DESIGNING NOVEL HOST MATERIALS FOR BLUE PHOSPHORESCENT ORGANIC LIGHT-EMITTING DIODES

DISSERTATION

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Summary

The overall efficiency of an organic light-emitting diode (OLED) is always limited to the efficiency of its individual components. The most important component is the emission layer, where excitons are formed and light is generated. This thesis deals with the improvement of one class of OLED component, namely host materials for blue phosphorescent emitters. Three generations of 1,3,5-triazine-based materials with varying donor-substituents are presented in this work. In the first generation carbazole units are bound to the triazine core. The second generation consists of triazines with diarylamino substituents. The third generation compounds are a combination of disubtituted triazines from the first two generations and a phenoxy-carbazole unit. While the first and second generation comprise substituents that are directly bound to the triazine core, in the third generation triazines the phenylcarbazole-donor is attached via a nonconjugated ether bond. Within each generation various properties are tailored to fulfill the complex profile of requirements for host materials.

Known nucleophilic substitution reactions were further improved to enable the efficient synthesis of novel host materials in very high purity and high yields. The sequential replacement of the chlorines of cyanuric chloride is dependent on temperature, actual ring substitution and the nature of the nucleophile. Effective methods were developed to yield asymmetrically substituted triazines in a controlled manner.

The thermal properties, including the thermal stability to enable the processing by vapor deposition and the glass forming properties to result in a morphological stability of prepared thin emission layers, were controlled by systematic investigation of different substitution patterns. Thus, glass transition temperatures up to 170 °C are presented. Studies of the long term stability of amorphous host films, carried out for several materials, revealed its importance for long term efficient devices.

The electrochemical properties of the novel compounds were investigated by cyclic voltammetry to study the energetic position of the HOMO and the LUMO as well as the stability of the material upon oxidation and reduction. Using this method the injection properties of the materials were determined. The blocking of activated positions resulted in reversible redox behavior. Furthermore the ionization potential was decreased for the third generation triazines to yield an improved hole injection into these materials. Additionally computational calculations were carried out to understand and further improve the energy levels by substituent exchange. This led directly to the development of bipolar host materials with separated hole and electron transport units within one molecule. Furthermore single carrier devices were fabricated to demonstrate the benefits of the transport bipolar characteristics.

For the efficient operation of a device the triplet energy of the host material has to be higher compared to the emitter. First generation triazines exhibit triplet energies up to 2.96 eV and therefore enable the use of light and middle blue phosphorescent emitters. Second generation triazines comprise exceptionally high triplet energies up to 3.24 eV. These are amongst the highest values reported in the literature and facilitate the use of deep blue phosphorescent emitters. For hosts of the third generation the triplet energy depends on the choice of the triazine moiety. They are therefore suited for light and deep blue emitter. Extensive photo physical characterizations of all materials have been carried out in solutions, neat films and doped films. Energy transfer experiments with several emitters additionally gained valuable information about the compatibility of host and guest molecules

All generations of triazines are tested as host material in OLEDs. The optimization of the device configurations was carried out by combinatorial evaporation. The sequential adaption of layer thickness and composition helped to improve the device performance. The stepwise optimization of the host material properties resulted in an enduring progression concerning the luminance and efficiency. For the third generation triazines 11.5 % external quantum efficiency and a high brightness of 33000 cd/m^2 were achieved.

Zusammenfassung

Die Gesamteffizienz einer organischen Leuchtdiode (OLED) wird durch die Effizienzen ihrer Einzelkomponenten, aus denen sie aufgebaut ist, bestimmt. Der wichtigste Bestandteil ist die Emitterschicht, in der Exzitonen gebildet werden und Licht erzeugt wird. Diese Dissertation beschäftigt sich mit der Optimierung einer Klasse an OLED Materialien, genauer den Matrixmaterialien für blaue Phosphoreszenzemitter. In dieser Arbeit werden drei Generationen von 1,3,5-Triazinen mit verschiedenen Donorsubstituenten vorgestellt. In der ersten Generation sind Carbazoleinheiten direkt an den Triazinkern geknüpft und bei der zweiten Generation wurden diese durch Diarylaminogruppen ersetzt. Die dritte Generation ist eine Kombination aus den disubstituierten Triazinen der ersten beiden Generationen und einer Phenoxycarbazoleinheit. Während in den ersten beiden Generationen die Donorsubstituenten direkt an den Kern gebunden sind, so ist in der dritten Generation der Phenoxycarbazoldonor nicht konjugiert über eine Etherbrücke angebunden. Innerhalb einer jeden Generation werden verschiedene Eigenschaften maßgeschneidert um dem komplexen Anforderungsprofil der Matrixmaterialien gerecht zu werden.

