White Top-Emitting OLEDs on Metal Substrates

Dissertation

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In the beginning [..], the earth hath existed waste and void,
and darkness is on the face of the deep [..]

“Let light be”; and light is.

Gen 1:1-3 [1]
Abstract

This work focusses on the development of top-emitting white organic light-emitting diodes (OLEDs), which can be fabricated on metal substrates. Bottom-emitting OLEDs have been studied intensively over the years and show promising perspectives for future commercial applications in general lighting. The development of top-emitting devices has fallen behind despite the opportunities to produce these devices also on low-cost opaque substrates. This is due to the challenges of top-light-emission concerning the achievement of a broad and well-balanced white emission spectrum in presence of a strong microcavity. The following work is a further step towards the detailed understanding and optimization of white top-emitting OLEDs.

First, the available metal substrates and the deposited silver electrodes are examined microscopically to determine their surface characteristics and morphology in order to assess their applicability for thin-film organic stacks of OLEDs. The examination shows the suitability for untreated Alanod metal substrates, which display low surface roughness and almost no surface defects. For the deposited silver anodes, investigations via AFM show a strong influence of the deposition rate on the surface roughness.

In the main part of the work top-emissive devices with both hybrid and all-phosphorescent architecture are investigated, in which three or four emitter materials are utilized to achieve maximum performance. The feasibility for top-emitting white OLEDs in first and second order devices is investigated via optical simulations, using the example of a three-color hybrid OLED. Here, the concept of a dielectric capping layer on top of the cathode is an essential criterion for broadband and nearly angle independent light emission. The main focus concerning the investigation of fabricated devices is the optimization of the organic stacks to achieve high efficiencies as well as excellent color quality of warm white emission.

The optimization of the hybrid layer structure based on three emitter materials using a combined aluminum-silver anode mirror resulted in luminous efficacies up to 13.3 lm W$^{-1}$ and 5.3 % external quantum efficiency. Optical analysis by means of simulation revealed a superior position concerning internal quantum efficiency compared to bottom-emitting devices with similar layer structure. The devices show an enhanced emission in forward direction compared to an ideal Lambertian emitter, which is highly preferred for lighting applications. The color quality – especially for devices based on a pure Al anode – is showing excellent color coordinates near the Planckian locus and color rendering indices up to 77. The introduction of an additional yellow emitter material improves the luminous efficacy up to values of 16.1 lm W$^{-1}$ and external quantum efficiencies of 5.9 %.

With the choice of a all-phosphorescent approach, using orange-red, light blue and green emitter materials, luminous efficacies of 21.7 lm W$^{-1}$ are realized with external quantum efficiencies of 8.5 %. Thereby, color coordinates of $(x, y) = (0.41, 0.45)$ are
achieved. Moreover, the application of different crystalline capping layers and alternative cathode materials aim at a scattering of light that further reduces the angular dependence of emission. Experiments with the crystallizing material BPhen and thin carbon nanotube films (CNT) are performed. Heated BPhen capping layer with a thickness of 250 nm show a lower color shift compared to the NPB reference capping layer. Using CNT films as cathode leads to a broadband white emission at a cavity thickness of 160 nm. However, due to very high driving voltages needed, the device shows low luminous efficacy.

Finally, white top-emitting organic LEDs are successfully processed on metal substrates. A comparison of three and four color based hybrid devices reveal similar performance for the devices on glass and metal substrate. Only the devices on metal substrate show slightly higher leakaged currents. During repeated mechanical bending experiments with white devices deposited on 0.3 mm thin flexible Alanod substrates, bending radii up to 1.0 cm can be realized without device failure.
Kurzfassung

Diese Arbeit richtet ihren Schwerpunkt auf die Entwicklung von top-emittierenden weißen organischen Leuchtdioden (OLEDs), welche auch auf Metallssubstraten gefertigt werden können. Im Laufe der letzten Jahre wurden bottom-emittierende OLEDs sehr intensiv studiert, da sie vielversprechende Perspektiven für zukünftige kommerzielle Anwendungen in der Allgemeinbeleuchtung bieten. Trotz der Möglichkeit, OLEDs auch auf kostengünstigen lichtdurchlässigen Substraten fertigen zu können, blieb die Entwicklung von top-emittierenden Bauteilen dabei allerdings zurück. Dies läßt sich auf die enormen Herausforderungen von top-emittierenden OLEDs zurückführen, ein breites und ausgeglichenes weißes Abstrahlungsspektrum in Gegenwart einer Mikrokavität zu generieren. Die folgende Arbeit liefert einen Beitrag zum detaillierten Verständnis und der Optimierung von weißen top-emittierenden OLEDs.


Im Rahmen der Optimierung von hybriden Schichtstrukturen basierend auf drei Emittermaterialien resultiert die Verwendung eines kombinierten Aluminium-Silber Anodenspiegels in einer Lichtausbeute von 13.3 lm W⁻¹ und einer externen Quanteneffizienz von 5.3 %. Eine optische Analyse mit Hilfe von Simulationen zeigt eine überlegene Stellung hinsichtlich der internen Quanteneffizienz verglichen mit bottom-emittierenden Dioden ähnlicher Schichtstruktur. Die Dioden zeigen eine verstärkte vorwärtsgerichtete Emission im Vergleich zu einem idealen Lambertschen Emitter, welche in hohem Maße für Beleuchtungsanwendungen erwünscht ist. Es kann eine ausgezeichnete Farbqualität erreicht werden – insbesondere für Dioden basierend auf einer reinen
Aluminiumanode – mit Farbkoordinaten nahe der Planckschen Strahlungskurve und Farbwiedergabefähigkeit bis zu 77. Die weitere Einführung eines zusätzlichen gelben Emittermaterials verbessert die Lichtausbeute auf Werte von 16.1 lm W⁻¹ und die externe Quanteneffizienz auf 5.9 %.

Mit der Wahl eines voll-phosphoreszenten Ansatzes unter Verwendung eines orange-roten, hellblauen und grünen Emittermaterials werden Lichtausbeuten von 21.7 lm W⁻¹ und externe Quanteneffizienzen von 8.5 % erzielt. Damit werden Farbkoordinaten von (x, y) = (0.41, 0.45) erreicht.


Schließlich werden weiße top-emittierende organische Leuchtdioden erfolgreich auf Metallssubstraten prozessiert. Ein Vergleich von drei- und vierfarb-basierten hybriden Bauteilen zeigt ähnliche Leistungsmerkmale für Dioden auf Glas- und Metallssubstraten. Während wiederholten mechanischen Biegeexperimenten mit weißen Dioden auf 0.3 mm dicken flexiblen Aluminiumsubstraten können Biegeradien bis zu 1.0 cm ohne Bauteilausfall realisiert werden.
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List of Publications

In the course of this thesis, the following articles and conference contributions have resulted:

Articles


Conference Contributions


(3) P. Freitag, G. Schwartz, and K. Leo, “White top-emitting OLEDs”, *The 7th International Conference on Electroluminescence of Molecular Materials and Related Phenomena (ICEL)*, OR 8a-1, 173 (2008)


1 Introduction

The development of organic light-emitting devices (OLEDs) started in the 1970’s, when the emission of electrically generated light in single anthracene crystals [2, 3] was observed for the first time. Since the pioneering work of Tang and van Slyke in 1987 [4], where the first efficient two-layered organic light-emitting device has been developed at the Eastman Kodak research laboratories in Rochester, considerable efforts have been put into the further development and optimization of OLEDs. Over the years, the layer structure and material utilization have undergone a strong development. Nowadays, highly purified organic material can be produced and a large number of diverse organic materials with specifically designed properties were developed. Due to the development of new stable and highly efficient emitter materials spanning the whole visible wavelength spectrum, partly incorporating rare earth or heavy metal atoms, OLEDs with improved efficiency and device lifetime were developed. Finally, the approach of electrical doping [5, 6] allowed much lower driving voltages.

Besides scientific research, also companies got increasingly interested in organic light-emitting devices and related technology. Nowadays, a large number of OLED applications already entered the consumer market and speed up to market acceptance. Besides displays for mobile phones (Samsung, HTC, and Nokia), music players (Sony, Samsung), digital cameras (Samsung, Nikon, and Kodak) and PC monitors (Samsung, Panasonic, etc.), a new generation of OLED TVs from Sony (11”) [7] and LG (15”) [8] are based on the organic LED technology. Recently, 3D OLED glasses have been demonstrated by the company Carl Zeiss [9] for home theater and gaming applications. These display applications particularly impress with their brilliant colors, high contrast level, and large viewing angle. In the quickly growing field of organic electronics, organic memories and transistors as well as organic photovoltaic (OPV) [10] are also under scientific investigation.

Especially within the industry sector of lighting and signage, OLEDs are the key technologies of the future. They show large potential for green and efficient light sources for general lighting, automotive lighting, architectural lighting, and safety signage. Since 1994, when the first white OLED was reported by Kido et al. [11], the race for the development of white light-emitting devices for illumination purposes started. Consequently, the academic and industrial interest grew tremendously. Due to the numerous
possibilities of color mixing for white light emission, many different white nuances can be created for different fields of application. In terms of standardization, one basically distinguishes between cold white and warm white. Cold white – or also called neutral white – is preferred in the Far East, e.g. Japan, China, Korea, etc. Western consumers rather prefer warm light, which features a higher red fraction in the emission spectrum and is comparable to the light emitted by an incandescent lamp, which is still highly preferred by consumers. However, compared to incandescent light sources, OLEDs are much more efficient.

In the last decades, the demand of artificial light grew considerably. About 19% of all produced electrical energy is used for lighting applications. To highly encourage the consumer to use more energy-efficient lighting alternatives, the European Commission [12] banned conventional 100 W incandescent light bulbs in September 2009. Until 2012 bulbs with 75 W, 60 W and 40 W will follow stepwise. Likewise, other nations are planning scheduled phase-outs or have already done. Consequently, consumers are looking for highly efficient new light sources providing excellent color quality. Organic light-emitting devices can potentially fulfill this need and fill the gap in the supply of illuminants. The ban as well as the high energy prize may shorten the transition in the lighting industry. However, a real paradigm shift is required to replace the common light bulbs by energy efficient technologies in solid state lighting based on LEDs and OLEDs. To compete with conventional light sources, both the efficiency and the cost levels of OLEDs have to become comparable at least with fluorescent lamps to push this transition towards OLED lighting.

Therefore, numerous research projects (OLLA, OLED100, Rollex, R2Flex, So-light, CombOLED, etc.) have been set up by many countries as well as the European Commission in the last years. Thereby, many universities, companies and new start up companies dealing with organic light-emitting devices have been supported to expedite the electrical and optical development of OLED technology. Based on this large support, organic LEDs have been pushed to high efficacy and external quantum efficiency as well as long lifetimes at high brightnesses. Furthermore, good color properties, including excellent color coordinates and color rendering (>80) have been achieved, which is a prerequisite for the lighting market. Lighting experts agree that OLEDs have a large potential and many advantages to revolutionize the concepts of lighting and architecture. OLEDs are flat self-luminous light sources and provide nice and pleasant bright light without any glaring effect, as it can be observed in incandescent lamps, and are fully dimmable. Due to their low driving voltage and high temperature stability, they are highly efficient and environmentally acceptable. Furthermore, the devices can be produced on extremely thin and even flexible substrates. OLEDs further offer a wide range of novel designs and application options as recently demonstrated in OLED design contests (see Figure 1.1). The visions reach from decorative room dividers, integrated OLED panels, large ceiling tiles, and Venetian blinds to beautiful futuristic luminaires with unique shaped lighting segments providing new lighting solutions for in- and outdoors. The two ultimate functionalities for designers –
Figure 1.1: OLED luminaire prototypes developed at the OLED design contests in Korea (ETRI 2009 & 2010): (a) Windmill, (b) Poom, (c) Coronight, (d) Flower, (e) Overturned Lighting, (f) prominence, and (g) plug & combination; and in the framework of the project CombOLED (2010): (h) Newlight, (i) Time/4, and (j) Lucifero [13–15].

unique to OLED lighting – are flexibility and transparency (cf. Figure 1.2). Transparent OLEDs may be implemented even into window glass, to provide unrestricted view at day and a large area light source during night. With self-luminous flexible OLED sheets, numerous amazing designs can be made possible.

However, to take advantage of the enormous potential of OLED lighting, a mass manufacturing equipment and customized processes with high throughput fabrication have to be developed to achieve low cost devices on large areas. Besides, the future lighting tiles have to be highly convenient, which requires light-weight, slim as well as unbreakable substrates and encapsulation solutions. These needs can economically be realized with roll-to-roll fabrication (cf. Figure 1.3) of OLEDs on low cost, flexible, thin, and robust substrates like aluminum [20].
1 Introduction

Figure 1.2: Large-area white OLED lighting tiles: (a) flexible [16] and (b) transparent [17].

However, for this application on opaque substrates, a top-emitting device architecture is required. So far, OLED research for lighting applications strongly concentrated on bottom-emitting devices on transparent substrates. Consequently, the first white OLED devices for lighting applications have been predominantly processed on top of transparent but brittle glass substrates.

The top-emitting layer structure, though, provides advantages, which should not be overlooked. Besides the fact that the production is no longer bound to special substrate types, the expensive transparent material ITO can be replaced by common metal films.

Figure 1.3: Roll-to-roll production line developed in the framework of the projects Rollex and R2Flex: (a) Photograph of the R2R-line [18] and (b) sketch of the vacuum deposition and rolling transport system [19]. The machine allows direct deposition of organic thin films on metal foils with high throughput.
Furthermore, top-emitting OLEDs can easily be implemented into inorganic semiconductor technology like Si- or TFT-backplanes for displays. So far a detailed investigation of OLEDs generating white light by a top-emitting structure primarily failed due to the non-availability of highly transparent cathode materials and the challenges of the microcavity when using transparent metal electrodes instead. Due to optical microcavity effects, the emission spectra, which is coupled out from microcavity devices, show strong spectral narrowing and a blue shift with higher viewing angle. Consequently, only very few studies about top-emitting white OLEDs have been published (see listing in Appendix B). This work will therefore contribute to the next step towards the realization of top-emitting white lighting applications on flexible substrates.

**Short Overview over the Following Chapters**

This thesis focuses on the development of white organic light-emitting devices with top-emitting layer architectures and their deposition on metal substrates. The investigation includes the characterization of substrate surfaces, optical device simulation, device preparation, and stack optimization using different device structures and emitting dyes.

The thesis is organized as follows: The first four chapters (Chapter 2 - Chapter 5) deal with the theoretical aspects of organic light-emitting devices including preparation and characterization. In Chapter 2, some general characteristics of light are presented, which are essential for light emitting systems. After a brief introduction into the electromagnetic radiation and the human visual system, the chapter deals with the detection and definition of light. The color and color related specifications are given thereafter. Additionally, the main features of white light sources are summarized in the end. Chapter 3 reviews the basic physics of organic molecules and solids. Starting with the basic concepts of organic molecules, the properties of organic molecules and molecular semiconducting solids are discussed, followed by an review of optical processes in organic solids. The electrical and optical properties of organic light-emitting devices are presented in Chapter 4. This chapter also includes an overview over the contributions to the electroluminescence efficiency and a brief review of the possible OLED structures. Chapter 5 describes the utilized substrates and materials for the preparation of organic light-emitting devices. Furthermore, experimental preparation techniques and the equipment for the characterization of the devices are introduced. Subsequently, the determination of the device performance is reviewed, which is essential for white top-emitting devices due to the altered emission characteristics compared to common bottom-emitting devices. Finally, some further measurement techniques including optical, microscopic, and photoelectron spectroscopic analysis are briefly introduced.

Throughout the following chapters (Chapter 6 - Chapter 10), the experimental results are presented and discussed. In Chapter 6 the surface quality of the available Alanod
substrates are examined microscopically and compared to the commonly used glass substrates with regard to defects and surface roughness. Furthermore, the morphology and surface quality of deposited silver anode layers are investigated in detail concerning the evaporation parameters deposition rate and thickness. The following Chapter 7 is dedicated to the hybrid approach of OLEDs utilizing fluorescent as well as phosphorescent emitter materials. The devices are based on three or four emissive dyes generating warm white emission. First, optical simulations are performed for first and second order devices to identify the theoretical feasibility for white light emission. The optical simulation study is followed by optimization studies, to investigate the influences and effects of different parameters on electrical and optical characteristics of the devices, especially spectra, efficiencies, and color coordinates. After the insertion of a forth yellow emitter, hybrid devices based on four emitting dyes are additionally discussed in terms of device performance and emission characteristics. Chapter 8 deals with the investigation of top-emissive devices using the all-phosphorescent approach. Several optimization steps are discussed. In Chapter 9, different capping layer materials, which are known to crystallize due to some post-processing, are investigated to act as scattering capping layer. Furthermore an alternative cathode material is tested. This study targets at the improvement of the angular independent emission characteristics of the developed devices discussed beforehand. The developed hybrid stack is transferred onto metal substrates in Chapter 10, where additionally simple bending experiments are performed. Finally, Chapter 11 summarizes this work and provides an outlook for future possible fields of work for device improvement to compete with bottom-emitting devices.

Additionally, experiments based on two emission colors for cold white light emission have been done, which are discussed in Appendix A. Appendix B gives an overview over the studies about top-emitting white OLEDs published so far.
In this chapter the general aspects of light are introduced. After a short introduction on the range of electromagnetic radiation, a detailed overview over the physiological function and sensitivity of the human eye is given in the first section. Subsequently, some technical definitions for measuring light are given, starting with the introduction of the general basics of radiometry and photometry as well as the photon flux. Afterwards, a short description of possible radiation patterns and the determination of the main parameters of light sources follows. The fourth section deals with color and chromaticity as well as two other phenomena closely related to color: color temperature and color rendering, as they play a fundamental role in lighting. Finally, a short overview over the common natural and artificial light sources is given and the standard illuminants and standard sources are described.

2.1 Electromagnetic Radiation

Electromagnetic radiation is described as the oscillation of electric and magnetic field components, $\vec{E}$ and $\vec{B}$, that propagate in the same direction $\vec{k}$ with the same speed $c$ and form waves with distinct wavelength $\lambda$ and frequency $\nu$. The electromagnetic spectra extends from cosmic rays of the magnitude of femtometers to long-wave radio waves of even some meters, evident from Figure 2.1. The fact that radiation between 380 nm to 780 nm can be detected by the human eye (and is commonly called “light”) distinguishes this wavelength region from the rest of the electromagnetic spectrum [21].
2.2 The Human Visual System

The perception of light is influenced by the sensitivity of the human visual eye. Therefore, a detailed insight into the human visual system and its functioning is essential to be able to exactly define and understand light as well as color.

2.2.1 The Eye

The eye – the human light-detector – is approximately spherical with a diameter of about 24 mm and is comprised of a multitude of optical elements, as illustrated in Figure 2.2a. The integral parts for receiving light and color are explained in the following. The eye consists of three concentric layers enclosing its inner parts, which mainly consist of the vitreous humor, the aqueous humor, and the eye lens. The outermost layer is called sclera, which is usually white but bulges up at the front and becomes transparent forming the cornea. The middle layer, the choroid, contains blood vessels to supply the following layer, the retina, with oxygen and nutrients. At the transition to the aqueous humor, the retina covers about two third of the internal surface with a transparent film of about 0.3 mm thickness [22]. This layer contains different types of cells responsible for light perception and signal processing and is illustrated in Figure 2.2b. When light is incident in the eye through the cornea, it is focused on the retina. The portion of incident light can thereby be adjusted via the iris. After passing the transparent optic nerve cells (retinal ganglion cells and collector cells [23]), the light reaches the photo-
2.2 The Human Visual System

Figure 2.2: Schematic cross-section of (a) the human eye and (b) the structure of the retina, after [22, 23]

sensitive neuro-epithelial layer. This layer consists of two different types of detector cells, the rods and the cones, named by their appearance under a microscope. Different pigments within these receptors absorb different wavelength-portions of light and cause photochemical reactions that change the pigmental structure [22]. The occurring electrochemical signals are then transmitted to the neurons in the optic nerve layer and sent to the brain via the eye-nerve for further image processing. Due to the eye-nerve, there is a small area without any detector cells, which is called the blind spot. The different detector types are not randomly distributed on the retina, but arranged around the fovea centralis, as depicted in Figure 2.3. The approximately eight million cones are mainly concentrated in the center of the fovea, whereas the rods (around 120 million) [23] are located in the outer part of the retina and are especially responsible for peripheral vision. According to the level of luminance from the outer environment, either rods or cones are responsible for the perception of light. For day vision – also called photopic\(^1\) vision – mainly cones are used at luminances at a level of around \(1\)-\(3\) cd m\(^{-2}\). At lower illumination levels (\(<1\)-\(3\) \(\times\) \(10^{-3}\) cd m\(^{-2}\)) mainly rods are dominating light perception for night vision or scotopic\(^2\) vision. In the transition zone (mesopic vision) both detector types are involved. As the rods contain only one pigment they are not sensitive to color, but to small changes in the lower luminance level. The color sensitive cones can be further distinguished in three different types containing three different pigments enabling a wavelength sensitive responsiveness. They are named l-type or long wavelength cones, m-type or middle-wavelength cones and s-type or short-wavelength cones. About 5 \%

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\(^1\)from Greek φῶς (phos) – light [24]
\(^2\)from Greek σκότος (skotos) – darkness [24]
Figure 2.3: Distribution of rods and cones located at the retina of a human eye, after [22].
2.2 The Human Visual System

![Graph showing difference spectra of visual pigments in single cones (s, m, and l) of the parafoveal region of the human retina, after [26].](image)

**Figure 2.4:** Difference spectra of visual pigments in single cones (s, m, and l) of the parafoveal region of the human retina, after [26].

...of all cones in each human eye are s-cones, whereas the ratio of m- and l-cones can vary from person to person, in which long-wavelength cones are dominant in number [25]. The spectral response functions of the three different cones are illustrated in Figure 2.4.

### 2.2.2 The Spectral Luminous Efficacy Function

As mentioned in the former subsection, the illumination conditions assign the sort of the used detector cells contributing to the human vision. Rods and cones have different absorption spectra due to different pigments. Therefore the human's eye sensitivity differs for photopic and scotopic vision.

To determine the relative eye spectral sensitivity for both conditions, several experiments have been carried out repeatedly, involving several people with normal color vision. Thereby wavelength dependent functions have been derived following the spectral responsiveness of rods for scotopic and of cones for photopic vision. Based on these experiments, the International Lighting Commission, *Commission Internationale de l’Eclairage (CIE)*, standardized the relative spectral luminous efficacy functions $V(\lambda)$ for photopic vision in 1924 and $V'(\lambda)$ for scotopic vision in 1951. Although later...
experiments revealed that the spectral luminous efficacy function \( V(\lambda) \) is inaccurate both in the low-wavelength range below 520 nm (where it has been underestimated) and above 680 nm (where it is too sensitive \([27]\)), the CIE 1931 is commonly used in photometry and colorimetry and also applied in this work.

For photopic vision the maximum possible luminous efficacy \( K_m^{\text{phot}} \) (m for maximum) is given for a wavelength of \( \lambda=555 \text{ nm} \) (cf. Figure 2.5) with a maximum value of 683 lm W\(^{-1}\). This value is especially needed to calculate the portion of light as shown in the following sections.

### 2.3 Technical Light Detection and Definitions

The next section deals with the description of technical light detection. Therefore, an introduction into radiometry and photometry is given in the first subsection, followed by a short description of the photon flux. After treating different emission pattern of light sources, the efficiency of light sources is briefly addressed.
2.3 Technical Light Detection and Definitions

2.3.1 Radiometry and Photometry – The Wave Nature of Light

To measure light as the visible part of the electromagnetic spectrum, one firstly has to deal with the science of radiometry before defining photometric quantities. In the following, quantities in radiometry are labeled with the subscripted e for “energy” and photometric quantities show a subscripted v for “visible”.

The fundamental measure of radiometry is radiant flux $\Phi_e$, which is the radiant energy $Q$ that is transferred through a surface or region of space per unit time. The radiant energy $Q$ is defined as the radiant energy per unit wavelength interval at the specific wavelength $\lambda$ [21]. All relevant radiometric quantities are deduced from the radiant flux $\Phi_e$. Radiant intensity $I_e$ is defined as radiant flux per unit solid angle $\omega$; irradiance $E_e$ is the radiant flux per unit area $S_0$ and radiance $L_e$ is the radiant flux per unit projected area $A$ and unit solid angle $\omega$ (cf. Figure 2.6). Herein, the projected area $A$ is defined by the area $A_0$ and the angle $\theta$ according to $dA = dA_0 \cos(\theta)$. Usually irradiance is used to describe the radiation incident on a specified surface. However, if radiation emerges from a surface, the term of radiant emittance $M_e$ is used, which has the same defining equation and units as the irradiance.

The photometric quantities $X_v$ can be easily derived from radiometry by weighing the spectral radiometric quantities $X_e(\lambda)$ with the spectral luminous efficacy function $V(\lambda)$.

![Figure 2.6](image)

**Figure 2.6:** Schematical illustration of the definition of radiometric and photometric quantities, with radiant flux $\Phi_e$, luminous flux $\Phi_v$, solid angle element $d\omega$, element of the area in plane $dA_0$, and element of the projected area $dA$. 
\textbf{Table 2.1: Basic quantities of radiometry and photometry, their definitions and units.}

<table>
<thead>
<tr>
<th>RADIOMETRY</th>
<th>PHOTOMETRY</th>
</tr>
</thead>
<tbody>
<tr>
<td>quantity</td>
<td>Definition</td>
</tr>
<tr>
<td>radiant flux</td>
<td>$\Phi_e := \frac{dQ}{dt}$</td>
</tr>
<tr>
<td>radiant intensity</td>
<td>$I_e := \frac{d\Phi_e}{d\omega}$</td>
</tr>
<tr>
<td>irradiance</td>
<td>$E_e := \frac{d\Phi_e}{dA_0}$</td>
</tr>
<tr>
<td>radiance</td>
<td>$L_e := \frac{d^2\Phi_e}{dA_0 d\omega}$</td>
</tr>
</tbody>
</table>

using the following equation

\[ X_v = K_m \int_{380}^{780} X_e(\lambda)V(\lambda)d\lambda \quad (2.1) \]

with $X$ representing each respective quantity like $\Phi$, $I$, $E$ or $L$ and $K_m$ the maximum luminous efficacy for photopic vision. A summary of all relevant radiometric and photometric quantities together with their definitions is given in Table 2.1.

\subsection*{2.3.2 Photon Flux – The Particle Nature of Light}

Besides its wave character, electromagnetic radiation can, according to the quantum theory, also be described as propagation of discrete packages of energy. These defined portions or quanta of energy

\[ E_p = h\nu = \frac{hc}{\lambda} \quad (2.2) \]

with $h$ the Planck’s constant, $\nu$ the frequency, $c$ the velocity of light in vacuum, and $\lambda$ the wavelength, are called photons. For some applications or calculations (e.g. external quantum efficiency (cf. Subsection 5.5.3) it is important to describe light as quantities of photon propagation, compared to the wave based description via radiometry and photometry. Based on the number of photons

\[ N_p = \frac{1}{hc} \int Q(\lambda)\lambda d\lambda \quad (2.3) \]

emitted by a source or propagation onto, through, or emerging from a specified surface of a given area in a given period of time [21], the definitions concerning the particle character of light are straightforward compared to radiometry and summed up in Table 2.2.
2.3 Technical Light Detection and Definitions

Table 2.2: Basic quantities for photons $p$, their definitions and units.

<table>
<thead>
<tr>
<th>quantity</th>
<th>Symbol</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>photon flux</td>
<td>$\Phi_p$</td>
<td>$\frac{dN_p}{dt}$</td>
</tr>
<tr>
<td>photon intensity</td>
<td>$I_p$</td>
<td>$\frac{d\Phi_p}{d\omega}$</td>
</tr>
<tr>
<td>photon irradiance</td>
<td>$E_p$</td>
<td>$\frac{d\Phi_p}{dA_0}$</td>
</tr>
<tr>
<td>photon radiance</td>
<td>$L_p$</td>
<td>$\frac{d\Phi_p}{d\omega dA}$</td>
</tr>
</tbody>
</table>

2.3.3 Emission Pattern of Radiation

Light emitted by an object can be distributed within space in different characteristics of radiation as depicted in Figure 2.7. Spherical emitters have a continuous emission of flux $\Phi_{e,v}$ in every direction of space and therefore constant radiant/luminous intensity $I_{e,v}$. For an ideal diffuse emission, one speaks of a Lambertian or cosine emitter (cf. Figure 2.7b), as the radiant/luminous intensity $I_{e,v}$ is proportional to the cosine of the emission angle $\theta$:

$$I_{e,v}(\lambda) = I_{e,v}^0(\lambda) \cos(\theta)$$  (2.4)

with $I_{e,v}^0(\lambda)$ the radiant/luminous intensity at perpendicular light emission at $0^\circ$. As the projected area $A$ depends on the viewing angle $\theta$, the radiance/luminance $L_{e,v}$ is independent on the angle according to:

$$L_{e,v} = \frac{dI_{e,v}(\lambda)}{dA} = \frac{dI_{e,v}^0(\lambda)\cos(\theta)}{dA_0\cos(\theta)} = \frac{dI_{e,v}^0(\lambda)}{dA_0} = \text{const.}$$  (2.5)

Figure 2.7: Different emission patterns of light sources: (a) spherical emitter; (b) Lambertian emitter; (c) forward emitter; and (d) emitter with special emission pattern.
Light emission from a cone like emitter is directed in the forward direction, which is favored for most lighting applications. Besides these general kinds of emission pattern, a further variety of special emission pattern exist (e.g. Figure 2.7d), which one can for example find in inorganic light emitting diodes.

To simplify calculations, Lambertian emission is usually assumed. However, this is only justified in few cases. To exactly determine angular distribution of radiation and further the efficiency of the light source, the angular dependent emission has to be measured either with a Goniometer setup or an integrating sphere, which both are described in detail in the Subsections 5.4.2 and 5.4.3.

2.3.4 Efficiency Parameters of a Light Source

In general, the efficiency of a system is described by the ratio of energy output from the system to the energy input into the system and is measured in percent (%). Dealing with lighting applications, the output is usually visible radiation and the input is an electrical quantity, leading to measures of specific dimensions.

The distinction between the efficiency (dimensionless or unit of %) and other measures with special units is, however, not always maintained carefully in published literature and common language use. For example, the luminous efficacy (units of lm W$^{-1}$) of a light source is often referred as power efficiency leading to misunderstandings. This shall be avoided in this work. In the following, the common quantities for OLED characterization is briefly discussed with special attention to the luminous efficacy.

Luminous Efficacy

The efficacy of light sources is described by the ratio of the photometric quantity luminous flux $\Phi_v$ ($[\Phi_v]=\text{lm}$) to the input power, which is measured in W. Depending on the chosen context, the inserted power can be either the radiant flux $\Phi_e$ referring to the photometric output from the considered light source or the electrical power $P_{el}$ consumed by the source. This leads to either the luminous efficacy of radiation $K$ (cf. Subsection 2.2.2) or the lighting system luminous efficacy $\eta_l$.

The luminous efficacy of radiation $K$ is a characteristic of the emitted spectrum of the considered light source. It is a measure of the effectiveness of stimulating the perception of light in the human eye and defined via the equation:

$$K = \frac{\Phi_v}{\Phi_e} = \frac{\int V(\lambda)X_e(\lambda)d\lambda}{\int \lambda X_e(\lambda)d\lambda} \quad (2.6)$$
Table 2.3: Luminous efficacy of radiation $K$ for some light sources.

<table>
<thead>
<tr>
<th>light source</th>
<th>$K$ (lm W(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ideal black body radiator at 6000 K</td>
<td>95 [28]</td>
</tr>
<tr>
<td>white light, constant over visible spectrum</td>
<td>220 [21]</td>
</tr>
<tr>
<td>direct beam sunlight, extraterrestrial</td>
<td>99.3 [21]</td>
</tr>
<tr>
<td>blue sky light</td>
<td>125-140 [21]</td>
</tr>
<tr>
<td>radiation from typical tungsten filament lamp</td>
<td>53 [21]</td>
</tr>
<tr>
<td>phosphorescence of cool white fluorescent lamp</td>
<td>348 [21]</td>
</tr>
</tbody>
</table>

With respect to day and night vision (cf. Subsection 2.2.2) the maximum possible values of 683 lm W\(^{-1}\) (photopic) or 1700 lm W\(^{-1}\) (scotopic) can be reached for monochromatic light with a wavelength of 555 nm or 507 nm, respectively. Some luminous efficacies of radiation for common light source spectra are listed in Table 2.3.

The lighting system luminous efficacy of an artificial light source $\eta_l$ is the efficacy of radiation $K$ multiplied by the radiation yield $\eta_{el}$ for converting electrical energy to radiation energy:

$$\eta_l = \frac{\Phi_v}{\Phi_e} \cdot \frac{\Phi_e}{P_{el}} = K \cdot \eta_{el} = \frac{\Phi_v}{P_{el}}$$

(2.7)

The radiation yield is therefore defined as the ratio of the produced radiant flux $\Phi_e$ to the electrical power $P_{el}$ consumed by the light source. This yield evaluates, which portion of the electric energy supplied to the lighting system is converted into visible light. For the discussion in this work the lighting system luminous efficacy is evaluated, which is referred to as simple luminous efficacy $\eta_l$. Some examples of luminous efficacies for artificial light sources can be found in Subsection 2.5.1.

Further Definitions

For organic light emitting diodes, two further definitions are usually given. To describe the performance of a light source with respect to the ratio of the emitted number of photons $n_p$ to the injected number of electrons $n_e$, the external quantum efficiency $\eta_{eqe}$ is calculated. This radiometric based quantity is independent from the eye sensitivity and is therefore a real efficiency, dimensionless and measured in percent (%).

The current “efficiency” $\eta_c$ ([$\eta_c$]=cd A\(^{-1}\)) defines the ratio of the perpendicular radiated luminance $L_{v0}^\theta$ to the current $I$ flowing through the substrate and is frequently used for OLED applications.

The derivations of both quantities are explained in detail in Subsection 5.5.
2.4 Color and Related Specifications

The Commission Internationale de l’Eclairage sets special regimentation to determine the color of objects within defined color spaces to standardize the description of color. In the next sections, a short summary of the most important and commonly used colorimetry systems and color spaces is given, followed by the introduction of the color temperature and the color rendering index, which is essential concerning the determination of color quality.

2.4.1 Chromaticity

The perception of color is a subjective phenomenon that varies from person to person. Over the years it has been a great challenge for scientists to describe color in a way that is appropriate for applications and it is still under discussion. As there are several models, the description given here will be limited only to the basic concepts, which have been used in this work.

The color perception spans the whole visible region, where each wavelength raises a different unique monochromatic color impression. However, further color impressions beyond monochromatic light are given by a mixture of different wavelengths. As the retina contains three different color detectors – having different absorption spectra – one can take the sensitivity of the three detectors as basis for developing a description of color perception. Unfortunately, they are too broad and show too much overlap to be taken as a useful basis.

Experiments show that almost all colors can be imitated by a combination of three appropriate primary standard spectra – called stimuli – by properly mixing them. This special set is referred to as trichromatic system and consists of three imaginary stimuli \( X \), \( Y \) and \( Z \), which are called primary color stimuli of the CIE 1931 Colorimetric System. The stimuli were determined via color matching experiments under viewing angles of 2° to avoid any participation of rod vision. Thus, this set is also called the CIE 2° Colorimetric System. Within this system three color-matching functions \( \bar{x} \), \( \bar{y} \) and \( \bar{z} \) were defined (cf. Figure 2.8), in which \( \bar{y} \) was identically chosen as the spectral luminous function \( V(\lambda) \). The three color-matching functions are weighing a spectral radiation distribution \( \Phi_e(\lambda) \) (radiant flux \( \Phi_e(\lambda) \), spectral irradiance \( E_e \), or spectral radiance \( L_e \)) to receive the tristimulus values as follows [22]:

\[
X = k \int_{380}^{780} \Phi_e(\lambda) \bar{x}(\lambda) d\lambda
\]  

(2.8a)
2.4 Color and Related Specifications

\[ Y = k \int_{380}^{780} \Phi_e(\lambda) \bar{y}(\lambda) d\lambda \]  
\[ Z = k \int_{380}^{780} \Phi_e(\lambda) \bar{z}(\lambda) d\lambda \quad \text{with} \quad k = \text{const.} \]  

For simplification of the color analysis, the tristimuli are further normalized defining the chromaticity coordinates \( x, y \) and \( z \) via

\[ x = \frac{X}{X + Y + Z} \]  
\[ y = \frac{Y}{X + Y + Z} \]  
\[ z = \frac{Z}{X + Y + Z}. \]  

The chromaticity coordinates \( x \) and \( y \) span a two-dimensional tristimulus color space, where each pair corresponds to a special color impression, shown in Figure 2.9a. However, one characteristic of this system is that – despite identical calculated color coordinates or color stimuli – two different specimen may show different spectral flux distributions. This phenomenon is called metamerism and plays a fundamental role in colorimetry.

\[ \text{Figure 2.8: The three color matching functions } \bar{x}, \bar{y}, \text{ and } \bar{z} \text{ of the CIE 1931 Colorimetric system.} \]
The upper border of the CIE 1931 color space represents all visible monochromatic colors from 360 nm to 780 nm. The connection from 780 nm to 360 nm of the bottom of the color space is called the purple curve having no counterpart in monochromatic light. As $x$, $y$, and $z$ are normalized to 1, each color can be described by a set of different $x$ and $y$. The point of equal energy with $x=y=z=0.3$ is also called the cold white point E.

In 1964 the *Commission Internationale de l’Eclairage* introduced an additional color system, which was based on experiments with 10° field of view, as 2° are normally too narrow for common color estimation. Nevertheless today the 2° CIE 1931 Colorimetric System is still used for general colorimetry.

However, both systems lack in a proper reproduction of differences in colors. That is, color differences represented by equal distances in the chromaticity diagram are not perceived as being equal. Therefore, a uniform chromaticity scale was introduced in 1960, which was proposed by MacAdams [29]. He performed experiments concerning standard deviations of colors within the $xy$-coordinate diagram and introduced the MacAdams ellipses. These elliptical pattern can be seen as a measure of the standard deviation around a central color. Ideally, the MacAdams ellipses should be circles to give a presentation of the chromaticity diagram. The uniform chromaticity scale (UCS) improves the non-uniformity of the color space relative to the $xy$-diagram by transforming the 1931 chromaticity diagram with $x$, $y$, and $z$ in a new $uv$-chromaticity diagram (cf. Figure 2.9b) using following equations:

$$
u = \frac{4x}{-2x + 12y + 3} \quad (2.10a)$$

$$v = \frac{6y}{-2x + 12y + 3} \quad (2.10b)$$

With this modification, the uniformity of the color diagram was improved, but is still not perfect. However the $uv$-color space could now – among other benefits – be used to describe the correlated color temperature (CCT) (see next Subsection 2.4.2).

Some years later the 1960 UCS was modified again and finally led to the 1964 Uniform Space (1964 UCS) [30]. Based on the 1960 chromaticity diagram the variables $W^*$, $U^*$, and $V^*$ were introduced. The total color difference $\Delta E$ between to colors could now be calculated using the Color-Difference Formula [31]

$$\Delta E = \sqrt{(\Delta U^*)^2 + (V^*)^2 + (W^*)^2}, \quad (2.11)$$

which is used to determine the color rendering index (CRI) (cf. Subsection 2.4.3).
2.4.2 Color Temperature

The concept of color temperature is based on the spectral radiation from a black body at a temperature $T$, which can be described by Planck’s law [21]

$$M(\lambda) = \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda kT}} - 1}, \quad [M] = \frac{W}{m^2 \mu m \text{ sr}}.$$  \hspace{1cm} (2.12)

with $M(\lambda)$ the spectral emittance of the black body, $h$ Planck’s constant, $c$ the velocity of light in vacuum, $k$ Boltzmann’s constant, and $\lambda$ the wavelength. Depending on the temperature the radiated light is perceived as warm or cold. Figure 2.10 shows the spectral black body radiation at different temperatures, exhibiting a spectral color shift from red to blue with increasing temperatures. The absolute color temperature $T$ applied to an illuminant is defined as the temperature of a black body, whose chromaticity is the same as that of the illuminant.

Based on the spectral distribution at a fixed temperature, the chromaticity of a black body radiator can be calculated using the Equations (2.12) and (2.8-2.10). A collection of all chromaticities can be included into the chromaticity diagram and generates a line (cf. Figure 2.11), which is called the Planckian locus (or black-body-curve) that defines ideal white light. Light sources whose chromaticity does not exactly match the Planckian locus can only be described with the correlated color temperature $T_c$ (or CCT). This is the temperature of a black body, whose chromaticity is nearest to that of the illuminant. Chromaticities with the same correlated color temperature are lo-
Figure 2.10: The spectral blackbody radiation for different temperatures $T$ (K). The maximum of the radiant power shifts towards lower wavelength with increasing temperature.

cated on isothermal straight lines perpendicular to the Planckian locus in the CIE 1960 uniform color diagram (cf. Figure 2.11a). Although the correlated temperature can be calculated for any light source, it is only meaningful within a maximum distance of

$$\Delta uv = \sqrt{(u_t - u_r)^2 + (v_t - v_r)^2} = \pm 0.05$$

(2.13)

with $u_t$ and $v_t$ the chromaticities of the test illuminant and $u_r$ and $v_r$ the reference chromaticities on the Planckian locus [32]. In general, the Planckian locus can also be used in the $xy$ CIE 1931 chromaticity diagram. However, the lines of equal temperature are then not perpendicular to the Planckian locus anymore, which is due to the nonlinearity of this diagram (see Figure 2.11b).

2.4.3 The Color Rendering Index

When illuminating an object with a light source, the reflected light is altered in accordance to the absorption spectrum of the object, so that the chromaticity coordinates
Figure 2.11: The Planckian locus, the points of discrete color temperature $T$ (K), and the isothermal lines within (a) the uv 1960 (UCS) and (b) the xy 1931 color space. The definition range $\Delta uv = \pm 0.05$ of the correlated color temperature is marked with red lines. The insets shows the position of the Planckian locus within the whole (a) uv and (b) xy color space.
of the reflected light are shifted. The appearance of objects therefore depends on the spectral distribution of the illumination, which determines how well a color can be reproduced. This effect is called color rendering \([22]\), which plays an important role in lighting. The standard light sources, to which the color rendering properties of other illuminants are compared, are usually daylight or incandescent light (cf. Subsection 2.5.1). In 1965 the Commission Internationale de l’Eclairage recommended a procedure for measuring the color rendering properties of two different light sources (test illuminant and reference illuminant) \([31]\). The method uses eight different test color samples\(^1\), whose spectral reflectances are illustrated in Figure 2.12.

The reference illuminant \((u_r, v_r)\) has to show the same or nearly the same chromaticity as the lamp to be tested \((u_t, v_t)\), having a maximal chromaticity difference of

\[
\Delta uv < 5.4 \cdot 10^{-3} \tag{2.14}
\]

in the 1960 color space. Below correlated color temperatures of \(T_c=5000\) K, a Planckian radiator, above 5000 K, an appropriate daylight illuminant has to be used. Color rendering indices calculated with higher chromaticity differences \(\Delta uv\) than claimed,

---

\(^1\)Munsell notation: 1) 7.5R6/4, 2) 5Y6/4, 3) 5GY6/8, 4) 2.5G6/6, 5) 10BG6/4, 6) 5PB6/8, 7) 2.5P6/8, and 8) 10P6/8
are therefore less accurate. The procedure determines the differences in the resultant color shifts by illuminating the eight test color samples with both the test and the reference illuminant, taking the adaptive color shift into account, which occurs when our eyes adapt to changed illumination.

For that purpose the \( uv\)-chromaticity coordinates of both test \((t)\) and reference \((r)\) illuminant as well as the chromaticity coordinates of each test color sample \(i\) have to be determined in the 1960 USC color space. Therefore, the test color samples are illuminated with both test illuminant \(\left((u, v)_{t,i}\right)\) and reference illuminant \(\left((u, v)_{r,i}\right)\) and the 1960 color coordinates of the reflected light is determined as stated in Subsection 2.4.1. Due to the different state of chromatic adaption under both illuminants, the adaptive color shifts have to be regarded by a von Kries transformation. The resultant color shifts \(\Delta E_i\) are calculated in the 1964 UCS color space by using Equation (2.11). This results in the special color rendering indices for each test color sample \(R_i\) and the general color rendering index \(R_a\):

\[
R_i = 100 - 4.6 \cdot \Delta E_i \quad \text{and} \quad (2.15)
\]

\[
R_a = \frac{1}{8} \sum_{i=1}^{8} R_i. \quad (2.16)
\]

The general color rendering index \(R_a\) – commonly also called CRI – indicates the average deviation of the color rendition of the tested lamp from the reference illuminant and evaluates the light rendering quality of an illuminant in a scale up to 100. Test light sources with high color rendering indices of 90-100 have almost equivalent color rendering properties compared to the reference source.

In the field of scientific development with respect to organic light-emitting diodes, the color coordinates of the devices often have larger distance to the Planckian locus than required in Equation (2.14), which is often due to parallel optimization of different device parameters. Consequently, the developed devices can not always fulfil the strict demands for the CRI definition. However, the color rendering index is a very helpful criterion with respect to development, improvement, and evaluation of the color quality of OLED light sources. In the following, the CRI will thus also be stated for color coordinates, which exhibit little larger distance to the Planckian locus than claimed in the definition.

### 2.5 White Light Sources

The following section gives an overview over the most important natural and artificial light sources, before the standard illuminants and standard sources defined by the Commission Internationale de l’Eclairage are stated.
Figure 2.13: The extraterrestrial and direct/circumsolar solar radiation spectrum. The holes in the direct/circumsolar spectrum can be assigned to absorption bands in the atmosphere.

2.5.1 Natural and Artificial Light

Over centuries, major light sources for human beings have been the sun during day and the moon during night. Thus, light sources that produce light close to daylight are highly desired and play a very important role in every-days life. One characteristic of daylight is its variability, as the spectral distributions strongly depends on the time of the day, the weather conditions, the season, the geographical location, and further the solar activities. Strictly speaking, incident daylight is a composition of direct light emitted from the sun and diffuse skylight after scattering from the atmosphere, further also including the effect of clouds. Due to water vapor, waste particles, and ozone, some components of the direct sunlight is absorbed by the atmosphere. The continuous terrestrial solar spectral irradiance\(^1\) is illustrated in Figure 2.13 [33], providing illuminances from only 1000 lux in winter up to 150 000 lux in summer [23]. The spectral distribution is almost equal to a black body radiator of about 5800 K.

