Co-sensitization of 3D Bulky Phenothiazine-cored Photosensitizer with Planar Squaraine Dye for Efficient Dye-Sensitized Solar Cells

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Scheme S1. Synthetic routes for TP1–TP4. (a) KOH, RBr, DMSO, rt; (b) Cu, K₂CO₃, 18-crown-6, RBr, o-dichlorobenzene, reflux; (c) DMF, POCI₃, CICH₂CH₂Cl, reflux; (d) NBS, THF, 0°C; (e) Pd(PPh₃)₄, 4-(diphenylamino)phenyl boronic acid, 2N K₂CO₃, THF, reflux; (f) cyanoacetic acid, CH₃COOH, CH₃COONH₄, 120°C.

Synthetic procedure

10-Hexyl-10H-phenothiazine (1a)

Phenothiazine (5.0g, 25.1mmol) and 1-bromohexane (8.7g, 26mmol) were dissolved in 50mL DMSO and stirred for 30min at room temperature. Potassium hydroxide (2.8g, 50mmol) was slowly added and stirred for overnight at room temperature. The reaction mixture was poured into water and extracted with chloroform. The organic layer was separated and dried with anhydrous magnesium sulfate. The product was purified using column chromatography with hexane as the solvent. The product was obtained as light yellow oil. Yield: 6.0 g (85%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.118–7.148 (m, 4H), 6.828–6.855 (m, 4H), 3.340 (t, J = 6.9 Hz,
2H), 1.741–1.869 (m, 2H), 1.255–1.426 (m, 6H), 0.867 (t, J = 5.1 Hz, 3H). HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{18}H_{21}NS) 283.1445; found, 283.1456.

**General procedures for the preparation of compounds 1b-1d.**

A mixture of 10H-phenothiazine (2.0 g, 10 mmol), 1-(hexyloxy)-4-iodobenzene (or 9-hexyl-3-iodo-9H-carbazole or 9,9-dihexyl-2-iodo-9H-fluorene) (11 mmol), K_{2}CO_{3} (1.7 g, 12.5 mmol), copper powder (0.4 g, 6.2 mmol) and 18-crown-6 (0.08 g, 0.3 mmol) in o-dichlorobenzene (20 mL) was heated to reflux overnight under a N₂ atmosphere. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 4:1 mixture of hexane and CH_{2}Cl_{2} as eluent to afford the products as white solid.

**10-(4-(Hexyloxy)phenyl)-10H-phenothiazine (1b)** Yield: 2.43g, (65%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.30 (t, J = 2.8 Hz, 1H), 7.28 (t, J = 2.8 Hz, 1H), 7.10 (t, J = 2.8 Hz, 1H), 7.08 (t, J = 2.8 Hz, 1H), 6.99 (d, J = 1.6 Hz, 1H), 6.97 (d, J = 1.6 Hz, 1H), 6.76-6.85 (m, 4H), 4.03 (t, J = 7.2 Hz, 2H), 1.82–1.86 (m, 2H), 1.40–1.53 (m, 2H), 1.36–1.39 (m, 4H), 0.86 (t, J = 7.2 Hz, 3H). ¹³C NMR (400 MHz, CDCl₃): δ (ppm) 158.87, 146.43, 140.55, 139.01, 132.66, 131.44, 130.09, 129.08, 128.98, 127.10, 126.24, 126.00, 125.33, 124.55, 122.89, 121.84, 119.09, 114.66, 119.62, 116.37, 115.65, 68.34, 31.62, 29.27, 25.79, 22.64, 14.07. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{24}H_{25}NOS) 375.1717; found, 375.1720.

