

# Journal of Photonics for Energy

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Daniel Volz, "Review of organic light-emitting diodes with thermally activated delayed fluorescence emitters for energy-efficient sustainable light sources and displays," *J. Photon. Energy* **6**(2), 020901 (), doi: 10.1117/1.JPE.6.020901.

# Review of organic light-emitting diodes with thermally activated delayed fluorescence emitters for energy-efficient sustainable light sources and displays

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**Abstract.** Thermally activated delayed fluorescence (TADF) is an emerging hot topic. Even though this photophysical mechanism itself has been described more than 50 years ago and optoelectronic devices with organic matter have been studied, improved, and even commercialized for decades now, the realization of the potential of TADF organic light-emitting diodes (OLEDs) happened only recently. TADF has been proven to be an attractive and very efficient alternative for phosphorescent materials, such as dopants in OLEDs, light-emitting electrochemical cells as well as potent emitters for chemiluminescence. In this review, the TADF concept is introduced in terms that are also understandable for nonchemists. The basic concepts behind this mechanism as well as state-of-the-art examples are discussed. In addition, the future economic impact, especially for the lighting and display market, is addressed here. We conclude that TADF materials are especially helpful to realize efficient, durable deep blue and white displays. © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: [10.1117/1.JPE.6.020901](https://doi.org/10.1117/1.JPE.6.020901)]

**Keywords:** organic light-emitting diode; display; solid state lighting; thermally activated delayed fluorescence; singlet harvesting.

Paper 16024MVSS received Mar. 1, 2016; accepted for publication Mar. 31, 2016; published online Apr. 25, 2016.

## 1 Introduction

### 1.1 Thermally Activated Delayed Fluorescence as an Emerging Trend in Optoelectronics

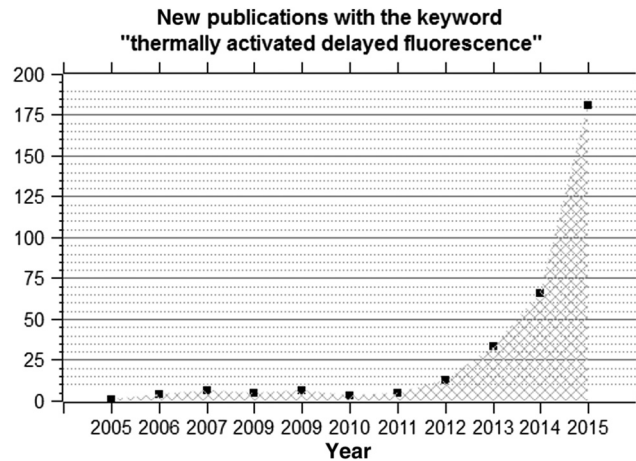
The transformation of electrical energy into visible light has remained an important issue for scientists and engineers, even more than a century after the development of the incandescent lightbulb by Swan, Edison, and others.<sup>1,2</sup> One of the new emerging topics in this niche of material sciences is emitting materials that feature thermally activated delayed fluorescence (TADF). Although TADF has been known since 1960,<sup>3</sup> the potential use of TADF emitters in optoelectronic devices has been proposed independently by several groups led by Adachi et al.<sup>4-6</sup> (organic and tin emitters), Deaton et al.,<sup>7</sup> Yersin et al.,<sup>8</sup> and others.<sup>9-12</sup> The rise of the TADF-topic is reflected by an exploding number of new peer-reviewed publications dealing with it in general (Fig. 1), peaking close to 200 in 2015. Note that Refs. 4-8, which propose and show the use of such materials in organic light-emitting diodes (OLEDs) for the first time, have been published between 2009 and 2012, suggesting that the rise of this concept was directly related to a potential (industrial) application in OLEDs. Occasionally, synonyms such as “singlet harvesting”<sup>13-16</sup> or “E-type fluorescence”<sup>7,17,18</sup> are also being used in the literature.

The aim of this review article is to briefly introduce this concept and outline its impact on photonics, especially with respect to its potential concerning the realization of energy-efficient solid-state lighting and display devices. The scope of this article does not include any in-depth

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This review manuscript is also part of the section on “Breakthroughs in Photonics and Energy,” highlighting primarily recent advances in the last three years.



