

## Supporting Information

# A $\text{H}_2@C_{60}$ $^1\text{H}$ NMR Probe for Sensitively Detecting the Supramolecular Interactions Between a Molecular Tweezer and $C_{60}$

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# 1. Experimental section

## 1.1 General

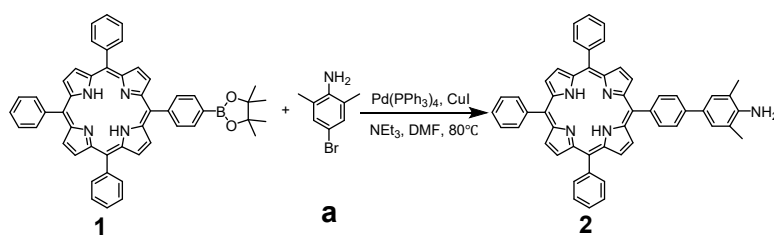
Commercially available solvents and reagents were used without further purification unless otherwise mentioned. Compound **1**, **2**, **a**, **b** was synthesized according to reported procedures<sup>1-3</sup>, the synthesis of  $H_2@C_{60}$  was performed by Komatsu's eight-step "molecular surgery" method<sup>4-6</sup>. Thin-layer chromatography (TLC) was carried out on HSGF 254 silica gel plates with a coating layer thickness of about 0.2 mm (Yantai Xincheng Silica Gel Materials Co., Ltd., Yantai, China). <sup>1</sup>H NMR spectra were recorded on a Bruker Bruker Avance III 400 MHz at 298 K, and the chemical shifts were reported relative to tetramethylsilane (TMS,  $\delta = 0$ ) in ppm. <sup>13</sup>C NMR spectra were on a Bruker Bruker Avance III 400 MHz at 298 K and the chemical shifts were reported relative to CDCl<sub>3</sub> ( $\delta = 77.00$ ) in ppm. HRMS were performed using a Shimadzu LCMS-IT-TOF spectrometer. UV-Vis absorption spectra were recorded on a Shimadzu UV2600 spectrophotometer and all absorption spectra were recorded at room temperature.

## 1.2 Crystallography

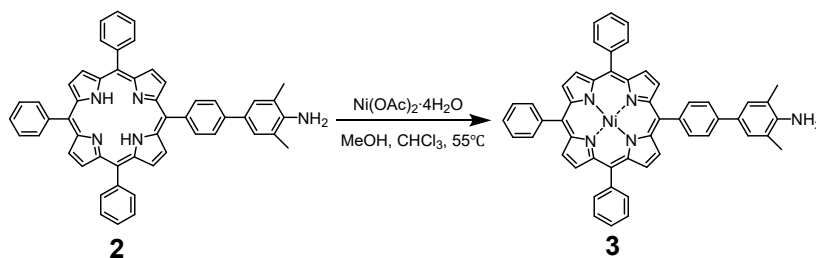
X-ray analyses were performed on a SMART APEX equipped with CCD detector (Bruker) using GaK $\alpha$  (graphite, monochromated,  $\lambda = 1.3414$  Å). The structures were solved by the direct method of SHELXS-2013/2014 and refined using the SHELXS-2013/2014 program.<sup>7-9</sup> The positional parameters and thermal parameters of non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares method. Hydrogen atoms were placed at calculated positions and refined riding on their corresponding carbon atoms. Single crystals of **5** was obtained slow diffusion of isopropanol into the 1,2-dichloroethane solution of molecular tweezer **5** at room temperature.

CCDC 2346340 (**5**), contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

## 1.3 Synthetic details

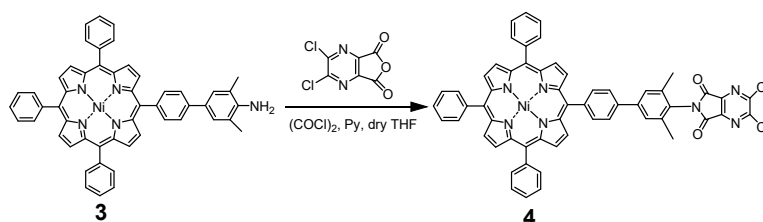


Compound **1**, **a** and **2** was synthesized according to reported procedures<sup>1-3</sup>.



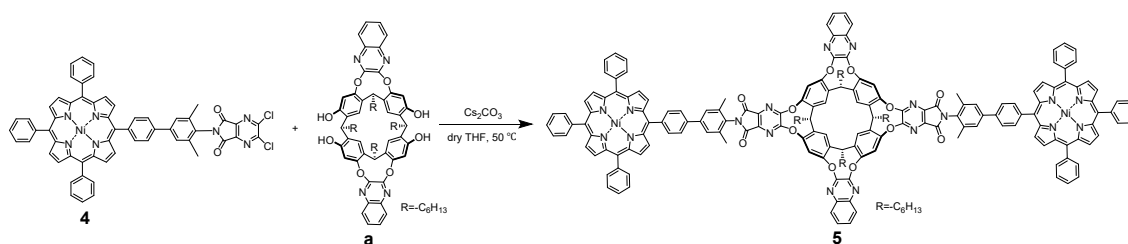
**3:** Under argon atmosphere, compound **2** (500 mg, 0.68 mmol), nickel acetate tetrahydrate (1.6 g, 6.8 mmol), methanol (100 mL) and chloroform (200 mL) were added to 500 mL three-neck flask, stirring to dissolve the raw materials completely. Reflux was heated to 65°C for about 6 hours, and the reaction progress was monitored with TLC. After the reaction was completed, the reaction was quenched with water, extracted with CH<sub>2</sub>Cl<sub>2</sub> and washed with brine. The organic phase was then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and the solvent was removed *in vacuo*. The raw product was purified on silica gel columns using petroleum ether (PE)/dichloromethane (DCM) = 3/4 (v/v) as the eluent., compound **3** was obtained as a red solid (470 mg 87.3%).

**3:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.84 (d, *J* = 4.9 Hz, 2H), 8.75 – 8.72 (m, 6H), 8.02 – 7.98 (m, 8H), 7.84 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.62 (m, 9H), 7.48 (s, 2H), 2.35 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 142.91, 142.79, 142.76, 142.74, 141.05, 140.74, 138.85, 134.27, 133.86, 132.48, 132.32, 127.86, 127.44, 127.01, 125.05, 123.20, 119.19, 119.08, 119.04, 18.22. HRMS (MALDI-TOF-MS): *m/z*: [M+H]<sup>+</sup>: calcd for C<sub>52</sub>H<sub>38</sub>N<sub>5</sub>Ni<sup>+</sup> = 790.2481; found: 790.2496.



