Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

A Study of Oligothiophene-Acceptor Dyes in P-Type Dye-Sensitized Solar Cells

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Spectroelectrochemistry:

Spectroelectrochemistry was performed in a three-electrode electrochemical cell with a platinum mesh working electrode, glassy carbon counter electrode and Ag/$AgNO_3$ (10mM/MeCN) as reference electrode. The electrochemical cell was set up in a quartz cuvette whit an optical pathway of 1 mm. The sample was dissolved in a 0.1 M t-Bu_4NPF_6 / DCM electrolyte solution. The counter electrode was kept separate from the main solution by a salt bridge with glass frit tip. The potential was applied with an Autolab PGSTAT302 potentiostat/galvanostat, while the spectra were acquired with an Agilent 8453 UV-Vis spectrophotometer. Experiments were carried out in a glovebox (MBraun) maintained at < 0.1 ppm O_2 and < 0.1 ppm H_2O.

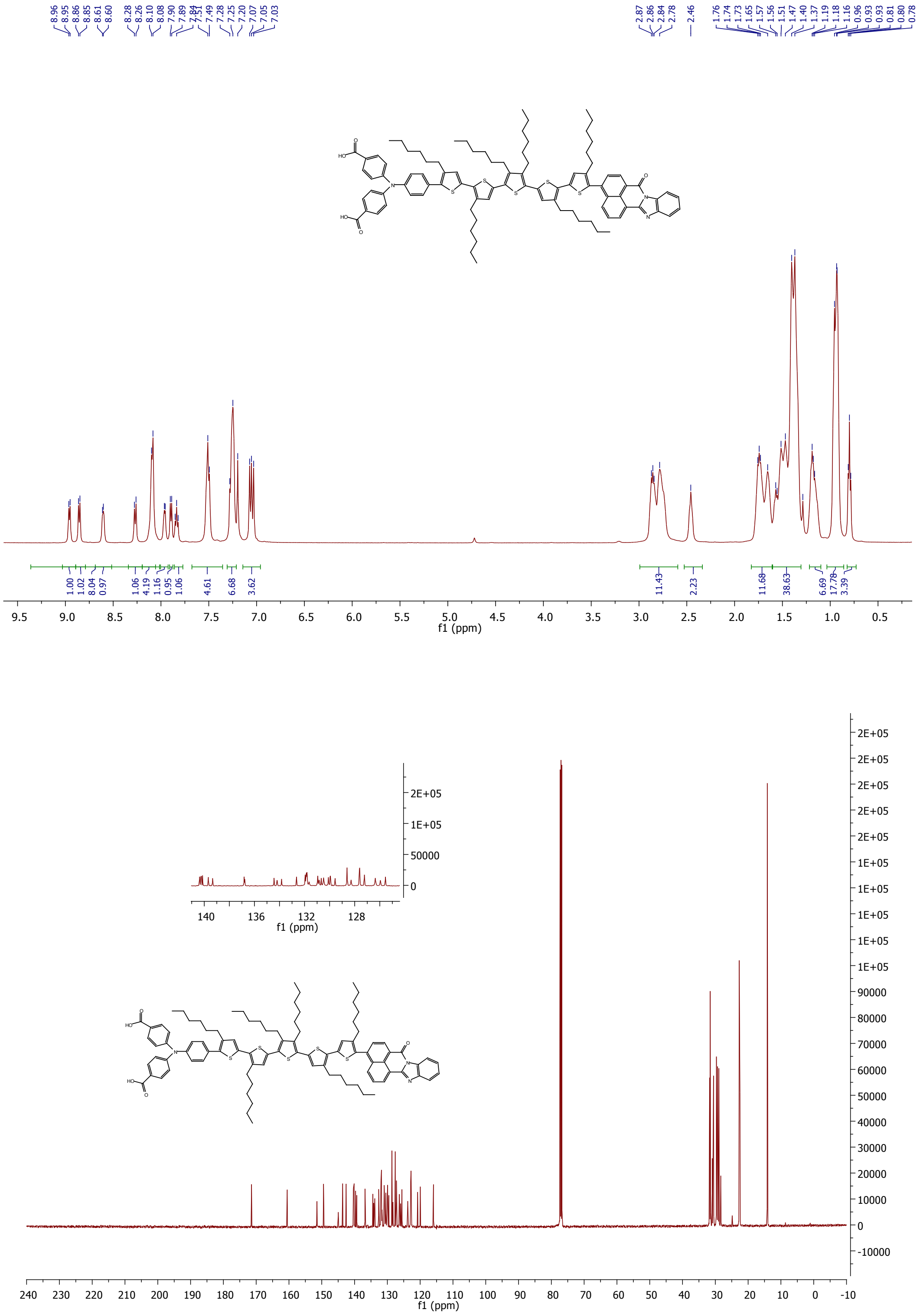

Figure S1. ^{1}H NMR and ^{13}C NMR (CDCl$_3$) spectra of **E1**

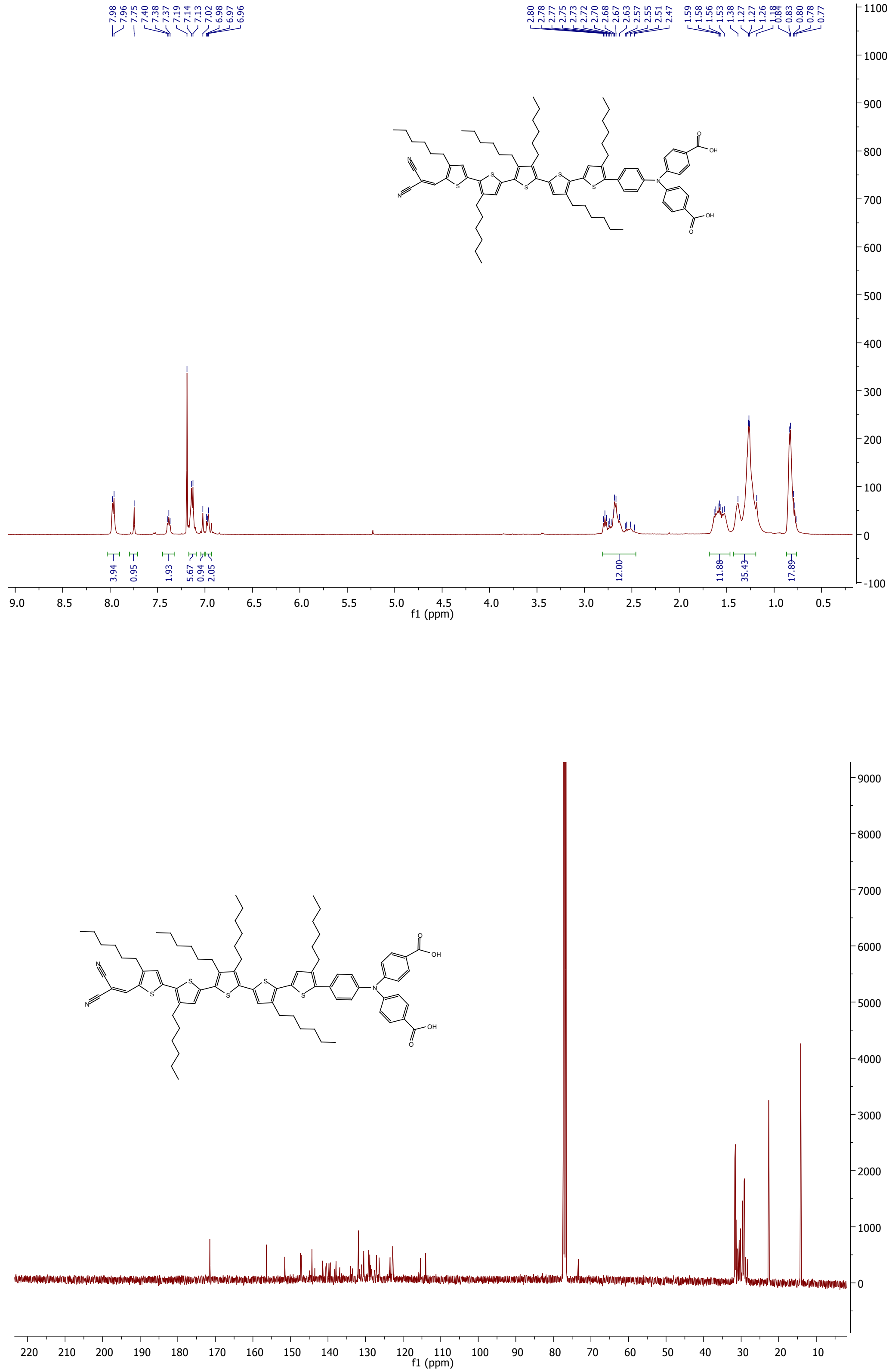

Figure S2. ^{1}H NMR and ^{13}C NMR ($CDCl_3$) spectra of **E2**

