Electronic Supplementary Information

Contents

Experimental Section	Pages S2~S8
Characterization data for the compounds	Pages S9~S18
Absorption and emission data	Pages S18~S21
Electrochemical data and the corresponding energy level data	Pages S21~S22
Frontier molecular orbital profiles of the dyes	Page S22
The photovoltaic parameters of the DSSCs	Page S23
Chemical capacitance, interfacial charge transfer resistance and electron li	fetime Page S24
The stability studies	Pages S25~S26
The photovoltaic parameters for optimization of the cosensitized DSSCs	Page S27
Photovoltaic parameters of the DSSCs using quasi-solid-state electrolyte	Page S28

Experimental Section

General information

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. THF was dried over 4 Å molecular sieves, and distilled under nitrogen from sodium benzophenone prior to use. Tetrabutylammonium hexafluorophosphate (TBAPF₆) was vacuum-dried for 48 h. The transparent FTO conducting glass (fluorine-doped SnO₂, transmission >90% in the visible range, sheet resistance 15Ω /square) and the TiO₂ paste was purchased from Geao Science and Educational Co. Ltd. The FTO conducting glass was washed with a detergent solution, deionized water, ethanol, and acetone successively under ultrasonication for 30 min before use. 3,7-dibromo-10-hexyl-10H-phenothiazine, 4-(hexyloxy) phenylboronic acid, 3,6-bis(4-bromophenyl)-2,5-dihexylpyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione, 5-ethynyl-3-hexylthiophene-2-carbaldehyde and 5-ethynylthiophene-2-carbaldehyde were prepared according to reported procedures.^{S1}

Equipments and apparatus

¹H NMR spectra were collected using a Bruker AM 400 spectrometer. HRMS measurements were performed using a Waters LCT Premier XE spectrometer. UV-Vis absorption spectra were recorded on a Varian Cary 100 spectrophotometer and fluorescence spectra were recorded on a Varian Cray Eclipse fluorescence spectrophotometer. The cyclic voltammograms of the dyes were determined with a Versastat II electrochemical workstation (Princeton Applied Research) using a three-electrode cell with a Pt working electrode, a Pt wire auxiliary electrode, and a saturated calomel (SCE) reference electrode in saturated KCl solution, 0.1 M TBAPF₆ was used as the supporting electrolyte in CH_2Cl_2 . Ferrocene was added to each sample solution at the end of the experiments, and the ferrocenium/ferrocene (Fe/Fe⁺) redox couple was used as an internal potential reference. The scan rate was 100 mV s⁻¹.

Photovoltaic measurements were performed by employing an AM 1.5 solar simulator equipped with a 300 W xenon lamp (model no. 91160, Oriel). The power of the simulated light was calibrated to 100 mW cm⁻² using a Newport Oriel PV reference cell system (model 91150 V). J–V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a model 2400 source meter (Keithley Instruments, Inc. USA). The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640). The electrochemical impedance spectroscopy (EIS) measurements of all the DSSCs were performed using a Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany), with the frequency range of 0.1 Hz–100 kHz and the alternative signal of 10 mV. The ZSimpWin software was used to fit the experimental EIS data of the DSSCs. Photostability of the dyes adsorbed on the nanocrystalline films was evaluated by visible-light (>420 nm) irradiation from a solar simulator operating at AM 1.5 (100 mW cm⁻²) with an ultraviolet cutoff filter.

Synthesis of the dyes



Scheme S1. Synthetic routes for the intermediates and the dyes. Reaction conditions: (i) 4-(hexyloxy)phenyl boronic acid, Pd(PPh₃)₄, THF, K₂CO₃ solution (2.0 M); (ii) THF, n-butyl lithium (2.4 M in hexane), trimethyl borate; (iii) 3,6-bis(4-bromophenyl)-2,5-dihexylpyrrolo [3,4-c]pyrrole-1,4(2H,5H)-dione, Pd(PPh₃)₄, K₂CO₃ solution (2.0 M); (iv) 5-formylthiophen- 2-yl-boronic acid, Pd(PPh₃)₄, THF, K₂CO₃ solution (2.0 M); (v) Pd₂(dba)₃, AsPh₃, THF, Et₃N; (vi) 2-cyanoacetic acid, piperidine, THF.

