Kurzzusammenfassung

In den letzten Jahren haben sich Organische Leuchtdioden (OLED) zu einer der vielversprechendsten Beleuchtungstechnologien entwickelt. Sie bestechen nicht nur durch ihre Effizienz und ihr Energieeinsparpotenzial, sondern vor allem durch die Tatsache, dass transparente und flexible Displays realisiert werden können. Die Optimierung von Flüssigprozessierungsverfahren ist hierzu aktuell eine der dominantesten prozesstechnischen Hürden für die Herstellung von großflächigen OLED Displays. Der vielversprechendste Ansatz für effiziente Lichterzeugung in OLEDs ist das Prinzip der *thermally activated delayed fluorescence* (TADF).

In dieser Arbeit wurden neue TADF Materialien für flüssigprozesierbare OLEDs untersucht. Bestehende TADF-Emitterstrukturen auf Basis des Isophthalnitril-Akzeptors wurden chemisch modifiziert und der Einfluss auf die optoelektronischen Eigenschaften studiert, um ein besseres Verständnis der Struktur-Eigenschaftsbeziehungen zu gewinnen. Abhängig von den Modifizierungen konnte die Emissionsfarbe zwischen 438 nm und 541 nm variiert werden. Die vielversprechendsten Emitter wurden in OLEDs getestet und zeigten eine maximale *external quantum efficiency* (EQE) von bis zu 16 %. Der modulare Ansatz ermöglichte die Einführung einer Vielzahl an funktionellen Gruppen und Strukturelementen. Anküpfstellen wurden geschaffen, um die TADF-Emitter an weitere Funktionalitäten wie Biotransporter zu binden. So diente die Kombination eines TADF-Emitters mit einem Biotransporter oder monodispersen Stäbchenoligomeren zur Untersuchung von Fluoreszenzbildgebung und von photophysikalischen Phänomenen wie Ladungsträgertransport.

In einem weiteren Ansatz wurden Phthalimid-basierte TADF-Emitter gezielt an Akzeptor und Donoreinheiten modifiziert und der Einfluss auf die optoelektronischen Eigenschaften und die Löslichkeit im Hinblick auf Flüssigprozessierbarkeit untersucht. Die Emissionswellenlänge konnte inkrementell in bis zu 2 nm Schritten zwischen 437 nm und 522 nm eingestellt werden.

Zuletzt wurde der Tris[1,2,4]triazolo[1,3,5]triazin Kern (TTT) als neue Akzeptorgruppe für TADF-Emitter erfolgreich evaluiert. Dazu wurde eine Synthese entwickelt, die den TTT-Kern mit peripheren Donoreinheiten dekoriert. Die Anzahl und Sträke der Donorgruppen beeinflusst maßgeblich die Emissionsfarbe (398–466 nm), während der Diederwinkel entscheidend für den TADF Charakter dieser Systeme ist. Die ersten himmelblauen OLEDs zeigen eine maximale EQE von 5.8 % und 11 %.

Abstract

Organic light-emitting diodes (OLEDs) are one of the most promising lighting technologies of the recent years not only due to their efficiency and energy saving capabilities, but also for their unique features in the realization of transparent and flexible display solutions. The commercial realization of large-area OLED panels is still limited by the dominant and cost-intensive vacuum processing techniques and challenges in solution processed device fabrication. Thermally activated delayed fluorescence (TADF) is considered as the most promising mechanism for electroluminescence for OLED application as this allows a complete conversion of excitons to photons.

In this thesis, the development of TADF materials for solution processed OLED devices was investigated. Existing isophthalonitrile-based TADF emitters were chemically modified in order to study the structure-to-property relationships with regards to the optoelectronic behavior. Based on the chemical modifications to the parent emitter, the emission color was varied in the range of 438 nm to 541 nm. Most promising emitters were employed in OLED devices, resulting in external quantum efficiencies (EQE) of up to 16%. A modular approach allowed the introduction of various functional groups and structural motives. Binding sites on TADF emitters were created in order to permit conjugation to other molecules or biotransporters. Combined systems of TADF emitter and biotransporter or rod-like monodisperse oligomers were used for fluorescence imaging or for the investigation of photophysical phenomena such as exciton transport and charge separation.

Phthalimide-based TADF emitters were thoroughly investigated with derivatization on the acceptor and donor groups to adjust optoelectronic properties and solubility for solution processing. For the emission color, a range of 437 nm to 522 nm was covered with typically small increments of 2 nm.

Lastly, the tris[1,2,4]triazolo[1,3,5]triazine (TTT) core was successfully implemented as novel acceptor group for TADF emitters. Hence, a synthesis for the TTT core with peripheral donor groups was developed. The concept was successfully extended to related systems yielding mono-triazolo triazines and bis-triazolo triazines. The donor strength and count were identified as key drivers for the emission color (398–466 nm) and the dihedral angle as critical measure for TADF characteristics. The initial sky-blue OLED devices showed maximum EQEs of 5.8% and 11%, respectively.

1   Introduction

"Light is a unifying symbol that signifies wisdom and excites the imagination across the world. Paintings and murals in all cultures show how artists have used light, shade and colour to illustrate mood and create atmosphere. Light is used in some therapies to promote health, and in religious ceremonies as aid to worship and reflection. On the most fundamental level through photosynthesis, light is necessary to the existence of life itself. Light science has revolutionized medicine, agriculture and energy, and optical technologies are part of the basic infrastructure of modern communications. For these reasons and more, light sciences are a cross-cutting discipline in the 21st century. As we strive to end poverty and promote shared prosperity, light technologies can offer practical solutions to global challenges. They will be particularly important in advancing progress towards the Millennium Development Goals, achieving the future sustainable development goals and addressing climate change. […] This will mean more light in homes, hospitals and enterprises – and that will translate into a safer, healthier and more productive future." This is how Ban Ki-moon who served as the eighth Secretary-General of the United Nations, illustrated the importance of this research field at the opening ceremony of the International Year of Light and Light-based Technologies 2015.[1,2]

The sun as the most natural source of energy served nature and humanity since their dawn and brought them warmth and light. Fearing darkness and needing a heat source, the human race tamed one of nature's most destructive elements, fire.[3] Uncompeted for millennia, fire and all of its derived lighting sources like torches, oil lamps or candles, were substituted with the development of the incandescent light bulb by Thomas Alva Edison based on the observations of Louis Jacques de Thénard who found that current-carrying metal wires emit light and heat.[4,5] As most of the energy is lost as unwanted heat, the efficiency of the incandescent light bulb is merely 5%. Given this major drawback, the use of these in Europe is prohibited since 2009. However, the following generation of halogen bulbs with an energy saving of up to 30% also found their end with the production ban since 2018. The compact fluorescent lamp was believed to be a promising successor, however, the necessity of mercury as well as the relatively long time until maximum luminance renders them as an interim solution at most.[6] All of the light sources discussed so far generate light through detours, either by harvesting solely a small share of the

injected energy via glowing metal wires with typical emission maxima in the infrared region (1000 nm) in incandescent light bulbs or by converting the initially created UV light into visible light as in compact fluorescent lamps. The development of light-emitting diodes through the utilization of an exciton generated in organic or inorganic semi-conductors by applying an electrical current is the first technique which allows the direct conversion of electrical energy to light.[5,7]

