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Photophysical Characterisation of Thermally Activated Delayed Fluorescence (TADF) Materials[†]

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In this work we present a brief characterization of thermally activated delayed fluorescence (TADF) emitters and describe the spectroscopic methods used to investigate them. Both steady state and time-resolved methods are presented. The effect of oxygen on delayed fluorescence is described. Three different TADF emitters are compared to evaluate the effect of different electron-donating groups on their spectroscopic properties.

Keywords: TADF, OLED, photophysics, delayed fluorescence, phosphorescence, charge transfer

1. INTRODUCTION

Thermally activated delayed fluorescence (TADF) has been widely investigated in recent years as an alternative for heavy metal phosphorescent complexes in organic light emitting diodes (OLEDs). [1-6] The purpose is that a purely organic fluorescent molecule that shows TADF enables to achieve up to 100% triplet harvesting [7] what in the past could only be achieved by phosphorescent complexes. [8]

In principle, thermally activated delayed fluorescent compound has a small singlet-triplet energy gap (ΔE_{ST}) that enables to convert triplet excitons

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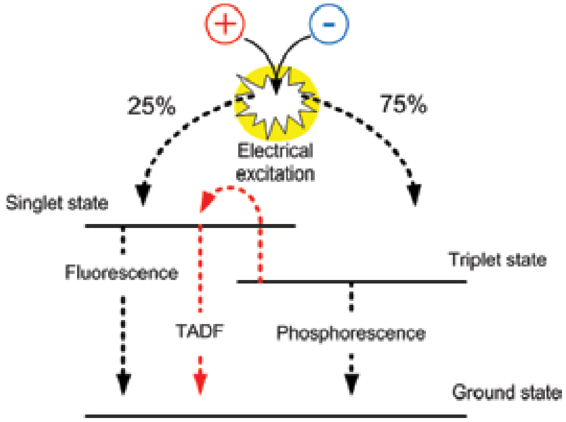

FIGURE 1
Schematic diagram of triplet harvesting in TADF OLED emitter under electrical excitation.

into singlet excitons only with aid of thermal energy. [1-7] Therefore, under electrical excitation of the molecule, both the 75% of triplet excitons and 25% of singlet excitons that are generated in an OLED can be harvested by a TADF emitter. [1-7] As a result the external quantum efficiency (EQE) that for a conventional fluorescent OLED is limited to ≈ 5% can be increased by the use of a TADF emitter up to ≈20%. [1,2,9]

Triplet recycling achieved in TADF emitters results in a specific behavior that fluorescence arrives in two waves. The first one that comes originally from a singlet state is called prompt fluorescence due to its short lifetime. The second one that originates from the lowest triplet state and due to spin-forbidden nature of the triplet-singlet transition, the emission, which is called a delayed fluorescence, has relatively long lifetime (please see FIGURE 1). [1-7,9]

The growing number of currently known efficient TADF OLED emitters shows how big is demand for such kind of molecules. The number of reported molecules is big and still increasing, however not very much is known about all the processes that are involved into TADF. Scientists are still discovering the TADF phenomenon with the use of photophysical methods. In this work we present a basic description on how the photophysical investigation of a typical TADF molecule can be performed by the use of steady-state and time-resolved spectrofluorimetry.

2. EXPLANATION OF TADF MECHANISM

Thermally activated delayed fluorescence is a process that involves triplet states. Regardless of how the molecular population is excited: electrically or photonically, triplet states are always formed. In electrical excitation, due to spin statistics, the population of triplets is formed initially. Under photoin-

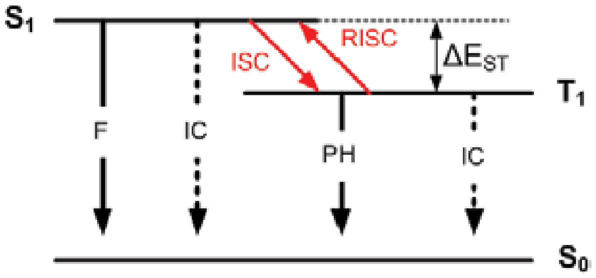

FIGURE 2
Explanation of TADF mechanism. Reverse intersystem crossing (RISC) is crucial to observe TADF. S_1 – lowest singlet excited state; T_1 – lowest triplet excited state; S_0 – ground state; F – fluorescence; PH – phosphorescence; IC – internal conversion (non-radiative decay); ISC – intersystem crossing; RISC – reverse intersystem crossing; ΔE_{ST} – singlet-triplet energy splitting.

duced excitation only singlet states are produced and some of them relax to the triplet state by intersystem crossing (see FIGURE 2).

