Supporting Information

Kinetic versus Thermodynamic Metalation Enables Synthesis of Isostructural Homo- and Heterometallic Trinuclear Clusters

Sung-Min Hyun, Apoorva Upadhyay, Anuvab Das, Corey P. Burns, Siyoung Sung, Jeremy D. Beaty, Nattamai Bhuvanesh, Michael Nippe*, David C. Powers*

[†] *Department of Chemistry, Texas A&M University, College Station, Texas 77843, United States*

Email: nippe@chem.tamu.edu, powers@chem.tamu.edu

Table of Contents

A. General Considerations

General Anhydrous THF, pentane, and acetonitrile were obtained from a drying column and stored over activated 4 Å molecular sieves.[1] Diethyl ether was purchased from Sigma Aldrich, refluxed over Na and benzophenone, distilled under an N_2 atmosphere, and stored over 4 Å molecular sieves. Triethylorthoformate was purchased from Acros Organics, degassed by freeze-pump-thaw, and dried over 4 Å molecular sieves. Pyrrole was purchased from BeanTown Chemical, refluxed over CaH_2, and distilled under an N_2 atmosphere. All other solvents were ACS reagent grade and were used as received. Ethyl acetate was obtained from EMD Millipore. Diethyl ether, hexanes, and CH_2Cl_2 were obtained from Sigma Aldrich. Silica gel (0.060 – 0.200 mm, 60 Å for column chromatography), LiHMDS and NaHMDS were obtained from Acros Organics. Sodium hydride (57–63% dispersion in mineral oil), anhydrous $ZnCl_2$, chlorotrimethylsilane, and nitrosonium tetrafluoroborate were obtained from BeanTown Chemical. 2-Bromopyridine, JohnPhos, and 2-mesitylmagnesium bromide (1.0 M solution in THF) were obtained from Sigma Aldrich. $Pd(OAc)_2$ and anhydrous $FeCl_2$ were obtained from Strem. NMR solvents were obtained from Cambridge Isotope Laboratories; THF-d_8 was stored over 4 Å molecular sieves and others were used as received.

Characterization Details NMR spectra were recorded on an Inova-300, an Inova-500, or a NMRS-500 FT NMR spectrometer. Spectra were referenced against solvent resonances: $CDCl_3$ (7.26 ppm, ^1H; 77.16 ppm, ^{13}C), THF-d_8 (1.72, 3.58 ppm, ^1H).[2] ^1H NMR data are reported as follows: chemical shift (δ, ppm), (multiplicity: s (singlet), d (doublet), t (triplet), m (multiplet), br (broad), integration). ^{13}C NMR data are reported as follows: chemical shift (δ, ppm). UV-vis spectra were recorded at 293 K in quartz cuvettes on an Ocean Optics Flame-S miniature spectrometer with DH-mini UV-vis NIR light source and were blanked against the appropriate solvents. IR spectra were recorded on a Shimadzu Affinity-1S IR spectrometer. Spectra were blanked against air and were determined as the average of 128 scans. IR data are reported as follows: wavenumber (cm^{-1}), (peak intensity: s, strong; m, medium; w, weak). For electrochemistry experiments, a glassy carbon working electrode, Pt counter electrode, and Ag reference electrode were used (obtained from CH Instruments). An anhydrous THF solution of analyte (0.7 mM) with NBu_4PF_6 (0.1 M) as a supporting electrolyte was used for measurements. Reference electrodes were prepared using 0.1 M solution of $[TBA]PF_6$ in acetonitrile with 1.0 mM $AgNO_3$. MALDI data were obtained using a Bruker Microflex LRF MALDI-TOF using reflectron-TOF modes. Mass Spectrometry (ESI) data were obtained using an Orbitrap Fusion^{TM} Tribrid^{TM} mass spectrometer from ThermoFisher Scientific. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were carried out on a PerkinElmer NexION 300D Quadruple in pulse mode with ASX-520 Autosampler. The collected data were analyzed by NexION software version 1.3. The solids were digested in conc. HNO_3 by sonication and diluted with ultrapure water to make 1% HNO_3 solution. The concentration of Fe and Zn was determined by the calibration curves (^{57}Fe, $R^2 = 0.997$ and ^{64}Zn, $R^2 = 0.998$). ^{57}Fe Mössbauer spectra were collected on a model MS4 WRC low-field, variable-temperature spectrometer (See Co., Edina, MN).

X-ray Crystallography Details Crystals of $Fe_3(TPM)_2$, $Zn_3(TPM)_2$, and $Fe_2Zn(TPM)_2$ suitable for X-ray diffraction were obtained by cooling a concentrated THF solution at –35 °C. A Leica MZ 75 microscope was used to identify a suitable crystal. For $Fe_3(TPM)_2$ sample, a red-orange crystal (0.1 mm × 0.05 mm × 0.02 mm) was mounted on a MiTeGen dual-thickness micromount and placed under a cold N_2 stream (Oxford) maintained at 110 K. A BRUKER APEX 2 Duo X-ray (three-circle) diffractometer was used for crystal screening, unit cell determination, and data collection.

The X-ray radiation employed was generated from a Mo sealed X-ray tube (Kα = 0.70173 Å with a potential of 40 kV and a current of 40 mA). Bruker AXS APEX II software was used for data collection and reduction. Absorption corrections were applied using the program SADABS.[3] A solution was obtained using XT/XS in APEX2 and refined in Olex2.[4-6] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The structure was refined (weighted least squares refinement on F^2) to convergence. In the structure of $Fe_3(TPM)_2$, one of the two independent tetrahydrofuran solvates is disordered and was modelled using two parts. The bond distances and thermal ellipsoids in the disordered THF were restrained using the SADI and EADP commands. The restraints SIMU and DELU were also used on the disordered parts.

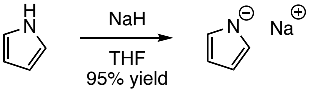
Variable-temperature (VT) X-ray diffraction data for $Fe_3(TPM)_2$ was collected using synchrotron radiation (0.41328 Å) at ChemMatCARS located at the Advanced Photon Source (APS) housed at Argonne National Laboratory (ANL). Crystals suitable for X-ray diffraction were mounted on a glass fiber pin with Paratone N oil. The data was collected at 10 K, 30 K, and 50 K using an Oxford Diffraction Helijet operating between 10–70 K and a vertically mounted Bruker D8 three-circle platform goniometer equipped with a PILATUS3 X CdTe 1M detector. Data was collected as a series of φ scans. Data were integrated using SAINT and scaled with a multi-scan absorption correction using SADABS. Data were integrated using SAINT and scaled with a multi-scan absorption correction using SADABS. Structures were solved by intrinsic phasing using SHELXT (Apex2 program suite v2014.1) and refined against F2 on all data by full matrix least squares with SHELXL97. All non-hydrogen atoms were refined anisotropically. H atoms were placed at idealized positions and refined using a riding model.

For $Zn_3(TPM)_2$, a colorless block with very well-defined faces with dimensions (0.11 mm × 0.08 mm × 0.06 mm) from a representative sample of crystals of the same habit was mounted on a nylon loop and was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.[7] The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418Å with a potential of 50 kV and a current of 1.0mA). 45 data frames were taken at widths of 0.5°. These reflections were used to determine the unit cell. There were indications suggesting a satellite crystal. Data was collected at a crystal to detector distance of 150 mm to resolve the overlapping reflections from the satellite crystal. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (45 sets) was initiated using omega and phi scans. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[7] The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[3] was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily using XT/XS in APEX3.[5-8] Two molecules of THF and 0.18 molecules of water were found solvated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Elongated thermal ellipsoids and the nearby residual electron density peaks suggested disorder on one of the THF molecule and was successfully modelled between two positions with an occupancy ratio close to 0.82:0.18. The occupancy ratio was fixed to those values during final least square refinement cycles. Appropriate restraints and constraints were used to keep the bond distances, angles, and thermal ellipsoids of the disordered groups meaningful. Absence of additional symmetry or void were confirmed using PLATON (ADDSYM).[9] The structure was refined (weighted least squares refinement on F^2) to convergence.[4-6, 8] Olex2 was employed for the final data presentation and structure plots.[4]

For $Fe_2Zn(TPM)_2$, a suitable orange plate with very well-defined faces with dimensions (0.20 mm × 0.20 mm × 0.04 mm) from a representative sample of crystals of the same habit was mounted on a nylon loop, and was then placed in a cold nitrogen stream (Oxford) maintained at 110 K. A BRUKER Venture X-ray (kappa geometry) diffractometer was employed for crystal screening, unit cell determination, and data collection. The goniometer was controlled using the APEX3 software suite.[7] The X-ray radiation employed was generated from a Cu-Iμs X-ray tube (K_α = 1.5418Å with a potential of 50 kV and a current of 1.0mA). 45 data frames were taken at widths of 1°. These reflections were used to determine the unit cell. The unit cell was verified by examination of the *h k l* overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (32 sets) was initiated using omega and phi scans. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[7] The integration method employed a three-dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, as well as for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[3] was employed to correct the data for absorption effects. Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/c$. A solution was obtained readily using XT/XS in APEX3.[5-8] Fe to Zn ratio of 2:1 was confirmed using HRMS (ESI+) and ICP-MS. Fe and Zn composition was refined with a restraint ratio of 2 : 1 in the three sites Fe1/Zn1, Fe2/Zn2, and Fe3/Zn3. All the three Fe/Zn sites refined to a ratio close to 0.66666:0.33333. The respective occupancies were constrained to these values during the final refinement. Our trials assuming all the three metal sites with only Fe (no Zn) resulted in R1 and wR2 values of 3.51% and 8.33%. On the other hand, assuming all the three metal sites with only Zn (no Fe) resulted with corresponding values of 5.18% and 15.58%. Our current results with the restraint of 2Fe:1Zn gave 3.33% and 8.23%. Two molecules of THF [(O1s, C2s-C5S) and (O6s, C7s-C10s)] were found solvated. Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The elongated thermal ellipsoids and nearby residual electron density peaks on both the solvated THF molecules indicated possible disorder, which were refined between two positions each with an occupancy ratio of [(0.65:0.35) and (0.56:0.44)] respectively. Appropriate restraints and constraints were added to keep the bond distances, angles, and thermal ellipsoids, of disordered atoms/groups meaningful. Absence of additional symmetry or void were confirmed using PLATON (ADDSYM).[9] The structure was refined (weighted least squares refinement on F^2) to convergence.[4-6, 8] Olex2 was employed for the final data presentation and structure plots.[4]

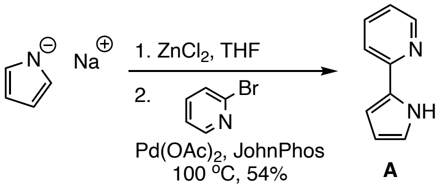
B. Synthesis and Characterization

Synthesis of sodium pyrrolide



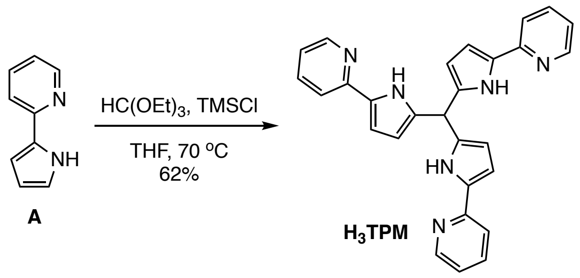
Sodium pyrrolide was prepared according to a previously reported method.[10] NaH was rinsed three times with THF and kept in an N_2-filled glovebox. A 100-mL round bottom flask was charged with NaH (2.86 g, 0.119 mol, 2.00 equiv) and anhydrous THF (20 mL). Pyrrole (4.00 g, 0.0596 mol, 1.00 equiv) was added dropwise to the NaH suspension over 30 min. The suspension was stirred at 23 °C for 30 min. The reaction mixture was filtered and the filtrate was concentrated *in vacuo* to afford 5.07 g of the title compound (95% yield).

Synthesis of 2-(2'-pyridyl)-1H-pyrrole (A).



Under an N_2 atmosphere, a 250-ml Schlenk tube was charged with sodium pyrrolide (6.00 g, 67.4 mmol, 3.01 equiv) and $ZnCl_2$ (9.18 g, 67.4 mmol, 3.01 equiv). With vigorous stirring, THF (30 mL) was slowly added to the reaction vessel, and the reaction mixture was allowed to stir at 23 °C for 1 h. To the reaction mixture, JohnPhos (33.0 mg, 0.111 mmol, 0.5 mol%) and $Pd(OAc)_2$ (25.0 mg, 0.111 mmol, 0.5 mol%) were added. After stirring for 5 min, 2-bromopyridine (2.14 ml, 22.4 mmol, 1.00 equiv) was added. The reaction vessel was sealed with a Teflon stopper and the reaction mixture was heated at 100 °C for 21 h. The reaction mixture was cooled to 23 °C. Under an ambient atmosphere, distilled water (15 mL) and diethyl ether (15 mL) were added to the reaction mixture, and the organic layer was extracted with diethyl ether (3 × 15 ml) and dried over $MgSO_4$. Solvent was removed *in vacuo* and the residue was purified by SiO_2 chromatography (4 : 1 hexanes : ethyl acetate) to afford 1.75 g of the title compound (54% yield). ^{1}H NMR (δ, 23 °C, $CDCl_3$): δ 9.81 (s, 1H), 8.46 (ddd, J = 4.9, 1.8, 1.0 Hz, 1H), 7.62 (ddd, J = 8.0, 7.4, 1.8 Hz, 1H), 7.55 (dt, J = 8.0, 1.0 Hz, 1H), 7.03 (ddd, J = 7.4, 4.9, 1.2 Hz, 1H), 6.91 (td, J = 2.6, 1.4 Hz, 1H), 6.72 (ddd, J = 3.7, 2.4, 1.3 Hz, 1H), 6.30 (dt, J = 3.6, 2.6 Hz, 1H). ^{13}C NMR (δ, 23 °C, $CDCl_3$) 150.7, 149.0, 136.6, 120.6, 120.0, 118.3, 110.3, 107.2 ppm. The recorded spectral data are in good agreement with those reported in literature.[11]

Synthesis of tris(2-(2’-pyridyl)-1H-pyrrolyl)methane (H_3TPM).