**4:** Compound **3** (500 mg, 0.63 mmol), 2,3-Dichlorofuro[3,4-b]pyrazine-5,7-dione (166 mg, 0.76 mmol) and anhydrous 1,4-dioxane (80 mL) were added to a 250 mL three-necked flask, stirred to dissolve the raw materials completely, and heated to 90 °C for 1 hour. After the reaction, it was cooled to room temperature, 128 μL pyridine (1.18 mmol) was added, 61 μL oxalyl chloride (0.59 mmol) was dissolved in 10 mL anhydrous 1, 4-dioxane and slowly added to the reaction system. After the drip is finished, the reaction is heated to 80°C for 12 hours. After the reaction was completed, the filtrate was pumped and collected. The raw product was purified on silica gel columns using petroleum ether (PE)/dichloromethane (DCM) = 1/1 (v/v) as the eluent. Compound **4** was obtained as a red solid (170 mg, 27.2%).

**4:** <sup>1</sup>H NMR (400 MHz, acetone-*d*<sub>6</sub>): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 8.86 – 8.70 (m, 9H), 8.09 (d, *J* = 7.7 Hz, 2H), 8.04 – 7.98 (m, 6H), 7.89 (d, *J* = 7.7 Hz, 2H), 7.68 (t, *J* = 4.6 Hz, 12H), 2.32 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm): δ 161.26, 154.29, 143.41, 142.96, 142.72, 142.70, 142.59, 140.89, 140.56, 139.45, 136.99, 134.22, 133.72, 132.31, 132.24, 132.10, 127.91, 127.79, 127.76, 126.88, 125.77, 119.06, 118.39, 18.46. HRMS (MALDI-TOF-MS): *m/z*: [M]<sup>+</sup>: calcd for C<sub>58</sub>H<sub>35</sub>Cl<sub>2</sub>N<sub>7</sub>NiO<sub>2</sub><sup>+</sup>: 991.1599; found: 991.1578.



**5:** Under argon atmosphere, compound **a** (10.75 mg, 0.01 mmol), compound **4** (21.3 mg, 0.02 mmol), cesium carbonate (13 mg, 0.04 mmol) and anhydrous tetrahydrofuran (25 mL) were added to a 50 mL three-necked flask. Reaction at 50°C for about 6 hours. At the end of the reaction, the solvent was

removed by vacuum, The raw product was purified on silica gel columns using petroleum ether (PE)/dichloromethane (DCM) = 1/4 (v/v). Compound **5** was obtained as a red solid (21.2 mg, 73.1%).

**5**:  $^1\text{H}$  NMR (400 MHz, Chloroform-d, ppm):  $\delta$  8.73 (d,  $J = 4.9$  Hz, 4H), 8.62 (d,  $J = 5.0$  Hz, 4H), 8.54 (dd,  $J = 8.7, 4.9$  Hz, 8H), 8.30 (s, 4H), 8.08 (d,  $J = 7.9$  Hz, 4H), 8.04–7.95 (m, 8H), 7.99–7.96 (m, 4H), 7.82 (s, 2H), 7.76 (d,  $J = 21.2$  Hz, 2H), 7.69–7.6 (m, 14H), 7.46–7.44 (dd,  $J = 6.3, 3.5$  Hz, 4H), 7.40–7.36 (m, 6H), 7.30 (d, 10H), 5.70 (t,  $J = 8.0$  Hz, 2H), 5.63 (t,  $J = 8.1$  Hz, 2H), 2.36 (s, 12H), 1.76 (s, 8H), 1.37–1.35 (m, 16H), 1.30–1.23 (m, 16H).  $^{13}\text{C}$  NMR (101 MHz, Chloroform-d, ppm):  $\delta$  160.82, 156.77, 152.11, 151.25, 151.04, 141.57, 141.50, 141.40, 140.57, 139.97, 139.57, 138.85, 137.38, 135.83, 134.67, 133.22, 132.67, 132.43, 131.14, 131.04, 127.42, 126.42, 125.80, 125.56, 124.79, 117.75, 30.86, 30.49, 29.12, 28.68, 28.35, 26.94, 21.66, 17.48, 13.06. HRMS (MALDI-TOF-MS):  $m/z$ ;  $[\text{M}]^+$ : calcd for  $\text{C}_{184}\text{H}_{142}\text{N}_{18}\text{Ni}_2\text{O}_{12}^+$ : 2910.9762; found: 2910.9759.

## 2. Characterization spectra for the compounds

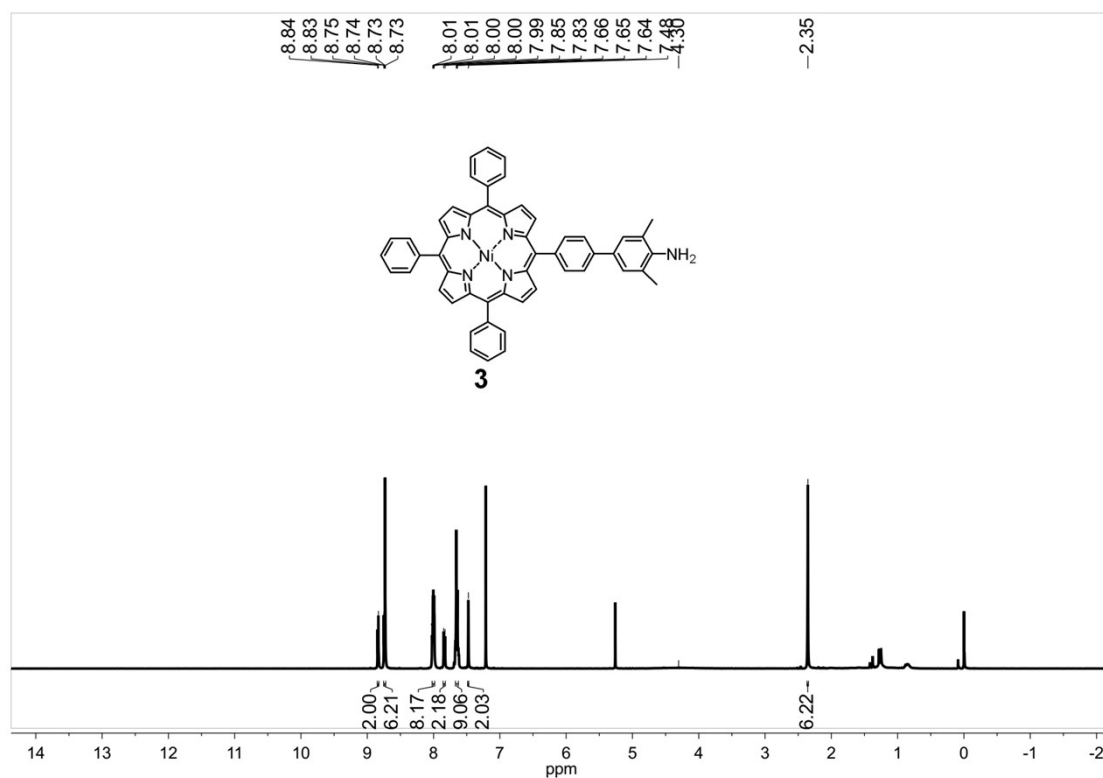


Figure S1. <sup>1</sup>H NMR (400 MHz) spectrum of **3** in CDCl<sub>3</sub>.

