Electronic Supplementary Information

Molecular Engineering of New Phenothiazine-based D-A-π-A Dyes for Dye-Sensitized Solar Cells

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Experimental section

Synthesis and characterization of dyes.

Figure S1 Synthetic routes of intermediates. (a) SOCl₂, NEt₃, CH₂Cl₂; (b) Br₂, HBr
(aq); (c) bis(pinacolato)diboron, Pd(PPh$_3$)$_2$Cl$_2$, KOAc, toluene; (d) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, DME/H$_2$O; (e) NaH, n-BuBr, THF; (f) NBS, THF; (g) NBS, THF; (h) Pd$_2$(dba)$_3$,

'Bu$_3$P, t-BuOK, diphenylamine, 1,4-dioxane; (i) NBS, DMF; (j) bis(pinacolato)diboron, Pd(PPh$_3$)$_2$Cl$_2$, KOAc, toluene; (k) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, DME/H$_2$O; (l) n-C$_8$H$_{13}$Br, K$_2$CO$_3$, acetone; (m) bis(pinacolato)diboron, Pd(PPh$_3$)$_2$Cl$_2$, KOAc, toluene; (n) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, DME/H$_2$O; (o) DMF, POCl$_3$, CH$_2$Cl$_2$; (p) cyanoacetic acid, piperidine, CHCl$_3$.

Dye of T2-1, compound 2, 3, 5, 6, 8, A-1, 9, 11, 12, 14, 15 and 16 were synthesized according to literatures.$^{1-6}$ Their $^1$H NMR spectra were consistent with that in references. The synthetic procedures and NMR data for other intermediates and new dyes are detailed as follows.

**Preparation of A-2~4**

**A-2**: Under argon, 3,7-dibromo-10-butyl-10H-phenothiazine (compound 9) (6.20 g, 15 mmol), Pd$_2$(dba)$_3$ (41.2 mg, 0.045 mmol), HP(t-Bu)$_3$BF$_4$ (43.5 mg, 0.15 mmol), and t-BuOK (1.00 g, 9 mmol) were dissolved in dry 1,4-dioxane (50 mL). The reaction mixture was stirred at 70 °C for 5 minutes and then diphenylamine (0.51 g, 3 mmol) was added and the mixture was heated to 105 °C for 14 h. After cooling to room temperature, solvents were removed by rotary evaporation. The residue was purified using column chromatography to give a pale green solid (1.00 g, 66.8 %). $^1$H NMR (300 MHz, Acetone-$d_6$): $\delta$ 7.33 (dd, $J = 6.9$, 1.8 Hz, 1 H), 7.27 (m, 5 H), 7.00 (m, 7 H), 6.93 (2 H, m), 6.85 (1 H, d, $J = 2.4$ Hz), 3.91 (t, $J = 7.2$ Hz, 2 H), 1.77 (m, 2
\( H \), 1.47 (m, 2 H), 0.93 (t, \( J = 7.2 \) Hz, 3 H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \( \delta \) 147.82, 144.65, 143.09, 140.76, 130.03, 129.79, 129.36, 126.84, 125.22, 124.34, 124.21, 123.63, 122.55, 116.51, 116.09, 114.34, 47.39, 29.06, 20.35, 14.03.

**A-3:** Compound 12 (0.63 g, 1.7 mmol) was treated with 9 (2.81 g, 6.8 mmol) in the presence of Pd(PPh\(_3\))\(_4\) (0.10 g, 0.08 mmol), 1 N aqueous solution of K\(_2\)CO\(_3\) (2.5 mL) and 1,2-dimethoxyethane (22.5 mL). The mixture was degassed for three times and refluxed for 48 h. After cooling and addition of AcOEt (50 mL), the mixture was washed with water and dried on magnesium sulfate. Solvents were removed by rotary evaporation and the residue was purified by silica gel column chromatography with petroleum ether:AcOEt (10:1, v:v) as eluent to give A-3 as a pale yellow oil (0.64 g, 67.2%). \(^1\)H NMR (300 MHz, Acetone-d\(_6\)): \( \delta \) 7.48 (dd, \( J = 6.9, 2.4 \) Hz, 2H), 7.41 (dd, \( J = 8.1, 2.4 \) Hz, 1H), 7.35 (d, \( J = 2.4 \) Hz, 1H), 7.27 (m, 6H), 7.03 (m, 9H), 6.88 (d, \( J = 8.7 \) Hz, 1H), 3.88 (t, \( J = 6.9 \) Hz, 2H), 1.73 (m, 2H), 1.44 (m, 2H), 0.89 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (75 MHz, Acetone-d\(_6\)): \( \delta \) 148.57, 147.91, 145.42, 144.61, 144.61, 135.89, 134.47, 130.95, 130.29, 130.04, 127.95, 127.62, 126.52, 125.75, 125.20, 125.10, 124.67, 123.97, 117.99, 117.03, 114.78, 47.67, 29.55, 20.63, 14.14.

