

## Supporting Information

### **Solvent-free mechanochemistry for the preparation of mixed- ligand cuboctahedral porous coordination cages**

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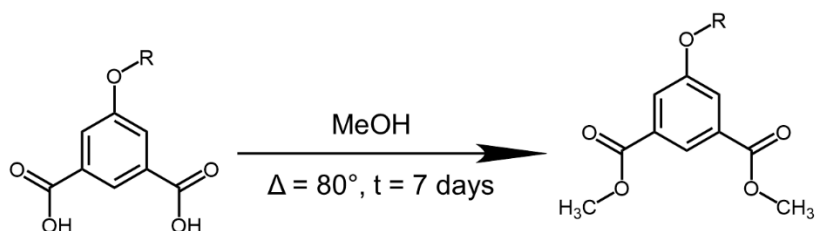
## 1. Experimental

### Sample preparation

All commercial reagents were used as obtained without further purification. Air sensitive reactions were performed in an inert box using dry solvents. All the synthesized cages were activated at 100 °C under N<sub>2</sub> flow to remove the trapped volatile solvents in avoiding solvent effect while grinding. Excess amount of benzene was used to remove the unreacted 5-octadecoxy-bdc and corresponding Cu and Cr cages. The final ground insoluble solids were separated by decanting the above benzene solution after centrifugation. Decanted benzene was vacuumed off to recover the unreacted benzene washed octadecoxy-bdc cage for cage-cage grinding otherwise cage-ligand grinding. Both the insoluble solid and vacuum dried filtrate were further activated at 100 °C before performing corresponding characterizations. Adsorption standard samples were activated at RT under dynamic vacuum.

### Methanol wash: Removal of benzene insoluble excess carboxylate ligands through esterification from cage-free ligands grinding

Mechanochemically replaced or unreacted excess R-bdc (R = hexoxy, octadecoxy, H, OH, CH<sub>3</sub>, and CN) ligands, generated from different cage-free ligands grinding were removed from the post-ground solids utilizing the MeOH solubility of these ligands in ester form. With a view to ester conversion of these free carboxylate ligands, resultant ground solids were first washed with benzene to remove octadecoxy-bdc cage/ligand and then dispersed into MeOH. The dispersed MeOH suspensions were then refluxed at 80 °C for 7 days under N<sub>2</sub> flow conditions. After 7 days, the resultant mixture was centrifuged and separated out both the MeOH soluble filtrate and insoluble solid cage. The MeOH solvent was then vacuumed off leaving the white carboxylate ester powder of the carboxylate bdc ligands. On the other hand, the insoluble solid cage was vacuum-dried for NMR characterization.



### Sample digestion for NMR

10 mg of the corresponding sample was taken into a 4 ml vial followed by adding a single drop of DCl. 700  $\mu$ l DMSO-d<sub>6</sub> was added to the vial and sonicated for 5 min making the sample sufficiently soluble in DMSO-d<sub>6</sub>. The sample solution was then transferred into an NMR tube for spectroscopic analysis.

### Instruments

A typical mortar pestle was used for mechanical grinding and each sample was continuously ground for 10 minutes. <sup>1</sup>H-NMR spectra were recorded using an AV 400 spectrometer whereas ALPHA II

of Bruker series provided the Infrared (IR) spectra measurement. The absorbance measurement was carried out using AvaSpec-ULS2048CL.

## 2. Ligand synthesis

### Synthesis of 5-hexoxy-1,3-benzenedicarboxylic acid (5-hexoxy-bdc)

The corresponding ligand was synthesized followed by one of the previous group papers with necessary modifications.<sup>1</sup> Dimethyl-5-OH-isophthalate (4g, 19 mmol), 1-iodohexane (3.1 ml, 21 mmol), and potassium carbonate (2.9 g, 21 mmol) were added in a 250 ml RBF followed by adding 80 ml acetone and stirring at 55 °C for next 12 hours. The generated white solid powder was then separated by vacuum filtration. The filtrate was then undergone through another 12 hours base-catalyzed hydrolysis at 55 °C by adding potassium hydroxide (2.46 g, 43.8 mmol), and 80 ml of DI water. The concentrated solution (removal of acetone) was later brought under acidic treatment (pH = 1) by adding conc. HCl (1 M). Then, the final deprotected product was then isolated via vacuum filtration and dried overnight at 75 °C. <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  = 13.28 (s, 2H, OH), 8.05 (t, 1H, CH aromatic ring), 7.62 (d, 2H, CH aromatic ring), 4.06 (d, 2H, OCH<sub>2</sub>), 1.72 (p, 2H, CH<sub>2</sub>) 1.30 (m, 6H, C<sub>3</sub>H<sub>6</sub>), 0.87 (t, 3H, CH<sub>3</sub>).

### Synthesis of 5-octadecoxy-1,3-benzenedicarboxylic acid (5-octadecoxy-bdc)

The following ligand was synthesized accordingly with the stoichiometric adjustment of the reactants. Dimethyl-5-OH-isophthalate (4g, 19 mmol), 1-iodooctadecane (4.7 g, 21 mmol), and potassium carbonate (2.9 g, 21 mmol) were stirred in 80 ml acetone at 60 °C for 12 hours followed by base-catalyzed hydrolysis (2.46 g, 43.8 mmol potassium hydroxide, 80 ml of DI water) at 60 °C for 12 hours and HCl acidification (pH = 1) after the vacuum filtration. The deprotected ligand was finally isolated via vacuum filtration and dried overnight at 75 °C in the oven. <sup>1</sup>H-NMR (400 MHz, DMSO):  $\delta$  = 13.25 (s, 2H, OH), 8.05 (t, 1H, CH aromatic ring), 7.62 (d, 2H, CH aromatic ring), 4.06 (d, 2H, OCH<sub>2</sub>), 1.73 (p, 2H, CH<sub>2</sub>) 1.21 (m, 6H, C<sub>3</sub>H<sub>6</sub>), 0.83 (t, 3H, CH<sub>3</sub>).

## 3. Cage synthesis

### Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub>

Cu(NO<sub>3</sub>)<sub>2</sub>·2.5H<sub>2</sub>O (0.754 g, 3.24 mmol) and 5-hexoxy-1,3-benzenedicarboxylic acid (0.862 g, 3.24 mmol) were transferred into a 500 ml jar with 72 ml DMF and 228 ml EtOH and heated then at 80 °C for 2 days. The resulting blue crystals were then pipetted out and dispersed in methanol for 12 hours. Three additional methanol washes were done each for 12 hours to completely remove the amide solvent. The final product was then vacuum dried and activated at 100 °C under N<sub>2</sub> flow to remove trapped volatile methanol solvent.<sup>1</sup>

### Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub>

Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (0.082 g, 0.41 mmol) and 5-octadecoxy-1,3-benzenedicarboxylic acid (0.1893 g, 0.42 mmol) were dissolved in 10 ml DMF solvents separately in 20 ml vials. The solutions were then transferred into a 100 ml jar and heated at 80 °C for 2 hours. 15 ml MeOH was then added to the jar to precipitate the blue powder. The suspended powder was then separated and redispersed in MeOH for 12 hours followed by three more overnight methanol washes. The final powder was then vacuum dried and activated at 100 °C under N<sub>2</sub> flow.

