

## **Electronic Supplementary Information**

**for**

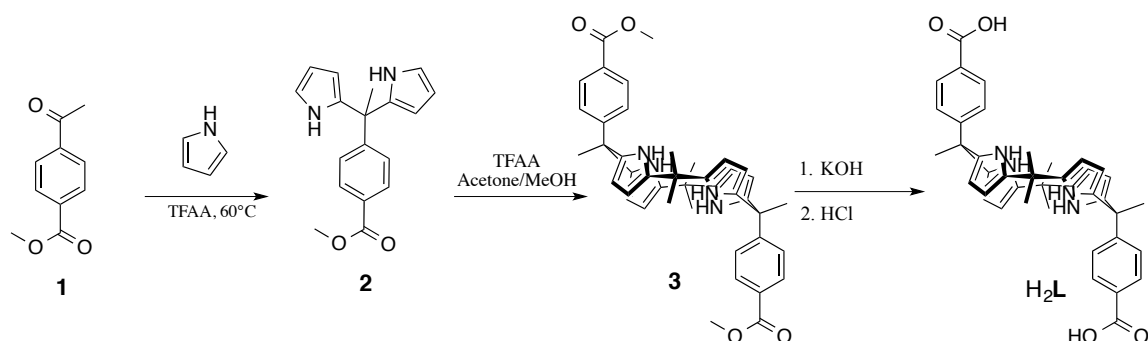
### **Ship in a breakable bottle: Fluoride-induced release of an organic molecule from a Pr(III)-linked molecular cage**

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### Scheme S1. Synthesis of H<sub>2</sub>L



All solvents and chemicals used were purchased from Aldrich, TCI, and Acros and used without further purification. NMR spectra were recorded on a Varian Mercury 400 instrument. The NMR spectra were referenced to solvent and the spectroscopic solvents were purchased from either the Cambridge Isotope Laboratories or the Aldrich Chemical Co. Chemical ionization (CI) and electrospray ionization (ESI) mass spectra were recorded on a VG ZAB-2E instrument and a VG AutoSpec apparatus, respectively. Sorbent Technologies silica gel (200 nm) sheets were used for TLC analyses. Column chromatography was performed on Sorbent silica gel 60 (40-63 mm).

#### Compound 2

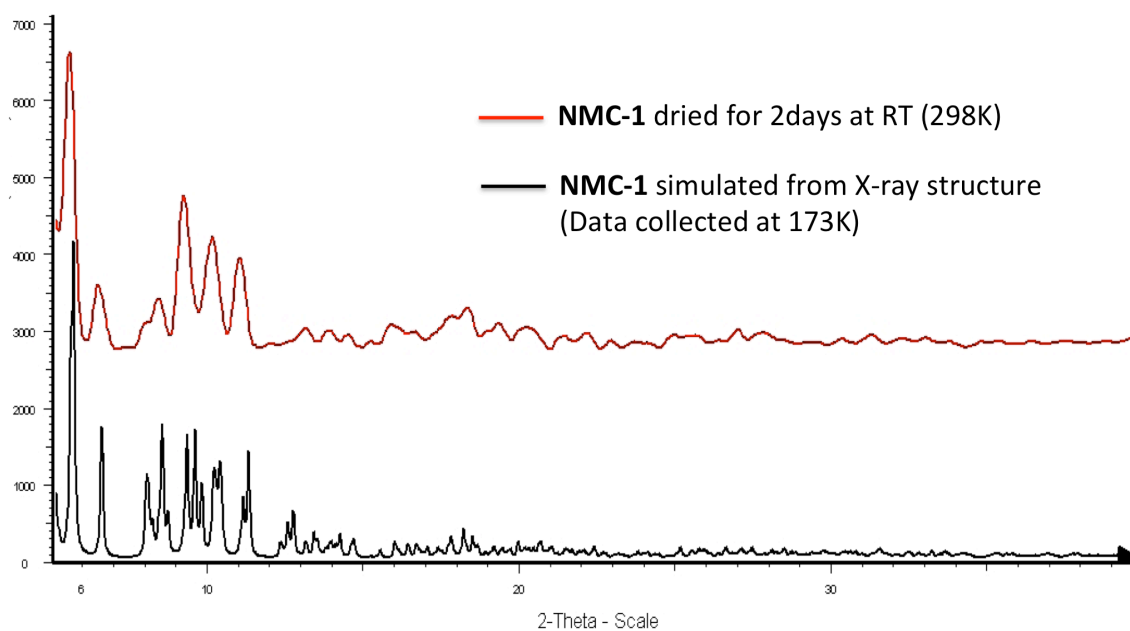
To methyl 4-acetylbenzoate (1) (5.00 g, 28.06 mmol) in pyrrole (100 mL) was added TFAA (trifluoroacetic anhydride, 2.1 mL, 14.80 mmol). The mixture was stirred for 10 hours at 60 °C. The resulting solution was evaporated *in vacuo* to remove pyrrole and other volatiles. The material obtained in this way was purified by column chromatography over silica gel (eluent: dichloromethane) to afford a pale yellow oil. Crystallization from a mixture of dichloromethane and hexanes gave 5.91 g (72% yield) of 2 as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.95-7.92 (d, 2H, ArH), 7.80 (br s, 2H, pyrrole-NH), 7.20-7.18 (d, 2H, ArH), 6.71-6.69 (m, 2H, ArH (pyrrole)), 6.19-6.17 (m, 2H, ArH (pyrrole)), 5.97-5.95 (m, 2H, ArH (pyrrole)), 3.90 (s, 3H, CH<sub>3</sub>), 2.06 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 167.1, 152.7, 136.7, 129.6, 128.7, 127.6, 117.4, 108.5, 106.7, 52.3, 45.1, 28.7. HRMS (ESI) *m/z* 295.14450 [M + H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> found 295.14410.

### Compound **3**

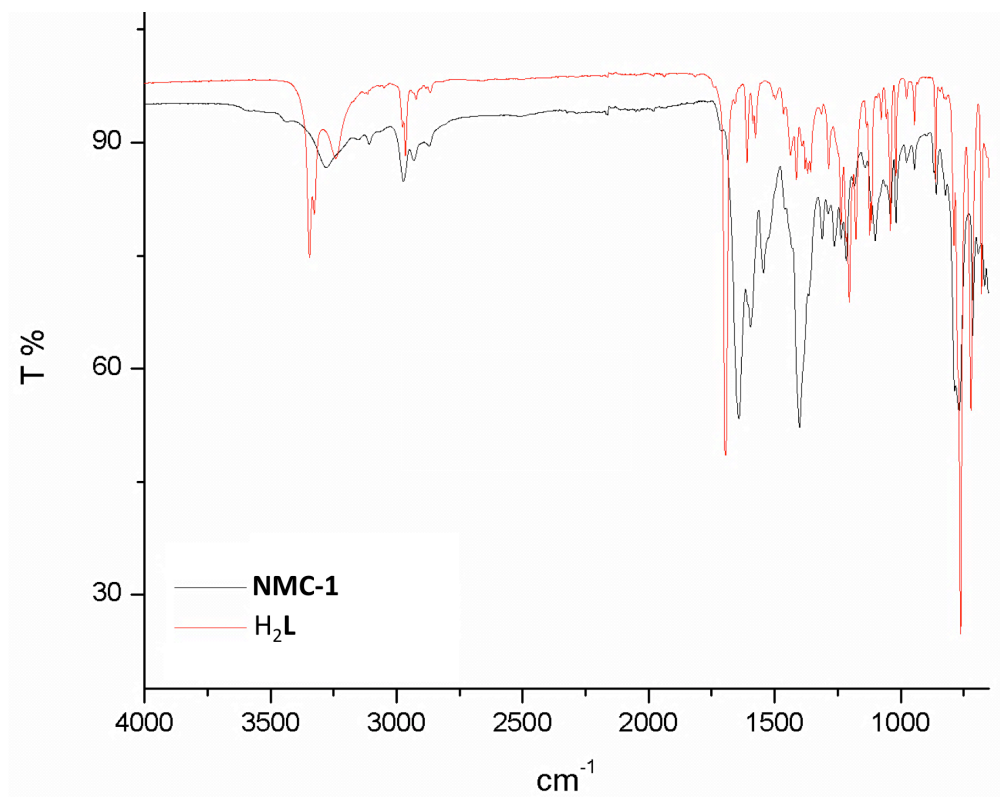
To a mixture of compound **2** (5.91 g, 20.09 mmol) and methanol/acetone (1:1, 300 mL), TFAA (trifluoroacetic anhydride, 1.42 mL, 10.00 mmol) was added at 0 °C and stirred for 1 hour. The solution was then stirred for 10 hours at room temperature and quenched with triethylamine. The resulting solution was evaporated *in vacuo* and re-dissolved in dichloromethane, washed with brine, and dried over Na<sub>2</sub>SO<sub>4</sub>. Column chromatography over silica gel (ethyl acetate/hexanes = 1/9) gave compound **3** (964 mg, 7% yield) as a white solid. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 7.94-7.91 (d, 4H, ArH), 7.21-7.19 (d, 4H, ArH), 7.18 (br s, 4H, pyrrole NH), 5.94-5.92 (t, 4H, ArH (pyrrole)), 5.76-5.74 (t, 4H, ArH (pyrrole)), 3.90 (s, 6H, CH<sub>3</sub>), 1.91 (s, 6H, CH<sub>3</sub>), 1.53 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, CDCl<sub>3</sub>): δ 166.9, 152.0, 138.7, 135.7, 129.2, 128.4, 127.4, 105.9, 103.3, 52.1, 44.9, 35.3, 29.2. HRMS (ESI) *m/z* 669.34370 (M + H)<sup>+</sup> calcd for C<sub>42</sub>H<sub>44</sub>N<sub>4</sub>O<sub>4</sub>, found 669.34350.

