

## Supporting Information

### Electron-poor trifluoromethyl-substituted sub-components alter the properties of $M_4L_4$ tetrahedral cages

N.Struch,<sup>[a]</sup> F. Topic,<sup>[b]</sup> K. Rissanen,<sup>[b]</sup> A. Lützen<sup>[a]</sup>

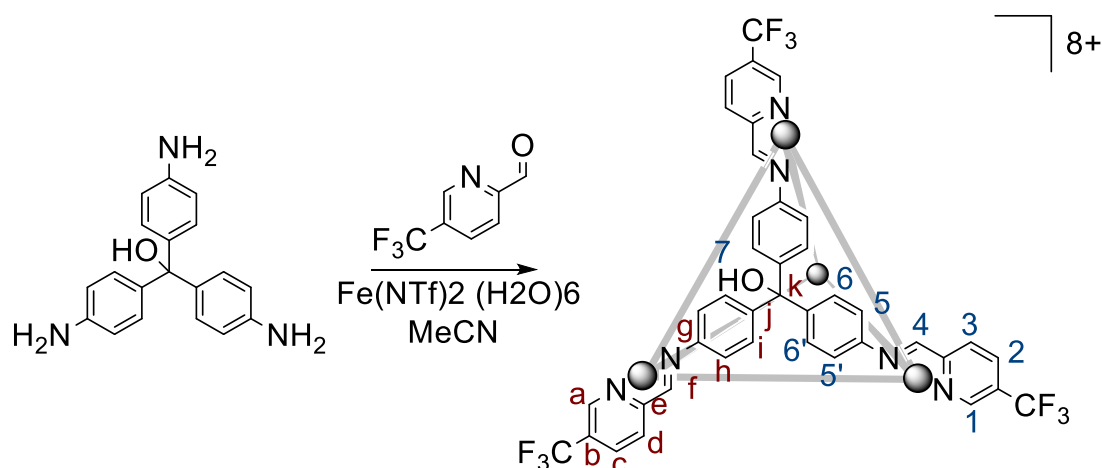
[a] N. Struch, A. Lützen  
Kekulé-Institut für Organische Chemie und Biochemie  
Rheinische Friedrich-Wilhelms-Universität Bonn  
Gerhard-Domagk-Straße 1, D-53121 Bonn  
E-Mail: arne.luetzen@uni-bonn.de

[b] F. Topić, K. Rissanen  
University of Jyväskylä  
Department of Chemistry, Nanoscience Center  
P.O. Box 35, 40014 Jyväskylä, Finland

## Table of contents

Synthesis and characterisation of <b>1</b> .....	2
NMR-Spectra of <b>1</b> .....	3
Mass spectra of <b>1</b> .....	7
UV-Vis spectrum of <b>1</b> .....	8
Synthesis and Characterisation of <b>2</b> .....	9
NMR spectra of <b>2</b> .....	10
Mass spectra of <b>2</b> .....	14
UV-Vis spectrum of <b>2</b> and comparison of UV-Vis spectra of cages <b>1</b> and <b>2</b> , the parent cage, and pararosanine.....	16
Synthetic transformation of <b>1</b> .....	18
Transformation from <b>1</b> to the parent structure.....	18
NMR spectra .....	18
Synthesis and characterisation of $NO_3^-@1$ .....	21
NMR spectra of $NO_3^-@1$ .....	22
Mass spectra of $NO_3^-@1$ .....	25
UV-Vis spectrum of $NO_3^-@1$ .....	28
Crystallographic analysis of <b>1</b> _PF6_TfO .....	28

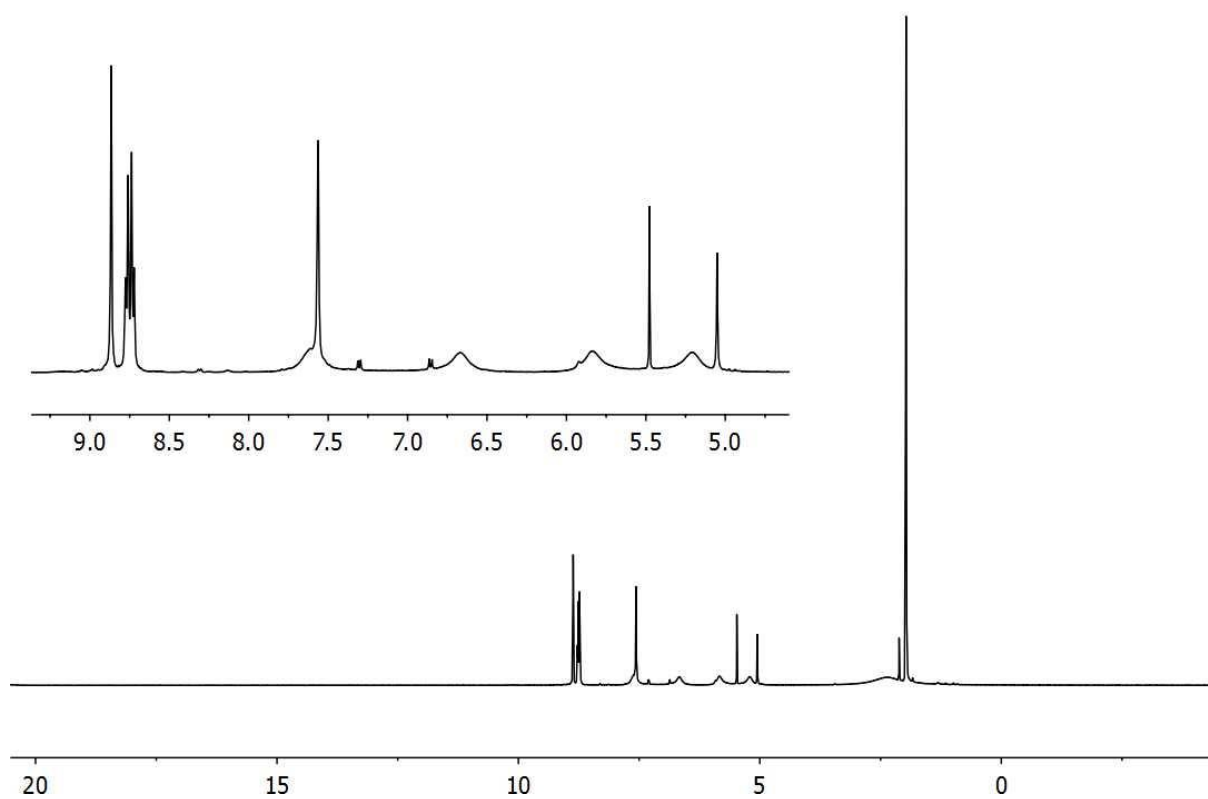
## Synthesis and characterisation of 1



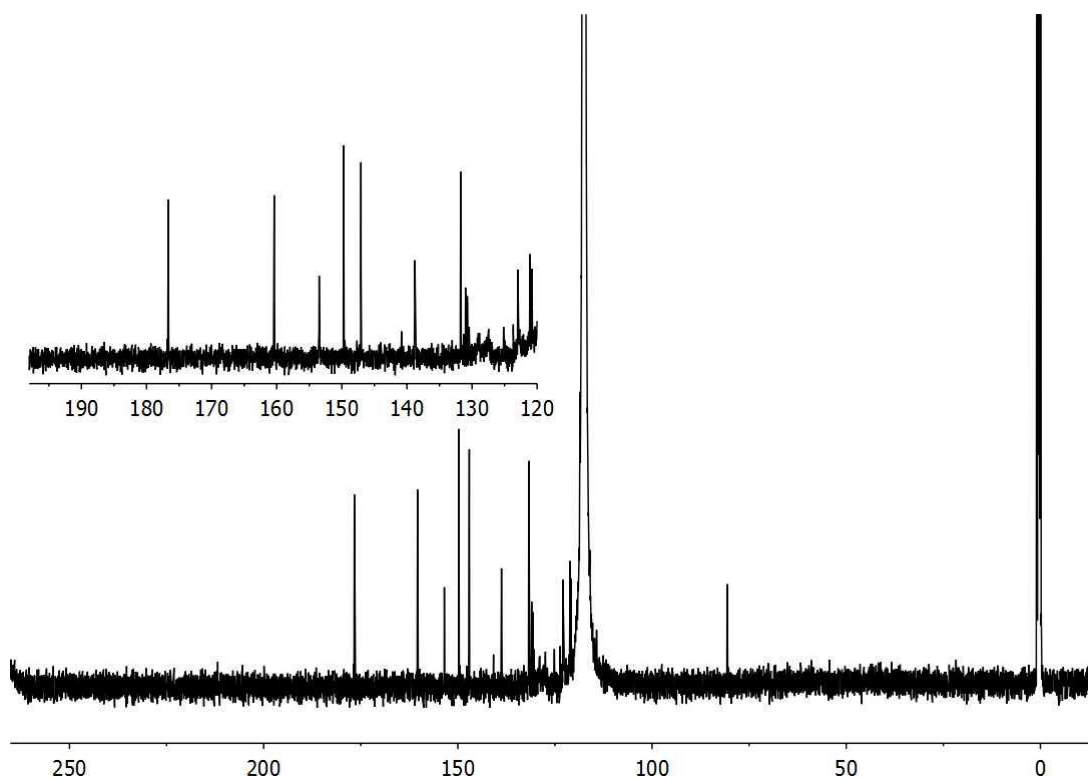
A solution of 15 mg pararosanine base (0.05 mmol, 4 eq), 25 mg 5-(trifluoromethyl)-pyridin-2-carbaldehyde (0.15 mmol, 12 eq) and 37 mg iron(II) triflimide hexahydrate (0.5 mmol, 4 eq) in 2 mL acetonitrile (HPLC grade) were degassed by one freeze-pump-thaw cycle and flushed with argon and heated to 65 °C for 18 hours. After cooling the solution to room temperature the solution was poured in 20 mL diethyl ether, the precipitate was filtered off, washed with dichloromethane and generous amounts of diethyl ether and dried in a stream of air to yield 59 mg (0.01 mmol, 85 %) purple-pink powder.  $^1\text{H-NMR}$  (acetonitrile- $d_3$ , 298 K, 500.1 MHz,  $\delta$  in ppm) = 8.84 (s, 3H, H4), 8.74 (d,  $^3J_{\text{H}_3\text{H}_2}=8.7$  Hz, 3H, H3), 8.70 (d,  $^3J_{\text{H}_2\text{H}_3}=8.7$  Hz, 3H, H2), 7.59 (brs, 3H, H5/6\*), 7.54 (s, 3H, H1), 6.65 (brs, 3H, H5/6\*), 5.81 (brs, 3H, H5/6\*), 5.81 (brs, 3H, H5/6\*), 5.02 (s, 1H, H7);  $^{13}\text{C-NMR}$  (acetonitrile- $d_3$ , 298 K, 156.4 MHz  $\delta$  in ppm) = 176.7 (f), 160.4 (b), 153.5 (a), 149.8 (e), 147.6 (j), 140.9 (g), 138.8 (d), 131.7 (c), 130.8 (q,  $\text{CF}_3$ ), 123.0 (h/i\*), 121.1 (h/i\*), 120.8 (h/i\*), 118.6 (h/i\*), 80.5 (k);  $^{19}\text{F-NMR}$  (acetonitrile- $d_3$ , 298 K, 282.4 MHz,  $\delta$  in ppm) = -63.4 ( $-\text{CF}_3$ ), -79.9 (NTf); high resolution ESI-MS (acetonitrile, positive mode,  $m/z$ ) = 515.6343 (calcd. for  $(\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Fe}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)]^{7+}$  515,6341), 648.2262 (calcd. for  $[\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Fe}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)_2]^{6+}$  648,2260), 834.0540 (calcd. for  $[\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Fe}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)_3]^{5+}$  834.0546); UV-Vis (acetonitrile, 298 K,  $\lambda$  in nm) = 234, 282, 326, 538, 580.

\*Due to the broad nature of the signals no significant cross-peaks can be observed in the 2D spectra.

## NMR-Spectra of **1**



**Figure S01:**  $^1\text{H-NMR}$  of **1**, acetonitrile- $d_3$ , 298 K, 499.1 MHz.



**Figure S02:**  $^{13}\text{C-NMR}$  of **1**, acetonitrile- $d_3$ , 298 K, 125.5 MHz.

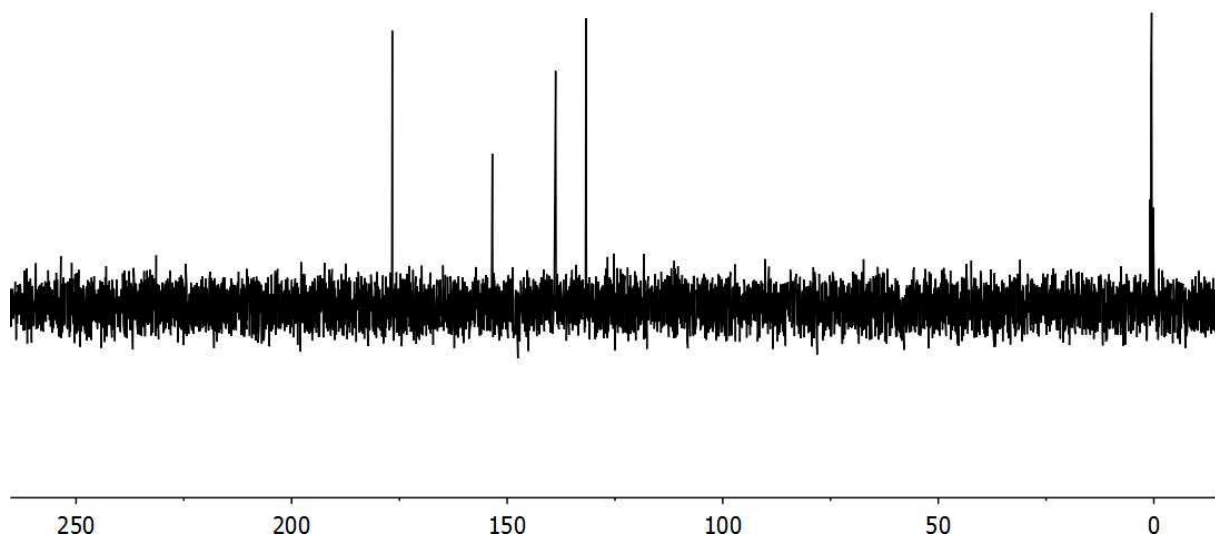


Figure S03:  $^{135}\text{DEPT-NMR}$  of **1**, acetonitrile- $d_3$ , 298 K, 125.5 MHz.