**10-(9-Hexyl-9H-carbazol-2-yl)-10H-phenothiazine (1c)**

Yield: 2.77g, (62%). ¹H NMR (400 MHz, CDCl₃): δ = 8.25 (s, 1H), 8.21 (d, J = 8.0 Hz, 2H), 7.88 (t, J = 8.0 Hz, 2H), 7.65 (d, J = 8.0 Hz, 2H), 7.45–7.50 (m, 2H), 7.17 (t, J = 8.0 Hz, 2H), 6.77–6.85 (m, 4H), 4.44 (t, J = 7.2 Hz, 2H), 1.74–1.86 (m, 2H), 1.24–1.25 (m, 6H), 0.8 (t, J = 7.2 Hz, 3H) ppm. ¹³C NMR (400 MHz, CDCl₃): δ = 146.43, 140.55, 139.01, 132.66, 131.44, 130.09, 129.08, 128.98, 127.10, 126.24, 126.00, 125.33, 124.55, 122.89, 121.84, 119.09, 114.66,
111.40, 43.34, 31.95, 28.50, 26.14, 22.09, 13.87 ppm. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\textsubscript{30}H\textsubscript{28}N\textsubscript{2}S) 448.2067; found, 448.2069.

10-(9,9-Dihexyl-9\textsubscript{H}-fluoren-2-yl)-10\textsubscript{H}-phenothiazine (1d)

Yield: 3.77g, (71%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 8.12\) (s, 1H), 7.90-7.94 (m, 1H), 7.67 (d, \( J = 8.0\) Hz, 2H), 7.18-7.22 (m, 4H), 7.05 (d, \( J = 8.0\) Hz, 2H), 6.86-6.97 (m, 4H), 6.76 (s, 1H), 3.45 (t, \( J = 8.8\) Hz, 4H), 1.45–1.47 (m, 4H), 1.28–1.37 (m, 12H), 0.88 (t, \( J = 8.8\) Hz, 6H) ppm. \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \( \delta = 154.76, 150.35, 142.77, 136.77, 135.89, 133.45, 131.96, 130.51, 127.65, 127.59, 125.27, 124.73, 123.90, 123.23, 115.92, 115.86, 114.95, 93.5, 65.78, 48.16, 31.39, 26.71, 26.52, 22.60, 14.00\) ppm. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\textsubscript{37}H\textsubscript{41}NS) 531.3087; found, 531.3090.

General procedures for the preparation of 2a-2d.

1a-1d (10mmol) and dry DMF (0.73g, 10mmol) was dissolved in 1,2-dichloroethane (20mL), then phosphorous oxychloride (1.54g, 10mmol) was added slowly at 0 °C in an ice water bath. The mixture was heated to reflux for overnight was and quenched with water and extracted three times with chloroform. The combined organic fraction was washed with brine and dried over MgSO\textsubscript{4}. The solvent was removed under reduced pressure and the residue was purified by column chromatography using silica gel and n-hexane/ethylacetate (8/2; v/v) as the eluent to give yellow solids, respectively.

10-Hexyl-10\textsubscript{H}-phenothiazine-3-carbaldehyde (2a)

Yield: 1.71 g (55%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \( \delta \) (ppm) 9.78 (s, 1H), 7.63 (d, \( J = 8.0\) Hz, 1H), 7.56 (s, 1H), 7.11 (t, \( J = 8.0\) Hz, 1H), 7.10 (d, \( J = 8.0\) Hz, 1H), 6.95 (d, \( J = 8.0\) Hz, 1H), 6.86 (t, \( J = 8.0\) Hz, 1H), 3.87 (t, \( J = 6.4\) Hz, 2H), 1.27–1.32 (m, 6H), 0.85 (t, \( J = 6.4\) Hz, 3H). HRMS (MALDI-TOF, m/z): [M+] calcd for (C\textsubscript{19}H\textsubscript{21}NOS) 311.1355; found, 311.1366.
10-(4-(Hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (2b)
Yield: 1.82 g, (70%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.80 (s, 1H), 7.33 (t, J= 8.0 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.25 (t, J = 8.0 Hz, 1H), 7.13 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.97 (d, J = 8.0 Hz, 2H), 6.67-6.78 (m, 4H), 4.13 (t, J = 7.2 Hz, 2H), 1.83-1.86 (m, 2H), 1.42-1.56 (m, 2H), 1.34–1.38 (m, 4H), 0.88 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 188.98, 162.87, 145.75, 134.21, 129.38, 127.81, 126.57, 122.27, 119.68, 116.77, 115.69, 68.64, 30.45, 29.28, 25.77, 22.66, 14.03. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{25}$H$_{25}$NO$_2$S) 403.1677; found, 403.1686.

