#### Tom CARDEYNAELS

Hasselt University, Institute for Materials Research (IMO-IMOMEC), Design & Synthesis of Organic Semiconductors (DSOS), Agoralaan 1, 3590 Diepenbeek, Belgium

University of Namur, Laboratory of Theoretical Chemistry, Theoretical and Structural Physical Chemistry Unit, Namur Institute of Structured Matter, Rue de Bruxelles 61, 5000 Namur, Belgium tom.cardeynaels@uhasselt.be

# An overview of organic light-emitting diodes: from past generations to modern light emission principles

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# Abstract

Organic light-emitting diodes (OLEDs) have entered our everyday life as we can nowadays find them in smartphone and television screens. Their widespread use can be attributed to their ability to outperform technologies based on classical semiconductors, whereas this is not possible or not yet achieved in other fields of organic optoelectronics such as solar cells. Current OLED efficiencies, i.e. the light output versus the power input, match or even surpass those of inorganic LEDs. Furthermore, the ability for ultra-thin processing and direct color emission, instead of having to rely on liquid crystals, makes them very successful in display technologies. Herein, a brief historic overview of the development of OLEDs is given with a focus on the organic emitters designed for the different OLED 'generations'. At the end, a short summary of our contributions to the field – joint computational/synthetic efforts on donor-acceptor chromophores displaying thermally activated delayed fluorescence (TADF) *– is provided as well.* 

# **1. 1<sup>st</sup> Generation OLEDs**

Organic light-emitting diodes (OLEDs) have come a long way since the discovery of electroluminescence in 1936 [1], when Destriau showed that ZnS can emit light when an electric field is applied. In 1953, Bernanose et al. for the first time observed electroluminescence in organic materials by introducing acridine orange (Figure 1) in a cellulose matrix and applying an alternating electric field.[2]. 10 years later, Pope et al. placed a layer of single crystal anthracene between two silver electrodes and applied a voltage to it (Figure 1) [3]. At over 400 V, the result was a faint, but typical emission for anthracene. When anthracene was mixed with tetracene, the fluorescence emission of tetracene was observed.

In 1987, Tang and VanSlyke created the first electroluminescent device that paved the way for modern-day OLEDs at the Eastman Kodak Company (Figure 2) [4].



Figure 1. Molecular structure of acridine orange (left) and the device architecture and active materials used by Pope et al. [3] (right).



Figure 2. Device architecture applied by Tang and VanSlyke and molecular structures of Alq<sub>3</sub>, the diamine layer and the colored emitters coumarin 540, DCM1 and DCM2 [4, 5]. Reproduced from ref. 4, with the permission of AIP Publishing.

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They described their device as being a double layer diode, wherein two organic layers consisting of Alq<sub>3</sub> and a diamine were used. Alq<sub>3</sub> acts as a green emitter, whereas the diamine layer is used for monopolar charge carrier (hole) transport. Around the same time, Adachi et al. published a series of papers in which they expanded the device structure to three layers, including hole transport (HTL) and electron transport layers (ETL) between which the emitting layer is sandwiched [6, 7]. Various emitter materials such as anthracene, coronene and perylene [6] and a 12-phthaloperinone derivative [7] were used. The two-layer architecture from Tang and VanSlyke worked rather well because the emitters have relatively good electron-transporting properties. Switching to the three-layer architecture removed this need as both barrier layers provide enhanced charge carrier transport and so the pool of emitter materials could be expanded. Adachi and coworkers further illustrated this by incorporating a hole transport layer with emitting properties, effectively combining the emitter and hole-transporting layer into one [8].

In 1989, Tang *et al.* were able to reach substantial device efficiencies by sandwiching an Alq<sub>3</sub> layer doped with green and orange-red emitters between two layers of pure Alq<sub>3</sub> (Figure 2) [5]. The higher photoluminescence quantum yield (PLQY), *i.e.* the ratio of emitted to absorbed photons, of the doped films, 3 to 5 times larger with respect to that of pure Alq<sub>3</sub> (PLQY = 8%), was expected to afford an increased device performance. Whereas devices using Alq<sub>3</sub> as the sole emitter afforded an efficiency of 1%, the new sensitized devices reached up to 3%. The device efficiency is defined here as the ratio of the number of photons emitted by the device to the number of charges injected into the device.

In these types of sensitized devices, electrons and holes that are injected from the anode and cathode move through the device until they encounter each other and recombine to form excitons (*i.e.* bound electron-hole pairs). Device tuning, making use of additional layers such as the hole and electron transporting layers, ensures that the electrons and holes recombine in the so-called active layer. This active layer usually consists of a 'host' material, *i.e.* a large energy gap semiconducting material capable of transporting the charge carriers to their destination, and an emitting material, on which the charges recombine.

Soon afterwards, in 1990, Burroughes *et al.* took a different route with the advent of organic conjugated polymers [9]. Their work involved the synthesis of a poly(*p*-phenylene vinylene) (PPV) derivative (Figure 3). The main advantage foreseen for a polymer emitter would be an improvement of the device stability as small molecule devices often suffer from recrystallization and other structural changes. However, due to the insolubility of the final polymer, a precursor polymer had to be processed from solution onto the bottom electrode, which

itself was deposited on a suitable substrate, followed by a thermal annealing step in vacuum in which the final PPV structure is formed. Indium tin oxide (ITO) was chosen as the bottom contact because of its semi-transparency, whereas a thin layer of aluminum was used as the top contact. In this device architecture, the polymer acts as the host and emitter at the same time, allowing charge recombination to occur on the polymer chains, followed by exciton diffusion until they decay and light is emitted. Unfortunately, the device efficiencies only reached up to 0.05%, which was attributed to failures at the polymer/ thin metal interface.

Since then, several strategies have been used to synthesize soluble, and thus readily processable, polymers for OLED applications. These strategies often encompass the incorporation of large, sometimes branched, aliphatic chains as these prevent stacking (and thereby emission quenching) between the conjugated polymer backbones. Other aromatic motifs such as thiophene, fluorene and phenylene have been used. Changing the polymer backbone leads to a variation in emission color, but could also lead to changes in device stability and



Figure 3. Polymer structures used in 1st generation OLED devices.

processability. Ohmori et al. (1991) made devices with poly(3-alkylthiophene) (P3AT) [10] and poly(9,9-dihexylfluorene) [11] as the active materials (Figure 3) because both polymers are well soluble with emission in the orange-red and blue, respectively. Unfortunately, efficiencies have not been reported for these devices. In 1992, Grem et al. prepared a poly(pphenylene) (Figure 3) based device, similar to that of Burroughes et al., in which a precursor polymer was processed and the final polymer was obtained after thermal annealing [12]. With blue emission, the device only managed to reach efficiencies of 0.01-0.05%, similar to the results with unfunctionalized PPV polymers. In the meantime, progress was made using PPV polymers and D. Braun and A.J. Heeger went on to functionalize the original PPV polymer with methoxy and 2'-ethylhexyloxy side chains to create poly(2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene) or MEH-PPV (Figure 3) [13]. This functionalized PPV polymer has the benefit of being soluble in organic solvents, allowing facile processing without a thermal annealing step.

Development in the field of polymer OLEDs has continued, although polymers such as MEH-PPV are still being used as prototypical reference materials. One notable example is the PDY-132 developed by Merck Gmbh, which is also dubbed "super-yellow" (Figure 3) [14]. This PPV-based copolymer has a high PLQY in the yellow region and devices with 5.3% efficiency have been obtained, which is among the highest values reported for polymer-based OLEDs. Early incorporations of polymer OLEDs can be found in for example the Norelco electric shaver by Philips [15].