### Compound H<sub>2</sub>L

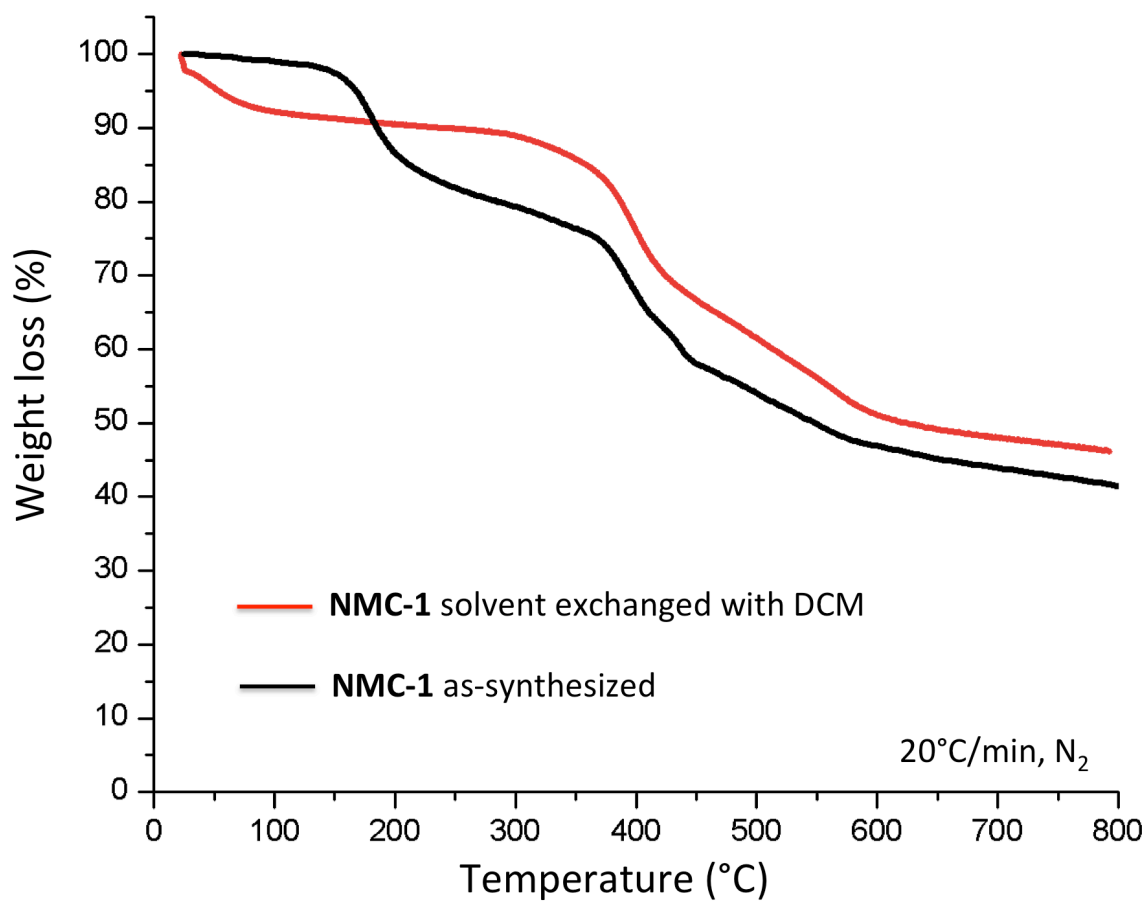
A mixture of compound **3** (964 mg, 1.44 mmol) and KOH (2.4 g, 43.20 mmol) in H<sub>2</sub>O/2-propanol (1:1, 100 mL) was heated at reflux for 10 hours. The reaction was cooled to room temperature and then further cooled to 0 °C. The solution was acidified with hydrochloric acid until it reached pH = 2. The white precipitate obtained in this way was filtered and washed with water until the washings were neutral. The resulting solid was dried in the air to give compound H<sub>2</sub>L (877 mg, 95% yield). <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ 12.75 (br s, 2H, COOH), 9.69 (s, 4H, pyrrole NH), 7.77-7.75 (d, 4H, ArH), 7.22-7.20 (d, 4H, ArH), 5.73-5.72 (d, 8H, ArH (pyrrole)), 1.75 (s, 6H, CH<sub>3</sub>), 1.47 (s, 12H, CH<sub>3</sub>). <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 167.2, 154.3, 139.4, 135.7, 128.9, 128.4, 127.3, 104.9, 102.1, 44.5, 35.1, 30.8, 30.4. HRMS (ESI) *m/z* 641.31250 (M + H)<sup>+</sup> calcd for C<sub>40</sub>H<sub>40</sub>N<sub>4</sub>O<sub>4</sub>, found 641.31220.



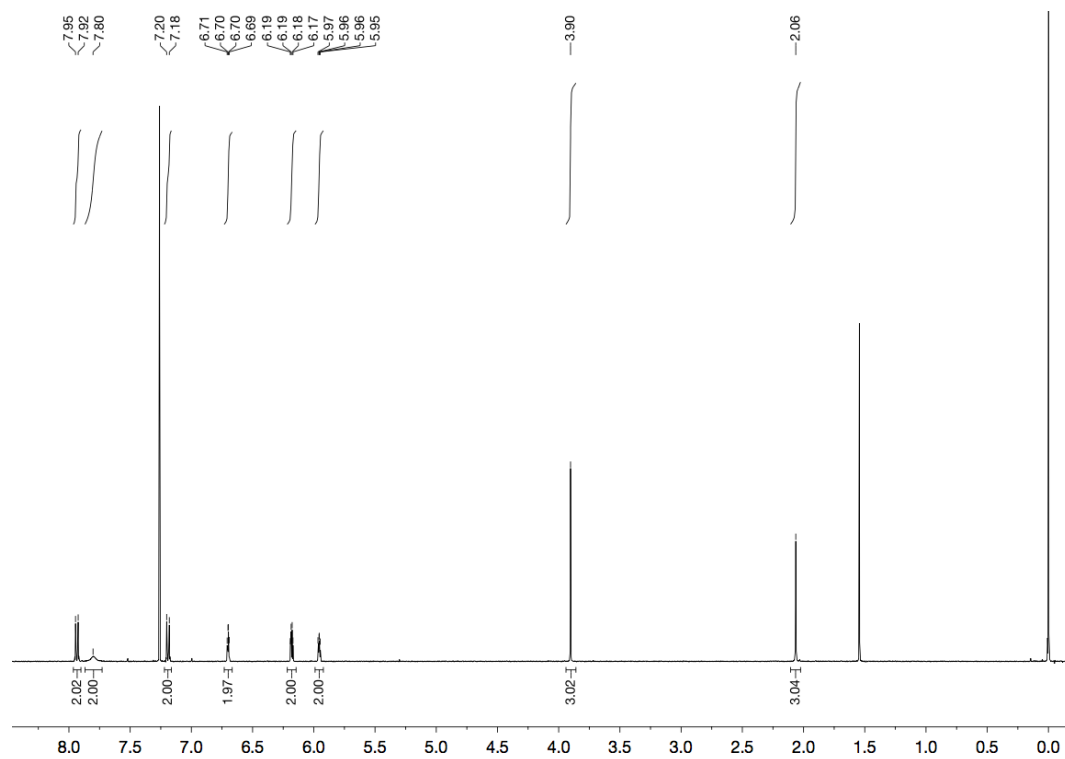
**Figure S1.** Powder X-ray diffraction data of **NMC-1** (red) after being air dried and the simulated powder pattern deduced from the solved crystal structure of **NMC-1** (black).



