

Supplementary Information

Self-Assembly of an Iron(II)-Based M_5L_6 Metallosupramolecular Cage

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Physical Measurements. ^1H NMR spectra were recorded on a Bruker DPX300 (300 MHz) or a Bruker AV400 (400 MHz) NMR spectrometers. All measurements were carried out in CD_3CN , using the residual solvent peak as the internal reference. ESI-mass spectra were obtained with a Waters Micromass ZQ spectrometer in the positive ion mode. The extraction cone voltage was set to 10 V to avoid fragmentations. In all the cases, a well-resolved isotopic pattern consisting of monoisotopic peaks separated by $1/z$ Da was obtained. UV/vis absorption spectra were recorded on a Shimadzu UV-2501PC spectrophotometer with 1 cm pathlength quartz cells. For the calculation of ϵ we have considered $[\text{Fe}_5(\text{L})_6]^{10+}$ as the predominant species in solution. This leads to a concentration of $2.5 \cdot 10^{-4}$ M. Elemental analysis was carried out at the Centro de Microanálisis Elemental, Universidad Complutense de Madrid.

Computational Details. Geometrical optimization of the structure was performed with the density functional theory (DFT) approach using the Becke's three parameter exchange with the Lee–Yang–Parr correlation functional (B3LYP).¹ The basis used was 6-31G for C, H, O and N atoms and Los Alamos LANL2DZ split-valence set² for Fe atoms. The optimization convergence criteria were set to a maximum step size of 0.001 a.u. and an RMS force of 0.0003 a.u. All computations were performed with the GAUSSIAN 03 program.³

$[\text{Fe}_5(\text{L})_6](\text{PF}_6)_{10}$ (1). A solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (28 mg, 0.10 mmol) in water (5 mL) was added dropwise to a stirred solution of L^4 (64 mg, 0.12 mmol) in refluxing acetone (5 mL). After stirring under argon at 60 °C for 30 min the mixture was cooled to room temperature and excess of aqueous KPF_6 was added. The resulting precipitate

was filtered off, washed with water and dried under vacuum to afford **1** (97 mg, quantitative) as a deep red solid. IR (KBr): $\nu = 3422$ (s), 3072, 2360, 1606 (s), 1518, 1435, 1251 (s), 841 (vs) and 557 (s) cm^{-1} . UV/vis (CH_3CN): $\lambda_{\text{max}} = 534$ nm ($\epsilon = 23700 \text{ M}^{-1}\text{cm}^{-1}$); ^1H NMR (300 MHz, CD_3CN): δ 9.06 (d, $J = 8.0$ Hz, 1H; T_5'), 9.02 (d, $J = 8.0$ Hz, 1H; T_3'), 8.91 (t, $J = 8.0$ Hz, 1H; T_4'), 8.73 (d, $J = 1.6$ Hz, 1H; P_7), 8.45 (d, $J = 8.2$ Hz, 1H; T_3''), 8.29 (d, $J = 2.7$ Hz, 2H; P_5 , P_6), 8.13 (d, $J = 8.4$ Hz, 1H; T_3), 8.09 (d, $J = 1.6$ Hz, 1H; P_4), 7.68 (br. d, $J \sim 8.2$ Hz, 1H; T_4''), 7.61 (d, $J = 1.6$ Hz, 1H; P_2), 7.49 (d, $J = 1.6$ Hz, 1H; P_9), 7.35 (d, $J = 1.6$ Hz, 1H; T_6), 7.11 (d, $J = 8.9$ Hz, 2H; H_0), 6.83 (d, $J = 8.9$ Hz, 2H; H_m), 6.80 (dd, $J = 8.4$ and 1.6 Hz, 1H, T_4), 6.70 (s 1H; T_6''), 3.71 (s, 3H; OCH_3), 1.93 (s, 3H; CH_3); ^{19}F NMR (282 MHz, CD_3CN): δ -73.1 (d, $J = 707$ Hz); MS (ESI): m/z (%) = 1495.0 (5) $[\text{M}-3\text{PF}_6]^{3+}$ (calcd 1495.2), 1085.1 (17) $[\text{M}-4\text{PF}_6]^{4+}$ (calcd 1085.4), 839.1 (25) $[\text{M}-5\text{PF}_6]^{5+}$ (calcd 839.6), 675.1 (20) $[\text{M}-6\text{PF}_6]^{6+}$ (calcd 675.6), 559.5 (100) $[\text{Fe}(\text{L})_2]^{2+}$ (calcd 559.7). Elemental analysis (%) calcd. for $\text{C}_{210}\text{H}_{150}\text{N}_{30}\text{O}_6\text{P}_{10}\text{F}_{60}\text{Fe}_5(\text{H}_2\text{O})_8$: C, 49.82; H, 3.31; N, 8.30. Found: C, 49.88; H, 3.39; N, 8.50.

