Achiral Endohedral Functionality Provides Stereochemical Control in Fe(II)-Based Self-Assemblies

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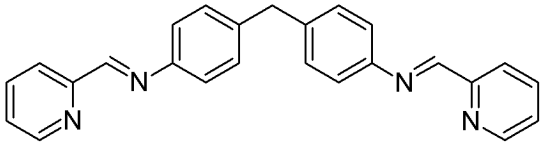
Electronic Supplementary Information

1. General Information

^{1}H and ^{13}C spectra were recorded on a Varian Inova 400 MHz or Varian Inova 500 MHz NMR spectrometer. DOSY spectra were recorded on a Bruker Avance 600 MHz spectrometer. Proton (^{1}H) chemical shifts are reported in parts per million (δ) with respect to tetramethylsilane (TMS, δ=0), and referenced internally with respect to the protio solvent impurity. Deuterated NMR solvents were obtained from Cambridge Isotope Laboratories, Inc., Andover, MA, and used without further purification. Mass spectra were recorded on an Agilent 6210 LC TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 v and processed with an Agilent MassHunter Operating System. All other materials were obtained from Aldrich Chemical Company, St. Louis, MO, or TCI, Tokyo, Japan and were used as received. Solvents were dried through a commercial solvent purification system (Pure Process Technologies, Inc.). Molecular modeling (semi-empirical calculations) was performed using the AM1 force field using SPARTAN.[1]

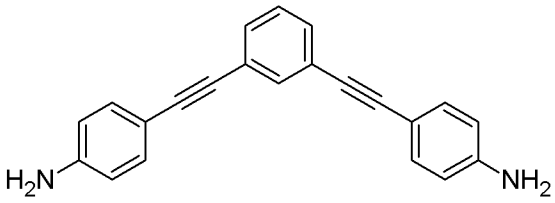
2. Synthesis of Compounds



4,4'-Methylene-bis[N-(2-pyridinylmethylene)benzenamine (7):

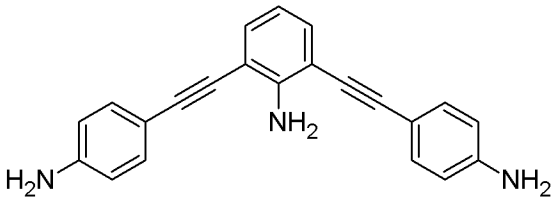
4,4'-diaminodiphenylmethane (512 mg, 2.58 mmol) and 2-pyridinecarboxaldehyde (500 μL, 5.27 mmol) were combined in a 50 mL Erlenmeyer flask with stir bar. MeOH (25 mL) was added, followed by stirring for 24 h, after which point a precipitate was filtered. The crude

product was rinsed with hexanes (25 mL) and dried to give a cream solid (712 mg, 73%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.73 (dq, *J* = 4.8, 0.8 Hz, 2H), 8.65 (s, 2H), 8.22 (d, *J* = 7.8 Hz, 2H), 7.82 (td, *J* = 7.8, 1.1 Hz, 2H), 7.38 (ddd, *J* = 7.8, 4.8, 1.1 Hz, 2H), 7.29 (s, 8H), 4.07 (s, 2H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.1, 154.8, 149.8, 149.1, 139.9, 136.8, 129.9, 125.1, 122.0, 121.5, 41.2. HRMS (ESI) m/z calcd for $C_{25}H_{20}N_4$ ($[M+H]^+$) 377.1760, found 377.1719.



1,3-Bis[(4-aminophenyl)ethynyl]benzene (A):

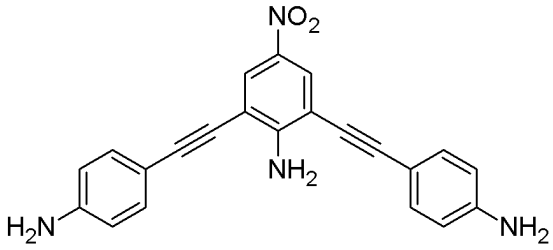
m-Diiodobenzene (500 mg, 1.52 mmol) was combined with 4-ethynylaniline (443 mg, 3.78 mmol), [1,1′-Bis-(diphenylphosphino)ferrocene] dichloropalladium(II) complexed with CH_2Cl_2 (62 mg, 76 μmol), and copper iodide (14 mg, 74 μmol) in a 25 mL round-bottomed flask with attached reflux condenser. The system was purged using a Schlenk line. Anhydrous iPr_2NH (2 mL) and anhydrous PhMe (8 mL) were added, followed by three additional purge cycles. The reaction was then heated to 100°C for 48 h. After cooling, the reaction was diluted with Et_2O (250 mL) and filtered through celite. The solvent was then evaporated *in vacuo*. The residue from this was purified by column chromatography (SiO_2; hexanes/ethyl acetate 3:1 + 1% Et_3N to hexanes/ethyl acetate 1:1 + 1% Et_3N). Collection of fractions and evaporation of solvent *in vacuo* gave product as a dull yellow solid (132 mg, 28%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.63 (s, 1H), 7.39 (dd, *J* = 7.5, 1.1 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 4H), 7.28 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.6 Hz, 4H), 3.82 (br, 4H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 146.9, 134.2, 133.2, 130.6, 128.4, 124.3, 114.9, 90.7, 86.9. HRMS (ESI) m/z calcd for $C_{22}H_{16}N_2$ ($[M+H]^+$) 309.1386, found 309.1389.



2,6-Bis[(4-aminophenyl)ethynyl)]aniline (B):

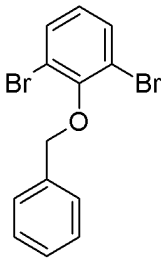
2,6-Dibromoaniline (380 mg, 1.51 mmol), 4-ethynylaniline (443 mg, 3.78 mmol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane (62 mg,

76 μmol), and copper iodide (14 mg, 74 μmol) were combined in a 25 mL round-bottomed flask with attached reflux condenser. The system was purged using a Schlenk line. Anhydrous iPr_2NH (2 mL) and anhydrous PhMe (8 mL) were added, followed by three additional purge cycles. The reaction was then heated to 100°C for 48 h. After cooling, the reaction was diluted with Et_2O (250 mL) and filtered through celite. The solvent was then evaporated *in vacuo*. The residue from this was purified by column chromatography (SiO_2; hexanes/ethyl acetate 3:1 + 1% Et_3N to hexanes/ethyl acetate 1:1 + 1% Et_3N). Collection of fractions and evaporation of solvent *in vacuo* gave product as an orange solid (102 mg, 21%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 4H), 7.28 (d, *J* = 7.5 Hz, 2H), 6.65 (t, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.4 Hz, 4H), , 4.86 (br, 2H), 3.83 (br, 4H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 148.7, 146.8, 133.0, 131.8, 117.3, 114.9, 112.7, 108.2, 95.7, 83.5. HRMS (ESI) m/z calcd for $C_{22}H_{17}N_3$ ($[M^{\bullet}]^+$) 323.1417, found 323.1427.



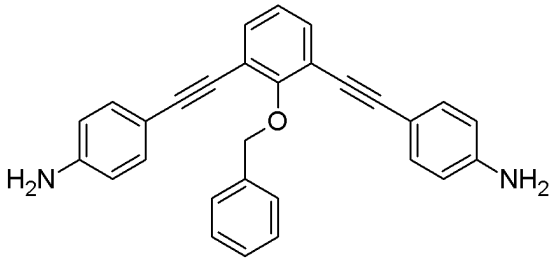
2,6-Bis[(4-aminophenyl)ethynyl]4-nitroaniline (C):

To a 2-neck 25 mL round-bottom flask equipped with a stir bar and reflux condenser was added 2,6-diiodo-4-nitroaniline (100 mg, 25 mmol), 4-ethynylaniline (58 mg, 50 mmol), bis(triphenylphosphino)dichloropalladium(II) (17.5 mg 2.5 mmol) and copper iodide (2.5 mg 1.3 mmol). The mixture was placed under nitrogen and anhydrous iPr_2NH (5 mL) was added. The reaction was stirred at room temperature for 40 h. The solvent was removed by rotary evaporation and the remaining solid was dissolved in a mixture of methylene chloride and methanol. The mixture was then filtered through celite and the solvent from the filtrate was removed by rotary evaporation. The product was recrystallized from methylene chloride twice to give an orange powder (32 mg, 33% yield). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.19 (s, 2H), 7.34 (d, *J* = 8.6 Hz, 4H), 6.66 (d, *J* = 8.6 Hz, 4H), 5.53 (br, 2H), 3.91 (br, 4H); ^{1}H NMR (400 MHz; DMSO-d_6) δ= 8.00 (s, 2H), 7.34 (d, *J* = 8.6 Hz, 4H), 6.68 (br, 2H), 6.57 (d, *J* = 8.6 Hz, 4H), 5.64 (br, 4H). ^{13}C NMR (100 MHz; DMSO-d_6) δ 153.4, 149.8, 136.1, 133.0, 126.5, 113.4, 107.5, 107.0, 98.0, 81.1. HRMS (ESI) m/z calcd for $C_{22}H_{16}N_4O_2$ ($[M+H]^+$) 369.1346, found 369.1382.



Benzyl 2,6-Dibromophenyl Ether (*S-1*):

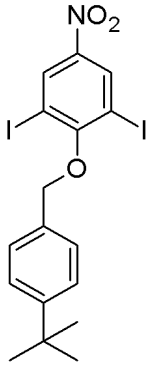
2,6-Dibromophenol (580 mg, 2.3 mmol), benzyl bromide (274 μL, 2.3 mmol), potassium carbonate (479 mg, 3.47 mmol), and sodium iodide (33 mg, 0.22 mmol) were combined in a 25 mL round-bottomed flask with attached reflux condenser. MeCN (7 mL) was added, and reaction was heated under reflux for 16 h. After cooling, water was added, followed by extraction with Et_2O. The combined organic fractions were washed with brine, dried over $MgSO_4$, followed by evaporation of solvent *in vacuo*. The crude product was then filtered through a silica plug with hexanes to yield a white solid (645 mg, 82%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.61 (d, *J* = 7.2 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.44-7.35 (m, 3H), 6.90 (t, *J* = 8.0 Hz, 1H), 5.04 (s, 2H) . ^{13}C NMR (100 MHz; $CDCl_3$) δ 153.0, 136.4, 132.9, 128.6, 128.5, 126.6, 118.9, 74.7 (two resonances are overlapping). HRMS (ESI) m/z calcd for $C_{13}H_{14}Br_2NO$ ($[M+NH_4]^+$) 359.9417, found 359.9432.



O-Benzyl 2,6-bis[(4-aminophenyl)ethynyl]phenol (D):

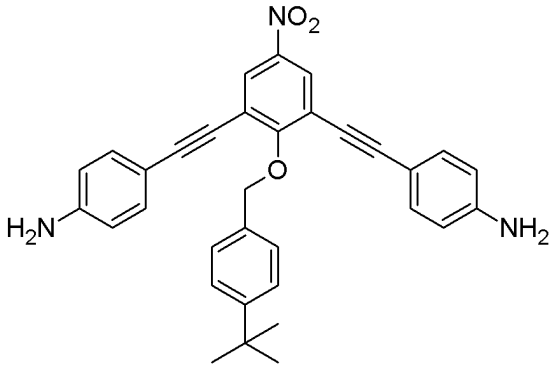
S-1 (250 mg, 0.73 mmol), 4-ethynylaniline (214 mg, 1.83 mmol), bis(triphenylphosphino)dichloropalladium(II) (60 mg, 0.09 mmol), and copper iodide (14 mg, 0.07 mmol) were combined in a 25 mL round-bottomed flask with attached reflux condenser. The system was purged using a Schlenk line. Anhydrous iPr_2NH (8 mL) and anhydrous THF (8 mL) were added, followed by three additional purge cycles. The reaction was then heated under reflux for 72 h. After cooling, the reaction was diluted with Et_2O (400 mL) and filtered through celite. The solvent was then evaporated *in vacuo*. The residue from this was triturated in 3 M aqueous KOH (20 mL) in an ultrasonication bath, followed by filtration and drying. The solid

was purified by column chromatography (SiO_2; hexanes/ethyl acetate 3:1 + 1% Et_3N to hexanes/ethyl acetate 1:1 + 1% Et_3N). Collection of fractions and evaporation of solvent *in vacuo* gave product as a light orange solid (32 mg, 10%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.32 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.04 (t, *J* = 7.7 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 4H), 5.34 (s, 2H), 3.83 (br, 4H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 160.1, 146.9, 137.7, 133.1, 132.7, 128.6, 128.5, 128.0, 123.8, 118.7, 114.9, 112.7, 94.9, 83.7, 75.6. HRMS (ESI) m/z calcd for $C_{29}H_{22}N_2O$ ($[M+Na]^+$) 437.1624, found 437.1646.



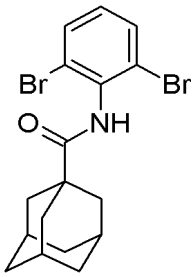
4-(t-Butyl)benzyl 2,6-Diiodo-4-nitrophenyl Ether (*S-2*):

2,6-Diiodo-4-nitrophenol (640 mg, 1.64 mmol), 4-(t-butyl) benzyl bromide (300 µL, 1.64 mmol), and potassium carbonate (283 mg, 2.05 mmol) were combined in a 25 mL round-bottomed flask with attached reflux condenser. MeCN (10 mL) was added, and reaction was heated under refluxed for 24 h. After cooling, water (100 mL) was added, followed by extraction with CH_2Cl_2 (3 x 50 mL). The combined organic fractions were dried over $MgSO_4$, followed by evaporation of solvent *in vacuo* to give a faint yellow solid (708 mg, 80%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.69 (s, 2H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 5.06 (s, 2H), 1.37 (s, 9H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 162.9, 152.1, 144.8, 135.2, 132.2, 128.6, 125.7, 90.6, 75.0, 34.8, 31.5. HRMS (ESI) m/z calcd for $C_{17}H_{17}I_2NO_3$ ($[M]^{\bullet+}$) 536.9292, found 536.9290.