**Fig. 1** TADF-related publications per year according to Scifinder as of February 2016.

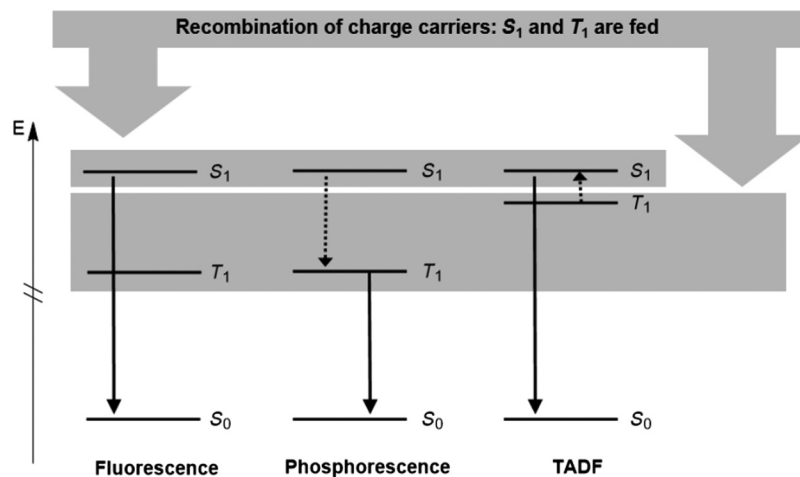
discussion of the molecular structure of TADF molecules or device architectures, which can be found elsewhere.<sup>19–22</sup>

### 1.2 What Is Thermally Activated Delayed Fluorescence?

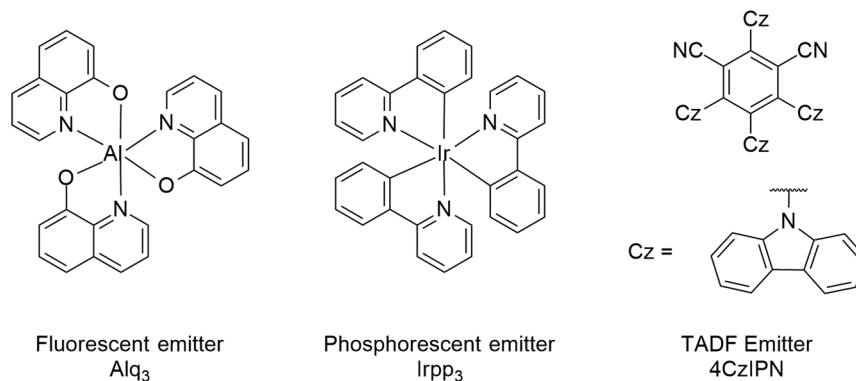
Upon recombination of charge carriers in any electroluminescent device, two different types of excitons are formed: singlet excitons having a spin  $S = 0$  and triplet excitons with  $S = 1$ .<sup>23</sup> Due to quantum statistics, the relative probability for the formation of singlet and triplet excitons is 25% to 75%.<sup>13,24,25</sup> In order to realize efficient OLEDs, it is crucial to harvest both singlet and triplet excitons for the generation of photons. Currently, there are three main emissive mechanisms available to harvest excitons: fluorescence, phosphorescence as well as TADF. A schematic overview of these mechanisms is shown in Fig. 2.

On a side note, there are also more complex schemes, which usually require at least a bimolecular, often trimolecular emitting mechanism (e.g., multiple species between which energy can be transferred) such as *P*-type delayed fluorescence or triplet–triplet annihilation,<sup>26–29</sup> hyperfluorescence,<sup>30</sup> exciplex emission,<sup>6</sup> and exciplex-assisted emission.<sup>31–34</sup> These mechanisms will not be covered in this article.

Fluorescent molecules have a relatively large energetic difference between the  $S_1$  and  $T_1$  state. This difference is also known as the singlet–triplet splitting or  $\Delta E (S-T)$ .<sup>13</sup> In addition,



**Fig. 2** Schematic comparison between fluorescence, phosphorescence, and TADF. Straight arrows represent emissive transitions, while dotted arrows indicate up- or down-conversion processes (ISC and rISC).



