

Thermally Activated Delayed Fluorescence: Excited State Engineering

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*Recent results on fluorescent materials for organic LED based on thermally activated delayed fluorescence (TADF) are summarized. **Keywords:** Thermally-activated delayed fluorescence, emitting materials*

Organic light-emitting devices, OLED, are entering the display market. In these devices electrons and holes injected into an active material recombine in an exciton that eventually decays emitting light. However, spin statistics limit the internal efficiency of light emission to 25% and several strategies have been proposed to break this limit. Thermally-activated delayed fluorescence (TADF) offers a valuable strategy towards efficient OLEDs with high color purity in purely organic materials, without the need to introduce heavy metal atoms. TADF indeed allows to harvest light from the non-fluorescent triplet states, via a precise engineering of the excited states of the material. The close proximity between lowest singlet and triplet energy levels allows for reverse intersystem crossing (RISC), i.e. a transfer of population from the dark triplet states towards the fluorescent singlets.

The efficiency of TADF emitters is affected by—(a) nature of excited states, (b) spin-orbit coupling, (c) conformational degrees of freedom, (d) environmental effects, etc. A proper understanding of these interrelated factors is very much necessary to improve the design of TADF materials. Density functional theory (DFT) and time-dependent density functional (TD-DFT) are the most widely used methods to study ground and excited states of medium to large molecular systems. Relative position of excited states largely depends on the choice of functional. We find a possible solution using tuned-range functional. Addressing conformational and environmental effects is a fairly delicate issue. We propose an original essential state model (ESM) approach to explain the behavior of excited states and their interaction (spin-orbit coupling) for a simple dipolar dye. ESM can be used to understand the interplay between conformational degrees of freedom and coupling between states. The model has been validated against the TD-DFT. Environmental effects are also introduced in terms electronic and orientational solvent degrees of freedom. Specifically, we exploit a novel antiadiabatic approach to describe the coupling between the TADF molecule and the electronic degrees of freedom of the environment (1).

The theoretical machinery is applied to the TADF emitter DMAC-TRZ shown in Figure 1. The low-energy weak transition at 350–400 nm is a charge-transfer transition. The strong solvatochromism of emission spectra of DMAC-TRZ is

well reproduced by ESM. At low temperature in a glassy solvent (2MeTHF, 77K), DMAC-TRZ shows a long-lived emission, which is assigned to a triplet state with a predominant charge-transfer character.

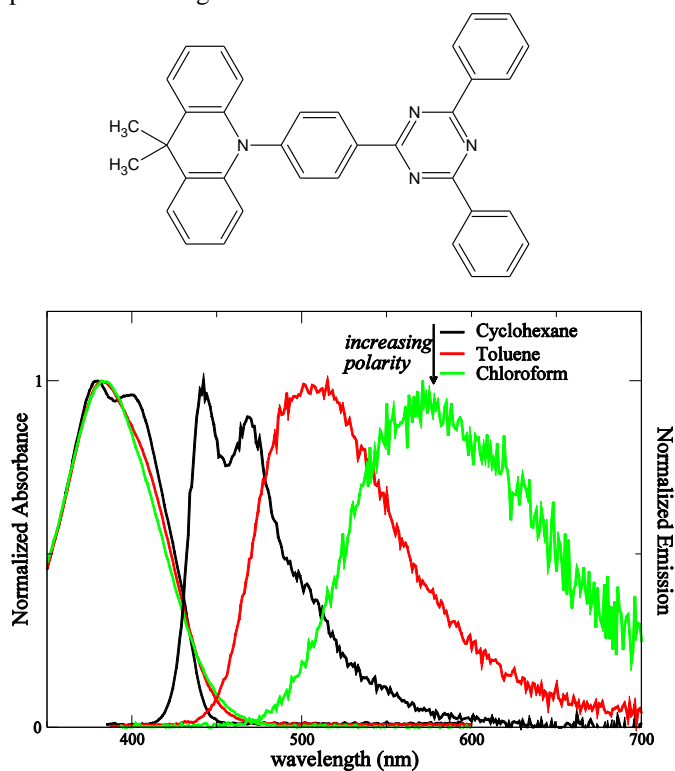


Fig. 1 Top: molecular structure of DMAC-TRZ. Bottom: absorption and emission spectra of DMAC-TRZ in solvents of different polarity.

Acknowledgements

This project received funding from the European Union Horizon 2020 research and innovation programme under grant agreement No 812872 (TADFlife). The work benefited of the COMP-HUB Initiative, funded by the ‘Departments of Excellence’ program of the Italian Ministry for Education, University and Research (MIUR, 2018-2022).

References

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