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“Development of high-performance, hyperfluorescence OLEDs for use in display applications and solid state lighting”

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D3.6 Report on TADF host properties

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The H2020 HyperOLED project is a three-year EC funded project entitled “Development of high-performance, hyperfluorescence OLEDs for use in display applications and solid state lighting”. The project will run from January 2017 to December 2019.

The overall goal of the HyperOLED project is to develop materials and matching device architectures for high performance, hyperfluorescence organic light emitting diodes (OLEDs) for use in display applications and solid state lighting. The innovative OLEDs will be realised by combining thermally activated delayed fluorescence (TADF) molecular hosts with novel shielded fluorescence emitters, targeting saturated blue emission of very high efficiency, especially at high-brightness levels.

Further efficiency gains will be achieved through molecular alignment to enhance light outcoupling from the hyperfluorescence OLEDs. Using shielded emitters will enable simpler device structures to be used, keeping drive voltages low to be compatible with low voltage CMOS backplane electronics. This will enable demonstration of the concept’s feasibility for high-brightness, full-colour OLED microdisplays as one application example.

To develop the hyperfluorescence OLEDs, the following scientific and technical objectives will be targeted:

- Objective 1: Develop shielded emitters
- Objective 2: Develop TADF hosts
- Objective 3: Photo-physically characterise the shielded emitters and TADF hosts
- Objective 4: Anisotropic molecular orientation for enhanced performance
- Objective 5: Design and test prototype hyperfluorescence OLEDs
- Objective 6: Fabricate and evaluate demonstration hyperfluorescence microdisplays

To show the project’s overall goal has been achieved, blue and white stack unit prototypes will be integrated into a high-brightness microdisplay demonstrator (based on MICROOLED’s 0.38” WVGA CMOS backplane) and tested to demonstrate significant improvements in functionality, performance, manufacturability and reliability.

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1. Introduction

OLEDs usually contain five or more layers, some of which are mixes of different materials in varying ratios. For example, the emission layer always contains at least both a host material and the emissive material at around 5-15%. The interplay between all the materials in the device has a significant impact on its performance. In particular, the host material in the emission layer plays an important role and needs to be chosen carefully. This is true for all OLEDs, but in hyperfluorescent devices is especially complicated as the emission layer additionally contains a thermally activated delayed fluorescence (TADF) material which converts triplet excitons to singlet excitons to boost efficiency. The nature of the TADF mechanism entails that the host material has a particularly strong impact in these devices. This report will explain the reasons for this, which type of host materials are favourable for device performance, and how to adjust TADF materials to work in combination with suitable host materials.

1.1. Choice of host materials

Many deep blue TADF materials reported in the literature require so called high polarity host materials, with phosphine oxide based DPEPO being a prominent example. However, these high polarity materials are often not stable under device operation which severely limits the choice of the host. The situation is further complicated when targeting blue OLEDs, where the host selection is further limited by the high triplet level required. It would be highly preferential regarding device lifetime if low polarity hosts could be used. These materials are much more common, making the choice of a stable host much easier. To achieve this, we need to design TADF materials which work efficiently in combination with such host materials. The prerequisite to do so is to understand the interplay between the host and the TADF material. This was done by investigating the optical properties of newly synthesised TADF materials in combination with hosts of different polarity.

1.2. Influence of the host

Emission *via* the thermally activated delayed fluorescence (TADF) mechanism uses thermal energy to convert triplet excitons, which are not emissive at room temperature in organic molecules, into emissive singlet states, thereby surpassing the 25% internal quantum efficiency limit for normal fluorescent devices. The thermal energy is required to up-convert the lower energy triplet excitons into higher energy singlet ones. In more detail, the TADF mechanism vibronically couples localised (³LE) and charge transfer (³CT) triplet states which enhances spin orbit coupling (SOC) between this mixed triplet state and the emissive singlet ¹CT state.

One requirement to increase the efficiency of the TADF mechanism is to minimize the energy splitting (ΔE_{ST}) between singlet and triplet states. Recent experimental and theoretical work identified that the SOC mechanism in TADF systems is a complex second order process requiring vibronic coupling between ³CT and ³LE to mediate the spin flip back to the ¹CT state [1]. CT states are very sensitive to the environment (the host material) while the local triplet states are not. Therefore, the choice of the host affects the energy gap between these states which directly changes the rate of reverse intersystem crossing (rISC), and thus TADF efficiency. As the rate of rISC depends exponentially on the magnitude of the energy barrier, even a small energy change in ΔE_{ST} has a very profound effect on the rISC rate. This shows that the effect of the host environment must be taken into account and tuned to optimise device performance by maximising the TADF efficiency.

In the context of blue hyperfluorescence, the TADF material must fulfil two critical functions, i) it must harvest triplet states at near 100% efficiency which requires a low value for ΔE_{ST} in the employed host and ii) the TADF emission must be sufficiently deep blue so that the fluorescent emitter can be excited by Förster energy transfer.