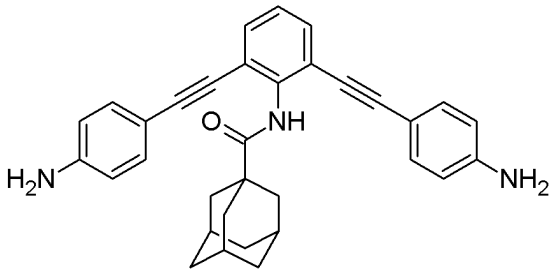
O-4-(t-Butyl)benzyl Bis[(4-aminophenyl)ethynyl]4-nitrophenol (E):

S-2 (638 mg, 1.19 mmol), 4-ethynylaniline (348 mg, 2.97 mmol), bis(triphenylphosphino)dichloropalladium(II) (42 mg, 0.06 μmol), and copper iodide (12 mg, 0.06 μmol) were combined in a 50 mL round-bottomed flask with attached reflux condenser. The system was purged using a Schlenk line. Anhydrous iPr_2NH (10 mL) and anhydrous PhMe (10 mL) were added, followed by three additional purge cycles. The reaction was then heated under reflux for 68 h. After cooling, the solvent was diluted with Et_2O (200 mL), followed by filtering through celite. The solvent was then removed *in vacuo*. The residue was dissolved in EtOAc (10 mL), followed by addition of hexanes (90 mL) to give a precipitate. The mixture was filtered through celite and rinsed with additional hexanes (100 mL), causing new precipitate to form. The fine solid was filtered through celite, rinsed with hexanes (50 mL), then washed off of the celite with EtOAc (50 mL). Solvent was removed *in vacuo* to give product as an orange solid (264 mg, 41%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 8.23 (s, 2H), 7.52 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.4 Hz, 4H), 6.63 (d, J = 8.4 Hz, 4H), 5.48 (s, 2H), 3.71 (br, 2H), 1.33 (s, 9H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 164.5, 151.4, 147.5, 143.1, 133.8, 133.3, 128.3, 127.3, 125.5, 119.3, 114.8, 111.6, 97.3, 82.3, 75.7, 34.7, 31.5. HRMS (ESI) m/z calcd for $C_{33}H_{29}N_3O_3$ ($[M+H]^+$) 516.2281, found 516.2354.



1-(N-(2,6-Dibromophenyl))Adamantane Carboxamide (*S-3*):

2,6-Dibromoaniline (250 mg, 1.0 mmol) and 1-adamantanecarboxylic acid chloride (160 mg, 0.81 mmol) were combined in a 10 mL round-bottomed flask with attached reflux condenser. System was purged using a Schlenk line, followed by addition of anhydrous PhMe (5 mL). Reaction was heated under reflux for 28 h, followed by cooling and then evaporating the solvent *in vacuo*. The residue was then recrystallized from 95% EtOH to give the product as a white powder (103 mg, 31%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 2H), 7.21 (br, 1H), 6.99 (t, *J* = 8.1 Hz, 1H), 2.10 (s, 3H), 2.05 (s, 6H), 1.77 (s, 6H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 175.6, 135.1, 132.3, 129.3, 124.0, 41.6, 39.3, 36.6, 28.3. HRMS (ESI) m/z calcd for $C_{17}H_{19}Br_2NO$ ($[M+H]^+$) 411.9906, found 411.9913.



N-(2,6-bis[(4-aminophenyl)ethynyl]phenyl)adamantanecarboxamide (F):

S-3 (103 mg, 0.25 mmol), 4-ethynylaniline (73 mg, 0.62 mmol), bis(triphenylphosphino)dichloropalladium(II) (18 mg, 0.03 μmols), and copper iodide (5 mg, 0.03 μmols) were combined in a 25 mL round-bottomed flask with attached reflux condenser. The system was purged using a Schlenk line. Anhydrous iPr_2NH (5 mL) and anhydrous PhMe (10 mL) were added, followed by three additional purge cycles. The reaction was then heated under reflux for 72 h. After cooling, the reaction was filtered through celite, followed by removal of solvent *in vacuo*. The residue was then purified by column chromatography (SiO_2; hexanes/ethyl acetate 2:1 + 1% Et_3N to hexanes/ethyl acetate 1:1 + 1% Et_3N) to give the product as a light orange solid (17 mg, 14%). ^{1}H NMR (400 MHz; $CDCl_3$) δ 7.56 (br, 1H), 7.45 (d, *J* = Hz, 2H), 7.30 (d, *J* = Hz, 4H), 7.15 (t, *J* = Hz, 1H), 6.62 (d, *J* = Hz, 4H), 3.87 (br, 4H), 2.07 (s,

9H), 1.75 (s, 6 H). ^{13}C NMR (100 MHz; $CDCl_3$) δ 175.5, 146.9, 138.8, 133.1, 131.8, 125.9, 121.5, 114.9, 112.6, 95.5, 84.3, 41.6, 39.7, 36.7, 28.4. HRMS (ESI) m/z calcd for $C_{33}H_{31}N_3O$ ($[M+H]^+$) 486.2539, found 486.2609.

Complex Formation

7_3·Fe_2·$(ClO_4)_4$ (Method A):

7 (25.0 mg, 66.0 μmol) and $Fe(ClO_4)_2$•xH_2O (17.2 mg) were combined in anhydrous MeCN (10 mL) in a 25 mL round-bottomed flask under a blanket of N_2, followed by submerging in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (200 mL), followed by filtration of the resulting precipitate. After drying, product was isolated as a purple solid (35.5 mg, 98%).

7_3·Fe_2·$(ClO_4)_4$ (Method B):

4,4'-Diaminodiphenylmethane (66 mg, 330 μmol) and 2-pyridinecarboxaldehyde (59 μL, 670 μmol) were combined in anhydrous MeCN (2 mL) in a 10 mL round-bottomed flask under a blanket of N_2. To this solution was added $Fe(ClO_4)_2$•xH_2O (122 mg). The mixture was then submerged in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (14 mL), and cooled to -25°C. This gave a fine precipitate which was collected by centrifugation to give a purple solid (183 mg, 82%). ^{1}H NMR (400 MHz; CD_3CN) δ 8.93 (s, 2H), 8.56 (d, *J* = 7.7 Hz, 2H), 8.37 (t, *J* = 7.7 Hz, 2H), 7.75 (t, *J* = 6.7 Hz, 2H), 7.35 (d, *J* = 5.2 Hz, 2H), 6.94 (br s, 4H), 5.52 (br s, 4H), 4.01 (s, 2H).

1_3·Fe_2·$(ClO_4)_4$:

A (3.9 mg, 13 μmol) and 2-pyridinecarboxaldehyde (2.5 μL, 26 μmol) were combined in anhydrous MeCN (1 mL) in a 10 mL round-bottomed flask under a blanket of N_2. To this solution was added $Fe(ClO_4)_2$•xH_2O (3.0 mg). The mixture was then submerged in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (14 mL), and cooled to -25°C. This gave a fine precipitate which was collected by centrifugation to give a purple solid (7.5 mg, 90%). ^{1}H NMR (500 MHz; CD_3CN) δ 8.93 (s, 2H), 8.54 (d, *J* = 7.5 Hz, 2H), 8.39 (t, *J* = 7.72 Hz, 2H), 7.85 (s, 1H), 7.79 (t, *J* = 6.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 2H),

7.45 (m, 7H), 5.33 (d, *J* = 8.2 Hz, 4H). HRMS (ESI) m/z calcd for $C_{102}H_{66}Cl_4Fe_2N_{12}O_{16}$ ($[M+2H]^{2+}$) 984.1159, found 984.1167.

2_3·Fe_2·$(ClO_4)_4$:

B (8.5 mg, 26 μmol) and 2-pyridinecarboxaldehyde (5.5 μL, 58 μmol) were combined in anhydrous MeCN (1 mL) in a 10 mL round-bottomed flask under a blanket of N_2. To this solution was added $Fe(ClO_4)_2$•xH_2O (7.1 mg). The mixture was then submerged in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (14 mL), and cooled to -25°C. This gave a fine precipitate which was collected by centrifugation to give a purple solid (49.2 mg, 94%). ^{1}H NMR (400 MHz; CD_3CN) δ 8.89 (s, 2H), 8.52 (d, *J* = 7.6 Hz, 2H), 8.39 (t, *J* = 7.6 Hz, 2H), 7.77 (t, *J* = 6.1 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 4H), 7.38 (m, 4H), 6.71 (t, *J* = 7.6 Hz, 1H), 5.47 (br, 2H), 5.31 (d, *J* = 8.4 Hz, 4H). HRMS (ESI) m/z calcd for $C_{102}H_{69}Cl_4Fe_2N_{15}O_{16}$ ($[M-3(ClO_4)]^{3+}$) 571.4676, found 571.4686.

3_3·Fe_2·$(ClO_4)_4$:

C (10.6 mg, 29 μmol) and 2-pyridinecarboxaldehyde (6.0 μL, 63 μmol) were combined in anhydrous MeCN (1 mL) in a 10 mL round-bottomed flask under a blanket of N_2. To this solution was added $Fe(ClO_4)_2$•xH_2O (7.0 mg). The mixture was then submerged in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (14 mL), and cooled to -25°C. This gave a fine precipitate which was collected by centrifugation to give a purple solid (15.6 mg, 76 %). ^{1}H NMR (500 MHz; CD_3CN) δ 8.87 (s, 2H), 8.53 (t, *J* = 8.2 Hz, 2H), 8.39 (t, *J* = 7.5 Hz, 2H), 8.24 (s, 2H), 7.77 (m, 2H), 7.57 (m, 4H), 7.39 (d, *J* = 8.1 Hz, 2H), 6.57 (br, 2H), 5.32 (d, *J* = 8.1 Hz, 4H). HRMS (ESI) m/z calcd for $C_{102}H_{66}Cl_4Fe_2N_{18}O_{22}$ ($[M-3(ClO_4)]^{3+}$) 616.4526, found 616.4522.

4_3·Fe_2·$(ClO_4)_4$:

D (23.8 mg, 57 μmol) and 2-pyridinecarboxaldehyde (11.0 μL, 116 μmol) were combined in anhydrous MeCN (1 mL) in a 10 mL round-bottomed flask under a blanket of N_2. To this solution was added $Fe(ClO_4)_2$•xH_2O (13.9 mg). The mixture was then submerged in an ultrasonication bath for two minutes. The solution was then diluted with Et_2O (14 mL), and cooled to -25°C. This gave a fine precipitate which was collected by centrifugation to give a

purple solid (35.8 mg, 82%). ^{1}H NMR (400 MHz; CD_3CN) δ 8.91 (s, 2H), 8.54 (d, *J* = 7.6 Hz, 2H), 8.39 (t, *J* = 8.0 Hz, 2H), 7.79 (t, *J* = 5.8 Hz, 2H), 7.59 (d, *J* = 7.6 Hz, 2H), 7.43 (m, 4H), 7.28 (d, *J* = 7.7 Hz, 4H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.09 (t, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 7.7 Hz, 1H), 5.36 (d, *J* = 7.7 Hz, 4H), 5.19 (s, 2H). HRMS (ESI) m/z calcd for $C_{123}H_{84}Cl_4Fe_2N_{12}O_{19}$ ($[M-2(ClO_4)]^{2+}$) 1043.2223, found 1043.2203.

5_3·Fe_2·$(ClO_4)_4$:

E (54.6 mg, 0.11 mmols) and 2-pyridinecarboxaldehyde (21 μL, 0.22 mmols) were combined in anhydrous MeCN (5 mL) in a 10 mL round-bottomed flask under a blanket of N_2. To this solution was added $Fe(ClO_4)_2$•xH_2O (26 mg). The mixture was then submerged in an ultrasonication bath for five minutes. The solution was then diluted with Et_2O (10 mL), and cooled to -25°C. This gave a fine precipitate which was collected by centrifugation to give a purple solid (41.4 mg, 45%). ^{1}H NMR (500 MHz; CD_3CN) δ 8.81 (s, 2H), 8.58 (d, *J* = 7.3 Hz, 2H), 8.42 (s, 2H), 8.40 (m, 2H), 7.77 (dd, *J* = 9.8 Hz, 3.7 Hz, 2H), 7.34 (d, *J* = 5.4 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 4H), 7.13 (d, *J* = 8.2 Hz, 2H), 5.7 (s, 2H), 5.17 (d, *J* = 8.0 Hz, 4H), 1.09 (s, 9H). HRMS (ESI) m/z calcd for $C_{135}H_{105}Cl_4Fe_2N_{15}O_{25}$ ($[M-4(ClO_4)]^{4+}$) 547.9224, found 547.9227.

3. NMR Spectral Data

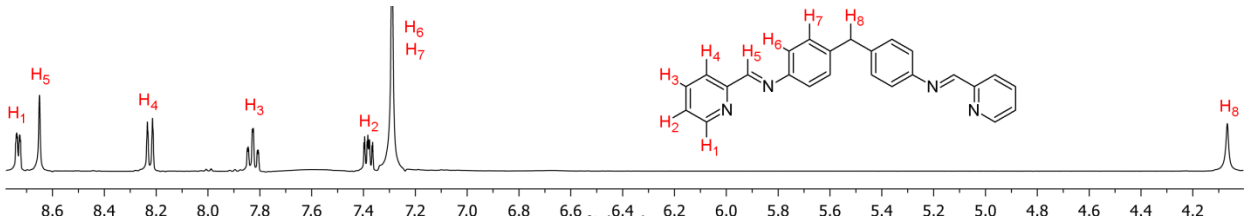


Figure S-1. ^{1}H NMR spectrum of **7** ($CDCl_3$, 400 MHz, 298 K).

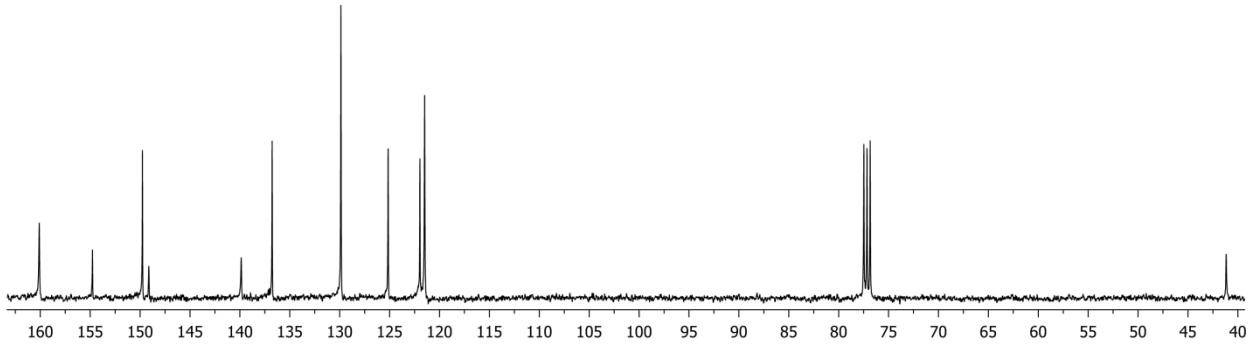


Figure S-2. ^{13}C NMR spectrum of **7** ($CDCl_3$, 100 MHz, 298 K).

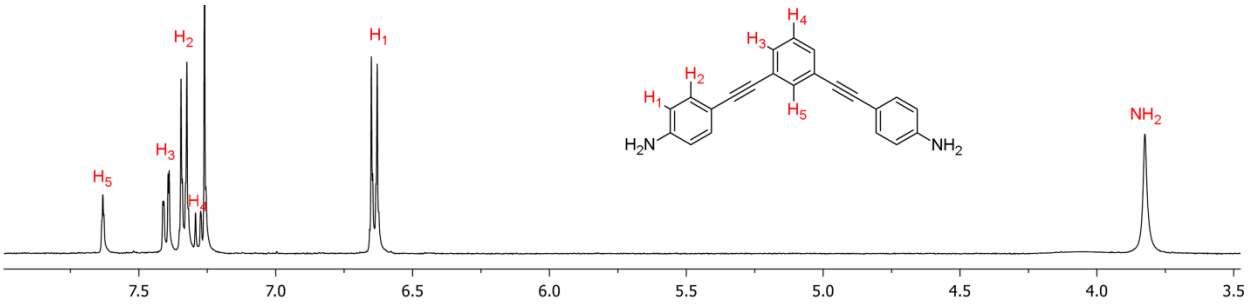


Figure S-3. ^{1}H NMR spectrum of **A** ($CDCl_3$, 400 MHz, 298 K).

