

Supporting information

Light-induced interfacial dynamics dramatically improve the photocurrent in dye-sensitized solar cells: An electrolyte effect

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Experimental details

Materials

All chemicals were purchased from Sigma Aldrich unless otherwise noted: Fluorine-doped tin oxide (FTO; Pilkington, TEC 15 Ω/cm^2 & TEC 7 Ω/cm^2), TiO₂ pastes (Dyesol Ltd., DSL 18NR-T and WER2-O), Surlyn frame (Solaronix). The dyes (PD2 and LEG1) and the tetracyanoborate or hexafluorophosphate salts of tris(2, 2'-bipyridine-2N, N') cobalt(II/III) were all purchased from Dyenamo AB, Sweden. All chemicals were reagent grade and used without further purification.

Solar cell fabrication and characterization

Details of solar cell fabrication have been reported previously.¹ A transparent TiO₂ layer (diluted paste: a mixture of 60 wt % TiO₂ paste (DSL 18NR-T) with 36 wt % terpineol and 4 wt % ethyl cellulose; area: 0.5×0.5 cm², thickness: 5 μm) and a scattering layer (WER2-O, 3 μm) were in succession screen-printed on a FTO substrate (Pilkington, TEC 15 Ω/cm^2) with a TiO₂ blocking layer pre-deposited by a simple hydrothermal method. The working electrodes were sintered in ambient atmosphere (325 °C for 25 min, thermostatic for 30 min, up to 500 °C for 25 min, thermostatic for 30 min and natural cooling), and post-treated with an aqueous TiCl₄ solution. The working electrodes were dipped in a 0.25 mM D35/ethanol dye bath in the dark overnight. The platinized counter electrode was prepared by drop-casting 20 μl 4.8 mM H₂PtCl₆ isopropanol solution on a pre-drilled and cleaned FTO (Pilkington, TEC 7 Ω/cm^2) glass substrate and then sintered in air at 400 °C for 30 min. The DSSCs were fabricated by assembling the sensitized TiO₂ electrodes with the Pt counter electrodes into a sandwich-type cell using a 25 μm thick hot-melt Surlyn frame (inner area: 0.6×0.6 cm²) as the sealant, introducing the electrolytes through pre-drilled holes under atmospheric pressure, and sealing by a 50 μm thermoplastic sheet and a glass coverslip. A metal contact was soldered on the edge of the FTO film to increase conductivity.

Current density-voltage (J - V) characteristics were conducted with a light-shading metal mask (0.7 ×0.7 cm²) on top of the cell under a standard irradiation (AM 1.5, 100 mW cm⁻²) supplied by a Newport solar simulator (model 91160-1000). Light illumination for incident photon-to-current conversion efficiency (IPCE) measurements was provided by a computer-controlled set-up assembled with a xenon arc lamp (300 W Cermax, ILC Technology), a monochromator (CVI Digikrom CM 110) and appropriate filters. Both J - V curves and IPCE spectra were recorded by a computerized Keithley 2400 source meter calibrated using a certified reference solar cell (Fraunhofer ISE). Photoelectrochemical measurements were performed using a white LED (Luxeon Star 1W) as the light source. Voltage and current traces were recorded using a 16-bit resolution digital acquisition board (National Instruments) in combination with a current amplifier (Stanford Research Systems SR570) and a custom-made system using electromagnetic switches. The methods of measurement have been reported previously.²⁻³ The relationship between voltage and extracted charge (Q_{oc}) under open-circuit conditions was studied using a combined voltage decay/charge-extraction method.⁴ Electron diffusion time (τ_d) and lifetime (τ_n) were determined by monitoring the photocurrent and photovoltage transients at different light intensities upon applying a small square-wave modulation to the

base light intensity. These transient responses were fitted using first-order kinetics in order to obtain the time constants. The data used in the figures visualizing the photoelectrochemical results were based on the cells that exhibited the best performance for each electrolyte.

Light exposure treatments performed on open-circuit devices and electrolyte samples were performed under continuous irradiation ($\sim 100 \text{ mW cm}^{-2}$, 390 nm UV cut-off; ATLAS Suntest XLS) in a sample compartment maintaining a temperature of 60°C.

Spectroscopic characterization

UV-*vis* absorption spectra of the dye-loaded, transparent films (2 μm thick) and dye solution in a quartz sample cell (0.5 cm path length), were recorded on a Cary 300 spectrophotometer respectively.

The photoinduced absorption (PIA) setup has been described previously.⁵ Excitation was provided by on/off modulation of a green diode laser (532 nm, Lasermate) at 9.3 Hz. Samples for transient absorption measurements were the same as the solar cells fabricated above, except that the photocathode contained only a transparent TiO_2 layer. Nanosecond transient absorption measurements were performed using an Edinburgh Instrument LP920 laser flash photolysis spectrometer with continuous wave xenon light as the probe light and a photomultiplier tube detector (system response time, $\sim 1 \mu\text{s}$). Scattering light from the excitation was suppressed with a 715 nm cut-on filter in front of the detector. Laser pulses were supplied by a Continuum Surelight II, Nd:YAG laser at 10 Hz repetition rate in combination with an OPO (Continuum Surelight). The pulse intensity was attenuated to 0.2 \sim 3 mJ per pulse with the use of natural density filters. The pump light wavelength was selected to 530 nm. Kinetic traces of absorbance were detected at 760 nm, averaged over 50 to 100 pulses per sample. Three samples were prepared for each electrolyte composition, and the measurement error was estimated from the averaged derivation. The overlaid curves were fitted from a KWW function only for visualization. The kinetics of the system were characterized by the half time, $t_{1/2}$, of the decay of the initial absorption difference.⁶ For the femtosecond transient absorption in the infrared region (IR), femtosecond laser pulses of 800 nm with a repetition rate of 3 kHz were used to generate an excitation wavelength of 520 nm with a power of 110-170 μW , and a probe pulse with a centered wavelength of ca. 5000 nm ($\sim 2000 \text{ cm}^{-1}$). More details about the femtosecond setup can be found in previously published work.⁷