10-(9-Hexyl-9H-carbazol-2-yl)-10H-phenothiazine-3-carbaldehyde (2c)
Yield: 1.67 g, (56%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.85 (s, 1H), 8.17 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.65 (s, 1H), 7.45-7.48 (m, 2H), 7.29-7.31 (m, 2H), 7.16 (d, J = 8.0 Hz, 1H), 6.77-6.85 (m, 4H), 4.47 (t, J = 7.2 Hz, 2H), 1.79-1.85 (m, 2H), 1.26–1.28 (m, 6H), 0.82 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 187.89, 144.41, 140.53, 139.21, 130.96, 127.98, 127.14, 126.38, 126.30, 122.54, 121.82, 120.88, 119.03, 118.40, 115.68, 111.40, 19.55, 42.38, 30.94, 28.55, 26.16, 22.03, 13.83. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{31}$H$_{28}$N$_2$OS) 476.1984; found, 476.1986.

10-(9,9-Dihexyl-9H-fluoren-2-yl)-10H-phenothiazine-3-carbaldehyde (2d)
Yield: 1.83 g, (67%). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 9.87 (s, 1H), 7.87 (d, J = 6.4 Hz, 1H), 7.55 (d, J = 6.4 Hz, 2H), 7.47 (s, 1H), 7.39-7.43 (m, 2H), 7.32-7.38 (m, 2H), 7.28 (t, J = 6.4 Hz, 2H), 6.83-6.90 (m, 2H), 6.27-6.29 (m, 2H), 4.35 (t, J = 7.6 Hz, 4H), 1.94-1.99 (m, 4H), 1.37-1.41 (m, 4H), 1.32-1.35 (m, 8H) 0.87-0.89 (t, J = 5.2 Hz, 6H). $^{13}$C NMR (400 MHz, CDCl$_3$): δ (ppm) 188.04, 154.39, 148.65, 143.47, 141.23, 139.97, 132.18, 131.31, 129.86, 128.89, 127.15, 126.78, 125.13, 124.56, 123.86, 122.29, 121.43, 120.11, 119.58, 118.89, 117.93, 115.96, 110.96,
NBS (411 mg, 2.31 mmol) was added in one portion to the solution of 2a-2d (2.0 mmol) in THF (50 mL) at 0 °C. The mixture was allowed to warm to room temperature and continued the stirring for 1.5 h. Then the reaction was quenched by addition of water (50 mL), and extracted with DCM. The collected organic layer was evaporated under vacuum and the residue was purified by column chromatography on silica gel with CH$_2$Cl$_2$ as eluent to give the products as yellow solid.

**7-Bromo-10-hexyl-10H-phenothiazine-3-carbaldehyde (3a)**

Yield: 700 mg, (90%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.80 (s, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.13 (t, $J = 8.0$ Hz, 1H), 7.10 (d, $J = 8.0$ Hz, 1H), 6.91 (d, $J = 8.0$ Hz, 1H), 6.85 (t, $J = 8.0$ Hz, 1H), 3.89 (t, $J = 6.4$ Hz, 2H), 1.78-1.90 (m, 2H), 1.28–1.32 (m, 6H), 0.86 (t, $J = 6.4$ Hz, 3H).