**Fig. 3** Molecular structure of Alq<sub>3</sub>, Irpp<sub>3</sub>, and 4CzIPN.

they usually show very weak intersystem crossing (ISC) and reverse intersystem crossing (rISC), meaning that the transformation of singlet ( $S_1$ ) into triplet excitons ( $T_1$ ) and vice versa is quantum-mechanically forbidden, therefore both slow and unlikely.<sup>23</sup> The same is true for any transitions between  $T_1$  and the singlet ground state  $S_0$ .<sup>35,36</sup> Because of these limitations, triplet excitons cannot be harvested with fluorescence, limiting the overall efficiency of such OLEDs to 25%.<sup>13</sup> An archetypical fluorescent OLED emitter is aluminum-tris-(8-hydroxyquinoline) (Alq<sub>3</sub>; Fig. 3).<sup>37–40</sup>

Phosphorescent molecules<sup>41</sup> share a rather larger  $\Delta E$  ( $S-T$ ) value with their fluorescent counterparts. On the other hand, ISC is very strong, leading to a prompt transformation of any singlet into triplet excitons. Because of the ISC, which is the result of the presence of heavy transition metals such as iridium, platinum, and osmium, the transition between  $T_1$  and  $S_0$  is possible.<sup>35,36</sup> Connected to this is the term triplet harvesting, because all excitons are harvested via the triplet state  $T_1$ .<sup>13</sup> With this, it was first possible to harvest all generated excitons, which resulted in highly efficient OLEDs.<sup>42,43</sup> An archetypical phosphorescent OLED emitter is iridium-tris-(2-phenylpyridine) (Irppy<sub>3</sub>; Fig. 3).<sup>44,45</sup>

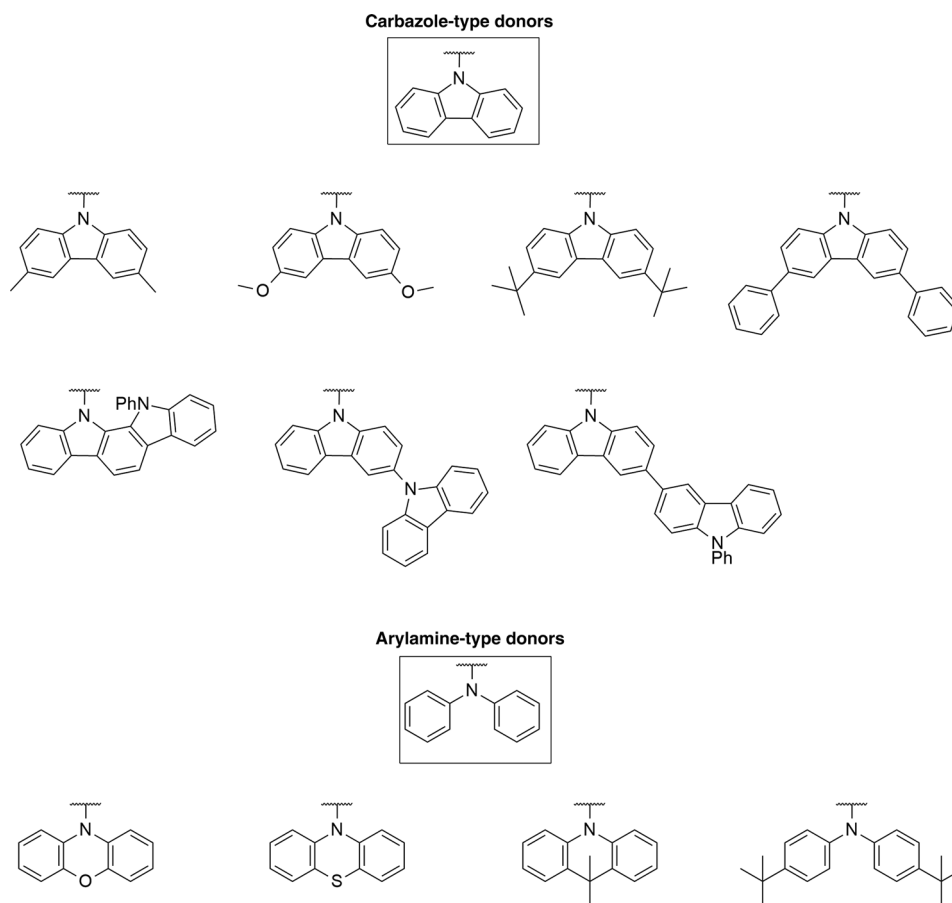
TADF molecules have a low  $\Delta E$  ( $S-T$ ), typically in the order of several hundreds of meV, and mediocre ISC and rISC.<sup>21</sup> Although direct transitions between  $T_1$  and  $S_0$  are still forbidden, it is possible to go from  $T_1$  back to  $S_1$  by means of rISC, if the thermal energy  $k_bT$  is sufficient. Compared with normal fluorescence, where the excited-state lifetime is in the order of ns, the excited-state lifetime is longer, often in the order of  $\mu$ s or more—the term TADF accounts for these observations. Occasionally, the term singlet harvesting<sup>14–16,46</sup> is used, because all excitons are harvested via the singlet state  $S_1$ .<sup>13</sup> A typical TADF emitter is tetrakis-*N*-carbazoyl-isophthalonitrile (4CzIPN; Fig. 3).<sup>5,47–49</sup>

