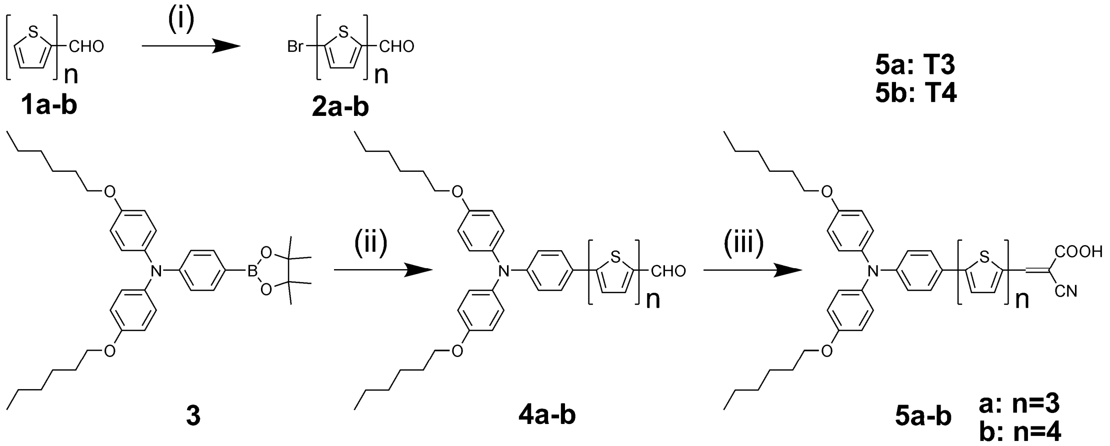
Electronic Supplementary Information

Oligothiophene dye-sensitized solar cells

Jingyuan Liu,[a,b] Renzhi Li,[a,c] Xiaoying Si,[a,b] Difei Zhou,[a,c] Yushuai Shi,[a,c] Yinghui Wang,[a] Xiaoyan Jing[b] and Peng Wang*[a]

Scheme S1. Synthetic route of T3−T4.[a]



[a]Reagents: (i) 1.1 equiv NBS, THF, r.t., 24 h; (ii) **2**, 2% Pd(OAc)$_2$, 2% 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos), 5.0 equiv K$_3$PO$_4$, dioxane:H$_2$O (5:1), 40 °C, 2 h; (iii) 3.0 equiv cyanoacetic acid, 7.0 equiv piperidine, CHCl$_3$, reflux, 18 h.

Experimental Details

1. Materials

All solvents and reagents, unless otherwise stated, were of analytical quality and used as received. Lithium iodide (LiI), iodine and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Sigma-Aldrich. Guanidinium thiocyanate (GNCS), 4-*tert*-butylpyridine (TBP), 3α,7α-dihyroxy-5β-cholic acid (cheno) and valeronitrile (VN) were purchased from Fluka. Acetonitrile (AN) and tetrahydrofuran (THF) were both distilled before use. 2,2':5',5''-Terthiophene-5-carbaldehyde (**1a**),[S1] 5'''-formyl-2,2':5',5'':2'',2'''-quaterthiophene (**1b**),[S2] 2''-bromo-2,2':5',5''-terthiophene-5-carbaldehyde (**2a**),[S1] 4,4,5,5-tetramethyl-2-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-1,3,2-dioxaborolane (**3**),[S3] 1,3-dimethylimidazolium iodide (DMII),[S4] dimethylimidazolium bis(trifluoromethanesulfonyl)imide (DMITFSI),[S4] 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI),[S4] **T1**,[S5] and **T2**[S6] were synthesized according to the literature methods. The scattering TiO_2 paste (WER2-O) was received as a gift from Dyesol.

2. Synthesis

2.1 Synthesis of 5'''-bromo-2,2':5',5'':2'',2'''-quaterthiophene-5-carbaldehyde (**2b**). To a solution of **1b** (0.232 g, 0.64 mmol) in THF (80 mL) was added *N*-bromosuccinimide (0.130 g, 0.73 mmol) at room temperature under argon. The reaction mixture was stirred at room temperature for 24 h. Then the mixture was filtrated, washed with petroleum ether and water, respectively, to yield a yellow solid (0.211 g, 76% yield). ^{1}H NMR (600 MHz, DMSO) δ: 9.89 (s, 1H), 8.01 (d, J=3.6 Hz, 1H), 7.61 (d, J=4.2 Hz, 1H), 7.58 (d, J=4.2 Hz, 1H), 7.43 (d, J=3.6 Hz, 1H), 7.42 (d, J=3.6 Hz, 1H), 7.34 (d, J=3.6 Hz, 1H), 7.26 (d, J=3.6 Hz, 1H), 7.23 (d, J=3.6 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ: 182.40, 146.60, 141.77, 138.52, 137.30, 136.15, 135.55, 134.81, 130.79, 129.03, 128.22, 126.98, 125.01, 124.78, 124.74, 124.16, 124.10. MS (ESI) *m/z* calcd. for ($C_{17}H_9BrOS_4$): 435.9. Found: 436.8 ($[M+H]^+$). Anal. Calcd. for $C_{17}H_9BrOS_4$: C, 46.68; H, 2.07. Found: C, 46.65; H, 2.10.