The main feature of a TADF molecule is that its singlet-triplet energy gap is narrow. When the gap is small enough, the triplet state, through reverse intersystem crossing, can be converted into a singlet state only by the use of thermal energy from the surrounding. When the excited molecule achieves the singlet state it usually very quickly relaxes by radiative or non-radiative way (internal conversion). The radiative relaxation in this case is called a delayed fluorescence since the reverse intersystem crossing that is involved into the process is also rather slow. Reverse intersystem crossing (RISC) as well as intersystem crossing (ISC) are spin-forbidden processes and their rate constants are much smaller than the rate constant of singlet radiative relaxation (fluorescence). Radiative (phosphorescence) and non-radiative (internal conversion) relaxation of the triplet state are processes that compete with RISC. Phosphorescence is also spin-forbidden, therefore its rate constant is very small and, at room temperature, significantly lower than that of RISC in a typical TADF emitter. [1-7,9-14]

The singlet and triplet energy are given by equations (2.1) and (2.2) where E_{HOMO} and E_{LUMO} are the energy of HOMO and LUMO level respectively and J is the spin exchange energy. Therefore the energy difference between singlet and triplet state is 2J (2.3). The key to obtain small ΔE_{ST} is to reduce the spin exchange energy – this is achieved by separation of frontier molecular orbitals.

$$E_S = E_{HOMO} - E_{LUMO} + J \tag{2.1}$$

$$E_T = E_{HOMO} - E_{LUMO} - J \tag{2.2}$$

$$\Delta E_{ST} = E_S - E_T = 2J \tag{2.3}$$

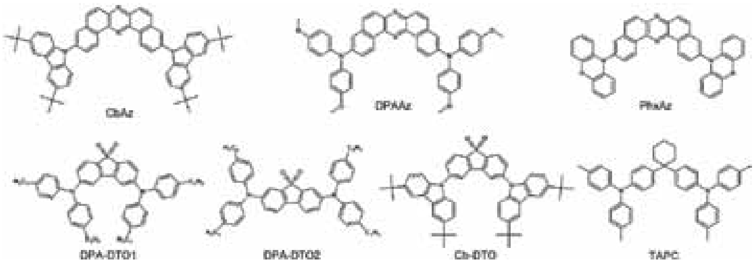

FIGURE 3
Compounds investigated in this article. The materials presented were described in previous works. [3,7] TAPC was purchased from Sigma Aldrich.

As mentioned in the previous paragraph, to achieve a small ΔE_{ST} in a molecule the HOMO and LUMO must be separated from each other. To obtain this effect, the donor-acceptor structure is used. [1-7,9-16] With such a donor-acceptor structure the HOMO is placed mostly on the donor, whereas LUMO mostly over the acceptor part. It means usually that the dipole moment of the molecule is different in ground and excited state. Excited state of a molecule with such a different dipole moment is called a charge transfer (CT) state since the electron density is partially transferred from the donor to the acceptor part. [7]

3. EXPERIMENTAL STUDIES OF TADF MOLECULES

The experimental study was performed on different types of donor-acceptor-donor (D-A-D) molecules that show TADF (CbAz, DPAAz, PhxAz) in solid film or in solution (DPA-DTO1). One molecule was shown as an example of a TTA (*Triplet-Triplet Annihilation*) emitter (DPA-DTO2). The other two molecules: Cb-DTO and TAPC form an exciplex in a solid-state blend. The detailed study of all presented compounds can be found in cited literature. [3,7,10]

3.1. Solvatochromism of fluorescence in donor-acceptor molecules

Since most of the known TADF emitters are donor-acceptor molecules, the charge transfer (CT) excited state and its energy is of vital importance. The donor-acceptor molecule that forms a charge transfer state in polar media shows a broad and featureless emission, whereas in non-polar media a narrow and usually resolved emission is observed. Charge transfer excited state is a state where the dipole moment of the molecule is significantly larger in excited state than in the ground state. Therefore polar media, like ethanol, tetrahydrofuran and other polar solvents favor the CT state, lowering its energy – the charge transfer emission spectrum will therefore shift to longer wavelengths with increasing solvent polarity. It was also observed that the CT