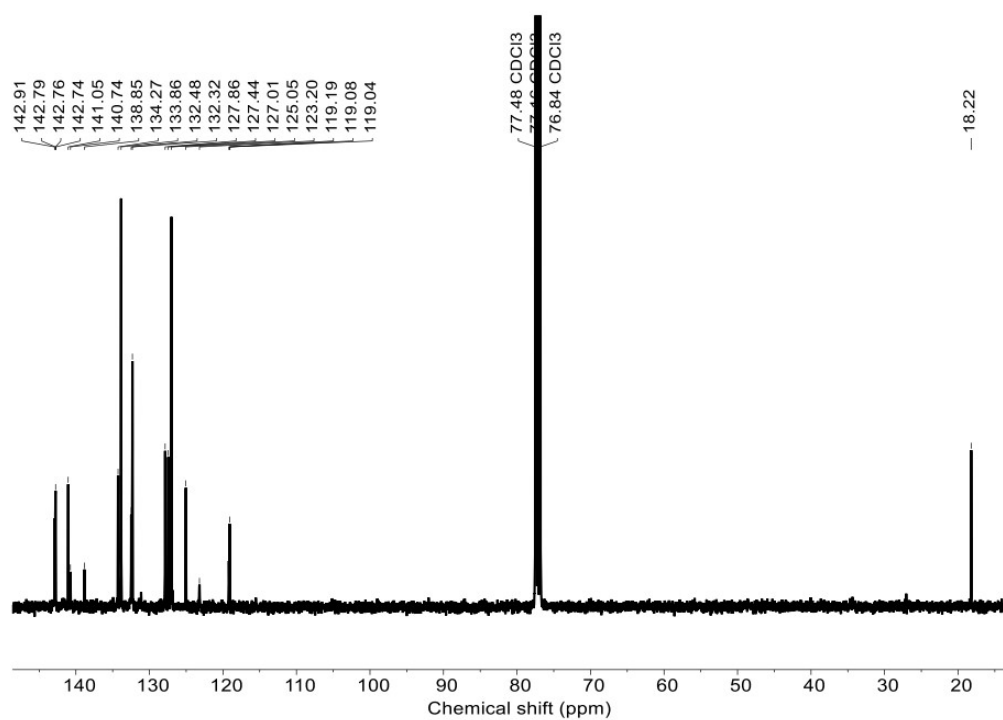
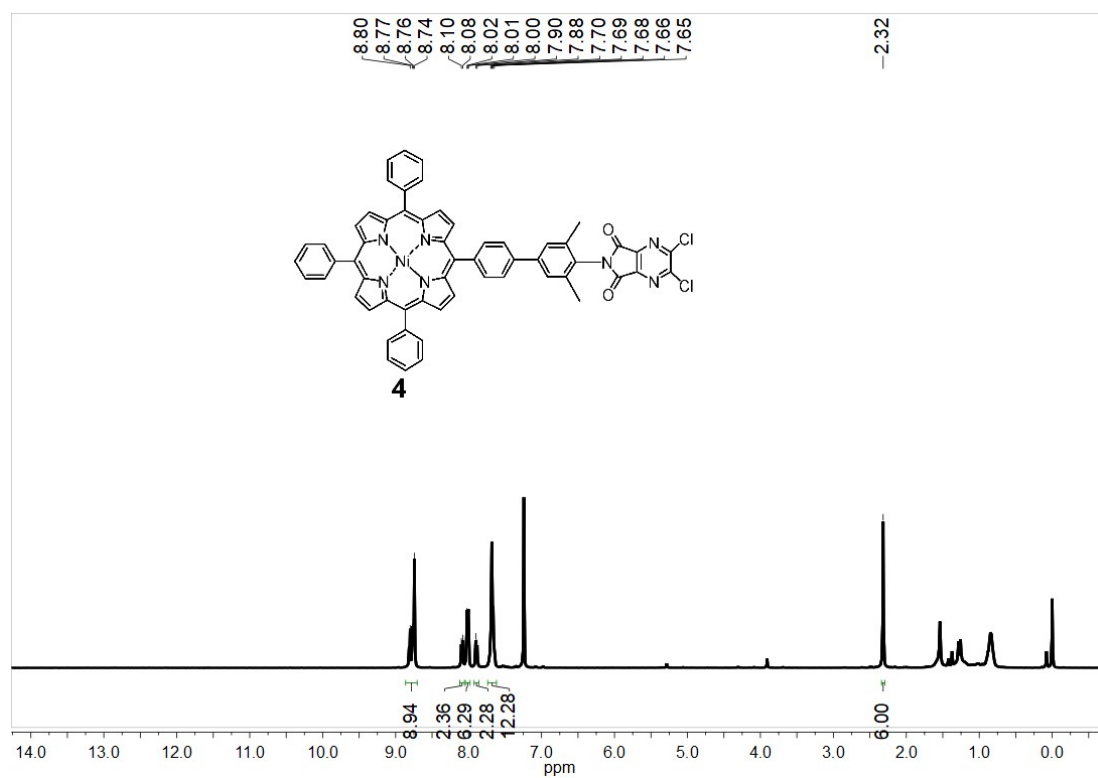
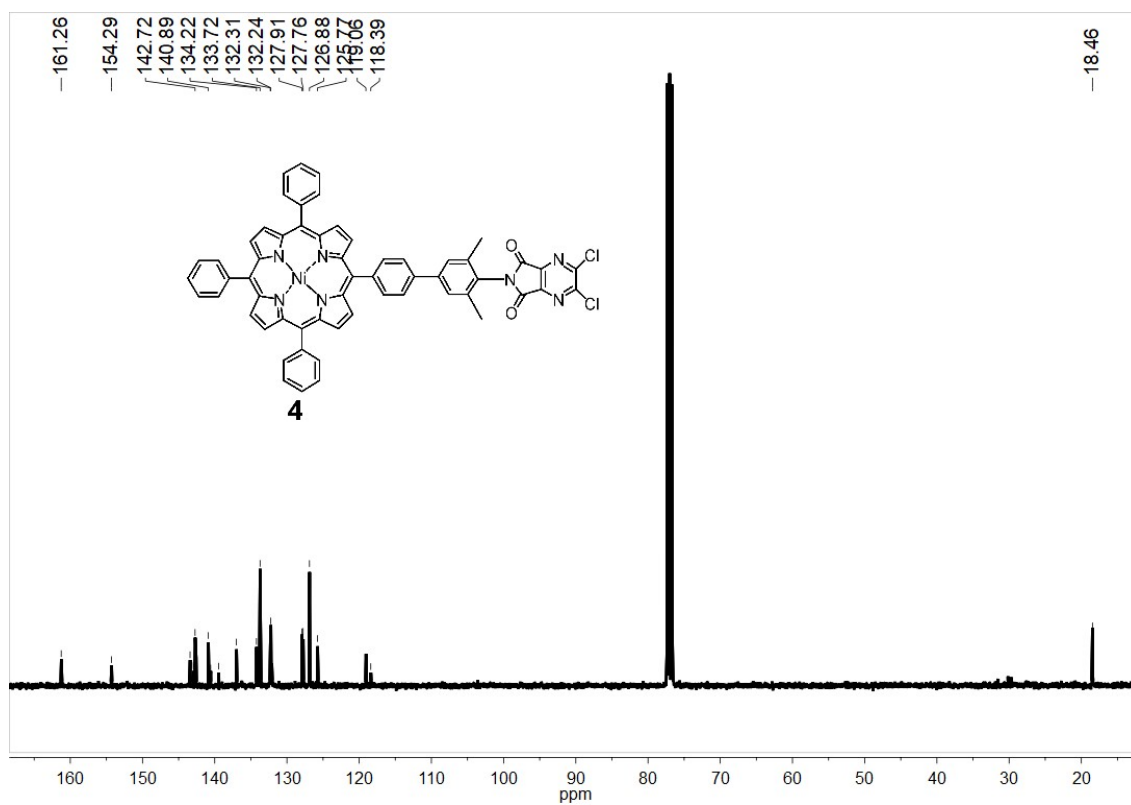


