Electronic Supplementary Material (ESI) for Energy and Environmental Science
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Supporting Information

for

Photoinitiated Multistep Charge Separation in Ferrocene-Zinc Porphyrin-Diiron Hydrogenase Model Complex Triads

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General

All commercial compounds were purchased from Sigma-Aldrich and used without further purification. Solvents were ACS reagent grade, unless otherwise specified. Toluene, methylene chloride (CH_2Cl_2), tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF) were dried using a Glass Contour solvent system. All reactions were performed in air-free conditions under nitrogen. Column chromatography was performed on standard silica gel, 60 angstrom, 32-63 μm (Sorbent Technologies). ^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on a Bruker Avance III using TMS as an internal standard. Laser desorption mass spectra were recorded on a Bruker Daltonics AutoFlex III MALDI-TOF, and high resolution electrospray ionization (HR-ESI) mass spectra were recorded on an Agilent 6210 LC-TOF. Characterization studies were performed at the Integrated Molecular Structure Education and Research Center (IMSERC) at Northwestern University.

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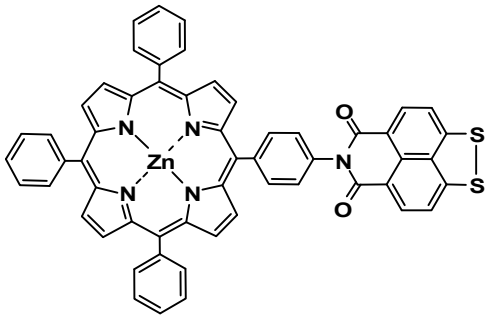
Synthesis

Starting materials 1,8-naphthalic anhydride-4,5-disulfide ($NMAS_2$),[1] 5-(*p*-aminophenyl)-10,15,20-triphenylporphyrin (TPP-NH_2),[2-4] 5-phenyldipyrromethane[5] and 4-iodophenyferrocene (Fc-Ph-I)[6] were synthesized according to reported methods.

ZnTPP-$NMIS_2$:



$NMAS_2$[1] (0.056 g, 0.22 mmol), TPP-NH_2 (0.880 g, 0.14 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.107 g, 0.49 mmol) and 40 mL of pyridine were added to a 100 mL round bottom flask and refluxed under N_2 for 72 hours. The solvent was removed by rotary evaporation and column chromatography was performed using CH_2Cl_2 as the eluent to provide ZnTPP-$NMIS_2$ in a 65% yield (0.085 g, 0.09 mmol). ^{1}H NMR δ ($CDCl_3$): 9.08 (d, J = 4.5 Hz, 2H), 8.92 (d, J = 4.5 Hz, 2H), 8.90 (s, 4H), 8.54 (d, J = 8.0 Hz, 2H), 8.39 (d, J = 8.0 Hz, 2H), 8.22 (d, J = 6.4 Hz, 6H), 7.75 (m, 9H), 7.67 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H). MS (MALDI+): *m/z* 933.364 [M^+], Calcd. 933.121 for $C_{56}H_{31}N_5O_2S_2Zn$.

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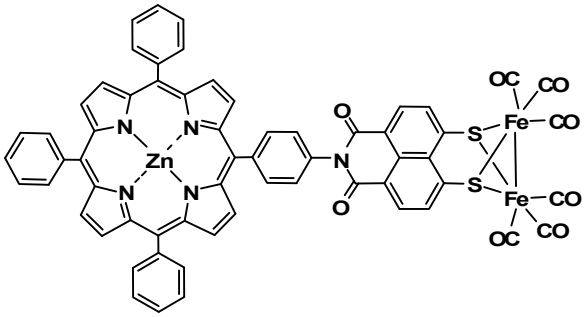
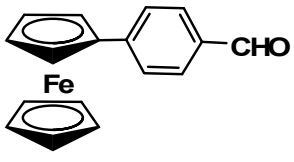
ZnTPP-[NMI-Fe^{I}-Fe^{I}-S$_2$(CO)$_6$] (dyad 3):



ZnTPP-NMIS$_2$ (0.050 g, 0.05 mmol) was added to a 100 ml round bottom flask with 60 ml of THF. Fe$_3$(CO)$_{12}$ (0.035 g, 0.07 mmol) was added to the flask and the reaction was refluxed for 2 hours. The solvent was removed by rotary evaporation and column chromatography was performed using CH_2Cl_2 as the eluent to provide ZnTPP-[NMI-Fe^{I}-Fe^{I}-S$_2$(CO)$_6$] in a 45% yield (0.029 g, 0.02 mmol). ^{1}H NMR δ ($CDCl_3$): 9.09 (d, J = 4.7 Hz, 2H), 8.98 (d, J = 4.7 Hz, 2H), 8.96 (s, 4H), 8.61 (d, J = 7.6 Hz, 2H), 8.54 (d, J = 7.6 Hz, 2H), 8.40 (d, J = 8.1 Hz, 2H), 8.23 (m, 6H), 7.78 (m, 9H), 7.68 (d, J = 8.1 Hz, 2H). ^{13}C NMR (125 MHz, δ $CDCl_3$): 206.74, 163.67, 150.25, 150.03, 143.50, 142.76, 135.64, 135.24, 134.48, 134.15, 133.23, 132.22, 132.07, 130.19, 129.71, 129.06, 128.25, 127.56, 126.77, 126.61, 126.58, 126.13, 125.31, 125.17,121.36, 121.29, 119.79, 66.30. ESI-HRMS: *m/z* 1219.9604 $[M+H]^+$, Calcd. 1219.0074 for $C_{62}H_{37}Fe_2N_2O_8S_2Zn$.