In summary, TADF is an alternate concept, which can help to realize efficient OLEDs with maximum efficiency. It competes with phosphorescence, the commercial state-of-the-art solution for efficient OLEDs.

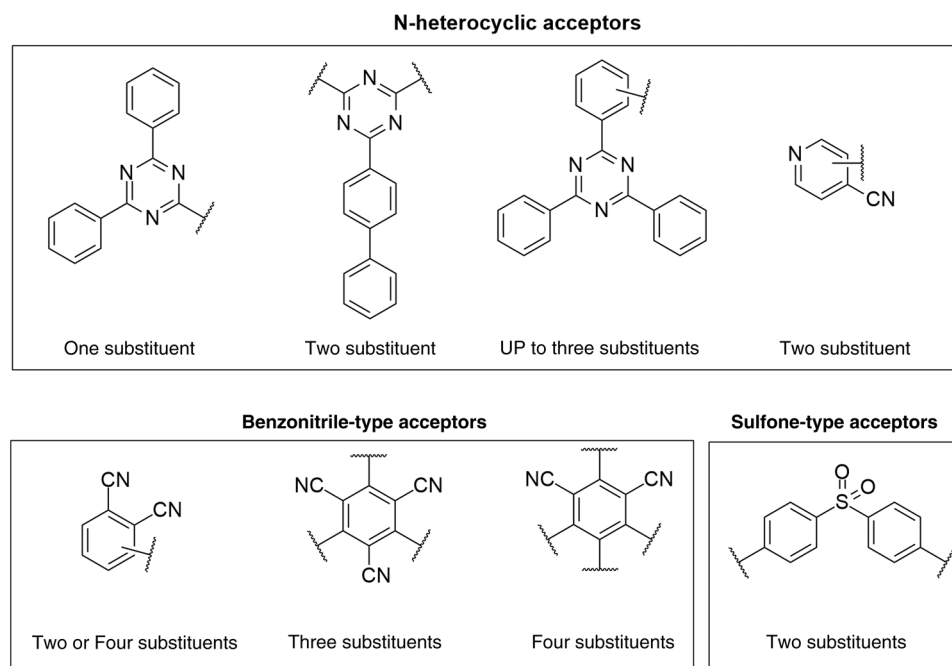
## 2 Conceptual Background of Thermally Activated Delayed Fluorescence

### 2.1 Molecular Design Principles

Without going too much into detail, all TADF emitters consist of donor and acceptor moieties. In a way, they are similar to so-called ambipolar host molecules and often even contain similar building blocks, which are either arranged in a different way or used in different combinations in order to realize the large bandgap, which is needed to accommodate dopant molecules.<sup>50–55</sup> In both hosts and TADF emitters, donor moieties are electron-rich functional units that have a rather deep HOMO, which allow them to be oxidized easily and partake in the transport of holes. Contrarily, acceptor moieties are electron-deficient functional units with a deep LUMO. They can be reduced and thus partake in the transport of electrons. Figure 4 contains the molecular structure of various donor units, while acceptor units are shown in Fig. 5.