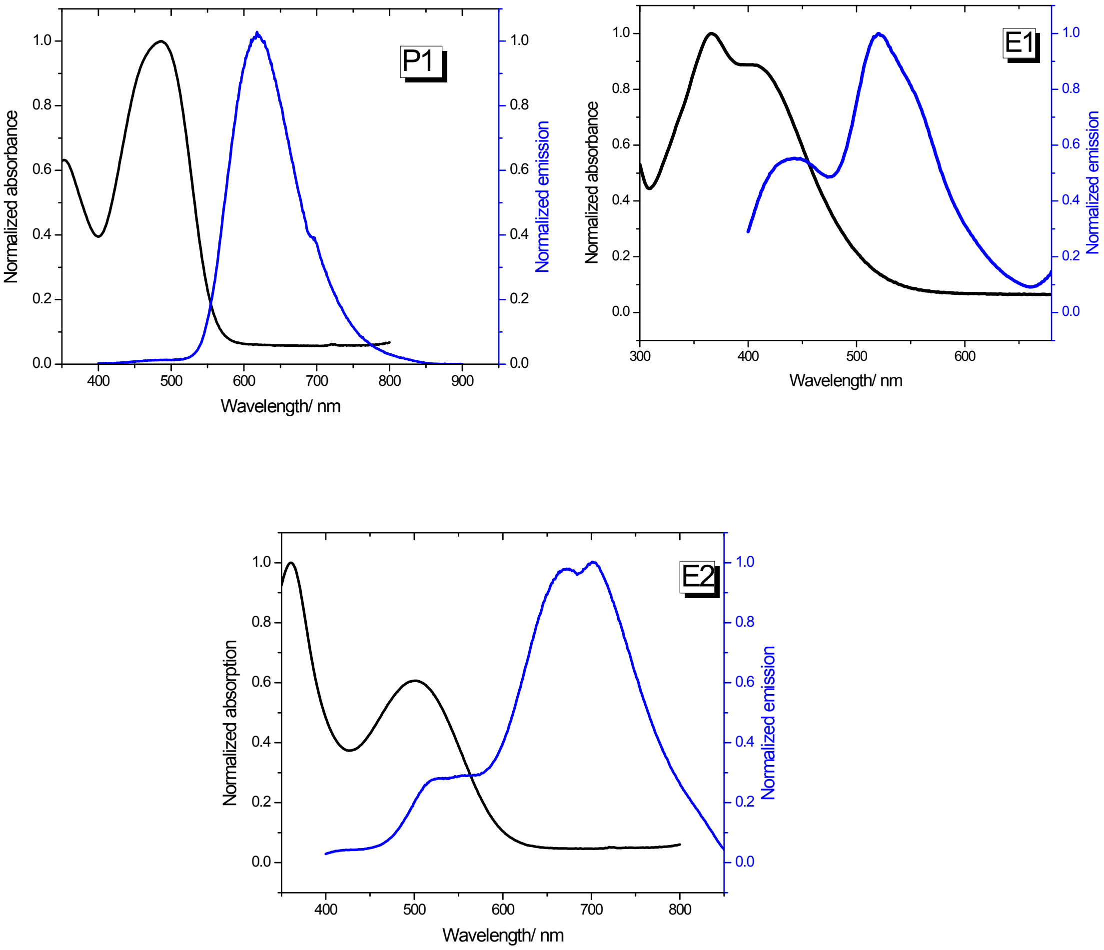

Figure S3. Normalized UV-Visible absorption and photoluminescence of **P1, E1**and **E2** tried in DCM (10^{-5} M).

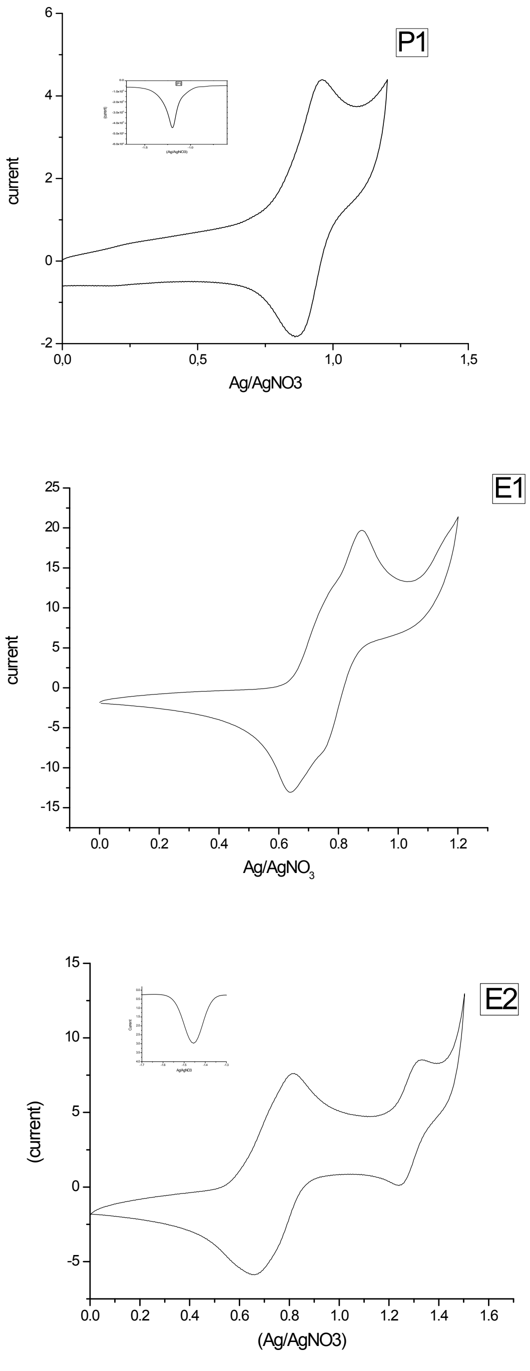

Figure S4. Cyclic voltammograms of **P1** in acetonitrile and **E1** and **E2** in THF containing 0.1 M TBAPF$_6$ with 100 mV scan rate and differential pulse voltammetry (inset) spectra of **P1** and **E2**.