Despite the rapid development of increasingly efficient lighting techniques, approximately 15% of the global power consumption is still accounted to the electricity used for lighting, which then accounts for roughly 5% of the global greenhouse gas emission.[8] Despite introducing recent technologies in more developed countries such as the United States of America, the total electricity consumed for lighting in the U.S. still amounts to 6%.[9] In the same manner as the energy savings through novel lighting technologies rose, the general light output drastically increased as well, as illustrated in Figure 1 for central Europe. As the production costs for light sources decreased at the same time, illumination of previously unlit areas is increasingly available for more safety, convenience or comfort.[10,11] Apart from the need of solutions for more targeted alignment of lighting to avoid light pollution, the growing demand for lighting sources has still to be tackled by satisfyingly energy efficient technologies as Ban Ki-moon stated.
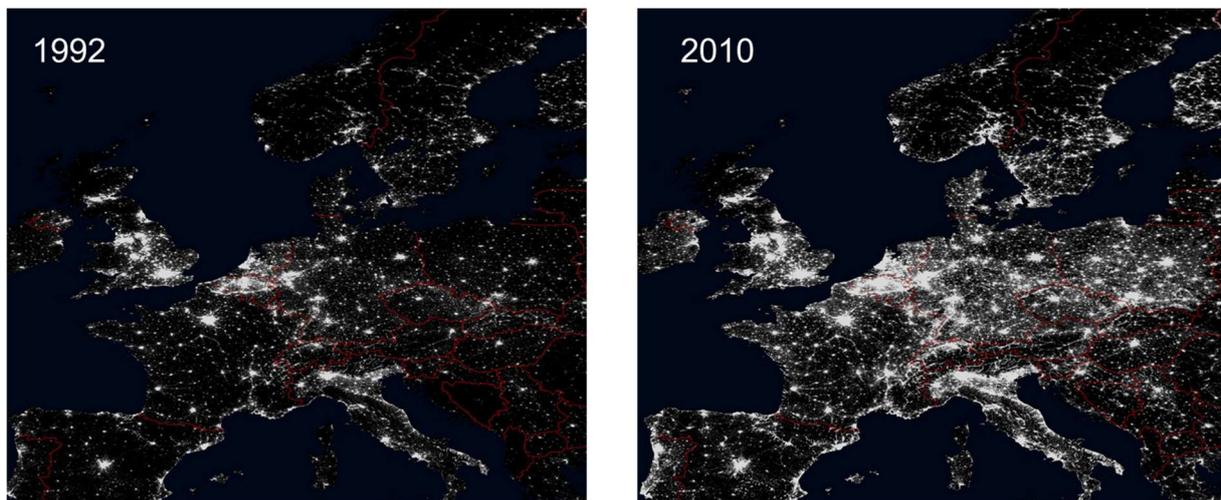

Figure 1. Nocturnal shot of central Europe from a satellite of the Defense Meteorological Satellite Program in 1992 (left) and in 2010 (right). Bright spots are caused by actual light emission on the ground. National borders were added afterwards for orientation purposes with red lines. Copyright: NGDC/DMSP/ESA.[10]

One of the most promising lighting technologies both for energy saving purposes as well as for innovative applications are organic light-emitting diodes (OLEDs). In contrast to the inorganic LED, where crystalline semiconductors are used as light source, the OLED is based on organic semiconducting emitters which can be processed in a thin film. The absence of crystalline materials allows solution-based processing techniques like inkjet printing,[12] spin-coating or photo-crosslinking[13] which are not only cost-efficient but also easily adoptable to a larger scale enabling the fabrication of large-area lighting solutions.[14] Already applied in commercial display solutions for smartphones or TV screens, OLEDs bring along another innovative solution: the realization of transparent[15] or flexible displays (Figure 2).[16] Besides these unique features, OLED displays are still impressive as they show high contrast, luminance and the realization of a true black. Hence, OLEDs fulfill modern demands for display solutions and also find application in the automotive industry as taillights[17,18] or by replacing the side-view mirror by a small camera and an indoor OLED display (Figure 2).[19]

Figure 2. OLED applications: replacement of the side-view mirror by an OLED display (left, copyright: Audi AG),[19] transparent display (center, copyright: LG Display),[15] flexible display (right, copyright: Samsung).[16]

1.1   Organic Light-Emitting Diodes (OLEDs)

The key phenomenon exploited in an OLED is the electroluminescence, which was first observed by Henry Joseph Round in 1907 when he witnessed light emission from silicium carbide upon the application of an electric current with a voltage of 10 V.[20] Later in 1955, this phenomenon was investigated by Bernanose *et al.* who measured phosphorescent dyes in a polymer matrix in dielectric cells,[21] while Pope and co-workers investigated the basic mechanisms on anthracene crystals in 1963.[22,23] Then, 24 years later, Tang and van Slyke   reported   the   first   OLED   device   based   on   the   fluorescent   tris(8-

hydroxyquinolinato)aluminum, which emitted green light at 550 nm with a brightness of 1000 cd m^{-2} at an external quantum efficiency of 1%.[24] Then, Heeger and co-workers' pioneering work on semiconducting and metal-like polymers was honored with the Nobel Prize in Chemistry in 2000, which paved the way for the commercial application of OLEDs.[25]

1.1.1   Working Principle and Architecture of OLEDs

The basic working principle of a simplified OLED, solely consisting of an organic emissive layer sandwiched between two electrodes is shown in Figure 3.[26,27] The work functions of the electrodes should be matched in such a fashion that the highest occupied molecular orbital (HOMO) is slightly lower in energy to the work function of the anode, while the lowest unoccupied molecular orbital (LUMO) needs to be slightly higher in energy to the work function of the cathode. This allows the injection of charge carriers into the organic material. Upon applying an external voltage to the electrodes, electrons are injected into the LUMO of the organic material at the interface from the cathode, while holes are generated by extracting electrons from the HOMO of the organic material at the interface of the anode. Next, the charges migrate towards the electrodes of the opposite polarity due to the external electric field. This is believed to follow a hopping mechanism accounted to the distinct molecular orbitals.[28] As the conductivity is critical for the efficiency, π-stacking,[29] as well as conjugated π-systems were found to increase these processes.[30] When two opposite charge carriers approach each other closer than the Coulomb radius, they recombine to form an exciton located at an organic molecule. An exciton on a molecule, also described as excited state, can relax via different pathways. The emission of a photon by relaxation to the ground state is called electroluminescence.
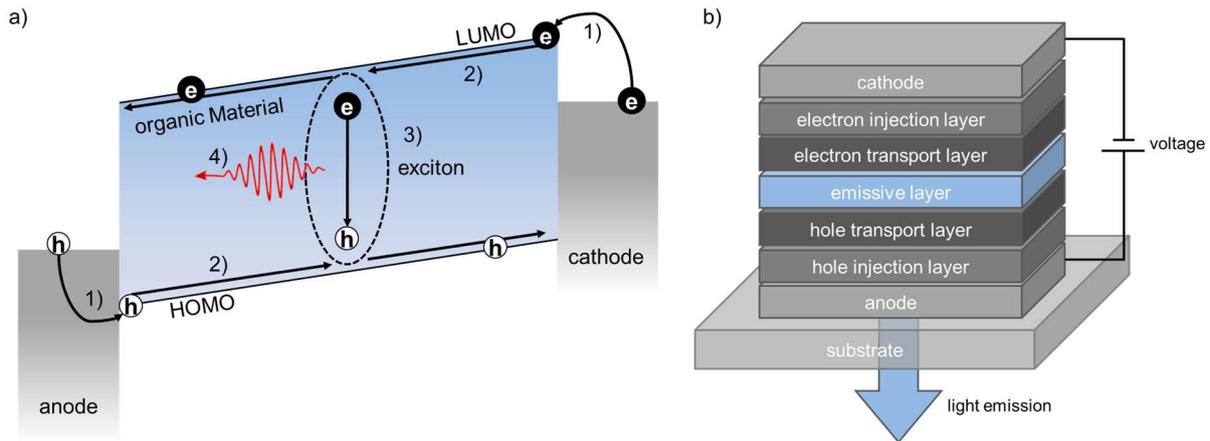
Figure 3. a) Simplified scheme of a single-layer OLED with the following elementary steps: 1) injection of charge carriers, 2) transport of charge carriers, 3) recombination of charge carriers, exciton generation, 4) light emission. b) Simplified OLED stack architecture. Figures recreated in accordance with literature.[31,32]