**Fig. 4** Schematic structures of various donor units.



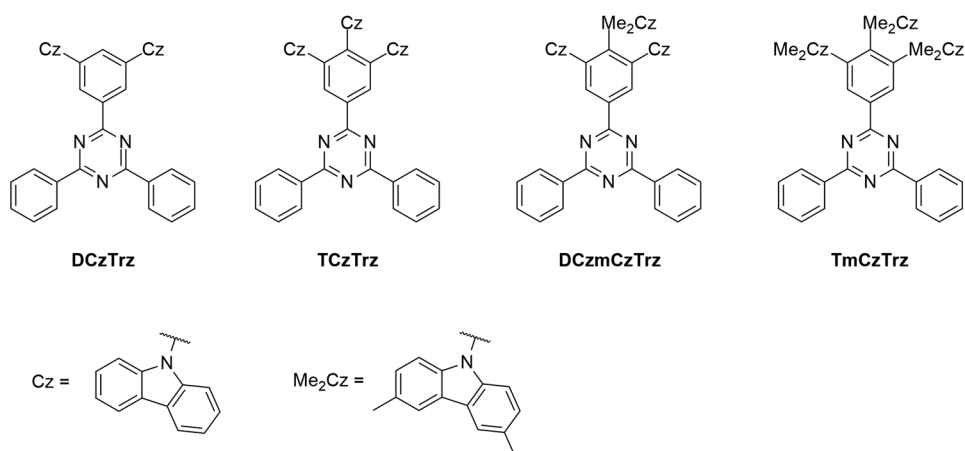
**Fig. 5** Schematic structures of various acceptor units.

It is apparent that—as of today—there is much more variation found on the acceptor part than on the donor part of TADF emitters.<sup>19</sup> As indicated in Fig. 4, the vast majority of all published organic TADF emitters contain substituted carbazole<sup>56–59</sup> or arylamine-type donors.<sup>60–62</sup> In most cases, the connection to the acceptors is realized via the aromatic nitrogen. On the acceptor-side (Fig. 5), one can find a plethora of nitrogen-containing heterocycles,<sup>63,64</sup> as well as various benzonitriles.<sup>47–49,56,57,59,65,66</sup> A third acceptor-class is sulfones,<sup>31,54,58,60,67,68</sup> which seems to be particularly useful to realize deep-blue TADF emission.

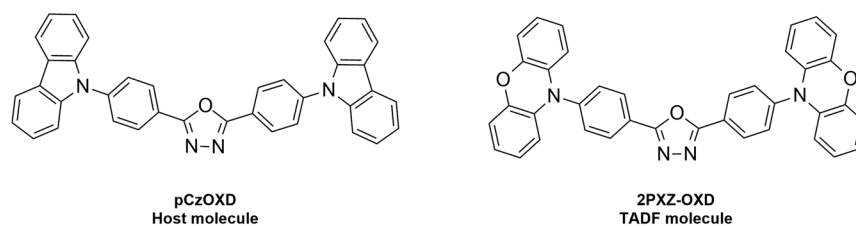
The color of the TADF emitter depends on the choice of the donor and acceptor moieties. Approximately, the choice of the donor dictates the HOMO, while the acceptor dictates the LUMO. The energetic difference between HOMO and LUMO is the bandgap, which is closely connected to the emission color of the emitter. Roughly, a bandgap of ca. 2.8 eV (450 nm) relates to blue emission, while 1.9 eV (650 nm) gives red emission.<sup>23</sup> In Sec. 1,  $\Delta E (S-T)$  was introduced as the most crucial parameter for TADF. This parameter is highly dependent of the localization of the Frontier orbitals HOMO and LUMO.<sup>69,70</sup> The better the separation (or the smaller the overlap between HOMO and LUMO), the smaller  $\Delta E (S-T)$ , which facilitates efficient ISC and rISC. From a design point of view, the overlap of HOMO and LUMO can be manipulated by the way in which the donor and acceptor moieties are connected. This is emphasized by analyzing the properties of different combinations of triphenyltriazine-type acceptors (Trz) with carbazole-type donors (Cz and mCz or Me<sub>2</sub>Cz), which have been published by Lee et al.<sup>71,72</sup> This work led to the TADF emitters DCzTrz, TCzTrz, DCzmCzTrz, and TmCzTrz, which are shown in Fig. 6. Addition of an additional carbazole or dimethylcarbazole to DCzTrz changes the triplet energy  $\Delta E (S-T)$  from 0.23 to 0.16 and 0.07 eV, respectively, in TCzTrz and DCzmCzTrz.

