Supporting Information

Multichromophoric di-anchoring sensitizers incorporating a ruthenium complex and an organic triphenyl amine dye for efficient dye-sensitized solar cells

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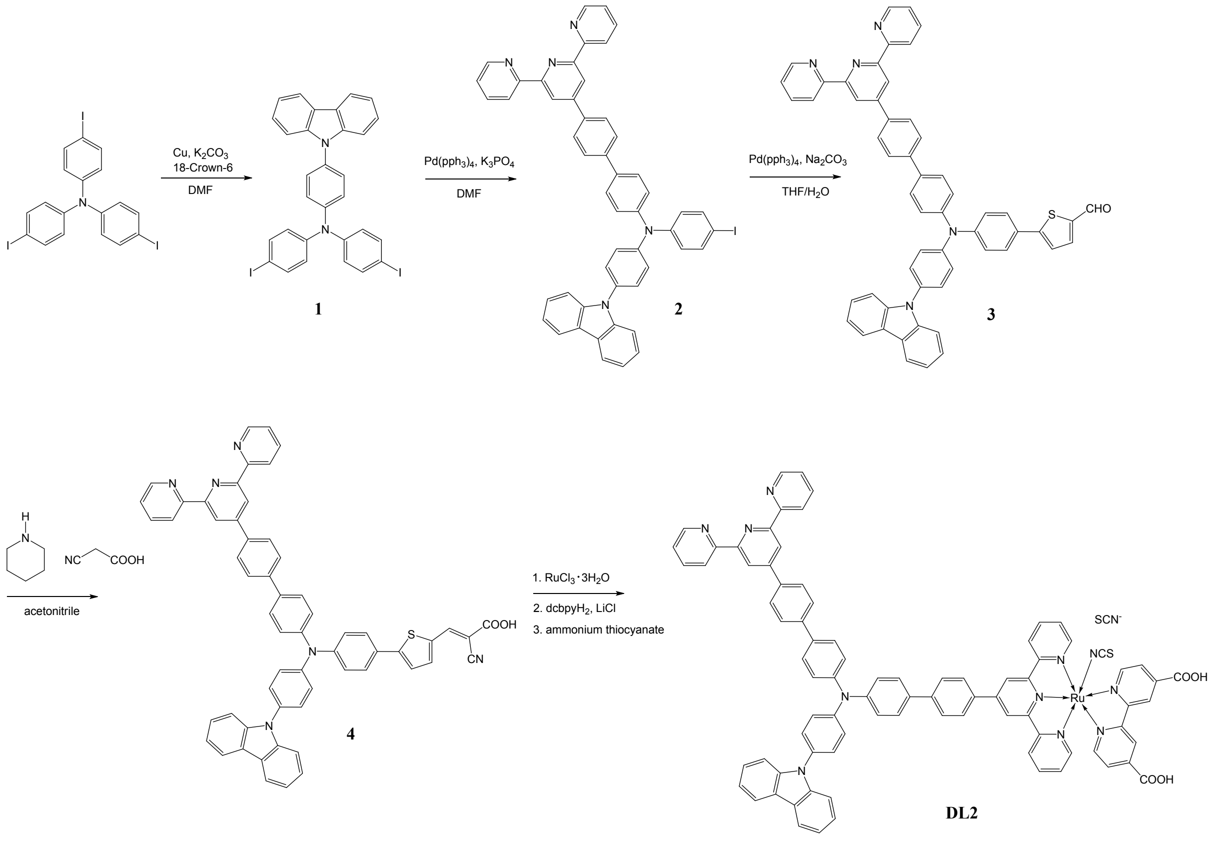
1. Experimental section

1.1 Materials and Reagents.

Tetrahydrofuran, toluene, and chloroform were purified using MBRAUN MB SPS-800 system. Methanol and acetonitrile were dried over molecular sieve without normal pressure distillation. Anhydrous solvents used in Suzuki coupling reaction were degassed by N_2 bubbling for 20 min. Optically transparent fluorine doped SnO_2 (FTO) conducting glass was purchased from Nippon Sheet Glass, Japan, (15 Ω/square), and cleaned by a standard procedure. All other chemicals and reagents were used as received from commercial sources without further purification.