3-bromo-10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazine(1). 3,7-dibromo-10-hexyl-10Hphenothiazine (300 mg, 0.68 mmol), 4-(hexyloxy)phenylboronic acid (126.5 mg, 0.57 mmol), Pd(PPh₃)₄ (65.9 mg, 0.057 mmol), 30 mL of dry THF, 2 mL aqueous of K₂CO₃ solution (2.0 M) were placed in a Schlenk flask and flushed with nitrogen. The mixture was vigorously stirred and heated to reflux for 12 h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with petroleum ether and dichloromethane as the eluent to give 1 (220 mg, 60%). ¹H NMR (400 MHz, $CDCl_3$, 25 °C, TMS): $\delta = 0.86-0.93$ (m, 6H, hexyl-CH₃), 1.28-1.37 (m, 8H), 1.39-1.49 (m, 4H), 1.75-1.83 (m, 4H), 3.81 (t, J = 7.2 Hz, 2H, NCH₂), 3.98 (t, J = 6.8 Hz, 2H, OCH₂), 6.69 (d, J = 8.4 Hz, 1H, phenyl), 6.87 (d, J = 8.4 Hz, 1H, phenyl), 6.91-6.95 (m, 2H, phenyl), 7.21-7.25 (m, 2H, phenyl), 7.29 (d, J = 2 Hz, 1H, phenyl), 7.32 (dd, J = 2.4 Hz, 8.4 Hz, 1H, phenyl), 7.41-7.45 (m, 2H, phenyl). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 26.02, 26.79, 26.83, 29.54, 31.86, 47.63, 68.15, 114.42, 114.93, 115.74, 116.46, 124.43, 125.40, 125.67, 126.86, 127.53, 128.62, 128.69, 128.84, 129.65, 129.98, 132.17, 133.81, 134.00, 135.54, 143.46, 144.39, 158.74. HRMS (ESI, m/z, $[M + H]^+$). Calcd for $C_{30}H_{37}BrNOS$: 538.1779. Found: 538.1781.

3-(4-bromophenyl)-2,5-dihexyl-6-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)pyrrolo[3,4-c]pyrrole-1,4(2H, 5H)-dione (2).

To a solution of 1 (1.8 g, 3.35 mmol) in dry THF (50 mL) at -78 °C, n-butyl lithium (2.6 mL, 6.03 mmol, 2.4 M in hexane) was added dropwise. The mixture was stirred at -78 °C for 1 h. Then, trimethyl borate (0.8 mL) was added rapidly to the solution and the mixture was stirred for another 2 h. After the resultant mixture was warmed up to room temperature and stirred overnight, the solution was then injected into a mixture of 3,6-bis(4-bromophenyl)-2,5-dihexylpyrrolo[3,4-c] pyrrole-1,4(2H,5H)-dione (2.06 g, 3.35 mmol), Pd(PPh₃)₄ (194 mg, 0.17 mmol) and 5.1 mL aqueous of K_2CO_3 solution (2.0 M) in a Schlenk flask, which was charged with nitrogen. The mixture was vigorously stirred and heated to reflux for 12 h. After cooling to room temperature, the mixture was dissolved in CH_2Cl_2 and washed with brine, dried over anhydrous Na_2SO_4 , evaporated and purified by a silica gel column to afford a dark red solid (830 mg, 25%). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 0.81-0.84$ (m, 6H, hexyl-CH₃), 0.87-0.93 (m, 6H, hexyl-CH₃), 1.21-1.22 (m, 12H), 1.31-1.36 (m, 8H), 1.45-1.48 (m, 4H), 1.53-1.63 (m, 4H), 1.76-1.88 (m, 4H), 3.71-3.79 (m, 4H, NCH₂), 3.87 (s, 2H, NCH₂), 3.98 (t, *J* = 6.4 Hz, 2H, OCH₂), 6.87-6.95 (m, 4H, phenyl), 7.31-7.33 (m, 2H, phenyl), 7.41-7.46 (m, 4H, phenyl), 7.62-7.69 (m, 6H, phenyl), 7.86 (d, J = 8.4 Hz, 2H, phenyl). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 25.73$, 26.36, 26.39, 26.67, 29.25, 29.36, 31.20, 41.79, 42.00, 47.54, 68.04, 109.47, 110.03, 114.73, 115.40, 115.46, 125.48, 125.96, 126.35, 126.50, 127.05, 127.43, 129.25, 130.10, 132.07, 142.52, 146.54, 148.70, 158.52, 162.40, 162.66. HRMS (ESI, m/z, [M + Na]⁺). Calcd for C₆₀H₇₀BrN₃NaO₃S: 1014.4219. Found: 1014.4207.

5-(4-(2,5-dihexyl-4-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)thiophene-2-carbaldehyde (3a).