Ultra-violet Photoelectron Spectroscopy (UPS) and metastable induced electron spectroscopy are electron spectroscopy methods for analysing the valence electron structure of surfaces. In UPS the sample is usually irradiated with photons of the He I photon line (21.2 eV excitation energy). The valence electrons are responsible for crystal/molecular bonding and charge transport in electronic devices. The probing depth depends on the electron mean free path and is in the order of a few nm. In contrast to UPS, MIES is probing exclusively the composition and electronic structure of the outermost layer of a sample. The surface sensitivity of MIES is due to the fact that the object carrying the energy used to excite the target electrons (e.g. the metastable atom) cannot penetrate the material in its excited state; it releases its energy to the surface at a distance of a few Å. Thus in a MIES experiment, the surface sensitivity does not originate from the mean free path of the emitted electrons but from the fact that only electrons in the outermost layer can be excited. Therefore, MIES probes the composition of that region which is important for interactions and reactions at surfaces or interfaces. MIES spectra are evaluated quantitatively and directly reveal the density of states (DOS) of the valence electrons. Fitting procedure enables to resolve each electron

orbital contribution in the UP and MIE Spectra. Each of gaussian curves are developed in a certain position, and its FWHM, position and intensity are set as parameters which will be optimised such that the sum of those gaussian forms a curve which fit to the measured spectrum. Firstly, the spectrum obtained from the fresh dyed nanoporous TiO₂ layer is used as a blank spectrum. Secondly, the spectrum can be obtained by applying fitting procedure through some parameters (e.g. FWHM, intensity, position, and background). Once the spectrum is well fitted, the next step is using the spectrum as a model to run the fitting procedure for other measured spectra from electrolyte-exposed samples. By comparing between the spectrum from fresh sample and exposed sample, then it can be seen their changes or how difference they are after the electrolyte immersion.

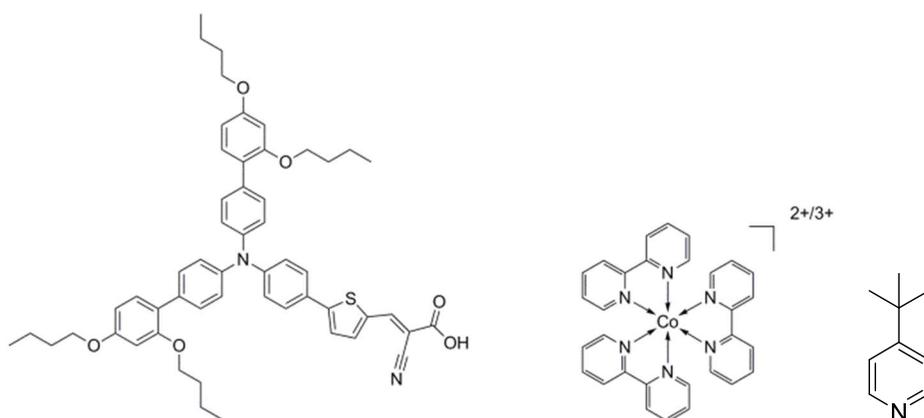


Figure S1. Chemical structures of dye D35 (left), the tris(2,2'-bipyridine) cobalt (II/III) complex (middle) and TBP (right).

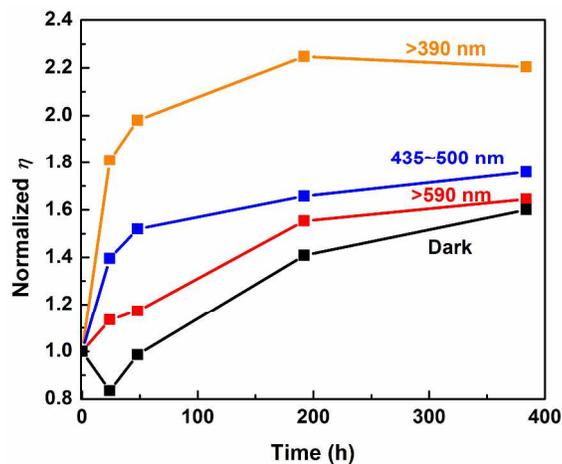


Figure S2. The evolution of efficiency normalized against the initial value of fresh PD2-sensitized solar cells during light soaking exposure. The spectral range of the light is limited by using color glass filters.