The photoluminescence quantum yield and excited-state lifetime are—in this case—connected to  $\Delta E (S-T)$ : it changes from 43% at 31  $\mu$ s (DCzTrz) to 100% at 14  $\mu$ s (TCzTrz) and 99% at 14  $\mu$ s (DCzmCzTrz). Note that the color of the four emitters shown in Fig. 6 depends on the choice of the donor unit. The carbazole-emitters DCzTrz and TCzTrz show peak electroluminescence around 480 nm, while the emitters with dimethylcarbazole, Me<sub>2</sub>Cz, emit around 500 nm. This can be attributed to a variation of the HOMO energy of carbazole, which is slightly raised when electron-rich methyl groups are added.

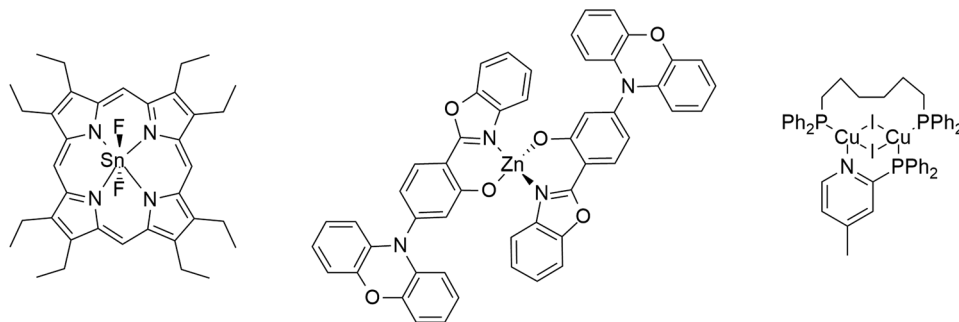
When comparing ambipolar host molecules with TADF dopands, the differences are often subtle. Examples are pCzOXD,<sup>73</sup> a fluorescent, ambipolar host molecule and 2PXZ-OXD,<sup>74</sup> a TADF emitter, which are shown in Fig. 7. They both feature diphenyloxadiazole (OXD) as the acceptor unit (not shown in Fig. 5) as well two carbazole- (Cz) or phenoxazine-donors (PXZ) per molecule. Apart from the different HOMO energy, which leads to a smaller bandgap for 2PXZ-OXD due to the shallower HOMO of phenoxazine, the twist angle between the donor and the phenyl-substituent is different with a reported value based on DFT calculation of 52 deg for pCzOXD<sup>73</sup> and 75 deg for 2PXZ-OXD.<sup>74</sup> The larger twist breaks the conjugation between the donor and acceptor, which leads to a well-separated HOMO and LUMO and a small



**Fig. 6** Impact of the connectivity of donors and acceptors on photophysical properties.<sup>71,72</sup>



**Fig. 7** Differences between ambipolar host molecules<sup>73</sup> and TADF emitters<sup>74</sup> are often subtle.



**Fig. 8** Examples for metal–organic TADF emitters.<sup>4,76,77</sup>

$\Delta E (S-T)$  for 2PXZ-OXD,<sup>74</sup> while the HOMO is totally delocalized for 2PXZ-OXD, as suggested by DFT calculations.<sup>73</sup>

## 2.2 Organic Versus Copper Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes

In Sec. 2.1, we highlighted organic, small-molecule TADF emitters. For metal–organic TADF emitters, the same design principles are also essentially true (Fig. 8). In this case, the HOMO is often located on metal (or metal-halide) centered orbitals, while N-heterocyclic ligands (which are also being used in organic TADF emitters, refer to Fig. 5) house the LUMO. The same is also true for polymeric TADF emitters, where the HOMO and LUMO are located on different monomers of the polymer strand.<sup>75</sup>

