

Electronics Supplementary Information

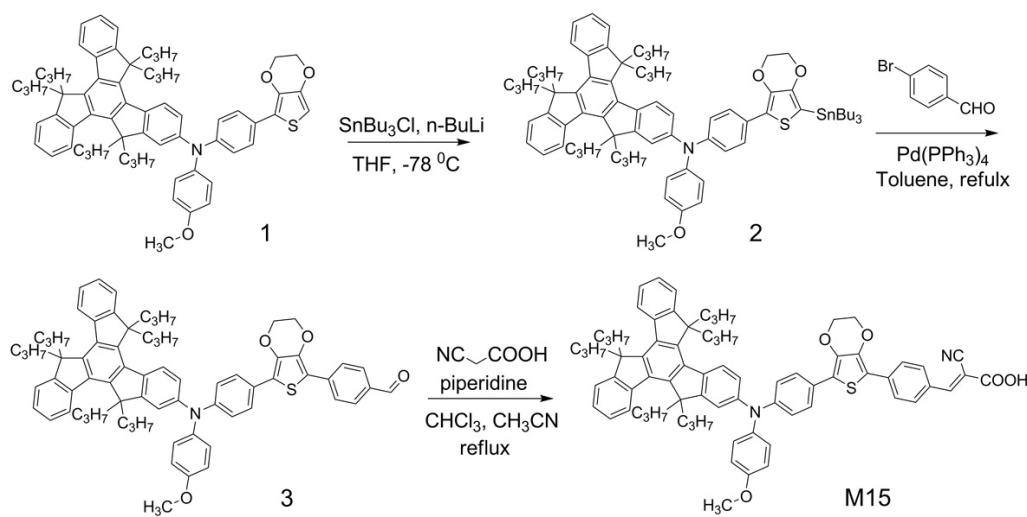
Efficient iodine-free dye-sensitized solar cells employing
truxene-based organic dyes

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1. Synthesis and characterization of dyes.



Scheme S1. Synthetic route to the M15

Synthesis of compound 2

A solution of compound **1** (852 mg, 0.914 mmol) in dry THF (15 mL) was cooled to -78°C under N_2 atmosphere was added $n\text{-BuLi}$ (0.762 mL, 2.4 M in hexane, 1.83 mmol) dropwise and stirred for 1 h. Subsequently, the mixture was cooled to -78°C again and then added Bu_3SnCl (357 mg, 1.10 mmol). The mixture was stirred overnight at room temperature. After extraction with ethyl acetate, the organic fractions were combined and dried over with MgSO_4 . The resulting oil was evaporated to give a yellow solid **2** (1.03 g, 0.844 mmol, 92.3 % yield). Crude **2** was obtained and used for the next step without any purification.

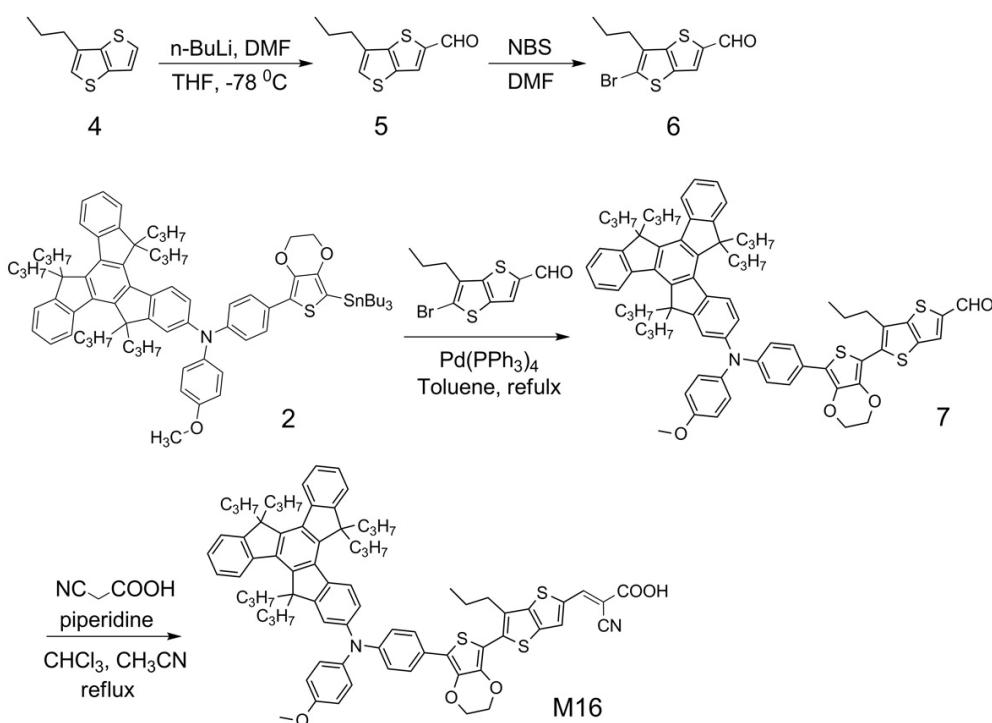
Synthesis of aldehyde 3

Crude **2** (300 mg, 0.253 mmol), 4-bromo-bezenealdehyde (51.5 mg, 0.278 mmol), and $\text{Pd}(\text{PPh}_3)_4$ (40 mg) in 10 mL of toluene were heated to reflux under a nitrogen atmosphere for four hours. After cooling to room temperature, 20 mL of water was added into the flask, followed by extraction with dichloromethane. The combined organic phase was dried over anhydrous Mg_2SO_4 . The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography with silica gel to yield **3** (143 mg, 0.138 mmol, 54.6%). Mp: 178–179 °C; IR (KBr): 2957, 2927, 2870, 1692, 1598, 1480, 1244, 1084

cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 9.89 (s, 1H), 8.27 (d, $J = 7.6$ Hz, 1H), 8.21 (d, $J = 7.2$ Hz, 1H), 8.08 (d, $J = 8.6$ Hz, 1H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.42-7.35 (m, 2H), 7.35-7.28 (m, 4H), 7.19-7.11 (m, 4H), 7.08 (d, $J = 8.6$ Hz, 2H), 6.84 (d, $J = 8.8$ Hz, 2H), 4.38-4.27 (m, 4H), 3.77 (s, 3H), 2.88-2.71 (m, 6H), 2.05-1.92 (m, 4H), 1.88-1.79 (m, 2H), 0.57-0.38 (m, 30H); ^{13}C NMR (100 MHz, CDCl_3): δ 191.2, 156.4, 155.1, 153.6, 153.5, 147.3, 146.0, 144.7, 144.1, 140.7, 140.3, 140.2, 139.2, 138.1, 138.0, 137.8, 134.9, 133.7, 130.1, 127.3, 127.0, 126.2, 125.9, 125.6, 125.5, 125.2, 124.6, 124.5, 122.2, 121.1, 118.5, 117.0, 114.8, 112.8, 64.7, 64.4, 55.6, 55.5, 55.4, 42.3, 39.3, 39.2, 34.7, 26.8, 18.7, 18.3, 17.3, 17.2, 14.4. HRMS (ESI) calcd for $\text{C}_{71}\text{H}_{73}\text{NO}_4\text{S} (\text{M}+\text{H}^+)$: 1036.5338. Found: 1036.5345.

Synthesis of M15

To a stirred solution of aldehyde 3 (280 mg, 0.270 mmol) and cyanoacetic acid (45.9 mg, 0.54 mmol) in a 1:2 mixture of chloroform and acetonitrile was added piperidine (46 μL). The reaction mixture was refluxed for 5 h and then the solvent was removed in vacuo. The resulting solid was extracted with DCM and sequentially washed with brine and dried with anhydrous Na_2SO_4 . The solvent was evaporated, and the remaining crude product was purified by column chromatography to give a red solid of M15 (280 mg, 0.254 mmol, 93.9%). Mp: 237–238 °C; IR (KBr): 3439, 2956, 2869, 1713, 1697, 1577, 1287, 1085 cm^{-1} . ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 8.32 (d, $J = 7.5$ Hz, 1H), 8.29-8.23 (m, 2H), 8.20 (d, $J = 8.0$ Hz, 1H), 8.05 (s, 1H), 7.88 (d, $J = 8.2$ Hz, 2H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.61-7.54 (m, 2H), 7.47-7.35 (m, 4H), 7.29-7.24 (m, 1H), 7.16 (d, $J = 8.4$ Hz, 2H), 7.09-6.98 (m, 5H), 4.52-4.35 (m, 4H), 3.78 (s, 3H), 2.90-2.74 (m, 6H), 2.18-2.02 (m, 4H), 1.98-1.84 (m, 2H), 0.63-0.34 (m, 30H); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 163.5, 156.3, 154.5, 153.0, 152.9, 146.7, 145.7, 143.9, 143.4, 141.3, 139.4, 139.3, 138.2, 137.8, 137.7, 137.6, 137.1, 134.1, 131.4, 128.9, 127.3, 126.8, 126.6, 126.3, 125.1, 124.0, 122.3, 121.5, 121.2, 117.0, 116.4, 115.1, 111.7, 102.0, 64.8, 64.4, 64.3, 55.2, 55.0, 38.5, 38.4, 24.6, 21.0, 16.9, 16.8, 14.2, 14.1. HRMS (ESI) calcd for $\text{C}_{74}\text{H}_{74}\text{N}_2\text{O}_5\text{S} (\text{M}+\text{H}^+)$: 1103.5396. Found: 1103.5389.



Scheme S2. Synthetic route to the M16

Synthesis of Compound 5.

A solution of compound 4 (1.00 g, 5.49 mmol) in dry THF (15 mL) was cooled to -78 °C under N₂ atmosphere was added n-BuLi (2.75 mL, 2.4 M in hexane, 6.59 mmol) dropwise and stirred for 1 h. Subsequently, the mixture was cooled to -78 °C again and then added anhydrous DMF (0.425 mL, 5.49 mmol). The mixture was stirred for 12 h at room temperature. After extraction with ethyl acetate, the organic fractions were combined and dried over with MgSO₄. The resulting oil was purified by column chromatography on silica gel (petroleum: dichloromethane = 4 : 1 as eluent) to give a yellow solid 5 (0.813 g, 3.87 mmol, 70.5 % yield). Mp: 61-63 °C; IR (KBr): 3092, 2962, 2817, 1654, 1231, 1129 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 9.88 (s, 1H), 7.84 (s, 1H), 7.24 (s, 1H), 2.66 (t, J = 7.4 Hz, 2H), 1.78-1.64 (m, 2H), 0.92 (t, J = 7.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): δ 182.4, 145.3, 143.8, 137.6, 134.3, 128.5, 127.5, 30.6, 20.7, 12.8. HRMS (ESI) calcd for C₁₀H₁₀OS₂(M+H⁺): 211.0251. Found: 211.0245.