1. 2 Synthetic procedure and characterization data

a)



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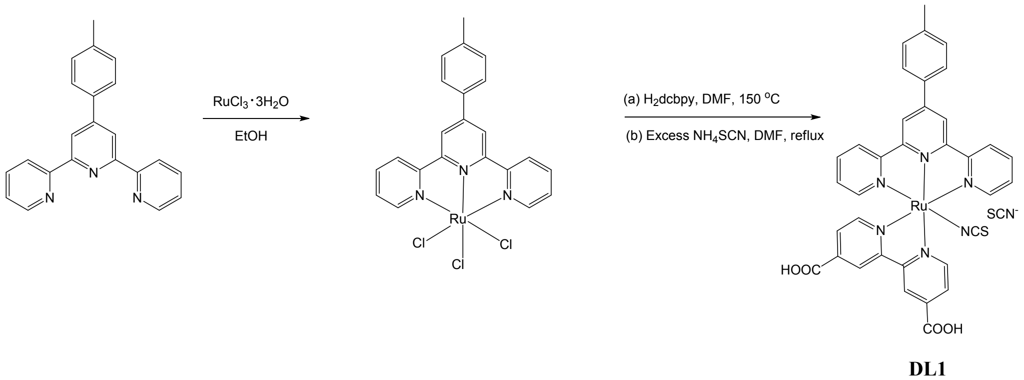

DL1

Scheme S1 Synthesis of **DL1** and **DL2**

Synthesis of Bis(N-4-iodophenyl)-N-4-(9H-carbazol-9-yl)phenyl (1)

Compound tris(4-iodophenyl)amine (3.738 g, 6 mmol), copper powder (45.7 mg, 0.715 mmol), potassium carbonate (690 mg, 5 mmol), 1, 4, 7, 10, 13, 16-Hexaoxacyclooctadecan (633 mg, 0.125 mmol), and carbazole (334 mg, 2 mmol) were dissolved in DMF (70 mL). The reaction solution was then heated at 150 °C for 2 h. After cooling down to room temperature，excess of water was added. The mixture was vacuum-filtrated to get raw product which was further purifed by silica-gel column chromatography to give 350 mg of yellow solid. Yield: 40%. ^{1}H-NMR (300 MHz, $CDCl_3$) δ (ppm): 8.14 (d, J = 7.8 Hz, 2H,), 7.57 (d, J = 2.1 Hz, 2H), 7.46-7.38 (m, 6H), 7.37-7.24 (m, 6H), 7.18 (d, J = 7.2 Hz, 2H), 6.91 (d, J = 3.0 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 144.6, 142.7, 139.5, 138.9, 131.9, 126.3, 124.6, 123.8, 122.3, 121.9, 119.3, 116.2, 109.5, 89.1. ESI-MS: m/z 537.2 ([M-I]$^-$).

Synthesis of 4-[N-4-iodophenyl-N-4-(9H-carbazol-9-yl)phenyl]amino-4'- {4-[2,6 -di(pyridin-2-yl)]pyridin-4-yl} biphenyl (2)