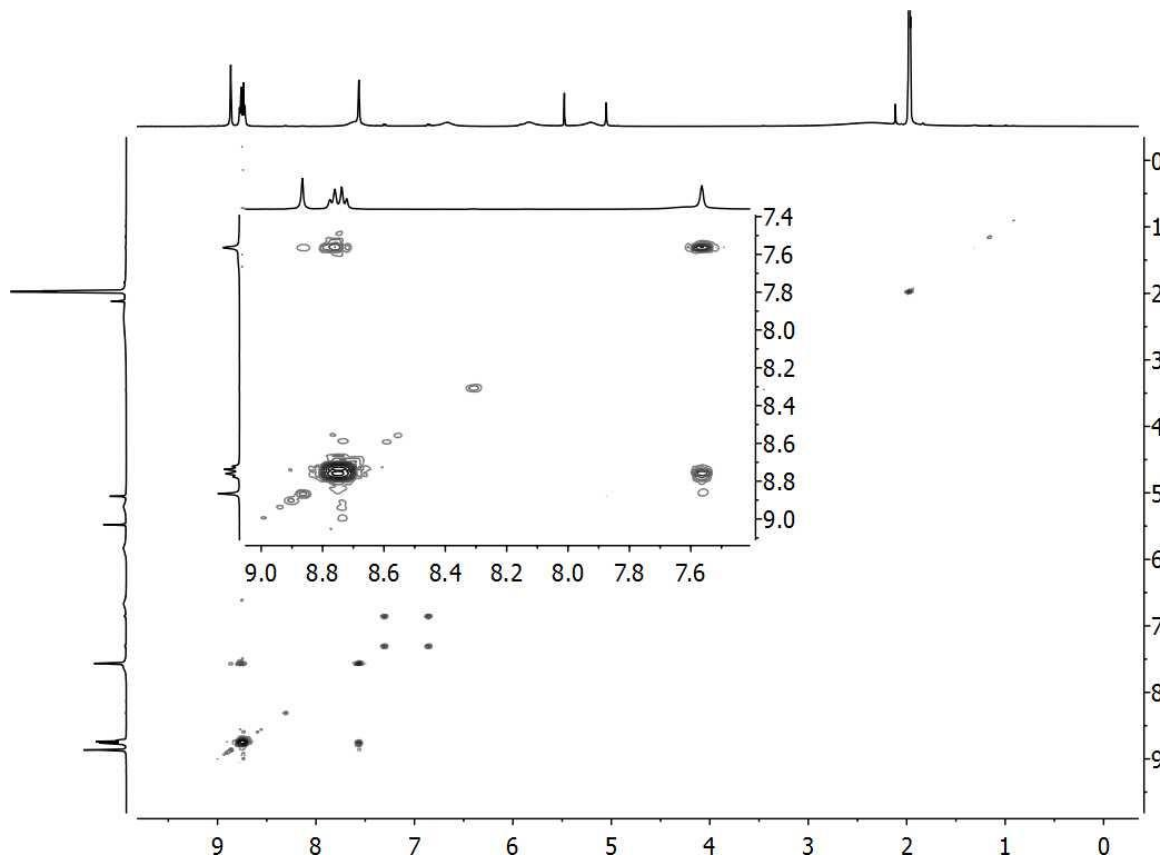
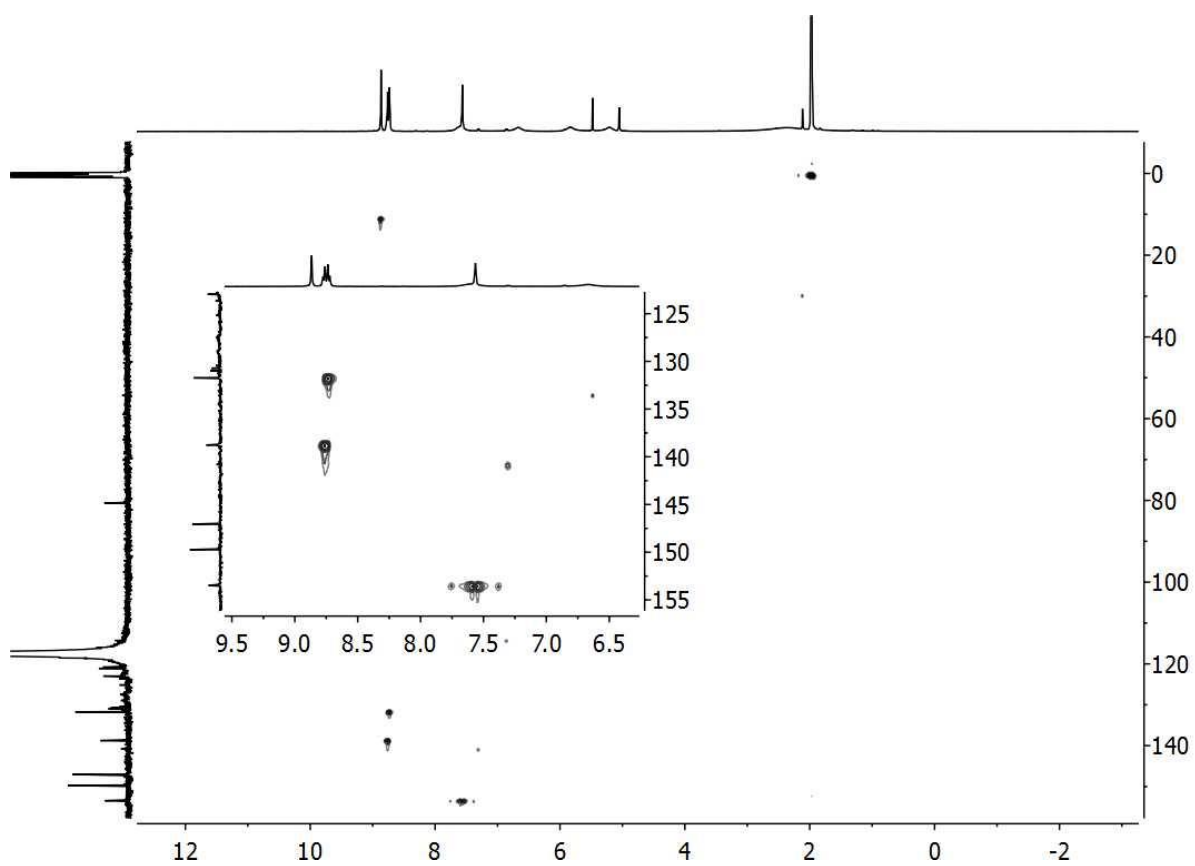
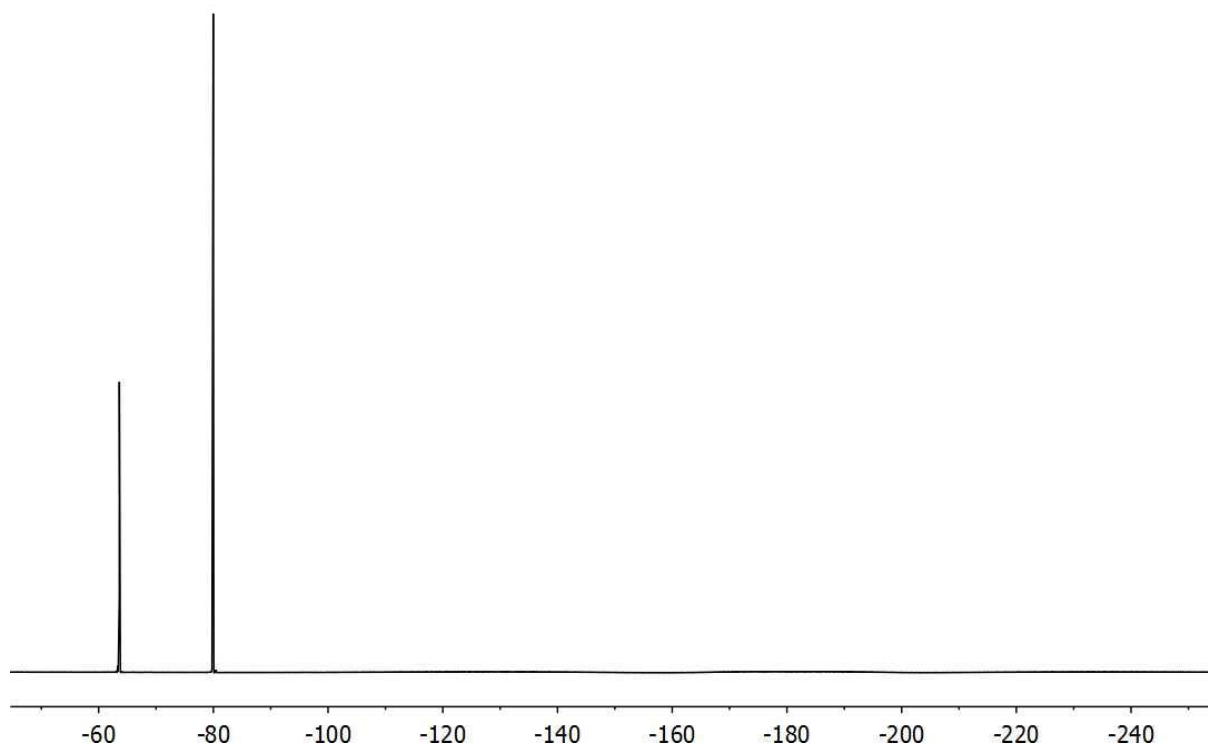


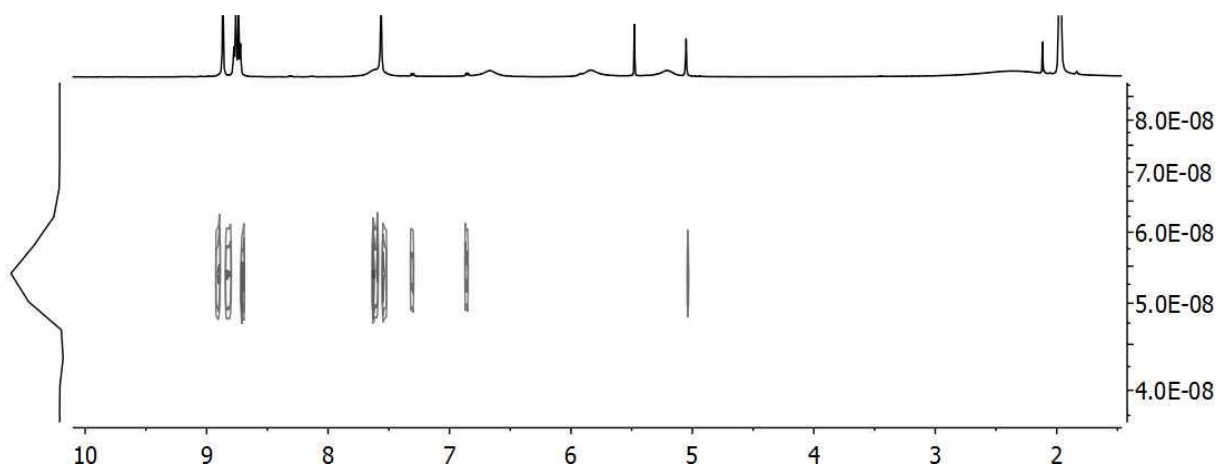
Figure S04:  $^1\text{H},^1\text{H-COSY-NMR}$  of **1**, acetonitrile- $d_3$ , 298 K, 499.1 MHz.



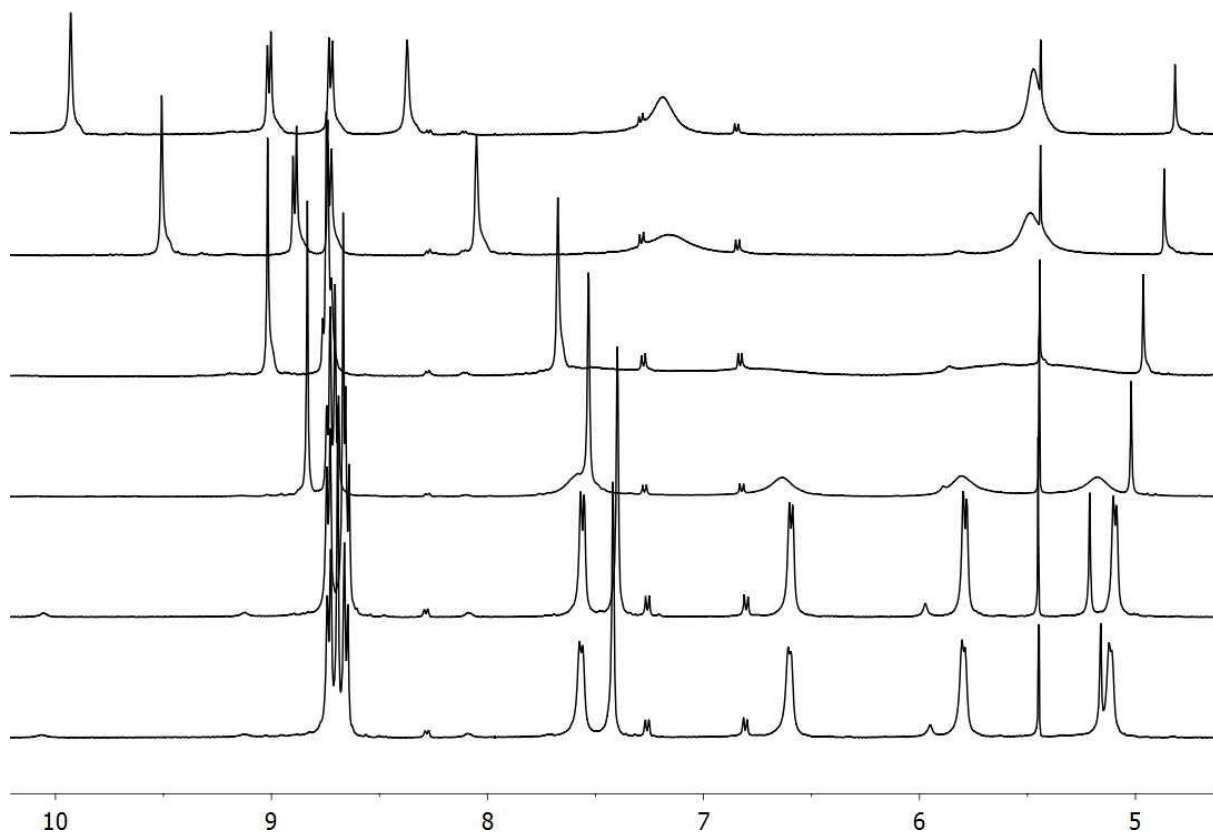
**Figure S05:**  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC-NMR of **1**, acetonitrile- $d_3$ , 298 K, 499.1 MHz, 125.5 MHz.



**Figure S06:**  $^{19}\text{F}$ -NMR of **1**, acetonitrile- $d_3$ , 298 K, 469.6 MHz.



**Figure S07:**  $^1\text{H}$ -DOSY-NMR of **1**, acetonitrile- $d_3$ , 298 K, 499.1 MHz



**Figure S08:** Temperature dependent  $^1\text{H}$ -NMR of **1**, acetonitrile- $d_3$ , 298 K, 499.1 MHz. 343 K, 333 K, 313K, 298 K, 283 K, 273 K (top to bottom).

## Mass spectra of 1

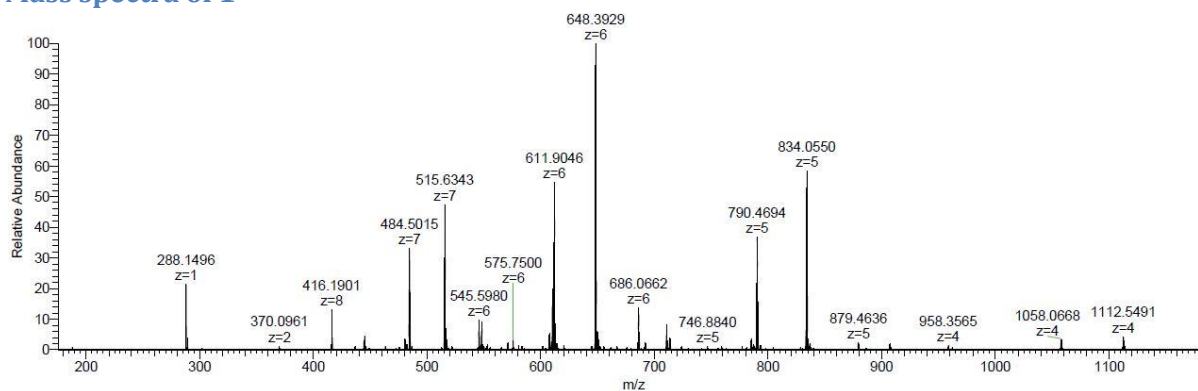


Figure S08: High resolution ESI(+) mass spectrum (acetonitrile) of 1.

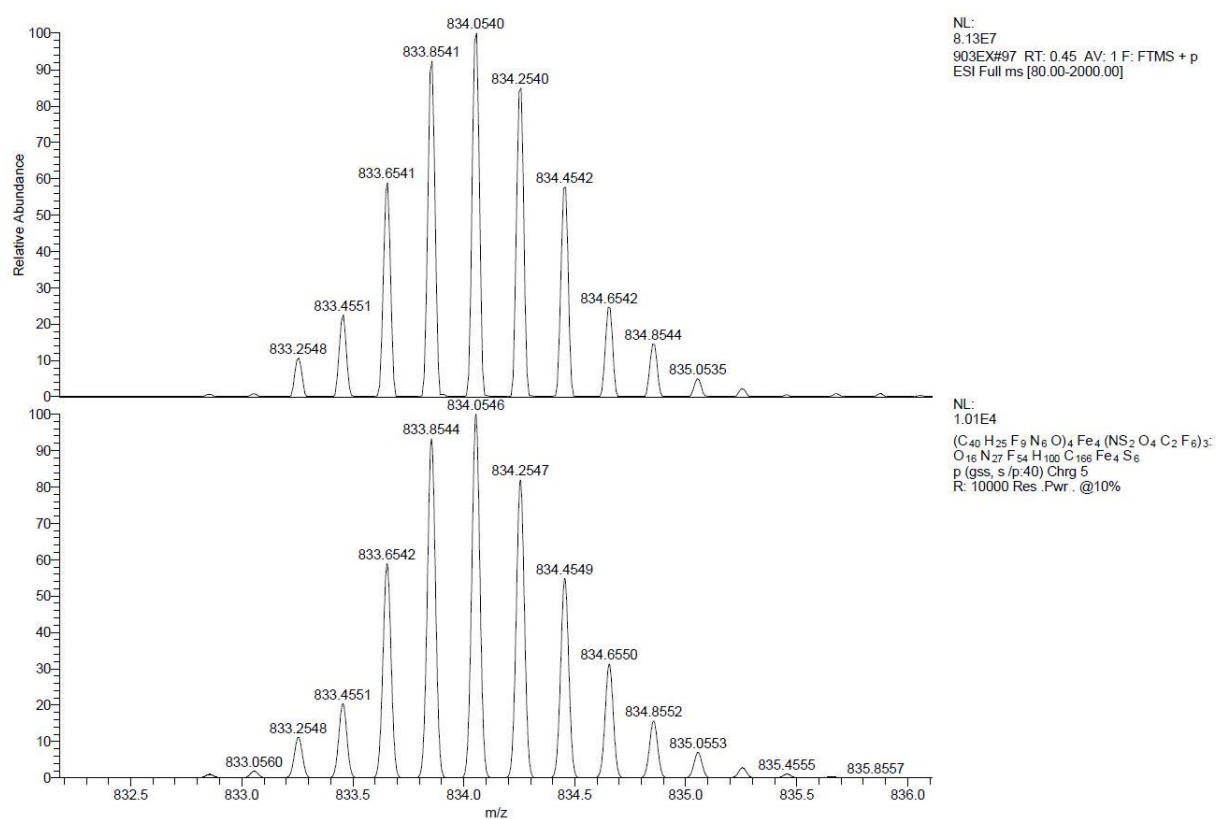
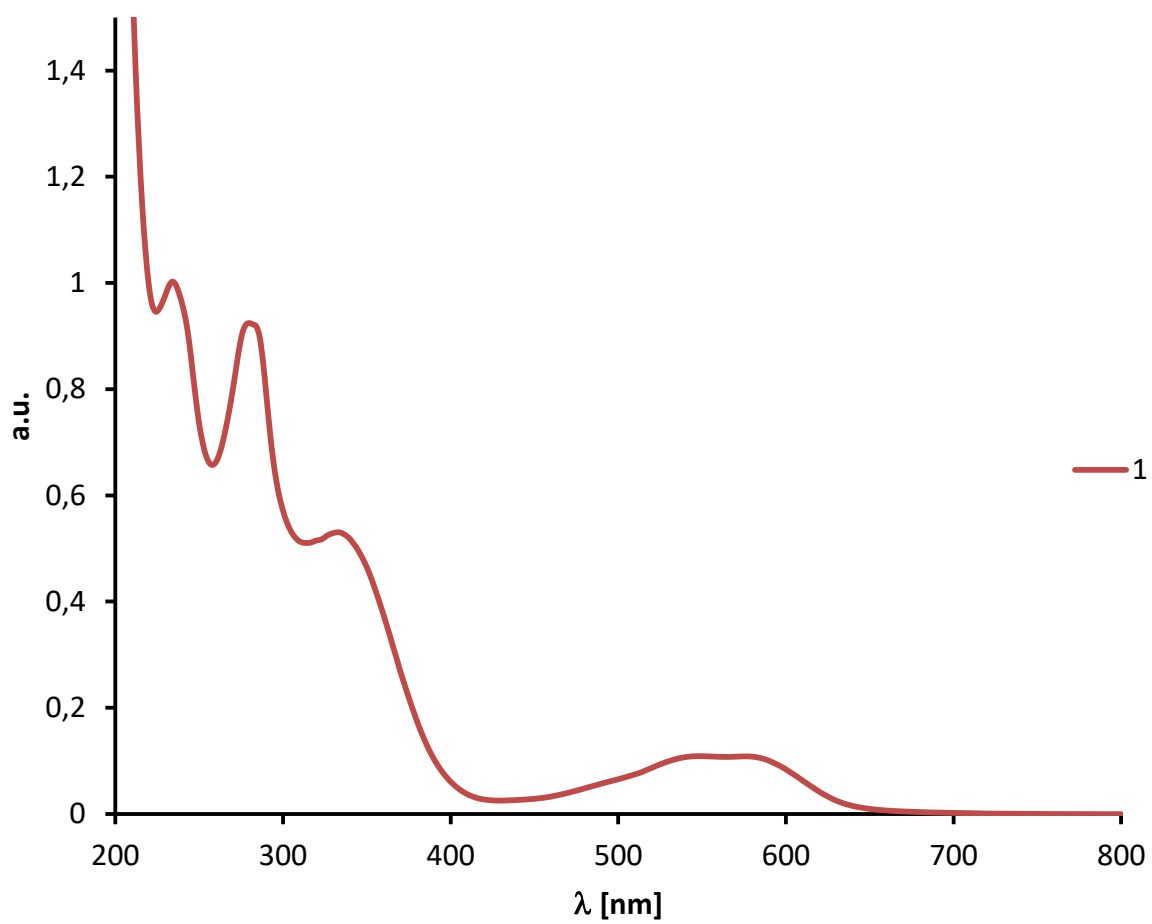


Figure S09: Isotope pattern (top) and calculated isotope pattern of  $[(C_{40}H_{25}F_9N_6O)_4Fe_4(NS_2O_4C_2F_6)_3]^{5+}$ .