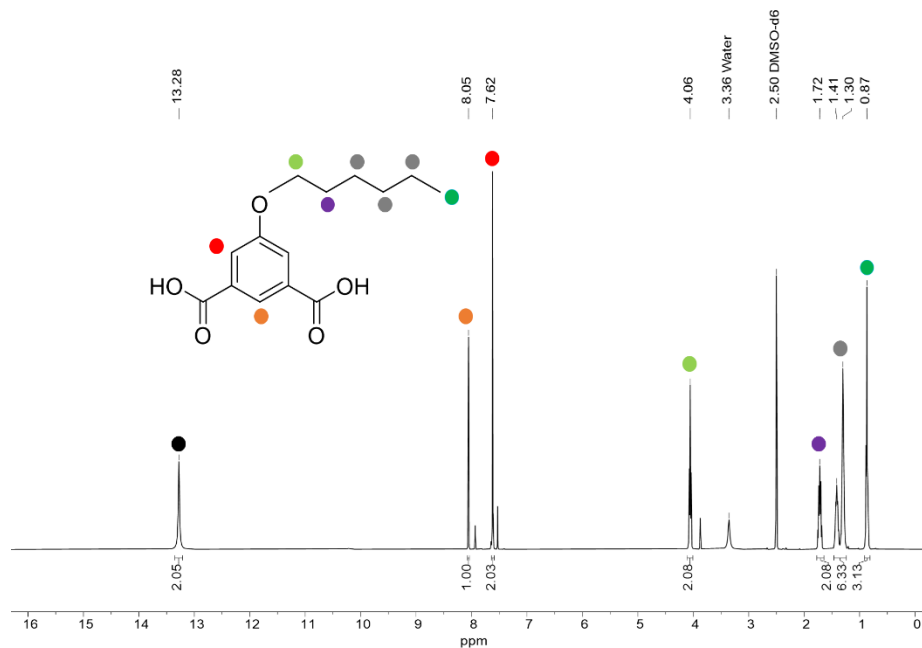
### **Cr<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub>**

Cr<sub>2</sub>(OAc)<sub>4</sub> (0.1 g, 0.266 mmol) and 5-hexoxy-1,3-benzenedicarboxylic acid (0.1404 g, 0.532 mmol) were dissolved into 12 ml DMF and 3 ml MeOH solvent in a 20 ml vial and heated at 75 °C for 2 days. 5 ml MeOH was then layered on the top of the solution and allowed them to diffuse slowly. Slow diffusion made the cage precipitate overnight. The final washing was performed in THF (3x) every 12 hours and vacuum dried at 100 °C.

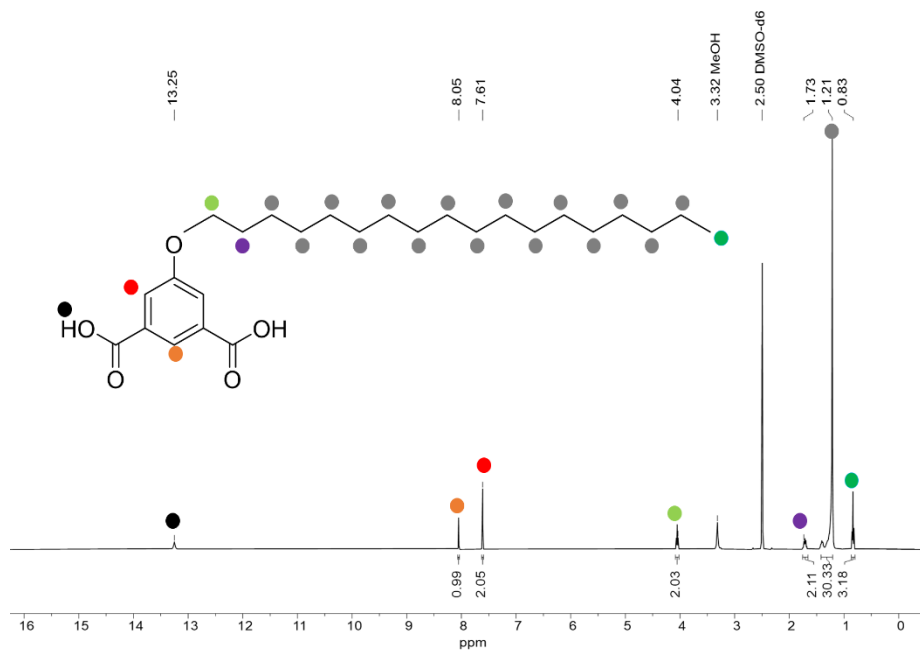
### **Cr<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub>**

Cr<sub>2</sub>(OAc)<sub>4</sub> (0.1 g, 0.266 mmol) and 5-octadecoxy-1,3-benzenedicarboxylic acid (0.229 g, 0.532 mmol) were added in a 20 ml vial and dissolved into 12 ml DMF and 3 ml MeOH. The solution was then heated at 75 °C for 2 days. Additional MeOH was layered on the solution top to allow slow diffusion, resulting in the precipitation of the cage overnight. The resultant cage was then washed off with THF three times, replacing fresh THF every 12 hours, and vacuum dried at 100 °C.