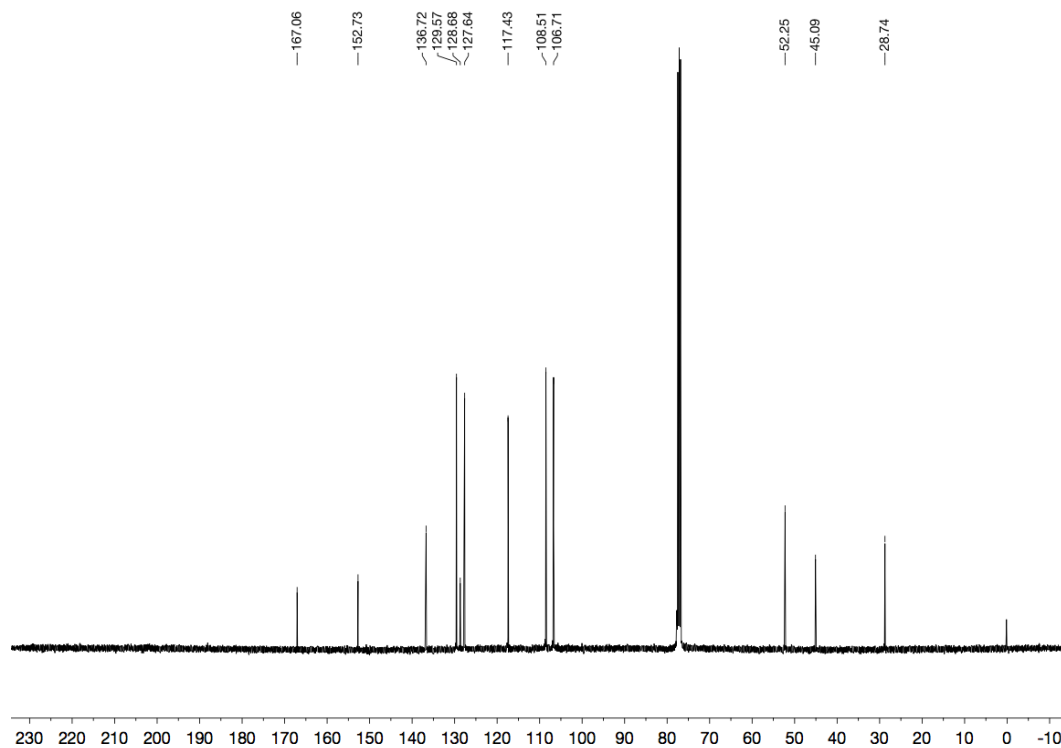
**Figure S2.** Overlaid infrared spectra of **NMC-1** (black) and **H<sub>2</sub>L** (red).



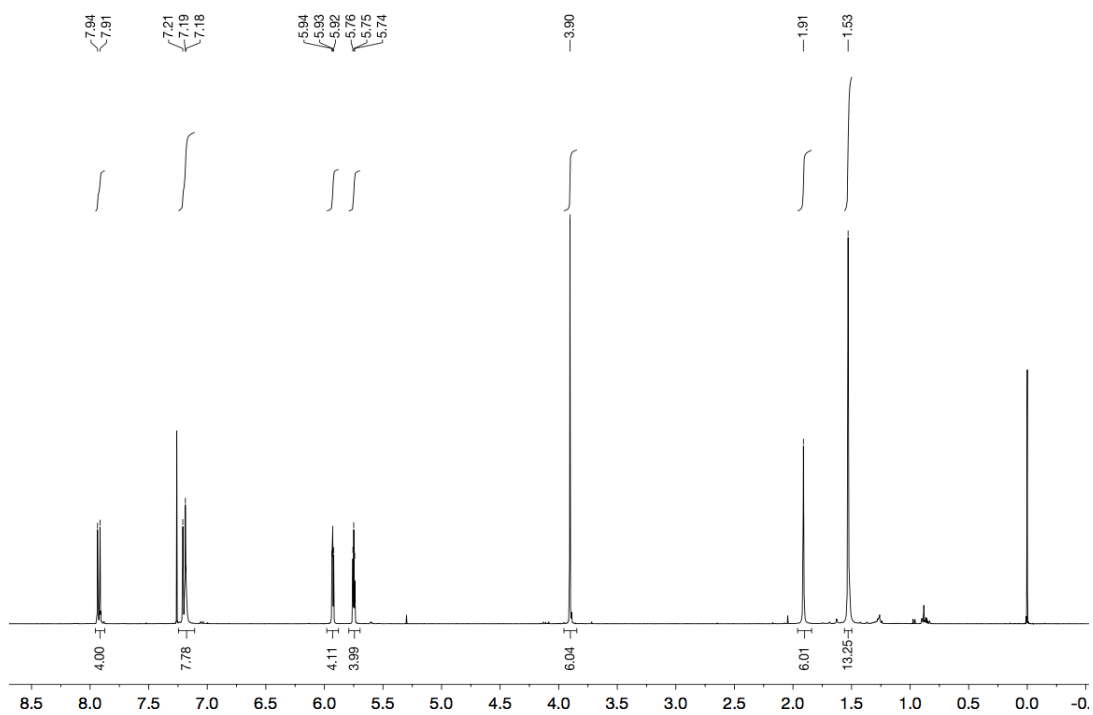
**Figure S3.** Thermogravimetric analysis data of as-synthesized **NMC-1** (black) and dichloromethane (DCM)-exchanged **NMC-1** (red).



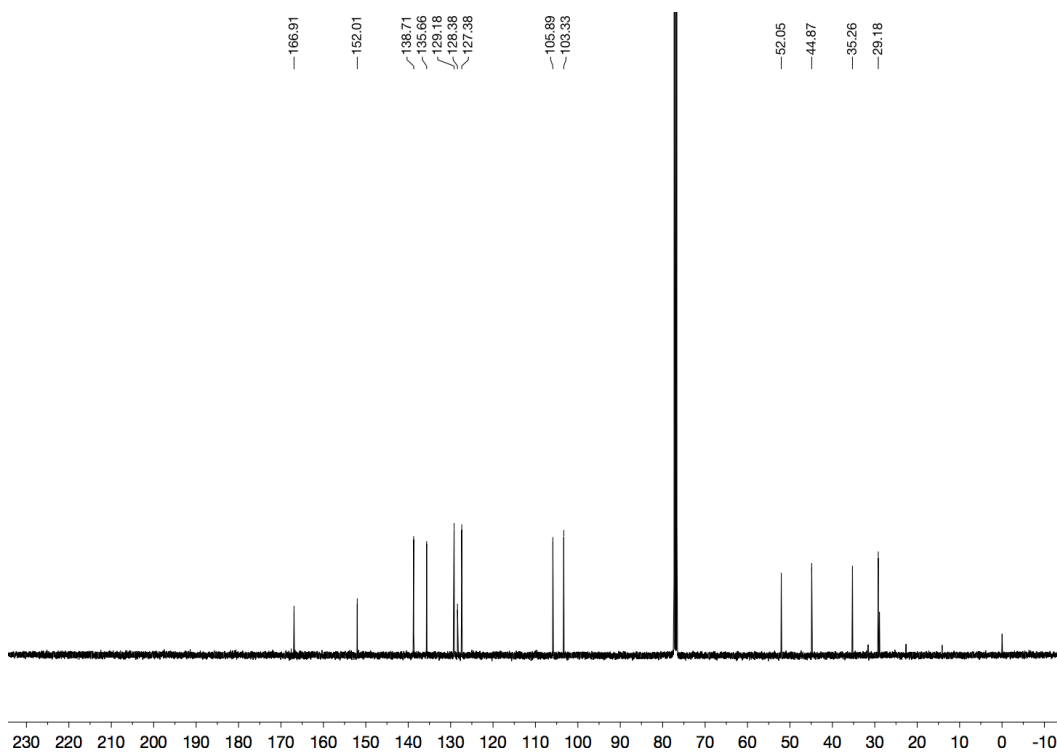
**Figure S4.**  $^1\text{H}$ -NMR spectrum of **2** recorded in  $\text{CDCl}_3$ .



