



DESIGN AND APPLICATION OF CHIRALLY PERTURBED TADF EMITTERS USING BENZENE-1,2-DITHIOL AS ELECTRON DONORS

L. Estaque¹, **P. Rajagopal**¹, **M. Remond**², **B. Racine**³, **L. Frédéric**⁴, **G. Clavier**⁴ and **G. Pieters**¹

¹ *Université Paris-Saclay, CEA, Service de Chimie Bio-organique et Marquage, DMTS, Gif-sur-Yvette F-91191, France*

² *Université d'Angers, UMR CNRS, MOLTECH-Anjou, SFR MATRIX, Angers F-49000, France,*

³ *Université Grenoble-Alpes, CEA, LETI, Grenoble 38054, France*

⁴ *Université Paris-Saclay, ENS Paris-Saclay, CNRS, PPSM, Gif-sur-Yvette F-91190, France*

Electroluminescent devices are multilayer systems, composed of an anode and a cathode, which are respectively responsible for the injection of holes and electrons. The recombination of these charges leads to the formation of excitons. These excited states can undergo radiative relaxation and produce light. Statistically, 25% and 75% of the excitons are located in the singlet and triplet states, respectively. Since the introduction of the first organic light-emitting diode (OLED) by Kodak in 1987¹, several generations have followed. The first generation of OLED is based on prompt fluorescence, using the transition between the first singlet excited state and the ground state ($S_1 \rightarrow S_0$) to produce light. The second generation introduces a phosphorescence process², where the triplet state-to-ground state transition ($T_1 \rightarrow S_0$) is exploited to generate light. The Internal Quantum Efficiency (IQE), an extremely important parameter in OLED devices, has reached 100% for certain second-generation systems. However, since phosphorescent emitters involve precious metals such as Ir or Pt, the quest to find a more sustainable and cost-effective strategy remains.

The breakthrough in 2012 by Adachi and his group provided a solution to this problem. They reported the first pure organic dye displaying Thermally Activated Delayed Fluorescence (TADF), which demonstrated remarkable performances in OLED devices³. The purpose of TADF is to harvest most of the excitons formed in the triplet state, thanks to Reverse Intersystem Crossing (rISC). The latter is enhanced when the energy gap between the S_1 and T_1 levels is smaller than 0.3 eV. In another hands, in conventional OLED displays, up to 50% of emitted light can be wasted due to the anti-glare filter. Therefore, it became important to develop chromophores with Circularly Polarized Luminescence (CPL), in which the emitted light is predominantly left- or right-oriented⁴.

In this context, we designed chiral TADF molecules featuring a dithiophenol moiety as an electron donor, with cyanopyridine and terephthalonitrile as electron acceptors, and a BINOL unit as a chiral perturbed unit. These molecules exhibit exceptionally high photoluminescence quantum yield (PLQY), reaching a maximum of 0.98 in doped thin films (using 1,3-bis-Carbazolyl-benzene as the host), with TADF properties leading to long fluorescence lifetimes up to 2.4 ms. Regarding chiroptical properties, these systems display unusual differences in dissymmetry factors between the ground and excited states. This has been explained by significant geometrical differences between ground and excited state geometries, as revealed by density functional theory (DFT) calculations. These readily synthesized emitters have been successfully implemented as emissive dopants in top-emission OLED devices, which are currently undergoing characterization.

References

¹ C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.*, **1987**, 51, 913

² M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature.*, **1998**, 395, 6698

³ H. Uoyama, K. Goushi, K. Shizu, H. Nomura, C. Adachi, *Nature.*, **2012**, 492, 7428.

⁴ L. Frédéric, A. Desmarchelier, R. Plais, L. Lavnevich, G. Muller, C. Villafuerte, G. Clavier, E. Quesnel, B. Racine, S. Meunier-Della-Gatta, J. P. Dognon, P. Thuéry, J. Crassous, L. Favereau and G. Pieters, *Adv. Funct. Mat.*, **2020**, 30, 43.

⁵ L. Mengke, X. Wentao, C. Xinyi, P. Xiaomei, L. Kunkun, G. Qing, Z. Jiadong, Q. Weidong, C. Zijian, G. Yiyang, S.-J. Su, *Angew. Chem.*, **2022**, 61, 35.