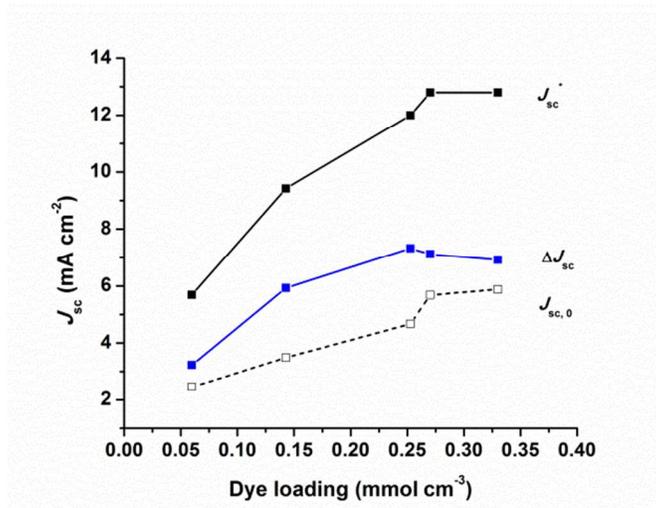
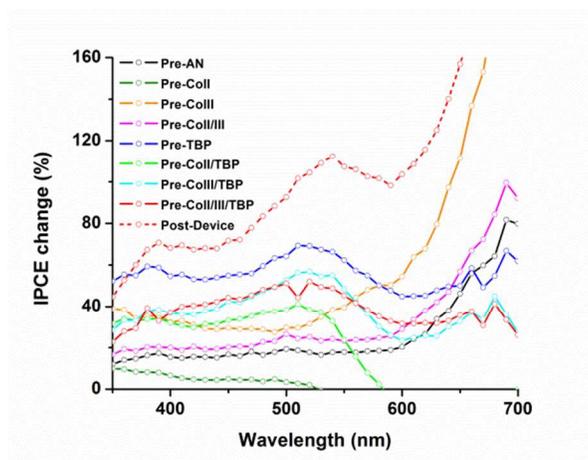
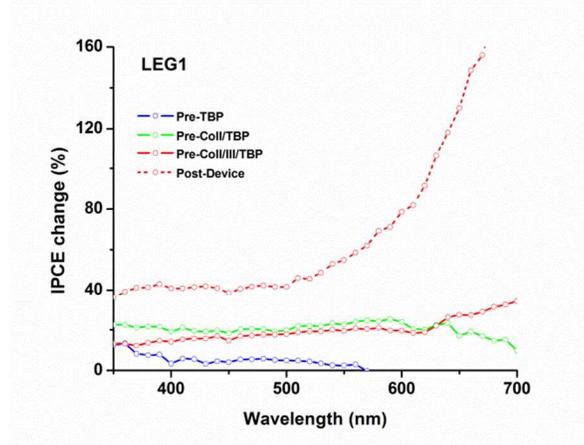


Figure S3. Short circuit current of PD2-sensitized solar cells measured before ($J_{sc,0}$) and after (J_{sc}^*) light soaking exposure of 500 h; the calculated difference is the maximum current increase (ΔJ_{sc}).

(a)



(b)



(c)

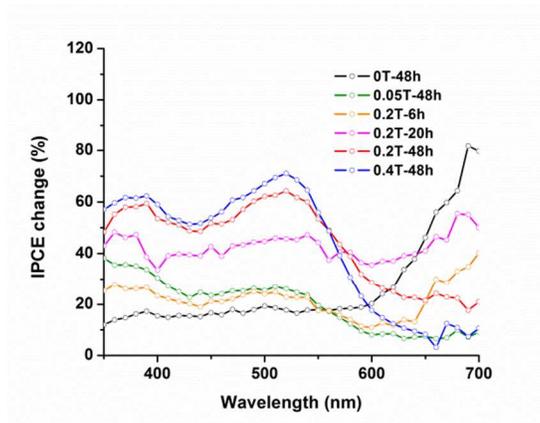


Figure S4. The change in the IPCE (%) of PD2- (a) and LEG1- (b) sensitized DSSCs treated according to *pre* strategy in the electrolyte varying the composition and to *post* strategy respectively for 48 h by comparison to non-treated ones; c) PD2-sensitized DSSCs treated according to *pre* strategy in the electrolyte varying the composition and treatment time by comparison to non-treated ones.

Table S1 Photovoltaic parameters and integrated current based on IPCE for PD2-based DSSCs pre-treated in different concentrations of TBP for different time.

TBP con.	Pre-treating time	V_{oc} /mV	J_{sc} / mA cm ⁻²	FF	η^b /%	J_{IPCE} / mA cm ⁻²
0 M	48h	0.69	6.9	0.68	3.2	4.6
0.2 M	0h	0.68	6.3	0.59	2.5	3.9
0.05 M	48h	0.68	6.8	0.62	2.9	4.7
0.2 M	48h	0.71	8.2	0.66	3.9	5.8
0.4 M	48h	0.70	8.6	0.63	3.8	5.9
0.2 M	6h	0.70	7.3	0.62	3.2	4.7