2.2 General synthesis of **4.** To a suspended solution of **2a or 2b** (1.50 mmol), $Pd(OAc)_2$ (0.006 g, 0.03 mmol), SPhos (0.011 g, 0.03 mmol) and K_3PO_4 (1.480 g, 7.50 mmol) in dioxane:H_2O (5:1) (24 mL) was added **3** (1.80 mmol). The reaction mixture was reacted at 40 ^{o}C for 2 h under argon and then water (50 mL) added. The crude compound was extracted into ethyl acetate, washed with brine and water, and dried over anhydrous sodium sulfate. After removing solvent under reduced pressure, the residue was purified by column chromatography.

2''-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-2,2':5',5''-terthiophene-5-carbaldehyde **(4a)**. Ethyl acetate/petroleum ether 60–90 °C (1/100, *v*/*v*) was used as eluent to yield an orange solid (yield 81%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.89 (s, 1H), 8.00 (d, *J*=4.0 Hz, 1H), 7.59 (d, *J*=4.0 Hz, 1H), 7.55 (d, *J*=4.0 Hz, 1H), 7.48 (d, *J*=8.8 Hz, 2H), 7.40 (d, *J*=4.0 Hz, 1H), 7.37 (d, *J*=4.0 Hz, 1H), 7.34 (d, *J*=4.0 Hz, 1H), 7.05 (d, *J*=8.8 Hz, 4H), 6.92 (d, *J*=8.8 Hz, 4H), 6.76 (d, *J*=8.8 Hz, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 1.70 (m, 4H), 1.42 (m, 4H), 1.32 (m, 8H), 0.88 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.29, 155.44, 148.31, 144.90, 143.77, 141.13, 139.42, 138.58, 138.20, 133.24, 132.96, 127.75, 126.72, 126.05, 125.99, 124.87, 124.69, 124.48, 122.96, 118.96, 115.52, 67.72, 30.72, 28.50, 24.92, 21.73, 13.51. MS (ESI) *m*/*z* calcd. for ($C_{43}H_{45}NO_3S_3$): 719.3; Found: 720.2 ($[M+H]^+$). Anal. Calcd. for $C_{43}H_{45}NO_3S_3$: C, 71.73; H, 6.30; N, 1.95. Found: C, 71.67; H, 6.28; N, 1.90.

5'''-{4-[*N*,*N*-Bis(4-hexyloxyphenyl)amino]phenyl}-2,2':5',5'':2'',2'''-quaterthiophene-5-carbaldehyde **(4b)**. Ethyl acetate/petroleum ether 60–90 °C (1/50, *v*/*v*) was used as eluent to yield a reddish orange solid (yield 88%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.89 (s, 1H), 8.00 (d, *J*=4.0 Hz, 1H), 7.60 (d, *J*=4.0 Hz, 1H), 7.56 (d, *J*=4.0 Hz, 1H), 7.48 (d, *J*=8.8 Hz, 2H), 7.41 (d, *J*=4.0 Hz, 1H), 7.33 (m, 3H), 7.04 (d, *J*=8.8 Hz, 4H), 6.92 (d, *J*=8.8 Hz, 4H), 6.77 (d, *J*=8.8 Hz, 2H), 3.94 (t, *J*=6.4 Hz, 4H), 1.72 (m, 4H), 1.42 (m, 4H), 1.32 (m, 8H), 0.88 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 183.19, 155.32, 148.13, 144.59, 143.19, 141.20, 139.35, 138.42, 137.41, 136.35, 133.64, 133.61, 133.17, 127.71, 126.58, 125.91, 125.79, 125.39, 125.14, 124.95, 124.49, 124.42, 122.80, 118.92, 115.41, 67.60, 30.61, 28.4, 24.81, 21.62, 13.41. MS (ESI) *m*/*z* calcd. for ($C_{47}H_{47}NO_3S_4$): 801.2; Found: 802.3 ($[M+H]^+$). Anal. Calcd. for $C_{47}H_{47}NO_3S_4$: C, 70.37; H, 5.91; N, 1.75. Found: C, 70.35; H, 5.87; N, 1.73.