Synthesis of Compound 6.

Under exclusion of light, NBS (364 mg, 2.05 mmol) was added to a solution of 5 (430 mg, 2.05 mmol) in 5 mL DMF at room temperature. The mixture was stirred for 12 h before

quenching with water and the product was extracted with dichloromethane. The combined organic layers were washed with brine and dried with anhydrous Mg₂SO₄. The solvent was evaporated to give a yellow powder **6** (483 mg, 1.67 mmol, 81.6% yield). Crude **6** was obtained and used for the next step without any purification.

Synthesis of aldehyde 7

Crude **2** (885 mg, 0.725 mmol), crude **6** (230 mg, 0.797 mmol), and Pd(PPh₃)₄ (90 mg) in 15 mL of toluene were heated to reflux under a nitrogen atmosphere for five hours. After cooling to room temperature, 20 mL of water was added into the flask, followed by extraction with dichloromethane, and the combined organic phase was dried over anhydrous Mg₂SO₄. The organic portion was combined and removed by rotary evaporation. The residue was purified by column chromatography with silica gel to yield **9** (599 mg, 0.525 mmol, 72.4%). Mp: 162–164 °C; IR (KBr): 2956, 2928, 2869, 1665, 1598, 1480, 1244, 1084 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 9.86 (s, 1H), 8.28 (d, *J* = 7.6 Hz, 1H), 8.21 (d, *J* = 7.3 Hz, 1H), 8.07 (d, *J* = 8.6 Hz, 1H), 7.78 (s, 1H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.43-7.34 (m, 2H), 7.35-7.28 (m, 4H), 7.18 (s, 1H), 7.17-7.11 (m, 3H), 7.08 (d, *J* = 9.4 Hz, 2H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.30 (s, 4H), 3.77 (s, 3H), 2.91-2.71 (m, 8H), 2.09-1.91 (m, 4H), 1.91-1.78 (m, 2H), 1.78-1.68 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.57-0.35 (m, 30H); ¹³C NMR (100 MHz, CDCl₃): δ 182.9, 156.3, 155.0, 153.6, 153.5, 147.8, 147.2, 145.9, 144.6, 144.1, 144.0, 143.6, 140.3, 140.2, 140.1, 139.6, 138.1, 138.0, 137.9, 137.0, 136.9, 136.6, 134.8, 131.7, 129.1, 127.2, 126.9, 126.1, 125.8, 125.3, 125.1, 124.5, 122.2, 121.0, 118.8, 116.9, 115.7, 106.7, 64.7, 64.4, 58.3, 55.5, 55.4, 42.2, 39.3, 39.1, 34.6, 31.1, 26.8, 21.9, 18.6, 18.3, 17.5, 17.3, 17.2, 14.4, 14.1. HRMS (ESI) calcd for C₇₄H₇₇NO₄S₃(M+H⁺): 1140.5093. Found: 1140.5098.

Synthesis of M16

To a stirred solution of aldehyde **7** (450 mg, 0.394 mmol) and cyanoacetic acid (72 mg, 0.848 mmol) in a 1:2 mixture of chloroform and acetonitrile was added piperidine (72 μL). The reaction mixture was refluxed for 4 h and then the solvent was removed in vacuo. The resulting solid was dissolved in DCM and sequentially washed with brine and dried with anhydrous Na₂SO₄. The solvent was evaporated, and the remaining crude product was purified by column chromatography to give a purple solid of M16 (377 mg, 0.312 mmol,

79.1%). Mp: > 300 °C; IR (KBr): 3431, 2956, 2928, 2869, 1655, 1577, 1362, 1242, 1087 cm⁻¹. ¹H NMR (400 MHz, DMSO-d₆): δ 8.29-8.20(m, 4H), 8.05 (s, 1H), 7.65-7.54 (m, 4H), 7.48-7.35 (m, 4H), 7.31-7.20 (m, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.07-6.17 (m, 5H), 4.50-4.31 (m, 4H), 3.79 (s, 3H), 2.96-2.73 (m, 8H), 2.20-2.01 (m, 4H), 1.98-1.86 (m, 2H), 1.81-1.66 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H), 0.67-0.16 (m, 30H); ¹³C NMR (100 MHz, Pyridine-d₅): δ 157.2, 155.7, 154.1, 154.0, 150.3, 149.3, 149.2, 147.5, 147.0, 145.1, 144.5, 140.6, 140.5, 140.4, 138.8, 138.7, 138.1, 137.9, 137.6, 135.9, 135.8, 135.5, 135.2, 134.9, 131.6, 128.0, 127.5, 127.2, 126.8, 126.5, 125.8, 125.0, 123.9, 123.5, 123.3, 123.0, 122.8, 117.0, 115.5, 64.8, 56.0, 55.9, 55.4, 39.6, 39.5, 31.3, 22.3, 18.0, 17.8, 14.6, 14.5, 14.2. HRMS (ESI) calcd for C₇₇H₇₈N₂O₅S₃(M+H⁺): 1207.5151. Found: 1207.5160.

Materials and Methods.

N,N-Dimethylformamide was dried over and distilled from CaH₂ under an atmosphere of nitrogen. 1,10-Phenanthroline (phen) and Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from J&K Scientific Ltd. All other solvents and chemicals used in this work were analytical grade and used without further purification.