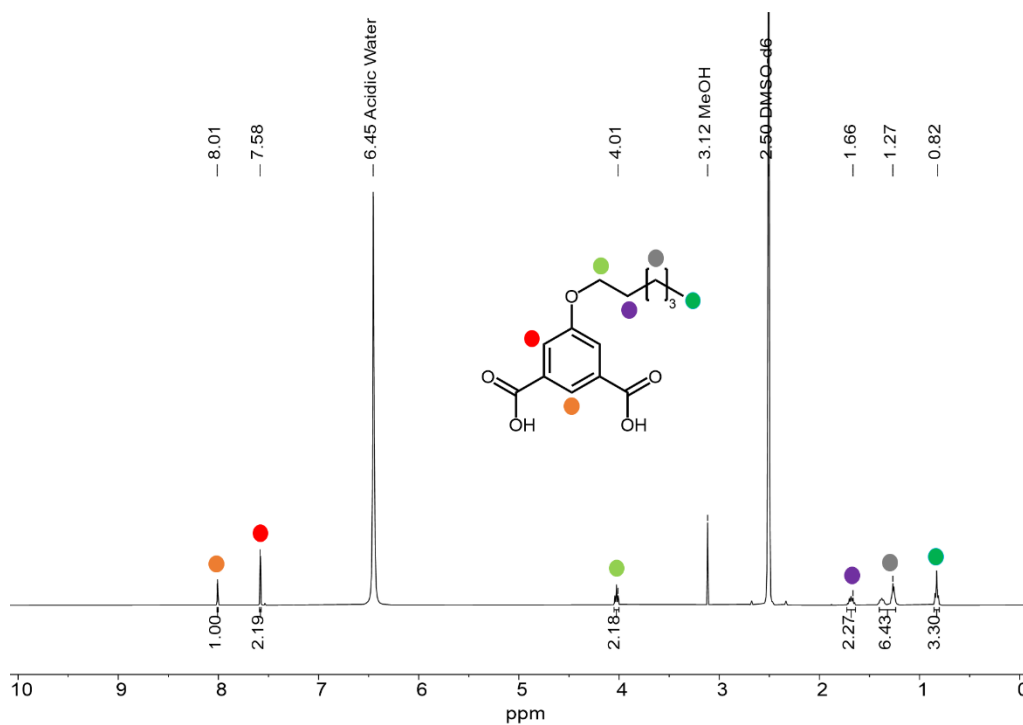
## 4. <sup>1</sup>H-NMR Spectra



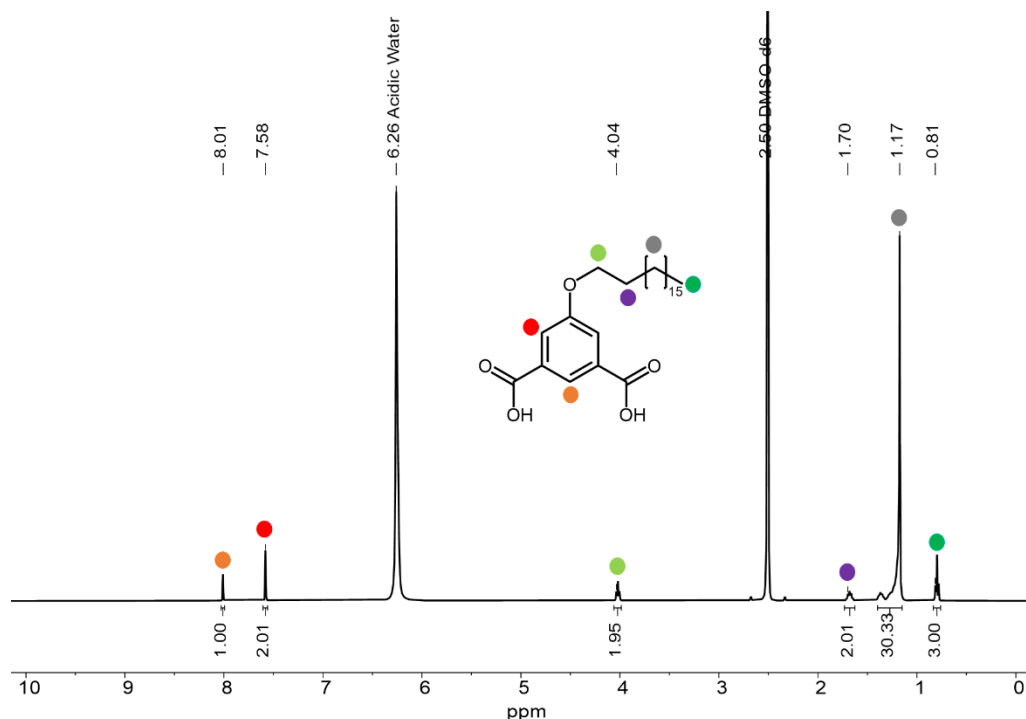
**Figure S1.** <sup>1</sup>H-NMR spectrum of 5-hexoxy-1,3-benzenedicarboxylic acid in DMSO-d<sub>6</sub>.



**Figure S2.**  $^1\text{H-NMR}$  spectrum of 5-octadecoxy-1,3-benzenedicarboxylic acid in  $\text{DMSO-d}_6$ .



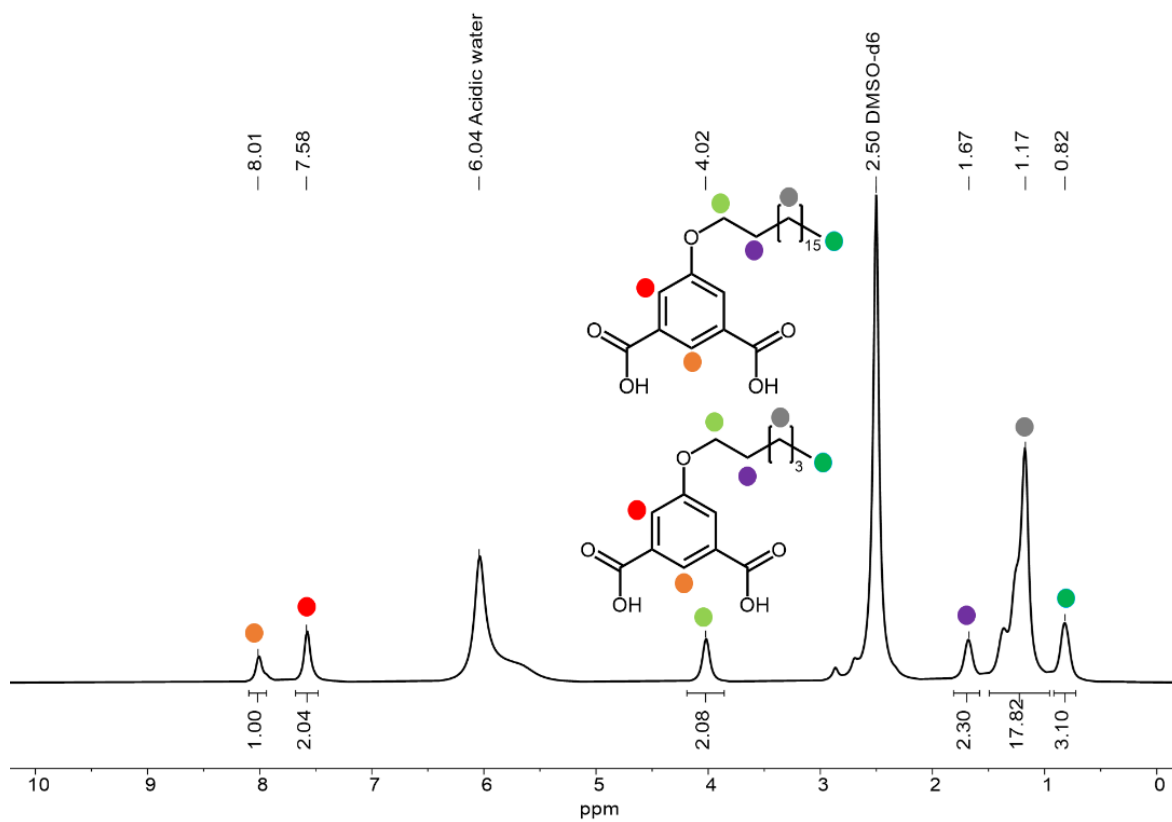
**Figure S3.**  $^1\text{H-NMR}$  spectrum of DCl digested  $\text{Cu}_{24}(\text{5-hexoxy-1,3-bdc})_{24}$  in  $\text{DMSO-d}_6$ .



**Figure S4.** <sup>1</sup>H-NMR spectrum of DCl digested Cu<sub>24</sub>(5-octadecoxy-1,3-bdc)<sub>24</sub> in DMSO-d<sub>6</sub>.

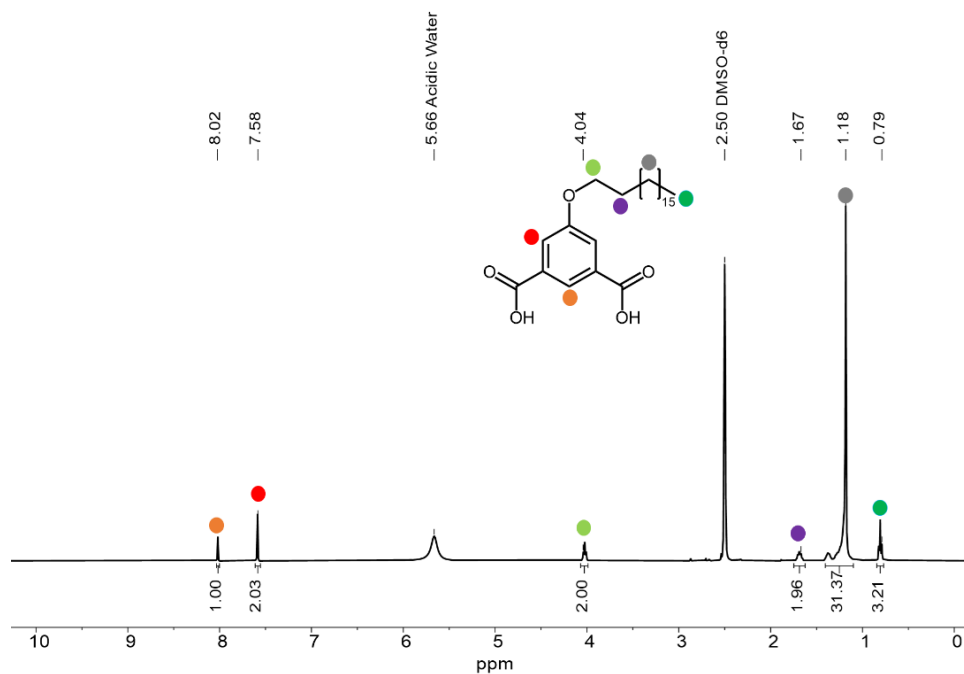
#### 4. 1 Mechanochemical grinding of cage and free ligands