In addition to polymer OLEDs, researchers have investigated different ways of combining facile solution processing with excellent photophysical properties. Dendrimers can be designed to have extended  $\pi$ -conjugated structures, giving them semiconducting properties, but because of their branched nature, they are far more soluble than their polymer counterparts. Early designs were based on an emissive core surrounded by either a fully conjugated or partially saturated periphery. Using conjugated or partially conjugated branches, the charge transport from the electrodes to the active material could be improved. In 1996, Wang et al. built a dendrimer around an anthracene unit using phenylene ethynylene units to create the branches (Figure 4) [16]. Unfortunately, the devices suffered from solid-state aggregation and self-quenching. Pillow et al. designed a dendrimer with a porphyrin core and stilbene branches (Figure 4), resulting in red emission [17]. Kwok and Wong used distyrylbenzenes with poly(benzyl ether) type dendritic wedges (Figure 4) [18]. Their dendrimer showed blue emission and despite its non-conjugated periphery, it was found that energy transfer does occur between the branches and the core. In 2003, six-arm starshaped oligofluorenes were synthesized by Zou et al. (Figure 4), affording blue emission and a maximum device efficiency of 6.8% [19].

Despite substantial efforts towards solutionprocessable polymer and dendrimer OLEDs, small molecule OLEDs have remained the main area of interest. This is mainly due to the lower device efficiencies obtained using polymer and dendrimer active materials, which themselves are a result of device defects that are introduced via solution processing and defects in the polymer backbones introduced during their synthesis. Device defects occur as the hole/ electron transporting/blocking layers are often small molecule organic materials, which can partially redissolve during the addition of novel layers, making pin-holes more likely and leading to a poor active layer morphology. In contrast to polymers, small molecule emitters can be readily purified using sublimation techniques and they allow device fabrication via vapor deposition, affording a higher degree of control over the layers and their morphology in multi-layer device stacks.

In the above section, a brief summary of the history of the first generation OLEDs, based on simple fluorescent emitters, is provided. While some historically important studies are mentioned, the overview on fluorescent OLEDs given here is far from exhaustive.



Figure 4. Dendritic active materials studied by Wang *et al.* [16] (top left), Pillow *et al.* [17] (top right), Kwok and Wong [18] (bottom left) and Zou *et al.* [19] (bottom right).

# 2. 2<sup>nd</sup> Generation OLEDs

Shortly after the initial discovery by Tang and VanSlyke [4], an alternative emission mechanism in the form of phosphorescence was used to develop OLED devices. Phosphorescence is the emission from the triplet state and is not commonly observed in organic fluorophores (e.g. in the materials from the previous section) (Figure 5). The underlying mechanism can be explained using quantum mechanics. For most organic materials, the ground state is of singlet nature. Absorption of a photon leads to excitation from the singlet ground state to one of the singlet excited states, depending on the energy of that photon. Because the excited triplet states have a different spin configuration, a change of spin is required to go from the singlet to the triplet state. Because of the laws of conservation of momentum, the change in spin angular momentum should be paired with a change of momentum elsewhere, typically in the orbital angular momentum. Hence, the term spinorbit coupling (SOC) is coined to describe the connection between the spin and orbital angular momentum in systems ranging from atoms to large organic compounds. Large SOC values are typically observed when heavy atoms such as lead (Pb), platinum (Pt) or iridium (Ir) are introduced, whereas intermediate values can be found for the heavy halogens iodine (I) and bromine (Br).

To reach the triplet state and subsequent emission back to the ground state, a certain amount of SOC is needed. The lack of SOC in common organic molecules, however, makes them unable to show phosphorescence. Furthermore, when an electron and a hole recombine in an OLED device, the formed exciton can be either of singlet or triplet nature. Because there is only one possible singlet and three possible triplet configurations, the excitons are formed in a ratio of 25% singlets and 75% triplets. Since phosphorescence is not



Figure 5. Jablonski diagram showing possible transitions.  $S_x$  and  $T_x$  = various singlet and triplet states; VR = vibrational relaxation; IC = internal conversion; ISC = intersystem crossing; Abs. = absorption; Fl. = fluorescence; Phos. = phosphorescence. The solid lines represent radiative transitions whereas the dashed lines represent non-radiative transitions.

possible for the 1<sup>st</sup> generation OLED emitters, the maximum internal quantum efficiency (IQE) can only be around 25% [20]. The EQE is dependent on the light outcoupling efficiency, in which nearly 75% of all emitted light is lost. Light outcoupling is mainly diminished by internal reflection and destructive interference within the OLED device [21].

The second generation OLED materials were designed to overcome these issues by the incorporation of heavy atoms. As they lead to an increase in spin-orbit coupling, giving rise to phosphorescence, intersystem crossing (ISC) becomes viable (Figure 5). The same SOC that leads to phosphorescence also enables ISC from the singlet to the triplet excited state. In an OLED device with such a heavy-metal containing emissive material, the 75% of triplet excitons that are inherently formed during charge recombination can now be exploited through the phosphorescent pathway. Subsequently, the 25% singlet excitons can be converted to the triplet state via ISC, leading to a maximal IQE of 100%. Nevertheless, even with an IQE of 100%, light outcoupling efficiencies of around 25% prevent EQEs of more than 25%.

In 1990, Kido *et al.* used a terbium  $(Tb^{3+})$  complex of acetylacetonate to construct a twolayer device with  $N^4, N^4$ '-diphenyl- $N^4, N^4$ '-di-*m*- tolyl-[1,1'-biphenyl]-4,4'-diamine (TPD) as the hole-transporting layer (Figure 6) [22]. The device emitted green light with a very narrow spectral width, another advantage of using heavy-metal complexes making them ideally suitable for display applications. In 1993, Kido *et al.* reported on a red-emitting tris(thienyltrifluoroacetylacetonato)  $Eu^{3+}$  complex which was spin-coated in a poly(methylphenylsilane) film because it was not possible to evaporate this complex (Figure 6) [23].



Figure 6. Terbium and europium complexes used by Kido *et al.*, with TPD as the hole-transporting material [22, 23].

These two complexes are among the first examples of heavy-metal complexes being applied to the field of OLEDs with the intent of boosting the device performance in terms of EQE and color purity. Baldo *et al.* used a phosphorescent 2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphyrine platinum(II) (PtOEP) (Figure 7) dye as the emitter doped in Alq<sub>3</sub> [24]. With this combination, more than 90% energy transfer from the Alq<sub>3</sub> host to the porphyrin emitter was obtained, leading to an IQE and EQE of 23% and 4%, respectively. At the time,

this was a record efficiency for a red-emissive OLED. The same research groups then reported two more red-emitting porphyrin-based (Figure 7) OLEDs, again using Alq, as the host material [25]. 2,7,13,17-Tetraethyl-3,8,12,18-tetramethyl-21H,23H-porphyrine platinum(II) (PtOX) and 5,15-diphenyl-21*H*,23*H*-porphyrine platinum(II) (PtDPP) showed similar red-shifted emission as PtOEP, but with varying photoluminescence quantum yields. PtOX and PtOEP have quantum yields of 0.44 and 0.55, respectively, as expected due to the minimal structural change. PtDPP has a PLQY of only 0.16 as the phenyl groups on the porphyrin meso-positions likely lead to more nonradiative losses. As a result, the devices obtained with PtOX and PtOEP showed similar EQEs, whereas the devices containing PtDPP lagged behind.



Figure 7. Phosphorescent Pt(II)-porphyrin emitters used by Baldo *et al.* [24] and Kwong *et al.* [25].