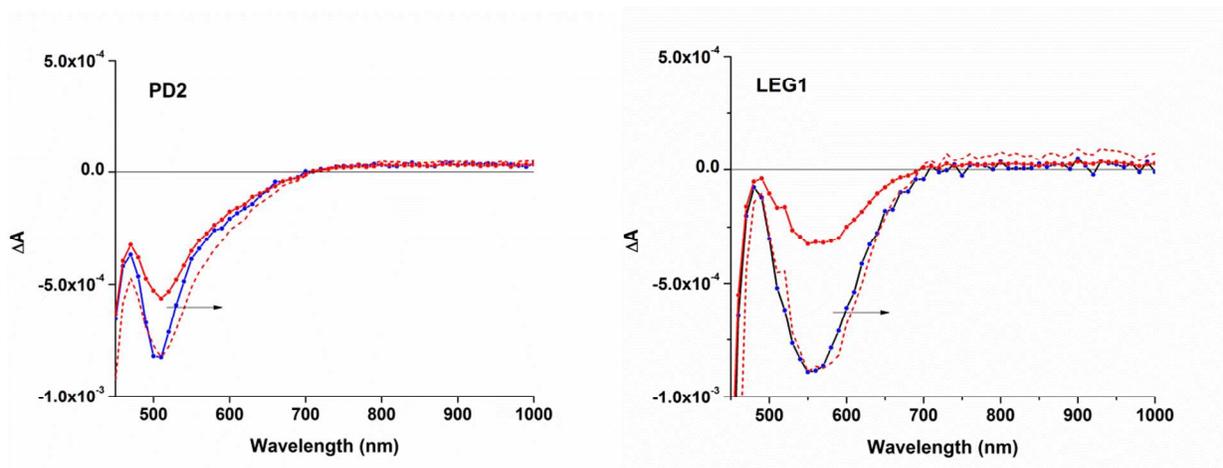


Figure S5. Photo-induced absorption of PD2 (left) and LEG1 (right) adsorbed on the mesoporous TiO₂ film in the cobalt electrolyte before (blue) and after (red) light soaking exposure for 48 h. Dashed lines were obtained by normalizing the spectra of samples after exposure against the absorbance at 510 nm and 550 nm respectively. The arrows indicate the spectral shift.

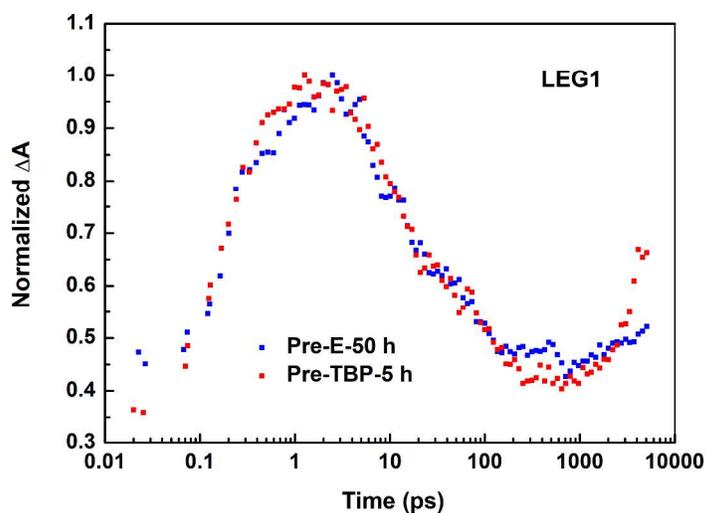


Figure S6. The normalized kinetic curves of electron injection/recombination processes for LEG1-sensitized TiO₂ films after *pre* treatment in 0.2 M TBP/acetonitrile solution (**Pre-TBP**) and complete electrolyte (**Pre-E**) for different time as labelled, recorded in contact with normal cobalt electrolytes.

Table S2. Electron transfer kinetic halftimes at LEG1/TiO₂ interface after *pre* treatment for different time as labelled.

Samples	Electron Injection		Electron Recombination			
	$\tau_{inj, 1}$	$\tau_{inj, 2}^*$	$\tau_{rec, 1}$	$\tau_{rec, 2}$	$\tau_{rec, long}$ (> 5 ns)	$\tau_{rec, averaged}$ (< 5 ns)

Pre-TBP- 5h	0.3	ns	12 (6)	175 (4)	τ_3 (90)
Pre-E-50h	0.4	-	5(38)	55(24)	τ_3 (38)

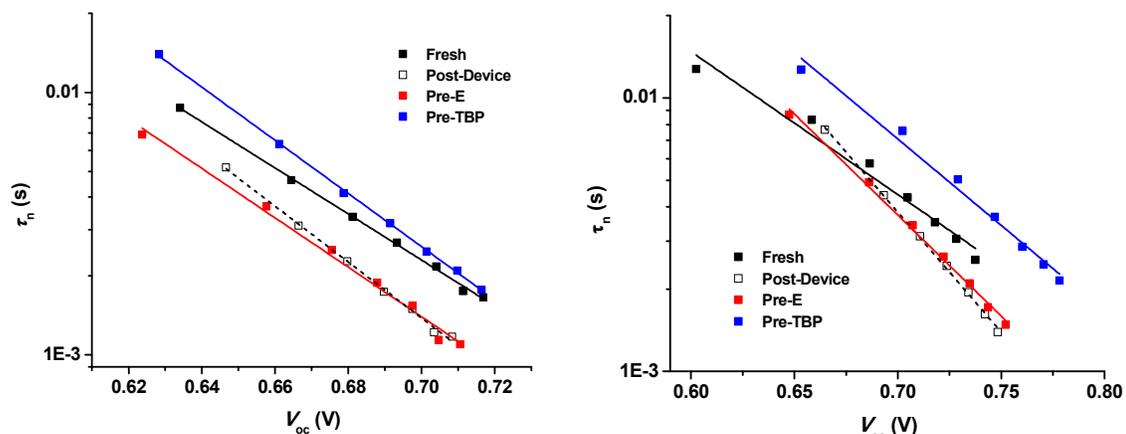


Figure S7. Electron lifetime (τ_n) of PD2 (left) and LEG1 (right) based DSSCs: **Fresh** and *pre*-treated in TBP only (**Pre-TBP**) and the normal electrolyte (**Pre-E**) respectively under light soaking for 50 h and after *post* treatment. Plots were linear fitted against logarithmic value of τ_n .