$[\text{Fe}(\text{L})_2](\text{PF}_6)_2$ (2**)**. A solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (28 mg, 0.10 mmol) in water (5 mL) was added dropwise to a stirred solution of L^4 (0.11 g, 0.20 mmol) in refluxing acetone (10 mL). After stirring under argon at 60 °C for 30 min the mixture was cooled to room temperature and excess of aqueous KPF_6 was added. The resulting precipitate was filtered off, washed with water and dried to yield **2** (140 mg, quantitative) as a dark red solid. IR (KBr): $\nu = 3415$ (s), 2925 (m), 2360, (m), 1606 (s), 1519 (m), 1436 (s), 1249 (m), 833 (vs) (P-F) and 559 (vs) (F-P-F) cm^{-1} . ^1H NMR (400 MHz, CD_3CN): δ 9.39 (d, $J = 2.0$ Hz, 1H; P_9), 8.98 (d, $J = 8.0$ Hz, 1H; T_3), 8.90 (d, $J = 8.0$ Hz, 1H; T_5), 8.89 (d, $J = 2.0$ Hz, 1H; P_2), 8.73 (t, $J = 8.0$ Hz, 1H, T_4), 8.64 (d, $J = 8.2$ Hz, 1H; T_3), 8.56 (d, $J = 2.0$ Hz, 1H; P_7), 8.39 (d, $J = 8.0$ Hz, 1H; T_3''), 8.33 (dd, $J = 8.2$ and 1.6 Hz, 1H; T_4), 8.29 (d, $J = 2.0$ Hz, 1H; P_4), 7.99 (d, $J = 9.0$ Hz, 1H; P_6), 7.88 (d, $J = 9.0$ Hz, 1H; P_5), 7.84 (d, $J = 8.8$ Hz, 2H; H_0), 7.72 (d, $J = 8.0$ Hz, 1H; T_4''), 7.33 (d, $J = 1.6$ Hz, 1H; T_6), 7.15 (d, $J = 8.8$ Hz, 2H, H_m), 6.98 (s, 1H; T_6''), 3.88 (s, 3H; OCH_3), 2.01 (s, 3H; CH_3); HRMS (ESI): m/z (%) = 727.53 (26) $[\text{M}+2\text{Na}]^{2+}$ (calcd 727.63), 716.57 (11) $[\text{M}+\text{Na}+\text{H}]^{2+}$ (calcd 716.64), 643.56 (46) $[\text{M}-\text{PF}_6+\text{Na}]^{2+}$ (calcd 643.66), 632.60 $[\text{M}-\text{PF}_6+\text{H}]^{2+}$ (calcd 632.67), 559.60 (100) $[\text{M}-2\text{PF}_6]^{2+}$ (calcd 559.68).

2D-NMR spectra of compounds 1 and 2.