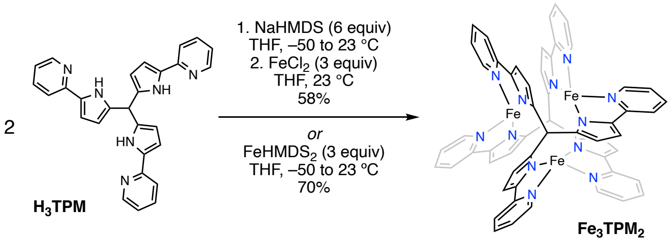
Under an N_2 atmosphere, a 20-mL scintillation vial was charged with 2-(2’-pyridyl)-1H-pyrrole (**A**, 244 mg, 1.70 mmol, 3.00 equiv), triethylorthoformate (136 mg, 0.918 mmol, 1.62 equiv), trimethylsilyl chloride (TMSCl, 0.5 mL, 3.94 mmol, 6.95 equiv), and THF (2 mL). The reaction vessel was sealed with a Teflon-lined cap and heated at 70 °C for 12 h. The reaction mixture was cooled to 23 °C, at which time a red solid was observed. Under an ambient atmosphere, the supernatant was decanted and CH_2Cl_2 (100 mL) and water (20 mL) were added to the residue. The organic layer was separated. To the aqueous layer, sat. aq. $NaHCO_3$ solution (10 mL) was added and the aqueous layer was re-extracted (3 × 10 mL) with CH_2Cl_2. The combined organic layer was dried over $MgSO_4$, solvent was removed *in vacuo*, and the residue was purified by SiO_2 chromatography (eluent from 4:1 to 1 : 1 hexanes : ethyl acetate) to afford 156 mg of the title compound (62% yield). ^{1}H NMR (δ, 23 °C, $CDCl_3$): δ 9.69 (s, 3H), 8.37 (ddd, *J* = 4.9, 1.7, 1.0 Hz, 3H), 7.57 (td, *J* = 7.7, 1.8 Hz, 3H), 7.49 (dt, *J* = 8.1, 1.0 Hz, 3H), 6.96 (ddd, *J* = 7.3, 5.0, 1.1 Hz, 3H), 6.62 (dd, *J* = 3.5, 2.3 Hz, 3H), 6.09 (t, *J* = 2.8 Hz, 3H), 5.60 (s, 1H). ^{13}C NMR (δ, 23 °C, $CDCl_3$) 150.7, 148.8, 136.5, 133.3, 131.5, 120.4, 118.1, 109.4, 107.8, 38.2 ppm. HRMS (ESI$^+$): calcd. for $C_{28}H_{22}N_6Na$ $[M+Na]^+$ 465.1798. Found: 465.1801.

Synthesis of iron bis(trimethylsilyl)amide ($Fe(HMDS)_2$)

$$\mathrm{FeCl_2} \xrightarrow[\substack{\mathrm{Et_2O},\ -50\ \text{to}\ 23\ ^\circ\mathrm{C},\ 20\ \mathrm{h} \\ 55\%\ \text{yield}}]{\text{Li(HMDS) (2 equiv)}} \mathrm{FeHMDS_2}$$

Iron bis(trimethylsilyl)amide ($Fe(HMDS)_2$) was prepared according to a previously reported method in an N_2-filled glovebox.[12] A 250-mL Erlenmeyer flask was charged with anhydrous $FeCl_2$ (0.760 g, 6.00 mmol, 1.00 equiv) and Et_2O (20 mL). A 40-mL scintillation vial was charged with Li(HMDS) (2.00 g, 12.0 mmol, 2.00 equiv) and Et_2O (40 mL). The suspension of $FeCl_2$ and the solution of Li(HMDS) were cooled to –50 °C in a glovebox cold well (cooled with dry ice and acetone) before the Li(HMDS) solution was added to the $FeCl_2$ suspension dropwise over 15 min. The suspension was allowed to warm slowly to 23 °C and was stirred for 20 h. The mixture was concentrated under vacuum, and the dark green residue was extracted with pentane (3 × 5 mL). The combined extracts were filtered into a 100-mL round bottom flask and concentrated under vacuum to afford a dark green oil. The round bottom flask was connected to a distillation apparatus with a 25-mL Schlenk flask in the glovebox, and the oil was distilled under reduced pressure at 110 °C to afford a pyrophoric green oil. The distillation apparatus was transferred back into a N_2-filled glovebox, and the product was transferred to a 20-mL scintillation flask and solidified in the freezer (–35 °C) to afford a green solid (1.24 g, 55% yield).

Synthesis of $Fe_3(TPM)_2$.



Method A. The following synthesis was carried out in an N_2-filled glovebox. In separate 20-mL scintillation vials, a suspension of $FeCl_2$ (13 mg, 0.10 mmol, 1.5 equiv) in THF (2 mL), and solutions of NaHMDS (40 mg, 0.22 mmol, 3.2 equiv) in THF (2 mL) and H_3TPM (30 mg, 0.068 mmol, 1.0 equiv) in THF (2 mL), were prepared. The suspension and solutions were cooled to –50 °C in a glovebox cold well (cooled with dry ice and acetone). With stirring, the NaHMDS solution was added to the H_3TPM solution, dropwise. The resulting reaction mixture was warmed to 23 °C and was stirred for 1 h. Then, $FeCl_2$ suspension was added to deprotonated ligand solutions and the reaction mixture was stirred at 23 °C for 24 h. At this time, the reaction mixture was filtered through Celite and the filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized in concentrated THF at –35°C to afford 21 mg of the title compound (58% yield).

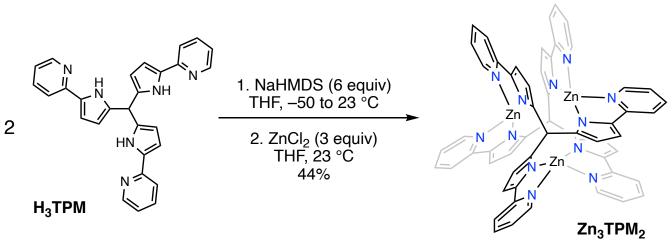
Method B. The following synthesis was carried out in an N_2-filled glovebox. In separate 20-mL scintillation vials, solutions of $Fe(HMDS)_2$ (38 mg, 0.050 mmol, 1.47 equiv) in THF (2 mL) and H_3TPM (30 mg, 0.068 mmol, 1.0 equiv) in THF (2 mL), were prepared. Both solutions were cooled to –50 °C in a glovebox cold well (cooled with dry ice and acetone). With stirring, the $Fe(HMDS)_2$ solution was added to the H_3TPM solution, dropwise. The resulting reaction mixture was warmed to 23 °C and was stirred for 24 h. At this time, the reaction mixture was filtered through Celite and the filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized in concentrated THF at –35°C to afford 25 mg of the title compound (70% yield).[a]

^1H NMR (δ, 23 °C, THF-d_8): 136.2 (3H), 55.6 (3H), 49.2 (3H), 35.4 (3H), 30.6 (1H), 21.3 (3H), –6.1 (3H) ppm. UV-vis (THF), λ_{max} (nm, ε (M^{-1} cm^{-1})): 285 (3.0×10^4), 322 (2.6×10^4), 382 nm (1.2×10^4), 496 (2.1×10^3), 614 (4.9×10^2). IR (cm^{-1}): 3078 (w), 2972 (w), 2847 (w), 1600 (s), 1556 (w), 1533 (m), 1469 (s), 1439 (m), 1401 (w), 1331 (w), 1310 (m), 1263 (w), 1240 (m), 1237 (m), 1149 (m), 1112 (m), 1055 (s), 1008 (m), 866 (w), 805 (w), 745 (s). MALDI-TOF-MS: calcd. for $C_{56}H_{38}Fe_3N_{12}$ $[M]^+$ m/z 1046.139. Found: 1046.058. Elemental Analysis (EA) for $[[Fe_3(C_{28}H_{19}N_6)_2]]$: calcd. C, 64.27; H, 3.66; N, 16.06; found C, 65.03; H 4.59; N, 15.66.

---

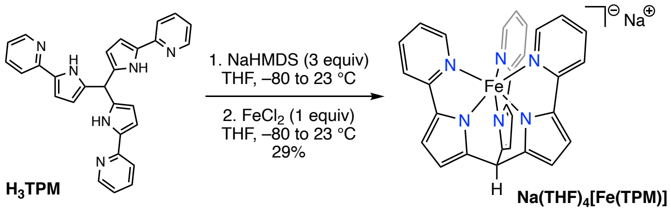
[a] To evaluate the impact of metal loading on the aggregation of the obtained product, we have also carried out this procedure using 1.0 equivalents of $FeCl_2$ in place of the described 1.5 equivalents. By ^1H NMR, a mixture of products was obtained, but the major species in Fe_3TPM_2 which confirms that this compound is the thermodynamic product of metalation and not generated simply due to metal loading.

Synthesis of $Zn_3(TPM)_2$.



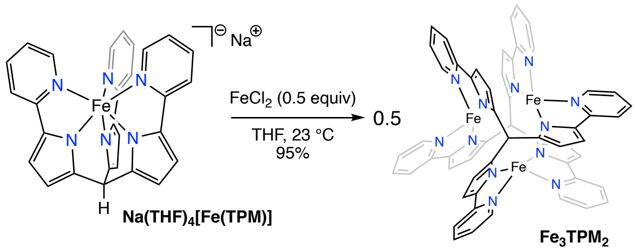
In separate 20-mL scintillation vials, solutions of $ZnCl_2$ (13 mg, 0.10 mmol, 1.5 equiv) in THF (2 mL), NaHMDS (40 mg, 0.22 mmol, 3.2 equiv) in THF (2 mL), and H_3TPM (30 mg, 0.068 mmol, 1.0 equiv) in THF (2 mL), were prepared. All solutions were cooled to –50 °C in a glovebox cold well (cooled with dry ice and acetone). With stirring, the NaHMDS solution was added to the H_3TPM solution, dropwise. The resulting reaction mixture was warmed to 23 °C and was stirred for 1 h. Then, $ZnCl_2$ suspension was added to deprotonated ligand solutions and the reaction mixture was stirred for 24 h. At this time, the reaction mixture was filtered through Celite and the filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized in concentrated THF at –35°C to afford 16 mg of the title compound (44% yield). ^1H NMR (δ, 23 °C, THF-d_8): 7.39 (ddd, $J = 8.4, 7.1, 1.5$ Hz, 3H), 6.95-6.94 (m, 3H), 6.89-6.87 (m, 3H), 6.45 (ddd, $J = 7.2, 5.3, 1.1$ Hz, 3H), 5.79 (d, $J = 1.0$ Hz, 6H), 5.70 (s, 1H). ^{13}C NMR (δ, 23 °C, THF-d_8): 153.4, 147.1, 146.0, 137.8, 135.9, 116.6, 116.5, 110.8, 44.4 ppm. UV-vis (THF), λ_{max} (nm, ε (M^{-1} cm^{-1})): 285 (3.0×10^4), 336 (2.0×10^4), 580 (4.8×10^2). IR (cm^{-1}): 3078 (w), 2954 (w), 2924(w), 2858 (w), 1605 (s), 1555 (w), 1528 (s), 1466 (s), 1439 (m), 1412 (m), 1339 (w), 1323 (m), 1265 (w), 1246 (m), 1204 (w), 1149 (m), 1115 (m), 1053 (s), 1011 (m), 934 (w), 868 (w), 810 (w), 775 (w), 740 (s) 706 (w), 679 (w), 644 (w). HRMS (ESI$^+$): calcd. for $C_{56}H_{38}Zn_3N_{12}$ $[M+H]^+$ m/z 1073.126. Found: 1073.121. Elemental Analysis (EA) for $[[Zn_3(C_{28}H_{19}N_6)_2]]$: calcd. C, 62.55; H, 3.56; N, 15.63; found. C, 62.33; H, 4.27; N, 14.03.

Synthesis of Na(THF)$_4$[FeTPM].



In separate 20-mL scintillation vials, solutions of FeCl$_2$ (9.0 mg, 0.071 mmol, 1.0 equiv) in THF (2 mL), NaHMDS (40 mg, 0.22 mmol, 3.2 equiv) in THF (2 mL), and H$_3$TPM (30 mg, 0.068 mmol, 1.0 equiv) in THF (2 mL), were prepared. All solutions were cooled to –80 °C in a glovebox cold well (cooled with liquid nitrogen). With stirring, the NaHMDS solution was added to the H$_3$TPM solution, dropwise. The resulting reaction mixture was warmed to 23 °C, was stirred for 1 h, and was cooled to –80 °C in a cold well. The FeCl$_2$ suspension was added to the deprotonated ligand solution and the reaction was allowed to slowly warm to 23°C, at which temperature the reaction was stirred for 6 h. The reaction mixture was filtered through Celite and the filtrate was concentrated to dryness *in vacuo*. The residue was recrystallized in concentrated THF at –35°C to afford 16 mg of the title compound (29% yield). ^{1}H NMR (δ, 23 °C, THF-d_8): 79.3 (3H), 45.4 (3H), 40.8 (3H), 29.0 (3H), 5.4-5.2 (4H), –1.8 (3H) ppm. MALDI-TOF-MS: calcd. for [$C_{28}H_{19}N_6Fe$]$^+$ m/z = 495.103. Found: 494.839.[b] UV vis (THF), λ_{max} (nm, ε (M^{-1} cm^{-1})): 337 (4.0 × 10^5), 580 (1.3 × 10^4). IR (cm^{-1}): 3437 (w), 3071 (w), 2951 (w), 2862 (w), 1593 (s), 1555 (w), 1520 (m), 1497 (s), 1454 (s), 1443 (s), 1396 (m), 1339 (w), 1304 (m), 1246 (m), 1204 (w), 1184(w), 1150 (m), 1111 (w), 1076 (w), 1045 (s), 995 (m), 934 (m), 883 (w), 837 (w), 772 (m), 745 (s) 706 (m), 679 (m), 644 (w).