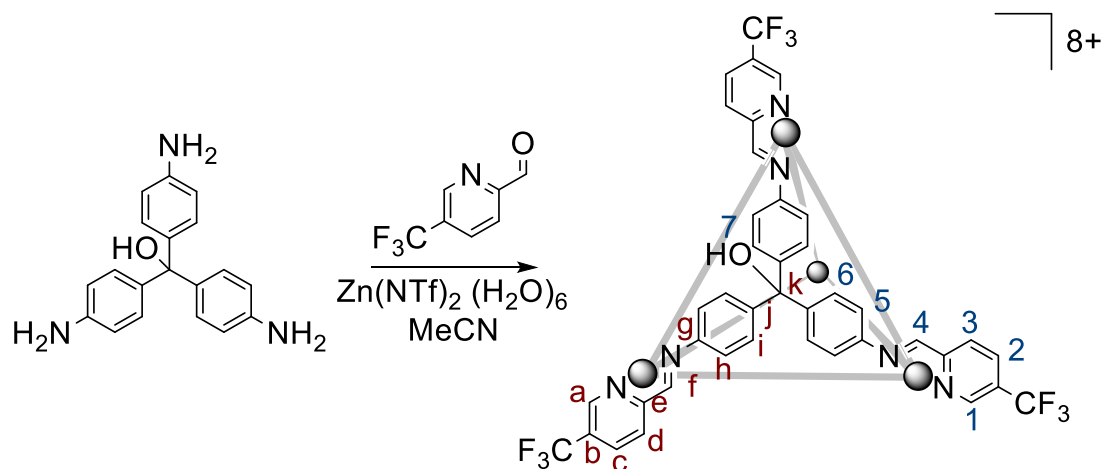
### UV-Vis spectrum of **1**



**Figure S10:** UV-Vis spectrum of **1**, acetonitrile (HPLC grade), 20  $\mu$ M, 298 K.

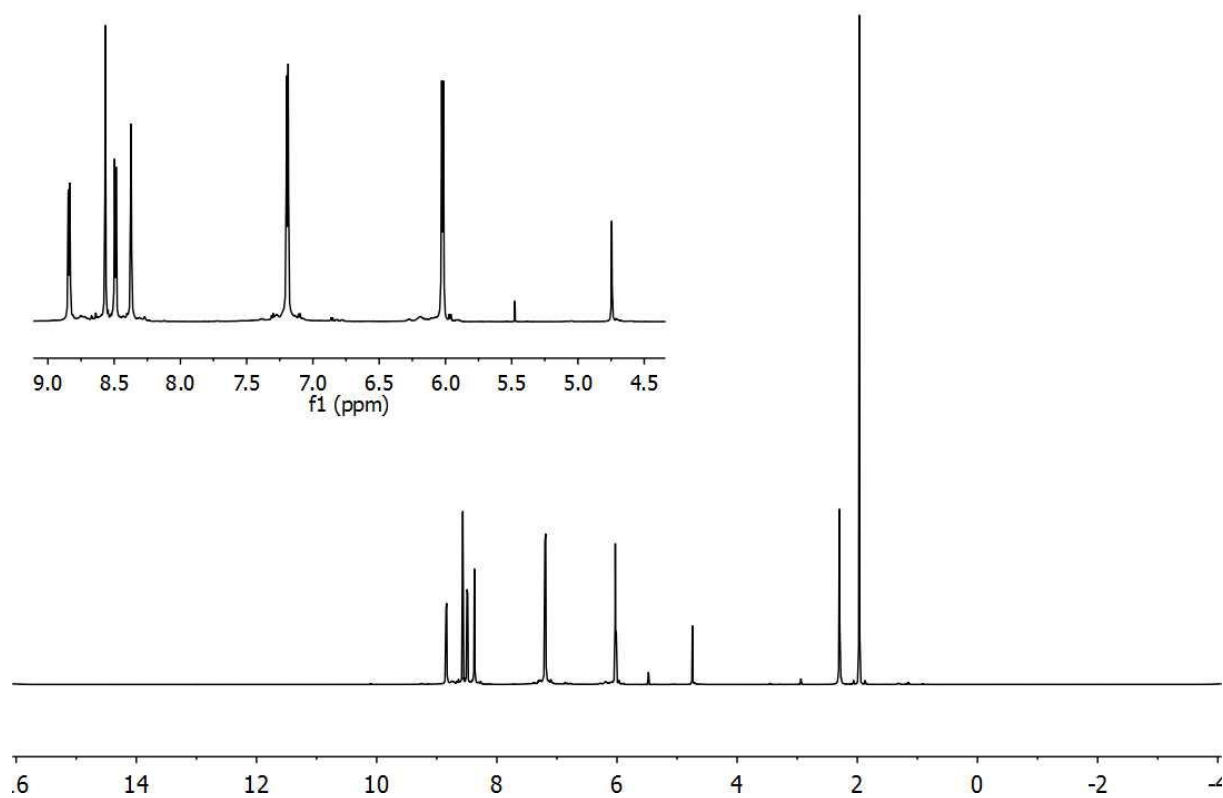


## Synthesis and Characterisation of 2

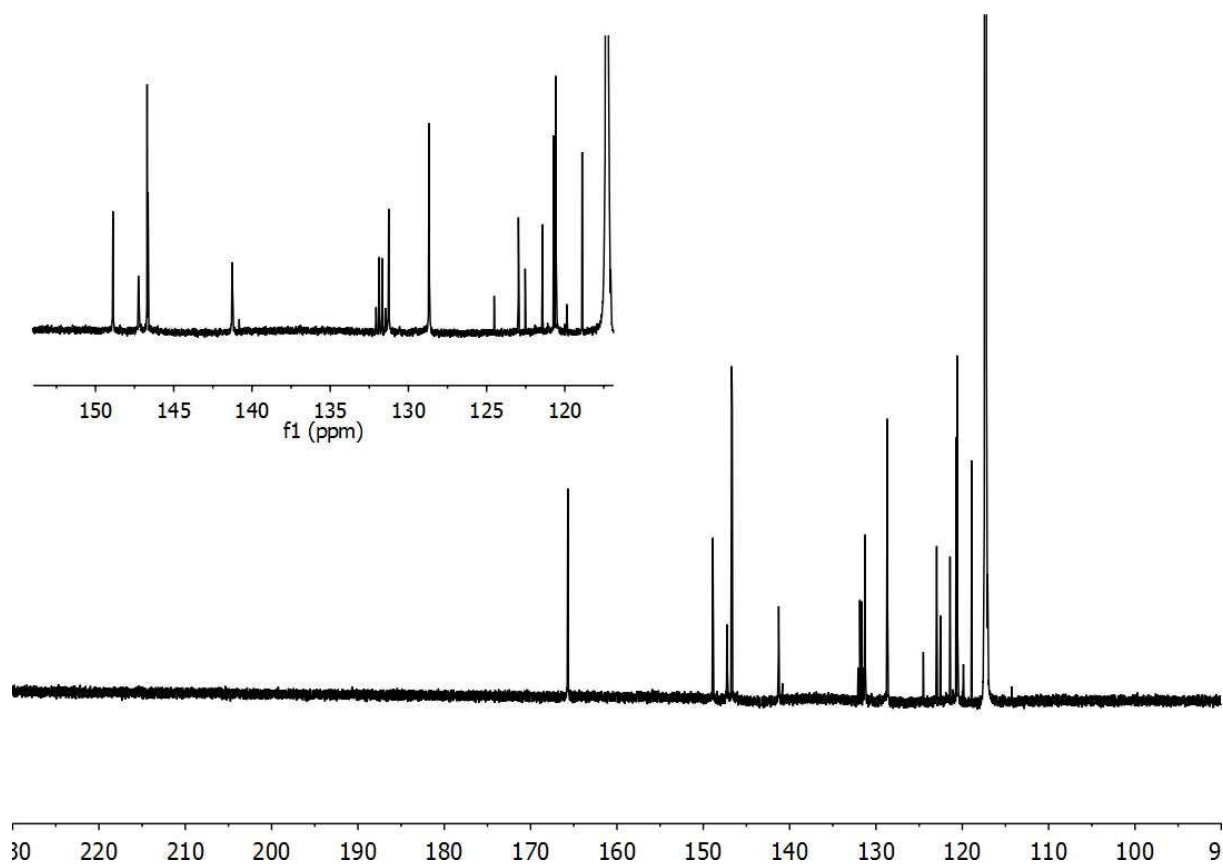


A solution of 15 mg pararosanine base (0.05 mmol, 4 eq), 25 mg 5-(trifluoromethyl)pyridin-2-carbaldehyde (0.15 mmol, 12 eq) and 37 mg zinc(II) triflimide hexahydrate (0.5 mmol, 4 eq) in 2 mL acetonitrile (HPLC grade) was degassed by one freeze-pump-thaw cycle and flushed with argon and heated to 65 °C for 18 hours. After cooling the solution to room temperature the solution was poured in 20 mL diethyl ether, the precipitate was filtered off, washed with dichloromethane and generous amounts of diethyl ether and dried in a stream of air to yield 61 mg (0.01 mmol, 86%) bright pink powder.  $^1\text{H-NMR}$  (acetonitrile- $d_3$ , 298 K, 700.1 MHz,  $\delta$  in ppm) = 8.81 (dd,  $^3J_{\text{H}_3\text{H}_2}=8.2$  Hz,  $^5J_{\text{H}_3\text{H}_1}=1.6$  Hz, 3H, H3), 8.54 (s, 3H, H4), 8.46 (d,  $^3J_{\text{H}_2\text{H}_3}=8.2$  Hz, 3H, H2), 8.34 (brs, 3H, H1), 7.16 (d,  $^3J_{\text{H}_5\text{H}_6}=8.4$  Hz, 6H, H5), 5.99 (d,  $^3J_{\text{H}_6\text{H}_5}=8.4$  Hz, 6H, H6), 4.71 (s, 3H, H7);  $^{13}\text{C-NMR}$  (acetonitrile- $d_3$ , 298 K, 156.4 MHz  $\delta$  in ppm) = 165.7 (f), 148.9 (b), 147.3 (a), 146.7 (g), 146.6 (j), 141.3 (d), 131.7 (q,  $-\text{CF}_3$ ), 131.3 (c), 128.7 (i), 123.0 (h), 120.6 (e), 80.7 (k);  $^{19}\text{F-NMR}$  (acetonitrile- $d_3$ , 298 K, 282.4 MHz  $\delta$  in ppm) = -63.35 ( $-\text{CF}_3$ ), -80.13 (NTf); high resolution ESI-MS (acetonitrile, positive mode,  $m/z$ ) = 420.936 (calcd. for  $\text{C}_{160}\text{H}_{100}\text{F}_{36}\text{N}_{24}\text{O}_4\text{Zn}_4^{8+}$  420.936), 521.059 (calcd. for  $[(\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Zn}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)]^{7+}$  521.058), 654.554 (calcd. for  $[(\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Zn}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)_2]^{6+}$  645.576), 841.649 (calcd. for  $[(\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Zn}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)_3]^{5+}$  841.649), 1122.041 (calcd. for  $[(\text{C}_{40}\text{H}_{25}\text{F}_9\text{N}_6\text{O})_4\text{Zn}_4(\text{NS}_2\text{O}_4\text{C}_2\text{F}_6)_4]^{4+}$  1122.040); UV-Vis (acetonitrile, 298 K,  $\lambda$  in nm) = 230, 286, 342, 504, 530.

## NMR spectra of 2



**Figure S11:**  $^1\text{H-NMR}$  of **2**, acetonitrile- $d_3$ , 298 K, 700.41 MHz.



**Figure S12:**  $^{13}\text{C-NMR}$  of **2**, acetonitrile- $d_3$ , 298 K, 176.1 MHz.

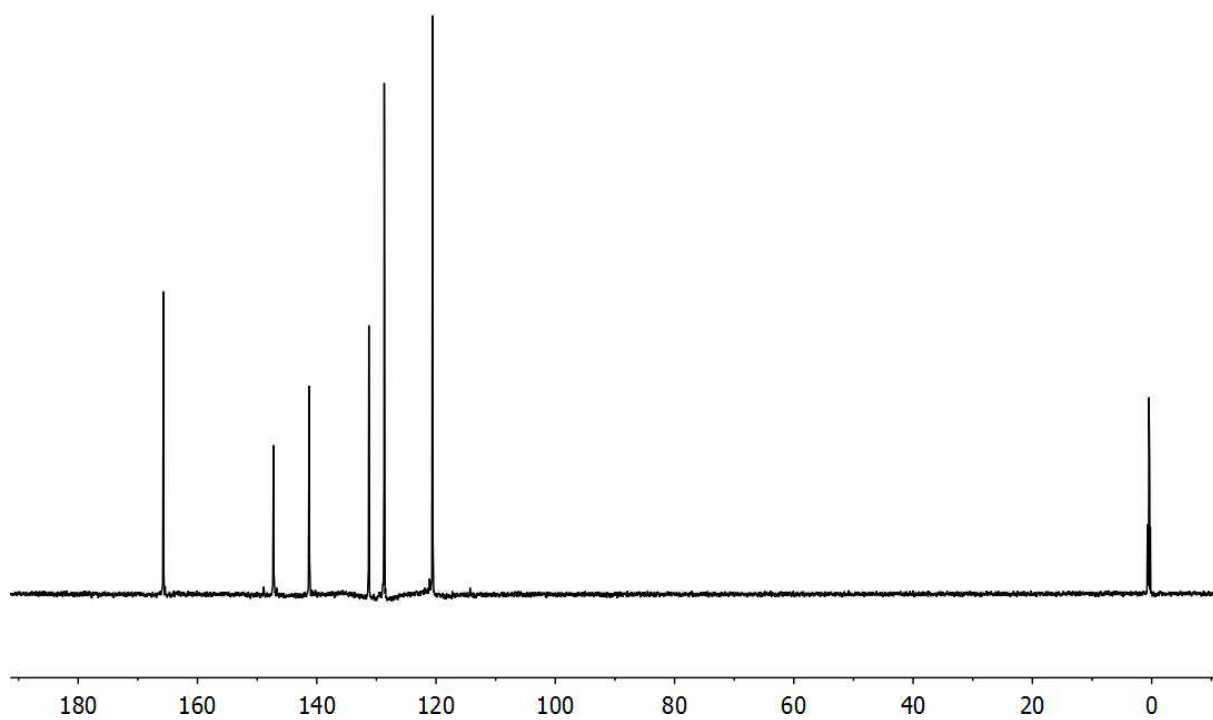


Figure S13:  $^{135}\text{C}$  DEPT-NMR of **2**, acetonitrile- $d_3$ , 298 K, 176.1 MHz.

