

Supporting Information for

**Fuel-Controlled Reassembly of Metal-Organic Architectures**

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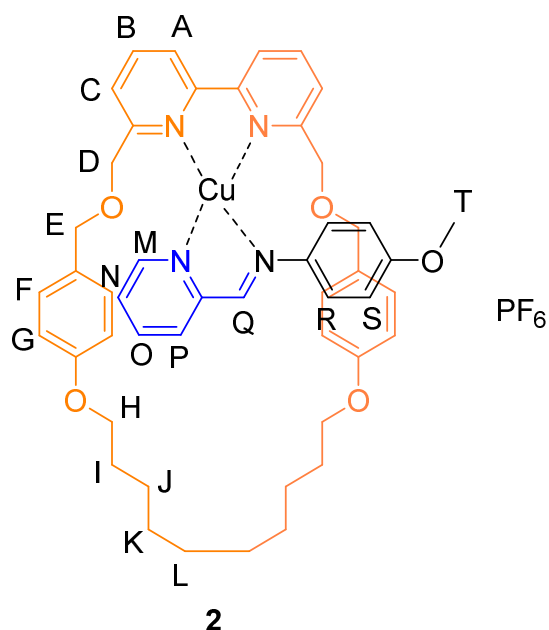
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## 1. General Experimental Section

Tetrakis(acetonitrile)copper(I) hexafluorophosphate, Tetrakis(acetonitrile)copper(I) trifluoromethanesulfonate, *p*-methoxyaniline, 2-pyridinecarboxaldehyde, and acetonitrile were purchased from Sigma-Aldrich and used as received. **1**,<sup>1</sup> **4**,<sup>2</sup> ReCat,<sup>3</sup> and MoCat<sup>4</sup> were prepared according to literature procedure.

NMR spectra were recorded on a Bruker Avance DRX-400, Bruker Avance 500 BB ATM, or Bruker Avance 500 Cryo spectrometers. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C were reported in ppm on the  $\delta$  scale; <sup>1</sup>H and <sup>13</sup>C were referenced to the solvent residual peak. Coupling constants (J) are reported in hertz (Hz). The following abbreviations are used to describe signal multiplicity for <sup>1</sup>H and <sup>13</sup>C spectra: s: singlet, d: doublet, t: triplet, m: multiplet, br: broad. Maximum gradient strength was 6.57 G/cmA. The standard Bruker pulse program, ledbpgp2s, employing a stimulated echo and longitudinal eddy-current delay (LED) using bipolar gradient pulses for diffusion using 2 spoil gradients was utilized. Rectangular gradients were used with a total duration of 1.5 ms. Gradient recovery delays were 875-1150  $\mu$ s. Diffusion times were 100 ms. Individual rows of the S4 quasi-2D diffusion databases were phased and baseline corrected. High resolution electrospray ionization mass spectrometry (HRMS) experiments were performed on a Thermo Scientific LTQ Orbitrap instrument. Samples were diluted in acetonitrile, and introduced into the ion source at flow rates of 5-10  $\mu$ L/min. The parameters for tube lens voltage (60 V), capillary voltage (-0.05 V) as well as ion optic were optimized for maximum abundances of the desired complex ions. Gas flow rates were optimised to the normalised values of: sheath gas (4.0) and auxiliary gas (5.0). Multiple scans (up to 21) were averaged to improve signal-to-noise ratio. Absorbance spectra were measured with a Perkin Elmer Lambda 750 UV/Vis/NIR spectrometer. Elemental analyses were obtained on an Exeter Analytical CE-440 Elemental Analyser.

## 2. Synthesis of 2



**2** (20 mg, 3.5  $\mu\text{mol}$ ) was dissolved in DCM (5 mL) under a N<sub>2</sub> atmosphere. 2-pyridinecarboxaldehyde (3.8 mg, 3.5  $\mu\text{mol}$ ) and *p*-anisidine (4.3 mg, 3.5  $\mu\text{mol}$ ) were added and the mixture stirred for five minutes. Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (13.15 mg, 3.5  $\mu\text{mol}$ ) was added and the mixture stirred at 303 K overnight. Solvent was removed under reduced pressure and the resulting residue was washed with Et<sub>2</sub>O (3 x 5 mL). Drying under vacuum gave **2** as a brown solid (33.4 mg, 96%). <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN)  $\delta$  8.80 (s, br, 1H, H<sub>Q</sub>), 8.33 (d,  $J$  = 8.0 Hz, 2H, H<sub>A</sub>), 8.18 (t,  $J$  = 7.9 Hz, 2H, H<sub>B</sub>), 8.02-8.12 (m, 1H, H<sub>M-P</sub>), 7.90-7.98 (m, 1H, H<sub>M-P</sub>), 7.74 (d,  $J$  = 7.7 Hz, 2H, H<sub>C</sub>), 7.68 – 7.50 (m, 1H, H<sub>M-P</sub>), 7.17 (m, 2H, H<sub>R</sub>), 6.81 (m, 4H, H<sub>F, S</sub>), 6.61 (d,  $J$  = 8.1 Hz 4H, H<sub>G</sub>), 4.34 (s, 4H, H<sub>E</sub>), 4.02 (s, 4H, H<sub>D</sub>), 3.90 (t,  $J$  = 6.5 Hz, 4H, H<sub>H</sub>), 3.76 (br, 3H, H<sub>T</sub>), 1.76-1.83 (m, , 4H, H<sub>I</sub>), 1.53-63 (m, , 4H, H<sub>J</sub>), 1.43-1.52 (m, , 8H, H<sub>K,L</sub>), <sup>13</sup>C NMR (126 MHz, CD<sub>3</sub>CN)  $\delta$  161.39, 159.69, 158.62, 155.54, 152.21, 151.88, 150.04, 140.62, 140.06, 138.89, 130.38, 129.54, 128.87, 128.47, 124.73, 124.49, 121.62, 115.42, 114.99, 72.79, 70.93, 68.58, 56.23, 29.42, 29.24, 29.09, 26.28. ESI-MS: 841.3389 [**2**]<sup>+</sup>. Elemental

Analysis (%) calcd for  $C_{49}H_{54}CuF_6N_4O_5P \cdot MeCN \cdot Et_2O$ : C 59.6, H 5.51, N 5.67; found: C 60.01, H 5.44, N: 5.58.

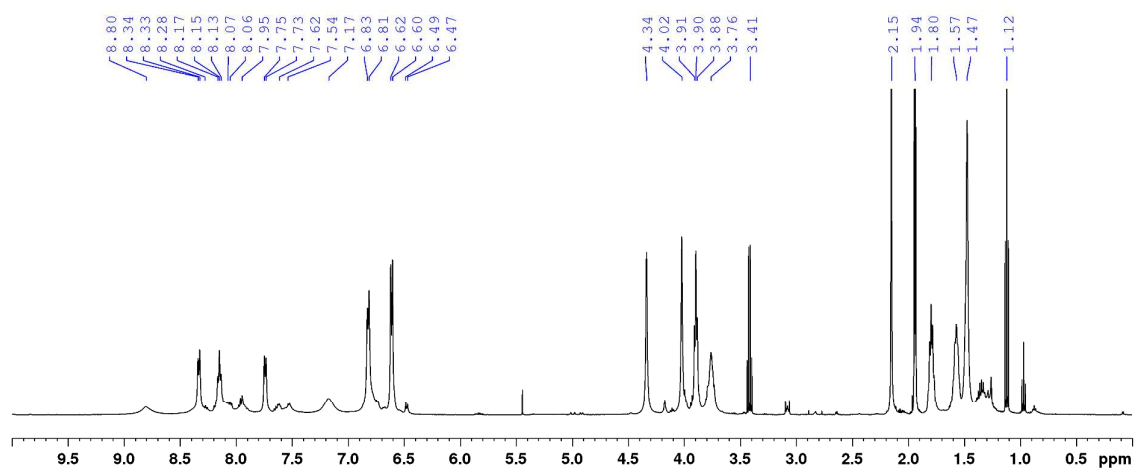


Figure S1.  $^1H$  NMR spectrum of 2.

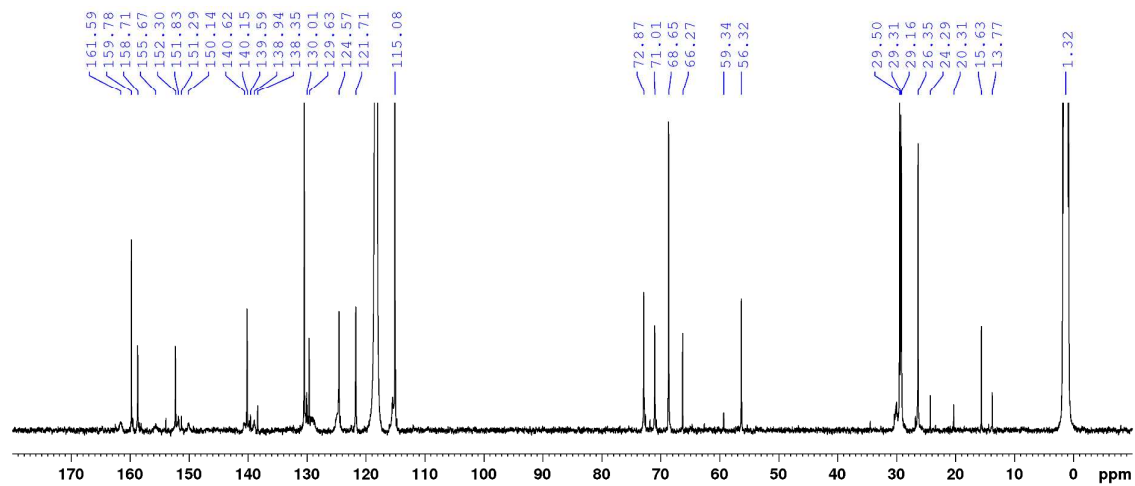
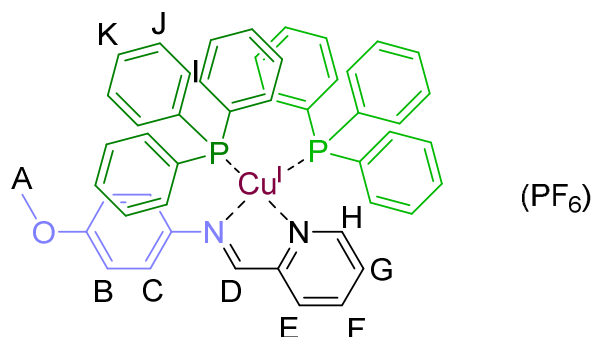


Figure S2. (i)  $^{13}C$  NMR spectrum of 2.

