Supporting information

Effect of porphyrin loading on performance of dye sensitized solar cells based on iodide/tri-iodide and cobalt electrolytes

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1.- Experimental conditions

Synthetic procedures were carried out under inert argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and were used without further purification. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040-0.063 mm). Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. $^1$H NMR spectra were obtained on Bruker TopSpin AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl$_3$, 7.27 ppm). $^{13}$C NMR chemical shifts are reported relative to the solvent residual peak (CDCl$_3$, 77.00 ppm). UV-Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH$_2$Cl$_2$, HPLC grade, with absorption between 0.1-1 of absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Mass spectra (MALDI-TOF) were recorded on a VOYAGER DE™ STR mass spectrometer using dithranol as matrix. Melting points are uncorrected.

The molecular geometries and frontier molecular orbitals of these new dyes have been optimized by density functional theory (DFT) calculations at the B3LYP/6-31G* level.$^1$

Cyclic voltammetry was performed in THF (4:1) solutions. Tetrabutylammonium perchlorate (0.1 M as supporting electrolyte) were purchased from Acros and used without purification. Solutions were deoxygenated by argon bubbling prior to each experiment which was run under argon atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode (ϕ = 2 mm) and a platinum wire counter electrode. An Ag/AgCl electrode was used as reference and checked against the ferrocene/ferrocinium couple (Fc/Fc$^+$) before and after each experiment.

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2. **$^1$H NMR, $^{13}$C NMR, FT-IR and MALDI-TOF**

![Figure S1. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 1a.](image1)

![Figure S2. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 1a.](image2)
Figure S3. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 1b.

Figure S4. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 1b.
Figure S5. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2a.

Figure S6. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2a.
Figure S7. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2b.

Figure S8. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2b.
Figure S9. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3a.

Figure S10. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3a.
Figure S11. $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3b.

Figure S12. $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3b.
Figure S13. MALDI-MS spectrum of compound 1a (Matrix: Ditranol).

Figure S14. MALDI-MS spectrum of compound 1b (Matrix: Ditranol).
Figure S15. MALDI-MS spectrum of compound 2a (Matrix: Ditranol).

Figure S16. MALDI-MS spectrum of compound 2b (Matrix: Ditranol).
**Figure S17.** MALDI-MS spectrum of compound 3a (Matrix: Ditranol).

**Figure S18.** MALDI-MS spectrum of compound 3b (Matrix: Ditranol).
Figure S19. FT-IR spectrum of compound 1a (KBr).

Figure S20. FT-IR spectrum of compound 1b.
**Figure S21.** FT-IR spectrum of compound 2a.

**Figure S22.** FT-IR spectrum of compound 2b.
**Figure S23.** FT-IR spectrum of compound 3a.

**Figure S24.** FT-IR spectrum of compound 3b.
3.- UV-Visible and emission spectroscopies

Figure S25. UV-Vis absorption spectra of compounds 1a (A) and 1b (B) in CH₂Cl₂.

Figure S26. Normalized UV-Vis absorption and fluorescence emission spectra of compounds 1a (A, λᵥₑₓ = 450 nm) and 1b (B, λᵥₑₓ = 449 nm) in CH₂Cl₂.
Figure S27. Fluorescence emission spectra in absence (solid line) and presence of TiO₂ (dash line) of 1b in CH₂Cl₂ of compounds 1a (A, λ_exc = 450 nm) and 1b (B, λ_exc = 449 nm) in CH₂Cl₂.

Figure S28. Normalized UV-Vis absorption spectra of compounds 2a (A) and 2b (B) in CH₂Cl₂.

Figure S29. Normalized UV-Vis absorption spectra of compounds 3a (A) and 3b (B) in CH₂Cl₂.
4. Square Wave plots of 1a and 1b

**Figure S30.** Cyclic Voltammetry (cathodic window) of compounds 1a (black line) and 1b (red line) (referred to Fc/Fc\(^+\)).

**Figure S31.** Square Wave Voltammetry plot (cathodic window) of compounds 1a (black line) and 1b (red line) (referred to Fc/Fc\(^-\)).
Figure S32. Square Ware Voltammetry plot (anodic window) of compounds 1a (black line) and 1b (red line) (referred to Fc/Fc').
6. Thermogravimetric analysis of 1a and 1b

![Graph showing thermogravimetric analysis of 1a](image)

**Figure S33.** Thermogravimetric analysis of 1a.

![Graph showing thermogravimetric analysis of 1b](image)

**Figure S34.** Thermogravimetric analysis of 1b.