**A-4:** Compound 12 (0.61 g, 2 mmol) was treated with 9 (4.13 g, 10 mmol) in the presence of Pd(PPh\(_3\))\(_4\) (115.6 mg, 0.1 mmol), 1 N aqueous solution of K\(_2\)CO\(_3\) (5 mL) and 1,2-dimethoxyethane (45 mL). The mixture was degassed for three times and refluxed for 48 h. After cooling and addition of AcOEt (80 mL), the mixture was washed with water and dried on magnesium sulfate. Solvents were removed by rotary evaporation and the residue was purified by silica gel column chromatography with
petroleum ether:AcOEt (10:1, v:v) as eluent to give A-4 as a pale yellow oil (0.69 g, 67.5%). ¹H NMR (300 MHz, Acetone-d₆): δ 7.54 (dd, J = 6.9, 2.4 Hz, 2H), 7.44 (dd, J = 8.7, 2.4 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 7.31 (m, 2H), 7.08 (d, J = 8.1 Hz, 1H), 6.97 (m, 3H), 4.02 (t, J = 6.6 Hz, 2H), 3.95 (t, J = 6.9 Hz, 2H), 1.78 (m, 4H), 1.49 (m, 4H), 1.36 (m, 4H), 0.92 (m, 6H).

**General synthetic procedure for compounds B-n⁷⁻⁸**

A mixture of A-n (1.0 mmol), bis(pinacolato)diboron (0.31 g, 1.2 mmol), Pd(PPh₃)₂Cl₂ (17.8 mg, 25 μmol) and KOAc (0.30 g, 3 mmol) in dry toluene (25 mL) was heated to 120 °C under argon for 12 h. After cooling, the solvents were evaporated in vacuum. The residue was chromatographed with petroleum ether:AcOEt (10:1, v:v) to give B-n as a pale green oil.

**B-1**: 0.36 g, yield 94.5%. ¹H NMR (300 MHz, DMSO-d₆): δ 7.49 (d, J = 8.1 Hz, 1H), 7.36 (s, 1H), 7.20 (t, J = 7.2 Hz, 1H), 7.13 (d, J = 7.8 Hz, 1H), 7.02 (m, 2H), 6.98 (t, J = 7.2 Hz, 1H), 3.84 (t, J = 6.9 Hz, 2H), 1.68 (m, 2H), 1.31 (s, 12 H), 0.92 (t, J = 7.8 Hz, 3H).