**Figure S5.**  $^{13}\text{C}$ -NMR spectrum of **2** recorded in  $\text{CDCl}_3$ .

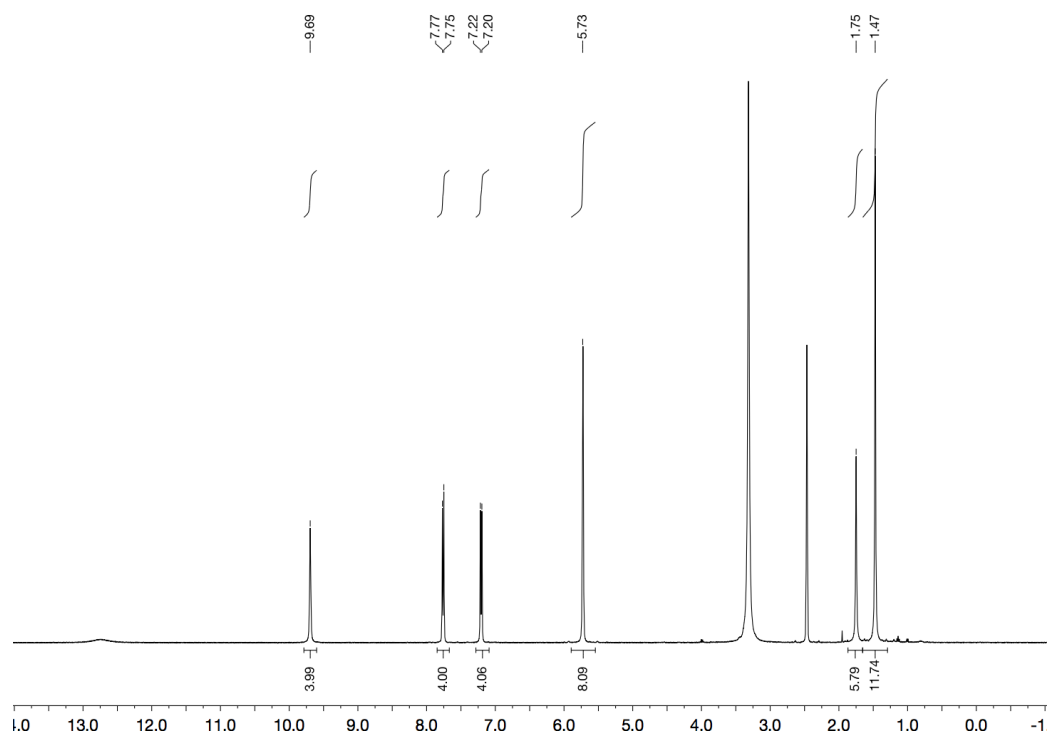


**Figure S6.** <sup>1</sup>H-NMR spectrum of **3** recorded in CDCl<sub>3</sub>.

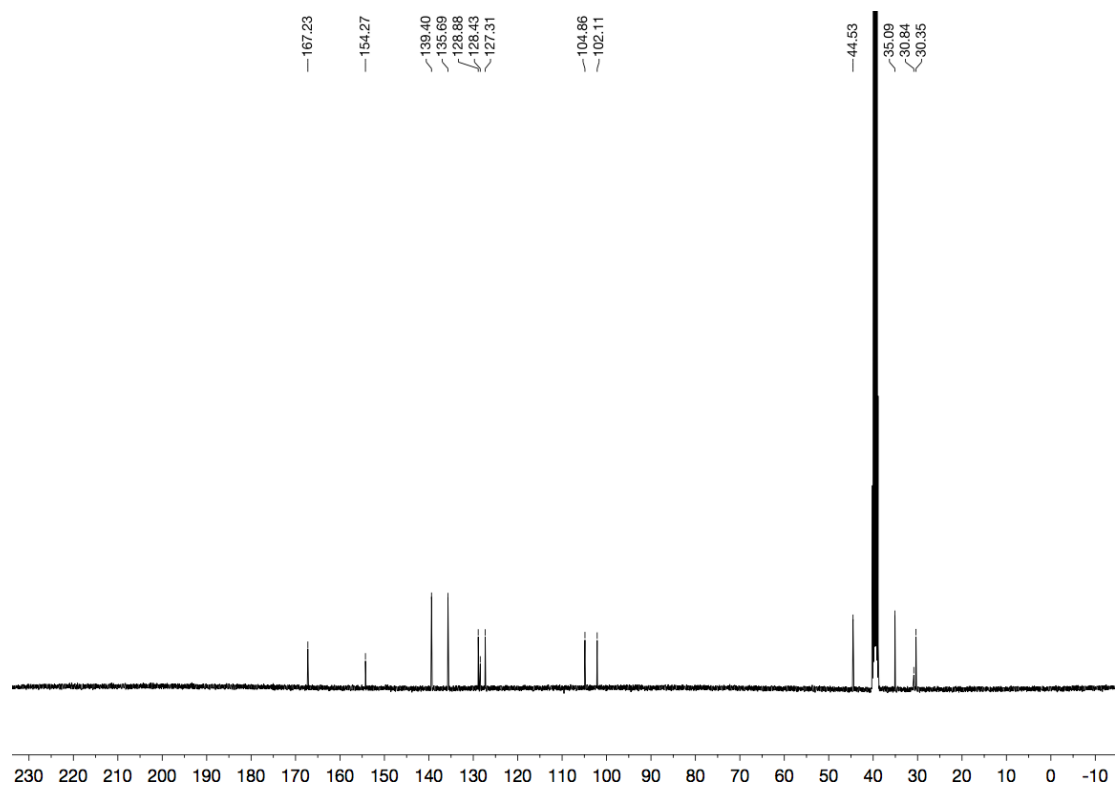


**Figure S7.** <sup>13</sup>C-NMR spectrum of **3** recorded in CDCl<sub>3</sub>.