Figure S2. <sup>13</sup>C NMR (101 MHz) spectrum of **3** in CDCl<sub>3</sub>.



**Figure S3.** <sup>1</sup>H NMR (400 MHz) spectrum of **4** in CDCl<sub>3</sub>.



**Figure S4.** <sup>13</sup>C NMR (101 MHz) spectrum of **4** in CDCl<sub>3</sub>.

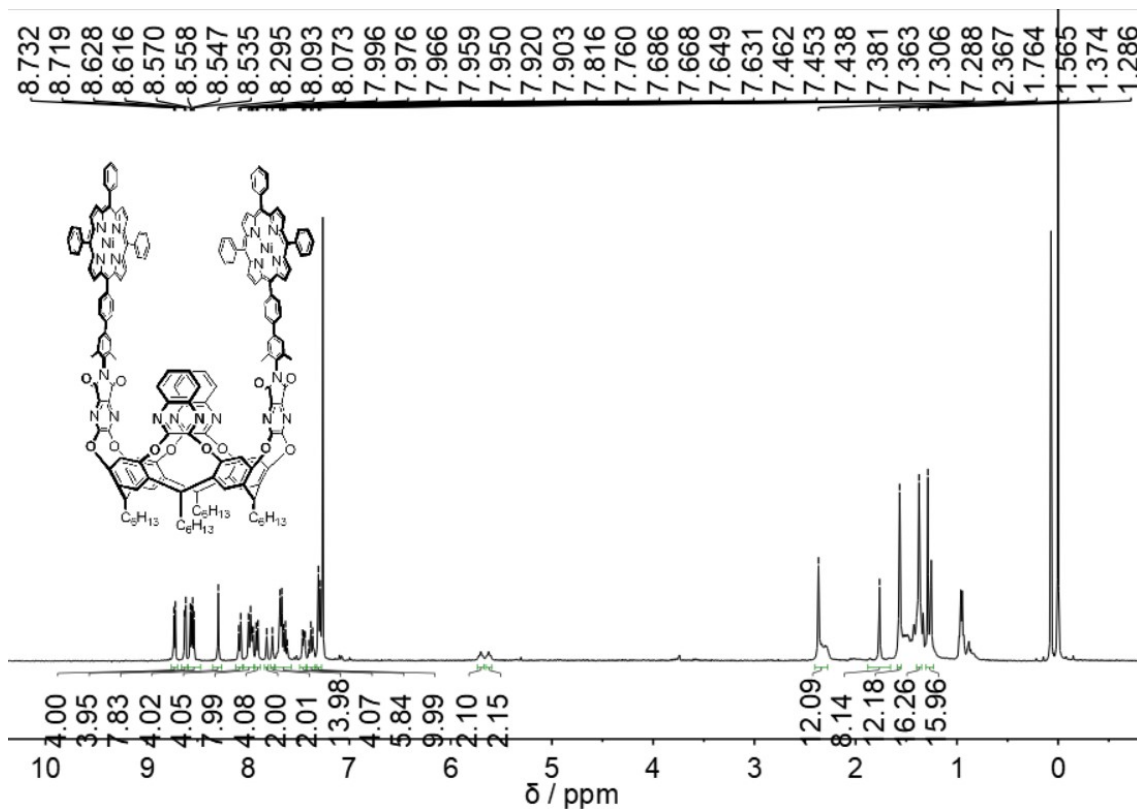


Figure S5.  $^1H$  NMR (400 MHz) spectrum of **5** in  $CDCl_3$ .