**B-2**: 0.47 g, yield 86.7 %. ¹H NMR (300 MHz, Acetone-d₆): δ 7.56 (dd, J = 1.2, 8.1 Hz, 1H), 7.41 (d, J = 1.2 Hz, 1H), 7.26 (m, 4H), 7.00 (m, 8H), 6.89 (dd, J = 8.7, 2.7 Hz, 1H), 6.84 (d, J = 2.7 Hz, 1H), 3.94 (t, J = 6.9 Hz, 2H), 1.73 (m, 2H), 1.48 (m, 2H), 1.30 (s, 12 H), 0.93 (t, J = 7.2 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃): δ 147.95, 147.83, 142.94, 140.64, 134.34, 133.97, 129.29, 125.90, 124.24, 124.09, 123.59, 123.52, 122.41, 115.99, 114.64, 83.75, 47.27, 29.85, 29.08, 24.98, 20.31, 14.01. HRMS (EIS): m/z [M]⁺ calcd for C₃₄H₃₇BN₂O₂S: 548.2335; found: 548.2358.
**B-3:** 0.46 g, yield 73.7 %. $^1$H NMR (300 MHz, DMSO-\textsubscript{d}$_6$): $\delta$ 7.56 (d, $J$ = 8.7 Hz, 2H), 7.41 (m, 2H), 7.39 (d, $J$ = 2.1 Hz, 1H), 7.32 (m, 5H), 7.03 (m, 10H), 3.90 (t, $J$ = 6.9 Hz, 2H), 1.68 (m, 2H), 1.41 (m, 2H), 1.27 (s, 12 H), 0.88 (t, $J$ = 7.2 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 147.85, 147.03, 143.68, 135.30, 134.17, 134.00, 129.63, 129.44, 129.23, 127.30, 125.28, 124.69, 124.50, 124.33, 124.20, 123.69, 123.02, 115.71, 114.75, 83.86, 47.37, 29.07, 25.35, 25.03, 20.33, 14.04. HRMS (EIS): m/z [M]$^+$ calcd for C$_{40}$H$_{41}$BN$_2$O$_2$S: 624.2976; found: 624.2964.

**B-4:** 0.43 g, yield 77.4 %. $^1$H NMR (300 MHz, DMSO-\textsubscript{d}$_6$): $\delta$ 7.55 (m, 3H), 7.44 (m, 2H), 7.36 (d, $J$ = 2.1 Hz, 1H), 7.06 (dd, $J$ = 12.9, 8.1 Hz, 2H), 6.98 (d, $J$ = 9.0 Hz, 2H), 4.01 (m, 4H), 1.74 (m, 4H), 1.48 (m, 4H), 1.35 (m, 16H), 0.92 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 158.67, 147.88, 143.49, 135.58, 134.34, 133.99, 132.50, 127.63, 125.53, 125.43, 125.29, 123.75, 115.70, 114.94, 114.73, 83.84, 68.25, 47.33, 31.80, 29.91, 29.46, 29.09, 25.94, 25.02, 22.82, 20.32, 14.26, 14.02. HRMS (EIS): m/z [M+1]$^+$ calcd for C$_{34}$H$_{44}$BNO$_3$S: 558.3208; found: 558.3192.

**General synthetic procedure for compounds C-n**

Compound **B-n** (0.5 mmol) was treated with **6** (0.6 mmol) in the presence of Pd(PPh$_3$)$_4$ (57.8 mg, 50 μmol), 1 N aqueous solution of K$_2$CO$_3$ (3 mL) and 1,2-dimethoxyethane (22 mL). The mixture was degassed for three times and refluxed for 48 h. After cooling and addition of AcOEt (50 mL), the mixture was washed with water and dried on magnesium sulfate. Solvents were removed by rotary evaporation and the residue was purified by silica gel column chromatography with petroleum ether:AcOEt (10:1, v:v) as eluent to give **C-n** as an orange solid.
**C-1**: 173.8 mg, yield 70.5 %. $^1$H NMR (300 MHz, Acetone-$d_6$): $\delta$ 10.16 (s, 1H), 8.31 (d, $J = 8.7$ Hz, 2H), 8.09 (m, 3H), 7.96 (m, 3H), 7.22 (m, 3H), 7.10 (d, $J = 6.9$ Hz, 1H), 6.99 (t, $J = 7.8$ Hz, 1H), 4.06 (t, $J = 6.9$ Hz, 2H), 1.86 (m, 2H), 1.53 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.74, 153.62, 153.58, 145.46, 144.48, 143.10, 135.51, 132.93, 132.92, 130.80, 129.75, 129.59, 128.79, 128.22, 127.63, 127.35, 127.26, 126.53, 124.67, 124.00, 122.52, 115.33, 115.01, 47.16, 28.81, 20.12, 13.80. Anal. Calcd. for C$_{29}$H$_{23}$N$_3$O$_2$·1/6 CH$_2$Cl$_2$: C, 68.99; H, 4.63; N, 8.28. Found: C, 69.15; H, 4.36; N, 8.07. HRMS (ESI): calcd for C$_{29}$H$_{23}$N$_3$O$_2$ m/z: 493.1557, found: 493.1546.