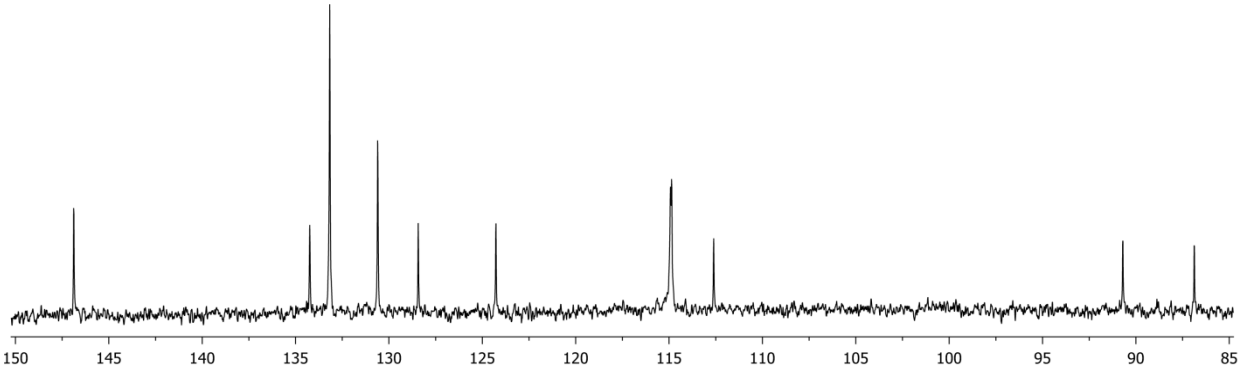


Figure S-4. ^{13}C NMR spectrum of **A** ($CDCl_3$, 100 MHz, 298 K).

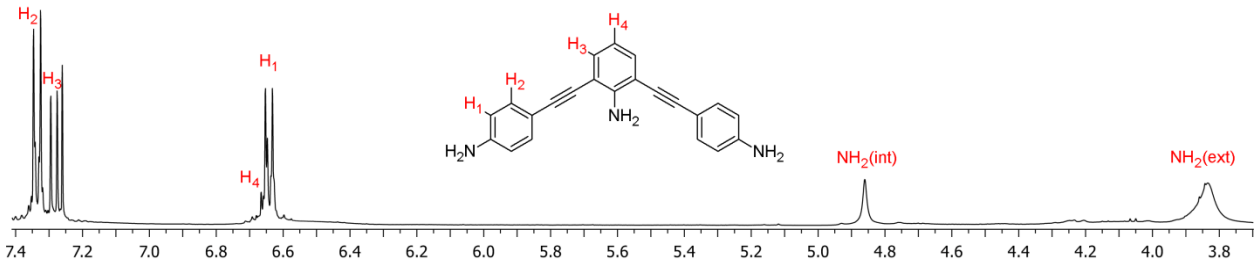


Figure S-5. ^{1}H NMR spectrum of **B** ($CDCl_3$, 400 MHz, 298 K).

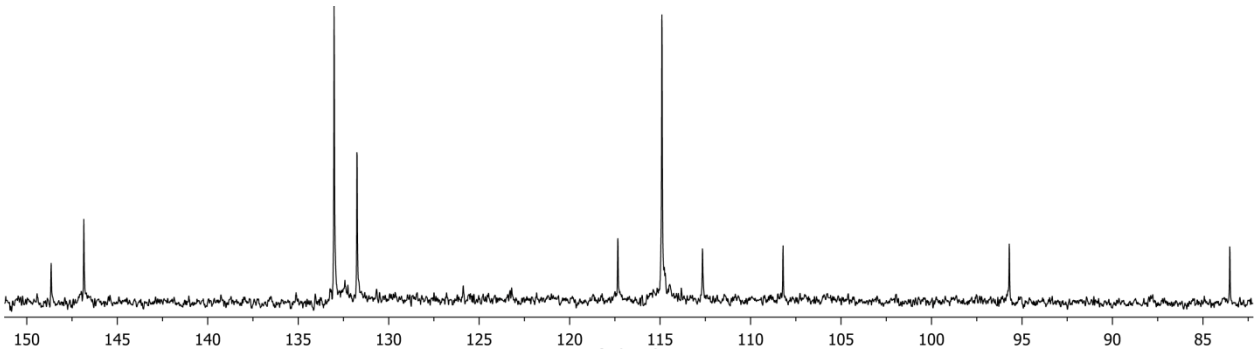


Figure S-6. ^{13}C NMR spectrum of **B** ($CDCl_3$, 100 MHz, 298 K).

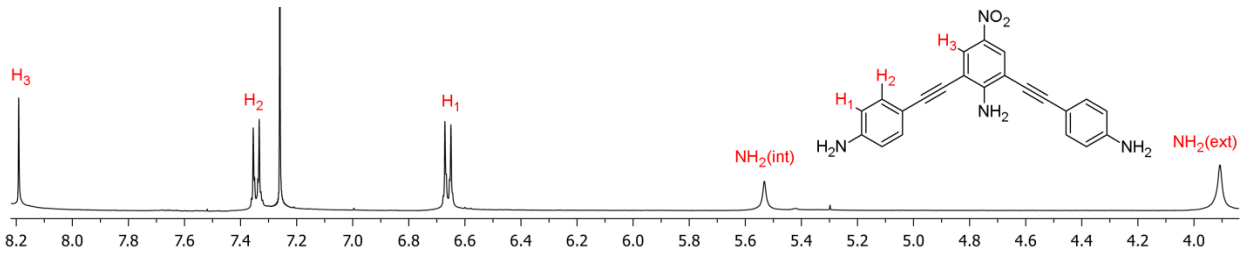


Figure S-7. ^{1}H NMR spectrum of **C** ($CDCl_3$, 400 MHz, 298 K).

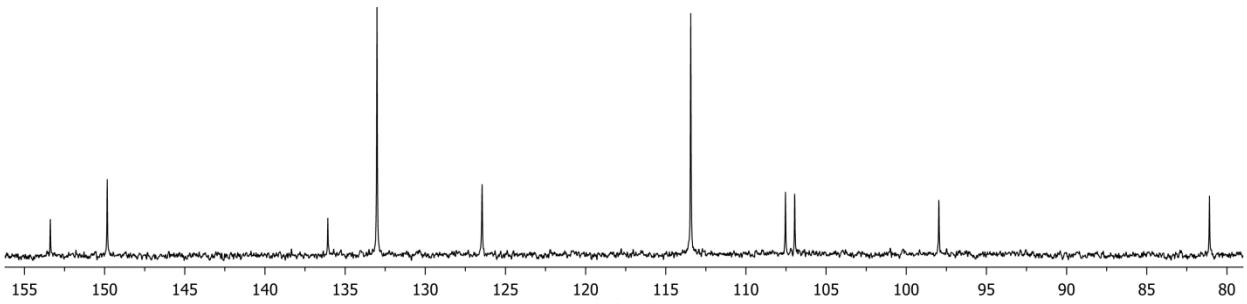


Figure S-8. ^{13}C NMR spectrum of **C** ($CDCl_3$, 100 MHz, 298 K).

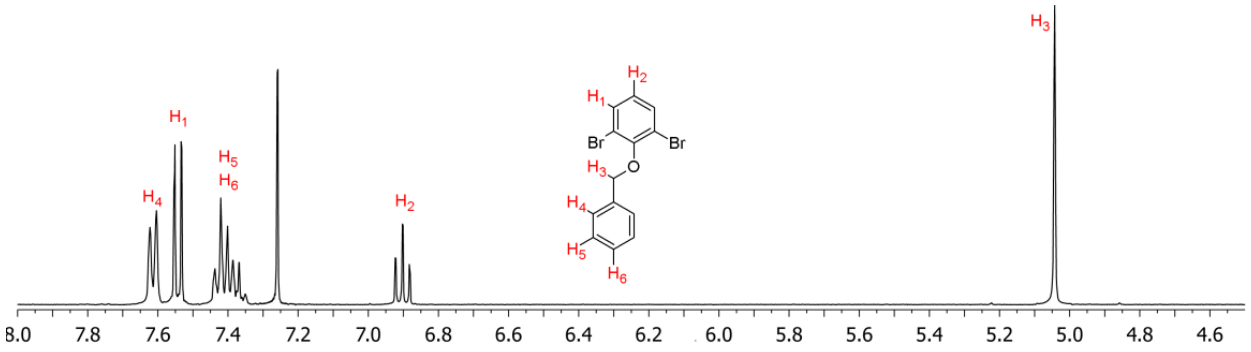


Figure S-9. ^{1}H NMR spectrum of ***S-1*** ($CDCl_3$, 400 MHz, 298 K).

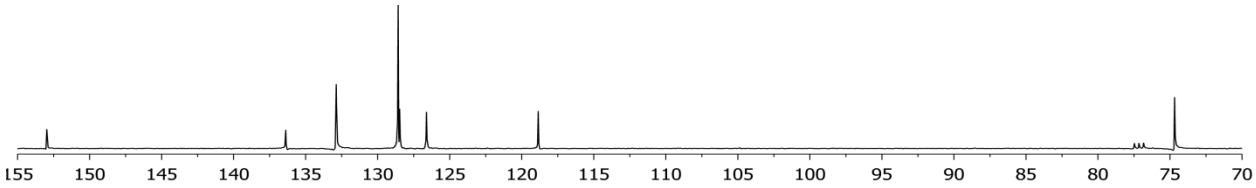


Figure S-10. ^{13}C NMR spectrum of ***S-1*** ($CDCl_3$, 100 MHz, 298 K).

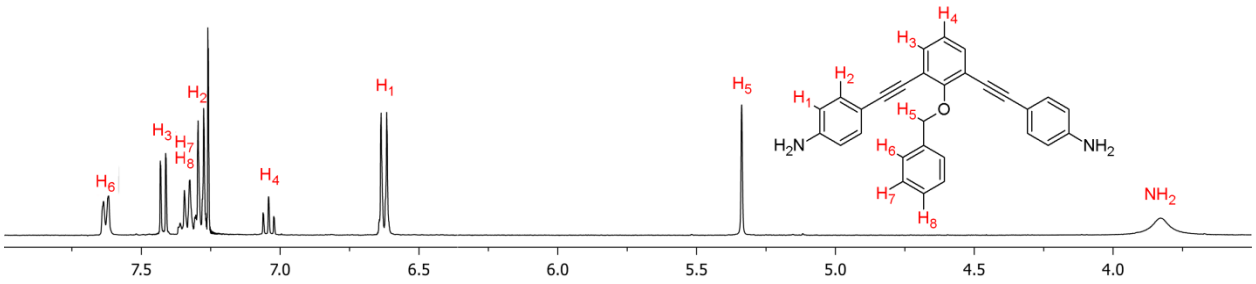


Figure S-11. ^{1}H NMR spectrum of **D** ($CDCl_3$, 400 MHz, 298 K).

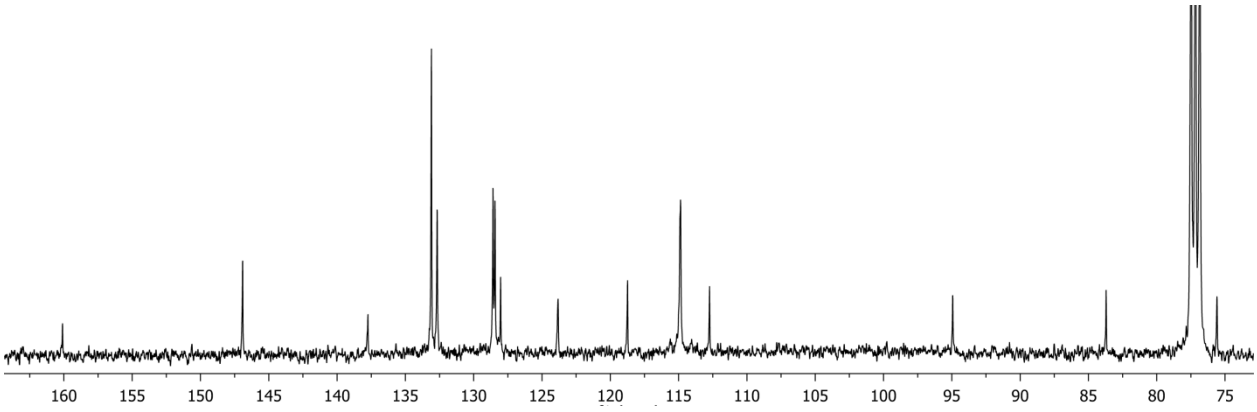


Figure S-12. ^{13}C NMR spectrum of **D** ($CDCl_3$, 100 MHz, 298 K).

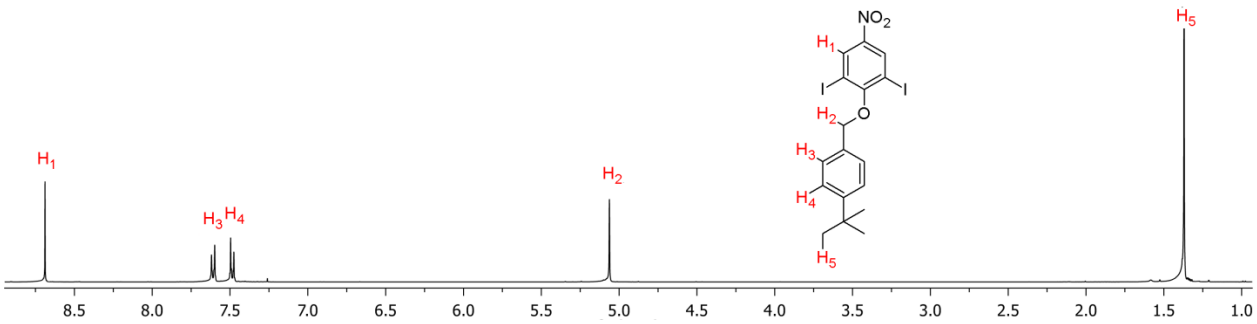


Figure S-13. ^{1}H NMR spectrum of ***S-2*** ($CDCl_3$, 400 MHz, 298 K).