### 3. Synthesis of **3**



PPh<sub>3</sub> (0.26 g, 1 mmol) and Cu(MeCN)<sub>4</sub>PF<sub>6</sub> (0.18 g 0.5 mmol) were dissolved in a 1:1 mixture of MeCN/DCM (20 mL). *p*-Anisidine (0.62 g, 0.5 mmol) and 2-pyridinecarboxaldehyde (44 μL, 0.5 mmol) were added and the resulting orange solution heated at 308 K for 5 hours. Solvent was removed under reduced pressure and the residue washed with Et<sub>2</sub>O (3 x 5mL). Drying under vacuum gave **3** as an orange solid (0.45 g, 93%). <sup>1</sup>H NMR (400 MHz, Acetonitrile-*d*<sub>3</sub>) δ 8.81 (s, 1H, H<sub>D</sub>), 8.40 (d, *J* = 5.0 Hz, 1H, H<sub>H</sub>), 8.05 (m, 1H, H<sub>F</sub>), 7.99 (d, *J* = Hz, 1H, H<sub>e</sub>), 7.48 (m, 1H, H<sub>G</sub>), 7.42 (t, *J* = 7.5 Hz, 6H, H<sub>K</sub>), 7.27 (t, *J* = 7.6 Hz, 12H, H<sub>J</sub>), 7.18 (d, *J* = 8.5 Hz, 2H, H<sub>C</sub>), 7.11 (br, 12H, H<sub>I</sub>), 6.78 (d, *J* = 8.5 Hz, 2H, H<sub>B</sub>), 3.78 (s, 3H, H<sub>A</sub>). <sup>13</sup>C NMR (101 MHz, CD<sub>3</sub>CN) δ 161.32, 158.52, 151.92, 151.03, 141.55, 139.95, 134.10, 134.03, 133.21, 132.98, 131.34, 129.95, 129.73, 128.73, 125.12, 115.48, 56.40. <sup>31</sup>P NMR (162 MHz, 298 K, DMSO): δ = 1.23 (br, s, PPh<sub>3</sub>) -144.0 ppm (heptet, *J* = 710.3 Hz, PF<sub>6</sub><sup>-</sup>). ESI-MS: 799.2055 [**3**]<sup>+</sup>; Elemental Analysis (%) calcd for C<sub>51</sub>H<sub>48</sub>CuF<sub>6</sub>N<sub>2</sub>OP<sub>3</sub>·MeCN: C 62.63, H 5.06, N 4.13; found: C 62.68, H 4.98, N: 4.17.

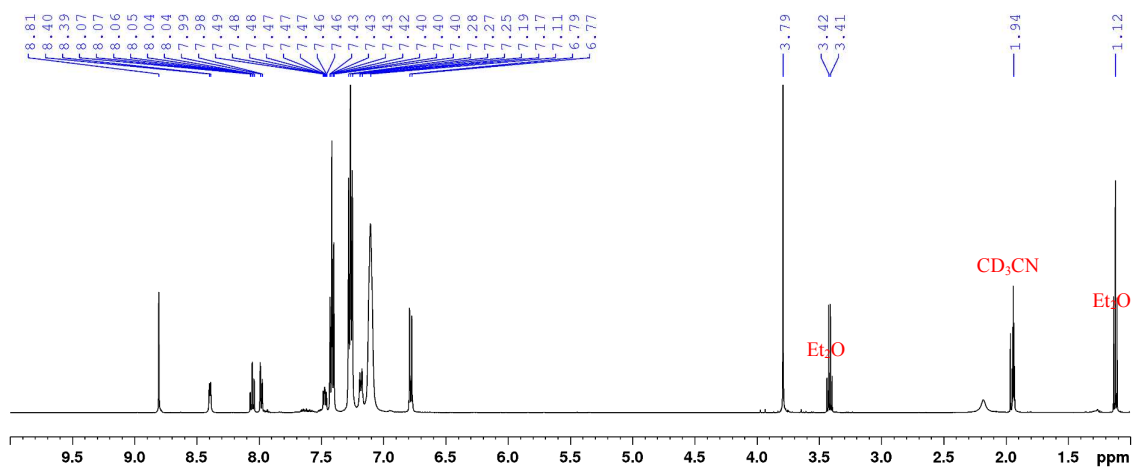


Figure S3. <sup>1</sup>H NMR spectrum of **3**.

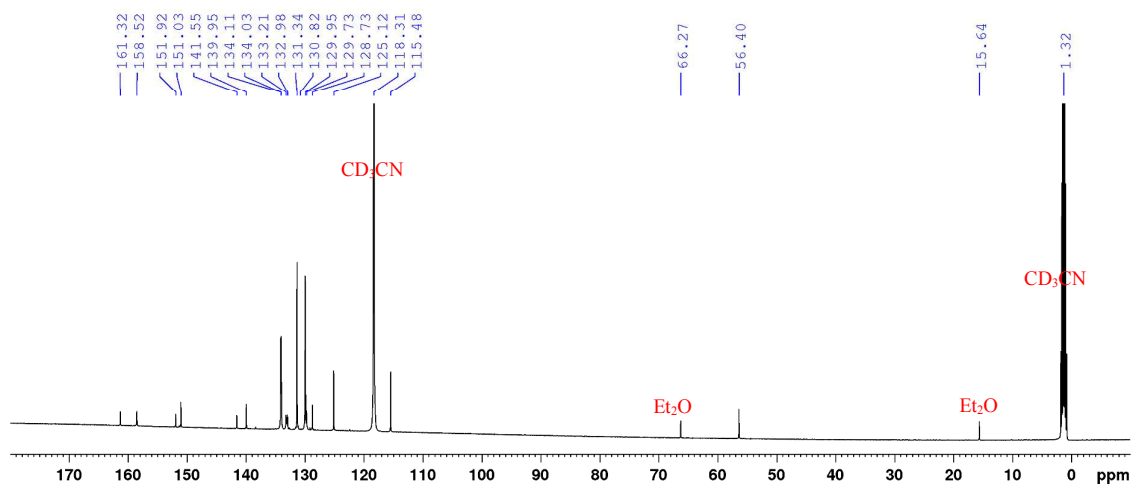


Figure S4. <sup>13</sup>C NMR spectrum of **3**.

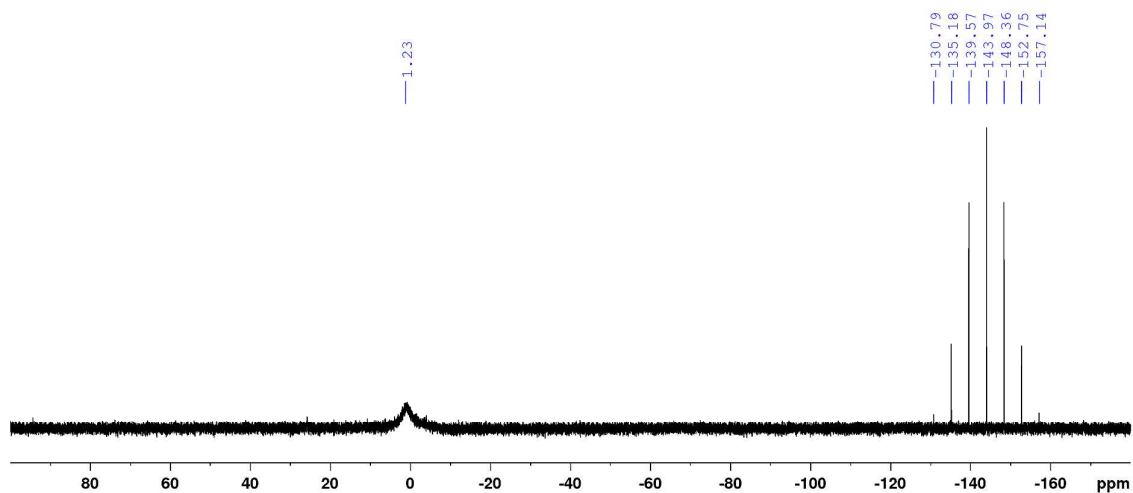
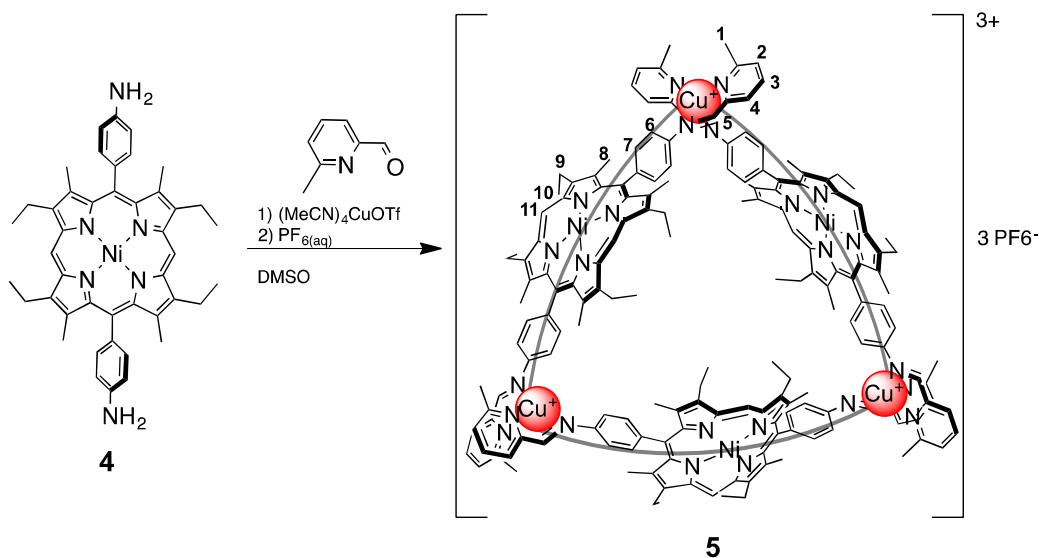