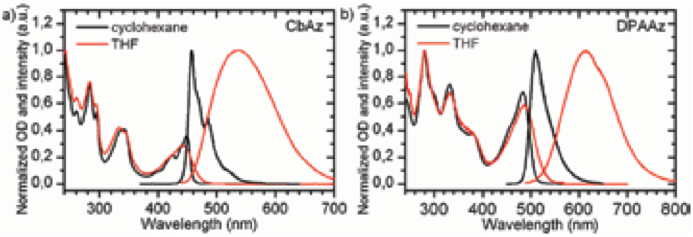

FIGURE 4
Solvatochromic effect on the photoluminescence spectrum of donor-acceptor-donor (D-A-D) molecules. The broad and featureless emission observed in THF indicates charge transfer origin, whereas in cyclohexane fluorescence has a localized character. [3]

emission can be quenched in some polar media if the compound presents strong charge transfer character. CT emission is also commonly observed in solid films of TADF compounds dispersed in OLED host matrices. [2-6]

The CT state has a very small ΔE_{ST} that is usually difficult to measure. [7,10,11] The energy of the CT state is strongly environment-dependent, therefore when the charge transfer state becomes the lowest singlet state, it will decrease the ΔE_{ST} gap which is usually desired. [1-3,7,9]

3.2. Effect of the oxygen on fluorescence intensity

Since TADF emission comes originally from a triplet state, therefore any process that affects the triplet state population will also affect the intensity and lifetime of TADF. Triplet oxygen from air interacts with triplet states of molecules quenching them. Therefore in both liquid and solid samples (only in air-permeable materials) the TADF emission can be observed only in oxygen-free conditions, whereas in air-equilibrated conditions delayed fluorescence is not observed or its intensity and lifetime is significantly reduced. In consequence, reliable characteristics of TADF materials must include experiments in air-free conditions.

In particular, solid samples like those prepared with a use of a polymer matrix (polystyrene, Zeonex®, etc.) can be degassed using a vacuum pump, whereas solutions must be degassed using nitrogen/argon bubbling or with several freeze / thaw cycles in a special degassing cuvette. [1-7,9-18] The difference in fluorescence intensity between air-equilibrated and degassed conditions can be low or very high regarding on the contribution of delayed fluorescence in overall steady-state emission. [12] The assumption that delayed fluorescence is totally quenched in an air-equilibrated solution is usually correct, therefore the steady-state fluorescence measured in those conditions can be attributed to prompt fluorescence, whereas the sum of prompt fluorescence (PF) and TADF is observed after removal of oxygen. The degassing experiment is the easiest way to confirm the presence of delayed fluorescence or more strictly, emission with

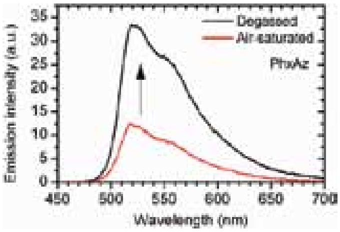

FIGURE 5
Effect of oxygen on steady-state emission of a TADF emitter in cyclohexane solution. Oxygen quenches the most of delayed fluorescence, therefore this experiment enables to estimate the contribution of TADF in steady-state photoluminescence.

an origin in a triplet state, and to determine the lowest limit for its contribution to overall emission.

3.3. Fluorescence decay

The fluorescence decay of a TADF emitter in a degassed solution or a solid film under vacuum consists of two species: prompt fluorescence and delayed fluorescence. Whereas the prompt fluorescence lifetime usually varies in a range of 1-100 ns as for normal fluorescence, the delayed fluorescence has a lifetime of typically 1 μs to 100 ms. [1-7,9-18] Prompt fluorescence lifetime and intensity change only slightly upon temperature with longer lifetime and higher intensity at low temperatures due to suppressing of the non-radiative decay pathways. Delayed fluorescence is at this point strongly dependent upon temperature and both intensity and lifetime change with temperature. Both the intensity and lifetime of TADF follow the Arrhenius-type kinetics (3.1) which is a result of Boltzmann's singlet and triplet state thermal equilibrium. [7,11,13] There can be also drawn a relation between steady state intensity ($I_{SS}{}^{TADF}$) of TADF and temperature which, after joining the equations (3.1) and (3.2), gives an equation identical to the Arrhenius equation (3.3). [7,11,13] For more details please see section 3.5.