Table S1. The HOMO/LUMO energy levels of the dyes

dye	HOMO [a] ev	LOMO [a] ev
E1	-6.02	-2.17
E2	-6.18	-2.61

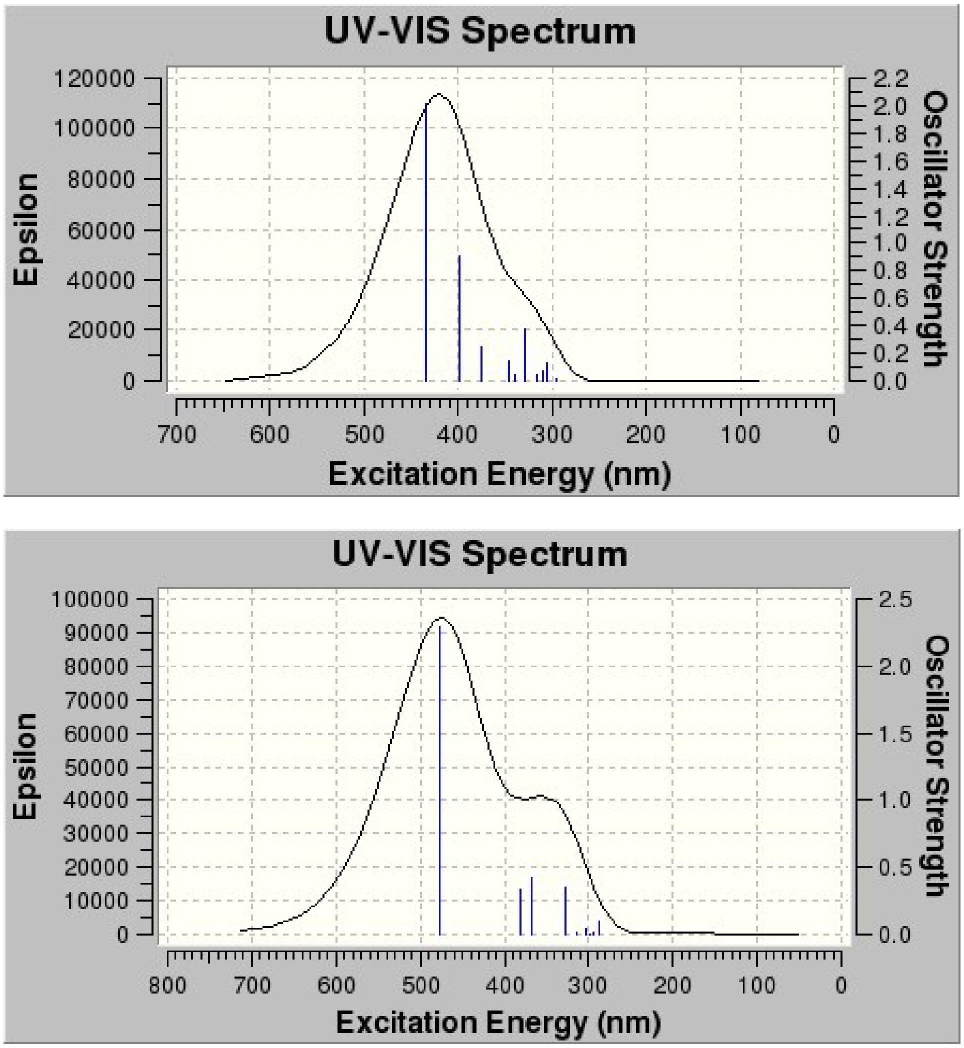

Figure S5. The simulated absorption spectra of E1 and E2 (from the top down).

Table S2. Time constants obtained from four-exponential fit of P1 and E2 in solution

	t_1 (ps)	t_2 (ps)	t_3 (ps)	t_4 (ps)
P1/ACN	0.098 ± 0.013	1.83 ± 0.24	9.74 ± 0.03	34.1 ± 0.3
E2/DCM	0.174 ± 0.021	0.864 ± 0.072	20.5 ± 0.26	941 ± 32