Hierzu wurden bekannte nukleophile Substitutionen weiter verbessert, um Matrixmaterialien effizient, hochrein und in guten Ausbeuten herzustellen. Das schrittweise Ersetzen von Chlorsubstituenten des Cyanursäurechlorides ist abhängig von der Reaktionstemperatur, des Substitutionsmusters am Ring und der Natur des Nukleophils. In dieser Arbeit wurden effektive Methoden entwickelt, um asymmetrisch-substituierte Triazine in kontrollierter Weise zu erhalten.

Die thermischen Eigenschaften, welche die thermische Stabilität und die Glasbildungseigenschaften beinhalten, wurden durch systematisches Untersuchen von verschiedenen Substitutionsmustern kontrolliert. Eine hohe thermische Stabilität ermöglicht das physikalische Aufdampfen der Materialien. Gute Glasbildungseigenschaften führen zu morphologisch stabilen Emissionsschichten. Hierzu werden Verbindungen mit hohen

Glasübergangstemperaturen von bis zu 170°C vorgestellt. Untersuchungen zur Langzeitstabilität von amorphen Matrixmaterialfilmen, die für verschiedene Materialien durchgeführt wurden, demonstrieren die Bedeutung für eine hohe Lebensdauer und Effizienz der Bauteile.

Die elektrochemischen Eigenschaften der neuen Verbindungen wurden hinsichtlich der Lage der HOMO und LUMO Energieniveaus sowie der Stabilität der Materialien gegen Oxidation und Reduktion untersucht. Weiterhin wurden mit dieser Methode die Injektionseigenschaften gegenüber den Ladungsträgern bestimmt. Das Blockieren von reaktiven Positionen am Molekül resultierte reversiblem Redoxverhalten. Zusätzlich wurden Computerberechnungen durchgeführt um die Lage oder Verschiebung der Energieniveaus zu verstehen und durch Substituentenaustausch weiter zu verbessern. Das führte zur Entwicklung von bipolaren Matrixmaterialien, bei denen innerhalb eines Moleküls separate Einheiten für den Loch- und Elektronentransport vorhanden sind. Es wurden ‚Single-Carrier-Devices‘ hergestellt um die Vorteile der beschriebenen bipolaren Transportcharakteristik der Materialien aufzuzeigen.

Für einen effizienten Betrieb der OLED zu gewährleisten muss weiterhin das Tripletniveau des Matrixmaterials höher sein als das Tripletniveau des Emitters. Die Triazine der ersten Generation zeigen Triplettenergien von bis zu 2.96 eV und sind deshalb für leicht- und mittelblaue Emitter geeignet. Die Triplettniveaus der zweiten Triazingeneration sind mit bis zu 3.24 eV außerordenlich hoch. Das sind Werte, die sich unter den höchsten jemals in der Literatur vorgestellten Triplettenergien befinden. Bei den Verbindungen der dritten Generation hängt die Lage des Tripletniveau von der Wahl der Triazineinheit ab. Sie sind deshalb sowohl für leicht- als auch für tiefblaue Emitter geeignet. An den Materialien wurden intensive photophysikalische Untersuchungen sowohl in Lösungs als auch als auch an reinen und dotierten Filmen durchgeführt. In Energietransferexperimenten dotierter Schichten konnten wertvolle Informationen bezüglich Effizienz und Verträglichkeit der Matrix-Emitter Kombinationen gewonnen werden.

Vertreter aus allen Triazingenerationen wurden als Matrixmaterialien in OLEDs getestet. Die Optimierung der Bauteile erfolgte durch kombinatorische Aufdampfexperimente, wobei sowohl die Schichtdickenabhängigkeit als auch der Dotiergrad variiert wurde. Durch die generationsweise Optimierung der Matrixmaterialien konnten die Leuchtdichten und die Effizienzen der OLEDs stetig verbessert werden. In der dritten Generation wurden eine externe Quantenausbeute von 11.5% und eine maximale Leuchtdichte von 33000 cd/m^2 erreicht.