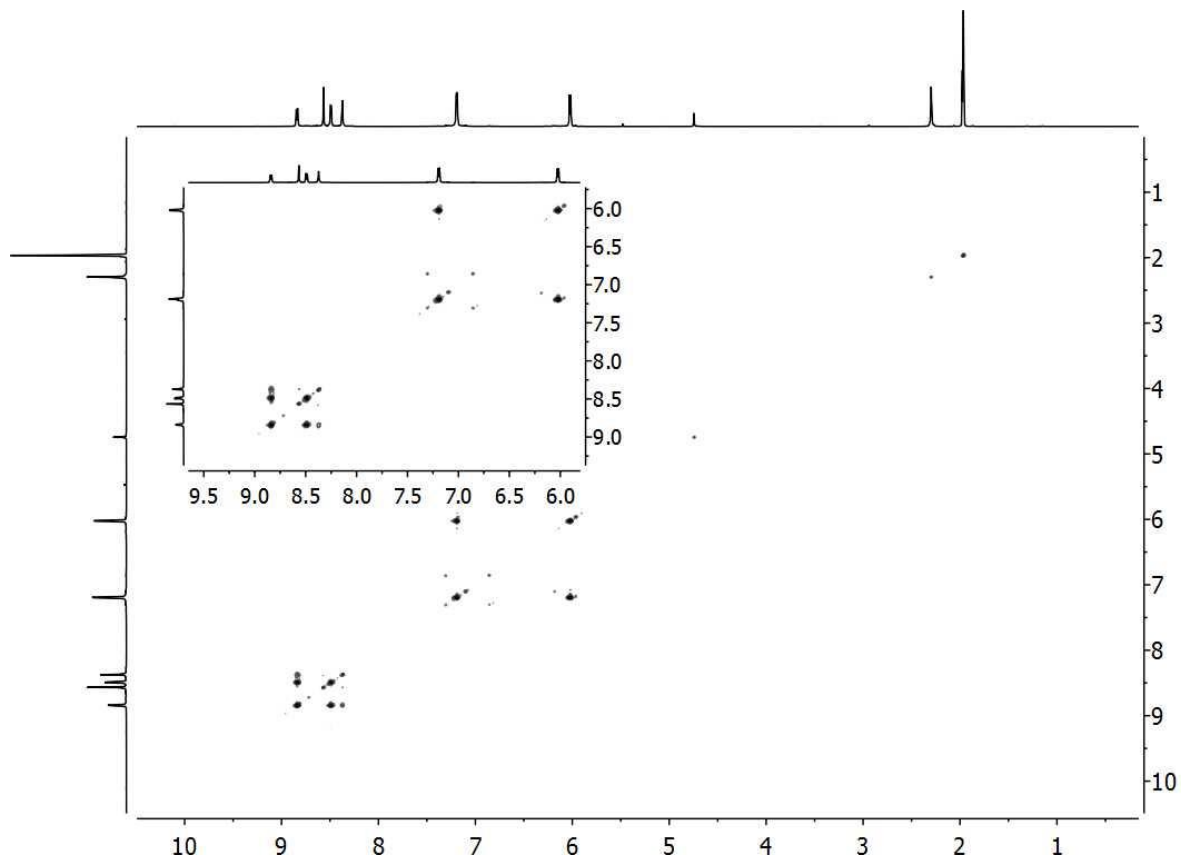
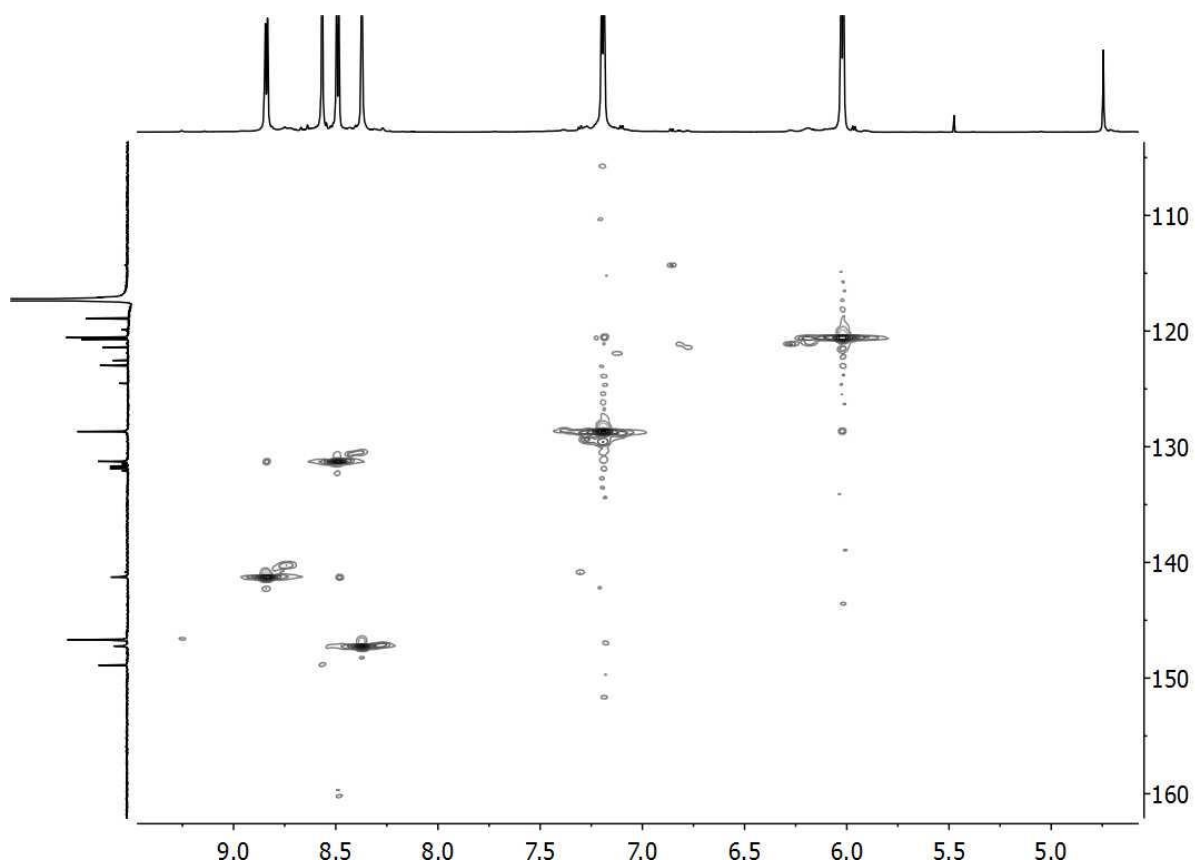
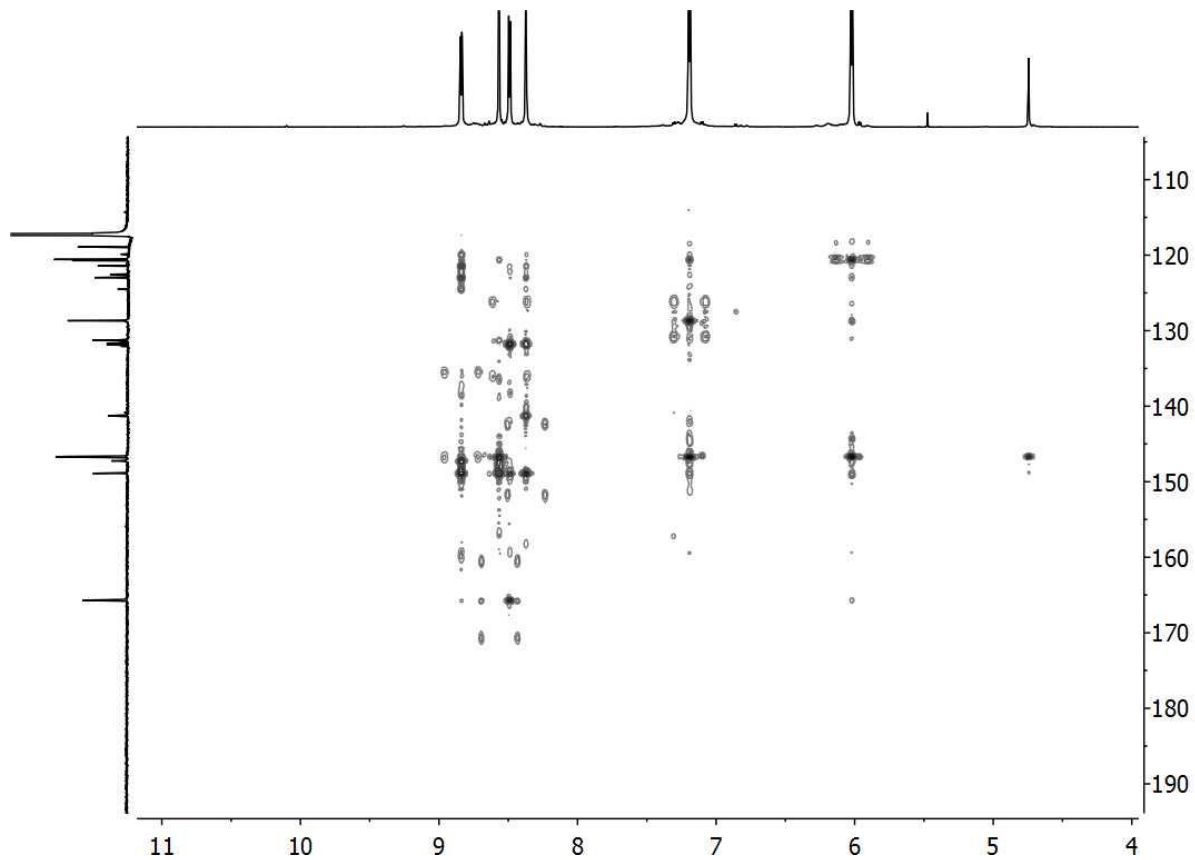


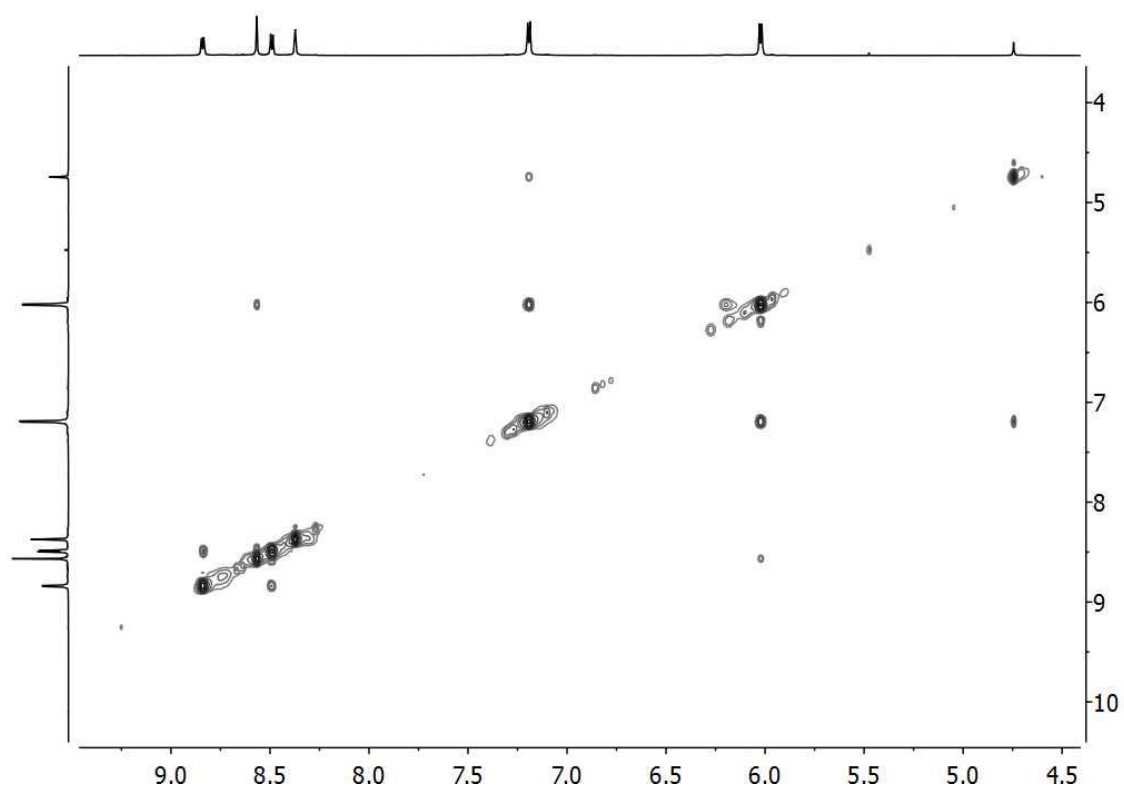
Figure S14:  $^1\text{H},^1\text{H}$ -COSY of **2**, acetonitrile- $d_3$ , 298 K, 700.1 MHz.



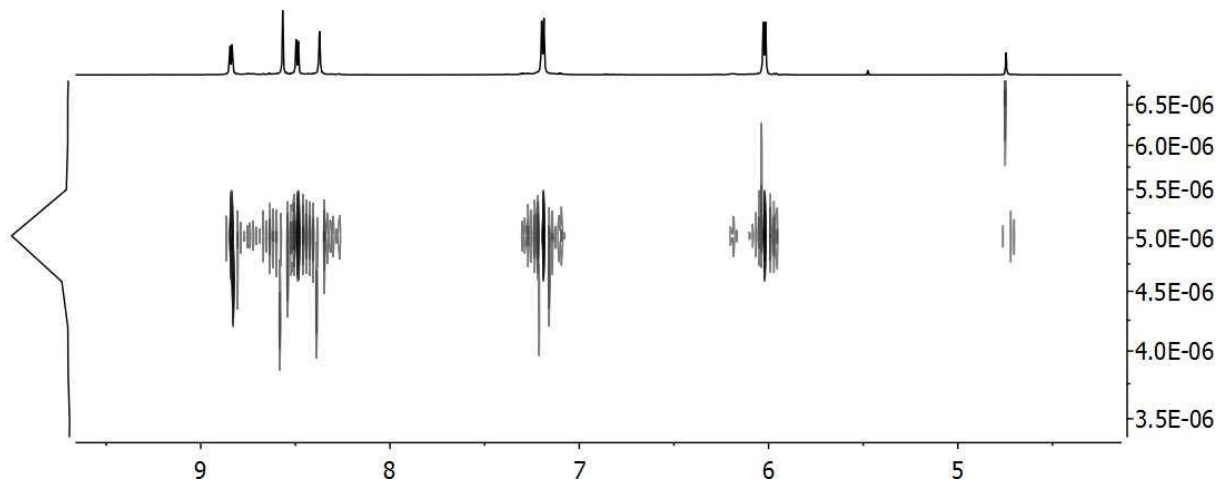
**Figure S15:** Excerpt from the  $^1\text{H}$ ,  $^{13}\text{C}$ -HSQC-NMR of **2**, acetonitrile- $d_3$ , 298 K, 700.1 MHz, 176.1 MHz.



**Figure S16:** Excerpt from the  $^1\text{H}$ ,  $^{13}\text{C}$ -HMBC-NMR of **2**, acetonitrile- $d_3$ , 298 K, 700.1 MHz, 176.1 MHz.



**Figure S17:** Excerpt from the  $^1\text{H},^1\text{H}$ -NOESY-NMR of **2**, acetonitrile- $d_3$ , 298 K, 700.1 MHz.



**Figure S18:**  $^1\text{H}$ -DOSY-NMR of **2**, acetonitrile- $d_3$ , 298 K, 700.1 MHz.

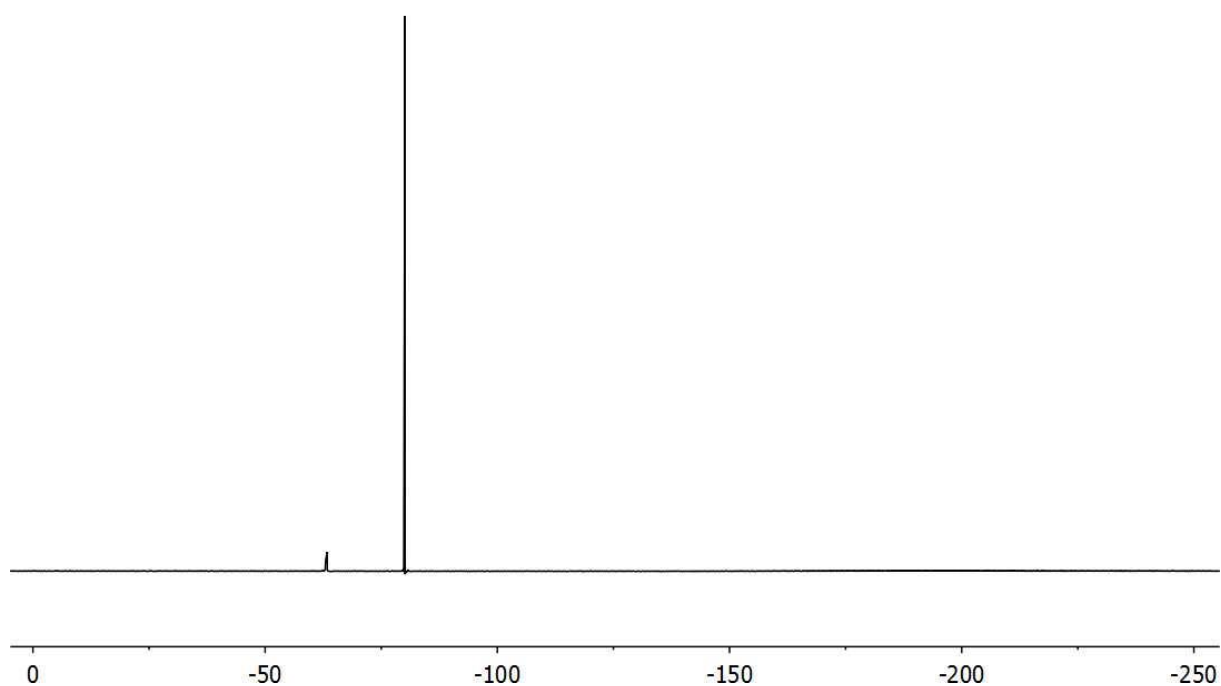


Figure S19:  $^{19}\text{F}$ -NMR of **2**, acetonitrile- $d_3$ , 298 K, 282.4 MHz.

### Mass spectra of **2**

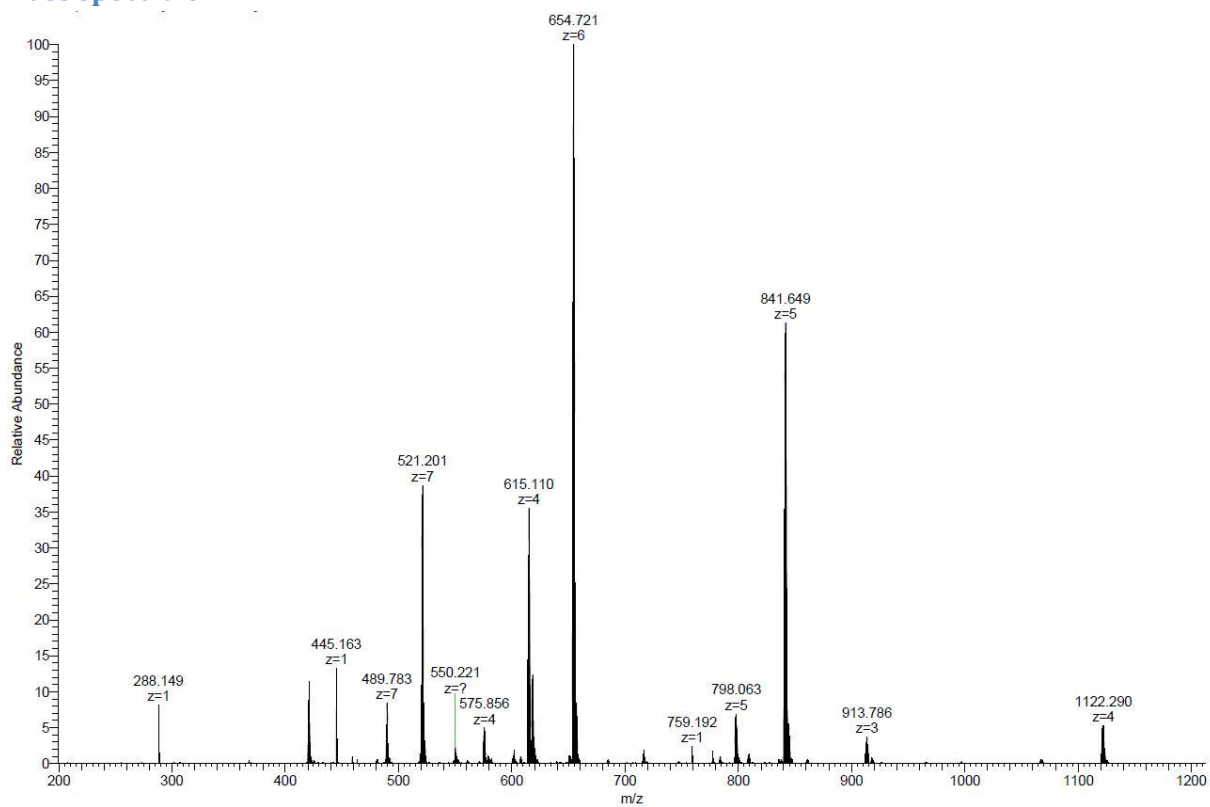
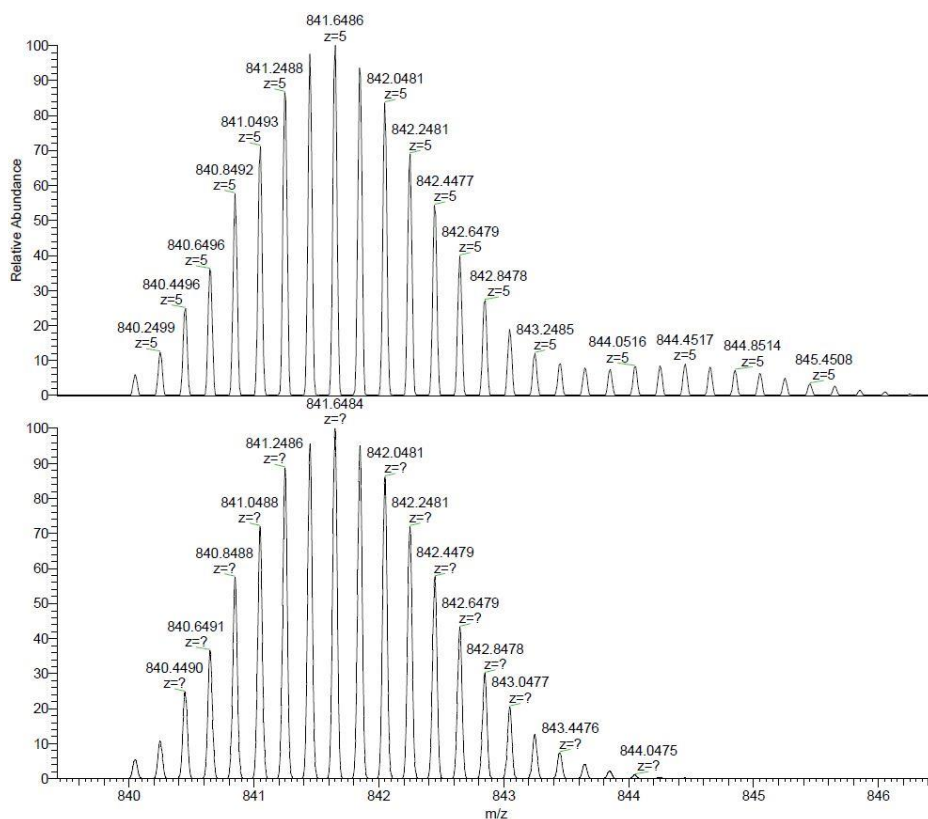