Free octadecoxy-bdc ligand was ground with Cu<sub>24</sub>(hexoxy-bdc)<sub>24</sub> cage in 24:1 equivalent ratio to happen to be exchanged with hexoxy-bdc ligand affording a mixed ligand cage of Cu<sub>24</sub>(octadecoxy-bdc)<sub>12</sub>(hexoxy-bdc)<sub>12</sub> upon benzene wash to remove octadecoxy-bdc ligand. Similarly, free hexoxy-bdc ligands were sequentially ground with Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage to observe successive free ligand (hexoxy-bdc) incorporation into Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage. 24 equivalent hexoxy-bdc ligands were initially ground with 1 equivalent Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage resulting in a mixed ligand cage of Cu<sub>24</sub>(octadecoxy-bdc)<sub>12</sub>(hexoxy-bdc)<sub>12</sub> upon benzene wash and MeOH reflux to remove unreacted Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage and excess hexoxy-bdc ligands respectively. The resultant Cu<sub>24</sub>(octadecoxy-bdc)<sub>12</sub>(hexoxy-bdc)<sub>12</sub> cage was then dried and ground with another 24 equivalent hexoxy-bdc ligands resulting in a mixed ligand cage of Cu<sub>24</sub>(octadecoxy-bdc)<sub>3</sub>(hexoxy-bdc)<sub>21</sub> upon MeOH refluxing to remove excess hexoxy-bdc and exchanged octadecoxy-bdc ligands. Benzene-washed Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage and MeOH soluble hexoxy-bdc ligands were characterized by <sup>1</sup>H-NMR upon vacuum drying.

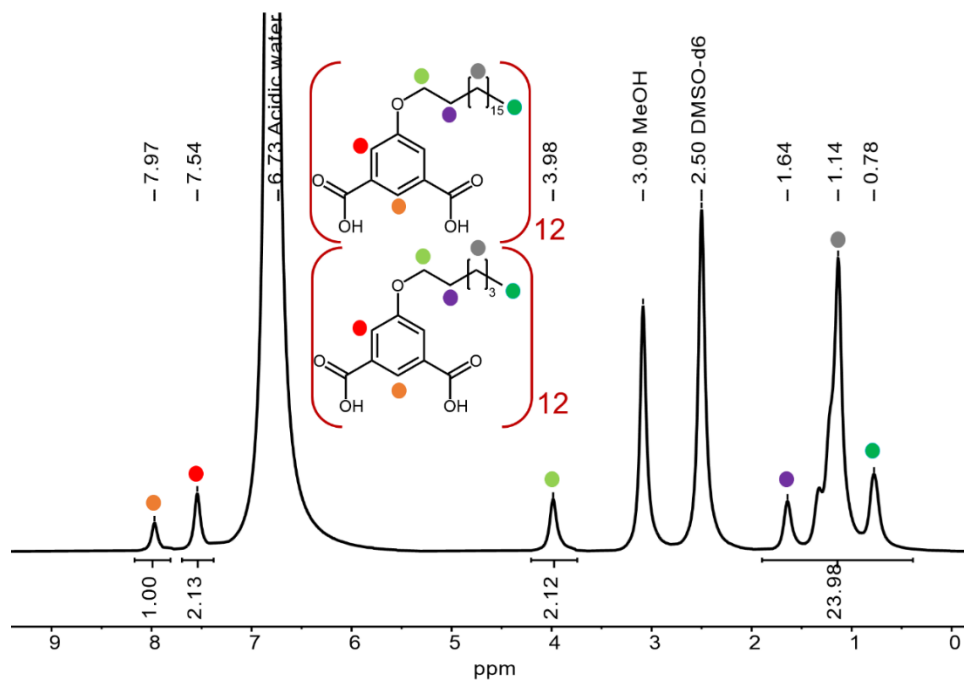


**Figure S5.** <sup>1</sup>H-NMR spectrum of DCI digested ground insoluble solid of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>12</sub>(5-hexoxy-bdc)<sub>12</sub> in DMSO-d<sub>6</sub> obtained from grinding of Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> and free octadecoxy-bdc ligand in 1:24 equivalent ratio.