Synthesis of Fe$_3$(TPM)$_2$ from Na(THF)$_4$[FeTPM].

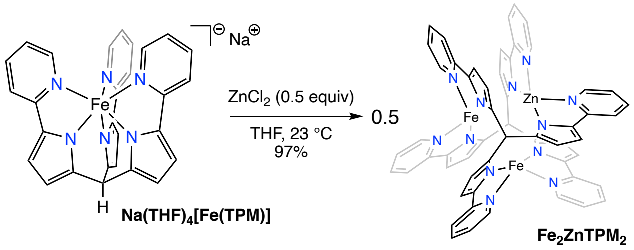


Under an N$_2$ atmosphere, a 20-mL scintillation vial was charged with Na(THF)$_4$[FeTPM] (19 mg, 0.024 mmol, 1.0 equiv), FeCl$_2$ (1.5 mg, 0.012 mmol, 0.50 equiv), and THF (3 mL). The reaction mixture solution was stirred at 23 °C for 6 h, and then was filtered through Celite. The filtrate was concentrated and stored at –35 °C for recrystallization, affording 24 mg of the Fe$_3$(TPM)$_2$ (95% yield).

---

[b] These mass spectrometry datawere not obtained under air-free conditions. We speculate that Na(THF)$_4$[Fe(TPM)] is oxidized in air to afford Fe(TPM). The reported data was detected in positive mode.

Synthesis of Fe_2ZnTPM_2.



Under an N_2 atmosphere, a 20-mL scintillation vial was charged with $Na(THF)_4[FeTPM]$ (15 mg, 0.019 mmol, 1.0 equiv), $ZnCl_2$ (1.2 mg, 0.0088 mmol, 0.46 equiv), and THF (3 mL). The reaction mixture solution was stirred at 23 °C for 6 h, and then was filtered through Celite. The filtrate was concentrated and stored at –35 °C for recrystallization, affording 9 mg of the Fe_2ZnTPM_2 (97% yield). UV vis (THF), λ_{max} (nm, ε (M^{-1} cm^{-1})): 285 (2.5×10^4), 334 (1.9×10^4), 381 nm (1.4×10^4), 522 (1.8×10^3), 603 (1.1×10^3). IR (cm^{-1}): 3082 (w), 2947 (w), 2920 (w), 2862 (w), 1666 (w), 1601 (s), 1555 (w), 1528 (s), 1466 (s), 1439 (s), 1408 (m), 1331 (w), 1312 (m), 1242 (m), 1204 (w), 1184(w), 1150 (m), 1111 (w), 1084 (w), 1053 (s), 1011 (m), 934 (w), 864 (w), 810 (m), 775 (m), 741 (s) 706 (m), 683 (m), 644 (w), 602 (w).

C. Supporting Data

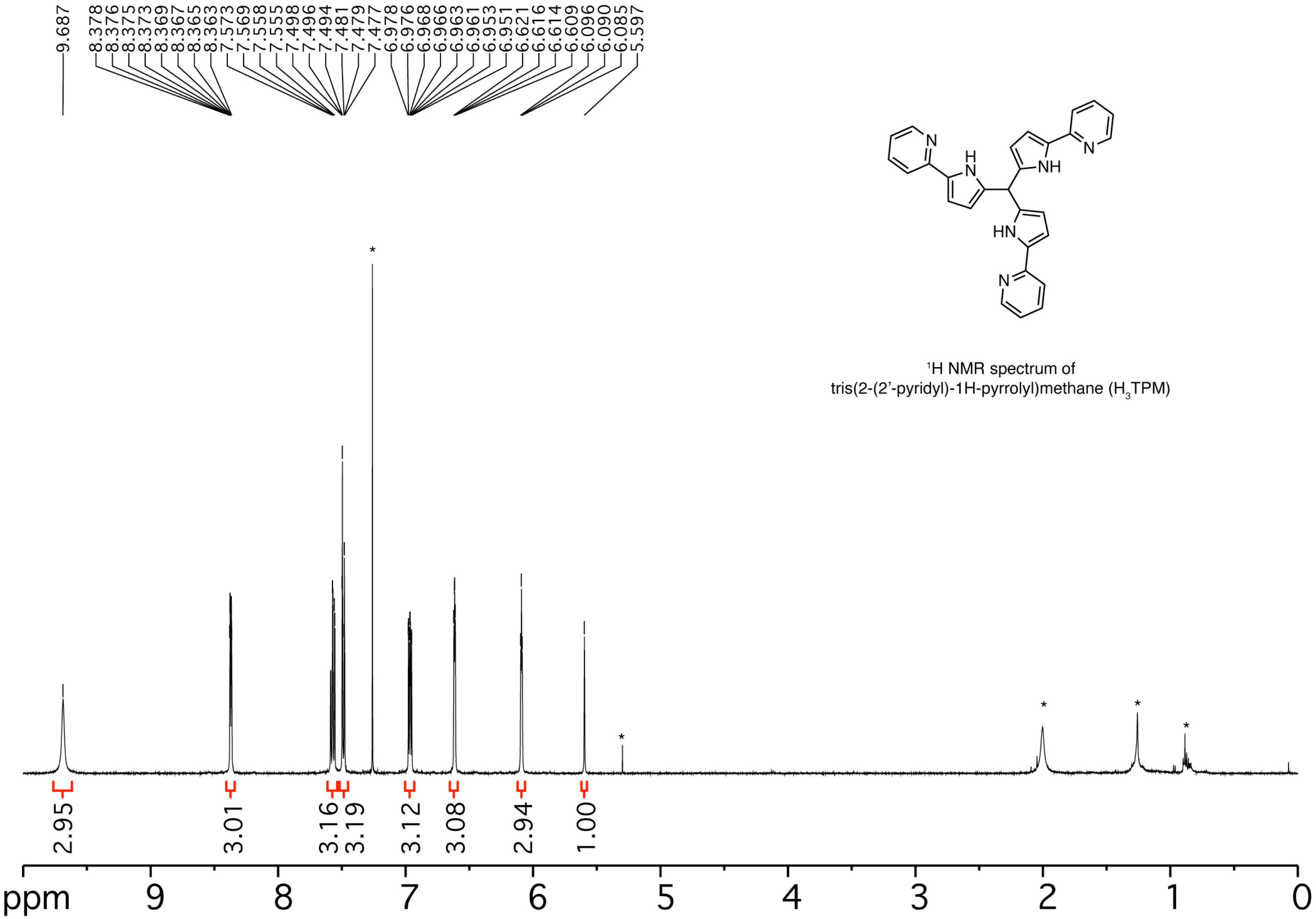


Figure S1. ^{1}H NMR spectrum of H_3TPM measured in $CDCl_3$ at 23 °C; $CDCl_3$, solvent (CH_2Cl_2), and grease peaks are marked with *.

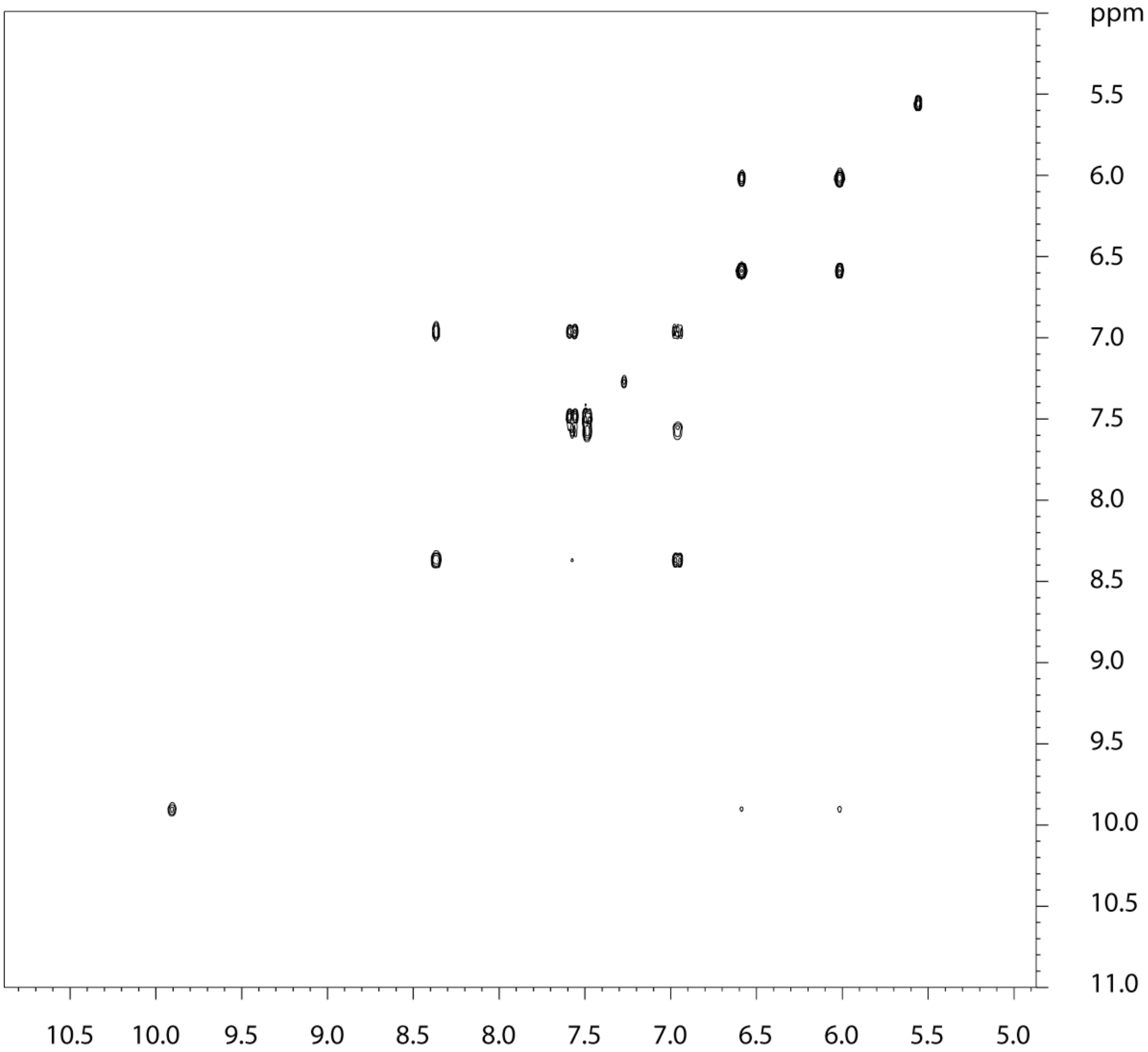


Figure S2. COSY spectrum of H_3TPM measured in $CDCl_3$ at 23 °C.

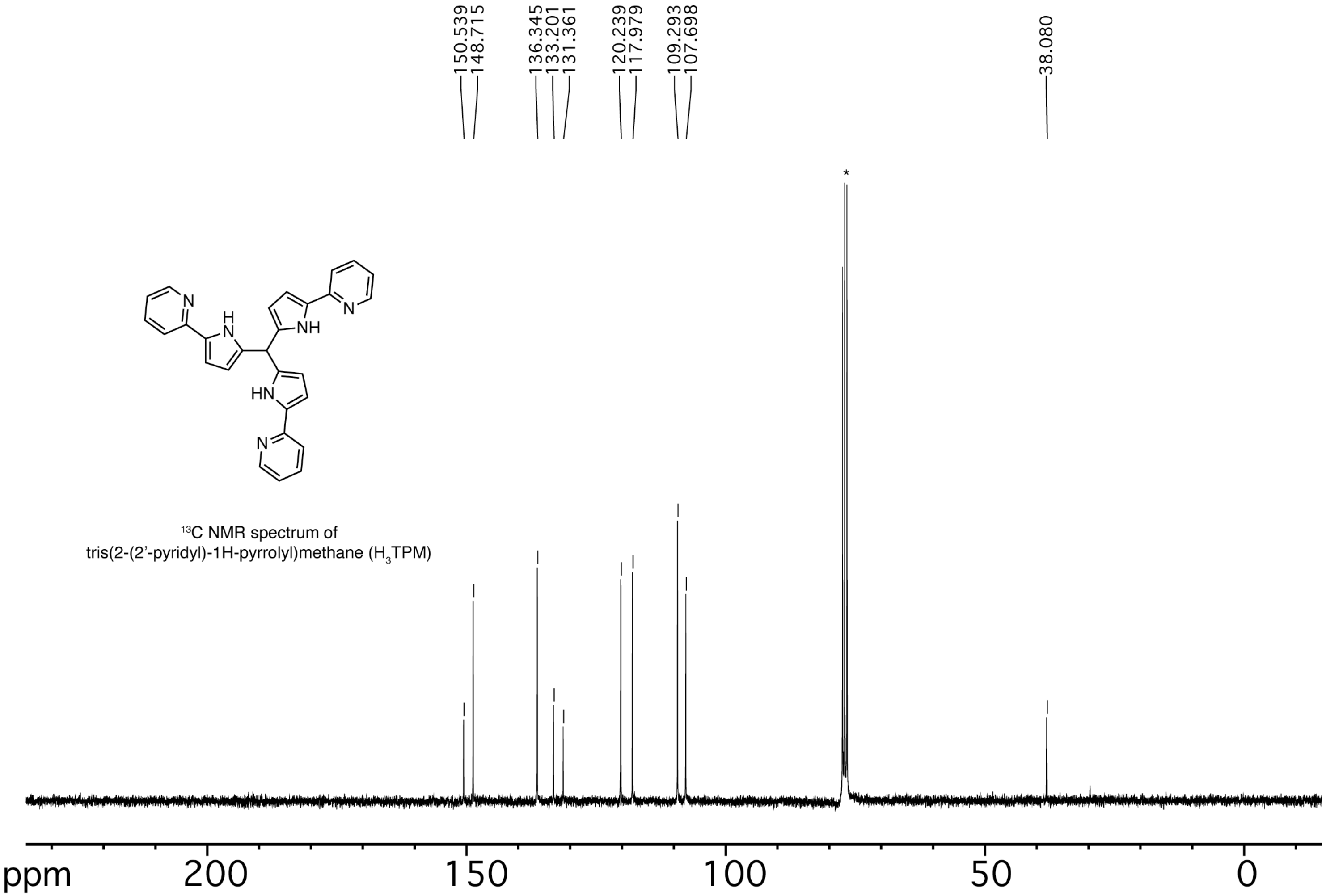


Figure S3. ^{13}C NMR spectrum of H_3TPM measured in $CDCl_3$ at 23 °C; $CDCl_3$ peak is marked with *.

