

Supporting Information for

**Synthesis and characterisation of an integratively self-sorted  
[Fe<sub>4</sub>L<sub>6</sub>]<sup>8+</sup> tetrahedron**

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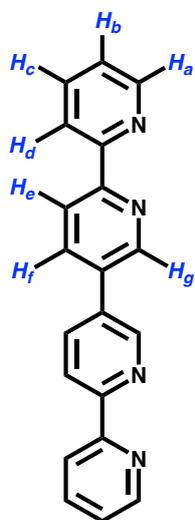
# S1 Synthesis and Characterisation

## S1.1 General Experimental Details

Unless stated otherwise, all chemicals were supplied from Sigma-Aldrich, Fluorochem, Fisher Scientific, Alfa Aesar or Scientific Laboratory Supplies Ltd and used without further purification. Deuterated NMR solvents were supplied from Sigma-Aldrich and NMR spectra were recorded on a B500 Bruker Advance II+ 500 MHz spectrometer. Chemical shifts are reported in parts per million (ppm). Coupling constants ( $J$ ) are reported in hertz (Hz). Standard abbreviations indicating multiplicity were used as follows: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet.  $^1\text{H}$  and  $^{13}\text{C}$  assignments were made using 2D NMR methods (COSY, NOESY). High-resolution mass spectra were obtained using a Thermo Orbitrap Exactive Plus Extended Mass Range mass spectrometer. Elemental analyses were performed by the microanalytical services of The University of Manchester with a CFlash 2000 elemental analyser for the analyses of carbon, hydrogen and nitrogen.

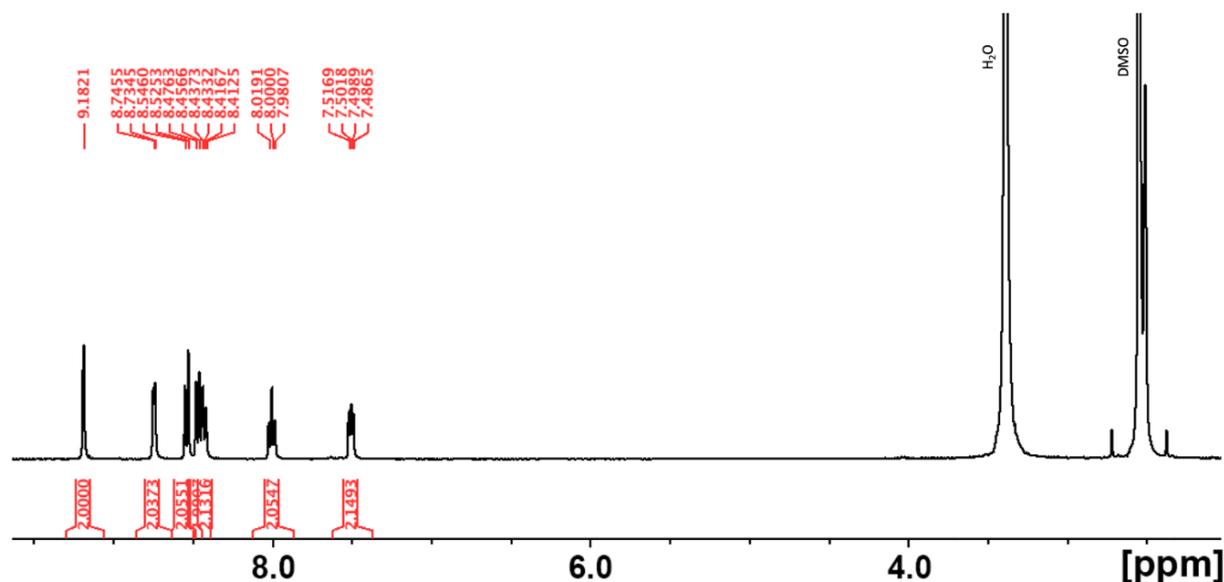
## S1.2 Ligand Synthesis

**2,2':5',3'':6'',2'''-quaterpyridine (L1):** Synthesis was adapted from Cerfontaine *et al.*<sup>1</sup>



Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.56 g, 0.86 mmol) was added to anhydrous DMF (10 mL) and the mixture was stirred until it turned blue (rt, 5 min). Zinc dust (0.065 g, 0.99 mmol) was added and the mixture was stirred under N<sub>2</sub> until it turned brown (rt, 45 min). 5-Bromo-2,2'-bipyridine (0.20 g, 0.85 mmol) was added and the solution was stirred (rt, 24 hr). NH<sub>4</sub>OH (2 M, 150 mL) was added and the resulting grey solution was extracted with ethyl acetate (3 x 50 mL). The combined organic layers were dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure to give the crude white solid. The crude product was added to ethyl acetate and the mixture was centrifuged (5 min).

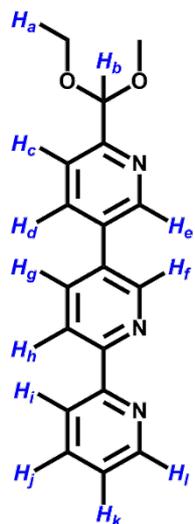
The supernatant was removed and the resultant white solid was washed with diethyl ether, diisopropyl ether and hexane, before being dissolved in DMSO and precipitated out with diethyl ether leaving a white solid (43 mg, 0.14 mmol, 16%). <sup>1</sup>H (400 MHz, 298 K, DMSO-d<sub>6</sub>): 9.18 (s, 2H, H<sub>g</sub>), 8.74 (s, 2H, H<sub>a</sub>), 8.54 (d, 2H, J = 8.28 Hz, H<sub>e</sub>), 8.47 (d, 2H, J = 7.91 Hz, H<sub>d</sub>), 8.43 (d, 2H, J = 8.25 Hz, H<sub>f</sub>), 8.00 (t, 2H, J = 7.68 Hz, H<sub>c</sub>), 7.50 (t, 2H, J = 6.07 Hz, H<sub>b</sub>). <sup>13</sup>C (400 MHz, 298 K, DMSO-d<sub>6</sub>): 155.2, 149.9, 147.9, 144.5, 141.7, 137.9, 135.9, 135.6, 132.9, 121.0. [Accurate mass, m/z]: expected: 310.1218, found: 333.1097 [M + Na]<sup>+</sup>. Elemental analysis (%) calculated for C<sub>20</sub>H<sub>14</sub>N<sub>4</sub>: C 77.40, H 4.55, N 18.05; found: C 77.03, H 4.49, N 17.77.



**Figure S1.** <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>, 298 K) spectrum of L1.

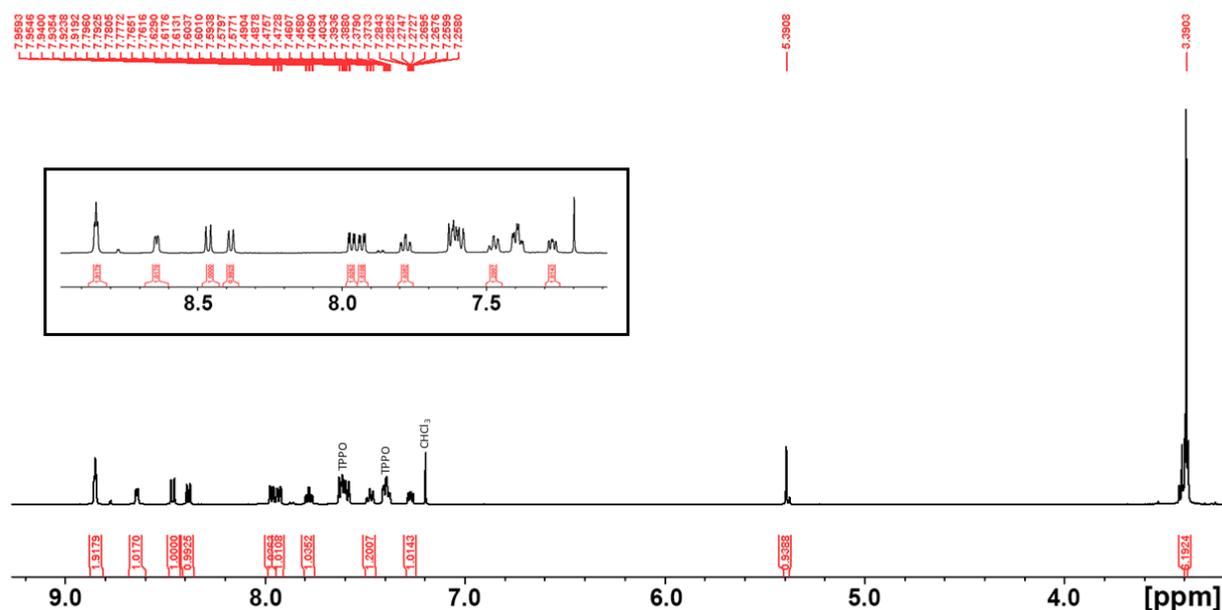
The following synthesis was adapted from a previously reported protocol.<sup>2</sup>

**6''-(dimethoxymethyl)-2,2':5',3''-terpyridine (L2')**: 2-(Dimethoxymethyl)-5-(4,4,5,5-



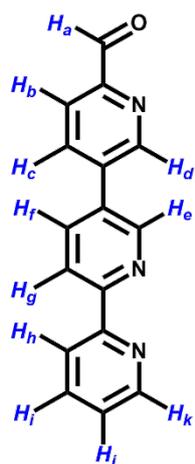
tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (1.2 g, 4.27 mmol), 5-bromo-2,2'-bipyridine (0.53 g, 2.25 mmol), Na<sub>2</sub>CO<sub>3</sub> (0.76 g, 7.17 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.29 g, 0.25 mmol) were dissolved in a 10:1 mixture of DMF:H<sub>2</sub>O (22 mL). The yellow solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being stirred under a flow of N<sub>2</sub> (70°C, 24 hr). The resulting brown solution was cooled and diluted in water before being extracted with dichloromethane (3 x 20 mL). The combined organic layers were then washed with water (3 x 10 mL) and dried over Na<sub>2</sub>SO<sub>4</sub> before the solvent was removed to give the crude product as a brown solid (0.61 g, 1.98 mmol, 88%),

this was sufficiently pure for the next step. <sup>1</sup>H (500 MHz, 298 K, CDCl<sub>3</sub>): 8.85 (t, 2H, H<sub>f</sub>, H<sub>e</sub>), 8.64 (s, 1H, H<sub>i</sub>), 8.46 (d, J = 8.24 Hz, 1H, H<sub>h</sub>) 8.38 (d, J = 7.96 Hz, 1H, H<sub>c</sub>), 7.97 (dd, J = 8.25 Hz, H<sub>d</sub>), 7.93 (dd, J = 8.11 Hz, H<sub>g</sub>), 7.71 (td, 1H, J = 11.58 Hz, H<sub>j</sub>), 7.60 (TPPO), 7.47 (td, 1H, J = 7.60 Hz, H<sub>i</sub>), 7.39 (TPPO), 7.27 (ddd, 1H, J = 4.85 Hz, H<sub>k</sub>), 5.39 (s, 1H, H<sub>b</sub>), 3.39 (s, 6H, H<sub>a</sub>). [ESI, m/z]: expected: 307.1, found: 330.1 [M + Na]<sup>+</sup>.

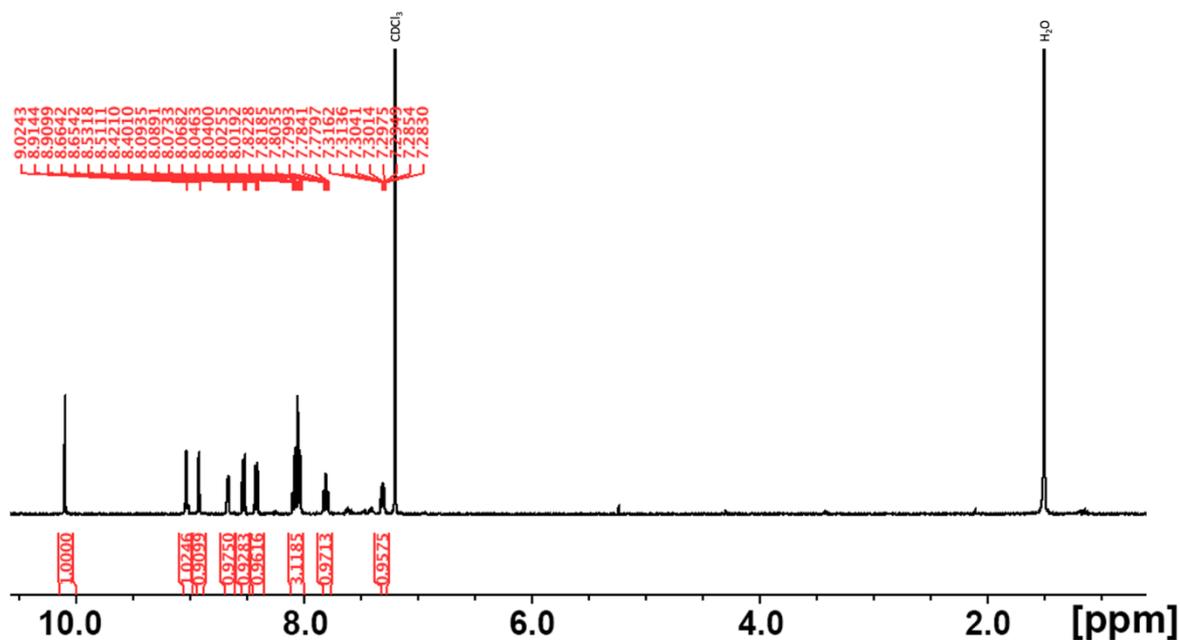


**Figure S2.** <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>, 298 K) spectrum of L2'. Insert highlights the aromatic region splitting. TPPO: triphenylphosphine oxide impurity from the catalyst.

**[2,2':5',3''-Terpyridine]-6''-carbaldehyde (L2):** 6''-(dimethoxymethyl)-2,2':5',3''-terpyridine



(2.3 g, 7.49 mmol) was dissolved in THF (7.3 mL) and HCl (2 M, 14.2 mL) was added. The yellow solution was sealed under N<sub>2</sub> and heated (40°C, 22 hr) before being neutralised by the addition of saturated NaHCO<sub>3</sub>, resulting in the formation of a white precipitate. The white solid was dissolved in a 3:1 mixture of CHCl<sub>3</sub>:2-propanol and the aqueous layer was washed with CHCl<sub>3</sub> (3 x 5 mL) before being dried over MgSO<sub>4</sub> and filtered to give a grey solid (1.4 g, 0.52 mmol, 72%). <sup>1</sup>H (500 MHz, 298 K, CDCl<sub>3</sub>): 10.09 (s, 1H, H<sub>a</sub>), 9.03 (s, 1H, H<sub>d</sub>), 8.91 (s, 1H, H<sub>e</sub>), 8.66 (d, *J* = 3.98 Hz, 1H, H<sub>h</sub>), 8.52 (d, *J* = 8.27 Hz, H<sub>g</sub>), 8.41 (d, *J* = 7.98 Hz, H<sub>b</sub>), 8.05 (m, 3H, H<sub>f</sub>, H<sub>c</sub>, H<sub>k</sub>), 7.79 (td, 1H, *J* = 11.59 Hz, H<sub>i</sub>), 7.29 (ddd, 1H, *J* = 7.45 Hz, H<sub>j</sub>). <sup>13</sup>C (126 MHz, 298 K, CD<sub>3</sub>CN): δ 194.12, 157.13, 156.10, 153.13, 150.37, 149.56, 148.86, 138.15, 138.05, 136.82, 136.48, 133.21, 125.28, 122.57, 121.81, 121.70. [Accurate mass, *m/z*]: expected: 261.0902, found: 262.0969 [M + H]<sup>+</sup>.