Introduction of a dopant into a host material was already described by Pope *et al.* as they showed doping of tetracene in anthracene gave predominant emission of the former [3]. Tang and VanSlyke used Alq<sub>3</sub> as a host for various fluorescent emitters [5] and the same host material was used for the porphyrin-based OLEDs by Baldo et al. [24] and Kwong et al. [25]. Doping of an emitter material in a suitable host has, in these examples, been shown to be advantageous for the overall efficiency of the devices. One of the key factors in achieving good efficiencies is a proper energy level alignment of the emitter and host molecules [26]. Ideally, the energy levels of the host encompass those of the emitter to ensure exciton formation on the dye molecules. In the case of exciton formation on the host molecules, exciton diffusion can occur and they will migrate to the dye, which essentially acts as an exciton trap (Figure 8). The emitter can therefore achieve higher IQE values as emission from the host or other device layers is minimized. Additionally, energy transfer from the host to the emitter should be as high as possible and ideally approach 100%.



Figure 8. Simplified schematic of the energy levels in an OLED, ensuring exciton formation in the emitting layer. Adapted from *Journal* of Chemical Information and Modeling, 2018, 58, 2440-2449., with permission of the American Chemical Society [27].

Another advantage of using doping is that doped devices often give narrower electroluminescence than non-doped devices [26]. This is particularly interesting when looking at full color displays where mixing of the primary colors red, green and blue (RGB) is necessary to obtain white light. A lower color purity (*i.e.* broad emission) leads to washed out colors. Doping also enhances stability as the emitter is no longer crystalline and the ETL and HTL have less tendency to crystallize. As doping is typically done in low amounts (<20%), the emitter molecules experience less self-quenching and ultimately less material is needed to construct efficient devices. This is particularly useful as the emitter is usually the most expensive component of an OLED device.

The next important improvement on the device architecture came with the introduction of additional layers to enhance charge carrier confinement in the emitting layer and thereby improve the overall device efficiencies. Up until this point, only two-layer (holetransporting and emitting) or three-layer (hole and electron-transporting and emitting layer) architectures were used. Ikai *et al.* introduced a hole and exciton-blocking layer consisting of perfluorinated compounds in a four-layer architecture (Figure 9) [28]. The device consisted of electron (Alq<sub>3</sub>) and hole ( $\alpha$ -NPD) transporting layers between which the hole/exciton-blocking layer and emitting layer are sandwiched. The hole/exciton-blocking layer is deposited between the emitting and electron-transporting layer to ensure that either holes or excitons are not able to migrate into the electron-transporting layer for charge recombination or relaxation (Figure 9).

This is possible due to the low-lying highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) which are necessary for effective blocking of holes and injection of electrons, respectively. The green emitter tris[2-phenylpyridinato-C2,N] iridium(III), better known as Ir(ppy)<sub>3</sub>, was doped in 4,4',4"-tri(*N*-carbazolyl)triphenylamine (TCTA),



Figure 9. Device architecture and materials used in the work of Ikai *et al.* [28]. Adapted from *Applied Physics Letters*, 2001, 79, 156-158., with the permission of AIP Publishing.

which also has hole-transporting properties. Additional layers include an aluminum cathode, a lithium fluoride (LiF) electron injection layer and an ITO anode (Figure 9). EQEs of up to 19.2% were obtained using this device architecture.

Iridium arose as one of the most suitable heavy metals to obtain highly emissive complexes with color tuneability, owing to the strong SOC of the iridium atom and strong metal-ligand charge transfer. In 2001, Adachi et al. reported three novel iridium complexes with modified ligands to obtain blue-emissive complexes [29]. Due to the requirement of having highenergy singlet and triplet states, blue-emissive complexes are more difficult to obtain than their green or red counterparts. By gradually making the ligands more electron poor (Ir(ppy),(acac) to  $Ir(Fppy)_{2}(acac)$  and by switching an acetylacetonato ligand for a picolinate (FIrpic) (Figure 10), the emission was shifted from 516 to 465 nm in dilute chloroform solution. Using FIrpic, an EQE of  $5.7 \pm 0.3\%$  was obtained, which was a significant improvement at that time for a blue emitter.



Figure 10. Iridium complexes reported by Adachi et al. [29, 30].

In the same year, Adachi et al. also reported on the highly efficient red-emitting complex  $bis(2-(2'-benzo[4,5-\alpha]thienyl)pyridinato N,C^{3'}$ )iridium(acetylacetonate) [btp\_Ir(acac)] (Figure 10) [30]. With an electroluminescence maximum at 616 nm, it comes close to the ideal color coordinates for video display standards. A maximum EQE of 7.5% was achieved, which is a significant increase over the 4% reported for the red-emitting PtOEP porphyrin (vide supra). Tuning of the emission color was further exploited by Tsuboyama et al., who reported on a large number of red-emitting iridium complexes (Figure 11) in which the ligand character was made more donating or accepting depending on the addition of specific functional groups such as methyl or CF<sub>3</sub> [31]. Varying the ligand strength not only changes the emission color, but also has implications on the phosphorescence quantum yield ( $\phi_{Ph}$ ), as it changes the positions of the singlet and triplet energy levels. Ir(piq)<sub>3</sub> was found to give very efficient red emission ( $\lambda_{max,Ph}$ = 603 nm,  $\phi_p$  = 0.26) and a maximum EQE of 10.3 % [31].

Next to platinum and iridium-based complexes, other heavy metals such as ruthenium, osmium and rhenium have also been used [32]. Due to the higher oxidation potentials of these materials with respect to iridium, the prerequisites for the ligands are stricter and less design freedom is available. In combination with the (generally) higher EQEs for iridium-based devices, iridium has received most attention [33-36].



Figure 1. Iridium complexes synthesized by Tsuboyama et al. [31].

## 3. 3<sup>rd</sup> Generation OLEDs

The commercial success of the second generation OLEDs has inspired researchers to investigate the possibilities to further improve the device performance in terms of stability, lifetime and sustainability. Instead of utilizing the emissive triplet state, research has focused on upconversion of the triplet excitons to the singlet state. This can be achieved via triplet-triplet annihilation (TTA), thermally activated delayed fluorescence (TADF) or the hybrid locally excited charge transfer (HLCT) mechanism. The most extensively studied mechanism is that of TADF and therefore, this is discussed in greater detail in this section.

# 3.1. The history of delayed fluorescence

The discovery of TADF dates back to the beginning of the 20th century. In 1929, Delorme and Perrin discovered delayed fluorescence emission from certain uranium salts, both in the solid state and in solution [37]. Measuring the emission of the salts at room temperature and at -180 °C (liquid oxygen), they observed a decrease in the emission lifetime, whereas the phosphorescence lifetime should go up upon decreasing the temperature. They therefore attributed the emission to some kind of delayed fluorescence. More than a decade later, Lewis et al. investigated the fluorescein molecule (Figure 12) in a solid state boric acid glass medium and found delayed emission by carefully looking at the emission and its lifetime at various temperatures [38]. In 1961, Parker et al. measured the time-resolved emission of eosin (Figure 12) in glycerol and ethanol and found the first example of temperature dependent delayed emission in solution [39].



Figure 12. Chemical structures of fluorescein, eosin Y and phenanthrene.

that triplet-triplet quenching (also known as TTA or triplet fusion) was most likely responsible for the formation of singlet excitons at very long lifetimes [40]. This phenomenon occurs when two excited molecules in the triplet state are in close proximity and energy transfer from one molecule to the other takes place. Two triplet excited states are converted to one singlet excited state and one molecule in the ground state, after which the singlet excited state can decay as delayed fluorescence. The process of TTA was originally named P-type delayed fluorescence after the molecule phenanthrene for which it was first discovered. TTA is here only mentioned because of its historical relevance. The detailed mechanism will be discussed later on when comparing the various triplet upconversion strategies.

Nishikawa *et al.* found E-type delayed fluorescence when trying to analyze porphyrinoid materials (Figure 13) based on their phosphorescence, but instead discovered delayed emission with a similar spectral position as the regular fluorescence [41, 42].



Figure 13. Porphyrinoids used by Nishikawa et al. [40, 41].