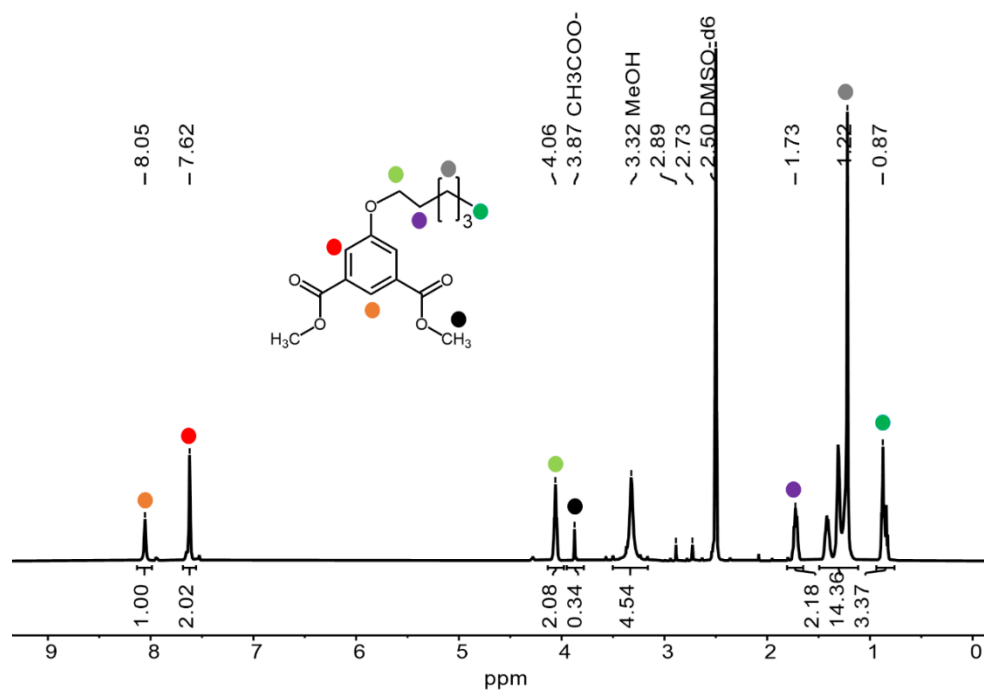




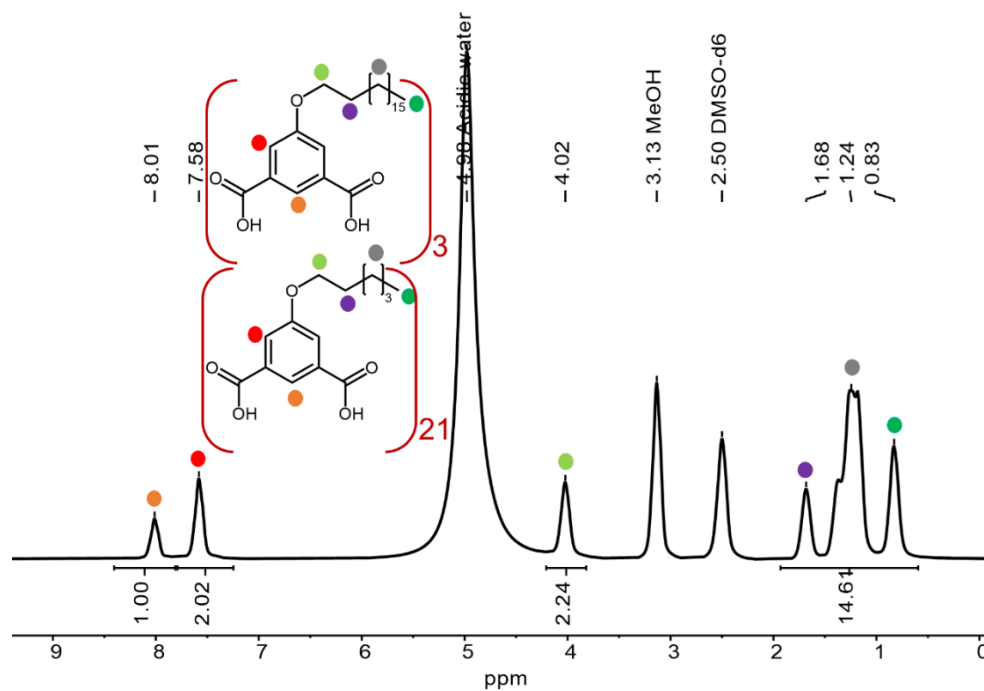
**Figure S6.**  $^1\text{H}$ -NMR spectrum of DCI digested benzene washed filtrate in  $\text{DMSO-d}_6$  obtained from the grinding of  $\text{Cu}_{24}(\text{5-hexoxy-bdc})_{24}$  cage and free 5-octadecoxy-bdc ligands in 1:24 equivalent ratio.



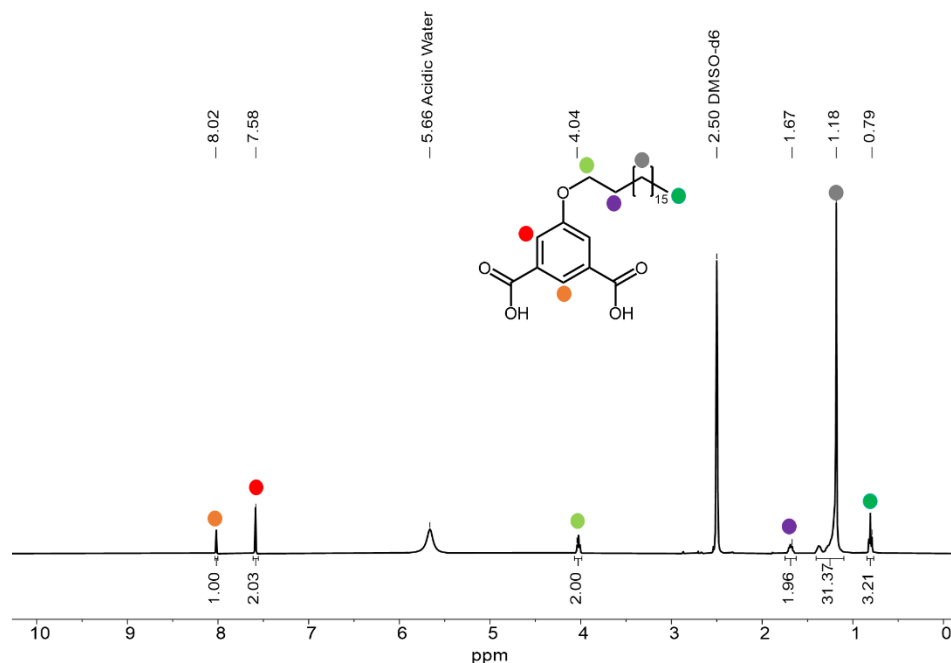
**Figure S7.**  $^1\text{H}$ -NMR spectrum of DCI digested ground insoluble solid of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{12}(\text{5-hexoxy-bdc})_{12}$  in  $\text{DMSO-d}_6$  resulting from initial 1:24 equivalent grinding of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  and free hexoxy-bdc ligands.



**Figure S8.**  $^1\text{H-NMR}$  spectrum of methanol soluble hexoxy-bdc ligands obtained from MeOH reflux of sequentially ground  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  cage and free 5-hexoxy-bdc ligands.



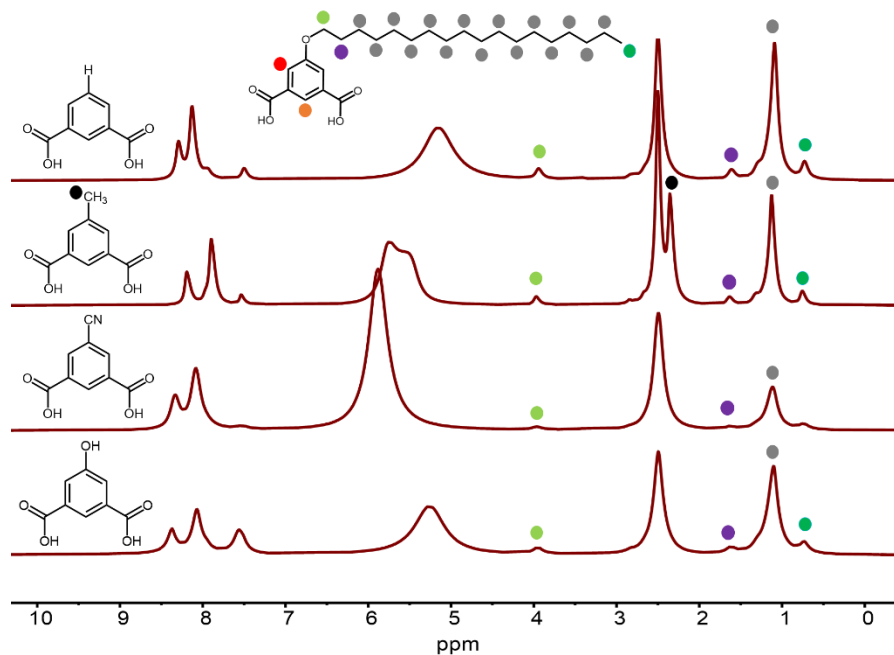
**Figure S9.**  $^1\text{H-NMR}$  spectrum of DCl digested ground insoluble solid of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_3(\text{5-hexoxy-bdc})_{21}$  in  $\text{DMSO-d}_6$  resulting from additional 24 equivalent grinding of 5-hexoxy-bdc ligands and initially obtained  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{12}(\text{5-hexoxy-bdc})_{12}$ .