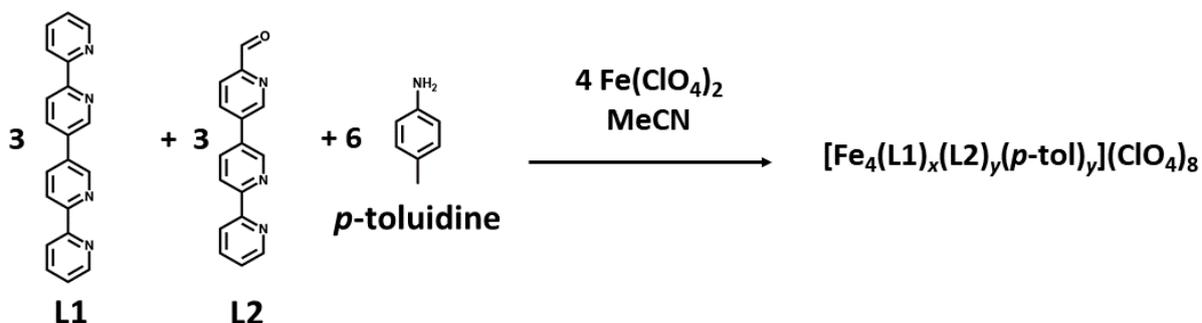


**Figure S3.** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, 298 K) spectrum of L2.

## S1.3 Complexation Reactions

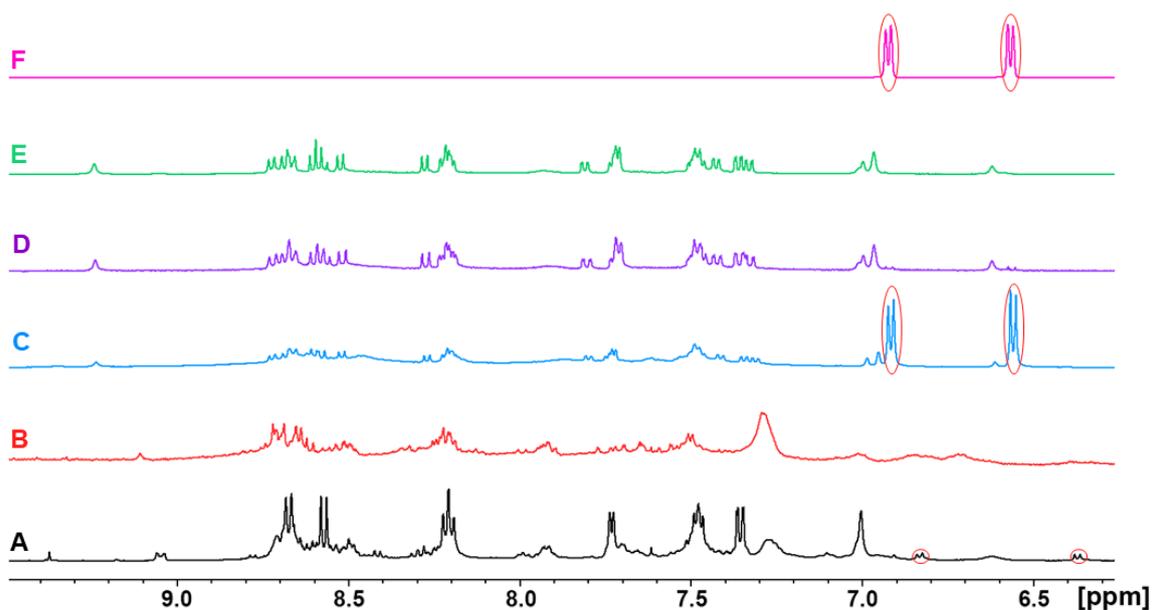
### S1.3.1 Reactions with *p*-Toluidine

**Scheme S1.** General reaction scheme for the formation of tetrahedral architectures with general formula  $[\text{Fe}_4(\text{L1})_x(\text{L2})_y(\textit{p-tol})_y](\text{ClO}_4)_8$  from ligands **L1**, **L2**,  $\text{Fe}(\text{ClO}_4)_2$  and *p*-toluidine.

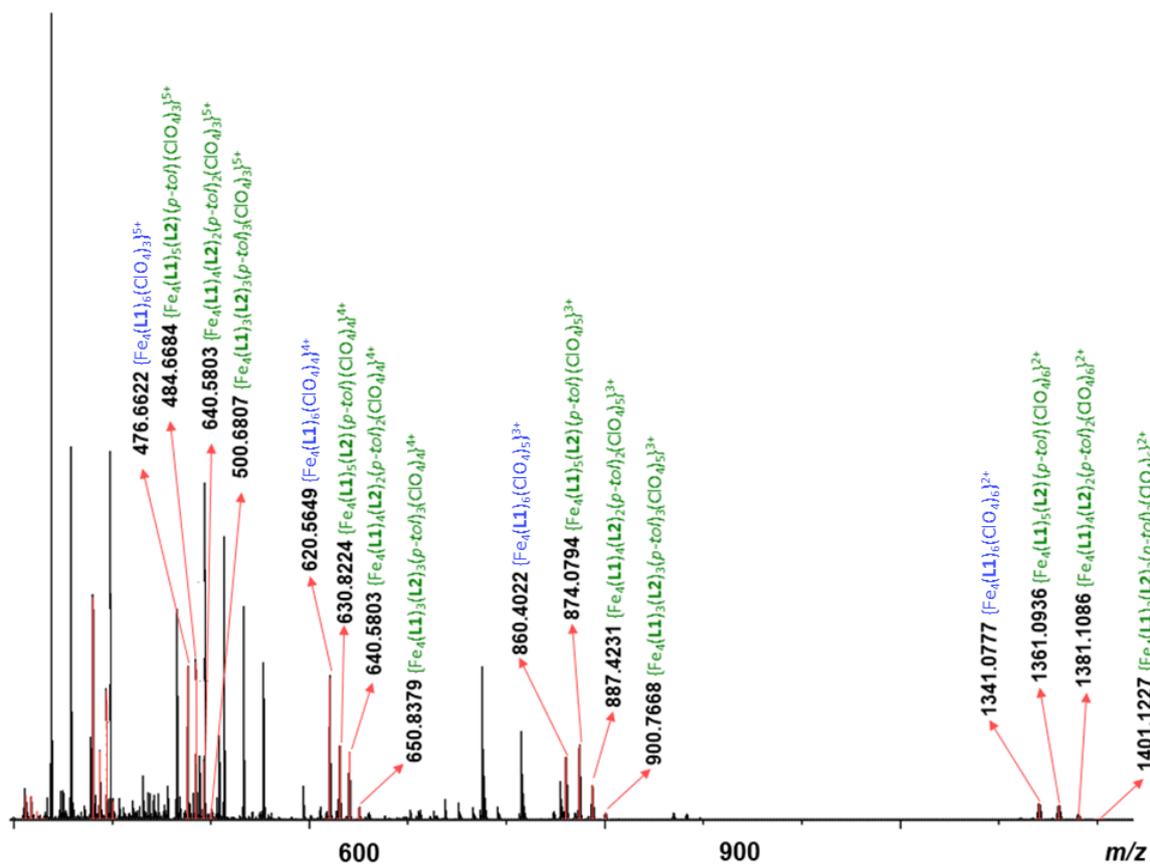


$[\text{Fe}_4(\text{L1})_x(\text{L2})_y(\textit{p-tol})_y](\text{ClO}_4)_8$

**L1** (3.6 mg, 11.6  $\mu\text{mol}$ , 3 equiv), **L2** (3.0 mg, 11.6  $\mu\text{mol}$ , 3 equiv),  $\text{Fe}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$  (3.9 mg, 15.3  $\mu\text{mol}$ , 4 equiv) and *p*-toluidine (1.2 mg, 11.5  $\mu\text{mol}$ , 3 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting pink solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/ $\text{N}_2$  fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a pink solid. [Accurate mass,  $m/z$ ]:  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3(\textit{p-tol})_3(\text{ClO}_4)\}^{7+} = 329.3581$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3(\textit{p-tol})_3(\text{ClO}_4)_2\}^{6+} = 400.7427$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3(\textit{p-tol})_3(\text{ClO}_4)_3\}^{5+} = 500.6807$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3(\textit{p-tol})_3(\text{ClO}_4)_4\}^{4+} = 650.8379$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3(\textit{p-tol})_3(\text{ClO}_4)_5\}^{3+} = 900.7668$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3(\textit{p-tol})_3(\text{ClO}_4)_6\}^{2+} = 1401.1227$ .  $\{\text{Fe}_4(\text{L1})_4(\text{L2})_2(\textit{p-tol})_2(\text{ClO}_4)\}^{7+} = 323.4965$ ,  $\{\text{Fe}_4(\text{L1})_4(\text{L2})_2(\textit{p-tol})_2(\text{ClO}_4)_2\}^{6+} = 393.9042$ ,  $\{\text{Fe}_4(\text{L1})_4(\text{L2})_2(\textit{p-tol})_2(\text{ClO}_4)_3\}^{5+} = 492.6746$ ,  $\{\text{Fe}_4(\text{L1})_4(\text{L2})_2(\textit{p-tol})_2(\text{ClO}_4)_4\}^{4+} = 640.5803$ ,  $\{\text{Fe}_4(\text{L1})_4(\text{L2})_2(\textit{p-tol})_2(\text{ClO}_4)_5\}^{3+} = 887.4231$ ,  $\{\text{Fe}_4(\text{L1})_4(\text{L2})_2(\textit{p-tol})_2(\text{ClO}_4)_6\}^{2+} = 1381.1086$ .  $\{\text{Fe}_4(\text{L1})_5(\text{L2})(\textit{p-tol})(\text{ClO}_4)\}^{7+} = 317.7777$ ,  $\{\text{Fe}_4(\text{L1})_5(\text{L2})(\textit{p-tol})(\text{ClO}_4)_2\}^{6+} = 387.2322$ ,  $\{\text{Fe}_4(\text{L1})_5(\text{L2})(\textit{p-tol})(\text{ClO}_4)_3\}^{5+} = 484.6684$ ,  $\{\text{Fe}_4(\text{L1})_5(\text{L2})(\textit{p-tol})(\text{ClO}_4)_4\}^{4+} = 630.8224$ ,  $\{\text{Fe}_4(\text{L1})_5(\text{L2})(\textit{p-tol})(\text{ClO}_4)_5\}^{3+} = 874.0794$ ,  $\{\text{Fe}_4(\text{L1})_5(\text{L2})(\textit{p-tol})(\text{ClO}_4)_6\}^{2+} = 1361.0936$ .  $\{\text{Fe}_4(\text{L1})_6(\text{ClO}_4)\}^{7+} = 312.0593$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{ClO}_4)_2\}^{6+} = 380.7264$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{ClO}_4)_3\}^{5+} = 476.6622$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{ClO}_4)_4\}^{4+} = 620.5644$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{ClO}_4)_5\}^{3+} = 860.7353$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{ClO}_4)_6\}^{2+} = 1341.0775$ .



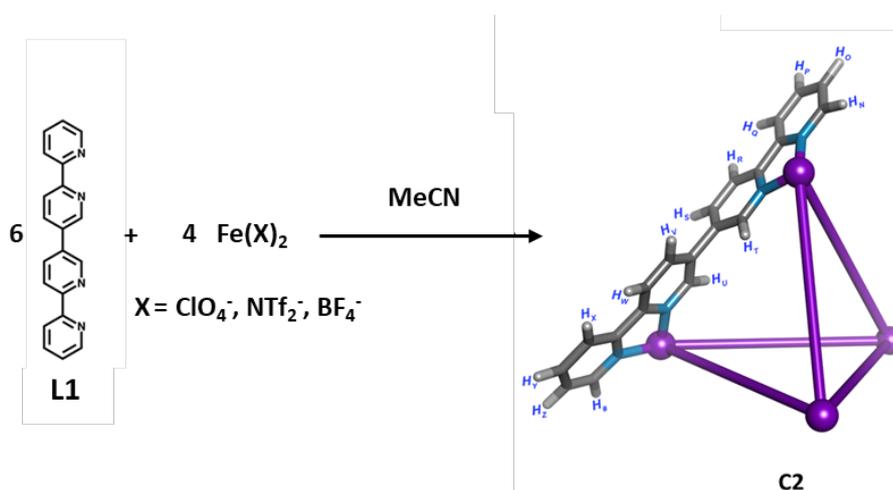
**Figure S4.** Stacked  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectra of the aromatic region of **A**: system containing  $[\text{Fe}_4(\mathbf{L1})_x(\mathbf{L2})_y(p\text{-tol})_z](\text{ClO}_4)_8$ , where the dominant species (incorporating 67% of **L1**) observed by NMR is  $[\text{Fe}_4(\mathbf{L1})_6](\text{ClO}_4)_8$ , with minor peaks for *p*-toluidine in red circles. **B**: control reaction of **L2** (6 equiv), *p*-toluidine (6 equiv) and  $\text{Fe}(\text{ClO}_4)_2$  (4 equiv), **C**: addition of TREN (1 equiv) into solution **A**, highlighting the ejection of free *p*-toluidine into solution (red circles) and the formation of the mixed-ligand tetrahedron  $[\mathbf{C1}](\text{ClO}_4)_8$ , **D**: precipitation of solution **C** with diethyl ether, removing the free *p*-toluidine from the solution and leaving  $[\mathbf{C2}](\text{ClO}_4)_8$  exclusively, **E**: reference spectrum of  $[\mathbf{C1}](\text{ClO}_4)_8$ , **F**: *p*-toluidine in solution.



**Figure S5.** High-resolution mass spectrum for an acetonitrile solution of  $[\text{Fe}_4(\mathbf{L1})_x(\mathbf{L2})_y(\text{p-tol})_z](\text{ClO}_4)_8$  (green). Patterns for the 2+ to 5+ peaks are annotated, whilst the 6+ and 7+ peaks are highlighted in red.

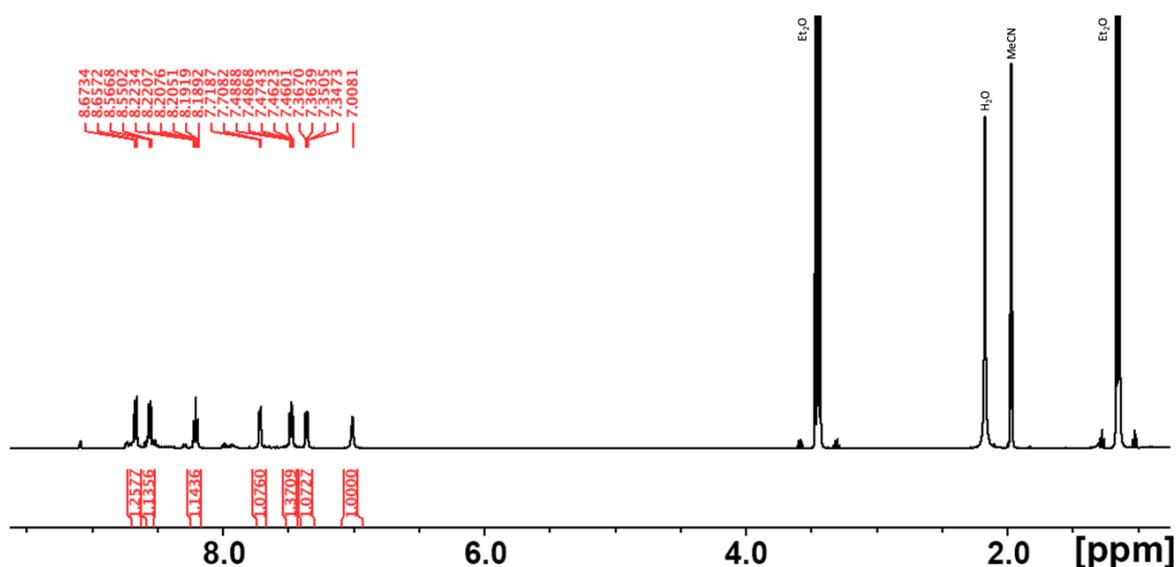
### S1.3.2 Synthesis and Characterisation of C2 Homotetrahedra

**Scheme S2.** General reaction scheme for the formation of homotetrahedron **C2** with general formula  $[\text{Fe}_4(\mathbf{L1})_6](\text{X})_8$ .