2 Introduction

Since C. W. Tang and S. A. van Slyke reported the first multilayer organic light-emitting diodes (OLEDs) in 1987, research groups around the world made tremendous progress in the understanding and manufacture of those devices.[1] Nowadays several companies fabricate full color OLED displays. The market for these flat-screen displays is worth billions of Euros per year. But there is another upcoming lucrative market for organic LEDs in white lighting applications. A recent study showed that about 20 % of the total primary energy is consumed by lighting.[2] This enormous amount of energy mainly originates from the use of inefficient light sources like incandescent lamps, which turn about 95 % of the energy into heat. Considering the concerns about global warming, Germany as well as many other states legislated for a general ban on inefficient light sources.[3] Well-established replacements like halogen lamps and compact fluorescent lights are equally inefficient or slightly better and generate about 20 lm/W or 60 lm/W, respectively. Only inorganic LEDs enable efficiencies beyond 120 lm/W but since they are spotlights they are not well suited as general lighting source. In the past years it has been shown with great effort that OLEDs are on the best way to become a serious competitor in the lighting market. In early 2009, the lighting companies OSRAM and PHILIPS commercialized first OLED panels whereon designers presented prototypes of desk lamps and visions of transparent luminescent windows (Figure 1).

Figure 1: (left to right) OSRAM white light OLED panel; Prototype desk lamp by I. Maurer; Vision of transparent OLED windows; (source: http://www.osram.de). This visionary study impressively illustrates one major advantage of OLEDs: the possibility of a large-area source of diffuse light.

Not only in industrial development departments but also in academic research various strategies have been developed to improve known OLED devices. Very recently K. Leo and co-workers reported a white organic light-emitting diode with fluorescent tube efficiency of 90 lm/W.[4] This step towards highly efficient lighting was only possible due to the discovery of efficient phosphorescent emitters by Forrest and Thompson in 1998.[5] From spin statistics it is known that the ratio of singlet and triplet excitons is 1:3 in small organic molecules.[6] Thus taking all loss pathways into account the maximum external quantum efficiency (EQE) of a fluorescent OLED is limited to 5 %.[7] In contrast to that an OLED that harvests singlet and triplet excitons can theoretically reach an EQE of about 20 %. For a single-color emitting system this goal was reached surprisingly early. In 2001 Forrest and co-workers presented a green OLED with 19 % EQE.[7] In the last decade several reports of 20% EQE or even slightly more emerged in scientific literature. Nowadays also red and blue OLEDs with high EQEs are well described.[8,9] However the EQE is not the only important measure for OLEDs. Especially for lighting applications the power efficiency is considered to be more important. That means additional device optimizations concerning charge carrier injection and transport have to be taken into account. In consideration of competing with modern and future lighting tubes power efficiencies above 100 lm/W are desirable. OLED lighting projects funded by the U.S. Department of Energy are intended to achieve 150 lm/W until 2015.[10]

In order to generate white light several possibilities are discussed. The most popular involves a red-green-blue (RGB) color-mixing system, where the single colors are either organized horizontally or vertically. In the horizontal approach the output spectrum can be adjusted during the operation due to the separation of the colors. This is a major advantage over the vertical stack, where the output-color is fixed once the device is fabricated. However the horizontal stack design is complicated and therefore expensive in fabrication.[11] This limits its application. The vertical approach on the other hand is ideal for a cheap large area processing. The disadvantage of this design is related to the different aging of the three sub-colors. This may result in a color shift during the lifetime of the device. Generally speaking, the lifetime of OLED materials is still a major goal toward the commercial success of the devices. Especially the blue emitting systems tend to degrade faster than other components.[12] This fact emphasizes the importance of the further improvement of existing blue emitting systems or the development of novel ones. In Figure 2 a newly published white OLED stack by K. Leo and co-workers is compared to the first published multi-layer OLED by C. W. Tang and S. A. van Slyke. This shows the increasing complexity in this field.