$^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.91, 150.32, 142.63, 131.33, 130.35, 130.12, 129.38, 128.54, 126.61, 124.44, 117.41, 115.48, 115.20, 48.10, 31.43, 26.56, 26.64, 22.36, 14.01. HRMS (MALDI-TOF, m/z): [M$^+$] calcd for (C$_{19}$H$_{20}$BrNOS) 389.0413; found, 389.0422.

**7-Bromo-10-(4-(hexyloxy)phenyl)-10H-phenothiazine-3-carbaldehyde (3b)**

Yield: 580 mg, (89%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.69 (s, 1H), 7.27-7.29 (m, 1H), 7.21-7.23 (m, 2H), 7.10-7.14 (m, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 6.88-6.91 (m, 1H), 6.18 (d, $J = 8.0$ Hz, 1H), 5.99 (d, $J = 8.0$ Hz, 1H), 4.03 (t, $J = 6.4$ Hz, 2H), 1.78-1.84 (m, 2H), 1.50-1.61 (m, 2H), 1.36–1.38 (m, 4H), 0.93 (t, $J = 6.4$ Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.65, 159.45, 149.13, 142.19, 131.69, 131.45, 131.13, 130.09, 129.75, 128.75, 127.49, 121.20, 119.31,
117.61, 116.48, 115.70, 115.20, 68.45, 31.60, 29.21, 25.77, 22.63, 14.06. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{25}H_{24}BrNO_{2}S) 481.0713; found, 481.0721.

7-Bromo-10-(9-hexyl-9H-carbazol-3-yl)-10H-phenothiazine-3-carbaldehyde (3c)
Yield: 500 mg, (87%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.68 (s, 1H), 8.05-8.07 (m, 2H), 7.62-7.65 (m, 2H), 7.48-7.54 (m, 2H), 7.45 (t, \(J = 7.2\) Hz, 2H), 7.35-7.38 (m, 2H), 7.29 (d, \(J = 7.2\) Hz, 1H), 7.22-7.25 (m, 1H), 6.83-6.86 (m, 1H), 4.38 (t, \(J = 6.4\) Hz, 2H), 1.91-1.97 (m, 2H), 1.41-1.49 (m, 2H), 1.28–1.37 (m, 4H), 0.94 (t, \(J = 6.4\) Hz, 3H). \(^1^3\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 189.65, 149.54, 142.60, 142.48, 141.06, 139.94, 131.08, 131.00, 130.39, 130.14, 129.70, 129.43, 128.71, 128.62, 127.36, 126.74, 124.80, 122.25, 121.16, 115.60, 115.45, 115.40, 111.36, 111.06, 109.27, 43.50, 31.63, 29.05, 27.07, 22.62, 14.08. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{31}H_{27}BrN_{2}OS) 554.1012; found, 554.1025.

7-Bromo-10-(9,9-dihexyl-9H-fluoren-2-yl)-10H-phenothiazine-3-carbaldehyde (3d)
Yield: 460 mg, (91%). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 9.69 (s, 1H), 7.94 (d, \(J = 6.4\) Hz, 1H), 7.76-7.78 (m, 1H), 7.46 (d, \(J = 6.4\) Hz, 1H), 7.39-7.40 (m, 3H), 7.29-7.31 (m, 2H), 7.24-7.28 (m, 2H), 7.09 (d, \(J = 7.2\) Hz, 1H), 6.85-6.88 (m, 2H), 2.01 (t, \(J = 6.4\) Hz, 4H), 1.31-1.37 (m, 4H), 1.17-1.25 (m, 4H), 1.07-1.23 (m, 8H), 0.78 (t, \(J = 6.4\) Hz, 6H). \(^1^3\)C NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 189.67, 148.56, 143.61, 141.43, 141.02, 139.95, 131.01, 131.00, 130.27, 130.15, 129.76, 129.41, 128.73, 128.34, 127.37, 126.75, 124.90, 123.23, 121.16, 115.61, 115.40, 114.40, 112.36, 111.15, 109.29, 65.78, 43.51, 31.77, 29.01, 27.08, 22.34, 14.00. HRMS (MALDI-TOF, m/z): [M+] calcd for (C_{38}H_{46}BrNOS) 637.2011; found, 637.1921.