Fc-Ph-CHO:



p-Bromobenzaldehyde (0.518 g, 2.80 mmol) was added to a 100 ml round bottom flask with 50 ml of toluene. Sodium carbonate (4.759 g, 44.90 mmol), bis(triphenylphosphine)palladium(II)

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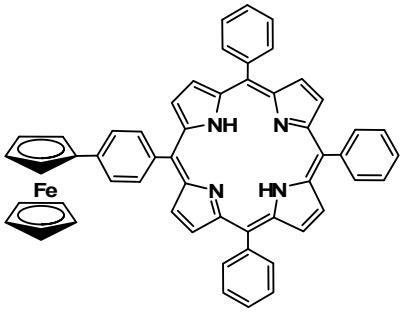
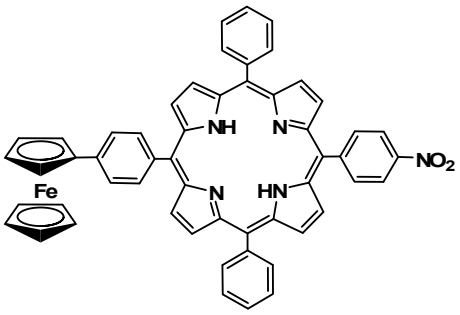
dichloride (0.060 g, 0.085 mmol) and ferroceneboronic acid (0.837 g, 3.64 mmol) were added and the reaction mixture was heated at 90 °C under N_2 for 16 hours. The solvent was removed by rotary evaporation and Fc-Ph-CHO (0.792 g, 2.73 mmol) was obtained in a 75% yield after column chromatography using CH_2Cl_2 as the eluent. ^{1}H NMR δ ($CDCl_3$): 9.97 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 4.74 (s, 2H), 4.44 (s, 2H), 4.05 (s, 5H). ESI-HRMS: *m/z* 290.040 $[M+H]^+$, Calcd. 290.039 for $C_{17}H_{14}FeO$.

Fc-TPP and Fc-TPP-NO_2:



Fc-TPP



Fc-TPP-NO_2

5-Phenyldipyrromethane (2.22 g, 10.0 mmol), Fc-Ph-CHO (1.450 g, 5.00 mmol), 4-nitrobenzaldehyde (0.755 g, 5.00 mmol) and 1000 ml of CH_2Cl_2 were added to a 2000 ml round bottom flask. Trifluoroacetic acid (1.37 ml, 17.80 mmol) was added slowly over 30 s. The reaction mixture was stirred at room temperature for 30 min. *N*,*N*-Diisopropylethylamine (3.00 ml, 18.00 mmol) was added followed by a solution of *p*-chloranil (3.700 g, 15.00 mmol) in THF (200 ml). The mixture was stirred at room temperature for an additional 6 hours. The solvent was removed by rotary evaporation and column chromatography using 50/50 (*v/v*) hexanes/CH_2Cl_2 as the eluent provided Fc-TPP (0.030 g, 0.07 mmol) in 2% yield. Fc-TPP-NO_2 (0.200 g, 0.07 mmol) was obtained using 30/70 (*v/v*) hexanes/CH_2Cl_2 as the eluent in 8% yield (overall yield). Fc-TPP: ^{1}H NMR δ ($CDCl_3$): 8.94 (d, *J* = 4.6 Hz, 2H), 8.87 (d, *J* = 4.6 Hz, 2H), 8.85 (s, 4H), 8.23 (m,

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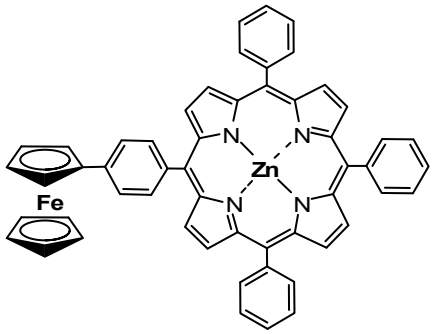
6H), 8.14 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.77 (m, 9H), 4.92 (t, 2H), 4.48 (t, 2H), 4.25 (s, 5H), –2.75 (s, 2H). MS (MALDI+): *m/z* 799.095 [M^+], Calcd. 798.244 for $C_{54}H_{38}FeN_4$.