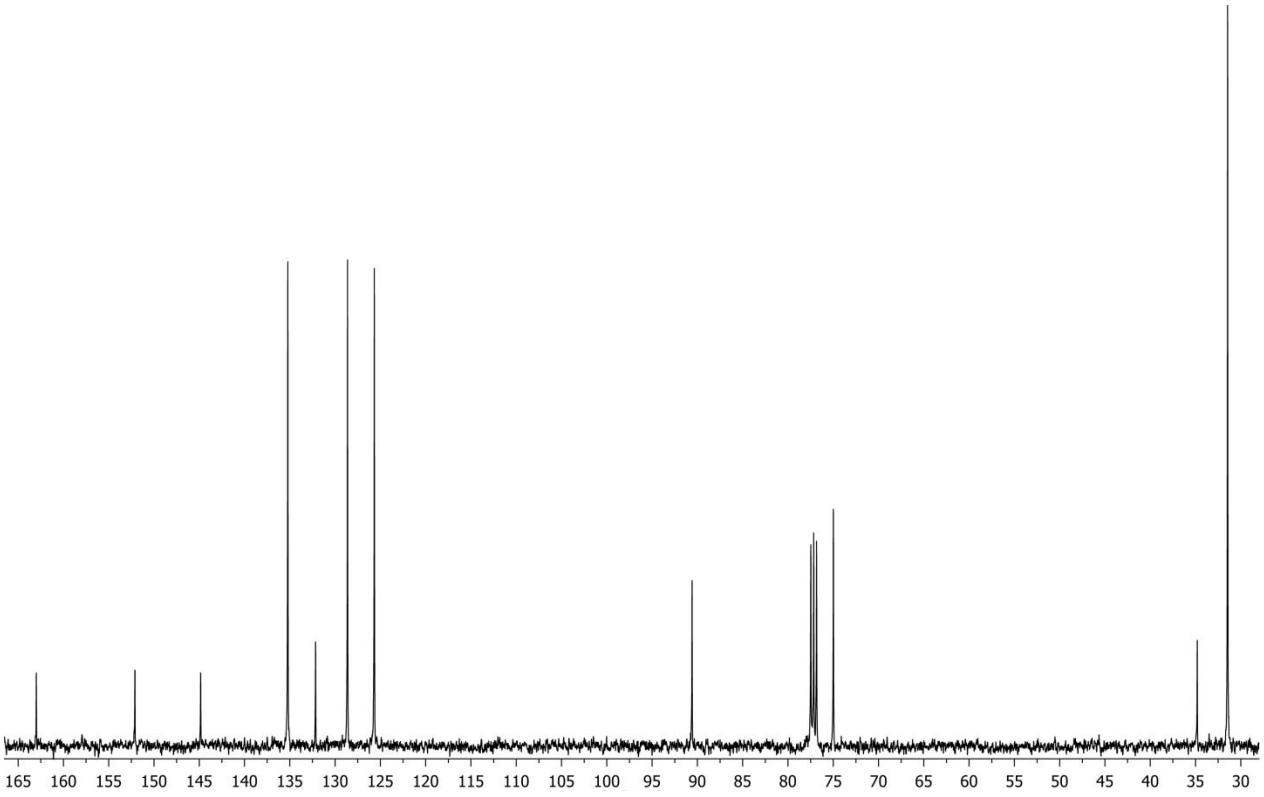


Figure S-14. ^{13}C NMR spectrum of ***S-2*** ($CDCl_3$, 100 MHz, 298 K).

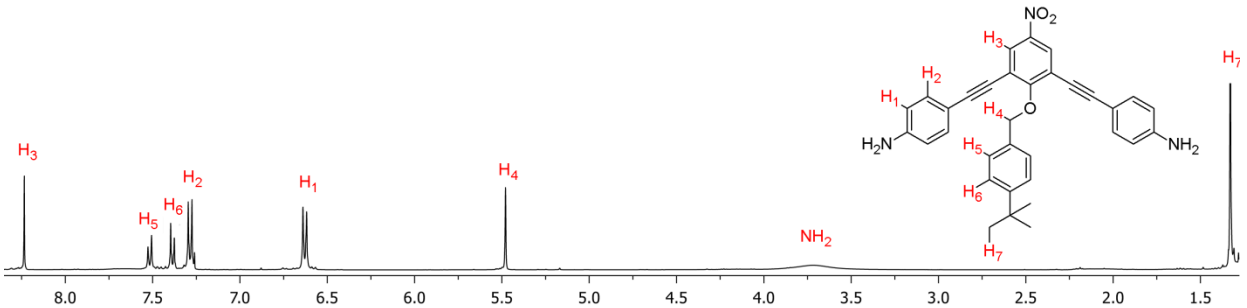


Figure S-15. ^{1}H NMR spectrum of **E** ($CDCl_3$, 400 MHz, 298 K).

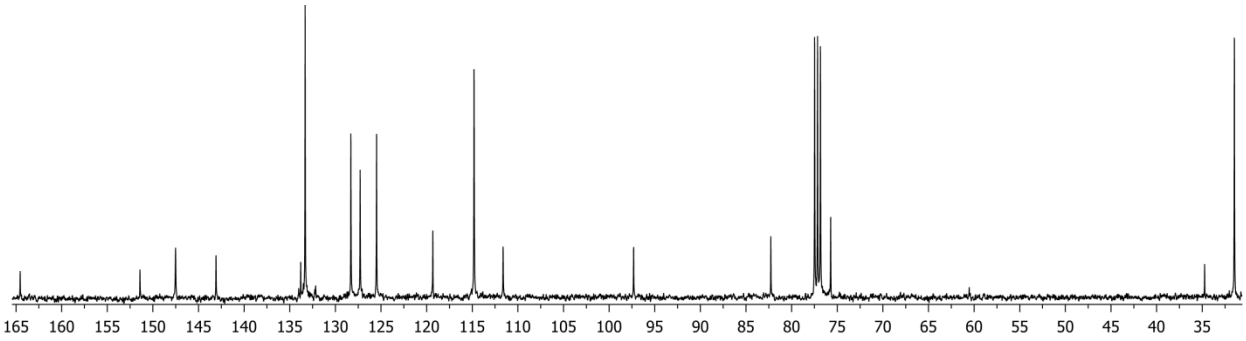


Figure S-16. ^{13}C NMR spectrum of **E** ($CDCl_3$, 100 MHz, 298 K).

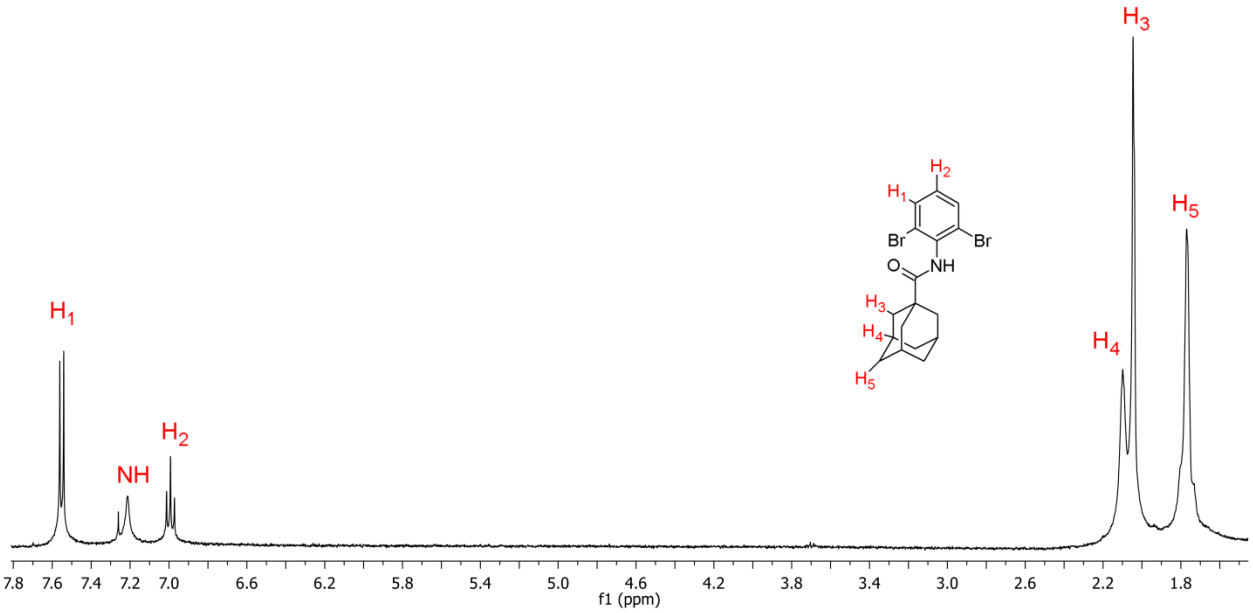


Figure S-17. ^{1}H NMR spectrum of ***S-3*** ($CDCl_3$, 400 MHz, 298 K).

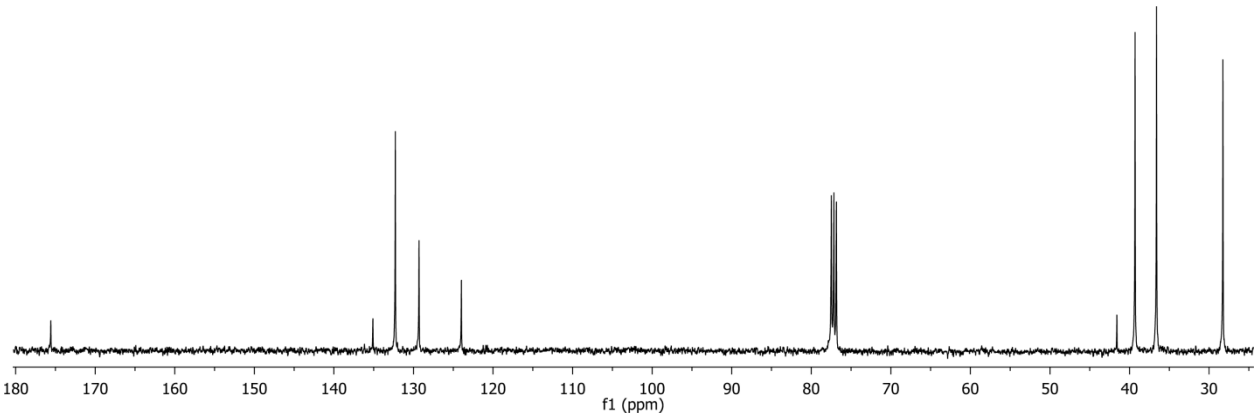


Figure S-18. ^{13}C NMR spectrum of ***S-3*** ($CDCl_3$, 100 MHz, 298 K).

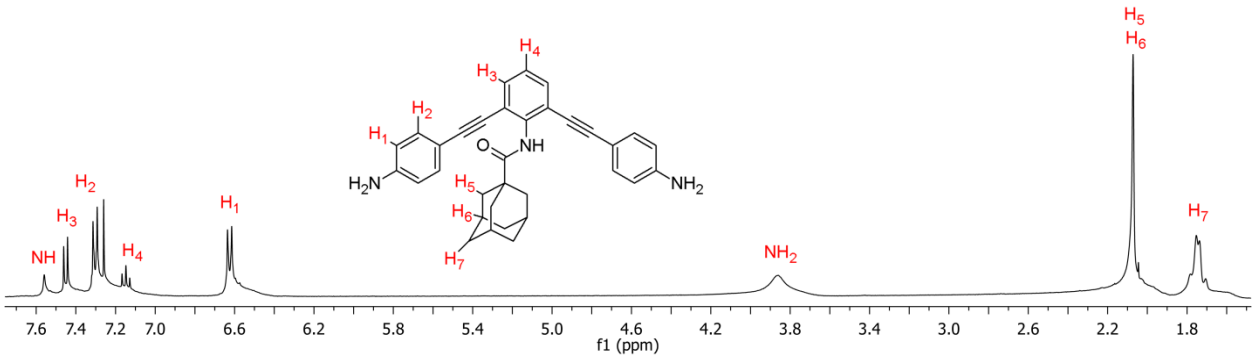


Figure S-19. ^{1}H NMR spectrum of **F** ($CDCl_3$, 400 MHz, 298 K).

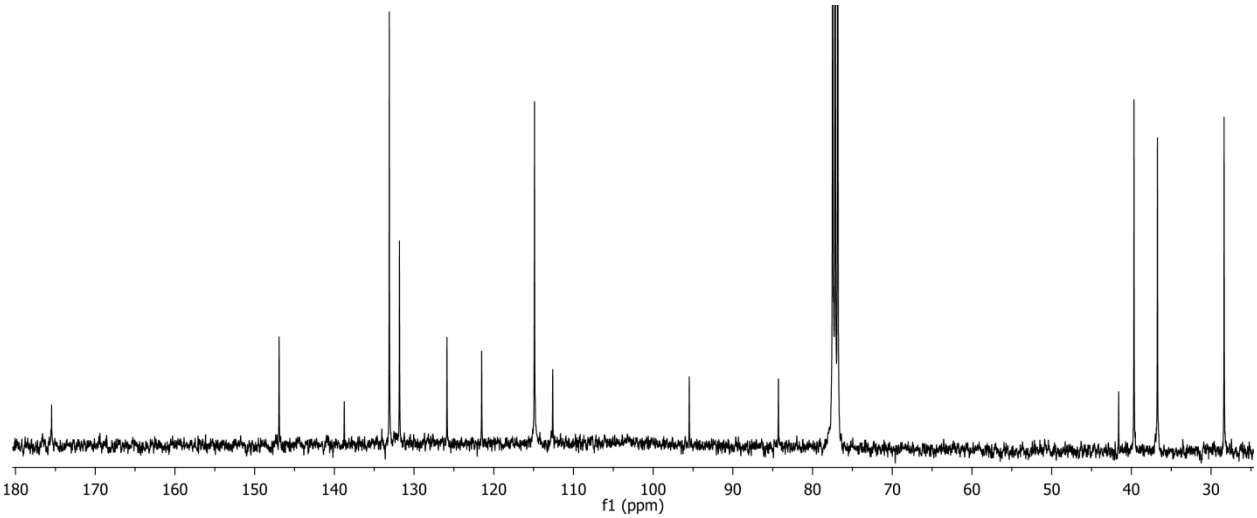


Figure S-20. ^{13}C NMR spectrum of **F** ($CDCl_3$, 100 MHz, 298 K).

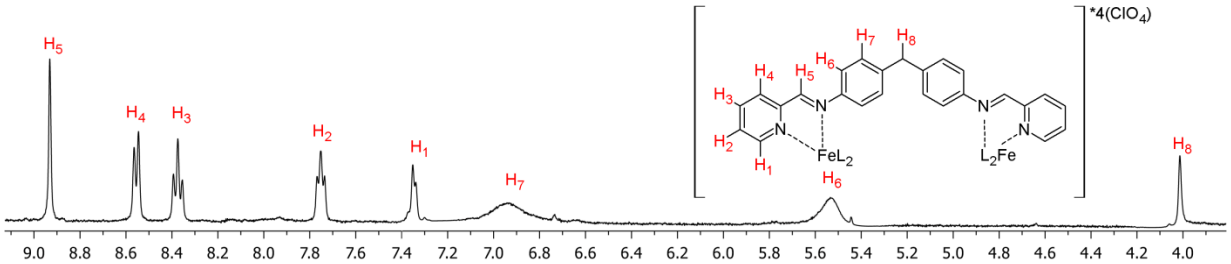


Figure S-21. ^{1}H NMR spectrum of $\mathbf{7_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 400 MHz, 298 K).