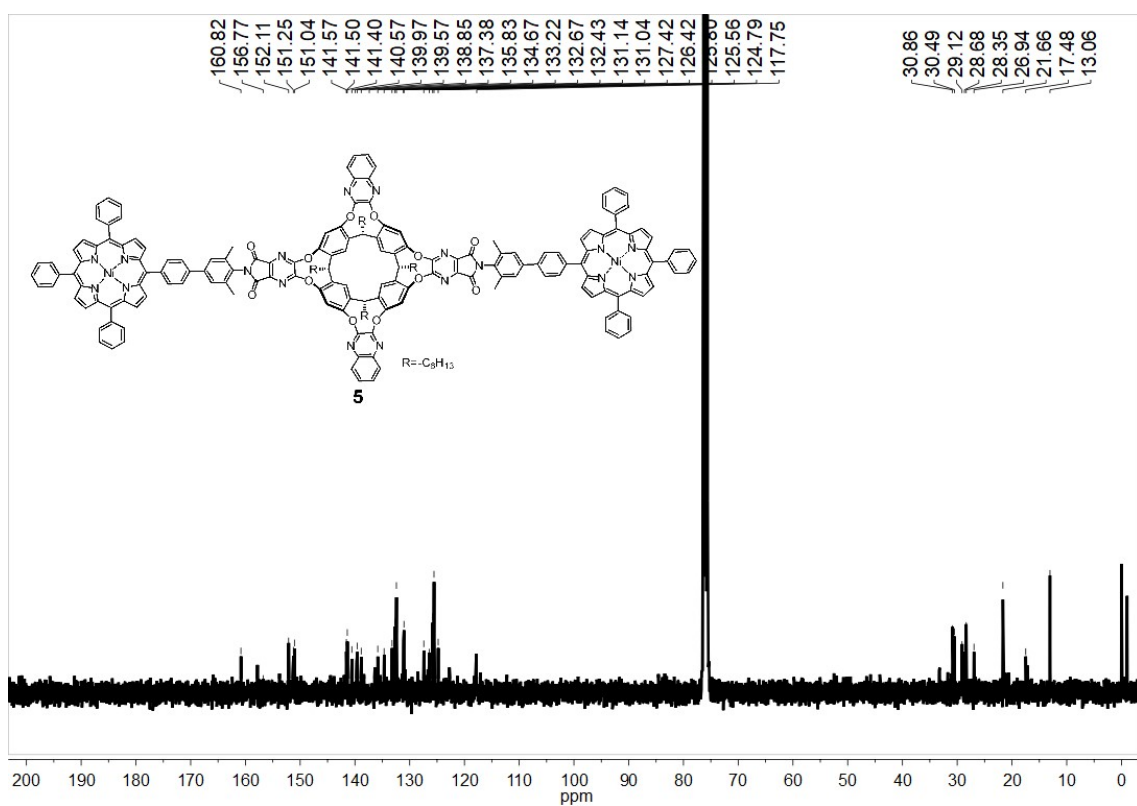
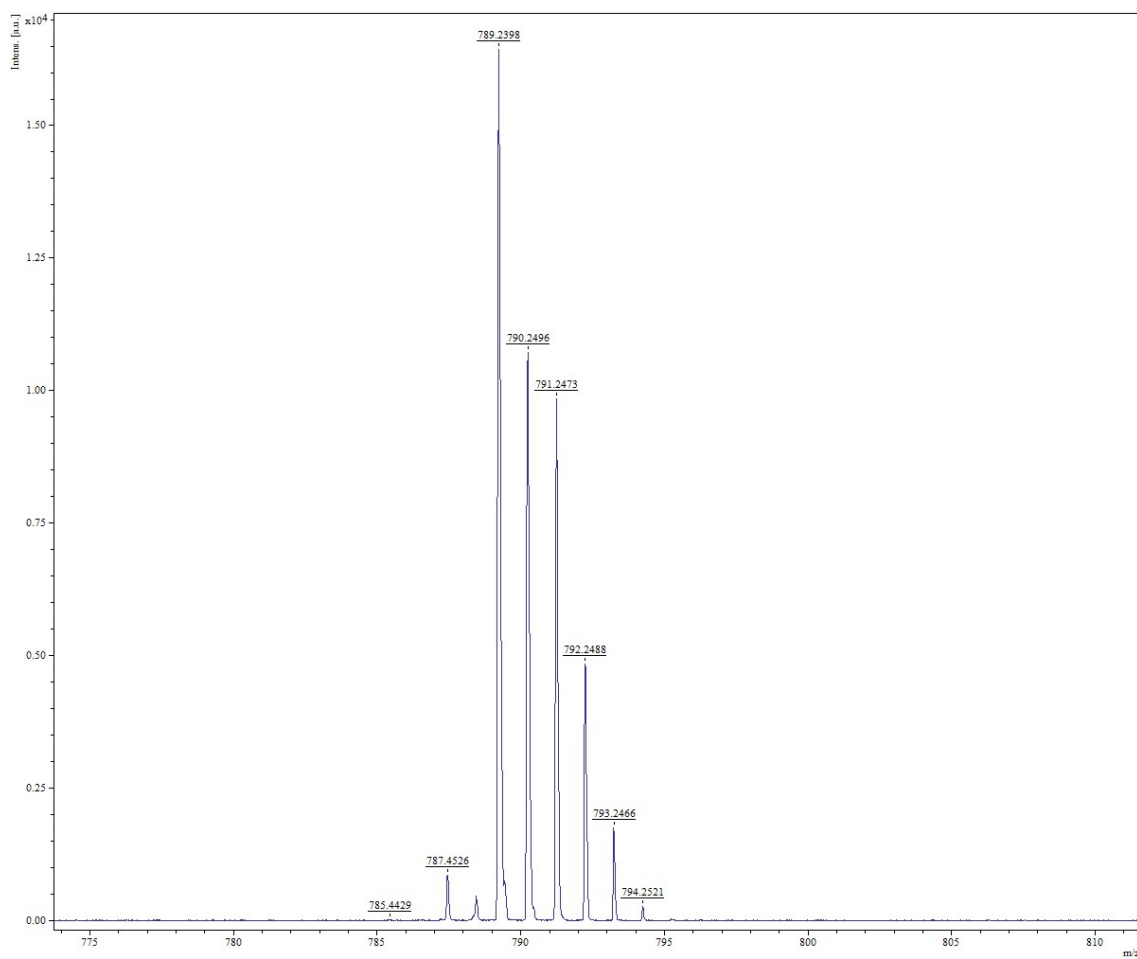
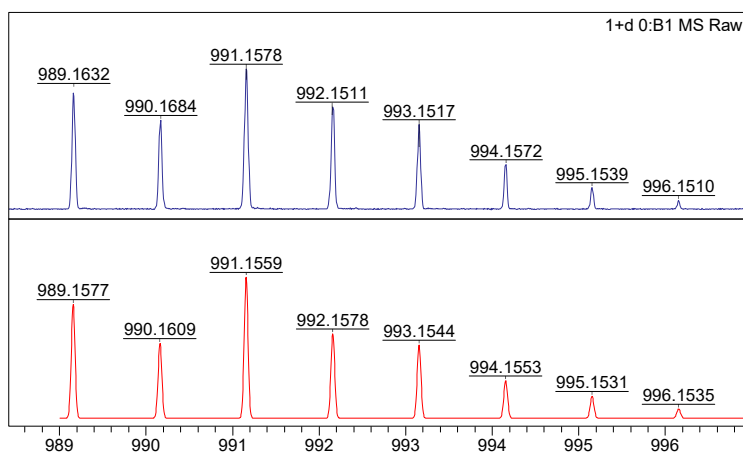


Figure S6.  $^{13}C$  NMR (101 MHz) spectrum of **5** in  $CDCl_3$ .