Melting points of the samples were taken on an RY-1 melting point apparatus (Tianfen, China). ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-400 spectrometer. The reported chemical shifts were against TMS. High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer.

Optical and Electrochemical Measurements.

The absorption spectra of the dyes either in solution or on the adsorbed TiO₂ film were measured by HITACHI U-3310 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer. FT-IR spectra were obtained with a Bio-Rad FTS 135 FT-IR instrument.

Cyclic voltammetry measurements for dye-sensitized films were performed at room temperature on a computer controlled LK2005A electrochemical workstation with dye sensitized TiO₂ film on conducting glass as the working electrode, Pt-wires as the counter electrode, and a Ag/AgCl electrode as the reference electrode at a scan rate of 100 mV s⁻¹. Tetrabutylammonium perchlorate (TBAP, 0.1 mol/L) and MeCN were used as supporting

electrolyte and solvent, respectively. The measurements were calibrated using ferrocene as standard. The redox potential of ferrocene internal reference is taken as 0.63 V vs NHE. Electrochemical impedance spectroscopy (EIS) in the frequency range of 100 mHz to 100 kHz was performed with a PARSTAT 2273 potentiostat/galvanostat/FRA in the dark with the alternate current amplitude set at 10 mV.

Fabrication and Characterization of DSCs.

The TiO₂ paste (particle size, 20 nm) consisting of 18 wt.% TiO₂, 9 wt.% ethyl cellulose and 73 wt.% terpineol was firstly prepared,^{S1} which was printed on a conducting glass (Nippon Sheet Glass, Hyogo, Japan, fluorine-doped SnO₂ over layer, sheet resistance of 10 Ω/sq) using a screen printing technique. The thickness of the TiO₂ films is 5.5 μm and the active area of cells is 0.12~0.15 cm². The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. The heated electrodes were impregnated with a 0.05 M titanium tetrachloride solution in a water-saturated desiccator at 70 °C for 30 min and sintered again to give a mesoscopic TiO₂ film. The TiO₂ electrode was stained by immersing it into a dye solution containing 300 μM sensitizers (ethanol–dichloromethane 1:1) for 24 h at room temperature. Then the sensitized-electrode was rinsed with dry ethanol and dried by a dry air flow. Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution (40 mM in ethanol) with the heat treatment at 395 °C for 15 min to give photoanode. The dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell by a 25 μm-thick Surlyn (DuPont) hot-melt gasket and sealed up by heating. The cobalt electrolyte, is composed of 0.25 M [Co(II)(phen)₃](PF₆)₂, 0.05 M [Co(III) (phen)₃](PF₆)₃, 0.5 M TBP and 0.1M LiTFSI in acetonitrile. The cobalt electrolytes with different concentration of TBP were prepared for DSCs application. For comparison, an iodine electrolyte consisting of 0.25 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPIMI), 0.1 M LiTFSI, 0.05 M I₂, and 0.5 M tertbutylpyridine in acetonitrile was formulated.

The photocurrent–voltage (*J*–*V*) characteristics of the solar cells were carried out using a Keithley 2400 digital source meter controlled by a computer and a standard AM1.5 solar simulator–Oriel 91160–1000 (300W) SOLAR SIMULATOR 2 x 2 BEAM. The light intensity was calibrated by an Oriel reference solar cell. A metal mask with an aperture area of 0.16

cm² was covered on a testing cell during all measurements. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cell were performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTECH, USA). We estimated the short circuit current density of cells based on the two dyes by integrating the IPCE values versus the sun AM1.5G spectrum, which is slightly lower than the measured short circuit photocurrent density and that calculated from the overlap integral of the IPCE curve with the standard AM1.5G solar emission spectra, implying that there existed a spectral mismatch between our solar simulating system and the standard AM1.5G irradiation. Similar phenomena have been reported by other groups.^{S2} In addition, the integration is performed only from 400 to 800 nm. The contribution from wavelength shorter than 400 nm is ignored, so that the calculated current may be underestimated. However, in view of the same conditions in the test, our approach is reliable for fair evaluation of the photovoltaic performance of the two dyes discussed in this work.

[S1] Ito, S.; Murakami, T. N.; Comte, P.; Liska, P.; Grätzel, C.; Nazeeruddin,M. K.; Grätzel, M. *Thin Solid Films* **2008**, *516*, 4613

[S2] (a) Wang, Z; Koumura, N; Cui, Y; Takahashi, M; Sekiguchi, H; Mori, A; Kubo, T; Furube, A; Hara, K. *Chem. Mater.* **2008**, *20*, 3993. (b) Liu, W. H.; Wu, I. C.; Lai, C. H.; Lai, C. H.; Chou, P. T.; Li, Y. T.; Chen, C. L.; Hsu, Y. Y.; Chi, Y. *Chem. Commun.* **2008**, 5152.

Table S1. Optical properties and electrochemical properties of the dyes.