As explained above, the TADF materials for hyperfluorescent devices are tuned by the charge transporting host material as was demonstrated by Dos Santos et al [2]. This implies strict requirements for the host material, both in terms of very high triplet level, but also in terms of polarity to optimally tune the TADF material. As hosts of high polarity are not very common, the latter criterion means that TADF materials which require a weakly or non-polar environment to achieve minimum ΔE_{ST} are favourable. This would make a much wider range of host materials accessible, giving more freedom to optimise device performance.

Here, we show how simple substitution on donor or acceptor units of the investigated Donor-Acceptor-Donor (D-A-D) molecules can be used to decrease the polarity requirement of the host material to yield minimal ΔE_{ST} in a range of highly efficient blue emitter TADF materials.

2. Experimental Details

We have synthesised four different blue emitting D-A-D type TADF materials which only differ in simple substituents on the donor or acceptor parts. The materials were characterised in different host materials which were (in order of increasing polarity) Zeonex, TSPO1, BCPO and DPEPO. The thin films required for the investigation were fabricated from mixed solutions of the TADF and host materials and were either drop or spin cast on quartz substrates. Photoluminescence spectroscopy was carried out on the films to determine the energies of the 1CT charge transfer states. Time resolved measurements were used to determine delayed fluorescence characteristics and triplet energies. After laser excitation, the time resolved luminescence spectra are recorded by an intensified charge-coupled device (iCCD) camera coupled to a spectrograph (see Figure 1). Triplet energies are obtained from low temperature (80K) luminescence at delay times above 500 μs .

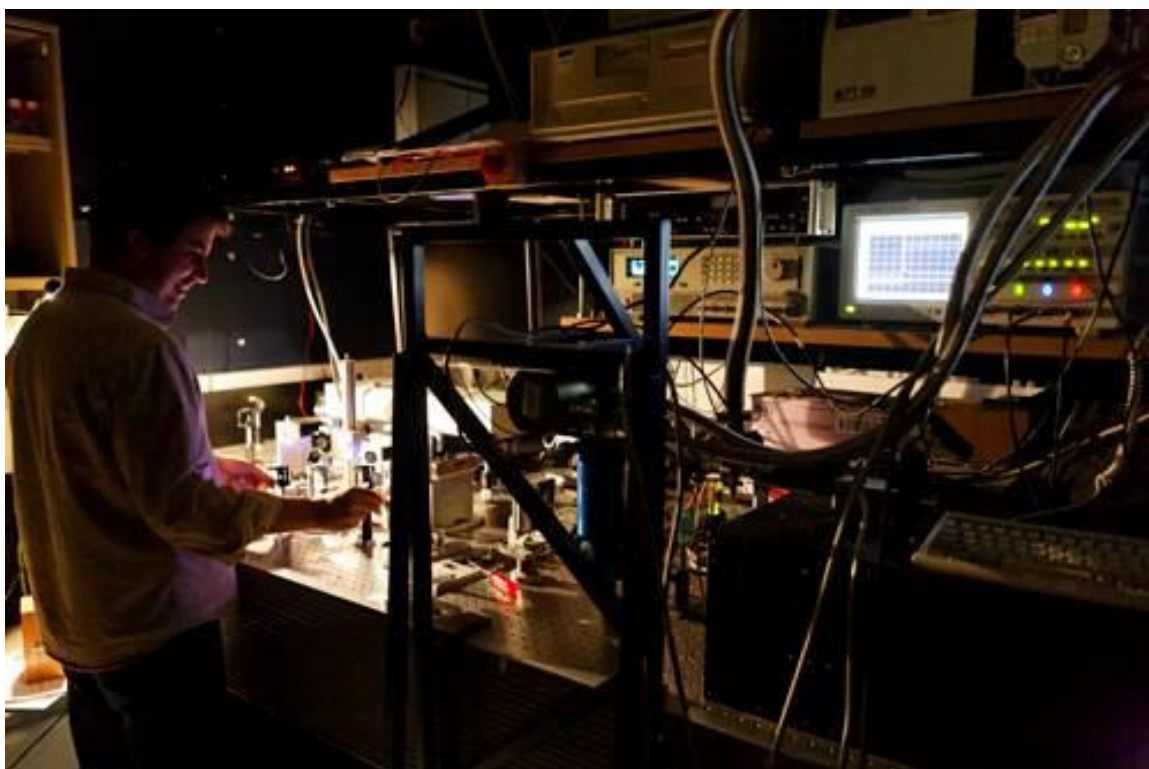


Figure 1: Nanosecond to millisecond time resolved emission spectrometer setup used to record emission decays and phosphorescence from samples.