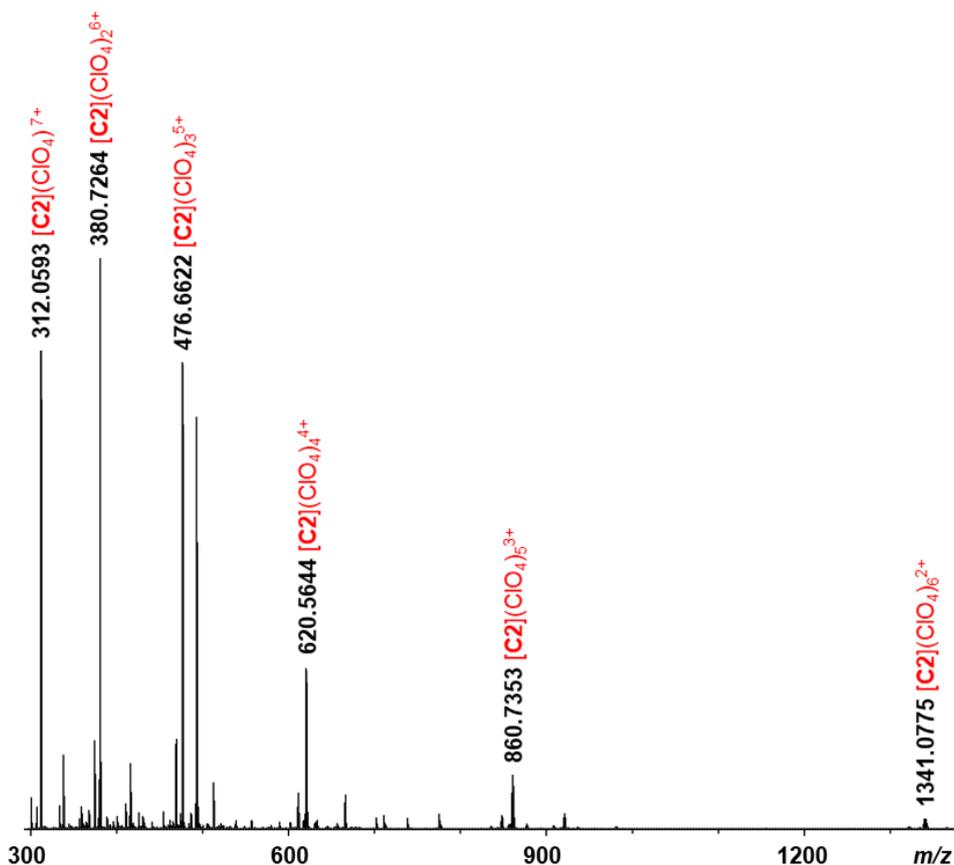


**[Fe<sub>4</sub>(L1)<sub>6</sub>](ClO<sub>4</sub>)<sub>8</sub>.**

**L1** (2.8 mg, 9.0 μmol, 6 equiv) and Fe(ClO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O (1.5 mg, 5.9 μmol, 4 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting pink solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a pink solid. <sup>1</sup>H (500 MHz, 298 K, CD<sub>3</sub>CN): 8.67 (d, 2H, *J* = 8.09 Hz, *H<sub>Q</sub>*, *H<sub>X</sub>*), 8.56 (d, 2H, *J* = 8.30 Hz, *H<sub>R</sub>*, *H<sub>W</sub>*), 8.21 (t, 2H, *J* = 7.89 Hz, *H<sub>P</sub>*, *H<sub>V</sub>*), 7.71 (d, 2H, *J* = 5.25 Hz, *H<sub>S</sub>*, *H<sub>V</sub>*), 7.36 (t, 2H, *J* = 6.67 Hz, *H<sub>O</sub>*, *H<sub>Z</sub>*), 7.36 (dd, 2H, *J* = 8.23 Hz, *H<sub>N</sub>*, *H<sub>#</sub>*), 7.01 (s, 2H, *H<sub>T</sub>*, *H<sub>U</sub>*). [Accurate mass, *m/z*]: {Fe<sub>4</sub>(L1)<sub>6</sub>(ClO<sub>4</sub>)<sub>7</sub>}<sup>7+</sup> = 312.0593, {Fe<sub>4</sub>(L1)<sub>6</sub>(ClO<sub>4</sub>)<sub>2</sub>}<sup>6+</sup> = 380.7264, {Fe<sub>4</sub>(L1)<sub>6</sub>(ClO<sub>4</sub>)<sub>3</sub>}<sup>5+</sup> = 476.6622, {Fe<sub>4</sub>(L1)<sub>6</sub>(ClO<sub>4</sub>)<sub>4</sub>}<sup>4+</sup> = 620.5644, {Fe<sub>4</sub>(L1)<sub>6</sub>(ClO<sub>4</sub>)<sub>5</sub>}<sup>3+</sup> = 860.7353, {Fe<sub>4</sub>(L1)<sub>6</sub>(ClO<sub>4</sub>)<sub>6</sub>}<sup>2+</sup> = 1341.0775.



**Figure S6.** <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K) spectrum of homotetrahedron [C2](ClO<sub>4</sub>)<sub>8</sub>.



**Figure S7.** High-resolution mass spectrum for an acetonitrile solution of homotetrahedron [C2](ClO<sub>4</sub>)<sub>8</sub> (red).

### [Fe<sub>4</sub>(L1)<sub>6</sub>](NTf<sub>2</sub>)<sub>8</sub>

**L1** (4.3 mg, 13.9 μmol, 6 equiv) and Fe(NTf<sub>2</sub>)<sub>2</sub>·7H<sub>2</sub>O (6.7 mg, 9.0 μmol, 4 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting red solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the red solution, causing a red precipitate to appear. Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a red solid. <sup>1</sup>H (500 MHz, 298 K, CD<sub>3</sub>CN): 8.73 (d, 2H, *J* = 7.88 Hz, *H<sub>O</sub>*, *H<sub>X</sub>*), 8.52 (d, 2H, *J* = 8.30 Hz, *H<sub>R</sub>*, *H<sub>W</sub>*), 8.24 (m, 2H, *H<sub>P</sub>*, *H<sub>Y</sub>*), 7.53 (t, 2H, *J* = 4.47 Hz *H<sub>S</sub>*, *H<sub>V</sub>*), 7.48 (dd, 2H, *J* = 8.29 Hz, *H<sub>O</sub>*, *H<sub>Z</sub>*), 7.40 (d, 2H, *J* = 5.30 Hz, *H<sub>N</sub>*, *H<sub>#</sub>*), 7.09 (s, 2H, *H<sub>T</sub>*, *H<sub>U</sub>*). [Accurate mass, *m/z*]: {Fe<sub>4</sub>(L1)<sub>6</sub>(NTf<sub>2</sub>)<sub>7</sub>}<sup>7+</sup> = 338.0867, {Fe<sub>4</sub>(L1)<sub>6</sub>(NTf<sub>2</sub>)<sub>2</sub>}<sup>6+</sup> = 440.7159, {Fe<sub>4</sub>(L1)<sub>6</sub>(NTf<sub>2</sub>)<sub>3</sub>}<sup>5+</sup> = 585.0429, {Fe<sub>4</sub>(L1)<sub>6</sub>(NTf<sub>2</sub>)<sub>4</sub>}<sup>4+</sup> = 801.0327, {Fe<sub>4</sub>(L1)<sub>6</sub>(NTf<sub>2</sub>)<sub>5</sub>}<sup>3+</sup> = 1162.0928, {Fe<sub>4</sub>(L1)<sub>6</sub>(NTf<sub>2</sub>)<sub>6</sub>}<sup>2+</sup> = 1882.9839.



### [Fe<sub>4</sub>(L1)<sub>6</sub>](BF<sub>4</sub>)<sub>8</sub>

L1 (1.9 mg, 6.12 μmol, 6 equiv) and Fe(BF<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.8 mg, 5.33 μmol, 4 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting red solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a red solid. Suitable crystals for X-ray diffraction (Section S2) were grown through slow vapour diffusion of diethyl ether into an acetonitrile solution. <sup>1</sup>H (500 MHz, 298 K, CD<sub>3</sub>CN): 8.67 (d, 2H, *J* = 7.92 Hz, *H<sub>Q</sub>*, *H<sub>X</sub>*), 8.49 (d, 2H, *J* = 8.22 Hz, *H<sub>R</sub>*, *H<sub>W</sub>*), 8.19 (t, 2H, *J* = 7.58 Hz, *H<sub>P</sub>*, *H<sub>Y</sub>*), 7.59 (s, 2H, *H<sub>S</sub>*, *H<sub>V</sub>*), 7.45 (t, 2H, *J* = 6.28 Hz, *H<sub>O</sub>*, *H<sub>Z</sub>*), 7.38 (d, 2H, *J* = 7.99 Hz, *H<sub>N</sub>*, *H<sub>#</sub>*), 7.19 (s, 2H, *H<sub>T</sub>*, *H<sub>U</sub>*). [Accurate mass, *m/z*]: {Fe<sub>4</sub>(L1)<sub>6</sub>(BF<sub>4</sub>)<sub>7</sub>}<sup>7+</sup> = 310.3528, {Fe<sub>4</sub>(L1)<sub>6</sub>(BF<sub>4</sub>)<sub>2</sub>}<sup>6+</sup> = 376.5791, {Fe<sub>4</sub>(L1)<sub>6</sub>(BF<sub>4</sub>)<sub>3</sub>}<sup>5+</sup> = 469.0956, {Fe<sub>4</sub>(L1)<sub>6</sub>(BF<sub>4</sub>)<sub>4</sub>}<sup>4+</sup> = 608.1202, {Fe<sub>4</sub>(L1)<sub>6</sub>(BF<sub>4</sub>)<sub>5</sub>}<sup>3+</sup> = 839.8284, {Fe<sub>4</sub>(L1)<sub>6</sub>(BF<sub>4</sub>)<sub>6</sub>}<sup>2+</sup> = 1303.2453.

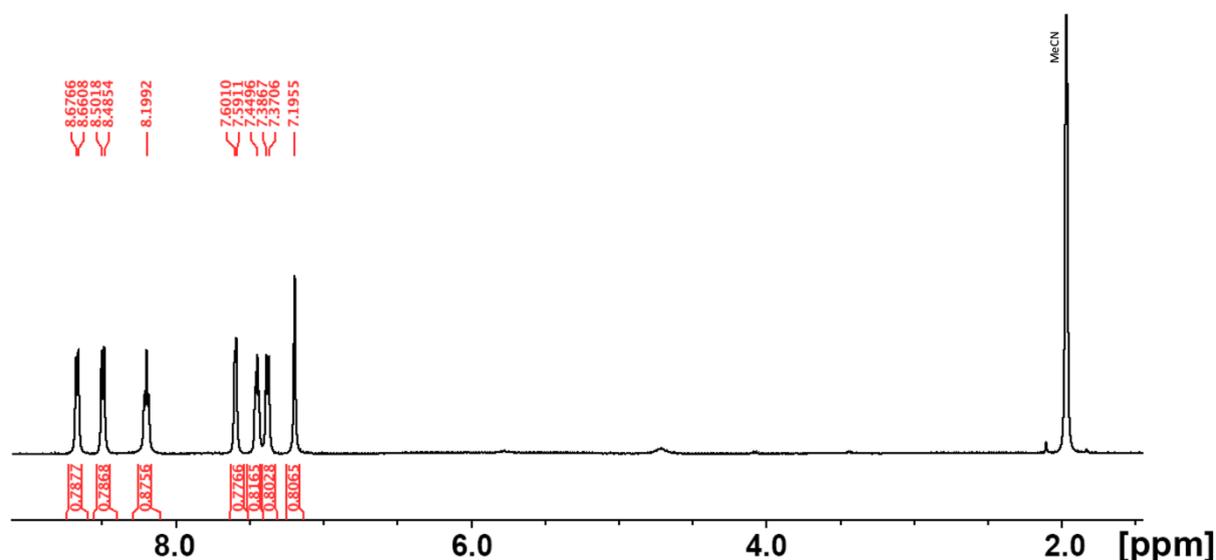
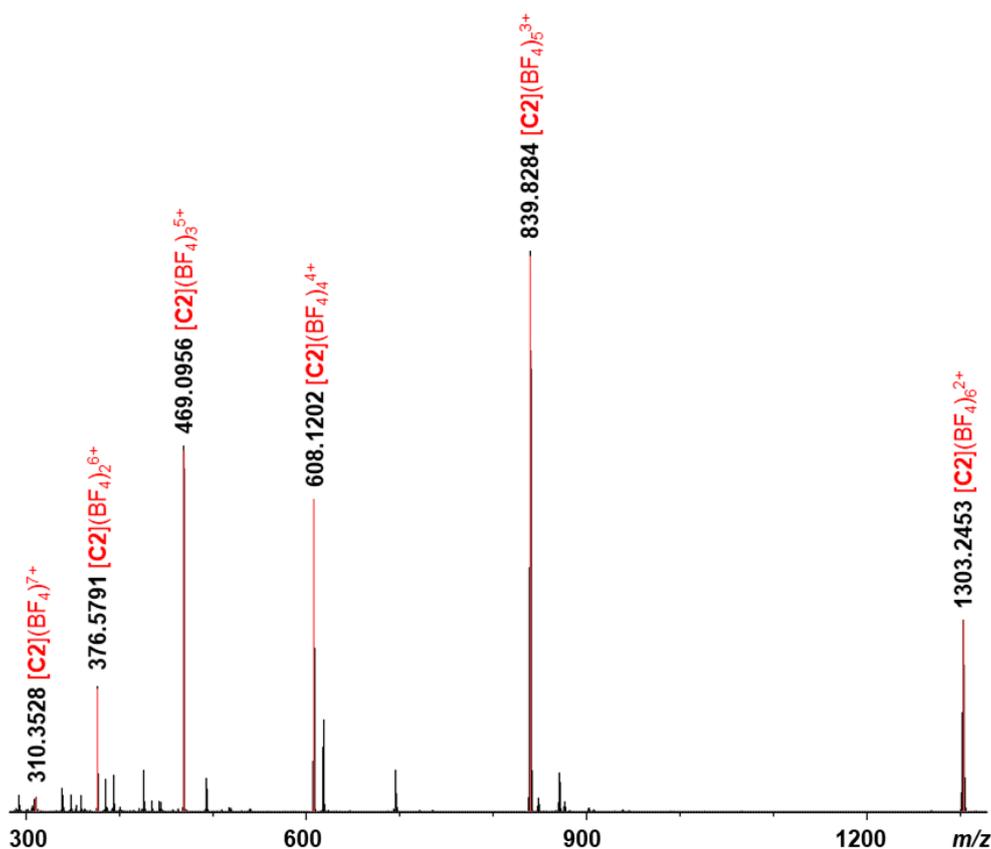


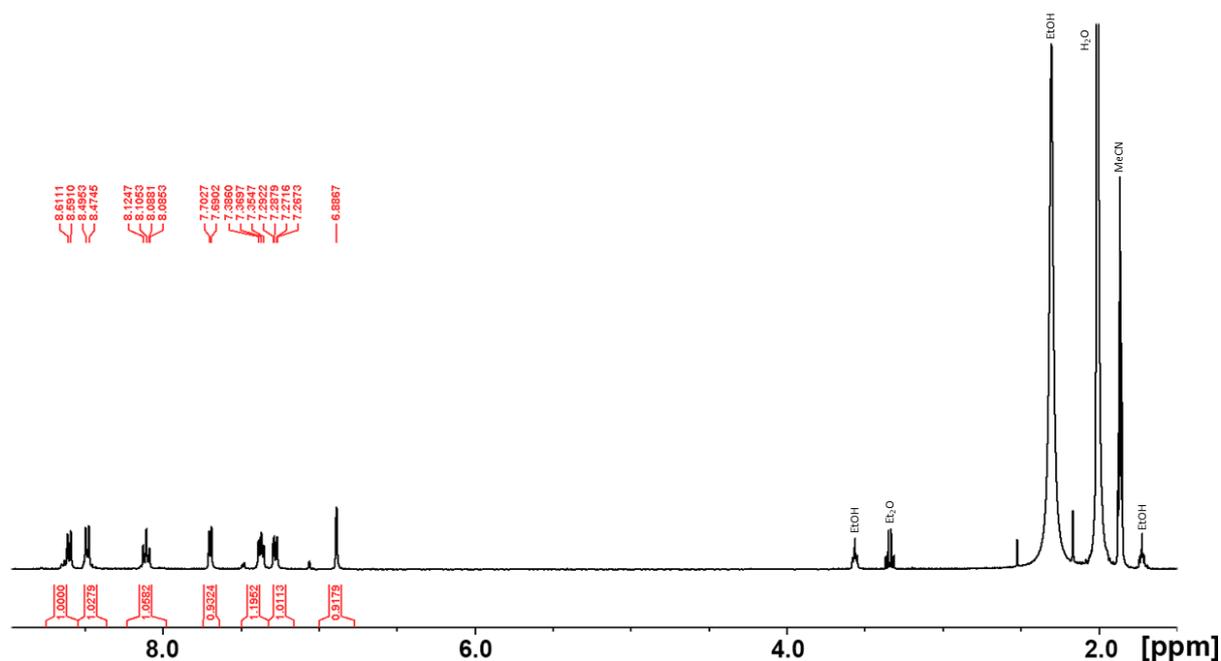
Figure S10. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K) spectrum of homotetrahedron [C2](BF<sub>4</sub>)<sub>8</sub>.