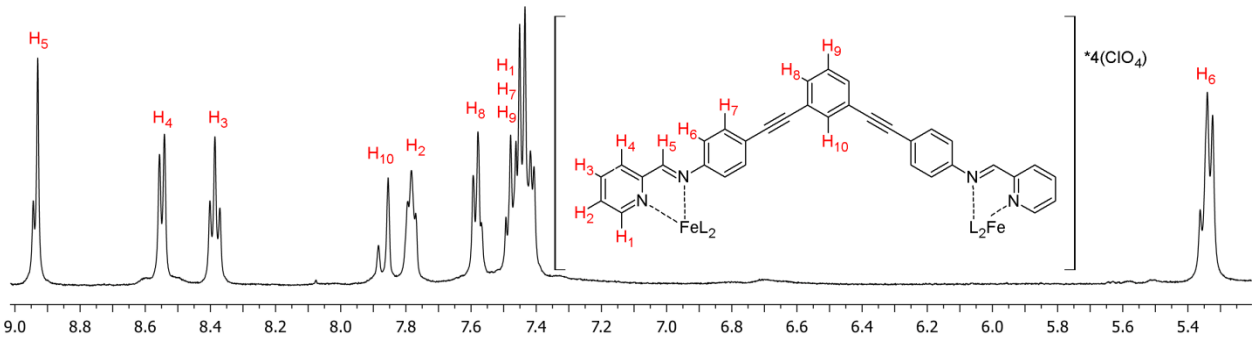


Figure S-22. ^{1}H NMR spectrum of $\mathbf{1_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 500 MHz, 298 K).

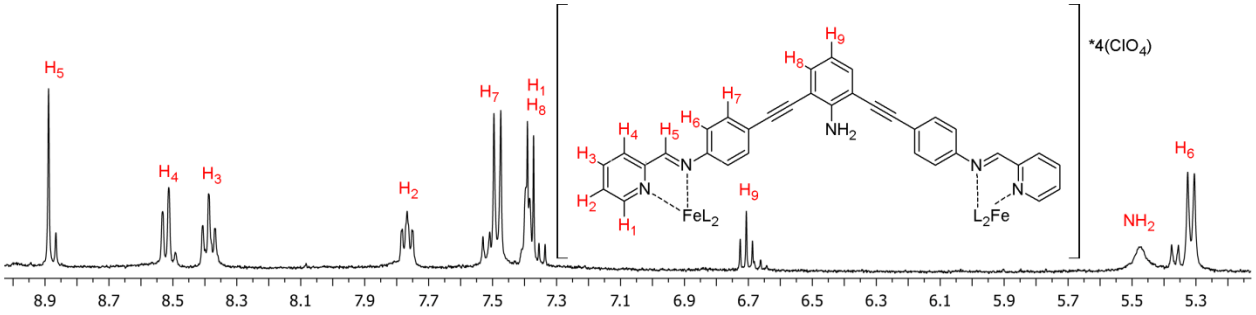


Figure S-23. ^{1}H NMR spectrum of $\mathbf{2_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 400 MHz, 298 K).

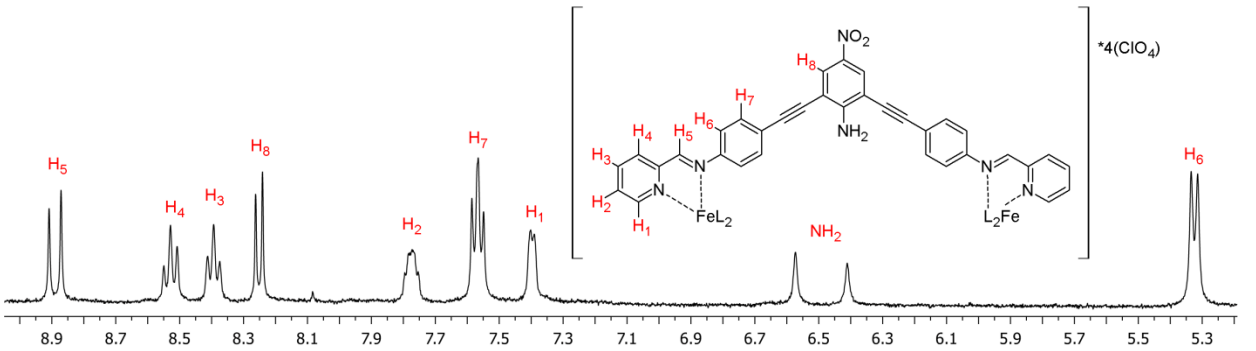


Figure S-24. ^{1}H NMR spectrum of $\mathbf{3_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 400 MHz, 298 K).

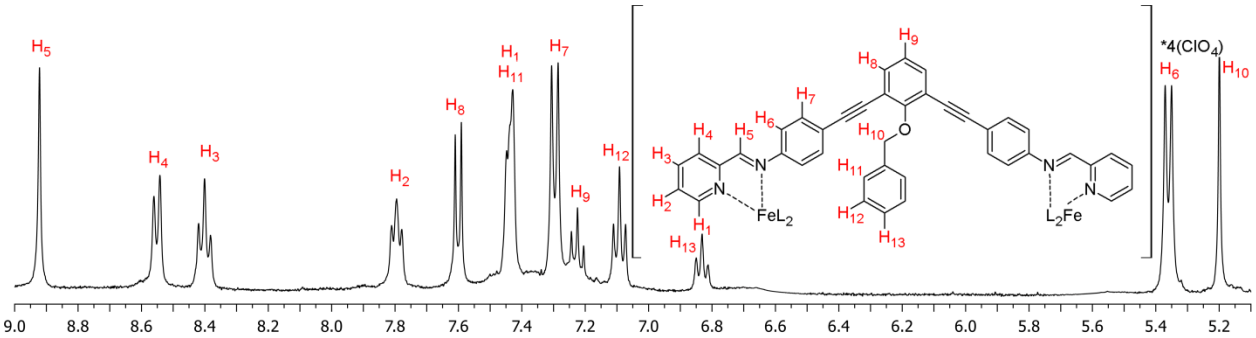


Figure S-25. ^{1}H NMR spectrum of $\mathbf{4_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K).

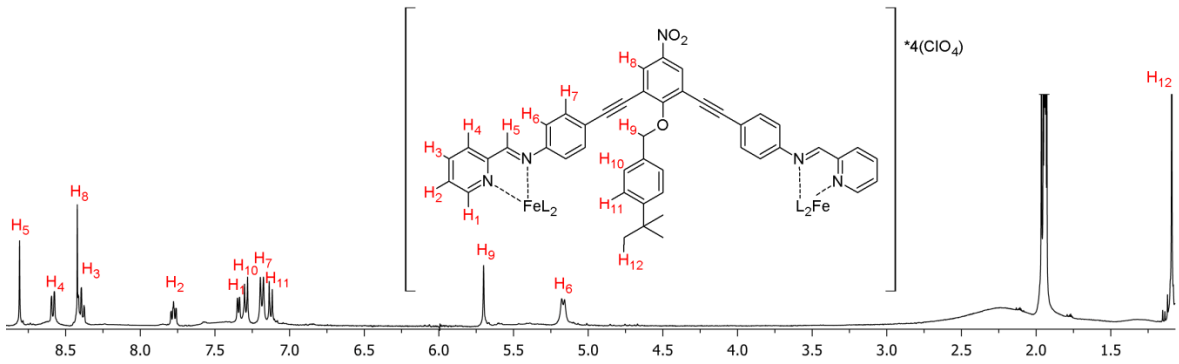


Figure S-26. ^{1}H NMR spectrum of $\mathbf{5_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 400 MHz, 298 K).

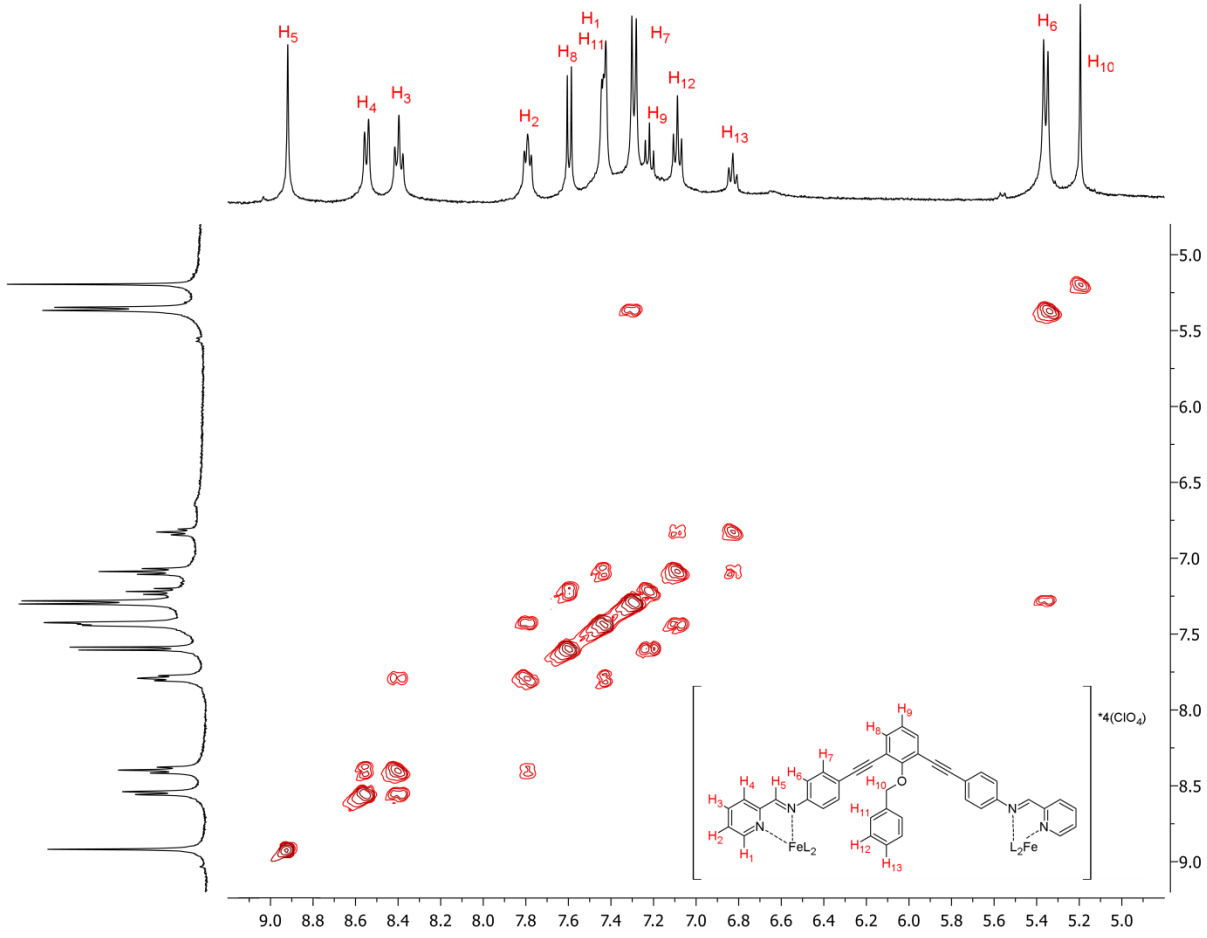


Figure S-27. COSY NMR Spectrum of $\mathbf{4_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 500 MHz, 298 K).

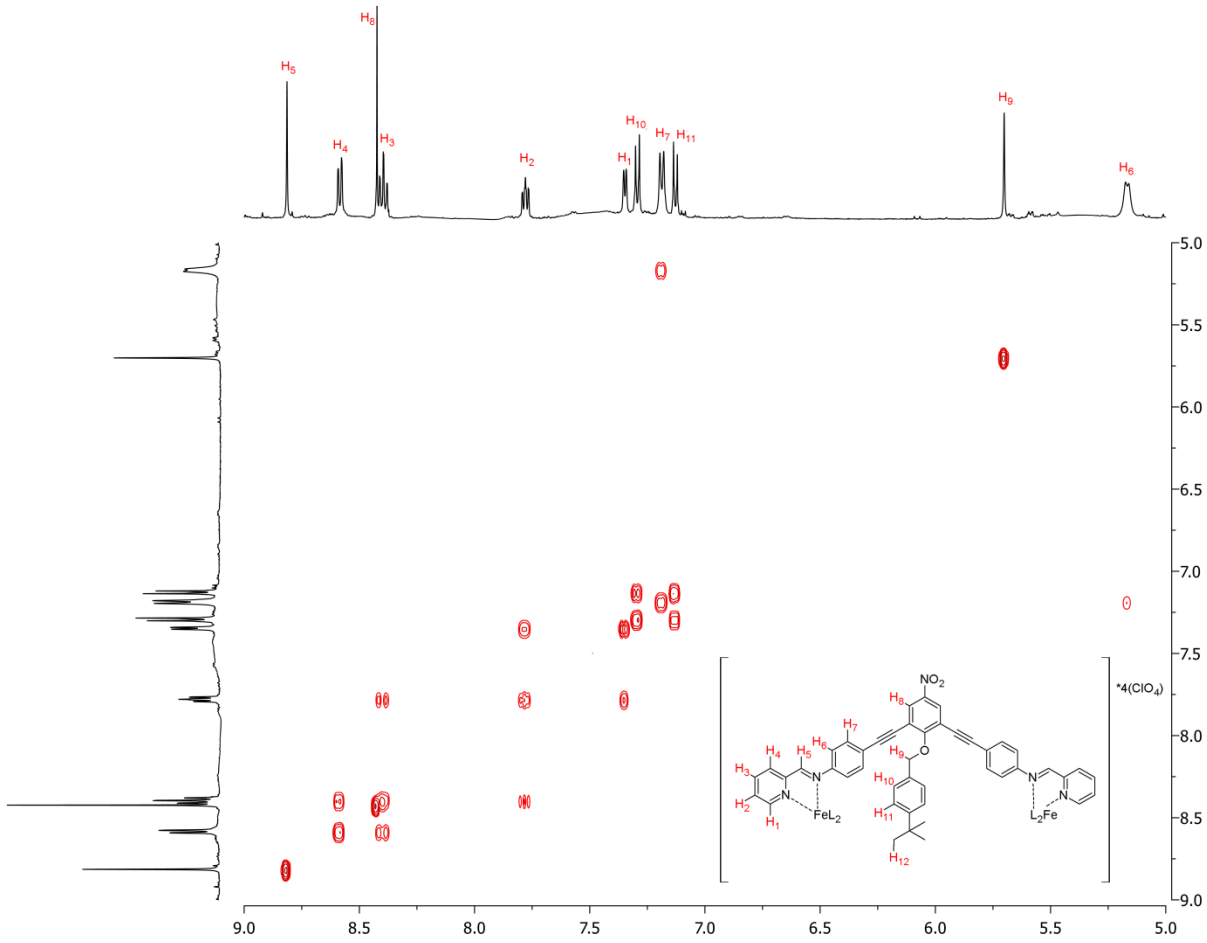


Figure S-28. COSY NMR Spectrum of $\mathbf{5_3 \cdot Fe_2 \cdot (ClO_4)_4}$ (CD_3CN, 500 MHz, 298 K)