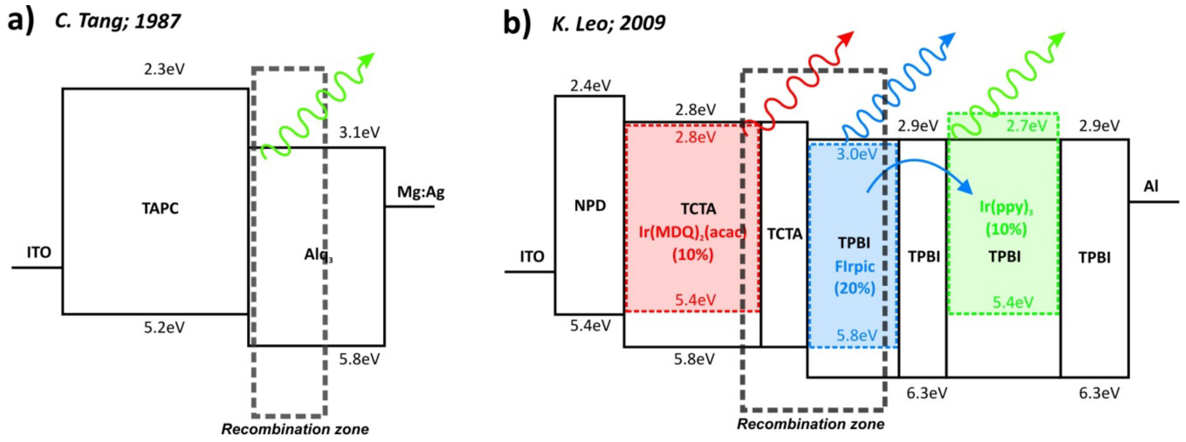

Figure 2: Energy diagram of: **a)** first published multi-layer OLED by C. Tang consisting of a hole conducting layer of TAPC, an electron conducting layer of Alq_3; **b)** state-of-the-art multi-layer white OLED stack by K. Leo and co-workers consisting of a hole and electron conducting layer as well as a complex emission layer comprising three phosphorescence emitting host guest systems (explanation of abbreviations in the respective chapter).

The Tang-device consisted of 2 layers, where TAPC acts as hole conductor and Alq_3 serves as electron conductor and emitter. This is mainly because the injection barrier for electrons from Alq_3 to TAPC is very high (0.8 eV) and therefore all excitons are generated in the Alq_3 layer. In vast contrast to that the Leo-device is a 7-layer stack involving 3 doped emission layers which are separated by thin organic layers. The charge carrier balance is extremely important in this setup to yield pure white emission. Excitons have to be generated in a narrow recombination zone and the separating layers must only permit a exciton transfer from blue to green. This illustrates the complexity of this highly optimized OLED stack. The replacement of one material would result in a complete re-design of the whole stack to guarantee efficient white emission.

OLED setup and working principle

In general there are two predominant methods to fabricate OLEDs. The organic material is either deposited from the gas phase or from solution. The vapor deposition technique is limited to small organic molecules, which can be thermally evaporated in high vacuum. Processing from solution on the other hand is also possible with high molecular weight polymers. However it is very challenging to fabricate a multi-layer organic device from solution.[13] For this purpose vapor deposition methods are very powerful. Therefore almost all state-of-the-art OLEDs are deposited from the gas phase.

The simplest setup of an organic light emitting diode is composed of an organic emissive layer, which is sandwiched between two electrodes. The first device of this kind was published by R. Friend and co-workers in 1990.[14] The device consisted of a 70 nm thick poly(p-phenylene vinylene) (PPV) layer, an indium-tin oxide bottom contact and a top contact of aluminum (Figure 3a). Although this simple OLED exhibits a poor performance regarding brightness and efficiency it exemplifies its working principle.