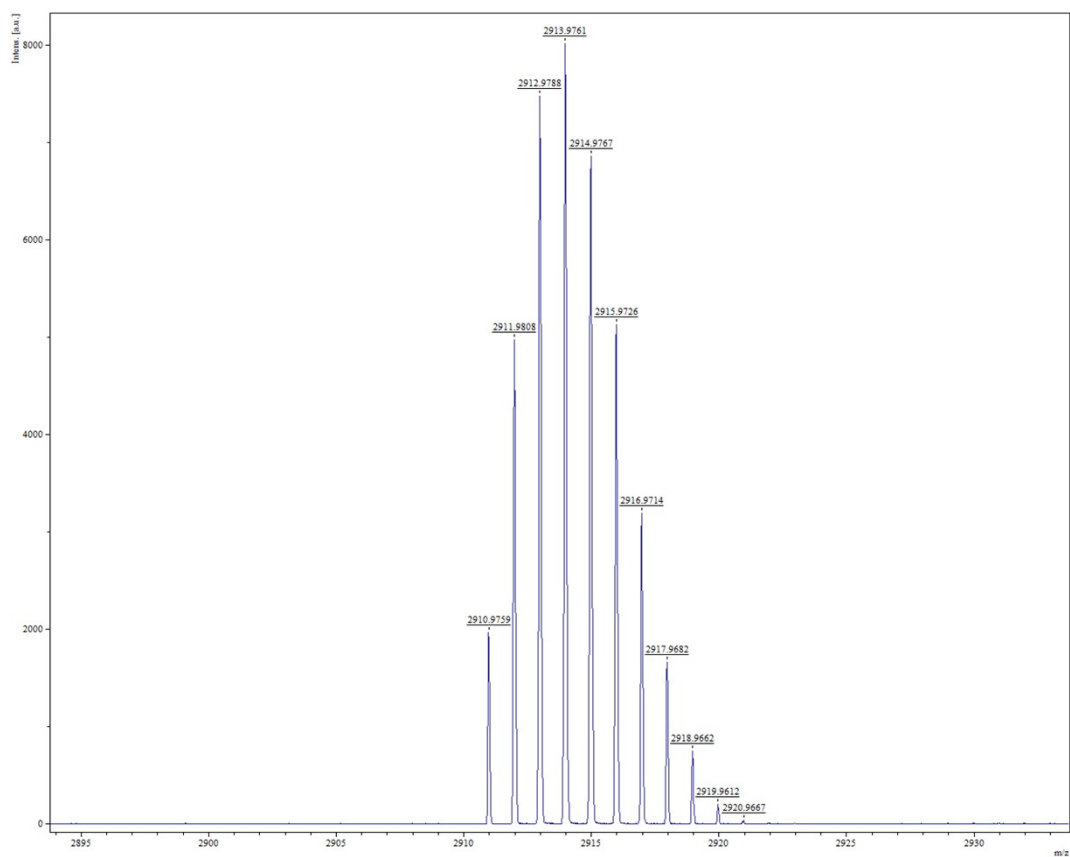


**Figure S7.** HRMS (MALDI-TOF-MS) of **3** in CH<sub>2</sub>Cl<sub>2</sub>.

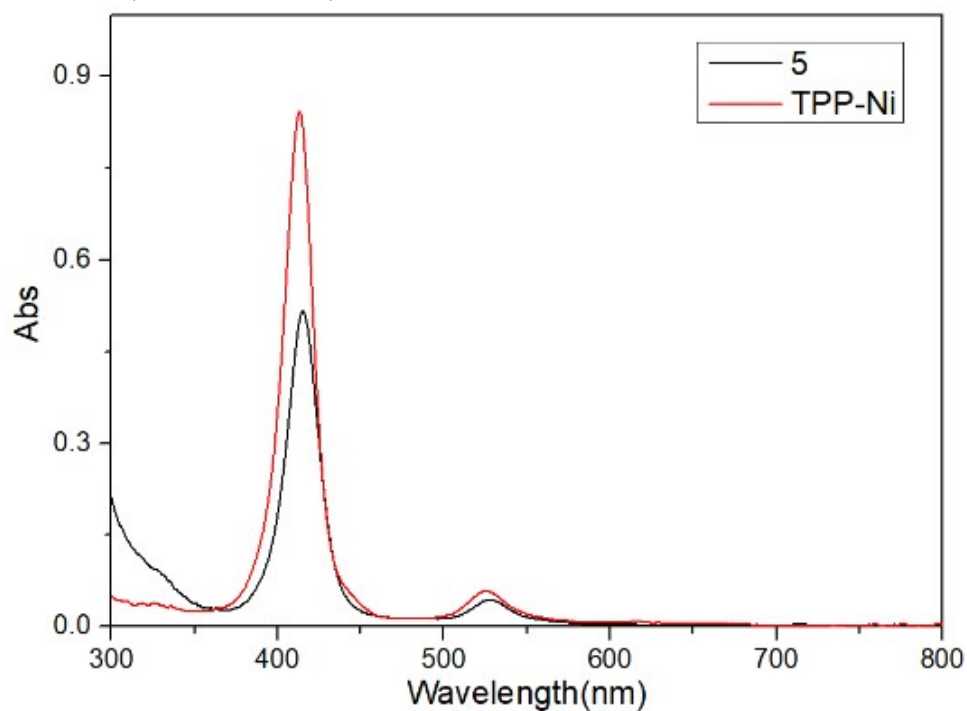


**Figure S8.** HRMS (MALDI-TOF-MS) of **4** in CH<sub>2</sub>Cl<sub>2</sub>.





**Figure S9.** HRMS (MALDI-TOF-MS) of **5** in  $\text{CH}_2\text{Cl}_2$ .



**Figure S10.** The UV/vis absorption of **5** ( $2 \mu\text{M}$ ) and **TPP-Ni** ( $2 \mu\text{M}$ ) in  $\text{CH}_2\text{Cl}_2$ .

## Association constants measurements

The changes in chemical shifts ( $\Delta\delta$ ) of selected protons were plotted as a function of the molar fraction of the guest, and the resulting curve was fitted by a nonlinear method using the global analysis approach according to the following equations assuming a 1:1 equilibrium:

$$Ka = \frac{[HG]}{[H][G]}$$

Changes in chemical shifts upon NMR titration are expressed:

$$\Delta\delta = \Delta\delta_{max} \left( \frac{[HG]}{[H_0]} \right)$$

Where:

[HG] is the concentration of the guest of the complex, and is calculated using the following equation:

$$[HG] = \frac{1}{2} \left( [G_0] + [H_0] + \frac{1}{Ka} \right) - \sqrt{\left( [G_0] + [H_0] + \frac{1}{Ka} \right)^2 - 4[G_0][H_0]}$$

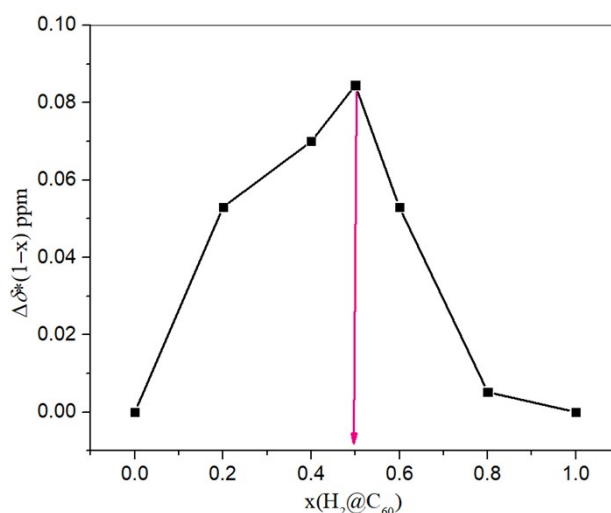
[G<sub>0</sub>]: total concentration of the guest (**5**).

[H<sub>0</sub>]: total concentration of the host (H<sub>2</sub>@C<sub>60</sub>).

