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SUPPLEMENTARY INFORMATION

Eugenic Metal-free Sensitizers with Double Anchors for High Performance Dye-Sensitized Solar Cells

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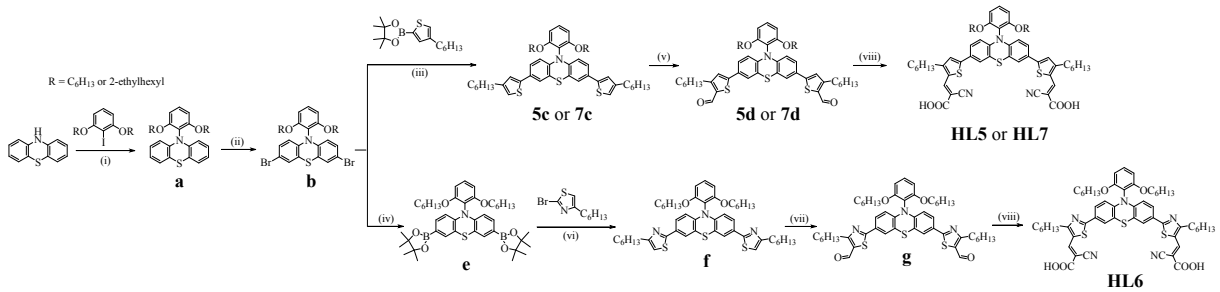
Materials and Reagents. Unless otherwise specified, all reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were dried by standard procedures. Dye bis(tetrabutylammonium)-*cis*-di(thiocyanato)-*N*,*N'*-bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine)ruthenium) (coded as N719) and TiO_2 paste were purchased from Solaronix S. A., Switzerland.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Mass spectra (FAB) were recorded on a VG70-250S mass spectrometer. Elementary analyses were performed on a Perkin-Elmer 2400 CHN analyzer. Absorption spectra were recorded on a Dynamica DB-20 probe UV/Vis spectrophotometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer. Cyclic voltammetry experiments were performed with a CHI-621A electrochemical analyzer. All measurements were carried out at room temperature with a conventional three electrode configuration consisting of a platinum working electrode, an auxiliary electrode and a non-aqueous $Ag/AgNO_3$ reference electrode. The photoelectrochemical characterizations on the solar cells were carried out using an Oriel Class AAA solar simulator (Oriel 94043 A, Newport Corp.). Photocurrent-voltage characteristics of the DSSCs were recorded with a potentiostat/galvanostat (CHI650B, CH Instruments, Inc.) at a light intensity of 100 mW/cm^2 calibrated by an Oriel reference solar cell (Oriel 91150, Newport Corp.). The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100, Newport Corp.) at short circuit condition. The intensity of each wavelength was in the range of 1 to 3 mW/cm^2. Electrochemical impedance spectra (EIS) were recorded for DSSC under illumination at open-circuit voltage (V_{oc}) or dark at -0.55 V potential at room temperature. The frequencies explored ranged from 10 mHz to 100 kHz. Intensity-modulated photovoltage spectroscopy (IMVS) was carried out on the electrochemical workstation (Zahner, Zennium) with a frequency response analyzer under an intensity modulated (10 to 300 W m^{-2}) white light emitting diode driven by a Zahner (0982wlr02) source supply. The frequency range was set from 100 KHz to 10 mHz.

Assembly and characterization of DSSCs. The photoanode used was the TiO_2 thin film (12 μm of 20 nm particles as the absorbing layer and 6 μm of 400 nm particles as the scattering layer) coated on FTO glass substrate with a dimension of 0.4 × 0.4 cm^2, and the film thickness measurement by a profilometer (Dektak3, Veeco/Sloan Instruments Inc., USA). The TiO_2 thin film was dipped into the THF solution containing 3×10^{-4} M dye sensitizers for at least 12 h. For the coadsorbed solar cell, chenodeoxycholic acid (CDCA) was added into the dye solutions at a concentration of 30 mM. After rinsing with THF, the photoanode adhered with a polyimide tape of 30 μm in thickness and with a square aperture of 0.36 cm^2 was placed on top of the counter electrode and tightly clipping them together to form a cell. Electrolyte was then injected into the seam between two electrodes. The electrolyte was composed of 0.5 M lithium iodide (LiI), 0.05 M iodine (I_2), and 0.5 M 4-*tert*-butylpyridine dissolved in acetonitrile.