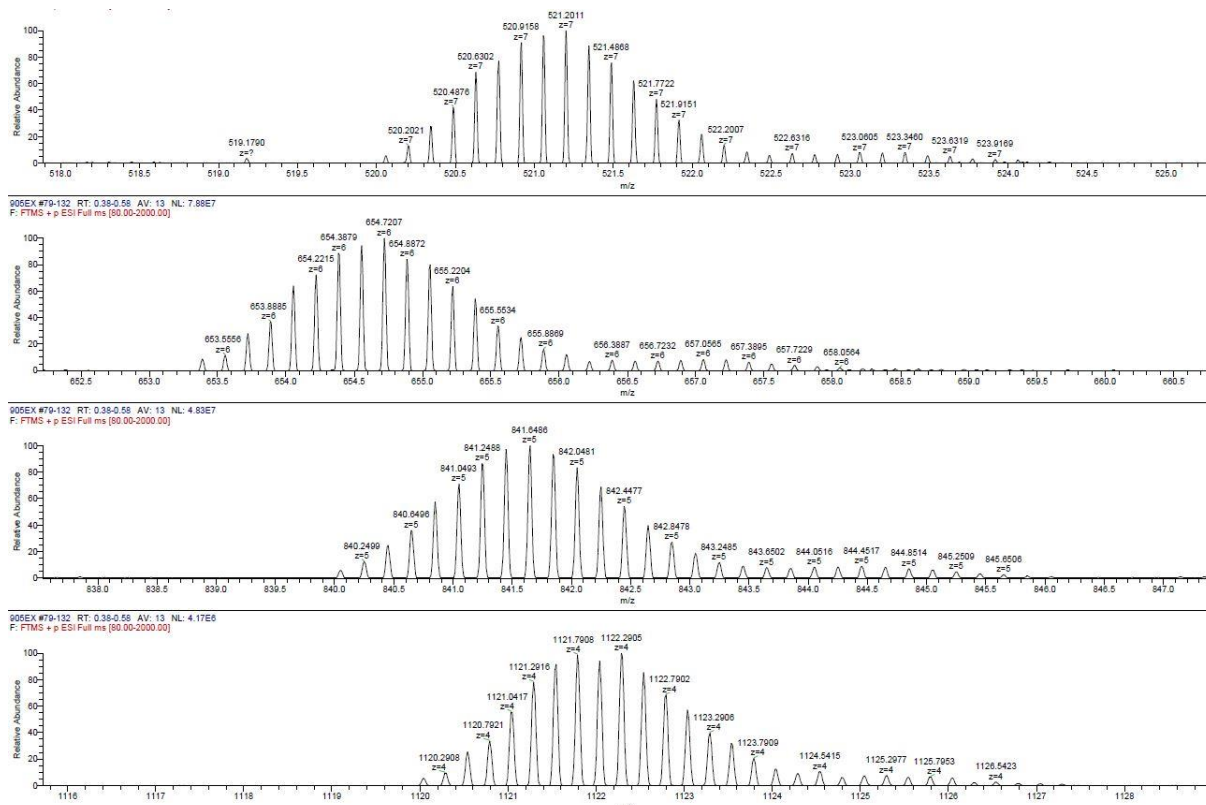
Figure S20: High resolution ESI(+) mass spectrum of **2** (acetonitrile).



NL:  
4.83E7  
905EX#79-132 RT: 0.38-0.58 AV: 13 F:  
FTMS + p ESI Full ms [80.00-2000.00]

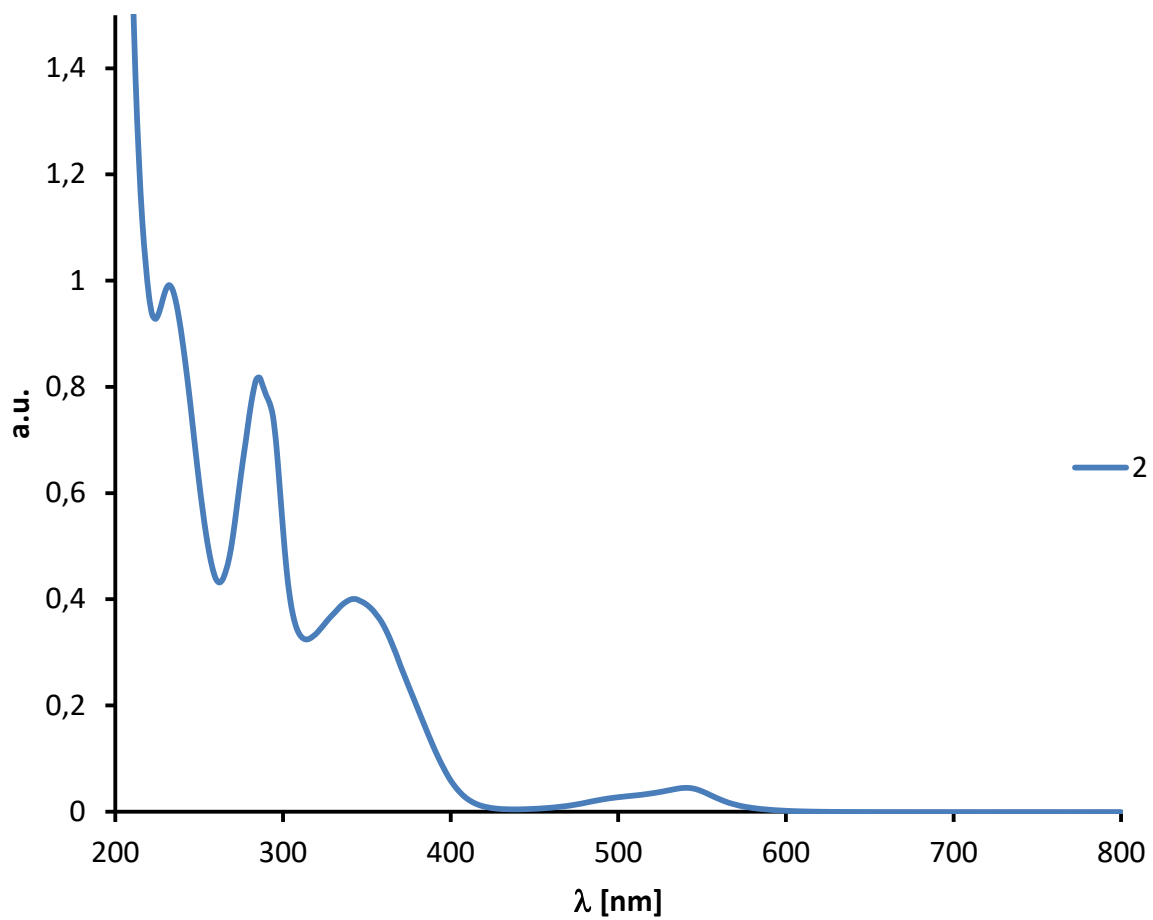
NL:  
5.24E3  
(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Zn<sub>4</sub>(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>3</sub>:  
O<sub>16</sub>N<sub>27</sub>F<sub>54</sub>H<sub>100</sub>C<sub>166</sub>Zn<sub>4</sub>S<sub>6</sub>  
p (gss, s/p:40) Chrg 5  
R: 10000 Res. Pwr. @10%

**Figure S21:** Isotope pattern (top) and calculated isotope pattern (bottom) of  $[(C_{40}H_{25}F_9N_6O)_4Zn_4(NS_2O_4C_2F_6)_3]^{5+}$ .



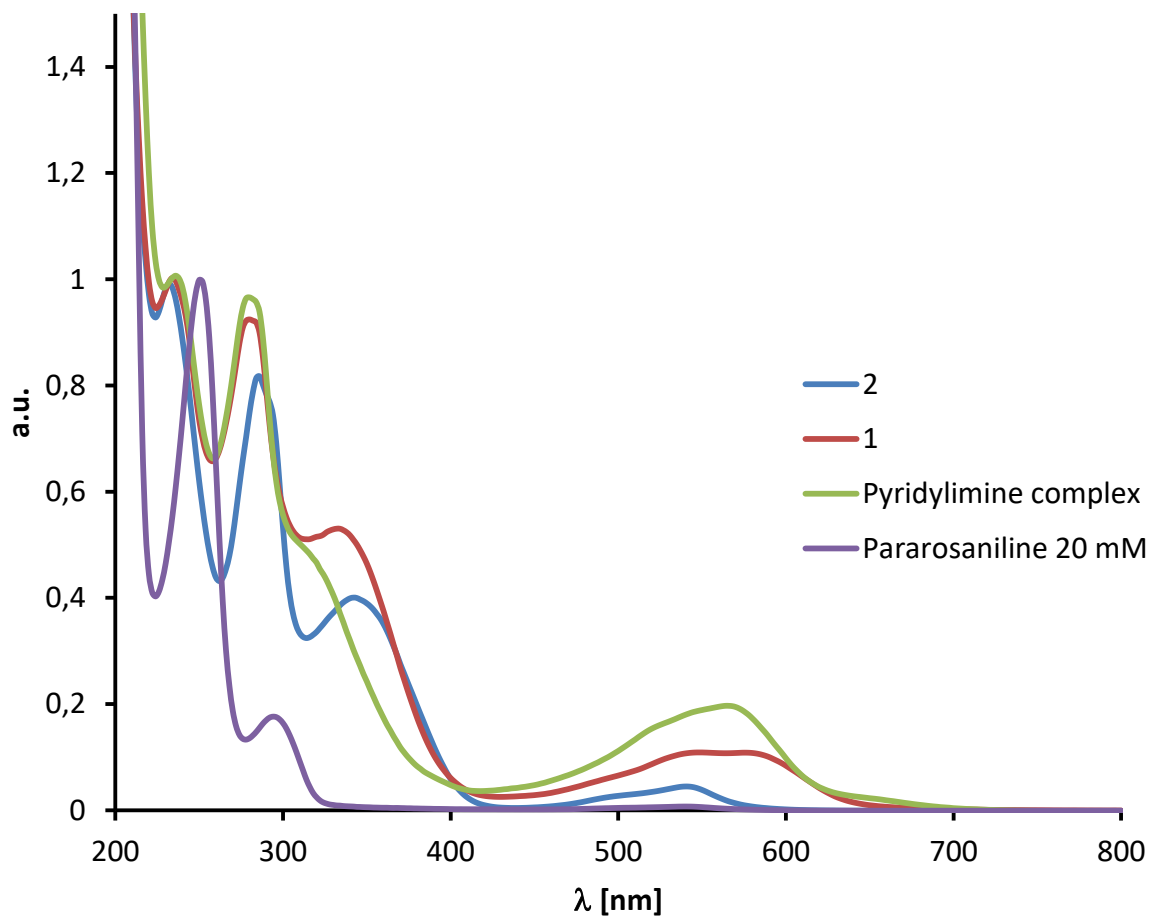
**Figure S22:** Isotope pattern of  $[(C_{40}H_{25}F_9N_6O)_4Zn_4(NS_2O_4C_2F_6)_1]^{7+}$ ,  $[(C_{40}H_{25}F_9N_6O)_4Zn_4(NS_2O_4C_2F_6)_2]^{6+}$ ,  $[(C_{40}H_{25}F_9N_6O)_4Zn_4(NS_2O_4C_2F_6)_3]^{5+}$ ,  $[(C_{40}H_{25}F_9N_6O)_4Zn_4(NS_2O_4C_2F_6)_4]^{4+}$ .

UV-Vis spectrum of **2** and comparison of UV-Vis spectra of cages **1** and **2**, the parent cage, and pararosanine



**Figure S23:** UV-Vis spectrum of **2**, acetonitrile (HPLC grade), 20  $\mu$ M, 298 K.





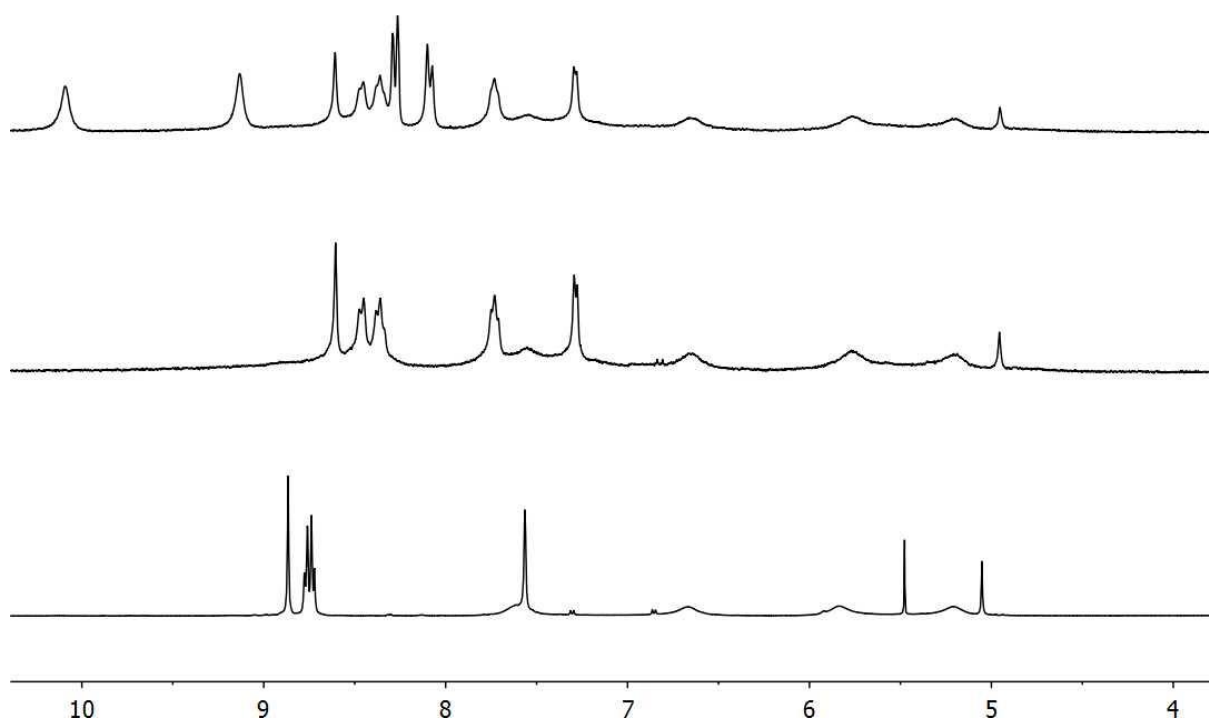
**Figure S24:** Comparison of the UV-Vis spectra of **1** (red), **2** (blue), the parent structure (green) and free pararosaniline base (purple).

## Synthetic transformation of **1**

### Transformation from **1** to the parent structure

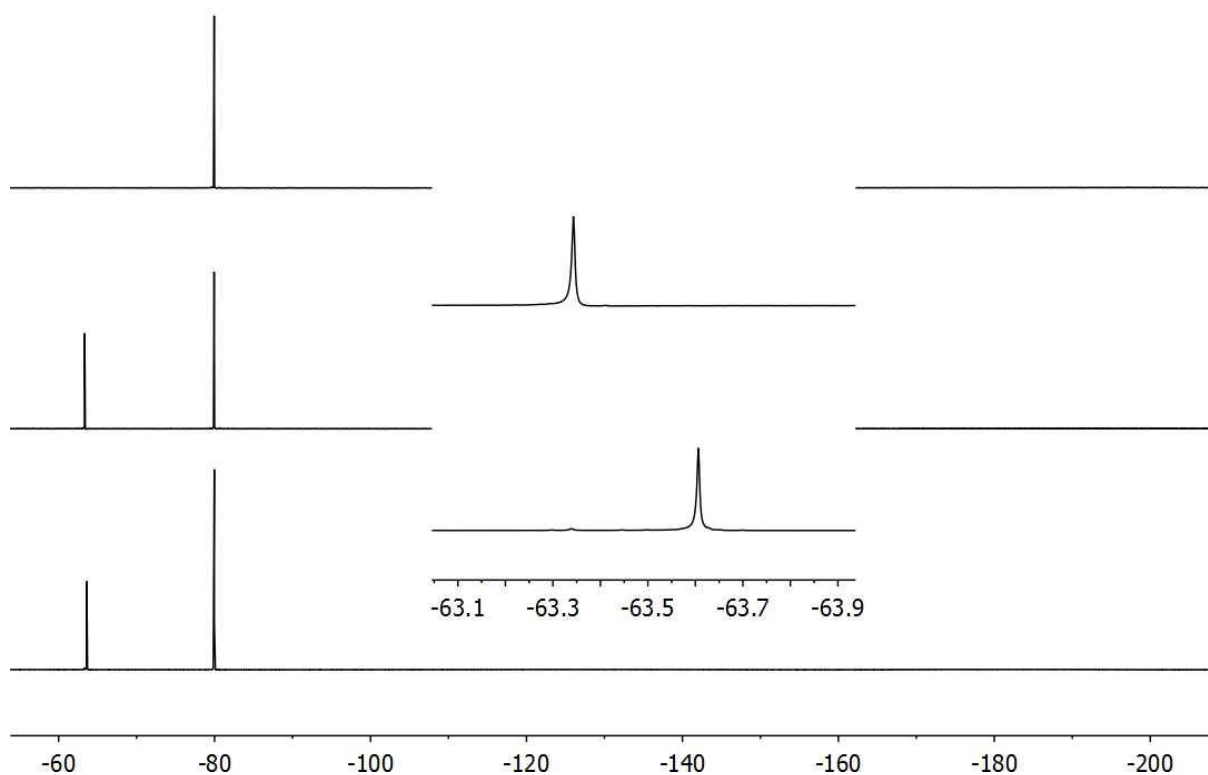
A solution of 10.0 mg (0.0017 mmol, 1 eq) **1** and 2.5 mg (0.023 mmol, 13.2 eq) pyridyl-2-carbaldehyde in 0.6 mL acetonitrile-*d*3 was heated to 50 °C for 18 hours. The resulting mixture was analysed by NMR-spectroscopy. Afterwards the solution was poured in diethyl ether, filtered, the remaining precipitate was washed with dichloromethane and diethyl ether and dried in a stream of air to yield the pure parent compound in 6 mg (0.0013 mmol, 72%) isolated yield. The resulting <sup>1</sup>H-NMR spectrum is in accordance with previously published NMR data.<sup>1</sup>