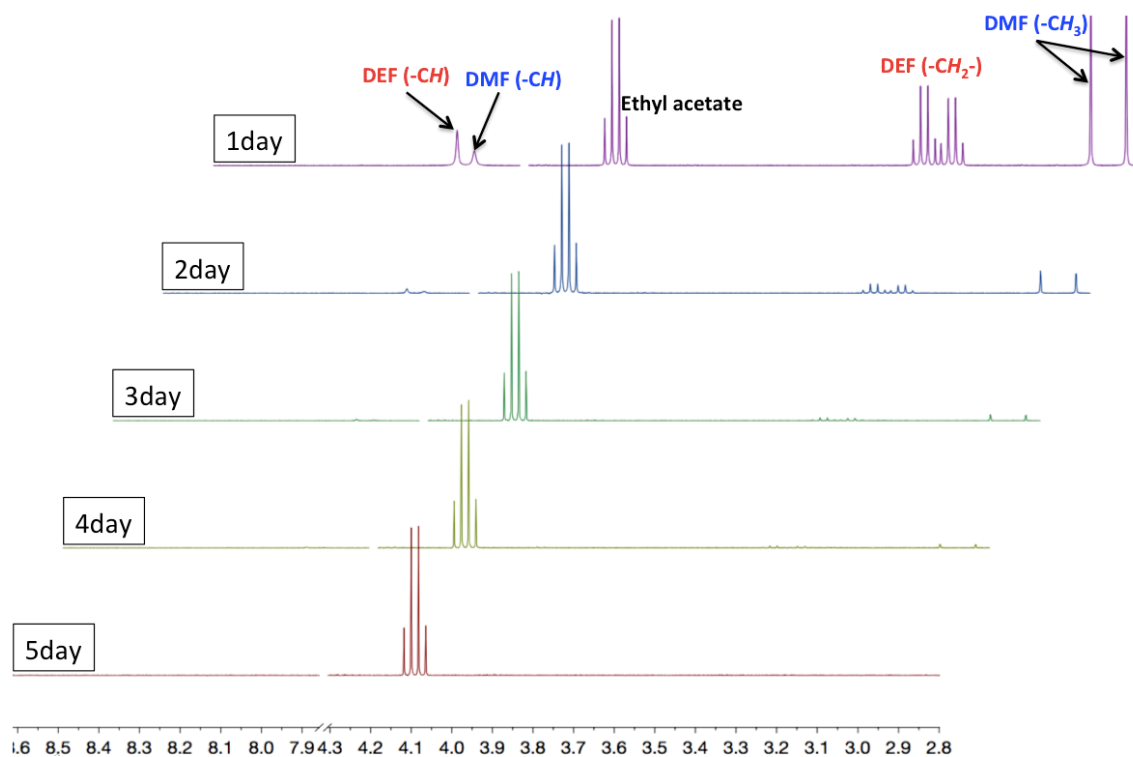




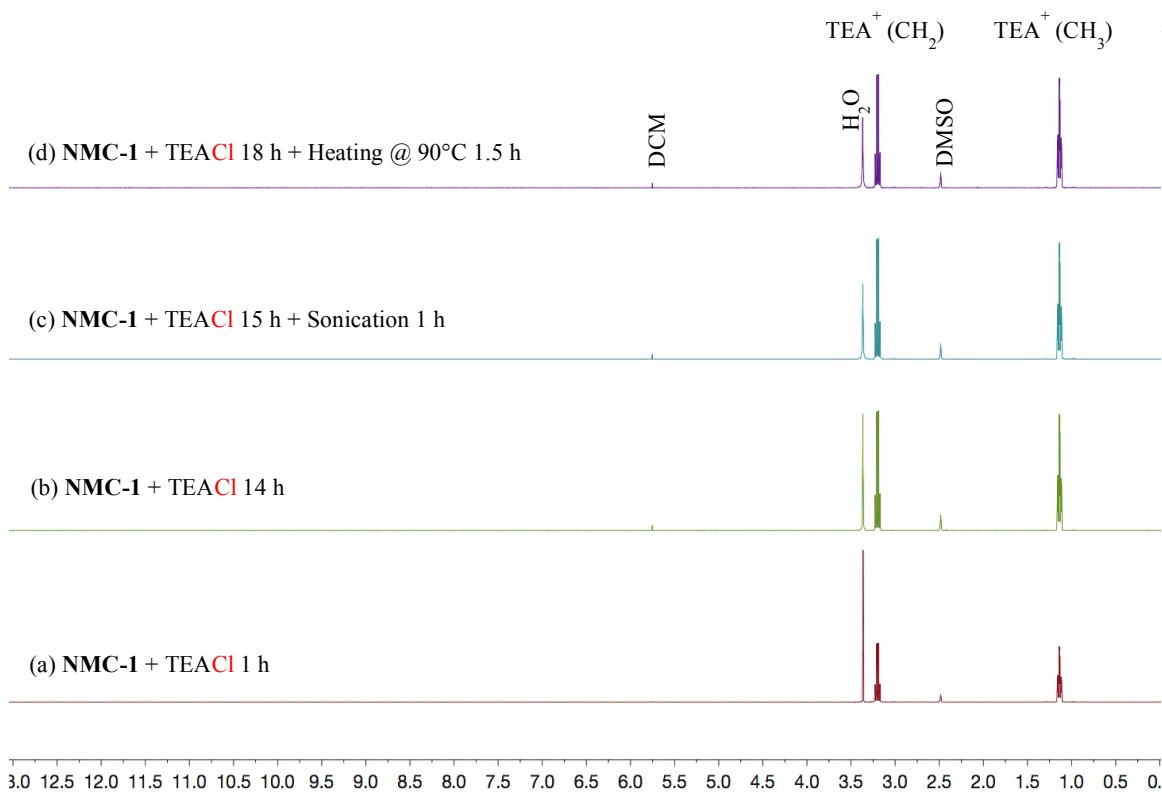
**Figure S8.** <sup>1</sup>H-NMR spectrum of H<sub>2</sub>L recorded in DMSO-*d*<sub>6</sub>.



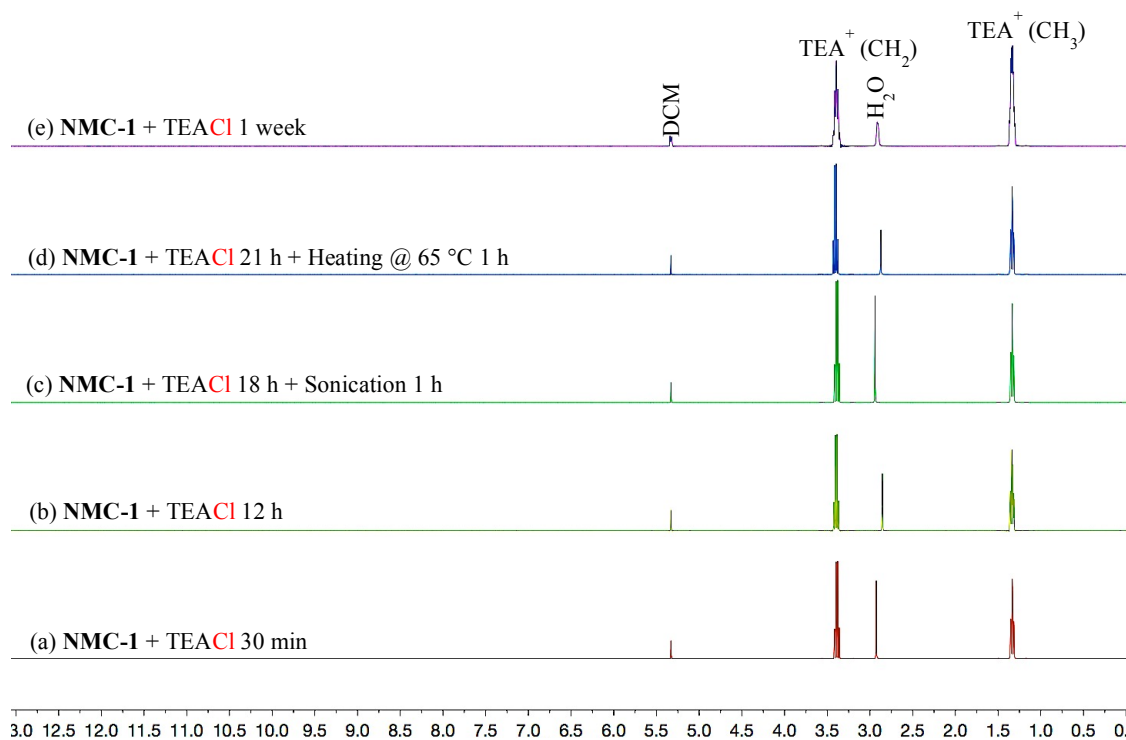
**Figure S9.** <sup>13</sup>C-NMR spectrum of H<sub>2</sub>L recorded in DMSO-*d*<sub>6</sub>.