Fc-TPP-NO_2 ^{1}H NMR δ ($CDCl_3$): 9.02-8.70 (m, 8H), 8.64 (d, *J* = 8.2 Hz, 2H), 8.41 (dd, *J* = 2.7 and 5.8 Hz, 2H), 8.23 (d, *J* = 6.4 Hz, 4H), 8.13 (d, *J* = 7.0 Hz, 2H), 7.86 (d, *J* = 7.7 Hz, 2H), 7.77 (m, 6H), 4.92 (s, 2H), 4.48 (s, 2H), 4.24 (s, 5H), –2.75 (s, 2H). MS (MALDI+): *m/z* 844.274 [M^+], Calcd. 843.229 for $C_{54}H_{37}FeN_5O_2$.

Fc-ZnTPP (dyad 4):



Fc-TPP (0.03 g, 0.04 mmol) and $CHCl_3$ (50 ml) were added to a 100 ml round bottom flask. $Zn(OAc)_2{\cdot}2H_2O$ (0.041 g, 0.19 mmol) dissolved in MeOH (15 ml) was added and the reaction was stirred for 2 hours. The reaction mixture was then washed with water and dried over sodium sulfate. Column chromatography using 30/70 (*v/v*) hexanes/CH_2Cl_2 as the eluent gave Fc-ZnTPP. (0.027 g, 0.03 mmol) in a 85% yield. ^{1}H NMR δ ($CDCl_3$): 9.04 (d, *J* = 4.6 Hz, 2H), 8.97 (d, *J* = 4.6 Hz, 2H), 8.95 (s, 4H), 8.23 (d, *J* = 7.6 Hz, 6H), 8.15 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 7.9 Hz, 2H), 7.76 (m, 9H), 4.93 (s, 2H), 4.48 (s, 2H), 4.25 (s, 5H). MS (MALDI+): *m/z* 860.609 [M^+], Calcd. 860.158 for $C_{54}H_{36}FeN_4Zn$.

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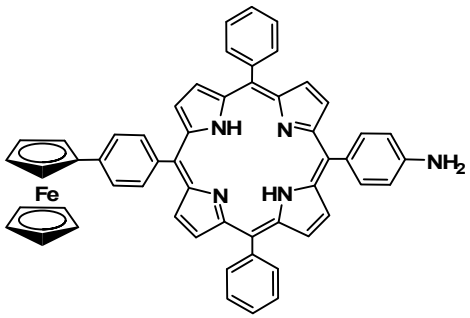
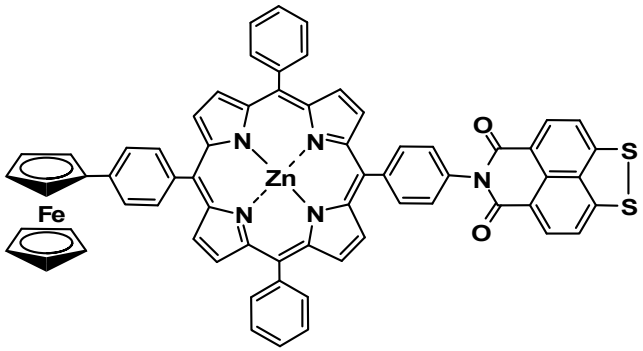
Fc-TPP-NH_2:



Fc-TPP-NO_2 (0.330 g, 0.39 mmol), concentrated HCl (20 mL) and $SnCl_2{\cdot}2H_2O$ (0.680 g, 3.00 mmol) were added to a 100 ml round bottom flask. The reaction was stirred at room temperature for 45 min and then heated at 65 °C for 30 min. The solution was cooled in ice and concentrated ammonia was added to neutralize the acid. Chloroform (500 mL) was added and the mixture was stirred for 1 hour. The layers were separated and the organic layer was washed twice with H_2O. The organic layer was dried over sodium sulfate and the solvent was removed by rotary evaporation. Fc-TPP-NH_2 (0.187 g, 0.23 mmol) was obtained in 65% yield after column chromatography using CH_2Cl_2 as the eluent. ^{1}H NMR δ ($CDCl_3$): 9.00-8.80 (m, 8H), 8.21 (d, J = 7.0 Hz, 2H), 8.13 (d, J = 7.8 Hz, 4H), 8.00 (d, J = 8.1 Hz, 6H), 7.84 (d, J = 8.1 Hz, 2H), 7.75 (m, 2H), 7. 07 (d, J = 8.0 Hz, 9H), 4.92 (s, 2H), 4.47 (s, 2H), 4.24 (d, J = 2.6 Hz , 5H), 4.04 (bs, 2H), –2.75 (s, 2H). MS (MALDI+): *m/z* 814.307 [M^+], Calcd. 813.255 for $C_{54}H_{39}FeN_5$.