### NMR spectra

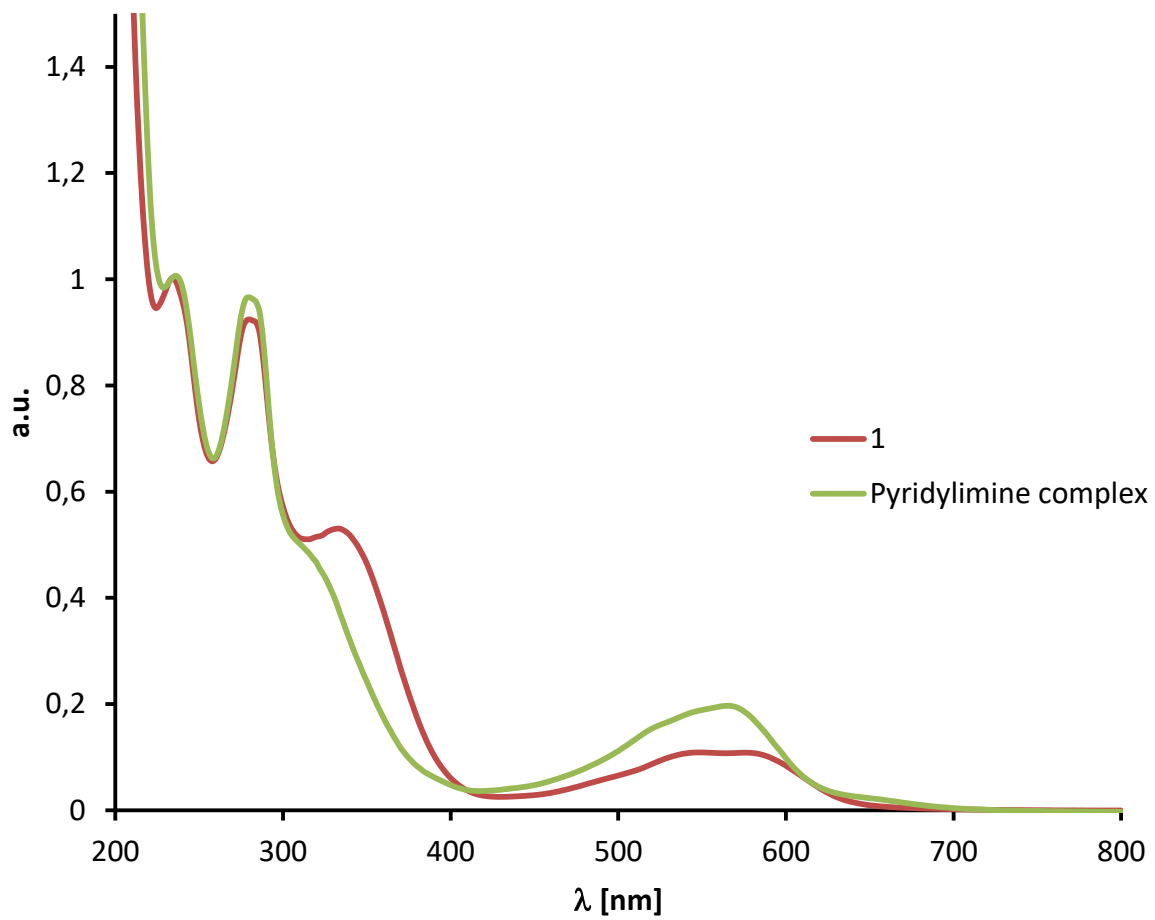


**Figure S30:** Comparison of the crude <sup>1</sup>H-NMR of the transformation of **1** to the parent structure (top) and the sample of the pure parent structure (middle) and **1** (bottom), acetonitrile-*d*3, 300.1 MHz, 298 K.

<sup>1</sup> R. A. Bilbesi, J. K. Clegg, N. Elgrishi, X. de Hatten, M. Devillard, B. Breiner, P. Mal, J. R. Nitschke, *J. Am. Chem. Soc.* **2012**, 134, 5110 – 5119.

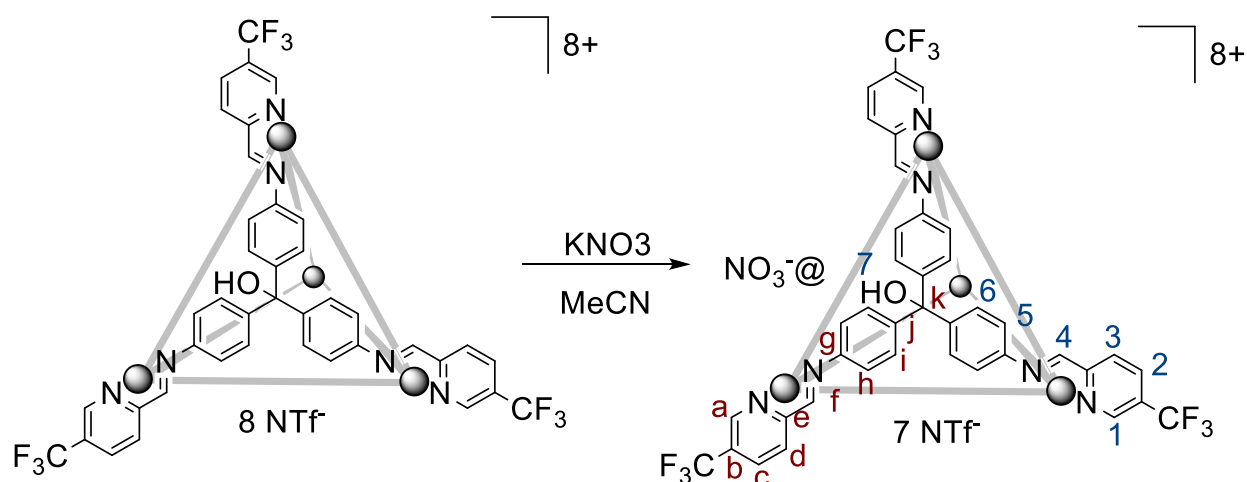


**Figure S31:** Comparison of the  $^{19}\text{F}$ -NMR of the parent structure (top), the crude parent structure after the transformation and **1** (bottom), acetonitrile- $d_3$ , 282.4 MHz, 298 K. Inset showing the signal of the  $\text{CF}_3$ -group from the free ligand after the transformation (top) and the signal of the  $\text{CF}_3$ -group in complex **1** (bottom).



**Figure S32:** Comparison of the UV-Vis spectra of the purified parent complex (green) and **1** (20  $\mu$ M, acetonitrile, 298 K).

## Synthesis and characterisation of NO<sub>3</sub><sup>-</sup>@1

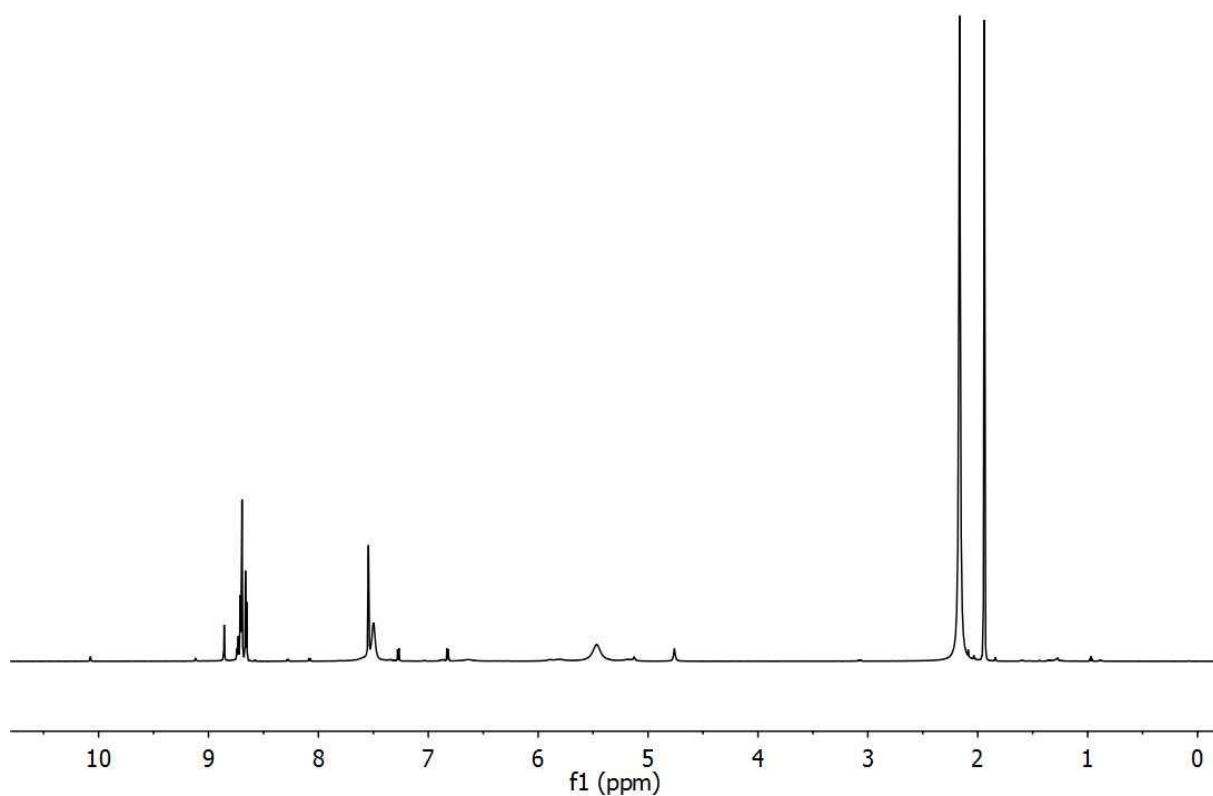


A solution of 10.0 mg (0.0017 mmol, 1 eq) **1** and 0.17 mg (0.0017 mmol, 1.0 eq) KNO<sub>3</sub> in 0.6 mL acetonitrile-*d*<sub>3</sub> was heated to 60 °C for 2 hours and the resulting solution was analysed by NMR spectroscopy.

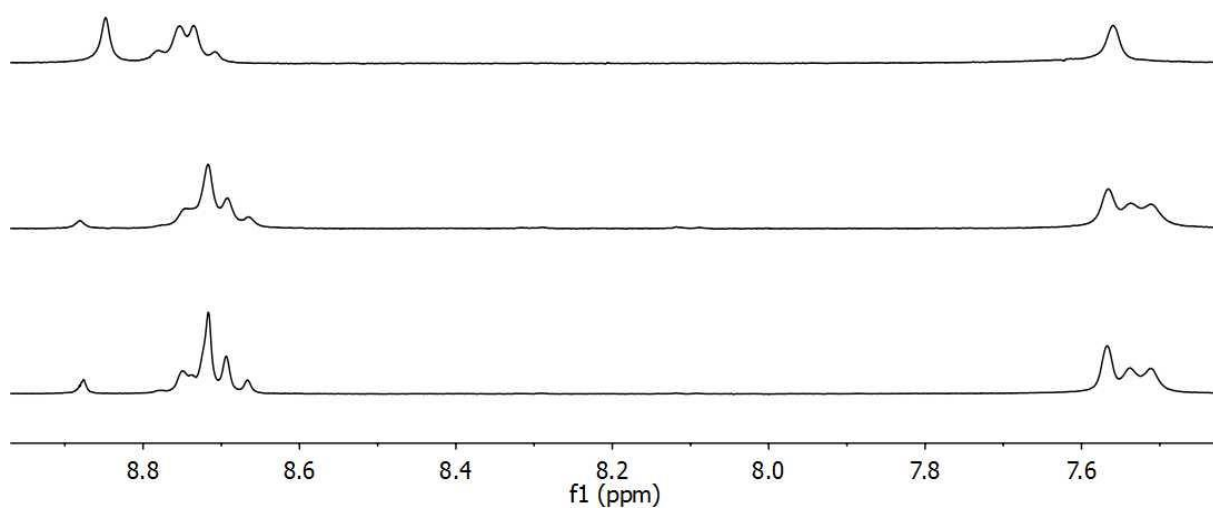
<sup>1</sup>H-NMR (acetonitrile-*d*<sub>3</sub>, 298 K, 700.1 MHz,  $\delta$  in ppm) = 8.65 – 8.75 (m, 6 H, H2/H3), 8.70 (s, 3 H, H4), 7.53 (s, 3H, H1), 7.50 (brs, 6 H, H5/6\*), 5.47 (brs, 6H, H5/6\*), 4.76 (s, 1H, H7); <sup>13</sup>C-NMR (acetonitrile-*d*<sub>3</sub>, 298 K, 156.4 MHz  $\delta$  in ppm) = 175.5 (f), 160.8 (b), 153.1 (a), 149.2 (e), 147.1 (j), 140.8 (g), 138.4 (d), 130.7 (c), 130.6 (q, CF<sub>3</sub>), 122.0 (h/i\*), 120.7 (h/i\*), 120.3 (h/i\*), 118.9 (h/i\*), 81.1 (k); <sup>19</sup>F-NMR (acetonitrile-*d*<sub>3</sub>, 298 K, 282.4 MHz,  $\delta$  in ppm) = -65.4 (-CF<sub>3</sub>), -79.9 (NTf); high resolution ESI-MS (acetonitrile, positive mode, *m/z*) = 484.503 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>]<sup>7+</sup> 484.501), 575.752 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NO<sub>3</sub>)]<sup>6+</sup> 575.582), 703.101 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub>]<sup>5+</sup> 703.101), 746.687 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NO<sub>3</sub>)<sub>1</sub>(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)]<sup>5+</sup> 746.685), 790.471 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>2</sub>]<sup>5+</sup> 790.469), 1003.586 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NO<sub>3</sub>)(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>2</sub>]<sup>4+</sup> 1003.581), 1504.065 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>4</sub>]<sup>3+</sup> 1504.060), 1058.068 (calcd. for [NO<sub>3</sub>@(C<sub>40</sub>H<sub>25</sub>F<sub>9</sub>N<sub>6</sub>O)<sub>4</sub>Fe<sub>4</sub>(NO<sub>3</sub>)(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>3</sub>]<sup>4+</sup> 1058.065), UV-Vis (acetonitrile, 298 K,  $\lambda$  in nm) = 235, 275, 337, 543, 583.

\*Due to the broad nature of the peaks no significant cross peaks could be assigned in the 2D spectra. Due to the procedure without any purification a small amount of free ligand can be observed.

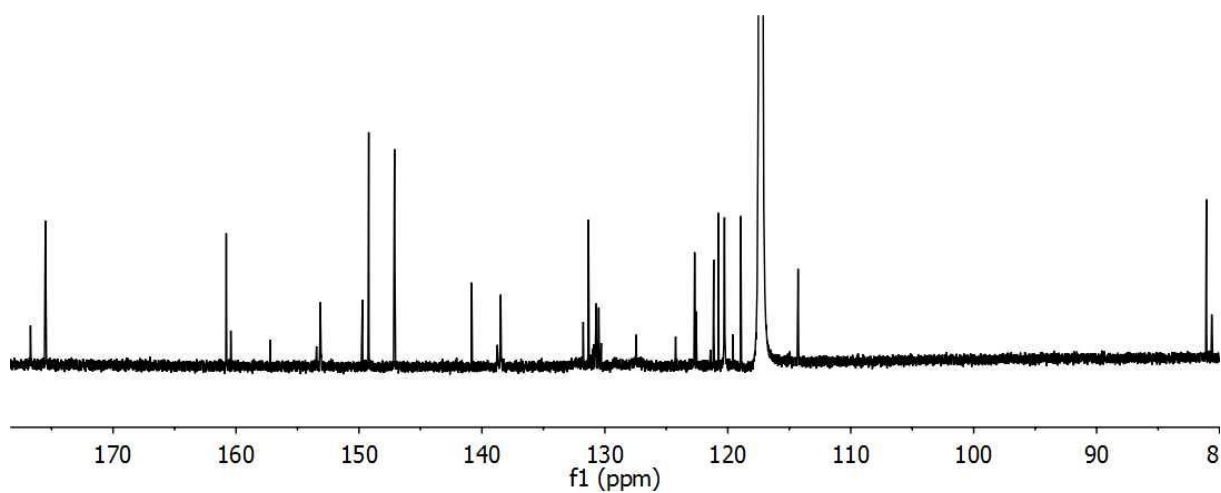
## NMR spectra of $\text{NO}_3^-@1$



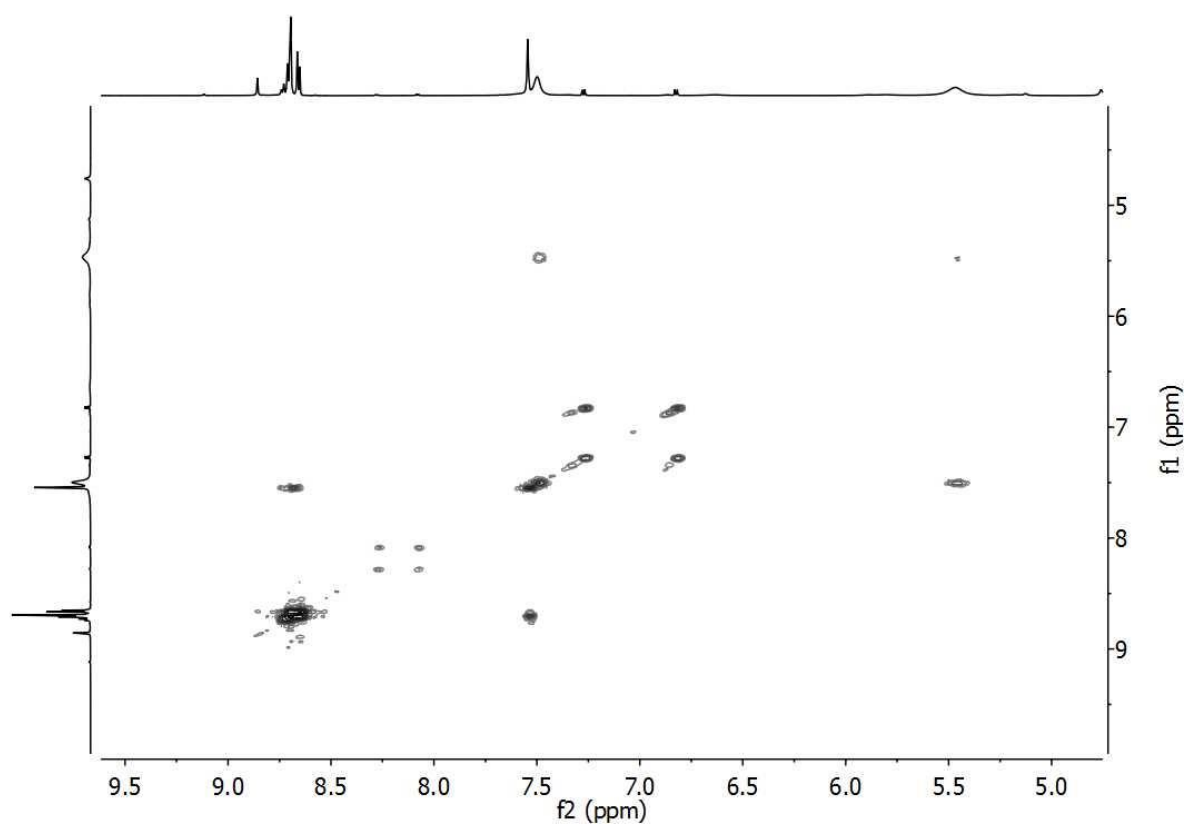
**Figure S33:**  $^1\text{H}$ -NMR-spectrum of crude  $\text{NO}_3^-@1$ , acetonitrile- $d_3$ , 298 K, 700.1 MHz.