In a typical TADF emitter a strong delayed fluorescence is observed at room temperature and no phosphorescence can be noticed, whereas upon

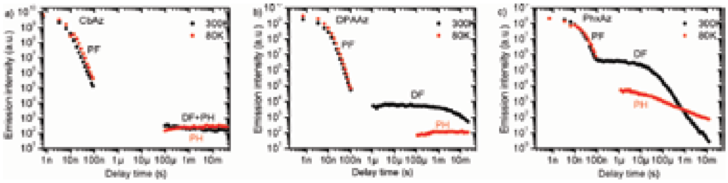

FIGURE 6
Photoluminescence decay of TADF emitters in a rigid Zeonex® matrix at 300 K and at 80 K. PF – prompt fluorescence; DF – delayed fluorescence; PH – phosphorescence. [3]

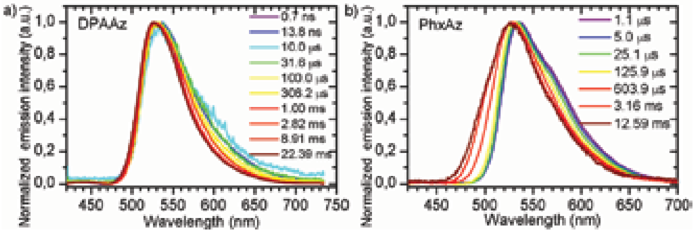

FIGURE 7
Time-resolved spectra of TADF emitters dispersed in a Zeonex® matrix, 300 K. [3]

decreasing temperature the amount of TADF decreases and the phosphorescence starts to be observed. At sufficiently low temperatures such as around 77K (liquid nitrogen) the TADF is not usually observed and now the phosphorescence dominates. When the ΔE_{ST} is very small the thermal energy at 77K is still sufficient to allow triplet-singlet up-conversion of excitons.

3.4. Time-resolved spectra

The principle of TADF is that the spectrum of prompt and delayed fluorescence are identical because the emission arises from the same singlet excited state. This statement is generally correct in all cases. However, in some cases and especially when a sensitive gated iCCD camera is used, some changes in time-resolved spectra are observed. [2,3,10,11] This also shows that investigation of TADF emitters only with a time-correlated single photon counting (TCSPC) equipment is insufficient and gives only the information about the lifetime of the delayed fluorescence without the information about changes in the photoluminescence spectrum.

There are several reasons for changes in the spectra depending on the form of the sample (solid or liquid). In some cases the prompt fluorescence can be blue-shifted or another emission band can be observed at very early times after excitation. [2] The mentioned emission arises usually from the donor or the acceptor of the D-A molecule. Red- or blue-shifting of the emission with time can also be observed and may be caused by the presence of conformers that have slightly different energy levels. Shifting of the time-resolved emission spectra is also observed in exciplexes where it can be explained by random distribution of donor and acceptor molecules in a solid film. [10,11] Donor and acceptor molecules in an exciplex blend are distributed randomly therefore upon excitation a whole distribution of excited states is formed with different energy and photoluminescence lifetime.

3.5. Determination of ΔE_{ST} and E_a^{TADF}

Since TADF mechanism involves RISC from the lowest triplet level to the lowest singlet level, the energy of those states is crucial to understand the whole process. ΔE_{ST} is the most important parameter describing a TADF molecule that determines the lifetime of delayed fluorescence as well as the DF/PF (delayed fluorescence / prompt fluorescence) ratio. In general, with lowering of the ΔE_{ST} the DF lifetime becomes shorter and the DF/PF ratio increases. The most efficient TADF-based OLEDs reported use low ΔE_{ST} TADF materials as emitters. [1-6,9]

ΔE_{ST} is drawn directly from prompt fluorescence and phosphorescence spectra as a difference of the energy of the lowest singlet E_{S1} and triplet E_{T1} excited states (2.3). There are two main methods for estimating the excited state energy: from *onset* and from *maximum*. There are several advantages and disadvantages of those methods which are not to be discussed in this article. It can be noted that in case of low ΔE_{ST} materials ($\approx$ 0.01 eV) it is vital to cool down the sample to a very low temperature (4-20 K) to observe phosphorescence since at the temperature of liquid nitrogen (77 K) TADF is still present. What is more, in compounds with a small ΔE_{ST} the fluorescence and phosphorescence spectra are almost indistinguishable. [15,16] It is also worth to mention that the phosphorescence of TADF emitters, can have its origin in donor's or acceptor's triplet level (depending on which triplet level is the lowest). In this case the phosphorescence spectrum is identical to the phosphorescence of a single donor or acceptor molecule in the same conditions. [2,3,12,14]