Fc-ZnTPP-$NMIS_2$:



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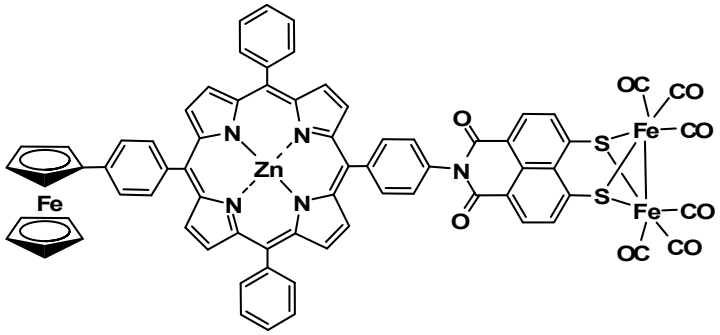
$NMAS_2$[1] (0.072 g, 0.26 mmol), Fc-TPP-NH_2 (0.150 g, 0.18 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.141 g, 0.64 mmol) and 40 mL of pyridine were added to a 100 ml round bottom flask and refluxed under N_2 for 72 hours. The solvent was removed by rotary evaporation and column chromatography was performed using CH_2Cl_2 as the eluent to provide Fc-ZnTPP-$NMIS_2$ in a 65% yield (0.134 g, 0.120 mmol). ^{1}H NMR δ ($CDCl_3$): 9.20-8.90 (m, 8H), 8.49 (m, 2H), 8.40 (d, *J* = 7.7 Hz, 2H), 8.25 (d, *J* = 6.0 Hz, 4H), 8.15 (m, 2H), 7.90-7.72 (m, 8H), 7.67 (d, *J* = 7.9 Hz, 2H), 7.45 (m, 2H), 4.91 (s, 2H), 4.46 (s, 2H), 4.24 (s, 5H). MS (MALDI+): *m/z* 1117.154 [M^+], Calcd. 1117.118 for $C_{66}H_{39}FeN_5O_2S_2Zn$.

Fc-ZnTPP-[NMI-Fe^I-Fe^I-$S_2(CO)_6$] (triad 1):



Fc-ZnTPP-$NMIS_2$ (0.100 g, 0.09 mmol) was added to a 100 ml round bottom flask with 60 ml of THF. $Fe_3(CO)_{12}$ (0.059 g, 0.12 mmol) was added to the flask and the reaction was refluxed for 2 hours. The solvent was removed by rotary evaporation and Fc-ZnTPP-[NMI-Fe^I-Fe^I-$S_2(CO)_6$] (0.056 g, 0.040 mmol) was obtained in a 45% yield after column chromatography using CH_2Cl_2 as the eluent. ^{1}H NMR δ ($CDCl_3$): 9.13-8.95 (m, 8H), 8.60 (dd, *J* = 2.2 and 5.2 Hz, 2H), 8.55 (dd, *J* = 2.3 and 5.2 Hz, 2H), 8.39 (d, *J* = 8.1 Hz, 2H), 8.25 (d, *J* = 6.3, 4H), 8.14 (m, 2H), 7.86-7.72 (m, 8H), 7.64 (d, *J* = 8.0 Hz, 2H), 4.89 (d, *J* = 5.6 Hz, 2H), 4.45 (s, 2H), 4.23 (d, *J* = 5.6 Hz, 5H). ^{13}C NMR (125 MHz, δ $CDCl_3$): 205.77, 162.56, 149.22, 142.43, 141.71, 139.24, 137.56, 134.56, 134.20, 133.56, 133.41, 135.05, 132.21, 131.18, 131.07, 129.15, 128.67, 126.50, 125.68,

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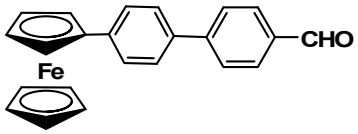
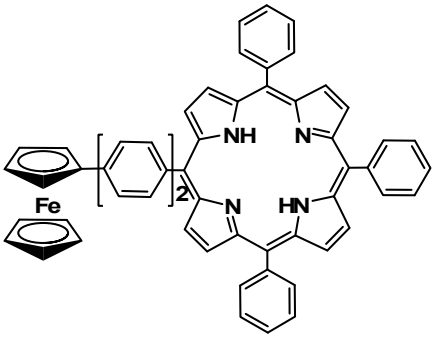
125.60, 125.06, 124.16, 123.20, 120.25, 118.69, 84.01, 68.81, 68.27, 65.75, 52.46. ESI-HRMS: *m/z* 1403.9567 $[M+H]^+$, Calcd. 1403.0049 for $C_{72}H_{45}Fe_3N_5O_8S_2Zn$.