They found evidence for thermally activated ISC as well as direct ISC from an upper vibrational energy level of the singlet state to the triplet state. A prerequisite for these processes to occur efficiently is the proximity of the lowest excited singlet and triplet states, so that a small thermal barrier is left for either the ISC or the reverse ISC (rISC) process. The term E-type (E for eosin) delayed fluorescence was coined to describe the phenomenon. A year later, when investigating solutions of anthracene and phenanthrene (Figure 12), they observed similar delayed emission, but from singlet and triplet states that were further apart in energy. Therefore, a thermally activated process was ruled out. Instead, Parker *et al.* found On top of the thermally activated nature, they postulated that the energy gap between the first excited singlet and triplet states should be less than 11 kcal mol<sup>-1</sup> (0.5 eV) as compounds exhibiting a larger singlet-triplet gap would not show delayed fluorescence [42]. Substituting the free-base porphyrins with a metal ion influences the rate of ISC and rISC according to the atomic number of the substituted metal ion, affording increased rates when going from H to Mg<sup>2+</sup> and Zn<sup>2+</sup>. While E-type or thermally activated delayed fluorescence was found in numerous small molecules, such as the aforementioned ones but also in C70 fullerenes [43], benzophenones [44] and aromatic thiones [45], a suitable application was not found.

## 3.2. The theory of TADF

In 2009, Endo *et al.* discovered TADF in tin(IV)porphyrins (Figure 14) and decided to implement them in OLED devices [46]. Their results were in line with the findings of Nishikawa *et al.* [42] that substituting the free-base porphyrins can lead to a significant increase in the observed TADF intensity. Although the compounds still contained a heavy-metal atom, this report sparked the interest in the field and the search for new TADF materials began as scientists started to understand the design principles behind TADF in fully organic molecules.

Following Endo's 2009 work on tin-porphyrins [46], the amount of literature on TADF increased significantly and fully organic emitters for OLED applications were reported soon thereafter. In 2011, the Adachi group published 2-biphenyl-4,6-bis(12-phenylindolo[2,3-*a*]carbazole-11-yl)-1,3,5-triazine (PIC-TRZ; Figure 15) as the first metal-free TADF compound for OLED applications, affording an EQE of 5.3% when doped in 1,3-bis(*N*-carbazolyl)benzene (mCP, 6 wt%) [47]. In the next two years, 10 reports with new emitters were published [48-57]. The best performing compounds from these reports are displayed in Figure 15 and some experimental

data are listed in Table 1. Although these data were obtained through varying methods for the different compounds, they provide a preliminary means of comparison. With EQEs ranging from 4.4% for the earliest work to >13% in the later studies, a huge improvement in OLED efficiency was already achieved. The emission maxima ranged between 485 and 553 for most of the materials and the compounds were largely greenyellow emitting. Only one blue OLED device (based on DBTDO-*t*BuCBZ) had been reported until this point, with red TADF OLEDs not being reported at all.

Compound	$\lambda_{\text{max,em}}$ a	$\Delta E_{ST}$ (meV) <sup>b</sup>	Max EQE (%)	Reference
PIC-TRZ	466	110	5.3	46
Spiro-CN	540	57	4.4	47
CC2TA	490	c	11.0	48
SDB-tBuCbz	424	c	9.9	49
PXZ-TRZ	544	c	12.5	50
ACRFLCN	485	100	10.1	51
4CzIPN	508	83	19.3	52
2PXZ-OXD	517	150	14.9	53
DBTDO-tBuCbz	416	350	c	56
tri-PXZ-TRZ	553	c	13.3	54
ACRSA	494	30	16.5	55

Table 1. Overview of fully organic TADF reports from 2011-2013

- <sup>a</sup> Estimated from electroluminescence or doped-film photoluminescence spectra.
- <sup>b</sup> Calculated from the onset of the prompt fluorescence and phosphorescence or via an Arrhenius plot.
- <sup>c</sup> These values were not reported.



Figure 14. SnF<sub>2</sub>-porphyrins used by Endo et al. to construct TADF-based OLEDs [45].



Figure 15. Chemical structures of the early full-organic TADF emitters listed in Table 1.

As was found by Parker et al. [39] and Nishikawa et al. [42], the mechanism of thermally activated delayed fluorescence relies on a series of excited state processes (Figure 16). When talking in terms of photoluminescence, a photon is absorbed and an electron is promoted from the (generally) singlet ground state to a singlet excited state according to the energy of the absorbed photon and the position of the singlet energy levels of the molecule in question. The excited state rapidly decays to the first excited singlet state in accordance to Kasha's rule [58], which states that internal conversion (IC) from a higher energy excited state to the lowest energy excited state of the same multiplicity occurs faster than any other excited state pathway. After the IC step, ISC from the singlet to the triplet state can occur. As previously discussed for the 2<sup>nd</sup> generation OLEDs, a change in the spin angular momentum has to be overcome by a change of orbital angular momentum through spin-orbit coupling. The use of heavymetal atoms facilitates this transition due to their inherently larger SOC effect. However, the compounds used by Parker et al. [39] and Nishikawa et al. [42] did not contain heavymetal atoms. The intersystem crossing rate  $(k_{ISC})$  is dependent on both the energy difference between the respective singlet and triplet states as well as the amplitude of SOC. A smaller energy difference between the singlet and triplet states leads to a larger  $k_{ISC}$ . Following the initial intersystem crossing, reverse ISC (rISC) can occur, whereupon the exciton goes from the triplet state back to the singlet state. Because the triplet configuration is generally lower in energy than the singlet configuration for a given state in organic compounds, this rISC process is endoenergetic and an energy barrier needs to be overcome. As the name TADF implies, this barrier is overcome using thermal energy. This also means the barrier cannot be too large. Whereas Nishikawa et al. postulated a barrier of approximately 0.5 eV [42], it should be at least below 0.2 eV for efficient rISC [59]. Once the exciton returns to its singlet configuration,

there are two options: either the exciton decays radiatively through fluorescence or it undergoes a second cycle of ISC/rISC. All these processes are dependent on their mutual rates. As was briefly touched upon, IC is typically very fast («  $10^{-9}$  s), while fluorescence occurs at ~ $10^{-9}$  s. ISC and rISC take place on much slower timescales of around  $10^{-7}$  s and  $10^{-6} - 10^{-5}$  s, respectively. The latter is especially slow due to the endoenergetic nature of the process. While phosphorescence is spin-forbidden, it is not entirely impossible. However, due to the SOC dependence, it occurs only at around 10<sup>-3</sup> s. Given these rates, the rate of TADF is effectively governed by the rate of rISC, as it is the slowest step. Delayed emission in TADF emitters is therefore often observed in the microsecond domain [59]. As the singlet state from which radiative decay occurs is the

same for the prompt (~10<sup>-9</sup> s) and the delayed (~10<sup>-6</sup> s) emission, their spectral shape should be identical, as was observed by Parker *et al.* [39] and Nishikawa *et al.* [42], and led them to believe the observed delayed emission could not be coming from phosphorescence.