A mixture of **1** (662 mg, 1 mmol), boron ester (421 mg, 1 mmol), $Pd(pph_3)_4$ (23 mg, 0.02 mmol) and potassium phosphate (318 mg, 1.5 mmol)was added to DMF (50 mL) under nitrogen atmosphere. The reaction solution was heated at 100 °C for 24 h. Upon cooling to room temperature, the resulting mixture was dissolved in CH_2Cl_2 and the organic phase was washed with water. The combined organic extracts were subsequently dried over anhydrous magnesium sulfate. After removal of solvent, raw product was obtained. The product was purified by silica-gel column chromatography to obtain 210 mg pure product. Yield: 24.8%. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 8.75 (s, 2H), 8.67 (d, J = 6.8 Hz, 2H), 8.24 (d , J = 7.2 Hz, 2H), 8.04 (m, 4H), 7.88 (d, J = 7.0 Hz, 2H), 7.78 (m, 2H), 7.69 (d, J = 6.9 Hz, 2H), 7.49-7.46 (m, 4H), 7.44-7.40 (m, 4H), 7.21-7.18 (m, 6H), 7.17 (t, J = 7.0 Hz, 2H), 7.01 (d, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 172.67, 164.39, 156.29, 155.53, 149.95, 149.44, 148.48, 146.68, 145.97, 140.96, 140.79, 138.08, 136.66, 135.24, 134.83, 132.83, 128.73, 128.63, 128.21, 128.11, 127.82, 127.31, 126.87, 126.32, 125.67, 125.18, 124.82, 123.96, 123.31, 121.59, 121.20, 120.68, 118.34, 117.86, 110.40. ESI-MS: *m/z* 844.4 [M+H]$^+$.

Synthesis of 4-[N-4-(5-formylthiophen-2-yl)phenyl-N-4-(9H-carbazol-9-yl) phenyl]amino-4'-{4-[2,6-di(pyridin-2-yl)]pyridin-4-yl}biphenyl (3)

A mixture of **2** (253 mg, 0.3 mmol), 5-formyl-2-thiopheneboronic acid (51.4 mg, 0.33 mmol), sodium carbonate (795 mg, 7.5 mmol) and Pd(pph$_3$)$_4$ (13.86 mg, 0.012 mmol) was added to a 100 mL Schlenk flask under nitrogen atmosphere, and then THF (15 mL) and degassed water (15 mL) were added. The reaction solution was heated at 65 °C for 26 h. After cooling to room temperature, distilled water was added. The resulting mixture was adjusted to pH=6 and extracted with dichloromethane. The extract was washed successively with water and dried over anhydrous magnesium sulfate, filtered and evaporated to afford raw product which was further purified by silica-gel column chromatography to give 100 mg pure product. Yield: 40.3%. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 9.86 (s, 1H), 8.76 (s, 2H), 8.68 (d, J = 7.2 Hz, 2H), 8.22 (d, J = 7.20 Hz, 2H), 8.00-7.98 (m, 4H), 7.84-7.82 (m, 2H), 7.81-7.79 (m, 4H), 7.69-7.66 (m, 6H), 7.52-7.50 (m, 2H), 7.45-7.42 (m, 12H). ^{13}C NMR (75 MHz, DMSO-d_6) δ (ppm): 182.4, 155.9, 155.3, 150.3, 149.5, 148.6, 145.3, 144.8, 141.6, 140.0, 139.8, 137.8, 137.2, 128.1, 127.7, 126.6, 123.6, 121.4, 119.8, 118.0, 116.9. ESI-MS: *m/z* 828.5 [M+H]$^+$.

Synthesis of 4-[N-(E)-4-(5-(2-carboxy-2-cyanovinyl)thiophen-2-yl)phenyl-N-4-(9H-carbazol-9-yl)phenyl]amino-4'-{4-[2,6-di(pyridin-2-yl)]pyridin-4-yl}biphenyl (4)

A mixture of **3** (82.7 mg, 0.1 mmol), piperidine (18.36 mg, 0.216 mmol) and cyanoacetic acid (12.75 mg, 0.15 mmol) was added acetonitrile (20 mL) under nitrogen atmosphere. The reaction solution was heated at 80 °C for 24 h. After cooling to room temperature, distilled water was added. The resulting mixture was adjusted to pH=6 and extracted with dichloromethane. The extract was washed successively with water, filtered and evaporated to afford raw product which was further purified by silica-gel column chromatography to give 20 mg pure product. Yield: 22.3%. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 7.40 (m, 13H), 7.50 (m, 2H), 7.62 (m, 3H), 7.80 (m, 4H), 7.92 (m, 3H), 8.02 (m, 4H), 8.22 (d, 2H), 8.36 (s, 1H), 8.65 (d, 2H), 8.76 (s, 3H), 11.5 (s, 1H). ^{13}C NMR (75 MHz, DMSO-d$_6$) δ (ppm): 172.60, 164.41, 156.27, 155.52, 149.94, 149.41, 148.43, 146.67, 145.96, 140.95, 140.78, 138.07, 136.64, 135.21, 134.87, 132.80, 128.62, 128.10, 127.80, 127.33, 126.86, 126.31, 125.63, 125.17, 123.96, 123.30, 121.58, 121.19, 120.68, 118.32, 110.39. ESI-MS: *m/z* 895.27 [M+H]$^+$.