Since reverse intersystem crossing is a process with activation energy, the RISC rate constant is dependent upon temperature and this relation can be described by the Arrhenius equation (3.1). Estimation of the activation energy of TADF is more difficult and requires measurement of lifetime or intensity of delayed fluorescence in wide range of temperatures. That requires a gated camera to integrate only the delayed emission or a TCSPC equipment coupled with a cryostat. The E_a^{TADF} can be drawn from Arrhenius plot where DF intensity (3.3) or k_{RISC} (3.4, 3.5) is plotted against T^{-1}, where k_{RISC} is the delayed fluorescence rate constant and T temperature. [7,13] Usually the E_a^{TADF} is close to ΔE_{ST} but very often the values stay in relation $\Delta E_{ST} \geq E_a^{TADF}$. [3a,7] The equation (3.3) is a result of joining equations (3.1) and (3.2). It must be noted that equations (3.2) and (3.3) are presented in a simplified form which is correct only in the temperature region where Arrhenius plot is linear (please see FIGURE 8). Equation (3.5) is shown in a simplified form, where $\Phi_{DF} >> \Phi_{PF}$ and therefore $\Phi_{RISC} \approx 1$ in equation (3.4). These are the conditions that describe an ideal TADF emitter in case of application in OLED devices, such emitters have already been shown. [1,2] We can assume here also that respective quantum yields are proportional to integrals given there. Equations (3.1-3.5), along with their modified forms, have been presented elsewhere or drawn from the equations from there. [13]

$$k_{RISC} = k_{ISC}^{-T} \; e^{\frac{-E_a}{RT}} \tag{3.1}$$

$$I_{SS}^{TADF} = f_{inst} k_{f0} \frac{T_0 k_{RISC}}{k_f k_{PH}} \tag{3.2}$$

$$I_{SS}^{TADF} = f_{inst} k_{f0} \frac{T_0}{k_f k_{PH}} k_{ISC}^{-T} e^{\frac{-E_a}{RT}} \tag{3.3}$$

$$k_{RISC} = \frac{\Phi_{RISC}}{\tau_{TADF}} \frac{\Phi_{PF} + \Phi_{DF}}{\Phi_{PF}} \tag{3.4}$$

$$k_{RISC} = \frac{\int_0^\infty I_{TADF}(t)\,dt}{\int_0^\infty I_{PF}(t)\,dt} \frac{1}{\tau_{TADF}} \tag{3.5}$$

Where: k_{RISC} – reverse intersystem crossing rate constant, s^{-1}; k_{ISC}^{-T} – intersystem crossing from upper triplet levels to lowest singlet level rate constant, s^{-1}; E_a – TADF activation energy, J mol^{-1}; R – gas constant, J mol^{-1} K^{-1}; T – temperature, K^{-1}; I_{SS}^{TADF} – steady state intensity of TADF, a.u.; f_{inst} – instrumental factor, a.u.; k_{f0} – natural radiative decay rate constant, s^{-1}; T_0 – constant of integration, a.u.; k_f – fluorescence rate constant, s^{-1}; k_{PH} – phosphorescence rate constant, s^{-1}; τ_{TADF} – TADF lifetime, s; Φ_{RISC} – reverse intersystem crossing yield, a.u.; Φ_{PF} – prompt fluorescence quantum yield, a.u.; Φ_{DF} – delayed fluorescence quantum yield, a.u.; $I_{TADF}(t)$ – TADF time profile, a.u.; $I_{PF}(t)$ – prompt fluorescence time profile, a.u.

In general, the calculation of E_a^{TADF} based on changes in the k_{RISC} constant (so based on the changes in the lifetime of delayed fluorescence) upon temperature are easy to do in solutions. Solution is an ideal medium because of its homogeneity, but solid-state samples also have to be considered, especially in OLED applications. Fluorescence decay of a solid film is very often multiexponential, therefore there is a distribution of DF lifetimes. In consequence, the method of calculating E_a^{TADF} based on the delayed fluorescence intensity is more useful and works in all cases. For more detailed information please refer to cited literature. [1,3,7,13]

As it is seen from the data provided, the activation energy of TADF is gained from the linear part of the Arrhenius plot (DF intensity vs. T^{-1}). The equation (3.3) fits to the linear part of the plot. Usually, the non-radiative