Moving to OLEDs, where excitons are formed by recombination of electrons and holes rather than via absorption of a photon, the processes involved are the same, with the exception that ISC is no longer a prerequisite for rISC to occur as the excitons are formed in a 25/75 ratio of singlets/triplets (Figure 16). Upconversion of the 75% formed triplet excitons via rISC gives TADF OLEDs the possibility to achieve up to 100% IQE. The former method of analysis via photon absorption rather than electrical



Figure 16. Schematic representation of the photophysical processes occurring upon photon absorption (top) or electrical excitation (bottom). IC = internal conversion,  $k_{nr}^{s}/k_{nr}^{T}$  = rate of non-radiative relaxation from the singlet or triplet state,  $k_{pF}$  = rate of prompt fluorescence,  $k_{DF}$  = rate of delayed fluorescence,  $k_{ISC}/k_{rISC}$  = rate of (reverse) intersystem crossing,  $k_{ph}$  = rate of phosphorescence. Adapted from *Adv. Mater.*, 2014, 26, 7931–7958, with the permission of John Wiley and Sons.

excitation still plays a crucial role as potential emitters are typically characterized in this way before being tested in actual OLED devices. While we discussed the crucial excited state processes for efficient TADF, these are not the only possible pathways for the excitons to traverse along. Non-radiative transitions, such as IC, can also occur between the lowest excited singlet or triplet states and the ground state, resulting in a loss of the exciton energy without the irradiation of visible light. These non-radiative transitions are often coupled with vibrations, rotations of specific functional groups or the molecules as a whole and collisions with other molecules (e.g. in solution) need to be minimized. The key to avoiding these is making the molecule very rigid, so that the possibility for the vibrations and rotations to occur is very low. Therefore, in TADF design, as can be seen in Figure 15, the emitters generally consist of large conjugated and often heteroaromatic systems.

Next to being rigid, the key to designing efficient TADF emitters is to minimize the energy difference between the first excited singlet  $(S_1)$ and triplet  $(T_1)$  states. From quantum mechanics within the single transition approximation (STA), the singlet ( $\Delta E_s$ ) and triplet ( $\Delta E_T$ ) state energies can be written as Eq. 1.1 and 1.2, in which subscripts i and a are used to describe the occupied (often the highest, *i.e.* HOMO) and unoccupied (often the lowest, *i.e.* LUMO) molecular orbitals (MOs;  $\varphi$ ), respectively.  $J_{ai}$  is the Coulomb interaction and  $K_{ai}$  is the exchange interaction between the occupied and unoccupied MOs. The energy difference  $\Delta E_{\rm ST}$  can then be written as Eq. 1.3. The value of  $K_{ia}$  is related to the overlap between  $\phi_i$  and  $\phi_a,$  as indicated in Eq. 1.4. Spatial separation of  $\varphi_i$  and  $\varphi_a$  should therefore lead to a small  $K_{ia}$  and hence a small  $\Delta E_{\rm ST}$ 

$$\Delta E_S = {}^{1}\Delta E_{ai} = (\varepsilon_a - \varepsilon_i) - J_{ai} + 2K_{ai} \qquad \text{Eq. 1}$$

$$\Delta E_T = {}^3 \Delta E_{ai} = (\varepsilon_a - \varepsilon_i) - J_{ai}$$
 Eq. 2

$$\Delta E_{ST} = {}^{1}\Delta E_{ai} - {}^{3}\Delta E_{ai} = 2K_{ai}$$
 Eq. 3

$$K_{ai} = \iint dr \, dr' \varphi_a(r) \varphi_i(r) \frac{1}{|r-r'|} \varphi_a(r') \varphi_i(r') \quad \text{Eq. 4}$$

While the single-transition approximation presents limitations that are corrected using time-dependent density functional theory (TDDFT) calculations (most excited states have contributions from several single-particle transitions), it served as a first design criterion for novel TADF emitters.

In organic materials, the HOMO is typically located on the electron rich parts of the molecule, whereas the LUMO is typically located on the electron poor parts. By connecting an electron-rich moiety (often called electron-donating group or donor "D") to an electron-deficient unit (often called electron-accepting group or acceptor "A") via a covalent bond, localization of the frontier orbitals is only achieved to a given extent so that overlap remains present, leading to relatively large values of  $\Delta E_{sT}$ . By spatially twisting the D and A groups in a molecule, the conjugation will decrease as the  $\pi$ -orbital overlap diminishes (Figure 17). This also leads to a better separation of the HOMO and LUMO [59]. Therefore, the most used strategy to obtain a small  $\Delta E_{\rm st}$  is to provide sufficient steric hindrance between the D and A parts of a molecule to ensure a large dihedral angle between the two moieties [60]. Color tuning is then done by combining weaker or stronger donor or acceptor units to obtain more blue or red-shifted emission, respectively [61]. Alternatively, sp<sup>3</sup>-hybridized linkages such as a spiro conjugation can be applied as the lack of non-hybridized p-orbitals in an sp<sup>3</sup>-hybridized atom breaks up the conjugation and also leads to HOMO-LUMO separation (Figure 17) [62]. Unfortunately, a trade-off exists between the frontier orbital overlap and the rate of fluorescence  $(k_{PF})$  [59]. The oscillator strength determines the strength of the coupling between the singlet ground and excited state. Excitations with a smaller oscillator strength show weaker absorption and emission intensity than excitations with a large oscillator strength. The size of the oscillator strength is determined by the overlap between the orbitals that are involved in the given transition. For a HOMO→LUMO transition for example, a large overlap between the HOMO and LUMO will lead to a large oscillator strength, if the symmetry conditions are also fulfilled, and a localized excited state (<sup>1</sup>LE state, superscript 1 for

singlet and 3 for triplet states), whereas a small overlap leads to a charge-transfer state (<sup>1</sup>CT state, superscript 1 for singlet and 3 for triplet states) with a small oscillator strength. As the requirements for TADF include a small orbital overlap, typically for the HOMO and LUMO, these transitions are paired with a small oscillator strength, which is unfavorable for the fluorescence efficiency. Luckily, TADF emitters with a high  $k_{\rm PF}$  and fluorescence quantum yield have been reported, indicating a less straightforward relationship between  $\Delta E_{\rm ST}$  and  $k_{\rm PF}$ .

#### 3.3. The spin-vibronic mechanism of TADF

Due to the structural design of TADF emitters, they often exhibit charge-transfer character in their transitions. Initially, the mechanism of TADF was therefore expected to result from direct (r)ISC between the first singlet and triplet excited CT states (*i.e.* <sup>1</sup>CT and <sup>3</sup>CT). However, the law of conservation of momentum forbids a change in spin angular momentum without a corresponding change in orbital angular momentum, or in other words, a <sup>1</sup>CT $\rightarrow$ <sup>3</sup>CT transition between states of the same nature is not possible as there is no change in orbital angular momentum [63, 64], which is also known as El-Sayed's rule [63]. Hyperfine coupling induced ISC was proposed as an alternative mechanism based on timeresolved electron paramagnetic resonance (EPR) methods [65], but due to the small values for hyperfine interactions (HFI), usually in the range of 10<sup>-4</sup> meV, it is unlikely that HFI alone can induce strong (r)ISC in these systems [66]. Furthermore, two experimental reports showed that the rate of reverse intersystem crossing  $(k_{rISC})$  is not directly related to the size of  $\Delta E_{ST}$ [67] and that, in some systems, it is possible to tune the excited states involved in the rISC step independently by changing the surrounding of the emitter [57, 68]. These findings lead to a more dynamic rISC process, which is not strictly governed by  $\Delta E_{\rm ST}$  and not strictly occurring between CT states. Chen et al. tried to calculate  $k_{rISC}$  occurring via SOC, but found a significant deviation from experimental values, even for the  $^{1}CT \rightarrow ^{3}LE$  transition, which is allowed according to El-Sayed's rule [69]. Marian used multireference methods to show that direct SOC was too small to explain the efficient rISC observed in TADF, in agreement with the work by Chen et al. [69]. Instead, she proposed vibrational mixing between the <sup>3</sup>CT and an energetically close <sup>3</sup>LE state to be responsible for the efficient rISC [70-72]. Gibson et al. further elaborated on this and



Figure 17. Optimized geometries, HOMO and LUMO topologies for a spiro conjugated (ACRFLCN) and a D-A based (DBTDO-tBuCbz) TADF emitter obtained using DFT (M06/6-311G(d)) (structures in Figure 15).

showed, through quantum dynamics simulations, the role of vibrational-electronic (vibronic) coupling of excited triplet states on  $k_{ISC}$  and  $k_{rISC}$  [66]. These results show how vibronic coupling helps to explain why compounds with an apparently large  $\Delta E_{ST}$  can still show TADF.