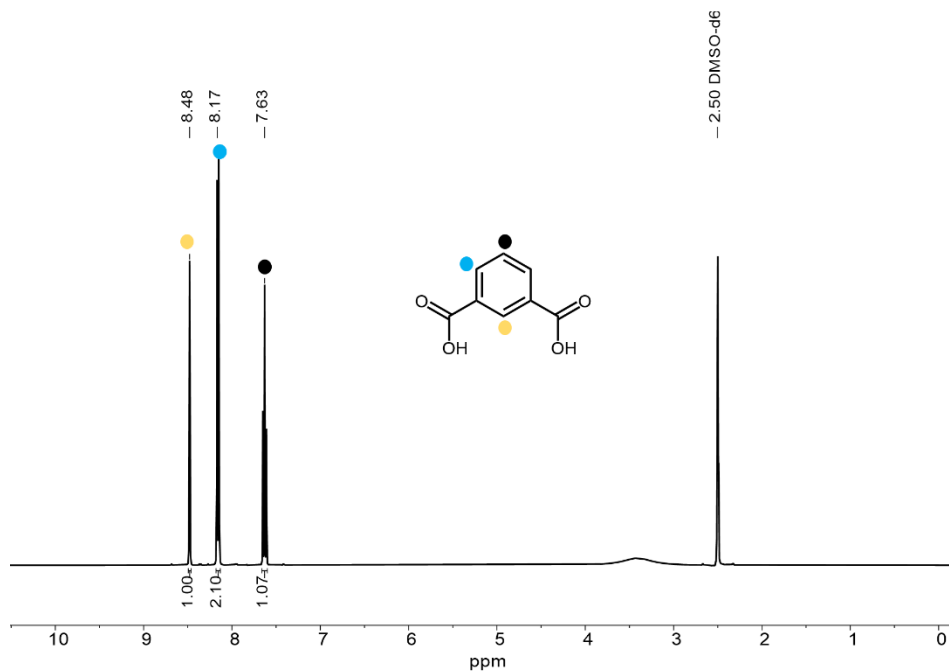
**Figure S10.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene-washed filtrate in  $\text{DMSO-d}_6$  obtained from sequential grinding of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  cage and free 5-hexoxy-bdc ligands.

#### 4.2 Mechanochemical grinding of $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$ cage and other free ligands

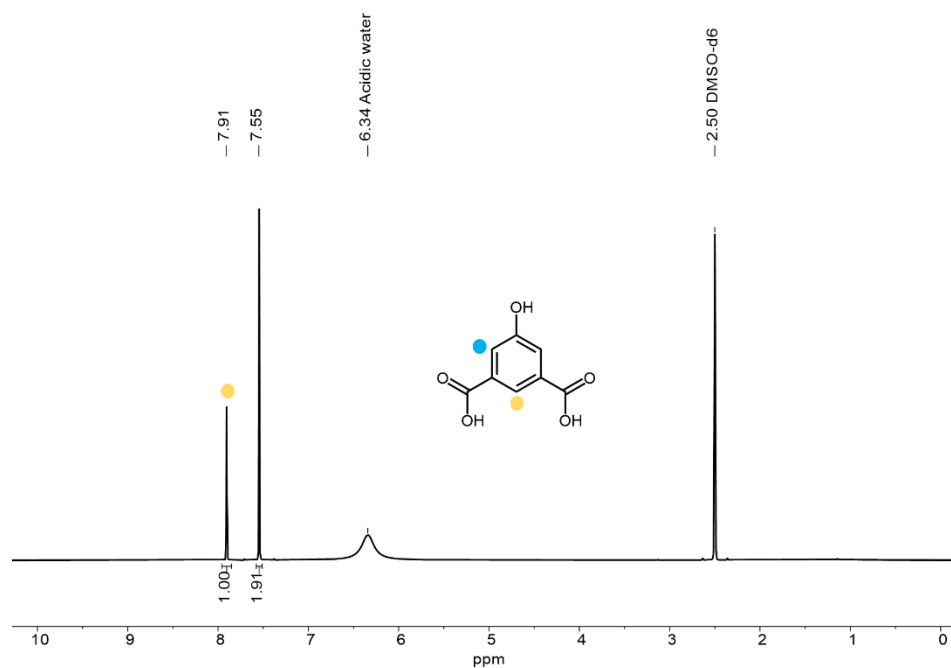
A series of other free bdc ligands, R-bdc (R = H,  $\text{CH}_3$ , OH, CN) functionalized at 5 position were mechanochemically ground with  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$  cage in 24:1 equivalent ratio resulting in a mixed ligand cage of octadecoxy-bdc and free bdc ligands along with an excess amount of insoluble free ligands. Therefore, an optimum amount (4-8 equivalent) free ligands were ground with  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$  cage and benzene washed followed by MeOH refluxing.



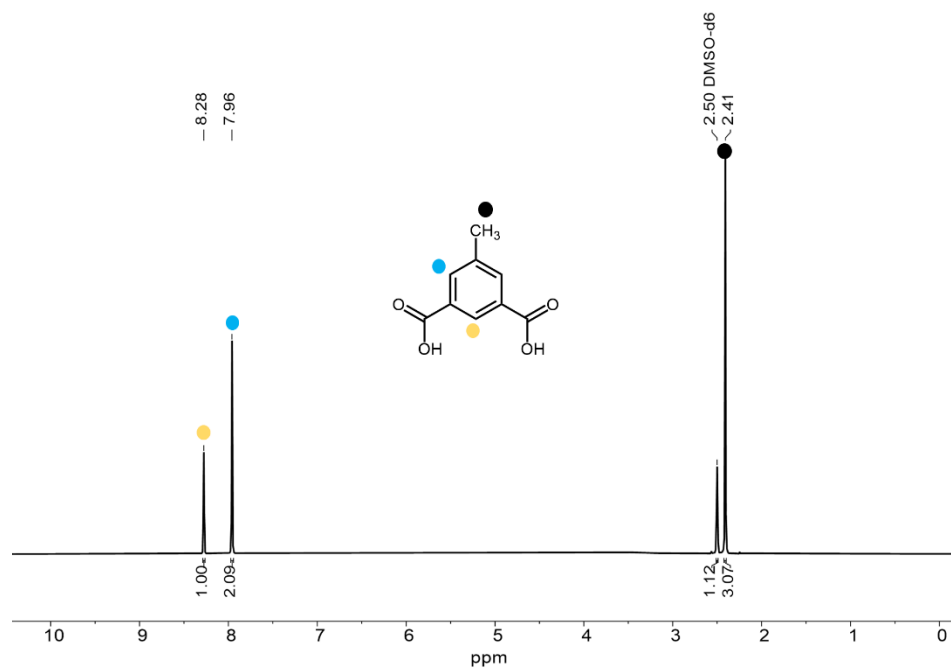
**Figure S11.**  $^1\text{H-NMR}$  spectrum of DCl digested insoluble solids obtained from grinding of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{24}$  cage and R-bdc (R = H,  $\text{CH}_3$ , OH, CN) free ligands in 1:24 equivalent ratio.