As the transport rate of charge carriers is different for holes and electrons, with the transport of holes known to be faster in organic semiconductors,[33] a multilayer device architecture with optimized layer thicknesses was found to be more efficient for OLEDs (Figure 3) to mitigate these issues. The **substrate** is needed to carry the OLED stack and typically consists of transparent polymers or glass. Like the substrate, the **anode** also must be transparent to allow light out-coupling. Transparent conductive oxides (TCO) like indium tin oxide (ITO, $(In_2O_3)_{0.9}(SnO_2)_{0.1}$) or non-indium-based TCOs are usually applied.[34] The **hole injection layer** (HIL) flattens out the usually rough surface of the anode material and facilitates the charge injection from the anode to the material by aligning the HOMO levels. PEDOT:PSS, a conductive polythiophene mixed with a sulfonic acid derivative is often used for this purpose.[5] As the name already suggests, the **hole transport layer** (HTL), facilitates the charge transport to the emissive layer. It is often built from electron rich heterocycles like triarylamines or carbazole derivatives. Furthermore, it acts as an **electron blocking layer** (EBL) preventing the electrons from entering this side of the stack. The **emissive layer** (EML) often consists of either solely the emitting molecule, or two or even three different materials forming a guest/host system. In this layer, the charges recombine in order to form excited emitter molecules (excitons) which then relax via emission of a photon. Like the HTL, the **electron transport layer** (ETL) simplifies the electron transfer via the LUMO while also preventing positive charge carriers from leaving the emissive layer. Lastly, the **electron injection layer** (EIL) as well as the **cathode** complete the device stack serving contrary tasks as the

HIL and anode. The cathode typically consists of readily available metals like magnesium, aluminum or different alloys.[5,32,35] Upon electrical excitation, the recombination of electron and hole results in the population of 25% excited singlet states and 75% excited triplet states according to the Fermi-Dirac statistics (Scheme 1).
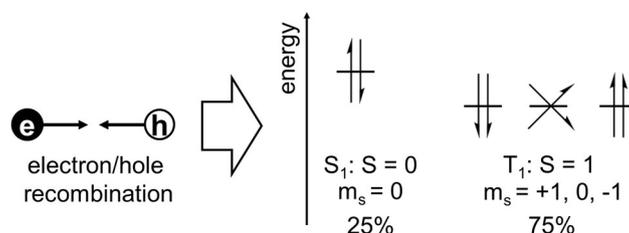
Scheme 1. Population of excited states upon charge carrier recombination.

1.2   Thermally Activated Delayed Fluorescence (TADF)

The relaxation from the excited singlet state S_1 to the ground state S_0 accompanied by the emission of light is called fluorescence (Scheme 2). Furthermore, the continuous population of the excited triplet state T_1 from S_1 via intersystem crossing (ISC) competes with the relaxation via fluorescence. As the excitons in the T_1 state cannot be used for light generation in conventional fluorescent emitters due to the forbidden $T_1 \rightarrow S_1$ transition, the maximum internal quantum efficiency is 25%. Typically, this is even lower as the ISC competes with fluorescence[36] and other non-radiative relaxation pathways.[37] Lastly, the populated triplet states can lead to additional unfavorable processes like triplet-triplet-annihilation (TTA) or radical mechanisms, which decrease the overall device lifetime. The first fluorescent molecule used in an OLED device, tris(8-hydroxyquinolinato)aluminum (Alq$_3$, **1**) is a coordination complex of aluminum with three bidentate 8-hydroxyquinoline ligands (Figure 4) and emitted green light with a maximum of 550 nm in the first OLED device.[24]
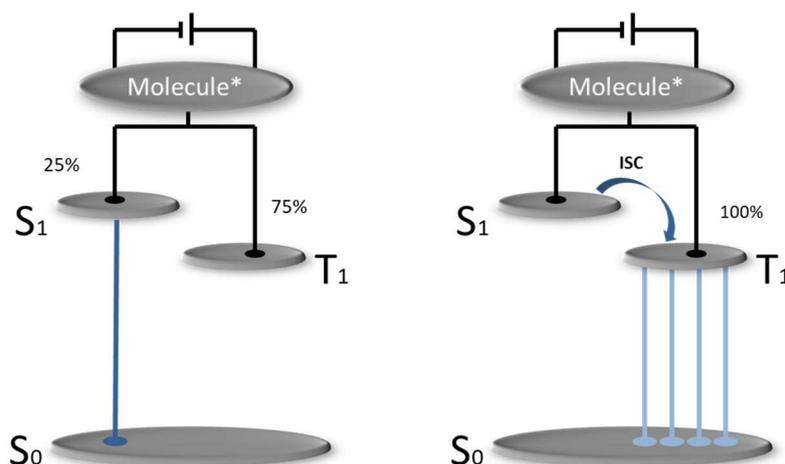
Scheme 2. Simplified Jablonksi diagrams for purely fluorescent emitter (left) and phosphorescent emitter (right). Applying voltage excites a molecule indicated with *. Basic pathways include $S_1 \rightarrow S_0$ (fluorescence), $T_1 \rightarrow S_0$ (phosphorescence) and $S_1 \rightarrow T_1$ (intersystem crossing (ISC)).

The second generation of OLEDs exploits that very triplet excitons by using heavy atom-based complexes to enhance not only the ISC from the excited singlet to the triplet state, but also to facilitate the $T_1 \rightarrow S_0$ transition accompanied by the emission of light (phosphorescence, Scheme 2) by spin-orbit coupling.[38,39] This class of metal complexes that are predominantly based on iridium,[39–42] but also on other heavy atoms like osmium[43,44], platinum[45,46], and ruthenium,[47,48] has found application in commercial electrophosphorescent devices. One of the most prominent phosphorescent dyes called Irppy3 (**2**)[36,39,49] is shown in Figure 4. It is often used as the standard for relative quantum yield measurements.[50] With this class of triplet-harvesting molecules, up to 100% of the generated excitons can be used for light generation. However, the precious metals needed for this emitter class is also considered as its bottleneck as they are cost-intensive, scarce and a limited resource. Lastly, the singlet excitons are converted to the triplet excitons which results in a loss of energy. As a consequence, the $T_1 \rightarrow S_0$ transition is slightly red-shifted in comparison to the $S_1 \rightarrow S_0$ transition.
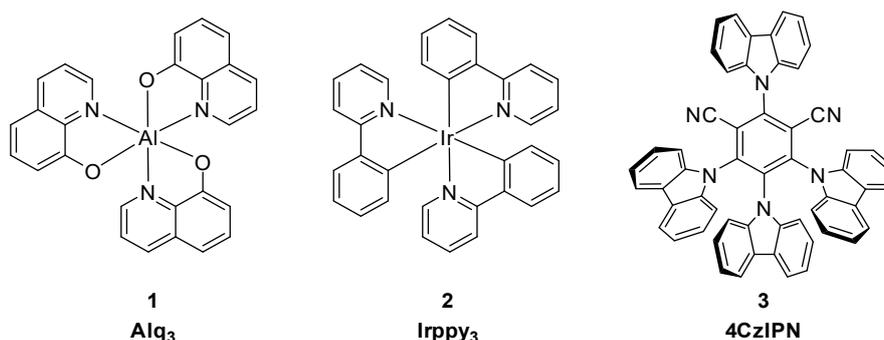
Figure 4. Fluorescent (left), phosphorescent (center), and TADF (right) dyes for OLEDs.