**General procedures for the preparation of 4a-4d.**

A mixture of 3a-3d (0.30 mmol), (4-(diphenylamino)phenyl)boronic acid (115 mg, 0.40 mmol), Pd(PPh\(_3\))\(_4\) (25 mg, 0.04 mmol) and 2N aqueous solution of K\(_2\)CO\(_3\) (2 mL) in THF (10 mL) was
heated to reflux under a N\textsubscript{2} atmosphere for about 12 hrs. Then, the solvent was removed under vacuum and the residue was purified by column chromatography on silica gel using a 1:4 mixture of hexane and CH\textsubscript{2}Cl\textsubscript{2} as eluent to afford 4a–4d as red solids, respectively.

7-(4-(Diphenylamino)phenyl)-10-hexyl-10\textsubscript{H}-phenothiazine-3-carbaldehyde (4a)

Yield: 120 mg, (71%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 9.65 (s, 1H), 7.90-7.93 (m, 1H), 7.79 (d, \(J = 2.0\) Hz, 1H), 7.56 (d, \(J = 2.0\) Hz, 2H), 7.41-7.46 (m, 1H), 7.40 (d, \(J = 2.0\) Hz, 1H), 7.32 (t, \(J = 7.6\) Hz, 4H), 7.11 (d, \(J = 7.6\) Hz, 1H), 6.87-6.94 (m, 10H), 3.94 (t, \(J = 6.8\) Hz, 4H), 1.67-1.70 (m, 2H), 1.34-1.40 (m, 2H), 1.24-1.26 (m, 4H), 0.84 (t, \(J = 6.8\) Hz, 3H). \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 189.77, 148.40, 146.88, 141.12, 134.95, 132.43, 130.09, 129.51, 129.00, 128.02, 125.44, 124.19, 123.88, 123.13, 122.98, 122.65, 122.54, 116.88, 116.23, 115.45, 99.60, 46.94, 30.69, 26.01, 25.68, 22.06, 14.01. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\textsubscript{37}H\textsubscript{34}N\textsubscript{2}OS) 554.2419; found, 554.2422.

7-(4-(Diphenylamino)phenyl)-10-(4-(hexyloxy)phenyl)-10\textsubscript{H}-phenothiazine-3-carbaldehyde (4b)

Yield: 100 mg, (68%). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 9.67 (s, 1H), 7.38 (d, \(J = 8.0\) Hz, 1H), 7.22-7.25 (m, 2H), 7.18-7.22 (m, 7H), 7.07-7.11 (m, 2H), 6.99-7.06 (m, 6H), 6.95-6.97 (m, 2H), 6.10-6.13 (m, 2H), 3.97 (t, \(J = 7.6\) Hz, 2H), 1.75-1.79 (m, 2H), 1.44-1.50 (m, 2H), 1.20-1.31 (m, 4H), 0.84 (t, \(J = 4.0\) Hz, 3H). \textsuperscript{13}C NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) 189.75, 159.33, 149.36, 147.60, 141.61, 136.18, 133.27, 132.06, 131.60, 130.86, 129.98, 129.30, 128.83, 127.50, 126.99, 126.37, 125.09, 124.53, 124.46, 123.81, 123.01, 119.73, 119.33, 116.76, 115.00, 68.44, 31.61, 29.24, 25.79, 22.64, 14.08. HRMS (MALDI-TOF, m/z): [M+] calcd for (C\textsubscript{43}H\textsubscript{38}N\textsubscript{2}O\textsubscript{2}S) 646.2712; found, 646.2713.
7-(4-(Diphenylamino)phenyl)-10-(9-hexyl-9\textit{H}-carbazol-3-yl)-10\textit{H}-phenothiazine-3-carbaldehyde (4c)