3. Measurement results

Figure 2 shows the emission from the ^1CT state of the TADF materials in different hosts. Also shown are the phosphorescence spectra (“Phosph.”). As the relevant triplet level of the ^3LE state does not change significantly with the polarity of the host, we only show the phosphorescence spectra in the host material Zeonex in the graphs. The closer the short wavelength onset of ^1CT emission and phosphorescence, the smaller the singlet-triplet gap ΔE_{ST} , which mainly determines the efficiency of the TADF process.

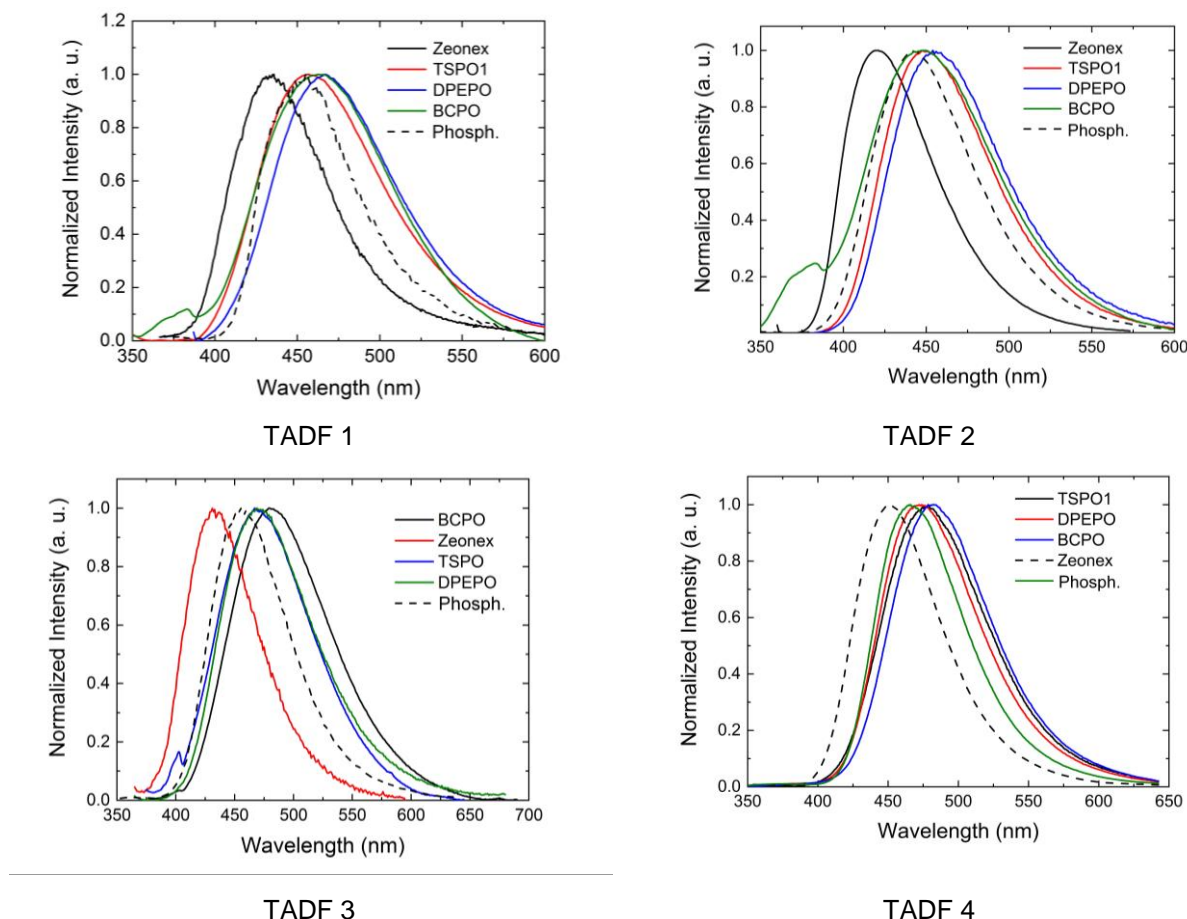


Figure 2: Emission spectra of new blue TADF emitters synthesised in the project. The ^1CT emission from the different TADF materials are named according to the employed host. “Phosph.” designates the phosphorescence from samples with Zeonex host.

TADF 1 was the starting point of our investigation. The spectra show that we obtain the smallest singlet-triplet gap in the host DPEPO for this material. As can be seen, we do not obtain a sufficiently small ΔE_{ST} for any of the different TADF materials in the non-polar host Zeonex. However, the substitution patterns allow us to tune the energy levels of the TADF materials so that for TADF 2-4 we can push the triplet energy (onset of phosphorescence) up in energy compared to TADF 1. It also matches well with the ^1CT emission in hosts TSPO1 and BCPO, which means that DPEPO is not needed for efficient TADF in the materials 2-4.