$\Delta\delta_{max}$  is  $\Delta\delta$  at maximum complexation (100% supramolecular complex formation).

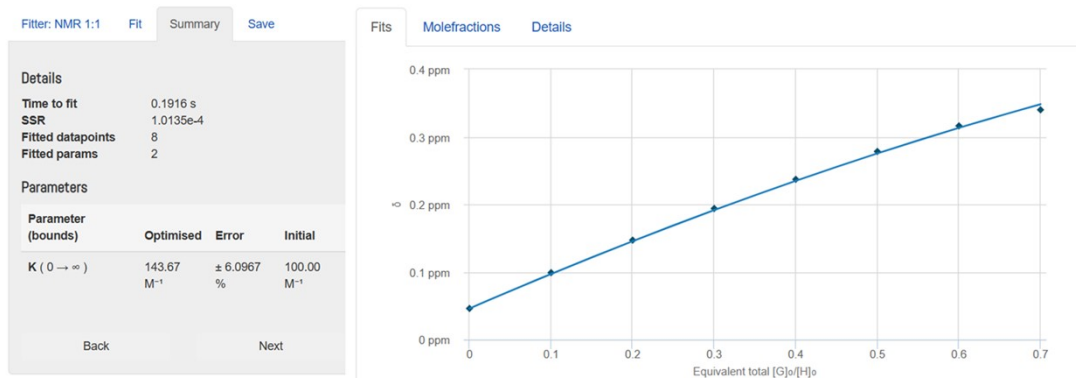
$Ka$  is the estimated association constant for 1:1 equilibrium.

$\Delta\delta_{max}$  and  $Ka$  for a 1:1 equilibrium were extracted by using the non-linear fitting tool provided by the open access web portal Supramolecular.org (<http://supramolecular.org>) applying equations 2 and 3.<sup>10</sup>

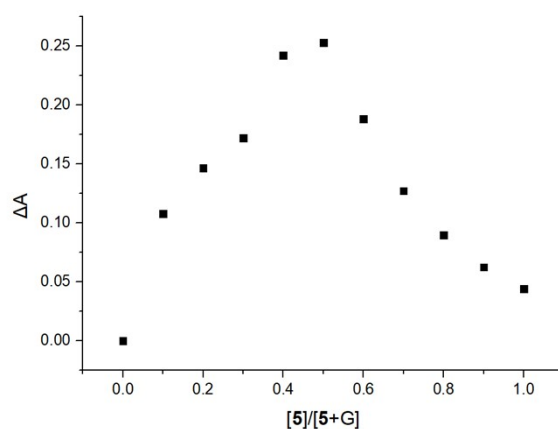


**Figure S11.** Job's plot of H<sub>2</sub>@C<sub>60</sub> investigated by <sup>1</sup>H NMR spectra in CS<sub>2</sub>/CDCl<sub>3</sub> = 1/1 (v/v) at 298 K.

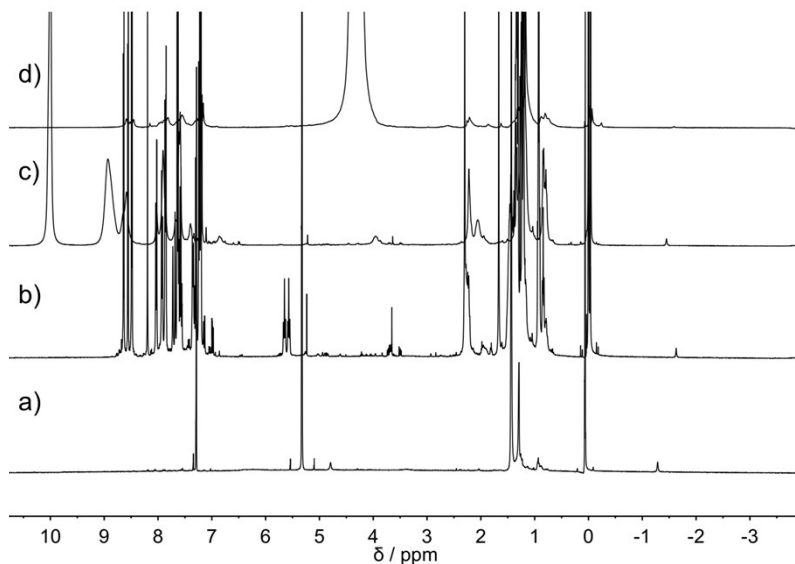
[H<sub>2</sub>@C<sub>60</sub>] = 0.15 Mm



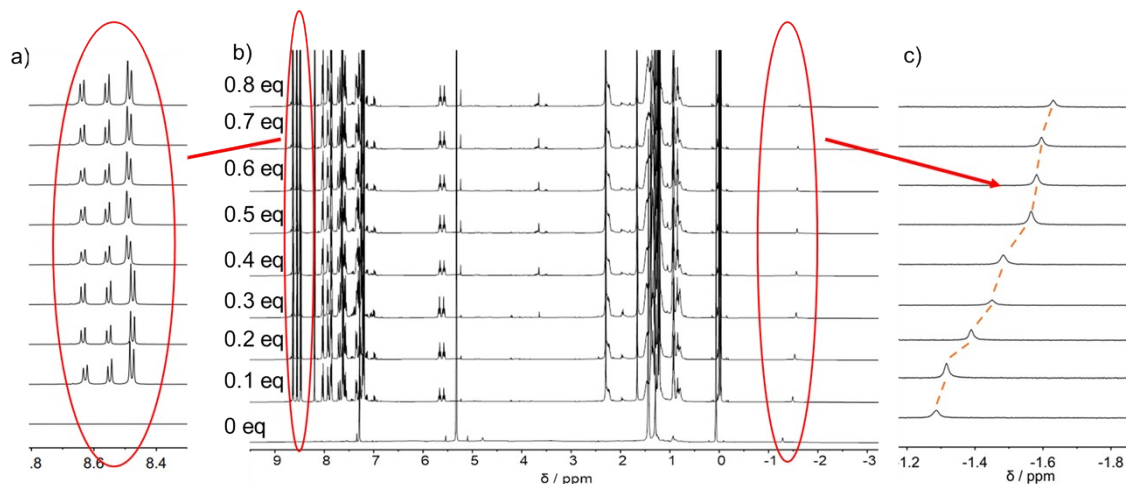
**Figure S12.** Nonlinear fitting of  $\Delta\delta$  for hydrogen proton inside  $C_{60}$  according to a 1 : 1 binding stoichiometry.



