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New Tetraphenylethylene-based luminescent dyes for parabolic concentrators

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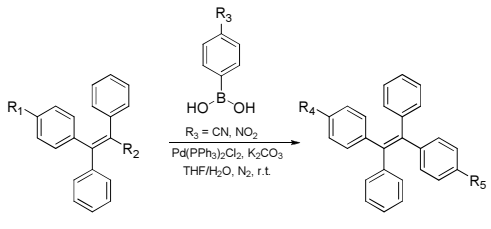
Introduction

In the scope of IDEAS project a novel low-cost building integrated renewable energy system maximizing the output tuneable for different climatic conditions is under development, through novel luminescent dyes and quantum dots (QD) and geometric concentrator techniques leading to current solar system efficiencies being exceeded electrically. A thin film luminescent downshifting (LDS) layer will be fabricated to enhance electricity generation which is placed as a top layer (or aperture) on the overall photovoltaic (PV) system. For this purpose a series of new tetraphenylethylene (TPE)-based luminescent dyes were design to fulfil certain conditions from the optical point of view: (i) unity Luminescent Quantum Yield (LQY), (ii) a wide absorption band in the region 300-400 nm where the External Quantum Efficiency (EQE) of the cell is low; (iii) a high absorption coefficient; (iv) a narrow emission band, coinciding with the peak of the cell EQE; (v) a large Stokes shift, *i.e* a good separation between the absorption and emission bands in order to minimize losses due to re-absorption.

Methods



Scheme 1 – Synthesis of dyes [1].

All dyes were structurally characterized by FTIR, NMR and HR-MS, and their optical and electrochemical properties were studied. Theoretical calculations were performed with Density Functional Theory (DFT) using the Gaussian 03 Package [2], with B3LYP/6-31G (d) functional and basis set in the gas phase.

Results

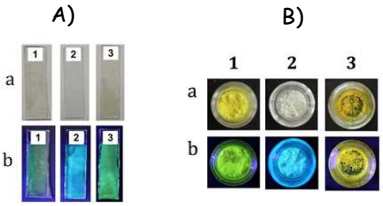


Figure 1 – Images of luminescent dyes **1**, **2**, **3** under white (a) and UV light of 365 nm (b), in solid films (Zeonex) (A) and powders (B).

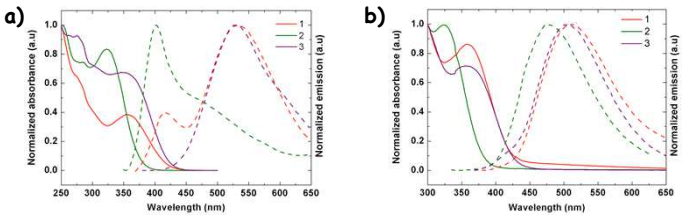


Figure 2 – Normalized absorption (solid line) and emission (dashed line) spectra of dyes **1**, **2**, **3**, in dioxane solution (a) and solid films (b).

Table 1 – Photophysical properties of dyes **1**, **2**, **3** in 1,4-dioxane and solid films.

	Dyes	UV-Vis absorption λ_{max} (nm)	Fluorescence emission λ (nm)	Stokes shift (nm)
Dioxane	1	355	415, 532 (355)*	177
	2	323	401, 483 (323)	78
	3	345	529 (345)	184
Film	1	359	512 (359)	153
	2	325	479 (323)	154
	3	357	505 (357)	148

*The values in parentheses are excitation wavelengths.

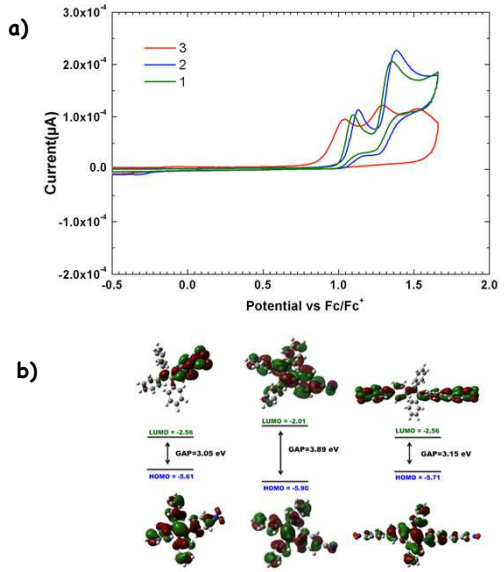


Figure 3 – (a) Cyclic voltammograms of the dyes **1**, **2**, **3**, in acetonitrile solution (b) Electron density distributions of HOMO and LUMO orbitals and corresponding energy levels (isovalue=0.004).

Table 2 – Experimental and theoretical electrochemical properties of dyes **1**, **2**, **3**

				Experimental (CV)		Theoretical (DFT)	
Dyes	E^{ox} (onset) vs Fc/Fc+	λ int[a] (nm)	$E_{0\text{-}0}$ (eV)[b]	E HOMO (eV)[c]	E LUMO (eV)[d]	E HOMO (eV)	E LUMO (eV)
1	1.04	429	2.89	-5.84	-2.95	-5.61	-2.56
2	1.02	394	3.15	-5.82	-2.67	-5.9	-2.01
3	0.88	419	2.96	-5.68	-2.72	-5.71	-2.56

[a] The intersect of the normalized absorption and the emission spectra.
[b] $E_{0\text{-}0}$ values were estimated from the intercept of the normalized absorption and emission spectra in film (Zeonex).
[c] Deduced from the equation E HOMO = - (E^{ox} $_{onset}$ + 4.80).
[d] Deduced from the equation E LUMO = E HOMO - $E_{0\text{-}0}$.

- Cyclic voltammograms of **1** and **2** show quasi-reversible waves with two oxidation peaks whereas in dye **3** the oxidation process is irreversible.
- The calculated energy levels of HOMO and LUMO orbitals of dyes 1-3 are consistent with the energy determined experimentally by cyclic voltammetry measurements.

Conclusions

- TPE-based dyes **1-3** display intense absorption in the UV range (323 nm to 359 nm), an emission maximum higher than 500 nm and Stoke shifts between 148 and 154 nm, which allow to minimize losses due to re-absorption.
- These dyes exhibit aggregation-induced emission (AIE) characteristics (very low fluorescence in solution but quite high in solid state, Figure 1) due to the TPE structures [3,4].
- The preliminary results of photophysical studies allow us to conclude that the new synthesized TPE-based dyes have the potential to be used as luminescent species for fabrication of LDS layers.
- Fabrication and characterization of LDS layers based on these dyes is underway.

References

[1] Y. Li, Z. Li, T. Ablekim, T. Ren, W-J. Dong, Phys.Chem.Chem.Phys. 16 (2014) 26193-26202.
[2] M. Frish, G. Trucks, H. Schlegel, G.S.- Inc., Gaussian 03, Revision D. 02, Gaussian Inc, Pittsburgh PA. (2003).
[3] R. Hou, G. Zhao, Y. Xia, Molecules, 23 (6) (2018) 1446.
[4] H-Q Peng, X. Zheng, T. Han, R. T. K. Kwok, J. W. Y. Lam, X. Huang, B. Zhong Tang, J. Am. Chem. Soc. 139 (2017) 10150-10156.

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