Electrochemical measurements: The electrochemical properties of the organic dyes were measured by cyclic voltammetry (CV) in THF solutions with ferrocene/ferrocenium as the internal reference. This first oxidation potential (E_{ox}) together with the zero-zero excitation energy ($E_{0\text{-}0}$) can be used to deduce the excited state potential ($E_{0\text{-}0}$*) of the sensitizer, i.e., $E_{0\text{-}0}^* = E_{ox} - E_{0\text{-}0}$. Electron injection from the excited dye to the TiO_2 is energetically favored as the $E_{0\text{-}0}$* value of the dye (-0.90 to -1.09 V vs. NHE) is more negative than the conduction band edge of TiO_2 (-0.5 V vs. NHE).[1] Dye regeneration should also be energetically favored as the first oxidation potentials of the dyes (0.94 to 1.16 V vs. NHE) are more positive than that of the I^-/I_3^- redox couple (0.4 V vs. NHE).[2]

Quantum chemistry computation: The computations were performed with Q-Chem4.0 software.[3] Geometry optimization of the molecules was performed using hybrid B3LYP functional and 6-31G* basis set. For each molecule, a number of possible conformations were examined and the one with the lowest energy was used. The same functional was also applied for the calculation of excited states usingtime-dependent density functional theory (TD–DFT). There exist a number of previous works that employed TD–DFT to characterize excited states with charge-transfer character.[4,5] In some cases underestimation of the excitation energies was seen.[6] Therefore, in the present work, we use TD–DFT to visualize the extent of transition moments as well as their charge-transfer characters, and avoid drawing conclusions from the excitation energy.



Scheme S1. Synthetic routes of **HL5**–**HL7**.

10-(2,6-Bis-hexyloxy-phenyl)-10*H*-phenothiazine (a). To a 250 mL two-neck round flask were added phenothiazine (2.46 g, 12.37 mmol), 1,3-bis(hexyloxy)-2-iodobenzene (5.00 g, 12.37 mmol), sodium *tert*-butoxide (1.78 g, 18.55 mmol) and $Pd(dba)_2$ (0.36 g, 0.62 mmol) under nitrogen. Dry toluene (25 mL) and tri(*tert*-butyl)phosphine (0.494 M, 2.52 mL) were injected into the mixture. The mixture was heated at 130 °C for overnight. The mixture was poured into dichloromethane and product was washed with water. The organic extract was dried over anhydrous $MgSO_4$, filtered, and pumped dry. The crude product was further purified by column chromatography on silica gel using hexane/dichloromethane (8 : 1 by vol.) as the eluent to give **a** as a light yellow oil (3.28 g, 56%). ^{1}H NMR (400 MHz, acetone-d_6): δ7.42 (t, J = 8.4 Hz, 1H), 6.89 (d, J = 7.6 Hz, 2H), 6.85-6.79 (m, 4H), 6.72 (t, J = 7.4 Hz, 2H), 6.11 (d, J = 8.0 Hz, 2H), 4.01 (t, J = 6.2 Hz, 4H), 1.62-1.56 (m, 4H), 1.26-1.21 (m, 4H), 1.14-1.13 (m, 8H), 0.77 (t, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, acetone-d_6): δ 158.85, 143.90, 130.84, 127.57, 126.71, 122.61, 120.66, 119.06, 116.25, 106.83, 69.25, 32.14, 26.26, 23.23, 14.33. MS-LR-MALDI, *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{37}NO_2S$, 475.2; found, 475.1.

10-(2,6-Bis-hexyloxy-phenyl)-3,7-dibromo-10*H*-phenothiazine (b). To a flask containing **a** (2.28 g, 4.79 mmol) was added DMF (5 mL). Then NBS (1.8 g, 10.07 mmol) in DMF (5.0 mL) was added slowly at 0 °C. The reaction mixture was brought to room temperature and stirred overnight. The mixture was poured into H_2O (100 mL) and extracted with CH_2Cl_2. The crude product was purified by column chromatography using hexanes/CH_2Cl_2 (10:1 by vol.) as the eluent to afford **b** as a colorless oil (2.10 g, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, J = 8.6 Hz, 1H), 6.97 (s, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 5.89 (d, J = 8.4 Hz, 2H), 3.92 (t, J = 6.0 Hz, 4H), 1.63-1.57(m, 4H), 1.22-1.14 (m, 12H), 0.79 (t, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.93, 142.08, 130.28, 129.78, 128.40, 121.80, 117.76, 116.87, 114.08, 105.92, 68.90, 31.56, 29.28, 25.72, 22.79, 14.15. MS-LR-MALDI, *m*/*z*: $[M + H]^+$ calcd for $C_{30}H_{35}Br_2NO_2S$, 631.1; found, 632.9.