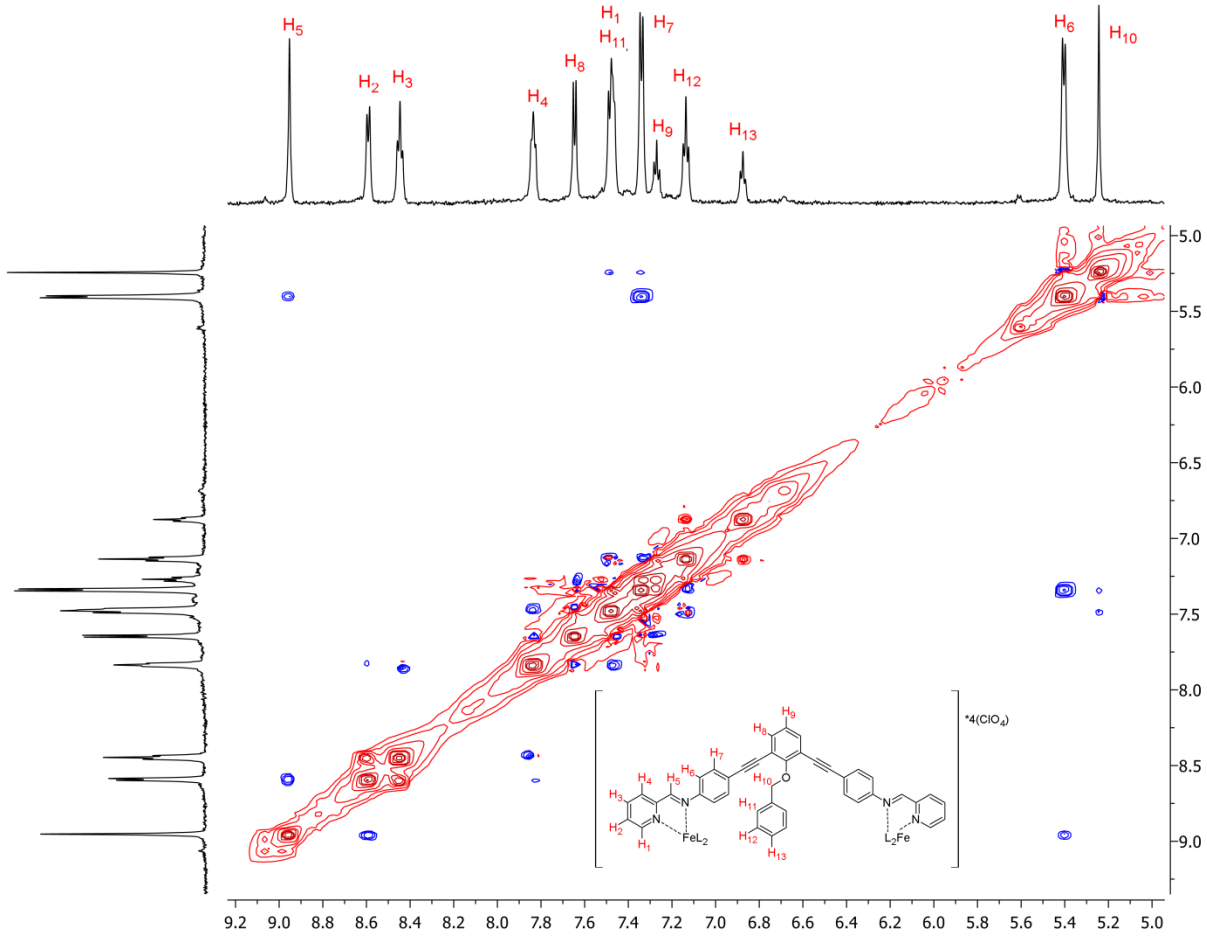


Figure S-29. 2D-ROESY NMR Spectrum of $\mathbf{4_3 \cdot Fe_2 \cdot (ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K)

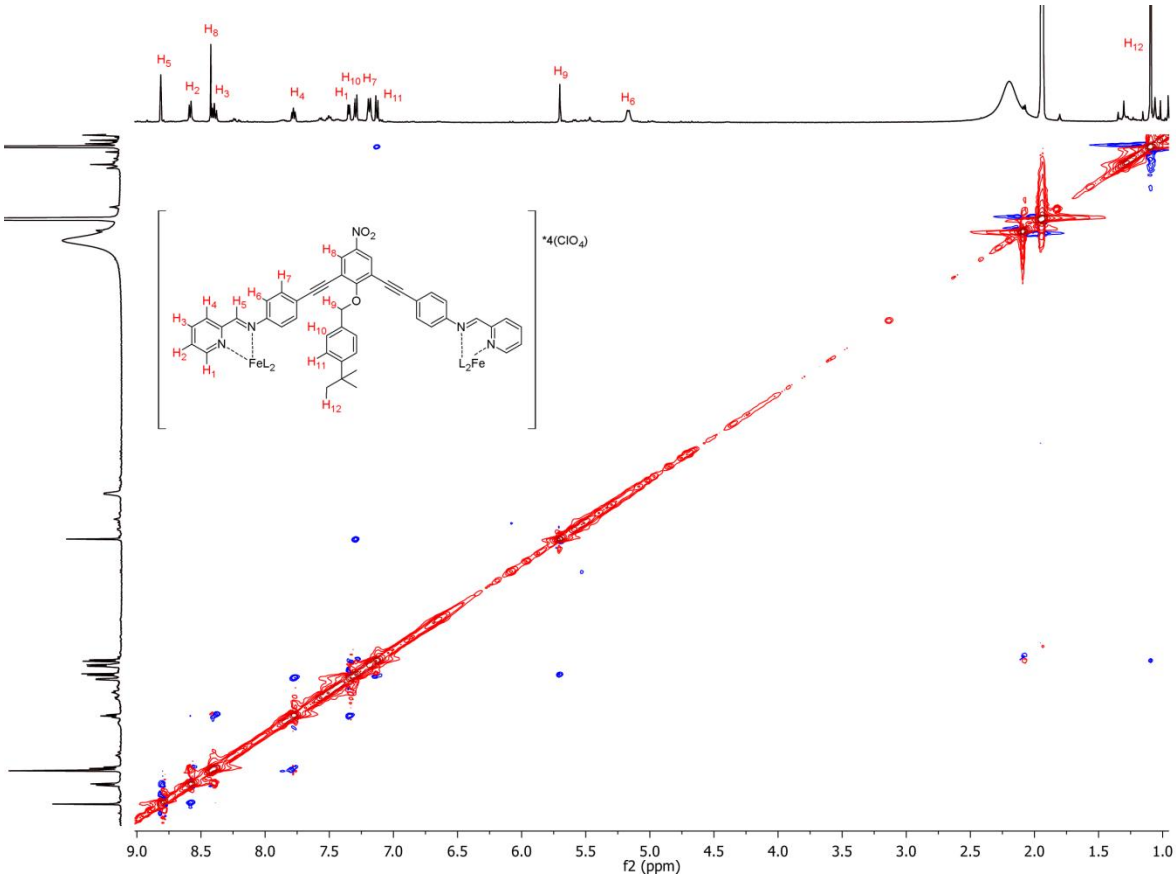


Figure S-30. 2D-ROESY NMR Spectrum of $\mathbf{5_3 \cdot Fe_2 \cdot (ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K)

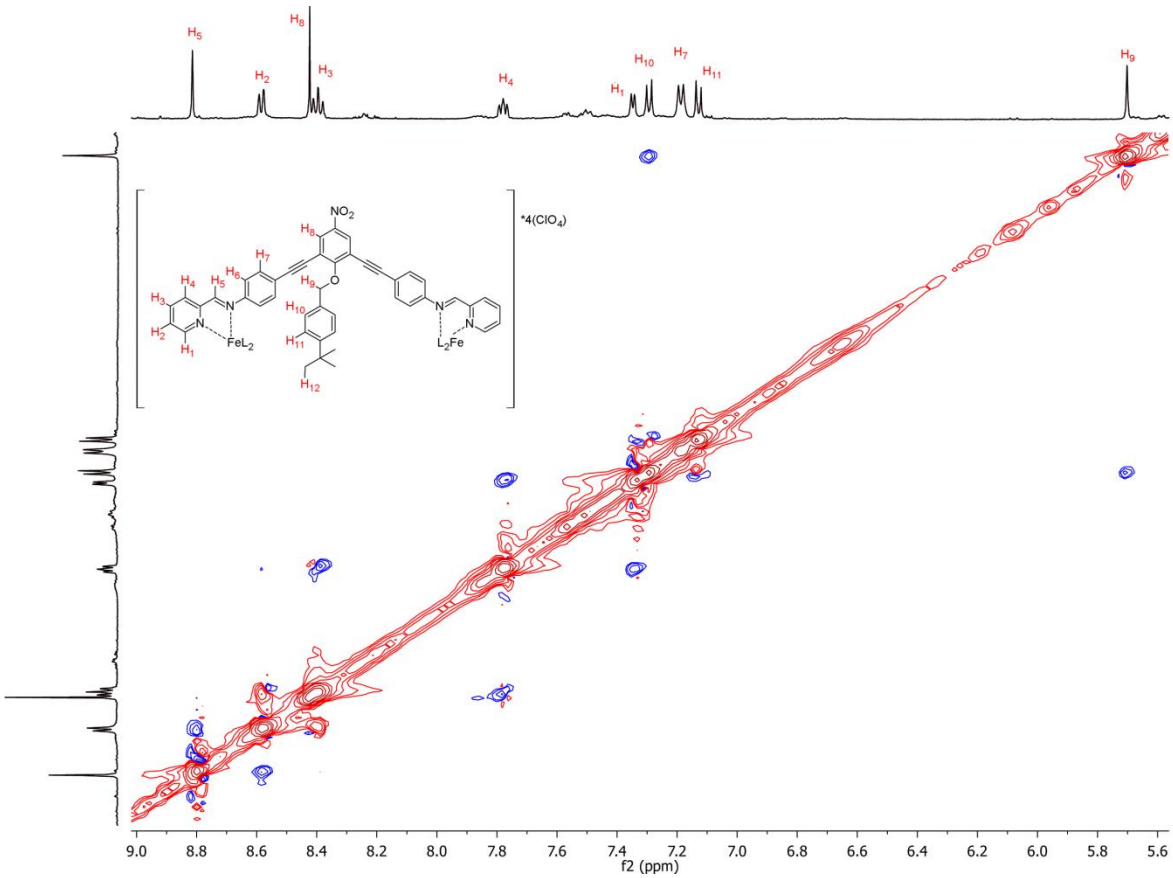


Figure S-31. Expanded 2D-ROESY NMR Spectrum of $\mathbf{5_3 \cdot Fe_2 \cdot (ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K)

4. Mass Spectral Data

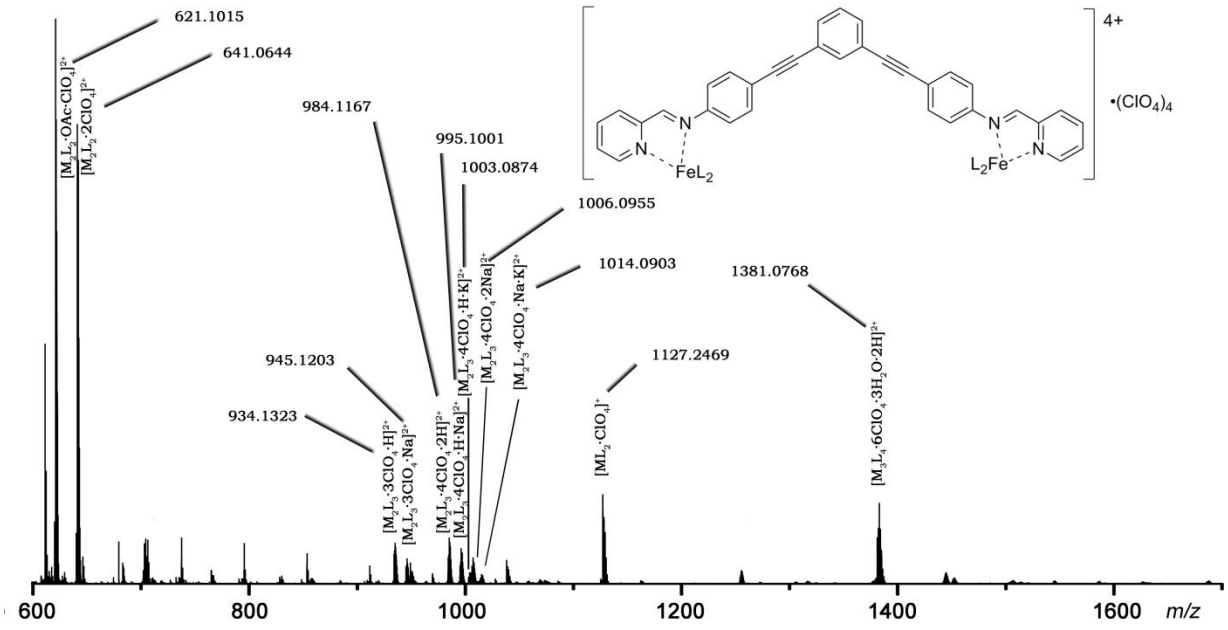


Figure S-32. ESI-MS spectrum (MeCN) of $\mathbf{1_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$.

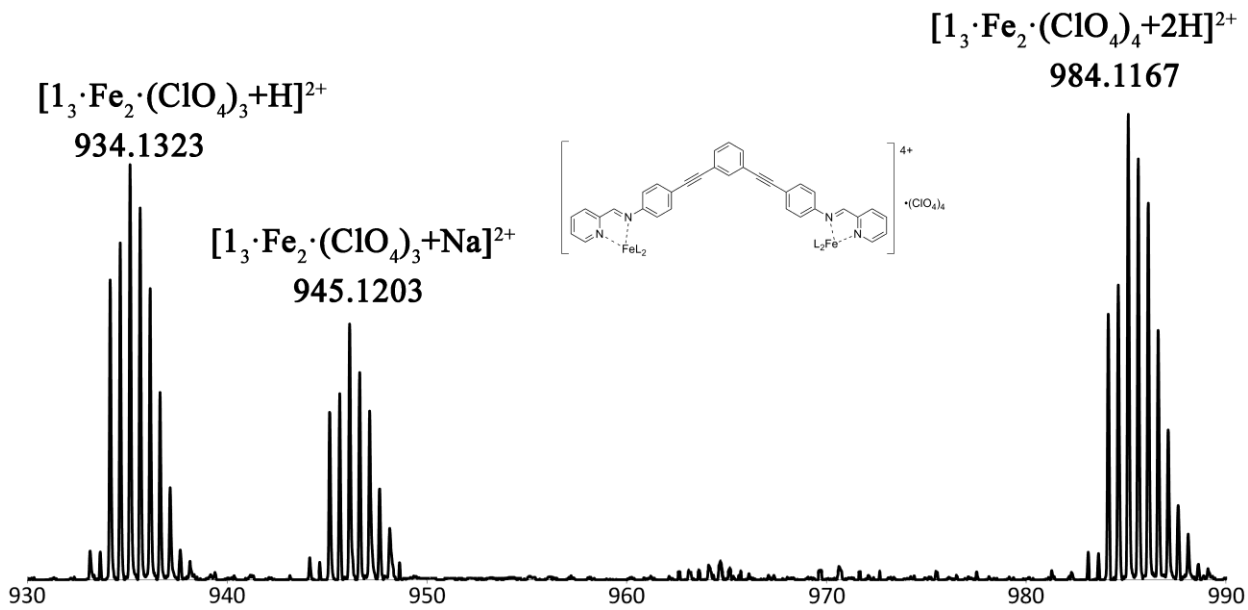


Figure S-33. ESI-MS spectrum expansion (MeCN) of $\mathbf{1_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$.