2.3 General synthesis of **5**. To a stirred solution of **4a** or **4b** (1.00 mmol) and cyanoacetic acid (7.00 mmol) in chloroform (30 mL) was added piperidine (3.00 mmol). The reaction mixture was refluxed under argon for 18 h and then acidified with 2 M hydrochloric acid aqueous solution (30 mL). The crude product was extracted into chloroform, washed with water. After removing solvent under reduced pressure, the residue was purified by flash chromatography with chloroform and methanol/chloroform (1/10, *v*/*v*) in turn as the eluent to yield the product.

2-Cyano-3-{2''-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-2,2':5',5''-terthienyl-5-yl}acrylic acid (**5a**, T3, C221). Yield: 81%.^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.68 (s, 1H), 8.48 (s, 1H), 7.98 (d, *J*=3.6 Hz, 1H), 7.58 (d, *J*=3.6 Hz, 2H), 7.47 (d, *J*=8.4 Hz, 2H), 7.41 (d, *J*=3.6 Hz, 1H), 7.36 (d, *J*=3.6 Hz, 1H), 7.33 (d, *J*=3.6 Hz, 1H), 7.03 (d, *J*=8.4 Hz, 4H), 6.91 (d, *J*=8.4 Hz, 4H), 6.76 (d, *J*=8.4 Hz, 2H), 3.94 (t, *J*=6.6 Hz, 4H), 1.70 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.09, 155.35, 148.24, 145.69, 144.92, 143.79, 140.52, 139.32, 138.37, 133.68, 132.93, 132.86, 127.76, 126.62, 126.00, 125.96, 124.73, 124.70, 124.37, 122.90, 118.85, 116.03, 115.43, 98.00, 67.62, 30.60, 28.40, 24.81, 21.61, 13.39. HR-MS (ESI) *m*/*z* calcd. for ($C_{46}H_{46}N_2O_4S_3$): 786.26197. Found: 786.26185 (M^+). Anal. Calcd. for $C_{46}H_{46}N_2O_4S_3$: C, 70.20; H, 5.89; N, 3.56. Found: C, 70.17; H, 5.85; N, 3.54.

2-Cyano-3-{5'''-{4-[*N*,*N*-bis(4-hexyloxyphenyl)amino]phenyl}-2,2':5',5'':2'',2'''-quaterthienyl-5-yl}acrylic acid (**5b**, T4, C222). Yield: 80%. ^{1}H NMR (600 MHz, DMSO-d_6) δ: 13.77 (s, 1H), 8.48 (s, 1H), 7.98 (d, *J*=3.6 Hz, 1H), 7.61 (d, *J*=3.6 Hz, 2H), 7.48 (d, *J*=9.0 Hz, 2H), 7.44 (d, *J*=4.2 Hz, 1H), 7.42 (d, *J*=4.2 Hz, 1H), 7.35 (d, *J*=3.6 Hz, 1H), 7.33 (m, 2H), 7.05 (d, *J*=9.0 Hz, 4H), 6.92 (d, *J*=9.0 Hz, 4H), 6.77 (d, *J*=9.0 Hz, 2H), 3.94 (t, *J*=6.6 Hz, 4H), 1.70 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.88 (t, *J*=7.2 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d_6) δ: 163.58, 155.42, 148.16, 145.96, 144.98, 143.28, 141.19, 139.43, 137.91, 136.62, 134.05, 133.75, 133.57, 133.36, 128.08, 126.85, 126.12, 126.06, 125.62, 125.44, 124.97, 124.60, 124.55, 122.97, 118.96, 116.59, 115.41, 98.34, 67.60, 31.01, 28.71, 25.21, 22.07, 13.88. HR-MS (ESI) *m*/*z* calcd. for ($C_{50}H_{48}N_2O_4S_4$): 868.24969. Found: 868.24593 (M^+). Anal. Calcd. for $C_{50}H_{48}N_2O_4S_4$: C, 69.09; H, 5.57; N, 3.22. Found: C, 69.07; H, 5.59; N, 3.19.

3. UV-vis/near-IR and voltammetric measurements

Electronic absorption spectra were recorded on a Perkin Elmer Lambda 900 spectrophotometer. A CHI660C electrochemical workstation was used for square-wave voltammetry measurements in combination with a three-electrode electrochemical cell equipped with a platinum gauze as counter electrode, a Ag/AgCl (sat. KCl) as auxillary electrode and a 5-μm-radius Pt ultramicroelectrode as working electrode. The dye-coated titania films on fluorine-doped tin oxide (FTO) were used as working electrode for spectroelectrochemical measurements. The redox potentials reported in this paper were calibrated with ferrocene as the internal reference (–5.14 V versus vacuum).

