nanoGe
Hybrid and Organic Photovoltaics
11-14 MAY 2014 - LAUSANNE -SWITZERLAND
HOPV14

Synthesis, Optical and Electrochemical Properties of Perylene Dyes for Solar Cells Applications

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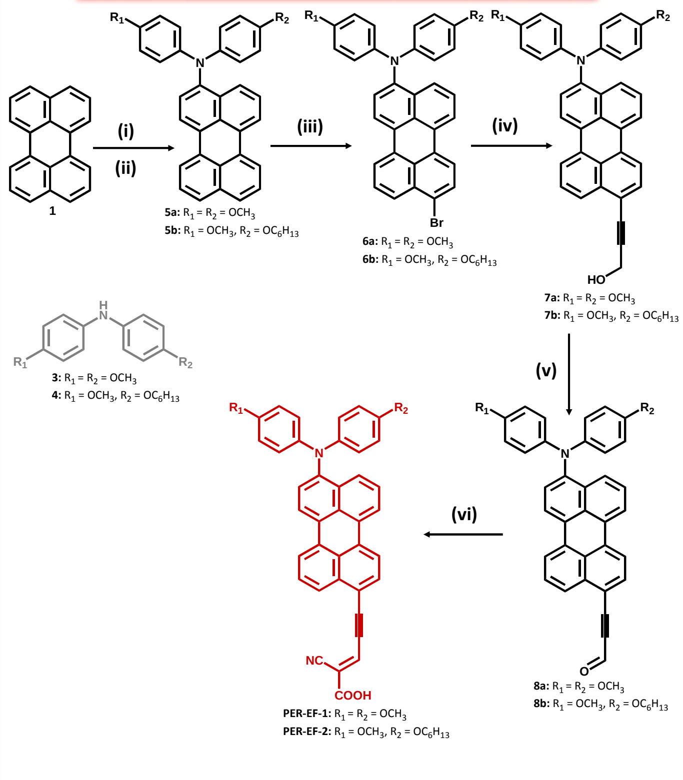
Introduction

Perylene monoimides or monoanhydrides are being intensively investigated as sensitizers in DSSCs. Keeping only one acceptor group, i.e. imide or anhydride, and introducing a donor group in the 9-position (such as diarylamine) proved to be important in order to obtain a favorable orbital partitioning strength and dipole moment of perylene compounds for DSSCs [1]. One way to control optical and electrochemical properties of perylene dyes is achieved by functionalizing *peri* and *bay* positions of perylene core with different substituents. In a simplified view, the *peri* groups coarsely tune the spectroscopic and electrochemical properties whereas the *bay* functional groups provide an additional fine tuning [2,3].

Here we report the design and synthesis of new perylene dyes (Scheme 1) comprising: (1) a 4-alkoxyphenylamino moiety in the 9-position as a strong donating group, (2) a cyanoacrylic acid as electron acceptor and anchoring group and (3) a triple bond as short and rigid linker between perylene core and the acceptor group [4].

Synthesis of Perylene Dyes



Scheme 1: (i) NBS (1.0 equiv), anhydrous THF, 24 h, r.t.; (ii) diarylamine (1.0 equiv), $Pd(OAc)_2$ (0.020 equiv), $P(t\text{-}Bu)_3$ (0.04 equiv), NaOt-Bu (1.5 equiv), anhydrous toluene, 120 ºC; (iii), NBS (1.0 equiv), anhydrous THF, 24 h, r.t.; (iv) $Pd(PPh_3)_4$ (0.1 equiv), PPh_3 (0.1 equiv), CuI (0.1 equiv), 2-propyn-1-ol (2.0 equiv), anhydrous THF and diisopropylamine, 90 °C; (v) Dess-Martin, anhydrous CH_2Cl_2, 24 h; (vi) cyanoacetic acid (1.5 equiv), ammonium acetate (0.4 equiv), glacial acetic acid, 120 °C.

Optical and Electrochemical Properties

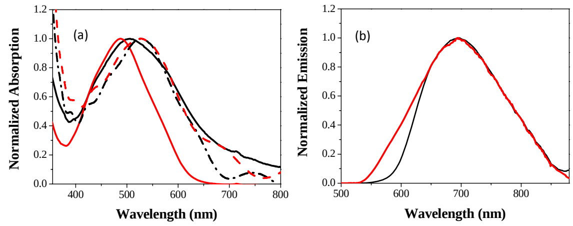


Figure 1: (a) Normalized absorption of PER-EF-1 (black) and PER-EF-2 (red) in toluene (2.5×10^{-5} M) and adsorbed on TiO_2 films; (b) Normalized emission spectra in toluene (2.5×10^{-5} M).

Table 1: Photophysical properties of dyes (2.5×10^{-5} M) in toluene at room temperature.

Dye	λ_{max} (nm) (ε/ M^{-1} cm^{-1})[a]	λ_{max} (nm)[b]		τ (ns)[d]	k_r (s^{-1})[e]	k_{nr} (s^{-1})[f]
PER-EF-1	506 (41,000)	695	0.89	5.1	1.75×10^8	2.16×10^7
PER-EF-2	488 (40,000)	695	0.88	5.1	1.74×10^8	2.37×10^7

[a] Maximum of absorption spectra and respective molar absorption coefficient.
[b] Maximum of emission spectra.
[c] Fluorescence quantum yield.
[d] Fluorescence lifetime.
[e] Radiative decay constant.
[f] Nonradiative decay constant.

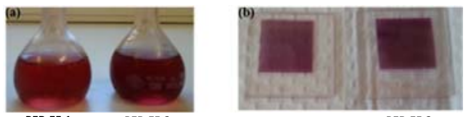


Figure 2: (a) Dyes in toluene solution and (b) adsorbed on TiO_2 films.

Table 2: Electrochemical properties of perylene dyes in DMF.

Dye	λ_{int} (nm)[a]	$E_{0\text{-}0}$ (eV)[b]	E_{HOMO} (eV)[c]	E_{LUMO} (eV)[d]
PER-EF-1	600	2.07	-5.88	-3.81
PER-EF-2	557	2.22	-5.81	-3.59

[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
[c] Deduced from the equation $E_{HOMO} = -(E_{ox}^{onset} + 4.75)$.
[d] Deduced from the equation $E_{LUMO} = E_{HOMO} - E_{0\text{-}0}$.

Results and Discussion

- We have successfully designed and synthesized new perylene dyes following a synthetic strategy and purification procedures liable for scale-up.
- **PER-EF-1** and **PER-EF-2** displayed intense absorption in the visible and NIR spectral range. The CV of both dyes showed one irreversible oxidation reaction.
- Both dyes exhibit LUMO levels more positive than the conduction band of TiO_2 (-4.26 eV) and hence should in theory have enough driving force for effective injection, when used as sensitizers in DSSCs.
- These dyes exhibit high molar absorption coefficients which make them good light harvesting materials for ss-DSSCs because of their ability to absorb light effectively in thin films.

References

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Acknowledgments: This work was supported by ***Fundação para a Ciência e Tecnologia*** through project PTDC/CTM-CER/11590/2009 and a doctoral grant (SFRH/BD/73999/2010).

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