**Figure S11.** High-resolution mass spectrum for an acetonitrile solution of homotetrahedron [C2](BF<sub>4</sub>)<sub>8</sub> (red).

### [Fe<sub>4</sub>(L1)<sub>6</sub>](OTf)<sub>8</sub>

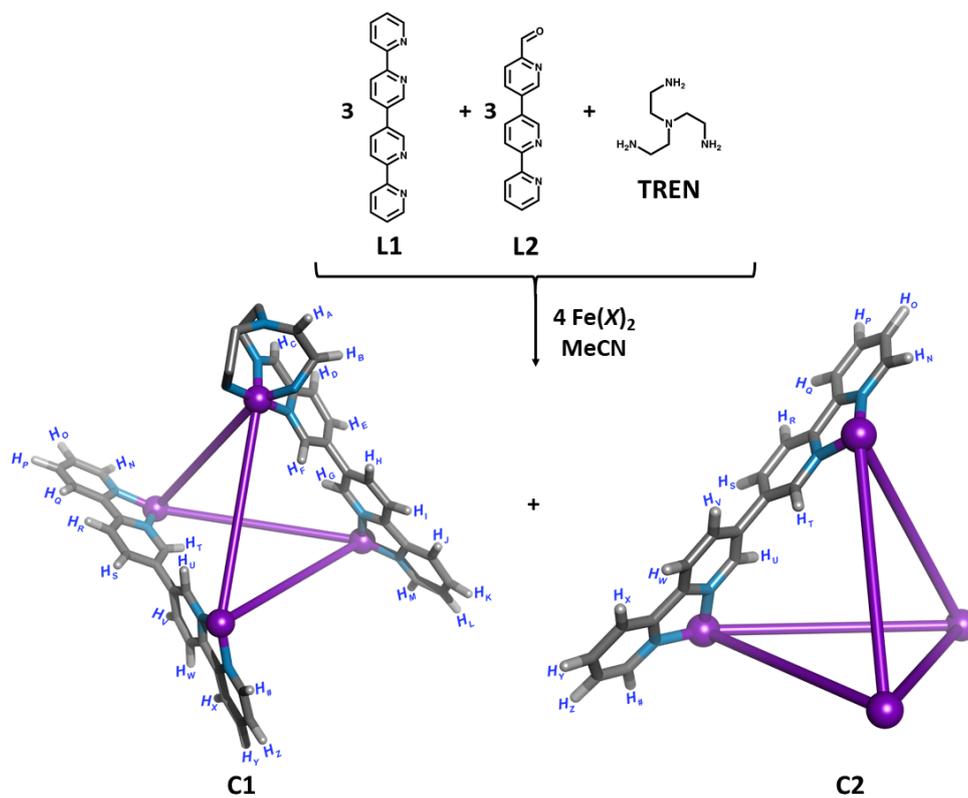
**L1** (2.4 mg, 7.7 μmol, 6 equiv) and Fe(OTf)<sub>2</sub> (1.8 mg, 5.1 μmol, 4 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting purple solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a purple solid. Suitable crystals for X-ray diffraction (Section S2) were grown through slow vapour diffusion of diethyl ether into an acetonitrile solution. <sup>1</sup>H NMR(500 MHz, 298 K, CD<sub>3</sub>CN): 8.60 (d, 2H, *J* = 8.04 Hz, *H<sub>O</sub>*, *H<sub>X</sub>*), 8.48 (d, 2H, *J* = 8.32 Hz, *H<sub>R</sub>*, *H<sub>W</sub>*), 8.09 (td, 2H, *J* = 11.7 Hz, *H<sub>P</sub>*, *H<sub>Y</sub>*), 7.69 (d, 2H, *J* = 5.00 Hz, *H<sub>S</sub>*, *H<sub>V</sub>*), 7.37 (t, 2H, *J* = 6.26 Hz, *H<sub>O</sub>*, *H<sub>Z</sub>*), 7.28 (dd, 2H, *J* = 8.36 Hz, *H<sub>N</sub>*, *H<sub>#</sub>*), 6.89 (s, 2H, *H<sub>T</sub>*, *H<sub>U</sub>*). [Accurate mass, *m/z*]: {Fe<sub>4</sub>(L1)<sub>6</sub>(OTf)<sub>3</sub>}<sup>5+</sup> = 506.4666, {Fe<sub>4</sub>(L1)<sub>6</sub>(OTf)<sub>4</sub>}<sup>4+</sup> = 670.5705, {Fe<sub>4</sub>(L1)<sub>6</sub>(OTf)<sub>5</sub>}<sup>3+</sup> = 943.4110, {Fe<sub>4</sub>(L1)<sub>6</sub>(OTf)<sub>6</sub>}<sup>2+</sup> = 1489.5942.



**Figure S12.**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectrum of homotetrahedron  $[\text{C}_2](\text{OTf})_3$ .

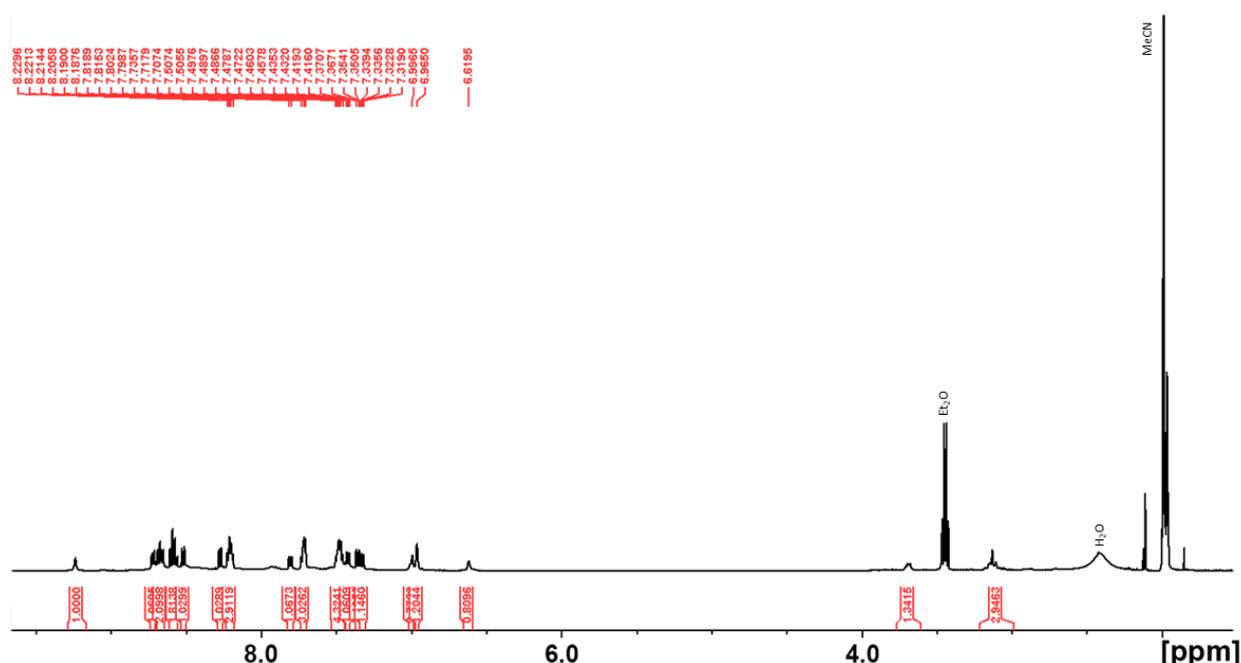
### S1.3.3 Reactions with TREN

**Scheme S3.** General reaction scheme for the formation of **C1** and/or **C2**. All hydrogen atoms are labelled for NMR assignment.

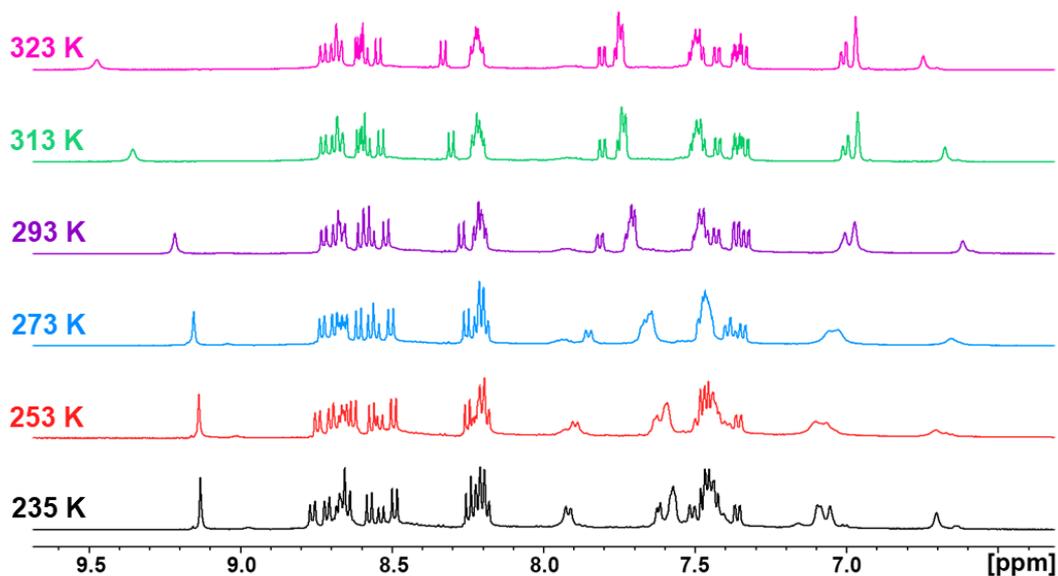


**[Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T](ClO<sub>4</sub>)<sub>8</sub>.**

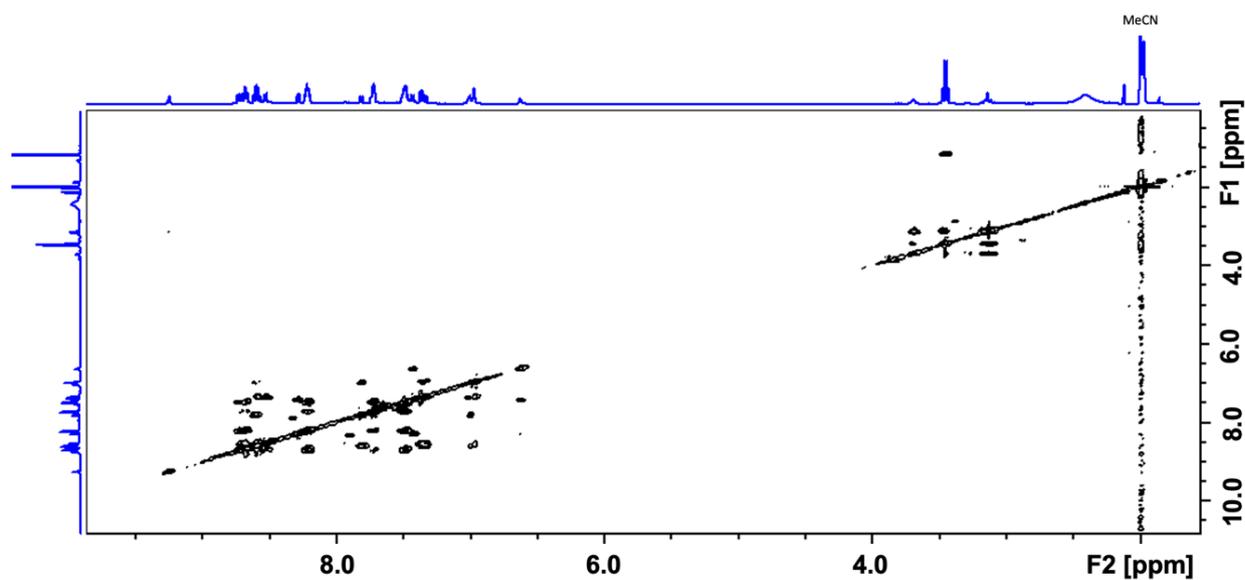
**L1** (3.7 mg, 11.9 μmol, 3 equiv), **L2** (2.6 mg, 10.0 μmol, 3 equiv), Fe(ClO<sub>4</sub>)<sub>2</sub>.xH<sub>2</sub>O (3.7 mg, 14.5 μmol, 4 equiv) and *tris*(2-aminoethyl)amine (0.50 μL, 3.3 μmol, 1 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting pink solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a pink solid. <sup>1</sup>H (500 MHz, 298 K, CD<sub>3</sub>CN): 9.24 (s, 1H, H<sub>C</sub>), 8.72 (d, 1H, J = 8.11 Hz, H<sub>Q</sub>), 8.67 (m, 3H, H<sub>X</sub>, H<sub>R</sub>, H<sub>W</sub>), 8.60 (d, 1H, J = 8.27 Hz, H<sub>F</sub>), 8.57 (d, 1H, J = 8.33 Hz, H<sub>G</sub>), 8.52 (d, 1H, J = 8.33 Hz, H<sub>H</sub>), 8.28 (d, 1H, J = 7.92 Hz, H<sub>E</sub>), 8.21 (m, 3H, J = 6.56 Hz, H<sub>P</sub>, H<sub>V</sub>, H<sub>S</sub>), 7.81 (d, 1H, J = 8.39 Hz, H<sub>D</sub>), 7.72 (m, 3H, J = 7.08 Hz, H<sub>V</sub>, H<sub>O</sub>, H<sub>Z</sub>), 7.48 (m, 3H, J = 7.73 Hz, H<sub>N</sub>, H<sub>T</sub>, H<sub>U</sub>), 7.42 (d, 1H, J = 7.96, H<sub>#</sub>), 7.36 (d, 1H, J = 8.24 Hz, H<sub>I</sub>), 7.33 (d, 1H, J = 8.24 Hz, H<sub>M</sub>), 6.99 (s, 1H, H<sub>K</sub>), 6.96 (s, 1H, H<sub>L</sub>), 6.62 (s, 1H, H<sub>J</sub>). [Accurate mass, *m/z*]: {Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T(ClO<sub>4</sub>)<sub>7</sub>}<sup>7+</sup> = 304.2057, {Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T(ClO<sub>4</sub>)<sub>2</sub>}<sup>6+</sup> = 371.5649, {Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T(ClO<sub>4</sub>)<sub>3</sub>}<sup>5+</sup> = 465.6632, {Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T(ClO<sub>4</sub>)<sub>4</sub>}<sup>4+</sup> = 606.8213, {Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T(ClO<sub>4</sub>)<sub>5</sub>}<sup>3+</sup> = 842.0778, {Fe<sub>4</sub>(L1)<sub>3</sub>(L2)<sub>3</sub>T(ClO<sub>4</sub>)<sub>6</sub>}<sup>2+</sup> = 1313.0922.



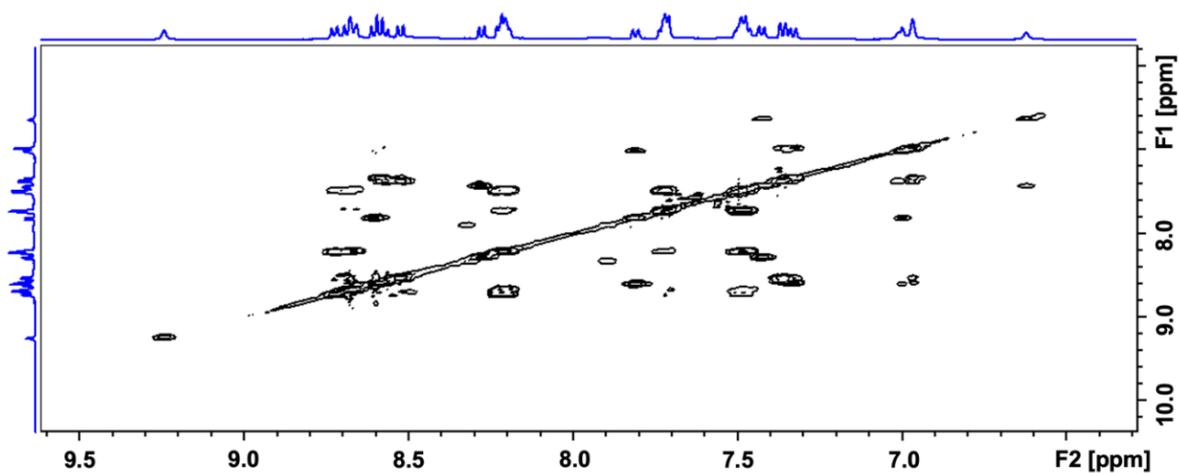
**Figure S13.** <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K) spectrum of iron perchlorate mixed ligand tetrahedron [C1](ClO<sub>4</sub>)<sub>8</sub>.