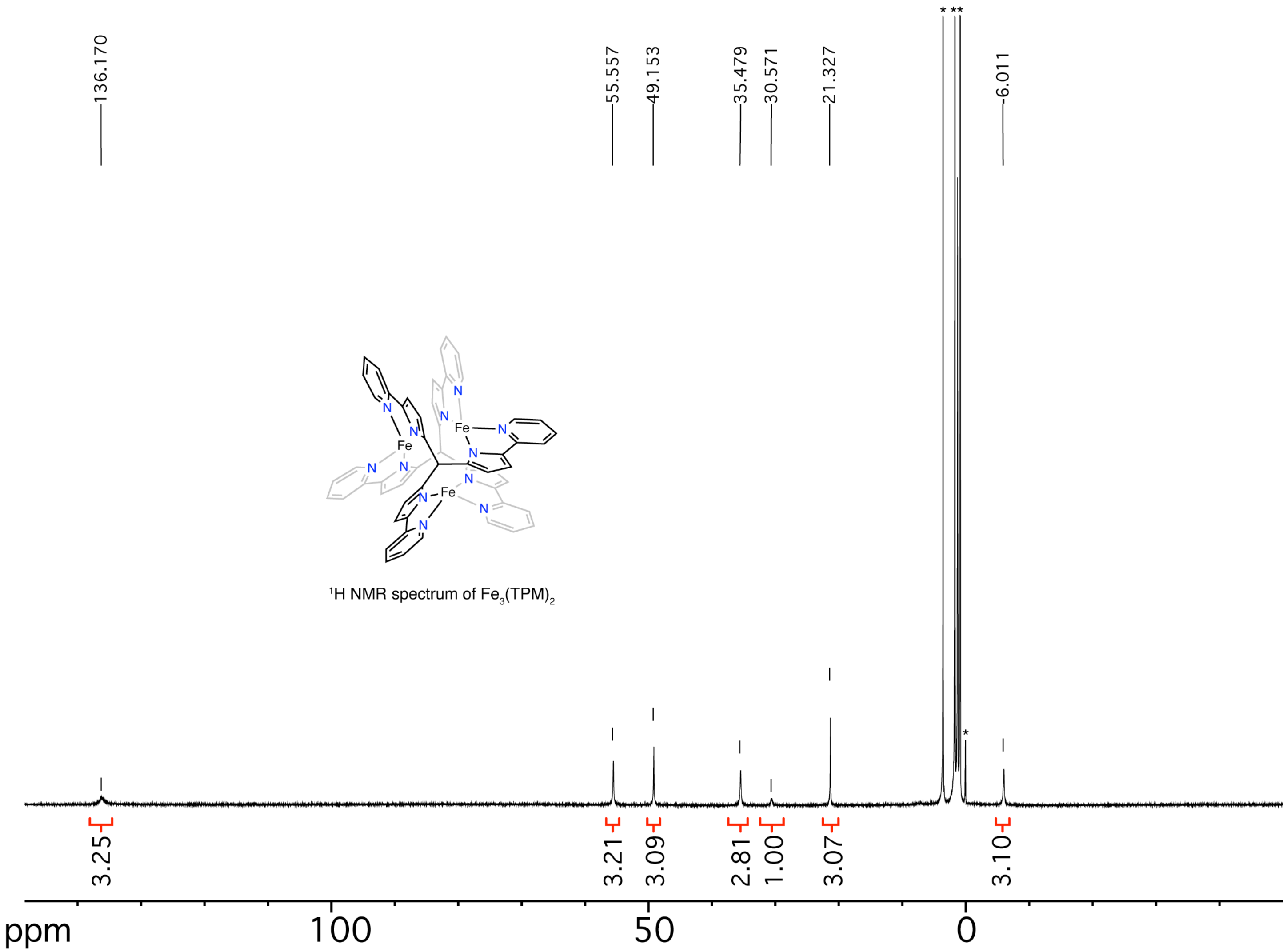


Figure S4. ^{1}H NMR spectrum of $Fe_3(TPM)_2$ measured in THF-d_8 at 23 °C; THF-d_8 and grease peaks are truncated and are marked with *

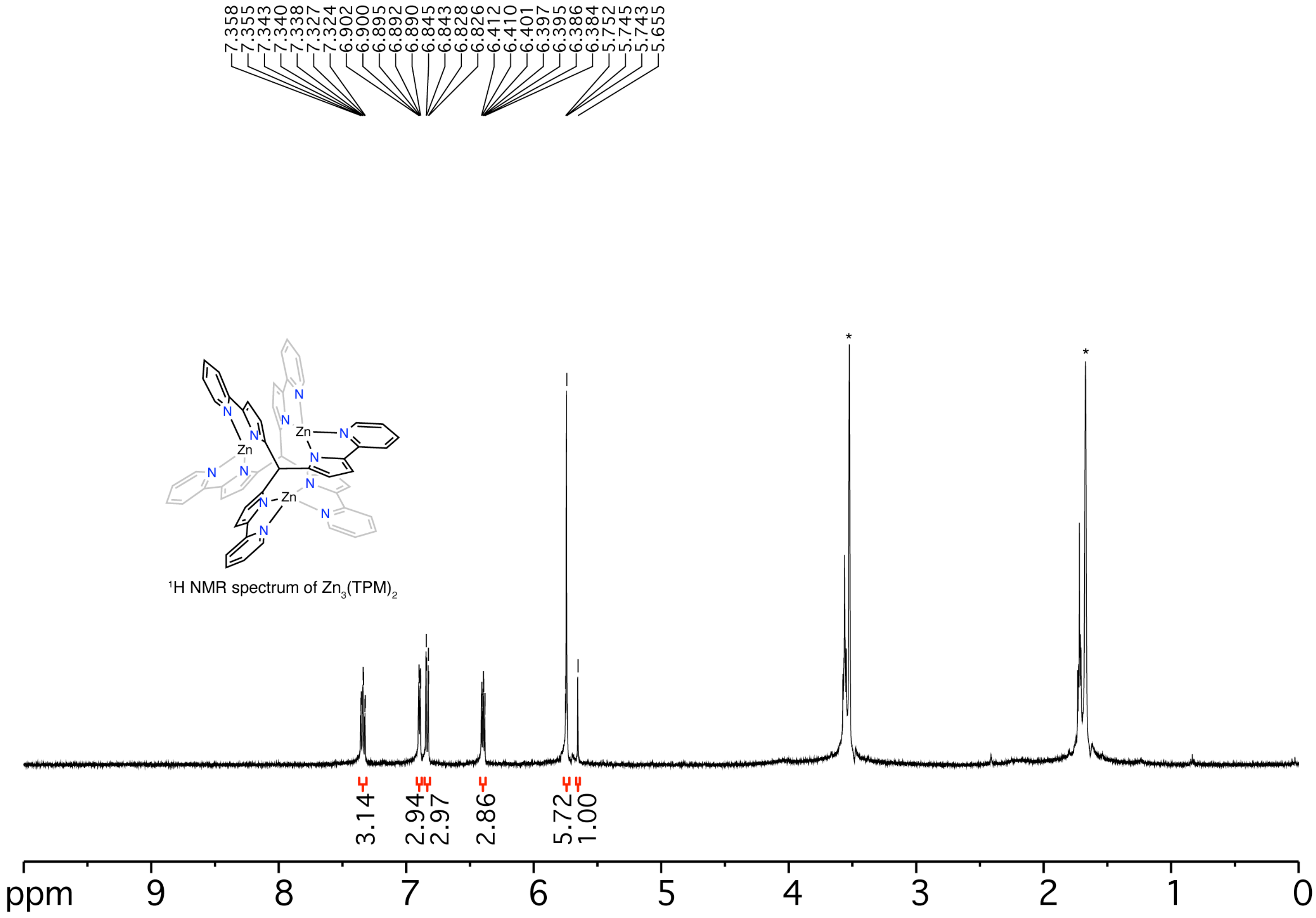


Figure S5. ^{1}H NMR spectrum of Zn$_3$(TPM)$_2$ measured in THF-d_8 at 23 °C; THF-d_8 peaks are marked with *.

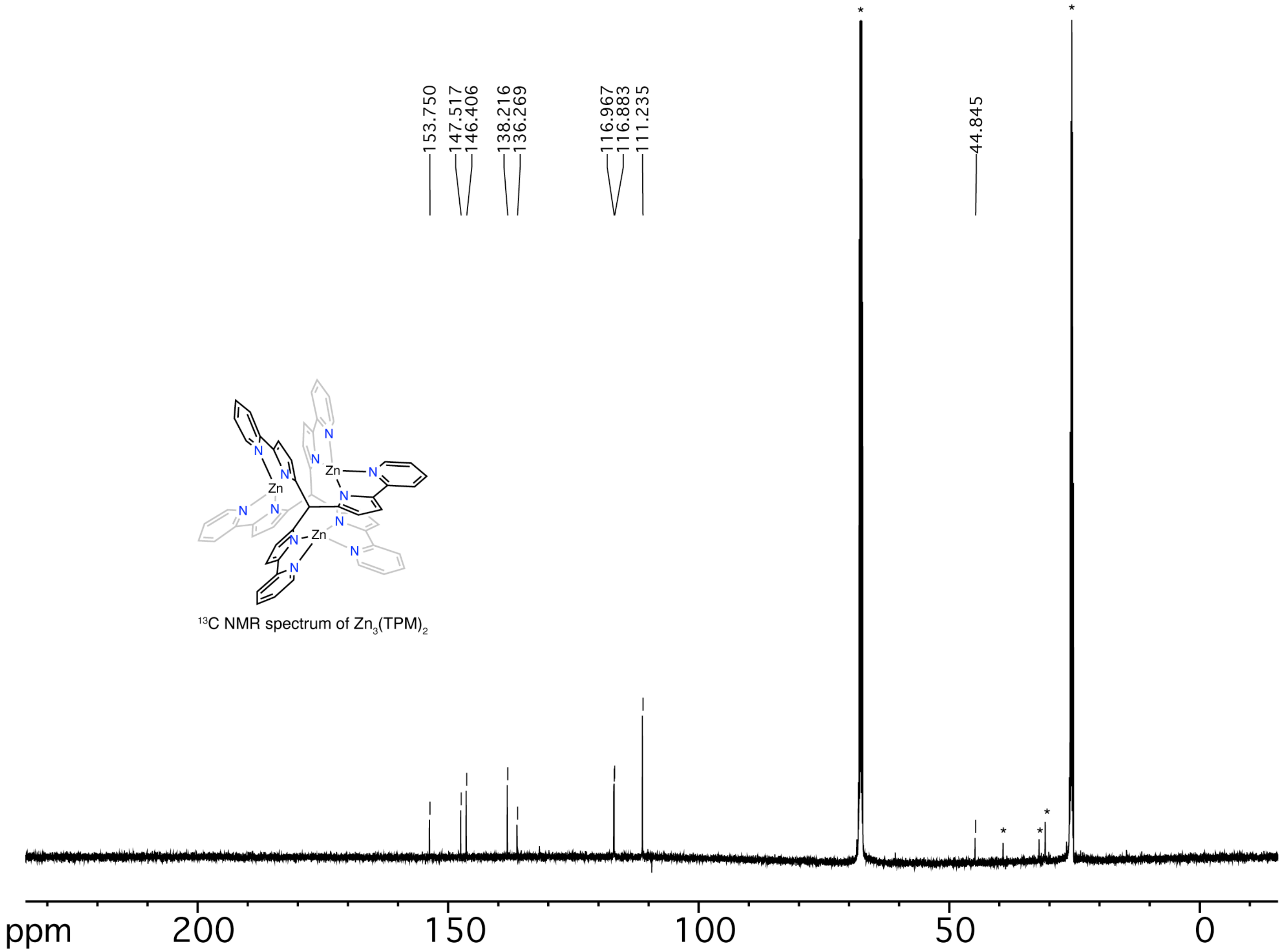


Figure S6 ^{13}C NMR spectrum of $Zn_3(TPM)_2$ measured in THF-d_8 at 23 °C; THF-d_8 solvent and grease peaks are marked with *.