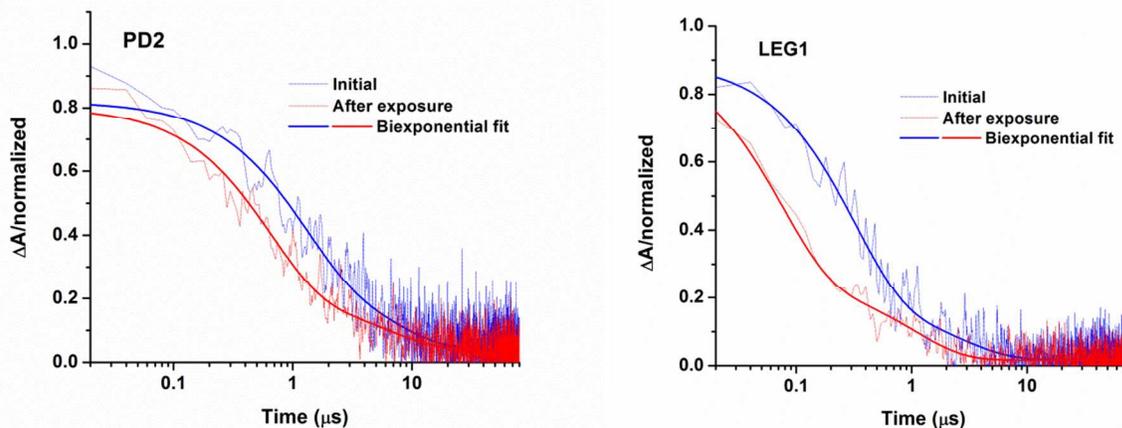


Figure S8 Normalized transient absorption traces (dotted lines) for PD2 (left) and LEG1 (right) absorbed on mesoporous TiO_2 in cobalt electrolyte ($0.3 \text{ M}/0.15 \text{ M Co}(\text{bpy})_3^{2+/3+}$ and 0.2 M TBP in acetonitrile) before (blue) and after light soaking exposure of 48 h. Signals were fitted (solid lines) according to biexponential decay functions.

Table S3 Biexponential fitting parameters of normalized transient absorption kinetic curves of PD2 and LEG1-sensitized cells before and after light soaking exposure, and accordingly obtained logarithmic weighted average lifetime (τ_{ave}) and observed kinetic rate (k_{obs}) of the absorption decay.

Dye-Time ^a	A_1	$\tau_1/\mu\text{s}$	A_2	$\tau_2/\mu\text{s}$	$\tau_{\text{ave}}^b/\mu\text{s}$	k_{obs}^c
PD2-0 h	0.53205	1166.525	0.24522	6527.363	2008.309	0.000498
PD2-48 h	0.59037	631.5645	0.17341	6171.783	1059.711	0.000944
LEG1-0 h	0.70699	311.7224	0.17123	2612.185	471.8185	0.002119
LEG1-48 h	0.23522	1047.707	0.66145	72.98501	146.807	0.006812

^a The time of a dummy cell consisting of dye-sensitized TiO_2 electrode, cobalt electrolyte and a blank FTO as the

counter electrode under light soaking exposure (full sun irradiation with 390 nm cut-off, 60°C);