Synthesis of 4 ligand-(4,4'-dicarboxyl-2,2'-bipyridine)-ruthenium (II) isothiocyanate (DL2)

4 (55.1 mg, 0.05 mmol) was dissolved in EtOH (30 mL) of and then $RuCl_3.3H_2O$ (13 mg, 0.05 mmol) was added. The mixture was heated to reflux for 1 h. After cooling to room temperature, resulting mixture was washed with EtOH and dried in vacuo. The pure product was obtained as dark orange solid. A mixture of the resulting product (130 mg, 0.086 mmol), 4,4'-Dicarboxy-2,2'-bipyridine (21 mg, 0.086 mmol) and the required amount of lithium chloride was added to DMF (20 mL) under nitrogen atmosphere. The reaction solution was heated at 150 °C for 12 h, and then excess of ammonium thiocyanate was added, the reaction mixture was reacted for another 12 h. Upon cooling to room temperature, distilled water was added to the mixture. Dark orange precipitation occurred and was filtered to afford a crude product. The pure product was obtained as orange crystals. Yield: 40%. ^{1}H-NMR(300 MHz, DMSO-d_6) δ (ppm): 9.30 (s, 1H), 9.20 (s, 1H), 9.16 (s, 1H), 9.05-9.02 (m, 2H), 8.89-8.86 (m, 4H), 8.81-8.78 (m, 2H), 8.75-8.72 (m, 2H), 8.65-8.62 (m, 4H), 8.19-8.17 (m, 4H), 8.08-

8.06 (m, 4H), 7.58-7.56 (m, 4H), 7.46-7.45 (m, 6H), 7.27-7.25 (m, 10H), 7.01-6.98 (m, 4H). ESI-MS: *m/z* 1428.3 [M-SCN]$^+$.

Synthesis of Ru[(TPy-CH_3)(dcbpyH_2)NCS](SCN^-)(DL1)

TPy-CH_3 ligands (0.13 g, 0.4 mmol) were dissolved in EtOH (100 ml) and then of $RuCl_3.3H_2O$ (0.104 g, 0.4 mmol) were added. The mixture was heated to reflux for 1 h. After cooling to room temperature, the resulting mixture was washed with EtOH and dried in vacuo. The pure product was obtained as dark orange solid. A mixture of the Ru(TPy-CH_3)Cl_3 (0.16 g, 0.3 mmol), 4,4'-Dicarboxy-2,2'-bipyridine (0.073 g, 0.3mmol) and the required amount of lithium chloride was added to DMF (100 mL) under nitrogen atmosphere. The reaction solution was heated at 150 °C for 12 h, and then excess of ammonium thiocyanate was added, and the reaction mixture was reacted for another 12 h. Upon cooling to room temperature, distilled water was added to the mixture. Dark orange precipitation occurred and was filtered to afford a crude product. The pure product was obtained as orange crystals. Yield: 40%. ^{1}H-NMR (300 MHz, DMSO-d_6) δ (ppm): 9.15 (s, 2H), 9.06 (d, J=7.4 Hz, 2H), 8.93 (d, J=7.4 Hz, 2H), 8.66 (s, 2H), 8.59 (d, J=8.0 Hz, 2H), 7.70 (d, J=7.5 Hz, 2H), 7.38 (d, J=6.9 Hz, 2H), 7.33-7.29 (m, 4H), 7.14 (d, J=7.3 Hz, 2H), 2.36 (s, 3H). ESI-MS: *m/z* 724.87 ([M-SCN-2H]$^-$). Anal. Calcd for RuTPy-$CH_3 \cdot CH_3OH \cdot 3H_2O$: C, 51.30; H, 4.05; N, 11.26. Found: C, 51.06, H, 4.10; N, 11.28.