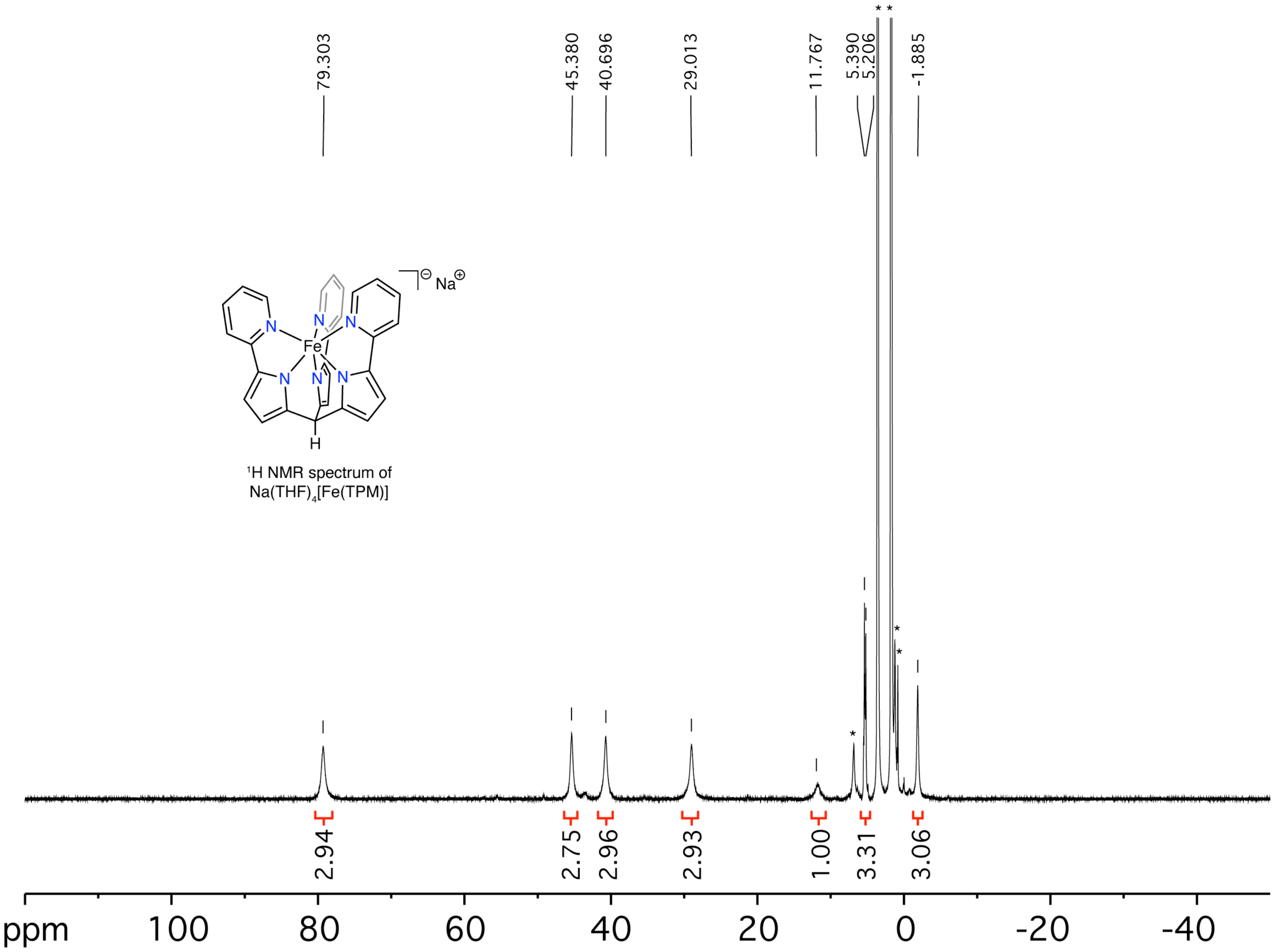


Figure S7. ^{1}H NMR spectrum of Na(THF)$_4$[Fe(TPM)] measured in THF-d_8 at 23 °C; THF-d_8 peaks are truncated and are marked with * along with grease and an unidentified impurity peak.

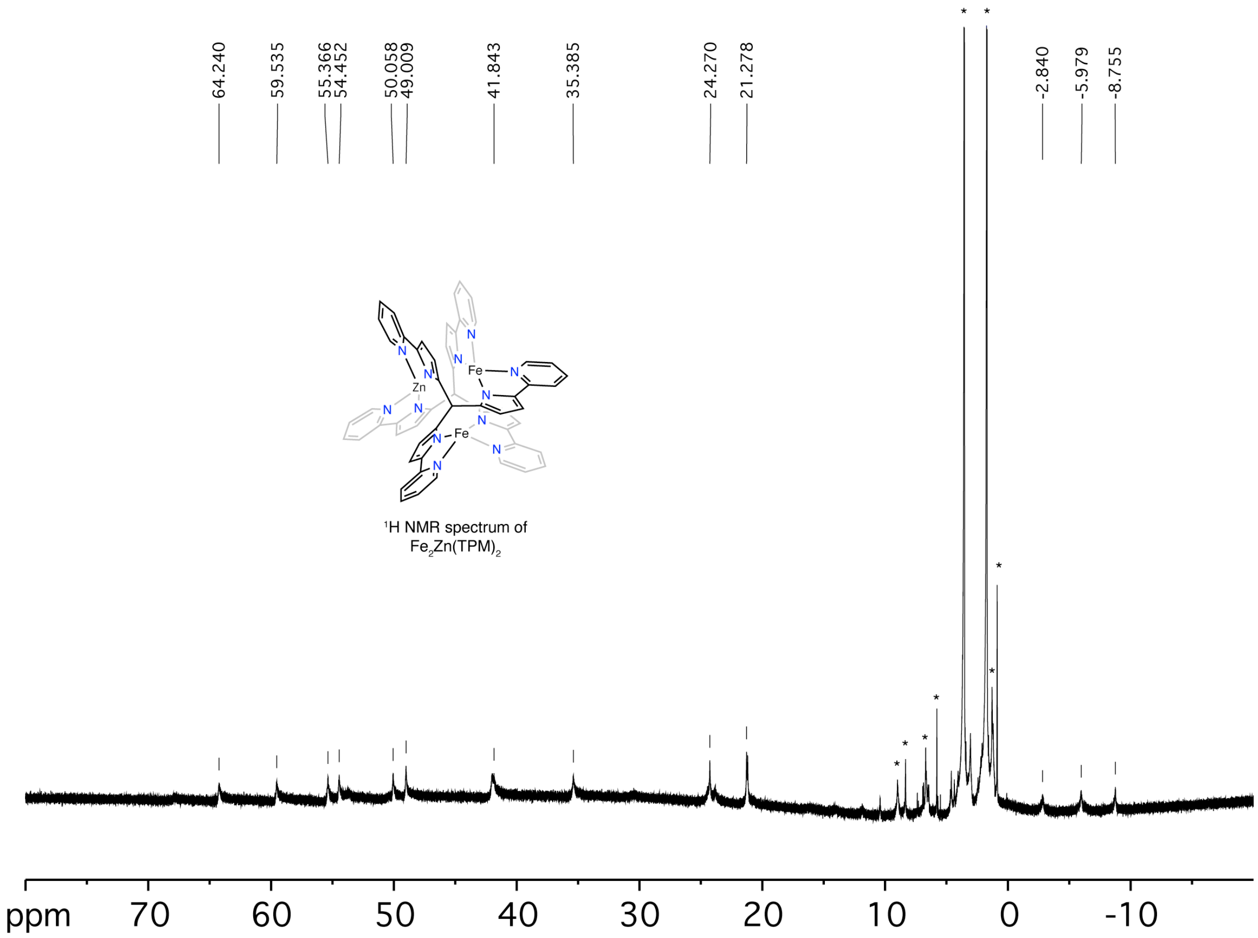


Figure S8. ^{1}H NMR spectrum of $Fe_2Zn(TPM)_2$ measured in THF-d_8 at 23 °C; THF-d_8 peaks are truncated and are marked with * along with grease and ligand peaks due to water present in the NMR solvent.

Examination of potential metal exchange between $Fe_3(TPM)_2$ and $Zn_3(TPM)_2$

A 20-mL scintillation vial was charged with THF-*d₈* (0.5 mL), $Fe_3(TPM)_2$ (10 mg, 0.0096 mmol, 1.0 equiv), and $Zn_3(TPM)_2$ (10 mg, 0.0093 mmol, 1.0 equiv). The reaction was stirred at 23 °C and was monitored periodically by ^{1}H NMR over 24 h.

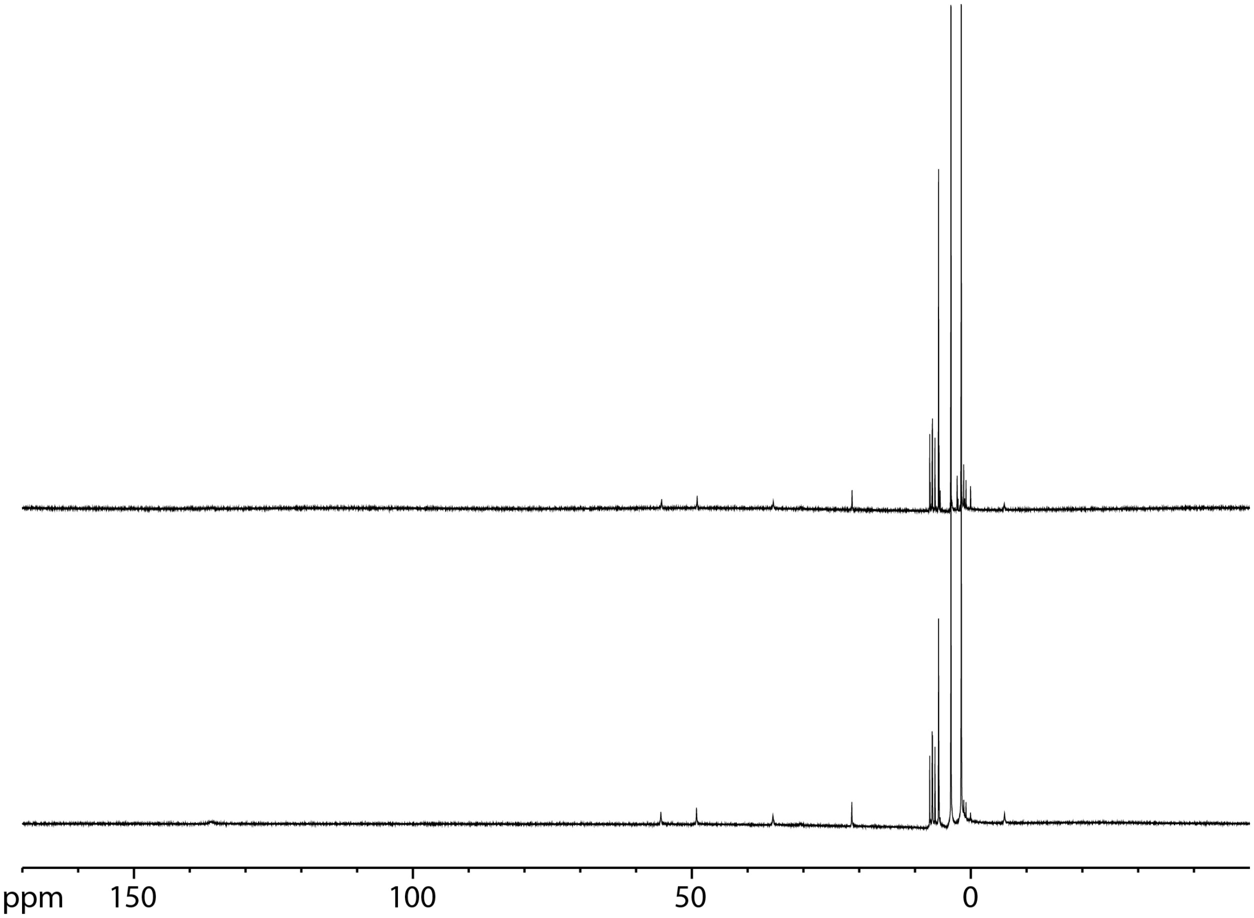


Figure S9. ^{1}H NMR spectra obtained from a THF-d_8 solution of $Fe_3(TPM)_2$ and $Zn_3(TPM)_2$ collected 1h (bottom) and 24 h (top) after the homometallic trinuclear complexes were combined.

Examination of potential metal exchange between $Fe_3(TPM)_2$ and $ZnCl_2$

A 20-mL scintillation vial was charged with THF (2 mL), $Fe_3(TPM)_2$ (10 mg, 0.0096 mmol, 1.0 equiv), and $ZnCl_2$ (4.0 mg, 0.029 mmol, 3.0 equiv). The reaction was stirred at 23 °C for 24 h, and then evacuated under reduced pressure. The result was analyzed by ^1H NMR in THF-d_8.