The concept of thermally activated delayed fluorescence (TADF) is considered to be one of the most promising mechanisms for electroluminescent devices. When the energy gap (ΔE_{ST}) between excited singlet S_1 and triplet T_1 state is sufficiently small, and the lifetime of T_1 long enough, the endothermic reverse intersystem crossing (RISC) from the T_1 to the S_1 state allows the harvesting of the triplet excitons via the fluorescent relaxation channel. The subsequent emission via the $S_1 \rightarrow S_0$ relaxation channel shows the same spectral distribution as the prompt fluorescence, but with a significantly longer decay time (Scheme 3). Developing TADF emitters that show these characteristics at ambient temperatures enables the usage of all electrically generated excitons in an OLED through singlet decay. This significantly increases the limit for fluorescent materials for internal efficiency from 25% to 100%.[51–54] Upon an increase in temperature, TADF emitters show a significant decrease of the fluorescence decay time indicating the efficient population of vibronic levels of T_1 followed by RISC (Scheme 3).
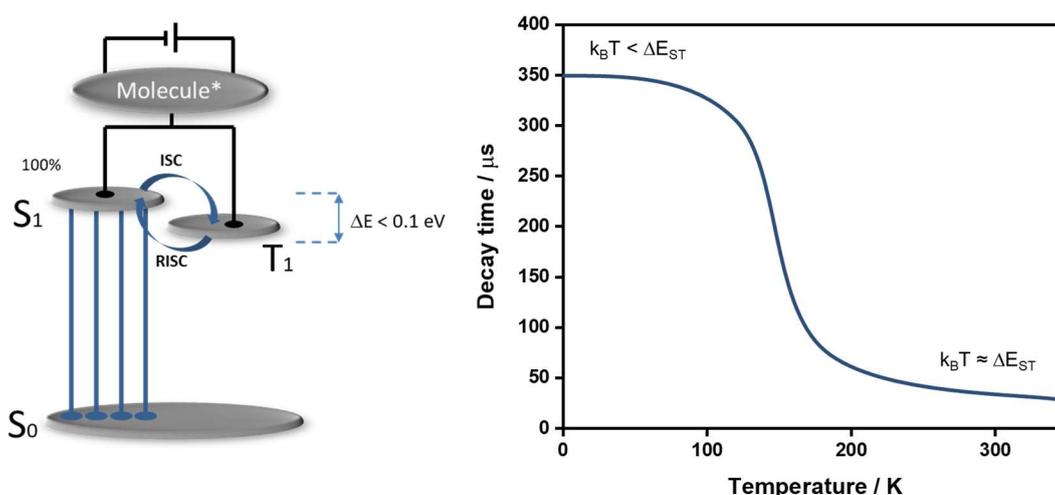
Scheme 3. Left: Simplified Jablonski diagram of a TADF emitter upon electrical excitation. Basic pathways include $S_1 \rightarrow S_0$ (fluorescence), $S_1 \rightarrow T_1$ (intersystem crossing (ISC)) and $T_1 \rightarrow S_1$ (reverse intersystem crossing (RISC)). Right: Temperature dependence of the emission decay time.

1.2.1   Working Principle of TADF

The working principle of TADF is under continuous investigation and has been summarized in numerous articles over the last years.[54–56]

The singlet-triplet energy gap (ΔE_{ST}) is the energy difference between the lowest excited triplet state (T_1) and lowest excited singlet state (S_1) and defines a system showing TADF characteristics. Thermal upconversion from the triplet state, followed by reverse intersystem-crossing (RISC), is possible when ΔE_{ST} is reasonably small (usually <0.1 eV).[51] Besides the prompt fluorescence from the S_1 to the S_0 state, TADF emitters usually show a second type of photoluminescence. The delayed fluorescence results from a triplet state converted to a singlet state via RISC prior to fluorescent emission.[51]

ΔE_{ST} is critical for efficient organic TADF materials as it directly influences the rate of RISC (k_{RISC}) according to the Boltzmann distribution (Equation (1), where k_B is Boltzmann's constant and T is the temperature).[37]

$$k_{\mathrm{RISC}} \propto \exp\left(-\frac{\Delta E_{ST}}{k_B T}\right) \tag{1}$$

As seen in Equation (1), a large ΔE_{ST} results in a slow k_{RISC} which then results in a longer delayed fluorescence lifetime (τ_d) and also decreases the rate of delayed fluorescence (k_{DF} = 1 / τ_d).[57,58] The delayed fluorescence lifetime is further expressed in Equation (2)[59] which shows a decreasing τ_d upon an increasing rate of ISC (k_{ISC})[60] or RISC (k_{RISC}),[58,61] where the radiative and nonradiative decay rate constants of the singlet state are expressed by k_r^S and k_{nr}^S.

$$\frac{1}{\tau_d} = k_{nr}^{T} + \left(1 - \frac{k_{ISC}}{k_r^S + k_{nr}^S + k_{ISC}}\right) k_{\mathrm{RISC}} \tag{2}$$

More importantly, the energy gap between the excited singlet (S_1) and triplet state (T_1) is dependent on the structure of the emitter and on the resulting exchange integral (J) as shown in Equation (3),[62] which itself is expressed by the density overlap between the frontier orbitals (HOMO and LUMO) under the assumption that the excited singlet (S_1) and triplet states (T_1) are dominated by a transition of LUMO to HOMO (Equation (4)). ϕ_{HOMO} and ϕ_{LUMO} are the spatial HOMO and LUMO distributions, and r_1 and r_2 are position

vectors.[63] Decreasing the spatial overlap between the HOMO and LUMO results in a decrease of the exchange integral (J) and thus, ΔE_{ST}.

$$\Delta E_{ST} = E_S - E_T = 2J \tag{3}$$

$$J = \iint \phi_{HOMO}(r_1)\phi_{LUMO}(r_2)\frac{1}{|r_2 - r_1|}\phi_{HOMO}(r_2)\phi_{LUMO}(r_1)dr_1dr_2 \tag{4}$$

In theory, ISC and RISC processes in pure organic TADF emitters are spin-forbidden. However, due to a small ΔE_{ST} these transitions are allowed as shown in Equation (5).[51] Here, λ stands for the first-order mixing coefficient between the singlet and the triplet states and H_{SO} represents the spin-orbit interaction. In organic molecules, H_{SO} is typically small, a reasonably small ΔE_{ST} however, leads to efficient ISC and RISC processes.

$$\lambda \propto \frac{H_{SO}}{\Delta E_{ST}} \tag{5}$$

Another effect caused by a small ΔE_{ST} is the diminishment of El-Sayed's rule,[64] that states that there must be a change in symmetry of the excited states for an efficient ISC and RISC. As hyperfine-coupling (HFC) plays an important role for small ΔE_{ST}, El-Sayed's rule can be neglected in this case. Furthermore, different symmetries for the excited states are given, if T_1 is represented by a locally excited state (LE), while S_1 is represented by a charge-transfer state (CT). Typically, in TADF emitters, the excited states are neither pure CT nor LE states, but often mixed CT-LE states with varying shares. Hence, El-Sayed's rule can be attenuated, resulting in fast rates for ISC (k_{ISC}) and RISC (k_{RISC}).[65]

Furthermore, the heavy atom effect has often been utilized to enhance ISC and RISC. For this, heavier atoms have been implemented in the emitter. Predominantly sulfur,[66,67] but also other elements like selenium[68] have been reported. In addition, the manipulation of the device architecture using heavy atom based layer materials can lead to an enhancement of these rates due to an external heavy-atom effect.[69,70]

1.2.2   History of TADF

The TADF phenomenon, although initially reported as E-type delayed fluorescence, was first observed in 1961 by Parker and Hatchard for Eosin (**4**) (Figure 5) at elevated

temperatures in ethanol.[71] Similar behaviors were later reported for benzophenone,[72] thioketones[73] and 9,10-anthraquinone.[74] In 1996, fullerene (**5**) was studied for its TADF properties and the rate equations for the description of the time-resolved processes of the TADF mechanism were derived (Figure 5).[75]