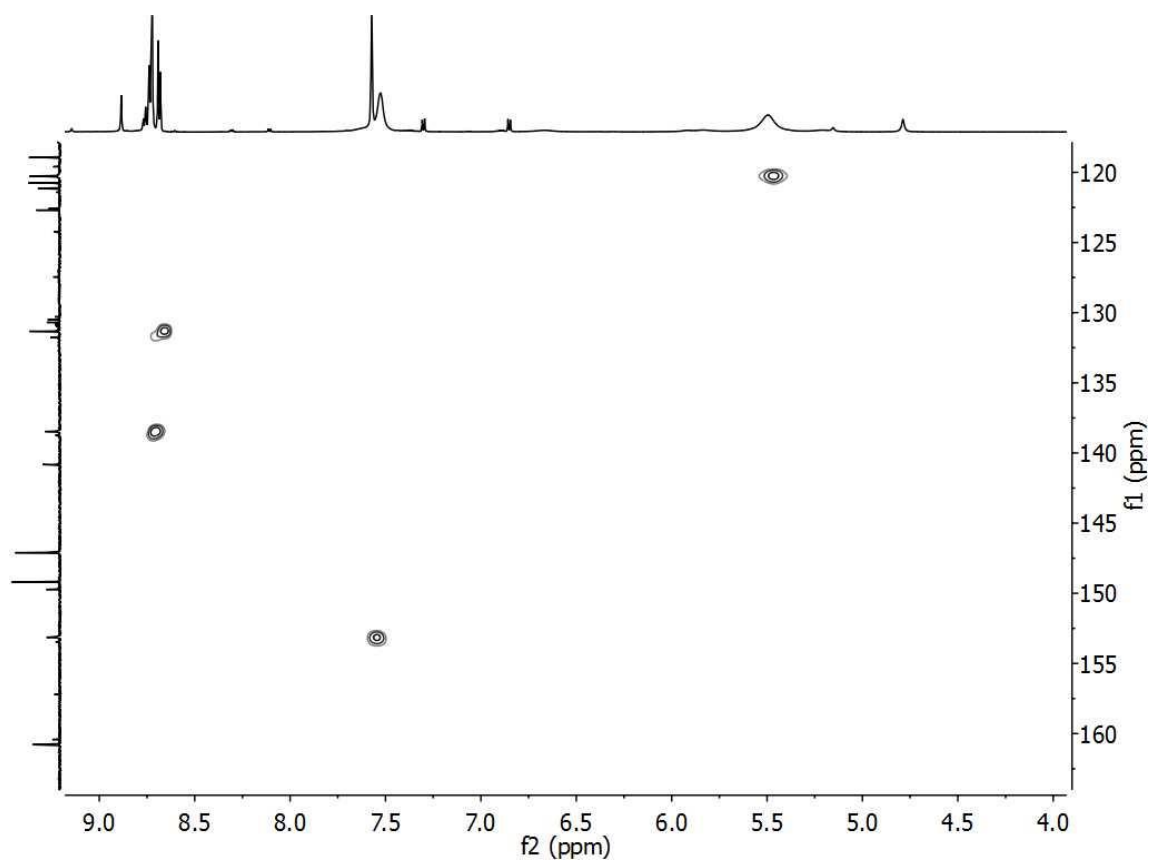
**Figure S34:**  $^1\text{H}$ -NMR-spectra of **1** (top), crude  $\text{NO}_3^-@1$  from addition of 1.0 equivalents  $\text{TBANO}_3$  (middle) and  $\text{NO}_3^-@1$  from addition of 1.0 equivalents of  $\text{KNO}_3$ , acetonitrile- $d_3$ , 298 K, 300.1 MHz.



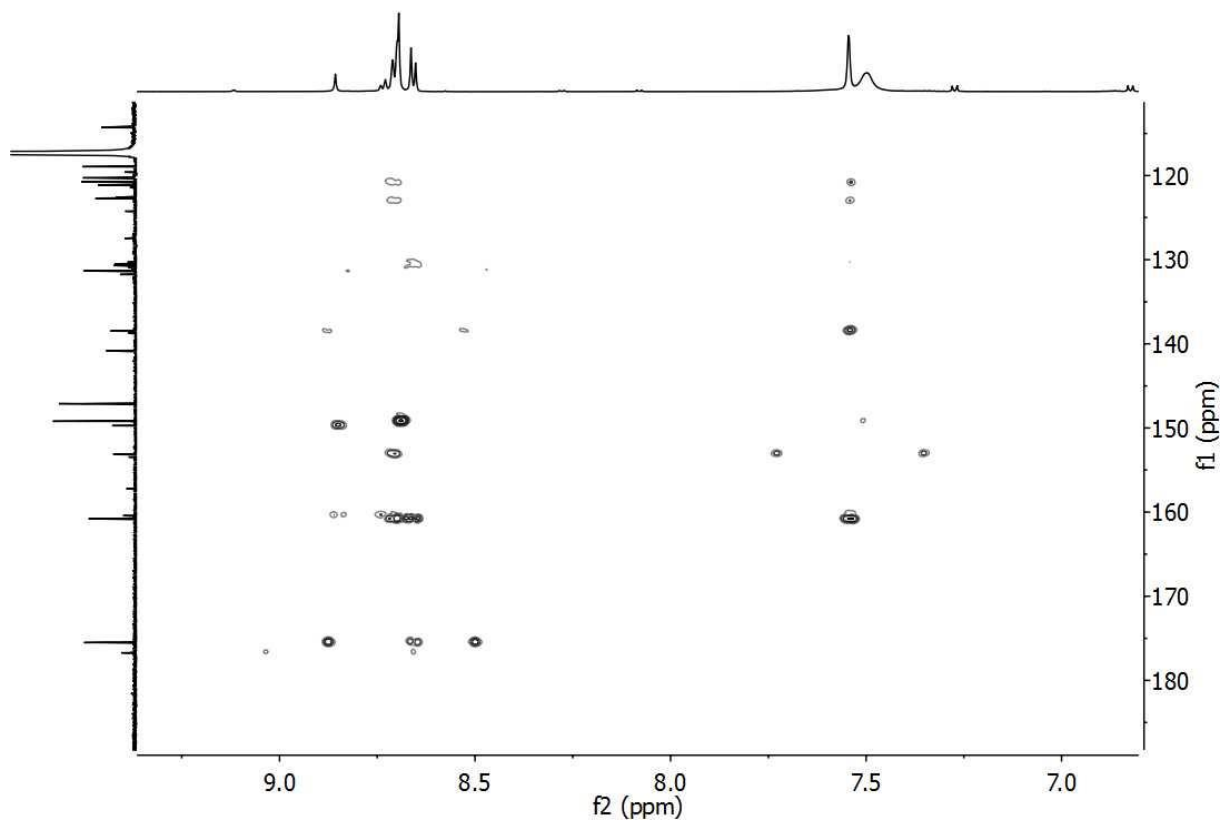
**Figure S35:**  $^{13}\text{C}$ -NMR-spectrum of  $\text{NO}_3^-$ @**1**, acetonitrile- $d_3$ , 298 K, 176.1 MHz.



**Figure S36:**  $^1\text{H},^1\text{H}$ -COSY-NMR of crude  $\text{NO}_3^-$ @**1**, acetonitrile- $d_3$ , 500.1 MHz.

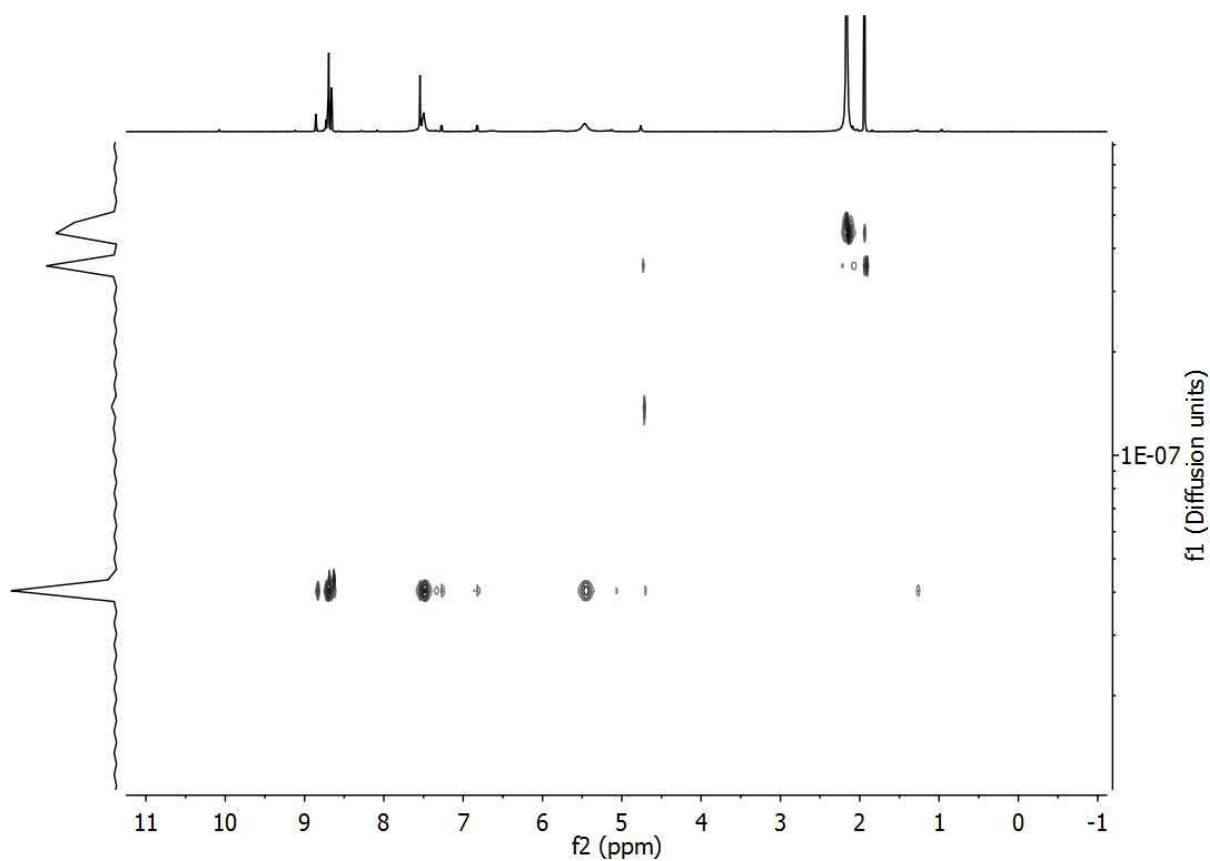


**Figure S37:**  $^1\text{H},^{13}\text{C}$ -HSQC-NMR of crude  $\text{NO}_3^-$ @**1**, acetonitrile- $d_3$ , 298 K, 500.1 MHz, 125.1 MHz.



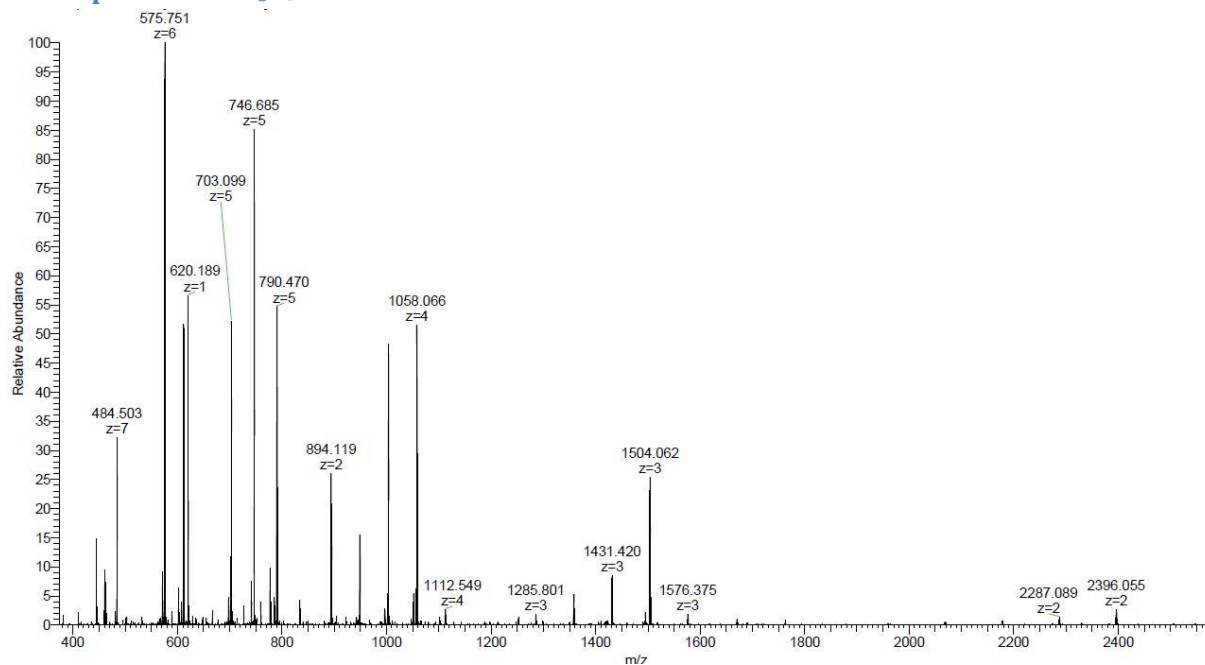
**Figure S38:**  $^1\text{H},^{13}\text{C}$ -HMBC-NMR of crude  $\text{NO}_3^-$ @**1**, acetonitrile- $d_3$ , 298 K, 500.1 MHz, 125.1 MHz.



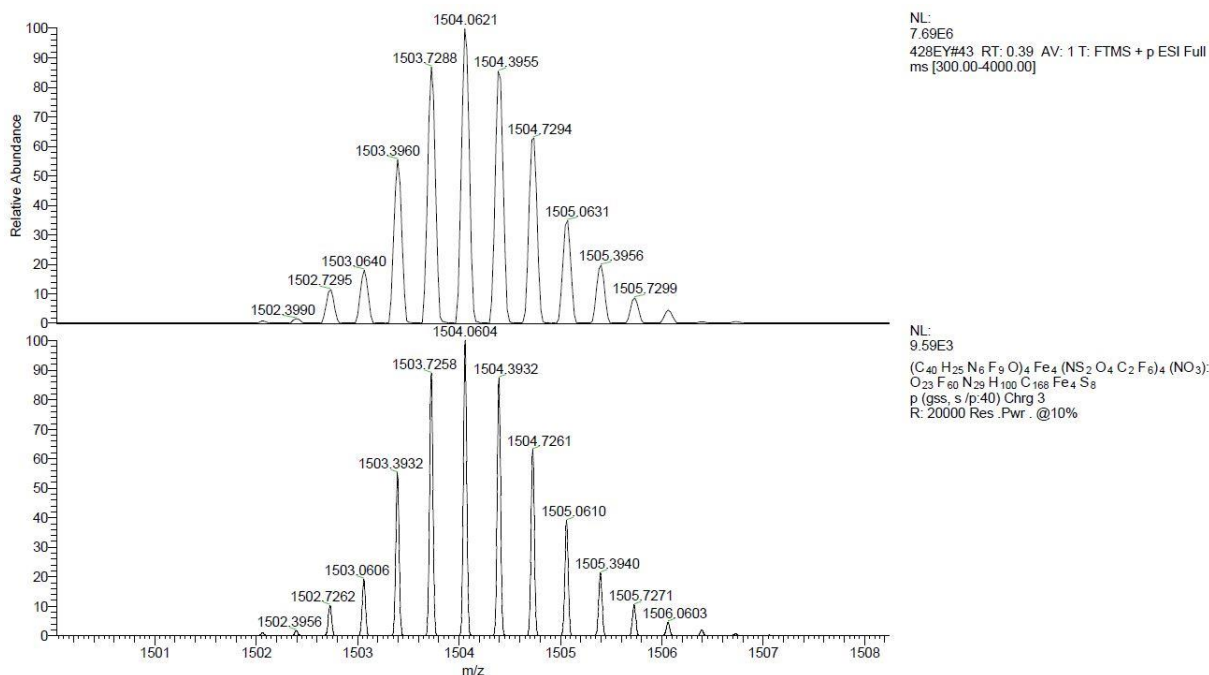


**Figure 39:**  $^1\text{H}$ -DOSY-NMR of crude  $\text{NO}_3^-@1$ , acetonitrile- $d_3$ , 298 K, 500.1 MHz.

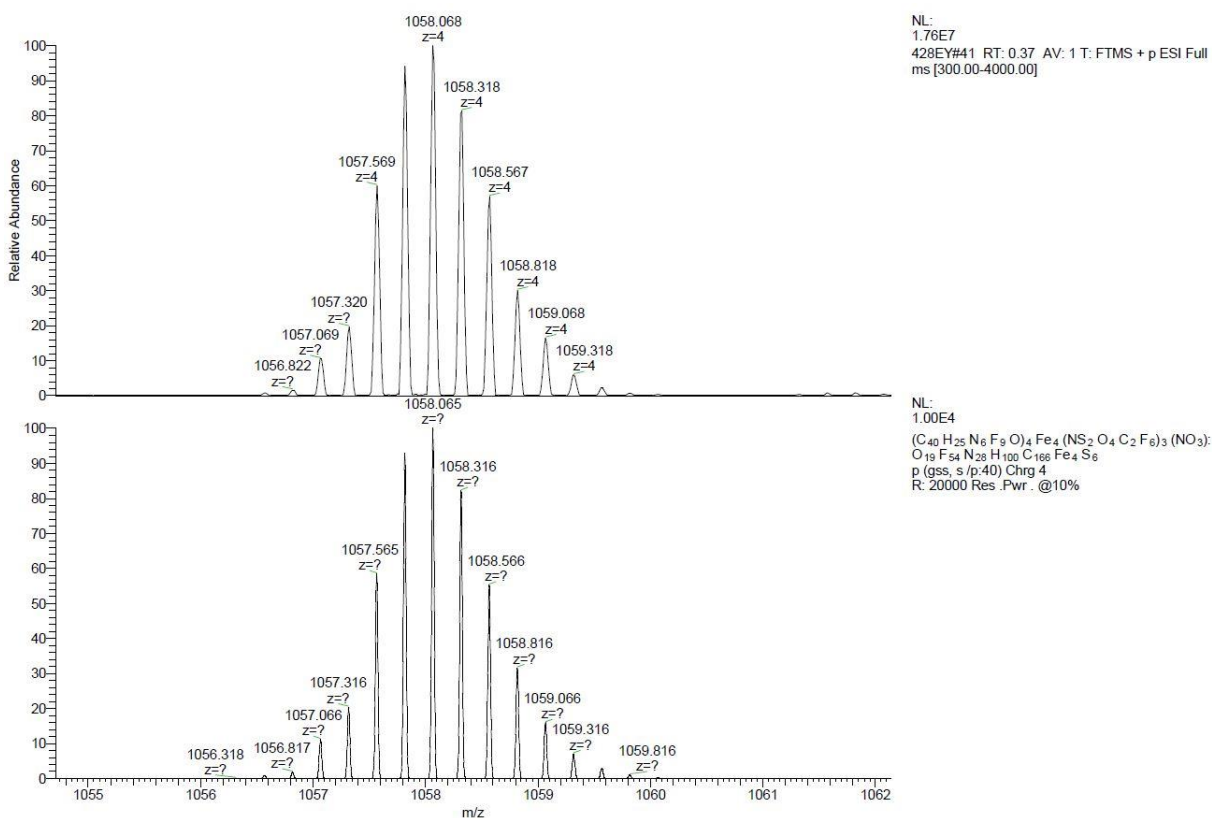
### Mass spectra of $\text{NO}_3^-@1$



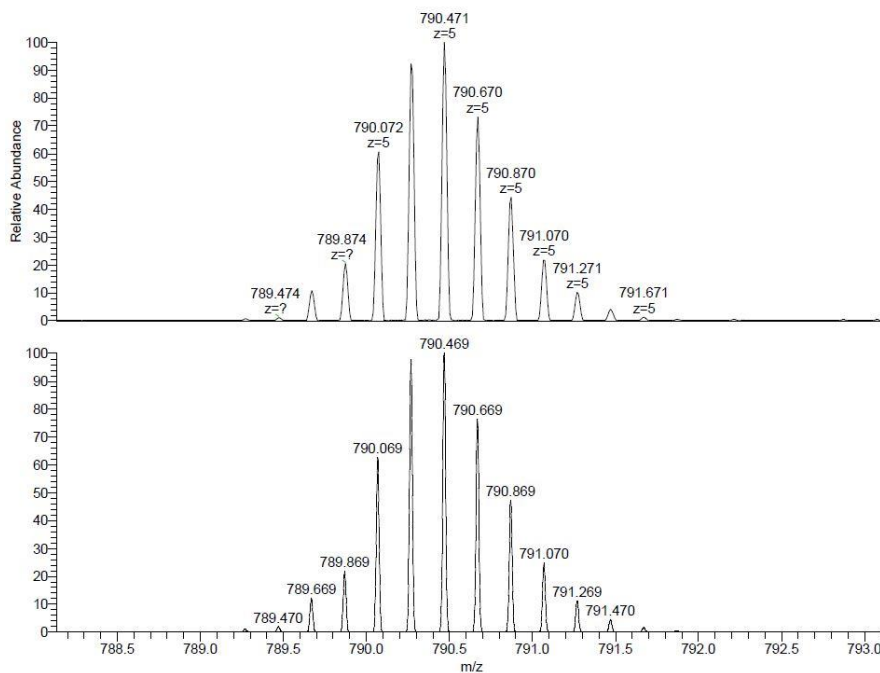
**Figure S 39:** High resolution ESI(+) mass spectrum of  $\text{NO}_3^-@1$ .