Experimentally,  $\Delta E_{sT}$  is obtained from the onset of the prompt fluorescence (singlet energy) at room temperature and delayed phosphorescence (triplet energy) at 80 K, both occurring from the lowest energy excited state for each multiplicity. The phosphorescence spectra are taken at 80 K because this transition is spin-forbidden and nonradiative losses dominate at room temperature. Decreasing the thermal energy and locking the conformation in a solid matrix allows the generally weak and red-shifted phosphorescence to be observed. The vibronic mechanism, however, couples the lowest excited triplet state to a higher energy excited triplet state to create 'mixed' states which are closer in energy to <sup>1</sup>CT. The energy gap that triplet excitons need to overcome to undergo rISC is therefore smaller than the experimental  $\Delta E_{sT}$  (Figure 18) [60].

#### 3.4. TADF emitters

In TADF literature, most reports deal with the design of novel (efficient) blue emitters. While  $2^{nd}$  generation phosphorescent OLEDs are commercially viable for green and red emission,

blue phosphorescent emitters suffer from instability due to the relatively weak metal-ligand bond and the inherently high triplet energy needed for blue emission. Blue TADF emitters might be able to overcome these issues, but their design is not straightforward. As mentioned before, blue CT emission can be achieved when relatively weak donor and acceptor units are coupled together. However, as their electron-donating and accepting properties become weaker, so does the CT character of their transitions and hence  $\Delta E_{\rm st}$  becomes larger. Another issue is the use of 9,9-dimethyl-9,10-dihydroacridine (DMAC), 10H-phenoxazine (PXZ) or 10H-phenothiazine (PTZ) as the electron-donating groups. While these groups provide large steric hindrance and good HOMO/LUMO separation, their strong electrondonating properties red-shift the emission, often leading to a blueish/green emission. Similarly, when the acceptor unit is too strong, the emission is also red-shifted and becomes green or even yellow. This explains why the first reported TADF materials were predominantly green or yellow emitters (Table 1, Figure 15). Nonetheless, the design of blue emitters has been successful, as demonstrated by the large amount of entries in review articles, some of them affording OLEDs with EQEs above 20% [36, 61, 73-76]. Unfortunately, most blue TADF emitters still suffer from rapid and significant roll-off of the device efficiency and more research to find stable blue emitters is required [77-80].



Figure 18. Schematic overview of the spin-vibronic mechanism for TADF. Vibronic coupling (VC) between  $T_1$  and  $T_2$  ensures population of the  $T_2$  state regardless of the available thermal energy, resulting in a smaller effective  $\Delta E_{sr}$ .

Another consequence of having strong CT character is the inherent broadness of the CT emission (FWHM > 50 nm), leading to reduced color purity, which is desired for OLED display applications. Recently, a new series of boronbased emitters has been proposed with extremely narrow (FWHM < 30 nm) emission profiles [81-863]. These emitters have been termed multi-resonance (MR) TADF emitters as they allow for a small  $\Delta E_{sT}$ , large  $k_{f}$ , high oscillator strengths and narrow emission via the opposing resonance effects of boron and nitrogen [81-83]. The emitters are based on the 5,9-diaza-13bboranaphtho[3,2,1-*de*]anthracene (DABNA) core and afford deep-blue emission. Variations on this core have been made by incorporation of several peripheral groups (DABNA-1 and DABNA-2) [84], tert-butyl groups (t-DABNA) [85] or by fusing two DABNA cores together (v-DABNA) [86]. While these MR-TADF materials still suffer from rapid roll-off, they are among the best performing and most promising blue TADF-based OLED materials to date.

On the other end of the spectrum are the red TADF emitters. These have received less initial interest because there are sufficient red-emitting phosphorescent complexes available (Figure 11), affording OLEDs with decent EQEs. While red emitters do not suffer so much from instability issues, their PLQY is often much lower due to the so-called energy gap law [87, 88]. As the energy gap between the ground and excited state becomes smaller, non-radiative transitions become more plausible as the upper vibrational states of the electronic ground state start to overlap with those of the electronic excited states. Because of this,

the highest EQEs reported are in the range of 10-20%, with a few outliers above 20% [61, 89]. In 2018, Chen et al. reported a summary of red emitters with a maximum electroluminescence wavelength of 600 nm or larger [90]. Additionally, due to their fully organic, and thus non-toxic nature, they have found application in other fields outside of OLEDs. In 2014, Xiong et al. showed that a fluorescein derivative showing delayed fluorescence could be used for time-resolved fluorescence imaging in biological cells. Due to the long-lived nature, the cell autofluorescence dies out before the fluorescein delayed emission, enabling to enhance the imaging contrast [91]. Furthermore, the red-shifted emission of such materials makes them viable for operation in the so-called phototherapeutic window (600-1200 nm). Several other reports using TADF emitters for time-resolved imaging have been made since [92-97].

Similar to the first generation OLED materials, researchers have tried to incorporate the principles of TADF in other types of molecules such as dendrimers and polymers. The main advantages of dendrimer and polymer structures include facile processing via spin- or spraycoating for large area applications such as television screens and solid-state lighting [76]. Both fully and partially conjugated dendrimers have been made (Figure 20). In both cases, the dendrimer core consists of a TADF emitter which is responsible for the photophysical properties. The dendrons in conjugated dendrimers often consist of extended carbazole networks [98-101], whereas in partially conjugated dendrimers a short aliphatic chain connects the core with



Figure 19. Chemical structures of some DABNA-based blue MR-TADF emitters [84-86].



Figure 20. Molecular structures of two types of dendritic TADF emitters based on fully<sup>98</sup> (left) and partially [102] (right) conjugated dendrons. The acceptor and donor units are indicated in red and blue, respectively.

the conjugated dendrons [102, 103]. For a more extensive overview of dendritic TADF materials, several reviews can be consulted [74, 76, 104].

For polymer-based TADF OLEDs, several design strategies are available. First, a distinction between non-conjugated and conjugated backbones can be made (Figure 21). Within the polymers with a conjugated backbone, a second division can be made between polymers in which the backbone consists of alternating D and A units (Figure 21b) and polymers in which the backbone consists of (a single or alternating) D units to which the A unit is grafted as a side chain (Figure 21c). The opposite case in which the backbone is constructed of A units is less straightforward as the reactive sites used for polymerization are the same as those used for the construction of the D-A bond. In nonconjugated polymers (Figure 21), the backbone is formed by polymerization of styrene-like [105-108] or acrylate [109] monomers via controlled free-radical polymerization techniques or by functionalized norbornenes [110] via ring-opening metathesis polymerization (ROMP). A TADF emitter is incorporated in the monomer structure and is copolymerized with another monomer containing a hole-transporting functionality such as carbazole.



Figure 21. Design motifs for TADF-based polymers. Adapted from *The Chemical Record*, 2019, 19, 1624-1643, with the permission of John Wiley and Sons.

Conjugated D-A alternating copolymers consisting of twisted D-A units suffer from poor charge transport along the polymer backbone and therefore these polymers need to have an additional charge-transporting host material in which they are imbedded [111]. To reduce self-quenching and to improve the charge carrier mobility, either a non-conjugated spacer can be incorporated between the various D-A blocks [112] or the D-A TADF emitters were copolymerized with an additional donor unit which acts as a kind of host material [113] The most employed strategy is copolymerization of multiple, typically one or two, donor units to one of which an acceptor unit is grafted. The other donor unit in the backbone then acts as a kind of host material, improving charge carrier mobility, and is sometimes functionalized to further improve these properties [74, 76, 111, 114-120].