Until then, the TADF characteristics of the systems were not found to be efficient due to large ΔE_{ST} and the absence of design rules for efficient TADF systems. It were Yersin and Monkowius in 2008 that filed a patent claiming multinuclear complexes based on metals like iridium, palladium, platinum, rhodium and gold with small singlet-triplet energy gaps for application in OLEDs.[76] This novel mechanism of TADF for electroluminescence was first implemented in an OLED device by Adachi and co-workers in 2009 when they reported TADF properties for the Sn^{4+} porphyrin **6** shown in Figure 5 and employed this as the emitting material in a device.[77] One year later, the bis(phosphino)diarylamido dinuclear copper(I) complex **7** (Figure 5) was used as emissive material in an OLED with a high EQE of 16.1%.[65] This initial copper-based TADF emitter inspired many research groups like Yersin,[78,79] Bräse[80–82] and more.[83,84]
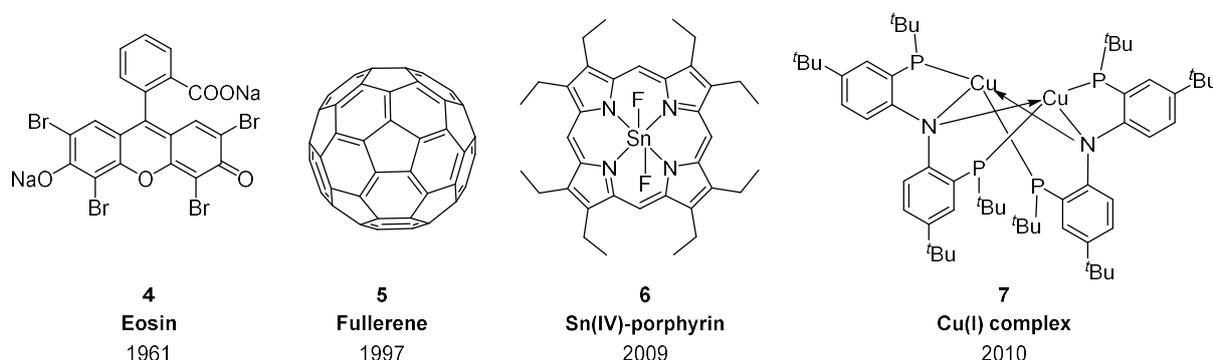

Figure 5. Historical outline of TADF emitters.

The breakthrough for TADF emitter design was in 2011, when Adachi and co-workers not only presented the first purely organic TADF molecule **PIC-TRZ** (**8**) (Figure 6) with a small ΔE_{ST} of 0.11 eV and an EQE of 5.3% in device, but also found the importance of reducing the overlap of the frontier orbitals to achieve a small ΔE_{ST} by quantum mechanical analysis. Hence, a molecular design was developed based on the combination of electron donor and acceptor groups in a twisted structure.[85] One year later, Adachi reported the prominent family of carbazolyl dicyanobenzenes (CDCB) by combining multiple carbazole groups as donor moieties with benzonitriles in different arrangements.[51] This class of emitters with its most prominent representative **4CzIPN**

(**3**) (Figure 6) with an outstanding performance with an EQE of up to 19.3% clearly demonstrated the harvesting process of both singlet and triplet excitons via the TADF pathway and demonstrated a significant breakthrough when compared to conventional fluorescence-based OLEDs. Since then, pure organic TADF emitters for application in electroluminescent devices are thoroughly investigated in literature not only for their potential to replace conventional fluorescent and phosphorescent emitting materials in already commercialized OLEDs but also for a better understanding of the mechanism and design principles for this special class of luminescent molecules, classified as "third generation emitters".[86]
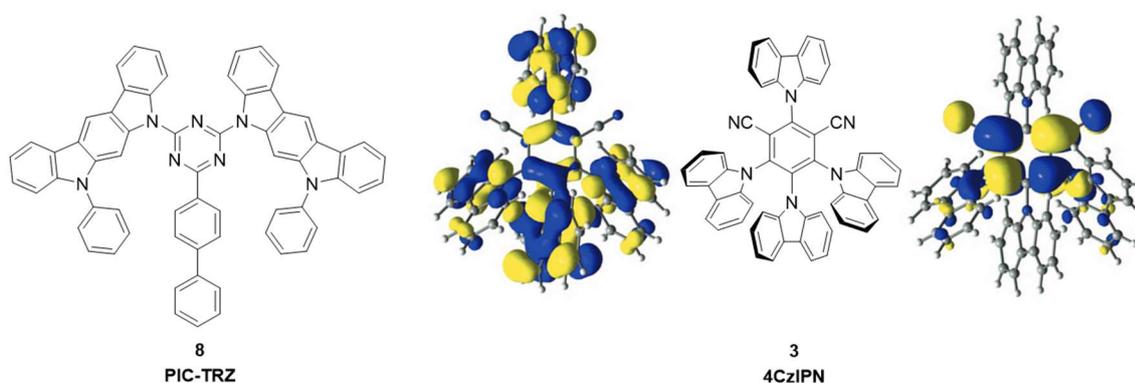

Figure 6. First pure organic TADF emitter (left) and **4CzIPN** (**3**) with its HOMO (left) and LUMO (right).

1.2.3   Molecular Design Strategies for TADF Emitters

Many design strategies for TADF emitters have been reported and were further refined since their advancement as OLED materials which can be followed in multiple review articles.[37,54–56,87] Most typically, the combination of donor and acceptor moieties is used to induce a charge transfer transition for efficient TADF characteristics. Most typically for donor groups, sterically demanding, annulated *N*-heterocycles like carbazole derivatives, triphenylamines or acridine-derived structures like phenoxazines, phenothiazine and 9,9-dimethyl-9,10-dihydroacridine (DMAC) are used. For acceptor groups, a vast plethora has already been reported. Predominantly however, benzonitriles, triazines, benzophenones, and sulfones are reported. Three distinct approaches have been proposed for molecular arrangement and design in order to create organic molecules with TADF properties.

1.2.3.1   Twist-Induced Charge Transfer

Based on the ground-breaking findings of Adachi and co-workers, one of the major design strategies uses the twist-induced charge transfer caused by a large steric hinderance between the acceptor and donor moieties. An increased dihedral angle between the acceptor and donor moieties separates the HOMO and LUMO orbitals and significantly reduces the exchange integral to a certain extent thus lowering the energy gap ΔE_{ST} as discussed earlier by localizing the HOMO on the donor groups and the LUMO on the acceptor groups.[56,88] The dihedral angle, mostly induced by the steric demand of the donor groups, can be varied depending on their relative arrangement. The prominent series of carbazolyl dicyanobenzenes (CDCB) by Adachi and co-workers squeezed up to four carbazole units and two nitrile groups to one central benzene unit, resulting in a highly twisted arrangement and separation of the frontier orbitals on the donor and acceptor groups (Figure 6).[51] Later, similar systems with up to five carbazole groups and one single acceptor unit such as **5CzBN** (**9**) were reported as efficient TADF emitters (Figure 7).[89,90]

In 2018, the group of Jun Yeob Lee investigated the dihedral angle control of two carbazoles linked via a phenyl unit to a diphenyltriazine acceptor. By investigating six isomers, it was found that the CT state, the singlet-triplet energy gap and the RISC rate could be affected by the dihedral angle. While the donor groups in 2-,6- and 2-,3- position showed the smallest energy gaps, substitution in 3-,4- and 3-,5- position was found to be not as efficient (**10**, Figure 7).[91] Another commonly used approach for increasing the dihedral angle is intentional installation of sterically demanding groups either on the donor group itself or on the respective spacer system. Often, the carbazole is methylated in the 1- and 8- position, or methyl groups are installed in *ortho* position to the donor group (**11**, Figure 7).[92] Furthermore, more profound modifications on the donor groups were also found to increase the dihedral angle and increase the TADF character of some molecules, like a triptycene modified carbazole[93] or the incorporation of the carbazole into a chiral [2.2]-paracyclophane (**12**) scaffold (Figure 7).[94]
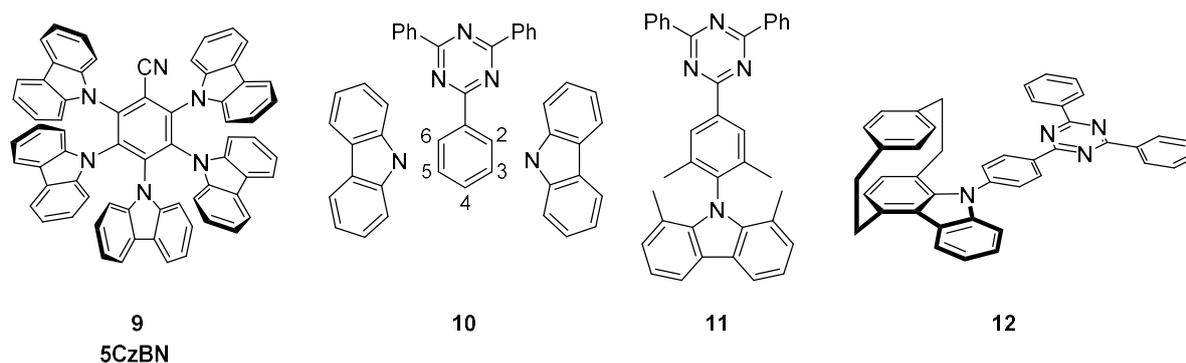
Figure 7. Different ways of adjusting the dihedral angle as crucial measure for a molecule showing TADF characteristics.