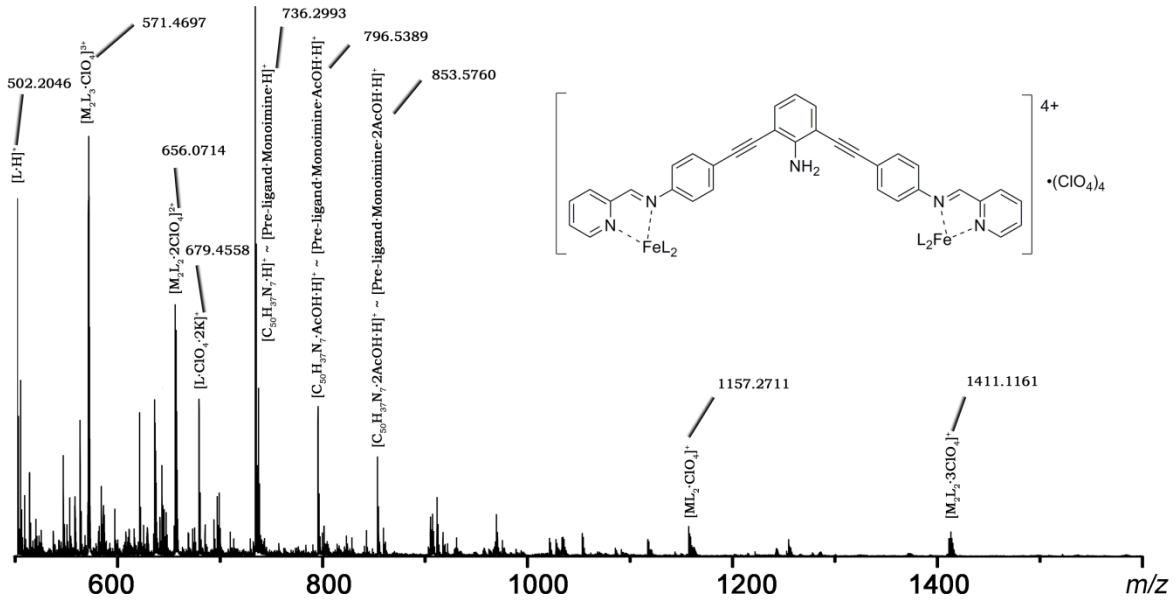


Figure S-34. ESI-MS spectra (MeCN) of $\mathbf{2_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$. Note M^{3+} ~572; singly charged complexes not observed, and other large peaks correspond to ligand.

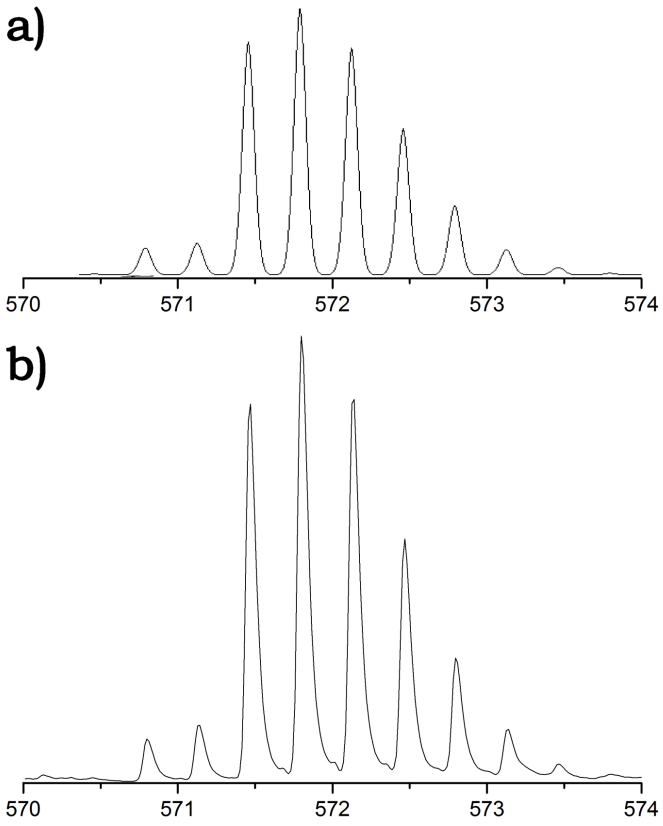


Figure S-35. ESI-MS spectra expansion of $\mathbf{[2_3Fe_2{\cdot}ClO_4]^{3+}}$: a) Predicted, b) Observed.

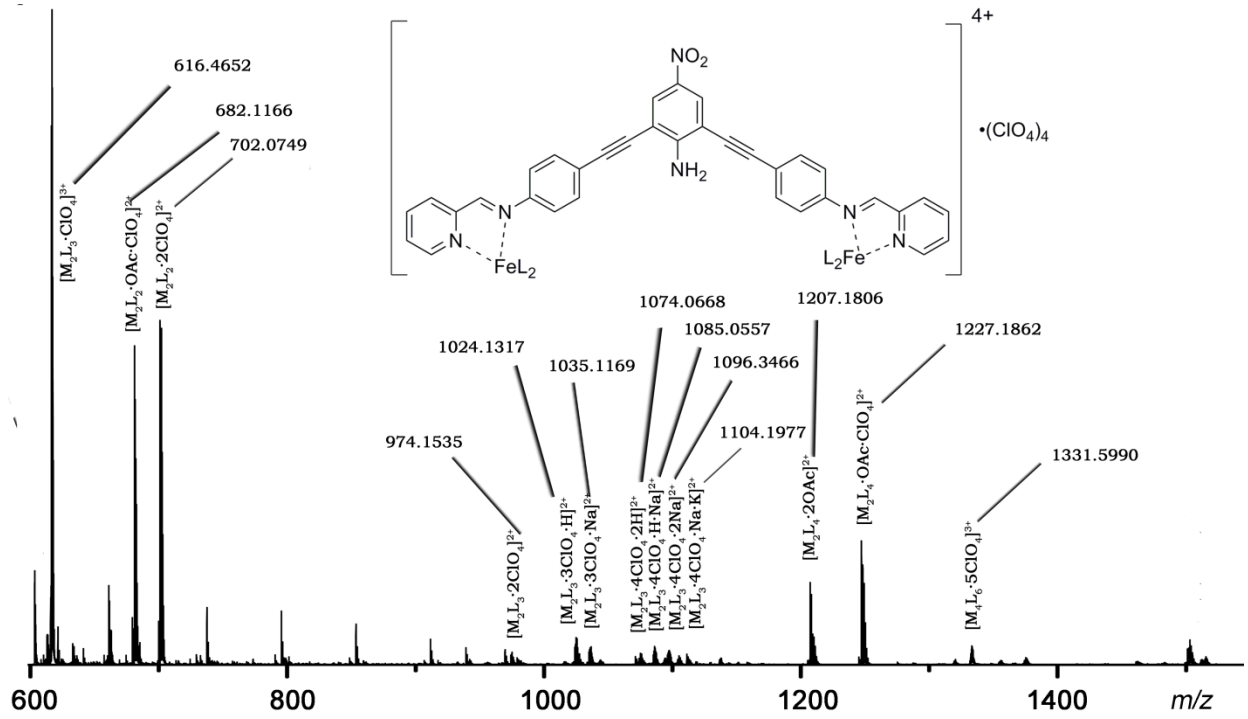


Figure S-36. ESI-MS spectra (MeCN) of $\mathbf{3_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$.

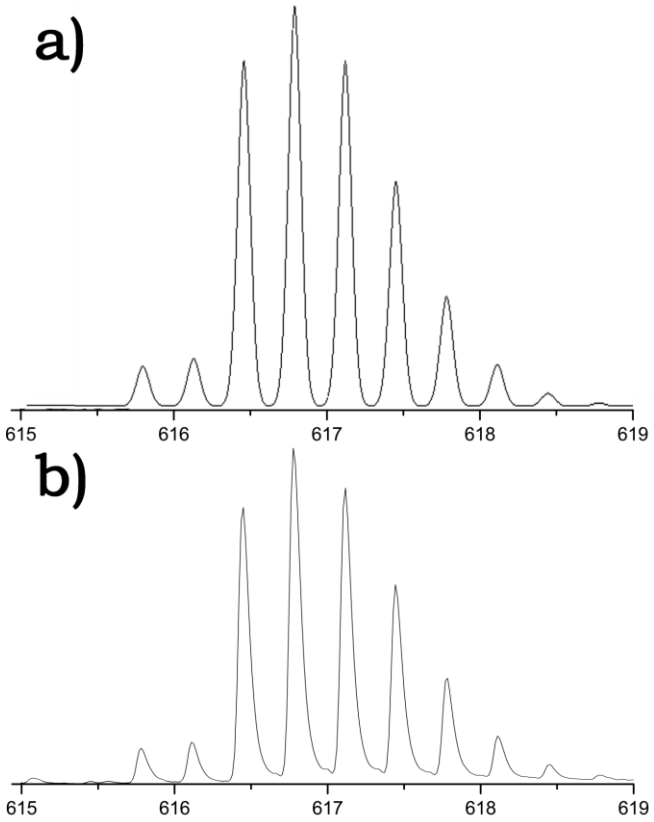


Figure S-37. ESI-MS spectra blow-up of $\mathbf{[3_3Fe_2{\cdot}ClO_4]^{3+}}$: a) Predicted, b) Observed.

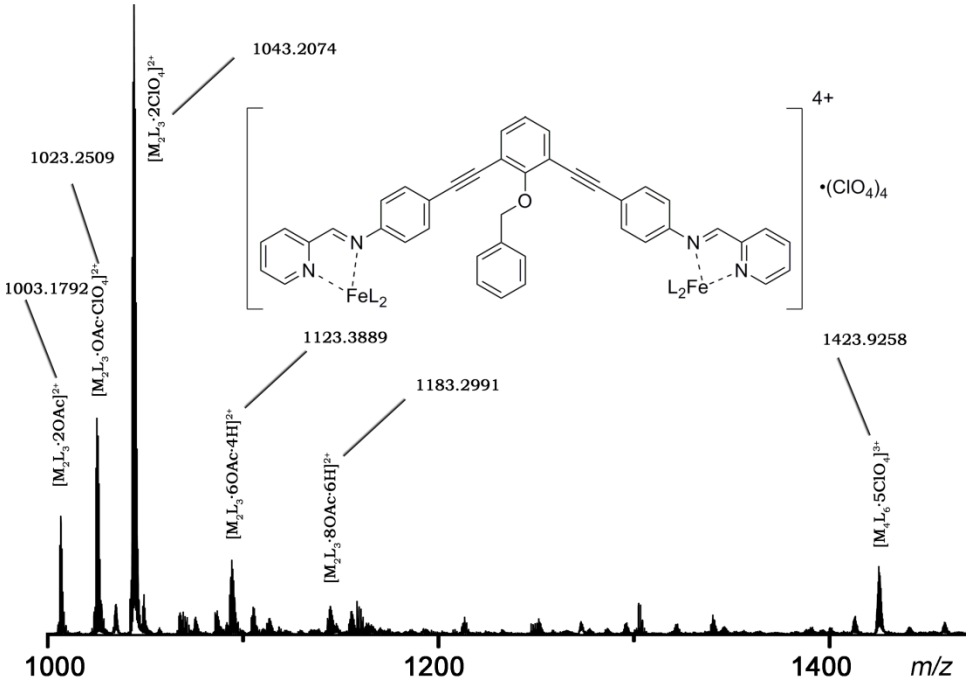


Figure S-38. ESI-MS spectra (MeCN) of $\mathbf{4_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$.

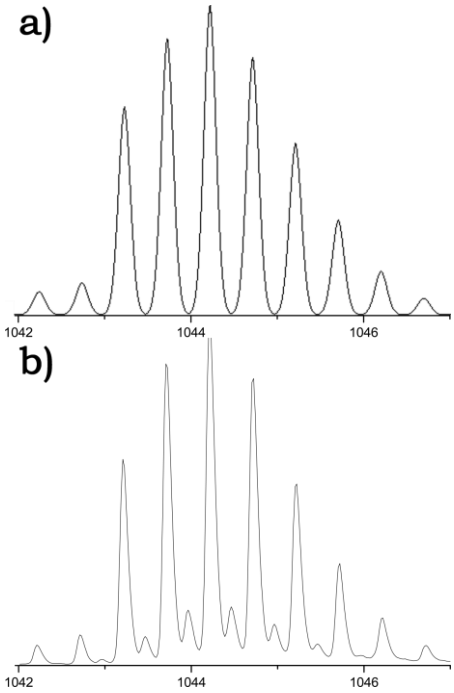


Figure S-39. ESI-MS spectra blow-up of $\mathbf{[4_3Fe_2{\cdot}2ClO_4]^{2+}}$: a) Predicted, b) Observed.

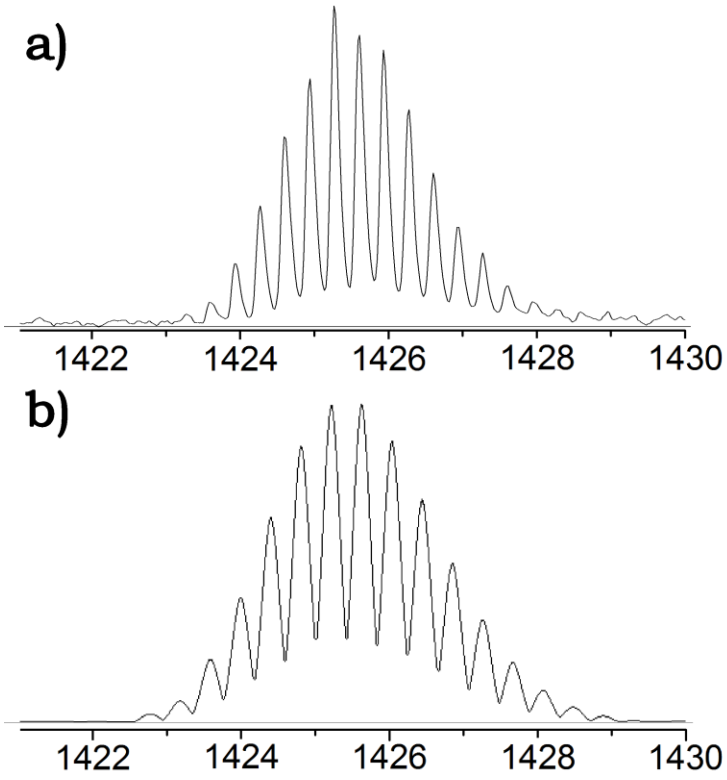


Figure S-40. ESI-MS spectra blow-up of $\mathbf{[4_6Fe_4{\cdot}5ClO_4]^{3+}}$: a) Predicted, b) Observed.