1.3 Characterizations.

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopies were performed on a BRUKER 400 MHz with tetramethylsilane (TMS) as internal standard. Elemental analyses were carried out with an Elementar Vario EL Cube instrument. Mass spectral data were obtained on an ultrafleX-treme MALDI-TOF/TOF mass spectrometer (Bruker Daltonics). The absorption spectra of the dyes (in solution and adsorbed on TiO_2 films) were observed with a Shimadzu UV- 2450 spectrometer and fluorescence spectra were measured with a Hitachi F-4500 spectrometer. Cyclic voltammogram (CV) curves were obtained with a CHI 832 electrochemical analyzer using a normal three-electrode cell with dye-sensitized photoanode as working electrode, a Pt wire counter electrode, and a regular Ag/AgCl reference electrode in saturated KCl solution which was calibrated with ferrocene/ferrocenium as external reference. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in $CHCl_3$.

1.4 Fabrication of Cells.

The anatase TiO_2 nanoparticles were synthesized according to our previous literature.[12] First, the $Ti(OBu)_4$ (10 mL) was added to the ethanol (20 mL) under stirring for 10 min. Then a mixture of deionized water (50 mL) and acetic acid (18 mL) was added to the solution with vigorous stirring for 1 h. The resulted solution was moved to an autoclave and heated at 200 °C for 12 h. Finally, the precipitations were washed with deionized water and ethanol for several times, respectively. The white powder was obtained after drying in air. The as-prepared TiO_2 nanoparticles were anatase crystals with diameters of about 20 nm, as confirmed by SEM, TEM, and XRD. The prepared TiO_2 powder (1.0 g) was ground for 40 min in the mixture of acetic acid (0.2 mL), ethanol (8.0 mL), ethyl cellulose (0.5 g), and terpineol (3.0 g) to form a slurry, and then the slurry was sonicated for 5 min to obtained a viscous white TiO_2 paste. The TiO_2 paste was then screen-printed onto the surface of FTO coated glass forming photoanode film. The thickness of films can be easily controlled through repeating screen-printing times. Afterwards, a programmed heating process was carried out to remove the organic substances in the film. The as-prepared TiO_2 films (~15 μm) were soaked in a 0.04 M aqueous solution of $TiCl_4$ for 30 min at 70 °C and then sintered at 520 °C for 30 min. After cooling to 80 °C, the TiO_2 electrodes were immersed into 0.3 mM optimal organic solution ($CHCl_3$/ACN/^{t}BuOH = 1/2/2) of the dyes and kept at room temperature for 6 h for cells with liquid electrolyte and for 12 h for cells with gel electrolyte, respectively. And then the prepared TiO_2 working electrodes were sandwiched together with Pt-counter electrode. The active area of the dye-coated TiO_2 film was 0.16 cm^2. The electrolyte was injected into the inter-electrode space. The liquid electrolyte are composed of 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), 0.10 M guanidinium thiocyanate (GuNCS), 0.03 M I_2, 0.5 M *tert*-butylpyridine (t-BP) in acetonitrile and valeronitrile (85:15, v/v). The dye-adsorbed TiO_2 film as working electrode was placed on the top of a Pt coated

FTO glass as counter electrode. The electrolyte was introduced into the space between two electrodes by capillary force.

1.5 Characterization of Cells.

The TiO_2 film thickness and active area of the dye-coated TiO_2 film was measured by using a profilometer (Ambios, XP-1). The current-density voltage (*J*-*V*) curves of the DSSCs were recorded by using a Keithley 2400 source meter under the illumination of AM 1.5 G simulated solar light. IPCEs of DSSCs were measured on the basis of a Spectral Products DK240 monochromator. Electrochemical impedance spectroscopy (EIS) was measured using an electrochemical workstation (Zahner, Zennium) with a frequency response analyzer at a bias potential of -800 mV in the dark with a frequency ranging from 10 mHz to 1 MHz. The dye-adsorbed amounts on the TiO_2 film were measured using a Shimadzu UV-2450 spectrometer.