4. Cell fabrication

A (7+5) μm double layer film of interconnected titania particles on the FTO (Nippon Sheet Glass, Solar, 4 mm thick) conducting glass was used as the negative electrode. A cycloidal TiO_2 electrode (~0.28 cm^2) was stained by immersing it into a dye solution containing 150 μM **Tn** and 30 mM cheno in THF overnight. After washing with acetonitrile and drying by air flow, the dye-coated titania electrode was assembled with a thermally platinized FTO electrode. The details on cell fabrication are described in our previous publication.[S3] The electrolyte composition is 1.0 M DMII and 30 mM iodine, 50 mM LiI, 0.5 M TBP, and 0.1 M GNCS in the mixed solvent of AN and VN (*v*/*v*, 85/15).

5. Photovoltaic characterization

A Keithley 2400 source meter and a Zolix Omni-λ300 monochromator equipped with a 500 W xenon lamp were used for photocurrent action spectrum measurements, with a wavelength sampling interval of 10 nm and a current sampling time of 2 s under the full computer control. Monochromatic incident photon-to-collected electron conversion efficiency (IPCE) is defined by $\mathrm{IPCE}(\lambda)=hcJ_{\mathrm{sc}}/e\phi\lambda$, where h is the Planck constant, c is the light speed in vacuum, e is the electronic charge, λ is the wavelength, J_{sc} is the short-circuit photocurrent density and ϕ is the incident radiative flux. A Hamamatsu S1337-1010BQ silicon diode used for IPCE measurements was calibrated in National Institute of Metrology, China. During the photocurrent action spectrum measurements, a white light-emitting diode was used to bias a testing cell with ~1.0 mA cm^{-2} background current. A model LS1000-4S-AM1.5G-1000W solar simulator (Solar Light Company, USA) in combination with a metal mesh was employed to give an irradiance of 100 mW cm^{-2}. The light intensity was tested with a PMA2144 pyranometer and a calibrated PMA 2100 dose control system. Current–voltage (J–V) characteristics were obtained by applying a bias potential to a testing cell and measuring photocurrent with a Keithley 2602 source meter under the full computer control. The measurements were fully automated using Labview 8.0. A metal mask with an aperture area of 0.158 cm^2 was covered on a testing cell during all measurements. An antireflection film (λ<380 nm, ARKTOP, ASAHI Glass) was adhered to the DSC photoanode during IPCE and J–V measurements. The short-circuit photocurrent densities measured under this solar simulator are well consistent with the integral of IPCEs over the AM1.5G spectrum (ASTM G173-03), within a 5% error.

6. Transient emission and absorption measurements

Photoluminescence decays were measured with the time-correlated single photon counting (TCSPC) technique on a LifeSpec-II fluorescence spectrometer. The EPL485 laser diode was used to supply an excitation light. Transient absorption kinetics were measured with a LP920 laser flash spectrometer. A nanosecond tunable OPOLett-355II laser was employed to generate the pump lights at different wavelengths. The sample was kept at a 45° angle with respect to the excitation beam. The probe light from a pulsed xenon arc lamp was passed through various optical elements, samples and a monochromator and detected by a fast photomultiplier tube in conjunction with a TDS 3012C digital signal analyzer.

7. Electrical impedance measurements

With an IM6ex electrochemical workstation, we performed electrical impedance measurements under illumination of a red light-emitting diode. We selected a frequency range from 50 mHz to 100 kHz and a potential modulation of 20 mV. To meet the zero current condition, a potential bias (V) equal the open-circuit photovoltage (V_{oc}) was applied to the illuminated cell. The measured impedance spectra were further fitted using the Z-view software (v2.80, Scribner Associates Inc.).

References

(S1) T. Nishizawa, K. Tajima and K. Hashimoto, *J. Mater. Chem.*, 2007, **17**, 2440.

(S2) N. R. Krishnaswamy and C. S. S. R.Kumar, *Indian J. Chem. B*, 1993, **32**, 766.

(S3) R. Li, J. Liu, N. Cai, M. Zhang and P. Wang, *J. Phys. Chem. B*, 2010, **114**, 4461.

(S4) P. Bonhôte, A. P. Dial, N. Papageorgiou, K. Kalyanasumdaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168.

(S5) R. Li, X. Lv, D. Shi, D. Zhou, Y. Cheng, G. Zhang and P. Wang, *J. Phys. Chem. C*, 2009, **113**, 7469.

(S6) J.-H.Yum, D. P. Hagberg, S.-J. Moon, K. M. Karlsoon, T. Marinado, L. Sun, A. Hagfeldt, M. K. Nazeeruddin and M. Grätzel, *Angew. Chem. Int. Ed.*, 2009, **48**, 1576.