1.2.3.2   Through-Space Induced Charge Transfer

The second, less explored design principle for TADF molecules is based on a through-space induced charge transfer. Typically connected via a direct σ-bond or through twisted π-conjugation, this class separates its acceptor and donor groups and thus the frontier orbitals via a through space homojunction within a rigid framework. Hence, the charge transfer process happens through space via aromatic π-bonds or via a sp³-hybridized carbon center.[56]

Swager and co-workers designed triptycene-based emitters (**13**), where the acceptor and donor groups are separated on different fins of the triptycene scaffold. The frontier orbitals can still communicate via a homoconjugation (Figure 8).[95] Later, these systems were further investigated and a variation on the π-conjugation length and the donor units was conducted as a measure to optimize this class of TADF emitter.[96]

Adachi and co-workers reported the first TADF molecule implementing a spiro-center to separate the donor and acceptor groups.[97] The molecular structure of the acridine-based emitter (**14**) is shown in Figure 8. Here, the sp³-hybridized carbon center prevents an electronic communication, resulting in a minimal HOMO/LUMO overlap induced by the orthogonal arrangement and spatial communication. The concept of separation via a spirojunction was further explored with adjustments on the molecular setup.[98–100]

Spuling *et al.* utilized the unique [2.2]-paracyclophane scaffold once more to fix the benzophenone acceptor and diphenylamine as donor group in certain orientations (Figure 8). The two paracyclophane decks with a distance of 3.09 Å to one another[101] are closer in distance than the van der Waals distance between layers of graphite (3.35 Å).[102] Although the photoluminescence quantum yields of these emitters (**15**) was poor, blue

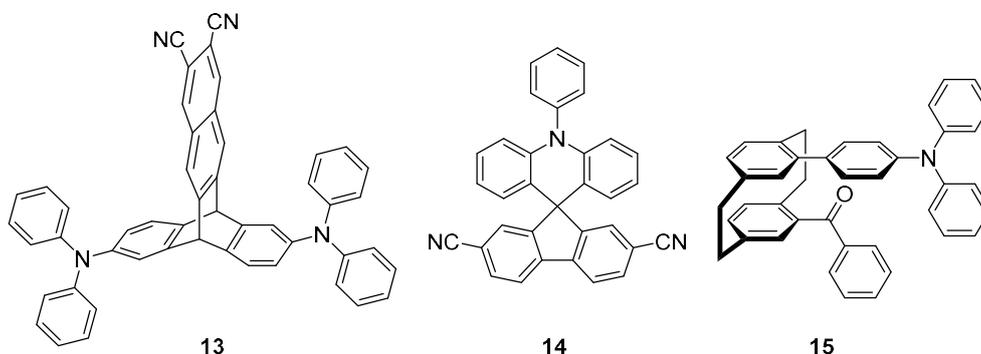TADF emission via a communication of the donor and acceptor group through-space was demonstrated.[103]

Figure 8. Emitters utilizing the through-space communication of acceptor and donor groups.

1.2.3.3   Multi-Resonance Effect

The pioneering work of Hatakeyama *et al.* in 2016 disregarded the conventional acceptor-donor design of TADF emitters and presented a class of organoboron-based emitters shown in Figure 9a.[104] In these molecules, the separation of the frontier orbitals is realized by "multi-resonance effects" where the HOMO and LUMO are alternated through the molecular framework. The boron atom localizes the center of the LUMO "mesh", while the HOMO is predominantly distributed on an alternative "mesh" centered at the nitrogen atoms. Both emitters, **DABNA-1** (**16**) and **DABNA-2** show excellent optoelectronic characteristics such as large oscillator strengths of 0.205 and 0.415, excellent photoluminescence quantum yields (PLQY) doped as 1 wt% in mCPB of 88% and 90% and high EQEs of 13.5% and 20.2% with CIE coordinates of (0.13, 0.09) and (0.12, 0.13). The main advantage of this new class of emitters lies in their significantly thinner full width at half maximum (FWHM) of only 28 nm (typically 70–100 nm for conventional TADF emitters). This leads to a superior color purity than for conventional TADF emitters, facilitating the accessibility of the deep blue color region for industrial applications.[56] Nakanotani *et al.* reported the light amplification abilities of **DABNA-2**,[105] while chemical modifications on the systems like extending the framework with additional boron and nitrogen atoms[106] or substitutions of donor groups on the framework,[107] mainly with the goal of developing a synthetic route and exploring the potential of this new TADF emitter class were conducted. The attachment of a carbazole group in *para* position to the boron atom conducted by Liang *et al.* led to a significant improvement of the efficiency of the resulting emitter (**17**) to be one of the best blue TADF-OLEDs up to date with an EQE

of 32.1% (Figure 9b).[108] In depth theoretical investigations were conducted in 2019 by Pershin *et al.* to study the origin of the multi-resonance (MR) TADF emitters. A local alternating rearrangement of the electronic density upon excitation was found by using highly correlated quantum-chemical calculations.[109] Furthermore, a series of π-extended graphene-like structures doped with boron and nitrogen atoms were proposed as promising candidates for MR-TADF emitters (**18**) as shown in Figure 9c.
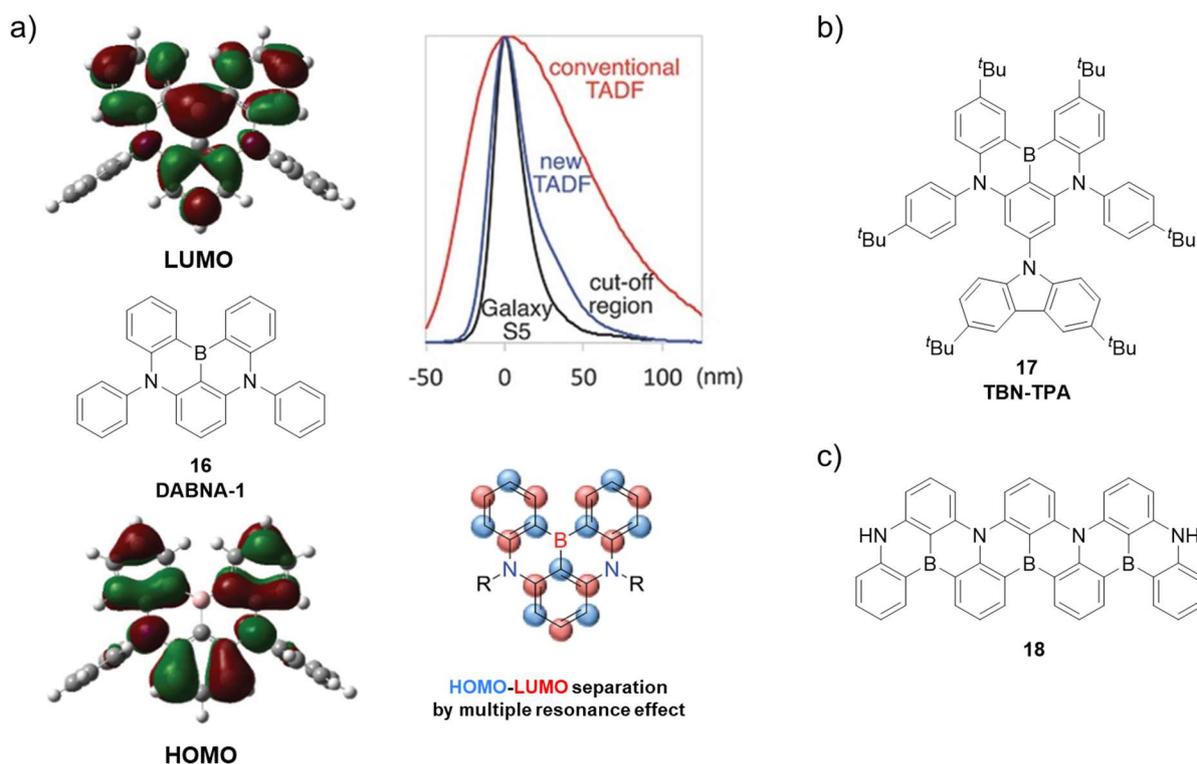