\(^1\)The data is an average for the 48 contiguous states of the United States of America (U.S.A.) over a period of one year
After utilization of fire and later oil-lamps, the development of current driven artificial light sources has been started with the discovery of electricity. Today many different electric light sources are widely used, wherein mainly three different ways of producing light can be distinguished.

The oldest but still very famous way is the heating of matter like it is done in incandescent lamps. Sometimes they are also called tungsten filament lamps, as light is produced via a glowing tungsten filament that is heated by the driving current. Atoms and molecules are excited and emit radiation in a continuous spectrum with a spectral distribution comparable to a black body radiator. To prevent a quick darkening of the bulb, arising from the evaporation of the filament, the glass bulbs have a certain minimum size, are evacuated, or contain inert gas or halogens. Since 1960 glass bulbs are also filled with low pressure halogen, which enables a redeposition of evaporated tungsten from inside the bulb back onto the filament. Thereby, halogen lamps allow higher temperatures due to the smaller design and therefore higher efficacies, which are in the range of 20 lm W$^{-1}$ compared to around 12 lm W$^{-1}$ for common incandescent lamps.

As radiation from incandescent lamps is based on a glowing filament, the emission color can be found to be on the Planckian locus at the specific heating temperature, having an ideal color rendering of 100. Due to their low price and good color properties, incandescent lamps have been the leading illumination source over years. However, they are now exchanged step by step by more energy saving light sources due to their inefficiency. Only about 10% of their consumed power is converted into light. The other 90% are lost as heat, which is due to the large infrared portion of the emission spectrum.

Secondly, light may also be produced by electrical discharge within a gas or metal vapor filled sealed glass tube under pressure. Accelerated by the electric field within the tube, electrons can excite gas atoms via collision ionization and photons are emitted, when the excited shell electrons fall back to lower energy levels.

One distinguishes low pressure discharge lamps (e.g. fluorescent lamps, compact fluorescent lamps, and sodium lamps), high pressure discharge lamps, and high intensity discharge lamps (e.g. mercury-vapor, metal halide, and sodium lamps). Compared to incandescent lamps, simple gas discharge lamps exhibit no continuous spectral distribution. The emission spectrum hence consists of a series of discrete spectral lines. To obtain a white spectrum, luminescent materials are applied to the tube walls, which absorb the monochromatic light and re-emit it at lower wavelength. Therefore a wide spectral range of emission and various color quality can be achieved from very poor – almost monochromatic light – to high-quality light with broad emission spectrum and color rendering above 80.

The most commonly used low pressure discharge lamp is the (compact-) fluorescent lamp, which is filled with mercury vapor and argon. The discharge of mercury mainly
produces UV light, which induces visible radiation in a composition of different luminescent materials on the inner tube walls. An accurate choice of several materials (mostly up to five) can assure high color qualities, with color rendering indices up to 95 [34, 35] and at color temperatures that span the whole range.

The third way of artificially producing light was made possible with the discovery that semiconducting material can emit light, if charge carrier are passing through [36, 37]. In a forward biased semiconductor diode, electrons and holes can recombine and produce photons. The emission color is determined by the energy gap of the semiconductor. This way of light generation has become very attractive in the last years as high efficacies, low energy consumption, and high lifetime can be provided. Generally, one distinguishes between inorganic light emitting diodes (LEDs), which are mainly point light sources, and surface-emitting organic light emitting diodes (OLEDs).

Inorganic LEDs are based on semiconducting solid state material consisting of elements from the second to the sixth (main-) group of the periodic table. The emission color of these solid state devices depends on the used semiconducting material combinations and concentrations. The most common materials are AlInGaP (for red to orange emission) and InGaN (for blue to green emission) [23]. Usually, emission from monochrome LEDs has a narrow spectrum. White light emission can be achieved by a combination of e.g. red, green, and blue separately driven LEDs (RGB LEDs or multicolored LEDs) or by so called conversion. Here, the emission from a blue LED stimulates emission from a yellow phosphor coating on top of the diode. This leads to broader ("nominally white") spectral distribution of radiation and improves the color rendering. Due to their robustness, LEDs are very attractive for vehicle lighting but also entered markets in the lighting industry in the last few years, especially for white lighting.

Organic light emitting diodes are mainly made from organic molecules with π-bonds. One can distinguish between either (high-molecular) polymer based devices (P-OLEDs) or (low-molecular) small-molecule based devices (SM-OLEDs), or a combination of both. Polymer OLEDs are mainly processed from solution phase via e.g. spin-coating, doctor-blading, or ink-jet printing. In this work solely small-molecule OLEDs are discussed, which are processed by evaporation of organic material (see Subsection 5.3.2). Both types can be produced on different substrates (e.g. flexible, steep, opaque, and transparent) as well as in different structures (e.g. bottom, top, transparent, inverse, multilayered, multi-doped, and stacked) providing a huge range of possible applications.

A short overview over the most commonly used light sources and their characteristics is given in Table 2.4. For the sake of completeness, the lifetimes of the light sources are additionally given, which are beyond the scope of this work.
Table 2.4: Commonly used light sources and their characteristics. Listed values are maximum values and were measured for different lamps.

<table>
<thead>
<tr>
<th>source</th>
<th>luminous efficacy (lm W(^{-1}))</th>
<th>CCT (10(^3) K)</th>
<th>CRI</th>
<th>lifetime (10(^3) h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>incandescent [23]</td>
<td>8-19</td>
<td>≈ 2.7</td>
<td>100</td>
<td>0.75-2.0</td>
</tr>
<tr>
<td>halogen [23]</td>
<td>8-20</td>
<td>≈ 2.9</td>
<td>100</td>
<td>2.0-6.0</td>
</tr>
<tr>
<td>tubular fluorescent [23]</td>
<td>60-110</td>
<td>3.0-5.0</td>
<td>50-95</td>
<td>9.0-20.0</td>
</tr>
<tr>
<td>compact fluorescent [23]</td>
<td>50-70</td>
<td>2.7-4.1</td>
<td>80-85</td>
<td>9.0-20.0</td>
</tr>
<tr>
<td>LED(^\d) [38]</td>
<td>50-70</td>
<td>-</td>
<td>-</td>
<td>50.0</td>
</tr>
<tr>
<td>OLED(^\d) [39]</td>
<td>23</td>
<td>2.8</td>
<td>-</td>
<td>&gt;5.0</td>
</tr>
</tbody>
</table>

\(^\d\) Best light source presently commercial available

2.5.2 Standard Illuminants and Standard Sources

The color impression of an object can be described by its color coordinates. However, these are dependent on the spectral distribution of the illuminant and may change for a different illumination source, as explained in Subsection 2.4.3. Hence, in 1931 the Commission Internationale de l’Eclairage proposed the use of a series of standard and supplementary illuminants having specified spectral distributions, illustrated in Figure 2.14. Further CIE standard sources (artificial light sources) were defined, that can realize the standard illuminants. Therefore, it is important to differentiate between the term source, referring to a real light source physically emitting light, and the term illuminant, defining a spectral power distribution that can not necessarily be realized by an actual source. The lighting industry is permanently searching for further improved sources that ideally represent illuminants. So far they succeeded in a few so called standard sources, which realizes the illuminants in practice.

The standard illuminant A represents the light from an incandescent light bulb with a relative spectral distribution of a Planckian radiator with the correlated color temperature of \(T=2856\, \text{K} \) [22]. With its chromaticity coordinates of \((x, y)=(0.448, 0.407)\) it is also referred as warm white point A. In the Western industrialized countries, the standard illuminant A is the most commonly used reference for white illumination, whereas Eastern industrialized countries rather prefer cold white, defined by the point of equal energy \(E\) with \((x, y)=(0.333, 0.333)\). The standard illuminant A can be realized with a gas-filled tungsten filament lamp referred as standard source A.

The D series of illuminants are constructed to represent natural daylight. The standard illuminant \(D_{65}\) represents average daylight and shows the spectral distribution illustrated in Figure 2.14 with a correlated color temperature of 6504 K. \(D_{50}\), \(D_{55}\) and
Figure 2.14: The spectral distribution of the CIE standard illuminants A and $D_{65}$ and the supplementary illuminants $D_{50}$, $D_{55}$ and $D_{75}$ [23].
Figure 2.15: The Planckian locus, the daylight locus, and the chromaticity points for CIE standard and supplementary illuminants within the 1931 color space. The inset illustrates the whole color space.

D₇₅ are supplementary illuminants with correlated color temperatures of approximately 5000 K, 5500 K and 7500 K, respectively. Actual light sources for daylight are difficult to produce artificially and until now no standard sources have been realized. However, simulators have been developed that provide approximate standard sources, e.g. xenon lamps for D₆₅. All daylight illuminants are located on the daylight locus, which was defined by the Commission Internationale de l’Eclairage in the 1960 UCS diagram by analyzing several daylight measurements [22]. The locus is parallel to the Planckian locus with a distance of about Δuv = 0.0003 and represents the average daylight as a function of correlated color temperature.

Figure 2.15 illustrates the location of the chromaticities of all defined illuminants in the xy chromaticity diagram. The point E describes an equal energy radiator (cf. Subsection 2.4.1).
3 Organic Molecules and Solids

This chapter summarizes the fundamental characteristics of single organic molecules and molecular solids. Starting with the basic quantum chemical concepts to describe the energy levels in a single molecule, the origin of semiconducting properties based on the formation of extended $\pi$-electron systems is discussed. Subsequently, the optical properties of organic molecules are stated. After a detailed discussion concerning spin states of excited molecules, the optical transitions in molecules are discussed. The next section deals with the formation of molecular solids, which finally leads to the transport of charge carriers within the molecular solid. Finally, optical processes in molecular solids are discussed, including the generation of electroluminescence via excitons, various energy transfer mechanisms, and excitonic processes.

3.1 Basic Concepts of Organic Molecules

The basic bricks of organic semiconductors are single organic molecules, which are internally covalently bound. To physically understand the semiconducting characteristics and properties of carbon based molecules as well as molecular based solid semiconductors, a closer look from the perspective of quantum chemistry is necessary, which will be given in the following.

3.1.1 From the Schrödinger Equation to the LCAO-Method

Generally, the physical properties of molecules can be described by a wave function $\Psi^n$, which solves the non-relativistic time independent Schrödinger equation

$$H\Psi^n = E^n\Psi^n$$

(3.1)
with the Hamilton operator $H$, leading to the allowed eigenstates $\Psi^\nu$ with the eigenvalues $E^\nu$ of the system. However, it is not possible to solve this equation analytically for a many-particle problem. Therefore, several approximations have to be made to find a solution to this problem.

The Born-Oppenheimer approximation accounts for the fact that the motion of the electrons (e) is much faster than that of the nuclei (N) to which they are bound. Due to the large difference between their masses ($m_e \ll m_N$), the electrons can almost instantaneously respond to any change of the nuclei configuration and the nuclei can be considered to remain stationary. Consequently, the Schrödinger equation can be solved for the electrons in the static potential of the nuclei $V$ by treating the problem separately for electrons (e) and nuclei (N). The Hamilton operator $H$ is then split up via

$$H = H^e + H^N = T^e + T^N + V,$$

with $T^e$ and $T^N$ denoting the kinetic energy of the electrons and nuclei, respectively, and $V$ the potential energy of the system. The total wave function $\psi$ is split in a product of an electronic wave-function $\psi^e(\vec{r}, \vec{R})$, which depends on the position of both electron ($r$) and the nuclei ($R$), and a nuclear wave-function $\psi^N(\vec{R})$ [40] via

$$\psi = \psi^e(\vec{r}, \vec{R})\psi^N(\vec{R}),$$

with

$$\psi^N = \psi_{\text{vib}}\psi_{\text{rot}}.$$

The nuclear wave function is further a combination of the vibrational $\psi_{\text{vib}}$ and rotational $\psi_{\text{rot}}$ portion of the molecular movement.

In a further simplification – the Hartree approximation – the numerous interactions between the single electrons are neglected [41]. The total electronic Hamiltonian is thereby obtained by the sum of core Hamiltonians $h_i$ for each electron $i$, each composed of the kinetic energy $t_{i\text{eff}}$ and the average effective potential $v_{i\text{eff}}$ of one electron $i$ in the neighborhood of all electrons:

$$H = \sum_i h_i$$

$$h_i = t_{i\text{eff}} + v_{i\text{eff}}$$

The electron wave function $\psi^e$ splits into a product of one-electron wave functions $\psi_j(i)$ for electron $i$ in orbital $j$, according to

$$\psi^e = \psi_a(1)\psi_b(2)\psi_c(3)\ldots\psi_n(n) = \prod_{i,j} \psi_j(i),$$
which solves the stationary one-electron Schrödinger equation

\[ \hat{h}_i \psi_j(i) = E_j \psi_j(i). \] (3.8)

In this independent-electron model \( E_j \) is the energy of an electron in orbital \( j \) and the total energy \( E \) is the sum of all one-electron energies \( E_j \).

To obey the Pauli principle, taking the electron spin into account, the total wave function – including spin – has to be antisymmetric under the exchange of any pair of identical electrons. Therefore, the overall wave function \( \psi^e \) is written as Slater-determinant

\[
\psi^e(i = 1, \ldots, n; j = a, \ldots, z) = \sqrt{\frac{1}{n!}} \begin{pmatrix}
\psi_a(1) & \psi_b(1) & \psi_c(1) & \cdots & \psi_z(1) \\
\psi_a(2) & \psi_b(2) & \psi_c(2) & \cdots & \psi_z(2) \\
\psi_a(3) & \psi_b(3) & \psi_c(3) & \cdots & \psi_z(3) \\
\vdots & \vdots & \vdots & \ddots & \vdots \\
\psi_a(n) & \cdots & \cdots & \cdots & \psi_z(n)
\end{pmatrix}.
\] (3.9)

Finally, the LCAO principle (Linear Combination of Atomic Orbitals) is applied. This approximation is motivated by the fact that the wave function of an electron near a nucleus can be expected to be similar to the wave function of an electron in a valence orbital of that atom. The molecular orbitals (MO) can be given by a linear combination of atomic orbitals \( \Phi_k \) via

\[
\psi^e_j(i) = \sum_k c_k \phi_k,
\] (3.10)

whose coefficients \( c_k \) have to be determined numerically.

The simplest example for the linear combination of atomic orbitals is the case of the molecule \( \text{H}_2 \), where two atomic orbitals (AO) \( \phi_A \) and \( \phi_B \) of two atoms A and B are combined to form a molecular orbital \( \psi_+ \) and \( \psi_- \) [42], according to

\[
\begin{align*}
\psi_+ & \propto \phi_A + \phi_B \\
\psi_- & \propto \phi_A - \phi_B,
\end{align*}
\] (3.11a)

(3.11b)

with the molecular orbital densities \( |\psi_+|^2 \) and \( |\psi_-|^2 \). The eigenvalues [41] can be calculated to

\[
E_{\pm} = \frac{\alpha \pm \beta}{1 \pm S},
\] (3.12)

with \( \alpha \) the Coulomb integral, \( \beta \) the resonance integral and \( S \) the overlap integral. As the energy levels are therefore split and electrons occupy the lowest energy level in their ground state, \( \psi_+ \) becomes the binding molecular orbital and \( \psi_- \) the anti-binding molecular orbital. Both binding- (\( \psi_+ \)) and anti-binding (\( \psi_- \)) molecular orbitals for this example as well as the energy level splitting of \( \text{H}_2 \) is graphically depicted in Figure 3.1.
Figure 3.1: Schematic description of (a) the binding and anti-binding molecular orbitals $\psi_+$ and $\psi_-$ as well as (b) the molecular orbital energy level diagram for a single $H_2$-molecule built from two $H$-atoms $A$ and $B$ with the atomic orbitals $\phi_A$ and $\phi_B$.

The binding molecular orbital is occupied by two electrons of each atomic orbital and according to Paulis principle with contrary spin number. However, the LCAO approach only gives an approximated description of the energy levels of a molecule. To exactly determine the orbital energies for a molecule containing $n$ molecules, all electron-electron interactions have to be taken into account.

### 3.1.2 Delocalized $\pi$-Electron Systems in Organic Molecules

Organic semiconducting molecules are mainly made from hydrocarbons (aromatic rings and/or conjugated double bonds), whose backbone structure is built from single carbon (C) molecules binding to hydrogen (H) atoms, but can further contain nitride (N), oxygen (O), sulfur (S), or other atoms like heavy metals. Due to their configuration ($1s^2$, $2s^2$, $2p^2$), carbon atoms usually form hybrid orbitals ($sp^3$, $sp^2$, or $sp$), where each atom holds four valence electrons. For electronic systems the $sp^2$-hybridization is of special interest, as this configuration leads to extended $\pi$-systems containing delocalized electrons, which is the precondition for the semiconducting properties of organic materials.

The $sp^2$-hybridization consists of three $sp^2$-orbitals lying in a horizontal plane and enclosing an angle of $120^\circ$ and one $p_z$-orbital perpendicular to the plane. Figure 3.2a shows a simple representative of hydrocarbons (ethylene: $C_2H_4$), built from two C-atoms. The two $sp^2$-orbitals at the axis connecting both carbon atoms are highly over-
Figure 3.2: Scheme of the orbitals, the bonds, and the energy levels of (a) an ethylene molecule and (b) a benzene ring. Due to the overlapping $p_z$-orbitals the molecules form $\pi$-bonds, which span over the whole molecule. Repeated $\pi$-bonds form extended $\pi$-electron systems leading to highest occupied and lowest unoccupied molecular energy levels.
lapping. This arrangement results in a fully occupied binding $\sigma$ orbital and an energetically higher lying unoccupied anti-binding $\sigma^*$ orbital. This $\sigma$-band determines the basic geometry of the molecule [43]. The remaining $sp^2$-orbitals, in the case of ethylene, bind to hydrogen atoms. Perpendicular to the plane, both $p_z$-orbitals can overlap to build $\pi$-bonds: occupied binding $\pi$ orbitals and unoccupied anti-binding $\pi^*$ orbitals. The overlap of the $p_z$ atomic orbitals is much smaller compared to the $\sigma$ overlap, but also stabilizes the molecule. The energetic splitting between binding and anti-binding MO is in the order of 10 meV to a few 100 meV [44]. However, these $\pi$-orbitals can extend across larger molecules. Repeated $\pi$-bonds within one extended molecule can form extended conjugated $\pi$-electron systems, as illustrated for benzene in Figure 3.2b. Here, the $p_z$-electrons are delocalized over the whole $\pi$-system and are thereby strongly determining the optical and electrical characteristics of the molecule. In typical organic molecules, the energetically highest occupied $\pi$-orbital forms the highest occupied molecular orbital (HOMO) and the lowest unoccupied $\pi^*$-orbital the lowest unoccupied molecular orbital (LUMO). Due to the Pauli Principle, the binding orbitals are occupied with pairs of electrons with anti-parallel spin, as equal fermions may never be in the same quantum state. The lowest possible excitation of a molecule is therefore given by a $\pi - \pi^*$-transition of an electron from the HOMO to the LUMO of the molecule.

Generally, the energetic gap between HOMO and LUMO decreases for an increased number of aromatic rings, as shown in Figure 3.3. The energetic gap is smaller for material in the solid state due to polarization effects, which will be discussed in Subsection 3.3.2. Therefore, the effective HOMO-LUMO levels as well as the energy gap $E_{\text{gap}}$ can be modified by adding, replacing, or removing molecular units of the organic molecule, as this influences the extended $\pi$-electron system. The energy gap varies in a range of 1.5 to 3 eV [43]. As the lowest possible excitation is dedicated to an $\pi - \pi^*$-transition of an electron from the HOMO to the LUMO of the molecule, this leads to light absorption or emission in the visible range of the electromagnetic spectrum. This excitation of organic molecules will be discussed in the following section.

### 3.2 Optical Properties of Organic Molecules

The following section deals with the basic concept of the generation of electromagnetic radiation from an optically excited molecule. After a short overview over the possible spin states of an excited molecule and the singlet-triplet splitting of excited energy level, the energy transitions in a molecule are explained including the generation of fluorescence and phosphorescence. Here, the mechanisms are only discussed for photoluminescence but can also be applied to electroluminescence as discussed in Section 3.4.
Figure 3.3: Dependence of the energy gap $E_{\text{gap}}$ of different polyacenes in the gas phase (g) and the crystalline state (c), after [45]. With increasing number of aromatic rings, the energy splitting of HOMO and LUMO energies is lowered. The gap is smaller for solid material due to polarization effects.
3.2.1 Excited States

To excite an organic molecule additional energy has to be applied. Molecules can either be excited optically by absorption of photons or electrically by a recombination of two charge carriers. As the latter process requires a pair of oppositely charged charge carriers, which have to be injected into a molecular system beforehand, this will be treated in the discussion of organic molecular solids in Section 3.4.1. With regard to the spin orientations (↑ and ↓) of two electrons a and b, there are generally four possible spin states (cf. Figure 3.4) containing one antisymmetric singlet state

\[ \chi_S = \frac{1}{\sqrt{2}} [\uparrow (a) \downarrow (b) - \downarrow (a) \uparrow (b)] \quad (S = 0; M_S = 0) \]  

(3.13)

and three symmetric triplet states

\[ \chi_T^{-1} = \uparrow (a) \uparrow (b) \quad (S = 1; M_S = -1) \]  

(3.14a)

\[ \chi_T^0 = \frac{1}{\sqrt{2}} [\uparrow (a) \downarrow (b) + \downarrow (a) \uparrow (b)] \quad (S = 1; M_S = 0) \]  

(3.14b)

\[ \chi_T^1 = \downarrow (a) \downarrow (b) \quad (S = 1; M_S = 1) \]  

(3.14c)

each with the quantum numbers S and M_S. Combined with the antisymmetric and symmetric orbital wave function \( \phi_{\text{anti-sym}} \) and \( \phi_{\text{sym}} \), they form the total antisymmetric wave function \( \psi \) of the molecule. Usually, a neutral molecule is in the singlet ground state \( \chi_S \) with both electron spins anti-parallel. During the excitation one of the electrons is lifted from the ground state into an energetically higher excited state. Due to the anti-parallel spin orientation of the excited electron and the remaining electron in the ground state, the arising excited molecule gets into the excited state \( S_1 \), which is also a singlet state \( \chi_S \) with quantum number S=0. However, inter-system-crossing processes (see Subsection 3.2.3) allow a spin flip of the excited electron, which results in a triplet state \( T \) \( (\chi_T) \) of the molecule with quantum number S=1.

3.2.2 Singlet and Triplet Energy States

As already stated before, the LCAO-theory introduced in Subsection 3.1.1 is qualitatively useful, but quantitatively incorrect, as the interactions of electrons are neglected. Therefore, the calculated molecular orbitals are only true for single electrons, which move in a mean field of all other electrons. The energetical gap for an molecular excitation in this simplified picture is given by the difference of HOMO and LUMO energy

\[ \Delta E_{\text{gap}}^{\text{LCAO}} = E^{\text{HOMO}} - E^{\text{LUMO}}. \]  

(3.15)
Figure 3.4: Possible spin states for two paired electrons with quantum number $S=0$ and $S=1$. The states are called singlet and triplet states, as there is only one realization possible for $S=0$, but three for $S=1$. 
However, for a more precise quantitative description of the energy gap, the electron-electron interactions have to be considered, which also accounts for the spin states of the electrons.

Here, the interactions between the electron $a$ in the ground state at $r_1$ and the electron $b$ in the excited state $r_2$ separated by a distance $r_{12}$ can be expressed via the Coulomb interaction integral $C_{a,b}$ and the exchange integral $X_{a,b}$. In both integrals the spin states of the electrons are included and both contribute to the total binding energy $E$. The Coulomb interaction integral \[ C_{a,b} = \int \int \psi^*_a(r_1)\psi^*_b(r_2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi_a(r_1)\psi_b(r_2) d^3r_1 d^3r_2, \] (3.16) is due to the electrostatic repulsive interaction between the delocalized charge densities $|\psi_a(r_1)|^2$ and $|\psi_b(r_2)|^2$ of the electrons in the orbitals $a$ and $b$. The exchange interaction integral is due to the exchange interaction between the two electrons and given by \[ X_{a,b} = \int \int \psi^*_a(r_1)\psi^*_b(r_2) \frac{e^2}{4\pi\varepsilon_0 r_{12}} \psi_b(r_1)\psi_a(r_2) d^3r_1 d^3r_2. \] (3.17) Thereby, each electron can either be found at position $r_1$ or $r_2$, as an exchange between both electrons can appear, if their orbitals can overlap. Hence, the exchange interaction integral scales with the spatial overlap of the wave functions in the ground state $\psi(r_1)$ and excited state $\psi(r_2)$.

In the triplet state, both electrons have parallel spin. Obeying the Pauli principle, there is a zero probability for the two electrons with the same spin orientation to be located at the same position. Thus, the average distance between the two electrons in the triplet state is larger than in the singlet state with anti-parallel oriented electrons, as they repel each other. In this case, the overall Coulomb interaction energy is lower. The energetically differences for singlet and triplet states with regard to the ground state are given by \[ \Delta E_S = E_b^{\text{LUMO}} - E_a^{\text{HOMO}} + C_{a,b} + X_{a,b} \] (3.18a) \[ \Delta E_T = E_b^{\text{LUMO}} - E_a^{\text{HOMO}} + C_{a,b} - X_{a,b} \] (3.18b) with \[ \Delta E_{ST} = \Delta E_S - \Delta E_T = 2K. \] (3.19) Consequently, the singlet state is less bound by twice the exchange integral $X$ compared to the triplet state. Therefore, the triplet energy is lower compared to the singlet energy as illustrated in Figures 3.5 and 3.7.
3.2.3 Franck-Condon-Principle and Photoluminescence

Optically excited molecules can undergo diverse transitions within the electronic structure of the molecule and finally radiatively relax to their ground state, which is called photoluminescence. Generally, the transition probability $P$ from an initial state $i$ to a final state $f$ is given by

$$P_{i \rightarrow f} \propto |M_{i \rightarrow f}|^2.$$  \hspace{1cm} (3.20)

The probability depends on the matrix dipole moment $M$ and the wave functions of the initial and final state due to Fermi's Golden Rule.

So far, electronic transitions in molecules have been treated in a static potential of the nuclei according to the Born-Oppenheimer approximation. To obtain a detailed description of all transitions in a molecule, besides the electronic contribution ($e$), the vibrational contributions ($v$) and the spin ($s$) have to be considered, too. The rotational portions can be neglected, due to their low energy contribution to the total energy $E$. Consequently, the wavefunction can be written according to

$$\psi = \psi_e \psi_v \psi_s.$$  \hspace{1cm} (3.21)

Transitions between an molecular initial ground state ($e\, v\, s$) and an final excited state ($e'\, v'\, s'$) can be described by the electric dipole transition moment $M$ given by

$$|M_{e\, v\, s \rightarrow e'\, v'\, s'}|^2 = \left| \langle \psi_{e'} \psi_{v'} \psi_{s'} | \mu | \psi_{e} \psi_{v} \psi_{s} \rangle \right|^2$$  \hspace{1cm} (3.22a)

$$= |\mu_{e \rightarrow e'}|^2 \cdot |\langle \psi_{v} | \psi_{v'} \rangle|^2 \cdot |\langle \psi_{s} | \psi_{s'} \rangle|^2,$$  \hspace{1cm} (3.22b)

with

$$\mu = \mu_e + \mu_N.$$  \hspace{1cm} (3.23)

The dipole moment vector of the molecule, composed of the contributions of the electron ($e$) and the nucleus ($N$). As the dipole term for the nucleus $N$ vanishes, the transition only depends on the electron dipole moment. The intensity of an electronic transition $|\mu_{e \rightarrow e'}|^2$ is therefore scaled with the overlap of the vibrational wave functions $\langle \psi_{v} | \psi_{v'} \rangle$, which is also called Franck-Condon-factor. Consequently, the probability is higher for transitions between vibrational states ($v\rightarrow v'$), whose wave functions is similar. This is the case, if both wave function amplitudes are maximum as schematically illustrated in the Franck-Condon-Diagram (cf. Figure 3.5).

The different possible transitions in an organic molecule are discussed in the following paragraphs. The singlet states are denoted with $S_i$ and the triplet states are denoted with $T_i$ as usual.
Absorption

Via absorption of an adequate amount of energy $h\nu$, the molecule is excited from the electronic and vibrational ground state ($S_0$, $v=0$) to an vibrational sub-level of an higher electronic state ($S_1$, $v=j$). Optical excitations from ground to triplet states are forbidden due to the different spin states. In the following, there are generally two possible radiative processes.

Fluorescence

If the molecule exclusively emits from the excited singlet state, conserving the spin during transitions, the process is called fluorescence ($S_1 \rightarrow S_0 + h\nu_{fl}$). After the absorption process, the excited molecule non-radiatively relaxes onto the vibrational ground state of the electronic excited state ($S_1$, $v'=0$) via vibrational relaxation due to the Kasha-rule that allows radiative transitions only from the lowest vibrational state of the excited state. After a typical lifetime of $10^{-9}$-10$^{-6}$ s [48], the relaxation to the lowest vibrational state is followed by the radiative transition back to the electrical

---

**Figure 3.5:** Franck-Condon-Diagram illustrating the various transitions in an organic molecule. Due to absorption of energy $h\nu$ one electron is lifted into the excited singlet state $S_1$ and can relax into the ground state $S_0$ via fluorescence.
3.2 Optical Properties of Organic Molecules

Figure 3.6: Absorption and fluorescence of an organic dye between ground state $S_0$ and excited state $S_1$. The fluorescence spectra is red-shifted (stokes-shift) and mirror-inverted compared to the absorption spectrum. The vibronic bands ($i-j$) indicate the transitions between the vibrational levels.

ground state ($S_0$). Thereby, the transition occurs again upright in the Franck-Condon-Diagram (cf. Figure 3.5), ending up in a higher vibrational state $v>0$. In a last step, the molecule relaxes back on the ground state ($S_0$, $v=0$) via vibrational conversion. As Figure 3.6 reveals, the fluorescence emission spectra is usually red-shifted (Stokes shift) compared to the absorption spectra of the molecule, because of the energy loss due to the relaxation processes. In solution or weakly doped films, the vibronic bands can be well detected, whereas in amorphous layers these bands are usually fused to a broad spectrum.

Inter-System-Crossing and Phosphorescence

Generally, the spin has to be conserved during all transitions, as the transition intensity scales with the spin-factor $\langle \psi_s | \psi_{s'} \rangle$ in Equation (3.22b). Consequently, transitions between singlet and triplet states are prohibited. However, this rule can be weakened due to spin-orbit-coupling, which leads to non-radiative inter-system-crossing (ISC) be-
tween excited singlet and triplet states. In organic molecules with incorporated heavy metals like platinum (Pt) or Iridium (Ir), this ISC-process is possible due to metal to ligand charge transfer. As a consequence, the molecule emits from the triplet state, which is called phosphorescence \( (T_1 \rightarrow S_0 + h\nu_{\text{phos}}) \). This transition is usually slower with a rate constant of about \( 10^{-2} - 10^6 \text{s}^{-1} \) compared to fluorescence.

As the excitation of singlet states can be easily transferred to triplet states, these phosphorescent materials can harvest emission from both singlet and triplet states. In organic light-emitting devices, where the singlet and triplet states are electrically excited with a ratio of 1:3, an internal quantum efficiency close to 100% can thereby be reach, which is four times higher compared to simple fluorescent emitters with only 25% (cf. Subsection 4.2).

**Internal Conversion**

However, transitions from excited states must not necessarily be radiative. They can also occur non-radiatively by internal conversion, e.g. caused by absorption processes. Thereby, the total quantum yield \( \Phi_q \) of luminescence will be lowered, according to

\[
\Phi_q = \frac{k_r}{k_r + k_{nr}},
\]

with \( k_r \) and \( k_{nr} \) the radiative and non-radiative transition rate, respectively.

In the diagram in Figure 3.7, the dynamics of excited molecular states are summarized including all relevant radiative and non-radiative transitions

### 3.3 Molecular Semiconducting Solids

A large number of single small organic molecules with saturated \( \pi \)-bonds are forming an organic semiconducting molecular solid. With regard to the internal arrangement of the molecules in the system, the range of possible morphologies spans from highly ordered organic crystals to disordered amorphous films. The molecules are bound by weak intermolecular van-der-Waals bonds, compared to inorganic semiconductors, which exclusively feature covalent and ionic bonds. As a consequence of these short-range bonds, the electrical as well as optical properties of the solids are still determined by the individual single molecules. The next section briefly discusses the electronic characteristics of organic solids concerning band structure, polarization effects as well as mobility and transport.
Figure 3.7: Jablonski diagram summarizing the most important radiative and non-radiative transitions within an excited molecule [49].
3.3.1 Electronic Band Structure

The formation of the electronic band structure of an organic solid, starting with the basic atomic brick, is illustrated in Figure 3.8 [50]. As already shown in Subsection 3.1.2, molecules are formed by single atoms, which can be described by electrons in atomic orbitals within a Coulombic potential well caused by the atomic nucleus, as shown in Figure 3.8a. In a polyatomic molecule, the effective potential well is formed by the atomic nuclei and the other electrons. As Figure 3.8b illustrates, the potential wells of each nuclei within the molecule are merged in the upper part to form a broad quantum well. Thereby, the upper atomic orbitals of the single atoms interact to compose delocalized molecular orbitals, whose outermost horizontal part of the potential well is again the vacuum level with energy $E_{\text{vac}}$. A combination of multiple single molecules, brought together to form a molecular solid, is shown in Figure 3.8c. As single electrons are strongly bound to their particular molecule, which only interact by weak van der Waals interactions, the molecular orbitals are still localized at each molecule. Therefore, the validity of the usual band theory assuming an unhindered transport of electrons is limited, as the electrons have to overcome the potential barrier and thereby move by hopping from molecule to molecule (see Subsection 3.3.3). Thus, the situation in Figure 3.8c is often simplified to a model system shown in Figure 3.8d. Here, also the Fermi level $E_F$ is indicated.

![Diagram](image-url)

**Figure 3.8:** Formation of the electronic band structure of molecular solids [50]. Based on single atoms (a), polyatomic molecules (b) and finally molecular solids (c) are formed, whose narrow bands are simplified to a model system (d).
3.3.2 Polarization Effects

So far, only neutral molecules (cf. Figure 3.9a) have been considered, when talking about organic molecular solids. However, the energy levels of the molecules will change, if charge carriers are injected into the solid. An electron brought or removed from the outside into the molecule, will always lead to deformations and redistributions within the electronic structure of the molecule, as there are various electron-electron interactions. This self-polarization of the molecule lowers the HOMO and LUMO energy levels of the neutral molecule within the solid as shown in Figure 3.9b. The localized positively or negatively charged isolated molecule within the solid will further interact with its surrounding neutral neighbors by polarizing their electron orbitals and inducing dipole moments. This weak intermolecular effect is called electrical polarization and is shown in Figure 3.10. Due to the fast electronic polarization process \(10^{-16} - 10^{-15}\) s [51], the polarization cloud follows the charge carrier and forms a quasi-particle, the polaron. The polarization energy \(P_{e,h}\) between the charge \(i\) and the induced dipole moment \(\mu\) can be estimated by

\[
P_{i \rightarrow \mu} \propto \sum_{m=1}^{N} \frac{e^2 \alpha}{2r_m^4},
\]

where \(\alpha\) denotes the average isotropic polarization and \(r_m\) the distance between the charge and the effected molecule \(m\) [48]. In aromatic hetero-cyclic molecular crystals, this energy \(P_{e,h}\) is in the range of \(1.5-2\) eV [51] and stabilizes the charged molecule energetically with respect to the energy levels of the isolated molecule (cf. Figure 3.9c).

\[\text{Figure 3.9: Diagram illustrating the energy levels of (a) a neutral molecule and a charged molecule, showing the effect of (b) self-polarization and (c) electrical polarization, induced by additionally inserted charge carriers.}\]
Figure 3.10: Electrical polarization of molecular crystals by a localized positive charge carrier \(i\) at the molecule \(m^*\) forming a polaron, which is manifested by spatial dislocated \(\pi\)-systems of the molecules \(m_{1,2}\) surrounding the charge. The distance between the charge \(i\) and the effected molecule \(m\) is denoted by \(r_m\), and \(\mu\) describes the induced dipole moment, after [51].

Thereby, the energy levels of the molecular ensemble are changed. The LUMO energy level is lowered by \(P^-\) for a negative inserted charge carrier and the HOMO energy level is increased by \(P^+\) for a positive inserted charge carrier.

As the ionization potential (IP) describes the energy, which is necessary to remove one electron from a molecule, the IP can be presumed to be equal to the resulting HOMO energy \(E^{\text{HOMO}}\) (Koopmans theorem [52]). Analogous, the energy of the LUMO \(E^{\text{LUMO}}\) is equal to the electron affinity (EA), which defines the energy that is gained, when an electron is added to the molecule. Therefore, the terms IP and HOMO as well as EA and LUMO are usually used synonymously, respectively. Both IP and EA can be measured via ultraviolet photoelectron spectroscopy (UPS) and X-ray photoelectron spectroscopy (XPS).

The arising levels \(E_h\) and \(E_e\) for positive and negative charge carriers form band-like charge transport states, whose energy difference is called electrical transport gap \(E_{\text{gap}}^{\text{el}}\). Due to statistically changed molecular distances (e.g. caused by disorder or vibrations), the levels are weakly broadened, hence, affecting the polarization energy \(P\), that scales with the distance between charge and molecule.

### 3.3.3 Charge Carrier Transport and Mobility

Generally, the transport of charge carriers in an arbitrary material in the presence of an external electric field \(\vec{E}\) can be described by the ohmic law according to

\[
\vec{j} = \sigma \vec{E},
\]

(3.26)
3.3 Molecular Semiconducting Solids

Figure 3.11: Density of transport states in an organic layer. The transport levels show a Gaussian distribution of density of states. Furthermore, traps states can be aroused by material impurities.

where the tensor $\tilde{\sigma}$ denotes the electrical conductivity of the material. For isotropic materials, the conductivity does not depend on the transport direction and can consequently be described via

$$\sigma = e n \mu,$$

(3.27)

with $e$ the electron charge, $n$ the charge carrier density, and $\mu$ the charge carrier mobility.

The transport mechanism is strongly dependent on the degree of order in the material. For organic semiconductors, therefore, two extreme cases can occur. For highly purified molecular crystals at not too high temperatures, band transport can be observed. Due to the reduced intermolecular overlap of the $\pi$-systems in organic crystals, these bands are narrow with a dimension of about 200-400 meV. However, the mobility at about $1 \text{ cm}^2 (\text{Vs})^{-1}$ [44] is relatively low compared to inorganic semiconductors ($\mu_{\text{inorg}} > 1000 \text{ cm}^2 (\text{Vs})^{-1}$) [53], which show ideal band transport based on Bloch-waves. In the other case of highly disordered amorphous layers, as they are usually used for the realization of light emitting devices, the mobility of charge carriers is some magnitudes lower in the range of $10^{-5} < \mu_{\text{am}} \ll 1 \text{ cm}^2 (\text{Vs})^{-1}$ [40, 43]. This results from the specific charge carrier transport in amorphous organic solids, which is realized by sequential hopping between localized states [54]. As the polarization energies $P_{\text{eh}}$ statistically fluctuate around a fixed value (cf. Subsection 3.3.2), one has to see the transport level as a accumulation of statistically spread states, which show a Gaussian distribution density of energy states (DOS), as it is schematically illustrated in Figure 3.11.
The mobility in amorphous solids is thermally activated and further depends on the electric field $E$ according to

$$\mu_{am}(E, T) \propto e^{-\frac{\Delta E}{k_B T}} e^{\frac{\beta E}{k_B T}}, \quad (3.28)$$

with $\Delta E$ the activation energy, $k_B$ the Boltzmann factor, and $\beta$ the field activation parameter [43], which is related to the disorder or level spread [55]. The typical width of the hopping states is in the range of 80-120 meV. However, the transport can also be constricted by trap states ($E_{trap}$) in between the transport level for holes ($E_h$) and electrons ($E_e$). They arise from chemical impurities in the materials or structural defects, but can be minimized by repeated material sublimation.

Furthermore, the amplitude of the current depends on the intrinsic charge carrier density $n_i$, which is given by the effective density of states $N_0$ and the transport gap $E^{el}$ via [43]

$$n_i = N_0 e^{-\frac{E_{gap}}{k_B T}}. \quad (3.29)$$

Using typical values for organic semiconductor materials of $E_{gap}^{el} = 2.5$ eV as well as $N_0 = 10^{21}$ cm$^{-3}$, a density of $n_i^{org}=1$ cm$^{-3}$ can be calculated for room temperature. This is indeed quite unrealistic and impurities will usually lead to much higher values. Compared to inorganic semiconductors with a calculated density of $n_i^{inorg}=10^{10}$ cm$^{-3}$ for $N_0=10^{19}$ cm$^{-3}$ and $E_{gap}^{el}=1.12$ eV, the current density of organic materials is still very low. However, the charge carrier density can be increased drastically by doping of organic layer, which will be discussed in Section 4.1.1.

For ohmic contacts adjacent to disordered undoped amorphous layers, the current is limited by space charges (SCLC: space charge limited current) that build up near the injection contacts and further hinder injection. The current density for most commonly used organic materials can therefore be approximately described by the Mott-Gurney equation (Child’s law) [48]

$$j_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu U^2 \frac{d^3}{dU^3}, \quad (3.30)$$

with $\varepsilon_0 \varepsilon_r$, the permittivity of the organic material, $U$ the applied voltage, and $d$ the thickness of the organic layer.

### 3.4 Optical Processes in Organic Solids

The optical processes in organic solids are strongly influenced by the properties of the single organic molecules. Besides optical excitation already discussed in Section 3.2, molecules can also be excited electrically. This excitation requires an oppo-
sitled charged pair of charge carriers. Radiation resulting from this kind of excitation is called electroluminescence, which is however very similar to photoluminescence. The generation of electroluminescence, the diverse transport mechanisms, and excitonic processes are discussed in the next subsections.

### 3.4.1 Excitons and Electroluminescence

As already stated in Subsection 3.2.1, the excitation of molecules can also be performed electrically by two charge carriers, which have been injected into the molecular solid. When these oppositely charged charge carriers, a hole and an electron, meet on a molecule within the organic solid, they form a quasi-particle, which is called exciton. The electron-hole pair is bound by electrostatic Coulomb attraction with the energy

\[ E_{\text{coul}} = \frac{1}{4\pi\varepsilon_0} \frac{q_e q_h}{r}, \]

with \( \varepsilon_0 \) the electric field constant, \( r \) the charge carrier distance, and \( q_e, q_h \) the charge of the electron and hole, respectively. Due to the weak intermolecular van der Waals forces in molecular solids, the excitons are strongly localized on a single molecule and called Frenkel excitons. The average spatial distance of electron and hole for Frenkel excitons, though, is in the range of the molecular dimension (<5 Å) with binding energies of about 0.5-1 eV [40] (see Figure 3.12a). They have to be distinguished from Mott-Wannier exciton, which usually appear in inorganic solids and have a quite large electron-hole radius of up to 10 nm and weak binding energies in the meV range (cf. Figure 3.12c). For the sake of completeness, the intermediate exciton type, the charge-transfer exciton, is depicted in Figure 3.12b. This exciton has an electron-hole radius

---

**Figure 3.12:** Illustration of (a) a Frenkel exciton, (b) a Charge-transfer exciton, and (c) a Mott-Wannier exciton. Whereas a Frenkel exciton is strongly bound on a molecule, a Wannier-Mott exciton can move freely through a highly ordered solid. The Charge-Transfer exciton describes the intermediate case.
and a binding energy between the two previously mentioned exciton types. A Charge-transfer exciton is neutral but polarized, as it is formed by two opposite charges located on two neighboring molecules, which form a pair of molecular ions.

The formation and decay of a Frenkel exciton in an amorphous solid is illustrated in Figure 3.13. Both oppositely charged carriers are transported on their energy levels \( E_e \) and \( E_h \) in the solid with an energetically distance of the transport gap \( \Delta E^\text{el}_{\text{gap}} \) depicted in Figure 3.13a. When an electron meets a hole an exciton is formed, while their energetic position is modified due to the Coulomb attraction between both charge carriers. Within the energy diagram of the excitation, the electron is lifted in a single or triplet excited state, whereas the hole remains on the ground state (cf. Figure 3.13b). This results in the so called optical gap with the energy \( \Delta E^\text{opt}_{\text{gap}} \), which is about 0-1.5 eV [56] lower compared to the transport gap \( \Delta E^\text{el}_{\text{gap}} \), previously discussed in Subsection 3.3.2. By a decay of the electrically generated exciton, electroluminescence is produced, which shows analogous properties compared to the optically excited photoluminescence. However, as both charge carriers are injected with statistically oriented spin, the ratio of singlet and triplet excitons formed by recombination is one quarter to three quarters, respectively (cf. Figure 3.13c). This is contrary to optical excitation, where only singlet states can be externally excited and phosphorescence can only be detected after inter-system-crossing processes. Consequently, up to 100 % phosphorescence can be detected, if the emission material is properly chosen to show high inter-system-crossing rates in which singlet states are additionally transferred to triplet states.

### 3.4.2 Energy Transfer Mechanisms in Organic Solids

Energy transfer in organic solids from one excited molecule (donor, \( D^* \)) to another molecule (acceptor, A) is implemented by different transfer mechanisms called trivial
reabsorption, Förster-transfer, and Dexter-transfer. These mechanisms are essential for organic light emitting diodes based on host-guest systems and shall be briefly explained in the following paragraphs.

### Photon Re-Absorption

The significant precondition for reabsorption is the spectral overlap of the emission spectrum of the donor molecule (D) with the absorption spectrum of the acceptor (A). Within the trivial emission-absorption process of a photon with the energy $h\nu$, the excitation energy can efficiently be transferred from the excited matrix molecule $D^*$ onto the emission molecule A, according to

$$D^* \rightarrow D + h\nu \quad \text{and}$$

$$A + h\nu \rightarrow D^*.$$ (3.32a)

Thus, this two step process has a large radius of operation of more than 10 nm [40]. Due to the Stokes-shift, this process is weak in organic molecules.