10-(2,6-Bis(hexyloxy)phenyl)-3,7-bis(4-hexylthiophen-2-yl)-10*H*-phenothiazine (5c). Toluene (10 mL), EtOH (2 mL) and H_2O (4 mL) were added to a flask containing a mixture of **b** (2.10 g, 3.32 mmol), 2-(4-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2.05 g, 8.29 mmol), $Pd(PPh_3)_4$ (0.19 g, 0.17 mmol) and Na_2CO_3 (1.05 g, 9.95 mmol), and the solution was heated at reflux for 18 h. The solution was cooled to room temperature and extracted with a mixture of CH_2Cl_2 and H_2O. The organic extract was dried over anhydrous $MgSO_4$, filtered, and pumped dry. The crude product was purified by column chromatography on aluminum oxide gel with hexane/DCM (9:1 by vol.) as the eluent to give 5**c** as a yellow oil (1.52 g, 57%). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.46 (t, J = 8.4 Hz, 1H), 7.19 (s, 2H), 7.16 (s, 2H), 7.08 (d, J = 8.4 Hz, 2H), 6.93 (s, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.10 (d, J = 8.8 Hz, 2H), 4.04 (t, J = 5.6 Hz, 4H), 2.59 (t, J = 7.8 Hz, 4H), 1.65-1.58 (m, 8H), 1.32-1.25 (m, 16H), 1.13-1.12 (m, 8H), 0.87-0.86 (m, 6H), 0.73 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, acetone-d_6): δ 158.65, 145.00, 143.78, 142.70, 131.24, 129.82, 125.10, 124.38, 123.64, 120.74, 119.47, 118.43, 116.51, 106.88, 69.34, 32.50, 32.24, 31.27, 30.01, 29.77, 26.44, 23.40, 14.47, 14.41. MS-LR-MALDI, *m*/*z*: $[M + H]^+$ calcd for $C_{50}H_{65}NO_2S_3$, 807.4; found, 807.3.

5,5'-(10-(2,6-Bis(hexyloxy)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(3-hexylthiophene-2-carbaldehyde) (5d). A solution of 5**c** (0.80 g, 0.99 mmol) in DMF (2.5 mL) was cooled to 0 °C under a N_2 atmosphere. $POCl_3$ (0.28 mL, 2.97 mmol) was added slowly via a syringe. The mixture was stirred for 30 min at 0 °C and 3 h at 65 °C. After cooling, the reaction was quenched with an aqueous solution of CH_3COONa and the resulting mixture was extracted with CH_2Cl_2 and H_2O. The organic extract was dried over anhydrous $MgSO_4$, filtered, and pumped dry. The crude product was purified by column chromatography on aluminum oxide gel using hexane/CH_2Cl_2 (2:3 by vol.) as the eluent to give 5**d** as an orange oil (0.66 g, 77%). ^{1}H NMR (400 MHz, acetone-d_6): δ 10.04 (s, 2H), 7.50 (t, J = 8.4 Hz, 1H), 7.40 (s, 2H), 7.36 (s, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.15 (d, J = 8.4 Hz, 2H), 4.06 (t, J = 5.8 Hz, 4H), 3.01 (t, J = 7.4 Hz, 4H), 1.77-1.71 (m, 4H), 1.69-1.59 (m, 4H), 1.41-1.23 (m, 20H), 1.20-1.07 (m, 8H), 0.88 (t, J = 6.0 Hz, 6H), 0.71 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, acetone-d_6): δ 182.27, 158.31, 154.88, 152.08, 143.91, 136.72, 131.64, 128.46, 126.73, 126.17, 124.29, 120.93, 117.68, 116.71, 106.90, 69.39, 32.41, 32.19, 29.98, 29.08, 26.45, 23.42, 23.32, 14.43, 14.39. MS-LR-MALDI, *m*/*z*: $[M + H]^+$ calcd for $C_{52}H_{65}NO_4S_3$, 863.4; found, 863.3.

Synthesis of **10-(2,6-Bis(2-ethylhexyloxy)phenyl)-3,7-bis(4-hexylthiophen-2-yl)-10*H*-phenothiazine (7c)**. Compound **7c** was synthesized according to a procedure similar to that described for **5c** except that the reaction temperature and time were 80 °C and 18 h, respectively. Yield: 72%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.44 (t, J =

8.4 Hz, 1H), 7.18 (d, J = 2.0 Hz, 4H), 7.04 (dd, J = 8.4, 2.0 Hz, 2H), 7.00 (s, 2H), 6.87 (d, J = 8.4 Hz, 2H), 5.95 (td, J = 8.4, 2.4 Hz, 2H), 3.90-3.82 (m, 4H), 2.55-2.50 (m, 4H), 1.59-1.56 (m, 4H), 1.49-1.45 (m, 2H), 1.31-1.27 (m, 12H), 1.20-1.11 (m, 6H), 1.07-0.96 (m, 10H), 0.85 (t, J = 6.8 Hz, 6H), 0.69 (t, J = 7.2 Hz, 6H), 0.64 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 156.93, 143.63, 141.96, 140.97, 130.42, 128.12, 123.94, 123.59, 122.24, 118.86, 118.71, 116.23, 115.00, 105.71, 69.89, 30.96, 29.93, 29.84, 29.71, 28.29, 28.24, 23.18, 22.36, 21.93, 13.81, 13.69, 10.86. MS-LR-MALDI, m/z: $[M + H]^+$ calcd for $C_{54}H_{73}NO_2S_3$, 863.5; found, 863.4.