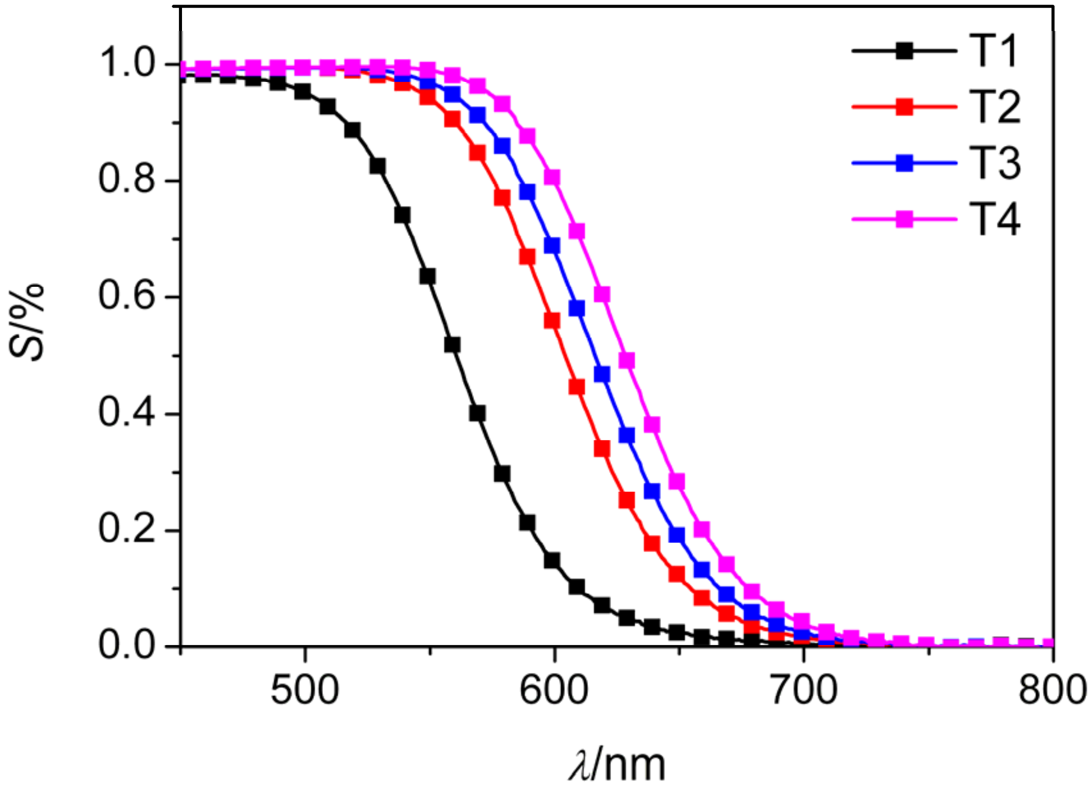


Fig. S1 Absorption percentage of a dummy cell possessing a transparent 7-μm-thick mesoporous titania film grafted with T1, T2, T3 or T4 in contact with the electrolyte for cell fabrication. Electrolyte composition: 1.0 M DMII, 50 mM LiI, 30 mM I_2, 0.5 M TBP and 0.1 M GNCS in the 85/15 mixture of AN and VN.