## 4. Alternative triplet upconversion strategies

## 4.1. Triplet-triplet annihilation

Since the discovery of TTA, sometimes called triplet fusion (TF), in 1962 by Parker et al. [40] (vide supra), it is well known as an upconversion mechanism to form singlet excited states. Proceeding via a Dexter energy transfer mechanism (Figure 22), two molecules with excited triplet configurations need to be in close proximity to form one de-excited molecule and one molecule with an excited singlet configuration. As twice the triplet excitation energy is generally larger than the first singlet excitation energy, it can occur that a higher singlet state  $(S_n)$  is formed first, after which IC takes place to arrive at the first excited singlet state  $(S_1)$ , followed by fluorescence (Figure 22). In time-resolved emission spectroscopy, TTA can be distinguished from other types of delayed

emission by varying the laser power and looking at the delayed emission intensity. When the emission intensity increases linearly with a slope of 2 in a log-log plot versus the laser energy, the emission is coming from TTA, whereas a slope of 1 indicates TADF. This is because the likelihood of two triplet excitons being in close proximity increases with high exciton formation. The TTA mechanism is especially prevalent under electrical excitation where, according to spin statistics, 75% of the excitons are formed in the triplet configuration. However, because two triplet states are converted to one singlet state, the IQE of a resulting OLED can only be 62.5% (initial 25% plus half of the triplet states formed), which is significantly lower than the 100% IQE achievable via phosphorescent or TADF-based OLEDs. Nevertheless, TTA has played a significant role in the development of early OLED devices, and to this day remains an attractive prospect for the fabrication of blueemitting OLEDs. As early fluorescent devices were only able to effectively use 25% of the formed excitons, the device EQEs were theoretically limited to  $\sim 5\%$ , taking into account a device outcoupling efficiency of approximately 20%. However, reports of fluorescent OLEDs with EQEs above the theoretical limit of 5% do exist. While other effects such as increased device outcoupling or improved selectivity for the generation of singlet excitons upon electrical excitation are possible, they are unable to account for the large increase in EQE. In 1998, Kido and Iizumi were



Figure 22. Schematic overview of Dexter energy transfer in TTA (left) and how it leads to singlet emission by combining 2 excited triplet states (right). ET = energy transfer, NR = non-radiative relaxation.

the first to suggest TTA as the plausible pathway for their record EQE (at the time) of 7.1% [121]. In 1999 and 2003, Partee et al. [122] and Sinha and Monkman [123] reported TTA as an efficiency boosting mechanism in PPV and MEH-PPV based OLEDs, respectively. In many other reports throughout the beginning of the 21st century, TTA is the likely candidate to explain EQEs above 5% for traditional fluorescent OLEDs. However, with the advent of phosphorescent and TADF-based OLEDs, research in this area has slowed down, with the exception of blue-emitting materials [117-119]. Despite the promise and achievement of higher EQEs for blue-emitting OLEDs using either phosphorescent iridium or TADF-based emitters, they both lack in device lifetime, while color purity is also an issue for the latter [124-126]. Poor electrochemical stability as a result of the fluorine substituents typically used for blue Ir-complexes (Figure 10) and instability of the metal-ligand bonds due to the high triplet energy (>2.7 eV) causes the blue phosphorescent OLEDs to have poor operation lifetimes [126]. While TADF emitters do not suffer from the same metalligand related issues, the inherently high triplet energy still causes deterioration of the emitter, with relatively short lifetimes as a result [126]. Furthermore, the CT character of the emission leads to broad emission peaks, affording inferior color purity with respect to the phosphorescent or fluorescent competitors. Blue fluorescent emitters suffer less from these instability issues due to their simpler molecular structures and as such are only hindered by the maximal attainable IQE of 25%. An upconversion mechanism such as TTA is able to boost this to 62.5% and hence can make blue emitters based on TTA viable, as apparent in recent literature [127-129].

## 4.2. Hybridized local and charge-transfer states

Proposed in 2013 by Ma and co-workers, hybridized local and charge-transfer (HLCT) poses an alternative but similar mechanism to that of TADF (Figure 23) [130]. The HLCT mechanism relies on intersystem crossing between an upper excited triplet state ( $T_n$ , n > 1) and an excited singlet state ( $S_n$ , n > 0). HLCT emitters rely on significant LE character in their first excited singlet state to ensure efficient coupling to the singlet ground state for a high PLQY. Two upper excited states of singlet and triplet multiplicity have to be in close energetic proximity for (r)ISC to occur. The lowest excited triplet state T<sub>1</sub>, typically of LE nature, has to be significantly below  $T_2$ , typically of CT nature, and  $S_1$  to reduce IC from  $T_2$  to  $T_1$ and to prevent TADF from happening from T<sub>1</sub> as large energy gaps reduce the coupling between the various states. ISC is enhanced when the upper states show hybrid LE/CT character [131], which circumvents El-Sayed's rule, but this is not a prerequisite for the HLCT mechanism to occur. Time-resolved emission measurements show that these emitters only have a single lifetime, instead of two as for TADF, indicating a k<sub>rISC</sub> larger than  $k_{PF}$ . The HLCT mechanism thus indirectly increases the amount of excitons in the singlet configuration beyond the statistical 25%, while HLCT materials act as regular fluorescent emitters beyond the initial rISC step. To obtain excited states with hybrid LE/CT character, twisted D-A structures are designed (Figure 23) and (TD)DFT calculations are performed to assess the character and the position of the upper excited states as these are difficult to determine experimentally.

IC is the favored transition according to Kasha's rule (*vide supra*) and the HLCT rISC mechanism is therefore not as efficient as the (r)ISC pathways of TADF can be. This means a significant portion of the 75% formed triplet excitons will still decay non-radiatively to  $T_1$  ( $k_{IC}$ ), where they are effectively trapped until they can further decay non-radiatively to the ground state ( $k_{nr}^T$ ). As a result, EQEs using this approach have only been around 10% [132, 133]. Because of its heavy reliance on quantum chemical calculations, lack of structure-property relationships that can be deduced and non-ideal working conditions, the HLCT mechanism is currently of less interest to obtain high-efficiency OLEDs.

# 5. TADF or TTA-sensitized fluorescence

Before the discovery of the multi-resonance DABNA emitters (*vide supra*), researchers were already looking for ways to decrease the emission



Figure 23. Simplified schematic overview of the HLCT triplet upconversion mechanism (left) and chemical structures of some highly efficient HLCT emitters: TPMCN [128], P-TXO2 [131], BTH-DMF [132] and TPA-NZP [130] (right).

width(toachievehighercolorpurity)andtoimprove on device stability. In 2014, an alternative OLED design strategy was reported by combining a TADF emitter with a fluorescent emitter doped in a wideenergy-gap host material in the active layer [134]. This strategy is sometimes called generation 3.5 and was termed hyperfluorescence<sup>TM</sup> by Kyulux. The TADF emitter is used as an assistant dopant and is chosen as such that its singlet and triplet energy levels are above those of the fluorescent emitter. Subsequently, exciton formation occurs on the assistant dopant and the triplet excitons are converted to the assistant dopant singlet state through rISC. Förster resonance energy transfer (FRET) allows transfer of the singlet excitons from the TADF assistant dopant to the narrowwidth, high-PLQY fluorescence emitter (Figure 24). The positioning of the energy levels of the assistant dopant and the fluorescent dopant are crucial and careful tuning is necessary to allow exciton formation solely on the assistant dopant and efficient energy transfer to the fluorescent dopant [135, 136]. To help achieving this, the assistant dopant is typically doped at 10–50 wt%, whereas the fluorescent emitter is doped at very low concentrations (below 5 wt%). This sensitized approach allows optimal usage of excitons (up to 100% IQE) in combination with the narrow emission width, high PLQY and large  $k_{pF}$  of the fluorescent emitter [135]. However, because an additional energy transfer step is required for the

fluorescent emitter, the design of these systems requires even more tuning of the energy levels of the OLED layers and active materials [136].