### Förster-Transfer

The non-radiative and single-step resonant Förster Transfer (cf. Figure 3.14a) also depends on an overlap between absorption spectrum of acceptor A and the emission spectrum of the donor D. This long-range transfer with distances of 5-10 nm [57] is based on a dipole-dipole interaction of donor and acceptor, according to

$$D^*_S + A_S \rightarrow D_S + A^*_S$$ (3.33a)

$$D^*_T + A_T \rightarrow D_T + A^*_T.$$ (3.33b)

During the transition, the spin of each molecule has to be conserved.

### Dexter-Transfer

Dexter transfer (see Figure 3.14b) is induced by an overlap of donor- and acceptor-orbitals, allowing a direct electron exchange between both participating molecules D and A [58] via

$$D^*_S + A_S \rightarrow D_S + A^*_S$$ (3.34a)

$$D^*_T + A_S \rightarrow D_S + A^*_T.$$ (3.34b)
Due to the spatially limited orbitals, this transfer mechanism is of short range order (< 1 nm [57]) but allows for singlet-singlet as well as triplet-triplet transfer, that can occur via exchange interactions. However, the total spin has to be conserved for the whole system.

### 3.4.3 Excitonic Processes in Molecular Solids

The following paragraphs give a short overview over the concept of exciton diffusion and summarize the various quenching processes of excitons.

**Exciton Diffusion**

Excitons can randomly move through organic materials via hopping from molecule to molecule by Förster or Dexter transfer, despite their strong localization on a single molecule [59]. The diffusion of excitons in a continuous medium can be described by Fick’s second law, where the change in exciton density over time is caused by a concentration gradient. In one dimension, the exciton diffusion equation can be written as

\[
\frac{\partial n}{\partial t} = G(z, t) - \frac{n}{\tau} - Q(n, z, t) + D \frac{\partial^2 n}{\partial z^2} \quad (3.35)
\]

including the exciton generation rate \( G \), the exciton decay rate \( n \tau^{-1} \), the exciton quenching rate \( Q \) and the diffusion coefficient \( D \). Thereby, \( \tau \) denotes the effective exciton lifetime considering radiative and non-radiative decay. In stacked organic layers one can
3.4 Optical Processes in Organic Solids

assume the exciton generation to be located at the interface of two layers, which are a blocking layer and the emission layer in pin-OLEDs (cf. Subsection 4.3.1). Therefore, the exciton density profile can be approximated by

\[ n = n_0 e^{-\frac{z}{L_D}} \]  

with

\[ L_D = \sqrt{D\tau}, \]  

where \( n_0 \) denotes the exciton density at the generation interface, \( z \) the direction perpendicular to the stacked layer, and \( L_D \) the diffusion length. Typically exciton diffusion lengths in molecular crystals are in the range of 0.1-10 \( \mu \)m [48], but are strongly reduced for high current densities due to triplet-triplet annihilation, which is explained in the following.

**Exciton Quenching**

Excitons can be quenched by triplet-triplet annihilation (TTA), singlet-triplet annihilation, singlet-singlet annihilation, or triplet-polaron annihilation. Triplet-triplet annihilation of two triplet excitons is caused by high concentrations of generated exciton triplet states, which is a result of the long lifetime of triplet excitons. This process occurs via the reaction paths

\[ T_1 + T_1 \rightarrow S_0 + S_n \rightarrow S_1 \quad \text{(delayed fluorescence)} \]  
\[ T_1 + T_1 \rightarrow S_0 + T_n \rightarrow T_1 \quad \text{(phosphorescence quenching),} \]  

where \( S_n \) or \( T_n \) denote a higher lying singlet and triplet state and \( S_1 \) and \( T_1 \) denote the first excited singlet and triplet state, respectively. In this process, one triplet exciton transfers its energy to another triplet exciton. Thereby, it relaxes to the ground state and leaves either an excited singlet or triplet state. This leads to reduced light emission, but can be hindered by spatial separation of emission molecules in host materials. Beyond TTA also singlet-triplet annihilation (STA) or singlet-singlet annihilation (SSA) can be detected, according the following paths:

\[ S_1 + T_1 \rightarrow S_0 + T_n \quad \text{(fluorescence quenching)} \]  
\[ S_1 + S_1 \rightarrow S_n^* + S_0 \rightarrow S_0 + h\nu \]  
\[ \rightarrow e^- + h^+ \quad \text{(electron-hole formation).} \]  

In the first process, the fluorescence is quenched by a relaxation of the excited singlet state into the ground state leaving an excited triplet state. In the second case, the excited state \( S_n^* \) can either decay back to the ground state giving off light or generate a pair of charge carriers.
4 Physics of Organic Light-Emitting Devices

This chapter deals with the physics of organic light-emitting devices concerning their electrical, structural, and optical character. The first section highlights the concept of electrical doping of transport layer as well as the charge carrier injection from the electrodes, which is required to fabricate OLEDs driven at low voltage. The next section gives an overview over the multiple factors influencing the external quantum efficiency of an OLED. Furthermore, different OLED structures are introduced starting with the general working principle of an organic layer system with one or more organic layers. Subsequently, the various OLED layer architectures are briefly addressed with special regard to white light emission. The fourth section deals with the optical properties of light-emitting diodes. After introducing the basic principles including dipole radiation and multilayer structures, special attention is drawn on microcavities and their effects on organic light-emitting diodes. Further, the outcoupling is addressed for bottom- and top-emitting OLEDs, introducing the concept of the dielectric capping layer.

4.1 Electrical Properties

Electrical doping of organic layers – similar to doping in inorganic semiconductors – as well as the improvement of charge carrier injection due to doped injection layers play a significant role in the development of organic devices with low driving voltages. Therefore, this technique is briefly discussed in the following.
4.1.1 Electrical Doping

In order to enhance the charge carrier density and reduce the voltage drop, organic materials can be effectively doped with acceptor and donor molecules [6, 61]. Comparable to their inorganic counterpart, the material is thereby systematically doped with molecules, which provide free charge carrier. For achieving p-type doping, acceptor molecules are mixed into the host matrix, where the LUMO of the guest has to be close to the HOMO of the host molecules (see Figure 4.1a).

The transfer of an electron from the HOMO of a host molecule to the LUMO of the guest molecule is energetically favorable and leads to a fixed negative charged guest molecule $A^-$ and a hole on the HOMO of the host material, which are assumed to be able to move freely through the film by a rearrangement of electrons.

For n-type doping, guest molecules with a HOMO level near the LUMO level of the host materials are chosen, enabling an electron transfer from the HOMO of the donor to the LUMO of the host molecules (cf. Figure 4.1b). Thereby a positive charged guest molecule is left and an additional free electron is gained for charge carrier transport. However, the material remains neutral in both cases with

\[
\begin{align*}
    p &= n + N_{A^-} \quad \text{(p-type doping)} \\
    n &= p + N_{D^+} \quad \text{(n-type doping)}.
\end{align*}
\]

Figure 4.1: Schematical illustration of (a) p-type and (b) n-type doping.
As a consequence of doping, the number of charge carriers is drastically increased, which leads to an improved conductivity \( \sigma > 10^{-6} \text{ S cm}^{-1} \) \([61, 63]\) and improved charge carrier injection, which is discussed in the following subsection. Further, the current through the layer is no longer limited by space charges. As the organic layer shows a quasi-ohmic behavior with \( j \propto U d^{-1} \), the driving current is only weakly dependent on the thickness of the doped layers. This leads to a lower voltage drop over the organic layer and allows to optically optimize the layer thicknesses without adverse electrical effects.

### 4.1.2 Charge Carrier Injection

The charge carrier injection from the electrodes into the organic layers demands electrode work functions \( \Phi_w \) close to the HOMO level for injection of holes and close to the LUMO level for injection of electrons. Due to the barrier height for charge carriers into intrinsic organic materials, this injection indeed is limited. However, a further advantage of doped transport layer arises in the improved injection from metal electrodes into the organic layer as it is shown in Figure 4.2, comparing the metal/organic interfaces for undoped and doped organic transport layer. In the undoped case, charge carrier from the metal cannot be easily injected into the organics because of the high energy barrier. Due to doping, a thin depletion region is formed at the interface to the metal with a thickness \( d \) of some nanometers \([64]\) depending on the dopant concentration \( N_{A/D} \propto N_{A/D}^{-1/2} \). Thereby, the transport energy levels are bent, which at high doping concentrations allows for efficient charge carrier tunneling into the organic layer and leads to a reduced voltage drop at the contact.

### 4.2 Electroluminescence Efficiency

Light generation of an OLED device results from various processes, where each involved process contributes with a special efficiency. Therefore, the external quantum efficiency (EQE) \( \eta_{\text{eqe}} \), which is one of the main parameters for light emitting devices, is a combination of several terms according to the following Equation \([65]\):

\[
\eta_{\text{eqe}} = \eta_{\text{iqe}} \cdot \eta_{\text{out}} = \gamma_{e,h} \cdot \xi_{S/T} \cdot \Phi_{\text{fl/ph}}^{\text{r}} \cdot \eta_{\text{out}}. \tag{4.3}
\]

Thus, the external quantum efficiency is composed of the internal quantum efficiency (IQE) \( \eta_{\text{iqe}} \) – formed by the charge-balance-factor \( \gamma_{e,h} \), the singlet-triplet-ratio \( \xi_{S/T} \), and the radiative quantum yield \( \Phi_{\text{fl/ph}}^{\text{r}} \) – and the outcoupling efficiency \( \eta_{\text{out}} \). The contribution factors are explained in the following and are schematically illustrated in Figure 4.3.
Figure 4.2: Charge carrier injection of (a) holes and (b) electrons from a metal M in (i) an undoped and (ii) a doped organic organic layer O. $\phi_w^M$ denotes the work function of the metal.

Figure 4.3: Flowchart of the contributions to electroluminescence of an OLED device. The transfer yields of the various steps in the light generation process determine the external quantum efficiency [66].
The charge-balance-factor $\gamma_{e,h} (\leq 1)$ describes the ratio of injected holes and electrons which recombine in the emission layer. It thereby depends on the electrical transport properties of the device. For an electrically balanced OLED the hole and electron current is equal to one. To ensure preferably high $\gamma$-values, equal and barrier-free injection of holes and electrons from both contacts as well as a confinement of charge carriers within the emission zone by blocking layers is required. The structural development of an OLED in order to achieve these conditions, will be discussed in Section 4.3.1. However, in multilayer devices the different transport properties of each material can lead to lower values.

Whereas optical excitation can only form singlet excitons, as the direct excitation from the ground state $S_0$ to an upper triplet state $T_n$ is spin-forbidden, electrically generated excitons can be both singlets or triplets. Thereby, the singlet-triplet ratio $\xi_{S/T}$ for the generated excitons is determined by spin statistics and turns out to be $\xi_S = 25\%$ for singlet and $\xi_T = 75\%$ for triplet states.

The intrinsic radiative efficiency $\Phi_{r,fl/ph}$ depends on the emitting material and is defined as the ratio of radiative recombination rate $k_r$ to the total recombination rate, including both radiative and non-radiative processes, according to

$$\Phi_r = \frac{k_r}{k_r + k_{nr}}.$$  

The radiative efficiency $\Phi_r$ can experimentally be measured via photoluminescence experiments, as it corresponds to the PL quantum yield

$$\Phi_t = \Phi_{PL} = \frac{\text{number of emitted photons}}{\text{number of absorbed photons}}.$$  

Generally, both fluorescent and phosphorescent materials can reach a yield of 100% with the assumption of no non-radiative processes at all [67, 68]. In fluorescent emitter materials, only singlet excitons can decay radiatively with an efficiency of $\Phi_{r,fl}$. However, there are also non-radiative decay rates ($\Phi_{nr,fl}$) as well as energy transfer via intersystem-crossing ($\eta_{isc}$) to triplet states. To enhance the overall efficiency, phosphorescent materials have been optimized for radiative triplet emission $\Phi_{r,ph}$ keeping the non-radiative rates $\Phi_{nr,ph}$ very low. Hereby, the spin-orbit-coupling is enhanced by the presence of heavy metal atoms like iridium (Ir) or platinum (Pt). Further, singlet excitons can be harvested to the triplet level due to high inter-system-crossing rates $\eta_{isc}$.

Considering the charge-balance-factor, the singlet-triplet ratio, and the intrinsic radiative efficiency, this results in an maximum internal quantum efficiency of 25% for fluorescent emitter materials and up to 100% for phosphorescent emitter materials.

Finally, due to total reflection and further power losses, generated radiation can only partially escape to air. The outcoupled fraction is given by the outcoupling efficiency.
\( \eta_{\text{out}} \), which is defined as the total number of outcoupled photons to the total number of photons emitted inside the cavity. This term strongly depends on the optical architecture of the device (cf. Section 4.4) and will be discussed in Subsection 4.4.2.

### 4.3 OLED Structures

This section gives a brief overview on the basic OLED working principle and the different device structures of organic light emitting diodes. The possible materials for electrodes and organic materials are listed in Subsection 5.2.

#### 4.3.1 General Working Principle

The general working principle of OLEDs is exemplary explained by different device structures, starting with the most simple one. The last paragraph is especially devoted to the emission layer, as it plays a special role in organic light emitting devices.

**Simple Single-Layer OLEDs**

The most simple possible device structure of OLEDs is realized by one organic layer sandwiched between two electrodes as it is schematically depicted in Figure 4.4. Positive and negative charge carriers are injected from both electrodes into the organic layer.

![Figure 4.4: Simple single-layer device under forward bias U. \( E_{\text{vac}} \) is the vacuum energy and the work functions of anode and cathode are denoted by \( \Phi^A \) and \( \Phi^C \), respectively.](image)
They approach each other by moving along their energy levels (HOMO/LUMO level) driven by the internal electric field and meet to recombine within a spatial confined recombination zone. The recombination of electrons and holes generates excitons, which preferentially decay radiatively to produce light. The position of the recombination zone depends on the mobilities of the carrier types for the organic material. It has to be chosen carefully to show approximately the same transport properties for both carrier types, preventing reduced efficiency for recombination near the electrodes. The decay of excitons within the recombination zone generates photons, which are emitted isotropically. These photons are then either reflected at the highly reflecting electrodes or transmitted through sufficiently transparent electrodes. To prevent internal absorption of photons, especially in thick transport layers, the transport materials have to be chosen adequately and usually exhibit large band gaps.

**Double- and Triple-Layer OLEDs**

However, there is usually no material, which fulfills the requirement for transporting both types of charge carriers. Therefore, two different materials have to be chosen for electron and hole conduction, forming a double layer device with hole transport layer (HTL) and electron transport layer (ETL) (see Figure 4.5a). This was first shown by Tang et al. [4], who used a hole transport layer in combination with a combined electron transporting and emission layer (EML/ETL). Due to the high LUMO of the hole transport layer, electrons face an energy barrier that prevents their penetration into the HTL. They accumulate at the interface and recombine with holes, which can easily overcome the low HOMO barrier of the EML/ETL. The recombination zone is therefore confined to the interface and can be placed in the middle of the layer stack, thereby electrons are no longer quenched at the anode.

By splitting the EML/ETL layer into two individual layers (cf. Figure 4.5b), the transport of holes into the ETL is further inhibited due to a low HOMO level of the ETL. The recombination zone can thus be efficiently confined to the emission layer, whose material can be chosen for different emission wavelengths (see Subsection 4.3.1), but always has to assure adequate HOMO and LUMO energy levels for sufficient charge carrier injection from the neighboring layers.

**pin OLEDs**

In order to enhance the charge carrier injection from both electrodes, the concept of electrical doping – already discussed in Subsection 4.1.1 – is employed in pin-devices. Here, both hole and electron transport layer are doped, thereby decreasing the driving voltage and improving the efficiency of the devices. The emission layer in between, however, remains undoped as dopants represent non-radiative recombination centers.
Figure 4.5: Double-layer device (a) and triple-layer device (b) under forward bias \( U \). \( E_{\text{vac}} \) is the vacuum energy and the work functions of anode and cathode are denoted by \( \phi_w^A \) and \( \phi_w^C \), respectively.

For hole and electron transport layers usually high gap materials are chosen, to inhibit light absorption within the OLED stack. To furthermore enhance the efficiency of the pin stack, two additional layers are inserted between the emission layer and the transport layers (cf. Figure 4.6). These blocking layers confine both charge carriers and excitons to the emission layer. On the one hand, the energy barrier between EML and blocking layer and/or the mobilities of the blocking layer have to be properly chosen in each charge carrier case. On the other hand, the singlet as well as the triplet energy level of the blocker materials have to be above the level of the emitting material. Thereby, exciton quenching in the transport layer is avoided, as especially triplet excitons usually show long diffusion length. Depending on the charge carrier transport properties of the emission layer, the recombination is fixed on one side of the emission layer at the interface to the blocking layer and the oppositely charged carriers will not reach the other blocking layer. To keep the voltage drop across the intrinsic layers low, the layers as a whole (EBL + EML + HBL) are very thin (< 25 nm).

In some devices applying both fluorescent as well as phosphorescent emission layer, a separation of the emission layer is further advantageous to avoid the diffusion of fluorescent blue excitons into phosphorescent layers and thus hinder exciton quenching. Therefore, an ambipolar interlayer has to be inserted between phosphorescent and fluorescent emission layers, which effectively blocks excitons by higher singlet and triplet energy level but is permeable for charge carrier transport.
4.3 OLED Structures

Figure 4.6: Pin-device with additional blocking layers under forward bias. $E_{\text{vac}}$ is the vacuum energy and the work functions of anode and cathode are denoted by $\Phi^A_w$ and $\Phi^C_w$, respectively.

Emission Layer

The emission layer can either be made of bulk dye material or it can consist of a host-guest system of a dye and a suitable matrix material. In the first case the luminescence efficiency is limited as non-radiatively decay paths appear due to impurities or quenching. Further, some dye materials cannot be used as bulk layers as they would form aggregates leading to a drop in efficiency [69]. Therefore, most dyes have to be doped into matrix materials to sufficiently separate the dye molecules and hinder dye aggregations. The matrix material has to be chosen to allow sufficient energy Förster transfer (see Subsection 3.4.2) to the dye. The dye molecule can hence be excited either by energy transfer from the matrix molecule, where electron and hole recombine to form excitons, or by trapping charge carriers that directly excite the dye via recombination with the opposite charged carrier. Depending on the dye concentration in the host material, the emission wavelength is slightly red shifted with higher concentrations [70], which is due to polarisation effects arising from agglomerated molecules, whose emission frequency is decreased.

4.3.2 OLED Architectures

OLEDs can be produced with different optical and electrical designs, depending on the arrangement and the choice of electrode materials as well as with respect to the choice of substrate types. Especially for white light generation several architectures have been
developed. In the following a short overview over the various possibilities is given, starting with the general OLED architectures.

**General Architectures**

To efficiently couple out light from the OLED layers, at least one electrode contact has to be semitransparent or fully transparent. Generally, one can distinguish between three possible types of devices, which are schematically depicted in Figure 4.7.

In bottom-emitting devices, light is transmitted through the bottom contact (see Figure 4.7a), which forms the anode in pin devices and is directly grown on the transparent substrate. Usually, indium tin oxide (ITO) is chosen as bottom-electrode material as it exhibits high transmission. However, also transparent and adequate conducting polymer films [71] as well as thin semitransparent Ag layers can be used, latter showing microcavity effects depending on the silver thickness (cf. Subsection 4.4.1). The top contact is commonly formed by a thick highly reflecting aluminum or silver layer. The device efficiency can be enhanced, if additional outcoupling structures are applied on top of the surface or a combination of high index substrate with outcoupling structures is used. Thereby, trapped light modes within the substrate can additionally be coupled out. However, due to the highly reflecting top-electrode, bottom-emitting devices are bound to transparent substrates like e.g. glass. This limits possible applications, as low-cost opaque substrates cannot be an alternative and in most cases the quite expensive ITO has to be used as bottom-electrode.

**Figure 4.7:** Schematical illustration of (a) a bottom-emitting, (2) a top-emitting, and (3) a transparent OLED device.
In contrary, top-emitting structures are not restricted to special substrate types, as the bottom contact is realized by a highly reflecting material. Therefore, all types of substrates can be used, from transparent to opaque substrates also including flexible ones. Hence, a large spectrum of possible low-cost and easy-processable fabrication methods like roll-to-roll production of large area devices can be provided. To adequately couple out light from top-emitting devices, the top contact has to be transmissive, for which either ITO or thin metal layers can be used. Conductive electrodes, which are usually spin-coated on the substrate from the liquid phase, will dissolve adjacent organic layers. As ITO is deposited on top of the layer stack via sputtering, which damages the upper organic layers [72], thin silver contacts are used in this work exclusively that can be applied via evaporation processes. However, adequate thin conducting silver layers are not fully transparent but semitransparent and thus form a microcavity, as some photons are reflected back into the organic layer stack. This microcavity causes effects which can be either advantageous or disadvantageous depending on the application, as it is described in Section 4.4. Light escaping from the top contact of the top-emitting stack, is further transmitted through inert gas atmosphere, enclosed between organic coated substrate and encapsulation glass, and finally through the encapsulation glass. Consequently, mechanically attached outcoupling structures have to possess an optical contact to the upper layer of the stack in order to modify the outcoupling.

In transparent OLEDs, both bottom anode and top cathode are realized by highly transmissive contacts, through which the generated light can be extracted.

All layer structures presented so far are based on the conventional pin layer structure (see Subsection 4.1.1). For the sake of completeness it should be mentioned that the order of layer deposition can also be electrically inverted, starting with the cathode and ending with the anode, which in view of doping is referred as nip device intended for implementation on n-CMOS structures. However, this layer architecture is not implemented in this work.

White Architectures

There are several ways to achieve white light emission from organic light-emitting diodes [73, 74]. The commonly used ways are depicted in Figure 4.8. Generally, one distinguishes between two main concepts: wavelength conversion and color mixing.

In the down conversion approach [75], an external color conversion layer – commonly containing phosphors – is added to a blue OLED, which converts the incident blue light into orange or red emission [76]. As the conversion layer is applied at the outside of the device, interference effects of device and conversion layer can be excluded and the devices can be optically optimized easily. However, these devices always suffer form energy losses due to the conversion technique. Furthermore, blue OLED emission is
Figure 4.8: Approaches for OLED stacks to achieve white light emission on the example of a top-emitting device. Besides down-conversion of radiation (a) from a blue OLED, white emission can be generated by color mixing (b-e). Here, the concepts of (b) laterally or (c) vertically stacking of individual colored OLEDs, (d) doping of dyes in one emission layer, and (e) individual layers within one stack are widely used.

The second concept utilizes multiple emitters within a single device. As light is a mixture of different components, white light can be composed of the emission of two or more emitters, each having different chromaticities. If one chooses any two points within a chromaticity diagram (Figure 2.4.1), then all the colors lying on a straight line between these two points can be achieved by mixing both colors in certain amounts. Similarly, taking three or four color points will result in color gamuts spanned by a triangle or a convex quadrangle. For achieving ideal white light, the spectral power distributions of different components are adjusted to obtain a homogeneous match to one of the blackbody radiators. The concept of color mixing includes a variety of different approaches, which will briefly be mentioned here.

Emission of white light can be achieved by stacking monochrome devices either horizontally [77] (adapted from display techniques) or vertically [78–81] (cf. Figure 4.8b and c). Each light-emitting unit can be separately optimized optically and electrically, which allows for color tuning of the devices and compensation of differential aging. However, stacked devices demand a high effort in deposition of multiple layers and in structuring, as each unit needs separate contacting. In the horizontal approach, white light can be achieved by very small non-resolvable pixels or an additional diffuser on top, requiring higher luminances due to the lower area and/or absorption losses. Ver-
tical stacks demand transparent electrodes or charge generation layers between each monochrome unit and higher driving voltages. Further, their optical optimization for broadband emission is quite challenging due to microcavity effects, discussed in Subsection 4.4.1.

White light emission from a single emission layer can be realized by doping different dyes into one single emission layer, as shown in Figure 4.8d. The emission layer can be either self emissive or a host for multiple dyes [11, 82, 83]. Thereby, the concentration of the dye has to be carefully adjusted to balance the energy transfer between host and guest and achieve homogeneous white emission spectra. However, this method also allows the greatest possible color and efficiency fine tuning.

The most popular method for achieving white light from an OLED stack is the multi-layer structure (see Figure 4.8e). Here, different separate emission layers with different emission colors are utilized within a single OLED stack. If required, the single emission layers are separated by different interlayers in order to better control the energy transfer between the dyes. The emission layers can be formed by fluorescent [84–86] or phosphorescent [81, 87, 88] emitting materials, the latter achieving highest efficiencies for white light emitting diodes based on organic materials reported so far [89]. Further, fluorescent and phosphorescent emitters can be combined to form so-called hybrid devices [90–93]. As stable deep blue emitter materials are not available so far, this hybrid approach represents a good alternative to achieve stable white light emission.

Besides down conversion and color mixing by different dyes, white light can also be achieved using the emission of eximers [94, 95] or exciplexes [96, 97] in organic compounds or by utilizing multi-mode resonant microcavities [98].

### 4.4 Optical Properties

Organic light emitting devices are built up by a number of thin organic films in between two electrodes. Due to this multilayer device structure, whose overall layer thickness is in the order of the wavelength, thin film optics play an essential role when considering light generation in such structures. Especially top-emitting devices show strong microcavity effects, as they usually contain highly reflecting bottom- and top-electrode mirrors made from aluminum (Al) or silver (Ag), which have higher reflectivities compared to ITO. Finally, the outcoupling from the organic stack into air has to be considered, which differs for bottom- and top-emitting devices and can further be modulated via applying an antireflecting coating on top-emitting structures. The following subsections give a short overview over the thin film optics of light-emitting devices and their outcoupling behaviour.
4.4.1 Thin Film Optics in OLEDs

A multilayer device is built from thin layers of different organic materials each with different properties, such as the refractive index \( n \) or the layer thickness \( d \), which is on the order of the wavelength. Depending on the reflectance of both electrodes, which can reflect an considerable amount of incident light produced in the active layer within the structure, microcavity effects can occur. In the next paragraphs, the most important issues concerning light generation and microcavities in multilayer structures are briefly summarized.

Multilayer Device Structure and Dipole Emission

A multilayer device structure consists of \( i \) organic layers with a layer thickness of \( d_i \) and the complex refractive index \( \tilde{n}_i(\lambda) = n_i + ik_i \) as illustrated in Figure 4.9. The assembly can include one or more active layers, which contain emitting molecules. The emitting molecules can be considered to be randomly oriented and homogeneously distributed in the organic solid. They can be described as classical radiating dipole antennas [99] that are assumed to deliver isotropic radiation. The spontaneous emission

![Figure 4.9: Sketch of a multilayered structure including an active layer containing randomly oriented emissive dipoles. Each layer \( i \) is characterized by its refractive index \( \tilde{n}_i \) and its thickness \( d_i \). The transmission and reflection at each interface are given by \( T_{i,i+1} \) and \( R_{i,i+1} \). Transmission and reflection at the organic interfaces lead to interference effects resulting in different angles \( \theta_i \) of radiation. The phase shifts at the bottom and top interface is denoted with \( \phi_{b,t} \).](image)
Figure 4.10: Emission pattern of (a) a vertical dipole in p-polarization (TM), (b) a horizontal dipole in p-polarization (TM), and (c) a horizontal dipole in s-polarization (TE) [99].

from an electrical dipole can be understood as a superposition of plane waves with the wave vector

$$\vec{k}_i = \frac{2\pi n_i \hat{e}_k}{\lambda},$$

where $n_i$ denotes the real part of the complex refractive index of the organic material, $\hat{e}_k$ the unit vector of the propagation direction of emission through the organic medium with thickness $d_i$ and $\lambda$ the wavelength. The electric fields $\vec{E}_i$ can be decomposed into three different components. This is illustrated in Figure 4.10 showing one vertical p-polarized (TM) component and two horizontal polarized components, the s-(TE) and p-polarized (TM) waves, where TM and TE denote transverse-magnetic and transverse-electric, respectively. In systems with more than one active layer, where the emitting dipoles are distributed among different layers, the emitted power from discrete subsources is summed up by weighing their coefficients.

Due to the reflection ($R_{i,i+1}$) and transmission ($T_{i,i+1}$) of planar waves at the layer interfaces, usually interference effects occur as given in Figure 4.11. Thereby wide-angle interference occurs between the directly emitted light and its reflection on the bottom

Figure 4.11: Illustration of (a) wide-angle interference and (b) multiple-beam interference between two interfaces of distance $d$ with $z_0$ the distance between dipole and highly reflecting interface [100].
layers, which is important if the generation region is only a fraction of a wavelength [100]. If the reflectivity of both interfaces is comparatively high, especially multiple-beam interference is important, which appears when light is reflected back and forth between top and bottom layers.

The whole multilayer system can be described with the transfer matrix formalism [101, 102] with Fresnel coefficients to fulfill the Maxwell equations including all appearing interference effects and phase changes occurring at reflection on layers. For thick incoherent substrate layers, the intensity matrix formalism is used, which is analogous to the transfer matrix formalism but only neglects interference effects [102].

Planar Microcavity

An optical resonator made from a pair of highly reflecting mirrors with a spacing in the order of the optical wavelength is called a microcavity. From an optical point of view, an OLED incorporating organic material between two reflecting mirrors can be treated as a planar Fabry-Perot microcavity. The quality factor of the microcavity with two mirrors is given by [103]

\[ Q = \frac{\lambda}{\Delta \lambda} = \frac{2\pi L_{\text{cav}}}{\lambda_{\text{res}}} \frac{1}{\ln \sqrt{R_b R_t}}, \]  

(4.7)

which is defined by the resonance wavelength \( \lambda_{\text{res}} \), the optical cavity length \( L_{\text{cav}} \) and the reflectivity of bottom \( (R_b) \) and top \( (R_t) \) contact.

The optical cavity length \( L_{\text{cav}} \) is further defined by the Equation [103, 104]

\[ L_{\text{cav}}(\lambda) = \sum_i n_i d_i + L_{\text{M}_t}(\lambda) + L_{\text{M}_b}(\lambda), \]  

(4.8)

where \( d_i \) represents the thickness of the organic layer \( i \) with the real refractive index \( n_i \).

The effective penetration depths of photons into the top- and bottom-reflecting metal mirror is defined by \( L_{\text{M}_t} \) and \( L_{\text{M}_b} \), respectively and depends on the phase shift at the metal reflector \( \phi^M \) according to [103]

\[ L^M(\lambda) = \frac{\lambda}{4\pi} \phi^M. \]  

(4.9)

The approximate theoretical external intensity \( I_{\text{cav}} \) emitted from a cavity [105] for spontaneous emission in a cavity with two metal mirrors is given by

\[ I_{\text{cav}}(\lambda, \theta) = T_t \frac{1 + R_b(\lambda) + 2\sqrt{R_b(\lambda)\cos(2k_z b(\lambda, \theta))}}{1 + R_t(\lambda)R_b(\lambda) - 2\sqrt{R_b(\lambda)R_t(\lambda)\cos(2k L_{\text{cav}}(\lambda, \theta))}} I_0(\lambda) \]  

(4.10a)

\[ = G(\lambda, \theta, z_b, L_{\text{cav}}, T_t, R_{t,b}) \cdot I_0(\lambda), \]  

(4.10b)
where $T_t$ denotes the transmittance through the top contact, $R_b(\lambda)$ and $R_t(\lambda)$ the reflectivity of the bottom and top metal contact, and $k$ the wave vector of propagation. The distance of the radiating molecule in the active layer to the highly reflecting bottom contact mirror is given by $z_b(\lambda, \theta)$ and the effective optical cavity length is $L_{cav}(\lambda, \theta)$. If the phase shifts on both electrodes are taken into account $[103, 106–109]$, both terms are given by

$$2kz_b(\lambda, \theta) = \frac{4\pi \sum_j n_j(\lambda)d_j \cos(\theta_j)}{\lambda} - \phi_b(\lambda) \quad \text{and} \quad (4.11a)$$

$$2kL_{cav}(\lambda, \theta) = \frac{4\pi \sum_i n_i(\lambda)d_i \cos(\theta_i)}{\lambda} - \phi_t(\lambda) - \phi_b(\lambda). \quad (4.11b)$$

with $n_j(\lambda)$, $d_j$ and $\theta_j$ the refractive index, the layer thickness and the angle of propagation of light within the layers $j$ between the emission layer and the reflecting metal mirror in the opposite emission direction. The phase shifts at the bottom and top contact is denoted by $\phi_{b,t}(\lambda)$, respectively, and $n_i(\lambda)$ is the refractive index of the organic layers $i$ with thickness $d_i$. The term $I_0(\lambda)$ in Equation (4.10) represents the spectral emission intensity of the dipole without any cavity. With regard to organic light emitting diodes, where the radiating dipoles are given by emitting molecules, $I_0$ illustrates their luminescence spectra.

This finally leads to a function $G$ (cf. Equation 4.10b) dependent on the wavelength $\lambda$ and various other parameters, which affects the spectral emission intensity $I_0(\lambda)$. The enumerator of $G$ shows the interference of initially oppositely propagating waves upon multiple reflections and transmissions out of the cavity. The denominator leads to the usual Fabry-Perot transmission spectrum $[105]$.

The resonance condition for light after one cycle ($m=0$) in the cavity is given by the phase shift

$$\Delta \phi = \frac{4\pi \sum_i n_i d_i \cos(\theta_i)}{\lambda_{res}} - \phi_t - \phi_b = 2\pi m \quad \text{with} \quad m \in \mathbb{N} \quad (4.12)$$

for the $m^{th}$ resonant mode and the propagation direction of light $\theta_i$. The resonator and accordingly the function $G$ can therefore be tuned to different resonance wavelengths by adjusting the cavity thickness $L_{cav}(\lambda)$, which leads to a redistribution of the photon density of states so that only certain wavelengths – corresponding to allowed cavity modes – are emitted in a specific direction. Furthermore, the function $G$ also depends on the position of the emission layer $z_b$ in the cavity, as the emitting dipoles couple to the internal spatial-dependent electric field and thereby modify the external outcoupling spectrum.

Depending on $G$, the light ($I_0$) emitted from the dipoles can consequently either be amplified or attenuated, as it is illustrated in Figure 4.12 for single emission wavelengths $\lambda_A$, $\lambda_B$, and $\lambda_C$. 

4.4 Optical Properties
Figure 4.12: Illustration of the enhancement or reduction function $G$, calculated according to Equation (4.10) for a cavity consisting of two silver mirrors with 100 nm (bottom) and 30 nm (top) layer thickness. The cavity incorporates material with a real refractive index of $n_o=1.75$ and a thickness of $L_{cav}=320$ nm, where the active area is placed at $z_b=230$ nm. The emission angle $\theta$ is assumed to be $0^\circ$ in this simplified calculation. The inset shows the amplification and attenuation of $G$ with regard to emission at the single wavelength $I_0=1$ at $\lambda_A=610$ nm, $\lambda_B=640$ nm, and $\lambda_C=660$ nm leading to the resulting emission intensity $I_{cav}$, which is lowered for the wavelengths A and C, but enhanced for wavelength B.

Cavity Effects

As a consequence of the microcavity structure, microcavity effects occur [110–113], which basically lead to a spectral narrowing and an angle dependence of the outcoupled spectrum. Due to the resonance condition, the emission of the device at certain wavelengths is enhanced, when it is in-resonance and suppressed, when it is off-resonance. Accordingly, the full width at half maximum (FWHM) of the emitted spectral modes of $G$ is narrowed and given by [114]

$$\Delta \lambda_G^{\text{FWHM}} = \frac{\lambda^2}{2\pi L_{cav}} \frac{1 - \sqrt{R_t R_b}}{(R_t R_b)^{1/4}}.$$ (4.13)
This limits the theoretical external emission wavelength range of a top-emitting device as shown in Figure 4.13. The intensity $I_0(\lambda)$ is given by the luminescence of the employed dye, which usually has a full width at half maximum of several tens of nanometers. Coupled with the enhancement function $G(\lambda)$, having quite narrow FWHM, the outcoupled emission spectrum is constricted and the luminescence spectrum is deformed due to partial enhancement or attenuation.

Furthermore, the emission regarding to intensity and spectral distribution also depends on the viewing angle $\theta$, which is directly connected to the internal propagation angles $\theta_i$ via Snell’s law. By a changed viewing angle $\theta$, the resonance wavelength ($\lambda_{\text{res}}$) in Equation (4.12) has to change in order to still fulfill the resonance condition. Consequently, the emission peak will favor a slightly different wavelength. Therefore, one can observe a blue shift of emission with increasing viewing angle, as the resonance wavelength of the microcavity decreases.

**Figure 4.13:** Resulting external emission intensity $I_{\text{cav}}$ for a radiating dipole, which emits a luminescence spectrum $I_0$, within a microcavity characterized by the function $G$. The cavity consists of two silver mirrors with 100 nm (bottom) and 30 nm (top) layer thickness incorporating organic material with a real refractive index of $n_o=1.75$ and a thickness of $L_{\text{cav}}=120$ nm, where the active area is placed at $z_b=60$ nm. The emission angle $\theta$ is assumed to be $0^\circ$ in this simplified calculation. Due to the narrow FWHM of $G$, the width of the cavity intensity $I_0$ is deformed and limited with respect to the original luminescence emission $I_0$. 
**Table 4.1:** Refractive indices for some materials averaged over a wavelength range of 380-780 nm.

<table>
<thead>
<tr>
<th>Material</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td>air</td>
<td>1.0003</td>
</tr>
<tr>
<td>common glass</td>
<td>1.5</td>
</tr>
<tr>
<td>ITO</td>
<td>$\approx 1.92$</td>
</tr>
<tr>
<td>organic material</td>
<td>$\approx 1.71-1.82$</td>
</tr>
</tbody>
</table>

Generally, microcavity effects play a role in all devices where at least one electrode is not fully transparent. However, due to the almost completely transparent ITO anode, the effects arising from the microcavity are low in bottom-emitting OLEDs. In top-emitting devices usually strong microcavity effects arise, which are crucial for the emission concerning the dependence of intensity, spectra, viewing angle, and emission pattern. A possible solution to modify the appearing effects is the application of a dielectric capping layer as antireflecting coating, which is discussed in the next subsection.

### 4.4.2 Outcoupling

The efficiency of outcoupling is defined as the number of photons emitted from the OLED into air divided by the number of photons generated inside the OLED. Not all photons that are generated within the thin film structure can be coupled out into air. Light produced in the stack can undergo total internal reflection at the interfaces due to a difference in the refractive index. The refractive indices for some common materials are shown in Table 4.1. Thus, light can be trapped within the organic layers and several guided modes can appear, whose power is basically transported along the plane of the multilayer and therefore lost for emission. Power can also be lost due to absorption within the structure or at the metal layer interfaces. Furthermore, coupling between free charges at the metal surface and the electromagnetic radiation from the dipoles may result in the generation of surface plasmon-polaritons, which are longitudinal fluctuations of the surface charge density that propagate along the interface and thereby further reduce the outcoupled power.

### Bottom-Emitting Structures

As the light from flat bottom-emitting devices is coupled out through glass, next to ITO-organic modes also substrate modes can appear. For flat bottom-emitting OLED devices the outcoupling factor can be roughly approximated to 22 % [115] using the
4.4 Optical Properties

The equation

\[ \eta_{\text{out}}^{\text{b-OLED}} = \frac{1}{2} \frac{n_{\text{air}}^2}{n_{\text{glass}}^2} \approx 0.22. \]  

(4.14)

This equation is derived from ray optics, where \( n_{\text{air}}, n_{\text{glass}} \) denotes the refractive indices of air and glass, respectively, neglecting microcavity interference or absorption effects. The outcoupling factor can be enhanced by utilizing weak microcavities within bottom-emitting OLEDs [68, 108, 112] or using high index glass substrates in combination with outcoupling structures, like a half sphere or patterned outcoupling foils containing pyramid or lens structures [89, 116, 117].

**Top-Emitting Structures**

Due to the changed architecture of top-emitting OLEDs, the outcoupling cannot be easily calculated by applying Equation (4.14), as the assumptions are no longer valid. Therefore, \( \eta_{\text{out}}^{\text{top}} \) always has to be calculated numerically for each layer architecture. Unfortunately, there are only very few publications dealing with this question, in which the outcoupling of top-emitting devices is presumed to be also about 20% [115, 118].

Generally, the width of the outcoupled spectra showing the external intensity \( I_{\text{cav}}(\lambda) \) emitted from a cavity depends on the overlap of the dye emission \( I_0(\lambda) \) and the spectral width of the enhancement function \( G(\lambda) \), which is given by Equation (4.13). Therefore, the strength of the optical interference is mainly influenced by the optical cavity thickness \( L_{\text{cav}} \) as well as the reflectivities \( R_{b,t} \) of the metal mirrors forming the microcavity. To enhance the outcoupling and alleviate the strong microcavity effects, either a short optical cavity length \( L_{\text{cav}} \) or a low reflectivity of the top contact \( R_t \) are favored. The optical cavity length can be easily adjusted by the choice of organic layer thicknesses \( d_i \). Varying the thickness of the top-electrode would further change its reflectivity. However, the latter consequently leads to increased absorption losses for thick metal mirrors and to insufficient conductivity for very thin metal contacts.

A possible solution to modify the electrode transmission is the application of a dielectric layer on top of the semitransparent metal top contact [111, 119–121], which thereby does not influence the electrical characteristics of the device. It is well known from the optics of metal coatings that a thin dielectric layer on top of a thin metal layer can be used to modulate the transmittance of the metal layer [122] and thereby improve the light output to air. However, the highest output or light emission is not achieved with maximum transmission, but is determined by a complex interplay between wide-angle and multiple-angle interference effects governed by the capping layer thickness [111, 123]. Thereby, the capping layer thickness significantly influences the spectral characteristics as a function of the different viewing angles.

It has been shown for monochromatic OLED devices that an adequate adjustment of the capping layer thickness [123, 124] can alleviate the cavity effects. Therefore, the
Table 4.2: Simplified stack structure for a top- and bottom-emitting device with a cavity thickness $d_{cav}$ of the organic material with refractive index $n=1.75$ and a capping layer thickness of $x$.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) top-emission:</td>
<td>(b) bottom-emission:</td>
</tr>
<tr>
<td>capping layer</td>
<td>Ag 100</td>
</tr>
<tr>
<td>$x$</td>
<td>organic material $d_{cav}$</td>
</tr>
<tr>
<td>Ag 15</td>
<td>ITO 90</td>
</tr>
<tr>
<td>organic material $d_{cav}$</td>
<td></td>
</tr>
<tr>
<td>Ag 100</td>
<td></td>
</tr>
</tbody>
</table>

angle dependence of the emission spectra can be reduced and the emission pattern can be modified to show forward enhanced light emission. Furthermore, this modification and an improved spontaneous emission within the microcavity device can lead to an overall enhanced efficiency of monochromic devices [124].

For the realization of white light emission from a microcavity, the challenge lies in the relatively narrowband emission of the devices due to the microcavity effect. However, by carefully adjusting both cavity length and the thickness of the anti-reflecting coating on top of the stack, an adequate broadband emission can be achieved [107, 109, 125–127] and the angle dependence can be reduced.

Figure 4.14a and b illustrate the enhancement function $G$ of two simplified top-emitting devices without emitting dyes according to Table 4.2a with ($x=50$ nm) and without ($x=0$ nm) dielectric capping layer. For reasons of comparison these data are compared to the enhancement function $G$ of a common bottom-emitting structure (cf. Figure 4.14c) with the layer structure shown in Table 4.2b. All data are derived from optical simulation employing the numerical tool, which is mentioned in Section 5.8.

The top-emitting structure with applied capping layer shows a broader full width of half maximum of $G$ compared to the structure without capping layer. However, a bottom-emitting structured device still features a much broader FWHM. Furthermore, the shift of the maxima, which denote the resonance wavelength of the device, is larger for the top-emitting structure with capping layer compared to the stack without additional layer. A bottom-emitting structure shows the lowest change of the resonance wavelength. Consequently, even small deviations in the organic layer thickness of top-emitting devices have a large impact on the function $G$ and consequently on the device emission. Particularly this fact is challenging to achieve a distinct device emission with specific color coordinates.

As the enhancement function $G$ describes the emission properties of the pure cavity independent from the emitter spectrum ($I_0=1$), the term cavity emission is used in the following to describe the emission from the cavity with an ideal wavelength-independent emitter, if not stated differently.
Figure 4.14: Simulation of the enhancement function $G$ of a simplified organic layer structure for (a) a top-emitting device without capping layer ($x=0$ nm), (b) a top-emitting device with capping layer ($x=50$ nm) and a bottom-emitting device. The simulated organic material stacks ($n=1.75$) exhibit a thickness of $d_{\text{ov}}=90, 100, \text{ or } 110\text{ nm}$. Applying the dielectric capping layer largely broadens the enhancement function $G$ of the top-emitting structure. However, the bottom-emitting structure still features a broader FWHM.
5 Experimental Techniques and Methods

This chapter gives an overview of the different experimental steps necessary to produce organic light emitting diodes. Furthermore, some methods for the characterization of surfaces and organic films concerning morphology, energy levels, and optical properties are presented. After a summary of the employed substrates and used materials, the general sample preparation of OLEDs is discussed. Subsequently, the electrical and optical characterization techniques for organic light-emitting devices are described, followed by the determination of the device performance. In the following, the determination of the quantum yield is introduced. Furthermore, the tools for optical characterization of thin organic single films and the techniques for optical simulations are briefly mentioned. To determine the quality of the substrate surfaces as well as the morphology of thin organic films, different microscopical techniques are used, which are shortly introduced afterwards. Further examinations of organic layers are carried out by optical measurements and ultraviolet photoelectron spectroscopy (UPS), which are briefly introduced at the end.