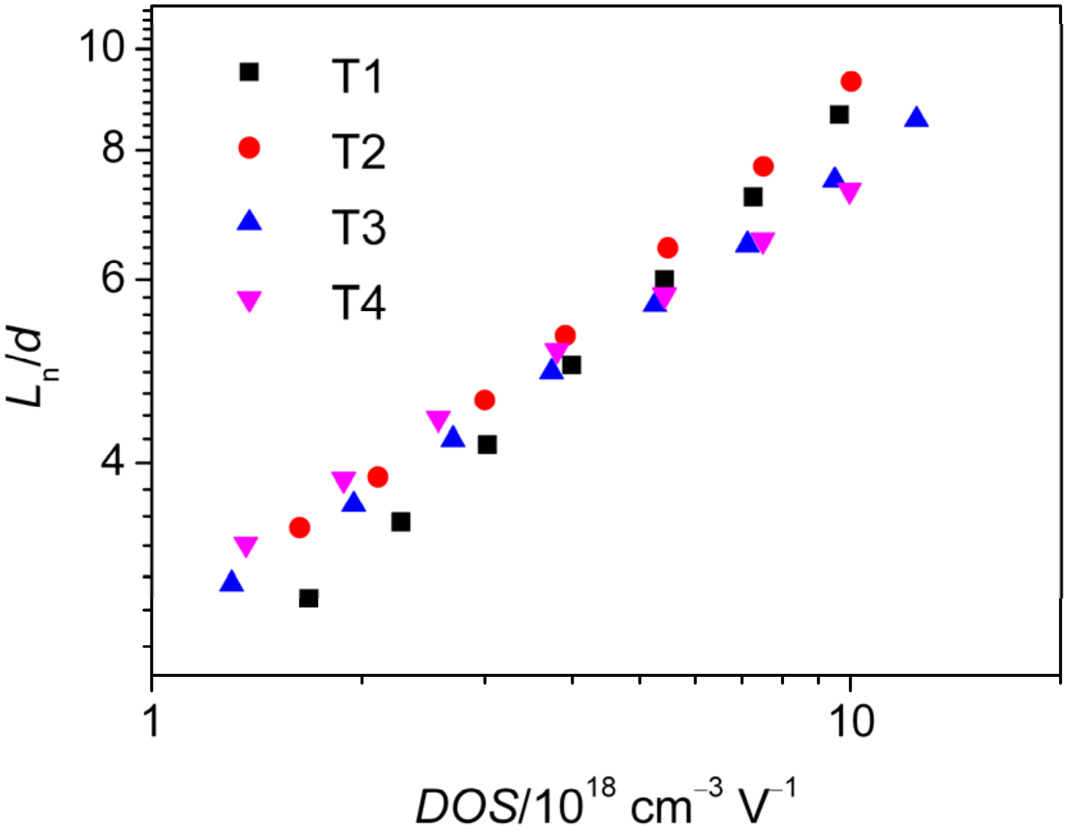


Fig. S2 The ratio of electron diffusion length (L_n) derived from impedance measurements relative to the titania film thickness (*d*).

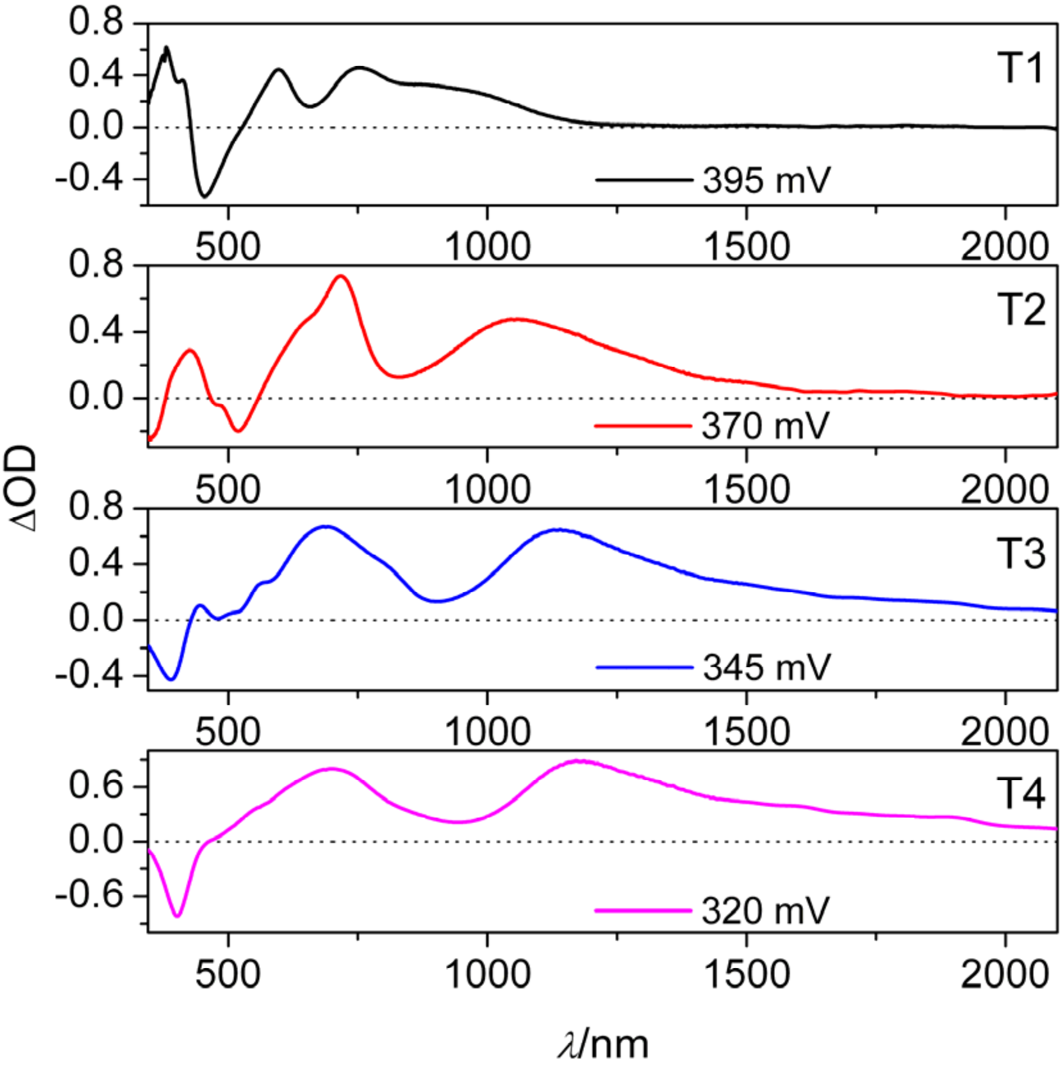


Fig. S3 Absorption change upon applying a positive potential bias (versus ferrocene) to a dye-coated titania film immersed in EMITFSI.