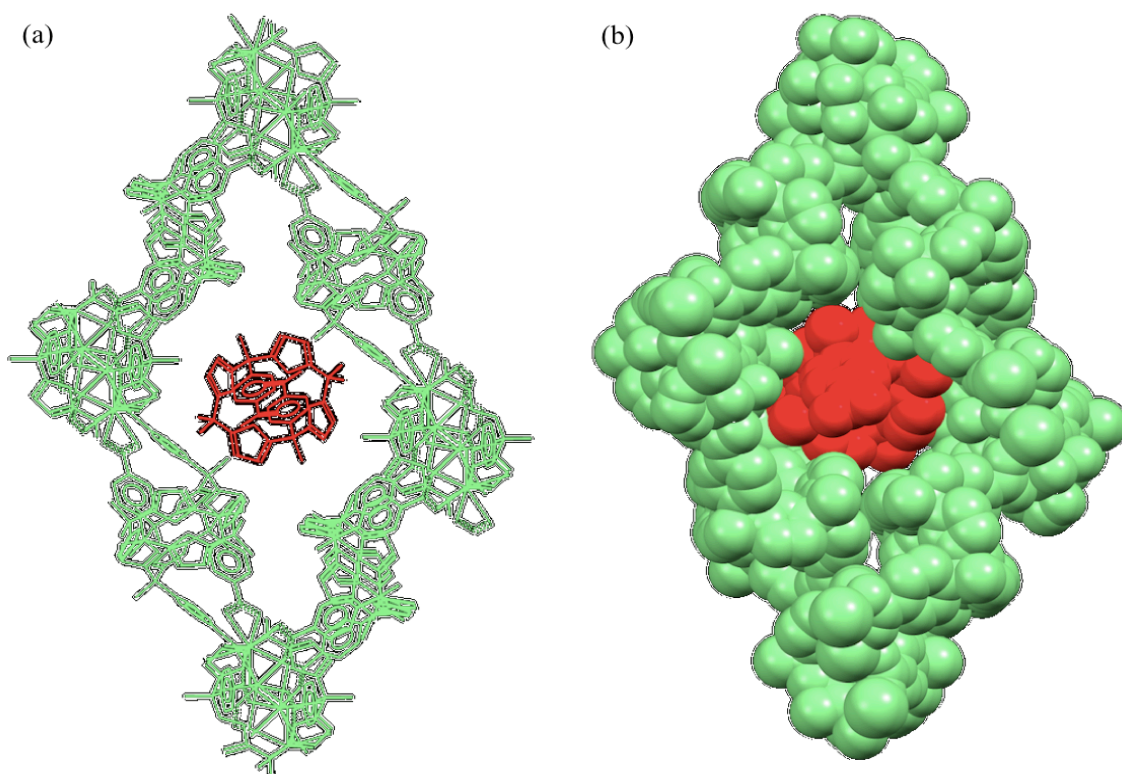
**Figure S10.** Time-dependent views of the upfield region of the  $^1\text{H}$ -NMR spectra of NMC-1 soaked in  $\text{CD}_2\text{Cl}_2$  in the presence of 1  $\mu\text{L}$  of ethyl acetate added as an internal standard.



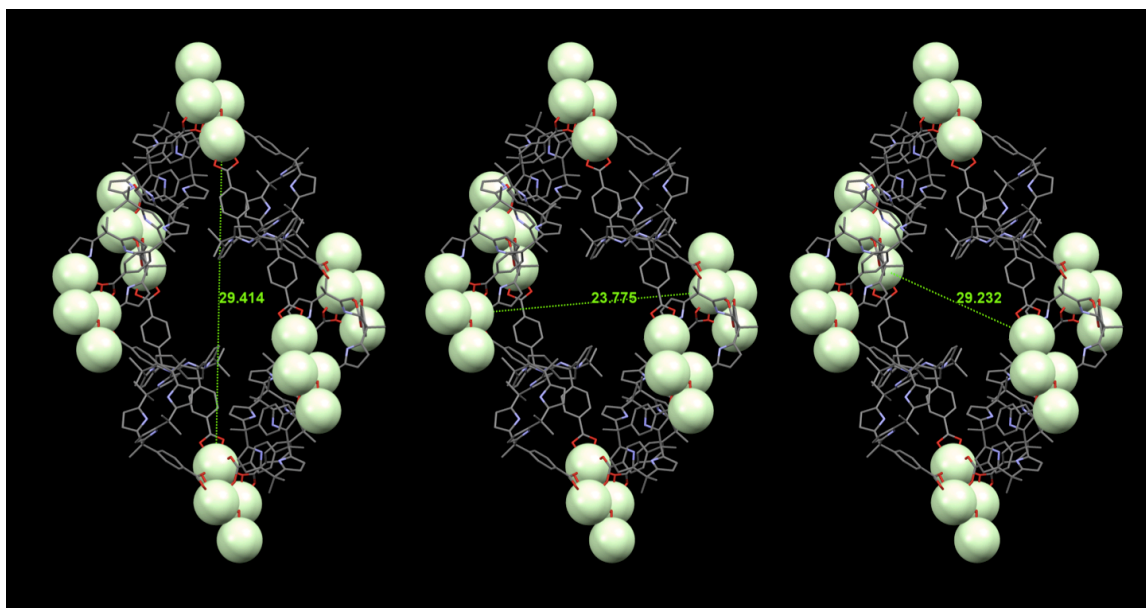
**Figure S11.**  $^1\text{H}$ -NMR spectra observations of NMC-1 in the presence of excess of TEACl recorded in  $\text{DMSO}-d_6$  under different conditions; (a) soaking for 1 h, (b) soaking for 14 h, (c) sonication for 1 h, following by soaking 15 h, (d) heating at  $90^\circ\text{C}$  for 1 h, following soaking for 18 h.



**Figure S12.** <sup>1</sup>H-NMR spectroscopic observations of **NMC-1** in the presence of excess TEA**Cl** recorded in CD<sub>2</sub>Cl<sub>2</sub> under different conditions; (a) soaking for 0.5 h, (b) soaking for 12 h, (c) sonication for 1 h, following soaking for 18 h, (d) heating at 65 °C for 1 h, following soaking for 21 h, (e) soaking for 1 week.

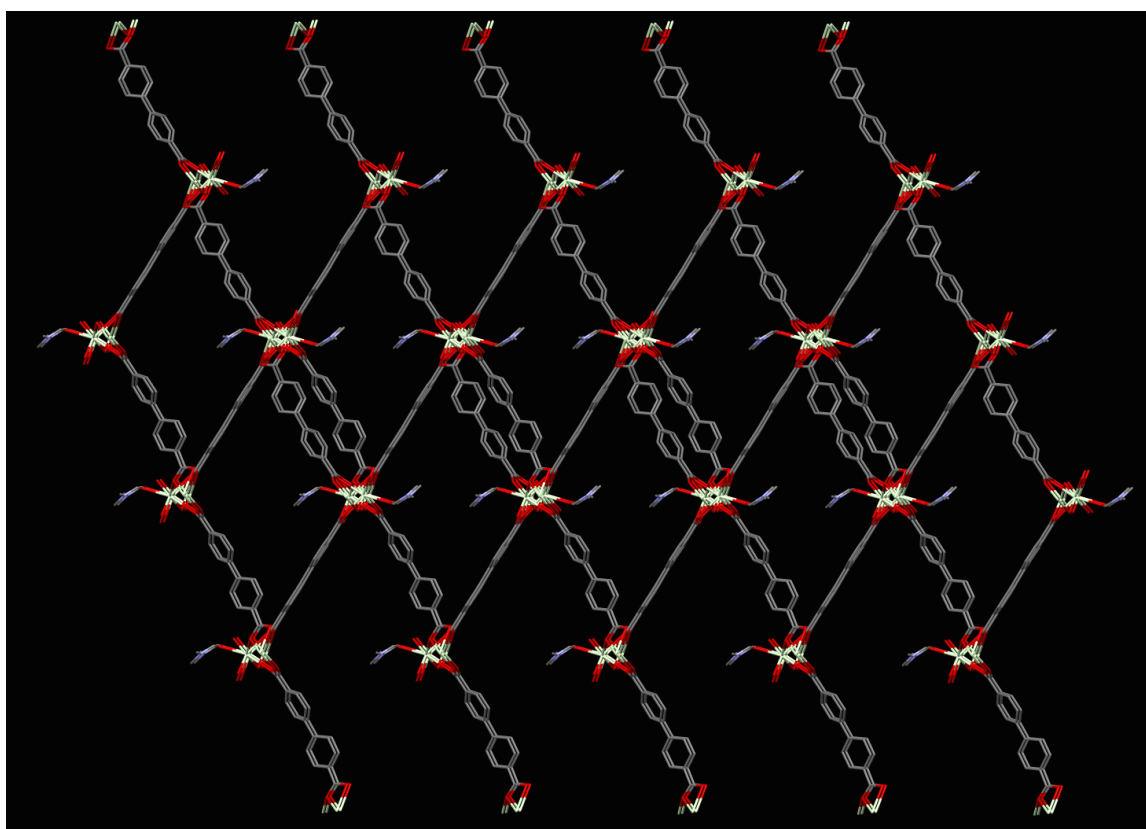
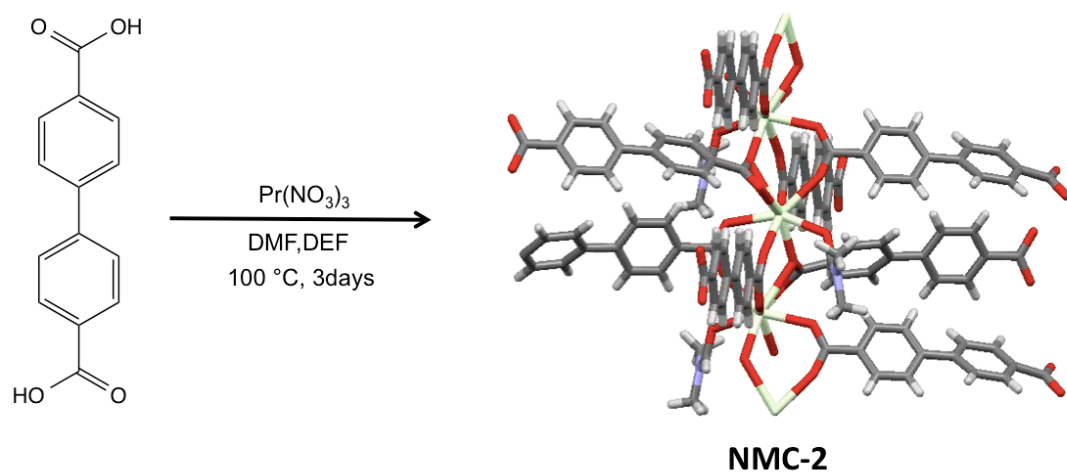