**C-2**: 221.8 mg, yield 67.2 %. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 10.12 (s, 1H), 8.17 (d, $J = 8.1$ Hz, 2H), 8.06 (d, $J = 8.1$ Hz, 2H), 7.84 (d, $J = 7.8$ Hz, 2H), 7.76 (d, $J = 8.4$ Hz, 2H), 7.24 (m, 4H), 7.01 (m, 5H), 6.94 (m, 4H), 6.79 (d, $J = 8.7$ Hz, 1H), 3.90 (t, $J = 6.9$ Hz, 2H), 1.87 (m, 2H), 1.54 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 191.92, 153.90, 153.83, 147.79, 143.36, 143.00, 140.45, 136.86, 135.76, 133.24, 132.41, 131.02, 130.00, 129.83, 129.30, 128.94, 128.50, 127.90, 126.77, 125.18, 124.43, 124.24, 123.55, 122.47, 115.99, 115.10, 47.43, 29.83, 20.40, 14.04. HRMS (ESI): m/z [M]$^+$ calcd for C$_{41}$H$_{32}$N$_4$O$_2$: 660.1794; found: 660.1814.

**C-3**: 264.2 mg, yield 71.8 %. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 10.07 (s, 1H), 8.12 (d, $J = 8.1$ Hz, 2H), 8.01 (d, $J = 8.1$ Hz, 2H), 7.81 (m, 3H), 7.70 (d, $J = 7.5$ Hz, 2H), 7.38 (m, 4H), 7.25 (t, $J = 7.8$ Hz, 4H), 7.11 (m, 4H), 7.01 (dd, $J = 7.2$, 12.9 Hz, 4H), 6.90 (d, $J = 8.7$ Hz, 1H), 3.90 (t, $J = 6.9$ Hz, 2H), 1.76 (m, 2H), 1.51 (m, 2H), 0.90 (t,
\( J = 7.2 \text{ Hz, 3H).} \) \(^{13}\text{C NMR (75 MHz, CDCl}_3\):} \( \delta \) 192.05, 153.97, 153.91, 147.78, 147.07, 145.59, 143.52, 143.47, 135.82, 135.34, 133.95, 133.33, 131.17, 130.50, 130.09, 129.90, 129.43, 129.10, 128.57, 128.15, 127.96, 127.24, 126.88, 125.65, 125.50, 124.59, 124.51, 124.12, 123.05, 115.71, 115.25, 47.51, 29.08, 20.40, 14.06.

HRMS (EIS): \( m/z \ [M]^+ \) calcd for \( \text{C}_{47}\text{H}_{36}\text{N}_4\text{O}_2\text{S}_2 \): 736.2325; found: 736.2313.

**C-4**: 205.0 mg, yield 61.3 %. \(^1\text{H NMR (300 MHz, CDCl}_3\):} \( \delta \) 10.06 (s, 1H), 8.10 (d, \( J = 7.2 \text{ Hz, 2H) \), 7.74 (m, 4H), 7.31 (m, 2H), 6.93 (m, 4H), 3.96 (m, 4H), 1.79 (m, 4H), 1.45 (m, 8H), 0.97 (m, 6H). \(^{13}\text{C NMR (75 MHz, CDCl}_3\):} \( \delta \) 192.12, 158.64, 153.81, 153.85, 147.08, 145.58, 143.44, 143.27, 135.73, 135.54, 133.26, 132.27, 131.07, 130.07, 129.86, 129.44, 129.09, 128.54, 127.91, 127.56, 126.84, 125.62, 125.49, 124.48, 115.67, 115.18, 114.88, 68.18, 47.43, 31.76, 29.40, 29.00, 25.90, 22.79, 20.37, 14.26, 14.05. HRMS (EIS): \( m/z \ [M]^+ \) calcd for \( \text{C}_{41}\text{H}_{39}\text{N}_3\text{O}_2\text{S}_2 \): 669.2478; found: 669.2467.