Figure S5. <sup>31</sup>P NMR spectrum of **3**.

#### 4. Synthesis of 5



4 (4.0 mg, 5.6  $\mu\text{mol}$ ), 6-methyl-2-formylpyridine (1.4 mg, 11.2  $\mu\text{mol}$ ) and  $\text{Cu}(\text{MeCN})_4\text{OTf}$  (2.1 mg, 5.6  $\mu\text{mol}$ ) were dissolved in DMSO (0.6 mL) then heated at 70°C under N<sub>2</sub> for 16h. The resultant dark red solution was added to a saturated solution of aqueous KPF<sub>6</sub> (3 mL) to precipitate a red solid. The precipitate was isolated over Celite, washed with water (2 x 2 mL) and then dissolved in a 1:1 solution of MeCN/DCM (3 mL). The solution was reduced to dryness to give a red solid (5.4 mg, 1.55  $\mu\text{mol}$ , 85%); <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  = 9.80 (1H, m, **5**), 9.49 (1H, m, **11**), 8.32 (1H, t, *J* = 7.5 Hz, **3**), 8.23 (1H, d, *J* = 5.0 Hz, **4**), 7.81-7.98 (5H, m, **2**, **6-7**), 3.42-3.71 (4H, bm, **9**), 2.49 (3H, m, **1**), 2.05-2.30 (6H, m, **8**), 1.20-1.49 (6H, m, **10**); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  = 160.22, 157.87, 150.44, 147.02, 145.73, 140.96, 139.22, 139.03, 138.04, 137.89, 133.86, 128.92, 126.77, 121.69, 115.38, 96.01, 24.74, 18.65, 17.09, 15.09; *m/z* (HRMS) = 986.9924 [**5**]<sup>3+</sup>; Elemental Analysis (%) calcd for C<sub>174</sub>H<sub>168</sub>Cu<sub>3</sub>F<sub>18</sub>N<sub>24</sub>Ni<sub>3</sub>P<sub>3</sub>·6DMSO·H<sub>2</sub>O: C 57.52, H 5.35, N 8.66; found: C 57.52, H 5.35, 8.66.



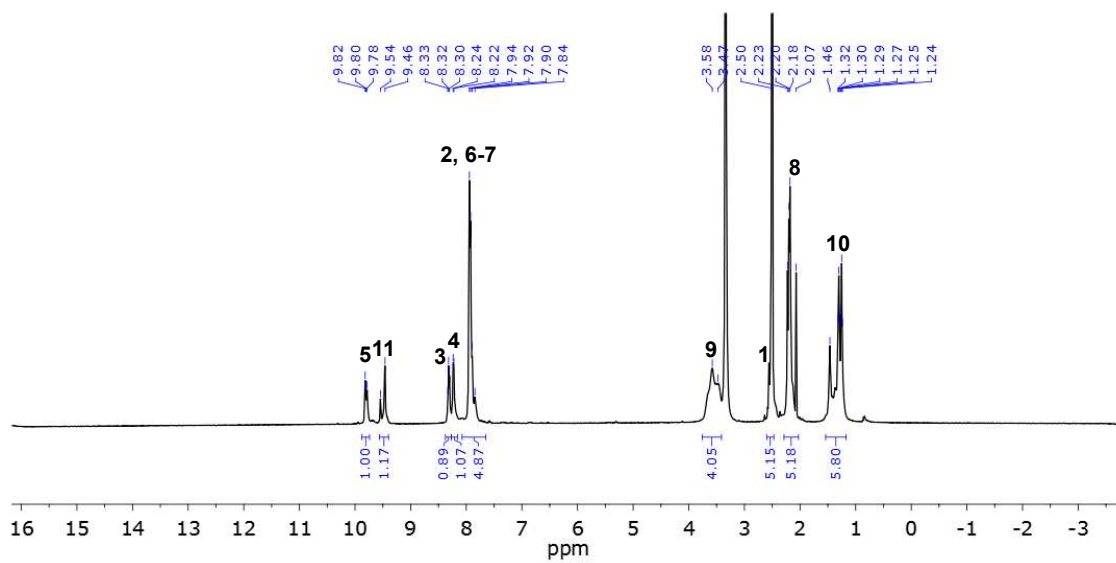


Figure S6.  $^1\text{H}$  NMR spectrum of **5**.

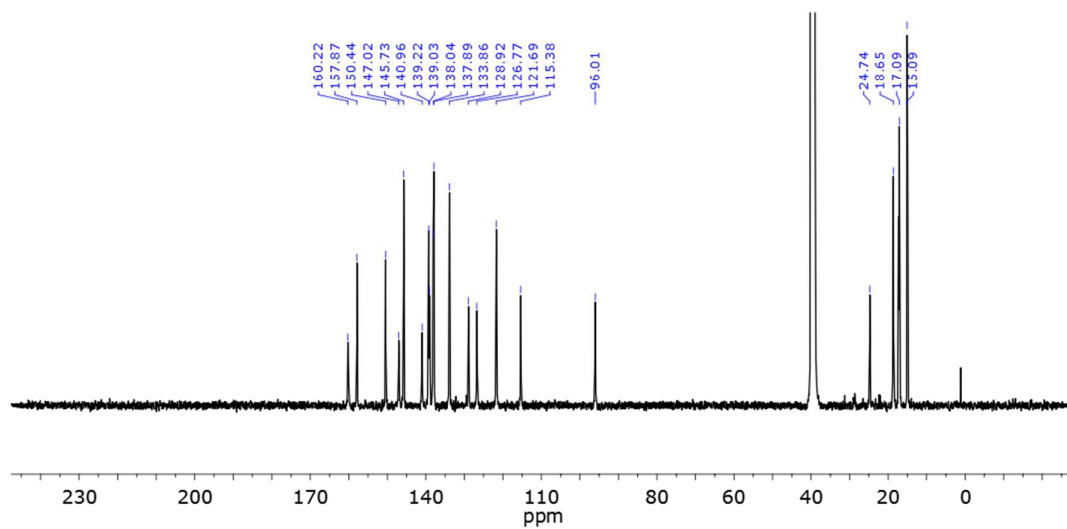
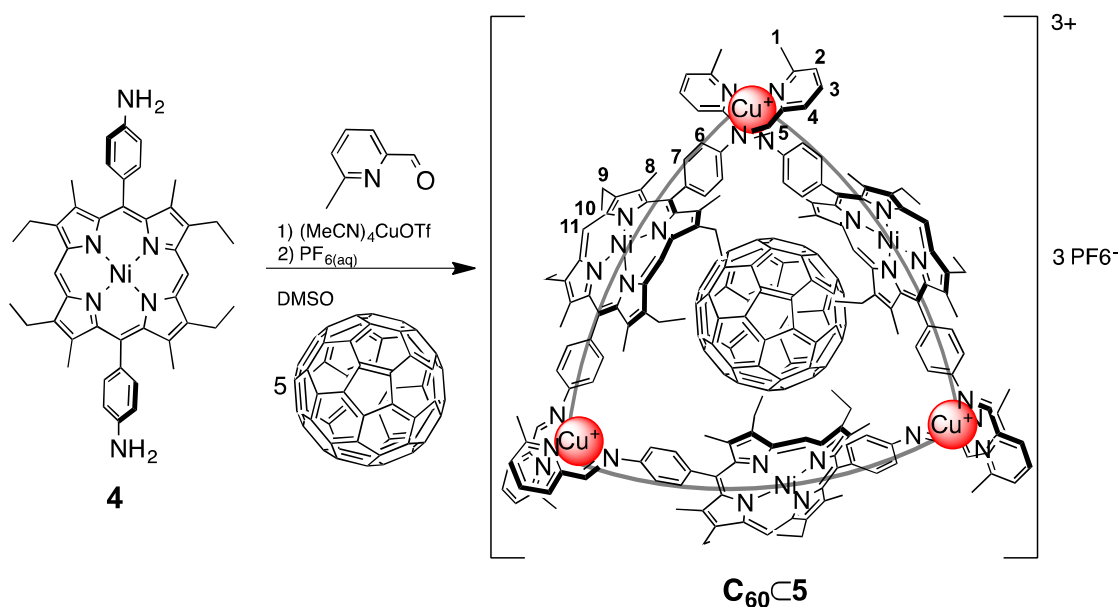


Figure S7.  $^{13}\text{C}$  NMR spectrum of **5**.