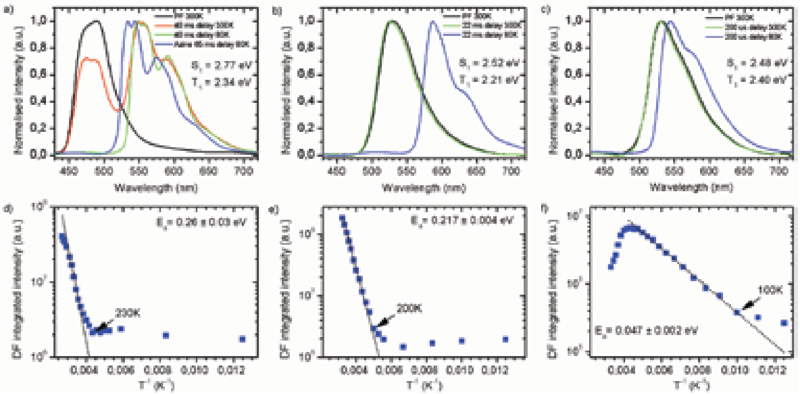

FIGURE 8
Prompt fluorescence, delayed fluorescence and phosphorescence spectra of investigated compounds. Temperature dependence of the delayed fluorescence in an Arrhenius plot. Recorded in Zeonex® matrix. Azine refers to the acceptor unit of all three presented compounds. [3]

decay process that affects triplet lifetime reduces the contribution of TADF in higher temperatures. Therefore to achieve strong TADF in an OLED device a host material that reduces the molecular motion and suppresses non-radiative decay is desired.

3.6. Power dependence of delayed fluorescence

Thermally activated delayed fluorescence is an unimolecular process, therefore only one excited molecule in a triplet state is involved. However, in molecules with long triplet lifetime and relatively large ΔE_{ST} the TADF may not be observed, but another phenomenon: triplet-triplet annihilation (TTA) is present. [7,13] TTA requires a direct contact of two molecules in a triplet excited state. So two triplet excited states can form one singlet excited state which can be observed as a delayed fluorescence. TTA is limited by diffusion rate, therefore it is also thermally activated. Since TTA is a bimolecular pro-

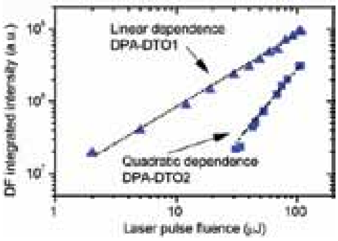

FIGURE 9
Power dependence of delayed fluorescence in ethanol for a TADF and a TTA emitter. Room temperature.[7]

TABLE 1
Properties of D-A-D TADF emitters in 1% Zeonex® films at 300 K. [3]

Compound name	τ_{PF}, ns[a]	τ_{DF}, ms[b]	S_1/T_1, eV[c]	ΔE_{ST}, eV[d]	E_a^{TADF}, eV[e]	Power dependence[f]	DF/PF ratio[g]
CbAz	3.3	148	2.77 / 2.34	0.43	0.26 ± 0.03	1.24	0.4
DPAAz	4.9	7.3	2.52 / 2.21	0.31	0.217 ± 0.004	1.00	3.8
PhxAz	10.2	$2.9 \cdot 10^{-2}$	2.48 / 2.40	0.08	0.047 ± 0.002	1.08	4.6

[a] Prompt fluorescence lifetime estimated from monoexponential decay fitting; [b] Averaged delayed fluorescence lifetime from biexponential fitting [11], note that delayed emission from CbAz is dominated by phosphorescence; [c] S_1 – singlet, T_1 – triplet energy measured from *onset* of the prompt fluorescence / phosphorescence spectra respectively; [d] Singlet-triplet energy gap; [e] TADF activation energy drawn from Arrhenius equation; [f] Exponent of the fitted power dependence of delayed fluorescence; note that measurement of CbAz was made at 370 K due to domination of phosphorescence at 300K; [g] Ratio between delayed fluorescence and prompt fluorescence steady state intensity.

cess its intensity is quadratically dependent upon excitation dose, whereas TADF has linear dependence. [7,13]

Power dependence experiment is a convenient way to reliably distinguish between TADF and TTA phenomena. TADF as a unimolecular process is linearly dependent upon excitation dose, whereas TTA is quadratically dependent. In some cases TTA and TADF can compete with each other so the power law is in between 1 and 2. [3]

4. STRUCTURE-PROPERTY RELATIONSHIP IN TADF EMITTERS

Photophysical investigation of series of donor-acceptor molecules gives an opportunity to study the structure-property relationship of TADF parameters. ICT character and HOMO-LUMO separation increase with increasing electron-donating properties of donors when the same acceptor is used. [3] To exemplify that relationship a group of three molecules with carbazole, triphenylamine and phenoxazine donors was studied and the data are presented in the TABLE 1.