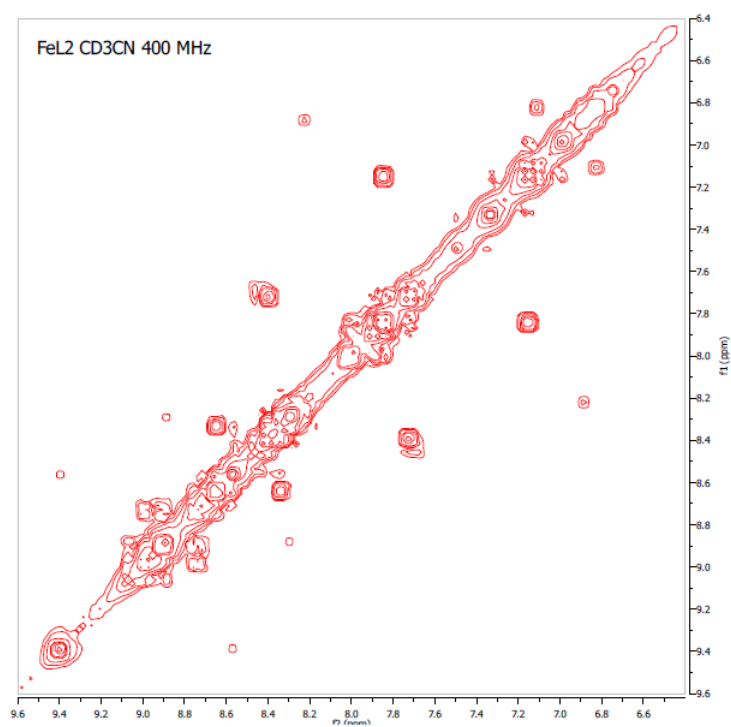


Figure S1. Partial ^1H - ^1H COSY spectrum (CD_3CN , 400 MHz) of $[\text{FeL}_2](\text{PF}_6)_2$.

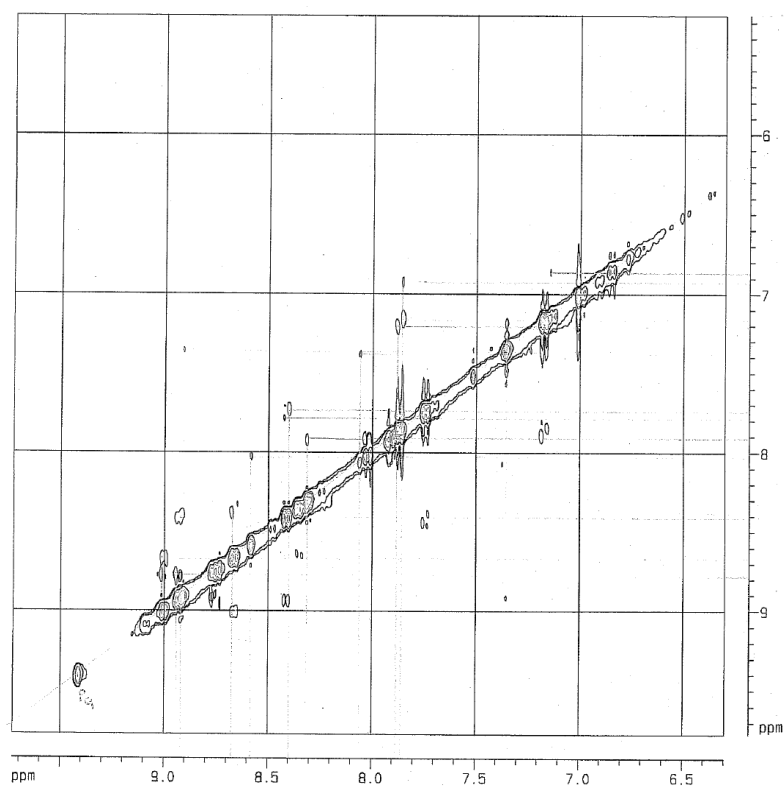


Figure S2. Partial ROESY spectrum (CD_3CN , 400 MHz) of $[\text{FeL}_2](\text{PF}_6)_2$.