Both organic<sup>66,78,79</sup> and metal–organic TADF emitters<sup>77</sup> have been shown to reach the maximum theoretical OLED efficiency, which is in the order of 20% to 25% external quantum efficiency in cases where no light-extraction technology is applied.<sup>13</sup> For clarity, the molecular structures of metal–organic TADF emitters are not discussed here. This has already been covered elsewhere.<sup>80–82</sup>

## 3 Current Strengths and Weaknesses of Thermally Activated Delayed Fluorescence–Organic Light-Emitting Diode

In terms of efficiency, TADF is already directly competing with phosphorescent OLEDs,<sup>66,78,79</sup> even though the first TADF OLED was published only 5 years ago.<sup>63</sup> In terms of stability, there are some promising results.<sup>72,83</sup> With 4CzIPN (see Fig. 2),  $L_T50$  values of over 10,000 h (starting luminance of 500  $\text{cd m}^{-2}$ ) have been reported. However, there still exists a gap that needs to be bridged prior to commercialization.

It has been pointed out that TADF emitters partake in the charge transport in the OLED architecture, which are currently used.<sup>83</sup> This is a result of the high doping concentrations, ranging from 6% up to neat emitter films that are usually being employed, which facilitate charge transport, as well as the current lack of host and blocking materials with properly aligned energy levels and high-triplet energies.<sup>84,85</sup> In another study, it was demonstrated that charge-carrier-induced formation of small (e.g., as a result of unimolecular processes) and large molecular

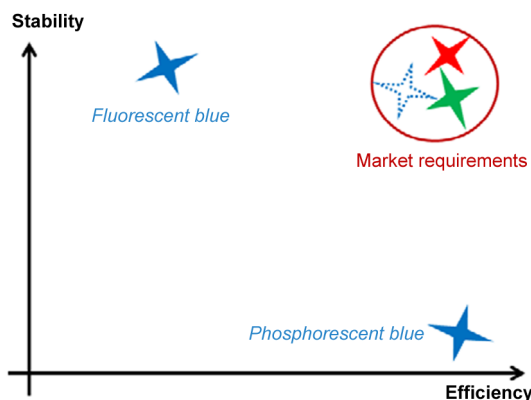
weight (e.g., as a result of multimolecular processes) degradation products occurs, which suggests bond formation as well as bond cleavage needs to be prevented. This is a general problem for all organic semiconductors, but is generally solvable when reaching a certain level of maturity.<sup>86</sup> The authors also pointed out that 3,3-Di(9H-carbazol-9-yl)biphenyl, a host that is often used with TADF emitters, is in fact not sufficiently stable upon UV irradiation.<sup>87</sup> This further suggests that the development of hosts and supporting materials needs to be investigated in parallel to the actual material development.

A big issue is the excited-state lifetime or emission decay time of materials. Apart from efficiency roll-off,<sup>88–90</sup> the loss of OLED efficiency at high currents, this is also likely to affect the operational stability. Unfortunately, no straightforward structure–property relation has yet been identified to systematically modify the excited-state lifetime of TADF emitters. Especially metal-free TADF emitters often suffer from long excited-state lifetimes up to the millisecond regime,<sup>65,90</sup> while ideally, the excited-state lifetime is in the order of 1  $\mu$ s or even less.<sup>13</sup> For the diphenylsulfone acceptor (see Fig. 5), excited-state lifetimes in the order of ms are achieved when donors such as *tert*-butyl-carbazole are used,<sup>68</sup> while in a similar system with dimethoxycarbazole, only several  $\mu$ s are reported.<sup>91</sup> This cannot be rationalized or predicted with the current level of understanding. At this point, no general design rules exist on how to specifically design TADF molecules with very low-excited-state lifetime.