In general, the increase of ICT character decreases the ΔE_{ST} and the E_a^{TADF} which is the consequence of better HOMO-LUMO separation. The lifetime of delayed fluorescence (τ_{DF}) decreases dramatically with decreasing ΔE_{ST}, but prompt fluorescence lifetime (τ_{PF}) slightly increases. The delayed fluorescence / prompt fluorescence ratio increases upon decrease of ΔE_{ST} due to lowering of the TADF energy barrier. CbAz with relatively wide ΔE_{ST} shows a mixed contribution of TADF and TTA in delayed fluorescence and the phosphorescence is here also observed at room temperature. DPAAz has lower ΔE_{ST} and shows pure TADF, as well as PhxAz which has very low $\Delta E_{ST} = 0.08$ eV. The values of E_a^{TADF} are lower than $\Delta E_{ST.}$ It is also worth to mention that the highest EQE of an OLED device was achieved for PhxAz as an emitter in 10% PhxAz : CBP emissive layer. [3] This is the consequence of a low $E_a^{TADF} \approx 0.02$ eV in

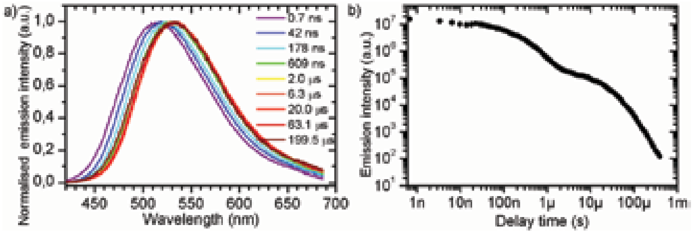

FIGURE 10
Time-resolved spectra (a) and photoluminescence decay (b) of an exciplex blend Cb-DTO : TAPC (30/70; w/w).

the OLED emissive layer that enables the reverse intersystem crossing (RISC) to be fast and very efficient.

5. EXCITON AND EXCIPLEX TADF EMITTERS: SIMILARITIES AND DISSIMILARITIES

The major difference between an exciton and exciplex TADF emitter is that the first one is unimolecular and the second one is bimolecular. Although the chemical formulation and the possible modifications of exciplex layer are different than that of a unimolecular TADF emitter, the photophysical characterization is here very similar (FIGURE 10). [10,11,17,18] The donor-acceptor exciton TADF emitter consists of (sometimes several) donor and acceptor units that are connected in a way to achieve separation of HOMO and LUMO. In an exciplex blend donor and acceptor molecules are dispersed in a random way so there are all possible relative locations of donors and acceptors present. Unimolecular TADF emitter is more ordered since the D and A locations are determined by chemical bonds. That is also the reason why the time-resolved photoluminescence study of an exciplex is more complicated than that of a unimolecular emitter. [10,11] Recent studies have shown that mechanism of efficient TADF is identical for exciplex and exciton emitters. [19,20]

As the exciplex emitter has similar photophysical properties to the exciton emitter all the measurements described above that are made with a solid film can be applied to an exciplex blend. The measurements in liquid state, however possible, are performed rarely because formation of an exciplex requires a contact of two different molecules (from which one is in excited state and another in ground state), which is more likely to happen in a blend containing only donor and acceptor rather than in a diluted solution of those materials.

More detailed study of the presented exciplex blend (see FIGURE 10) can be found elsewhere. [10]

6. CONCLUSIONS

A brief and general description of TADF has been shown as well as the methods used to investigate the TADF phenomenon in solid and liquid state for exciton and exciplex emitters. It is clear that the close photophysical study is recommended to understand and describe the processes regarding delayed fluorescence molecules reliably. Some of the methods described in the article do not require any additional equipment and can be done with a regular fluorometer, however most of them require substantial modifications of the equipment or specialized tools like cryostats and degassing cuvettes. This study is only a general description and every case has to be considered independently. It is recommended to check the references below for more details.

7. ACKNOWLEDGMENT

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