5-(10-(2,6-Bis(2-ethylhexyloxy)phenyl)-3-(5-formyl-4-hexylthiophen-2-yl)-10*H*-phenothiazin-7-yl)-3-hexylthiophene-2-carbaldehyde (7d). Compound **7d** was synthesized according to a procedure similar to that described for **5d**. Yield: 78%. ^{1}H NMR (400 MHz, acetone-d_6): δ 10.04 (s, 2H), 7.50 (t, J = 8.4 Hz, 1H), 7.40 (s, 2H), 7.37 (d, J = 2.4 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 6.91 (d, J = 8.8 Hz, 2H), 6.14 (td, J = 8.4, 2.8 Hz, 2H), 3.98-3.94 (m, 4H), 3.01 (t, J = 7.6 Hz, 4H), 1.75-1.69 (m, 4H), 1.56-1.55 (m, 2H),1.42-1.37 (m, 4H),1.35-1.24 (m, 16H), 1.22-1.01 (m, 8H), 0.87 (t, J = 6.8 Hz, 6H), 0.76 (t, J = 7.6 Hz, 6H), 0.69 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, acetone-d_6): δ 182.48, 158.39, 155.07, 152.15, 144.09, 136.76, 131.77, 128.52, 126.86, 126.21, 124.31, 120.83, 117.41, 116.67, 106.63, 71.16, 40.51, 32.39, 32.13, 31.52, 30.67, 29.03, 24.68, 23.81, 23.30, 14.42, 14.37, 11.61. MS-LR-MALDI, m/z: $[M + H]^+$calcd for $C_{56}H_{73}NO_4S_3$, 919.5; found, 919.3.

10-(2,6-Bis(hexyloxy)phenyl)-3,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10*H*-phenothiazine (e). To a 100 mL round flask was added **b** (2.15 g, 3.39 mmol) and THF (8 mL) was injected as the solvent under N_2. The solution was cooled to −78 °C and *n*-butyllithium (1.6 M in hexane, 4.6 mL) was injected slowly and stirred for 30 min. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.42 mL) was injected into the mixture and stirred at room temperature for 13 h. The reaction was quenched with water and the resulting mixture was extracted with ether. The organic extract was dried over anhydrous $MgSO_4$, filtered and pumped dry to give **e** as a yellow oil (1.98 g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31 (t, J = 8.4 Hz, 1H), 7.27 (d, J = 1.2 Hz, 2H), 7.14 (dd, J = 10.0, 1.0 Hz, 2H), 6.64 (d, J = 8.4 Hz, 2H), 5.95 (d, J = 8.4 Hz, 2H), 3.92-3.87 (m, 4H), 1.59-1.52 (m, 4H), 1.26 (s, 24H), 1.19-1.06 (m, 12H), 0.75-0.72 (m, 6H). MS-LR-MALDI, m/z: $[M + H]^+$ calcd for $C_{42}H_{59}B_2NO_6S$, 727.4; found, 727.2.

10-(2,6-Bis(hexyloxy)phenyl)-3,7-bis(4-hexylthiazol-2-yl)-10*H*-phenothiazine (f). Toluene (8.0 mL), EtOH (2.0 mL) and H_2O (4.0 mL) were added to a flask containing a mixture of **e** (1.98 g, 2.72 mmol), 2-bromo-4-hexylthiazole (1.42 g, 5.72 mmol), $Pd(PPh_3)_4$ (0.25 g, 0.22 mmol) and Na_2CO_3 (0.87 g, 8.17 mmol), and the solution was heated at 120 °C for 18 h. The solution was cooled to room temperature and extracted

with a mixture of CH_2Cl_2 and H_2O. The organic extract was dried over anhydrous $MgSO_4$, filtered, and pumped dry. The crude product was purified by column chromatography on aluminum oxide gel with hexane/EA (10:1 by vol.) as the eluent to give **f** as a yellow oil (0.89 g, 40%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 2.0 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 1H), 7.28 (dd, *J* = 8.4, 2.0 Hz, 2H), 6.72 (s, 2H), 6.67 (d, *J* = 8.8 Hz, 2H), 6.03 (d, *J* = 8.4 Hz, 2H), 3.93 (t, *J* = 6.2 Hz, 4H), 2.74 (t, *J* = 7.6 Hz, 4H), 1.74-1.66 (m, 4H), 1.63-1.56 (m, 4H), 1.37-1.29 (m, 12H), 1.25-1.23 (m, 4H), 1.21-1.05 (m, 8H), 0.87 (t, *J* = 6.8 Hz, 6H), 0.70 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.89, 158.75, 157.82, 143.64, 130.28, 128.39, 125.59, 124.13, 120.41, 117.74, 115.49, 111.63, 105.94, 68.95, 31.90, 31.55, 29.36, 29.27, 29.21, 25.68, 22.82, 22.75, 14.31, 14.13. MS-LR-MALDI, *m*/*z*: $[M + H]^+$ calcd for $C_{48}H_{63}N_3O_2S_3$, 809.4; found, 810.2.