Dye	λ_{max}/nm ($\varepsilon/10^3 \text{M}^{-1}\text{cm}^{-1}$) ^a	λ_{int}/nm ^b	E_{0-0}/eV ^c	$E(\text{S}/\text{S}^+)/\text{V}$ vs NHE ^d	$E(\text{S}^*/\text{S}^+)/\text{V}$ vs NHE ^e	Dye amount/ 10^{-7} mol cm^{-2} ^f
M15	374 (81), 498 (76)	564	2.19	0.91	-1.28	1.86
M16	381 (88), 500 (81)	573	2.16	0.90	-1.26	1.65

^aAbsorption spectra of dyes measured in CH_2Cl_2 with the concentrate of solution 1.0×10^{-5} M, ε is the extinction coefficient at λ_{max} of absorption. ^bThe intersect of the normalized absorbtion and the emission spectra. ^c E_{0-0} values were estimated from the intersections of normalized absorption and emission spectra in CH_2Cl_2 , λ_{int} : $E_{0-0} = 1240/\lambda_{int}$. ^d $E(\text{S}/\text{S}^+)$ was determined by the E1/2 value of CV, which is taken as the highest occupied molecular orbital (HOMO) level. ^e $E(\text{S}^*/\text{S}^+)$ can be derived from the ground-state oxidation potential and the zero-zero excitation energy (E_{0-0}) according to the following equation: $E(\text{S}^*/\text{S}^+) = E(\text{S}/\text{S}^+) - E_{0-0}$. The $E(\text{S}^*/\text{S}^+)$ is taken as the lowest unoccupied molecular orbital (LUMO) level. ^fThe dye amount was determined by comparing the absorbance change of a dye solution ($300 \mu\text{M}$) before and after dye up-taking with a titania film ($5.5 \mu\text{m}$).

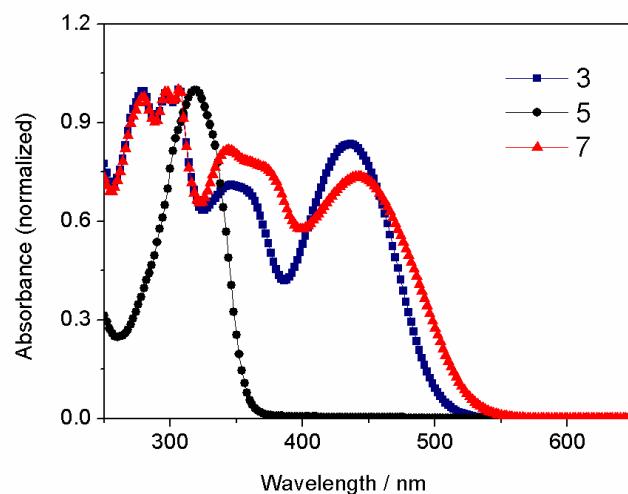


Figure S1. The UV-Vis absorption spectra of important intermediates 3, 5 and 7 in dichloromethane.

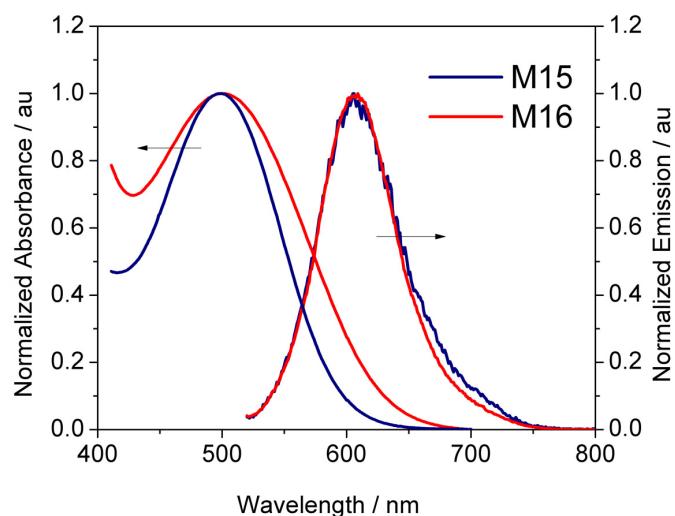


Figure S2. Normalized absorption and emission spectra of the dyes

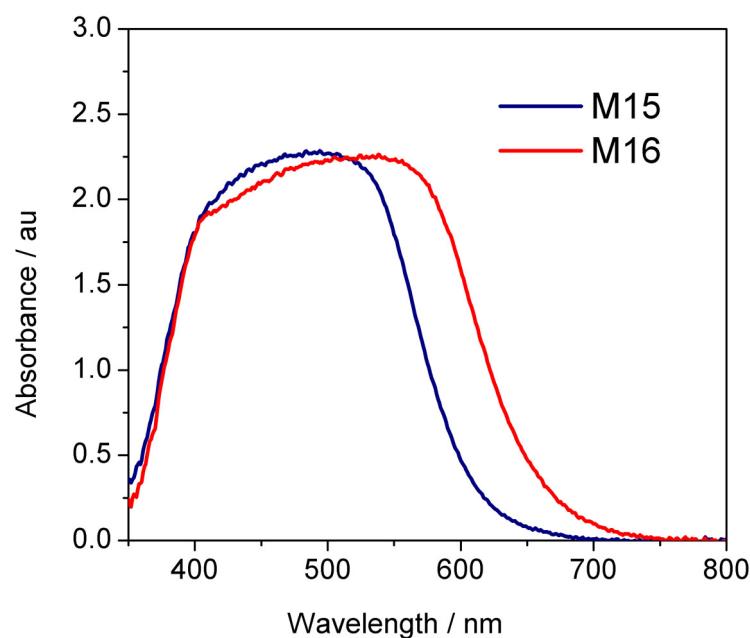


Figure S3. Absorption spectra of the dyes adsorbed TiO_2 films ($5.5 \mu\text{m}$)