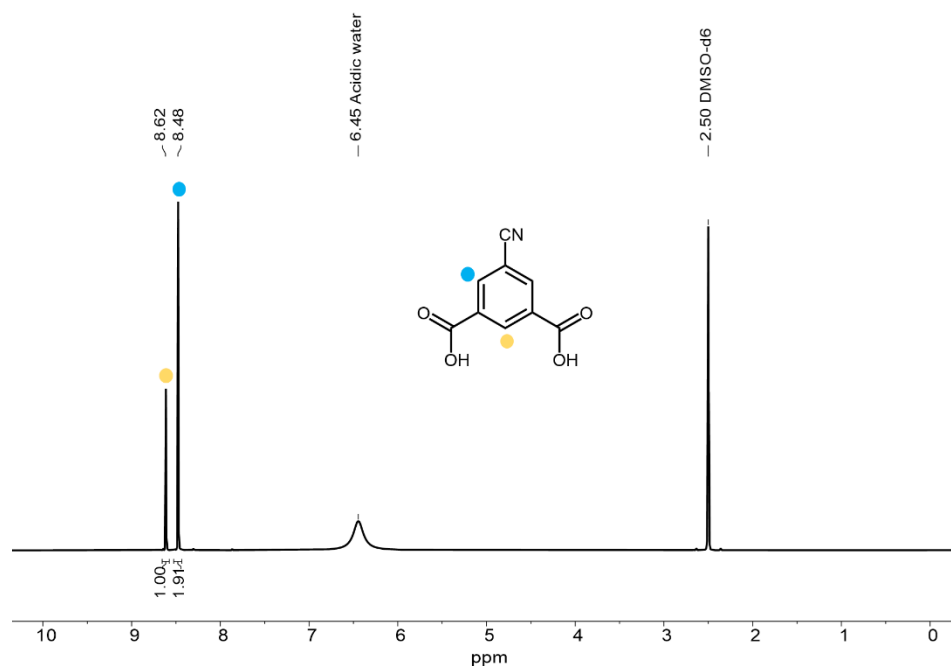
**Figure S12.**  $^1\text{H-NMR}$  spectrum of 1,3-benzenedicarboxylic acid in  $\text{DMSO-d}_6$ .



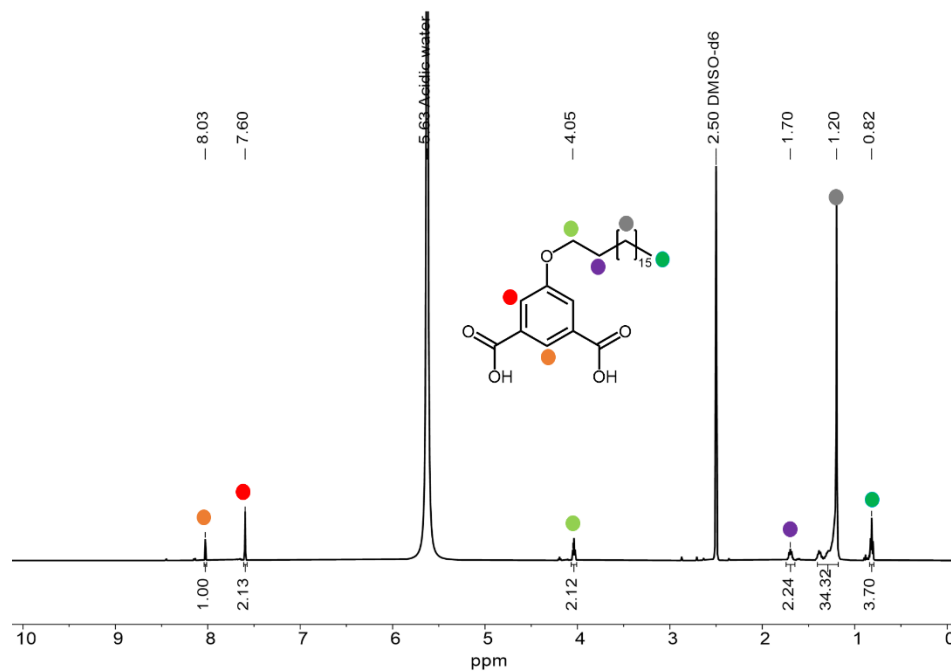
**Figure S13.**  $^1\text{H-NMR}$  spectrum of DCI digested 5-OH-1,3-benzenedicarboxylic acid in  $\text{DMSO-d}_6$ .



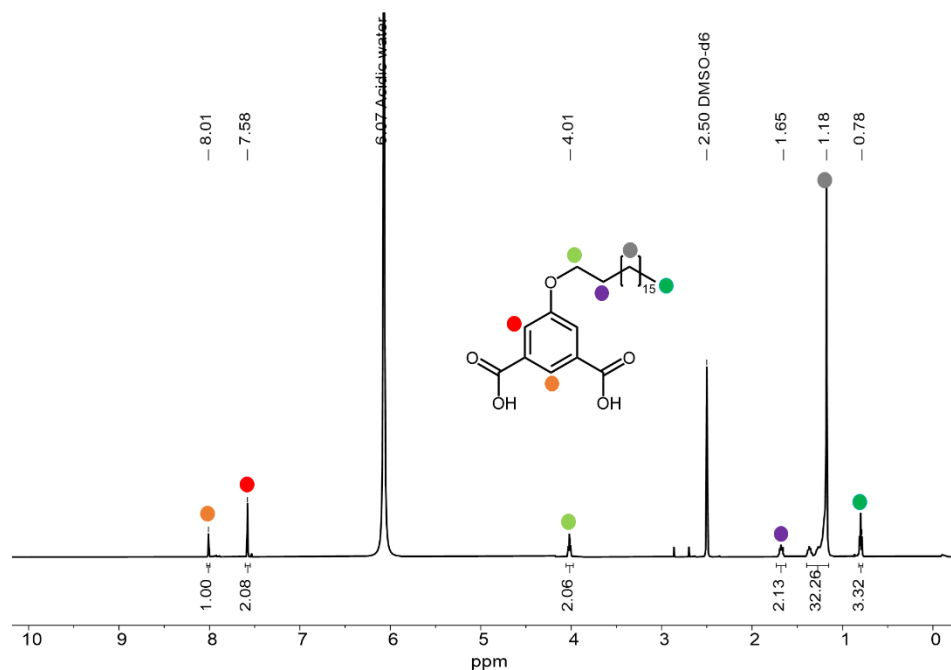
**Figure S14.**  $^1\text{H-NMR}$  spectrum of 5- $\text{CH}_3$ -1,3-benzenedicarboxylic acid in  $\text{DMSO-d}_6$ .



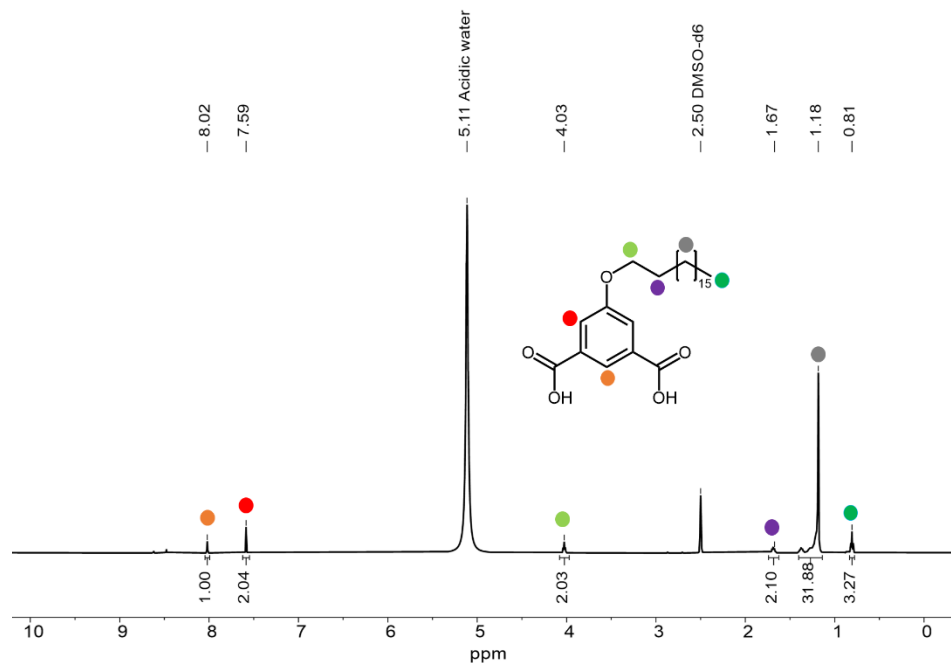
**Figure S15.**  $^1\text{H-NMR}$  spectrum of DCI digested 5-CN-1,3-benzenedicarboxylic acid in  $\text{DMSO-d}_6$ .