Fc-Ph$_2$-CHO:

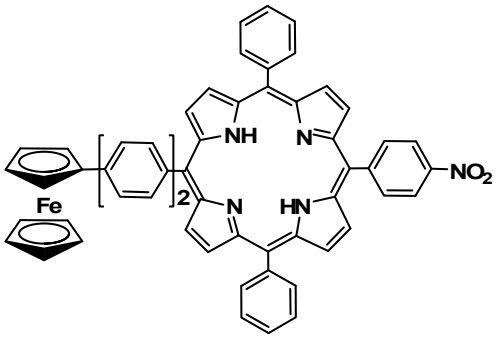


4-Formylbenzeneboronic acid (1.770 g, 11.80 mmol)**,** Fc-Ph-I (2.250 g, 5.80 mmol), $Ba(OH)_2$ (2.586 g, 8.20 mmol) and palladium(II)acetate (0.440 g, 1.96 mmol) were combined in a 100 ml round bottom flask with DMF (50 ml). The reaction mixture was refluxed under N_2 for 48 hours. The solvent was removed by rotary evaporation and Fc-Ph$_2$-CHO (1.276 g, 3.49 mmol) was obtained in a 60% yield after column chromatography using 40/60 (*v/v*) hexanes/CH_2Cl_2 as the eluent. ^{1}H NMR δ ($CDCl_3$): 10.08 (s, 1H), 7.98 (d, *J* = 7.0 Hz, 2H), 7.80 (d, *J* = 7.0 Hz, 2H), 7.59 (s, 4H), 4.77 (s, 2H), 4.43 (s, 2H), 4.13 (s, 5H). ESI-HRMS: *m/z* 366.073 $[M+H]^+$, Calcd. 366.070 for $C_{23}H_{18}FeO$.

Fc-Ph-TPP and Fc-Ph-TPP-NO$_2$:



Fc-Ph-TPP



Fc-Ph-TPP-NO$_2$

5-Phenyldipyrromethane (2.220 g, 10.0 mmol), Fc-Ph$_2$-CHO (1.830 g, 5.0 mmol), 4-nitrobenzaldehyde (0.755 g, 5.00 mmol) and 1000 ml of CH_2Cl_2 were added to a 2000 ml round bottom flask. Trifluoroacetic acid (1.37 ml, 17.80 mmol) was added slowly over 30 s. The

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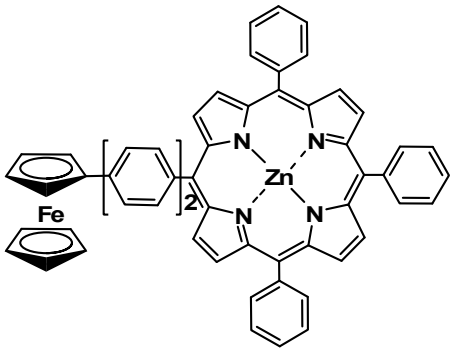
reaction mixture was stirred at room temperature for 30 min. *N*,*N*-Diisopropylethylamine (3.00 ml, 18.00 mmol) was added followed by a solution of *p*-chloranil (3.700 g, 15.00 mmol) in THF (200 ml). The mixture was stirred at room temperature for further 6 hours. The solvent was removed by rotary evaporation and column chromatography using 50/50 (*v*/*v*) hexanes/CH_2Cl_2 as the eluent provided Fc-Ph-TPP (0.030 g, 0.03 mmol) in 2% yield. Fc-Ph-TPP-NO_2 (0.200 g, 0.07 mmol) was obtained using 30/70 (*v*/*v*) hexanes/CH_2Cl_2 as the eluent in 8% yield (overall yield). Fc-Ph-TPP: ^{1}H NMR δ ($CDCl_3$): 8.95 (d, *J* = 4.7 Hz, 2H), 8.87 (d, *J* = 4.7 Hz, 2H), 8.86 (s, 4H), 8.29 (d, *J* = 8.1 Hz, 2H), 8.23 (d, *J* = 7.8 Hz, 6H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.76 (m, 9H), 7.69 (d, *J* = 8.1 Hz, 2H), 4.77 (s, 2H), 4.40 (s, 2H), 4.13 (s, 5H), –2.73 (s, 2H). MS (MALDI+): *m/z* 875.237 [M^+], Calcd. 874.275 for $C_{60}H_{42}FeN_4$. Fc-Ph-TPP-NO_2: ^{1}H NMR δ ($CDCl_3$): 9.00-8.70 (m, 8H), 8.60 (d, *J* = 8.5 Hz, 2H), 8.37 (dd, *J* = 2.3 and 6.1 Hz, 2H), 8.25 (d, *J* = 7.7 Hz, 2H), 8.22 (d, *J* = 6.4 Hz, 4H), 7.97 (d, *J* = 7.7 Hz, 2H), 7.78 (m, 8H), 7.65 (d, *J* = 8.0 Hz, 2H), 4.74 (s, 2H), 4.38 (s, 2H), 4.11 (s, 5H), –2.75 (bs, 2H). MS (MALDI+): *m/z* 920.012 [M^+], Calcd. 919.260 for $C_{60}H_{41}FeN_5O_2$.