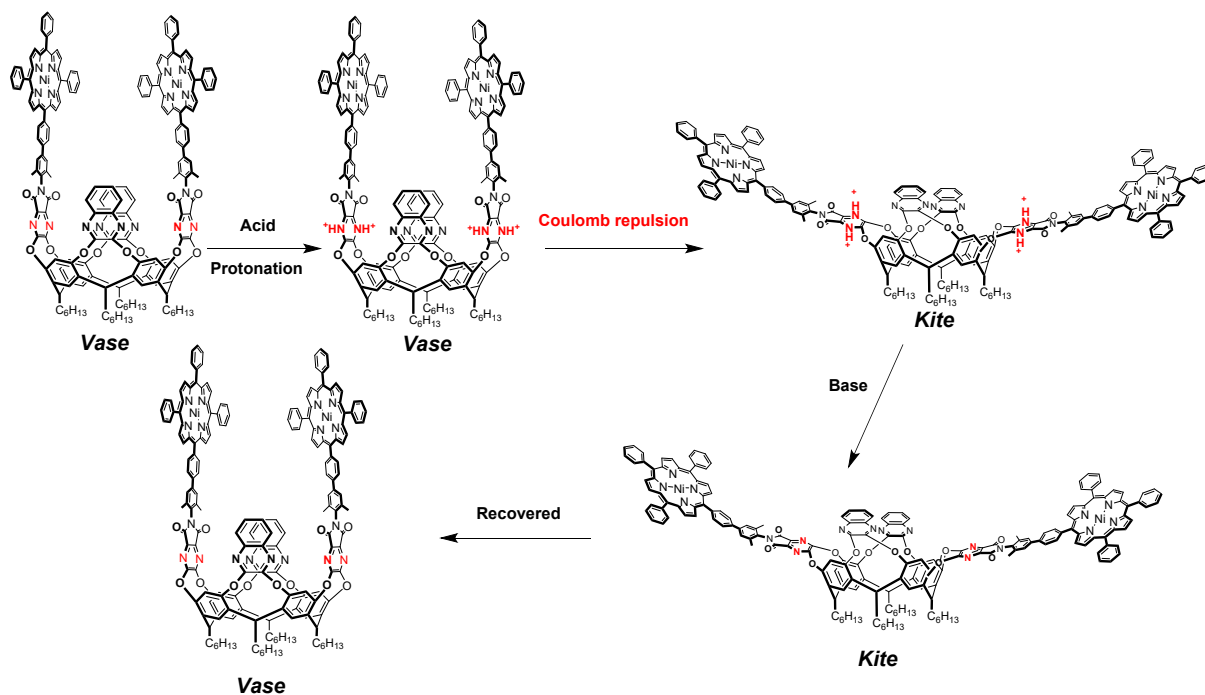
**Figure S13.** Job's plot : Absorbance change of **5** versus  $[5] / ([5] + [C_{60}])$  in toluene at 298 K.  $[5] + [C_{60}] = 2.0 \mu\text{M}$



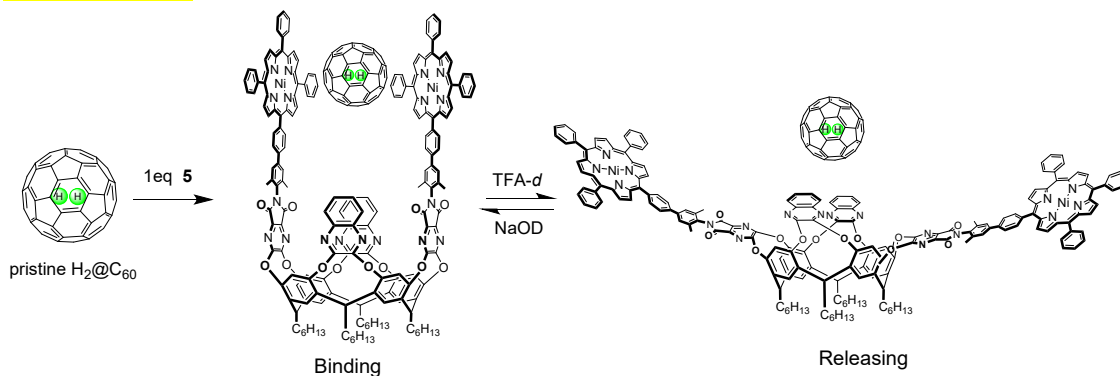
**Figure S14.** The open-close state of molecular tweezer **5** (0.15 mM) monitored using  $^1\text{H}$  NMR in  $\text{CDCl}_3/\text{CS}_2=1/1$ , a) signal of pristine  $\text{H}_2@C_{60}$ , b) signal of  $\text{H}_2@C_{60}+1\text{eq. 5}$ , c) signal of  $\text{H}_2@C_{60}+1\text{eq. 5} + \text{TFA-}d$ , d) Signal of  $\text{H}_2@C_{60}+1\text{eq. 5} + \text{TFA-}d + \text{NaOD}$ .



**Figure S15.** a) Magnified  $^1\text{H-NMR}$  spectra of Fig. S14b in the region of 8.61~8.67 ppm. b)  $^1\text{H-NMR}$  spectra of  $\text{H}_2@\text{C}_{60}$  (0.15 mM) in  $\text{CS}_2/\text{CDCl}_3$  at 298 K in the presence of 0-0.8 equiv of **5**. c) Magnified  $^1\text{H-NMR}$  spectra of picture S14b in the region of -1.2~-1.8 ppm.



**Figure S16.** The mechanism of opening and closing of bisporphyrin resorcinarene with the addition of the acid and base.



**Figure S17.** The mechanism of binding and releasing of bisporphyrin resorcinarene with the  $\text{H}_2@\text{C}_{60}$ .

### 3. Crystal data and structure refinements

**Table S1.** Crystal data and structure refinements of **5**.

Compounds	<b>5</b>
Formula	C <sub>184</sub> H <sub>142</sub> N <sub>18</sub> Ni <sub>2</sub> O <sub>12</sub>
Formula weight (g/mol)	2914.57
Crystal system	monoclinic
Temperature (K)	193.00
Crystal size (mm <sup>3</sup> )	0.13×0.12×0.1
Theta range for data collection (°)	4.342-107.81
Space group	C2/c
<i>a</i> (Å)	31.418(2)
<i>b</i> (Å)	40.637(3)
<i>c</i> (Å)	19.4953(12)
<i>α</i> (°)	90.00
<i>β</i> (°)	117.411(3)
<i>γ</i> (°)	90.00
Volume (Å <sup>3</sup> )	22096(2)
<i>Z</i>	4
$\rho_{\text{calc}}$ (g/cm <sup>3</sup> )	0.876
<i>F</i> (000)	6090.0
$\mu$ (mm <sup>-1</sup> )	1.176
	-37 ≤ <i>h</i> ≤ 37
Index ranges	-48 ≤ <i>k</i> ≤ 48
	-23 ≤ <i>l</i> ≤ 23
<i>R</i> <sub>1</sub> [ <i>I</i> >2σ( <i>I</i> )]	0.0986
<i>wR</i> <sub>2</sub> (all data)	0.3413
GOF	0.976
Reflections collected/Unique	82430 / 20157
CCDC number	2132255

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