Table S1 Overall reaction free energy (ΔG^0) and half-reaction time ($t_{1/2,\mathrm{dr}}$) for dye regeneration of T1−T4.

dye	ΔG^0/eV[a]	$t_{1/2,\mathrm{dr}}$/μs
T1	−0.425	1.26
T2	−0.371	11.46
T3	−0.362	20.52
T4	−0.343	50.64

[a] Derived from the redox potential difference between T1−T4 and the iodide/triiodide couple.

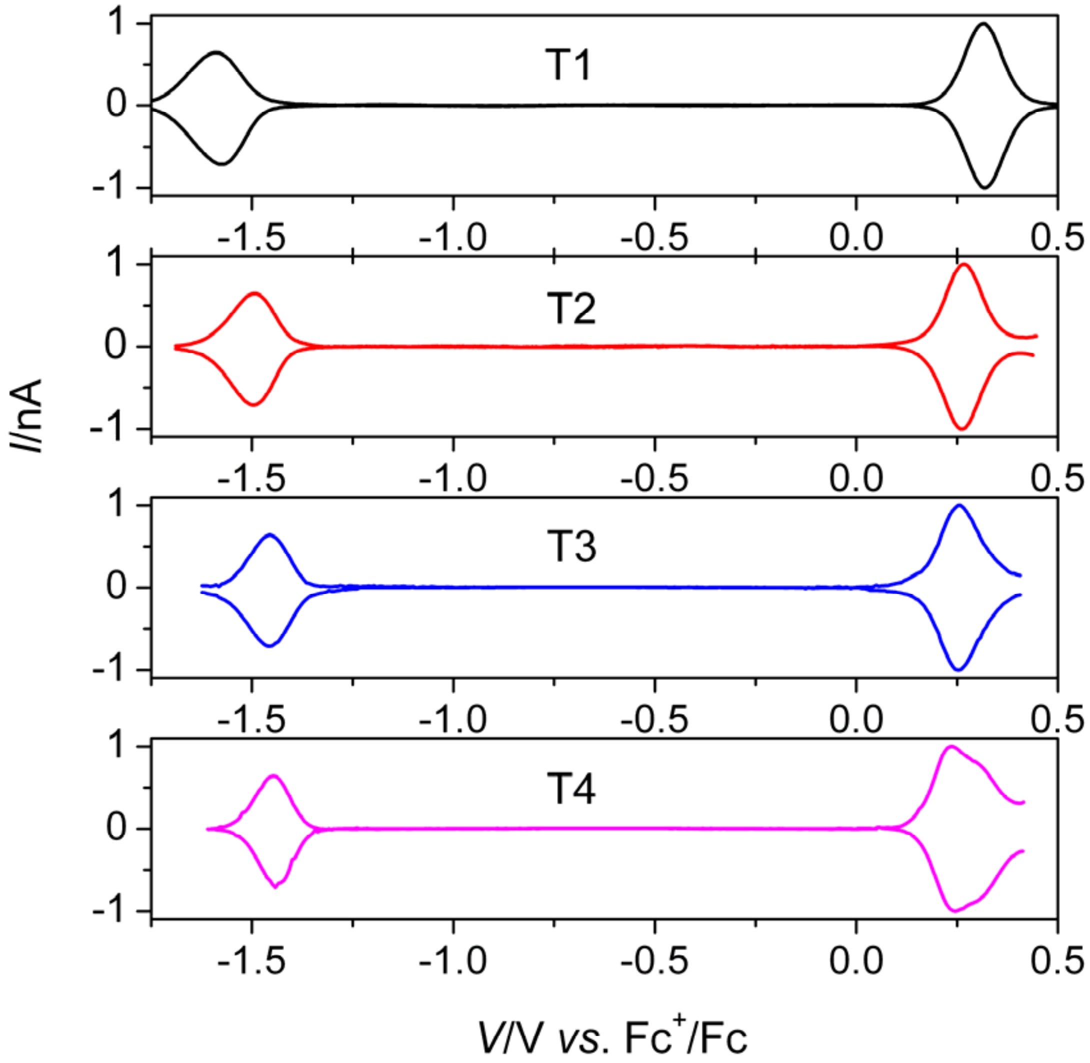


Fig. S4 Square-wave voltammograms of T1−T4 dissolved in *N*,*N*-dimethylformamide with 0.1 M tetra-*n*-butylammonium hexaflurophosphate as the supporting electrolyte.