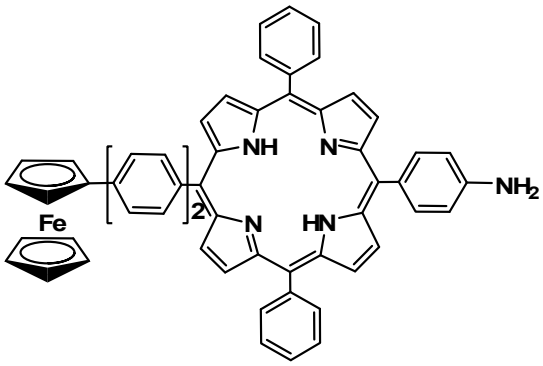
Fc-Ph-ZnTPP (dyad 5):



Fc-Ph-TPP (0.035 g, 0.04 mmol) and $CHCl_3$ (50 ml) were added to a 100 ml round bottom flask. $Zn(OAc)_2{\cdot}2H_2O$ (0.041 mg, 0.19 mmol) dissolved in MeOH (15 ml) was added and the solution was stirred for 2 hours. The solution was then washed with water and dried over sodium sulfate.

Column chromatography using 30/70 (*v/v*) hexanes/CH_2Cl_2 as the eluent gave Fc-Ph-ZnTPP. (0.071 g, 0.07 mmol) in a 52% yield. ^{1}H NMR δ ($CDCl_3$): 9.04 (d, *J* = 4.5 Hz, 2H), 8.97 (d, *J* = 4.7 Hz, 2H), 8.95 (s, 4H), 8.30 (d, *J* = 7.9 Hz, 2H), 8.23 (d, *J* = 7.4 Hz, 6H), 8.02 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 7.76 (m, 9H), 7.68 (d, *J* = 8.1 Hz, 2H), 4.77 (s, 2H), 4.39 (s, 2H), 4.13 (s, 5H). MS (MALDI+): *m/z* 936.342 [M^+], Calcd. 936.189 for $C_{60}H_{40}FeN_4Zn$.

Fc-Ph-TPP-NH_2:



Fc-Ph-TPP-NO_2 (0.359 g, 0.39 mmol), concentrated HCl (20 mL) and $SnCl_2{\cdot}2H_2O$ (0.680 g, 3.00 mmol) were added to a 100 ml flask. The reaction was stirred at room temperature for 45 min and then heated at 65 °C for 30 min. The solution was cooled in ice and concentrated ammonia was added to neutralize the acid. Chloroform (500 mL) was added and the mixture was stirred for 1 hour. The layers were separated and the organic layer was washed twice with H_2O. The organic layer was dried over sodium sulfate and the solvent was removed by rotary evaporation. Fc-Ph-TPP-NH_2 (0.226 g, 0.25 mmol) was obtained in 65% yield after column chromatography using CH_2Cl_2 as the eluent. ^{1}H NMR δ ($CDCl_3$): 9.00-8.80 (m, 8H), 8.29 (dd, *J* = 1.7 and 6.5 Hz, 2H), 8.23 (m, 4H), 8.01 (m, 4H), 7.86 (dd, *J* = 1.7 and 6.5 Hz, 2H), 7.76 (m, 6H), 7.70 (dd, *J* = 1.5 and 6.7 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 4.77 (s, 2H), 4.40 (s, 2H), 4.13 (d, *J* = 1.3 Hz, 5H), 4.04 (bs, 2H), –2.73 (s, 2H). MS (MALDI+): *m/z* 890.496 [M^+], Calcd. 889.286 for $C_{60}H_{43}FeN_5$.

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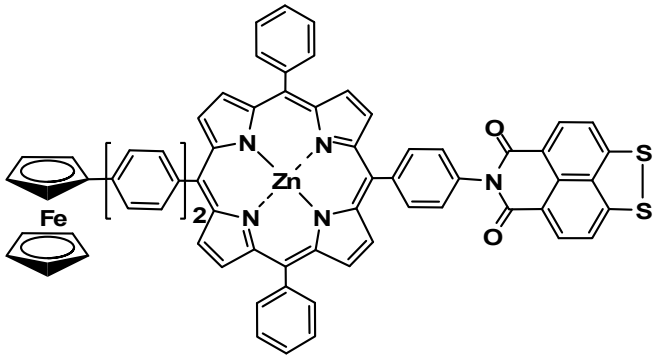
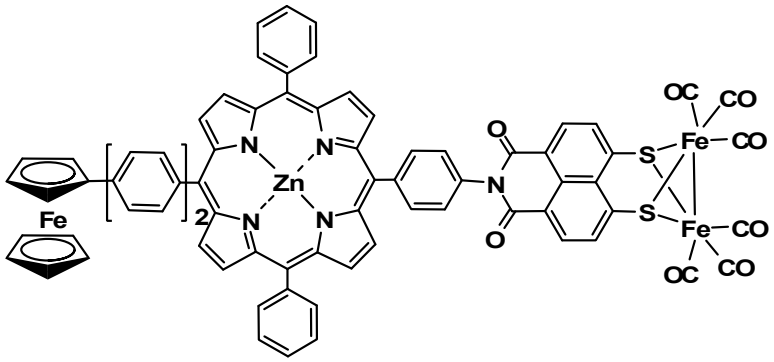
Fc-Ph-ZnTPP-NMIS$_2$:



$NMAS_2$ (0.072 g, 0.22 mmol), Fc-Ph-TPP-NH_2 (0.160 g, 0.18 mmol), $Zn(OAc)_2{\cdot}2H_2O$ (0.141 g, 0.64 mmol) and 40 mL of pyridine were added to a 100 ml round bottom flask and refluxed under N_2 for 72 hours. The solvent was removed by rotary evaporation and column chromatography CH_2Cl_2 as the eluent gave Fc-Ph-ZnTPP-$NMIS_2$ (0.145 g, 0.12 mmol) in a 70% yield. ^{1}H NMR δ ($CDCl_3$): 9.18-8.92 (m, 8H), 8.61 (d, *J* = 8.0 Hz, 2H), 8.41 (d, *J* = 7.9 Hz, 2H), 8.31 (d, 7.7 Hz, 2H), 8.24 (d, *J* = 6.6 Hz, 4H), 8.04 (d, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 7.0 Hz, 2H), 7.78 (m, 6H), 7.70 (d, *J* = 7.9 Hz, 4H), 7.60 (d, *J* = 7.9 Hz, 2H), 4.80 (s, 2H), 4.42 (s, 2H), 4.16 (s, 5H). MS (MALDI+): *m/z* 1193.404 [M^+], Calcd. 1193.149 for $C_{72}H_{43}FeN_5O_2S_2Zn$.

Fc-Ph$_2$-ZnTPP-[NMI-Fe^I-Fe^I-S$_2$(CO)$_6$] (triad 2):



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Fc-Ph-ZnTPP-$NMIS_2$ (0.107 g, 0.09 mmol) was added to a 100 ml round bottom flask with 60 ml of THF. $Fe_3(CO)_{12}$ (0.059 g, 0.12 mmol) was added to the flask and the reaction was refluxed for 2 hours. The solvent was removed by rotary evaporation and Fc-Ph-ZnTPP-[NMI-Fe^{I}-Fe^{I}-$S_2(CO)_6$] (0.066 g, 0.045 mmol) was obtained in a 50% yield after column chromatography using CH_2Cl_2 as the eluent. ^{1}H NMR δ ($CDCl_3$): 9.14-8.93 (m, 8H), 8.61 (d, *J* = 7.6 Hz, 2H), 8.54 (d, *J* = 7.6 Hz, 2H), 8.40 (dd, *J* = 2.3 and 6.0 Hz, 2H), 8.31 (m, 4H), 8.24 (m, 2H), 8.03 (m, 2H), 7.88 (m, 2H), 7.78 (m, 6H), 7.69 (m, 4H), 4.78 (m, 2H), 4.40 (m, 2H), 4.14 (d, J = 2.3 Hz, 5H). ^{13}C NMR (125 MHz, δ $CDCl_3$): 206.73, 163.63, 150.23, 143.46, 142.73, 141.55, 139.81, 138.78, 138.12, 135.61, 135.21, 135.00, 134.11, 133.19, 132.15, 130.15, 129.67, 127.54, 127.17, 126.64, 126.09, 125.13, 124.83, 38.81, 121.34, 121.05, 119.78, 84.88, 69.71, 69.13, 66.55. ESI-HRMS: *m/z* 1479.9858 $[M+H]^+$, Calcd. 1479.0368 for $C_{78}H_{49}Fe_3N_5O_8S_2Zn$.

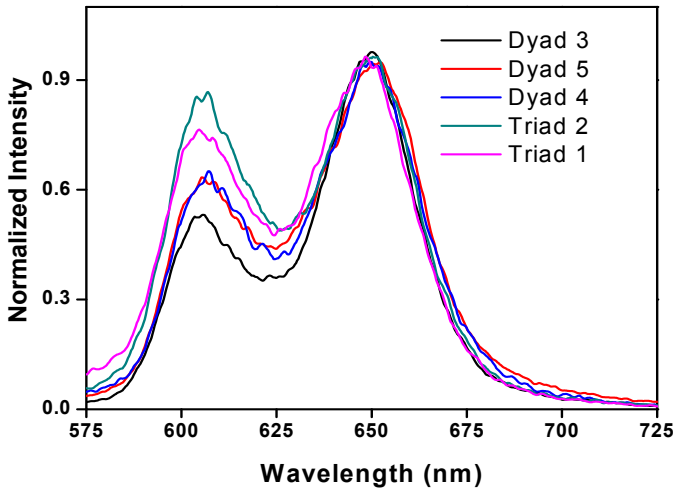

Figure S1. Normalized steady-state fluorescence spectra in CH_2Cl_2, λ_{ex} = 530 nm.