## 5. Preparation of C<sub>60</sub>⊂5



4 (4.0 mg, 5.6  $\mu\text{mol}$ ), 6-methyl-2-formylpyridine (1.4 mg, 11.2  $\mu\text{mol}$ ),  $\text{Cu}(\text{MeCN})_4\text{OTf}$  (2.1 mg, 5.6  $\mu\text{mol}$ ) and  $\text{C}_{60}$  (6.7 mg, 9.3  $\mu\text{mol}$ ) were mixed in DMSO (0.6 mL), sonicated and then heated at  $70^\circ\text{C}$  under  $\text{N}_2$  for 16h. The resultant dark red solution was filtered through Celite to remove undissolved  $\text{C}_{60}$  and then added to a saturated solution of aqueous  $\text{KPF}_6$  (3 mL) to precipitate a red solid. The precipitate was isolated over Celite, washed with water (2 x 2 mL) and then dissolved in a 1:1 solution of MeCN/DCM (3 mL). The solution was reduced to dryness to give a red solid (6.7 mg, 1.65  $\mu\text{mol}$ , 88%);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_7$ )  $\delta$  = 9.76 (1H, m, **5**), 9.44 (1H, m, **11**), 8.32 (1H, t,  $J$  = 7.5 Hz, **3**), 8.23 (1H, d,  $J$  = 5.0 Hz, **4**), 7.73-7.97 (5H, m, **2**, **6-7**), 3.43-3.70 (4H, bm, **9**), 2.57 (3H, m, **1**), 2.03-2.30 (6H, m, **8**), 1.16-1.49 (6H, m, **10**);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  = 160.26, 157.90, 150.42, 147.30, 145.71, 140.78, 139.65, 139.20, 139.02, 138.12, 137.95, 133.84, 128.91, 126.73, 121.63, 115.30, 96.06, 24.94, 18.66, 17.07, 15.01;  $m/z$  (HRMS) = 1227.3265 [ $\text{C}_{60}\subset\mathbf{5}$ ] $^{3+}$ ; Elemental Analysis (%) calcd for  $\text{C}_{234}\text{H}_{168}\text{Cu}_3\text{F}_{18}\text{N}_{24}\text{Ni}_3\text{P}_3 \cdot 17\text{H}_2\text{O}$ : C 63.65, H 4.59, N 7.61; found: C 62.84, H 4.96, N 8.43.

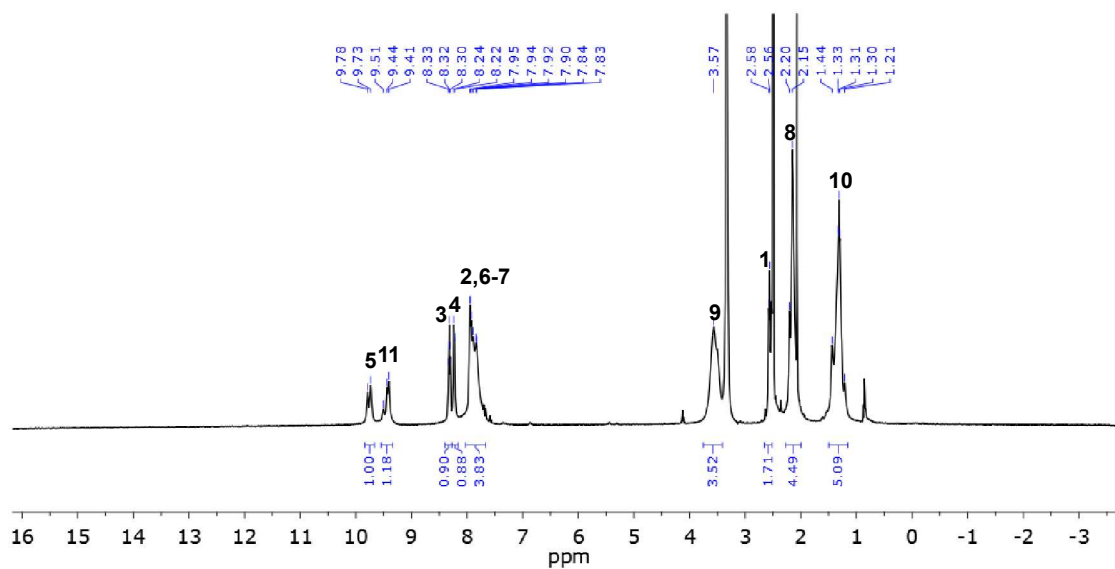


Figure S8.  $^1\text{H}$  NMR spectrum of  $\text{C}_{60}\text{C}_5$ .

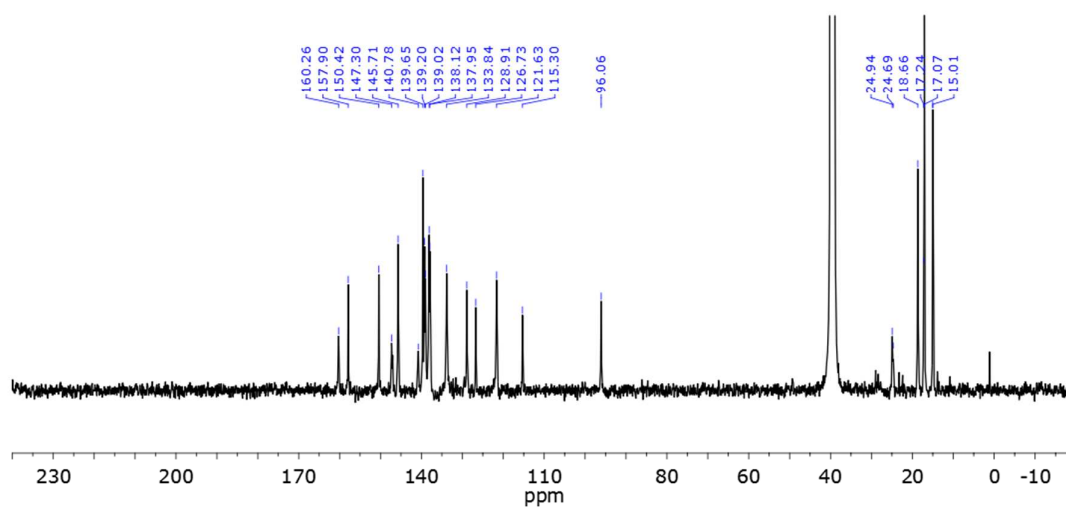
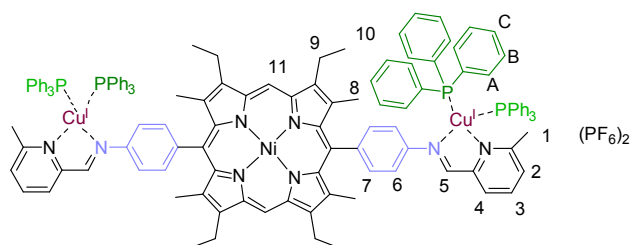


Figure S9.  $^{13}\text{C}$  NMR spectrum of  $\text{C}_{60}\text{C}_5$ .

## 6. Synthesis of 6



**4** (1.4 mg, 1.9  $\mu\text{mol}$ ), 6-methyl-2-formylpyridine (0.5 mg, 4.2  $\mu\text{mol}$ ),  $\text{PPh}_3$  (2.0 mg, 1  $\mu\text{mol}$ ) and  $\text{Cu}(\text{MeCN})_4\text{PF}_6$  (1.4 mg, 3.8  $\mu\text{mol}$ ) were mixed in DMSO (0.6 mL), sonicated and then heated at 70°C under  $\text{N}_2$  for 16 h. The resultant dark red solution was added to a saturated solution of aqueous  $\text{KPF}_6$  (3 mL) to precipitate a red solid. The precipitate was isolated over Celite, washed with water (2 x 2 mL) and then dissolved in a 1:1 solution of MeCN/DCM (3 mL). The solution was reduced to dryness to give a red solid (1.4 mg, 1.65  $\mu\text{mol}$ , 77 %);  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_7$ )  $\delta$  = 9.58 (1H, m, **11**), 9.41 (1H, m, **5**), 8.22-8.24 (1H, m, Hz, **3**), 8.16-18 (1H, d,  $J$  = 7.2 Hz, **4**), 7.54-7.73 (5H, m, **2**, **6-7**), 7.45-7.50 (6H, m, **c**), 7.39-7.44 (12H, m, **b**), 7.27-7.32 (12H, m, **a**), 3.65-3.73 (4H, br, m, **9**), 2.30 (3H, br, **1**), 2.04-2.07 (6H, m, br **8**), 1.52-1.58 (6H, m, **10**);  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO}-d_6$ )  $\delta$  162.28, 158.97, 150.09, 147.45, 145.89, 139.40, 138.25, 138.02, 137.90, 133.49, 133.19, 133.07, 132.67, 132.45, 131.60, 131.53, 130.42, 129.13, 129.08, 128.96, 128.89, 128.07, 127.48, 121.81, 115.27, 96.25, , 25.49, 18.83, 17.46, 15.17;  $^{31}\text{P}$  NMR (162 MHz, 298 K, DMSO):  $\delta$  = 1.1 (br, s,  $\text{PPh}_3$ ) -144.0 (heptet,  $J$  = 710.4 Hz,  $\text{PF}_6^-$ ).  $m/z$  (HRMS) = 1049.8109 [**6**] $^{2+}$ ; Elemental Analysis (%) calcd for  $\text{C}_{130}\text{H}_{146}\text{Cu}_2\text{F}_{12}\text{N}_8\text{NiO}_{15}\text{P}_6 \cdot 15 \text{H}_2\text{O}$ : C 58.69, H 5.53, N 4.21; found: C 58.79, H 4.18, N: 4.33.