5-(5-(10-(2,6-Bis(hexyloxy)phenyl)-3-(5-(5-formyl-4-hexylthiazol-2-yl)-10*H*-phenothiazine-7-yl)thiazol-2-yl)-3-hexylthiazol-2-carbaldehyde (g). To a 10 mL round flask was added **f** (0.89 g, 1.10 mmol) and THF (5.0 mL) was injected as the solvent under N_2. The solution was cooled to −78 °C and *n*-butyllithium (1.6 M in hexane, 1.51 mL) was injected slowly and stirred for 30 min. *N*-formylmorpholine (0.33 mL) was injected into the mixture and stirred at room temperature for 18 h. The reaction was quenched with an aqueous solution of NH_4Cl and the resulting mixture was extracted with CH_2Cl_2 and H_2O. The organic extract was dried over anhydrous $MgSO_4$, filtered and pumped dry. The produce was purified by column chromatography on aluminum oxide gel using hexane/EA (8:1 by vol.) as the eluent to give **g** as an orange oil (0.26 g, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (s, 2H), 7.57 (d, *J* = 2.0 Hz, 2H), 7.40-7.34 (m, 3H), 6.68 (d, *J* = 8.8 Hz, 2H), 6.06 (d, *J* = 8.8 Hz, 2H), 3.94 (t, *J* = 6.0 Hz, 4H), 3.01 (t, *J* = 7.2 Hz, 4H), 1.85-1.75 (m, 4H), 1.64-1.57 (m, 4H), 1.39-1.29 (m, 12H), 1.22-1.12 (m, 12H), 0.87 (t, *J* = 6.8 Hz, 6H), 0.69 (t, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 181.95, 172.93, 167.73, 157.38, 144.80, 131.87, 130.75, 127.54, 126.84, 124.74, 120.51, 116.80, 115.71, 105.81, 68.88, 31.72, 31.46, 30.51, 30.13, 29.18, 29.12, 25.65, 22.71, 14.21, 14.05. MS-LR-MALDI, *m*/*z*: $[M + H]^+$ calcd for $C_{50}H_{63}N_3O_4S_3$, 865.4; found, 866.2.

(2E,2'E)-3,3'-(5,5'-(10-(2,6-Bis(hexyloxy)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(2-cyanoacrylic acid) (HL5). To a flask containing mixture of 5**d** (100 mg, 0.12 mmol), cyanoacetic acid (59 mg, 0.69 mmol) and piperidine (2 drops) was added acetonitrile (1 mL) and THF (1 mL), and the solution was heated at 80 °C for 18 h. The solution was cooled to room temperature and filtered. The filtrate was pumped dry and the crude product was further purified through silica gel column chromatography using EA/acetic acid (100:1 by vol.) as the eluent to afford **HL5** as a black powder in 35%. ^{1}H NMR (400 MHz, DMSO-d_6): δ

8.25 (s, 2H), 7.54 (s, 2H), 7.48 (t, J = 8.0 Hz, 1H), 7.40 (s, 2H), 7.22 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 6.03 (d, J = 8.8 Hz, 2H), 4.02-3.98 (m, 4H), 2.78-2.75 (m, 4H), 1.60-1.53 (m, 8H), 1.28-1.16 (m, 16H), 1.01-1.05 (m, 8H), 0.86-0.82 (m, 6H), 0.65-0.61 (m, 6H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 164.05, 156.73, 155.92, 149.89, 142.59, 142.34, 131.05, 128.17, 126.82, 125.96, 125.68, 123.35, 119.29, 117.17, 115.99, 115.65, 106.36, 68.29, 30.98, 30.86, 28.78, 28.65, 28.40, 28.25, 25.16, 22.22, 22.05, 13.94, 13.75. MS-HR-MALDI, m/z: $[M + H]^+$ calcd for $C_{58}H_{67}N_3O_6S_3$, 997.4192; found, 997.4218. Anal. calcd for $C_{58}H_{67}N_3O_6S_3$: C 69.78, H 6.76, N 4.21; found: C 69.83, H 6.77, N 4.40.

(2E,2'E)-3,3'-(2,2'-(10-(2,6-Bis(hexyloxy)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(4-hexylthiazole-5,2-diyl))bis(2-cyanoacrylic acid) (HL6). Compound **HL6** was synthesized as a black powder in 47% yield according to the similar procedure as described for **HL5**. ^{1}H NMR (500 MHz, THF-d_8): δ 8.40 (s, 2H), 7.68 (d, J = 1.2 Hz, 2H), 7.51 (dd, J = 7.0, 1.4 Hz, 2H), 7.45 (t, J = 6.8 Hz, 1H), 6.84 (d, J = 6.8 Hz, 2H), 6.15 (d, J = 6.8 Hz, 2H), 4.02 (t, J = 5.0 Hz, 4H), 2.95 (t, J = 6.0 Hz, 4H), 1.86-1.73 (m, 4H), 1.67-1.61 (m, 4H), 1.39-1.25 (m, 16H), 1.19-1.13 (m, 8H), 0.89 (t, J = 5.4 Hz, 6H), 0.73 (t, J = 5.4 Hz, 6H). ^{13}C NMR (125 MHz, THF-d_8): δ 172.03, 169.55, 164.05, 158.28, 145.65, 143.38, 131.65, 128.36, 127.75, 125.65, 125.23, 121.32, 117.59, 116.78, 116.41, 106.60, 101.13, 69.48, 67.99, 32.58, 32.37, 30.83, 30.74, 30.05, 29.83, 26.55, 25.86, 23.55, 23.47, 14.43. MS-HR-MALDI, m/z: $[M + H]^+$ calcd for $C_{56}H_{65}N_5O_6S_3$, 1000.4175; found, 1000.4204. Anal. calcd for $C_{56}H_{65}N_5O_6S_3$: C 67.24, H 6.55, N 7.00; found: C 67.15, H 6.50, N 6.98.