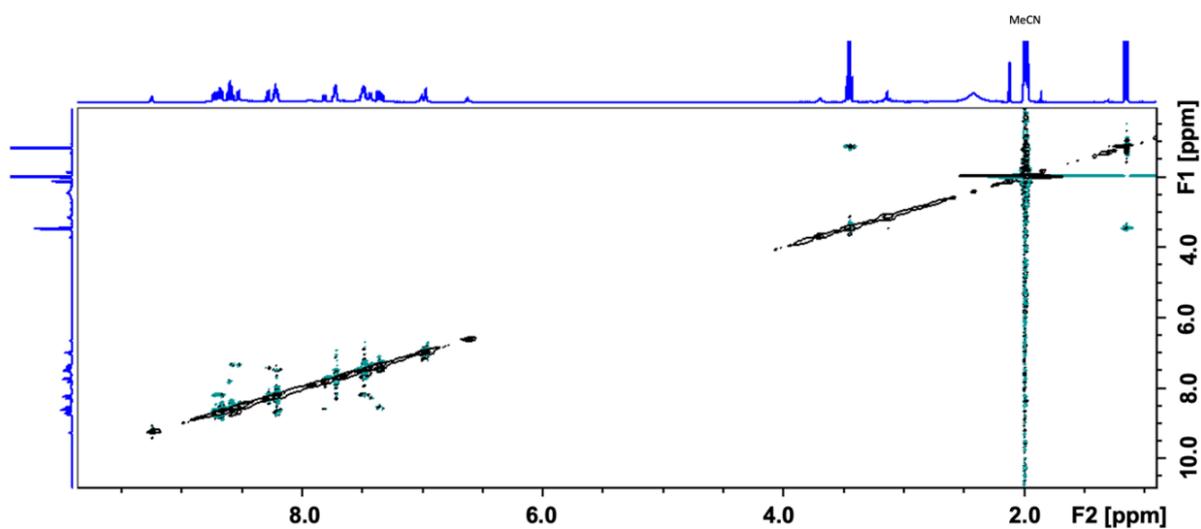
**Figure S14.** Stacked  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) variable temperature NMR spectra of iron perchlorate mixed ligand tetrahedron  $[\text{C1}](\text{ClO}_4)_8$ .



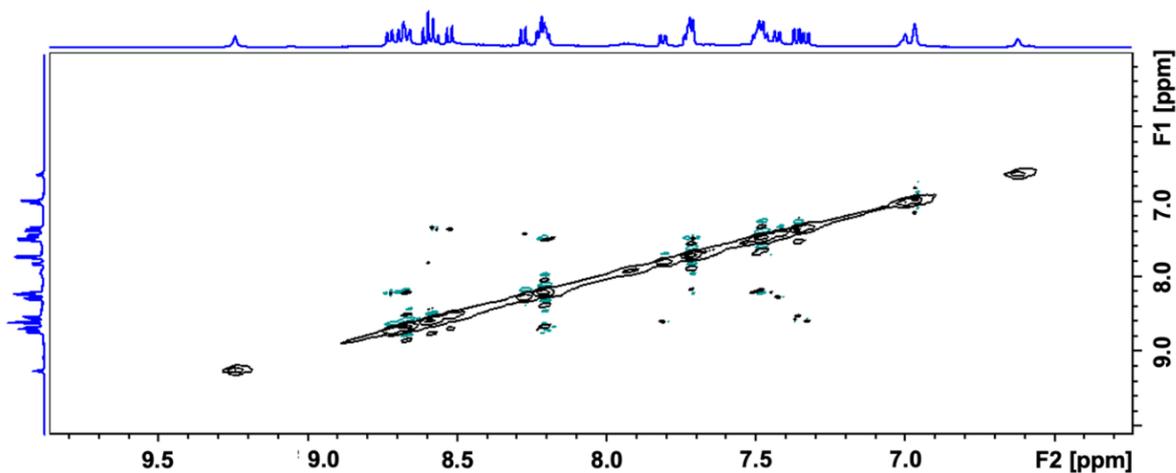
**Figure S15.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectrum of iron perchlorate mixed ligand tetrahedron  $[\text{C1}](\text{ClO}_4)_8$ .



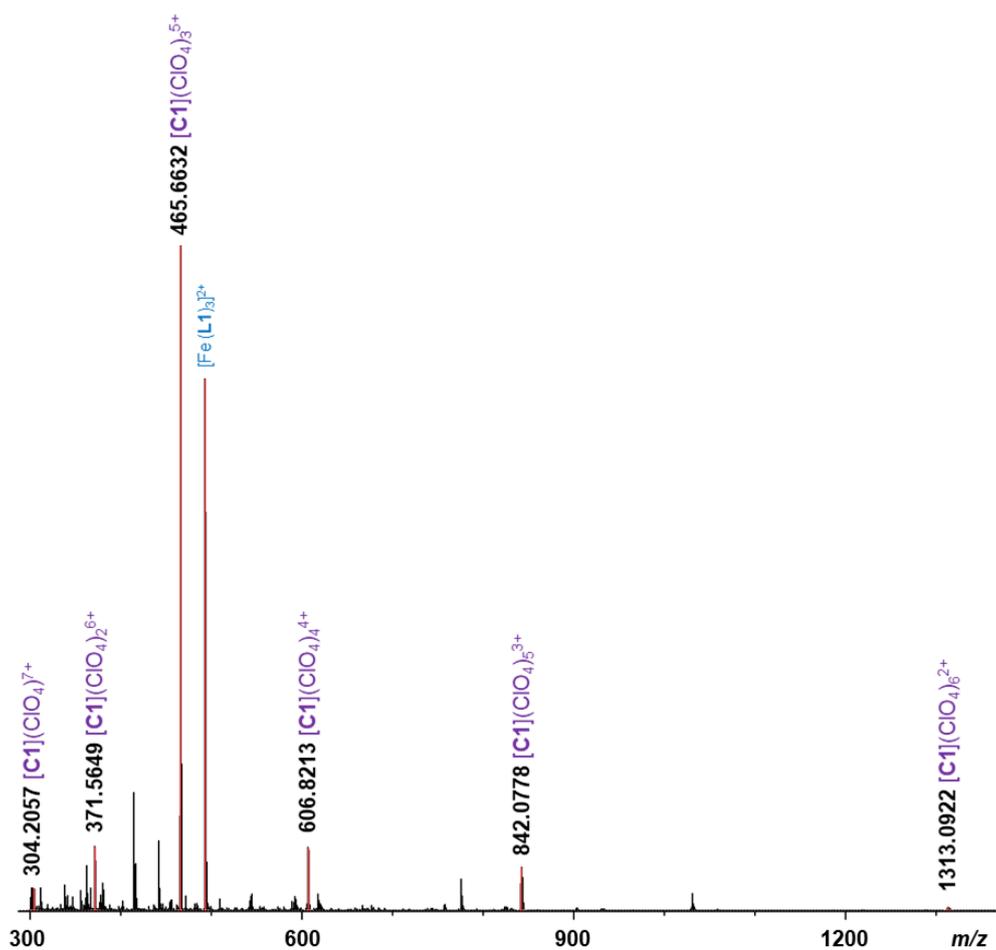
**Figure S16.** Zoomed in  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectrum of iron perchlorate mixed ligand tetrahedron  $[\text{C1}](\text{ClO}_4)_8$ .



**Figure S17.**  $^1\text{H}$ - $^1\text{H}$  NOESY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectrum of iron perchlorate mixed ligand tetrahedron  $[\text{C1}](\text{ClO}_4)_8$ .



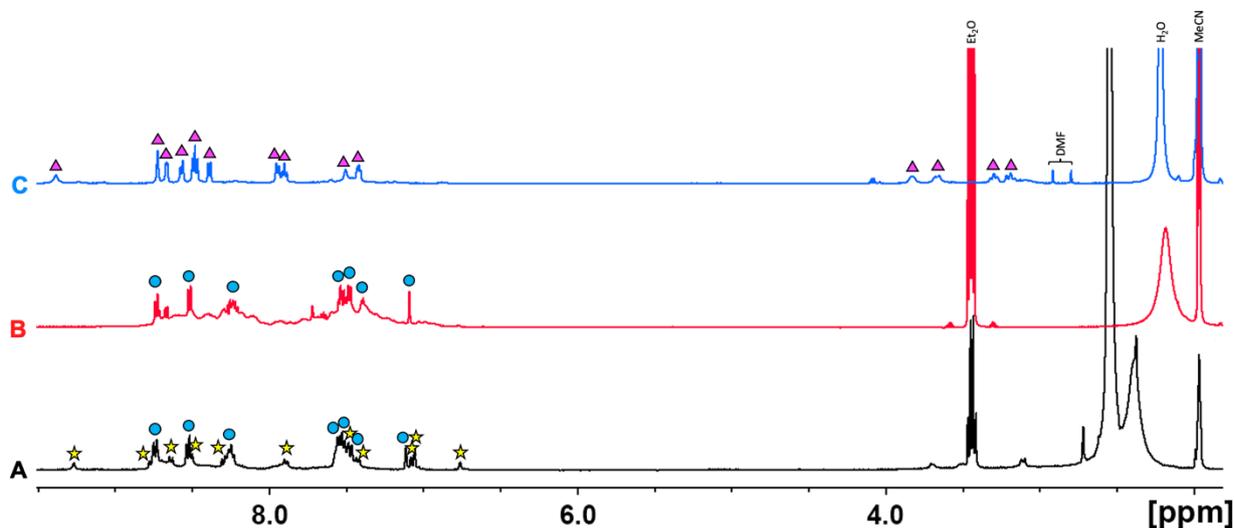
**Figure S18.** Zoomed in  $^1\text{H}$ - $^1\text{H}$  NOESY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectrum of iron perchlorate mixed ligand tetrahedron  $[\text{C1}](\text{ClO}_4)_8$ .



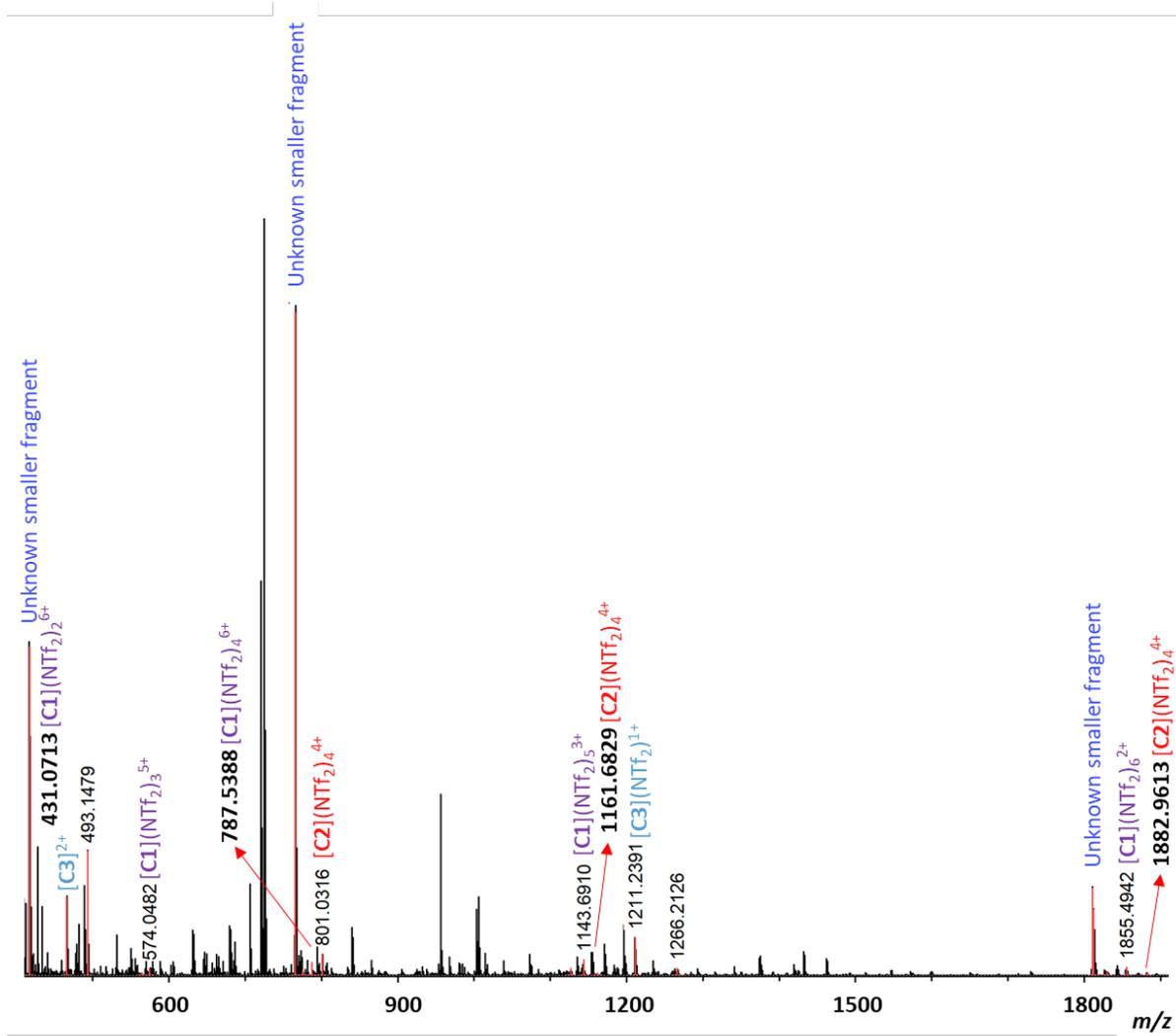
**Figure S19.** High-resolution mass spectrum for an acetonitrile solution of heterotetrahedral complex  $[\text{C1}](\text{ClO}_4)_8$  (purple).

### $[\text{Fe}_4(\text{L1})_3(\text{L2})_3](\text{NTf}_2)_8$

**L1** (2.5 mg, 8.1  $\mu\text{mol}$ , 3 equiv), **L2** (2.1 mg, 8.0  $\mu\text{mol}$ , 3 equiv),  $\text{Fe}(\text{NTf}_2)_2 \cdot 7\text{H}_2\text{O}$  (8.0 mg, 10.8  $\mu\text{mol}$ , 4 equiv) and *tris*(2-aminoethyl)amine (0.32  $\mu\text{L}$ , 2.1  $\mu\text{mol}$ , 1 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting dark purple solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/ $\text{N}_2$  fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a purple solid.  $^1\text{H}$  (400 MHz, 298 K,  $\text{CD}_3\text{CN}$ ):  $[\text{C1}](\text{NTf}_2)_8$   $\delta$  = 9.26 (s, 1H,  $H_C$ ), 8.77 (s, 1H), 8.63 (d, 1H,  $J$  = 8.48 Hz,  $H_F$ ), 8.49 (s, 1H), 8.30 (s, 1H), 7.88 (d, 1H,  $J$  = 8.28 Hz,  $H_D$ ), 7.50 (s, 1H), 7.42 (d, 1H,  $J$  = 8.56 Hz,  $H_\#$ ), 7.07 (s, 1H), 7.05 (s, 1H), 6.75 (s, 1H);  $[\text{C2}](\text{NTf}_2)_8$   $\delta$  = 8.73 (d, 2H,  $J$  = 8.28 Hz,  $H_O, H_X$ ), 8.52 (d, 2H,  $J$  = 8.12 Hz,  $H_R, H_W$ ), 8.24 (m, 2H,  $H_P, H_Y$ ), 7.53 (t, 2H,  $J$  = 5.72 Hz,  $H_S, H_V$ ), 7.46 (d, 2H,  $J$  = 8.32 Hz,  $H_Q, H_Z$ ), 7.10 (s, 2H,  $H_T, H_U$ ). [Accurate mass,  $m/z$ ]:  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{NTf}_2)_2\}^{6+}$  = 431.0713,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{NTf}_2)_3\}^{5+}$  = 574.0482,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{NTf}_2)_4\}^{4+}$  = 787.5388,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{NTf}_2)_5\}^{3+}$  = 1143.6910,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{NTf}_2)_6\}^{2+}$  = 1855.4942.  $\{\text{Fe}_4(\text{L1})_6(\text{NTf}_2)_4\}^{4+}$  = 801.0315,  $\{\text{Fe}_4(\text{L1})_6(\text{NTf}_2)_5\}^{3+}$  = 1161.6829,  $\{\text{Fe}_4(\text{L1})_6(\text{NTf}_2)_6\}^{2+}$  = 1882.9613.