Compound 2 (500 mg, 0.504 mmol), 5-formylthiophen-2-yl boronic acid (393.4 mg, 2.52 mmol), Pd(PPh₃)₄ (58.2 mg, 0.05 mmol), 50 mL of dry THF, 2 mL aqueous of K₂CO₃ solution (2.0 M) were placed in a Schlenk flask and flushed with nitrogen. The mixture was vigorously stirred and heated to reflux for 12 h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane, washed with brine, dried over anhydrous Na₂SO₄ and evaporated under reduced pressure. The crude product was purified by column chromatography on silica gel with dichloromethane as the eluent to give 3a (310 mg, 60%). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 0.82-0.85$ (m, 6H, hexyl-CH₃), 0.88-0.93 (m, 6H, hexyl-CH₃), 1.23-1.25 (m, 12H), 1.33-1.36 (m, 8H), 1.46-1.50 (m, 4H), 1.62-1.63 (m, 4H), 1.77-1.82 (m, 2H), 1.84-1.88 (m, 2H), 3.80 (t, J = 6.4 Hz, 4H, NCH₂), 3.90 (s, 2H, NCH₂), 3.99 (t, J = 6.4 Hz, 2H, OCH₂), 6.94-6.96 (m, 4H, phenyl), 7.35 (s, 2H, phenyl), 7.41-7.49 (m, 4H, phenyl, 1H, thienyl), 7.68 (d, J = 8.4 Hz, 2H, phenyl), 7.74 (d, J = 4 Hz, 1H, thienyl), 7.80 (d, J = 8.4 Hz, 2H, phenyl), 7.89 (t, J = 8.8 Hz, 4H, phenyl), 9.88 (s, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 22.47, 25.74, 26.40,$ 26.69, 26.79, 29.26, 29.34, 29.70, 31.21, 31.49, 41.85, 41.92, 47.63, 68.08, 109.53, 110.29, 114.79, 115.38, 115.53, 124.32, 124.67, 124.88, 125.37, 125.50, 125.92, 126.30, 126.41, 127.44, 128.84, 129.34, 129.51, 132.16, 133.57, 135.01, 135.43, 137.42, 142.33, 143.05, 143.22, 144.99, 146.66, 148.79, 152.56, 158.55, 162.46, 162.66, 182.84. HRMS (ESI, m/z, [M + H]⁺). Calcd for C₆₅H₇₄N₃O₄S₂: 1024.5121. Found: 1024.5126.

5-((4-(2,5-dihexyl-4-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethynyl)thiophene-2-carbaldehyde

(3b).

Compound 2 (274 mg, 0.28 mmol), 5-ethynylthiophene-2-carbaldehyde (113 mg, 0.83mmol), Pd₂(dba)₃ (127 mg, 0.14 mmol), AsPh₃ (199 mg, 0.55 mmol) were placed in a Schlenk flask, which was flushed with nitrogen and then charged with dry THF (40 mL) and Et₃N (6 mL). The mixture was stirred at 50 °C for 2 h. Then, the solvent was removed under reduced pressure, and the residue was dissolved in CH₂Cl₂ and washed with brine, dried over anhydrous Na₂SO₄, and evaporated. The residue was purified on a silica gel column to afford **3b** (159 mg, 55%). ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 0.82-0.87$ (m, 6H, hexyl-CH₃), 0.88-0.93 (m, 6H, hexyl-CH₃), 1.23-1.26 (m, 12H), 1.33-1.35 (m, 8H), 1.47 (s, 4H), 1.57-1.63 (m, 4H), 1.76-1.86 (m, 4H), 3.78 (q, J = 8.4 Hz, 4H, NCH₂), 3.86 (t, J = 6.8 Hz, 2H, NCH₂), 3.98 (t, J = 6.8 Hz, 2H, OCH₂), 6.87-6.95 (m, 4H, phenyl), 7.33 (d, J = 5.6 Hz, 2H, phenyl, 1H, thienyl), 7.44 (t, J = 8.8 Hz, 4H, phenyl), 7.62-7.67 (m, 4H, phenyl, 1H, thienyl), 7.82-7.87 (m, 4H, phenyl), 9.86 (s, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 22.46, 22.48, 25.74, 26.39, 26.41, 26.69, 26.78, 29.27, 29.38, 31.20, 31.22, 31.49, 41.96, 42.05, 47.67, 68.09, 84.42, 97.21, 109.64, 110.51, 114.79, 115.40, 115.47, 124.25, 124.28, 124.78, 125.36, 125.49, 125.63, 126.01, 126.32, 126.50, 127.43, 128.75, 129.32, 131.88, 132.20, 133.02, 133.70, 135.42, 135.98, 142.65, 143.22, 144.25, 145.07, 146.55, 148.99, 158.54, 162.50, 162.70, 182.38. HRMS (ESI, m/z, [M + H]⁺). Calcd for C₆₇H₇₄N₃O₄S₂: 1048.5121. Found: 1048.5101.

5-((4-(2,5-dihexyl-4-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethynyl)-3-hexylthiophene-2-carbaldehyde (3c).

The synthetic procedure was similar to that of **3b** and the compound was purified by column chromatography on silica gel to give a red solid. Yield: 157 mg, 53%. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): $\delta = 0.82$ -0.84 (m, 6H, hexyl-CH₃), 0.90-0.91 (m, 9H, hexyl-CH₃), 1.23-1.25 (m, 16H), 1.35 (s, 12H), 1.47 (s, 4H), 1.67-1.71 (m, 4H), 1.76-1.87 (m, 4H), 2.78 (t, *J* = 7.6 Hz, 2H, thienyl-CH₂), 3.79 (q, *J* = 7.6 Hz, 4H, NCH₂), 3.88 (t, *J* = 7.2 Hz, 2H, NCH₂), 3.99 (t, *J* = 6.4 Hz, 2H, OCH₂), 6.88-6.95 (m, 4H, phenyl), 7.34 (d, *J* = 6.4 Hz, 2H, phenyl), 7.44 (t, *J* = 7.6 Hz, 4H, phenyl), 7.55 (s, 1H, thienyl), 7.64-7.69 (m, 4H, phenyl), 7.87 (t, *J* = 8.8 Hz, 4H, phenyl), 9.83 (s, 1H, CHO). ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): $\delta = 22.48$, 25.74, 26.41, 26.69, 26.81, 28.90, 29.26, 29.42, 29.54, 29.70, 30.01, 31.22, 31.49, 42.01, 42.09, 47.65, 68.09, 84.28, 99.24, 109.67, 110.50, 114.78, 115.43, 115.50, 124.31, 124.70, 124.84, 125.38, 125.50, 125.67, 126.02, 126.35, 126.56, 127.45, 127.65, 128.58, 128.74, 129.31, 131.79, 132.22, 133.74, 135.44, 136.68, 142.63, 142.70, 143.27, 145.13, 146.62, 148.94, 149.21, 158.53, 162.55, 162.74, 182.52. HRMS (ESI, m/z, [M + H]⁺). Calcd for C₇₃H₈₆N₃O₄S₂: 1132.6060. Found: 1132.6049.