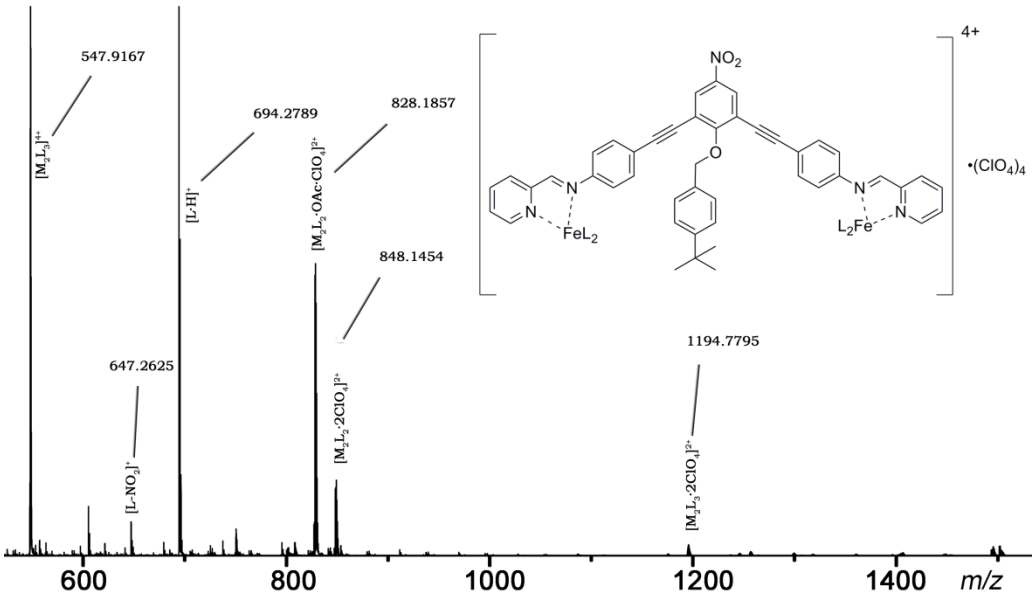


Figure S-41. ESI-MS spectra (MeCN) of $\mathbf{5_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$.

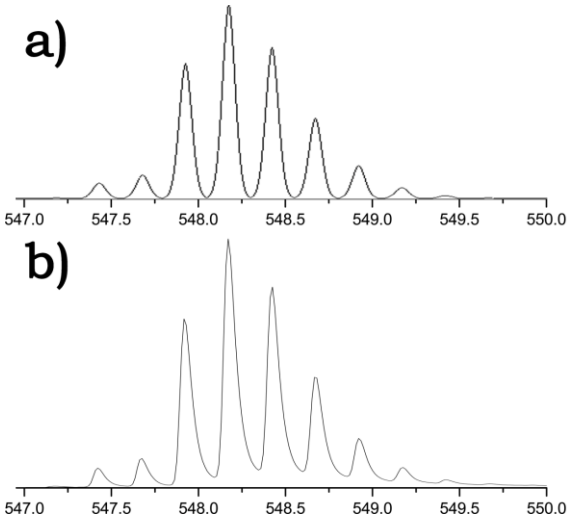


Figure S-42. ESI-MS spectra blow-up of $\mathbf{[5_3Fe_2]^{4+}}$: a) Predicted, b) Observed.

5. DOSY NMR Spectra of Self-Assemblies

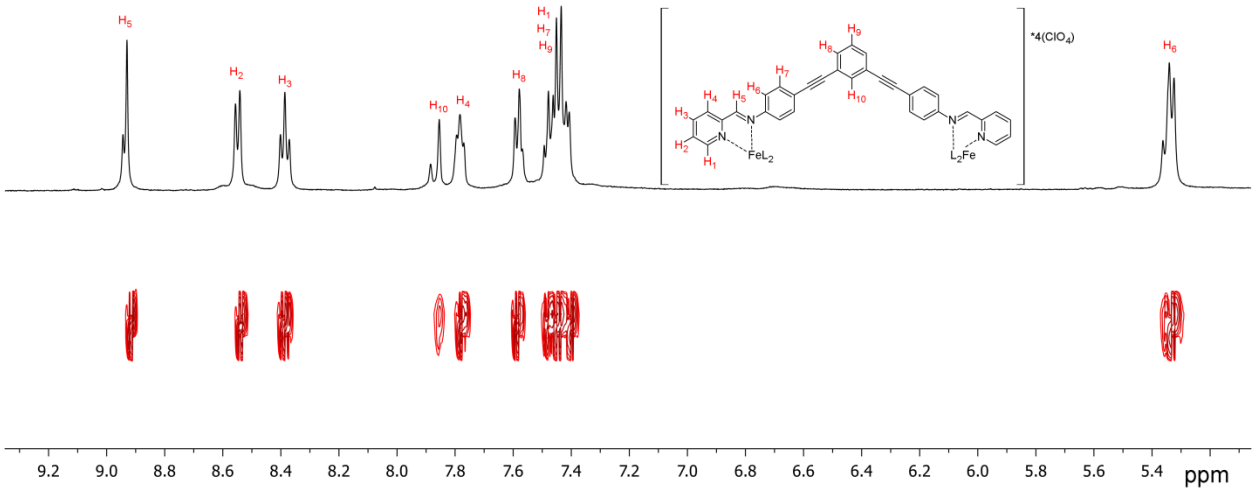


Figure S-43. ^{1}H-DOSY NMR spectrum of $\mathbf{1_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K, Δ = 17.0 ms, δ = 7000 µs, Diffusion Coefficient = 5.46×10^{-10} m^2/s vs. 3.85×10^{-9} m^2/s for the solvent).

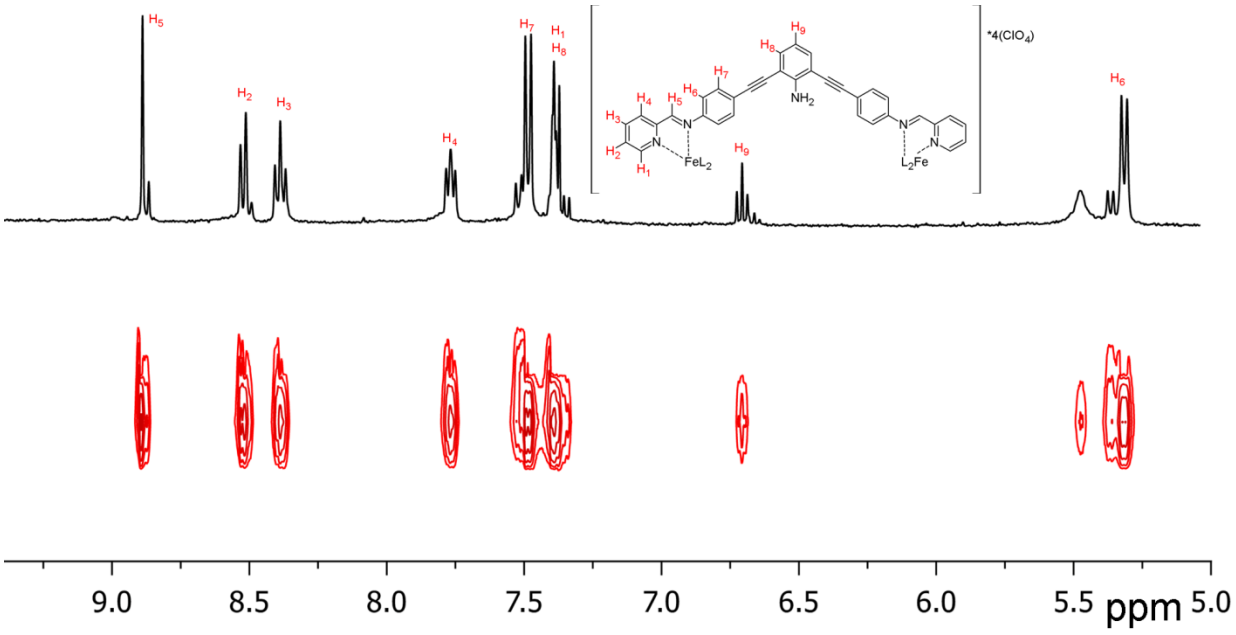


Figure S-44. ^{1}H-DOSY NMR spectrum of $\mathbf{2_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K, Δ = 17.0 ms, δ = 7000 µs, Diffusion Coefficient = 5.25×10^{-10} m^2/s vs. 3.47×10^{-9} m^2/s for the solvent).

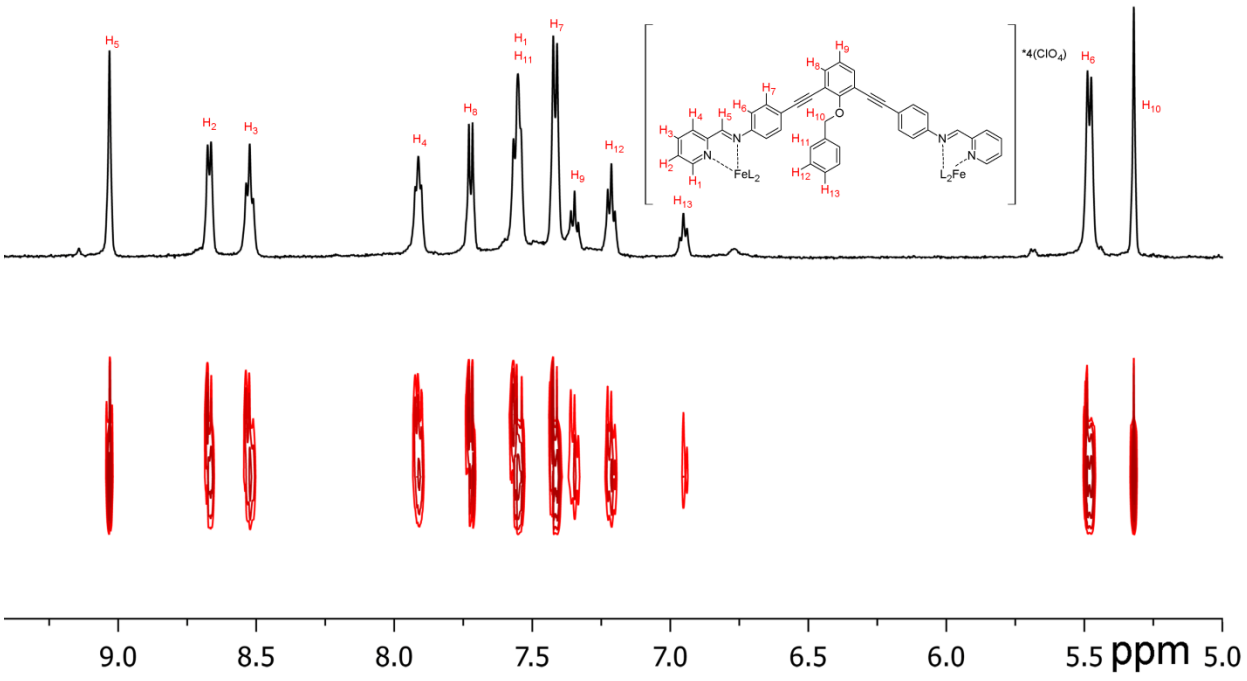


Figure S-45. ^{1}H-DOSY NMR spectrum of $\mathbf{4_3{\cdot}Fe_2{\cdot}(ClO_4)_4}$ (CD_3CN, 600 MHz, 298 K, Δ = 17.0 ms, δ = 7000 µs, Diffusion Coefficient = 5.51×10^{-10} m^2/s vs. 3.79×10^{-9} m^2/s for the solvent).

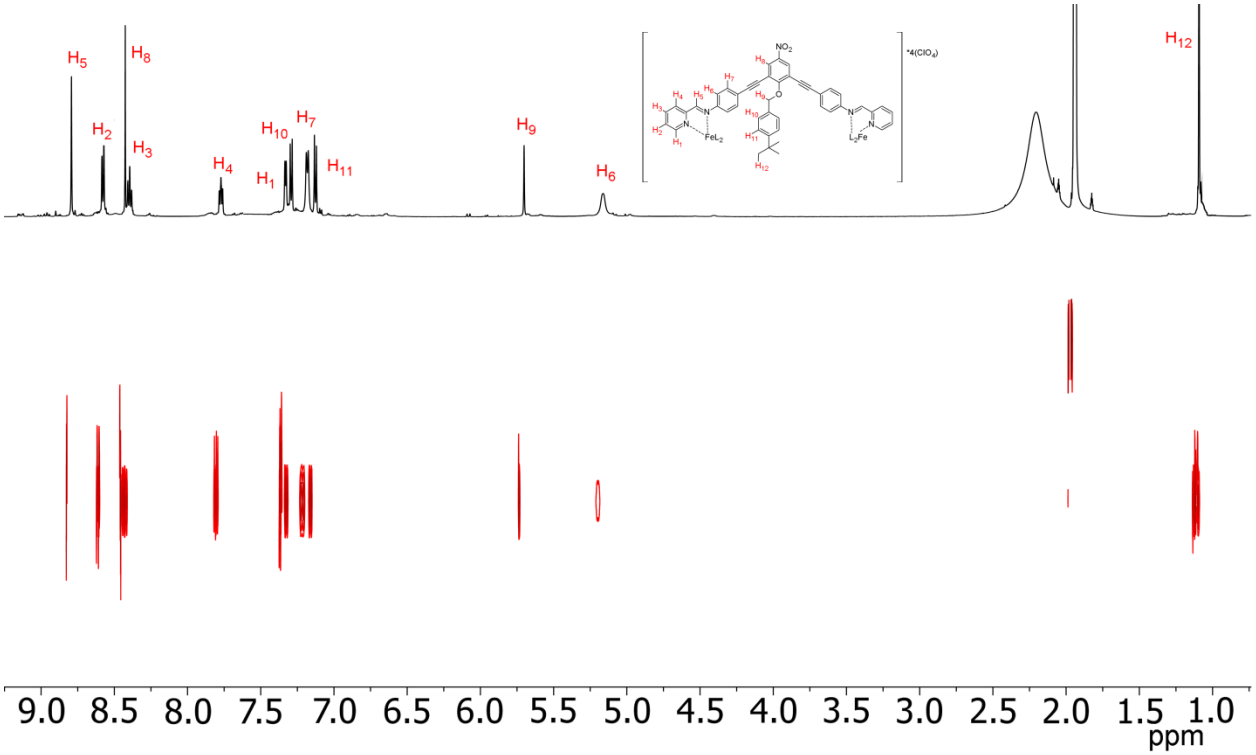


Figure S-46. 1H-DOSY NMR spectrum of **5_3·Fe_2·(ClO4)$_4$** (CD3CN, 600 MHz, 298 K, Δ = 17.0 ms, δ = 7000 μs, Diffusion Coefficient = 4.20x10^{-10} m^2/s vs. 3.79x10^{-10} m^2/s for the solvent).

6. References

1) M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.*, **1985**, *107*, 3902-3909; calculations performed on SPARTAN 06, Wavefunction Inc.