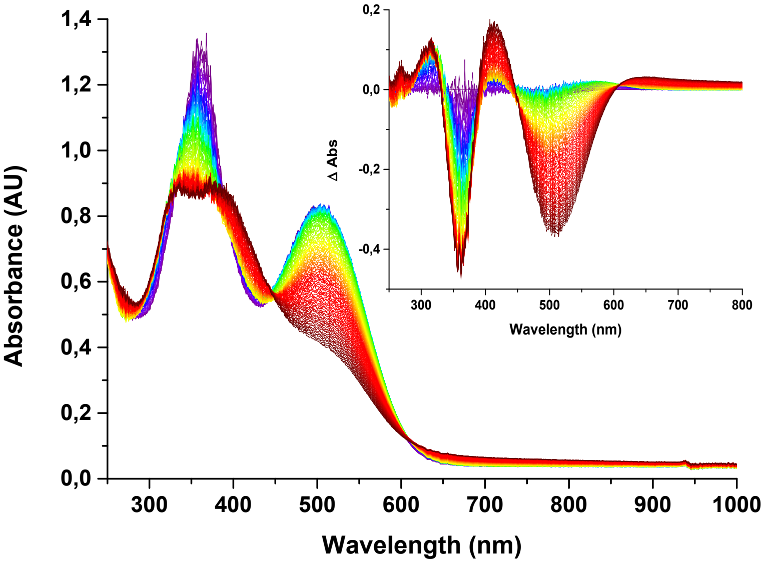

Figure S6. UV/Vis spectroscopic changes observed during controlled potential electrolysis of E2 dye (240 µM in 0.1 M t-Bu$_4$NPF$_6$ / DCM, 1 mm optical path length) at -1.4 V *vs*. Ag/AgNO$_3$ (10mM / MeCN). Inset shows the differential spectra.