**Figure S13.** (a) Capped stick- and (b) spacefilling-rendered views of free  $H_2L$  inside the NMC-1 pore.

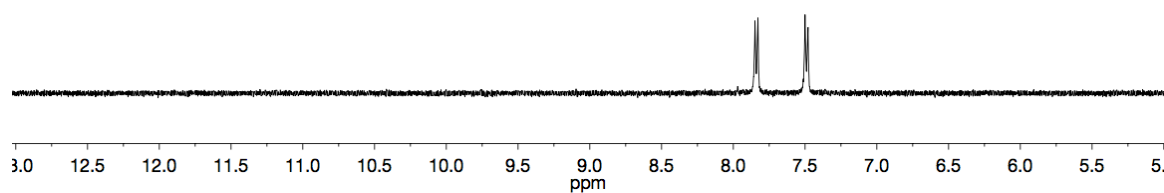


**Figure S14.** Distances between the opposing vertices established by the metal nodes of NMC-1.

**Scheme S2. Synthesis of NMC-2**



**Figure S15.** X-ray structure of NMC-2.



**Figure S16.** Partial  $^1\text{H}$ -NMR spectra of **NMC-2** in  $\text{DMSO}-d_6$  recorded 12 h after the addition of an excess of TEAF.

### X-ray Experimental for complex $\text{H}_2\text{L}\cdot(\text{DMF})_4$

Crystals grew as long, colorless needles by slow evaporation from DMF. The data crystal was cut from a larger crystal and had approximate dimensions; 0.34 x 0.04 x 0.02 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus Cu  $K\alpha$  radiation source ( $\lambda = 1.5418 \text{ \AA}$ ) with collimating mirror monochromators. A total of 1127 frames of data were collected using  $\omega$ -scans with a scan range of  $1^\circ$  and a counting time of 30 seconds per frame with a detector offset of  $\pm 40.3^\circ$  and 90 seconds per frame with a detector offset of  $\pm 108.9^\circ$ . The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.<sup>1</sup> The structure was solved by direct methods using SHELXT<sup>4</sup> and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.<sup>5</sup> Structure analysis was aided by use of the programs PLATON98<sup>6</sup> and WinGX.<sup>7</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

A small peak in the difference electron density map was found near C24. It was twice as large as the next peak and was considered likely to reflect a small amount of disorder in the DMF molecule. The disorder was ascribed to a 180 degree rotation about the N4-C24 bond. A disorder model was applied that only involved the oxygen atom, O4, of the affected DMF molecule. The variable x was assigned to the site occupancy for O4, while (1-x) was assigned to the site occupancy for O4a. A common isotropic displacement parameter was refined for the two atoms while refining x. The geometry of the two atoms was restrained to be equivalent throughout the refinement process. In this way, the site occupancy for O4 refined to 93(1)%. The function,  $\sum w(|F_o|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_o))^2 + (0.0707*P)^2 + (0.6968*P)]$  and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.138, with R(F) equal to 0.0483 and a goodness of fit,  $S$ , = 1.02. Definitions used for calculating R(F),  $R_w(F^2)$  and the goodness of fit,  $S$ , are given below.<sup>9</sup> The data were checked for secondary extinction effects but no correction was

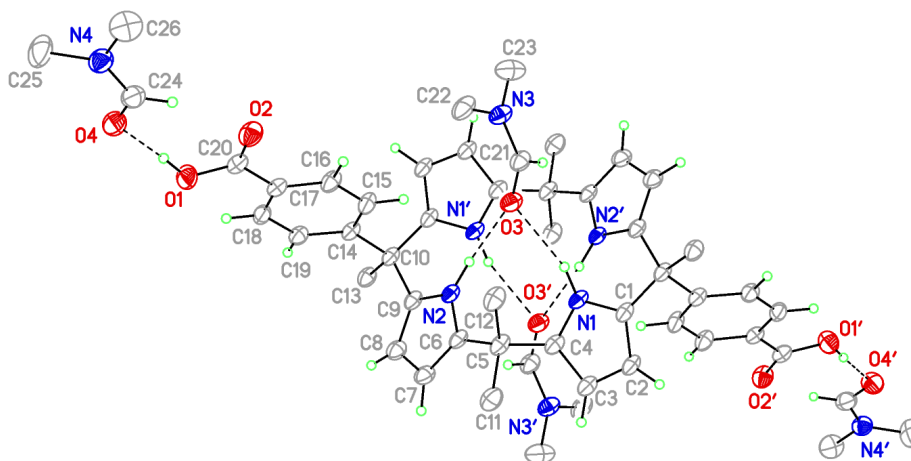


necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>10</sup> All figures were generated using SHELXTL/PC.<sup>11</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found in the CIF. CCDC deposition number: 1475464.

**Table S1.** Crystal data and structure refinement for H<sub>2</sub>L•(DMF)<sub>4</sub>.

Empirical formula	C <sub>52</sub> H <sub>68</sub> N <sub>8</sub> O <sub>8</sub>	
Formula weight	933.14	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	monoclinic	
Space group	P 2 <sub>1</sub> /n	
Unit cell dimensions	a = 17.4535(4) Å	α = 90°.
	b = 8.0246(2) Å	β = 97.847(2)°.
	c = 17.7712(4) Å	γ = 90°.
Volume	2465.68(10) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.257 Mg/m <sup>3</sup>	
Absorption coefficient	0.692 mm <sup>-1</sup>	
F(000)	1000	
Crystal size	0.02 x 0.04 x 0.34 mm <sup>3</sup>	
Theta range for data collection	3.329 to 74.139°.	
Index ranges	-21 ≤ h ≤ 20, -9 ≤ k ≤ 6, -21 ≤ l ≤ 21	
Reflections collected	13957	
Independent reflections	4904 [R(int) = 0.0407]	
Completeness to theta = 67.684°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.684	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4904 / 3 / 331	
Goodness-of-fit on F <sup>2</sup>	1.012	
Final R indices [I > 2σ(I)]	R1 = 0.0483, wR2 = 0.1235	
R indices (all data)	R1 = 0.0668, wR2 = 0.1383	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.333 and -0.260 e.Å <sup>-3</sup>	

**Figure S17.** View of  $\text{H}_2\text{L} \cdot (\text{DMF})_4$  showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The complex resides around a crystallographic inversion center at  $\frac{1}{2}, 1, 1$ . Atoms with labels appended by a ' are related by  $1-x, 2-y, 2-z$ . The methyl group H atoms were omitted for clarity.



## X-ray Experimental for NMC-1

Crystals grew as colorless prisms by solvothermal reaction of  $\text{H}_2\text{L}$  and  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with oxalic acid and sodium hydroxide in DMF/DEF mixture solvent at  $100^\circ\text{C}$ . The data crystal had approximate dimensions;  $0.17 \times 0.11 \times 0.06$  mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a  $\mu$ -focus  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.5418 \text{ \AA}$ ) with collimating mirror monochromators. A total of 1056 frames of data were collected using  $\omega$ -scans with a scan range of  $0.5^\circ$  and a counting time of 15 seconds per frame using a detector offset of  $\pm 40.5^\circ$  and a counting time of 43 seconds per frame using a detector offset of  $\pm 111.0^\circ$ . The data were collected at 100 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.<sup>1</sup> The structure was solved by direct methods using SIR2004<sup>2</sup> and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.<sup>5</sup> Structure analysis was aided by use of the programs PLATON98<sup>6</sup> and WinGX.<sup>7</sup> The hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to  $1.2 \times U_{\text{eq}}$  of the attached atom ( $1.5 \times U_{\text{eq}}$  for methyl hydrogen atoms).