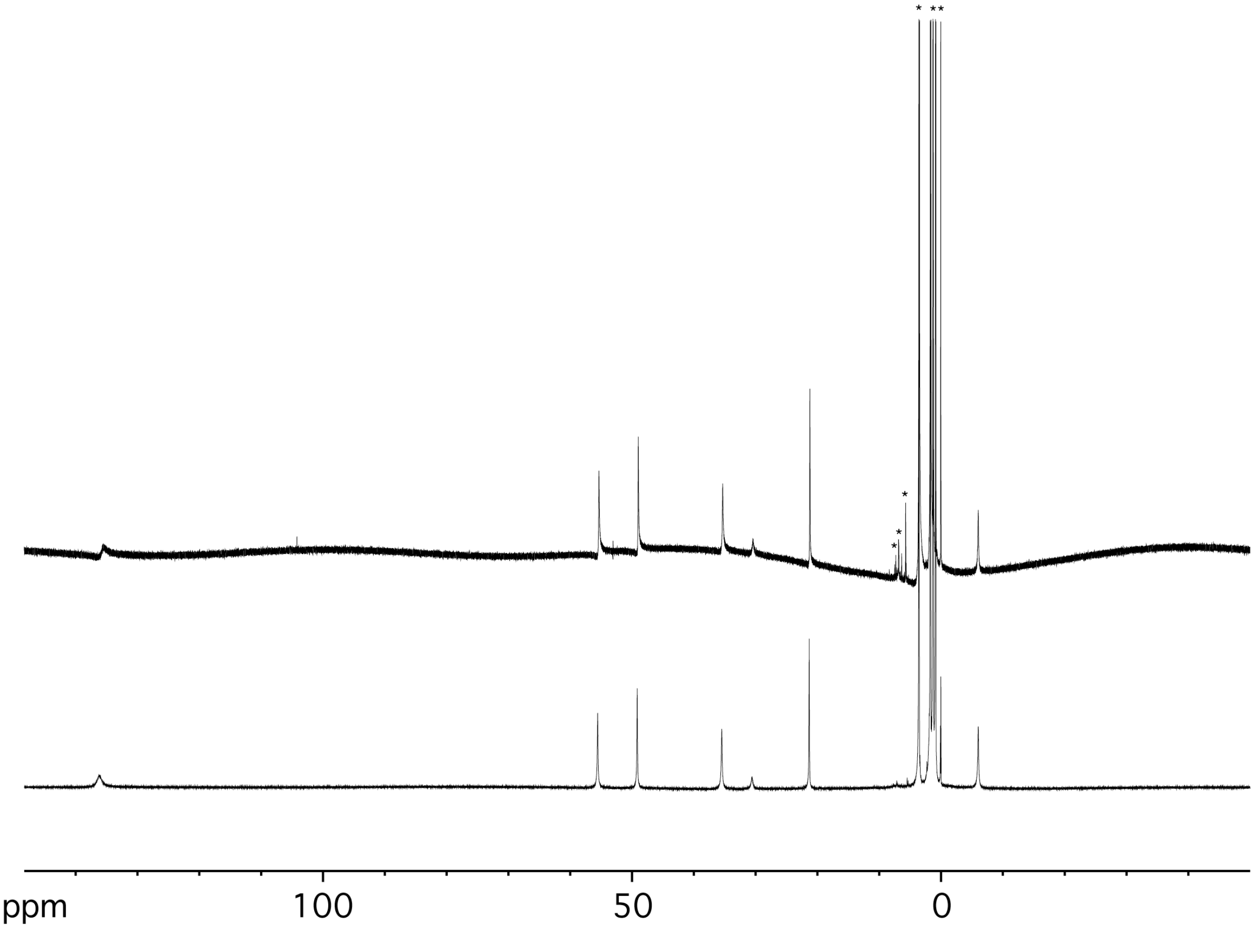


Figure S10. ^1H NMR spectra obtained from $Fe_3(TPM)_2$ before adding $ZnCl_2$ (bottom) and after a 24 h reaction of $Fe_3(TPM)_2$ and $ZnCl_2$ (top). THF-d_8 peaks are truncated and are marked with * along with grease and ligand peaks due to water present in the NMR solvent.

Table S1. The concentration and ratio of Fe and Zn observed in compound $Fe_2Zn(TPM)_2$ by ICP-MS.

	^{57}Fe	^{64}Zn
Concentration (ppb)	28.46 ± 0.98	15.45 ± 0.10
Molar ratio	2.07	1.00

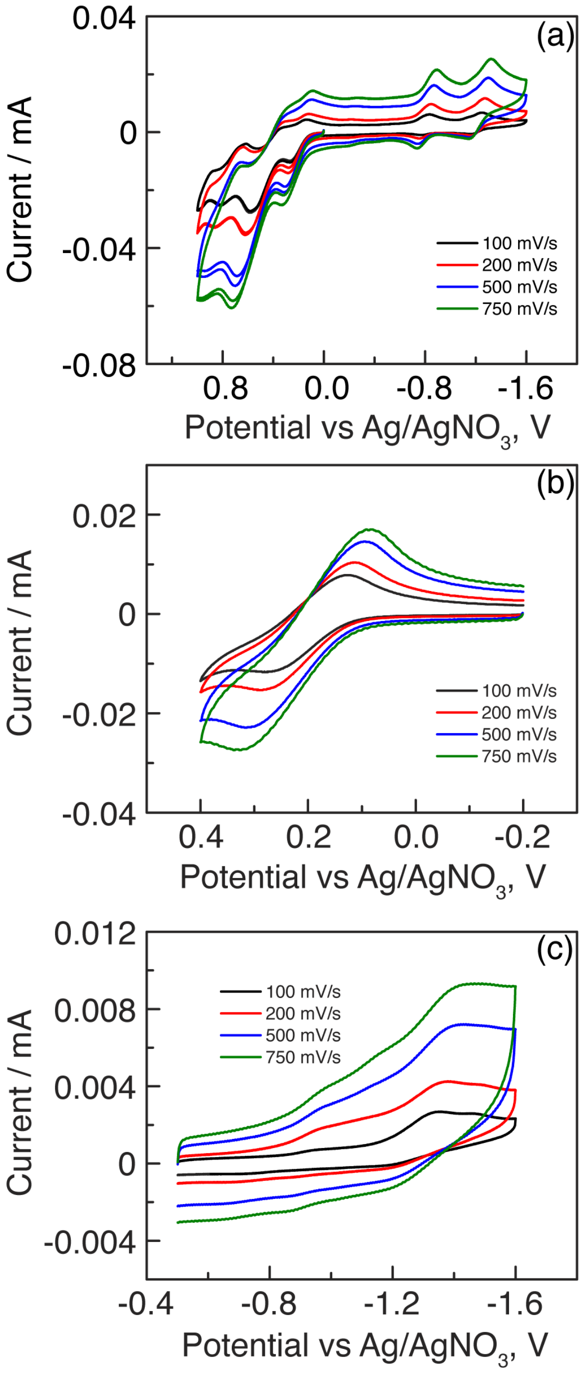


Figure S11. Cyclic voltammograms (CVs) of Fe$_3$(TPM)$_2$ (0.7 mM) in a 0.1 M [TBA]PF$_6$ solution of THF. (a) CVs measurements initiated at 0 V with 3 sweeps beginning anodically ranging 1.0 V to –1.6 V. (b) The initial reversible oxidation event, from –0.2 V to 0.4 V, was isolated. (c) The reduction peaks, from –0.4 V to –1.6V, were not observed without preceding oxidation events. CV conditions: glassy carbon working electrode, Pt counter electrode, and Ag/AgNO$_3$ as a reference. Fc$^{0/+}$ E$_{1/2}$ = 0.257 V vs Ag/AgNO$_3$.

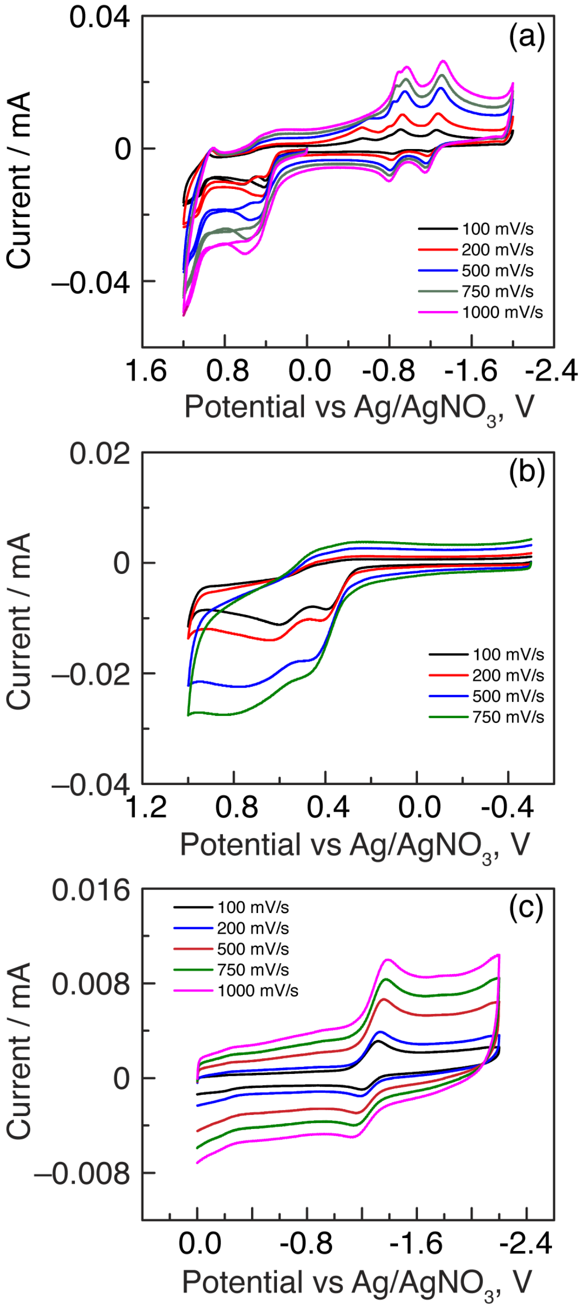


Figure S12. CVs of $Zn_3(TPM)_2$ (0.7 mM) in a 0.1 M $[TBA]PF_6$ solution of THF. (a) CV measurements initiated at 0 V with 3 sweeps beginning anodically from 1.2 V to –2.0 V. (b) No reversible oxidation event, starting from –0.5 V to 1.0 V, was observed for $Zn_3(TPM)_2$. (c) The reduction wave, which is reversible, was observed without preceding oxidation events (measurement started from 0.0 V to 2.2 V). CV conditions: glassy carbon working electrode, Pt counter electrode, and $Ag/AgNO_3$ as a reference. $Fc^{0/+}$ $E_{1/2}$ = 0.257 V vs $Ag/AgNO_3$.

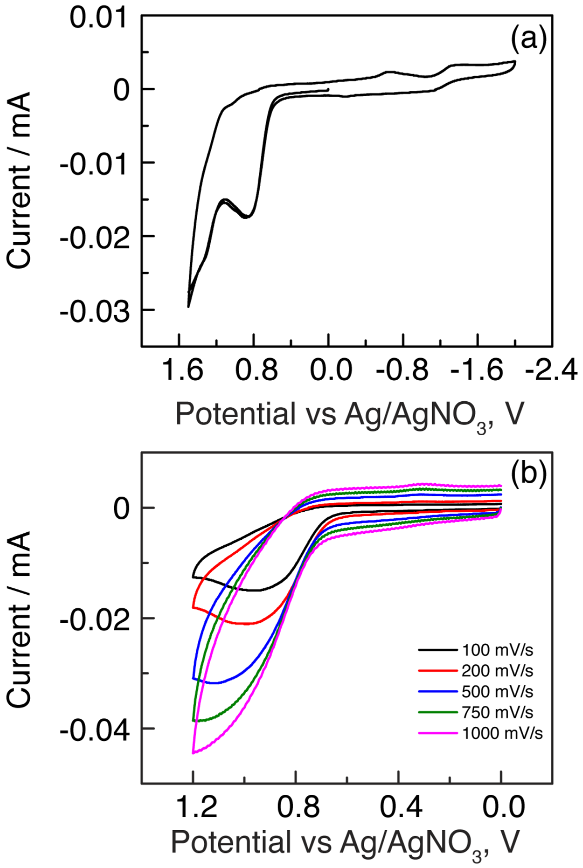


Figure S13. CV of H_3TPM. (1.0 mM) in a 0.1 M [TBA]PF_6 solution of THF. (a) CV measurements initiated at 0 V with 3 sweeps beginning anodically from 1.5 V to –2.2 V. (b) The initial oxidation event was not reversible even with increase of scan rate. CV conditions: glassy carbon working electrode, Pt counter electrode, and Ag/$AgNO_3$ as a reference. $Fc^{0/+}$ $E_{1/2}$ = 0.257 V vs Ag/$AgNO_3$.

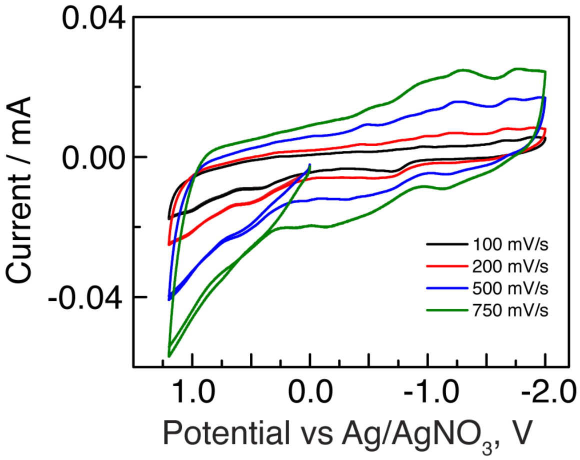


Figure S14. CV of Na(THF)$_4$[Fe(TPM]]. (0.7 mM) in a 0.1 M [TBA]PF$_6$ solution of THF. (a) CV measurements initiated at 0 V with 3 sweeps beginning anodically from 1.2 V to –2.0 V. No reversible redox event was observed and peak resolution was not improved by increasing scan rate. CV conditions: glassy carbon working electrode, Pt counter electrode, and Ag/AgNO$_3$ as a reference. Fc$^{0/+}$ E$_{1/2}$ = 0.257 V vs Ag/AgNO$_3$.