(2E,2'E)-3,3'-(5,5'-(10-(2,6-Bis((2-ethylhexyl)oxy)phenyl)-10*H*-phenothiazine-3,7-diyl)bis(3-hexylthiophene-5,2-diyl))bis(2-cyanoacrylic acid) (**HL7**). Compound **HL7** was synthesized as a black powder in 49% yield according to the similar procedure as described for **HL5**. ^{1}H NMR (400 MHz, THF-d_8): δ 8.37 (s, 2H), 7.43 (t, J = 8.6 Hz, 1H), 7.35-7.34 (m, 4H), 7.17 (dd, J = 9.0, 1.4 Hz, 2H), 6.83 (d, J = 8.8 Hz, 2H), 6.10 (td, J = 8.8, 1.8 Hz, 2H), 3.91-3.90 (m, 4H), 2.82 (t, J = 7.8 Hz, 4H), 1.68-1.64 (m, 4H), 1.58-1.56 (m, 2H), 1.40-1.26 (m, 18H), 1.18-1.07 (m, 10H), 0.89 (t, J = 6.8 Hz, 6H), 0.78-0.71 (m, 12H). ^{13}C NMR (125 MHz, THF-d_8): δ 164.78, 158.59, 156.59, 152.43, 144.22, 143.90, 131.56, 129.90, 128.35, 126.47, 125.59, 124.40, 121.22, 117.67, 116.95, 116.76, 106.39, 97.62, 71.41, 32.70, 32.33, 31.70, 30.11, 30.04, 29.85, 24.90, 24.09, 23.60, 14.59, 14.54, 11.64. MS-HR-MALDI, m/z: $[M + H]^+$ calcd for $C_{62}H_{75}N_3O_6S_3$, 1053.4812; found, 1053.4811. Anal. calcd for $C_{62}H_{75}N_3O_6S_3$: C 70.62, H 7.17, N 3.98; found: C 70.70, H 7.18, N 4.03.

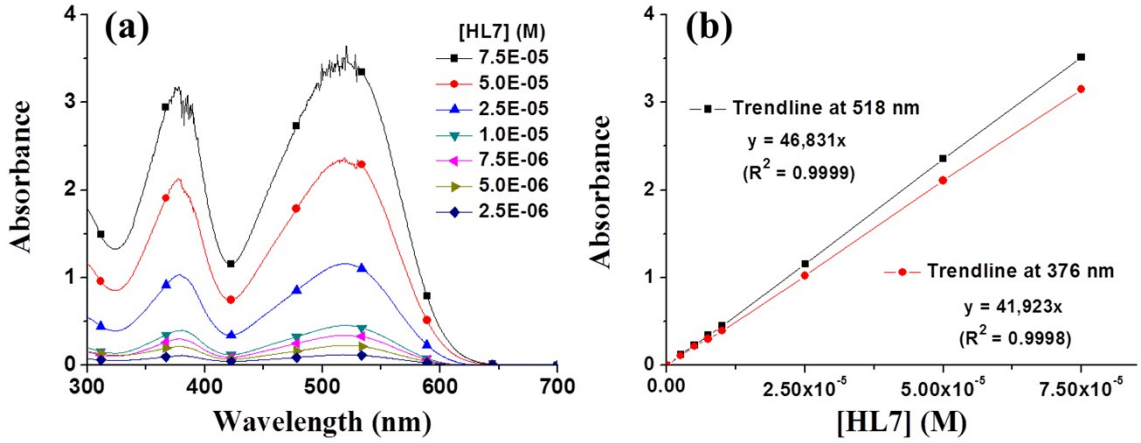


Fig. S1 (a) Normal absorption spectra of HL-7 in THF and (b) their trendline at 376 and 518 nm.

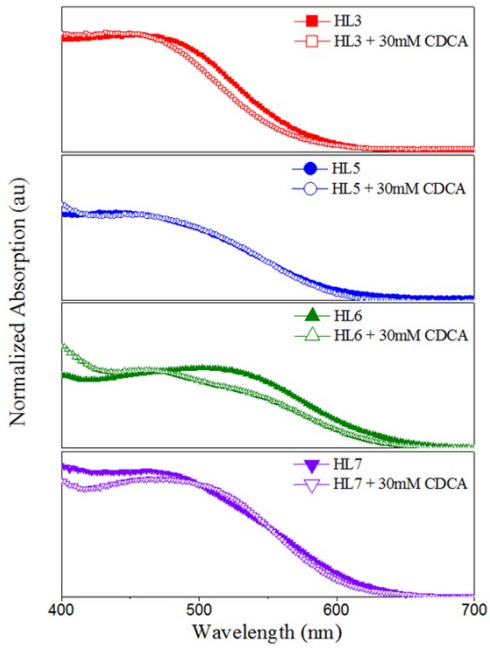


Fig. S2 Absorption spectra of the dyes on TiO_2 films.