**Synthesis of compounds PZ-n**

A CHCl\(_3\) (10 mL) solution of compound \( \text{C-n} \) (0.3 mmol), cyanoacetic acid (123.2 mg, 1.5 mmol) and piperidine (0.19 mL, 1.9 mmol) were charged sequentially into a three-necked flask under a nitrogen atmosphere and heated to reflux till no starting material \( \text{C-n} \) was detected by the TLC plate. After cooling to 0 \( \degree \text{C, 2M HCl (5mL) were added dropwisely into the flask and stirred for 1h. The mixture was washed with water and dried on anhydrous magnesium sulfate. Solvents were removed by rotary evaporation, and the residue was purified by silica gel column chromatography with CH\(_2\)Cl\(_2\):CH\(_3\)OH (10:1, v:v) as eluent to afford the dye \( \text{PZ-n} \) as a dark purple solid.
**PZ-1**: 116.3 mg, yield 69.2 %. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 14.07 (br, 1H), 8.42 (s, 1H), 8.23 (m, 4H), 8.06 (d, $J = 7.2$ Hz, 1H), 7.97 (d, $J = 7.2$ Hz, 1H), 7.91 (m, 2H), 7.31 (dd, $J = 9.3$, 40.5 Hz, 1H), 7.21 (m, 2H), 7.08 (d, $J = 7.8$ Hz, 1H), 6.99 (m, 1H), 3.95 (t, $J = 6.9$ Hz, 2H), 1.72 (m, 2H), 1.45 (m, 2H), 0.91 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$-CD$_3$OD): $\delta$ 164.06, 154.30, 153.80, 153.68, 145.64, 144.64, 143.86, 142.00, 133.16, 131.21, 130.97, 130.68, 129.77, 129.54, 128.86, 128.33, 127.72, 127.34, 126.80, 124.78, 124.11, 122.58, 116.55, 116.06, 115.45, 115.17, 47.20, 28.92, 20.14, 13.73. Anal. Calcd. for C$_{32}$H$_{24}$N$_4$O$_2$S$_2$·1/3 CH$_2$Cl$_2$·1/3 CH$_3$OH: C, 65.43; H, 4.37; N, 9.34. Found: C, 65.23; H, 4.05; N, 9.28. HRMS (ESI): m/z [M+1]$^+$ calcd for C$_{32}$H$_{24}$N$_4$O$_2$S$_2$·1/3 CH$_2$Cl$_2$·1/3 CH$_3$OH: 561.1413, found: 560.1420.

**PZ-2**: 171.2 mg, yield 78.5 %. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 14.09 (br, 1H), 8.40 (s, 1H), 8.22 (m, 4H), 8.07 (d, $J = 7.5$ Hz, 1H), 7.98 (d, $J = 7.5$ Hz, 1H), 7.91 (m, 1H), 7.86 (d, $J = 2.1$ Hz, 1H), 7.28 (m, 4H), 7.20 (d, $J = 8.7$ Hz, 1H), 6.99 (m, 9H), 3.92 (t, $J = 6.3$ Hz, 2H), 1.74 (m, 2H), 1.44 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$-CD$_3$OD): $\delta$ 164.48, 158.89, 154.12, 153.81, 153.70, 153.68, 147.74, 142.89, 142.54, 141.94, 141.92, 141.81, 141.63, 140.48, 131.20, 130.70, 129.77, 129.40, 129.18, 128.86, 128.45, 127.02, 126.75, 125.14, 124.19, 123.47, 122.35, 116.24, 116.04, 115.97, 47.32, 28.92, 20.24, 13.82. Anal. Calcd. for C$_{44}$H$_{33}$N$_5$O$_2$S$_2$·1/4 CH$_2$Cl$_2$: C, 70.95; H, 4.51; N, 9.35. Found: C, 70.72; H, 4.24; N, 9.41. HRMS (ESI): m/z [M]$^+$ calcd for C$_{44}$H$_{33}$N$_5$O$_2$S$_2$·1/4 CH$_2$Cl$_2$: 727.2070, found:727.2078.