5.1 Substrates

There are different types of substrates available for the production of organic light emitting devices. Besides glass substrates (Glas-Meyer & Söhne GmbH, Freiburg-Haslach and Princeoptics, Stromberg) and indium tin oxide (In$_2$O$_3$:SnO$_2$, ITO) coated glass substrates (Thin Film Devices Inc., Anaheim), also glass substrates coated with highly reflecting molybdenum-tantalum alloy (Institut für Systemtheorie und Bildschirmechnik, Universität Stuttgart) (referred to as MoTa-substrates) are used. Furthermore, sheets of aluminum (“325GK0”) (see Figure 5.1) are available, which allow to realize top-emitting OLEDs on thin metal substrates. The metal substrates, which are also re-
5.2 Materials

The next section will give a short overview of the used materials in this work. Except of the electrode materials and the inorganic n-dopant Cesium (Cs), all materials are based on small organic molecules. The purity of these organic material is of great importance in terms of device performance and lifetime. Therefore, the organic materials have been purified via repeated gradient sublimation in high vacuum before they are used.

5.2.1 Electrode Materials

To contact the OLED stack, different materials can be used as anode and cathode electrodes. Besides the commonly used almost transparent indium tin oxide (ITO) as transparent bottom contact in bottom-emitting diodes, aluminum (Al) or silver (Ag)
are usually used for contacting organic light-emitting OLEDs. The transmittance and reflectance of aluminum and silver layers can be adjusted via layer thickness, as for the bottom contact highly reflecting and for the top contact semitransparent layers are needed. The smoothness of the bottom contact layer is crucial to prevent failures of the devices. Pure aluminum layers are commonly smoother than thick silver layer, as the latter are known to grow in small clusters during deposition and can form even high peaks, which cause short cuts within the device. However, the reflectivity for Ag is in the average slightly larger compared to Al (see Figure 5.3). Silver layers feature higher reflectance in the higher wavelength region and lower reflectance in the high energy region in contrast to aluminum layer with the same thickness. Additionally, glass substrates covered with 70 nm thick layer of molybdenum-tantalum alloy were used, as these show a very smooth surface.

Indeed, a non reflecting and highly transmitting material would be the first choice for top-contacting of top-emitting devices, as this would alleviate the strong microcavity effects and allow good light extraction for all wavelengths. Unfortunately, there are no materials commercial available, which show sufficient transmittance as well as adequate conductivity – despite ITO. As ITO is commonly deposited via a sputtering process, a damage of the upper organic layers of a thin organic layer stacks cannot be avoided [72]. Consequently, apart from some experiments with alternative transparent top-electrodes in Chapter 9, 15 nm thin Ag layer are exclusively used for transparent top-contacting of top-emitting OLEDs.

In Table 5.1 and Figure 5.3 the general work functions and conductivities as well as the reflectance and transmittance of some electrode materials are shown.

### 5.2.2 Transport Materials and Electrical Dopants

To realize electrically p-doped organic hole transport layers, the hole transport material $N,N',N''$-Tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) is doped with either 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane ($F_4$-TCNQ) or NDP2. The latter material is a proprietary p-type dopant provided by the Novaled AG (Dresden), whose composition has not been revealed yet. Both p-doped systems are comparable, however $F_4$-TCNQ contaminates the evaporation chamber and can therefore not be used in the
Figure 5.3: Reflectance and transmittance of different electrode materials. The material silver shows the highest reflectance, whereas the transmittance of MoTa reaches up to 60%.

single-chamber evaporation tool.

Compared to p-type doping, n-type doping poses a greater challenge, as the HOMO and LUMO level of the organic guest molecules have to be above the host level. Thereby, the LUMO of the dopant is close to the vacuum level and thus susceptible to oxygen. Besides organic molecules also inorganic alkali metals like lithium (Li) or cesium (Cs) can be used for doping. In this work, exclusively Cs is used, due to the lower diffusivity compared to the relative small Li atoms, which consequently makes the devices more stable with regard to temperature. The n-transport layer is realized by co-evaporation of the electron transport matrix material 4,7-Diphenyl-1,10-phenanthroline (BPhen) with Cs from a dispenser, where the doping concentration is always chosen to achieve a conductivity of about $10^{-5}$ S cm$^{-1}$ of the doped layer. Alternatively, the Novaled electron-transporting system can be used, which consists of the matrix material NET5 and the dopant material NDN1. Similar to the p-dopant NDP2, the composition of n-side materials has not been revealed yet.

The chemical notations of the used transport and doping materials are given in Figure 5.4. Table 5.2 summarizes their characteristic ionization potentials (IP), electron affinities (EA), optical gap energies $E_{opt}$, and singlet energies $S_1$. 
5.2 Materials

Figure 5.4: Chemical structure of the materials (a) N,N,N′,N′-Tetrakis (4-methoxyphenyl)-benzidine (MeO-TPD), (b) 4,7-Diphenyl-1,10-phenanthroline (BPhen), and (c) 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ)

Table 5.2: Most important characteristic values of the used transport materials MeO-TPD and BPhen and the electrical dopant F₄-TCNQ. The singlet energies (S₁) are calculated from the fluorescence emission peak.

<table>
<thead>
<tr>
<th>short name</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>E^optgap (eV)</th>
<th>S₁ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO-TPD</td>
<td>-5.1 [132]</td>
<td>-1.9 [132]</td>
<td>2.96 [128]</td>
<td>2.53</td>
</tr>
<tr>
<td>BPhen</td>
<td>-6.38 [133]</td>
<td>-2.0 [128]</td>
<td>3.52 [128]</td>
<td>3.21</td>
</tr>
<tr>
<td>F₄-TCNQ</td>
<td>-8.34 [134]</td>
<td>-5.24 [134]</td>
<td>2.94 [135]</td>
<td></td>
</tr>
</tbody>
</table>

5.2.3 Blocking and Host Materials

Depending on their characteristic energy levels, their charge carrier mobility, and singlet/triplet level energies, organic materials can be used for charge carrier and exciton blocking (cf. Subsection 4.3.1) or as host matrices for emissive dyes (see Subsection 5.2.4). Figure 5.5 and Table 5.3 depict the chemical notation and the most important characteristic energy values for the materials, which are used in this thesis. The materials 2,2′,7,7′-Tetrakis-(N,N-diphenylamino)-9,9′-spirobifluoren (S-TAD), N,N′-Di (naphthalen-1-yl)-N,N′-diphenyl-benzidine (NPB), and 4,4′,4″-Tris(carbazol-9-yl)triphenylamine (TCTA) are predominantly hole-transporting and used as electron blocking layers. Besides intrinsic BPhen, the electron conducting materials Tris (8-hydroxy-quinolinato)-aluminium (Alq₃), Aluminum (III) bis(2-methyl-8-quinolinato)-4-phenyl-phenolate (BAIq₂) and 2,2′,2″-(1,3,5-Phenyl) tris (1-phenyl-1H-benzimidazol) (TPBi) are employed as hole blockers. Among those materials NPB and TCTA as well as TPBi are further used as suitable host materials for emissive dyes (see Subsec-
Figure 5.5: Chemical notation of the used host and/or blocking materials (a) 2,2’,7,7’-Tetrakis-(N,N-diphenylamino)-9,9’-spirobifluoren (S-TAD), (b) N,N’-Di(naphthalen-1-yl)-N,N’-diphenyl-benzidine (NPB), (c) 4,4’,4’’- Tris(carbazol-9-yl)-triphenylamine (TCTA), (d) Tris(8-hydroxy-quinolinato)-aluminium (Alq₃), (e) Aluminium(III) bis(2-methyl-8-quinolinato)-4-phenyl- phenolate (BAIq₂), and (f) 2,2’,2’’-(1,3,5-Phenylen) tris(1-phenyl-1H-benzimidazol) (TPBi).

Due to their high triplet energies of 2.82 eV and 2.64 eV, respectively, the materials TCTA and TPBi are further used to separate fluorescent and phosphorescent emitter materials by adequately blocking excitons. This exciton blocking interlayer is formed by a blend of both materials, in which the mobility of the interlayer can be adjusted by the ratio of both blend materials, as TCTA is rather hole- and TPBi is rather electron-transporting.

5.2.4 Emitter Materials

The emission layer can either be formed by a bulk layer of emissive material or by doping a dye into a suitable host matrix. Thereby, depending on the layer position within the OLED, wide-gap matrix materials are chosen for the charge carrier transport.
5.2 Materials

Table 5.3: Most characteristic energy values of the used hole and electron conductive host and/or blocking materials. The singlet energies ($S_1$) are calculated from the fluorescence emission peak.

<table>
<thead>
<tr>
<th>short name</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>$S_1$ (eV)</th>
<th>$T_1$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-TAD$^1$</td>
<td>-5.38$^4$</td>
<td>-2.3 [136]</td>
<td>3.04$^5$</td>
<td>3.07</td>
<td>-</td>
</tr>
<tr>
<td>NPB$^3$</td>
<td>-5.4 [133]</td>
<td>-2.52 [137]</td>
<td>3.12 [135]</td>
<td>2.80</td>
<td>2.29 [138]</td>
</tr>
<tr>
<td>TCTA$^2$</td>
<td>-5.9 [139]</td>
<td>-2.7 [139]</td>
<td>3.2 [139]</td>
<td>3.18</td>
<td>2.82 [140]</td>
</tr>
<tr>
<td>Alq$_3$$^1$</td>
<td>-5.8 [141]</td>
<td>-3.1 [141]</td>
<td>2.75 [135]</td>
<td>2.31</td>
<td>2.03 [142]</td>
</tr>
<tr>
<td>BAIk$_2$$^1$</td>
<td>-6.08 [128]</td>
<td>-3.0 [143]</td>
<td>3.44 [143]</td>
<td>2.51</td>
<td>2.18 [142]</td>
</tr>
<tr>
<td>TPBi$^3$</td>
<td>-6.3$^4$</td>
<td>-2.8$^4$</td>
<td>3.4 [144]</td>
<td>3.22</td>
<td>2.64 [140]</td>
</tr>
</tbody>
</table>

1 used for charge carrier blocking  
2 used for exciton blocking  
3 used as host matrices  
4 determined via UPS at the IAPP  
5 determined at the IAPP

In this work bulk emission layers are solely formed by the blue fluorescent materials 2,2’,7,7’-Tetrakis (2,2-diphenylvinyl) spiro-9,9’-bifluorene (Spiro-DPVBi) and 2-Methyl-9,10-bis (naphthalen-2-yl) anthracene (MADN) that show emission peaks at 470 nm and 452 nm, respectively. The deep blue fluorescent material MADN can further be used as suitable host for the blue fluorescent emissive dye 2,5,8,11-Tetra-tert-butylperylene (TBPe) ($\lambda_{\text{em}}=484$ nm).

The phosphorescent iridium (Ir) based emitter material Iridium (III) bis [(4,6-di fluorophenyl)-pyridinato-N,C2] picolinate (Flrpic) emits in the light blue color region ($\lambda_{\text{em}}=474$ nm) and is doped into the matrix material TPBi. For realization of green emission, the highly efficient and stable emissive material Tris (2-phenylpyridin) iridium (III) (Ir(ppy)$_3$) is used, which can either be doped into TCTA or TPBi. Yellow and orange-red emission is realized with the phosphorescent materials Bis (2-(9,9-dihexylfluorenly)-1-pyridine) (acetylacetonate) iridium (III) (Ir(dhfpy)$_2$(acac)) and Iridium (III) bis (2-methylidibeno-[f,h]chinoxalin) (acetylacetonat) (Ir(MDQ)$_2$(acac)) that are very efficient as well as stable and show emission peaks at 557 nm and 614 nm, respectively. Depending on the best achievable spectral color balance, the doping concentrations are varied in the range of 5-20 wt.% (weight percent) (with the exception of MADN:TBPe (1 wt.%) for highest achievable efficiency [145]). With increased dye concentration, the emission maxima are slightly shifted to higher wavelength.

To achieve white emission, one can either use exclusively phosphorescent emitter materials or utilize a hybrid approach, as discussed in Subsection 4.3.2. In the first case the stability and lifetime is significantly limited due to the blue phosphorescent dye. The hybrid approach utilizes stable blue fluorescent emitter materials, which are combined with highly stable and efficient phosphorescent emitters. This however leads to
lower efficiencies compared to an all-phosphorescent approach. For the design of top-emitting white OLEDs in this work, both approaches are tested with respect to achieve stable white organic light-emitting diodes on the one hand as well as highly efficient white OLEDs on the other hand. The phosphorescent blue emitter material FIrpic is used as a test material, which can be replaced by new deep blue phosphorescent emitter dyes, which are currently under development [146].

The chemical notation of both blue bulk materials and the emissive dopants are depicted in Figures 5.6 and 5.7, respectively. Table 5.4 summarizes their characteristic energy levels and emission wavelengths. The photoluminescence emission spectra are illustrated in Figure 5.8a for the blue dyes and in Figure 5.8b for the remaining green, yellow and orange-red dye.

### 5.3 Processing of OLED Samples

The following section will illustrate the different steps of processing organic light-emitting diodes, starting from cleaning procedures and preparation steps via processing to encapsulation.

#### 5.3.1 Substrate Cleaning and Preparation

Prior to material deposition, the substrates are cleaned to fully remove contaminations on the substrate surface. Otherwise short circuits or lowered device performance would be a direct consequence. Depending on the substrate type and size, different cleaning procedures are used. The cleaning steps using liquids are carried out...
5.3 Processing of OLED Samples

Figure 5.7: Chemical structure of the used emissive dyes (a) 2,5,8,11-Tetra-tert-butylperylene (TBPe), (b) Iridium (III) bis [(4,6-difluorophenyl)-pyridinato-N,C2] picolinate (FIRpic), (c) Tris (2-phenylpyridin) iridium (III) (Ir(ppy)3), (d) Bis (2-(9,9-dihexylfluorenyl)-1-pyridine) (acetylacetonate) iridium (III) (Ir(dhfpy)2(acac)), and (e) Iridium (III) bis (2-methyl dibenzo-[f,h]chinoxalin) (acetylacetonat) (Ir(MDQ)2(acac)).

Table 5.4: Characteristic energy values of the used fluorescent and phosphorescent emitting materials. The singlet (S1) or triplet (T1) energies are calculated from fluorescence or phosphorescence peaks, if not stated otherwise.

<table>
<thead>
<tr>
<th>short name</th>
<th>IP (eV)</th>
<th>EA (eV)</th>
<th>S1 (eV)</th>
<th>T1 (eV)</th>
<th>λem (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MADN</td>
<td>-5.6 [147]</td>
<td>-2.6 [147]</td>
<td>2.74</td>
<td>-</td>
<td>452</td>
</tr>
<tr>
<td>Spiro-DPVBi</td>
<td>-5.6 [148]</td>
<td>-2.8 [148]</td>
<td>2.64</td>
<td>-</td>
<td>470</td>
</tr>
<tr>
<td>TBPe</td>
<td>-5.3 [149]</td>
<td>-2.3 [149]</td>
<td>-</td>
<td>2.56</td>
<td>484</td>
</tr>
<tr>
<td>FIRpic</td>
<td>-5.8 [150]</td>
<td>-2.7 [150]</td>
<td>-</td>
<td>2.62 [140]</td>
<td>474</td>
</tr>
<tr>
<td>Ir(ppy)3</td>
<td>-5.4 [151]</td>
<td>-2.4 [151]</td>
<td>-</td>
<td>2.45</td>
<td>507</td>
</tr>
<tr>
<td>Ir(dhfpy)2(acac)</td>
<td>-5.12</td>
<td>-2.4 [2]</td>
<td>-</td>
<td>2.23</td>
<td>557</td>
</tr>
<tr>
<td>Ir(MDQ)2(acac)</td>
<td>-5.36 [128]</td>
<td>-2.76 [1]</td>
<td>-</td>
<td>2.01</td>
<td>614</td>
</tr>
</tbody>
</table>

1 measured via cyclic voltammetry
2 determined via optical gap and UPS measurements at the IAPP
Figure 5.8: Photoluminescence intensity of all used dyes: (a) fluorescent (MADN, TBPe, and Spiro-DPVBi) and phosphorescent (FIrpic) blue emitting dyes and (b) phosphorescent green (Ir(ppy)$_3$), yellow (Ir(dhfpy)$_2$(acac)), and orange-red (Ir(MDQ)$_2$(acac)) dye.

in an ultrasonic bath: i) The cleaning of small substrates is realized with acetone, ethanol and isopropanol, before drying with nitrogen. ii) Large glass substrates and MoTa-substrates are cleaned with N-Methyl-2-pyrrolidon (NMP), de-ionized water and ethanol. Afterwards substrates are dried with a spin-rinser (Semitool) and treated with UV-light (FHR Anlagenbau GmbH). iii) Aluminum substrates are cleaned with acetone and ethanol, followed by a cleaning with de-ionized water for large substrates or isopropanol for small substrates. Afterwards, the substrates are dried with nitrogen. As solvent molecules tend to soak into the silicon oxide coating during the cleaning process (cf. Figure 5.9), the metal substrates are heated at 100°C for one hour to remove the solvent. After cleaning, the substrates are mounted on substrate holders under laminar filtered air and transferred in ultra high vacuum (UHV, pressure $p < 10^{-7}$ mbar) via a glove-box filled with nitrogen.

5.3.2 Thin Film Processing

The evaporation of organic materials and metals is completely carried out in UHV without breaking the vacuum. For that purpose two different deposition tools can be used: a multi-chamber vacuum deposition cluster tool (Bestec) (cf. Figure 5.10), referred to as UFOII, and a single-chamber vacuum deposition tool (Kurt J. Lesker) shown in Figure 5.11, referred to as LESKER. Both systems employ the same evaporation technique but vary in dimension as well as in some other particular features, which will be discussed later. A schematic sketch of both tools is depicted in Figure 5.12.
5.3 Processing of OLED Samples

Figure 5.9: Microscopic pictures of an Alanod-substrate: (a) optical microscope picture after 15 min pre-cleaning with acetone, (b) AFM image of a point structure shown in (a), and (c) optical microscope picture after 20 min heating at 100°C. It is clearly recognizable that the surface is swollen around some point defects after solvent conditioning, what disappears after heating.

Figure 5.10: Multi-chamber deposition tool (UFOII). The tool comprises four chambers with organic sources and one chamber for metal evaporation.
Figure 5.11: Single-chamber vacuum deposition tool (LESKER). The evaporation chamber is directly connected to an glovebox filled with inert gas.

Figure 5.12: Schematical cross-section of both evaporation tools: (a) UFOH and (b) LESKER. In the LESKER tool, the substrate is rotated during evaporation.
5.3 Processing of OLED Samples

The two systems contain several sources at their chamber bottom basement, which are filled with purified organic material or metal. Each source has a separate shutter and an independent temperature control unit to adjust the cone shaped material evaporation beam and the material deposition on the substrate, which is forming thin amorphous layers. In the upper area of the chamber, the substrate holder is mounted and can be covered by a shutter, too. By using different shadow slit masks available beneath the substrate holder, the device layout of a sample can be defined. Each sample contains four independent OLED devices (pixels) (cf. Figure 5.13), which are defined by an anode-, an organic- and a cathode-mask. The pixel area \( A \) is between six and seven square millimeter and is dependent on the electrode layout used.

The layer thickness as well as the evaporation rate are controlled via quartz crystal monitors (QCMs) within the evaporation beam. These instruments are driven at a certain frequency and can determine the amount of deposited material by the material density and the frequency change during evaporation. The exact layer thickness on the substrate is determined with the aid of a second QCM, which is set on the substrate position and allows to calculate the geometrical factor between substrate position and reference QCM. As the position of the source and the reference QCM generally slightly varies after material refill or replacement of the crystal quartz, this factor has to be recalculated after every system change to obtain reliable deposition thicknesses. To achieve doped transport layers, doped emission layers, or ambipolar interlayer blends, co-evaporation of different materials is done by controlling two or more sources with independent QCMs.

Figure 5.13: Substrate layout of (a) a single OLED sample (prepared at the UFOII) and (b) a sample-wafer (prepared at the LESKER).
Multi-Chamber System

The multi-chamber evaporation system contains four organic chambers with each four to six available organic sources and one extra metal chamber with six available metals. As each chamber can hold only one small substrate for each evaporation step, the samples have to be grown successively via sequential deposition processes in different chambers.

Due to the high flexibility in material placement and co-evaporation, this tool is suitable for testing new materials, novel and complex layer structures, or special substrates. For detailed comparison of a series of OLEDs with the focus on effects of slightly different device structures, this tool is less convenient, as the comparability of OLEDs suffers from serial processing. Depending on the complexity of the device structure, two comparable samples may show differences in electrical and optical properties.

Single-Chamber System

The single-chamber evaporation tool has larger dimensions. Therefore, even large substrate wafers can be used. On one large substrate wafer (Figure 5.13) up to 36 samples, arranged in a $6 \times 6$ matrix, can be processed at the same time and under identical conditions. To investigate the influence of changes in the OLED structure – such as layer thickness or doping concentration – different samples can be prepared using slit masks for every row and column. However, there is a limitation of available materials to a maximum of 15 different materials for one OLED layer structure. Here, twelve sources for organic materials and the n-dopant Cs are circularly arranged enclosing three metal sources, located several centimeter below (Figure 5.12b).

Due to the larger dimensions of the whole evaporation tool as well as the dimension of the material crucibles, the sources cannot be arranged directly perpendicular below the substrate wafer. To achieve the highest possible homogeneity of the material distribution on the substrate wafer, the substrate holder is thereby rotating during every evaporation step. Despite that handling, measurements reveal a point symmetric profile of layer thickness, schematically shown in Figure 5.14. The thickness deviations from the center to the outer edges of the wafer can be as large as 13% for evaporated organic materials (Figure 5.15). The resulting profile is dependent on the evaporated material, the source position, the source adjustment, and the evaporation rate. By comparison, the metal sources – positioned directly beneath the substrate – show considerably lower deviations of 1-1.5%, which are negligible. As large inhomogeneities can particularly influence the optical properties of complex and thickness-sensitive OLEDs, a substrate layout of $4 \times 4$ single cells has been chosen for experiments in this work, if not stated differently. The experimental uncertainties of organic layer thickness for this area is about 5%.
5.3 Processing of OLED Samples

Figure 5.14: Sketch of the thickness deviations on a substrate wafer.

Figure 5.15: Measured organic thickness deviations on a substrate wafer. The thickness profile depends on the used organic material, the source position, and the evaporation rate.
5.3.3 Encapsulation

After the multilayer evaporation process, the samples are encapsulated in nitrogen atmosphere, avoiding further reactions with oxygen or humidity. The active area is covered by a small glass lid and sealed with special glue: epoxy glue for single UFOII samples, which has to dry for approximately two days in inert atmosphere, and UV-hardening glue for LESKER samples. Bottom-emitting OLEDs are further provided with some so-called "getter-material", which binds water vapor within the encapsulation. This is not possible for top-emitting devices, as these radiate through the encapsulation glass.

5.4 Characterization of OLED Devices

The next section deals with the electrical and optical characterization of OLEDs using three different measurement setups: an automated measuring system (referred as OLED-robot) for determination of electrical diode characteristics and forward directed spectra, a goniometric setup for angle-dependent measurements, and finally an integrating sphere for spectral measurements within the whole forward hemisphere.

5.4.1 OLED-Robot: IVL- and EL-Characterization

The preliminary characterization of the processed devices is carried out using an automated measuring setup consisting of a Keithley 2400 Source Meter in combination with an absolutely calibrated array-spectrometer (CAS 140CT-153) (Figure 5.16). Here, the current-voltage-luminance ($I$-$V$-$L^\theta_v$) characteristics of each single device can be measured. Due to the fixed perpendicular mounting of the spectrometer head above the OLED or OLED-wafer, the spectral measurements are limited to the forward direction ($\theta_v=0^\circ$). Further, the spectral radiance $L^\theta_v(\lambda, j)$ for perpendicular radiation is determined at various luminances ($L^\theta_v(\lambda, j)$) and currents ($I$).

Besides, three smaller spectrometer (USB4000 (calibrated), USB2000 (uncalibrated) and USB2000 (calibrated), Ocean Optics) are utilized for measurements with the self-developed goniometer setup (see Subsection 5.4.2) and for EL- and PL-measurements with the small integrating sphere (see Subsection 5.4.3), respectively.
5.4 Characterization of OLED Devices

5.4.2 Goniometer-Setup: Angle-Dependent Characterization

To determine the angle-dependent spectral radiance of each device, a goniometer setup has to be employed. During this work two different system types (three setups) are used, either a commercial available setup DMS401 (Autronic Melchers) from the cooperation partner IPMS, a self-made setup of our cooperation partner Novaled or a carefully adjusted self-developed setup, similar to the Novaled tool. The latter system including software has been developed in the time of this work. Whereas the commercial setup with implemented software exhibits a movable detection fiber, which can be arranged at angles of $-90^\circ$ to $+90^\circ$ around the fixed driven device, the self-made systems features a fixed fiber with a rotating device. As the latter mentioned self-developed setup is mainly used in this work, this shall be described in more detail in the following.

The goniometer setup – depicted in Figure 5.17 – is employed to determine the angle-dependent spectral radiance of each device. The active area of the OLED device is positioned in the center of a rotary table (OWIS GmbH) and stepwise rotated from $0^\circ$ to $90^\circ$. Thereby, the spectral irradiance $E_e(\lambda, \theta, i)$ of the device is measured after every rotation step at a discrete current $i$. To avoid unwanted contributions from the edges, the devices are covered with masks during the measurement. Due to these masks the detected irradiance of the device may be slightly reduced above angles of $70^\circ$. As the employed spectrometer (USB4000, Ocean Optics) is not an absolutely calibrated tool, the spectral radiant intensity $I_e(\lambda, \theta, i)$ of the discrete spectra have to be determined with the aid of the $0^\circ$-spectra from the array spectrometer, resulting in the normed spectral radiant intensity $I_e^{\text{norm}}(\lambda, \theta, i)$. The data is used to calculate the device performance parameter luminous efficacy, external quantum efficiency, and current efficiency as discussed in the next section. The exact measurement of the self-made system has been verified via comparisons of the performance of monochromatic devices determined by an integrating sphere.
As the measurement usually lasts some seconds – due to the stepwise detection of the angle-dependent OLED emission – this setup requires an adequate long-term stability of the devices. OLEDs with very short lifetime therefore have to be characterized using an integrating sphere, where the whole hemispherical radiation can be detected in a short measurement time. Otherwise degradation and angle dependence would interfere, leading to unreliable angle-dependent spectral data.

### 5.4.3 Integrating Sphere: Hemispherical Characterization

The used large integrating sphere (ISP 500, Instrument systems, Ø=500 mm) and its schematic working principle is shown in Figures 5.18 and 5.19. The device is mounted in the center of the diffuse reflecting sphere. Before starting the measurement of the device, the sphere has to be calibrated with a standard lamp to measure its self-absorption. To prevent edge emission and falsification of the measured spectra, the edges of the substrate are covered. The emitted light from the device (solid lines in Figure 5.19) undergoes multiple diffuse reflections in the sphere (dotted lines) before reaching the detecting fiber. The fiber is separated from the emissive device by a baffle to prevent direct irradiation. Therefore, multiple reflected light at every possible angle emitted from the device in the half-space can be measured. The resulting integrated spectra is measured employing an absolutely calibrated array-spectrometer (CAS 140CT-153).

For EL-measurements on unencapsulated devices or PL measurement on thin films within an inert gas atmosphere in a glovebox, a small integrating sphere (Labsphere, Ø=15 cm) is furthermore utilized. It’s working principle is identical to the large sphere described above.

![Photograph of the employed integrating sphere.](image1)

![Schematic illustration of the working principle of an integrating sphere.](image2)
5.5 Determination of OLED Performance

Based on the optical and electrical measurements, illustrated in the previous section, the device performance is determined regarding color, efficacy, and efficiency. The basic equations for calculations are given in this section.

5.5.1 Colorimetric Variables

The color coordinates, the color rendering indices, and the correlated color temperature of all detected spectra (0°-spectra (OLED-robot), angle-dependent spectra (goniometer), and integrated spectra (sphere)) are calculated as explained in Section 2.4.

5.5.2 Luminous Efficacy

As already mentioned in Subsection 2.3.4, the luminous efficacy of a lighting system is defined by the luminous flux $\Phi_v$ radiated from the source in the whole sphere divided by the consumed electrical power $P_{el} = UjA$, with $U$ the applied voltage, $j$ the current density, and $A$ the device area. The luminous flux is obtained by an integration of the spectral radiant intensity over wavelength $\lambda$ and volume $\Omega$. As light from an plain OLED is radiated only in the forward hemisphere, the problem can be simplified and the luminous efficacy can consequently be determined via [152]

$$\eta_l = \frac{2\pi K_m}{UjA} \int_\theta \int_\lambda I_e(\theta, \lambda, i^j)V(\lambda)sin(\theta)d\theta d\lambda$$

with $[\eta_l] = \frac{lm}{W}$, (5.1)

where $K_m$ denotes the maximum luminous efficacy for photopic vision, $I_e(\theta, \lambda, i^j)$ the spectral radiant intensity at a discrete current $i^j$, and $V(\lambda)$ the spectral luminous efficacy function for photopic vision. If one can assume Lambertian emission from the device, the determination of the luminous efficacy will simplify to

$$\eta_{lamb} = \frac{\pi L_{0}^e}{Uj}.$$  (5.2)

However, for top-emitting OLEDs Lambertian emission can only be a rough assumption. Considering the usually non-Lambertian emission characteristic of top-emitting OLEDs, the spectral radiant intensity $I_e(\theta, \lambda, i^j)$ in Equation (5.1) has to be substituted by $I_{e}^{norm}(\theta, \lambda, i^j)$, which is the measured spectral radiant intensity normalized to the forward directed spectrum of the absolute OLED-robot measurement.
For current stable spectral emission, the radiant intensity shape does not change with driving currents. Consequently, the progression of the luminous efficacy in dependence on the current $I$ or luminance $L^0\theta$ can be assumed to be parallel to the exact progression of luminous efficacy values throughout the whole range of measured current points. Hence, a scaling factor $s_i$ is introduced, which determines the difference of the luminous efficacies at a distinct measured current $j$ via

$$s_i = \frac{\eta_{\text{lamb}}^i (j, U, L^0\theta)}{\eta_{\text{exact}}^i (j, U, L^0\theta)}, \quad (5.3)$$

with $\eta_{\text{lamb}}^i$ the luminous efficacy calculated with the assumption of Lambertian emission and $\eta_{\text{exact}}^i$ the exactly luminous efficacy determined via goniometer measurements. The luminous efficacy at every current $j$ can thereby be determined via

$$\eta_{\text{exact}}^i (j, U, L^0\theta) = s_i \cdot \eta_{\text{lamb}}^i (j, U, L^0\theta), \quad (5.4)$$

by a single goniometer measurement that defines the scaling factor $s_i$.

However, the spectral emission depends on the driving current $j$ in most multilayered white devices. Due to the altered charge carrier balance within the layers, the recombination zones shift and the exciton production as well as their distribution within the emission layer are modified. Consequently, the contributions of the participating electroluminescence spectra are modifying the spectral shape. In this case, the luminous efficacy $\eta^i$ can only be determined for distinct currents $j$ and correlated luminances $L^0\theta$, if the radiant intensity $I_e(\theta, j)$ was measured before.

### 5.5.3 External Quantum Efficiency

The external quantum efficiency $\eta_{\text{leqe}}$ is defined as the quotient of the radiated photon rate $\dot{N}_p$ (see Subsection 2.3.2) and the injected electron rate $\dot{N}_{el}$:

$$\eta_{\text{leqe}} (j) = \frac{\dot{N}_p}{\dot{N}_{el} (j)}, \quad (5.5)$$

with

$$\dot{N}_{el} = \frac{e A j}{\epsilon} \quad \text{and} \quad (5.6)$$

$$\dot{N}_p = \frac{1}{\hbar c} \int_{\Omega} \int_{\lambda} \lambda I_e (\Omega, \lambda) d\Omega d\lambda, \quad (5.7)$$
5.5 Determination of OLED Performance

where \( j \) denotes the current density, \( A \) the area, \( e \) the electron charge, \( h \) Planck’s constant, \( c \) the velocity of light in vacuum, \( \Omega \) the whole solid angle, and \( \lambda \) the wavelength. The photon rate \( \dot{N}_p \) is thereby calculated according to the equations depicted in Table 2.2 in Subsection 2.3.2. Consequently, the external quantum efficiency – dependent on the wavelength and the measured radiant intensity – is given by [152]

\[
\eta_{eqe} = \frac{2\pi e}{jAhc} \int_{\theta} \int_{\lambda} \lambda I_{\theta}(\theta, \lambda, j) \sin(\theta)d\theta d\lambda \quad \text{with} \quad [\eta_{eqe}] = \%.
\] (5.8)

The equation can be simplified for an Lambertian emitter according to

\[
\eta_{eqe}^{\text{lamb}} = \frac{\pi e}{jAhc} \int_{\lambda} \lambda I_{\theta}^{\text{lamb}}(\lambda)d\lambda.
\] (5.9)

For non-Lambertian emission characteristics, the spectral radiant intensity \( I_{\theta}(\lambda, \theta, j) \) has to be replaced again by \( I_{\theta}^{\text{norm}}(\lambda, \theta, j) \).

If the spectrum is further stable with increasing current, the external quantum efficiency \( \eta_{eqe}^{\text{exact}} \) can be calculated via

\[
\eta_{eqe}^{\text{exact}}(j, L_{\theta}^{\text{Lamb}}) = i_s \eta_{eqe}^{\text{exact}}(j, L_{\theta}^{\text{Lamb}}) \quad \text{with} \quad \eta_{eqe}^{\text{lamb}}(j, L_{\theta}^{\text{Lamb}}) = \frac{i_s}{\eta_{eqe}^{\text{exact}}(j, L_{\theta}(\theta))},
\] (5.10)

where \( i_s \) denotes a scaling factor analog to the considerations for the luminous efficacy in Subsection 5.5.2. Otherwise, it is only allowed to calculate the external quantum efficiency \( \eta_{eqe} \) for distinct current points \( j \) and correlated luminances \( L_{\theta}^{\text{Lamb}} \).

5.5.4 Current “Efficiency”

The current efficiency \( \eta_c \) evaluates the radiation of light from the light source against the driving current \( (I_{el} = jA) \). Since the current efficiency \( \eta_c \) is a directed term, only the luminous intensity \( (L_{\theta}^{\text{Lamb}} := I_{\theta}^{\text{Lamb}} A^{-1}) \) in forward direction is relevant, which is measured within the \( IV/L_{\theta}^{\text{Lamb}} \)-measurement of the OLED-robot. Therefore, \( \eta_c \) can be calculated via

\[
\eta_c(j) = \frac{1}{I_{el}} \int_{\lambda} \frac{I_{\theta}^{\text{Lamb}}(\lambda)}{jA}d\lambda = \frac{L_{\theta}^{\text{Lamb}}}{jA} \quad \text{with} \quad [\eta_c] = \frac{\text{cd}}{A}.
\] (5.12)
To determine the absolute quantum yield of thin organic layers, a setup consisting of the small integrating sphere (Labsphere), a He-Cd laser (IK5651R, Kimmon Electric Co.) for excitation and the small calibrated spectrometer (USB2000, Ocean Optics) for detection is utilized [140]. One after the other, a clean uncoated quartz glass substrate and an organic coated quartz glass substrate are excited at a wavelength of $\lambda=325$ nm within the sphere. Both signals are detected with the spectrometer connected with the integrating sphere via fiber.

The PL quantum yield $\eta_{PL}$ is calculated by the difference between emitted photons from the laser $N_{abs}$ and absorbed photons $N_{abs}$ by the dye. Concerning the emission, the number of photons $N_p$ in a distinct time and wavelength interval ($\Delta t$ and $\Delta \lambda$, respectively) is given by

$$N_{p, em}(\Delta \lambda)(\Delta t) = \int_{\lambda_1}^{\lambda_2} \int_{t_1}^{t_2} \left( \frac{\partial \Phi_{em}}{\partial \lambda} \right) \frac{\lambda}{h} d\lambda dt,$$

(5.13)

with $\Phi_{em}$ the photon flux, $h$ the Planckian constant, and $c$ the velocity of light in vacuum. Assuming further an invariant photon flux in the time interval $\Delta t$ and small wavelength intervals $\Delta \lambda_n = \lambda_2 - \lambda_1$ the equation simplifies to:

$$N_{p, em}(\Delta \lambda_n)(\Delta t) = \frac{\lambda_n}{hc} \Phi_{em}(\Delta \lambda_n) \Delta t,$$

(5.14)

which is the number of photons emitted in a time interval $\Delta t$ and a wavelength interval $\Delta \lambda_n$. The detected signal $S_n$ of the spectrometer photocell $n$ depends on the impacting radiated power $\tilde{\Phi}(\Delta \lambda_n)$, the integration time $\Delta t$ of the spectrometer, and the spectral responsivity of the setup $\alpha(\Delta \lambda_n)$:

$$S_n \propto \tilde{\Phi}(\Delta \lambda_n) \Delta t \alpha(\Delta \lambda_n).$$

(5.15)

Since the integrating sphere assures a proportionality between the detected power $\tilde{\Phi}(\Delta \lambda_n)$ of the spectrometer and the emitted radiated power $\Phi_{em}(\Delta \lambda_n)$ of the sample, Equation (5.14) results in

$$N_{em} \propto \frac{\lambda_n}{hc} S_n \alpha^{-1}(\Delta \lambda_n).$$

(5.16)

A summation over all signals of the $n$ cells of the spectrometer within the emission area for each of the three contributions – the sample signal, the initial and final laser signal – leads to the following equation for the PL quantum yield

$$\eta_{PL} = \frac{N_{em}}{N_{abs}}$$

(5.17a)
5.7 Optical Measurements on Thin Layers

\[
\begin{align*}
= & \sum_{n}^{\text{em,s}} \frac{\lambda_n S_n \alpha^{-1}(\lambda_n)}{\sum_{n}^{\text{em,l-i}} \lambda_n S_n \alpha^{-1}(\lambda_n)} \\
= & \frac{A_{\text{em,s}}}{A_{\text{em,l-i}} - A_{\text{em,l-f}}} \\
\end{align*}
\]

(5.17b)

(5.17c)

where the subscripts s, l-i and l-f describe the contribution from the sample signal, the initial and final laser signal, respectively, and \( A \) denotes the respective area under the detected spectral graph. Figure 5.20 illustrates the spectrometer signals calibrated with the setup responsivity \( \alpha \).

As the measurement setup is currently under installation, the self-reflection of the integrating sphere has not been examined in detail so far, leading to an inexact setup calibration. For the calculation of the yield based on the measured spectral emission, the reflection is approximated to be independent from wavelength within the measurement range. Consequently, large measurement errors may appear, which can lead to calculated values of above 100%.

5.7 Optical Measurements on Thin Layers

For optical characterization of metal layers or thin films of organic materials, single layers are evaporated on top of glass or quartz glass substrates. The photoluminescence spectra of the emissive materials are detected with a spectrofluorometer (FluoroMax, SPEX and F900, Edinburgh Instruments). To determine the reflectance, transmittance, and absorption of the grown thin layers, a spectrophotometer (MPC-3100, Shimadzu and Lambda900, Perkin Elmer) is utilized. Based on the measurements of the spectrophotometer, the real and complex refraction index \( n \) and \( k \) of thin organic layers can be determined using an algorithm published by Fritz et al. [153].

5.8 Optical Simulations

For optical simulations of complete organic devices, a numerical tool [154] is utilized, which is able to simulate the optical performance of an OLED based thin film optics (cf. Section 4.4). The tool can calculate the characteristics of any desired organic multilayered stack, if the needed parameters are provided, which are the refractive indices \( n_i(\lambda) \) and \( k_i(\lambda) \) as well as the thickness \( d_i \) of each layer \( i \) and the layer arrangement within the stack. Furthermore, the PL-spectra of the employed emitters, their weighting factors \( w_i \), the position of the active layer, and the exciton distribution have to be introduced. This enables the calculation of diverse spectral values such as cavity emission,
Figure 5.20: Calibrated emission signals from a pure quartz glass substrate and a quartz glass substrate coated with organic film (NPB:Ir(MDQ)$_2$(acac), 5 wt.%) excited by a laser. The insets magnify the relevant spectral areas $A$ of (a) the initial and final laser emission ($A_{em,l-i}$ and $A_{em,l-f}$) and (b) the dye emission ($A_{em,s}$).
5.9 Microscopic Analysis of Surfaces

The layer quality and morphology of substrate surfaces and organic layers are determined using three different microscopical techniques illustrated in Figure 5.21a-c. Besides a light-optical microscope, a scanning electron microscope and an atomic force microscope is used. Their basic functions are shortly described in the following subsections. For more details beyond this short description, the reader is referred to further literature [155–159].
5.9.1 Light-Optical Microscope

For an optical characterization of large areas and surfaces, a light-optical microscope (LM) (JENAVAL, Carl Zeiss, Jena) is employed. This microscope uses a system of variable objective and ocular lenses to magnify the sample, which is irradiated with visible light on a wide-field area. The magnification can thereby be chosen by different lens arrangements. The magnified image of the sample is detected by either the bare eye or digitally by a CCD-camera. Due to the utilization of visible light, however, the resolution is limited by diffraction.

5.9.2 Scanning Electron Microscope

Especially substrate surfaces can further be determined by a scanning electron microscope (SEM) (CAM SCAN CS44) [160]. All measurements have been carried out by Dr. Enrico Langer (Institut für Oberflächenphysik und Mikrostrukturphysik, TU Dresden).

A scanning electron microscope uses a high-energy particle beam of electrons in UHV to create magnified images of objects. To prevent accumulation of static electric fields during electron irradiation, the objects under observation have to be electrically conductive. Non-conductive specimen are therefore usually covered by a ultra-thin gold (Au) film by sputtering or thermal evaporation. The high-energy electron beam is thermionically emitted by a cathode and focused by electrostatic and electromagnetic “lenses” to probe the sample. Primary electrons incident on the sample can either be reflected back by elastic scattering (back scattered electrons), lead to an emission of secondary electrons by inelastic scattering or result in emission of electromagnetic radiation (X-rays), each of which can be collected by specialized detectors. The signals from secondary electrons and back scattered electrons, obtained by scanning across a little rectangular area of the sample, are amplified by electronic amplifiers and usually displayed on a screen. The three-dimensional image thus created is therefore a distribution of an intensity signal emitted from the scanned area. Thus, the topography of a specimen or the morphology of the particles, making up the sample are indirectly shown. The detected X-rays can give information about the material composition of the sample via energy dispersive X-ray analysis (EDX). The scanning electron microscope generates high-resolution images of shapes of objects up to a few nanometers and shows a large depth of sharpness. However, differences in height and sample roughness cannot be detected.
5.9.3 Atomic Force Microscope

A more precise surface analysis of the topography of samples can be obtained by an atomic force microscope (AFM) (Nanoscope III, Digital Instruments, Veeco and ExplorerTM, TopoMetrix Corporation). It has a maximal scanning area of $15 \times 15 \, \text{µm}^2$, shows a resolution of 1 nm and is able to map differences in height on the sample.

An atomic force microscope consists of a cantilever with a sharp tiny tip at its end by which the specimens surface is probed. To scan the surface of the sample, the cantilever is mounted on piezoelectric elements, which move the cantilever above the sample. Thereby, atomic forces between surface molecules and the cantilever are detected. Deflections of the bent cantilever are measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. All measurements are carried out in tapping mode, where the cantilever is positioned in a minimum distance above the sample surface slightly tapping the surface. The cantilever is externally oscillated at its resonant frequency and moved above the surface in $x$- and $y$-direction driven by the piezo elements. During the scanning, the occurring tunneling current between the specimen surface and the tip is used as feedback signal to adjust the sample-tip distance. By this technique, a damage of the tip can be avoided, what is important especially for very rough samples. Thereby, the frequency is permanently hold constant. The topographic image of the sample surface is constructed by measuring the deflections of the cantilever with the help of the photodiode array.

An evaluation of the microscopic images with the software program WSxM (4.0 Develop 7.0, Nanotec Electronica S.L.) allows to extract information about the roughness of the measured surface. Thereby, each height data of the two dimensional surface was sorted in a histogram with 100 intervals. Next to the average or mean height $\bar{h}$ of the intervals and thereby the height distribution as well as the maximum height $h_{\text{max}}$ value describing the end of the histogram interval and therefore the highest elevation on the surface, also the root mean square of the roughness is calculated based on the equation

$$\text{rms} = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (\bar{h} - h_i)}, \quad (5.18)$$

where $n$ denotes the number of measured heights $h_i$ and $\bar{h}$ the average height. On the base of these numbers, several surfaces can be compared with regard to roughness.

5.10 UPS Measurements

For the determination of hole injection barriers within the layered device, the technique of Ultraviolet Photoelectron Spectroscopy (UPS) is employed, which utilizes the prin-
Figure 5.22: Sketch of (a) the working principle of the UPS system and (b) a typical resulting energy distribution of organic material on top of a metal layer.

Experimental Techniques and Methods

ciple of the external photo effect. All measurements at this tool were carried out by Dr. Selina Olthof (Institut für Angewandte Photophysik, TU Dresden).

Photons with the energy $E = h \nu$ are generated by an ideally monochromatic light source and directed on the sample, which can either be metal or semiconducting material. Each photon can excite an electron from the sample up to a depth of 2-3 monolayers, if the binding energy $E_B$ of the electron is lower than the incident photon energy. Photoelectrons are ejected from the bulk layer and can be detected by an electrostatic analyzer, which resolves the kinetic energy $E_{\text{kin}}$ of the electrons given by

$$E_{\text{kin}} = h \nu - E_B.$$  \hspace{1cm} (5.19)

Thereby, the density of states (DOS) of the bound electrons within metal or organic material can be observed.

The measurements are carried out under ultrahigh vacuum ($p < 1 \cdot 10^{-9}$ mbar) with a measuring setup (Phoibos100) using the helium (He) I line with an energy of 21.22 eV from a discharge lamp. The experimental error is below 50 meV and can be estimated from the reproducibility achieved in separate measurements. The organic layers for UPS measurements are grown in an multi-chamber evaporation system (similar to the system described in Subsection 5.3.2), which is directly connected to the UPS chamber. A sketch of the working principle and the resulting energy distribution are shown in Figures 5.22 and 5.23.

