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

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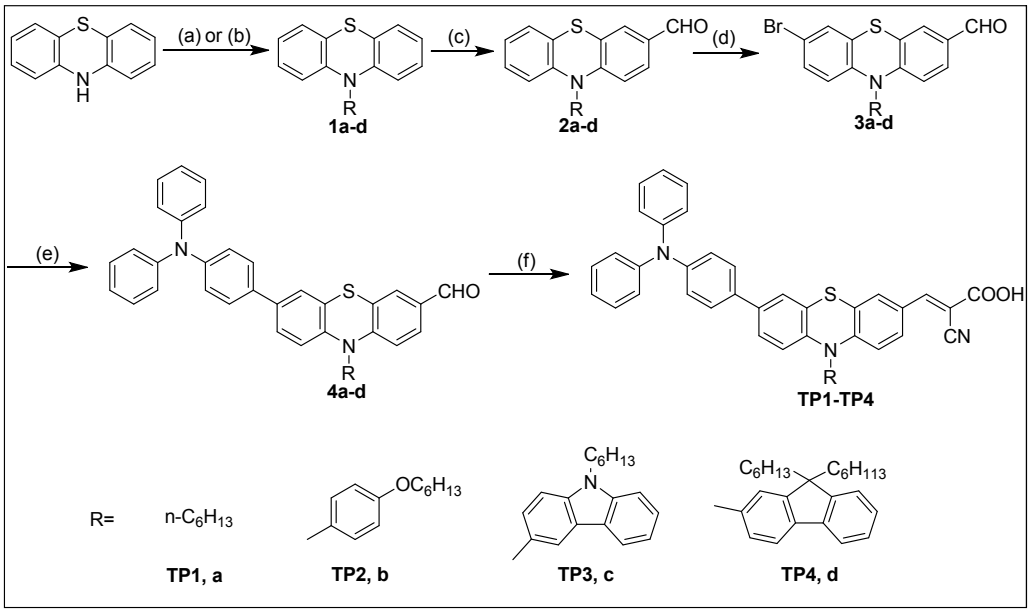


Scheme S1. Synthetic routes for **TP1–TP4**. (a) KOH, RBr, DMSO, rt; (b) Cu, K_2CO_3, 18-crown-6, RBr, *o*-dichlorobenzene, reflux; (c) DMF, $POCl_3$, $ClCH_2CH_2Cl$, reflux; (d) NBS, THF, 0°C; (e) $Pd(PPh_3)_4$, 4-(diphenylamino)phenyl boronic acid, 2N K_2CO_3, THF, reflux; (f) cyanoacetic acid, CH_3COOH, CH_3COONH_4, 120°C.

Synthetic procedure

10-Hexyl-10*H*-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%). ^{1}H NMR (400 MHz, $CDCl_3$): 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 10*H*-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_2CO_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 N_2 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_2Cl_2 as eluent to afford the products as white solid.

10-(4-(Hexyloxy)phenyl)-10*H*-phenothiazine (1b) Yield: 2.43g, (65%). ^{1}H NMR (400 MHz, $CDCl_3$): 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* = 1.6 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). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 158.87, 144.70, 132.21, 126.81, 126.59, 122.21, 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-9*H*-carbazol-2-yl)-10*H*-phenothiazine (1c)

Yield: 2.77g, (62%). ^{1}H NMR (400 MHz, $CDCl_3$): 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), 0.82 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (400 MHz, $CDCl_3$): 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 ($C_{30}H_{28}N_2S$) 448.2067; found, 448.2069.

10-(9,9-Dihexyl-9*H*-fluoren-2-yl)-10*H*-phenothiazine (1d)

Yield: 3.77g, (71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 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. ^{13}C NMR (400 MHz, $CDCl_3$): δ = 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 ($C_{37}H_{41}NS$) 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 phosphrous 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 $MgSO_4$. 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*H*-phenothiazine-3-carbaldehyde (2a)

Yield: 1.71 g (55%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (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 ($C_{19}H_{21}NOS$) 311.1355; found, 311.1366.

10-(4-(Hexyloxy)phenyl)-10*H*-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 ($C_{25}H_{25}NO_2S$) 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 ($C_{31}H_{28}N_2OS$) 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,

109.23, 92.38, 44.48, 31.98, 29.03, 27.65, 22.76, 14.03. HRMS (MALDI-TOF, m/z): [M^+] calcd for ($C_{38}H_{41}NOS$) 559.2912; found, 559.2916.

General procedures for the preparation of 3a-3d.

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_2Cl_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, $CDCl_3$): δ (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, $CDCl_3$): δ (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, $CDCl_3$): δ (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, $CDCl_3$): δ (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 ($C_{25}H_{24}BrNO_2S$) 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, $CDCl_3$): δ (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). ^{13}C NMR (400 MHz, $CDCl_3$): δ (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 ($C_{31}H_{27}BrN_2OS$) 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, $CDCl_3$): δ (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). ^{13}C NMR (400 MHz, $CDCl_3$): δ (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 ($C_{38}H_{40}BrNOS$) 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_2CO_3 (2 mL) in THF (10 mL) was

heated to reflux under a N_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_2Cl_2 as eluent to afford **4a**–**4d** as red solids, respectively.