Figure 9. Developments of MR-TADF emitters: a) Chemical structure of **DABNA-1** (**16**) and its frontier orbitals, narrow emission peak compared to conventional TADF and the visualized HOMO-LUMO separation, (copyright: Wiley-VCH)[104] b) Substituted **DABNA-1** derivative (**17**) used in the most efficient blue TADF-OLED up to date, c) π-extended proposed structure based on theoretical investigations.

1.2.4   Molecular Design Towards Efficient OLEDs

Zheng *et al.* further reviewed on molecular design strategies in order to obtain efficient OLEDs.[56] Besides having a highly luminescent emitter with a high internal quantum efficiency, the out-coupling efficiency, strongly dependent on the device architecture is of crucial importance to achieve excellent external quantum efficiencies. Typically, the light outcoupling involves several channels for losses and is in the range of 20% to 30% for OLEDs.[110] The light outcoupling can be enhanced by deploying transparent electrodes

and by targeted design of the refractive indices of the employed layers within the device. There are few possibilities for emitter design to enhance the light out-coupling, too.

1.2.4.1   Host-Free TADF-OLEDs

Typically, TADF emitters are doped in a host matrix to prevent exciton-exciton or exciton-polaron quenching. A less active emissive layer is also more gentle to the embedded molecules resulting in diminished efficiency roll-offs.[56] Recent studies found that the optimal doping concentration of TADF emitters is much larger than for fluorescent or phosphorescent emitting materials.[111] A fully host-free setup, solely using the pure emitter as emissive layer furthermore simplifies the device fabrication by preventing the need of depositing two materials simultaneously, resulting in lower costs in commercial applications and more reliable devices.[112–114] Still, it is necessary to suppress the non-radiative processes through interference of the molecular stacking or by largely twisted conformations.

The group of Adachi reported a set of sulfone and benzophenone based emitters (**19, 20**) (Figure 10) used in host-free OLEDs that were as efficient as the best doped OLEDs with maximum EQEs of 18.9% and 19.5%. They proposed that both, a large Stokes shift and weak $\pi-\pi$ stacking interactions, led to the suppression of the non-radiative processes.[115] The combination of the DMAC or phenoxazine donor with a triazine acceptor led to two similar TADF emitters, **DMAC-TRZ (21)** and **PXZ-TRZ (22)** (Figure 10). **DMAC-TRZ (21)** was not only found to result in highly efficient conventional doped OLEDS (EQE of 26.5%), but also in a device architecture employing a non-doped emitting layer with an EQE of 20%.[116] The possibility of achieving high efficiencies of one emitter in doped or non-doped OLEDs demonstrates the feasibility of device and fabrication simplification and ultimately cost reduction.
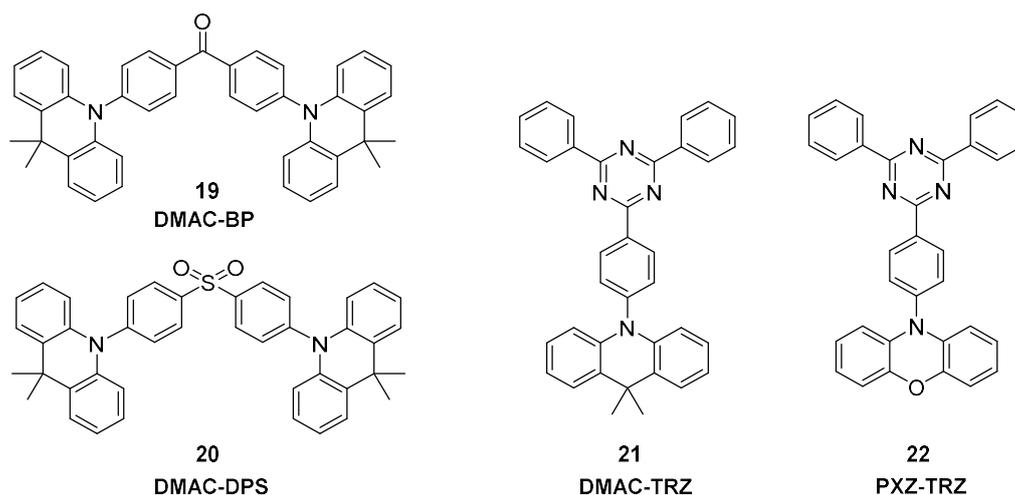
Figure 10. Efficient TADF emitters suitable for host-free device stacks.

1.2.4.2   Aggregation-Induced Emission

Another effect which was found and investigated to suppress concentration quenching was found in 2001 by Tang and co-workers and named aggregation-induced emission (AIE).[117–119] Molecules, showing this effect are non-luminescent in diluted solutions but show intense luminescence upon the formation of aggregates in solid state.

Wang *et al.* reported the first TADF emitter with AIE characteristics in 2014 by combining a thioxanthenone-dioxide acceptor with a *N*-phenyl carbazole and triphenylamine donor (Figure 11). The AIE properties were demonstrated by a significantly higher PLQY in solid state than in solutions. The investigation of the crystal structure and molecular packing gave evidence to understand the different emission behavior in solid state. As the molecules align themselves in a rigidified molecular conformation, the intramolecular rotation is hindered and non-radiative processes are suppressed. In solution, the emission is quenched by the enabled rotation of the donor units from the twisted conformation.[120,121] Although a non-doped device architecture was not reported, the doped OLEDs of **TXO-PhCz** (**23**) and **TXO-TPA** (**24**) showed maximum EQEs of 21.5% and 18.5%, respectively.

Groundbreaking results on AIE-based emitters were reported by Tang and coworkers in 2018 as they combined the 4-(phenoxazine-10-yl)benzoyl building block[122–125] with common host motifs like DCB, CBP, mCP and mCBP. Two of them, **DCB-BP-PXZ** (**25**) and **mCP-BP-PXZ** (**26**) are shown in Figure 11. The optoelectronic properties of this set of emitters were quite similar, mainly influenced by the 4-(phenoxazine-10-yl)benzoyl fragment. Almost non-fluorescent in solution, excellent PLQYs in non-doped films were

reported, as well as excellent performing OLEDs with almost 100% exciton use, negligible efficiency roll-offs even at a luminance of 1000 cd m^{-2} and maximum EQEs of 22.6% for **DCB-BP-PXZ** (**25**) and 22.1% for **mCP-BP-PXZ** (**26**). The emission quenching is suppressed by a highly twisted molecular geometry which also prevents the excitons at the central accepting benzoyl moiety from Dexter energy transfer. Lastly, the peripheral carbazole moieties are presumed to transfer excitons to the benzoyl moiety to further enhance the EL efficiencies.[126]