#### 4 Potential Economic Impact of Thermally Activated Delayed Fluorescence: Overcoming the Blue Gap

OLEDs have successfully been introduced in commercial products, such as tablet personal computers, smartwatches, and smartphones in the last few years, thanks to breakthroughs that led to the realization of stable devices with good efficiency. The first commercial successes should not distract from the fact that there is much room for improvement. Currently, the most pressing material issue in OLEDs is the bluegap (Fig. 9): In modern, commercial OLEDs, fluorescent materials<sup>92</sup> are used in addition to phosphorescent materials, even though this leads to an increased power consumption. The main reason for this is the unavailability of stable deep-blue phosphorescent emitters.<sup>93</sup>

Similar to any other display technology, OLEDs display consists of red, green, and blue pixels. While red and green pixels rely on energy-efficient, phosphorescent materials, blue phosphorescent OLEDs never reached the necessary color purity and stability to allow for commercialization. It needs to be said that academic and industrial institutions tried to solve this issue with blue phosphorescent materials without success for the last 15 years,<sup>94–100</sup> suggesting that much like the low efficiency of fluorescent OLED materials, the instability of blue phosphorescent materials might be an intrinsic property and that innovative material concepts are required to close the bluegap. This means that as of today, no efficient and stable blue OLED pixels are available. The consequences are drastic, because the human eye is relatively



**Fig. 9** The bluegap. So far, no commercial blue material has been shown to combine both efficiency and stability.



**Table 1** Representative size of AMOLED pixels for smartphones.

	Average area in a display ( $\mu\text{m}^2$ )	Relative area (%)
Red	354	34
Green	151	14
Blue	545	52
Sum	1050	Percentage of total active area

insensitive to blue light, which means that a fairly large amount of blue pixels is needed in any display.

The scope of this problem can be illustrated with a back-of-the-envelope calculation: typical OLED devices have displays with fluorescent blue emitter materials. Due to the aforementioned color sensitivity, 52% of the active display consists of blue pixels (Table 1). With a standard 2600-mAh-capacity battery, such a device plays up to 12.5 h of video.

Using a deep-blue TADF of phosphorescent emitter will allow for a reduction of the blue pixel area due to the greater light output. Assuming that the energy consumption of blue pixels is decreased by only 66% (corresponding to an efficiency increase by a factor of 3), the energy consumption of the whole display will be decreased by 33% and the battery lifetime of the video mode will be increased from 12.5 to more than 16 h. Note that the theoretical efficiency increase when using blue TADF or phosphorescence technology is even larger than assumed here (factor of 4 instead of 3!).

The first promising steps have already been made to put this into reality: in several cases, efficiency values of more than 20% have been demonstrated in deep-blue TADF OLEDs.<sup>64,68,71,72,101,102</sup> The lifetime of blue TADF OLEDs is currently in the order of 50 h ( $L_{T80}$ , starting luminance  $500 \text{ cd m}^{-2}$ ), which was achieved for derivatives of DDCzTrz (structure, see Fig. 6).<sup>72</sup>

Given that the issues that were outlined in Sec. 3 are adequately addressed, and TADF technology has the potential to close the bluegap.

## 5 Conclusion

Considering that first-world societies use up to 30% of their electric energy either for direct lighting or for the illumination of the displays of large-area TVs or portable devices, the development of stable and efficient deep-blue OLEDs is a problem with great economic relevance. It is evident that after many unsuccessful attempts to realize this with phosphorescent materials, new approaches such as TADF need to be investigated. Apart from aspects such as general chemical stability against dissociative and associative reactions, the focus of future work should be directed toward a more in-depth understanding of the parameters, which can be used to tune the excited-state lifetime. Without it, material development is highly dependent on empiric brute-force approaches and luck, which significantly reduces the probability of success.

In this review, the TADF concept was introduced. With a modular approach, TADF molecules can be designed from donor and acceptor units. Also, the current strengths, especially the very high device efficiency, as well as weaknesses such as the often long excited-state lifetime, have been addressed. The great economic potential of blue TADF technology was outlined, which is one of the main driving forces for future academic and industrial research in this field.

## Acknowledgments

This work has been sponsored by the German Federal Ministry of Education and Research. BMBF in the funding programs “cyCESH” and “cyFLEX.” Also, we acknowledge funding from the European Union in the LEO Project (H2020-ICT-2014-1 call). D.V. thanks the R&D Division of CYNORA and his collaboration partners, among them Stefan Bräse,

Clemens Heske, Uli Lemmer, and Christopher Barner-Kowollik (Karlsruhe Institute of Technology), Hartmut Yersin (University of Regensburg), and Franky So (North Carolina State University) for their continued support.

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