The distribution of the electron density is superimposed by a background electron signal, which is formed by secondary electrons that result from inelastic scattering processes before they escape the irradiated layer. As the kinetic energy of the photoelectrons, reaching the detector, is depending on their binding energy, strongest bound electrons will show lowest energy. The high binding energy cutoff (HBEC) energy ($E_{\text{HBEC}}$) of the detected energy distribution, therefore describes photoelectrons, which just have enough energy to escape from the solid. The work function of the material
\( \Phi_w \) is therefore defined according to

\[
\Phi_w = h\nu - E_{\text{HBEC}}. \quad (5.20)
\]

Electrons with highest detectable kinetic energy originate from the lowest occupied energy level, due to their weakest binding energy \( E_B = 0 \) eV, which is the Fermi energy level \( E_F \) for metals and the HOMO-level for organic material. These electrons define the HOMO cutoff (HC) position with the energy \( E_{\text{HC}} \) in semiconducting organic material. Therefore, the hole injection barrier (HIB) into the organics can be calculated via

\[
E_{\text{HIB}} = E_F - E_{\text{HC}}. \quad (5.21)
\]

The ionization potential (IP) of the organic layer can be determined via

\[
E_{\text{IP}} = h\nu - (E_{\text{HBEC}} - E_{\text{HC}}). \quad (5.22)
\]

Generally, an interface dipole \( \Delta \) appears at an interface of two materials A and B given by

\[
\Delta = E_{\text{HBEC}}^A - E_{\text{HBEC}}^B. \quad (5.23)
\]

Thus, vacuum level alignment is no longer given. For more details, the reader is referred to literature [161].

---

**Figure 5.23:** Schematic description of the process of the excitation in a sample comprising an organic layer on top of metal.
6 Metal Substrates and Bottom Electrode Layer

The first chapter is dedicated to the investigation of the surface morphology of the substrates and bottom electrode layers. Both, substrates and bottom electrode layers are essential for the processing of OLEDs, as their smoothness directly determines the production yield. Therefore, the chapter is split into two parts. The first part deals with the microscopical analysis of metal substrates, where the morphology of three different metal substrates (untreated, pretreated uncoated, and pretreated Ag-coated) is determined. In the second section, the evaporation of silver layers on top of metal and glass substrates is discussed. Here, the effect of the evaporation rate as well as the deposited layer thickness on the surface smoothness are determined.

6.1 Microscopic Analysis of Metal Substrates

The application of thin organic films requires a very smooth substrate surface, which avoids low device performance caused by high leakage current in backward driving direction as well as short circuits resulting from peaks or substrate defects in the dimension of the organic layer thickness that may lead to device failures. To assure adequate surface quality for OLED application, novel substrate types have to be carefully examined with regard to defects and surface roughness. Therefore, the surface quality of the different available substrates is discussed with a special focus on metal substrates. In the first subsection, the morphology of the untreated pure Alanod metal substrate is analyzed and compared to two different glass substrates. Subsequently, the characteristics of two different pretreated Alanod substrates (uncoated and silver coated) is presented. In contrast to the untreated pure substrate, these substrates both have passed a so called roll-process, where the surface has been contacted by rolls over the whole area. Here, the examination involves three differ-
ent microscopical techniques introduced in Section 5.9. The light-optical microscope is used for a first inspection of the surface quality and the location of large defects. The scanning electron microscope has a higher resolution and therefore gives a more detailed view on the substrate surface. Finally, the atomic force microscope provides a height profile and the surface roughness.

### 6.1.1 Alanod Metal Substrates

Generally, untreated Alanod metal substrates show a homogeneous surface morphology as depicted in Figure 6.1. All microscopical images with different resolution show small round and oval hills that cover the whole surface. In Figure 6.2 the surface morphology of an Alanod substrate is compared to a standard glass substrate and a high-quality glass substrate. In comparison to the very homogeneous surface of the Alanod substrate, both glass substrates show a few large hills, which are distributed across the whole substrate surface. With regard to the rms (1.86 nm) and average height $\bar{h}$ (5.69 nm), the Alanod substrate is comparable to a standard glass substrate as shown in Table 6.1. However, the maximum height of approximately 13 nm is lower for the
6.1 Microscopic Analysis of Metal Substrates

Figure 6.2: AFM image of (a) an Alanod substrate, (b) a standard glass, and (c) a high-quality glass. The inset shows the three-dimensional surface. In comparison to the surface morphology of the Alanod metal substrate, the glass substrates show a few larger hills on the top of the surface.

metal substrate compared to approximately 37 nm for the standard glass. Compared to a high-quality glass (cf. Figure 6.2c), which was for the first time available at the end of this thesis, the roughness data is about two times higher concerning the rms and average height, but comparable to the maximum roughness values. As the roughness values of the untreated Alanod substrate are comparable to standard glass substrates, this substrate type presents an alternative to the commonly used heavy and fragile glass substrate.

6.1.2 Pretreated Alanod Substrates

Besides the pure Alanod substrates, Alanod substrates with pre-fabricated 100-120 nm thick Ag electrode layer are available. The Ag coating is deposited in a UHV sputter chamber, in which the Alanod metal band has to be stepwise locked in from normal pressure to UHV and back. Thereby, the whole surface is exposed to several large heavy rolls on both substrate sides. During this locking process, the contact between rolls and...
Table 6.1: AFM roughness data of (a) an Alanod substrate, (b) a standard glass substrate, and (c) a Princeoptics glass substrate. Values are each extracted from \((5 \times 5) \mu m^2\) large areas.

<table>
<thead>
<tr>
<th></th>
<th>Alanod metal substrate</th>
<th>standard glass substrate(^1)</th>
<th>Princeoptics glass substrate(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>rms</td>
<td>1.86</td>
<td>1.92</td>
<td>0.93</td>
</tr>
<tr>
<td>(l_h)</td>
<td>5.69</td>
<td>4.95</td>
<td>2.33</td>
</tr>
<tr>
<td>(h_{\text{max}})</td>
<td>13.34</td>
<td>37.43</td>
<td>11.91</td>
</tr>
</tbody>
</table>

\(^1\) values averaged over two AFM measurements

Uncoated Alanod Substrates

Figure 6.3 shows microscopical images of the silicon oxide substrate surface, which has been in contact with the rolls. As the silicon oxide smoothing layer is transparent, a surface examination using the light-optical microscope (Figure 6.3a) can not reveal surface defects or other morphological damages. The visible stripes result either from the silicon oxide coating or the Al plate surface. The SEM images (see Figure 6.3b), using secondary electrons, does not show any large surface defects. Only some small particles are visible, which are likely dust and can easily be removed by further cleaning.

Microscopic AFM images (cf. Figure 6.3c) from the surface of the uncoated Alanod substrates show a few small holes and a couple of tiny scratches. The average roughness of the AFM images is 1.71 nm and the average height is 21.36 nm. The maximal height is measured to be 31.96 nm. Compared to the untreated Alanod substrate, the average and maximum height values are higher, whereas the rms is slightly decreased.

In conclusion, the contact of the uncoated substrate to the rolls barely affects the substrate surface. The roughness remains low and is in the range of the untreated Alanod substrate or the standard glass substrate (cf. Subsection 6.1.1), with a slight increase
6.1 Microscopic Analysis of Metal Substrates

Figure 6.3: Microscopical images of the rolled uncoated substrate surface, taken by (a) a light-optical microscope, (b) a SEM, and (c) an AFM. Due to the transparency of the silicon oxide smoothing layer, the light-optical microscope is not able to detect any surface damage. Despite some particles and holes on (b) the SEM and (c) the AFM image, no large defects can be detected.

of the average height. The treated substrates can therefore be used as substrates for organic devices, especially OLED applications, as their smoothness is appropriate for the deposition of thin organic layers.

Silver Coated Alanod Substrates

Furthermore, Alanod substrates with a prefabricated Ag electrode layer are examined. The microscopically taken images are shown in Figures 6.4, 6.5, and 6.6. In comparison to the uncoated silicon oxide, the Ag-coated Alanod substrates can be examined via light-optical microscopy due to the low transmittance of the Ag coating. The images reveal various defects, e.g. round and bulky defects visible in Figure 6.4b-d, but predominantly scratches in different variations (see Figure 6.4e-h). Next to the continuous and discontinuous scratches with undefined direction, also holes and dints can be detected. These defects most probably originate from tiny particles sticking to the rolls and pressing into the soft Ag layer during the locking process or improper substrate handling after deposition.

The SEM analysis shows a similar situation, illustrated in Figure 6.5. Along with scratches, dints (cf. Figure 6.5a) and material scratched out of the substrate (see Figure 6.5c) are detected. The EDX analysis shows that some deep scratches already reach the Al substrate. For example, only Al and Si could be detected in the large scratch in Figure 6.5c. As the insulating silicon oxide layer is broken, these deep defects will cause an electrical contact between substrate and anode and will cause short circuits. Furthermore, flakings and bulges are detectable (cf. Figures 6.5b and d). The origin of the round structures with small spherical particles (see Figure 6.5e), surrounding a large particle, is not yet resolved. This structure could be due to a particular deposition of sputtered Ag around dust particles.
Figure 6.4: Selected light-optical microscope images of Ag-coated Alanod substrate surfaces. The substrate surface is covered with numerous defects (a-d), mainly scratches (e-h).

Figure 6.5: Selected scanning microscope images of Ag-coated Alanod substrate surfaces. Particles (a), flakings (b), deep broad scratches (c), bulges (d), round particle structures (e) and bounded discontinuous scratches (f) can be detected.
6.1 Microscopic Analysis of Metal Substrates

In the AFM images, scratches up to a depth of 120 nm (see Figure 6.6c) can be detected. The average rms roughness value of the examined surfaces is 11.63 nm, which is almost seven times higher compared to the uncoated substrate. Furthermore, an average height of 57.32 nm and a maximum height of 153.01 nm are detected. These large height differences are detrimental for particularly thin organic layers deposited on top of this Ag-coated substrate.

Although several positions on the Alanod substrate band are examined, an accumulation of defects on one of these test positions cannot be detected. The defects are homogeneously distributed on the whole metal band surface.

In summary, the Ag-coated substrate is hardly applicable for organic devices, as short circuits cannot be avoided due to the large and deep surface defects. To fabricate usable metal coated substrates with a low number of defects, the locking process has to be optimized and the substrate handling has to be improved further. However, these substrate may be usable for OLED stacks with thick organic layers, e.g. in the second or third order, if appropriate insulation of the OLED stack to the metal substrate can be assured. Here, the number of peaks with a height in the order of the stack thickness is comparatively small. Though, a passivation coating has to be applied on the Ag surface to achieve a defined active area and to separate the cathode from the anode layer.

Figure 6.6: Representative atomic force microscope images of Ag-coated Alanod substrate surfaces. Deep scratches can be detected. They can reach a depth of even 120 nm, which is the layer thickness of the whole Ag electrode coating.
6.2 Roughness of the Silver Bottom Electrode Layer

This section deals with the bottom electrode layer made from silver films, which are evaporated on the substrate in UHV previous to the deposition of the organic material. Generally, electrode layers have to fulfill several requirements, where especially the surface morphology and roughness are crucial for the processing of efficient light emitting devices without energy losses due to leakage currents or short circuits. The morphology of the layer depends on several factors. In the following, the effect of the evaporation rate as well as the deposited layer thickness are analyzed. Thereby, special attention is drawn to the metal substrates. As for test samples, glass substrates are also used, the surface roughness of Ag on top of these samples is examined, too.

6.2.1 Requirements of Electrode Layers

Electrode materials have to meet special demands, if they are intended for the application in organic devices. One has to distinguish between the bottom contact, the anode in pin-devices, and the top contact, which serves as cathode.

In the top-emitting structure, the latter electrode is – besides the injection of electrons into the organic layers – responsible for the outcoupling of light from the device. This can be provided by using a very thin but closed metal layer, which ensures a sufficient transmission as well as an adequate conductivity. For the devices reported in this work, exclusively 15 nm Ag are used as top-electrode.

Compared to the top contact, the bottom contact – lying beneath the organic layers in the complete deposited layer stack – has to be highly reflecting. This ensures that light emitted in the anode direction is not absorbed by the electrode. Besides a good conductivity and a good injection of holes into the organic layers, the surface quality of this layer is crucial for a device with limited layer thickness. To prevent short circuits and device failure, the roughness of the bottom anode layer has to be very low without any large peaks.

As Alanod substrates with prefabricated Ag anode layer (see Subsection 6.1.2) cannot be used due to the high number of surface defects, the anode layer has to be deposited onto the substrates within the evaporation process of the whole organic device, which is done by thermal evaporation (cf. Subsection 5.3.2). Due to the higher reflectivity the metal Ag is so far mainly used as bottom contact of top-emitting devices. Therefore, the growth and the morphology of this metal is examined and reported in the following.
6.2 Roughness of the Silver Bottom Electrode Layer

6.2.2 Silver Anode Layer on Top of Metal Substrates

In order to evaluate the roughness of Ag on top of metal substrates, the layer thickness and the evaporation rate are varied separately. All metal evaporation experiments using the Alanod metal substrate are carried out in the multi-chamber deposition tool UFOII. The surfaces are subsequently examined via AFM.

Effect of the Evaporation Rate on the Surface Morphology

To examine the influence of the evaporation rate on the morphology and the roughness of Ag covered metal substrates, 20 nm Ag is evaporated on top of eight metal substrates using different evaporation rates. The rates are chosen within a range from 0.1 Å s\(^{-1}\) to 10.0 Å s\(^{-1}\) and are typically used for metal evaporation at the UFOII. The recorded AFM images and the determined roughness data are depicted in Figures 6.7a-h and 6.8, respectively. At low evaporation rates of 0.1 and 0.3 Å s\(^{-1}\), the surface morphology is comparable to the pure Alanod substrate (cf. Figure 6.1) and shows a homogeneous distribution of material on top of the Alanod substrate. Consequently, the roughness values are low with an average height of around 15-22 nm. With increasing rate (see Figure 6.7c), more and higher hills are growing, which are visible as bright spots on the

Figure 6.7: AFM images of Alanod metal substrates coated with 20 nm Ag using eight different evaporation rates (a) 0.1, (b) 0.3, (c) 0.5, (d) 0.7, (e) 1.0, (f) 2.0, (g) 5.0, and (h) 10.0 Å s\(^{-1}\). At lower rates (0.1 and 0.3 Å s\(^{-1}\)) the morphology equals the pure Alanod substrate surface (see Figure 6.2a). With increasing evaporation rate, larger Ag cluster are growing.
AFM image. In the medium evaporation range at 0.7-2.0 Å s\(^{-1}\), the hills on the surface are larger compared to the morphology at lower evaporation rates. Furthermore, some deep holes appear at higher deposition rates, where no or only a low amount of material is deposited. Therefore, the average height and the maximum height is strongly increased showing maximum height values of 75-95 nm in comparison to the low evaporation rates. However, the roughness at even higher rates (5.0 and 10.0 Å s\(^{-1}\)) are on the other hand decreased. This may be due to the large clusters of Ag (see Figure 6.7g), which are formed during the rapid evaporation and cover a large area of the sample, smoothening the surface.

**Effect of the Deposited Layer Thickness on the Surface Morphology**

The influence of the Ag layer thickness on the anode morphology and the surface is illustrated in Figures 6.9 and 6.10. All anode layers are evaporated at a constant evaporation rate of 0.3 Å s\(^{-1}\).
6.2 Roughness of the Silver Bottom Electrode Layer

Figure 6.9: AFM images of Alanod metal substrates coated with (a) 20, (b) 30, (c) 40, (d) 50, (e) 60, (f) 80, and (g) 100 nm Ag layer thickness at an evaporation rate of 0.3 Å s\(^{-1}\). The surface morphology does not significantly change with higher layer thickness.

In comparison to the evaporation rate, the morphology does not change significantly with an increased layer thickness. The images show homogeneously structured anode surfaces, which are comparable to each other and mostly composed of small oval to round hills containing larger Ag clusters from time to time. The roughness does not show a distinct dependency on the Ag layer thickness. The average height is in the range of 11±2 nm and the maximum height is between 16 and 24 nm.

6.2.3 Silver Anode Layer on Top of Glass Substrates

Besides using Alanod substrates, organic light-emitting diodes are also processed on top of glass substrates as test substrates. Consequently, Ag covered glass substrates also have to meet the requirements for a smooth electrode layer surface. To determine the roughness of Ag deposited on glass substrates, two standard glass substrates are covered with an 50 nm thick Ag layer using the multi-chamber evaporation tool and the single-chamber evaporation tool to furthermore compare the Ag deposition with respect to the available facilities. The results are compared to a measurement of a Ag-coated Alanod substrate processed in UFOII.

Figure 6.11 shows the AFM images of the examined substrate surfaces with the deposition parameters layer thickness and evaporation rate. The bar diagram in Figure 6.12 obviously shows a lower roughness for the Ag covered standard glass substrate, compared to the Alanod substrate. The morphology of the coated glass substrate, with a
Figure 6.10: AFM roughness values (root mean square, average height, and maximum height) of Ag films on top of Alanod substrates deposited with different layer thicknesses at an evaporation rate of 0.3 Å s⁻¹ with the standard deviation σ. The roughness values at 0 nm are taken from the uncoated Alanod substrate. With increasing Ag layer thickness, the roughness is not significantly changed.

Figure 6.11: AFM images of (a) an Alanod substrate and (b and c) two standard glass substrates covered with a Ag layer. The Ag deposition was carried out in the UFOII for the samples (a) and (b) and in the LESKER for sample (c).
6.2 Roughness of the Silver Bottom Electrode Layer

Figure 6.12: AFM roughness values of (a) an Alanod substrate and (b and c) two standard glass substrates covered with a Ag anode layer. The Ag deposition was carried out in the UFOII for the samples (a) and (b) and the LESKER for sample (c).

rm of 1.80 nm, an average height of 5.58 nm, and a maximum height of 29.28 nm, is comparable to an uncoated standard glass substrate shown in Subsection 6.1.1. If the evaporation is carried out in the large single-chamber evaporation tool, the roughness is strongly reduced. Here, the average height is below 1 nm and shows a very homogeneous surface morphology, which is comparable to the silicon oxide surface of the Alanod metal substrates. As for both samples (b) and (c) the same standard glass substrates are used, one can assume that the changed roughness is due to the evaporation tool.
7 Hybrid White Devices

This chapter focusses on hybrid white devices, which combine phosphorescent and fluorescent emitter materials to achieve warm white light emission. First, a short introduction to hybrid OLEDs is given, especially focusing on the separating interlayer. Subsequently, two layer stacks are presented, which realize warm white light based on three and four emissive dyes. The first part concentrates on devices containing three emissive dyes. Herein, the realization of first- and second-order top-emitting white devices is discussed, followed by an analysis of several optimization steps for achieving high efficiencies as well as good color quality. Hereafter, four selected white devices showing high efficiency as well as good color quality are discussed in detail. In the following section, the three-color approach is extended by another yellow emitter material for achieving higher luminous efficacies.

7.1 The Interlayer Approach in Hybrid Devices

Emission of white light can be achieved using several approaches (see Subsection 4.3.2). In this section, the generation of white light is based on a layered emission layer structure containing fluorescent as well as phosphorescent materials, resulting in so called hybrid devices. The utilization of both fluorescent and phosphorescent dyes is due to the fact that up to now, the available phosphorescent blue emitters are relatively unstable compared to very long living red and green phosphorescent dyes such as Ir(MDQ)$_2$(acac) or Ir(ppy)$_3$ [152, 162]. Therefore, the combination of phosphorescent and fluorescent emitters is a good compromise between stability and efficiency of OLEDs.

Combining fluorescent and phosphorescent emitter materials enables exciton exchange between both emitters, which is illustrated in Figure 7.1a. If the fluorescent blue emitter shows a very low lying triplet level, exciton transfer from the triplet level of the
phosphorescent emitters takes place, which leads to a loss of radiation due to the non-radiative character of the triplet level of the fluorescent emitter. Furthermore, the phosphorescent emitter quenches singlet excitons of the fluorescent dye, leading to highly reduced fluorescence. To avoid such mutual exciton quenching processes, both emission layers are separated by an interlayer with a higher singlet as well as a higher triplet level compared to the emitters (see Figure 7.1b). Thereby, Förster as well as Dexter transfer can be restricted and quenching of excitons can be avoided.

To assure furthermore an exciton generation at both sides of the interlayer at all, this layer must have ambipolar transport characteristics as well as low energy barriers for both charge carrier types to avoid blocking. As it is quite challenging to find a single material with ambipolar character carrying both holes and electrons, this need can be fulfilled by a blend of two materials [163]. In this blend, one material is predominantly hole transporting and the other predominantly electron conduction (e.g. NPB and BAlq₂ or TCTA and TPBi). The combination of two materials has the additional possibility to adjust the flow of charge carriers by changing the mixing ratio in the interlayer.

The charge carrier balance and the exciton generation are therefore – besides the interlayer thickness – highly influenced by the choice and the mixture ratio of the materials, which also determines the driving current and voltage. Consequently, these parameters have a strong impact on the performance as well as the spectrum of the device.

Figure 7.1: Illustration of the interlayer approach separating fluorescent and phosphorescent dyes: Interface between fluorescent and phosphorescent emitter material (a) without interlayer and (b) with interlayer. Due to the high lying triplet and singlet level of the interlayer, exciton exchange via Förster and Dexter transfer are suppressed, after [66].
7.2 White Emission Based on Three Emitters

To achieve high-quality white light, the emission range of the utilized dyes should span the whole visible spectrum. This requires at least three emitters to allow for high color rendering indices, as each emitter can cover a wavelength range of only 100 to maximum 200 nm. The white organic layer structure presented in this section is based on three emitter materials Ir(MDQ)$_2$(acac) for orange-red emission, Ir(ppy)$_3$ for green emission, and a third fluorescent emitter for blue emission. The first two highly stable phosphorescent dyes show high efficiencies, whereas the blue emitter is limited in efficiency. For photoluminescence emission spectra of the used dyes see Figure 5.8 in Subsection 5.2.4.

The basic layer arrangement of the three-color based devices is adapted from a bottom-
emitting OLED stack [90] and was applied to a top-emission layer architecture (see Figure 7.2), which required a change of layer thicknesses, electrodes as well as profound device optimization. Using this structure, firstly, the realization of white emission using a top-emitting device architecture is discussed including means of simulation. Subsequently, several optimization steps are described in the second subsection, resulting in high-quality devices, which are discussed in detail in the final part of this three-color section. In the following, the spectral radiance, the cavity emission, and the examined color coordinates are illustrated for a viewing angle of 0°, if not stated differently.

7.2.1 Realization of White Top-Emission

As already discussed in Subsection 4.4.2, white light emission from a top-emitting layer architecture is quite challenging due to microcavity effects (see Subsection 4.4.1). To predict and evaluate the optical characteristics for these devices, optical simulation (see Section 5.8) can be an assistive tool. With regard to a reasonable material utilization, OLED devices are in general produced up to the third order. Higher order devices exhibit an increased cavity thickness, which depends on the emission wavelength. In the following, the first and second order of a white cavity stack are evaluated by optical simulations. This is followed by the production of the device if appropriate.

Simulation of First-Order Cavity Devices

The used layer structure for the simulation is depicted in Table 7.1. Using simulation tools, one can get a rough prediction of the cavity emission and the spectral emission of the considered device. However, for detailed fitting of the spectral emission of a processed device, the measured data at several viewing angles has to be applied. Furthermore, the weighting factors for blue (b), green (g), and orange-red (r) emission of the dyes have to be precisely chosen in the simulation. Sometimes, it is also necessary to rearrange the thicknesses of the organic layer for the simulation in order to get a precise fit. This is mainly due to experimental uncertainties during evaporation with regard to layer thickness (see Subsection 5.3.2) and doping concentration, leading to different emission spectra despite using nominally identical materials, thicknesses, and stack structure. Some deviations in efficiency or spectral radiance appearing in the following sections may be due to this fact.

Starting with the first maximum cavity emission, the cavity length is modified by a change of the hole transport layer thickness (HTL) between x=0 and 50 nm, leading to an overall organic layer thickness of 80 to 130 nm. The HTL is chosen to ensure a
Table 7.1: Hybrid device structure based on three emitters with different cavity thickness $d_{cav}$, between 80 and 130 nm, arranged by a change of HTL thickness $x=0$ to 50 nm without ($y=0$ nm) and with ($y=50$ nm) dielectric capping layer. The RGB weighting of the emission is chosen to be $r=1$, $g=0.4$, and $b=0.4$.

<table>
<thead>
<tr>
<th>material</th>
<th>$d$ (nm)</th>
<th>weights $w$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO-TPD</td>
<td>$y$</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Spiro-DPVBi</td>
<td>20</td>
<td>$b$</td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>3</td>
<td>$g$</td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>20</td>
<td>$r$</td>
</tr>
<tr>
<td>Spiro-TAD</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:F$_4$-TCNQ</td>
<td>$x$</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

The RGB weighting of the emission is chosen to be $r=1$, $g=0.4$, and $b=0.4$.

As Figure 7.3 shows, the overall cavity thickness strongly effects the emission. The wavelength region — aimed at outcoupling and emission — is marked by the photoluminescence spectra of the three utilized emission materials. Their intensities are stepwise increased from blue to red, as one would expect RGB intensity arrangement for ideal well-balanced warm white emission. With increasing cavity thickness, the cavity emission is red-shifted across the whole visible wavelength region. The application of the dielectric capping layer can broaden the shape of the cavity emission, but it also decreases the intensity.

The maximum of the cavity emission is red-shifted with higher cavity thickness. Devices without capping layer exhibit high intensity with small spectral width. Supplementary, the distance between the maxima of the cavity emission is quite small compared to the devices with capping layer. These devices feature lower intensity but much broader spectral emission. Furthermore, the spectral shape changes, which leads to a modified full width of half maximum noted in Table 7.2. The maximum FWHM can be found at a HTL thickness of 20 nm with 100 nm cavity thickness. Furthermore, the blue contribution to the emission can be enhanced at this thickness. The strong dependence of the cavity emission on the cavity thickness further stresses the necessity to precisely control the layer thicknesses. A change in thickness of only a few nanometer changes the width of the possible emission, the contribution of each dye and thereby the shape of the spectral emission.
Figure 7.3: Simulation of the first-order cavity emission at different cavity thicknesses $d_{cav}$ arranged by varied HTL thickness $x$ nm, without ($y=0$ nm) and with ($y=50$ nm) capping layer of the device described in Table 7.1. For reasons of comparison the PL emission of the three utilized emitting dyes is shown. The devices without capping layer show quite narrow cavity emission, whereas the capping layer devices show much broader cavity emission.

Table 7.2: Full width of half maximum (FWHM) of the cavity emission for the layer structure without ($y=0$ nm) and with ($y=50$ nm) capping layer at different HTL thicknesses $x$ and cavity thicknesses $d_{cav}$ of the device described in Table 7.1.

<table>
<thead>
<tr>
<th>$x$ (nm)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d_{cav}$ (nm)</td>
<td>80</td>
<td>90</td>
<td>100</td>
<td>110</td>
<td>120</td>
<td>130</td>
</tr>
<tr>
<td>FWHM (nm) for $y=0$ nm</td>
<td>68</td>
<td>72</td>
<td>72</td>
<td>71</td>
<td>71</td>
<td>73</td>
</tr>
<tr>
<td>FWHM (nm) for $y=50$ nm</td>
<td>112</td>
<td>143</td>
<td>159</td>
<td>156</td>
<td>147</td>
<td>137</td>
</tr>
</tbody>
</table>
In Figure 7.4 the simulation of the spectral radiance is illustrated for cavity thicknesses between 80 nm and 130 nm ($x=0$ to 50 nm). It is clearly visible that a modified cavity thickness of $\pm 10$ nm is sufficient to change the shape of the spectral emission. A well balanced warm white emission spectrum can only be achieved for a hole transport layer thickness of 20 nm.

The angular dependence of the cavity emission is depicted in Figure 7.5. Without dielectric layer, a considerable green shift of 58 nm can be detected from $0^\circ$ to $70^\circ$. The application of the CL decreases this shift by two thirds to 19 nm. Thereby, the angular dependence of the spectral emission is decreased. The splitting into two peaks for angles above $60^\circ$ is due to changed p- and s-polarized contributions to the cavity emission.

Furthermore, the cavity is also influenced by the thickness of the capping layer. Figure 7.6 illustrates the cavity emission for a capping layer thickness of $y=40$ to 60 nm. With increased thickness of the capping layer, the cavity emission maximum shows a slight green shift and also a change in intensity. The broadest FWHM can be detected for a CL thickness of 50 nm (see Table 7.3).
Figure 7.5: Simulation of the angle-dependent cavity emission ($x=20$ nm, $d_{cav}=100$ nm) with and without capping layer in the face of the PL emission of the three utilized emitting dyes of the device described in Table 7.1. The green shift is largely alleviated by the applied dielectric capping layer.

Table 7.3: Cavity emission maximum and full width of half maximum (FWHM) of the cavity emission at different capping layer thicknesses $y$ of the device described in Table 7.1.

<table>
<thead>
<tr>
<th>$y$ (nm)</th>
<th>40</th>
<th>45</th>
<th>50</th>
<th>55</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>cavity emission maximum (nm)</td>
<td>520</td>
<td>525</td>
<td>538</td>
<td>552</td>
<td>558</td>
</tr>
<tr>
<td>FWHM (nm)</td>
<td>131</td>
<td>139</td>
<td>159</td>
<td>157</td>
<td>145</td>
</tr>
</tbody>
</table>
Figure 7.6: Simulation of the cavity emission \(x=20\,\text{nm}\) at different capping layer thicknesses \(y\) of the device described in Table 7.1. The emission shifts to lower wavelength and features a maximum FWHM at \(y=45\) and 50 nm.
Table 7.4: Hybrid device structure based on three emitters without \((x=0 \text{ nm})\) and with \((x=50 \text{ nm})\) dielectric capping layer processed on MoTa substrates.

<table>
<thead>
<tr>
<th>material</th>
<th>(c) (wt.%)</th>
<th>(r) ((p:q))</th>
<th>(d) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeO-TPD</td>
<td></td>
<td></td>
<td>(x)</td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spiro-DPVBi</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>3:1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)_3</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)_2(acac)</td>
<td>5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Spiro-TAD</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:F$_4$-TCNQ</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoTa</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Realization of First-Order Cavity Devices**

To verify the simulation, devices with a cavity length of 100 nm (see Table 7.4) are processed using the small multi-chamber evaporation tool UFOII. Using the anode material MoTa, which usually shows a very smooth surface and therefore prevents short circuits, a much higher device yield is achieved. Additionally, a thin silver layer is applied on top of the MoTa layer to increase the anode reflectivity, as MoTa shows a high transmission (see Table 5.3). To emphasize the importance of the dielectric capping layer for top-emitting devices, one device is processed without \((x=0 \text{ nm})\) and one with capping layer \((x=50 \text{ nm})\). The angular measurements of these devices are carried out with a commercial goniometer setup DMS401.

Figure 7.7 illustrates the cavity and spectral emission of the examined devices. Both devices feature the characteristics of the cavity emission in Figure 7.7a and b as already discussed in the previous paragraph. The spectral emission of the device is depicted in Figure 7.7c and d, directly below the cavity emission for comparison reasons. Both sets of spectral radiant intensity coincide very well with the simulated data. The device without capping layer features emission in a quite small wavelength region, which is shifted to lower wavelengths by \((\Delta x, \Delta y)=(0.160, 0.097)\). This effect originates from the microcavity effects. Thereby, the emission spectra strongly is deformed. The application of the 50 nm thick dielectric capping layer from MeO-TPD changes the optical properties, without influencing electrical characteristics of the device. Thereby, the microcavity effects (cf. Subsection 4.4.1) are alleviated, which leads to a broadband emission spectrum, where light from all three emitters is coupled out. Furthermore, the
Figure 7.7: Simulated cavity emission (a and b) and simulated and measured spectral radiant intensity (c and d) of the device described in Table 7.4 without and with capping layer (CL). Without CL the cavity emission and the spectral emission show both a narrow spectrum and a strong angular dependence, which is alleviated by applying a dielectric layer. The changed cavity emission shape for the angle of 60° is due to changed s- and p-polarization tendencies. Simulation and measurement of the spectral emission coincide very well.
Figure 7.8: Color coordinates (a) and normalized radiant intensity (b) of the devices described in Table 7.4 without and with capping layer (CL). The color coordinates without CL show a strong shift from $0^\circ$ to $60^\circ$, which is largely removed with the CL. Both devices show emission patterns almost similar to Lambertian emission.

The stabilized spectral emission with increasing viewing angle for the device with applied capping layer can be verified by pictures of the devices in Figure 7.9. The emission color is close to the warm white point A as visible in Figure 7.8a. Besides, the devices exhibit nearly Lambertian emission characteristic (Figure 7.8b) in both cases, especially at small viewing angles.

Simulation of Second-Order Cavity Devices

Since the thickness of first-order devices is low, they are prone to short circuits and device failures, if the roughness of the substrate is in the range of the layer thickness. Consequently, an increase in the cavity thickness would be advantageous to prevent such failures. Due to the high conductivity of the transport layers, the thickness of the HTL and ETL can be increased without significantly increasing the driving voltage. Thick HTL may act as buffer layer for rough substrates or electrodes. Furthermore, the emission layer is removed from the highly reflecting anode, which reduces the coupling to surface plasmon-polaritons [164, 165].
Therefore, a second-order white top-emitting device is explored in the following using simulations based on the stack shown in Table 7.1. In the simulation the cavity thickness is stepwise raised by increasing the HTL thickness $x$ from 0 nm to 260 nm in 20 nm steps. Figures 7.10a and b give an overview on the cavity emission in this region comparing first- and second-order devices.

The cavity emission in the second-order can be detected in the visible wavelength region above a cavity thickness of 200 nm ($x=120$ nm) (cf. Figure 7.10a). With increasing cavity thickness, the cavity emission is shifted towards the IR. It can be clearly detected that the second-order cavity emission is much narrower compared to the first-order cavity emission. The FWHM is as low as for devices without capping layer in the first maximum. The comparison of first, second, and third order reveals that an increase in cavity order leads to a narrowed spectrum. Furthermore, the distance between the maxima of two cavity emission curves at an increment of 20 nm is decreased compared to first-order devices. This situation inhibits a broadband emission of all three emitter and makes a balanced white emission impossible.

A more detailed view on the second-order simulations is given in Figure 7.11. The averaged FWHM of the cavity emission between 220 and 320 nm is 74 nm, which is only half of the FWHM of first-order devices (cf. Table 7.2), preventing broadband white emission.

As the capping layer thickness has only a small effect on the maximum and FWHM of the cavity emission, a thickness change does not improve the emission of second-order devices significantly. Since broadband emission for white color coordinates cannot be achieved by second-order devices, OLEDs were not realized experimentally.
Furthermore, the thin Al sub-layer, if not stated otherwise. For much easier de-
Figure 7.10: Simulation of the cavity emission at different cavity thicknesses $d_{\text{cav}}$
which does not form a closed layer. It is assumed that the thin Al layer acts as trap for
Ag, which otherwise diffuses into the device. Due to the stability, tend to failures, high leakage currents, and short circuits as well as discontin-
During the processing of several devices, it turned out that the devices show quite low
stability, tend to failures, high leakage currents, and short circuits as well as discontinu-
uous emission (flickering). A thin aluminum sub-layer – introduced between ETL and
the thin Ag cathode – reduces these problems and stabilizes the devices. Due to the positive effects on the device stability, almost all processed devices therefore contain
this stabilizing thin Al sub-cathode layer. To prevent absorption of light and a thereby
a strong influence on the emission spectrum, the thickness is chosen to be only 1 nm,
which does not form a closed layer. It is assumed that the thin Al layer acts as trap for
Ag, which otherwise diffuses into the device [166]. Furthermore, the thin Al sub-layer
may also lead to a better electron injection into the device.

7.2.2 Layer Adjustment and Device Optimization

Building on the results of the first white emitting device in Subsection 7.2.1, the or-
ganic stack is optimized to achieve good efficiencies and color quality. Due to the com-
plex layer system, various optimization steps can be performed to adjust both electrical
and optical properties of the emission stack. The devices are produced in the single-
chamber evaporation tool (LESKER) on top of common glass substrates. They are
characterized by the OLED-robot (see Subsection 5.4.1) as well as the self-developed
goniometer-setup (see Subsection 5.4.2), if not stated otherwise. For much easier de-
vice processing and handling, glass wafer are used as test substrates at first.

![Simulation of the cavity emission at different cavity thicknesses $d_{\text{cav}}$.](image)

(a) between 80 and 200 nm and (b) between 200 and 320 nm arranged by
changed HTL thickness $x$ for a device with 50 nm capping layer based on the
stack shown in Table 7.1. The FWHM of the cavity emission decreases with
higher order. Depending on the cavity thickness, the first-, second-, or even
third-order emission maxima are depicted.

**Figure 7.10:** Simulation of the cavity emission at different cavity thicknesses $d_{\text{cav}}$.
(a) between 80 and 200 nm and (b) between 200 and 320 nm arranged by
changed HTL thickness $x$ for a device with 50 nm capping layer based on the
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ous emission (flickering). A thin aluminum sub-layer – introduced between ETL and
the thin Ag cathode – reduces these problems and stabilizes the devices. Due to the positive effects on the device stability, almost all processed devices therefore contain
this stabilizing thin Al sub-cathode layer. To prevent absorption of light and a thereby
a strong influence on the emission spectrum, the thickness is chosen to be only 1 nm,
which does not form a closed layer. It is assumed that the thin Al layer acts as trap for
Ag, which otherwise diffuses into the device [166]. Furthermore, the thin Al sub-layer
may also lead to a better electron injection into the device.
Figure 7.11: Simulation of cavity emission and the spectral radiance at cavity thicknesses between 220 and 320 nm ($x=140$ to 240 nm) for a device with 50 nm capping layer based on the stack shown in Table 7.1. Due to the narrow cavity emission, a broadband spectral emission from the microcavity is impossible.
The devices based on the three color hybrid approach [90] show a dependence of the spectral emission shape as a function of current or luminance (see Figure 7.12). This results from a shifted electron-hole balance within the device and hence a shift of the recombination zone, leading to a different exciton distribution [91]. Thereby, the green and blue emission contribution in the spectrum is enhanced at higher driving current. Consequently, the emission spectrum, the color coordinates, and also the color rendering are tuned by device brightness. However, due to the current dependent emission spectra, the spectral shape of the emission at certain brightnesses has to be considered when calculating the efficiency of the device. This is usually done with a measurement at distinct driving currents or luminances (as explained in Subsections 5.5.2 and 5.5.3) with a goniometer setup, which additionally accounts for the emission characteristics of the device. For some devices, processed in an early state of this work, such a setup has not yet been available. Therefore, only preliminary efficiency data evaluated by assuming Lambertian emission (labelled with *) can be provided in this cases, which is generally only suited for comparison among one another.
7.2 White Emission Based on Three Emitters

Table 7.5: External quantum efficiency ($\eta_{eq}$) and lifetime ($t_{1/2}$) of the blue emitters Spiro-DPVBi [167] and MADN:TBPe [145] measured at distinct luminances $L$.

<table>
<thead>
<tr>
<th>$L$ (cd m$^{-2}$)</th>
<th>$\eta_{eq}$ (%)</th>
<th>$t_{1/2}$ (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spiro-DPVBi</td>
<td>3.8</td>
<td>87</td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>$\approx$6.1</td>
<td>$\approx$3000</td>
</tr>
</tbody>
</table>

Application of Different Blue Emitters

The spectral emission of the devices shown in Subsection 7.2.1 mainly lacks in spectral contributions from low wavelength to achieve balanced white light. To improve the blue emission in this three color device, an alternative fluorescent blue emitter was tested and compared to the bulk emitter Spiro-DPVBi. The emission spectra of both the new system MADN:TBPe and the previous emitter Spiro-DPVBi are depicted in Figure 5.8a in Subsection 5.2.4. Experiments on blue monochromatic bottom-emitting OLEDs reveal that utilizing the blue emitter material TBPe [145] can exceed the device performance of the common fluorescent material Spiro-DPVBi [167]. As depicted in Table 7.5, the external quantum efficiency of the blue fluorescent system MADN:TBPe can reach up to 5% in contrast to 3.8% for Spiro-DPVBi. Additionally, a much higher lifetime\(^1\) can be achieved for the blue system at adequate device conditions. OLEDs with the bulk emitter Spiro-DPVBi reach a lifetime of only 87 h at an initial luminance of 500 cd m$^{-2}$, whereas the system MADN:TBPe feature approximately 3000 hours. Furthermore, the photoluminescence color coordinates are more in the deep blue ($x$, $y$) = (0.133, 0.189) compared to Spiro-DPVBi with ($x$, $y$) = (0.15, 0.24). This allows a better color balance of the three emitters to achieve high-quality white emission.

To prevent short circuits and low device yield, another anode modification is implemented as depicted in Table 7.6. Here, 15 nm Ag are applied on top of a 40 nm thick Al layer, the latter assuring low transmission. The applied thin Ag layer leads to a higher reflectance compared to pure Al but prevents emerging peaks on its surface. Since a layer thickness above 10 nm on top of Aluminum does not show any significant spectral changes, which is due to a saturation in reflectance, a layer thickness of 15 nm is chosen to assure highest reflectivity at lowest material consumption.

Furthermore, the material NPB is used as capping layer due to economic reasons, as it shows similar optical properties compared to MeO-TPD but is much cheaper.

The application of the new emitter system MADN:TBPe leads to a significant increase of the blue and green emission compared to Spiro-DPVBi (see Figure 7.13b). The emis-

\(^1\)The lifetime of an OLED is defined by the half life $t_{1/2}$ of the device at an initial luminance $L_i$ $(L(t_{1/2}) = \frac{1}{2}L_i)$ and is given in hours (h).
Figure 7.13: Characteristics of the three-color based devices described in Table 7.8 with different blue emission material systems with a layer thickness of \( x \) nm: (a) normalized spectral emission measured at a luminance of approximately 1000 cd m\(^{-2}\), (b) luminous efficacy, and EQE. Using MADN:TBPe as blue emitter leads to increased blue and green emission, but a decrease in efficiency.
Table 7.6: Hybrid device structure based on three emitters employing different blue emitter materials $X$ (Spiro-DPVBi or MADN:TBPe). Besides, a pure Ag anode with $y=60$ nm an anode combination of $x=40$ nm and $y=15$ nm is used to prevent device failures which often appear for pure Ag anode layer.

<table>
<thead>
<tr>
<th>Material</th>
<th>$c$ (wt.%)</th>
<th>$r$ ($p:q$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>1</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>1:1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$ (acac)</td>
<td>5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>NPB</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>$y$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>$x$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

sion intensity of the blue as well as the green emission are more than doubled, whereas the anode modification does apparently not significantly influence the spectral emission characteristic of both devices with different blue emitter materials. Compared to Spiro-DPVBi, the devices using TBPe feature a decreased luminous efficacy and external quantum efficiency. This is due to the reduced orange-red emission from the highly efficient material Ir(MDQ)$_2$ (acac), whose proportion in the RGB ratio is decreased, since MADN:TBPe features more blue and green emission. The missing efficiency data for the Ag based MADN:TBPe device originates from a device failure due to the problems with pure Ag anodes. Concerning the anode modification for Spiro-DPVBi devices, the efficiencies are slightly lower using Al-Ag compared to pure Ag.

Applying Different Hole-Blocking Materials

The electron-hole balance and consequently the generation of excitons can be influenced by varying the HOMO and LUMO values of different blocker materials. With regard to the electron supply of the EML, especially the hole blocking layer influences this balance. To find the best material in terms of electrical characteristics and well balanced spectrum, three different hole blocking materials TPBi, BPhen, and Alq$_3$ are tested. The layer sequence used is illustrated in Table 7.7. In comparison to previous experiments, the emission layer thickness of MADN:TBPe is decreased to 10 nm.
Table 7.7: Hybrid device structure based on three emitters employing different hole blocking materials $X$: TPBi, BPhen or Alq$_3$.

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%)</th>
<th>$r$ ($p:q$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>1:1</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>S-TAD</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Due to the higher lying LUMO of Alq$_3$ ($E_{A_{Alq3}} = -3.1$ eV) and TPBi ($E_{A_{TPBi}} = -2.8$ eV) compared to BPhen with $E_{A_{BPhen}} = -2.0$ eV, the electron transport into the emission layer is limited. This leads to a lack of electrons in the orange-red sub-emission layer. Thereby, the recombination and exciton generation is decreased in this layer, whereas the emission of Ir(ppy)$_3$ and TBPe is increased, since an adequate amount of electrons is available to recombine with the holes present. Consequently, the green emission is enhanced for the materials TPBi and Alq$_3$ compared to BPhen (cf. Figure 7.14) that does not show an energy barrier for the injected electrons. The emission color points for TPBi and Alq$_3$ are hence shifted to lower $x$- and higher $y$-coordinates to the green edge of the color diagram and moved away from the Planckian locus. Only the device with BPhen shows a stepwise increase of the emission intensity from blue over green to orange-red. Furthermore, this device exhibits well color coordinates of $(x, y) = (0.468, 0.483)$ and the highest CRI value of 59. Under the assumption of Lambertian emission, the luminous efficacy and external quantum efficiency is highest for the BPhen device, as this material leads to the strongest orange-red emission from the highly efficient dye Ir(MDQ)$_2$(acac).

Emission Layer Thickness

The utilized hybrid layer structure has been taken from an optimized bottom-emitting device [90], which was optimized for a much larger cavity thickness of around 155 nm. The orange-red as well as the blue sub-emission layer thickness have been chosen to be
7.2 White Emission Based on Three Emitters

Figure 7.14: Characteristics of the three-color based devices described in Table 7.7 with different hole blocking materials X: (a) \( jV \)-characteristics, (b) spectral radiance divided by driving current, (c) luminous efficacy and EQE as well as (d) color coordinates, and (e) color rendering indices. Compared to TPBi and Alq3, the HBL material BPhen features a steplike spectral emission as well as higher efficiency and better color quality.
Table 7.8: Hybrid device structure based on three emitters employing different thicknesses \( x = 10 \) or \( 20 \) nm for the orange-red sub-emission layer. To keep the overall cavity thickness constant at 100 nm, the HTL thickness is simultaneously changed by \( y \).

<table>
<thead>
<tr>
<th>Material</th>
<th>( c ) (wt.%)</th>
<th>( r ) (p:q)</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td></td>
<td>1:2</td>
<td>2</td>
</tr>
<tr>
<td>TCTA:Ir(ppy)(_3)</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)(_2)(acac)</td>
<td>5</td>
<td>x</td>
<td></td>
</tr>
<tr>
<td>S-TAD</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>y</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

20 nm each in this bottom-emitting device. Since a top-emitting device needs a much thinner cavity thickness to adjust the cavity emission maximum in the visible wavelength region, a decrease of the sub-emission layers is advantageous. Thereby a better optimization of the position of the emission zone within the cavity can be achieved. The blue sub-emission layer has already been narrowed during the introduction of the new emitter system MADN:TBPe. In this paragraph, the decrease of the orange-red sub-emission layer will be discussed in detail. The utilized layer stack is depicted in Table 7.8.