$$b \log \tau_{ave} = \frac{\sum A_i \tau_i}{\sum A_i}$$

$$c \ k_{obs} = \frac{1}{\tau_{ave}}$$

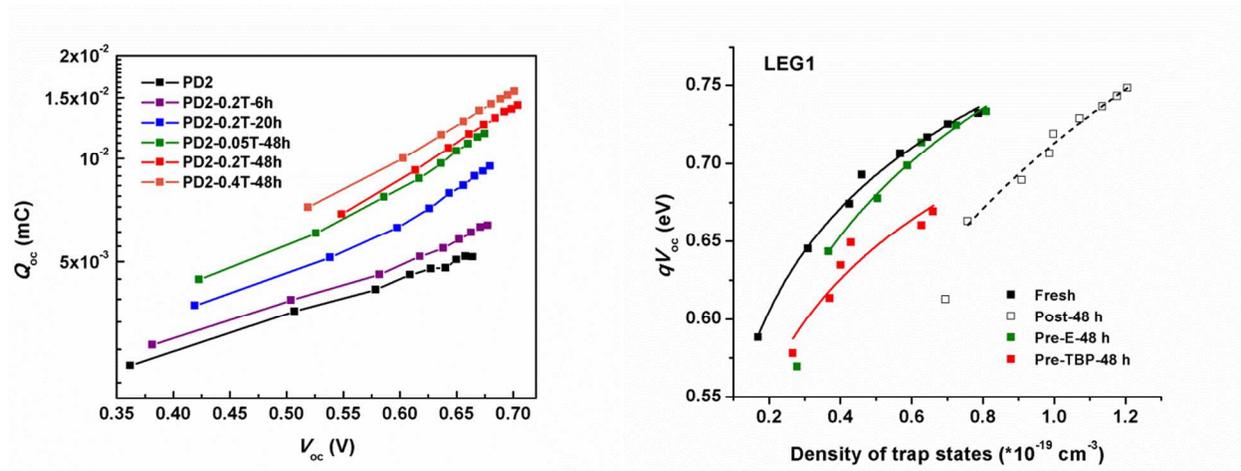


Figure S9. (a) Charge extraction of PD2-sensitized TiO₂ film before and after *pre*-treatment varying with TBP concentration in the electrolyte and treatment time; (b) trap state distribution in LEG1-sensitized TiO₂ films before and after *pre*-treatment varying with electrolyte components as labelled and *post* treatment under light soaking exposure of 48 h. Plots were fitted using exponential functions.

Table S4. Work function of each sample measured by UPS: A, B is PD2 and LEG1-sensitized TiO₂ sample; 1 is fresh films and 2 means those exposed to TBP solution and cobalt electrolyte respectively for PD2 and LEG1.

Sample	Work Function (eV)
A1	3.1
A2	3.5
B1	3.2
B2	3.5

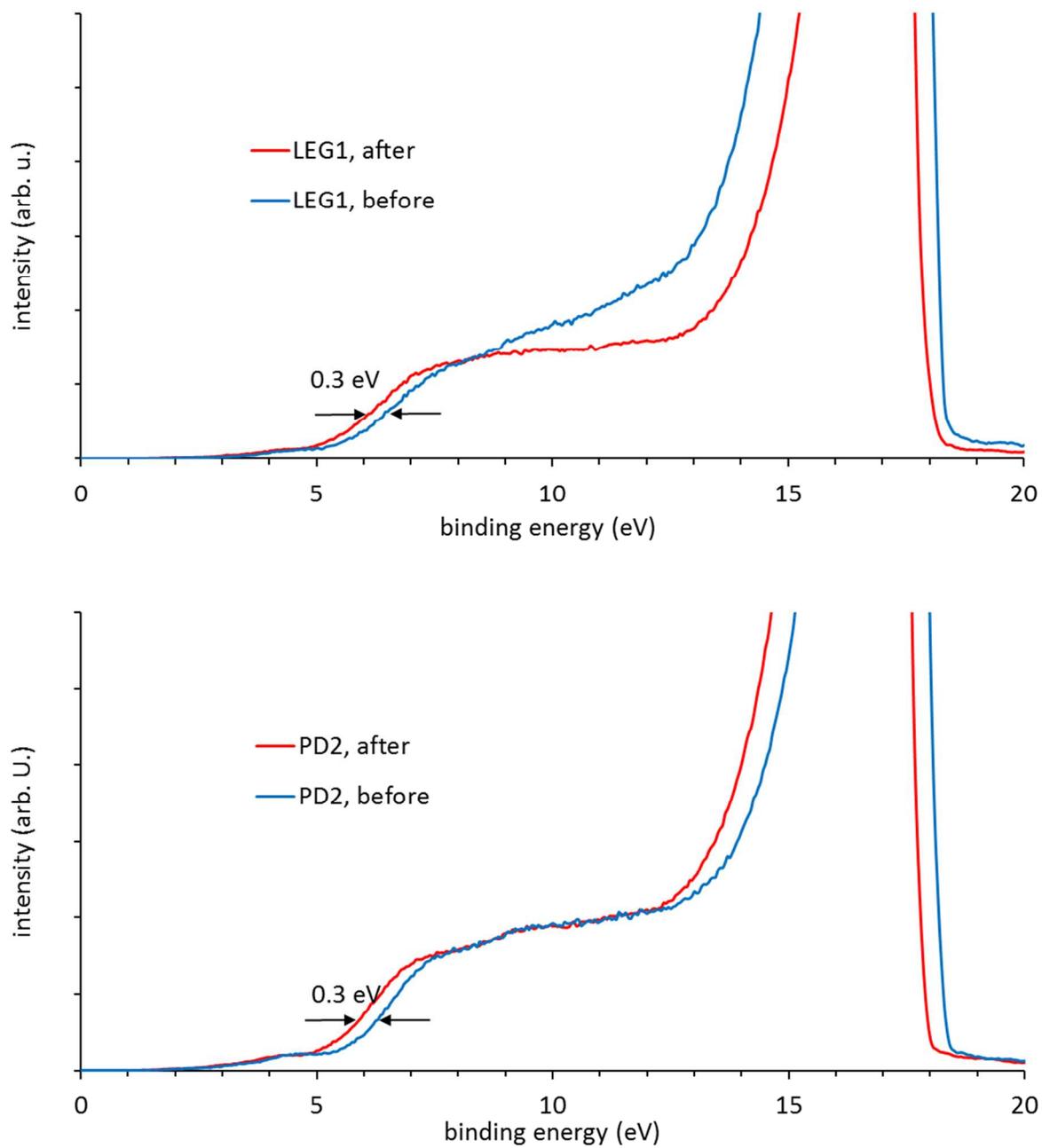


Figure S10. The UP Spectra of LEG1/TiO₂ (top) and PD2/TiO₂ film (bottom) before (blue) and after (red) exposed to the complete cobalt electrolyte and light. A shift of the spectrum with respect to that of the fresh film is shown in both spectra.