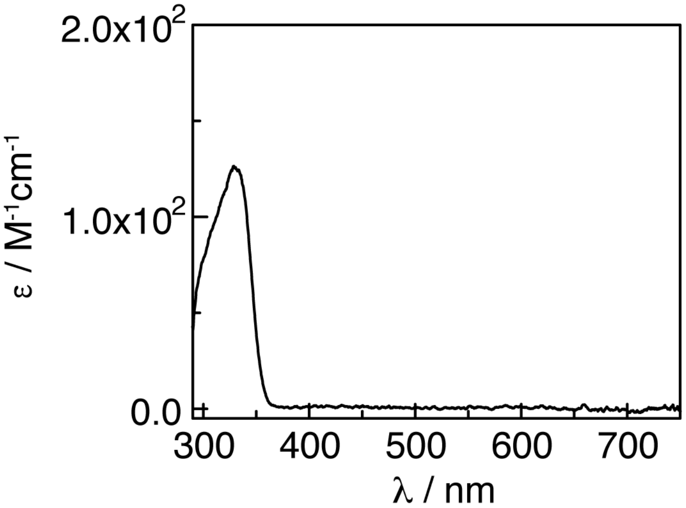


Figure S15. Extinction spectrum of H_3TPM measured in THF with a 7 mM solution.

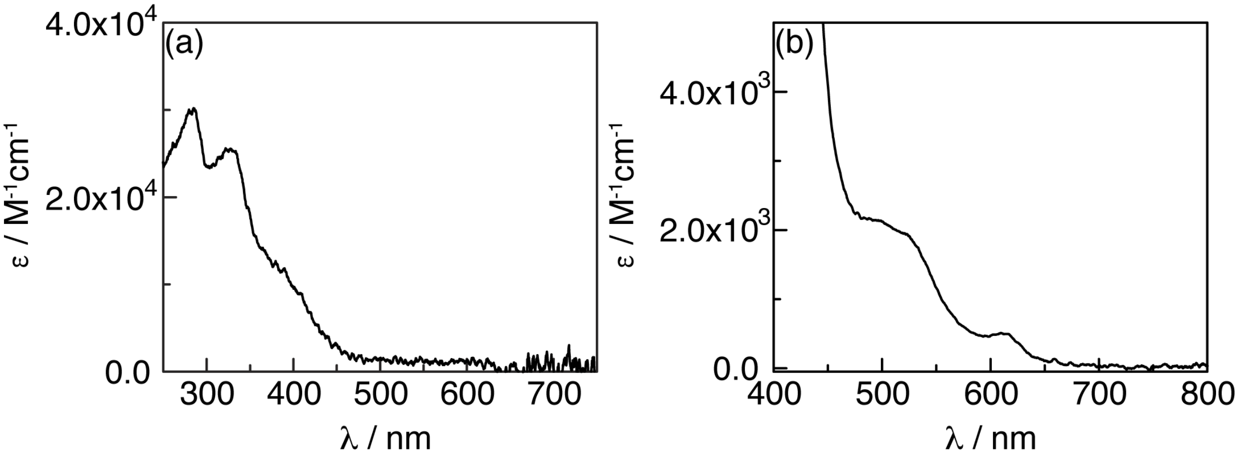


Figure S16. Extinction spectra of $Fe_3(TPM)_2$ measured in THF with (a) 0.01 mM and (b) 0.3 mM solutions.

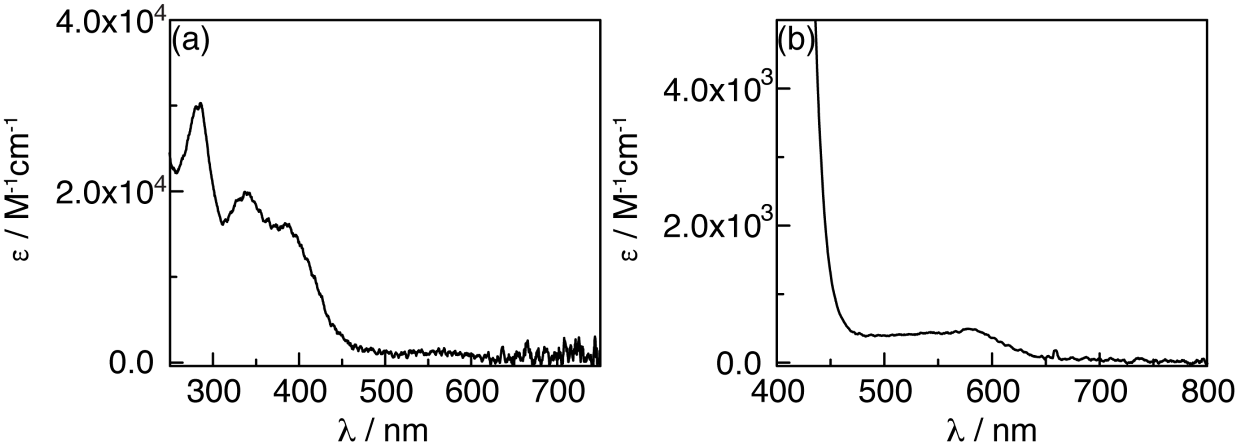


Figure S17. Extinction spectra of $Zn_3(TPM)_2$ measured in THF with (a) 0.01 mM and (b) 0.2 mM solutions.

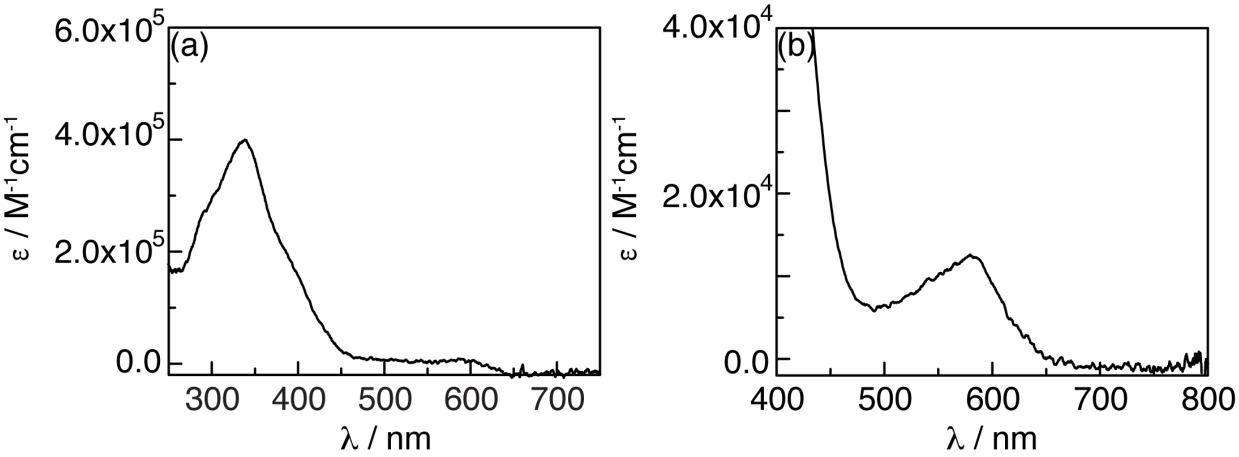


Figure S18. Extinction spectra of Na(THF)$_4$[Fe(TPM)] measured in THF with (a) 0.001 mM and (b) 0.01 mM solutions.

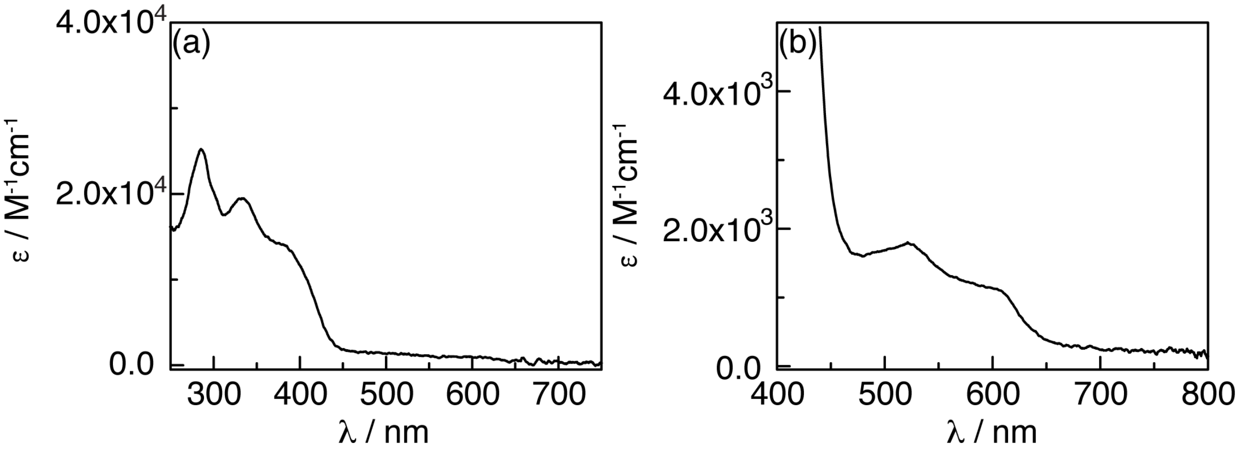


Figure S19. Extinction spectra of $Fe_2Zn(TPM)_2$ measured in THF with (a) 0.03 mM and (b) 0.3 mM solutions.

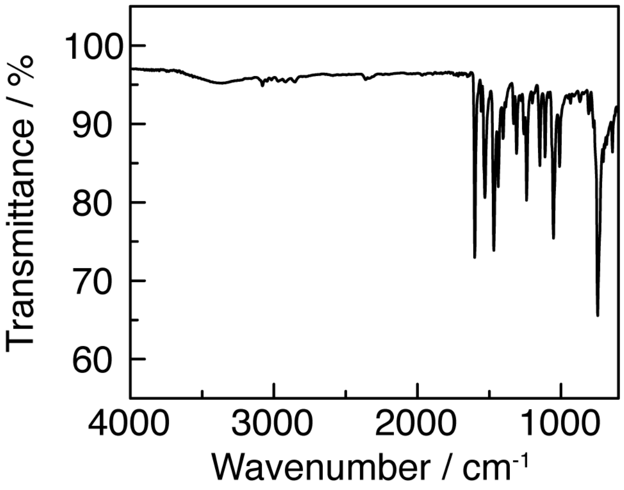


Figure S20. Infrared spectrum of $Fe_3(TPM)_2$. The spectrum was blanked against air and was determined as the average of 128 scans.

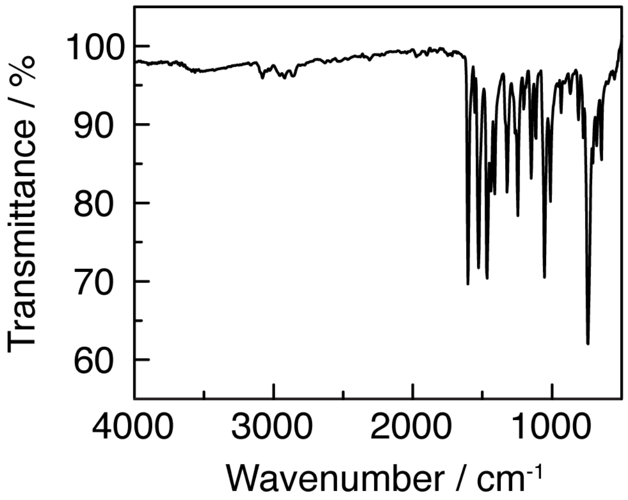


Figure S21. Infrared spectrum of $Zn_3(TPM)_2$. The spectrum was blanked against air and was determined as the average of 128 scans.

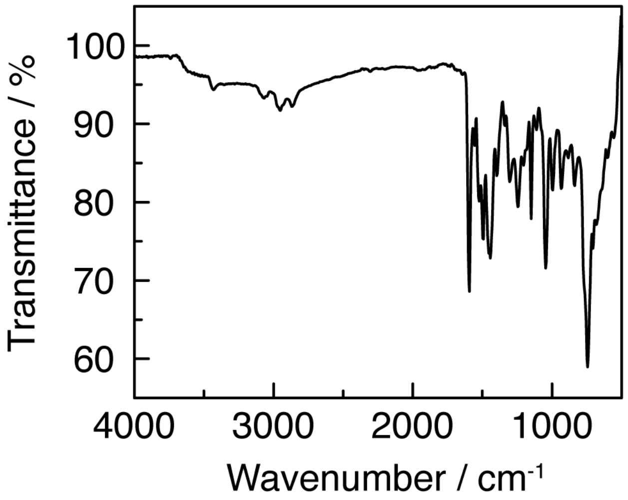


Figure S22. Infrared spectrum of Na(THF)$_4$[Fe(TPM)]. The spectrum was blanked against air and was determined as the average of 128 scans.

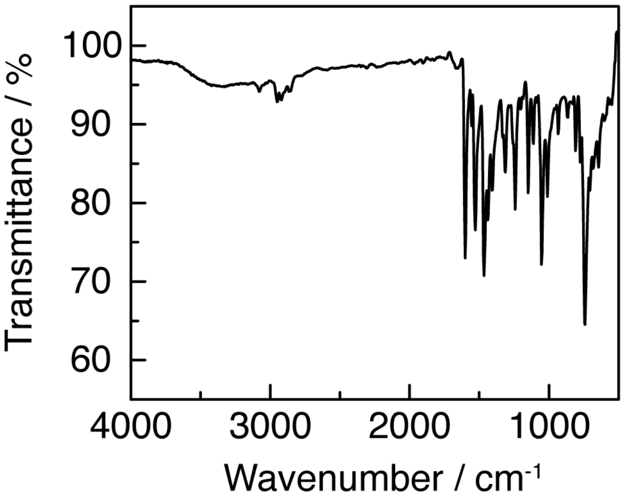


Figure S23. Infrared spectrum of $Fe_2Zn(TPM)_2$. The spectrum was blanked against air and was determined as the average of 128 scans.