While the advent of TADF sparked new hope for stable blue-emitting materials, large rolloff of the device efficiencies remained, even for blue TADF materials. The main problem is the inherently high-lying triplet state, a property that all blue phosphorescent and TADF materials share, which leads to rapid degradation of the OLED devices [126, 137-139]. Even with the TADF-sensitized fluorescent OLED approach, the concentration of the TADF dopant is sufficiently high to have a rapid decrease in device efficiency. Alternatively, TTA molecules can be used for triplet upconversion in combination with a fluorescent emitter via the same mechanism [140]. The benefit of TTA molecules is the presence of low-lying triplet states ( $S_1 \approx 2x T_1$ ), which give the TTA molecules greater stability [141]. The downside of the TTA mechanism is the limited IQE of 62.5 % which can be obtained when all triplet excitons are upconverted (vide supra). These TTA-sensitized fluorescent OLEDs will give lower overall device efficiencies but improved device lifetimes over their TADF counterparts. It is then up to industry to determine how to best manage these advantages and disadvantages in order for the development of OLEDs to move forward.



Figure 24. Schematic overview of the TADF-sensitized fluorescent OLED design.

# 6. Rational design of TADF emitters through a joint synthetic and computational chemistry approach

In the past couple of years, the author of this overview article has collaborated on the tailored design of novel TADF emitters by combining quantum-chemical (TDDFT), synthetic, and photophysical analysis efforts. In the final section, a short summary of the most important results obtained so far is given.

The use of TDDFT calculations to predict the excited state properties of conjugated materials has become commonplace in organic electronics research. To better understand how different exchange-correlation functionals (XCFs) influence the obtained excited state properties of potential TADF materials, a series of 10 prototypical donor-acceptor compounds were subjected to thorough investigation with DFT and TDDFT and their excited state properties such as the excitation energies and oscillator strengths were calculated using 19 different XCFs with various levels of complexity [142]. These values were benchmarked against a high level wavefunction method called resolution-ofthe-identity second order approximation coupledcluster (riCC2). The best performing functional was the long-range corrected LC-BLYP with a value for  $\omega$  of 0.17 bohr<sup>-1</sup>. Application of the Tamm-Dancoff approximation [143] (often used to overcome triplet instabilities) was found to improve the error on the triplet excitation energies with respect to those obtained using riCC2, and resulted in even smaller errors for the singlet-triplet energy splittings.

One of the main research lines in our research groups is to expand on the known pool of donor and acceptor moieties that can be used to construct D-A and D-A-D type emissive materials for 3<sup>rd</sup> generation OLEDs. To achieve this, other fields of organic electronics, most notably the field of organic photovoltaics (OPVs), serve as an inspiration for new building blocks that have not been applied before in the field of OLEDs. With the help of quantum chemistry methods such as those mentioned before, we are able to rationally design new emitters based on the findings from the calculations. One such donor unit that we have benzo[1,2-*b*:4,5-*b*']dithiophene introduced is (BDT), a well-known OPV donor unit as it possesses a high electron-donating strength, high planarity and often affords a high charge carrier mobility. Unfortunately, conventional coupling of this unit via the  $\alpha$ -positions would lead to planar D-A molecules, not likely to show TADF properties. As such, a synthetic pathway to couple the donor and acceptor units via the benzene core



Figure 25. Molecular structures of the BDT-TIPS, DMAC and DTP-based compounds.

of BDT had to be developed. The BDT unit was coupled to 3 different acceptors: 9,9-dimethyl-9H-thioxanthene-10,10-dioxide (TXO2) [144], dibenzo[a,c]phenazine-11,12-dicarbonitrile (CNQxP) [144] and difluorodithieno[3,2*a*:2',3'-*c*]phenazine (DTPz) (Figure 25) [145]. To compare their properties, the 9,9-dimethyl-9,10-dihydroacridine (DMAC) analogues were designed. On top of that, the DTPz unit is also a new strongly electron-accepting unit which has been used for the construction of TADF materials for the first time [145]. Photophysical characterization in zeonex films showed prompt and delayed emission for all 6 compounds (Figure 26). However, their nature differed. The DMAC-containing compounds showed TADF, whereas the BDT-based compounds showed room temperature phosphorescence (RTP) when TXO2 and DTPz were chosen as the acceptor and TADF when CNQxP was chosen as the acceptor. The RTP behavior of TXO2-BDT-TIPS (Figure 26a) is unusual and was attributed to the presence of multiple sulfur atoms in the BDT unit. Therefore, we investigated the BDT-TIPS donor unit by itself and found similar RTP behavior in zeonex film. The RTP emission of DTPz-BDT-TIPS differed from that of TXO2-BDT-TIPS and was attributed to phosphorescence coming from the DTPz core instead. CNQxP-BDT-TIPS and CNQxP-DMAC showed long-lived TADF with some TTA at

very long emission times. The main difference between TXO2-BDT-TIPS and CNQxP-BDT-TIPS is the acceptor strength. While the localized triplet state of the BDT-TIPS group, responsible for the phosphorescent behavior, is below the CT states for TXO2-BDT-TIPS, this is not the case for CNQxP-BDT-TIPS. The smaller experimental singlet-triplet energy splitting also resulted in the possibility of rISC to occur for CNQxP-BDT-TIPS, whereas this is not possible for TXO2-BDT-TIPS.

In addition to the introduction of the BDT and DTPz units, 4H-dithieno[3,2-b:2',3'-d] pyrrole (DTP; Figure 26) was chosen as the donor unit to replace 9H-carbazole in 4CzIPN (Figure 15) [146], originally reported by Adachi and coworkers [46]. It was further studied by Etherington et al. [147] and was found to show extensive dimer formation in doped OLED films originating from interactions between the carbazole units of different molecules. Dimer emission is undesired in OLED devices as it compromises the color purity. Synthesis of the DTP unit via a carbamate intermediate allows the free-base DTP to be obtained after which it can be used in nucleophilic aromatic substitution or Buchwald-Hartwig type reactions to form D-A or D-A-D type materials. The former was applied to construct 4DTP-IPN, using similar reaction conditions as for the synthesis of 4CzIPN. 4DTP-IPN showed red-shifted emission with respect to that of 4CzIPN and exhibited TADF properties in a variety of films and at different concentrations. Unfortunately, instead of removing the dimerization, the DTP unit enhances aggregation and it persists even at 0.01 wt% doping in polymer and small molecule films. While this enhances the color purity of the emission, the PLQY drops because of the aggregational quenching and this is obviously not desired for OLED applications.



Figure 26: Normalized time-resolved emission spectra for BDT-TIPS-based compounds (left) and DMAC-based compounds (right) in zeonex at room temperature. The colour intensity shows the emission wavelength at various emission times during the decay. When the delayed emission appears at the same wavelength as prompt emission, triplet upconversion mechanisms such as TADF and TTA are at play. For TXO2-BDT-TIPS and DTPz-BDT-TIPS, the delayed emission corresponds to the triplet emission at 80K. Adapted from *Dyes and Pigments*, 2021, 186, 109022 and *Dyes and Pigments*, 2021, 190, 109301, with the permission of Elsevier [143, 144].

## 7. Conclusions

In the presented work, a historic overview of some crucial discoveries in the field of organic light-emitting diodes is given. Special attention is devoted to the principle of thermally activated delayed fluorescence or TADF for triplet upconversion as this is the most researched sub-topic in the field at present. While device stability and lifetime for blue emitters is still an issue, solutions are presented by the TADF and TTA-sensitized fluorescent OLEDs and these technologies could bring additional relevance to the field of OLEDs in the years to come. The interplay of quantum-chemical calculations, synthesis efforts and detailed (time-resolved) photophysical analysis seems crucial to foster further progress.

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