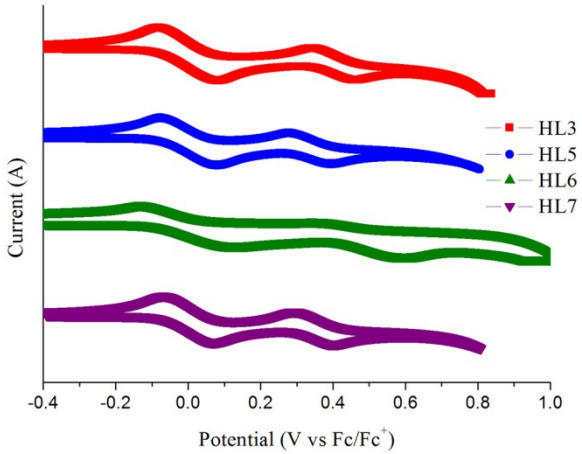


Fig. S3 Cyclic voltammograms of all dye in THF.

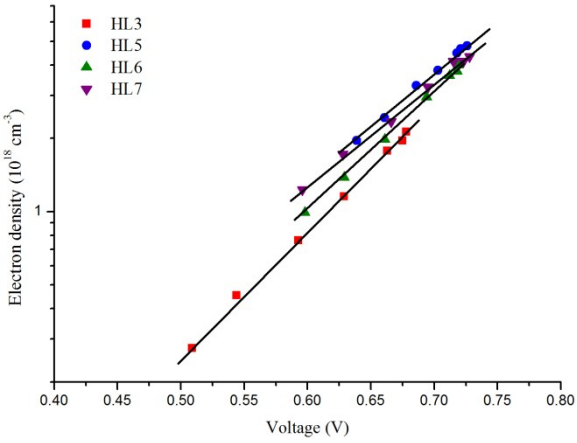


Fig. S4 Electron density vs. photovoltage of DSSCs based on charge extraction measurement.

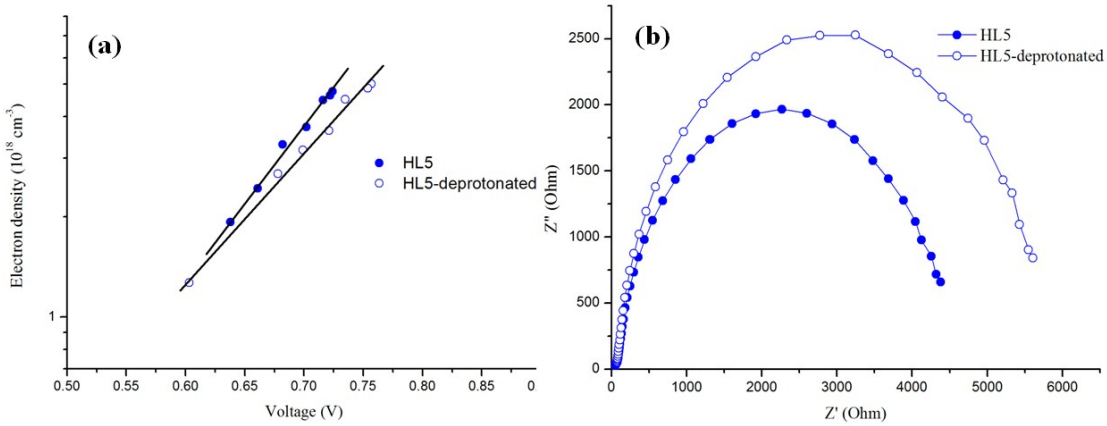


Fig. S5 HL5 with or without Et_3N treatment measured by electrochemical methods for (a) electron density vs. photovoltage and (b) Nyquist plot in the dark.

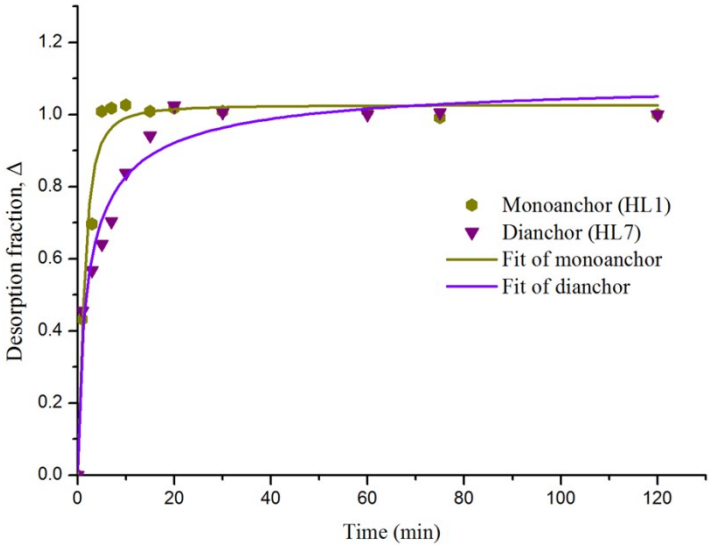


Fig. S6 Experimental time dependence of desorption fraction (Δ) for the dye with monoanchor (**HL1**) and dianchor (**HL7**).