7-(4-(Diphenylamino)phenyl)-10-hexyl-10*H*-phenothiazine-3-carbaldehyde (4a)

Yield: 120 mg, (71%). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ (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). ^{13}C NMR (400 MHz, $CDCl_3$): δ (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 ($C_{37}H_{34}N_2OS$) 554.2419; found, 554.2422.

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

Yield: 100 mg, (68%). ^{1}H NMR (400 MHz, $CDCl_3$): ^{1}H NMR (400 MHz, $CDCl_3$): δ (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). ^{13}C NMR (400 MHz, $CDCl_3$): δ (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 ($C_{43}H_{38}N_2O_2S$) 646.2712; found, 646.2713.

7-(4-(Diphenylamino)phenyl)-10-(9-hexyl-9*H*-carbazol-3-yl)-10*H*-phenothiazine-3-carbaldehyde (4c)

Yield: 112 mg, (66%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (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, $CDCl_3$): δ (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 ($C_{49}H_{41}N_3OS$) 719.3017; found, 719.3025.

10-(9,9-Dihexyl-9*H*-fluoren-2-yl)-7-(4-(diphenylamino)phenyl)-10*H*-phenothiazine-3-carbaldehyde (4d)

Yield: 130 mg, (72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 9.60 (s, 1H), 7.85-7.88 (m, 1H), 7.68-7.69 (m, 1H), 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), 1.91 (t, *J* = 6.0 Hz, 4H), 0.88-1.00 (m, 12H), 0.67 (t, *J* = 7.6 Hz, 6H), 0.59 (m, 4H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (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 ($C_{56}H_{54}N_2OS$) 802.4045; found, 802.4039.

YR6 was synthesized according to the reported method.

A blue solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ =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 C48H55N3O4S, 769.3913; found, 769.3918.

Ref: Y. R. Shi, R. B. M. Hill, J. H. Yum, A. Dualeh, S. Barlow, M. Grätzel, S. R. Marder, M. K. Nazeeruddin, *Angew. Chem. Int. Ed*. **2011**, *50*, 6619 –6621.

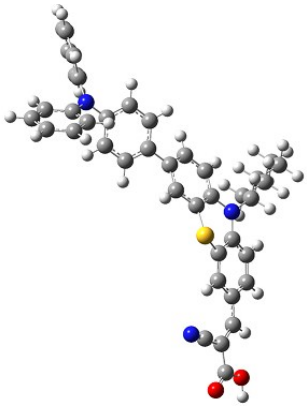
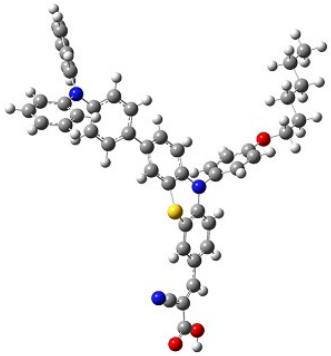
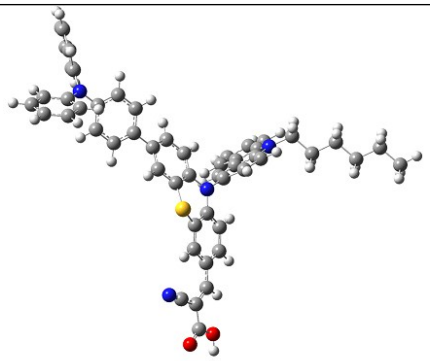
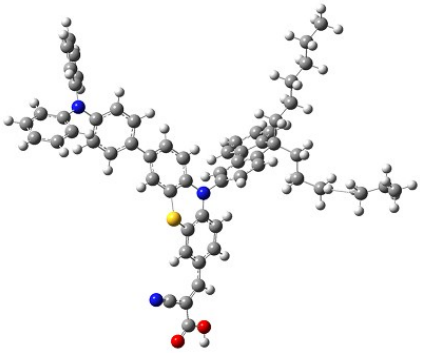
TP1	TP2
	
TP3	**TP4**
	

Figure S1. The optimized ground-state geometries of these dyes **TP1**–**TP4**.

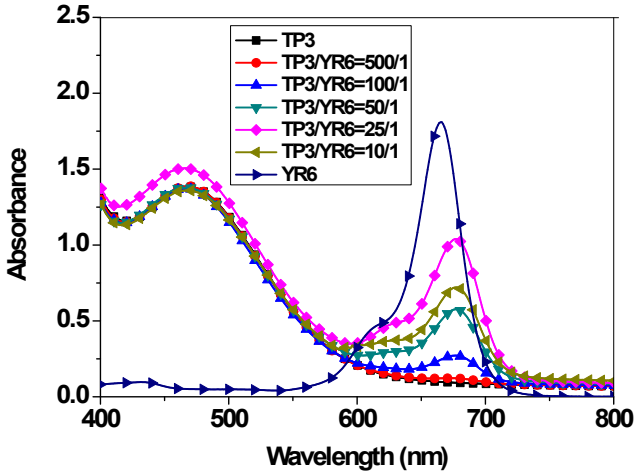


Figure S2. Absorption spectra of **TP3**, **YR6** and co-adsorption on TiO_2 films.