As the electric characteristics in Figure 7.15a reveal, the performance of the device can be improved by a narrowed sub-emission layer and a consequently increased thickness of the HTL. Thereby, the \( jV L \)-curve becomes much steeper leading to lower driving voltages at a fixed luminance. Furthermore, the emission spectrum shows an increased orange-red and decreased green emission (see Figure 7.15b), both leading to more balance white emission as the color point is moved towards the Planckian locus (cf. Figure 7.15d). However, the blue contribution to the emission spectra is not changed and still quite low. The efficiencies of both devices are quite similar. The device with the 10 nm thick orange-red emission layer exhibits luminous efficacies of 18.7 lm W\(^{-1}\) and 15.2 lm W\(^{-1}\) as well as external quantum efficiencies of 5.8 % and 5.1 % at luminances of about 500 and 2000 cd m\(^{-2}\), respectively.
Figure 7.15: Characteristics of the three-color based devices described in Table 7.8 with different orange-red sub-emission layer thicknesses of x nm: (a) $jV L$-characteristics, (b) spectral radiance divided by driving current, (c) luminous efficacy and EQE, and (d) color coordinates at about 2000 cd m$^{-2}$. With smaller orange-red emission layer thickness, both electrical and optical characteristics are improved, leading to a better balanced white device with higher color quality.
Table 7.9: Hybrid device structure based on three emitters employing a changed overall cavity thickness. The cavity thickness is decreased via reduction of the ETL thickness \( x = 35 \text{ nm} \) to \( x = 20 \text{ nm} \) in 5 nm steps.

<table>
<thead>
<tr>
<th>material</th>
<th>( c ) (wt.%)</th>
<th>( r ) (p:q)</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>( x )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>1:2</td>
<td>10</td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)(_3)</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)(_2)(acac)</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>S-TAD</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Optimizing the Cavity Thickness

To enhance the blue portion of the spectrum and thereby gain a more balanced color performance, the thickness of the cavity is decreased from 100 to 80 nm via a reduction of the ETL thickness, which leads to a shift of the cavity emission towards smaller wavelengths. The stack is illustrated in Table 7.9. The experimental results are depicted in Figure 7.16.

Unfortunately, the probability for device failures increases with decreased cavity thickness using the example of the device with \( x = 20 \text{ nm} \), whose efficiency could only be determined for one luminance. Furthermore, the devices exhibit very high leakage current as visible in Figure 7.16a, which give an indication for a low quality or rough substrate.

With decreasing cavity thickness, the cavity emission is blue-shifted and thus more and more detuned, as the cavity emission maximum is shifted to wavelength lower than the blue emission maximum. At a cavity thickness of 85 nm (\( x = 20 \text{ nm} \)), the cavity emission features a maximum of 448 nm, which is even below the maximum of the emission peak of TBPe. Thereby, the spectral emission shows a lowered orange-red contribution and increased green and blue emission. As a result of the change in the emission proportions, the luminous efficacy as well as the EQE are decreased and the color coordinates are shifted towards the green edge of the color diagram.

Due to the high failure rates of the devices with low cavity thickness, in future ex-
7.2 White Emission Based on Three Emitters

Figure 7.16: Characteristics of the three-color based devices described in Table 7.9 with decreased overall cavity layer thickness $x = 35, 30, 25, 20$ nm: (a) $jV L$-characteristics, (b) spectral radiance divided by driving current, (c) luminous efficacy and EQE, (d) color coordinates, and (e) color rendering indices measured at around 1000 cd m$^{-2}$. According to the green shift of the cavity emission, a decreased spectral orange-red and increased green and blue emission can be detected, leading to lower efficiency.
Table 7.10: Hybrid device structure based on three emitters employing increasing TPBi interlayer fraction $q=1, 2$ and $3$ with $p=1$.

<table>
<thead>
<tr>
<th>Material</th>
<th>$c$ (wt.%)</th>
<th>$r$ ($p:q$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B Phen:Cs</td>
<td>25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B Phen</td>
<td>10</td>
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<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>1:$q$</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>S-TAD</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>70</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experiments only cavity thicknesses of 100 nm are used to prevent short circuits. Thus, an overall decreased emission intensity due to the strongly detuned cavity can also be avoided.

Influence of Interlayer Ratio and Thickness

The interlayer separating fluorescent and phosphorescent material plays an important role in the hybrid device as discussed in Section 7.1. This paragraph reports on experiments using different blend ratios as well as blend thicknesses in order to achieve balanced white emission.

In the beginning, the attention is drawn to the ratio of the interlayer blend, where the fraction of TPBi ($q$) is varied within the interlayer blend. Thereby, the mainly electron transporting material is increased stepwise. The utilized layer structure as well as the interlayer composition can be extracted from Table 7.10.

As illustrated in Figure 7.17a, the electrical characteristics are almost identical for all devices with the exception of $q=1$, showing slightly lowered luminance. The spectral radiance, shown in Figure 7.17b, also illustrates a different spectral emission for the 1:1 blend ratio compared to $q=2$ and 3. By using the interlayer ratios 1:2 and 1:3, the orange-red emission is strongly increased and the blue emission is slightly increased, while the green emission is stable. For $q=2$ and 3, the spectral emission is similar featuring a very high contribution from the green emitter materials Ir(ppy)$_3$ as a consequence.
Figure 7.17: Characteristics of the three-color based devices described in Table 7.10 with increasing TPBi fraction in the interlayer blend of 1:1, 1:2 or 1:3: (a) \( \psi \)-characteristics, (b) spectral radiance divided by driving current, (c) luminous efficacy respectively EQE, and (d) color coordinates at approximately 1000 cd m\(^{-2}\). With increasing TPBi concentration, the orange-red contribution is increased and the color coordinates are red-shifted.
Table 7.11: Hybrid device structure based on three emitters employing different interlayer thicknesses $x$. The interlayer thickness is lowered from $x=2.0$ nm to $x=1.5$ nm.

<table>
<thead>
<tr>
<th>material</th>
<th>c (wt.%)</th>
<th>$r (p:q)$</th>
<th>d (nm)</th>
</tr>
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<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
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<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>1:2</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td></td>
<td></td>
<td>$x$</td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>8</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>S-TAD</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of a changed electron-hole balance. However, the emission intensity at wavelength of around 555 nm drops with higher TPBi concentration. This leads to a decreased luminous efficacy for $q=3$ (see Figure 7.17c) compared to $q=2$, which shows the highest efficiency performance with 13.1 lm W$^{-1}$ and 4.3 % at around 1000 cd m$^{-2}$ due to the large orange-red contribution in the emission spectrum. The color coordinates of the devices can be found in the whitish green part of the color diagram, especially if considering $q=1$ with the low orange-red emission. However, they are shifted towards the Planckian locus and the warm white point A for increased TPBi fraction.

Furthermore, the interlayer thickness is investigated. As depicted in Table 7.11, two different interlayer thicknesses $x=2$ nm and $x=1.5$ nm are chosen. As the $jV/L$-characteristics in Figure 7.18a show, the total charge current flow is not influenced by the changed thickness of the interlayer. In contrast, the spectral radiance illustrated in Figure 7.18b is modified. The green contribution to the spectrum is largely decreased for the interlayer thickness of 1.5 nm compared to $x=2$ nm. This is combined with a slight reduction of orange-red emission and increased blue contribution. The spectral modification may be due to a loss of excitons in the Ir(ppy)$_3$ doped TCTA sub-emission layer, as excitons probably permeate this thin interlayer and decay nonradiatively in the blue sub-emission layer. The EQE is stable at 5 %, whereas the luminous efficacy features a constant drop of about 2 lm W$^{-1}$ at each luminance (e.g. from 18.8 lm W$^{-1}$ to 16.5 lm W$^{-1}$ at 500 cd m$^{-2}$), which can be assessed as a consequence of the reduced green emission. Due to the large drop in green emission,
Figure 7.18: Characteristics of the three-color based devices described in Table 7.11 using an different interlayer thickness of either 1.5 nm or 2.0 nm: (a) $jV$-$L$-characteristics, (b) spectral radiance divided by driving current, (c) luminous efficacy and external quantum efficiency, (d) color coordinates, and (e) color rendering indices at about 1000 cd m$^{-2}$. 

7.2 White Emission Based on Three Emitters
Table 7.12: Hybrid device structure based on three emitters employing different doping concentrations for the green emitter Ir(ppy)$_3$ ($x=5$ or 8 wt.%) and the blue emitter TBPe ($y=0.5$, 1.0, 1.5, 2.0 wt.%).

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%)</th>
<th>$r$ $(p:q)$</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>$y$</td>
<td>1:2</td>
<td>10</td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td></td>
<td>1:2</td>
<td>1.5</td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>$x$</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>S-TAD</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

the color coordinates for the devices with $x=1.5$ nm are strongly shifted towards the Planckian locus. Furthermore, the color rendering is increased reaching almost 75 at a luminance of 3000 cd m$^{-2}$. This performance trend of increased green emission with higher interlayer thickness is confirmed by further experiments.

Applying Different Dye Doping Concentrations

The doping concentration of the sub-emission layer can also play an important role in the balancing of the RGB contributions to the white emission spectrum. Therefore, the influence of the doping concentration is examined in this paragraph to adjust the color coordinates if possible. To keep the orange-red emission as highest emission contribution, the doping concentration of Ir(MDQ)$_2$(acac) is not varied. The chosen layer structure with varied green $x$ and blue $y$ doping concentration in the sub-emission layer is illustrated in Table 7.12. Previously performed experiments showed large contributions from the green emitter material Ir(ppy)$_3$, leading to an unbalanced emission in regard to blue and red contributions. In order to modify the intensity of the green emission contribution, two doping concentrations ($x=8$ wt.% and $x=5$ wt.%) are tested. Furthermore, the doping concentration of the blue emitter TBPe is varied for device optimization. As it is known from experiments with monochromatic bottom-emitting devices [145], single blue devices comprising the system MADN:TBPe show highest efficiencies as well as highest
lifetime for doping concentrations around 1 wt.%. Therefore, doping concentrations around 1 wt.% are chosen for further experiments.

Figure 7.19 illustrates the results of the above described experiments. Neither the Ir(ppy)$_3$ nor the TBPe concentration – doped in the respective matrix material – do change the current-voltage characteristics of the devices. However, a decreased luminance (see Figure 7.19a) can be detected for the 5 wt.% doped devices compared to the 8 wt.% doping. This indicates a lowered exciton generation at the interface of the green sub-emission layer to the interlayer, which results in lower green and also lower orange-red emission, as less excitons can diffuse to the red sub-emission layer. On the other hand, this lowered exciton generation causes a larger supply of holes on the cathode facing side of the emission layer, leading to a higher amount of singlet excitons on the interface between interlayer and blue sub-emission layer. Consequently, the blue contribution is increased as visible in the current normalized spectral radiance in Figure 7.19b, but indeed by a much lower degree due to the loss of triplet excitons in fluorescent emitter materials. Thereby, also the green emission contribution is modified as a lower intensity can be detected for a Ir(ppy)$_3$ concentration of 5 wt.%. The slight red-shifted emission maximum can be due to the contribution from the second and third emission maximum of the MADN:TBPe emission at 490 and 534 nm, respectively, which is also raised with higher blue emission. This interferes with a strong reduction of Ir(ppy)$_3$ emission, as the overall emission decreases. Due to the reduced contribution from highly efficient green and orange-red emission, the luminous efficacy and the EQE are significantly reduced from about 15.3 lm W$^{-1}$ to 11.5 lm W$^{-1}$ and from about 5.5 % to 4.5 % at a luminance of approximately 1000 cd m$^{-2}$. Due to the modified spectral emission with decreased Ir(ppy)$_3$ doping concentration, the color coordinates approach the Planckian locus and are slightly blue-shifted.

Concerning the TBPe doping concentration, one can determine relatively independent device characteristics. Neither the electrical characteristics nor the spectral emission of the devices change with the doping concentration. Consequently, the luminous efficacy as well as the EQE do not exhibit significant changes. Exclusively, the color coordinates as well as the color rendering indices of the devices slightly shift.

**Location of the Emission Layer**

The emission layer can be shifted within the organic stack by varying the p- and n-transport layer thicknesses. Thereby, the device properties can be influenced with regard to the spectral emission of the device. As described in Table 7.13, the MeO-TPD:NDP2 (HTL) and BPhen:Cs (ETL) layer thicknesses $x$ and $y$, respectively, are stepwise changed from $x/y=35$ nm/$20$ nm to $x/y=20$ nm/$35$ nm, keeping the overall cavity thickness constant at 99.5 nm. Thus, the emission layer is shifted towards the anode.
**Figure 7.19:** Characteristics of the three-color based devices described in Table 7.12 using different different Ir(ppy)$_3$ and TBPe doping concentrations $x$ and $y$, respectively: (a) $JVL$-characteristics, (b) spectral radiance divided by driving current, (c) luminous efficacy and external quantum efficiency, (d) color coordinates, and (e) color rendering indices at luminances of approximately 100, 500, 1000, and 3000 cd m$^{-2}$. Devices with lower (5 wt.%) Ir(ppy)$_3$ concentration show lower efficiency performance but color coordinates more close to the Planckian locus, as well as blue enhanced spectral emission.
Table 7.13: Hybrid device structure based on three emitters employing different transport layer thicknesses. The hole transport layer thickness can be chosen to be $x=35, 30, 25, 20\,\text{nm}$, at which the ETL layer thickness is simultaneously changed from $y=20, 25, 30, 35\,\text{nm}$ holding the overall cavity thickness constant at 99.5 nm. The emission layer is thus shifted from the cathode to the anode facing region.

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%</th>
<th>$r$ ($p{:}q$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
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<td>NPB</td>
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</tr>
<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1.5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>1:2</td>
<td></td>
<td>1.5</td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>5</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>NPB</td>
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<td></td>
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</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
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<td>$x$</td>
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</tr>
<tr>
<td>Al</td>
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</tbody>
</table>

Figure 7.20 illustrates the device characteristics, which have been – apart from $jVL$-measurements – determined at a constant current of 3 mA. As the $jVL$-characteristics (Figure 7.20a) do not change, the differences in the spectral radiance can only be explained by a varied exciton distribution and/or by optical reasons. With decreased p-doped transport layer thickness, both blue and green emission intensities are increased. Whereas the orange-red emission first increases, it is subsequently lowered below its initial intensity. The cavity emission of the organic layer stack reveals that the change in the spectral emission of both blue and green emitters can be attributed to the blue-shifting cavity emission. However, the change in cavity emission does not explain the variation of the orange-red emission intensity in the spectral emission. These effects are not totally understood yet. The luminous efficacy as well as the EQE increase up to a thickness arrangement of $x/y=30\,\text{nm}/25\,\text{nm}$ (9.7 lm W$^{-1}$ and 4.6 %), but decrease afterwards. This is on one hand due to the changed orange-red emission intensity, but may also be attributed to another parameters. The color coordinates of the four devices are noticed to show a strong blue shift of 600 K in correlated color temperature (CCT).
Figure 7.20: Characteristics of the three-color based devices described in Table 7.13 using different transport layer thicknesses: (a) \( jV \) characteristics, (b) spectral radiance at a constant current of 3 mA, (c) luminous efficacy and EQE, and (d) color coordinates at 3 mA for each \( x/y \) combination. The \( jV \) as well as the \( VL \)-data do not differ and indicates no changes of the electrical device characteristics. Despite that, the spectral emission does apparently change and so do the efficiencies.
7.2 White Emission Based on Three Emitters

Table 7.14: Hybrid device structure based on three emitters employing two different anode mirrors as well as electron blocking layer materials X. Either S-TAD or NPB are used for electron blocking. The layer thickness of the anode silver layer is adjusted to be $x=0$ or $15$ nm forming a pure Al anode or a hybrid anode from Al and Ag, therewith changing the anode mirror and its reflectance.

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%</th>
<th>$r_{(p:q)}$</th>
<th>$d$ (nm)</th>
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<td>MADN:TBPe</td>
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</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
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</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
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</tr>
<tr>
<td>X</td>
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</tr>
<tr>
<td>MeO-TPD:NDP2</td>
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<td>20</td>
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</tr>
<tr>
<td>Ag</td>
<td>$x$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>60</td>
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</tbody>
</table>

7.2.3 Detailed Characterization of Four Selected Devices Featuring High-Quality White Emission

In the following, four devices are discussed in detail that show high efficiencies as well as white color coordinates. To examine the influence of the anode material on the emission spectrum, devices with an Al anode are compared to devices with a composite anode from Al and Ag. The additional $x=15$ nm thick Ag layer that is added on top of Al modifies the reflectance of the anode mirror. Furthermore, two materials S-TAD and NPB are tested with respect to the best device performance, where either S-TAD or NPB is placed as electron blocking layer within the layer sequence. The layer architecture utilized is illustrated in Table 7.14.

Influence of Different Anode Materials on the Spectral Emission

The reflectance of the electrode mirrors plays a large role for a microcavity, since it determines the cavity strength as well as the outcoupled spectra. As the optical simulation of the reflectance of different metal mirrors in an organic cavity – illustrated in
Figure 7.21: Simulated optical reflectance of a pure Al (60 nm), a pure Ag (60 nm), and a layered anode consisting of 60 nm Al and 15 nm Ag. The values are calculated with the program FilmWizard for reflection into air and organic material with an average refractive index of $n = 1.75$. While a pure Ag layer shows large reflectance in the high wavelength region, the reflectance for pure Al is predominantly high in the low wavelength region, showing lower reflectance for high wavelength. A combination of both materials leads to an almost equal reflectance over the whole visible wavelength region.
Figure 7.21 shows, aluminum predominantly reflects in the low wavelength region, whereas silver mainly shows a higher reflectance at high wavelength. The emission spectra of the devices at a luminance of about 1000 cd m$^{-2}$ are shown in Figure 7.22a. To verify the effect of different anodes and electron blocking layers, the forward directed cavity emission (cf. Section 5.8) of all four OLED systems are additionally illustrated in Figure 7.22c.

It is evident that the spectra based on the pure Al and the composite anode reveal a change of the spectral emission shape depending on the anode reflectance. This effect can be explained by a closer look on the cavity emission and the associated reflectivity of their anode mirrors. The resonance wavelength of Al based devices is calculated to be 471 nm, which is lower than for Al-Ag devices (495 nm). Accordingly, the cavity emission of Al based devices is enhanced for short wavelengths (below 477 nm) compared to the Al-Ag devices. Therefore, the emission at large wavelengths is enhanced, leading to larger contributions in the blue and a decreased red emission. On the other hand, using an Al-Ag anode, the resonant wavelength of the cavity is red-shifted by 25 nm, leading to enhanced light emission in the low energy region. This is related to the larger reflectance for composite Al-Ag anodes for wavelengths larger than 450 nm when compared to Al systems. As a consequence, devices with composite anodes present strongly enhanced red emission and suppressed blue contribution.

Due to the larger spectral contribution from the highly efficient phosphorescent orange-red emitting material Ir(MDQ)$_2$(acac), devices with the composite anode yield a higher luminous efficacy than OLEDs containing a pure Al anode (cf. Figure 7.23). With the electron blocker NPB, about 12.4 lm W$^{-1}$ are achieved for the composite anode at about 1000 cd m$^{-2}$ compared to 8.0 lm W$^{-1}$ using a pure Al anode. The large spectral blue contribution from the fluorescent emitter TBPe with much lower efficiency further corresponds to an EQE of 3.8 % in comparison to the highly red emitting Al-Ag based device with an EQE of 5.3 %. Table 7.15 summarizes the examined performance data at a luminance of about 1000 cd m$^{-2}$ of the devices under consideration.

**Analysis of Different Electron Blocking Materials**

To examine the influence of the electron blocking material on the device performance, the materials NPB and S-TAD are tested. As shown in Figure 7.22a and b, only small changes in the spectrum can be detected. Further, the luminous efficacies for both anodes can strongly be increased using S-TAD instead of NPB. These slight spectral changes as well as the increased luminous efficacies cannot be attributed to a different optical behavior for different blocking materials, since for both anodes the cavity emission of the organic layers is practically independent of the EBL material (see Figure 7.22c), due to very similar optical constants. Therefore, the differences have to be attributed to the different electrical behavior, which slightly changes the electron-hole balance and therefore alters the emission spectra.
Figure 7.22: Electroluminescence spectra (a and b) of the examined devices described in Table 7.14 comprising different anodes (Al, Al-Ag) and different electron blocking layers (NPB, S-TAD) and (c) the cavity emission determined via optical simulation based thin film optics. The spectra are measured in forward direction at a luminance of about 1000 cd m$^{-2}$ and scaled to their driving current for better comparison. Aluminum based devices feature higher blue contribution compared to the Al-Ag based devices, where more red emission can be detected. Changed electron blocking materials do not strongly influence the spectral emission. The cavity emission was determined via optical simulation and shows full coincidence for the data of NPB and S-TAD.
Figure 7.23: Luminous efficacy and external quantum efficiency of the four devices described in Table 7.14 derived from angular dependent measurements as a function of luminance. As the highly efficient phosphorescent orange-red emitting material Ir(MDQ)$_2$(acac) largely contributes to the spectral emission of the Al-Ag based devices, they yield a higher luminous efficacy than OLEDs with pure Al anode. Using the electron blocking material S-TAD can further increase the luminous efficacy.
Table 7.15: Key performance data of the devices described in Table 7.14. Besides the common efficiency data (voltage $V$, current $I$, luminance $L$, current efficiency $\eta_c$, luminous efficacy $\eta_l$ and external quantum efficiency $\eta_{eqe}$), the color coordinates (CIE) and color rendering indices (CRI) are given.

<table>
<thead>
<tr>
<th>$x$ (nm)</th>
<th>$X$</th>
<th>$V$ (V)</th>
<th>$I$ (mA)</th>
<th>$L$ (cd m$^{-2}$)</th>
<th>$\eta_c$ (cd A$^{-1}$)</th>
<th>$\eta_l$ (lm W$^{-1}$)</th>
<th>$\eta_{eqe}$ (%)</th>
<th>CIE</th>
<th>CRI</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>NPB</td>
<td>3.5</td>
<td>0.557</td>
<td>1151</td>
<td>14.0</td>
<td>8.0</td>
<td>3.8</td>
<td>0.420, 0.407</td>
<td>75.6</td>
</tr>
<tr>
<td>0</td>
<td>S-TAD</td>
<td>3.0</td>
<td>0.388</td>
<td>902</td>
<td>15.7</td>
<td>10.4</td>
<td>4.0</td>
<td>0.435, 0.429</td>
<td>74.8</td>
</tr>
<tr>
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<td>NPB</td>
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<td>0.350</td>
<td>1037</td>
<td>20.0</td>
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<td>0.472, 0.441</td>
<td>69.5</td>
</tr>
<tr>
<td>15</td>
<td>S-TAD</td>
<td>3.0</td>
<td>0.440</td>
<td>1220</td>
<td>18.7</td>
<td>13.3</td>
<td>4.9</td>
<td>0.466, 0.444</td>
<td>70.4</td>
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Figure 7.24 shows the $jVl$-characteristics of the processed devices. Devices using S-TAD as electron blocking layer material exhibit much steeper $jV$-curves compared to the devices with NPB, whose current-voltage characteristic is rather flat and requires 0.25 to 0.48 V higher voltage for the same luminance in the range of 100 to 10000 cd m$^{-2}$. As the driving voltage is lowered for the devices comprising S-TAD, their luminous efficacy is improved (see Figure 7.23), which reaches up to 11.3 and 15.0 lm W$^{-1}$ at 500 cd m$^{-2}$ for Al and Al-Ag based devices employing the electron blocking material S-TAD. However, the external quantum efficiency remains almost unchanged, as the spectra of the compared blocking materials – shown in Figures 7.22a and b – do not show large variations for both cases of anodes.

A possible explanation for the altered $jV$-characteristics might be found in different energy barriers from p-doped MeO-TPD to the applied electron blocking layer, S-TAD or NPB, respectively. Therefore, UPS measurements are performed at the interface of MeO-TPD:NDP2 to each blocker material to determine the hole injection barrier. The measurements and interface alignment between MeO-TPD:NDP2 and the applied electron blocking materials (NPB and S-TAD) are shown in Figure 7.25.

On top of two 10 nm thick 4 wt.% NDP2 doped MeO-TPD layers, either 5 nm S-TAD or 5 nm NPB are evaporated, respectively. Hence, for MeO-TPD:NDP2 a hole injection barrier from the Fermi level of 0.37 eV as well as a high binding energy cutoff of 16.50 eV is obtained, leading to an ionization potential of 5.09 eV. The following electron blocking layers show vacuum level alignment with the doped layer and the injection barriers to MeO-TPD are measured to be 0.31 eV for S-TAD and 0.38 eV for NPB with ionization potentials of 5.35 eV for S-TAD and 5.45 eV for NPB. Thus, the energy barrier for holes is 70 meV higher for NPB compared to S-TAD and is therefore
Figure 7.24: Current density-voltage and luminance-voltage characteristics for the processed devices described in Table 7.14. Curves reveal a dependence on the choice of the blocking material, leading to steeper curves and reduced driving voltage for the material S-TAD.
Figure 7.25: UPS characteristics of the interfaces between the hole transport material MeO-TPD:NDP2 and either NPB or S-TAD: (a) High binding energy cutoff (HBEC) and the HOMO region of the UPS He I spectra. The intersection of the tangents mark the HOMO cutoff positions. (b) Resulting schematic energy level diagram.
only slightly larger than the experimental error of 50 meV. Consequently, these small differences in the energy barrier for both electron blocking materials are unlikely to have such a strong influence on the electrical characteristics alone. Thus, it is more likely that the differences in the electrical characteristics are also influenced by an altered hole mobility within the blocking material.

To further investigate the origin of the different $jV$ characteristics for both electron blocking materials, hole-only devices (p-i-p and p-i-i-i-p) as listed below are fabricated. The parameter $X$ denotes either the material NPB or S-TAD:

**p-i-p devices:** ITO (90 nm)/ MeO-TPD:NDP2 (50 nm)/ $X$ (100 nm)/ MeO-TPD:NDP2 (50 nm)/ Al (100 nm)

**p-i-i-i-p devices:** ITO (90 nm)/ MeO-TPD:NDP2 (50 nm)/ $X$ (20 nm)/ NPB:Ir(MDQ)$_2$(acac) (30 nm; 4.63 wt.% or 4.76 wt.%)/ $X$ (50 nm)/ MeO-TPD:NDP2 (50 nm)/ Al (100 nm)

The intrinsic material is inserted in between two 50 nm thick hole transport layers of MeO-TPD:NDP2 with a doping concentration of approximately 4 wt.%. For p-i-p devices either 100 nm NPB or 100 nm S-TAD are used as intrinsic layer. The p-i-i-i-p devices contain a layer sequence of 20 nm EBL and 30 nm NPB:Ir(MDQ)$_2$(acac), again followed by the electron blocking material (50 nm), which was used before. The organic p-i-p as well as the p-i-i-i-p stack is evaporated on top of an indium tin oxide (ITO) coated glass substrate and covered with 100 nm aluminum cathode.

In Figure 7.26, the forward and backward measured current density for both p-i-p and both p-i-i-i-p devices is shown. All four devices exhibit symmetric $jV$ characteristics, whereas the devices containing NPB as electron blocking material show lower current flow compared to the devices with S-TAD. As the current density for NPB at a fixed applied voltage is much lower than for S-TAD, the flow of holes is hindered. Due to these different electrical characteristics of the device structure using either NPB or S-TAD as blocking material, the electron-hole balance within the device is modified. Consequently, this has an influence on the emission spectra and on the OLED efficiency, as the distribution of exciton generation is also changed.

**Color Quality**

The color coordinates and the color rendering indices of the devices are calculated by using the measured spectra at an angle of 0° and are illustrated in Figure 7.27. As the emission spectra are not stable with regard to driving current, the color coordinates as well as the color rendering indices vary as a function of the driving current respectively device brightness. For all devices, a shift of the color points towards the
Figure 7.26: Current density in forward and backward direction of the fabricated p-i-p and p-i-i-i-p devices. The curves for NPB exhibit lower current densities compared to S-TAD.
Figure 7.27: Color performance of the four devices described in Table 7.14: (a) Color coordinates (CIE) and (b) color rendering indices calculated from forward determined spectra at luminances of 100, 500, 1000, 3000 cd m\(^{-2}\) and currents of 3 and 5 mA. The color coordinates are situated close to the Planckian locus and the warm white point A. The shift of CIE and CRI is determined by current instability of the emission spectra. Brackets denote values measured at deviant luminances. The color rendering indices raise with higher brightness and reach values up to 77.
blue edge of the CIE chromaticity diagram can be detected with increasing luminance. Due to the increasing blue contribution with increasing OLED brightness, the color rendering indices are enhanced with luminance exhibiting values between 62 and 77 in a luminance range of 100 and 1000 cd m\(^{-2}\). A comparison of devices with different anode materials reveal a stronger dependence on the driving current for Al based devices. However, these devices exhibit a smaller distance to the Planckian locus and therefore feature higher quality white with superior CRI values. Particularly, the device combining an Al anode with the EBL material NPB features CIE coordinates of \((x, y)=(0.44, 0.41)\) at a luminance of 500 cd m\(^{-2}\), which is very close to the black body curve defining ideal white and almost matches the warm white point A with \((x, y)=(0.45, 0.41)\). Consequently, these devices show high color rendering values of 73 at a luminance of approximately 500 cd m\(^{-2}\) and 77 at about 3000 cd m\(^{-2}\). Due to the larger orange-red contribution in the spectral emission, devices with \(x=15\) nm show slightly more orange shifted color points. Considering different blocking layer materials, the distance to the Planckian locus can be adjusted, being larger for Al-Ag devices compared to devices with a pure Al anode mirror.

**Emission Characteristics**

Figure 7.28a and b show the spectral radiant intensity of the devices with \(x=0\) and 15 nm, utilizing NPB as electron blocking material. Therein, the emission shape at viewing angle between 0° and 70° are illustrated. The devices are driven at 3.5 V and 3.4 V at luminances of 1151 cd m\(^{-2}\) and 1037 cd m\(^{-2}\). The two other devices exhibit only slight spectral differences due to different EBL materials. As expected, the spectral radiance at different viewing angles shows a decreased intensity with increasing viewing angle, which coincides very well with the simulation data.

The emission peak wavelength is stable, however, the spectral weight of the three emitters is altered at higher viewing angles. This results in slightly blue-shifted color coordinates for higher viewing angles, as illustrated in Figure 7.28c. Surprisingly, the devices exhibit a light green shift starting from angles above 50°. This is caused by the unbalanced decrease of intensity for all three emitter peaks. Compared to the green and blue emission, the orange-red emission peak exhibits a stronger decrease in intensity. The strongly reduced orange-red contribution in the spectral emission leads to green-shifted color coordinates. As the additional 15 nm of Ag within the Al-Ag devices exhibit a higher reflectance, the microcavity effects are stronger for this device and the device exhibits a more pronounced resonance behavior. The relative decrease of orange-red emission in comparison to the green emission peak is much larger compared to the Al based device (cf. Figures 7.28a and b).

As the radiance behavior of the devices is equal (see Figure 7.29a), exemplarily the radiance of the device without Ag and NPB as EBL is shown in Figure 7.29c. Here, the
Figure 7.28: Emission characteristics of the devices described in Table 7.14: Experimental measured and simulated spectral radiant intensity of (a) the Al/NPB device and (b) the Al-Ag/NPB device, and (c) the measured color coordinates of all processed devices. The experimental and simulated spectral emission data coincide very well and the devices only show slight color changes with increased viewing angle.
measured data can also be fitted very well by optical simulation. Usually, organic light-emitting diodes are presumed to show Lambertian emission with constant radiance. The devices presented here, however, show considerably enhanced emission for small viewing angles. Compared to an ideal Lambertian emitter, with the same radiant power density per unit area (6.78 W m$^{-2}$ at 3.5 V forward bias), the device has larger radiance for viewing angles in the range of 0° to 50°.

In order to explain the observed small angular dependence and the enhanced emission in the forward direction, the cavity resonance wavelength is analyzed in detail. Figure 7.30a illustrates the spectral PL emission of the three utilized emitters TBPe, Ir(ppy)$_3$, and Ir(MDQ)$_2$(acac), which can be compared to the angular dependent resonance wavelength illustrated below in Figure 7.30b. The resonance wavelengths for TE- and TM-polarization as a function of the viewing angle are extracted from the respective simulated angular dependent cavity emission. Besides the fabricated devices with applied capping layer, devices without capping layer are simulated for reasons of comparison.

For the device containing an Al ($x=0$ nm) anode and the electron blocking material NPB, the resonance wavelength equals 471 nm in forward direction (0°). With increasing viewing angle, a blue shift in the resonance wavelength of 56 nm from 0° to 80° can be observed for TE-polarized radiation, whereas the TM-polarized light does not show any change. In comparison, the same device without a capping layer shows considerable shifts in both the TE- and TM-components (59 nm and 68 nm, respectively), featuring a resonance wavelength of 510 nm at an angle of 0°. It can be concluded that the capping layer is very effective in suppressing the blue shift of the TM-component, whereas the shift of the TE-component is left almost unchanged. Since the resonance conditions of the microcavity exhibit only a small overall angular dependence, the corresponding color coordinates of the emitted radiations are stable with increasing viewing angle.

The effect of forward directed light emission is related to the resonance wavelength of the microcavity. It can be observed that the resonance wavelength in the forward direction is smaller than the central emission wavelengths of both the green and orange-red emitters (525 nm and 610 nm, respectively) and slightly larger than the emission wavelength of the blue emitter TBPe (460 nm). With increasing viewing angle, the OLED cavity is in resonance at shorter wavelengths due to the blue shift in the resonance wavelength for TE-polarized light. Therefore, the overlap between the intrinsic cavity emission and the luminescence spectra of the emitters is reduced, especially when considering TBPe. This leads to a consistent and fast reduction in radiated power when considering off-normal directions. Consequently, light emission from the device exhibits a rather strong directionality, rather than a Lambertian behavior [168].

The Al-Ag based device ($x=15$ nm) exhibits a larger resonance wavelength (495 nm), but shows similar behavior compared to the Al based device. With an applied capping layer, the TE-component of the polarization strongly shifts to low wavelengths with
Figure 7.29: Radiance and emission pattern of the processed devices described in Table 7.14: (a) normalized radiance and (b) normalized radiant intensity of all processed devices. Measured and simulated (c) radiance and (d) radiant intensity of the Al based device incorporating the EBL NPB compared to an ideal Lambertian emission with the same total power. All four devices show nearly identical emission pattern and show strongly forward directed emission compared to an ideal Lambertian emitter.
Figure 7.30: Normalized photoluminescence emission of the three inserted emitters (a) and simulation of the resonance wavelength of the Al ($x=0$ nm) and the Al-Ag ($x=15$ nm) based devices at different viewing angles with capping layer (b). For reasons of comparison the resonance wavelength is additionally simulated for devices without capping layer. The resonance wavelength of the Al-Ag based devices are red-shifted due to the shifted cavity emission. The applied capping layer strongly stabilizes the TM-polarization component.
increasing viewing angle, whereas the TM-component is stable in wavelength. However, with an applied capping layer, the blue shift for the Al-Ag based device is much stronger compared to the Al based device and compared to the same device without capping layer.

### Analysis of the Device Efficiency

To compare the efficiency of the top-emitting devices with bottom-emitting devices, a brief comparison is given in this paragraph. A direct comparison between top- and bottom-emitting device is very complex, as the optics of the devices strongly differ. Therefore, the top-emitting device structure has to be significantly altered to obtain a bottom-emitting device with similar emission characteristics, which will make the devices incomparable regarding to their electrical characteristics. Consequently, devices are either incomparable concerning their optical characteristics (e.g. emission spectrum or emission pattern) or their electrical characteristics (e.g. \( jV^L \)-characteristics). This makes a straightforward comparison between top- and bottom-emitting devices very difficult. A much better understanding of the effects of the top-emitting structure can be obtained using optical simulations and performing a comparison of the internal quantum efficiency and outcoupling efficiency.

For that purpose, an inhouse developed optical model presented by Furno et al. [169] is employed to analyze the efficiencies of the top-emitting OLEDs and of equivalent bottom-emitting devices [90, 170] in order to provide meaningful comparisons to existing literature data. The first step of the modelling approach is the calculation of the outcoupling efficiency \( \eta_{\text{out}} \) [154] for each of the emission layers in the OLED stack.

An overall outcoupling efficiency for the white OLED is then derived as an averaged sum of the contribution of the three emitting units, the weights \( w \) being determined from the fitting of the electroluminescence spectrum of the device in the forward direction. As last step, the overall internal quantum efficiency \( \eta_{\text{iqe}} \) is obtained via the division of the measured external quantum efficiency \( \eta_{\text{eqe}} \) by the calculated outcoupling efficiency \( \eta_{\text{out}} \) according to Equation (4.3) in Section 4.2. This approach allows to obtain an approximate estimate of the internal quantum efficiency of the device and therefore allows to quantify the optical and electrical/excitonic efficiencies of the OLED stack under study.

As a representative of the above discussed devices, the Al-Ag based device with an NPB blocking layer is chosen, exhibiting the maximum external quantum efficiency \( \eta_{\text{eqe}}^{\text{top}} = 5.3 \% \) at 1000 cd m\(^{-2}\). The outcoupling efficiency values \( \eta_{\text{out},i}^{\text{top}} \) obtained for \( i \), the red, green, and blue emission layers, are 6.9 \%, 19.9 \%, and 19.3 \%, respectively. The low value obtained for the red emitter is related to the fact that the OLED cavity is strongly off-resonance for radiation at wavelengths in the range 600 to 700 nm, the resonance wavelength of the cavity being close to 490 nm. On the other hand, the OLED cavity resonates at wavelengths in the blue-green region of the visible spectrum.
and thus outcoupling of the green and blue components of the white OLED emission spectrum is favored. The weights $w_i^{\text{top}}$ of the three emitters in the OLED stack extracted from the forward emission spectrum of the device are equal to 0.72, 0.09, and 0.19 for the red, green, and blue emitter, respectively. From the analysis of the values quoted above, it is obvious that most of the recombination events are occurring within the red emission layer, whereas only recombination within the green and blue emission layers is comparably lower. The overall outcoupling efficiency (cf. Subsection 4.2) is finally evaluated according to the equation

$$\eta_{\text{out}} = w_{\text{red}} \cdot \eta_{\text{out}, \text{red}} + w_{\text{green}} \cdot \eta_{\text{out}, \text{green}} + w_{\text{blue}} \cdot \eta_{\text{out}, \text{blue}}$$ (7.1)

and results in $\eta_{\text{out}}^{\text{top}}=10.4\%$ for the top-emitting device. It is obvious that such a relatively low value is related, on the one hand, to the low outcoupling efficiency of the microcavity for red light and, on the other hand, to the low number of recombination events occurring in the green and blue emitters. From the comparison of the measured $\eta_{\text{eqe}}^{\text{top}}$ and the calculated $\eta_{\text{eqe}}^{\text{top}}$, the overall internal quantum efficiency is equal to $\eta_{\text{iqe}}^{\text{top}}=50.8\%$.

For comparison purposes, the efficiencies of the white bottom-emitting OLED [90, 170] are similarly calculated. These devices feature a very similar structure of the emission units. The main differences to the top-emitting stack are the blue fluorescent emitter Spiro-DPVBi instead of TPBe and some of the organic functional layers. The best external quantum efficiency for these devices at 1000 cd m$^{-2}$ is $\eta_{\text{eqe}}^{\text{bot}}=7.4\%$ [170]. The overall outcoupling efficiency of this device is calculated to be $\eta_{\text{out}}^{\text{bot}}=19.6\%$. From the comparison of calculation and experiments, the internal quantum efficiency at 1000 cd m$^{-2}$ is estimated to be $\eta_{\text{iqe}}^{\text{bot}}=37.8\%$.

These calculations reveal that the outcoupling efficiency of the top-emitting device under consideration is about half as high ($\eta_{\text{out}}^{\text{top}}=10.4\%$) compared to bottom-emission ($\eta_{\text{out}}^{\text{bot}}=19.6\%$). Therefore, the lower external quantum efficiency of the top-emitting devices is due to the decreased outcoupling efficiency, which is caused by the microcavity. However, the internal quantum efficiency of the bottom-emitting device is with $\eta_{\text{iqe}}^{\text{bot}}=37.8\%$ considerably lower than the internal quantum efficiency ($\eta_{\text{iqe}}^{\text{top}}=50.8\%$) of the top-emitting device. From the comparison of the estimated internal quantum efficiency values for the two device architectures, it can be concluded that the top-emitting OLED presented here exhibits a performance superior to similar devices in bottom-emitting configuration. The reasons for this can on the one hand be ascribed to a changed charge carrier balance. On the other hand, this results from an improved efficiency for the blue fluorescent emitter used for the top-emitting layer structure.
7.3 White Emission Based on Four Emitters

Despite the successful experiments with white top-emitting devices based on three different emission colors, there is still some room for optimization. Due to the choice of the phosphorescent green emitter Ir(ppy)$_3$, with an emission maximum of 507 nm and the orange-red emitter Ir(MDQ)$_2$(acac) with a maximum emission at a wavelength of $\lambda=614$ nm, the obtained spectra exhibit low intensity in the yellow-orange area, where the eye sensitivity is highest. As the spectral luminous efficacy function $V(\lambda)$ of the human eye with a maximum at 555 nm is directly connected to the calculation of the discussed luminous efficacy of the device (cf. Equation 5.1), the introduction of an additional yellow emitter Ir(hdfpy)$_2$(acac) with an emission maximum of $\lambda=557$ nm into the device structure has the potential for efficacy improvement. To avoid an additional emission layer, arousing additional interfaces, a modified electron-hole balance, and a completely different exciton distribution within the emission layer, the new yellow emitter is doped into the already existing Ir(MDQ)$_2$(acac) doped NPB layer [145]. To prove the potential of a luminous efficacy enhancement in regard to the additionally used yellow emitter, PL quantum yield measurements are performed. Subsequently, devices containing four emission materials, based on the stack shown in Figure 7.31, are discussed. They are compared to a common three-color device concerning the doping concentration and the used anode material. The shown spectral radiance, cavity emission, and color coordinates are determined for a viewing angle of $0^\circ$ if not stated otherwise.

7.3.1 Quantum Yields of the Yellow and Orange-Red Dye

To compare both emitters Ir(MDQ)$_2$(acac) (orange-red) and Ir(hdfpy)$_2$(acac) (yellow) with regard to their quantum yield, PL measurements are performed. Therefore, three organic layers (A, B, and C) are evaporated on top of quartz substrates in the small multi-chamber evaporation system:

A: NPB:Ir(MDQ)$_2$(acac) (100 nm, 2 wt.%)

B: NPB:Ir(hdfpy)$_2$(acac) (100 nm, 2 wt.%)

C: NPB:Ir(hdfpy)$_2$(acac):Ir(MDQ)$_2$(acac) (100 nm, 5 wt.%, 0.5 wt.%)

The measurements and calculations are performed according to the description in Subsection 5.6. Figure 7.32 shows the corrected PL emission of the three samples, which already have been calibrated with respect to the spectral responsivity of the setup.
Due to the uncalibrated measurement setup, absolute quantum yields cannot be measured. Thus, all quantum efficiencies are normalized to the PL efficiency of device A which should be close to 100%. Sample B shows a relative yield of 70.4%, allowing for an enhancement of efficiency with co-doping.

Furthermore, one can definitely expect increased luminous efficiencies due to a blue shifted spectral emission with higher overlap with the spectral luminous efficacy function $V(\lambda)$. As Figure 7.32 illustrates, the spectral emission for the co-doped NPB layer reveals a small shoulder at a wavelength of 555 nm, which is congruent with the first emission maximum of Ir(dhfpy)$_2$(acac). However, the emission is still dominated by the spectral emission of Ir(MDQ)$_2$(acac). This fact and the determined relative yield of 94.6% indicates a significant transfer of excitons from the Ir(dhfpy)$_2$(acac) to the Ir(MDQ)$_2$(acac), although the Ir (MDQ)$_2$(acac) concentration is low. For even lower Ir(MDQ)$_2$(acac) concentrations of $x < 0.5$ wt.% the yellow contribution can be expected to be higher. Consequently, the relative yield can be almost kept constant while the spectral emission is enlarged to lower wavelengths and shows a higher overlap with the $V(\lambda)$ curve, which will lead to higher luminous efficacies. The following experiments are performed in view of this enhancement.

**Figure 7.31:** Schematical illustration of the top-emitting layer architecture comprising four emitting dyes. The yellow emitter Ir(dhfpy)$_2$(acac) is supplementary doped into the orange-red emission layer via triple evaporation.
Figure 7.32: Corrected photoluminescence signal of the three samples measured in the integrating sphere. Sample C only shows a small contribution from the yellow emitter Ir(dhfpy)$_2$(acac) due to quenching by Ir(MDQ)$_2$(acac).
Table 7.16: Hybrid device structure based on four emitters employing different doping concentrations of the yellow and orange-red emitter. The doping concentration of the emitter materials Ir(dhfpy)$_2$(acac) (X) and Ir(MDQ)$_2$(acac) (Y) are denoted with $x$ and $y$, respectively. Further, the Ag sub-anode can be chosen to be $z = 0$ or 15 nm.

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<tr>
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<td>1.5</td>
<td></td>
</tr>
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<td></td>
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<tr>
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<tr>
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7.3.2 Examination of Devices Including Four Emitter Materials

In the following, devices incorporating four emitter materials are examined and compared to three-color reference devices. Therefore, the host material NPB is doped with both the yellow emitter Ir(dhfpy)$_2$(acac) and the orange-red emitter Ir(MDQ)$_2$(acac) in a triple evaporation process. Further, different anode mirror materials (Al or Al-Ag combination) are used. The layer structure including layer thicknesses and doping concentrations can be extracted from Table 7.16. The doping concentration of the yellow and the orange-red emitter are denoted with $x$ and $y$, respectively. The layer thickness of the Ag sub-anode is described by $z$.