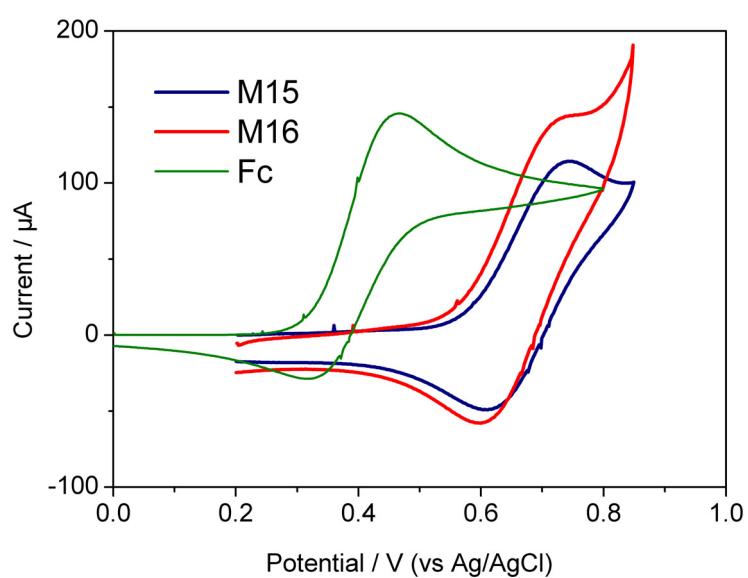


Figure S4. Cyclic voltammograms of the dyes–sensitized films.

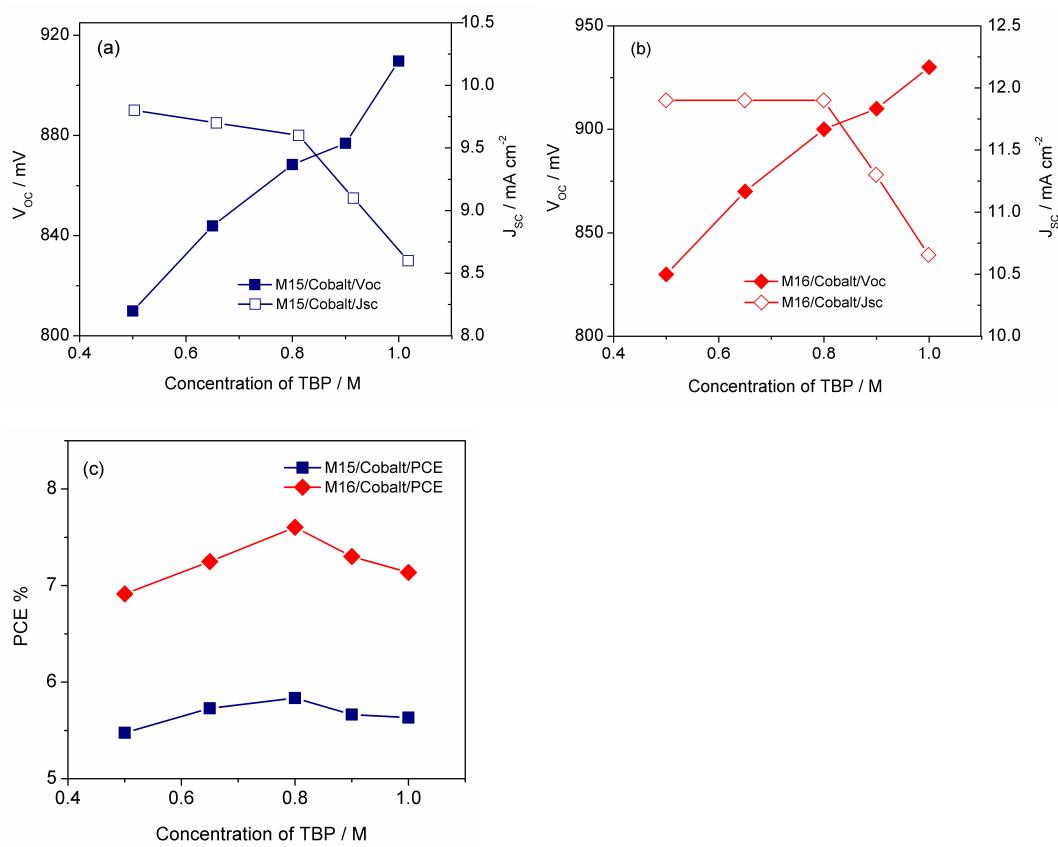


Figure S5. Optimization of Co(II/III)tris(phen)-based electrolytes by varying the concentrations of TBP in the electrolyte.

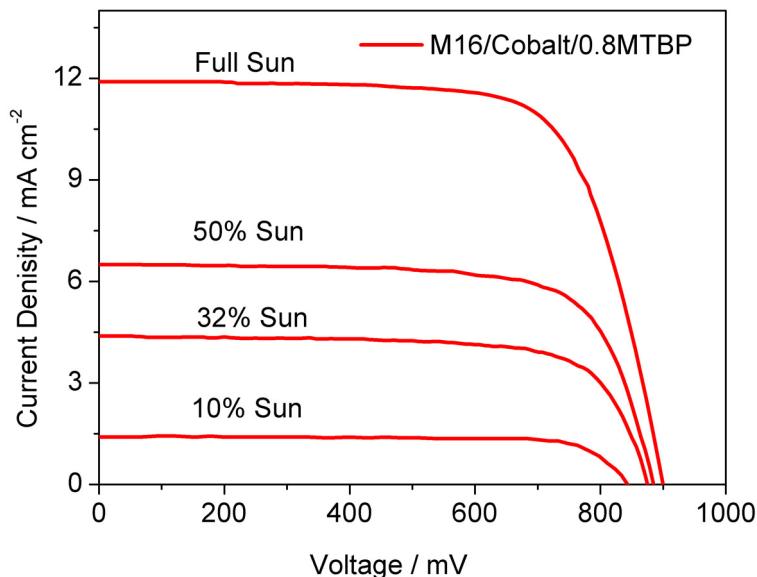


Figure S6. *J-V* characteristics of M16–sensitized DSCs measured under standard AM 1.5 global sunlight under various light intensities.