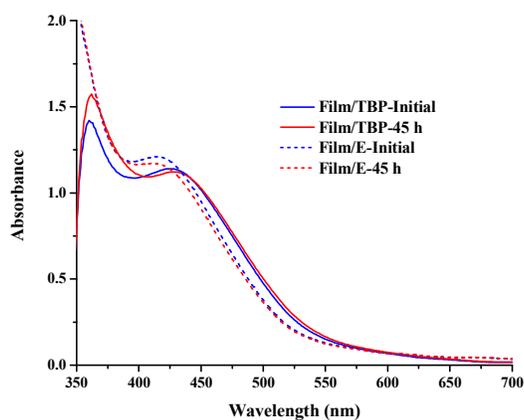
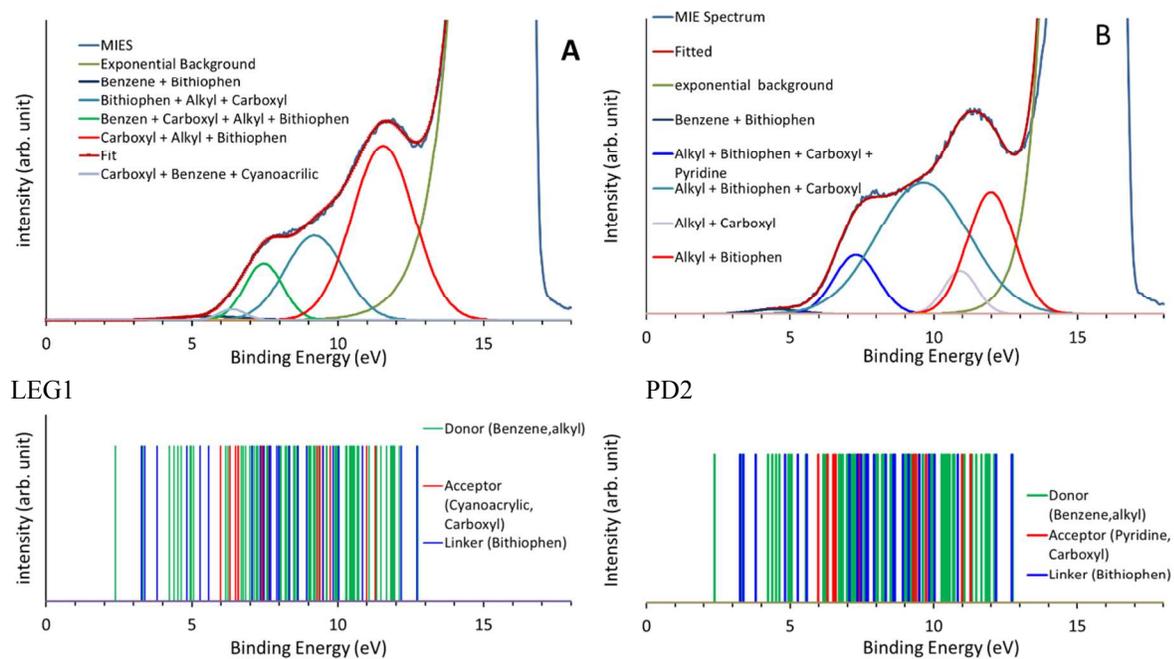


Figure S11. The UV-vis spectra of PD2/TiO₂ film in a dummy cell with 0.2 M TBP only (Film/TBP) and the normal electrolyte (Film/E) initially (blue) and after (red) light soaking for 45h.



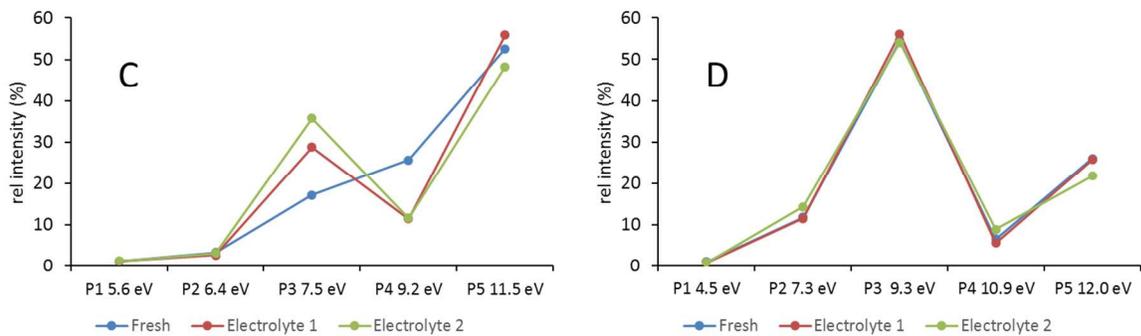


Figure S12. Top: molecular orbital contributions of MIE spectrum of LEG1 (A) and PD2 (B) dye assigned by comparing between the fitted spectrum and computational calculation. Bottom: variation of MIES peak intensity of LEG1 (C) and PD2 dye (D) after the dyed TiO₂ film non-treated (Fresh) and treated by electrolyte 1: working cobalt electrolyte containing 0.2M TBP and electrolyte 2: 0.2 M TBP in acetonitrile.