(Z)-2-cyano-3-(5-(4-(2,5-dihexyl-4-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)thiophen-2-yl)acrylic acid (XS1).

Compound **3a** (167 mg, 0.163 mmol), 2-cyanoacetic acid (69.4 mg, 0.816 mmol), and piperidine (0.5 mL) in 20 mL of THF were heated to reflux under a nitrogen atmosphere for 12 h. Then the solvent was removed by rotary evaporation and the residue was purified by column chromatography on silica gel to provide **XS1**. Yield: 151 mg, 85%. ¹H NMR (400 MHz, DMSO- d_6 : CDCl₃ = 10:1, 25 °C, TMS): δ = 0.78 (d, *J* = 3.6 Hz, 6H, hexyl-CH₃), 0.82-0.84 (m, 3H, hexyl-CH₃), 0.88-0.90 (m, 3H, hexyl-CH₃), 1.16 (s, 12H), 1.25 (m, 4H), 1.32-

1.33 (m, 4H), 1.42-1.43 (m, 8H), 1.71-1.75 (m, 4H), 3.71 (s, 4H, NCH₂), 3.82 (s, 2H, NCH₂), 3.96 (t, J = 6.4 Hz, 2H, OCH₂), 6.92-6.94 (m, 4H, phenyl), 7.35-7.38 (m, 2H, phenyl), 7.48 (t, J = 8 Hz, 4H, phenyl), 7.65 (s, 1H, thienyl), 7.70 (d, J = 4.4 Hz, 2H, phenyl, 1H, thienyl), 7.79 (s, 6H, phenyl), 8.12 (s, 1H, alkenyl). HRMS (ESI, m/z, $[M + H]^+$). Calcd for C₆₈H₇₅N₄O₅S₂: 1091.5179. Found: 1091.5148. IR (KBr pellet, cm⁻¹): 3142(br), 2927(m), 2856(m), 2214(w), 1677(m), 1637(w), 1616(s), 1515(w), 1494(w), 1466(s), 1385(s), 1240(s), 1092(s), 995(m), 842(w), 806(m), 746(w), 623(s), 475(m). Anal. Calcd for C₆₈H₇₄N₄O₅S₂: C, 74.83; H, 6.83; N, 5.13. Found: C, 74.48; H, 6.74; N, 4.73.

(E)-2-cyano-3-(5-((4-(2,5-dihexyl-4-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethynyl)thiophen-2-yl)acrylic acid (XS2).

The synthetic procedure was similar to that of **XS1** and the compound was purified by column chromatography on silica gel to give a red solid. Yield: 201 mg, 93%. ¹H NMR (400 MHz, DMSO- d_6 : CDCl₃ = 10 : 1, 25 °C, TMS): δ = 0.79 (s, 6H, hexyl-CH₃), 0.84-0.89 (m, 6H, hexyl-CH₃), 1.13-1.15 (m, 12H), 1.26-1.27 (m, 4H), 1.32-1.33 (m, 4H), 1.41 (s, 8H), 1.72 (t, *J* = 6.8 Hz, 4H), 3.73 (s, 4H, NCH₂), 3.87 (s, 2H, NCH₂), 3.97 (t, *J* = 6.4 Hz, 2H, OCH₂), 6.95 (d, *J* = 8.4 Hz, 2H, phenyl), 7.01 (t, *J* = 8.8 Hz, 2H, phenyl), 7.37-7.41 (m, 2H, phenyl), 7.49-7.53 (m, 4H, phenyl, 1H, thienyl), 7.63 (s, 1H, thienyl), 7.69 (d, *J* = 7.6 Hz, 2H, phenyl), 7.78 (d, *J* = 8 Hz, 2H, phenyl), 7.84 (s, 4H, phenyl), 8.09 (s, 1H, alkenyl). HRMS (ESI, m/z, [M + H]⁺). Calcd for C₇₀H₇₅N₄O₅S₂: 1115.5179. Found: 1115.5189. IR (KBr pellet, cm⁻¹): 3417(br), 2953(w), 2926(m), 2855(m), 2217(w), 1668(m), 1640(w), 1607(w), 1584(s), 1465(s), 1393(m), 1362(w), 1241(m), 1162(w), 1091(s), 1013(w), 937(w), 841(m), 808(m), 764(w), 745(w), 725(w), 623(m), 472(m). Anal. Calcd for C₇₀H₇₄N₄O₅S₂: C, 75.37; H, 6.69; N, 5.02. Found: C, 75.08; H, 6.43; N, 4.69.