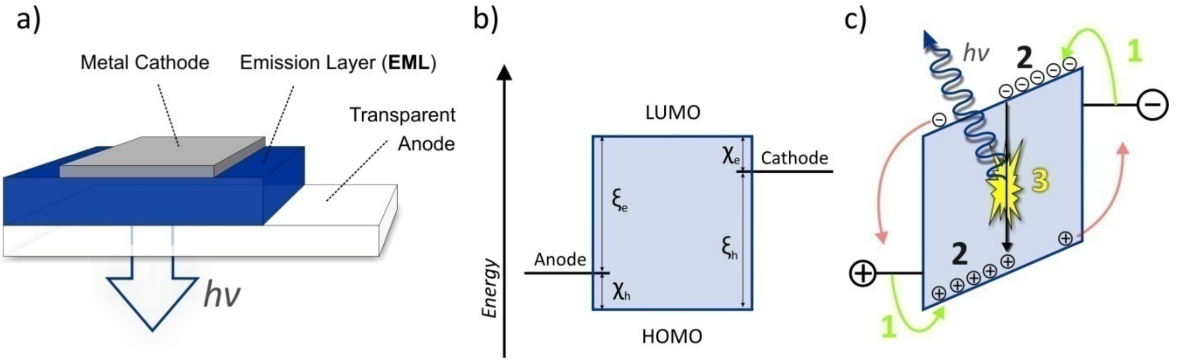

Figure 3: a) Schematic of a single-layer OLED consisting of transparent anode, emission layer (EML) and metal cathode; **b)** energy diagram of a single-layer OLED: χ_h: hole injection barrier from the anode to the HOMO of the EML; χ_e: electron injection barrier from the cathode to the LUMO of the EML; ξ_h and ξ_e: injection barriers for hole and electron from the respective counter electrode in reverse-biasing mode; **c)** energy diagram of a single-layer OLED upon applying an electric field; including three essential OLED processes: 1) injection 2) transport and 3) recombination of holes (⊕) and electrons (Θ), exciton diffusion and emission.

In Figure 3b) the energy diagram of a single layer OLED is illustrated. The injection barriers in conduction direction, χ_e for electrons and χ_h for holes, symbolize the potential difference from the Fermi level of the electrode to the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) of the organic material respectively. In reverse direction these barriers are symbolized by ξ_e and ξ_h. The ratio of χ to ξ is a measure for the injection balance of the diode.[15] Although the HOMO and LUMO levels are shown as line in the schematic they can be considered as a narrow Gaussian-like distribution of states.[16] Figure 3c shows the energy diagram of a single-layer OLED upon applying an electric field. The illustration includes three essential processes in an operating device, which are: the injection of charge carriers (1), the transport of hole (⊕) and electron (Θ) (2) and the formation of an exciton, exciton diffusion and its emissive decay (3).

Charge carrier injection (1)

The injection of a hole or an electron into an organic material means its oxidation or reduction respectively. As shown in Figure 3b), there are certain injection barriers χ_h and χ_e for these processes. For an efficient injection of holes and electrons they have to be as low as possible. Ideally the surface contacts are ohmic, which requires energy barriers below 0.3 eV.[17] Regarding this case the operation of the OLED is space-charge limited and no longer injection limited.[18] Additionally the injection barriers for holes and electrons should be equal to guarantee charge carrier balance in the emission layer. The injection process can be understood as a hopping process of a charge carrier from the Fermi level of the metal into tail states of the organic material.[19,20] The most common anode material for OLEDs is indium-tin oxide (ITO), which is sputtered onto a glass substrate. It is transparent and exhibits a low resistivity. The Fermi energy of ITO strongly depends on the pretreatment of the material and varies from 4.2 eV to 4.8 eV.[21] Therefore an ohmic contact is possible if the HOMO of the organic is below 5.1 eV. To avoid too strong limitations in material choice, the use of polymeric injection layers is widespread. Especially poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) (PEDOT:PSS) is well described in literature and enables ohmic injection into materials with HOMO energies up to 5.8 eV.[22] The variety of cathode metals is larger than for anode materials. Very favorable is a relatively low work function of the metal, like that of the alkaline earth metals barium (Φ = 2.7 eV), calcium (Φ = 2.9 eV) or magnesium (Φ = 3.5 eV). The vast disadvantage of these metals is their reactivity. Therefore they are often capped with aluminum (Φ = 4.0 eV) or silver (Φ = 4.3 eV). Because the injection barrier of most aluminum/organic interfaces is too large for ohmic behavior, the injection properties can be increased by the introduction of a thin lithium fluoride interlayer.[23] The LiF/Al cathode allows good electron injection into most organic electron conductors.