1.6 Computational Details

Calculations were performed using the software package TURBOMOLE with the basis set def2-TZVP for all atoms. The exchange and correlation energy was estimated using the functional B3LYP. Open-shell electronic configurations were computed using unrestricted density functional theory (DFT). The singlet to singlet transitions were calculated with time-dependent DFT (TDDFT)/COSMO using the same basis sets and exchange-correlation functional as for the ground-state calculations. The quasirelativistic Stuttgart/Dresden semicore SDD-ECP was used for the ruthenium atom.

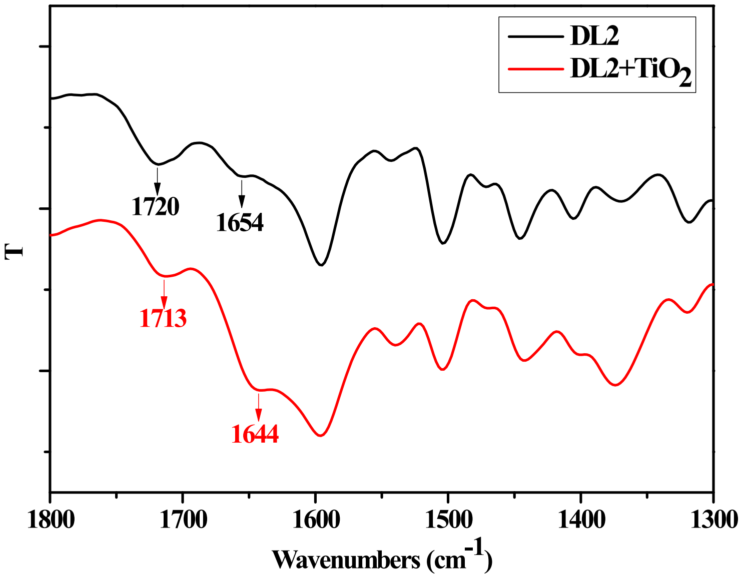

Figure S1 FTIR spectra of dye powders (black) and dyes adsorbed on TiO_2 nanoparticles (red) for **DL2**.