This is also demonstrated by the time resolved photoluminescence shown in figure 3. The strong delayed component (second “cascade” feature) in BCPO and in particular in the less polar host TSPO1 is a clear indication of efficient TADF. For the non-polar host Zeonex however this is not the case, though for TADF 4 the delayed component in Zeonex is stronger than for TADF 1.

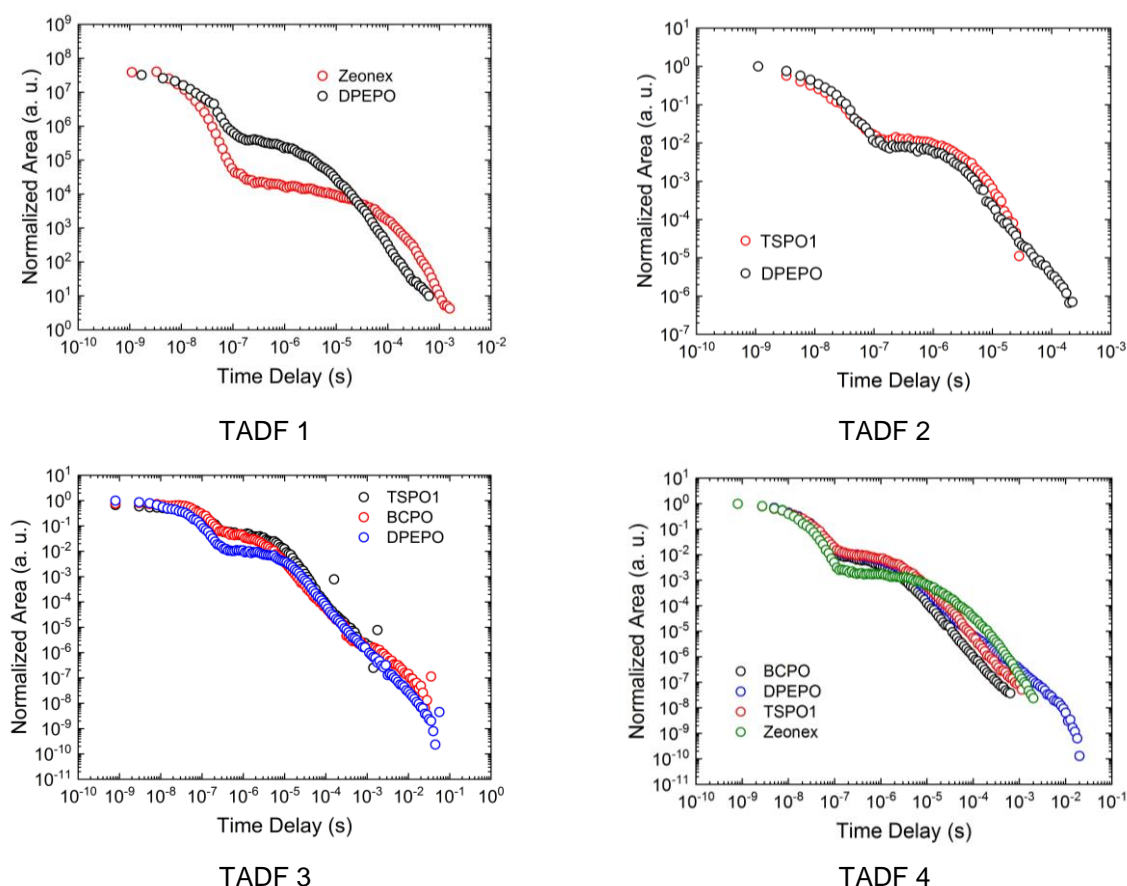


Figure 3: Photoluminescence decay of the new blue TADF emitters.

It should be mentioned that TADF 2 and 3 emit deeper in the blue than TADF 1, while TADF 4 only shows a slight redshift. This means that Förster energy transfer to blue fluorescent emitters is enhanced or only slightly decreased by the energy level tuning that was achieved.

4. Summary

With a new series of deep blue emitting TADF materials, we have been able to investigate the influence of the host material on the TADF efficiency. We have demonstrated that our deep blue TADF emitters can be modified to work in less polar hosts than DPEPO, namely TSPO1, without deteriorating emission color. This improvement has been achieved using simple substitutions on the donor or acceptor units and work currently continues to prepare and identify TADF materials suitable for devices with nonpolar host materials.

5. References

- [1] Penfold, T. J., et al. (2018). "Spin-Vibronic Mechanism for Intersystem Crossing." *Chemical Reviews* 118(15): 6975-7025.
- [2] Dos Santos, P. L., et al. (2016). "Using Guest-Host Interactions To Optimize the Efficiency of TADF OLEDs." *The Journal of Physical Chemistry Letters* 7(17): 3341-3346.