Charge carrier transport (2)

Once holes and electrons are injected into an organic layer they will propagate to the cathode and the anode respectively, due to the external electric field. This propagation can be understood as a series of redox processes. Considering the hole transport, an oxidized molecule acts as electron acceptor for a neutral neighboring molecule which acts as electron donor. Thus, on molecular level, a hole is a radical cation while an electron is a radical anion. This means, an electron is either transferred from the LUMO to the LUMO (electron transfer) or from the HOMO to the HOMO (hole transport) of two neighboring molecules. The transfer itself is interpreted as hopping.[24] The propagation speed of the charge carriers thereby is limited by the intrinsic mobility of the material. Additionally, it is influenced by the existence of trap states within the layer. These traps are energetically more favorable sites, which result from impurities, dopants and/or defects.[16] Therefore the mobility is high in perfect organic crystals and low in amorphous materials.

Charge carrier recombination, exciton diffusion and emission (3)

In order to emit light, a hole and an electron must recombine and form an exciton. The recombination can be regarded as a reaction between hole and electron, which is driven by the Coulomb interaction. At this point it is important to know that depending on the spin of the electrons, either singlet or triplet excitons are formed. There are 4 possible spin configurations, which can result from the recombination of 2 electrons with undefined spin (Figure 4).

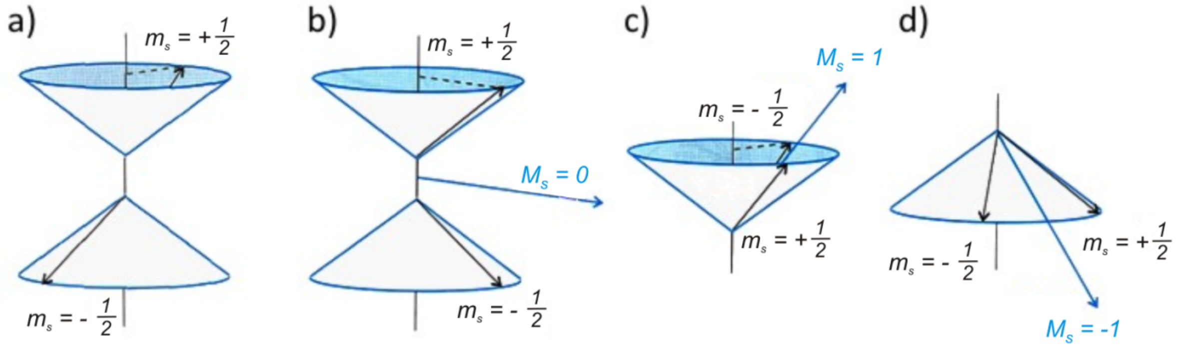

Figure 4: Possible spin configurations for the recombination of two electrons with anti-parallel spin (a) or parallel spin (b-d). While a) represents the singlet state, b)-d) are three possible triplet configurations.

If the spins (m_S) of two electrons are anti-parallel to each other, the total angular momentum (M_S) of the system is 0. This equates to a singlet exciton (Figure 4a). If the two spins are parallel the total angular momentum of the system can be +1, 0 and -1. Although the total angular momentum of configuration a) and b) are both 0, they represent different states. Since, in an OLED all injected electrons exhibit random spin all 4 configurations are possible. Thus the ratio of singlet to triplet excitons is 1 to 3. Once the exciton is formed, it can either undergo radiative decay or diffuse within the organic material. The typical lifetime of singlet or triplet exciton is in the range of nanoseconds or microseconds rerspectively. This can be translated into a typical diffusion length of about 10 nanometers. The diffusive energy transfer can be subdivided into two non-radiative mechanisms, the so-called Förster and Dexter transfer types, depending on the different intermolecular interaction. The Förster mechanism is a dipolar transfer between an excited donor molecule and a non-excited acceptor. Therefore the existence of a spectral overlap between donor-emission and acceptor-absorption is essential. Depending on the transfer efficiency the energy can be transferred over a distance of several nanometers. In contrast to that Dexter energy transfer is an electron transfer mechanism and therefore has a short range. Since the electrons are transferred by hopping an orbital overlap of donor and acceptor molecules is essential. The spin symmetry is persevered in this case, which means that both singlet and triplet excitons can be transferred. On the other side, a triplet-triplet exchange by Förster transfer in not possible. It is limited to singlet-singlet transfer in general and triplet-singlet transfer in individual cases.[25]