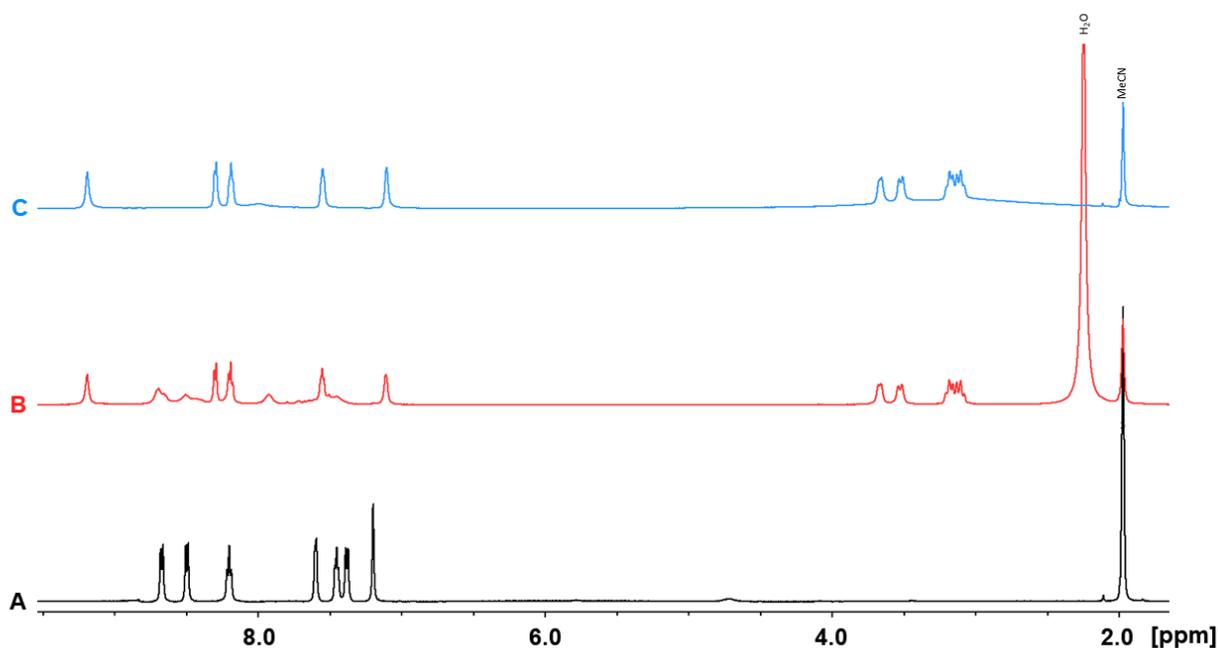
**Figure S20.** Stacked  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectra of **A**: iron triflimide mixed ligand system, **B**: iron triflimide homotetrahedron  $[\text{C2}](\text{NTf}_2)_8$  (blue circles). **C**: mononuclear complex  $[\text{C3}](\text{NTf}_2)_2$  (pink triangles). Peaks assigned to  $[\text{C1}](\text{NTf}_2)_8$  through comparison with the heterotetrahedron  $[\text{C1}](\text{ClO}_4)_8$  are denoted by yellow stars.



**Figure S21.** High-resolution mass spectrum for an acetonitrile solution of the tetrahedral mixture of complex  $[C1](NTf_2)_8$  (purple),  $[C2](NTf_2)_8$  (red) and  $[C3](NTf_2)_2$  (pale blue).

### S1.3.4 Addition of TREN and 2-Pyridinecarboxaldehyde to C2

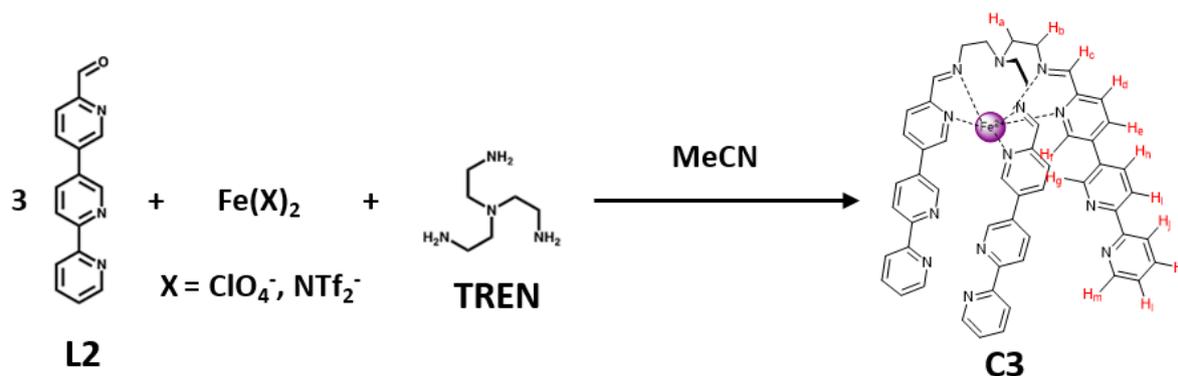
To a solution of  $[C2](BF_4)_8$  (4.48 mg, 1.61  $\mu$ mol) in deuterated acetonitrile (0.35 mL), *tris*(2-aminoethyl)amine (0.24  $\mu$ L, 1.60  $\mu$ mol, 1 equiv) and 2-pyridinecarboxaldehyde (0.46  $\mu$ L, 4.83  $\mu$ mol, 3 equiv) were added. The resulting solution was sealed in a J-Young NMR tube, and degassed by three vacuum/ $N_2$  fill cycles before being heated (50°C, 24 hr).



**Figure S22.** Stacked <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 298 K) spectra of **A**: homotetrahedron [C2](BF<sub>4</sub>)<sub>8</sub>, **B**: reaction mixture following addition of TREN (1 equiv) and 2-pyridinecarboxaldehyde (3 equiv) into a solution of homotetrahedron [C2](BF<sub>4</sub>)<sub>8</sub>, **C**: standard for the reaction of TREN (1 equiv), 2-pyridinecarboxaldehyde (3 equiv) and Fe(BF<sub>4</sub>)<sub>2</sub> (1 equiv).

### S1.3.5 Synthesis and Characterisation of Mononuclear Complex C3

**Scheme S4.** General reaction scheme for the formation of mononuclear complex **C3** with general formula [Fe(L1)<sub>3</sub>T](X)<sub>2</sub>.

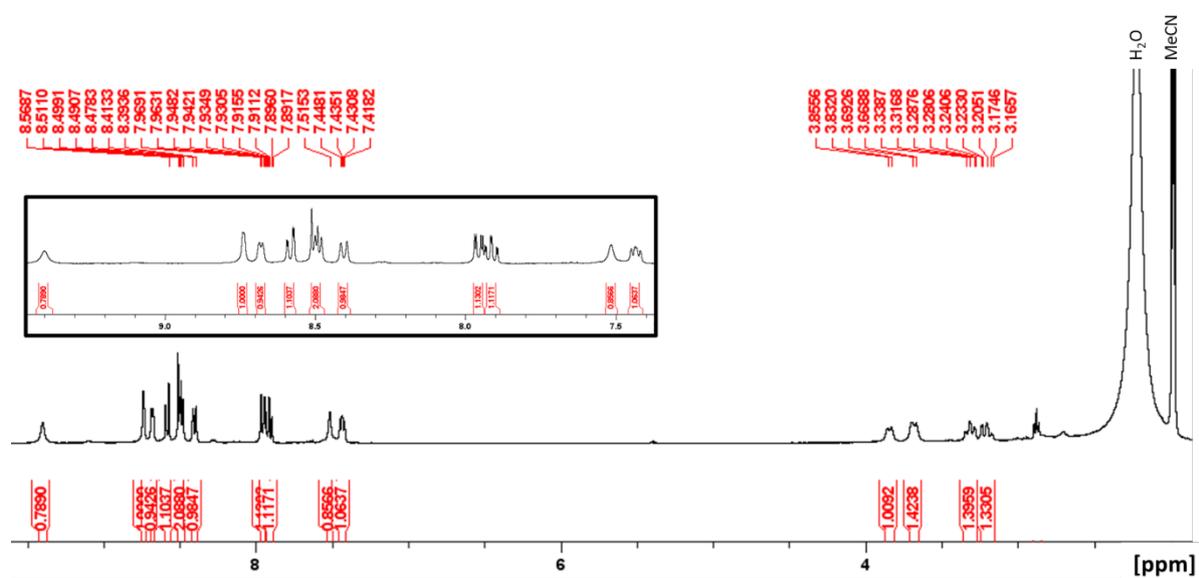


[Fe(L1)<sub>3</sub>T](X)<sub>2</sub>

**L2** (5 mg, 19.2 μmol, 3 equiv), Fe(X)<sub>2</sub> (6.4 μmol, 1 equiv, where X = ClO<sub>4</sub><sup>-</sup> or NTf<sub>2</sub><sup>-</sup>) and tris(2-aminoethyl)amine (0.93 μL, 6.4 μmol, 1 equiv) were dissolved in deuterated acetonitrile

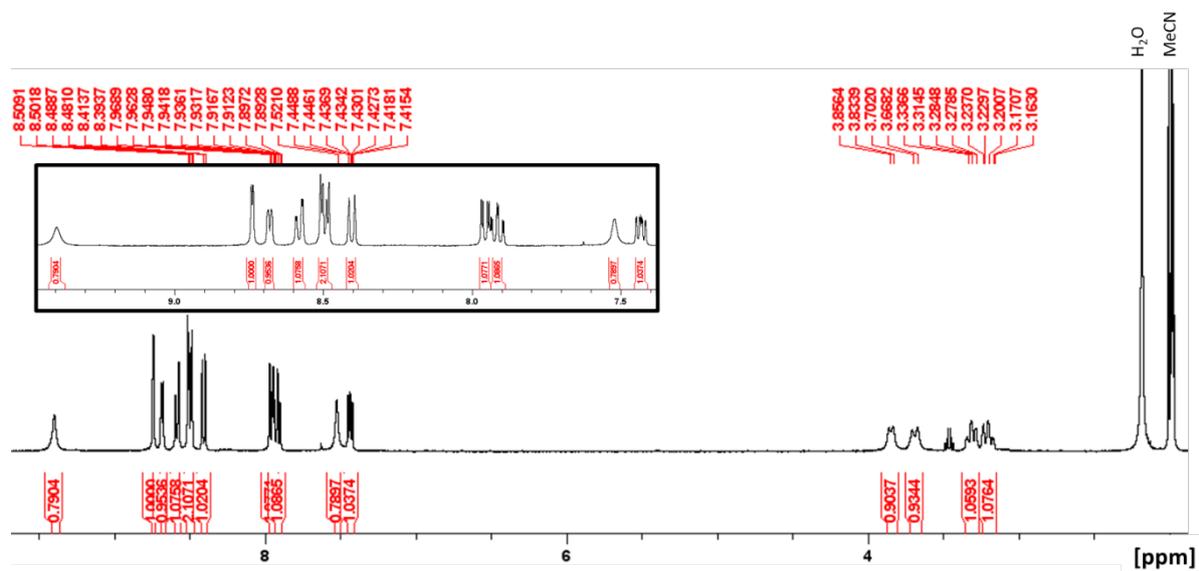
(0.35 mL) and the resulting solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (50°C, 24 hr).

**[C3](ClO<sub>4</sub>)<sub>2</sub>** <sup>1</sup>H NMR (400 MHz, 298 K, CD<sub>3</sub>CN): δ = 9.40 (s, 3H, H<sub>c</sub>), 8.74 (s, 3H, H<sub>f</sub>), 8.68 (d, 3H, *J* = 4.20 Hz, H<sub>m</sub>), 8.58 (dd, 3H, *J* = 8.04, 1.72 Hz, H<sub>d</sub>), 8.51-8.47 (m, 6H, H<sub>e</sub>, H<sub>h</sub>), 8.40 (d, 3H, *J* = 7.88 Hz, H<sub>i</sub>), 7.96 (dd, 3H, *J* = 8.24, 2.40 Hz, H<sub>j</sub>), 7.91 (td, 3H, *J* = 7.80, 1.72 Hz, H<sub>k</sub>), 7.52 (s, 3H, H<sub>g</sub>), 7.43 (t, 3H, *J* = 5.92 Hz, H<sub>l</sub>), 3.84 (broad d, 3H), 3.68 (broad d, 3H), 3.31 (t, 3H, H<sub>b</sub>), 3.20 (t, 3H, H<sub>a</sub>) ppm.



**Figure S23.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K) spectrum of iron perchlorate mononuclear complex [C3](ClO<sub>4</sub>)<sub>2</sub>.

**[C3](NTf<sub>2</sub>)<sub>2</sub>** <sup>1</sup>H NMR (400 MHz, 298 K, CD<sub>3</sub>CN): δ = 9.40 (s, 3H, H<sub>c</sub>), 8.74 (d, 3H, *J* = 1.88 Hz, H<sub>f</sub>), 8.68 (d, 3H, *J* = 4.64 Hz, H<sub>m</sub>), 8.58 (dd, 3H, *J* = 8.16, 1.64 Hz, H<sub>d</sub>), 8.49 (dd, 3H, *J* = 8.24, 2.92 Hz, H<sub>e</sub>, H<sub>h</sub>), 8.40 (d, 3H, *J* = 8.00 Hz, H<sub>i</sub>), 7.95 (dd, 3H, *J* = 8.36, 2.44 Hz, H<sub>j</sub>), 7.91 (td, 3H, *J* = 7.80, 1.76 Hz, H<sub>k</sub>), 7.52 (s, 3H, H<sub>g</sub>), 7.43 (broad t, 3H, *J* = 7.56 Hz, H<sub>l</sub>), 3.84 (broad d, 3H), 3.68 (broad d, 3H), 3.31 (t, 3H, H<sub>b</sub>), 3.20 (t, 3H, H<sub>a</sub>) ppm.

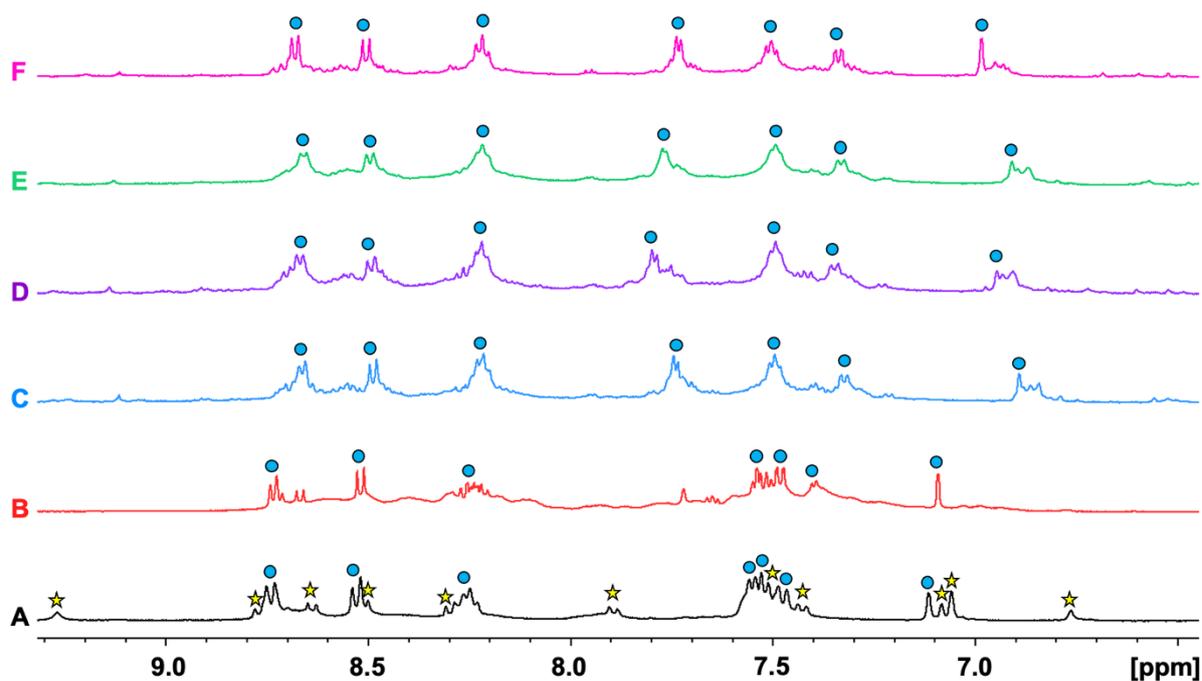


**Figure S24.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 298 K) spectrum of iron triflimide mononuclear complex [C3](NTf<sub>2</sub>)<sub>2</sub>.