(E)-2-cyano-3-(5-((4-(2,5-dihexyl-4-(4-(10-hexyl-7-(4-(hexyloxy)phenyl)-10H-phenothiazin-3-yl)phenyl)-3,6-dioxo-2,3,5,6-tetrahydropyrrolo[3,4-c]pyrrol-1-yl)phenyl)ethynyl)-3-hexylthiophen-2-yl)acrylic acid (XS3).

The synthetic procedure was similar to that of **XS1** and the compound was purified by column chromatography on silica gel to give a red solid. Yield: 148 mg, 90%. ¹H NMR (400 MHz, DMSO- d_6 : CDCl₃ = 10 : 1, 25 °C, TMS): δ = 0.77-0.79 (m, 6H, hexyl-CH₃), 0.85-0.89 (m, 9H, hexyl-CH₃), 1.16 (s, 12H), 1.28-1.32 (m, 14H), 1.43(s, 8H), 1.63-1.65 (m, 2H), 1.69-1.74 (m, 4H), 2.75 (s, 2H, thienyl-CH₂), 3.73 (s, 4H, NCH₂), 3.86 (s, 2H, NCH₂), 3.96 (t, *J* = 6.4 Hz, 2H, OCH₂), 6.92-6.99 (m, 4H, phenyl), 7.34 (s, 1H, thienyl), 7.39 (d, *J* = 8 Hz, 1H, phenyl), 7.49-7.56 (m, 4H, phenyl), 7.69 (s, 2H, phenyl), 7.77 (s, 2H, phenyl), 7.85 (s, 5H, phenyl), 8.40 (s, 1H, alkenyl). HRMS (ESI, m/z, [M + H]⁺). Calcd for C₇₆H₈₇N₄O₅S₂: 1199.6118. Found: 1199.6125. IR (KBr pellet, cm⁻¹): 3417(br), 2953(w), 2927(m), 2855(m), 2214(m), 1674(s), 1607(s), 1515(s), 1494(m), 1465(s), 1385(s), 1241(s), 1178(w), 1091(s), 1013(m), 938(w), 842(m), 807(s), 741(m), 667(w), 588(w), 530(w), 475(w). Anal. Calcd for C₇₆H₈₆N₄O₅S₂: C, 76.09; H, 7.23; N, 4.67. Found: C, 75.71; H, 7.28; N, 4.50.

Theoretical Approach

We employed density functional theory (DFT) calculations to optimize the ground state geometries of the sensitizers using the hybrid B3LYP functional^{S2} and the 6-31G(d,p) basis set.^{S3} At the optimized geometries, frontier molecular orbitals were computed using the range-separated

CAM-B3LYP functional^{S4} and Ahlrichs's triple-ζ basis set def-TZVP. ^{S5} Time-dependent DFT calculations were also carried out to gain insight into low-lying excitations of the sensitizer dyes, with solvent effects of tetrahydrofuran taken into account by the polarizable solvent model (PCM).^{S6} All calculations were carried out using the Gaussian09 program package.^{S7}

Photovoltaic Device Fabrication

The procedure for preparation of TiO_2 electrodes and fabrication of the sealed cells for photovoltaic measurements were adapted from that reported by Grätzel and co-workers.^{S8} A screen-printed double layer of TiO_2 particles was used as the photoelectrode. A 12-µm thick film of 13-nm-sized TiO₂ particles was first printed on the FTO conducting glass, which was kept in a clean box for 5 minutes, and then dried at 125 °C over 6 min, and further coated by a 5-µm thick second layer of 400-nm light-scattering anatase particles. Finally, the electrodes coated with the TiO₂ pastes were gradually sintered in a muffle furnace at 275 °C for 5 min, at 325 °C for 5 min, at 375 °C for 5 min, at 450 °C for 15 min and at 500 °C for 15 min, respectively. The size of the TiO₂ film was 0.25 cm². These films were immersed into a 40 mM aqueous TiCl₄ solution at 70 °C for 30 min, washed with water and ethanol, and then heated again at 450 °C for 30 min. The films were then immersed into a 0.3 mM solution of XS1-XS3 in a mixture of chloroform and ethanol (volume ratio of 3:2) or a 0.2 mM solution of the porphyrin dyes in a mixture of toluene and ethanol (volume ratio of 1 : 4) at 25 °C for 10 h at room temperature. For co-sensitization,⁸⁹ these porphyrin-sensitized films were washed with ethanol, dried in air, and immersed in a solution containing the cosensitizer (0.3 mM) in a mixture of chloroform and ethanol (volume ratio of 3 : 2) and kept at 25 °C for 1 h. For comparison, the films were immersed into a 0.3 mM solution of the reference dye N719 in ethanol at 25 °C for 10 h at room temperature. The counter electrode was prepared by sputtering with three drops of 0.02 M H₂PtCl₆ in 2-propanol followed by annealing treatment at 400 °C for 15 min. A hole (diameter of 0.8-mm) was drilled on the counter electrode. The perforated sheet was cleaned by ultrasound in an ethanol bath for 10 min. For the assembly of DSSCs, the dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 µm thickness made of ionomer Surlyn 1702 (DuPont). A drop of electrolyte solution was put on the hole in the back of the counter electrode, and introduced into the cell via vacuum backfilling. Finally, the hole was sealed using a UV-melt gum and a cover glass. The solar cells were measured with a black mask of 0.25 cm². The electrolyte solution LP was used for XS1-XS3, L130 was used for porphyrin dyes and the cosensitized system. L131 was used for N719. LP consists of 0.1 M LiI, 0.05 M I_2 , 0.6 M 1,2-Dimethyl-3-propylimidazolium bis(trifluoro- methylsulfonyl)imide (DPMII), and 0.5 M 4-tert-butylpyridine (TBP) in acetonitrile. L130 consists of 0.1 M LiI, 0.05 M I₂, 0.6 M 1-methyl-3-propyl-imidazolium iodide (PMII), and 0.5 M 4-tert-butylpyridine (TBP) in a mixture of acetonitrile and valeronitrile (volume ratio of 85:15). L131 consists of 0.1 M LiI, 0.05 M I₂, 0.6 M 1,2-dimethyl-3-propyl-imidazolium iodide (DMPII), and 0.5 M 4-tert-butylpyridine (TBP) in a mixture of acetonitrile and valeronitrile (volume ratio of 85:15).