A molecule of the calixpyrrole dibenzoic acid was located around a crystallographic inversion center at  $1, 1, \frac{1}{2}$ . This molecule was not coordinated to the Pr ions. It occupied a cavity in the 3D structure of the Pr complex. The electron density of the atoms of this calixpyrrole was lower than what is expected for a fully occupied molecule. The site occupancy for this calixpyrrole was estimated to be  $1/2$ . The complex contained several solvent molecules, both dimethyl formamide and diethyl formamide. Several of these molecules were disordered. Some were badly disordered and could not be modeled effectively. The contributions to the scattering factors due to this solvent molecule were removed by use of the utility SQUEEZE<sup>8</sup> in PLATON98. PLATON98 was used as incorporated in WinGX. The function,  $\sum w(|F_o|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_o))^2 + (0.0978 \times P)^2 + (9.1139 \times P)]$  and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.170, with  $R(F)$  equal to 0.0555 and a goodness of fit,  $S$ , = 1.08. Definitions

used for calculating  $R(F)$ ,  $R_w(F^2)$  and the goodness of fit,  $S$ , are given below.<sup>9</sup> The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>10</sup> All figures were generated using SHELXTL/PC.<sup>11</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found in the CIF. CCDC deposition number: 1475465.

**Table S2.** Crystal data and structure refinement for **NMC-1**.

Empirical formula	C286 H338 N38 O40 Pr4	
Formula weight	5511.56	
Temperature	173(2) K	
Wavelength	1.54184 Å	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 20.6712(4) Å	$\alpha = 62.477(2)^\circ$ .
	b = 21.0386(5) Å	$\beta = 79.558(2)^\circ$ .
	c = 21.6281(5) Å	$\gamma = 67.086(2)^\circ$ .
Volume	7683.2(3) Å <sup>3</sup>	
Z	1	
Density (calculated)	1.191 Mg/m <sup>3</sup>	
Absorption coefficient	5.329 mm <sup>-1</sup>	
F(000)	2876	
Crystal size	0.17 x 0.11 x 0.06 mm <sup>3</sup>	
Theta range for data collection	2.304 to 76.398°.	
Index ranges	-25 ≤ h ≤ 25, -26 ≤ k ≤ 24, -25 ≤ l ≤ 26	
Reflections collected	51735	
Independent reflections	30831 [R(int) = 0.0320]	
Completeness to theta = 67.684°	99.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.881	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	30831 / 2699 / 1746	
Goodness-of-fit on F <sup>2</sup>	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0555, wR2 = 0.1507	
R indices (all data)	R1 = 0.0733, wR2 = 0.1704	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.150 and -1.332 e.Å <sup>-3</sup>	

## X-ray Experimental for NMC-2

Crystals grew pale green prisms by solvothermal reaction of biphenyl-4,4'-dicarboxylic acid and  $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  in DMF/DEF mixture solvent at  $100^\circ\text{C}$ . The datum crystal was cut from a larger crystal and had approximate dimensions;  $0.2 \times 0.1 \times 0.05$  mm. The data were collected at  $-173^\circ\text{C}$  on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with  $\text{MoK}\alpha$  radiation ( $\lambda = 0.71075 \text{ \AA}$ ). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 868 frames of data were collected using  $\omega$ -scans with a scan range of  $0.5^\circ$  and a counting time of 76 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1. Data reduction were performed using SAINT V8.27B.<sup>3</sup> The structure was solved by direct methods using SIR97<sup>12</sup> and refined by full-matrix least-squares on  $F^2$  with anisotropic displacement parameters for the non-H atoms using SHELXL-2014/7.<sup>5</sup> Structure analysis was aided by use of the programs PLATON98<sup>6</sup> and WinGX.<sup>7</sup>

A cylindrical region parallel to the c-axis contained some disordered solvent. The solvent appeared to be a mixture of n-hexane and DMF. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE<sup>8</sup> in PLATON98.<sup>6</sup>

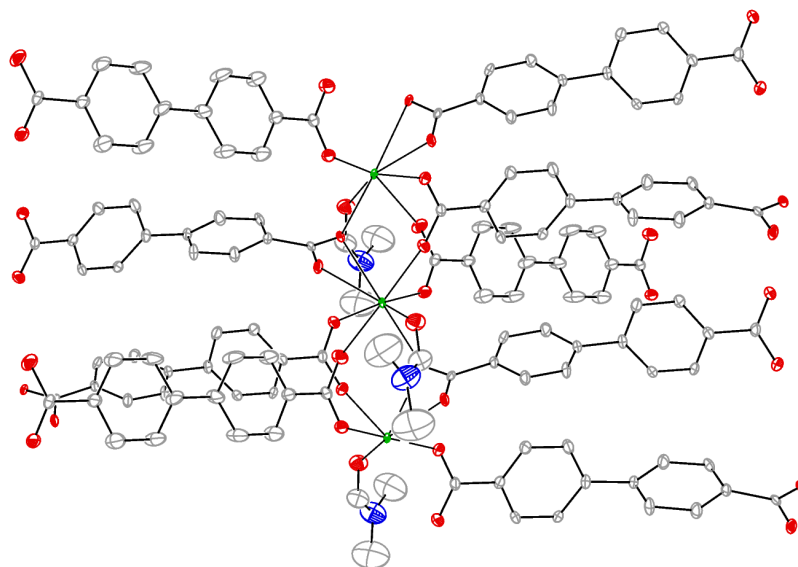
The function,  $\sum w(|F_o|^2 - |F_c|^2)^2$ , was minimized, where  $w = 1/[(\sigma(F_o))^2 + (0.0401 \cdot P)^2]$  and  $P = (|F_o|^2 + 2|F_c|^2)/3$ .  $R_w(F^2)$  refined to 0.0828, with  $R(F)$  equal to 0.0322 and a goodness of fit,  $S$ , = 1.04. Definitions used for calculating  $R(F)$ ,  $R_w(F^2)$  and the goodness of fit,  $S$ , are given below.<sup>9</sup> The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).<sup>10</sup> All figures were generated using SHELXTL/PC.<sup>11</sup> Tables of positional and thermal parameters, bond lengths and angles, torsion angles and figures are found in the CIF. CCDC deposition number: 1475466.

**Table S3.** Crystal data and structure refinement for **NMC-2**.

Empirical formula	C60 H68 N16 O4 Pr2	
Formula weight	1359.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	C 2	
Unit cell dimensions	a = 28.8960(9) Å	$\alpha = 90^\circ$ .
	b = 8.6749(3) Å	$\beta = 116.0560(10)^\circ$ .
	c = 14.2513(4) Å	$\gamma = 90^\circ$ .
Volume	3209.29(18) Å <sup>3</sup>	
Z	2	
Density (calculated)	1.406 Mg/m <sup>3</sup>	
Absorption coefficient	1.556 mm <sup>-1</sup>	
F(000)	1380	
Crystal size	0.2 x 0.1 x 0.05 mm <sup>3</sup>	
Theta range for data collection	2.475 to 33.678°.	
Index ranges	-44<= <i>h</i> <=28, -12<= <i>k</i> <=10, -17<= <i>l</i> <=21	
Reflections collected	10221	
Independent reflections	7556 [R(int) = 0.0255]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00 and 0.761	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	7556 / 413 / 392	
Goodness-of-fit on F <sup>2</sup>	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0322, wR2 = 0.0805	
R indices (all data)	R1 = 0.0391, wR2 = 0.0828	
Absolute structure parameter	0.110(19)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.785 and -0.589 e.Å <sup>-3</sup>	



**Figure S18.** View of **NMC-2** showing a portion of the 3-dimensional array. Displacement ellipsoids are scaled to the 50% probability level.



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 $R(F) = \sum (|F_o| - |F_c|) / \sum |F_o|$  for reflections with  $F_o > 4(\sigma(F_o))$ .  
 $S = [\sum w(|F_o|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$ , where n is the number of reflections and p is the number of refined parameters.
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