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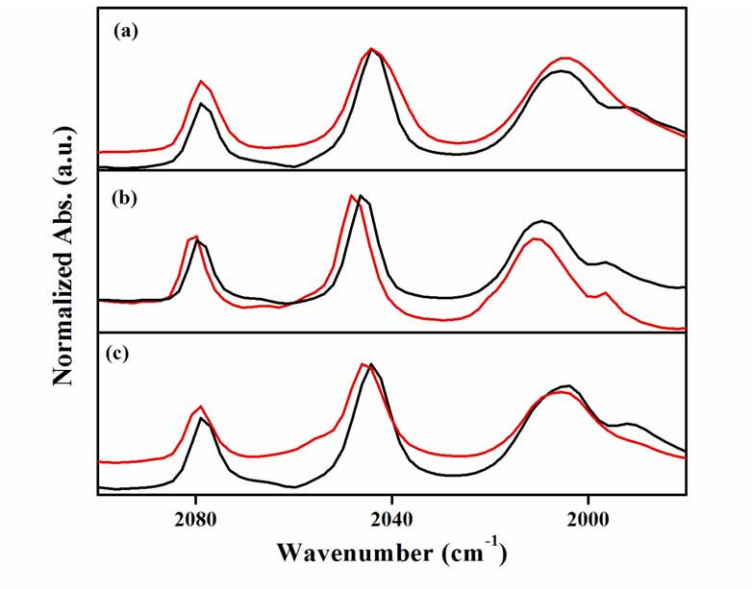

Figure S2. IR spectra of (a) **3**, (b) **1** and (c) **2** in toluene (black) and CH_2Cl_2 (red).

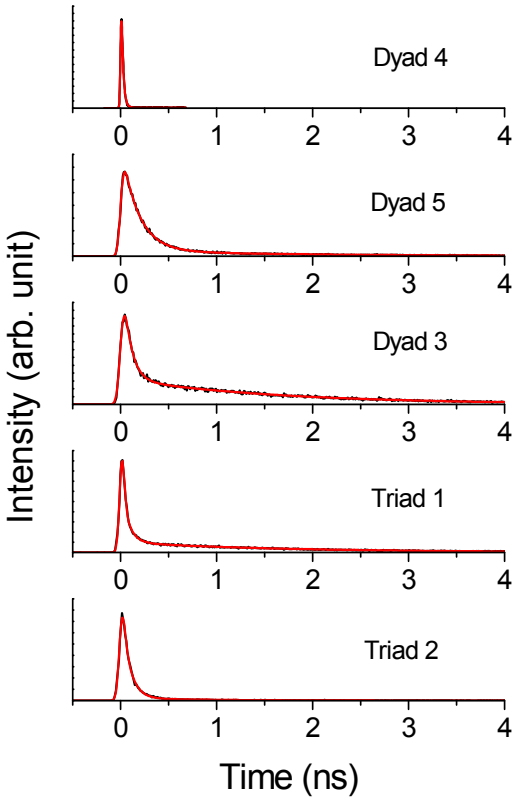

Figure S3. Time-resolved fluorescence signals (data: black curves, fits: red curves) in CH_2Cl_2. Detection wavelength was 650 nm.

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References:

1. M. Tesmer and H. Vahrenkamp, *Eur. J. Inorg. Chem.*, 2001, 1183-1188.

2. J. P. Collman, J. I. Brauman, K. M. Doxsee, T. R. Halbert, E. Bunnenberg, R. E. Linder, G. N. Lamar, J. Delgaudio, G. Lang and K. Spartalian, *J. Am. Chem. Soc.*, 1980, **102**, 4182-4192.

3. J. T. Landrum, D. Grimmett, K. J. Haller, W. R. Scheidt and C. A. Reed, *J. Am. Chem. Soc.*, 1981, **103**, 2640-2650.

4. F. A. Walker and M. Benson, *J. Am. Chem. Soc.*, 1980, **102**, 5530-5538.

5. B. J. Littler, M. A. Miller, C. H. Hung, R. W. Wagner, D. F. O'Shea, P. D. Boyle and J. S. Lindsey, *J. Org. Chem.*, 1999, **64**, 1391-1396.

6. F. D'Souza, P. M. Smith, S. Gadde, A. L. McCarty, M. J. Kullman, M. E. Zandler, M. Itou, Y. Araki and O. Ito, *J. Phys. Chem. B*, 2004, **108**, 11333-11343.