Table S5. Character of the peaks in the MIES spectra.

LEG1 dye						
	Position (eV)	5.6	6.4	7.5	9.2	11.5
	Main character	Benzene, alkyl, bithiophene	Cyanoacrylic, carboxyl	Benzene, alkyl,	Bithiophene	Benzene, alkyl
PD2 dye						
	Position (eV)	4.5	7.3	9.6	10.9	12.0
	Main character	Benzene, alkyl, bithiophene	Carboxyl, pyridine, bithiophene,	Benzene, alkyl, bithiophene, pyridine, carboxyl	All,	Benzene, alkyl,

Table S6. Photovoltaic parameters for DSSCs^a assembled with PD2-sensitized TiO₂ films untreated (Fresh) and pre-treated by different basic solution for different time.

Base ^b -treatment time	V_{oc}	J_{sc}	FF	η^c
	/mV	/mA cm ⁻²		/%
Fresh	0.71	6.5	0.68	3.1
TEA-1 min	0.68	5.5	0.57	2.1
TMAOH-10 s	0.67	4.4	0.56	1.6
TMAOH-1 min	0.51	2.8	0.43	0.6
TMAOH-2 min	0.26	1.5	0.47	0.2

^a DSSCs were assembled with electrolytes consisted of 0.3 M/0.15 M Co(bpy)₃^{2+/3+} and 0.2 M TBP in acetonitrile;
^b TEA contains 0.1 M triethylamine in acetonitrile; TMAOH contains 0.01 M tetramethylammonium hydroxide in dichloromethane: methanol (4:1, v/v);
^c Efficiencies were recorded under full sun irradiation (AG 1.5M, ~100 mW/cm²).

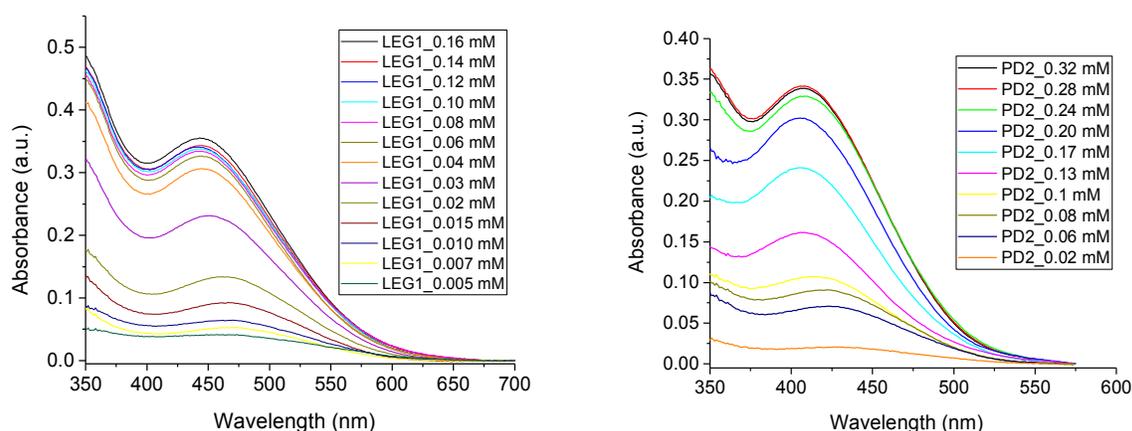


Figure S13. UV-vis absorption spectra of dye/TiO₂ film for LEG1 (left) and PD2 (right) after saturate adsorption in the dye bath of gradient concentrations for overnight.

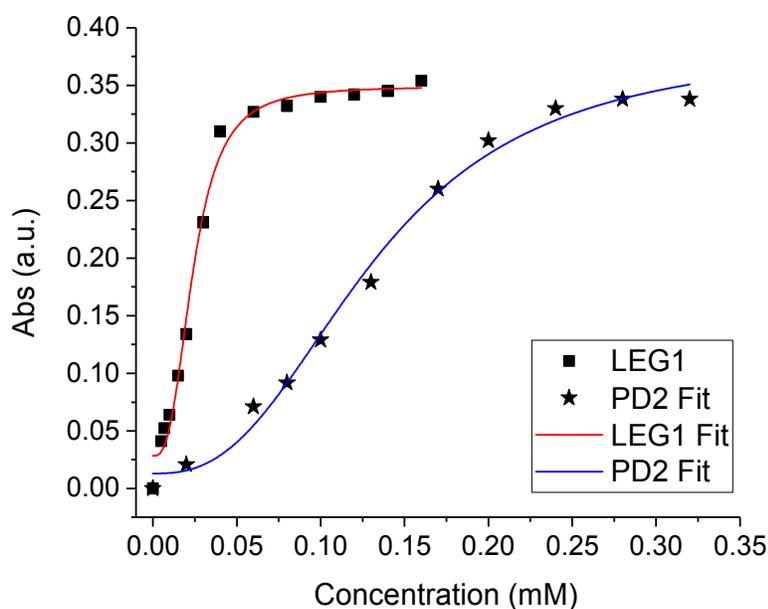


Figure S14. The adsorption isotherms profiles for LEG1 (square, red line) and PD2 (star, blue line).

Reference

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