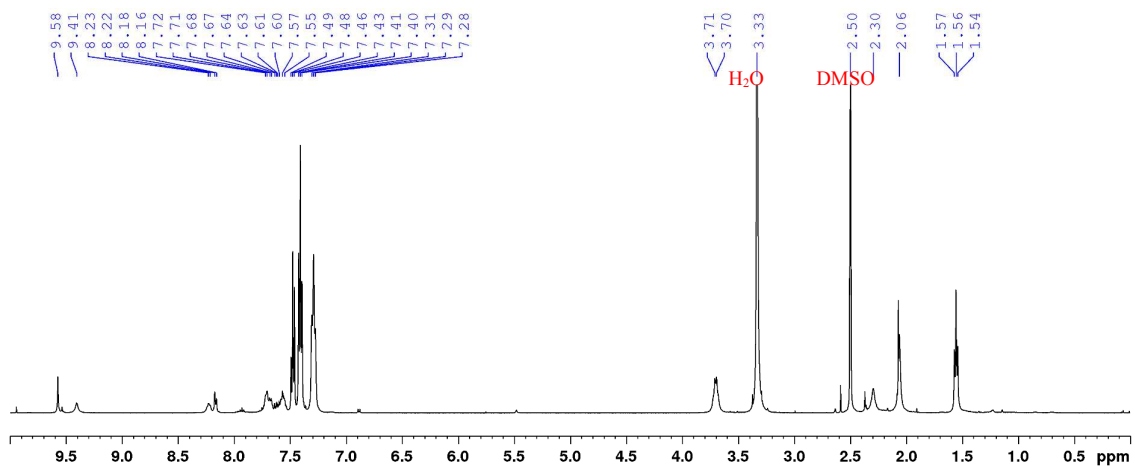


Figure S10. <sup>1</sup>H NMR spectrum of **6**.

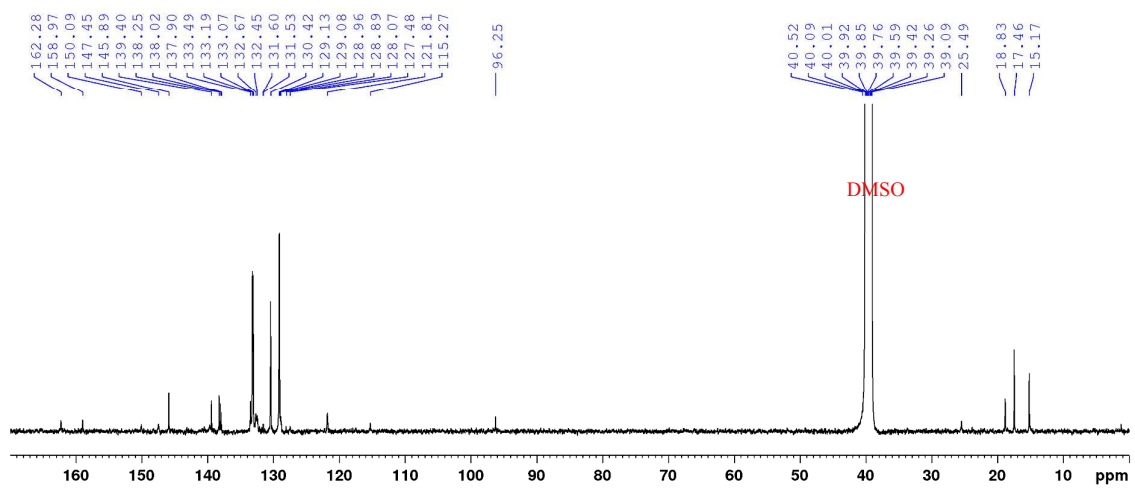


Figure S11. <sup>13</sup>C NMR spectrum of **6**.

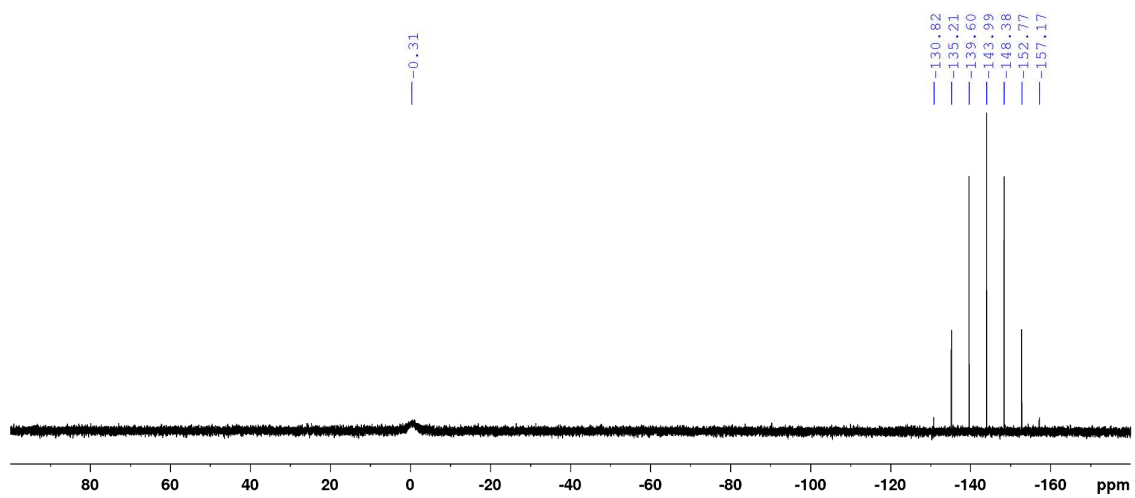
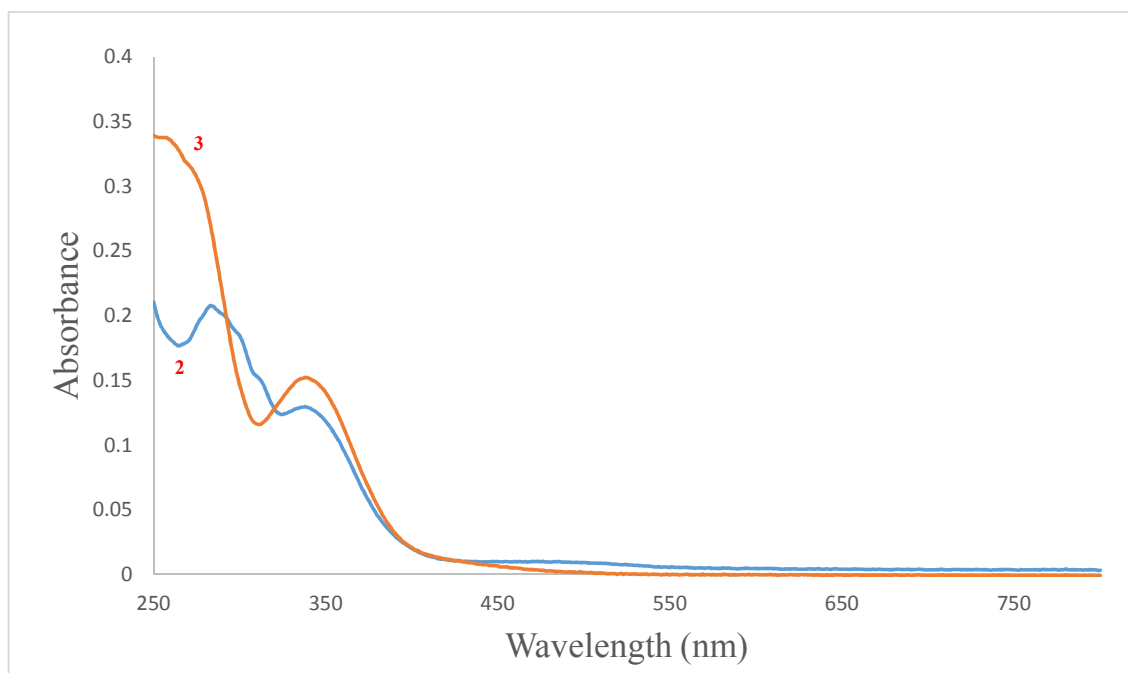
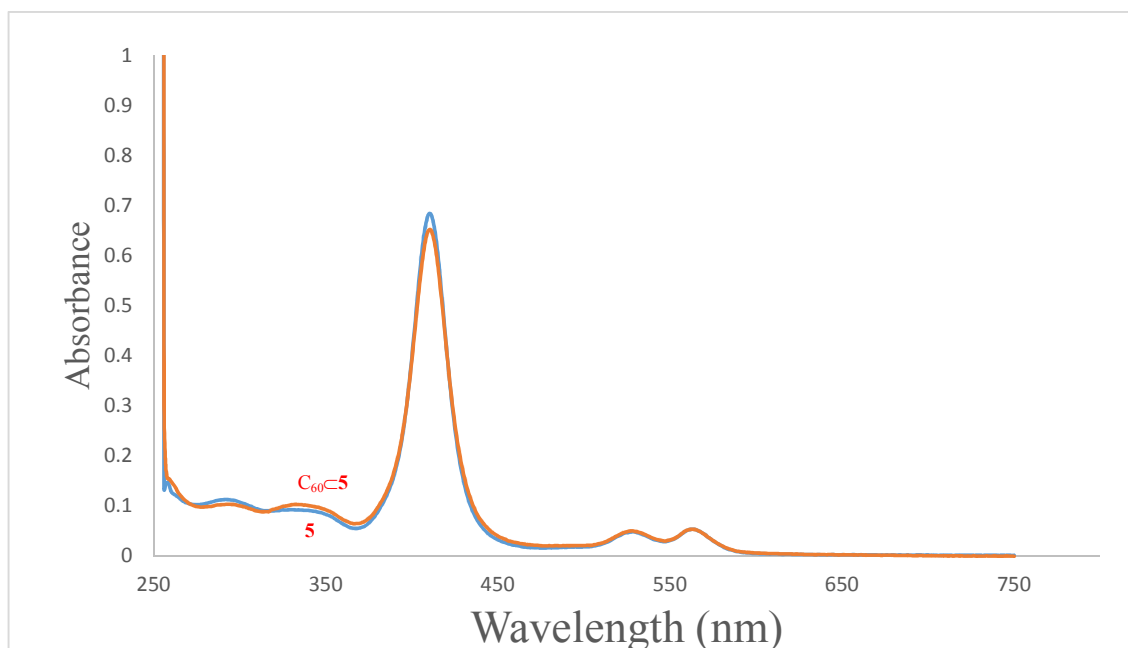