Table S2. Photovoltaic performance of DSCs (5.5 μm film) made with cobalt electrolyte and sensitized M16 dye at different light intensities.

dye	P_{in} (mW cm ⁻²)	J_{SC} (mA cm ⁻²)	V_{OC} (mV)	FF	PCE (%)
M16	100	11.9	900	0.71	7.6
	50	6.5	890	0.72	8.3
	32	4.4	875	0.72	8.5
	10	1.4	842	0.74	8.7

EL-Cobalt: 0.25 M [Co(II)(phen)₃](PF₆)₂, 0.05 M [Co(III) (phen)₃](PF₆)₃, 0.8 M TBP

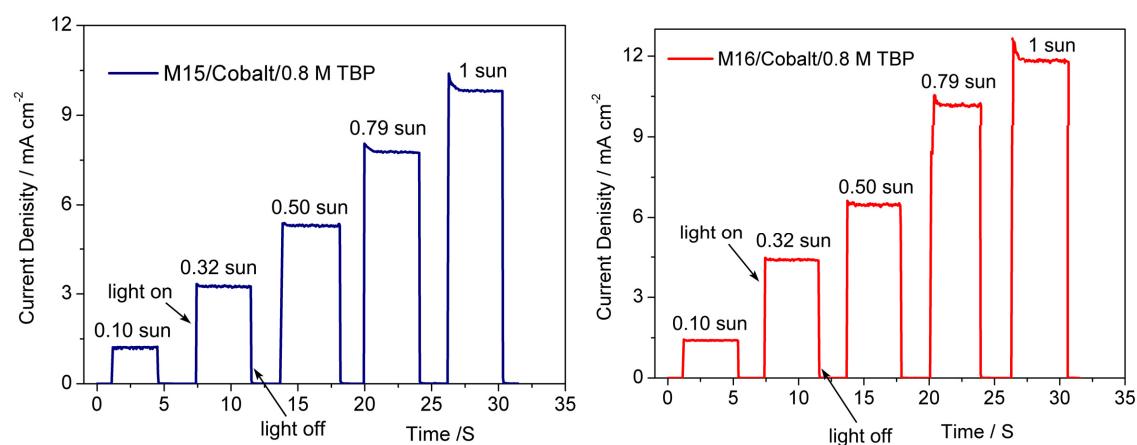


Fig. S7 Photo-current dynamics as a function of light intensity for the M15 (the left figure) and M16 (the right figure) –sensitized DSCs ($5.5 \mu\text{m}$ film) with cobalt electrolyte.

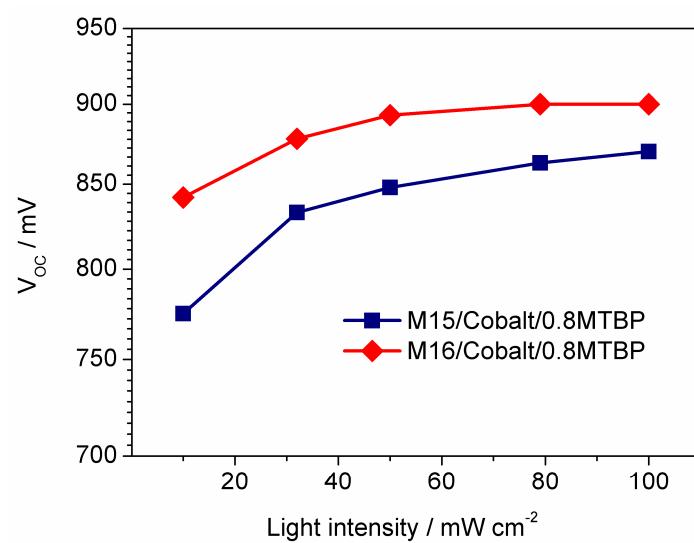


Fig. S8 Dependence of the V_{oc} on light intensity for a DSC with $\text{Co}^{II}/\text{III}$ tris(phen)-based electrolyte with the dyes.

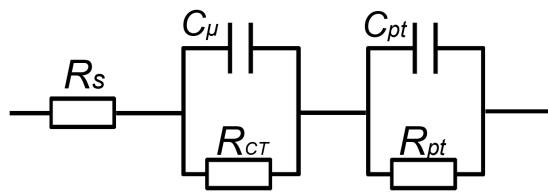


Figure S9. Equivalent circuit used to fit the impedance spectra.^{S3} R_s is the series resistance accounting for the transport resistance of the TCO and the electrolyte. C_μ and R_{CT} are the chemical capacitance and the charge recombination resistance at the TiO_2 /electrolyte interface. C_{pt} and R_{pt} are the interfacial capacitance and charge transport resistance at the Pt/electrolyte interface, respectively.

[S3] Fabregat-Santiago, F.; Garcia-Belmonte, G.; Bisquert, J.; Zaban, A.; Salvador, P. *J. Phys. Chem. B* **2002**, *106*, 334.