Yield: 112 mg, (66%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.68 (s, 1H), 7.61-7.68 (m, 1H), 7.50 (d, $J$ = 8.8 Hz, 2H), 7.33-7.45 (m, 5H), 7.27-7.29 (m, 2H), 7.16-7.20 (m, 12H), 7.00-7.14 (m, 2H), 6.22-6.24 (m, 2H), 4.39 (t, $J$ = 6.0 Hz, 2H), 1.81-1.87 (m, 2H), 1.33-1.40 (m, 2H), 1.20-1.26 (m, 4H), 0.84 (t, $J$ = 6.8 Hz, 3H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.78, 159.97, 148.66, 146.14, 146.09, 145.89, 141.88, 141.25, 140.77, 139.95, 139.23, 134.98, 132.28, 131.34, 129.78, 127.99, 127.55, 127.10, 126.67, 125.09, 124.13, 124.00, 123.93, 123.75, 123.28, 123.10, 122.78, 122.47, 119.20, 118.40, 118.12, 116.12, 115.52, 30.95, 30.68, 28.57, 26.16, 22.13, 14.02. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{49}$H$_{41}$N$_3$OS) 719.3017; found, 719.3025.

10-(9,9-Dihexyl-9\textit{H}-fluoren-2-yl)-7-(4-(diphenylamino)phenyl)-10\textit{H}-phenothiazine-3-carbaldehyde (4d)

Yield: 130 mg, (72%). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 9.60 (s, 1H), 7.85-7.88 (m, 1H), 7.68-7.69 (m, 2H), 7.39-7.41 (m, 1H), 7.27 (d, $J$ = 6.0 Hz, 2H), 7.21-7.24 (m, 4H), 7.14-7.17 (m, 4H), 6.93-7.00 (m, 5H), 6.89-6.92 (m, 4H), 6.69-6.77 (m, 3H), 6.07-6.11 (m, 2H), 0.88-1.00 (m, 12H), 0.67 (t, $J$ = 7.6 Hz, 6H), 0.59 (m, 4H). $^{13}$C NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 189.65, 154.08, 152.44, 151.09, 149.43, 147.61, 147.23, 142.06, 141.51, 139.87, 138.44, 136.27, 133.20, 130.94, 129.31, 129.06, 127.97, 126.97, 125.92, 125.69, 125.06, 124.68, 124.48, 123.97, 123.81, 123.65, 123.01, 122.19, 119.90, 119.22, 118.83, 116.62, 114.82, 55.57, 31.62, 29.55, 23.88, 22.69, 22.49, 14.05. HRMS (MALDI-TOF, m/z): [M+] calcd for (C$_{56}$H$_{54}$N$_2$OS) 802.4045; found, 802.4039.
YR6 was synthesized according to the reported method.

A blue solid. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$: 8.34 (s, 1H), 7.69 (s, 1H), 7.63 (d, $J$ = 6.4 Hz, 1H), 7.59 (m, 1H), 7.39 (m, 2H), 7.32 (t, $J$ = 6.4 Hz, 1H), 7.19 (t, $J$ = 6.4 Hz, 1H), 7.06 (d, $J$ = 6.4 Hz, 1H), 6.98 (d, $J$ = 6.8 Hz, 1H), 6.08 (s, 1H), 5.98 (s, 1H), 4.15 (m, 2H), 3.99 (m, 2H), 1.79 (m, 12H), 1.45–1.23 (m, 23H), 0.86 (t, $J$ = 6.4 Hz, 3H). HRMS (MALDI-TOF): m/z: [M+] calcd for C$_{48}$H$_{55}$N$_3$O$_4$S, 769.3913; found, 769.3918.

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**Figure S1.** The optimized ground-state geometries of these dyes TP1–TP4.
Figure S2. Absorption spectra of TP3, YR6 and co-adsorption on TiO$_2$ films.