Figure S12. <sup>31</sup>P NMR spectrum of **6**.

## 7. Electronic Absorption Spectra of 2 and 3

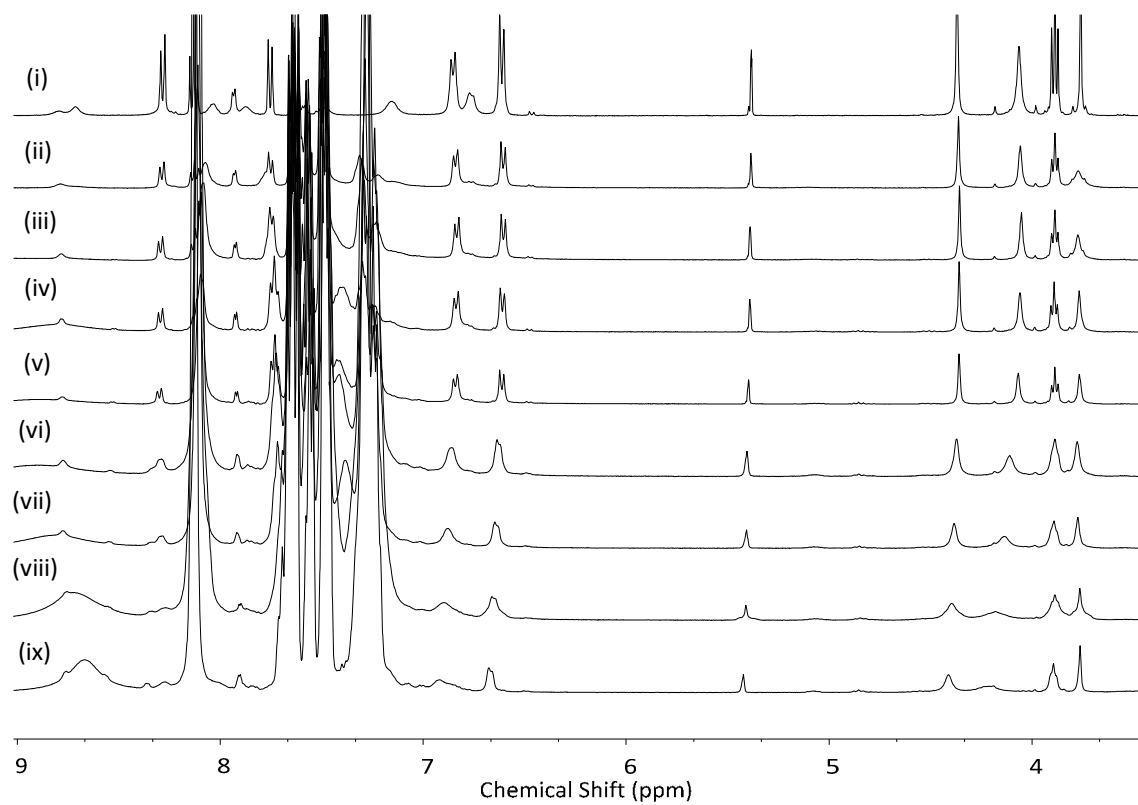


**Figure S13.** Comparison of the electronic absorption spectra of **2** (blue) and **3** (orange) in MeCN

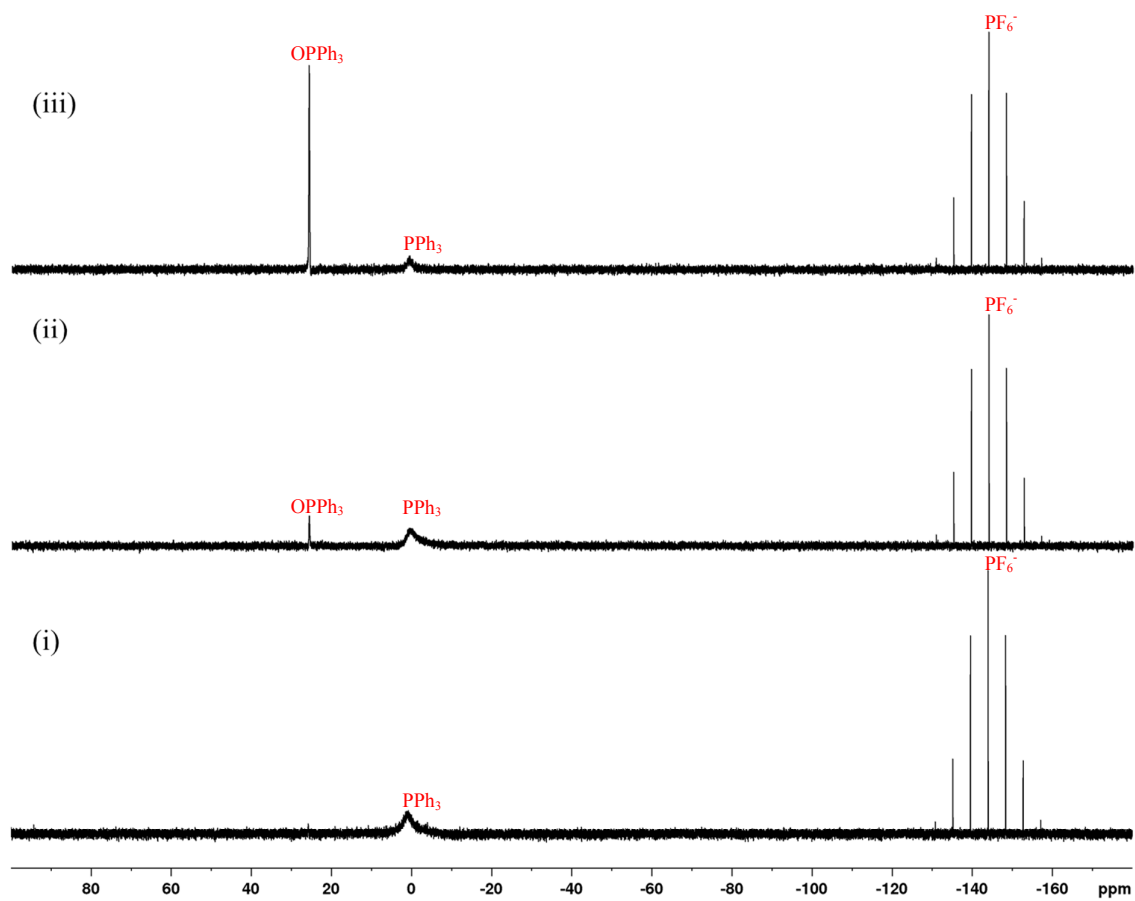


**Figure S14.** Electronic Absorption Spectra of **5** (blue) and C<sub>60</sub>-**5** (orange) in DMSO

## 8. $^1\text{H}$ NMR of De-threading/Rethreading of **2**



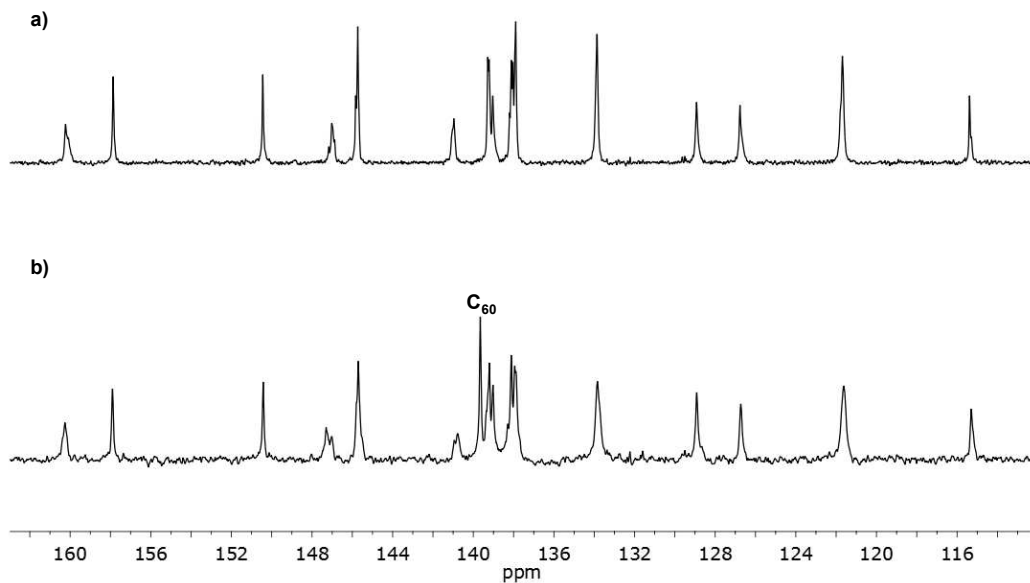
**Figure S15.** (i)  $^1\text{H}$  NMR spectrum of **2**. (ii) – (ix)  $^1\text{H}$  NMR spectrum of **2** after 2 – 8 oxidation cycles