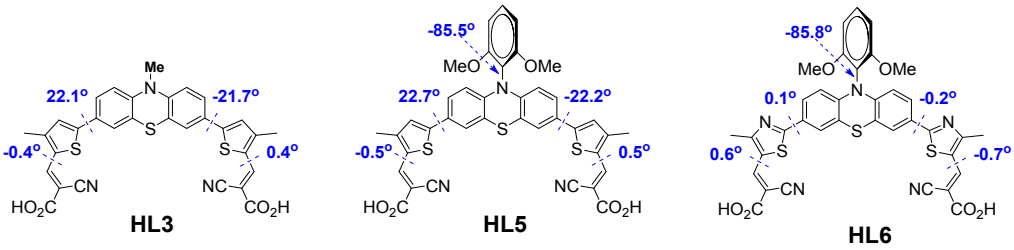


Fig. S7 Schematic division and dihedral angles of the molecules.

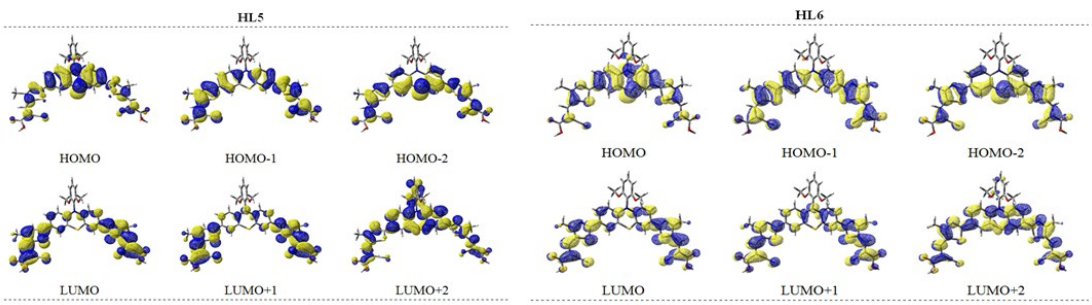


Fig. S8 Frontier orbitals of the dyes.

Table S1. Calculated lower-lying transitions of the dyes.[a]

dye	State	excitation[b]	λ_{cal},eV	f[b]	Δ(Mulliken charge),[d] |e|	$f \times \Delta q$	dye	State	excitation[b]	λ_{cal},eV	f[b]	Δ(Mulliken charge),[d] |e|	$f \times \Delta q$
HL3	S_1	H → L (99%)	2.33	0.59	Ac:-0.17	-0.20							
					T:-0.13								
					Ptz(Me):0.60								
					T':-0.13								
					Ac':-0.17								
	S_2	H → L1 (95%)	2.54	0.14	Ac:-0.20	-0.05							
					T:-0.13								
					Ptz(Me):0.66								
					T':-0.13								
					Ac':-0.19								
	S_3	H1→ L (89%)	3.18	0.35	Ac:-0.09	-0.06							
					T:0.01								
					Ptz(Me):0.14								
					T':0.02								
					Ac':-0.08								
HL5	S_1	H → L (99%)	2.14	0.61	Ac:-0.18	-0.22	**HL6**	S_1	H → L (99%)	2.09	0.65	Ac:-0.16	-0.21
					T:-0.14							Tha:-0.14	
					Ptz(Ph):0.63							Ptz(Ph):0.61	
					T':-0.14							Tha':-0.14	
					Ac':-0.18							Ac':-0.16	
	S_2	H→ L1 (97%)	2.37	0.17	Ac:-0.20	-0.07		S_2	H→ L1 (96%)	2.36	0.17	Ac:-0.19	-0.07
					T:-0.14							Tha:-0.14	
					Ptz(Ph):0.69							Ptz(Ph):0.67	
					T':-0.14							Tha':-0.14	
					Ac':-0.20							Ac':-0.20	
	S_3	H2→ L (95%)	3.10	0.26	Ac:-0.14	-0.07		S_3	H2→ L (95%)	3.04	0.30	Ac:-0.13	-0.08
					T:-0.08							Tha:-0.10	
					Ptz(Ph):0.44							Ptz(Ph):0.44	
					T':-0.09							Tha':-0.09	
					Ac':-0.14							Ac':-0.13	

[a] Results are based on gas-phase TD-DFT calculation. [b] H = HOMO, L = LUMO, H1 = The next highest occupied molecular orbital, or HOMO – 1, H2 = HOMO – 2, L1 = LUMO + 1, L2 = LUMO + 2. In parentheses is the population of a pair of MO excitations. [c] Oscillator strength. [d] The difference of the Mulliken charge between the ground state and excited state.

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