For investigating the cosensitization approach, the conditions were optimized as following. Initially, the TiO_2 electrode was immersed in a solution of the porphyrin dye and the cosensitizer (molar ratio: 2/1), and the results turned out to be unsatisfactory. Then we continued to check the stepwise approach for cosensitization and optimized the immersion time. The corresponding data are listed in Table S3.

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Characterization data for the compounds





Fig. S1 The ¹H NMR spectrum of 1 in CDCl₃.





Fig. S2 The 13 C NMR spectrum of 1 in CDCl₃.



Fig. S3 HRMS spectrum of 1.



Fig. S4 The ¹H NMR spectrum of 2 in CDCl₃.



Fig. S5 The ¹³C NMR spectrum of 2 in CDCl₃.



Fig. S6 HRMS spectrum of 2.



Fig. S7 The ¹H NMR spectrum of **3a** in CDCl₃.



Fig. S8 The ¹³C NMR spectrum of **3a** in CDCl₃.



Fig. S9 HRMS spectrum of 3a.



Fig. S10 The ¹H NMR spectrum of **3b** in CDCl₃.



Fig. S11 The ¹³C NMR spectrum of **3b** in CDCl₃.



Fig. S12 HRMS spectrum of 3b.

-9 833 -9 833 -9 833 -9 835 -9 837 -9 847 -9



Fig. S13 The ¹H NMR spectrum of 3c in CDCl₃.



Fig. S14 The ¹³C NMR spectrum of **3c** in CDCl₃.



Fig. S15 HRMS spectrum of 3c.



Fig. S16 The ¹H NMR spectrum of **XS1** in $CDCl_3$: DMSO- d_6 (1 : 4).



Fig. S17 HRMS spectrum of XS1.



Fig. S18 The ¹H NMR spectrum of **XS2** in CDCl₃ : DMSO- d_6 (1 : 4).



Fig. S19 HRMS spectrum of XS2.





Fig. S20 The ¹H NMR spectrum of **XS3** in $CDCl_3$: DMSO- d_6 (1 : 4).



Fig. S21 HRMS spectrum of XS3.

Table S1. Absorption and emission data for the dyes in THF.

Dyes	Absorption $\lambda_{max}/nm (\epsilon/10^3 \text{ M}^{-1} \text{ cm}^{-1})^a$	Emission λ_{max}/nm^a
XS1	389 (34.5), 522 (33.2)	639
XS2	391 (55.4), 519 (45.6)	608
XS3	409 (46.8), 516 (46.5)	602

^{*a*} The absorption and emission data were measured in THF. Excitation wavelengths/nm: 522 nm (**XS1**), 519 nm (**XS2**), 516 nm (**XS3**).



Fig. S22 Simulated absorption spectra of the cosensitizers.

Table S2. Excitation energies, wavelengths, oscillator strengths, and molecular orbital (MO) compositions of the low-lying excited states of the cosensitizers, computed from TD-DFT calculations.