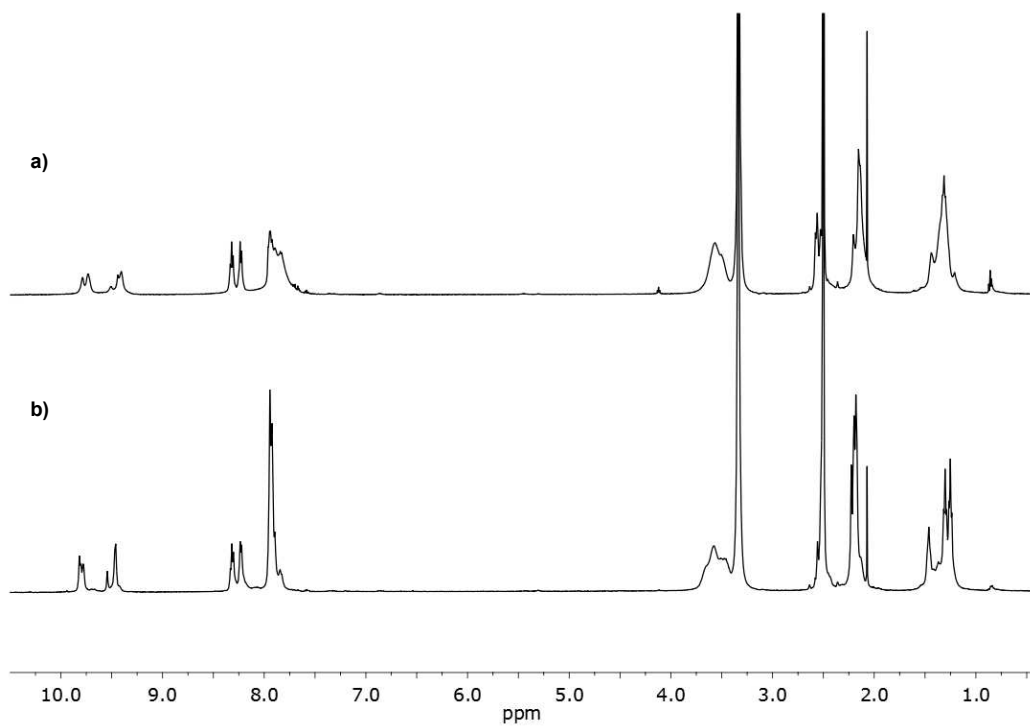
**Figure S16.** Representative  $^{31}\text{P}$  NMR spectra of the oxidation of dethreaded **2**; (i) **2** after the addition of 2 equiv. of  $\text{PPh}_3$ , (ii) Deathreaded **2** after the addition of MoCat (50 mol %) and heating at 65 °C for 90 minutes, (iii) Deathreaded **2** after 12 hours of heating and catalytic oxidation of  $\text{PPh}_3$ .



## 9. Host-Guest Chemistry of **5**

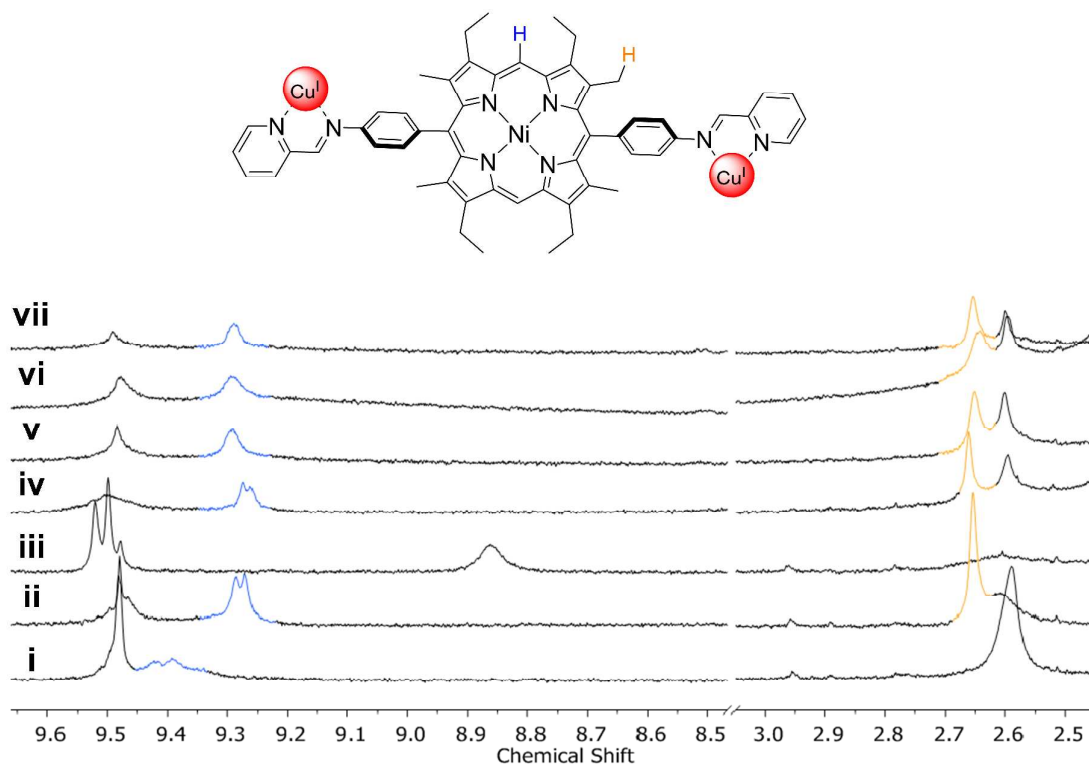


**Figure S17:** Selected region of  $^{13}\text{C}$  NMR spectra of a) **5** and b)  $\text{C}_{60}\text{C}_5$ , highlighting the resonance corresponding to  $\text{C}_{60}$ .



**Figure S18:**  $^1\text{H}$  NMR spectra for a) **5** and b)  $\text{C}_{60}\text{C}_5$ .

## 10. PPh<sub>3</sub> Fueled Uptake and Release of C<sub>60</sub>



**Figure S19:** **i** shows the <sup>1</sup>H NMR spectrum of **5** (blue and orange signals correspond to blue and orange labeled protons respectively), **ii** shows <sup>1</sup>H NMR of C<sub>60</sub>⊂**5**, **iii** shows <sup>1</sup>H NMR of reaction mixture after disassembly to a dynamic combinatorial library upon PPh<sub>3</sub> addition, disassembly of **5**, and release of C<sub>60</sub>, **iv** shows the mixture after all PPh<sub>3</sub> has been fully converted to OPPh<sub>3</sub> resulting in the reformation of C<sub>60</sub>⊂**5**, **v**, **vi**, and **vii** show the mixture after two, three, and four PPh<sub>3</sub> addition/oxidation cycles respectively (only peaks which show greatest shift upon C<sub>60</sub> binding ( are shown for clarity).

## 11. ESI-Mass Spectroscopy

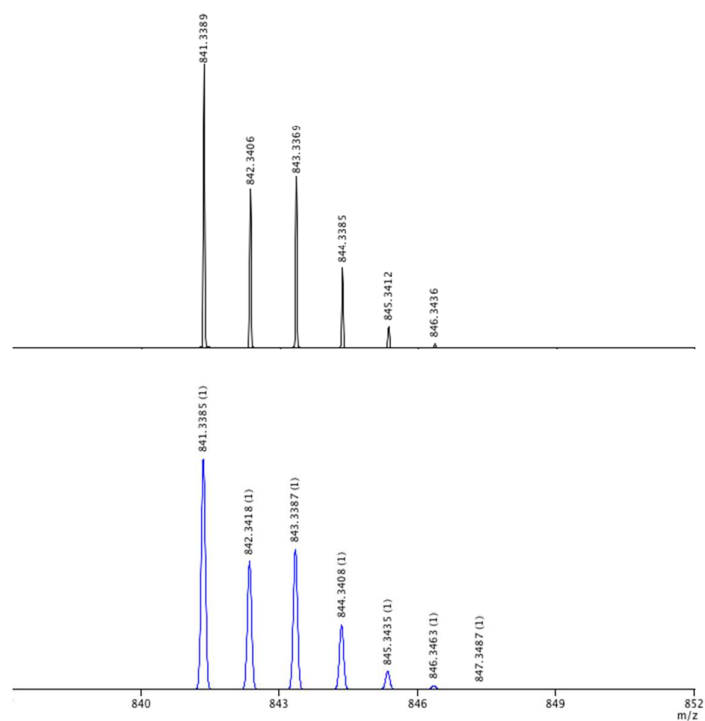


Figure S20: HRMS of  $[2]^{3+}$  (top = observed, bottom = theoretical).

