

Project:
HyperOLED
(Grant Agreement number 732013)

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

Funding Scheme: Research and Innovation Action

Call: ICT-02-2016 "Thin, Organic and Large Area Electronics"

Date of the latest version of ANNEX I: 12/10/2016

D2.6 Summary report on effects of donor substituents

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Report Issue Date:	26/07/2018

Document History (Revisions – Amendments)	
Version and date	Changes
1.0 –26/07/2018	First version

Dissemination Level		
PU	Public	X
PP	Restricted to other program participants (including the EC Services)	
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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, multiple blue and white stack unit prototypes (2 x 2 mm² on 30x30mm glass substrates with ITO) will be integrated into a high-brightness microdisplay demonstrator (based on MICROOLED’s 0.38” WVGA CMOS backplane) and tested that demonstrate significant improvements in functionality, performance, manufacturability and reliability.

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1. Introduction

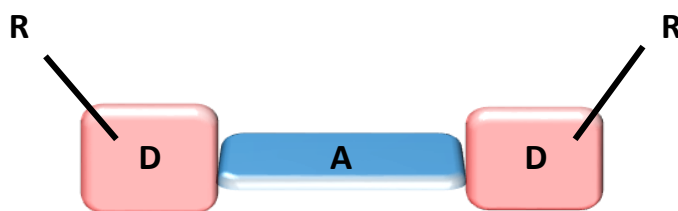
Hyperfluorescent OLEDs combine thermally activated delayed fluorescence (TADF) materials with fluorescent dopants to obtain improved performance compared to purely TADF based devices. The TADF material's job is to convert all electrical energy into singlet excitons which are transferred to the fluorescent dopant and emitted as light. This "detour" is used because fluorescent emitters show better emission characteristics than TADF materials but cannot use the triplet excitons created in the device. The HyperOLED project aims to improve hyperfluorescent OLEDs and so one obvious goal is the development of improved TADF materials, which is the subject of the present report. The focus lies on efficiency, stability and compatibility with the fluorescent dopants developed in the project.

The rate of reverse intersystem crossing (rISC) basically describes how fast the TADF material converts triplet into singlet excitons. Apart from the obvious fact that a high rISC rate is beneficial for device performance, we have identified the compatibility with low polarity host materials as an important requirement to obtain stable OLEDs. The reason is that the choice of high polarity host materials is quite limited, making it very difficult to find a stable material with the correct properties. As the host material has a big impact on device lifetime and performance in general, better devices are expected when one of the more widely available low polarity hosts can be used.

One approach to improve our TADF materials is based on the fact that attaching bulky substituents to the donor groups tunes the energy levels of the charge transfer as well as the local triplet states. Understanding the substituents' effect on the photo physical properties gives us the possibility to tune the emission colour which is important to obtain good energy transfer to the fluorescent dopant. Adjusting the energy gaps that govern the TADF mechanism by using optimised substituents allows us to find TADF materials that work in less polar host materials with high rates of intersystem crossing.

2. Investigated compounds

In our project, we investigate so called D-A-D (donor-acceptor-donor) molecules which can be depicted by the following sketch. The D-A-D structure gives rise to the charge transfer character of the materials which is one of the prerequisites for efficient TADF.



Molecule 1 R = H

Molecule 2 R = Steric Bulk group 1

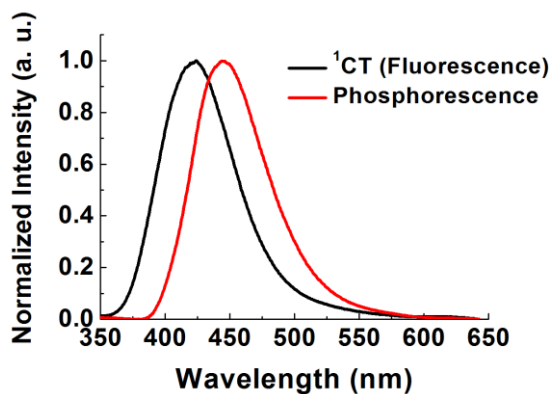
Molecule 3 R = Steric Bulk group 2

Two new molecules 2 and 3 have been successfully synthesised and characterised. Their structures were aimed at assessing how bulky substituents (R) on the donor will affect the properties compared to analogue 1 without the substituents. The groups on material 2 provide steric bulk on the donor and tune the electronic properties. The groups on 3 have very different electronic properties but provide a similar steric situation. The effect of steric bulk in combination with differing electronic properties can thus be probed within this series.

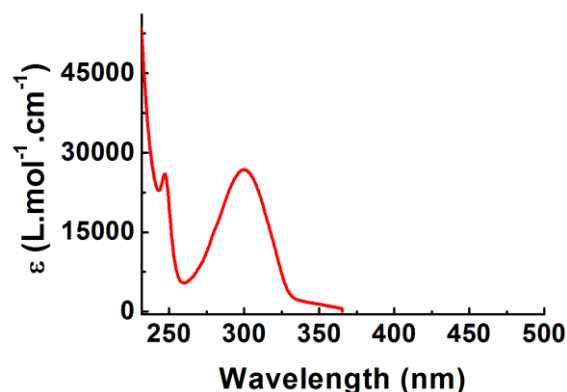
The new molecules were characterised by mass spectrometry and ^1H NMR spectroscopy to confirm their structure and to demonstrate isolation of clean and single products.