The combination of the benefits of host-free emissive layers for simplified device architectures and the outstanding performance of aggregation induced emission properties shows great potential for non-doped OLED devices with superior efficiency and stability.[56]
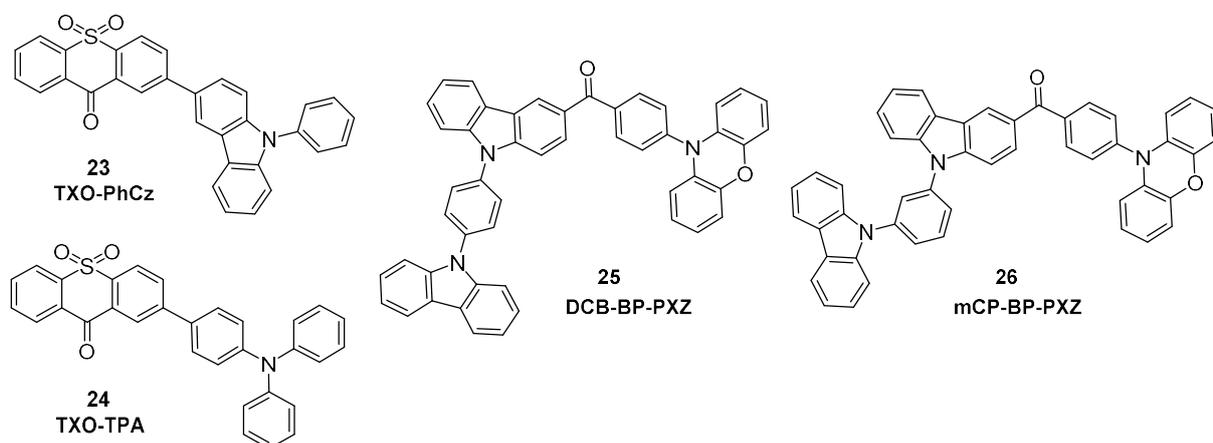

Figure 11. Emitters showing AIE properties: Thioxanthenone-dioxide based emitters (left) and the combination of common host groups with an emissive unit (right).

1.2.4.3   Orientation Controlled Emitters

The specific orientation of emissive molecules with respect to the device stacking direction is another tool for improving the device efficiency. The already mentioned out-coupling efficiency of 20% to 30%[110] is achieved upon an isotropic orientation of the emitting molecules. Studies have shown that a horizontal orientation of the emitters with respect to the substrate reduces the surface plasmon losses, and therefore significantly increases the out-coupling efficiencies.[127–130] The anisotropy factor Θ, defined as the share of vertically oriented dipoles (p_z) to the total dipole moments, as shown in Equation (6), can be used as a measure for the emitter orientation.[131]

$$\Theta = \frac{[p_z]}{[p_x] + [p_y] + [p_z]} \qquad (6)$$

The group of Brütting investigated the previously reported triazine-based emitter **CC2TA** (**27**)[132] (Figure 12) and found a preferential horizontal orientation of its transition dipole moments of 92% when doped in DPEPO as host. Due to the TADF properties of the emitter, they observed an increase of the internal quantum efficiency by a factor of 2.24. However, the horizontal orientation also increased the external quantum efficiency due to an increased light out-coupling by a factor of 1.46 resulting in an experimental EQE of 11% that clearly exceeds the theoretical value (3.4%) for conventional fluorescent emitters.[133] Typically, the orientation is determined by analyzing angular photoluminescence spectra.[134]

Adachi and co-workers found that by adjusting the film fabrication temperature, the orientation of the triazine-based emitter **PXZ-TRZ** (**22**) could be controlled.[135] This is attributed to the molecular interaction of the emitting molecule and the mCBP host. Later in 2016, the group of Adachi demonstrated a correlation between the degree of emitter planarity and the preference for horizontal orientation. Hence, they designed a series of carbazole-based TADF emitters varying in their molecular planarity. Attributed to a strong intermolecular interaction between the emitter molecule and the host (DPEPO), the most planar emitters **BDQC-2** and **BDQC-4** (**28**) (Figure 12) showed the highest share in horizontal orientation, also effecting the EL performance of the resulting OLEDs.[136]

In conclusion, controlling the orientation of the emitting molecules either by molecular design or by fabrication techniques is a suitable tool to further enhance the efficiencies of OLED devices beyond the conventional limits.
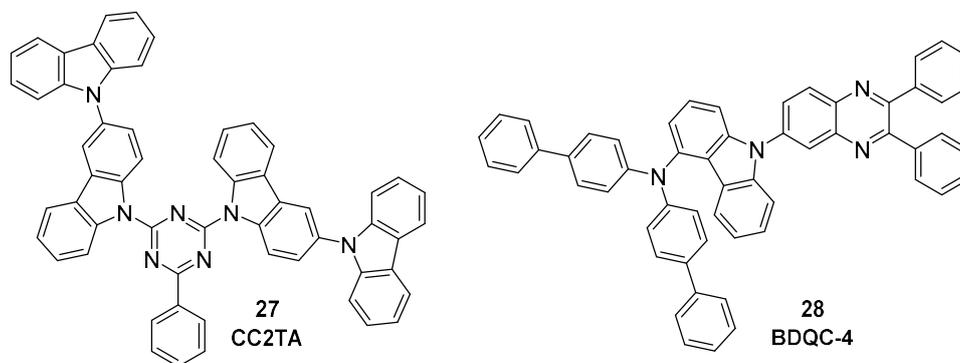

Figure 12. Reported molecules for horizontal orientation.

2   Objective

Lighting technologies are essential for working-around-the-clock modern society to provide basic services. Therefore, the continuous improvement towards higher efficiency is subject of lighting technology research to save energy, develop more environment-friendly processing techniques, and improve lifetimes of lighting devices to conserve resources.

In this regard, organic light-emitting diodes (OLEDs) have recently emerged as one of the most promising approaches, as they not only show favorable characteristics regarding large-scale fabrication and energy-saving capabilities, but in addition they possess unique advantages in the realization of novel display solutions such as flexible and transparent displays. In the field of OLEDs, the thermally activated delayed fluorescence (TADF) -based emitters are the most promising class for OLED application due to their excellent efficiencies and the absence of heavy metal ions in the molecular structures. Therefore, they are considered to be the 3rd generation of OLED materials. As not only the pure efficacy of an emitter is of great importance, but also the in depth understanding of the underlying fundamental mechanisms of TADF and structure-property relationships in order to fully understand the potential, increasing efforts have been devoted to explore the scope and limitations of TADF over the recent years.

The aim of this thesis was the synthetic development and in-depth characterization of three sets of TADF emitter classes for OLED application as well as for further less explored applications such as bioimaging and charge carrier transport investigations.

The rationale for the design is threefold: First, existing nitrile-based TADF emitters are chemically modified by transforming the nitrile acceptor groups into substituted tetrazoles or oxadiazoles as new accepting motifs. The modularity of this approach not only allows the adjustment of optoelectronic properties by altering the electron donating or withdrawing character, but the introduction of functional groups such as halides, alkynes, alkenes, and more offer pathways for follow-up chemistry and the attachment to other systems such as biomolecules or surfaces. Second, a phthalimide-based TADF emitter motif is thoroughly investigated through chemical modification with the aim to extensively explore structure-to-property relationships with the goal of realizing highly efficient, color tunable TADF emitters with enhanced properties for vacuum or solution processing. Lastly, the employment of the tristriazolotriazine (TTT) as acceptor motif is investigated in order to achieve a new family of TADF emitters. A synthetic protocol for

the TTT core with peripheral donor groups is developed. The influence of donor strength, count and arrangement as well as variations on the dihedral angle between donor and acceptor groups on the optoelectronic properties is studied.

All promising TADF emitters that are synthesized are thoroughly characterized to assess their suitability for OLED application. The most promising candidates are then embedded as emitting materials in OLED devices.

TADF emitters featuring binding sites for follow-up chemistry are subjected to conjugation to molecular transporters for bioimaging and in the context of the Collaborative Research Centre 1176 "Molecular Structuring of Soft Matter" to rigid, monodisperse oligomers to investigate photophysical phenomena such as exciton transport and charge separation.