### S1.3.6 Effect of Counterion on Composition of Self-Assembly Mixture

#### Addition of anions to mixture consisting of C1, C2 and C3 generated from Fe(NTf<sub>2</sub>)<sub>2</sub>

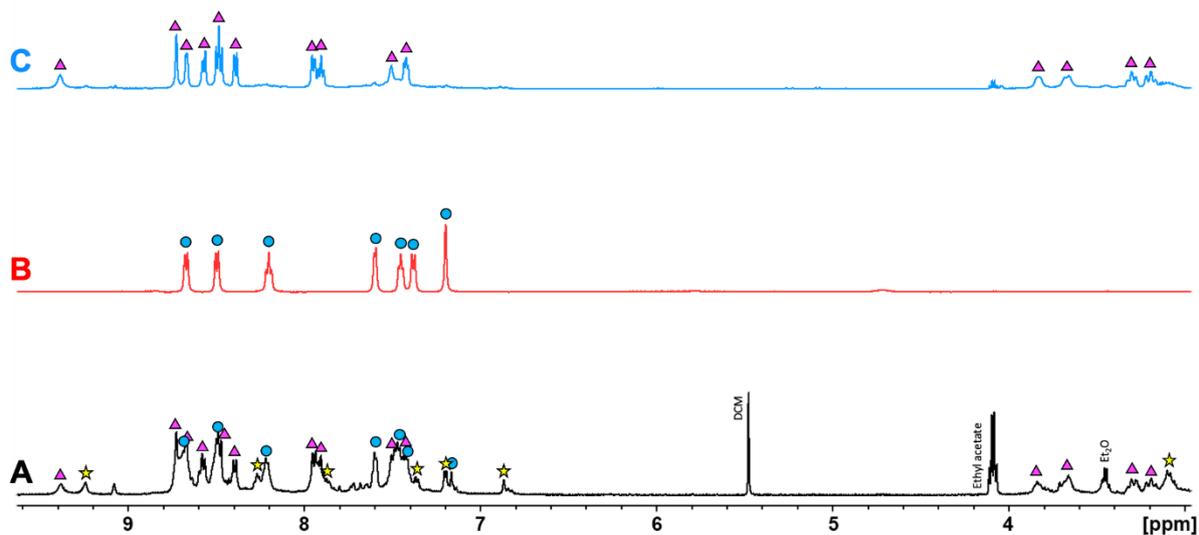
A stock solution of the mixture containing **C1**, **C2** and **C3** generated from **L1** (10.1 mg, 32.5 μmol, 3 equiv), **L2** (8.6 mg, 32.9 μmol, 3 equiv), *tris*(2-aminoethyl)amine (1.57 μL, 10.5 μmol, 1 equiv) and Fe(NTf<sub>2</sub>)<sub>2</sub>·7H<sub>2</sub>O (31.9 mg, 43.1 μmol, 4 equiv) was prepared in 1.75 mL of deuterated acetonitrile. Aliquots of 0.35 mL CD<sub>3</sub>CN were removed and 1 equiv of NaX/KX (where X = PF<sub>6</sub><sup>-</sup>, SbF<sub>6</sub><sup>-</sup>, AsF<sub>6</sub><sup>-</sup> or ReO<sub>4</sub><sup>-</sup>) was added individually to each solution. The resulting reaction mixtures were sealed in J-Young NMR tubes, and degassed by three vacuum/N<sub>2</sub> fill cycles before being heated (70°C, 24 hr) and analysed by <sup>1</sup>H NMR.



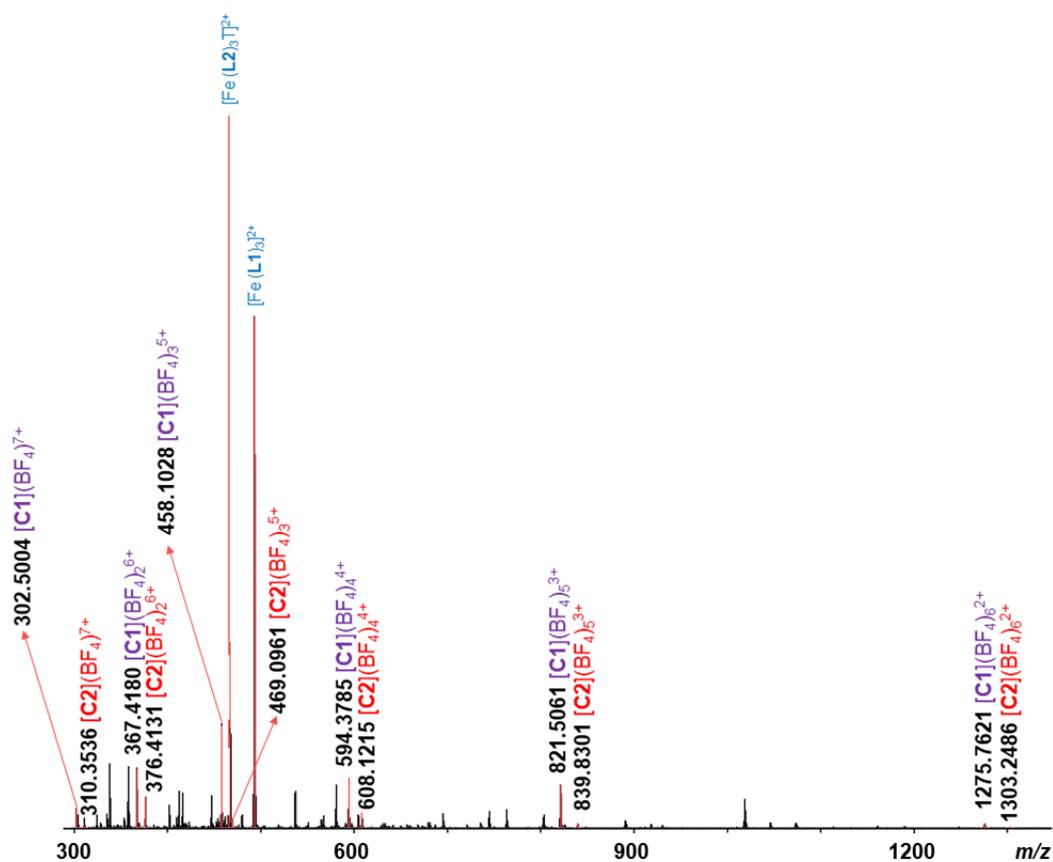
**Figure S25.** Stacked  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectra of **A**: iron triflimide mixed ligand system, **B**: iron triflimide homotetrahedron (*blue circles*), **C**: addition of  $\text{PF}_6^-$  to a solution of **A**, **D**: addition of  $\text{SbF}_6^-$  to a solution of **A**, **E**: addition of  $\text{AsF}_6^-$  to a solution of **A**, **F**: addition of  $\text{ReO}_4^-$  to a solution of **A**. Peaks for heterotetrahedron  $[\text{C1}](\text{NTf}_2)_8$  are denoted by yellow stars. In all four reactions (**C**, **D**, **E** and **F**) the homotetrahedron is the dominant complex observed in solution following anion addition.

### $[\text{Fe}_4(\text{L1})_6](\text{BF}_4)_8 / [\text{Fe}_4(\text{L1})_3(\text{L2})_3](\text{BF}_4)_8$

**L1** (1.8 mg, 5.8  $\mu\text{mol}$ , 3 equiv), **L2** (1.7 mg, 6.5  $\mu\text{mol}$ , 3 equiv),  $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (2.9 mg, 8.6  $\mu\text{mol}$ , 4 equiv) and *tris*(2-aminoethyl)amine (0.32  $\mu\text{L}$ , 2.1  $\mu\text{mol}$ , 1 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting dark blue solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/ $\text{N}_2$  fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a blue/black solid. [Accurate mass,  $m/z$ ]:  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{BF}_4)\}^{7+} = 302.5004$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{BF}_4)_2\}^{6+} = 367.4180$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{BF}_4)_3\}^{5+} = 458.1028$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{BF}_4)_4\}^{4+} = 594.3785$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{BF}_4)_5\}^{3+} = 821.5061$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{BF}_4)_6\}^{2+} = 1275.7621$ .  $\{\text{Fe}_4(\text{L1})_6(\text{BF}_4)\}^{7+} = 310.3536$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{BF}_4)_2\}^{6+} = 376.4131$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{BF}_4)_3\}^{5+} = 469.0961$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{BF}_4)_4\}^{4+} = 608.1215$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{BF}_4)_5\}^{3+} = 839.8301$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{BF}_4)_6\}^{2+} = 1303.2486$ .



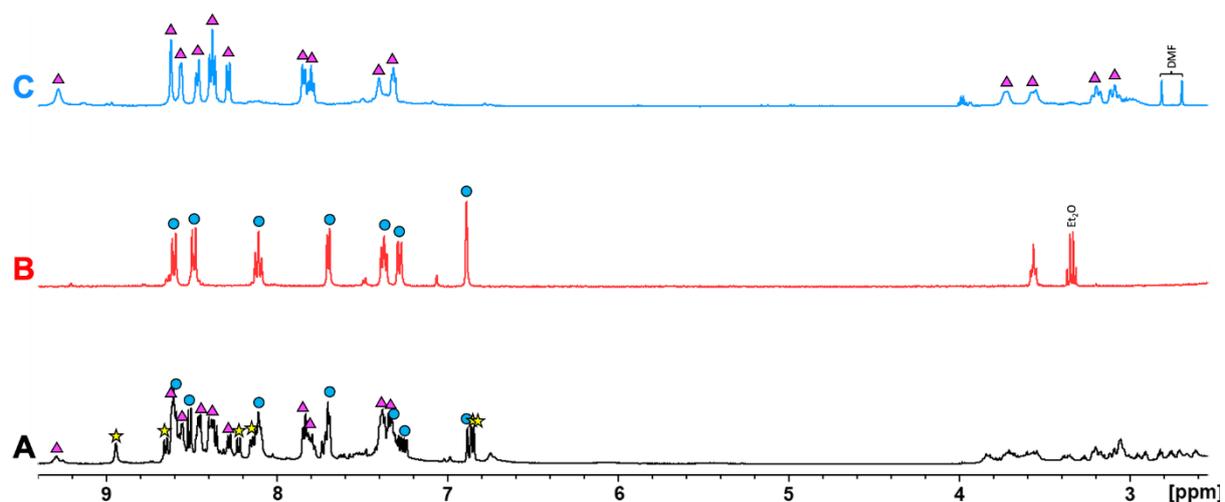
**Figure S26.** Stacked  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectra of **A**: iron tetrafluoroborate mixed ligand system, **B**: iron tetrafluoroborate homotetrahedron  $[\text{C}2](\text{ClO}_4)_8$  (blue circles), **C**: mononuclear complex  $[\text{C}3](\text{BF}_4)_2$  (pink triangles). Peaks assigned to  $[\text{C}1](\text{BF}_4)_8$  through comparison with the heterotetrahedron  $[\text{C}1](\text{ClO}_4)_8$  are denoted by yellow stars.



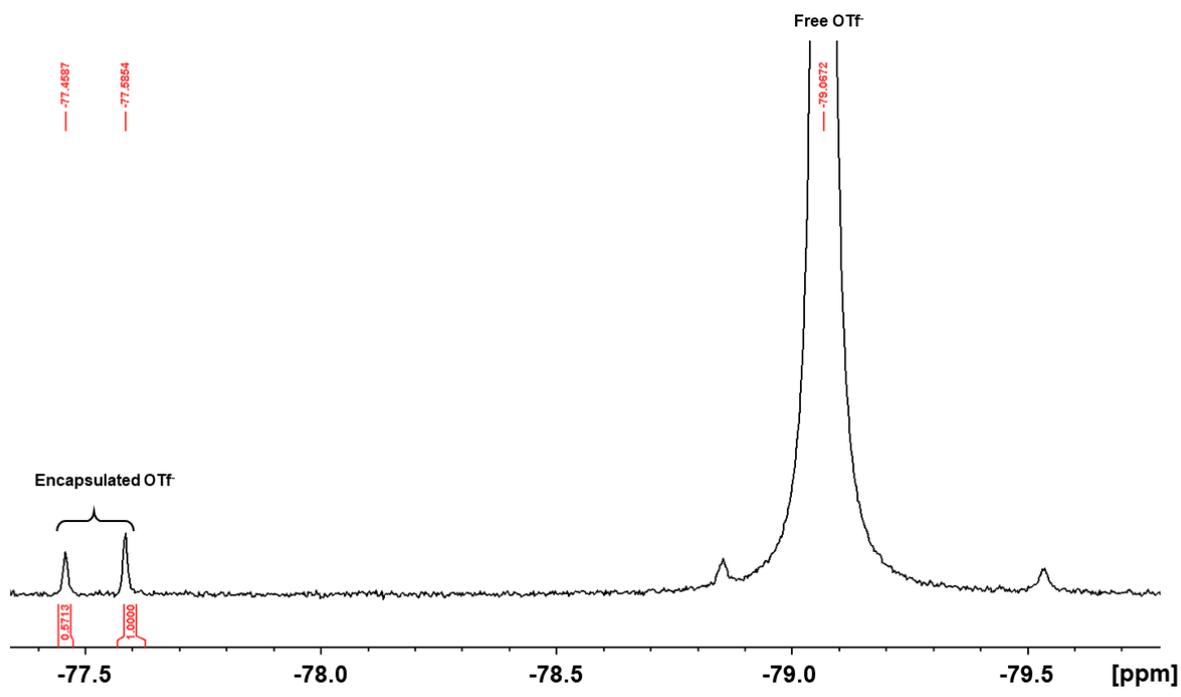
**Figure S27.** High-resolution mass spectrum for an acetonitrile solution of the tetrahedral mixture of complex  $\text{C}1(\text{BF}_4)_8$  (purple) and  $\text{C}2(\text{BF}_4)_8$  (red). Additional isotopic patterns are highlighted in blue.

**$[\text{Fe}_4(\text{L1})_6](\text{OTf})_8 / [\text{Fe}_4(\text{L1})_3(\text{L2})_3](\text{OTf})_8$**

**L1** (3.6 mg, 11.6  $\mu\text{mol}$ , 3 equiv), **L2** (3.0 mg, 11.5  $\mu\text{mol}$ , 3 equiv),  $\text{Fe}(\text{OTf})_2$  (5.4 mg, 15.2  $\mu\text{mol}$ , 4 equiv) and *tris*(2-aminoethyl)amine (0.56  $\mu\text{L}$ , 3.9  $\mu\text{mol}$ , 1 equiv) were dissolved in deuterated acetonitrile (0.35 mL) and the resulting pink solution was added to a J-Young NMR tube. The tube was sealed, and the solution was degassed by three vacuum/ $\text{N}_2$  fill cycles before being heated (50°C, 24 hr). Diethyl ether was added to the solution causing precipitation and the mixture was centrifuged (5 min). The supernatant was removed leaving the product as a pink solid. [Accurate mass,  $m/z$ ]:  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{OTf})_4\}^{4+} = 642.5834$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{OTf})_5\}^{3+} = 925.0872$ ,  $\{\text{Fe}_4(\text{L1})_3(\text{L2})_3\text{T}(\text{OTf})_6\}^{2+} = 1462.1077$ .  $\{\text{Fe}_4(\text{L1})_6(\text{OTf})_4\}^{4+} = 670.0698$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{OTf})_5\}^{3+} = 943.4112$ ,  $\{\text{Fe}_4(\text{L1})_6(\text{OTf})_6\}^{2+} = 1490.0951$ .



**Figure S28.** Stacked  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectra of **A**: iron triflate mixed ligand system, **B**: iron triflate homotetrahedron  $[\text{C2}](\text{OTf})_8$  (blue circles). **C**: mononuclear complex  $[\text{C3}](\text{OTf})_2$  (pink triangles). Peaks assigned to  $[\text{C1}](\text{OTf})_8$  through comparison with the heterotetrahedron  $[\text{C1}](\text{ClO}_4)_8$  are denoted by yellow stars.



**Figure S29.**  $^{19}\text{F}$  NMR (471 MHz,  $\text{CD}_3\text{CN}$ , 298 K) spectrum of the iron triflate mixed ligand system, highlighting the peak for free triflate anions as well as two additional peaks for triflate encapsulation in homotetrahedron **C2** (-77.46 ppm) and heterotetrahedron **C1** (-77.59 ppm).