3. Results

We found that for molecule 2, the ^1CT emission (fluorescence from the charge transfer state) is significantly blue shifted compared to molecule 1. The absorption is also significantly blue-shifted. This shows that the donor substituents can be effectively used for colour tuning. The phosphorescence onset however is too far away from the ^1CT onset as shown by the corresponding spectra in the following graph on the left. Consequently, this molecule does not show TADF.

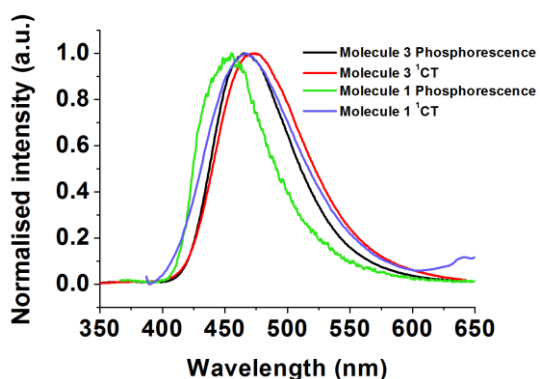


Emission spectra of molecule 2 in Zeonex

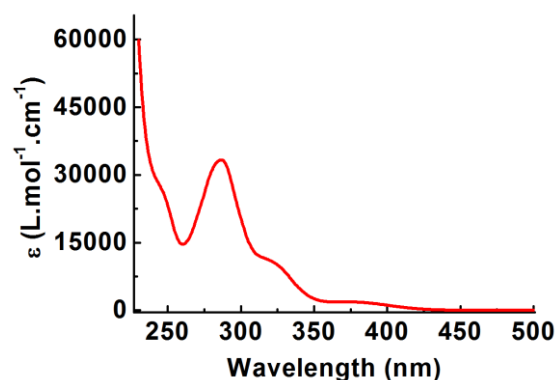


Absorption spectrum of molecule 2

In contrast, we find a slightly red-shifted ^1CT emission for compound 3 when compared to the unsubstituted material 1. This shows that the donor substituent on this compound has a very different electronic effect compared to the one used for material 2. The interesting feature is that the phosphorescence is also red-shifted as can be seen from the spectra in the following graph on the left.

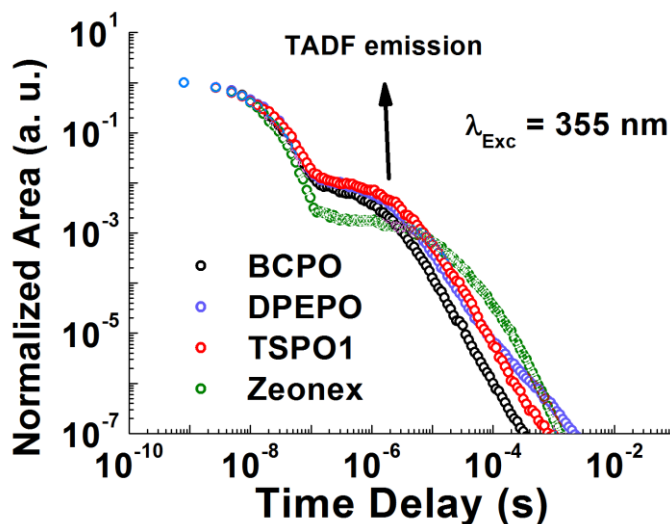


Emission spectra of molecules 1 and 3 in DPEPO



Absorption spectrum of molecule 3

As the shift in the phosphorescence onset is not as strong as that for the ^1CT emission, the singlet and triplet levels are pushed closer together compared to molecule 1, which should give rise to faster TADF. The time resolved photoluminescence (PL) shown in the following graph confirms this expectation.



Time resolved emission of molecule 3 in different hosts

The analysis of the time resolved PL data shows that the delayed component has a decay time of 2.5 μs for compound 3 in the host DPEPO. The unsubstituted material 1 has almost double this (4.4 μs) in the same host which shows we have effectively increased the rate of reverse intersystem crossing by substituting the donor unit. Time resolved PL was recorded in different host materials and though a delayed component is observed in the non-polar host Zeonex, it is far weaker than in the high polarity materials DPEPO, BCPO and TSP1. While we have not yet achieved compatibility with low polarity host materials, our results indicate the way how to tune the energy levels which is required to make the materials work in low polarity hosts.

4. Conclusion

We have analysed the effect of two different substituents on the donor part of our TADF molecules. Strong colour tuning to deeper blue was obtained but resulted in a loss of TADF. With another substituent, a decrease of the singlet-triplet gap and a significant improvement of the reverse intersystem crossing rate was achieved.