Compound	Stat	$\lambda_{ m abs}$	f	MO composition
	e			
XS1	\mathbf{S}_1	2.46 eV, 502	1.6212	$\text{H-1} \rightarrow \text{L+0} \text{ (47\%)}$
		nm		$\text{H-1} \rightarrow \text{L+1} \text{ (10\%)}$
				$\text{H-0} \rightarrow \text{L+0} \ (27\%)$
	S_2	3.19 eV, 388	0.3905	$\text{H-3} \rightarrow \text{L+0} \text{ (39\%)}$
		nm		H-1 \rightarrow L+1 (18%)
				$\text{H-0} \rightarrow \text{L+1} \text{ (16\%)}$
	S_3	3.38 eV, 367	0.4631	$\text{H-1} \rightarrow \text{L+0} \text{ (18\%)}$
		nm		$\text{H-1} \rightarrow \text{L+1} \text{ (15\%)}$
				$\text{H-0} \rightarrow \text{L+0} \text{ (35\%)}$
	\mathbf{S}_4	3.50 eV, 354	0.0027	$\text{H-6} \rightarrow \text{L+0} \text{ (49\%)}$
		nm		$\text{H-6} \rightarrow \text{L+1} (37\%)$
	S_5	3.71 eV, 334	0.3761	$\text{H-3} \rightarrow \text{L+0} \text{ (24\%)}$
		nm		H-1 \rightarrow L+1 (13%)
				$\text{H-0} \rightarrow \text{L+0} \text{ (16\%)}$
				$\text{H-0} \rightarrow \text{L+1} \text{ (19\%)}$
XS2	\mathbf{S}_1	2.44 eV, 507	1.8893	$\text{H-1} \rightarrow \text{L+0} \text{ (41\%)}$
		nm		$\text{H-1} \rightarrow \text{L+1} \text{ (14\%)}$
				$\text{H-0} \rightarrow \text{L+0} \ (24\%)$
				$\text{H-0} \rightarrow \text{L+1} (11\%)$
	S_2	3.05 eV, 407	f=0.4589	$\text{H-3} \rightarrow \text{L+0} \text{ (50\%)}$
		nm		$\text{H-1} \rightarrow \text{L+1} (16\%)$
				$\text{H-0} \rightarrow \text{L+1} \text{ (12\%)}$

	S_3	3.36 eV, 369	0.3492	H-1 \rightarrow L+0 (17%)
		nm		$H-1 \rightarrow L+1 (15\%)$
				$\text{H-0} \rightarrow \text{L+0} \text{ (32\%)}$
				$\text{H-0} \rightarrow \text{L+1} \text{ (10\%)}$
	S_4	3.49 eV, 354	0.0039	$\text{H-6} \rightarrow \text{L+0} \text{ (39\%)}$
		nm		$\text{H-6} \rightarrow \text{L+1} \text{ (47\%)}$
	S_5	3.64 eV, 340	0.2678	$\text{H-3} \rightarrow \text{L+0} \text{ (21\%)}$
		nm		$\text{H-1} \rightarrow \text{L+1} (11\%)$
				$\text{H-0} \rightarrow \text{L+0} \text{ (21\%)}$
				$\text{H-0} \rightarrow \text{L+1} \ (20\%)$
XS3	\mathbf{S}_1	2.43 eV, 509	1.9346	$\text{H-1} \rightarrow \text{L+0} \text{ (42\%)}$
		nm		$\text{H-1} \rightarrow \text{L+1} (12\%)$
				$\text{H-0} \rightarrow \text{L+0} \ (24\%)$
				$\text{H-0} \rightarrow \text{L+1} (10\%)$
	S_2	3.00 eV, 413	0.4024	$\text{H-3} \rightarrow \text{L+0} (41\%)$
		nm		$H-2 \rightarrow L+0 (14\%)$
				$H-1 \rightarrow L+1 (17\%)$
				$\text{H-0} \rightarrow \text{L+1} (12\%)$
	S_3	3.36 eV, 369	0.3325	$H-1 \rightarrow L+0 (18\%)$
		nm		$H-1 \rightarrow L+1 (14\%)$
				$\text{H-0} \rightarrow \text{L+0} (32\%)$
				$\text{H-0} \rightarrow \text{L+1} (11\%)$
	S_4	3.49 eV, 354	0.0044	$\text{H-6} \rightarrow \text{L+0} (39\%)$
		nm		$\text{H-6} \rightarrow \text{L+1} \text{ (46\%)}$
	S_5	3.63 eV, 341	0.2095	$H-3 \rightarrow L+0 (17\%)$
		nm		$H-1 \rightarrow L+1 (13\%)$
				$\text{H-0} \rightarrow \text{L+0} \text{ (21\%)}$
				$H-0 \rightarrow L+1 (20\%)$

 a H = HOMO, L = LUMO



Fig. S23 Normalized UV-visible spectra of the dyes in THF and on the TiO_2 films (5 μ m).



Fig. S24 Cyclic voltammograms of XS1–XS3 in CH₂Cl₂ solution.



Fig. S25 Schematic energy-level diagram of XS1-XS3 and XW3, XW4

Dyes	HOMO /V ^a	E_{0-0} / eV^b	LUMO/V ^c
XS1	0.63	2.19	-1.56
XS2	0.63	2.14	-1.51
XS3	0.66	2.18	-1.52
XW3	0.82	1.86	-1.04
XW4	0.83	1.86	-1.03

Table S3. Electrochemical data and the corresponding energy level data of the dyes.

^{*a*} HOMO levels were measured in CH_2Cl_2 with 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAPF₆) as electrolyte (working electrode: Pt; reference electrode: SCE; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an external reference. Counter electrode: Pt); ^{*b*} E₀₋₀ was estimated from the intersection wavelengths of the normalized UV-visible absorption and the fluorescence spectra; ^{*c*} The LUMO was calculated using the equation LUMO = HOMO - E₀₋₀.