## S2 X-Ray Crystallography

**Data Collection.** X-Ray data for compound **C2** were collected at a temperature of 100 K using a Rigaku Supernova with Mo-K $\alpha$  radiation equipped with a CCD-Eos detector and an Oxford Cryosystems nitrogen flow gas system. X-Ray data for compound [**C3**](ClO<sub>4</sub>)<sub>2</sub> was collected at a temperature of 100 K using a Rigaku FR-X with Cu-K $\alpha$  radiation equipped with a HypixHE6000 detector, equipped with an Oxford Cryosystems nitrogen flow gas system. X-Ray data for compounds **C1** and [**C3**](NTf<sub>2</sub>)<sub>2</sub> were collected at a temperature of 100 K using a synchrotron radiation ( $\lambda = 0.6889 \text{ \AA}$ ) at Diamond Light Source,<sup>3</sup> equipped with a Pilatus 2M detector and an Oxford Cryosystems nitrogen flow gas system. Data was measured using CrysAlisPro and GDA suite of programs.

**Crystal structure determinations and refinements.** X-Ray data were processed and reduced using CrysAlisPro suite of programmes. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles.<sup>4-6</sup> The crystal structure was solved and refined against all  $F^2$  values using the SHELXL and Olex 2 suite of programmes.<sup>7,8</sup> Despite the highly intense X-ray source, crystals of **C2** present a diffraction limit of 1  $\text{\AA}$ .

All atoms in crystal structures were refined anisotropically with the exception of the hydrogens atoms. Hydrogen atoms were placed in the calculated idealized positions for all crystal structures. BF<sub>4</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup> anions in crystal structures were disordered and modelled over two positions. The anions structure were constrained to have idealize structure. The atomic displacement parameters (adp) of the ligands have been restrained using similar Ueq and rigid bond (RIGU) and Similar Ueq (SIMU) restraints.

Compounds **C1** and **C2** present large voids filled with featureless electron density. Solvent mask software implemented in Olex2 shows an electron count of 2074 and 357 electrons, which correspond to 94 and 16 molecules of acetonitrile in the unit cell, respectively.

A number of A and B alerts were found for structure **C2** due to the poor resolution obtained and the large disorder found in the crystal structure.

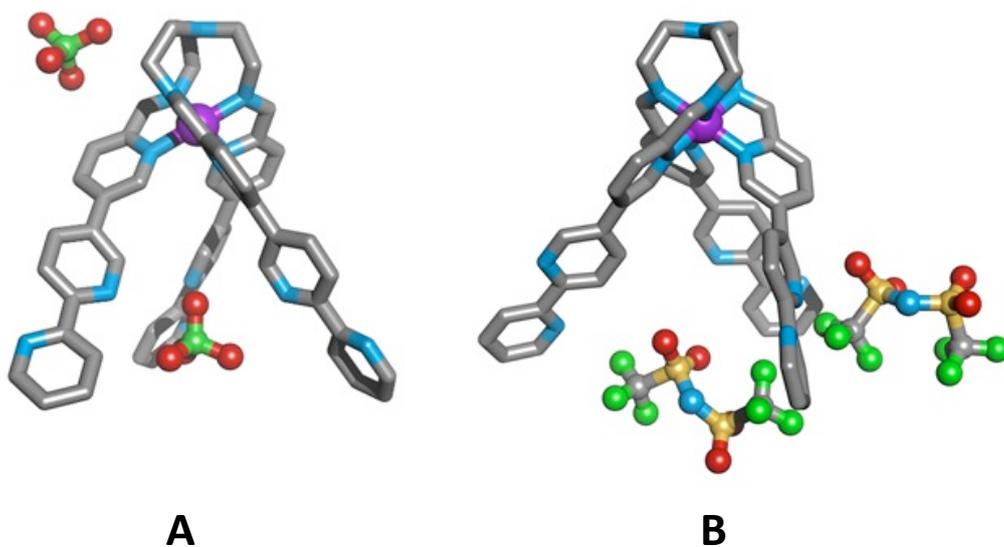
CCDC 2112326, 2112327, 2112329 and 2112640 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44)1223-336-033; or [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

**Table S1.** Crystallographic information for **C1** and **C2**.

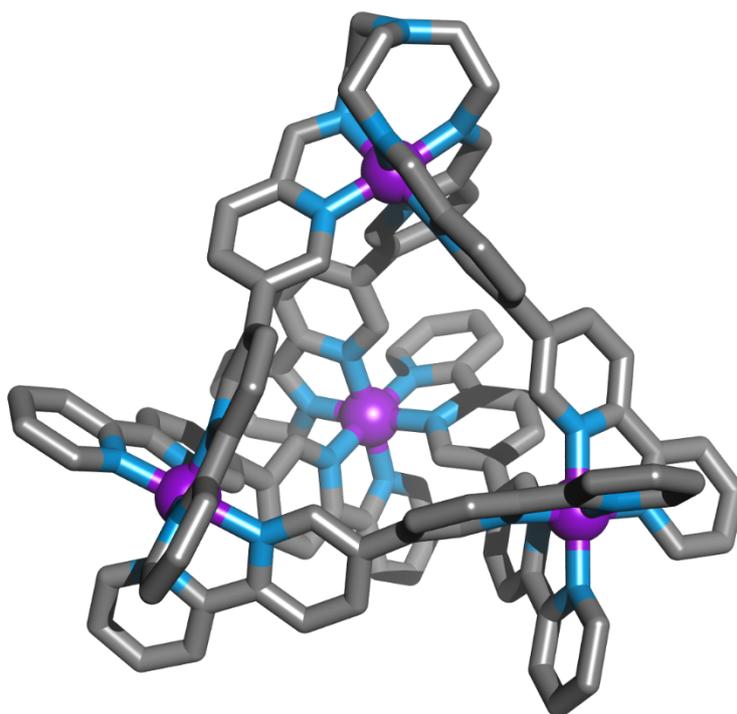
Identification code	<b>C1</b>	<b>C2</b>
Empirical formula	C <sub>120.39</sub> H <sub>94.58</sub> Cl <sub>8</sub> Fe <sub>4</sub> N <sub>28.19</sub> O <sub>32.99</sub>	C <sub>132</sub> H <sub>90</sub> F <sub>24</sub> Fe <sub>4</sub> N <sub>26</sub> O <sub>24</sub> S <sub>8</sub>
Formula weight	2971.07	3360.17
Temperature/K	293(2)	150.00(10)
Crystal system	trigonal	monoclinic
Space group	R-3	I2/a
a/Å	21.1400(7)	31.990(3)
b/Å	21.1400(7)	18.5196(12)
c/Å	67.0247(16)	28.075(2)
α/°	90	90
β/°	90	114.492(11)
γ/°	120	90
Volume/Å <sup>3</sup>	25940.3(18)	15136(2)
Z	6	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.141	1.475
μ/mm <sup>-1</sup>	0.480	0.590
F(000)	9109.0	6816.0
Crystal size/mm <sup>3</sup>	0.16 × 0.1 × 0.02	0.34 × 0.13 × 0.03
Radiation	Synchrotron (λ = 0.6889)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	3.194 to 49.034	5.434 to 41.628
Index ranges	-25 ≤ h ≤ 21, -25 ≤ k ≤ 23, -80 ≤ l ≤ 78	-31 ≤ h ≤ 25, -17 ≤ k ≤ 18, -27 ≤ l ≤ 28
Reflections collected	60877	27222
Independent reflections	10558 [R <sub>int</sub> = 0.0722, R <sub>sigma</sub> = 0.0487]	7890 [R <sub>int</sub> = 0.1191, R <sub>sigma</sub> = 0.1327]
Data/restraints/parameters	10558/283/605	7890/586/944
Goodness-of-fit on F <sup>2</sup>	1.244	1.280
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.1384, wR <sub>2</sub> = 0.3692	R <sub>1</sub> = 0.1348, wR <sub>2</sub> = 0.3475
Final R indexes [all data]	R <sub>1</sub> = 0.1947, wR <sub>2</sub> = 0.4153	R <sub>1</sub> = 0.2015, wR <sub>2</sub> = 0.3981
Largest diff. peak/hole / e Å <sup>-3</sup>	0.95/-0.43	1.20/-0.91

**Table S2.** Crystallographic information for [C3](ClO<sub>4</sub>)<sub>2</sub> and [C3](NTf<sub>2</sub>)<sub>2</sub>.

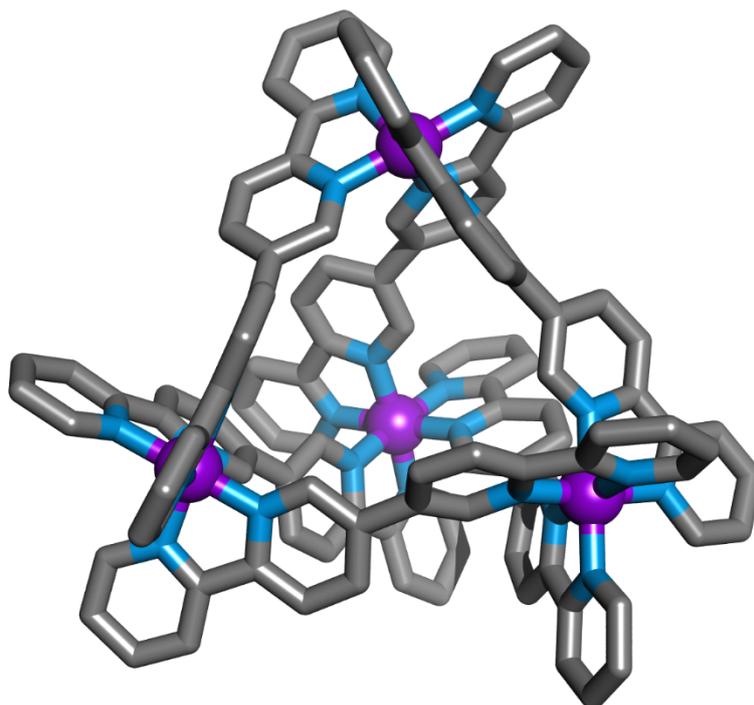
Identification code	[C3](ClO <sub>4</sub> ) <sub>2</sub>	[C3](NTf <sub>2</sub> ) <sub>2</sub>
Empirical formula	C <sub>60</sub> H <sub>54</sub> Cl <sub>2</sub> FeN <sub>16</sub> O <sub>8</sub>	C <sub>65.86</sub> H <sub>56.79</sub> F <sub>12</sub> FeN <sub>18.93</sub> O <sub>8</sub> S <sub>4</sub>
Formula weight	1253.94	1653.52
Temperature/K	99.96(10)	100
Crystal system	trigonal	trigonal
Space group	R-3c	P-1
a/Å	14.7047(2)	12.5031(2)
b/Å	14.7047(2)	15.5665(3)
c/Å	99.8911(10)	19.8576(4)
α/°	90	80.413(2)
β/°	90	72.158(2)
γ/°	120	77.821(2)
Volume/Å <sup>3</sup>	18705.5(5)	3574.56(13)
Z	12	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.336	1.536
μ/mm <sup>-1</sup>	3.279	0.396
F(000)	7800.0	1693.0
Crystal size/mm <sup>3</sup>	0.1 × 0.1 × 0.1	0.05 × 0.03 × 0.01
Radiation	Cu Kα (λ = 1.54184)	Synchrotron (λ = 0.6889)
2θ range for data collection/°	5.308 to 152.36	3.366 to 72.534
Index ranges	-15 ≤ h ≤ 17, -18 ≤ k ≤ 12, -122 ≤ l ≤ 123	-20 ≤ h ≤ 21, -26 ≤ k ≤ 26, -33 ≤ l ≤ 33
Reflections collected	41454	77550
Independent reflections	4330 [R <sub>int</sub> = 0.0385, R <sub>sigma</sub> = 0.0221]	32879 [R <sub>int</sub> = 0.0387, R <sub>sigma</sub> = 0.0411]
Data/restraints/parameters	4330/110/318	32879/724/1168
Goodness-of-fit on F <sup>2</sup>	1.611	1.082
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.1052, wR <sub>2</sub> = 0.3256	R <sub>1</sub> = 0.0422, wR <sub>2</sub> = 0.1232
Final R indexes [all data]	R <sub>1</sub> = 0.1108, wR <sub>2</sub> = 0.3372	R <sub>1</sub> = 0.0492, wR <sub>2</sub> = 0.1277
Largest diff. peak/hole / e Å <sup>-3</sup>	2.20/-2.21	0.78/-0.96



**Figure S30.** A: Single-crystal X-ray structures of mononuclear iron species **A**:  $[\mathbf{C3}](\text{ClO}_4)_2$ , where one  $\text{ClO}_4^-$  counteranion sits on the three-fold rotation axis of the complex, confined between the three ligands, **B**:  $[\mathbf{C3}](\text{NTf}_2)_2$ , where both counterions sit on the periphery of the complex.



**Figure S31.** Single-crystal X-ray structures of heterotetrahedron  $[\mathbf{C1}](\text{ClO}_4)_8$ . Counterions and hydrogens were omitted for clarity.



**Figure S32.** Single-crystal X-ray structures of homotetrahedron  $[\mathbf{C2}](\text{OTf})_8$ . The central OTf counterion, additional counterions and hydrogens were omitted for clarity.

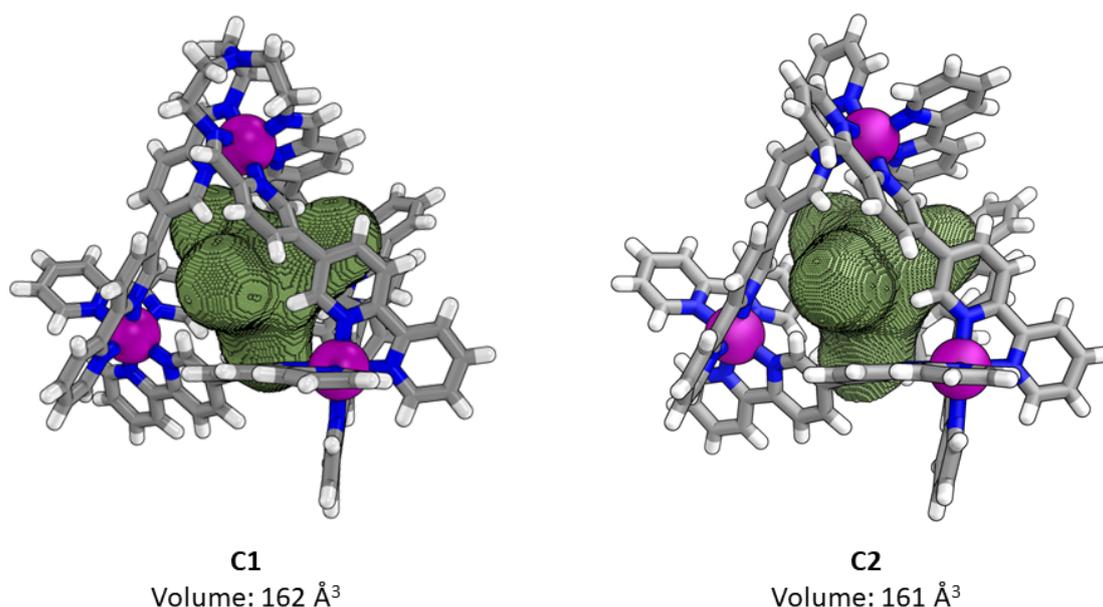
### S3 VOIDOO Calculations

Following removal of counterions and solvent from the single crystal X-ray structures of complexes **C1** and **C2** cavity calculations were run using VOIDOO.<sup>9</sup> The volume of the internal binding pocket within each structure was calculated using a probe of radius 1.6 Å, this was the minimum probe radius that allowed detection of discrete void spaces. Calculations run with smaller probe radii (1.4 and 1.5 Å) allowed the probe to roll out of the cavity and map space external to the cage.

The following parameters were used in the calculation:

Primary grid spacing	0.1
Number of detection cycles	10
Growth factor van der Waals radii	1.1
Min size of real cavities	1
Number of refinement cycles	30
Grid shrink factor	0.9
Convergence criterion (Å <sup>3</sup> )	0.1

Cavities were mapped as ccp4 files and visualised using Pymol v1.4.



**Figure S33.** VOIDOO structures of heteroleptic tetrahedron **C1** and homoleptic tetrahedron **C2** with calculated cavity volumes of 162 Å<sup>3</sup> and 161 Å<sup>3</sup>, respectively.

## S4 References

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