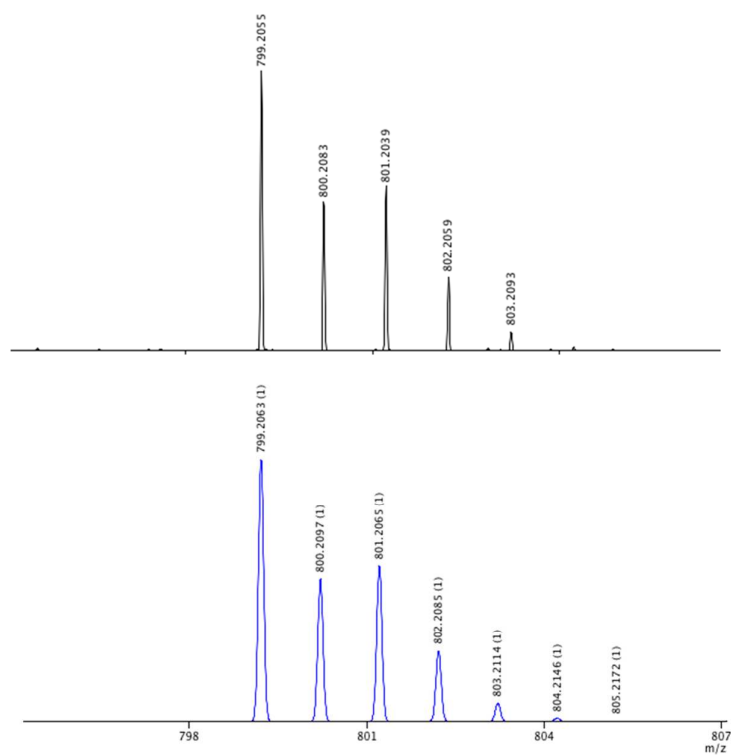


Figure S21: HRMS of  $[3]^{3+}$  (top = observed, bottom = theoretical).

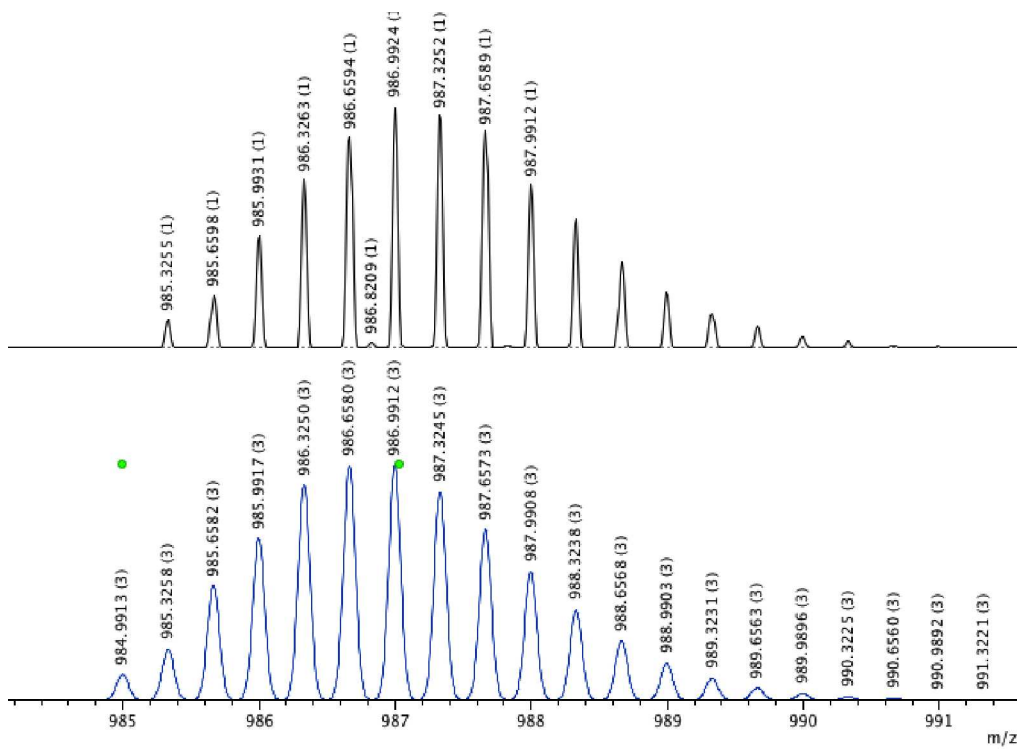


Figure S22: HRMS of  $[5]^{3+}$  (top = observed, bottom = theoretical).

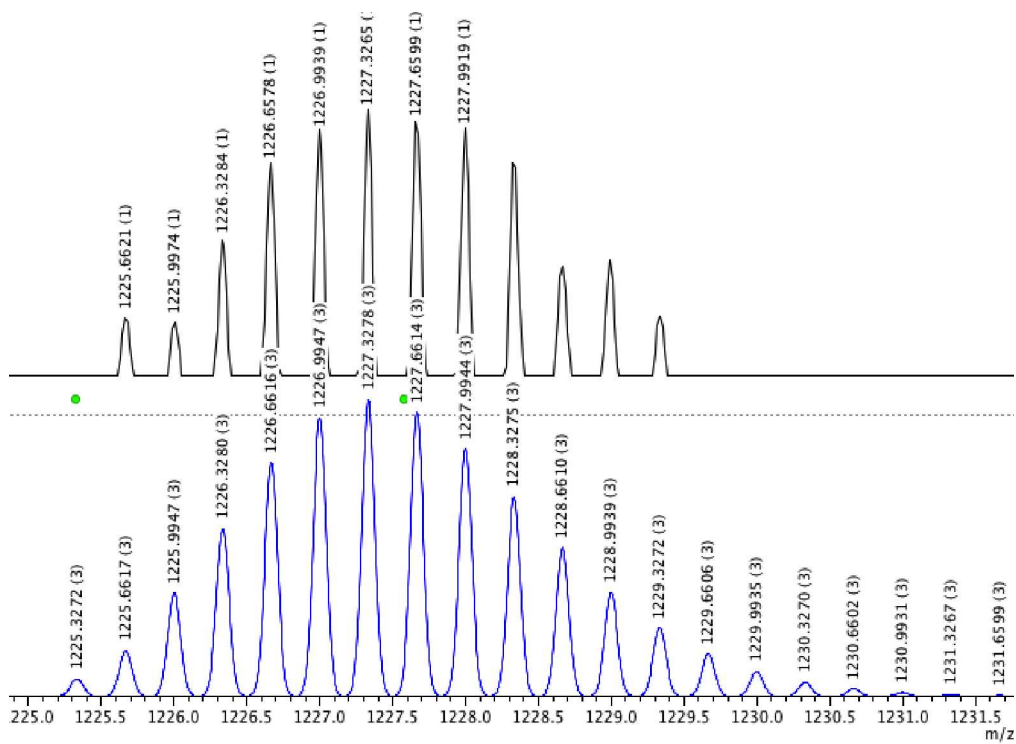
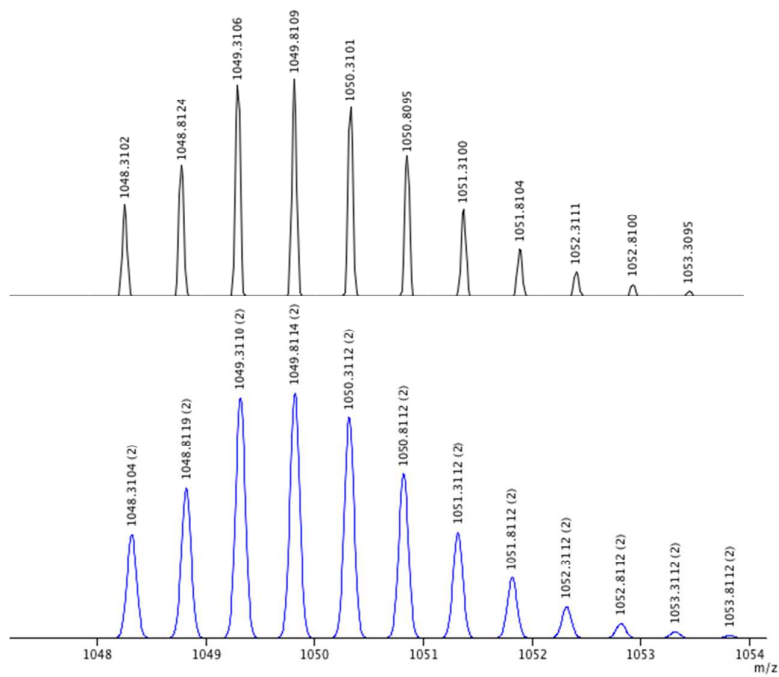


Figure S23: HRMS of  $[C_{60}C_5]^{3+}$  (top = observed, bottom = theoretical)



**Figure S24:** HRMS of  $6^{3+}$  (top = observed, bottom = theoretical)

## 12. References

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