Fig. S26 Frontier molecular orbital profiles of XS1–XS3 calculated by DFT.



Fig. S27 LHE as a function of wavelength for XS1–XS3 adsorbed on the surface of a 5- μ m-thick nanocrystalline TiO₂ film.



Fig. S28 APCE as a function of wavelength for XS1–XS3 adsorbed at the surface of a 5- μ m-thick nanocrystalline TiO₂ film in contact with iodide/triiodide–based electrolyte.



Fig. S29 (a) *J–V* characteristics of the cosensitized DSSCs and (b) IPCE action spectra for the cosensitized DSSCs.



Fig. S30 Chemical capacitance C_{μ} (a), interfacial charge transfer resistance R_{CT} (b), and electron lifetime τ (c) of the cells based on **XS1**, **XS2** and **XS3** as a function of bias voltage.



Fig. S31 Chemical capacitance C_{μ} (a), interfacial charge transfer resistance R_{CT} (b), and electron lifetime τ (c) of the cosensitized cells as a function of bias voltage.



Fig. S32 Absorption spectra of XS1, XS2 and XS3 adsorbed onto the TiO_2 films after irradiation for 0, 5, 15 and 30 min.



Fig. S33 Variation of photovoltaic parameters with aging time under visible-light soaking for DSSC devices based on **XS1–XS3**.



Fig. S34 Variation of photovoltaic parameters with aging time under visible-light soaking for DSSC devices based on **XS3/XW3** and **XS3/XW4**.

		u			
Dyes	Dye-loading	$J_{\rm sc}/{ m mA~cm^{-2}}$	V _{oc} /mV	FF	PCE/%
$XS1 + XW3^a$	10 h in XS1/XW3	18.78	681	0.70	8.93
$XS2 + XW3^{a}$	10 h in XS2/XW3	18.34	697	0.70	8.94
$XS3 + XW3^a$	10 h in XS3/XW3	18.83	701	0.70	9.31
$XS1 + XW4^a$	10 h in XS1/XW4	19.27	697	0.67	9.06
$XS2 + XW4^{a}$	10 h in XS2/XW4	19.15	699	0.69	9.19
$XS3 + XW4^a$	10 h in XS3/XW4	19.23	712	0.70	9.53
	10 h in XW3 + 0.5 h in XS1	18.84	671	0.67	8.53
XS1 + XW3	10 h in XW3 + 1 h in XS1	19.26	679	0.70	9.19
	10 h in XW3 + 2 h in XS1	18.48	696	0.68	8.76
XS2 + XW3	10 h in XW3 + 0.5 h in XS2	18.24	685	0.67	8.36
	10 h in XW3 + 1 h in XS2	19.10	688	0.69	9.04
	10 h in XW3 + 2 h in XS2	19.07	694	0.66	8.77
XS3 + XW3	10 h in XW3 + 0.5 h in XS3	19.63	692	0.66	9.01
	10 h in XW3 + 1 h in XS3	19.89	720	0.73	10.45
	10 h in XW3 + 2 h in XS3	19.31	723	0.71	9.91
	10 h in XW4 + 0.5 h in XS1	18.29	683	0.69	8.57
XS1 + XW4	10 h in XW4 + 1 h in XS1	19.62	700	0.70	9.58
	10 h in XW4 + 2 h in XS1	18.53	708	0.69	9.10
X82 + XW4	10 h in XW4 + 0.5 h in XS2	18.40	687	0.68	8.58
	10 h in XW4 + 1 h in XS2	19.85	696	0.68	9.43
	10 h in XW4 + 2 h in XS2	18.96	704	0.68	9.09
	10 h in XW4 + 0.5 h in XS3	19.17	717	0.70	9.62
XS3 + XW4	10 h in XW4 + 1 h in XS3	19.96	728	0.74	10.75
	10 h in XW4 + 2 h in XS3	19.03	731	0.71	9.88

Table S4. Photovoltaic parameters of the cosensitized DSSCs *vs.* immersion time in the solution of **XS** measured under simulated AM 1.5G illumination (power 100 mW cm⁻²).

^{*a*} The cocktail solutions contain the **XS** and **XW** dyes in a molar ratio of 1/2.

Table S5. Photovoltaic parameters of the DSSCs using the quasi-solid-state electrolyte measured under AM 1.5G illumination (power 100 mW cm⁻²).

Dye	$J_{\rm sc}/{\rm mA~cm^{-2}}$	$V_{\rm oc}/{ m mV}$	FF	η/%
XS3/XW3 ^a	18.85	704	0.60	8.02
XS3/XW4 ^a	19.88	700	0.58	8.12

^a The quasi-solid-state electrolyte was obtained from HeptaChroma (DMPII/DMII/BMII/PMII).



Fig. S35 (a) *J–V* characteristics of the cosensitized DSSCs based on **XS3/XW3** and **XS3/XW4** using the quasi-solid-state electrolyte and (b) IPCE action spectra for the cosensitized DSSCs.