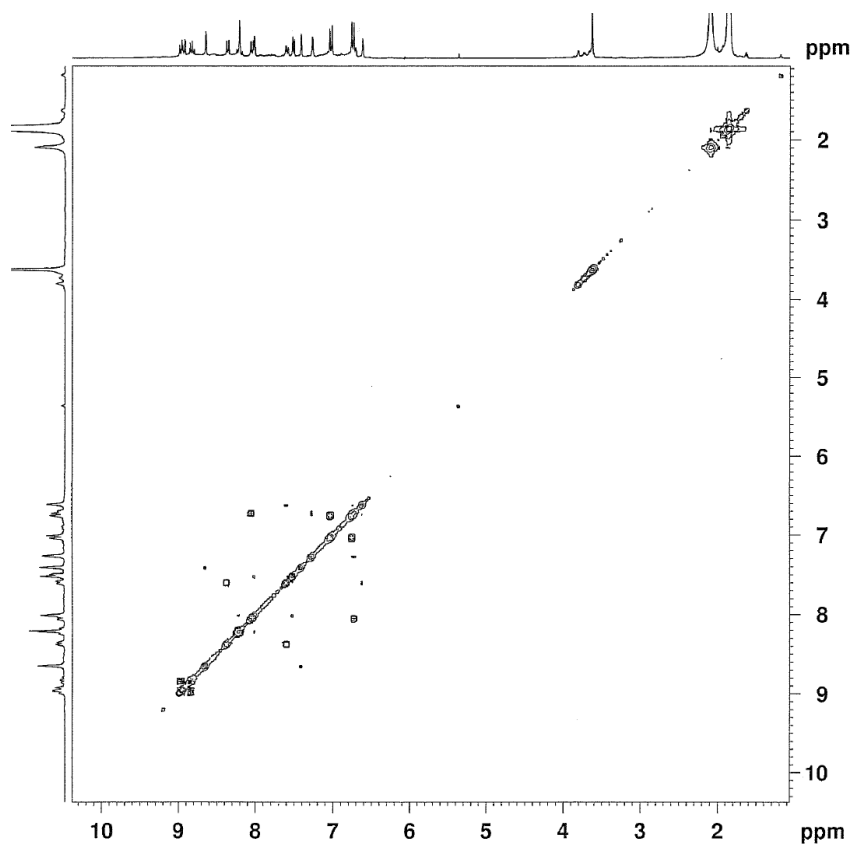


Figure S3. ^1H - ^1H COSY spectrum (CD_3CN , 300 MHz) of **1**.

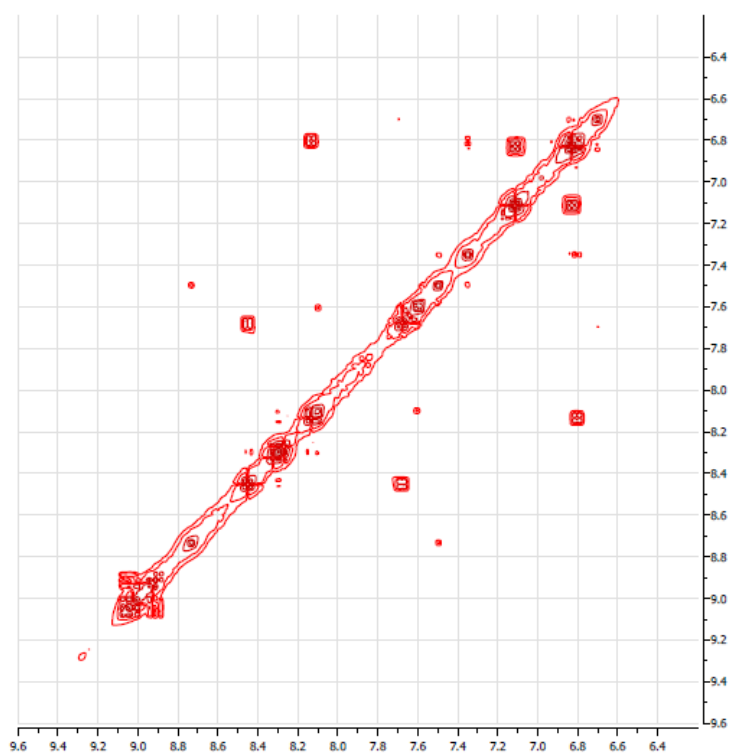


Figure S4. Partial COSY spectrum (CD_3CN , 300 MHz) of **1**.