Table S2 Photovoltaic parameters measured at the 100 mW cm^{-2} AM1.5G conditions.[a]

dye	J_{sc}/mA cm^{-2}	V_{oc}/mV	FF	η/%
T1	9.55	801	0.751	5.75
T2	13.09	784	0.745	7.65
T3	13.83	741	0.743	7.61
T4	15.35	722	0.728	8.06

[a] The spectral distribution of our light resource simulates AM 1.5G solar emission with a mismatch less than 5%. Lights at different intensities were obtained by attenuating the AM 1.5G full sunlight with a set of neutral meshes. Short-circuit photocurrent density: J_{sc}; Open-circuit photovoltage: V_{oc}; Fill factor: FF; Total power conversion efficiency: η. Cell area tested with a metal mask: 0.158 cm^2. An antireflection film was adhered to a testing cell during measurement.

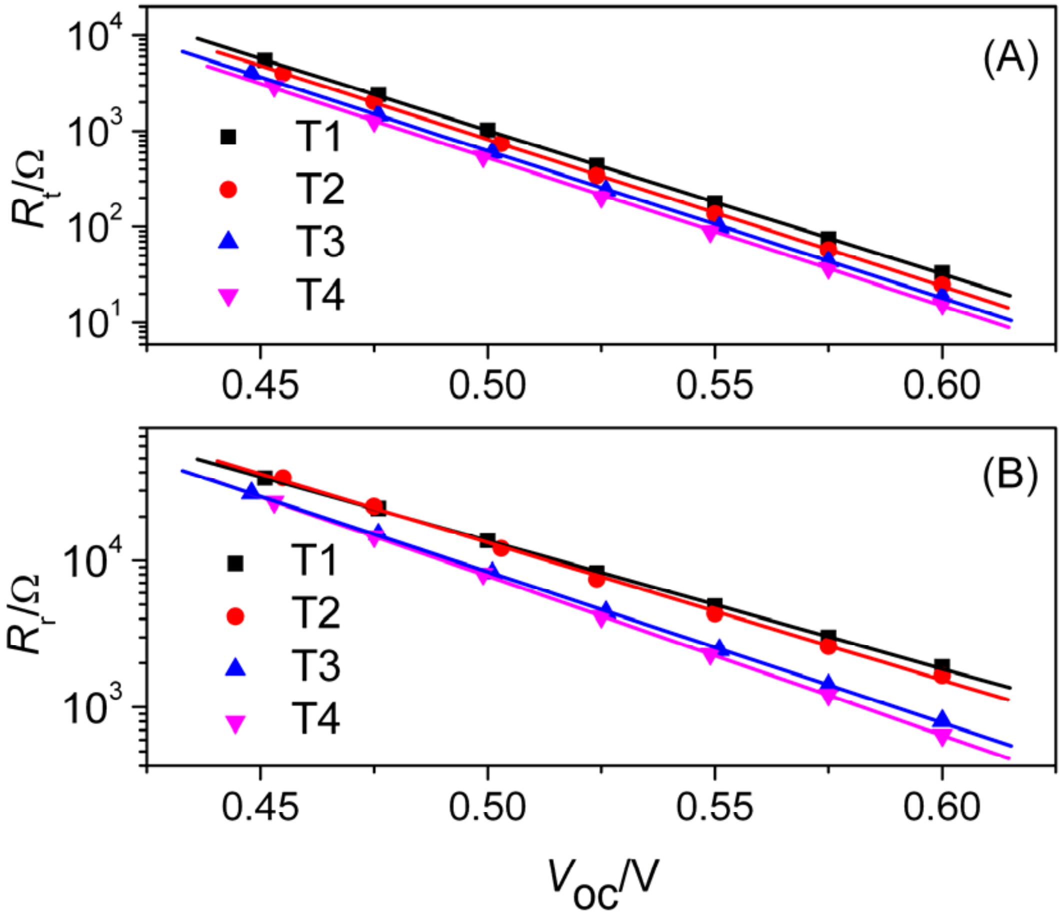


Fig. S5 Plots of (A) electron transport resistance and (B) interfacial charge recombination resistance versus the applied potential bias which is equal to the value of V_{oc} in impedance measurements. The solid lines are fittings in terms of proper functions.

Table S3 Parameters derived from mathematical fitting of the electron transport resistance and interfacial charge transfer resistance.

dye	E_c–$E_{F,redox}$/eV	γ	k_0/cm$^{-3(1-\gamma)}$ s^{-1}
T1	0.982	0.517	1.7×10^{9}
T2	0.965	0.555	5.4×10^{8}
T3	0.961	0.603	1.4×10^{8}
T4	0.949	0.641	4.3×10^{7}