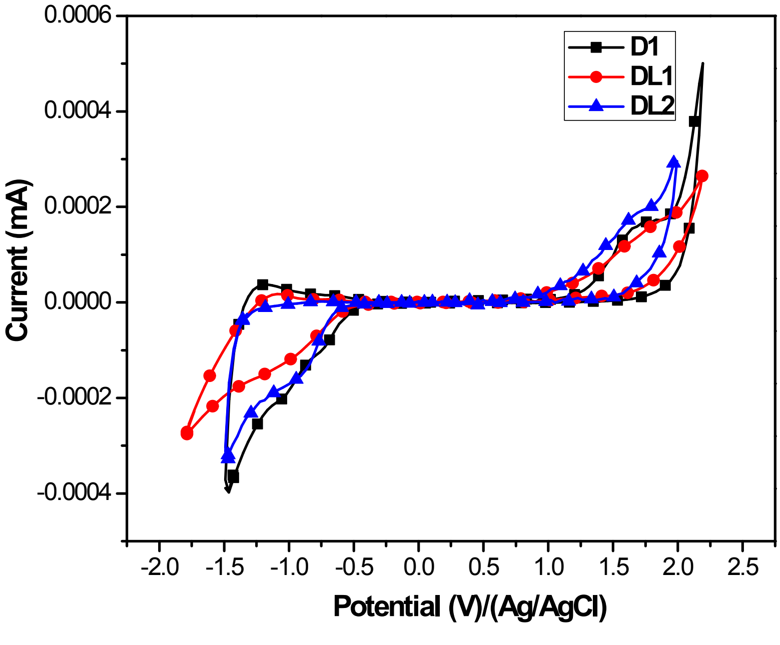

Figure S2 Cyclic voltammograms of **D1, DL1,** and **DL2** on TiO_2 film

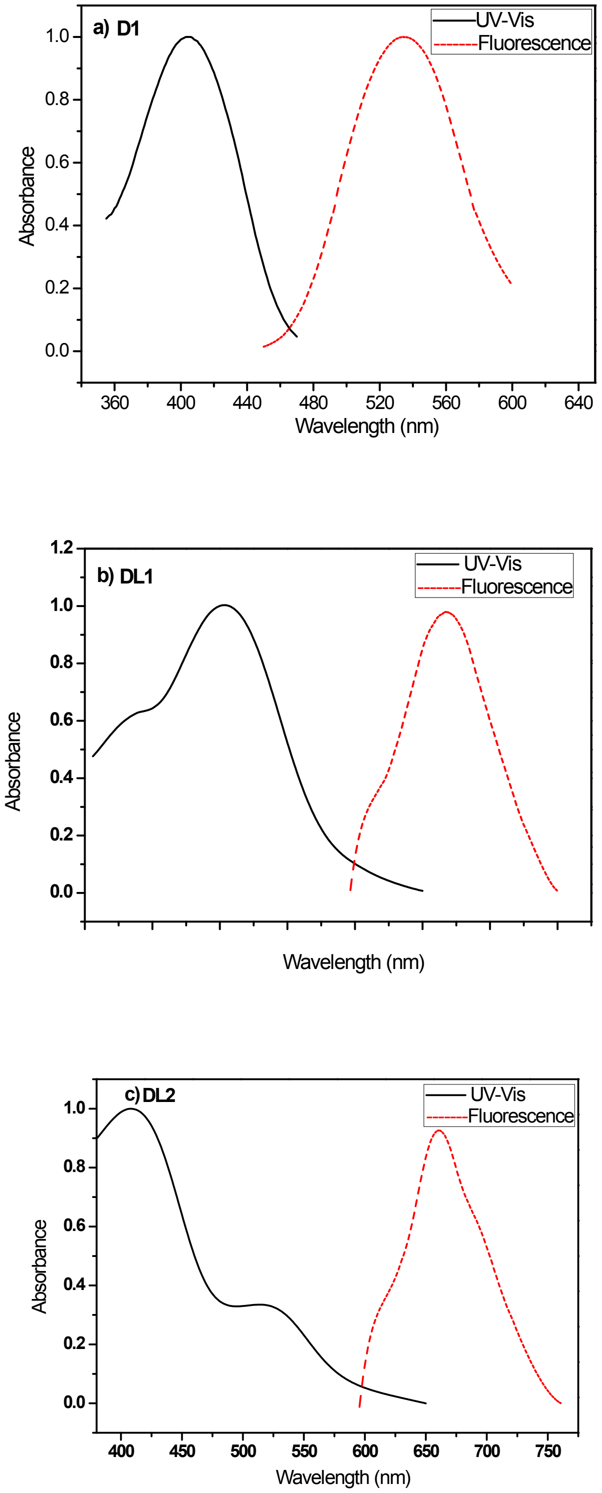

Figure S3 Absorption (black solid) and emission (red dash) spectra of a) **D1**, b) **DL1**, and c) **DL2** measured in DMF solution.

Table S1 Absorption and electrochemical data of the dyes.

dye	$\varepsilon/10^4\ M^{-1}\ cm^{-1}$ (λ_{max}/nm)	E_{HOMO}/eV	$^aE_{0-0}$/eV	E_{LUMO}/eV
D1	2.20 (409)	-5.79	2.68	-3.11
DL1	0.73 (509)	-5.93	2.07	-3.86
DL2	1.66 (519); 2.35 (409)	-5.87	2.07	-3.80

^{a} E_{0-0} was determined from the intersection of absorption and emission spectra in $CHCl_3$.

Table S2 Photovoltaic parameters of the cosensitization DSSCs under AM 1.5G illumination

Dye	J_{sc}/ m A cm^{-2}	V_{oc}/ mV	*FF*	η/%
6+6h	8.33	613	0.74	3.78
6+9h	9.98	625	0.71	4.43
6+12h	10.74	624	0.74	4.94