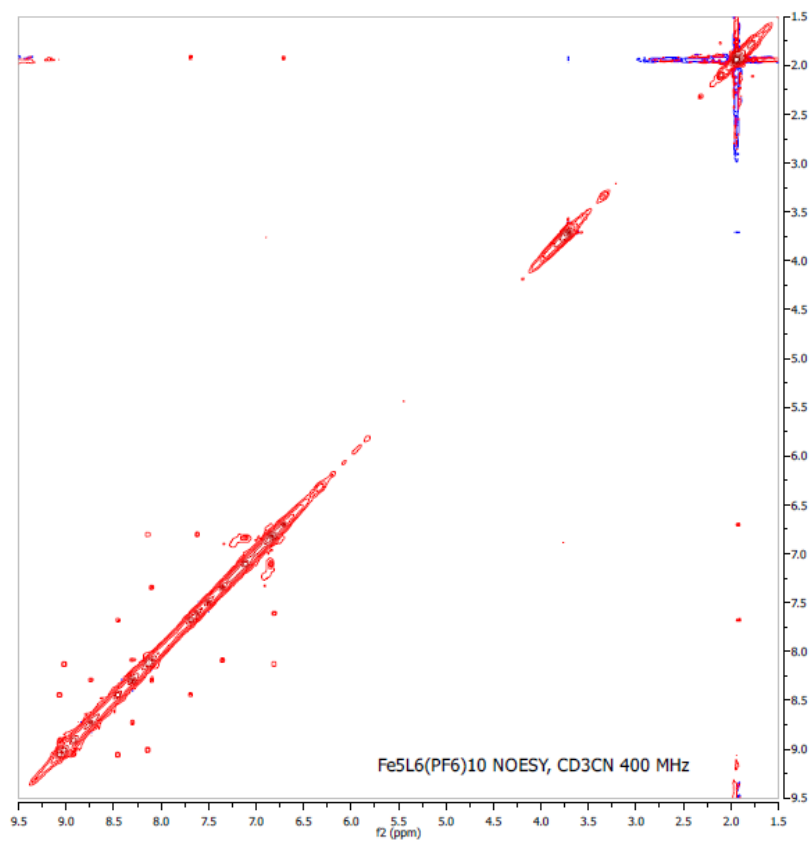


Figure S5. NOESY spectrum of **1** (CD₃CN, 400 MHz).

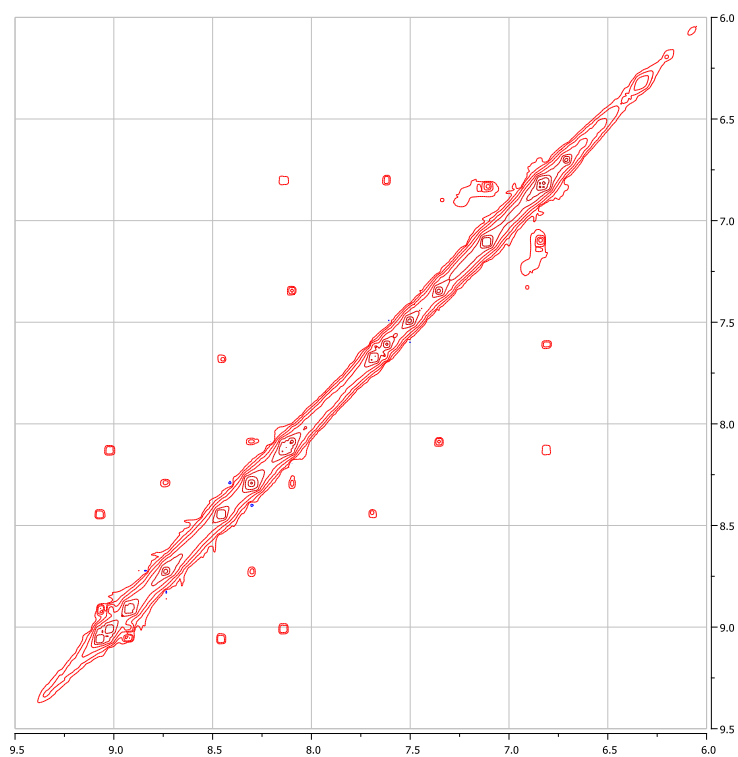


Figure S6. Partial NOESY spectrum of **1** (CD₃CN, 400 MHz).

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