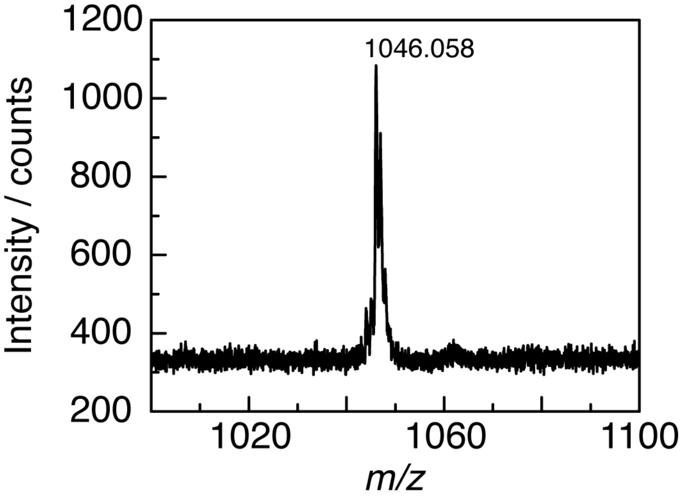


Figure S24. Mass spectrometry of $Fe_3(TPM)_2$ (MALDI-TOF).

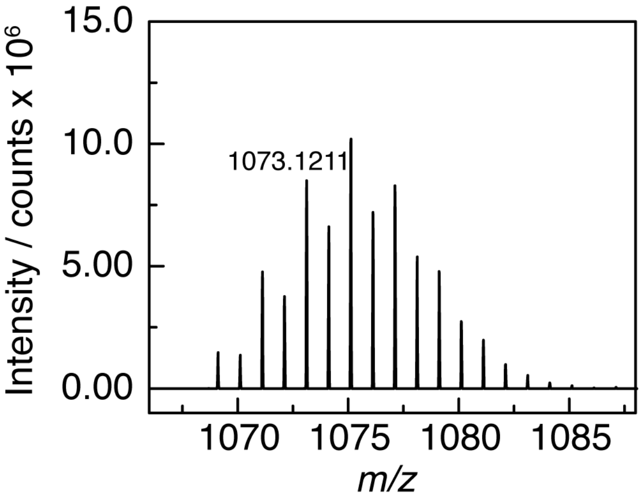


Figure S25. Mass spectrometry of $Zn_3(TPM)_2$ (HRMS-ESI$^+$).

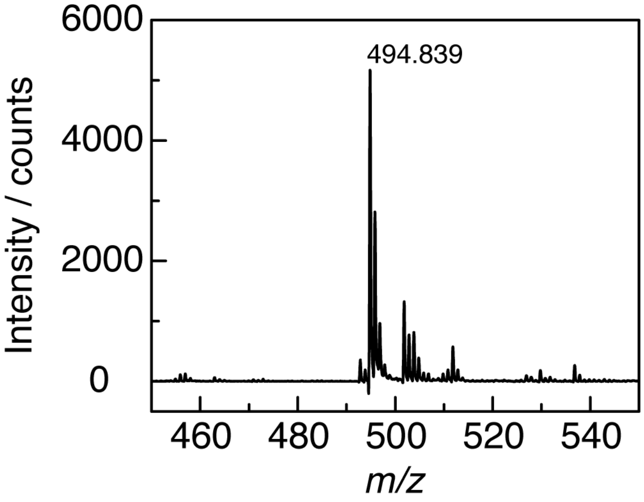


Figure S26. Mass spectrometry of Na(THF)$_4$[Fe(TPM)] (MALDI-TOF).

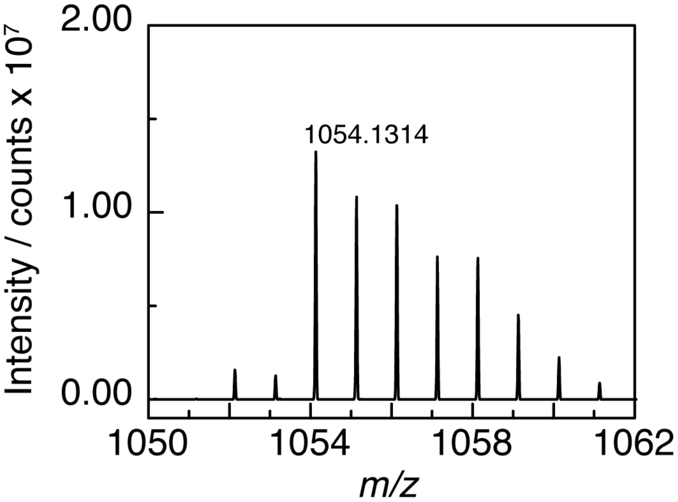


Figure S27. Mass spectrometry of $Fe_2Zn(TPM)_2$ (HRMS-ESI$^+$).

D. Crystallographic Data

Table S2. Crystallographic data for Fe$_3$(TPM)$_2$.

	Fe$_3$(TPM)$_2$·2THF			
Formula	$C_{64}H_{54}Fe_3N_{12}O_2$	$C_{64}H_{54}Fe_3N_{12}O_2$	$C_{64}H_{54}Fe_3N_{12}O_2$	$C_{64}H_{54}Fe_3N_{12}O_2$
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P2$_1$/n	P2$_1$/n	P2$_1$/n	P2$_1$/n
a, Å	11.719(9)	11.681(1)	11.681(1)	11.681(1)
b, Å	22.28(1)	22.210(1)	22.210(1)	22.210(1)
c, Å	20.34(1)	20.268(1)	20.268(1)	20.268(1)
α,°	90	90	90	90
β,°	91.485(8)	91.652(1)	91.652(1)	91.652(1)
γ, °	90	90	90	90
Volume, Å^3	5309(5)	5256.2(3)	5256.2(3)	5256.2(3)
Z	4	4	4	4
T, K	110	50	30	10
ρ_{calcd} (mg/m^3)	1.490	1.505	1.505	1.505
F(000)	2464	2464	2464	2464
Θ_{min}, Θ_{max}, °	1.356, 26.479	0.666, 0.744	0.674, 0.744	0.682, 0.744
R$_1$[a], wR$_2$[b] ($I > 2\sigma(I)$)	0.0589, 0.1106	0.0330, 0.0872	0.0326, 0.0849	0.0328, 0.0850
R$_1$[a], wR$_2$[b] (all data)	0.1457, 0.1397	0.0378, 0.0905	0.0368, 0.0876	0.0368, 0.0877

[a] $R_1 = 3||F_o|-|F_c||/3|F_o|$. [b] $wR_2 = [3[w(F_o^2 - F_c^2)^2]/3[w(F_o^2)^2]]^{½}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S3. Selected interatomic distances for Fe$_3$(TPM)$_2$ at 110 K.

distances, Å	
Fe1···Fe2	3.041(3)
Fe1···Fe3	3.313(3)
Fe2···Fe3	3.203(3)
Fe1–N	2.098(4), 1.981(4), 2.117(4), 1.999(4)
Fe2–N	1.992(4), 2.104(4), 2.108(4), 2.002(4)
Fe3–N	2.116(4), 1.978(4), 2.122(4), 1.980(4)

Table S4. Crystallographic data for $Fe_3(TPM)_2$ as a function of temperature

$Fe_3(TPM)_2$, 110K	$Fe_3(TPM)_2$, 50K	$Fe_3(TPM)_2$, 30K	$Fe_3(TPM)_2$, 10K
Monoclinic	Monoclinic	Monoclinic	Monoclinic
$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
a = 11.719(7) b = 22.28(1) c = 20.34(1) β = 91.485(8)	a = 11.681(1) b = 22.210(1) c = 20.268(1) β = 91.652(1)	a = 11.681(1) b = 22.210(1) c = 20.268(1) β = 91.652(1)	a = 11.681(1) b = 22.210(1) c = 20.268(1) β = 91.652(1)
Fe···Fe: 3.041(3) 3.203(3) 3.313(3)	Fe···Fe: 3.0057(1) 3.1879(1) 3.3155(1)	Fe···Fe: 3.0002(1) 3.1856(1) 3.3173(1)	Fe···Fe: 2.9965(6) 3.1827(6) 3.3213(6)
Fe–$N_{pyrrole}$ 1.989(2) Fe–$N_{pyridine}$ 2.111(2)	Fe–$N_{pyrrole}$ 1.993(1) Fe–$N_{pyridine}$ 2.111(1)	Fe–$N_{pyrrole}$ 1.994(1) Fe–$N_{pyridine}$ 2.113(1)	Fe–$N_{pyrrole}$ 1.994(1) Fe–$N_{pyridine}$ 2.114(1)

Table S5. Crystallographic Data for $Zn_3(TPM)_2$.

Compound	**$Zn_3(TPM)_2$·2THF·0.18(H_2O)**
Formula	$C_{64}H_{54.36}Zn_3N_{12}O_{2.18}$
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	11.592(1)
b, Å	22.523(2)
c, Å	20.574(2)
α,°	90
β,°	92.149(1)
γ, °	90
Volume, Å^3	5367.9(9)
Z	4
T, K	110
ρ_{calcd} (mg/m^3)	1.513
F(000)	2519
Θ_{min}, Θ_{max}, °	2.910, 65.123
R_1^{a}, wR_2^{b} (I > 2σ(I))	0.0350, 0.0853
R_1^{a}, wR_2^{b} (all data)	0.0367, 0.0876

$^a R_1 = 3||F_o|-|F_c||/3|F_o|$. $^b wR_2 = [3[w(F_o^2 - F_c^2)^2]/3[w(F_o^2)^2]]^{½}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0 \text{ or } F_o^2) + 2(F_c^2)]/3$.

Table S6. Selected interatomic distances for $Zn_3(TPM)_2$.

distances, Å	
Zn1···Zn2	3.5732(3)
Zn1···Zn3	3.6322(2)
Zn2···Zn3	3.7425(3)
Zn1–N	1.954(2), 2.065(2), 2.072(2), 1.958(2)
Zn2–N	1.955(2), 2.066(2), 2.069(2), 1.952(2)
Zn3–N	1.942(2), 2.081(2), 2.080(2), 1.945(2)

Table S7. Crystallographic Data for $Fe_2Zn(TPM)_2$.

Compound	**$Fe_2Zn\ (TPM)_2{\cdot}2THF$**
Formula	$C_{64}H_{54}Fe_2ZnN_{12}O_2$
Crystal system	Monoclinic
Space group	$P2_1/n$
a, Å	11.6640(7)
b, Å	22.457(1)
c, Å	20.421(1)
α,°	90
β,°	91.781(3)
γ, °	90
Volume, $Å^3$	5346.5(6)
Z	4
T, K	110
ρ_{calcd} (mg/m^3)	1.491
F(000)	2480
Θ_{min}, Θ_{max}, °	2.925, 70.174
R_1^a, wR_2^b ($I > 2\sigma(I)$)	0.0333, 0.0823
R_1^a, wR_2^b (all data)	0.0336, 0.0825

$^{a}R_1 = 3||F_o|-|F_c||/3|F_o|$. $^{b}wR_2 = [3[w(F_o^2 - F_c^2)^2]/3[w(F_o^2)^2]]^{½}$, $w = 1/\sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [\max(0$ or $F_o^2) + 2(F_c^2)]/3$.

Table S8. Selected interatomic distances for $Fe_2Zn(TPM)_2$.

distances, Å	
Fe···Fe	3.2017(2), 3.2888(1), 3.4152(2)
Zn···Zn	3.5323(2), 3.6110(1), 3.6865(2)
Fe···Zn	3.3601(2), 3.3754(2), 3.4400(1) 3.4625(2), 3.5479(2), 3.5577(2)
Fe1–N	2.133(4), 1.974(5), 2.124(5), 1.962(4)
Fe2–N	2.154(4), 1.953(4), 2.121(4), 1.972(4)
Fe3–N	2.126(4), 1.991(4), 2.137(4), 1.949(4)
Zn1–N	1.949(7), 1.993(7), 2.043(8), 2.016(7)
Zn2–N	2.005(6), 2.010(7), 2.066(7) ,1.978(7)
Zn3–N	2.033(7), 1.973(7), 2.001(7), 2.035(7)

E. References

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.
2. G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176–2179.
3. G. M. Sheldrick, *SADABS Program for Absorption Correction of Area Detector Frame*, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI, USA.
4. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.
5. G. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122.
6. G. Sheldrick, *Acta Crystallogr. Section C*, 2015, **71**, 3–8.
7. APEX3, “Program for Data Collection on Area Detectors” BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
8. G. Sheldrick, *Acta Crystallogr. A*, 2015, **71**, 3–8.
9. A. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7–13.
10. R. D. Rieth, N. P. Mankad, E. Calimano and J. P. Sadighi, *Org. Lett.*, 2004, **6**, 3981–3983.
11. C. Ducloiset, P. Jouin, E. Paredes, R. Guillot, M. Sircoglou, M. Orio, W. Leibl and A. Aukauloo, *Eur. J. Inorg. Chem.*, 2015, **2015**, 5405–5410.
12. D. L. J. Broere, I. Čorić, A. Brosnahan and P. L. Holland, *Inorg. Chem.*, 2017, **56**, 3140–3143.