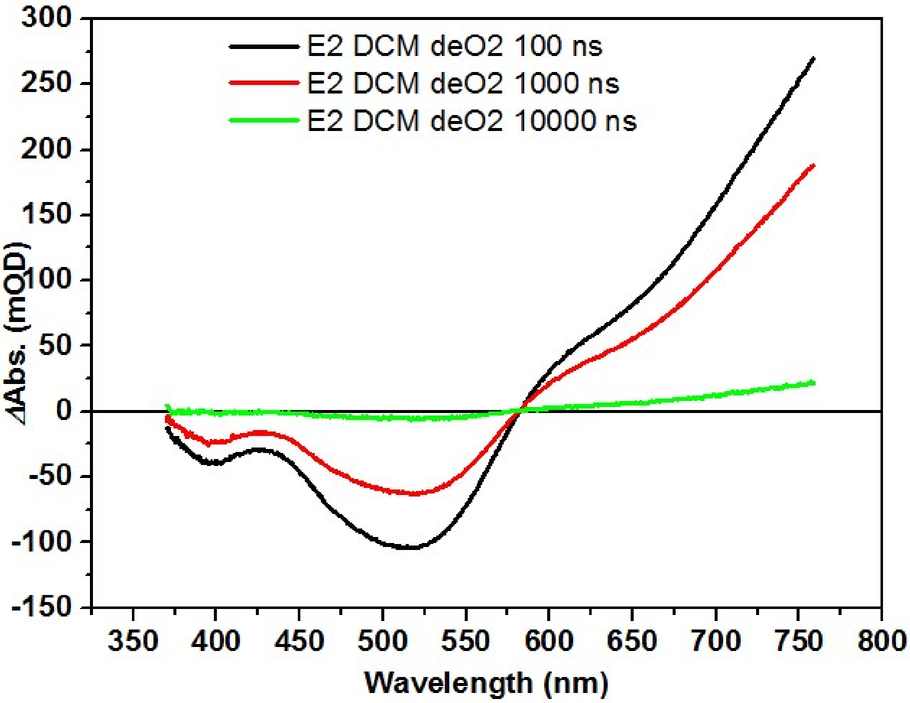

Figure S7. The transient absorption spectra of E2 in DCM excited at 532 nm

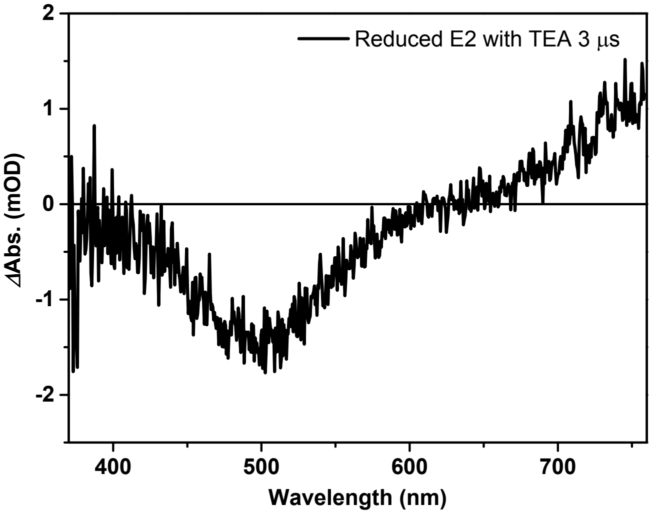

Figure S8. The TAS of **E2** in DCM in presence of triethylamine excited at 532 nm.

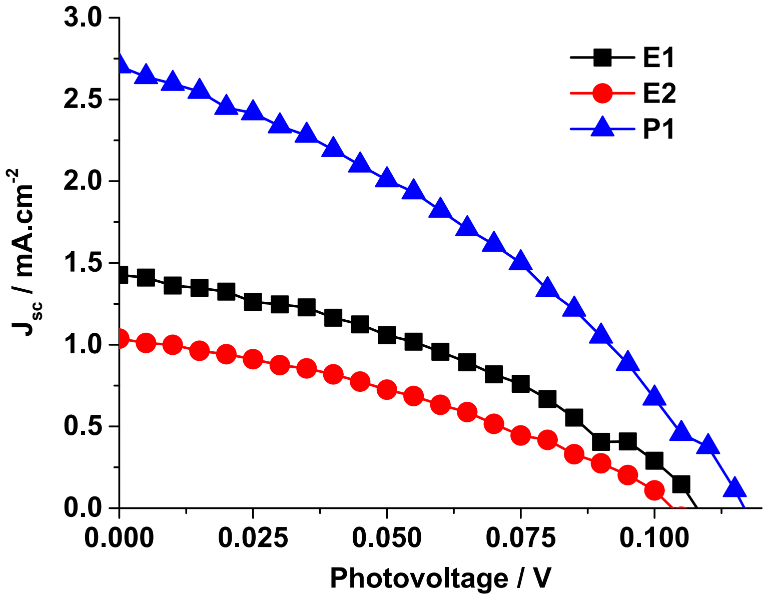

Figure S9. *J-V* curves of devices based the **E1**, **E2** and **P1** dyes using I^-/I_3^- electrolyte.

Table S3. Photovoltaic performance of DSCs based on **E1**, **E2** and **P1**-sensitized NiO and I^-/I_3^- electrolyte

dye	J_{SC} mA·cm^{-2}	V_{OC} mV	ff	η %
E1	1.4	110	0.37	0.056
E2	1.0	105	0.35	0.038
P1	2.7	115	0.36	0.113

Light intensity: 100 mW·cm^{-2}; solar cell area: 0.25 cm^2; Thickness of NiO: 2 μm. Electrolyte: 1 M LiI, 0.1 M I_2 in MeCN

As compared to the photovoltaic data of devices using cobalt electrolyte, the trend of photocurrent density of devices using I^-/I_3^- electrolyte is consistent with that from cobalt electrolyte. The devices using I^-/I_3^- indeed show enhanced photocurrent in comparison with those devices based on cobalt electrolyte. The slower mass transport issue of cobalt electrolyte should be responsible for the lower obtained photocurrent at 1 Sun illumination, which can be proved from J-V and IPCE shown in Figure 4. However, the photovoltage values of devices based on different dyes using I^-/I_3^- electrolyte are almost the same. It implies that the bulky structures of E1 and E2 cannot block I^- to reach NiO surface due to the smaller size of I^- in comparison with that of cobalt complex.