Analysis of Varied Yellow and Orange-Red Emitter Doping Concentrations

Due to the fact that the Ir(dhfpy)$_2$(acac) exhibits a higher triplet level (2.2 eV) compared to the orange-red emitter material Ir(MDQ)$_2$(acac) (2.0 eV), the excitons generated on the yellow emitting material can also be harvested by the Ir(MDQ)$_2$(acac). Therefore, the four color devices must exhibit a higher concentration $x$ of the yellow emitter com-
7.3 White Emission Based on Four Emitters

Figure 7.33: Spectral radiance of the reference device and the four-color devices described in Table 7.16 divided by driving current for better comparison. The devices are based on a pure Al anode \((z=0\text{ nm})\) and contain the yellow emitting material \(\text{Ir(dhfpy)}_2(\text{acac})\) \((X)\) and the orange-red emitting material \(\text{Ir(MDQ)}_2(\text{acac})\) \((Y)\) with doping concentrations of \(x\) and \(y\), respectively. The yellow emission peak is increased with decreased \(\text{Ir(MDQ)}_2(\text{acac})\) concentration.

pared to \(\text{Ir(MDQ)}_2(\text{acac})\), which is thus chosen to be 8 wt.%. The doping concentration of \(\text{Ir(MDQ)}_2(\text{acac})\) is varied between 0.5 to 1.5 wt.% in 0.5 wt.% steps. For reasons of comparison an additional device without yellow component \((x=0\text{ wt.\%})\) is processed, which has the doping concentration \(y\) of 5 wt.%. The emission spectra of the prepared devices with a pure Al anode are depicted in Figure 7.33. Figure 7.34 shows the electrical characteristics and the determined efficiencies.

At a doping concentration of \(y=5\text{ wt.\%}\), the three-color reference device achieves a luminous efficacy of 8.3 lm W\(^{-1}\) at an approximate luminance of 1000 cd m\(^{-2}\) (see Figure 7.34a). After the introduction of the yellow emitter with a doping concentration of \(x=8\text{ wt.\%}\) and a adjusted \(\text{Ir(MDQ)}_2(\text{acac})\) doping concentration of \(y=1.5\text{ wt.\%}\), a low additional emission from the yellow emitter at 555 nm can be detected. Compared to the reference device, the emission intensity of the orange-red emitter is increased due to the additional number of excitons harvested from the material \(\text{Ir(dhfpy)}_2(\text{acac})\). The
Related change of doping concentration leads further to a lower current density and luminance at the same driving voltage for the four-color devices (cf. Figure 7.34a). As a consequence of the changed electron-hole balance, the intensities of the blue and green emission contribution are raised.

With decreased concentration $y$, the yellow emission is increased, as less excitons are harvested on the Ir(MDQ)$_2$(acac). Consequently, the luminous efficacy is raised up to 15.6 lm W$^{-1}$ at approximately 1000 cd m$^{-2}$. The higher efficiency for a concentration of $y=1.0$ wt.% is due to the higher orange-red contribution in the emission spectrum. The external quantum efficiency is also increased with changed doping concentration $y$ from 4.1 to 6.1 % at around 1000 cd m$^{-2}$.

**Introduction of an Additional Silver Anode Layer**

To further enhance the device efficiency, an additional silver anode layer ($z=15$ nm) is applied on top of the Al anode according to experiments in Subsection 7.2.3. Figure 7.35a illustrates the change of the spectral radiance for the four-color devices and the three-color reference device with altered anode mirror. Despite a red shift of 21 nm for the device comprising an Al-Ag anode mirror ($z=15$ nm), the changes in the spectral radiance are small. However, the efficiency can be further enhanced as illustrated in Figure 7.35b. Compared to the pure Al based devices, both the reference device and the
Figure 7.35: Characteristics of the reference device and the four-color based devices described in Table 7.16 with different doping concentrations \( x \) and \( y \): (a) spectral radiance divided by driving current and associated simulated cavity emission, (b) \( jV \) and \( LV \)-characteristics and, (c) luminous efficacy and external quantum efficiency. Either pure Al (\( z=0 \) nm) or a composite Al-Ag layer (\( z=15 \) nm) is utilized as anode. The devices with hybrid Al-Ag anode feature steeper \( jV \) and \( LV \) characteristics, which is due to the better injection properties of the Al-Ag layer. The additional Ag layer leads to enhanced luminous efficacy and quantum efficiency.
four-color based device with $y = 0.5, 1.0$ and $1.5 \text{ wt.\%}$ feature higher luminous efficacies, even though the improvements at $y = 0.5$ and $1.5 \text{ wt.\%}$ are small. The enhancement is on one hand due to the steeper $jV_L$-characteristic as depicted in Figure 7.35c, resulting from better injection by the composite Al-Ag electrode. On the other hand, the composite anode mirror shifts the cavity emission (cf. Figure 7.35a) towards larger wavelengths, which leads to an increased yellow emission. The luminous efficacy can therefore be tuned to $16.1 \text{ lm W}^{-1}$ for $y = 0.5 \text{ wt.\%}$ and an increased external quantum efficiency of $5.6\%$ is detected for the device featuring a doping concentration of $1.0 \text{ wt.\%}$ Ir(MDQ)$_2$(acac) and $8.0 \text{ wt.\%}$ Ir(dhfpy)$_2$(acac).

**Emission Characteristics**

The emission characteristics of the devices with additional Ag layer ($z = 0 \text{ nm}$) – incorporating four emission materials – are similar to that of the reference device with only three emissive dyes. The spectral radiant intensities of the reference and the representative device with $y = 1.0 \text{ wt.\%}$ at $z = 0$ and $15 \text{ nm}$, which are presented in Figure 7.36, show the typical decrease of intensity with increased viewing angles. The radiance is therefore sub-Lambertian and equal for all measured devices (cf. Figure 7.37a) and presents a particularly forward directed light emission depicted in Figure 7.37b.

**Color Coordinates and Color Rendering Indices**

Besides the color coordinates and color rendering at a luminance of approximately $1000 \text{ cd m}^{-2}$, the devices are characterized for two different driving currents ($0.15$ and $1.0 \text{ mA}$). Due to the current dependent emission spectra, featuring higher blue contribution at higher driving currents, the color as well as the CRI is tunable (see Figure 7.38). In contrast to the three-color devices, the color coordinates of the four-color based devices are off the Planckian locus. The color coordinates have higher $y$ values, due to the enhanced green (and blue) emission visible in Figure 7.35a. With lowered concentration of Ir(MDQ)$_2$(acac), the orange-red contribution within the spectrum is decreased. This results in color coordinates that are shifted to the green edge of the color coordinate diagram. The Ag layer on top of the common Al anode leads to a shift towards the orange-yellow border of the CIE diagram, as the resonance wavelength is red-shifted favoring higher wavelength.

The color rendering indices are between 51 and 69 for a luminance of approximately $1000 \text{ cd m}^{-2}$, exhibiting higher values for higher driving currents. With the introduction of the yellow emitter, the color rendering is decreased and further reduced with smaller Ir(MDQ)$_2$(acac) doping concentration leads to lower color rendering indices. A photograph of a four-color based hybrid white device with a Al-Ag anode on top of a glass substrate is presented in Figure 7.39.
7.3 White Emission Based on Four Emitters

![Figure 7.36](image)

**Figure 7.36:** Spectral radiant intensity of (a and c) the three-color based reference device \((x=0\) and \(y=5.0\)) and (b and d) the four-color based devices described in Table 7.16 with \(x=8.0\) and \(y=1.0\), each based on a pure Al anode or a composite Al-Ag anode. The devices show a similar decrease of intensity for larger viewing angles.

![Figure 7.37](image)

**Figure 7.37:** Normalized radiance and radiant intensity of three- and four-color based devices described in Table 7.16. All devices feature the same sub-Lambertian emission characteristics with forward directed light emission.
Figure 7.38: Color coordinates and color rendering indices of the four-color based devices with different doping concentrations and the reference device described in Table 7.16 using both pure Al and hybrid Al-Ag anode. Due to current dependent emission, a color shift to the blue can be detected with higher driving currents. Thereby, the CRI values are rising to approximately 70.
7.3 White Emission Based on Four Emitters

Figure 7.39: White top-emitting organic light-emitting diode based on a hybrid layer structure with four emitters on top of a glass substrate.
8 All-Phosphorescent White Devices

In this chapter, white phosphorescent top-emitting devices are discussed, which have the potential to achieve very high efficiencies. The first section addresses the device structure as well as the general working principle of the utilized OLED stack. In the second section, experiments which are focussed on thickness modifications are presented. Besides the positioning of the emission layer within the device, the thicknesses of the blue sub-emission layer and the TCTA interlayer are examined, where especially the latter strongly influences the emission spectra.

8.1 Layer Structure and Working Principle

So far, the stack development of white top-emitting OLEDs was based on the hybrid approach combining fluorescent and phosphorescent materials. However, the fact that fluorescent materials can make use of only 25% of generated excitons, limits the intensity of the useable blue emission and leads to a loss of a large fraction of energy. Utilizing highly efficient phosphorescent blue emitter – comparable to the so far used phosphorescent green and orange-red dyes – have the potential to overcome these problems. However, commercial available phosphorescent blue emitting dyes still show strongly limited lifetimes. Furthermore, some highly efficient blue emitter materials only show sky blue color. Consequently, achieving broadband white emission remains challenging.

To discover the possible efficiency limits for white top-emission, an all-phosphorescent model system incorporating the emitter FIrpic is utilized in the following experiments. The sky-blue test-emitter material FIrpic may be replaced by a deep blue as well as more stable emitter material in the future if a suitable emitter is available.
The layer architecture is illustrated in Figure 8.1. The layer sequence in bottom-configuration has already been studied in detail for bottom emission [89, 171] with great success concerning efficiencies. The stack has been adopted for top-emission by changing the electrode mirrors and choosing a cavity thickness of 100 nm. The emission layer consists of three sub-emission layer with the phosphorescent emitter materials \( \text{Ir(MDQ)}_2(\text{acac}) \) (orange-red emission), \( \text{Flrpic} \) (sky blue emission), and \( \text{Ir(ppy)}_2 \) (green emission), which are separated by a thin intrinsic interlayer. Thicknesses, doping concentrations, and further used materials are listed in Table 8.1.

The choice of materials, their arrangement as well as their layer thicknesses with regard to their energetic properties has been optimized for controlling exciton generation and exciton diffusion within the complex layer structure. A diagram of the energy design is depicted in Figure 8.2.

Electrons and holes – injected from both electrodes – are transported through the organic layers to the exciton generation interface between the preferentially hole transporting material TCTA and electron transporting material TPBi within the EML. As the injection and transport is nearly barrier free, the charge carrier distribution remains unchanged for changed current and brightness, leading to color stable emission spectra.
8.1 Layer Structure and Working Principle

Table 8.1: Complete all-phosphorescent device structure using different transport layer thicknesses \( x \) and \( y \), different TCTA interlayer thicknesses and different blue emission layer thicknesses. The transport layer thicknesses are changed from \( x/y=15/45 \text{ nm} \) to \( x/y=45/15 \text{ nm} \), keeping the overall cavity thickness of approximately 100 nm constant. Furthermore, \( a \), \( b \), and \( c \) denote the thickness of the TCTA interlayer, the blue emission layer and the TPBi interlayer.

<table>
<thead>
<tr>
<th>material</th>
<th>( c ) (wt%)</th>
<th>( d ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>( y )</td>
<td></td>
</tr>
<tr>
<td>TPBi</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TPBi:Ir(ppy)(_3)(acac)</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>TPBi</td>
<td>( c )</td>
<td></td>
</tr>
<tr>
<td>TPBi:FIrpic</td>
<td>20</td>
<td>( b )</td>
</tr>
<tr>
<td>TCTA</td>
<td>( a )</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(MDQ)(_2)(acac)</td>
<td>10</td>
<td>6</td>
</tr>
<tr>
<td>NPB</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>( x )</td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

The intrinsic interlayers made from TCTA and TPBi are necessary to control the exciton distribution and the emitted color. The thin TCTA layer between the orange-red and blue emission layer suppresses Dexter diffusion from the blue to the orange-red emitter due to a step in triplet energy from \( T_1^{TPBi}=2.64 \text{ eV} \) for TPBi to \( T_1^{TCTA}=2.82 \text{ eV} \) for TCTA. Further, the interlayer can restrict the Förster energy transfer and consequently controls the transfer rate between blue and orange-red \([171]\). The TPBi interlayer between the Flrpic and the Ir(ppy)\(_3\) doped TPBi layer also restricts the Förster transfer between blue and green similar to the TCTA interlayer. However, the diffusive triplet energy Dexter transfer cannot be suppressed, as no energy barrier in triplet energy is existent. Therefore, the Ir(ppy)\(_3\) doped sub-emission layer can harvest triplet excitons that do not recombine within the blue emission layer. This consequently results in green emission. Due to the rather small layer thicknesses, the performance modifications by layer thickness changes due to processing is quite large. This may complicate a reproducible production.
Figure 8.2: Diagram of the energetic levels within the all-phosphorescent OLED stack described in Table 8.1. HOMO and LUMO energy is depicted as lines. The triplet energy of the emission layer is shown as colored area, after [89]
8.2 Experiments Based on Layer Thickness Variations

To tune this top-emissive stack in terms of efficiency, some modifications concerning the layer thicknesses are made, which are discussed in the following paragraphs. With a view to the position of the EML within the stack, which always plays a noticeable role, different p-doped and n-doped layer thicknesses are chosen, which are denoted as $x$ and $y$. Subsequently, the interest is focused on the blue emission layer with the thickness $b$. Furthermore, a change of the TCTA and TPBi interlayer thicknesses $a$ and $c$ are discussed, as the device performance is strongly influenced by especially the first interlayer thickness of intrinsic TCTA.

Due to short lifetime of the phosphorescent blue emitter, the correct luminous efficacy and external quantum efficiency can only be determined via measurements in an integrating sphere, if it was available. Otherwise, the efficiency has to be approximated by assuming Lambertian emission. Goniometer measurements of the OLEDs radiant intensity are distorted due to a large decrease of intensity during the angle dependent measurement. However, test measurements show emission characteristics similar to previously discussed hybrid top-emitting white devices (100 nm cavity thickness) with forward directed light emission pattern.

Location of the Emission Layer

Although the transport layers are thin in top-emitting devices, they can strongly influence the charge carrier balance and the optical emission of the device due to a changed arrangement of the EML, as already seen in Subsection 7.2.2. In order to examine the emission behavior and appropriate HTL and ETL layer thicknesses, both layer thicknesses $x$ and $y$ are varied as depicted in Table 8.1. The thickness of the interlayer layer $a$ and $c$ are arranged to be 1.8 nm and 2.0 nm. The FIrpic doped blue emission layer has a thickness of $b=4$ nm. The device performance data are illustrated in Figure 8.3.

As the $jV L$-graph (cf. Figure 8.3a) shows similar slopes, the electron-hole balance is stable while different p/n layer thicknesses are utilized. Only slightly less luminance can be detected for $x=15$ nm and 45 nm. The normalized electroluminescence in Figure 8.3b reveals a strong decrease of intensity from the green emitter Ir(ppy)$_3$ and a slight decrease of blue emission contribution with thicker hole transport layer $x$. Accordingly, the orange-red emission is increased, also showing a slight red shift of the emission maximum. This indicates a small shift of the exciton generation interface towards the orange-red sub-emission layer facing the anode of the device. Thereby, excitons are more likely to reach this sub-emission layer producing emission at about 600 nm. Due to the enlarged distance to the green sub-emission layer, the decay of excitons is increased before they reach the Ir(ppy)$_3$ doped layer. The lowered blue emission
Figure 8.3: Characteristics of the all-phosphorescent based devices described in Table 8.1 with varied p- and n-transport layer thicknesses: (a) \(jV-L\)-properties, (b) electroluminescence intensity in forward direction normalized to equal integrated area, (c) color coordinates calculated from emitted spectra, and (d) luminous efficacy and external quantum efficiency at a driving current of 0.45 mA calculated with Lambertian assumption. Increased HTL thickness leads to a strong decrease of green and an increase of orange-red emission shifting the color coordinates towards the Planckian locus.

may also be due to a lower concentration of excitons at the cathode side of this sub-emission layer due to the shifted exciton generation zone. Due to the arrangement of RGB contribution within the emission spectrum, the color coordinates shift towards the Planckian locus with increased HTL thickness. Concerning the luminous efficacy as well as the external quantum efficiency, a transport layer thickness combination of \(x=25\) nm and \(y=35\) nm leads to the highest values, with changes more pronounced for the luminous efficacy. This is on one hand due to the higher light emission at equal voltage (see \(L-V\) plot in Figure 8.3a) and on the other hand results from the high orange-red and green contributions of the highly efficient phosphorescent emitter materials.
Influence of the Blue Emission Layer Thickness

Due to the central adjustment of the blue sub-emission layer made from TPBi:FIrpic and the direct abutment on the exciton generation zone, this layer is investigated in more detail concerning its thickness influence. Despite the larger green emission contribution for thicker HTL layers and consequently green-shifted color coordinates, the hole transport layer thickness of $x=25$ nm is chosen in the following as this thickness arrangement promises high efficiencies. To keep the overall cavity thickness constant, the ETL thickness $y$ is modified accordingly. The thickness of the TCTA and TPBi interlayers are $a=1.8$ nm and $c=2.0$ nm. Figure 8.4 shows the determined performance with increased TPBi:FIrpic layer thickness $b$.

**Figure 8.4:** Characteristics of the all-phosphorescent based devices described in Table 8.1 with rearranged blue emission layer thickness $b$: (a) $jV L$-properties, (b) electroluminescence intensity in forward direction normalized to equal integrated area, (c) CIE coordinates calculated from forward emitted spectra, and (d) luminous efficacy and external quantum efficiency determined at a luminance of 1000 cd m$^{-2}$. With increasing layer thickness the blue emission maximum is increased.
As the $jVL$-graph in Figure 8.4a illustrates, the increased sub-emission layer thickness slightly changes the electron-hole balance and decreases the current density and luminance. With increasing thickness $b$, the emission intensity for green remains almost unchanged, which is accompanied by a slight blue shift (cf. Figure 8.4b). Also the orange-red emission remains unchanged. Most interestingly, the gap between both, green and orange-red emission maximum, deepens with higher TPBi:FIrpic layer thickness. On the contrary, the blue emission can strongly be increased, which can also be realized by a strong blue shift of the color coordinates (see Figure 8.4c). However, the coordinates are still too far in the green. The luminous efficacy reaches up to $19.6\text{ lm W}^{-1}$ at $1000\text{ cd m}^{-2}$ for $4\text{ nm TPBi:FIrpic}$ thickness, which decreases to $14.7\text{ lm W}^{-1}$ at $b=7\text{ nm}$. The external quantum efficiency slightly decreases with rising parameter $b$ to $8.1\%$, showing only a small roll-off compared to the steep slope of the luminous efficacy at larger brightness.

### Influence of the TCTA Interlayer Thickness

It is known from preceding experiments on bottom-emitting devices comprising this layer structure [171] that the emission spectra are strongly influenced by the TCTA interlayer thickness between orange-red and blue sub-emission layer. To estimate the possibility of tuning the device performance by this TCTA layer, a thickness change of $a=1.4\text{ nm}$ to $a=2.0\text{ nm}$ is investigated in this paragraph. The thickness of the blue sub-emission layer is chosen to be $b=4\text{ nm}$ featuring an according transport layer thickness $y$ of $35\text{ nm}$. The TPBi interlayer is $c=2\text{ nm}$ thick. Figure 8.5 gives the performance data of the studied devices. Although this thickness lies in the range of the evaporation accuracy, differences can be detected in the spectral emission, illustrated in Figure 8.5b, while the electron-hole balance remains unchanged (see Figure 8.5a).

With slightly decreased TCTA interlayer thickness, the blue and green emission intensity are decreased, whereas the orange-red emission increases. This originates from the lower exciton diffusion distance from the exciton generation layer to the orange-red sub-emission layer. Therefore, more excitons can arrive at the Ir(MDQ)$_2$(acac) doped NPB layer leading to higher orange-red emission. Compared to this, the other two emission intensities are relatively decreased and the color points are shifted towards the Planckian locus. However, with $x$ and $y$ coordinates between 0.32 and 0.39 respectively 0.47 and 0.5, the emitted color is far too green. The color rendering indices are calculated to be between 53 and 68. In comparison to the emission spectra, the efficiencies are not drastically changed. Only a slight decrease in luminous efficacy from $19.8\text{ lm W}^{-1}$ (2.0 nm TCTA) to $18.3\text{ lm W}^{-1}$ (1.4 nm TCTA) can be detected as shown in the diagram of Figure 8.5d. The external quantum efficiency is stable at around $7.6\pm0.3\%$. 
8.2 Experiments Based on Layer Thickness Variations

Figure 8.5: Characteristics of the all-phosphorescent based devices described in Table 8.1 with changed TCTA interlayer thickness $a$: (a) $jVL$-properties, (b) spectral radiance in forward direction normalized to driving current, (c) CIE coordinates calculated from forward emitted spectra, and (d) luminous efficacy and external quantum efficiency determined at a luminance of 1000 cd m$^{-2}$. A lower TCTA layer thickness leads to decreased blue and green emission with accompanying increase of orange-red intensity.

Influence of the TPBi Interlayer Thickness

The last experiment clearly showed that the red contribution rises for thinner TCTA interlayer. Therefore, the layer thickness is further decreased to $a=0.8$ nm to achieve color coordinates close to the Planckian locus. Secondly, the thickness of the TPBi interlayer $c$ between the blue and green sub-emission layer is varied to study its influence on the emission spectrum. With changed TPBi interlayer thickness, the blue sub-emission layer thickness $b$ is adapted to keep the overall layer thickness of the structure constant. Figure 8.6 illustrates the performance of six devices with transport layer thicknesses of $x=25$ nm and $y=35$ nm. For better comparison, the spectral radiance is normalized to the maximum of the orange-red emitter Ir(MDQ)$_2$(acac).
All six devices show similar $jV L$-characteristics. The spectral radiance of the inner four devices (ii, iii, iv, and v) show a drop in green emission contribution from Ir(ppy) with increased TPBi interlayer thickness $c$ from 0 to 2 nm. This agrees with a decrease in luminous efficacy (external quantum efficiency) from 21.7 lm W$^{-1}$ (8.5%) to 19.3 lm W$^{-1}$ (7.6%) (cf. Figure 8.6c). This loss is due to a restricted transport of excitons to the green sub-emission layer caused by the thicker intrinsic TPBi interlayer. However, due to better balanced emission of the three emitters, the color performance is enhanced (see Figure 8.6d and e).

Both devices (i) and (vi), which were processed at the edges of the LESKER wafer ($6 \times 6$ matrix), exhibit a decreased green and blue emission and thereby improved color.

**Figure 8.6:** Characteristics of the all-phosphorescent based devices described in Table 8.1 with changed TPBi interlayer thickness $c$ and rearranged blue emission layer thickness $b$: (a) $jV L$-properties, (b) spectral radiance in forward direction normalized to the emission maximum of the orange-red emitter Ir(MDQ)$_2$(acac), (c) luminous efficacy and external quantum efficiency determined at a luminance of approximately 1000 cd m$^{-2}$, and (d) CIE coordinates calculated from forward emitted spectra. With increasing TPBi interlayer thickness $c$, the Ir(ppy) contribution to the emission spectrum is decreasing.
characteristics. The high overall fraction of orange-red emission within the emission spectrum of these devices is mainly due to their position on the wafer. As the thickness reduction at the edges of the substrate can be up to 12% (cf. Subsection 5.3.2), the TCTA interlayer thickness is furthermore reduced, leading to higher \( \text{Ir(MDQ)}_2(\text{acac}) \) emission. Consequently, a well balanced warm white emission spectrum with color coordinates of \((0.40, 0.45)\) for device (i) and \((0.41, 0.45)\) for device (vi) is achieved. Furthermore, the color quality rises up to CRI 72.6 for device (vi). However, this effect is accompanied by a loss in efficiency.

Hence, there is still much room for further improvements and development, especially concerning the interplay between device structure and optical characteristics yielding high efficiency as well as high color quality of white emission.
9 Scattering Capping Layer

Despite the accurate adjustment of both cavity thickness and capping layer thickness, top-emitting devices still show a slight color shift at higher viewing angles. A scattering top-layer may prevent this angle dependence and lead to homogeneous radiation. In this chapter two ideas for a scattering capping layer are presented. The first section deals with organic materials, which crystallize after deposition on top of the OLED stack. Subsequently, a thin film of carbon nanotubes applied on top of the OLED stack is investigated.

9.1 Crystallized Organic Material

An angle-independent spectral radiation is a prerequisite for commercial application. Furthermore, it would be advantageous to achieve a homogeneous emission from organic light-emitting devices without the need to carefully adjust the microcavity and the capping layer, where even small changes in thickness strongly affect the cavity emission. For this reason a thin scattering layer on top of the OLED stack made of crystallizing materials may be a solution. Outcoupled light from the microcavity moving through the top electrode contact can be scattered at a number of tiny crystals in different directions and angles. This may lead to a mixture of spectral radiation uniformly distributed over the whole spectral region, achieving color stability for all viewing angles.

There are some organic materials known to crystallize at certain conditions, e.g. BPhen, anthracene, or pentacene. Figure 9.1 shows a crystalline structure from BPhen formed on top of the organic stack of the OLED. The structures appear after approximately one hour after deposition.

The basic OLED – onto which the capping layer materials $X$ are applied – is a common top-emitting white OLED stack with a cavity thickness of 99.5 nm without any capping layer. In the following the materials BPhen and pentacene are tested. An evaporation
of anthracene has not been possible due to technical restrictions (cf. Subsection 9.1.2).
The basic organic layer stack is depicted in Table 9.1. The devices are processed on top of one wafer (6×6 devices) at the LESKER evaporation tool, however, without a capping layer. After cutting and de-encapsulation, the different capping layer materials $X$ are applied in the small multi-chamber tool. Based on encapsulation problems, the choice of devices is randomly distributed over

Table 9.1: Hybrid device structure based on three emitters. The capping layer material ($X$) and its thickness ($x$) is varied.

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%)</th>
<th>$r$ ($p:q$)</th>
<th>$d$ (nm)</th>
</tr>
</thead>
<tbody>
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<td>$X$</td>
<td></td>
<td>$x$</td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td></td>
<td>15</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>B Phen:Cs</td>
<td></td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>B Phen</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1.5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td></td>
<td>1:2</td>
<td>1.5</td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Spiro-TAD</td>
<td></td>
<td>10</td>
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</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>
9.1 Crystallized Organic Material

the wafer. The devices are encapsulated and characterized with the OLED-robot and the goniometer setup.

For reference reasons one device is covered with $x=50$ nm NPB. This material has been used so far to alleviate the microcavity effects, leading to limited angle-dependent emission and broadband outcoupling. The spectral radiant intensity and corresponding color coordinates for this reference device is shown in Figure 9.2 for viewing angle between $0^\circ$ and $90^\circ$. The device exhibits stable emission maxima and sub-Lambertian emission leading to forward directed radiation. The color coordinates only show a slight color shift towards the blue edge of the chromaticity diagram up to angles of $50^\circ$.

![Figure 9.2: Emission characteristics of the reference device described in Table 9.1 with a 50 nm thick NPB capping layer: (a) spectral radiant intensity, (b) related color coordinates, (c) normalized radiance, and (d) emission pattern for angles between $0^\circ$ and $70^\circ$. The vertical arrows mark the emission maxima. The device emission shows stable emission maxima, week angle dependence of the color coordinates and forward directed light emission.](image)
9.1.1 The Material BPhen

The material BPhen crystallizes under application of heat [152] and during long-time storage in UHV. Therefore, two series of experiments are performed using each four pre-processed devices (cf. Table 9.1). After the transfer to UHV, the devices are covered with the organic material BPhen of different thicknesses $x=50$, 100, 250, and 500 nm and treated with heat or via long-time storage to evoke crystallization. After the re-encapsulation of the covered devices, light-optical microscope images are taken from the active areas of the devices. Furthermore, the devices are characterized concerning the $jV L_-$, EL-, and angle-dependent-characteristics with the OLED-robot and goniometer setup.

Heated BPhen Capping Layer

Before re-encapsulation, the prepared devices are heated on top of a heating plate at a temperature of $60 \degree C$ for a time period of $t=20$ min. Already with the bare eye small structures can be seen on top of the active areas. Illumination of the pixel areas using a laser beam reveals a scattering device surface. Figure 9.3 shows light-optical microscope images of the active areas of heated devices. The heated devices with a capping layer of $x=50$ nm and $x=100$ nm (cf. Figure 9.3a and b) show a structured surface containing presumably amorphous BPhen (dark) and crystallized BPhen (light), which form a homogeneous mixture. In contrast, devices with a thick BPhen layer (Figure 9.3c and d) exhibit a largely crystallized surface with only few round dark areas, which presumably still contain amorphous BPhen.

![Figure 9.3: Light-optical microscope images of the prepared OLED devices with heated BPhen capping layer with a layer thickness of (a) 50 nm, (b) 100 nm, (c) 250 nm, and (d) 500 nm. The active areas reveal a strongly structured material arrangement, especially for a thickness of 50 and 100 nm BPhen.](image-url)
9.1 Crystallized Organic Material

The spectral radiant intensities of these devices are depicted in Figures 9.4. The position of the emission maxima are only stable for a layer thickness of 250 nm over the whole angular region. The devices with a layer thickness of 50, 100, and 500 nm show slightly blue- or red-shifted emission at higher viewing angles. At a layer thickness of 500 nm, the emission intensity of TBPe is stable and only drops at a viewing angle of 50°. Furthermore, all heated devices show a lower light emission compared to the reference device as shown in Table 9.2. Here, the performance data of the devices with heated BPhen are summarized and compared to the data of the NPB reference device. Besides the luminance also the luminous efficacy is notably decreased. The color coordinate shifts of the devices are depicted in Figure 9.5 and compared to the reference device comprising a NPB capping layer. The color shift for the devices with $x\equiv50$, 100, and 500 nm show a large change of color coordinates with higher viewing angle due to a de-adjusted capping layer thickness of crystallized BPhen. However, a BPhen layer thickness of 250 nm leads to a smaller color shift in $x$ direction of $\Delta x\equiv0.009$ compared to the reference device ($\Delta x\equiv0.02$).
Table 9.2: Performance of the heated BPhen devices described in Table 9.1 compared to the NPB reference device.

<table>
<thead>
<tr>
<th>$x$ (nm)</th>
<th>NPB</th>
<th>BPhen</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>5024</td>
<td>1681</td>
</tr>
<tr>
<td>100</td>
<td>1875</td>
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<td>1505</td>
<td>1267</td>
</tr>
<tr>
<td>500</td>
<td>1505</td>
<td>1267</td>
</tr>
</tbody>
</table>

$L^1$ (cd m$^{-2}$), $\eta^2$ (lm W$^{-1}$), $\eta_{eqe}^3$ (%)

1. luminance measured at $I=1$ mA and $\theta=0^\circ$
2. luminous efficacy determined at $I=1$ mA
3. external quantum efficiency determined at $I=1$ mA

![Figure 9.5: Angle dependent color coordinates of the heated devices described in Table 9.1 comprising BPhen capping layer at different thicknesses $x$ and a NPB capping layer. The device with 250 nm heated BPhen exhibits a comparable or even lower color shift.](image)
In terms of the emission pattern of the devices – depicted in Figure 9.6 – a slightly more Lambertian emission characteristic is detected. However, the light emission is still sub-Lambertian.

**UHV Stored BPhen Capping Layer**

For the purpose of crystallization under vacuum, four devices with \( x = 50, 100, 250, \) and 500 nm are stored for 211 h at a pressure of approximately \( 3 \times 10^{-7} \) mbar in the storage of the multi-chamber evaporation system and re-encapsulated afterwards. In comparison to the heated devices, the active areas of the UHV stored devices look homogeneous when examined with the bare eye. Only at \( x = 50 \) nm, a lightly structured surface can be detected. Furthermore, some defects can be detected on the device surface, which originate from dirt particles during this long storage time. A laser beam irradiating the active area is only scattered weakly. Figure 9.7 shows the device surface of the UHV stored BPhen devices analyzed with an optical microscope. Only small structures can be detected on top of the cathode. The spectral radiant intensities of the devices are illustrated in Figure 9.8. Due to a very high leakage current, the performance data of the device with 50 nm BPhen capping layer could not be determined. The plots reveal a slightly changed spectral behavior with increasing viewing angle compared to the reference device. Besides an increasing blue emission up to angles of \( 40^\circ \), both blue as well as red shifts of the emission peaks
Figure 9.7: Light-optical microscope images of the OLED devices with BPhen capping layer after UHV storage with a layer thickness of (a) 50 nm, (b) 100 nm, (c) 250 nm, and (d) 500 nm. Only small structures can be observed.

Figure 9.8: Spectral radiant intensity of the devices described in Table 9.1 with BPhen capping layer after UHV storage measured at a driving current of 1 mA with a capping layer thickness of (b) 100, (c) 250, and (d) 500 nm. The vertical arrows mark the emission maxima. The emission maxima are no longer stable in most cases and show blue or red-shifted peaks with changed viewing angle. The device with the 50 nm thick capping layer could not be characterized due to high leakage current.
(RGB) can be detected for most thicknesses. Furthermore, at a thickness of 500 nm, the cavity emission is restricted in the high wavelength region, which can be deduced from the large intensity drop at 625 nm compared to the spectral radiant intensity of e.g. Figure 9.8c with 250 nm thick capping layer. The performance data for a thickness of 250 nm is equal to the common NPB capping layer device as depicted in Table 9.3. Due to the decreased intensity at higher layer thicknesses \((x=500 \text{ nm})\) the device performance is lowered. Most remarkably, the luminous efficacy and the external quantum efficiency at the layer thickness of 250 nm \((9.3 \text{ lm W}^{-1}, 4.1\%)\) is equal to the results from the reference device with 9.1 lm W\(^{-1}\) and 4.0 %, however much higher compared to a BPhen thickness of 100 and 500 nm.

Figure 9.9 shows the associated color coordinates for the three devices working with different BPhen capping layer thicknesses. Especially, the BPhen layers with \(x=100\) and 500 nm exhibit a large angle dependence. The emission characteristics are illustrated in Figure 9.10. All devices show a radiance similar to the reference device, which is lower compared to ideal Lambertian emission characteristics. Whereas the devices with \(x=100\) and 250 nm show slightly more Lambertian emission characteristics (especially for higher viewing angle), a BPhen layer thickness of \(x=500\) nm leads to lower emission up to an angle of 55°. For higher viewing angles, the emission is superior to the reference device.

<table>
<thead>
<tr>
<th>(X) (x) (nm)</th>
<th>NPB</th>
<th>BPhen</th>
</tr>
</thead>
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<td>-</td>
</tr>
<tr>
<td>50</td>
<td>1317</td>
<td>2061</td>
</tr>
<tr>
<td>100</td>
<td>1240</td>
<td>1240</td>
</tr>
</tbody>
</table>

\(L^1\) (cd m\(^{-2}\)) \(\eta^2\) (lm W\(^{-1}\)) \(\eta_{\text{eqe}}^3\) (%)
1 luminance measured at \(I=1\ mA\) and \(\theta=0^\circ\)
2 luminous efficacy determined at \(I=1\ mA\)
3 external quantum efficiency determined at \(I=1\ mA\)
Figure 9.9: Angle dependent color coordinates of the devices comprising a BPhen capping layer after UHV storage at different thicknesses $x$ and the NPB reference device. Devices with $x=100$ and 500 nm exhibit a large angle dependence.

### 9.1.2 Pentacene Capping Layer

Anthracene is widely known as a highly crystallizing organic material. However, all attempts to deposit thin films of anthracene on top of glass substrates with the available evaporation setups failed, although the material stuck to the QCM. This may be due to a different adhesion of anthracene on top of organic material on the QCM compared to the cleaned glass surface of the substrate, or to the temperature gradient between substrate and cooled QCM. A substrate cooling for further tests has not been available yet. Therefore, experiments with pentacene are performed, since a strong crystallization of pentacene on top of aluminum surfaces has been observed already. The chemical structure of anthracene and pentacene is shown in Figure 9.11. In the experiments performed here, a 50 and 100 nm thick layer of pentacene is evaporated on top of the OLED stack shown in Table 9.1. The active areas, however, reveal no structures either with the bare eye or the light-optical microscope.

The spectral emission at different viewing angle for the pentacene devices is presented in Figure 9.12. The peak emission homogeneously decreases with increased viewing
9.1 Crystallized Organic Material

**Figure 9.10:** Emission characteristics of the devices containing UHV stored BPhen as capping layer: (a) normalized radiance and (b) emission pattern for layer thicknesses of \( x = 50, 100, 250, \) and \( 500 \) nm as well as the reference device. All devices show sub-Lambertian emission and are slightly under or above the radiance of the reference device.

**Figure 9.11:** Chemical structure of (a) anthracene and (b) pentacene.

**Figure 9.12:** Spectral radiant intensity of the devices described in Table 9.1 with pentacene capping layer measured at a driving current of 1 mA with a capping layer thickness of (a) 50 and (b) 100 nm. The vertical arrows mark the emission maxima. The emission peaks are very stable with increasing viewing angle but additionally show higher emission in the long wavelength region.
angle and does not show any wavelength shift for both devices. However, in comparison to the devices with a capping layer made from NPB and BPhen, the emission spectra are altered. Between the wavelength of 550 and 700 nm there are three dips in the emission spectra. This originates from the limited transmission of Pentacene illustrated in Figure 9.13. Here, three minima in transmission can clearly be detected at 584, 633 and 670 nm.

The emission performance data are summarized in Table 9.4. Due to the quite thick pentacene capping layer of 100 nm, the luminance, the efficacy, and the external quantum efficiency are decreased compared to 50 nm capping layer.

The color coordinates show a strong color shift (see Figure 9.14). Especially for the device with the 50 nm thick pentacene capping layer, the color coordinates are shifted towards the blue edge of the CIE coordinate diagram along the Planckian locus. Concerning spectral emission characteristics (see Figure 9.15), the differences to the 50 nm NPB capping layer are insignificant and feature a forward directed light emission similar to the NPB reference device.

Figure 9.13: Transmission of a 100 nm thick pentacene film on a quartz substrate. At three distinct wavelengths, a drop in transmission is detected.
Table 9.4: Performance of the devices with pentacene capping layer compared to the NPB reference device.

<table>
<thead>
<tr>
<th>X (nm)</th>
<th>NPB</th>
<th>pentacene</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2024</td>
<td>1877</td>
</tr>
<tr>
<td>50</td>
<td>9.1</td>
<td>7.6</td>
</tr>
<tr>
<td>100</td>
<td>975</td>
<td>4.2</td>
</tr>
<tr>
<td>4.0</td>
<td>3.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

1 luminance measured at $I=1\,\text{mA}$ and $\theta=0^\circ$
2 luminous efficacy determined at $I=1\,\text{mA}$
3 external quantum efficiency determined at $I=1\,\text{mA}$

Figure 9.14: Angle dependent color coordinates of the devices comprising a pentacene capping layer at different thicknesses $x$ and the NPB reference device. At a thickness of 50 nm the coordinates are strongly blue-shifted.
9.2 Carbon Nanotubes

As an alternative to a scattering organic capping layer on top of the cathode, one can also use a semitransparent scattering top-electrode. One idea is the utilization of a thin film of carbon nanotubes (CNT) (University of Texas, Dallas) [172, 173] mechanically applied on top of the organic light-emitting device. The sheets are supplied in form of a network from one to five single carbon nanotube sheets with a single thickness of 15 nm. As there is also free space between the sheets, one CNT film has a thickness of about 40 nm [174].

**CNT on Top of a Silver Cathode**

Due to the crystallization of BPhen, the experiments can not be performed without the deposition of a metal top-contact that suppresses crystallization processes of the BPhen:C’s electron transport layer. Therefore, the CNT (X) mesh is first of all applied on top of the 15 nm thick Ag cathode of the common white top-emitting structure already shown in Table 9.1.

A light-optical microscope image of the carbon nanotube mesh on top of the OLED stack is illustrated in Figure 9.16. The mesh consists of numerous thin nanotubes,
which are all aligned in one direction. Compared to a device without any capping layer, shown in Figure 9.17b, the spectral radiant intensity of the CNT covered device shows a similar emission (cf. Figure 9.17a). Consequently, the color coordinates (cf. Figure 9.18) are similar to the device without any capping layer. The color shift of both devices is much larger compared to a device with NPB capping layer.

Figure 9.16: Light-optical microscope image of the active area with an applied CNT sheet. The tubes are aligned in one direction but leave free space between each other.

Figure 9.17: Spectral radiant intensity of the devices described in Table 9.1: (a) with an applied CNT sheet and (b) without any capping layer. The spectral emission of both devices is comparable.
Figure 9.18: Color coordinates of the devices with an applied CNT film, an applied NPB capping layer, and without capping layer. The color shift for the applied CNT is equal to the shift of the device without any capping layer.

Moreover, the CNTs do not strongly influence device performance compared to a device without capping layer (cf. Table 9.5). However, the luminance is slightly decreased due to the overall decreased transmission through the device as the carbon nanotube mesh shows a transmission of about 88%, which leads to a lower efficiency. The spectral emission pattern – illustrated in Figure 9.19 – furthermore reveals that the application of the mesh has no influence on the emission characteristics.

**CNT as Cathode**

Using the CNT films as cathode without the use of any metal film requires an electron transport material which does not crystallize. Consequently, the common system BPhen:Cs cannot be used anymore. An alternative electron transport system is the matrix material NET5 doped with the material NDN1. It is very susceptible to oxygen and has to be handled very carefully under exclusion of air in a flowbox.
Table 9.5: Performance of the device with applied CNT film compared to the reference device with 50 nm NPB capping layer and a device without capping layer.

<table>
<thead>
<tr>
<th>X</th>
<th>NPB without CL</th>
<th>CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>x (nm)</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>$L^1$ (cd m$^{-2}$)</td>
<td>2024</td>
<td>1829</td>
</tr>
<tr>
<td>$\eta_h^2$ (lm W$^{-1}$)</td>
<td>9.1</td>
<td>6.98</td>
</tr>
<tr>
<td>$\eta_{eqe}^3$ (%)</td>
<td>4.0</td>
<td>2.65</td>
</tr>
</tbody>
</table>

1 luminance measured at $I=1$ mA and $\theta=0^\circ$
2 luminous efficacy determined at $I=1$ mA
3 external quantum efficiency determined at $I=1$ mA

Figure 9.19: Emission characteristic of the device with an applied CNT film compared to the reference with an applied NPB capping layer and a device without any capping layer: (a) normalized spectral radiance and (b) normalized radiant intensity. The emission pattern for all three devices are similar.

The CNT films are applied on top of the ETL layer of the organic stack after de-encapsulation of the devices. The layer structure of the devices is shown in Table 9.6. As some CNT fibers may penetrate the electron transport layer and consequently could lead to short circuits due to the thin organic stack with a cavity thickness of 100 nm used so far, the ETL thickness is increased by 60 nm from 35 nm to 95 nm. Hence,
Table 9.6: Hybrid device structure based on three emitters with a 95 nm thick ETL layer from NET5 and NDN1 and a CNT cathode. Due to processing reasons, the EBL and HBL had to be changed, too. The cathode is realized with a single CNT film.

<table>
<thead>
<tr>
<th>material</th>
<th>c (wt.%)</th>
<th>r (p:q)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CNT</td>
<td>≈40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NET5:NDN1</td>
<td>95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NET5</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>1:2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)₃</td>
<td>5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)₂(acac)</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>NPB</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>60</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The device cannot be compared to the reference device with the NPB capping layer described at the beginning of this chapter. Figure 9.20 shows a microscopic image from the CNT cathode on top of the organic OLED stack. The single tubes can clearly be dissolved.

The pictures of the OLEDs in Figure 9.21, however, show a very homogeneous emission of light. Only at a low viewing distance and a low device luminance the individual carbon nanotubes can be detected. The performance of the determined diode with CNT cathode is illustrated in Figure 9.22. The electrical characteristics show rather flat $IV$- and $VL$- curves. Due to the high sheet resistance of the tubes (1460 Ω per □ [174]) compared to e.g. ITO (25±5 Ω per □ [71]), very high voltages are necessary to achieve a brightness above 100 cd m$^{-2}$. A brightness of up to 660 cd m$^{-2}$ can be reached at 40 V. Surprisingly, the emission spectra reveal broadband light outcoupling and a very well balanced white light emission with color coordinates very close to the Planckian locus and stable color rendering indices of 77. The luminous efficacy and the external quantum efficiency for the examined device at a luminance of 500 cd m$^{-2}$ is calculated to be 0.33 lm W$^{-1}$ and 2.1 %, respectively. The low luminous efficacy is owed to the high required voltages.

Figure 9.23 illustrates the spectral emission characteristics of the examined device. The spectral radiant intensity shows a strong decrease of blue and green emission contribution compared to the orange-red emission. Consequently, the color shift with higher viewing angle is rather high, although the color is shifted towards the orange edge of the color diagram along the Planckian locus. Concerning the emission pattern the device exhibits an almost Lambertian emission pattern as visible in Figure 9.23c and...
9.2 Carbon Nanotubes

Figure 9.20: Light-optial microscope image of a CNT cathode on top of the organic OLED stack. The single CNT fibres can still be detected and cover the full active area of 8.4 mm².

Figure 9.21: Photograph of an encapsulated OLED device with CNT cathode: (a) at approximately 0° viewing angle and (b) higher viewing angle. A homogeneous light emission can be detected.
Figure 9.22: Performance of a hybrid three-color based device described in Table 9.6 with CNT cathode on top of 95 nm ETL: (a) IVL-characteristics, (b) spectral radiance at different currents normalized to the maximum of the orange-red emission, (d) color coordinates, and (d) color rendering indices. The emission spectra show very well balanced white emission at high voltages.
9.2 Carbon Nanotubes

9.23d. This is presumably due to the high cavity thickness of 160 nm. Thereby, this experiment shows that broadband light emission from top-emitting devices can even be achieved with larger cavity thicknesses and is worth further investigation.