**PZ-3**: 174.4 mg, yield 72.4 %. $^1$H NMR (400 MHz, DMSO-d$_6$): $\delta$ 14.05 (s, 1H), 8.39 (s, 1H), 8.22 (dd, $J = 18.3$, 8.7 Hz, 4H), 8.06 (d, $J = 7.5$ Hz, 1H),
7.98 (d, J = 7.5 Hz, 1H), 7.91 (m, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.49 (dd, J = 8.5, 2.1 Hz, 1H), 7.44 (d, J = 2.1 Hz, 1H), 7.32 (dd, J = 8.2, 7.5 Hz, 4 H), 7.20 (d, J = 8.6 Hz, 1H), 7.11 (d, J = 8.6 Hz, 1H), 7.04 (m, 8H), 3.97 (t, J = 6.9 Hz, 2H), 1.75 (m, 2H), 1.46 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$-CD$_3$OD): $\delta$ 164.39, 153.96, 153.81, 153.68, 147.63, 146.91, 145.39, 143.38, 141.87, 135.12, 133.80, 133.11, 131.13, 131.00, 130.73, 129.75, 129.22, 128.84, 128.39, 127.89, 127.76, 127.03, 126.81, 126.00, 125.71, 125.44, 125.23, 124.42, 124.29, 123.91, 122.85, 116.22, 115.56, 115.11, 47.26, 28.88, 20.13, 13.71. Anal. Calcd. for C$_{50}$H$_{37}$N$_5$O$_2$S$_2$·CH$_3$OH: C, 73.27; H, 4.9 4; N, 8.38. Found: C, 73.19; H, 4.69; N, 8.39. HRMS (ESI): m/z [M+1]$^+$ calc d for C$_{50}$H$_{37}$N$_5$O$_2$S$_2$ m/z: 804.2461, found: 804.2460.

**PZ-4**: 181.9 mg, yield 82.4 %. $^1$H NMR (300 MHz, DMSO-d$_6$): $\delta$ 14.09 (br, 1H), 8.39 (s, 1H), 8.24 (d, J = 8.4 Hz, 2H), 8.20 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 7.2 Hz, 1H), 7.98 (d, J = 7.2 Hz, 1H), 7.91 (m, 2H), 7.56 (m, J = 8.7 Hz, 2H), 7.44 (m, 2H), 7.20 (d, J = 8.1 Hz, 1H), 7.10 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 3.98 (m, 4H), 1.71 (m, 4H), 1.31 (m, 8H), 0.92 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$-CD$_3$OD): $\delta$ 164.88, 158.36, 153.93, 153.68, 153.57, 145.29, 143.07, 141.76, 135.24, 132.93, 132.14, 131.03, 130.80, 130.51, 129.63, 128.75, 128.28, 127.62, 127.27, 126.66, 125.34, 125.11, 124.26, 124.20, 118.85, 116.20, 115.46, 114.95, 114.71, 106.01, 68.06, 47.17, 31.48, 29.13, 28.78, 25.60, 22.48, 20.05, 13.79, 13.61. Anal. Calcd. for C$_{44}$H$_{40}$N$_4$O$_3$S$_2$·1/3 CH$_2$Cl$_2$: C, 69.58; H, 5.36; N, 7.32. Found: C, 69.63; H, 5.22; N, 7.36. HRMS (ESI): m/z [M+1]$^+$ calc d for C$_{44}$H$_{40}$N$_4$O$_3$S$_2$ m/z: 737.2615, found:
References.


Results and discussion.

Photophysical and electrochemical properties.

Figure S2. CV curves of organic dyes and Fe/Fe$^{\text{+}}$ in THF.
NMR and HRMS spectra for our compounds.

A2-^1^H
A2-\textsuperscript{13}C

A3-\textsuperscript{1}H
B1-$^1$H

B2-$^1$H
B2-$^{13}$C
B3-\(^1\)H

B3-\(^{13}\)C
B3-HRMS

B4-$^1$H
B4-$^{13}$C

B4-HRMS
C1-^1H

C1-^{13}C
C1-HRMS
C2-^1^H

C2-^{13}C
C2-HRMS
C$_{3-13}^\text{C}$
C3-HRMS

C4-1H
C4-$^{13}$C

C4-HRMS
PZ-1-^1^H
PZ-1-$^{13}$C
PZ-1-HRMS

PZ-2-¹H
PZ-2-$^{13}$C
PZ-2-HRMS

PZ-3-^1^H
PZ-3\textsuperscript{13}C
PZ-4\textsuperscript{13}C

\[ \text{Diagram of molecular structure} \]