**Figure S40:** Isotope pattern (top) and calculated isotope pattern (bottom) of  $[(C_{40}H_{25}F_9N_6O)_4Fe_4(NS_2O_4C_2F_6)_4(NO_3)]^{4+}$



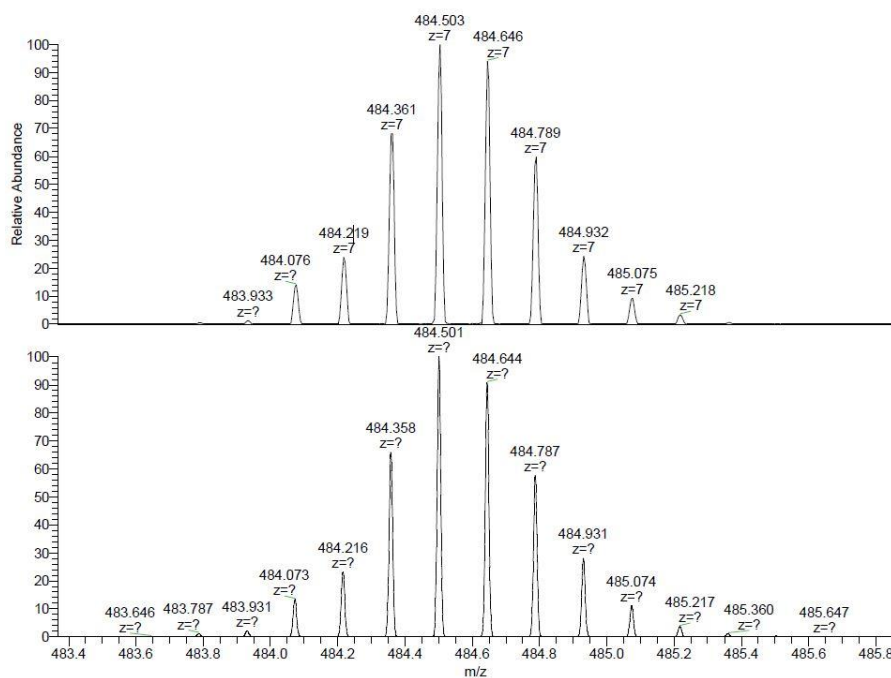
**Figure S41:** Isotope pattern (top) and calculated isotope pattern (bottom) of  $[(C_{40}H_{25}F_9N_6O)_4Fe_4(NS_2O_4C_2F_6)_3(NO_3)]^{4+}$



NL:  
2.52E7  
428EY#41 RT: 0.37 AV: 1 T: FTMS + p ESI Full  
ms [300.00-4000.00]

NL:  
1.04E4  
(C<sub>40</sub>H<sub>25</sub>N<sub>6</sub>F<sub>9</sub>O<sub>4</sub>)<sub>4</sub>Fe<sub>4</sub>(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>2</sub>(NO<sub>3</sub>):  
O<sub>15</sub>F<sub>48</sub>N<sub>27</sub>H<sub>100</sub>C<sub>164</sub>Fe<sub>4</sub>S<sub>4</sub>  
p (gss, s /p:40) Chrg 5  
R: 20000 Res. Pwr. @10%

**Figure S42:** Isotope pattern (top) and calculated isotope pattern (bottom) of  $[(C_{40}H_{25}F_9N_6O)_4Fe_4(NS_2O_4C_2F_6)_2(NO_3)]^{5+}$

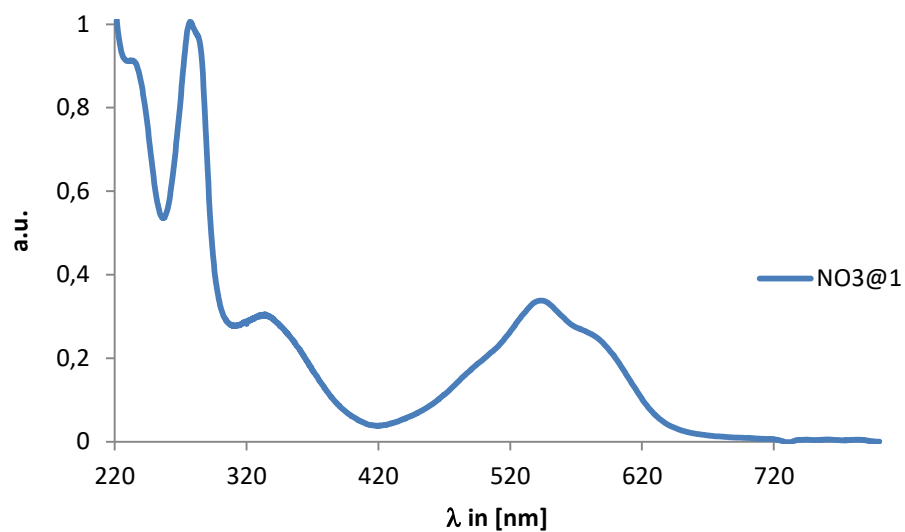


NL:  
1.49E7  
428EY#41 RT: 0.37 AV: 1 T: FTMS + p ESI Full  
ms [300.00-4000.00]

NL:  
1.22E4  
(C<sub>40</sub>H<sub>25</sub>N<sub>6</sub>F<sub>9</sub>O<sub>4</sub>)<sub>4</sub>Fe<sub>4</sub>(NS<sub>2</sub>O<sub>4</sub>C<sub>2</sub>F<sub>6</sub>)<sub>0</sub>(NO<sub>3</sub>):  
O<sub>7</sub>F<sub>36</sub>N<sub>25</sub>H<sub>100</sub>C<sub>160</sub>Fe<sub>4</sub>S<sub>0</sub>  
p (gss, s /p:40) Chrg 7  
R: 20000 Res. Pwr. @10%

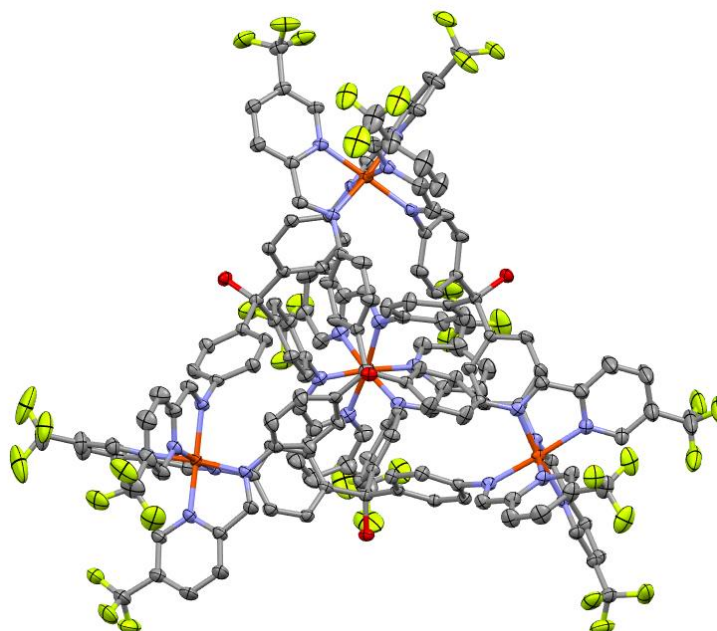
**Figure S43:** Isotope pattern (top) and calculated isotope pattern (bottom) of  $[(C_{40}H_{25}F_9N_6O)_4Fe_4(NO_3)]^{7+}$

### UV-Vis spectrum of $\text{NO}_3^-@1$

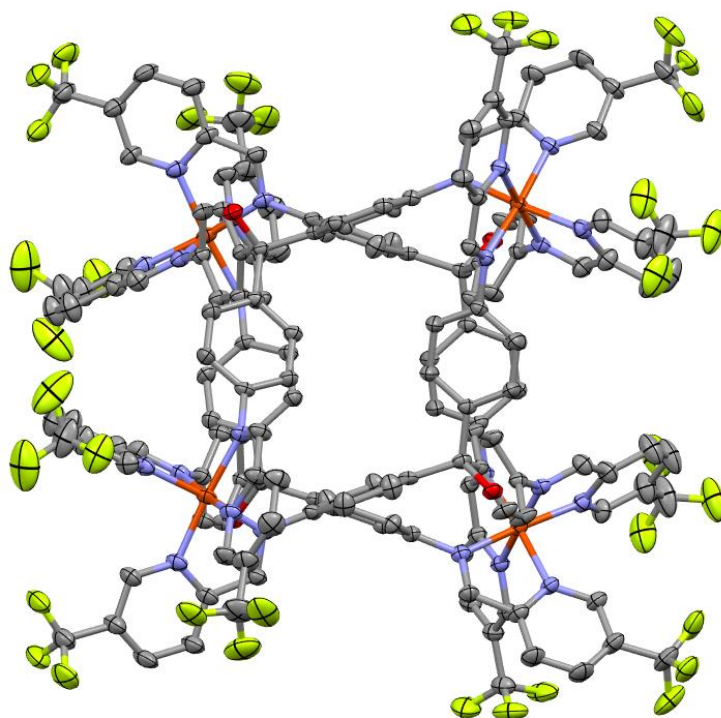


**Figure S44:** UV-Vis spectrum of  $\text{NO}_3^-@1$ , acetonitrile (HPLC grade), 20 mM, 0.01 mm cuvette, 298 K.

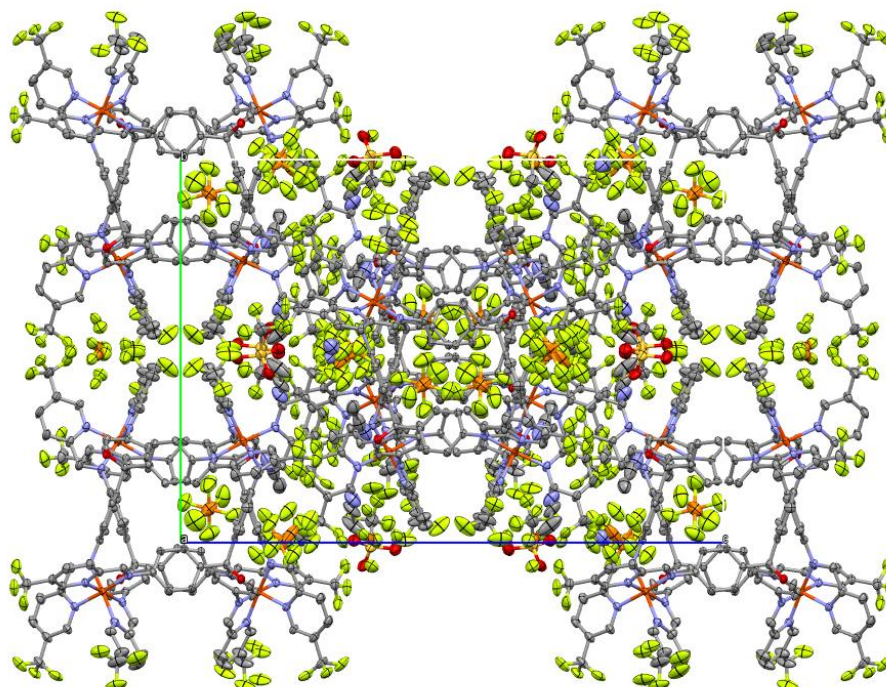
### Crystallographic analysis of 1\_Pf6\_TfO



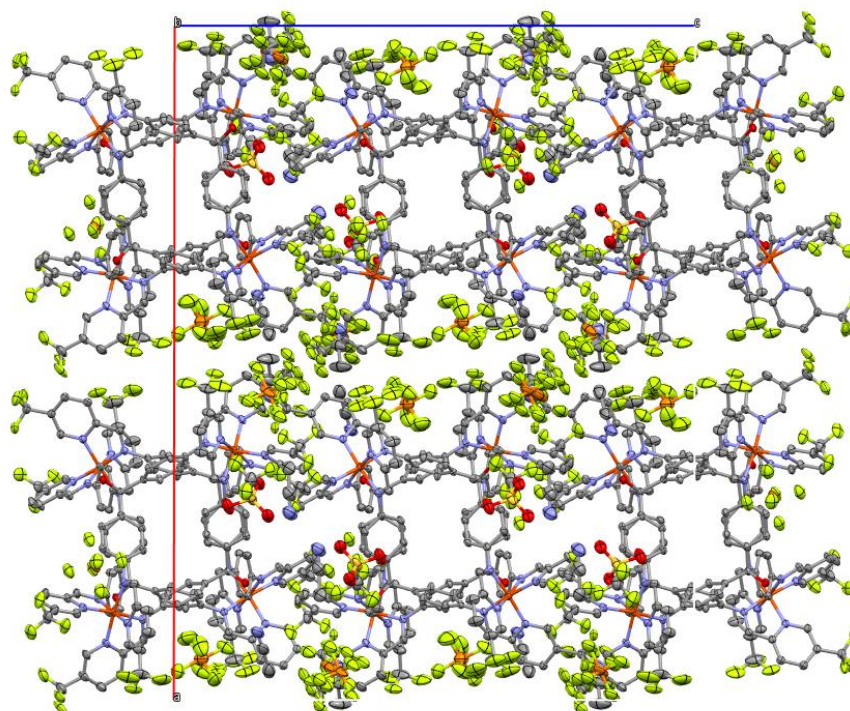
**Figure S45:** Cation 1 as observed in the crystal structure of 1\_Pf6\_OTf. View along the approximate molecular  $C_3$ -symmetry. Hydrogen atoms omitted for clarity. Displacement ellipsoids are drawn at 30% probability.



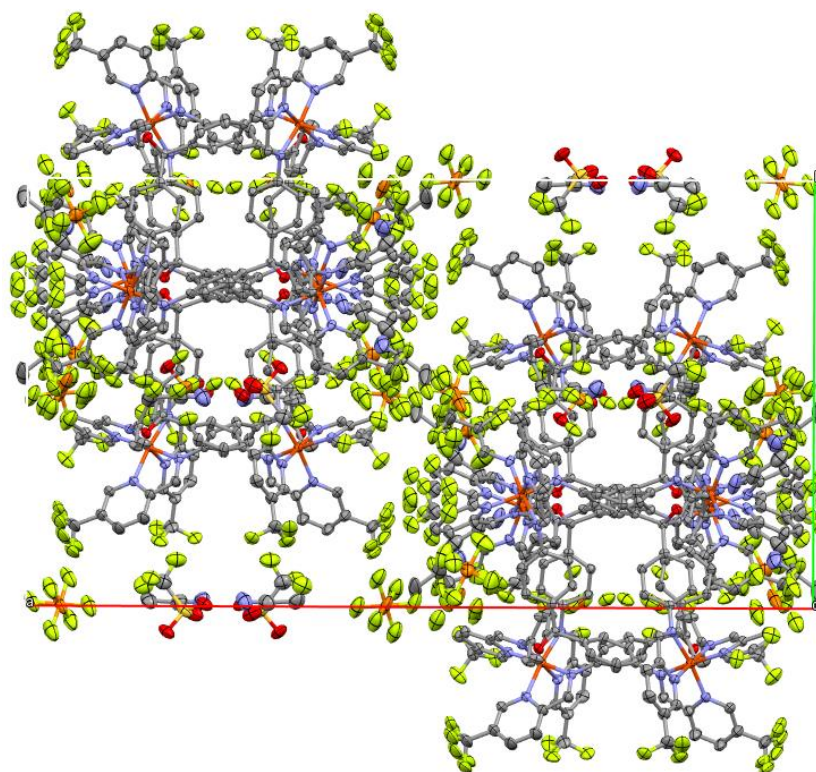
**Figure S46:** Cation **1** as observed in the crystal structure of **1**\_PF6\_OTf. View along the approximate molecular C<sub>2</sub>-symmetry parallel to the crystallographic *a*-axis. Hydrogen atoms omitted for clarity. Displacement ellipsoids are drawn at 30% probability.



**Figure S47:** Packing in the crystal structure of **1**\_PF6\_TfO as seen along crystallographic *a*-axis. Hydrogen atoms omitted for clarity. Displacement ellipsoids are drawn at 30% probability.



**Figure S48:** Packing in the crystal structure of **1**\_PF6\_TfO as seen along crystallographic *b*-axis. Hydrogen atoms omitted for clarity. Displacement ellipsoids are drawn at 30% probability.



**Figure S49:** Packing in the crystal structure of **1**\_PF6\_TfO as seen along crystallographic *c*-axis. Hydrogen atoms omitted for clarity. Displacement ellipsoids are drawn at 30% probability.