Figure 9.23: Spectral emission characteristics of a hybrid three-color based device described in Table 9.6 with CNT cathode on top of 95 nm ETL at 1 mA driving current: (a) spectral radiant intensity, (b) color coordinates at higher viewing angles, (c) normalized radiance, and (d) normalized radiant intensity. The emission pattern is almost Lamberian like.
In this chapter the deposition of white top-emitting OLED stacks on flexible metal substrates is presented. Compared to glass substrates, flexible metal foil offers opportunities in terms of large-scale, low-cost, and fast production, not to forget the numerous new design options for lighting applications based on these low-weight and slim devices. First, some general aspects of devices on metal substrates are mentioned followed by the direct comparison of devices on glass and metal substrates. Subsequently, the properties of bended metal based devices are discussed. This also includes the examination of device failures owed to too heavy or abrupt bending, discussed in the fourth section.

10.1 White Devices on Metal Substrates

Analogous to devices on top of large test substrate glass wafers, experiments on 0.3 mm and 0.5 mm thick uncoated and untreated Alanod metal substrates (see Section 6.1) are performed. For this purpose, the Alanod substrates are cleaned and heated according to the description in Subsection 5.3.1. The organic layer structure is chosen to be based on three and four emissive dyes as discussed in Subsection 7.2.3 and Section 7.3, respectively, due to the longer stability of hybrid devices. Due to a lack of thin film encapsulation, the common glass lids are used for airtight sealing which, however, only allow a flat device characterization. After encapsulation, the large metal wafer (see Figure 10.1) is cut into single devices by laser-beam cutting\(^1\). Figure 10.2 shows a photograph of demonstrator devices on metal plate under operation.

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\(^1\)Studentisches Produktions-, Forschungs- und Entwicklungscentrum GmbH (SPEZ), TU Dresden
Figure 10.1: Photograph of a metal wafer with 36 processed OLED devices encapsulated with glass lids.

Figure 10.2: Photograph of hybrid devices incorporating (a) three and (b) four emissive materials on top of a 0.5 mm thick metal substrate. The devices are contacted by silver paste on top of adhesive tape to protect the thin nanocomposite layer.
10.2 Comparison of Devices on Glass and Metal Substrates

To directly compare metal substrates and glass substrates with regard to the performance of the processed devices, the identical layer structure (cf. Table 10.1) is deposited on both glass substrate and Alanod substrate. The results of the comparison between glass substrate (I) and Alanod substrate (II) are shown in Figures 10.3 and 10.4, where the performance of two pixel (i and ii) of each device and substrate type is presented.

Generally, the devices show a similar performance on both substrate types. The \( jV L \)-characteristics are equal, apart from the higher leakage currents on top of the metal substrate. Concerning the spectral radiance, the devices on Alanod substrate exhibit a higher emission from the yellow and orange-red emitter material. The yellow and orange-red contributions for the four-color devices slightly vary. Both may be due to slightly changed processing preconditions, as both wafer were processed one after another at two days. However, the blue and green spectral contributions are remarkably

\begin{table}[h]
\centering
\begin{tabular}{lccc}
\hline
material & \( c \) (wt.\%) & \( r \) (p:q) & \( d \) (nm) \\
\hline
NPB & 50 & & \\
Ag & 15 & & \\
Al & 1 & & \\
BPhen:Cs & 35 & & \\
BPhen & 10 & & \\
MADN:TBPe & 1.5 & 10 & \\
TCTA:TPBi & 1:2 & 1.5 & \\
TCTA:Ir(ppy)\_3 & 5 & 3 & \\
NPB:Ir(dhfpy)\_2(acac):Ir(MDQ)\_2(acac) & \( x, y \) & 10 & \\
NPB & & 10 & \\
MeO-TPD:NDP2 & 4 & 20 & \\
Al & & 60 & \\
\hline
\end{tabular}
\caption{Hybrid device structure based on three or four emitters deposited on top of a substrate \( X \), which is either a glass test-substrate or an Alanod metal substrate. The Alanod substrate is 0.5 mm thick \((s=0.5 \cdot 10^6)\) and the glass substrate has a thickness of 1 mm \((s=1 \cdot 10^6)\). The doping concentration is chosen to be \( x=0 \) wt.% and \( y=5 \) wt.% for the three-color devices (upper half of the wafer) and \( x=8 \) wt.% and \( y=1 \) wt.% for the four-color devices (upper half of the wafer).}
\end{table}
similar. The luminous efficacy and external quantum efficiency are partly higher for the metal based substrates, which is due to slightly changed contributions of the highly efficient yellow and orange-red emitter materials to the emission spectra. The color quality is equal for both substrates and shows exceptionally white emission for the three-color based devices. The color coordinates are located exactly on the Planckian locus and show color rendering indices up to 76, which marks the limit for devices with this optical layer structure.

With respect to the degradation and lifetime of the devices on both substrate types, a faster degradation of the devices using metal substrates is observed. The degradation starts soon after processing and cutting and is characterized by a growth of dark spots without failure of the device. This accelerated degradation and the thereby associated
10.2 Comparison of Devices on Glass and Metal Substrates

Figure 10.4: Determined characteristics of the three- and four-color based devices on glass and metal substrate with the layer structure described in Table 10.1: (a) luminous efficacy and external quantum efficiency, (b) color coordinates, and (c) color rendering indices at different driving currents. Due to the higher contributions from the yellow and orange-red emitter in the four-color based spectra, the devices on top of the metal substrate have slightly higher efficacy. Nevertheless, the devices show very similar device performance.

The reduction of lifetime may be due to several reasons. On one hand, the available encapsulation via glass lids and UV-hardening glue is so far mainly tested on top of glass surfaces. Consequently, it can not be assumed that it is equally applicable to metal substrates, although the smoothing silicon oxide layer on top of the Alanod substrate is glass-like. Furthermore, in a long-term view, the encapsulation has to be made flexible to meet all processing and designing options. This requirement is a serious challenge and is already under investigation. On the other hand it is known, that solvents can penetrate the smoothing layer (see Subsection 5.3.1). Therefore, it is not certain whether a permeation of air as well as moisture through the
smoothing layer can take place. Furthermore, e.g. contamination on the smoothing layer or metal substrate – remaining from substrate production – may cause degradation and device failure. Finally, the OLED devices may be adversely affected by the cutting of the wafer in single pieces via a laser.

### 10.3 Bendable Devices on Flexible Metal Substrates

With regard to the targeted device production of OLEDs on metal substrates using a roll-to-roll evaporation system, the devices have to exhibit an adequate tolerance concerning bending. Furthermore, a bending test shall clarify the question, whether bending of the substrate effects the thickness of the organic material via compressing or stretching strain. Due to the very sensible microcavity a decrease of organic thickness originated by strain might lead to a change of the integrated spectral emission shape and a blue shift in emission. However, as the organic layer stack is already very thin, this effect should be quite small.

Due to the small device dimensions at the available evaporation system, the devices on 0.5 mm thick Alanod substrates turned out to be too stiff for bending. Therefore, a thinner 0.3 mm thick substrate is chosen for experiments concerning bending. The deposition is carried out at the small multi-chamber system, aligned to the small substrate dimensions. Metal substrate wafer with 0.3 mm thickness have not been available. Since the metal substrates cannot be encapsulated due to a lack of flexible encapsulation, all experiments are performed in inert gas atmosphere in a glovebox. Consequently, a detailed characterization, as illustrated in Section 5.4, cannot be carried. The integrated spectral emission is detected using the uncalibrated spectrometer in combination with the small integrating sphere. The organic stack used for these experiments is illustrated in Table 10.2.

After processing, the metal substrate based device is bent several times. As no appropriate measuring system for bending in the range of the small dimensions of the device is available, only relative information concerning the bending radii can be given. Consequently, the bending radius – illustrated in Figure 10.5 – can only be estimated. A large bending radius refers to a slight bending of the substrate, whereas a small radius indicates a strong bending of the substrate accompanied with a large curvature. The elasto-plastic metal based device can be bent repeatedly during operation without any failure or damage up to a bending radius of about 1.0 cm. Figure 10.6 shows some photographs of the metal based device in the flat and bent state.

To examine the spectral behavior of white devices under bending, the integrated spectral emission is measured. Thereby, the plain device is bent in two steps up to a bending ra-
Table 10.2: Hybrid device structure based on three emitters deposited on top of a thin Alanod metal substrate.

<table>
<thead>
<tr>
<th>material</th>
<th>c (wt.%)</th>
<th>r (p:q)</th>
<th>d (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NPB</td>
<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td>15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>1:2</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>TCTA:Ir(ppy)$_3$</td>
<td>5</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>NPB:Ir(MDQ)$_2$(acac)</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>S-TAD</td>
<td></td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>MeO-TPD:F$_4$ - TCNQ</td>
<td>4</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>metal</td>
<td></td>
<td>0.3 - $10^6$</td>
<td></td>
</tr>
</tbody>
</table>

dius of about 1.0 cm. At each bending state the integrated spectral emission is detected shown in Figure 10.7. The white device shows a wavelength shift of up to 0.3 nm and an intensity drop of about 2%. However, this marginal change can be negligible. Consequently, the experiment reveals that mechanical bending does not influence the emission of the device.

![Diagram](image)

Figure 10.5: Scheme of the bending radii $r_1$ and $r_2$ at two bending steps (1) and (2). The large bending radius refers to slight bending. At a strong bending of the substrate the bending radius is decreased.
Figure 10.6: Photographs of white OLEDs on thin Alanod substrate described in Table 10.2: (a) a plane substrate and (b) a bent substrate with a white top-emitting device under operation.

Figure 10.7: Integrated electroluminescence spectra of devices described in Table 10.2 determined via integrating sphere. The device is bent in two bending steps (1) and (2). The inset shows the magnified part of the detected EL spectra marked by the box. A spectral change of emission with smaller bending radius cannot be detected.
10.4 Mechanical Damage Owed to Bending

As already mentioned in the previous section, metal based devices are resistant against repeated bending up to bending radii of 1.0 cm. However, stronger bending with curvatures below 1.0 cm lead to device failures. This is owed to the fact that a large curvature damages both substrate and device. Furthermore, a damage of the sample can also be induced by abrupt and fast bending.

Figure 10.8 shows the surface of the prepared sample with applied organic material and electrodes, taken with a light-optical microscope. The samples have been subjected to a strong vertical strain, which resulted in a breaking of the silicon oxide nanocomposite smoothing layer of the horizontal aligned metal substrate. Especially, the very thin Ag cathode is susceptible to damages via bending as the contact to the power supply is disrupted. Despite this fact, even samples with broken nanocomposite smoothing layer may still be working, if an appropriate power supply is given as depicted in Figures 10.9. As the electrical energy supply is adjusted in one direction with the active areas, stripes of the OLED area are still emitting light.

However, one has to keep in mind that these experiments are performed on small device dimensions, which are not comparable to the large dimensioned roll-to-roll installation for large area devices. Usually the utilized coils for supplying substrate foil and recoiling the organic coated substrate as well as the the guiding rolls within the roll-to-roll coating system feature much larger dimensions (e.g. radii between 20 and 45 cm). Consequently, substrate and device damaging due to bending can be excluded at an adequate coil handling.

![Figure 10.8](image)
Figure 10.9: Photograph of a device under operation with broken nanocomposite layer owed to bending. Despite the broken silicon oxide layer the device is still working.
11 Summary and Outlook

Within this work, white organic light-emitting devices in top-emitting configuration on both glass and metal substrates were developed and investigated. In the following, a short summary of the results is given and an outlook is presented afterwards.

11.1 Summary

Metal Substrates and Bottom Electrode Layer

The deposition of white stacks on metal substrates requires an extremely smooth substrate surface to prevent short circuits and device failures. For that purpose, the surface morphology of metal substrates was investigated. With the help of light-optical microscopes, SEM, and AFM it was shown that the untreated Alanod metal sheets exhibit adequate surface properties for a successful utilization as substrate for organic light-emitting diodes. The substrate roughness values are comparable to glass substrates and provide a low-cost alternative to fragile and heavy glass substrates. Silver covered roll-process pre-treated substrates are not appropriate for OLED application, as they exhibit numerous defects on the substrate surface that will unavoidably lead to device failures. Since rough anode layers also cause device defects and high leakage currents, the surface morphology of Ag on top of Alanod substrates was examined via AFM in regard to evaporation rate and layer thickness. The lowest roughness values and the most homogeneous surface morphology was achieved for deposition rates below 0.5 Å s$^{-1}$ and above 5 Å s$^{-1}$. Changed layer thicknesses did not strongly influence the layer smoothness. Nevertheless, silver deposited on top of Alanod substrates is rougher than on glass substrate. However, due to changed evaporation conditions, the utilization of the single-chamber evaporation system can decrease the roughness. During experiments and optimization of the devices, a combination of both Al and Ag turned out to be more appropriate than pure Ag and still lowers the probability of high leakage currents and device short circuits.
White Organic Light-Emitting Devices

During this work, two different device structures were examined: the hybrid approach with both fluorescent and phosphorescent emitting material and the all-phosphorescent approach using only phosphorescent emitters. The examination of hybrid white devices was started with a detailed view on the realization of white emission in first- and second-order devices using optical simulation. The application of a dielectric capping layer on top of the top-electrode – acting as antireflection coating – allowed a broadband light emission in the first-order with almost angle independent spectral emission compared to devices without capping layer. However, the spectral emission is strongly influenced by the cavity emission of the stack set by its cavity thickness. By accurately adjusting the stack parameters, a first-order white-emitting cavity device was successfully prepared, whose spectral radiance coincides very well with optical simulations. Subsequently, a number of device optimization steps were performed to improve the device performance in terms of efficiency and color quality. Thereby, different parameters – e.g. the choice of materials, the layer thickness, the doping concentration, the interlayer mixture, etc. – were under investigation. The stack parameters were carefully arranged to achieve best device performance. Particularly, an altered anode material revealed a considerable influence on the spectral emission shape of the devices.

An optimal adjustment of the device parameters finally led to highly efficient devices with excellent color quality. The anode material (Al or composite Al-Ag) showed a considerable influence on the spectral emission shape of the devices, due to a changed cavity emission. Devices prepared on top of a composite Al-Ag anode electrode exhibit a current efficiency of 20.0 cd A$^{-1}$, a luminous efficacy of 12.5 lm W$^{-1}$ and external quantum efficiency of 5.3 % at approximately 1000 cd m$^{-2}$. By exchanging the electron blocker material NPB with S-TAD, an even higher luminous efficacy of 13.3 lm W$^{-1}$ was achieved due to a lowered driving voltage. With the choice of a pure Al anode, excellent color quality was achieved, featuring color coordinates very close to the Planckian locus (e.g. $(x, y) = (0.44, 0.41)$ at 500 cd m$^{-2}$) and excellent color quality with CRI up to 77. Furthermore, the color can be tuned along the Planckian locus via brightness. The devices exhibit stable emission maxima and particularly enhanced forward emission up to angles of 50°, which is especially preferred for applications in lighting industries. In comparison to comparable bottom-emitting devices, the presented top-emitting OLEDs feature superior internal quantum efficiency.

With the introduction of an additional fourth yellow emitter into the orange-red subEML layer of a Al anode based stack, the intensity at the maximum of the spectral luminous efficacy function – the highest sensitivity of the eye – was increased. Consequently, the luminous efficacy was nearly doubled from 8.3 lm W$^{-1}$ to 15.6 lm W$^{-1}$ at a luminance of 1000 cd m$^{-2}$. Furthermore, the external quantum efficiency was improved by a factor of 1.5 to a value of 6.1 %. Using the composite Al-Ag anode led to luminous efficacies of up to 16.1 lm W$^{-1}$ at 1000 cd m$^{-2}$. 


To further discover the limits in efficiency, an all-phosphorescent approach was modified for top-emission utilizing orange-red, green, and sky blue emitters. The devices were optimized concerning efficiency and spectral emission via the location of the EML, the blue sub-EML thickness, and the interlayer thicknesses TPBi and TCTA, the latter being particularly decisive for the spectral properties. With an optimally arranged device structure a luminous efficacy of 21.7 lm W$^{-1}$ with 8.5% external quantum efficiency was achieved. Although the emission spectrum is still dominated by the green emitter Ir(ppy)$_3$, color coordinates of $(x, y) = (0.40, 0.45)$ can be measured with a slightly lower efficiency. The color rendering is determined to be up to 72.

Owing to the rather few reports on white top-emitting devices (see Table B.1 in Appendix B), the results for the hybrid [175, 176] and all-phosphorescent approach presented here are the best reported so far concerning efficiency as well as color quality.

**Outcoupling**

Furthermore, experiments to optimize light outcoupling were performed. To improve the color stability with changing viewing angle, crystalline capping layer were investigated, which potentially scatter light in all directions. Devices with a BPhen capping layer thickness of 250 nm, which have been heated after capping layer deposition, show a smaller color shift in $x$ direction compared to the reference device with NPB capping layer. For UHV stored devices, a significant decrease of the spectral shift or a change of the spectral emission characteristics have not been determined. The applied pentacene capping layer did not have an effect on the spectral emission. Only the emission in the high wavelength region was altered due to material absorption. Carbon nanotube films on top of the device cathode did not have any effect on the spectral radiation of the devices. However, by using the CNT film as cathode of the device, a broadband white emission spectrum could be achieved at even a higher cavity thickness of 160 nm without using any additional capping layer. Although the device shows very low luminous efficacy of 0.33 lm W$^{-1}$ at 500 cd m$^{-2}$ due to the high voltages needed, the external quantum efficiency is measured to be 2.1%. Thus, this alternative approach is worth further investigation.

**White OLEDs on Top of Metal Substrates**

Finally, the hybrid white top-emitting layer structure was successfully applied onto metal substrates. The comparison between devices on both substrate types (glass and metal) revealed similar performance. Only the leakage currents of the devices on metal substrate are slightly higher. However, the lifetime of metal substrate based devices is low compared to those on top of common glass substrate.

Mechanical tests revealed a stable spectral emission concerning bending and hardly
spectral shift with smaller bending radii. The devices have a bending radius limit of approximately 1.0 cm. Smaller radii cause a breakage of the silicon oxide smoothing layer, which interrupts the power supply of both electrodes.

11.2 Outlook

The work presented here can only be a starting point for the investigation of white top-emissive systems and their applications on different substrates than glass. It is a long way to compete with bottom-emitting white devices, as top-emitting devices still suffer from optical limitations. However, the number of new opportunities for top-emissive OLEDs are worth further attention.

Although the device performance presented in this work exhibits excellent data for white top-emitting devices, an improvement is still possible and desirable in regard to future OLED products, which have to compete with bottom-emitting devices. There are several items that need further investigation to improve and optimize white top-emitting OLEDs.

Generally, white OLEDs suffer from a lack of available stable and highly efficient deep blue emitters. Both, device efficiency and color performance will benefit from such a fluorescent or phosphorescent blue emitter. Therefore, investigations and material development are highly desirable. The long time stability would further improve the lifetime of white OLEDs, which is required for lighting applications. To meet these requirements separately careful investigations have to be performed.

In terms of improving the device stability, other layer architectures are worth further attention. This work exclusively dealt with architectures using sub-EML concepts for the generation of white light. However, one can also think of achieving white light emission with e.g. multiple doped single EML or even stacked OLEDs. Thereby, an improved charge carrier balance for current stable devices without complicated inter-layer structures may potentially be possible. A stacked OLED can furthermore allow a direct control of emitted color via separate activation of each stack but requires extensive optical modelling or an upgraded outcoupling approach.

However, the main problem of top-emitting devices so far is their limited light extraction from the microcavity. Only a small portion of the light produced within the presented white devices can be coupled out due to the narrow cavity emission despite using an outcoupling layer. Therefore, new approaches for outcoupling have to be developed. This investigation may include the application of scattering particles or structures helping to eliminate the angle dependent color shift thereby leading to homogeneous emission. However, to compete with bottom-emitting devices, the ideal OLED structure must contain a highly transparent but adequate conducting top-electrode in combination with an outcoupling concept as recently presented by Novaled [177] using crystallizing scattering structures. This approach will hence avoid strong microcavity
effects and make top-emitting OLEDs competitive to bottom-emission. Furthermore, a better control of the reproducibility as well as color and color rendering indices can be achieved. Due to higher transparency and much broader cavity emission also higher efficiencies will be possible. This research has further to be combined with the development of an alternative concept for flexible thin film encapsulation of devices on flexible substrate, onto which additional outcoupling foils may be applied for an upgrade in efficiency as done for bottom-emissive devices.

Therewith, an essential requirement for roll-to-roll production will be implemented that paves the way for easy, quick, and low cost fabrication of OLEDs. However, high-quality substrates are essential for achieving high production yields. Since the presented experiments with metal substrates indicated a low lifetime of the processed OLEDs, the substrate stability has to be investigated further. With upscaling the evaporation systems and the OLED areas, the homogeneity and reproducibility of efficiency and color performance will further play an outstanding role.

Nowadays, very promising first steps towards industrial fabrication and commercialization have been done \cite{20, 178–181} for bottom-emitting devices. However, when the challenges mentioned can be met, also top-emitting devices will make up for the next generation of lighting into a bright future with OLEDs.
Appendix A  Cold White Emission Based on Two Emitters

Besides the comfortable warm light at the warm white point A (0.45, 0.41), also a much more neutral, colder emission color may be preferred for special applications. Here, the main focus is on the illumination of large working areas, e.g. offices, hallways, machine halls, or buildings. Especially, eastern costumers – like the Japanese or the Chinese – are strongly used to this much colder light impression. Furthermore, a drawback of the previously presented three- and four-color based devices producing warm white light is the instability of the spectral emission against changes in current and luminance. Thereby, the emission color cannot be kept with dimming light intensity. However, for commercial lighting devices stable color points are desired, which keep the emitted color with increased brightness.

Compared to the complex three- and four-color based devices, a much simpler OLED stack approach may cope with these challenges. Therefore, a simplified two color based stack structure (cf. Figure A.1) is furthermore investigated, which contains simply a yellow and a blue emitter. With this color combination, cold white emission can be achieved, as the connection line of the color points of both emitters almost intersects the cold white point E. However, a drawback will be the low CRI, as two emitting dyes cannot cover the whole visible emission spectrum due to the limited extentions of their emission spectra. Due to the symmetrical arrangement of both emission layers around the interlayer, a simplified adjustment of the electron-hole balance is assumed. To achieve well balanced cold white emission with this simplified layer architecture, several experiments are performed. Besides different fluorescent blue emitters, several materials for electron and hole blocking are tested. Further, the interlayer thickness and ratio is varied and cavity thickness variations are examined. The spectral radiance, cavity emission as well as the color coordinates and rendering indices are stated for forward directed emission, if not stated differently.
Figure A.1: Schematical illustration of the top-emitting layer architecture comprising two emitting dyes. The yellow emitter Ir(dhfpy)$_2$(acac) and the deep blue emitter TBPe are utilized to aim cold white emission.
A.1 Different Blue Emitting Materials

Generally, different blue emitter systems can be used for two-color devices. Here, the fluorescent blue emitting material MADN is used both as bulk layer and as host for the fluorescent blue emitter TBPe. The high-wavelength color component is realized with the phosphorescent yellow emitter Ir(dhfpy)$_2$(acac), which is doped into the matrix material NPB. This emitter is chosen due to its emission maximum at $\lambda = 557$ nm, which is almost exactly at the point of maximum eye sensitivity, which provides the possibility to reach high luminous efficacies. The combination of the deep blue and yellow dye furthermore assures a broad emission spectrum, without too low contributions within the green emission region, as especially the second emission maximum of TBPe is close to 500 nm. The chosen layer structure with the materials, doping concentrations, material ratios, and layer thicknesses are illustrated in Figure A.1.

Table A.1: Hybrid device structure based on two emitters using different deep blue emitter materials. Besides the orange-red emitting material Ir(dhfpy)$_2$(acac), the deep blue emitter material MADN is incorporated, which is either used as bulk emission material or as host for the fluorescent blue emitter TBPe. Hence, the doping concentration $x$ of TBPe is rather 0 or 1 wt.%.

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%)</th>
<th>$r$ (p:q)</th>
<th>$d$ (nm)</th>
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<tbody>
<tr>
<td>NPB</td>
<td>50</td>
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<tr>
<td>Ag</td>
<td>15</td>
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<tr>
<td>Al</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alq$_3$</td>
<td>10</td>
<td></td>
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</tr>
<tr>
<td>MADN:TBPe</td>
<td>$x$</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>2:1</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>NPB:Ir(dhfpy)$_2$(acac)</td>
<td>5</td>
<td></td>
<td>10</td>
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<tr>
<td>NPB</td>
<td>10</td>
<td></td>
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<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
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<td>Ag</td>
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The normalized spectral radiance examined for both devices (see Figure A.2a) reveals a strong yellow contribution compared to the low blue emission of both blue emitter materials. This is mainly due to electrical reasons, as the cavity emission of the 100 nm thick layer system has already been tuned for the low wavelength region (resonance wavelength is 490 nm) to enhance the blue emission. On the one hand, the fluorescent material anyway shows much lower efficiency compared to a phosphorescent emitter material, because of spin statistics. On the other hand, the electron-hole balance within
Figure A.2: Characteristics of the two-color based devices described in Table A.1 using different blue emitting materials: (a) intensity normalized spectral radiance and simulated cavity emission, (b) luminous efficacies and external quantum efficiencies. Despite a cavity tuning for blue emission, both devices show very strong yellow emission. However, the device containing MADN:TBPe exhibits little more blue contribution. Therefore, this device exhibits both enhanced luminous efficacy and external quantum efficiency.

Although the width of the spectrum is slightly limited in the blue range, the device with MADN:TBPe shows slightly blue shifted color coordinates of \((x, y) = (0.366, 0.466)\) compared to MADN with \((x, y) = (0.381, 0.477)\), which is still too yellow for cold white emission.

### A.2 Influence of Different Blocking Materials

To examine the influence of the blocking material on the electron-hole balance, different materials are tested as depicted in Table A.2. Besides the different electron blocking materials \((X)\) NPB and S-TAD, Alq3, the materials TPBi and BPhen are further used for hole blocking \((Y)\).
Table A.2: Hybrid device structure based on two emitters using different blocking materials $X$ and $Y$. With a layer thickness $d$ of 10 nm, the electron blocking materials NPB and S-TAD ($X$) as well as the hole blocking materials ($Y$) Alq$_3$, TPBi, and BPhen are tested.

<table>
<thead>
<tr>
<th>material</th>
<th>$c$ (wt.%)</th>
<th>$r$ ($p:q$)</th>
<th>$d$ (nm)</th>
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<tbody>
<tr>
<td>NPB</td>
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<td>Ag</td>
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<tr>
<td>Al</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>30</td>
<td></td>
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</tr>
<tr>
<td>$Y$</td>
<td>10</td>
<td></td>
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<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
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<tr>
<td>TCTA:TPBi</td>
<td></td>
<td>2:1</td>
<td>5</td>
</tr>
<tr>
<td>NPB:Ir(dhfpy)$_2$(acac)</td>
<td>5</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>$X$</td>
<td>10</td>
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<tr>
<td>MeO-TPD:NDP2</td>
<td>4</td>
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<td>Ag</td>
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In Figure A.3, the characteristics of the devices comprising different blocking materials are summarized. Due to the varied electrical conductivity as well as the different HOMO and LUMO energy levels of the materials, the devices show different current density and luminance (see Figure A.3a). As already discussed in Subsection 7.2.3, a change from NPB to S-TAD as blocking layer leads to lower driving voltages. Changing the hole blocking material causes a shift in the onset voltage of the device, wherein BPhen shows the lowest turn-on voltage of 2.6 V compared to Alq$_3$ and TPBi. Furthermore, the $jV$- as well as the $LV$-curves are slightly steeper compared to Alq$_3$ and TPBi.

The changed hole blocking materials also lead to different emission spectra as Figure A.3b shows. Compared to NPB, the blocking material S-TAD strongly decreases the emission of the yellow emitting material Ir(dhfpy)$_2$(acac), which is a hint for a changed exciton distribution within the device caused by different electron-hole recombination. Consequently, both luminous efficacy and external quantum efficiency are higher using NPB as electron blocker. Here, the efficacy rises from 5 to 7.5 lm W$^{-1}$ at a luminance of about 1000 cd m$^{-2}$ and the external quantum efficiency is increased to 3.2 % for NPB.

Concerning the hole blocking materials, the device containing TPBi shows reduced yellow emission but increased blue emission, which is due to an altered electron-hole balance with a smaller fraction of excitons being formed in the yellow sub-emission layer. Consequently, the luminous efficacy as well as the quantum efficiency are low. Due to the balanced intensities of blue and yellow emission, the color coordinates are
Figure A.3: Characteristics of the two-color based devices described in Table A.2 using different blocking materials: (a) $jV L$-characteristics, (b) spectral radiance divided by driving current, and (c) luminous efficacy and external quantum efficiency. The electron blocker material S-TAD combined with the hole-blocker material BPhen reaches the lowest voltage onset of 2.6 V, the smallest driving voltages and highest efficiency.

with $x=0.302$ and $y=0.401$ closer to the Planckian locus compared to the devices containing BPhen or Alq$_3$ as hole blocker. Utilizing the blocking material BPhen indeed leads to much higher efficacy values (9.1 lm W$^{-1}$ at 1000 cd m$^{-2}$), due to the large contributions from the highly efficient yellow emitter and a more balanced electron-hole distribution. However, the quality for cold white emission is poor with coordinates of $(x, y)=(0.39, 0.48)$ and a CRI of 33.

A detailed view on the current dependent spectral measurements of the four processed combinations for blocking materials (cf. Figure A.4a-d) reveals current stable emission spectra for the blocking material combination of S-TAD and BPhen only (Figure A.4d). Both combinations with Alq$_3$ (Figure A.4a and b) show a slightly changing spectral shape with changed driving current. The largest current dependence is given with the electron blocking material S-TAD combined with the hole blocking material TPBi (cf. Figure A.4c). Using the material combination S-TAD with BPhen leads to a constant emission shape and consequently invariant emission color and color rendering.
with driving current. However, despite current stable spectral emission, both luminous efficacy and external quantum efficiency have to be determined via angular measurements. Though, due to the invariance of the spectral shape with current variations, only one measurement is needed for exact efficiency determination, as explained in Subsection 5.5.2.

**A.3 Examination of Interlayer Characteristics**

The interlayer plays an decisive role in hybrid devices, as it controls the flow of electrons and holes by its thickness and its mixing ratio of both electron- and hole-conducting components. Furthermore, it controls the exciton exchange rates between both sub-EMLs. To examine the influence on the emission and the efficiency of the devices, two different thicknesses (3 and 5 nm) as well as different mixture ratios of TCTA and TPBi are analyzed as depicted in Table A.3.
Table A.3: Hybrid device structure based on two emitters using a different interlayer thickness \( x \) and mixing ratio \( r \). The interlayer thickness \( x \) is chosen to be 3 or 5 nm along with a cavity thickness of 98 or 100 nm. Within the interlayer ratio of TCTA and TPBi, the fraction of TCTA is varied by \( p \) resulting in ratios of 1:1, 2:1, 4:1, or 6:1.

<table>
<thead>
<tr>
<th>material</th>
<th>( c ) (wt.%)</th>
<th>( r ) ( (p:q) )</th>
<th>( d ) (nm)</th>
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<td>NPB</td>
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<tr>
<td>Al</td>
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<tr>
<td>BPhen:Cs</td>
<td>30</td>
<td></td>
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<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
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<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td>( p:1 )</td>
<td>( x )</td>
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</tr>
<tr>
<td>NPB:Ir(dhfpy)(_2)(\text{(acac)})</td>
<td>5</td>
<td>10</td>
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<tr>
<td>S-TAD</td>
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<td>MeO-TPD:NDP2</td>
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Figures A.5a and A.5b illustrate the influence of the interlayer thickness \( x \) on the spectral radiance and the device efficiencies for a fixed interlayer ratio of 2:1 \((p=2)\). Although the \( jV \)-characteristics (not shown here) are identical, an increased blue contribution is achieved with only 3 nm interlayer thickness instead of 5 nm. The fact that the cavity thickness is reduced by 2 nm may play a role in the increase of the blue emission, but is most likely not the only reason for the higher blue emission. Furthermore, despite the higher blue emission, the luminous efficacy as well as the external quantum efficiency are higher for thinner interlayer thicknesses, which points to an increased charge carrier flow through the interlayer.

Furthermore, different interlayer ratios are utilized to examine the influence of the TCTA fraction \( p \) within the mixed interlayer as denoted in Table A.3. The overall interlayer thickness is chosen to be 3 nm. Figure A.6 illustrates the characteristics of the four fabricated devices with the interlayer ratios of 1:1, 2:1, 4:1, and 6:1. Concerning the electrical characteristics, a similar but shifted current density and luminance is detected (see Figure A.6a), which indicates a change in hole and electron flow through the device. As the concentration of the predominantly hole conducting material TCTA within the interlayer is increased, the flow of electrons is restricted. This also explains the spectral radiance characteristics illustrated in Figure A.6b, where a decrease of yellow but an increase of blue emission is detected. As more holes reach the interface between interlayer and blue emission zone, more excitons are generated, which leads to an enhanced blue spectral emission. This is coupled with the restricted electron flow.
A.4 Influence of the Cavity Thickness

![Figure A.5](image)

**Figure A.5:** Characteristics of the two-color based devices described in Table A.3 using different interlayer thicknesses \(x\): (a) normalized spectral radiance and (b) luminous efficacy and external quantum efficiency. The interlayer mixing ratio of TCTA and TPBi is 2:1. For thinner interlayer thickness an increased blue emission contribution as well as a higher efficiency is detected.

through the interlayer leading to lower yellow emission. Consequently, the luminous efficacy as well as the external quantum efficiency drops for higher TCTA fractions \(p\) within the interlayer mixture (cf. Figure A.6c). For an increased TCTA fraction from \(p=2\) to \(p=4\) (2:1 to 4:1), the yellow emission does not change significantly, but the blue contribution is increased. Consequently, the luminous efficacy and external quantum efficiency are hardly changed for the interlayer ratio 4:1. The highest luminous efficacy (EQE) of 21.2 lm W\(^{-1}\) (5.2 \%) at 1000 cd m\(^{-2}\) is observed at a ratio of 1:1, the lowest efficacy (EQE) of 12.2 lm W\(^{-1}\) (2.9 \%) is realized with a TCTA fraction of \(p=6\).

Due to the large yellow and low blue contribution, the color is not well balanced for the interlayer ratio of 1:1, showing color coordinates of \((x, y) = (0.428, 0.529)\) at a luminance of 1277 cd m\(^{-2}\), whereas the device comprising a ratio of 6:1 features blue shifted coordinates of \(x=0.368\) and \(y=0.469\) due to the enhanced blue emission.

A.4 Influence of the Cavity Thickness

The devices can be optically tuned by changing their cavity thickness as already discussed in Subsection 7.2.2 for devices based on three emitting materials. Due to the thin overall device layer structure, the overall cavity thickness can only be reduced by decreasing the layer thickness of both p- and n-doped transport materials. Hereby, the blocking materials S-TAD and BPhen are used. Here, the layer thickness \(x\) and \(y\) of hole and electron transport layers is decreased in steps of 5 nm. The results of the device structure shown in Table A.4 is illustrated in Figure A.7.
Figure A.6: Characteristics of the two-color based devices described in Table A.3 using different interlayer ratios of p:1: (a) jV-L-characteristics, (b) spectral radiance at a driving current of 0.5 mA, and (c) luminous efficacy and external quantum efficiency. The interlayer thickness is chosen to be 3 nm. Due to the enhanced blue contributions for higher concentrations of TCTA within the interlayer, the emission spectrum gets more white balanced, but also suffers lower efficiencies.
Table A.4: Hybrid device structure based on two emitters featuring different p- and n-transport layer thicknesses \( x \) and \( y \). The changed transport layer thicknesses result in a changed overall cavity thickness.

<table>
<thead>
<tr>
<th>material</th>
<th>( c ) (wt.%)</th>
<th>( r ) (p:q)</th>
<th>( d ) (nm)</th>
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<tbody>
<tr>
<td>NPB</td>
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<tr>
<td>Ag</td>
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<tr>
<td>Al</td>
<td>1</td>
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<td></td>
</tr>
<tr>
<td>BPhen:Cs</td>
<td>( y )</td>
<td></td>
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<tr>
<td>BPhen</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MADN:TBPe</td>
<td>1</td>
<td>4:1</td>
<td>10</td>
</tr>
<tr>
<td>TCTA:TPBi</td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>NPB:Ir(dhfpy)(_2)(acac)</td>
<td>5</td>
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<tr>
<td>S-TAD</td>
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<td>MeO-TPD:NDP2</td>
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<td>( x )</td>
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The spectral radiance as well as the simulated cavity emission for all four devices are depicted in Figure A.7a. With decreasing overall cavity thickness, the maximum of the cavity emission is continuously shifted towards lower wavelengths. Due to the continuous change of the cavity emission, one expects a constant decrease of yellow emission and a simultaneously firstly rising and subsequently decreasing blue emission. However, the decrease of yellow and the increase of blue emission at a driving current of 0.5 mA is not continuous. The intensity of the first blue emission maximum at 464 nm does not change significantly with a changed ETL thickness between 20 and 25 nm as well as 25 and 30 nm. This change however leads to a decrease of Ir(dhfpy)\(_2\)(acac) emission. As the \( VL \)-diagram in Figure A.7b shows, the reduction of the ETL thickness is thereby accompanied by a large decrease in luminance, which is due to the lower emission of the efficient yellow emitter. The change of the HTL thickness from 25 to 20 nm, on the other hand, leads to an increased blue emission, while the yellow emission intensity is unchanged. As a consequence of the drop in yellow emission, both luminous efficacy and external quantum efficiency (see Figure A.7c) are decreased from 16.8 lm W\(^{-1}\) to 6.5 lm W\(^{-1}\) and from 5 % to 2.4 % at a driving current of 0.5 mA. In regard to the color balance for white emission, the decreased cavity thickness leads to shifted color coordinates towards the blue edge of the color diagram, steadily approaching the black body curve. Consequently, the color rendering is enhanced from 31 to 49.

The angle dependent spectral emission of all four devices is illustrated in Figure A.8. For all transport layer combinations \( x/y \), the yellow emission intensity constantly decreases with increasing viewing angle. However, the devices differ concerning the de-
Figure A.7: Characteristics of the two-color based devices described in Table A.4 using varied p- and n-layer thicknesses: (a) spectral radiance at a driving current of 0.5 mA and simulated cavity emission, (b) luminous efficacy and external quantum efficiency, (c) $jV L$-characteristics, (d) color coordinates, and (e) color rendering indices. The interlayer ratio is each chosen to be 4:1. Due to the blue shifted cavity emission the spectral radiance shows an overall increased blue and decreased yellow emission. Consequently, the luminous efficacy and the external quantum efficiency are lowest for the smallest cavity thickness. However, the color coordinates show well balanced white emission.
Figure A.8: Spectral radiant intensity of the four devices described in Table A.4 using varied p- and n-layer thicknesses. The decrease in yellow emission is always continuous but stronger for large cavity thicknesses compared to the decrease in blue emission. The intensity of the first maximum of TBPe is more stable for high ETL and HTL thicknesses.
Appendix A  Cold White Emission Based on Two Emitters

Figure A.9: Angle dependent color coordinates of the devices described in Table A.4 using varied p- and n-layer thicknesses. With higher viewing angle the color coordinates are blue shifted along the Planckian locus.

In Figure A.9, the angle-dependent color coordinates are depicted. The color points for all devices are shifted to the blue edge of the color diagram. Thereby, they move along the Planckian locus. The angle dependence is weakened with lower cavity thickness. Concerning the spectral emission pattern, all devices exhibit a forward directed light emission as illustrated in Figure A.10a and b. The normalized radiance shows equal behavior for all four devices with different cavity thickness.
Figure A.10: Normalized radiance (a) and normalized radiant intensity (b) of the devices described in Table A.4 using varied p- and n-layer thicknesses. All devices feature the same under-Lambertian emission characteristics with forward directed light emission.
Appendix B  White Top-Emission in Literature

Compared to bottom-emitting white organic light-emitting diodes, the top-emitting counterpart has not been frequently addressed in literature so far. The reason for this fact can be found in the optical properties of top-emitting devices, the challenge for broadband outcoupling and exactly meeting the requirements for high-quality white light emission.

Table B.1 gives a brief overview over the existing approaches and reports in the research of white top-emitting OLEDs up to the present.
Table B.1: Published papers concerning white top-emitting organic light-emitting diodes and their specifications. Besides the device performance (driving voltage $V$ (V), luminance $L$ (cd m$^{-2}$), current efficiency $\eta_c$ (cd A$^{-1}$), luminous efficacy $\eta_l$ (lm W$^{-1}$), external quantum efficiency $\eta_{eqe}$ (%), and driving current density $j$ (mA cm$^{-2}$)) the color quality (CIE color coordinates and CRI color rendering index) is given. (Abbreviations: CL=capping layer, y=yes, n=no, B=blue, G=green, and R=red).

<table>
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<tr>
<th>year</th>
<th>author</th>
<th>cavity</th>
<th>dye systems</th>
<th>CL</th>
<th>device performance</th>
<th>color quality</th>
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<tr>
<td>2001</td>
<td>T. Feng et al. [182]</td>
<td>y</td>
<td>fluorescent EML</td>
<td>n</td>
<td>7.94 V, 4.87 cd A$^{-1}$, 1.93 lm W$^{-1}$, 1.82% at 20 mA cm$^{-2}$</td>
<td>CIE (0.33, 0.41)</td>
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<tr>
<td>2005</td>
<td>S.-F. Hsu et al. [107, 183]</td>
<td>y</td>
<td>NPB:rubrene, MADN:DSA-ph</td>
<td>y</td>
<td>22.2 cd A$^{-1}$ and 9.6 lm W$^{-1}$ at 7.3 V</td>
<td>CIE (0.31, 0.47) at 7.3 V</td>
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<tr>
<td>2005</td>
<td>H. Kanno et al. [80]</td>
<td>n</td>
<td>UGH2:Ir(46dpyp)$_3$, CBP:PQIr</td>
<td>n</td>
<td>9.8 lm W$^{-1}$ and 10.4% at 1 mA cm$^{-2}$</td>
<td>CIE (0.42, 0.39) at 10 mA cm$^{-2}$</td>
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<tr>
<td>2006</td>
<td>S.-J. Lin et al. [184]</td>
<td>y</td>
<td>ADS082BE:DCJT</td>
<td>n</td>
<td>2527 cd m$^{-2}$ and 1.13 cd A$^{-1}$ at 12 V</td>
<td>CIE (0.30, 0.34)</td>
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<td>2007</td>
<td>X. Zhu et al. [125]</td>
<td>y</td>
<td>mCP:Ir(ppy)$_2$(acac), mCP:FIrpic, mCP:Ir(btp)$_2$(acac)</td>
<td>y</td>
<td>max.: 12.8 lm W$^{-1}$, 9.1% at $\approx$ 40 cd m$^{-2}$</td>
<td>CIE (0.37, 0.43) at 1445 cd m$^{-2}$</td>
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<td>2008</td>
<td>M.S. Kim et al. [126]</td>
<td>y</td>
<td>DPVBi:DCJTB</td>
<td>y</td>
<td>1.0 cd m$^{-2}$, 1.4 lm W$^{-1}$, maximum: 12700 cd m$^{-2}$ at 12.8 V</td>
<td>CIE (0.32, 0.34) at 1.0 cd m$^{-2}$</td>
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<td>2008</td>
<td>M.-T. Lee et al. [127]</td>
<td>y</td>
<td>TC-1556:TC-1776, TC-1556:TC-1754</td>
<td>y</td>
<td>3000 cd m$^{-2}$ and 4.6 cd/A at 5.3 V</td>
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<td>J.-J. Huang et al. [185]</td>
<td>y</td>
<td>ADS082BE:DCJT</td>
<td>n</td>
<td>max.: 3 cd A$^{-1}$ at 10 V, 3789 cd m$^{-2}$ at 13.5 V</td>
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Continued on next page...
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<th>Year</th>
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<th>CL</th>
<th>Device Performance</th>
<th>Color Quality</th>
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<td>J. Hou et al. [186]</td>
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<td>1.95 cd A$^{-1}$</td>
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<td>M. Thomschke et al. [109]</td>
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<td>Spiro-DPVBi, TCTA:Ir(ppy)$_3$, NPB:Ir(MDQ)$_2$(acac)</td>
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<td>W. Ji et al. [187]</td>
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<td>DPVBi, CBP:(F-BT)$_2$Ir(acac)</td>
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<td>8936 cd m$^{-2}$ at 11 V, max.: 8.4 cd A$^{-1}$ at $\approx$ 9 V</td>
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<td>max. 5.6 cd A$^{-1}$ at $\approx$ 6.5 mA cm$^{-2}$</td>
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<td>1037 cd m$^{-2}$, 20.0 cd A$^{-1}$, 12.4 lm W$^{-1}$ and 5.3% at 3.4 V</td>
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# List of Materials

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<td>Sulfur</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Silicon dioxide</td>
</tr>
<tr>
<td>Spiro-DPVBi</td>
<td>2,2’,7,7’-Tetrakis(2,2-diphenylvinyl)spiro-9,9’-bifluorene</td>
</tr>
<tr>
<td>S-TAD</td>
<td>2,2’,7,7’-Tetrakis-(<em>N</em>,<em>N</em>-diphenylamino)-9,9’-spirobifluoren</td>
</tr>
<tr>
<td>TBPe</td>
<td>2,5,8,11-Tetra-tert-butylperylene</td>
</tr>
<tr>
<td>TC-1556</td>
<td>from Tetrahedron Technology Co., Ltd</td>
</tr>
<tr>
<td>TC-1776</td>
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<td>TC-1556</td>
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<td>TC-1754</td>
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</tr>
<tr>
<td>TCTA</td>
<td>4,4’,4”-Tris(carbazol-9-yl)-triphenylamine</td>
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<tr>
<td>TPBi</td>
<td>2,2’,2”-(1,3,5-Phenyl)tris(1-phenyl-1H-benzimidazol)</td>
</tr>
<tr>
<td>UGH2</td>
<td><em>p</em>-Bis(triphenylsilyly)benzene</td>
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[8] LG UK. "LG releases 15 OLED TV, the largest available to consumers, this Spring". Press release April 2010.


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Ich versichere weiterhin, dass bislang keine Promotionsverfahren stattgefunden haben.


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Patricia Freitag