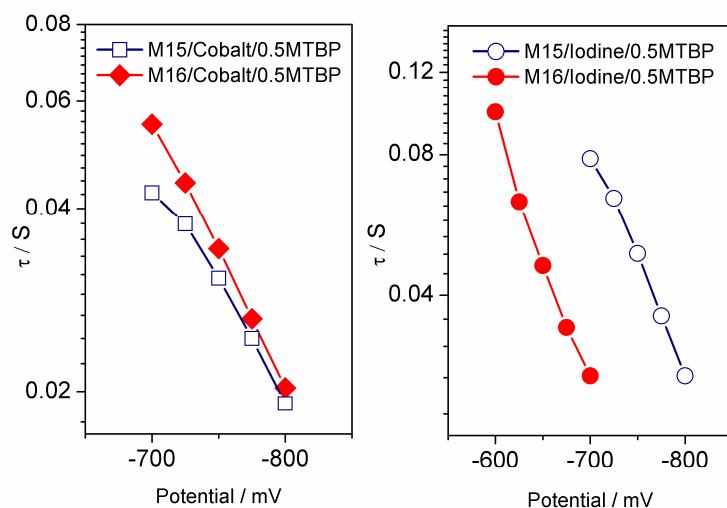


Figure S10. Electron lifetime τ fitted from impedance spectra under a series of applied potentials.

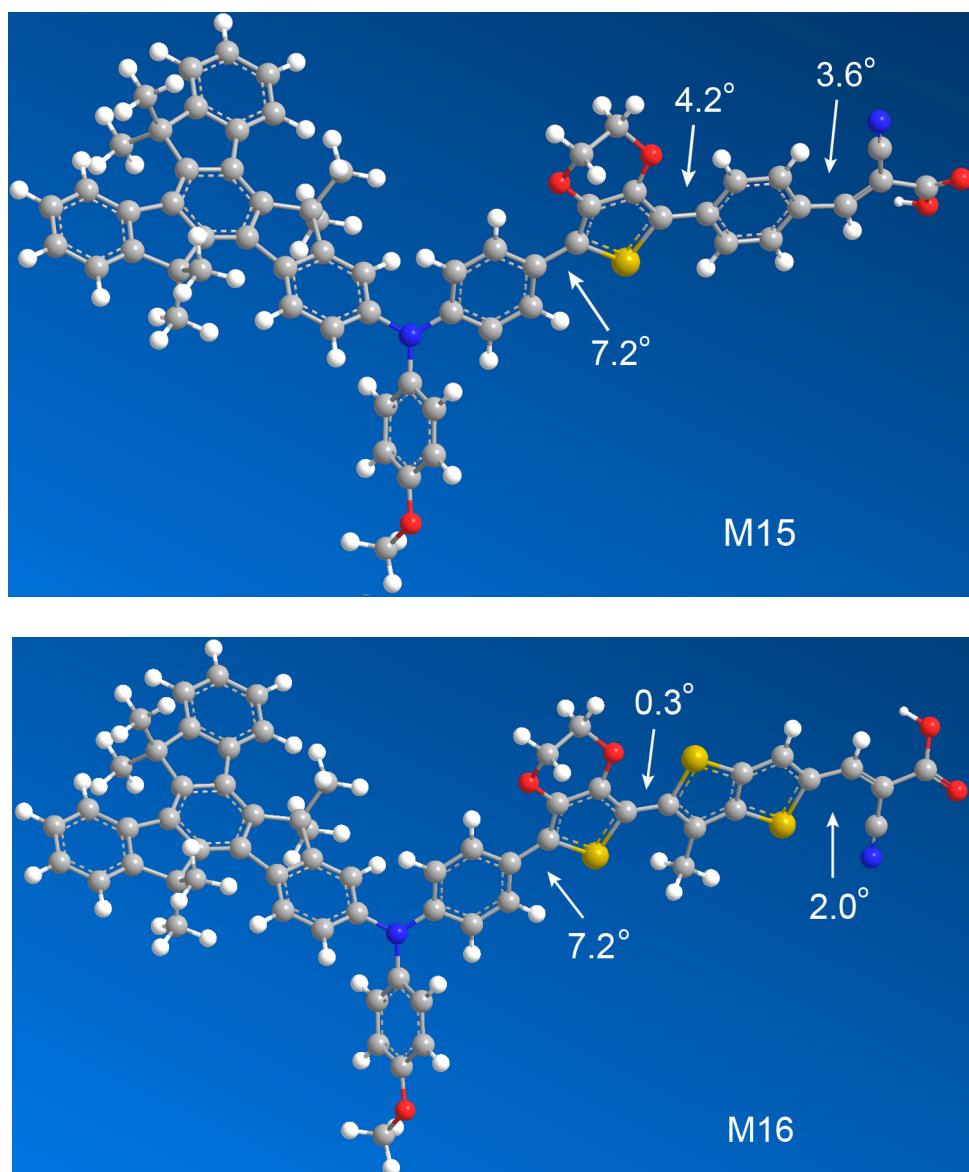


Figure S11. Optimized geometrical configuration of the dyes.

The geometrical structures of the two dyes were optimized by performed density functional theory (DFT) calculations and time-dependent DFT (TDDFT) calculations of the excited states at the B3LYP/6-31+G(d) level with the Gaussian 03W program package.^{S4}

[S4] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.;

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