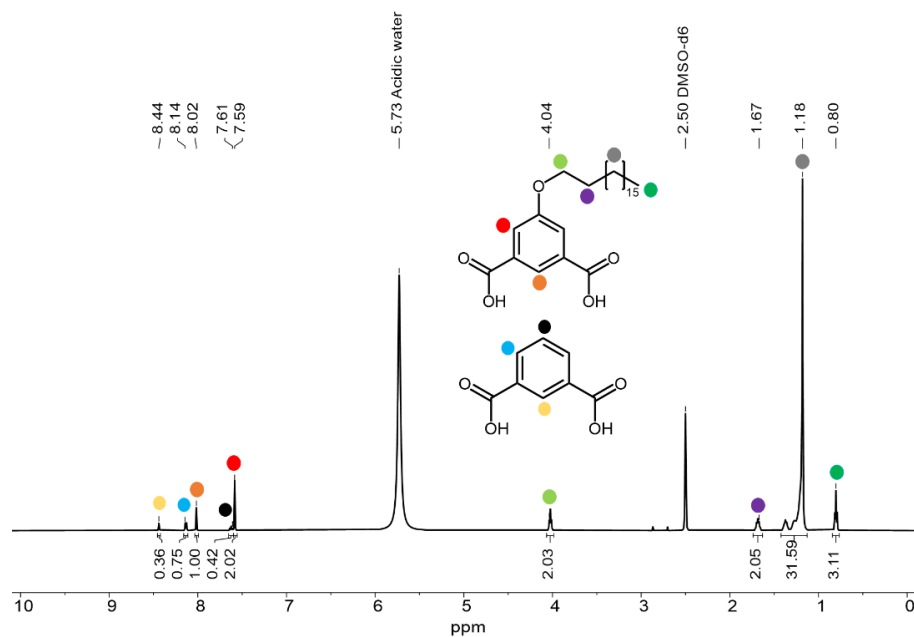
**Figure S16.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene-washed filtrate in  $\text{DMSO-d}_6$  obtained from grinding of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  cage and 1,3-benzenedicarboxylic acid in 1:8 equivalent ratio.



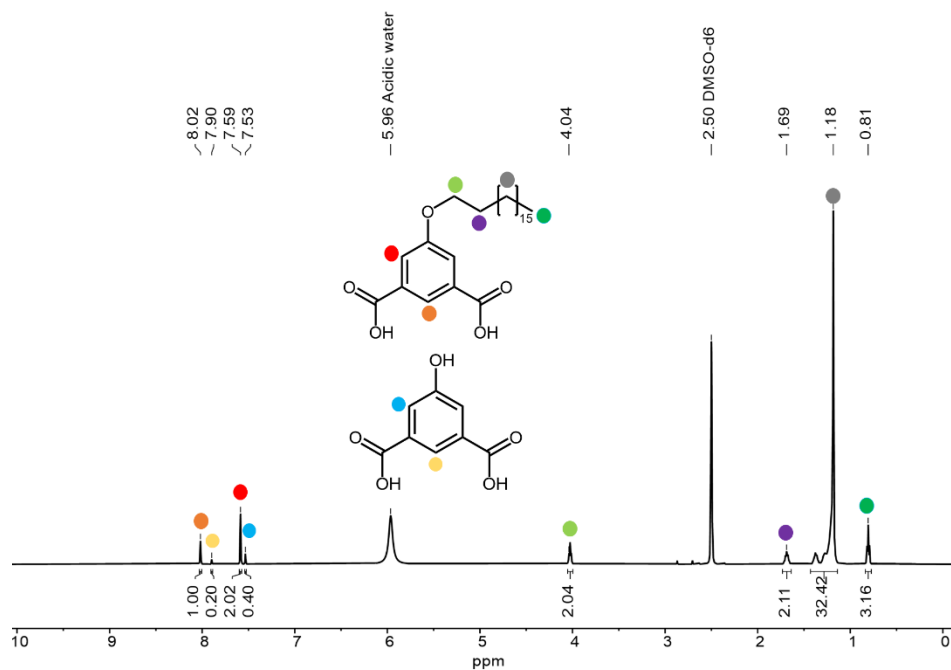
**Figure S17.** <sup>1</sup>H-NMR spectrum of DCI digested benzene-washed filtrate in DMSO-d<sub>6</sub> obtained from grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and 5-OH-1,3-benzenedicarboxylic acid ligand in 1:4 equivalent ratio.



**Figure S18.** <sup>1</sup>H-NMR spectrum of DCI digested benzene washed filtrate resulting from 1:8 equivalent grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and 5-CN-1,3-bdc free ligand.

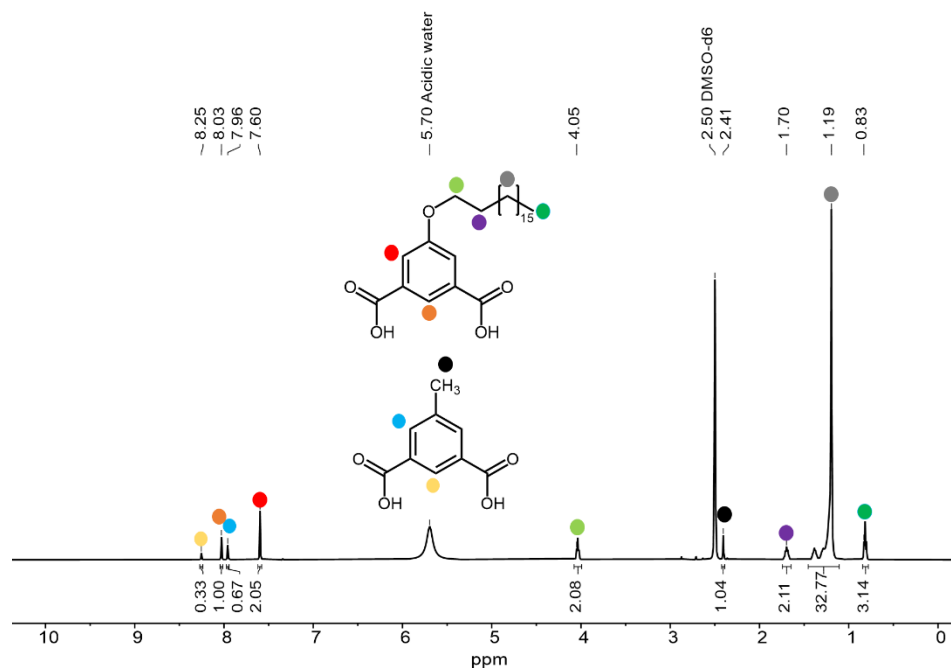


**Figure S19.**  $^1\text{H-NMR}$  spectrum of DCl digested insoluble solid of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{16}(\text{bdc})_8$  in  $\text{DMSO-d}_6$  obtained from grinding of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  and 1,3-benzenedicarboxylic acid in 1:8 equivalent ratio.

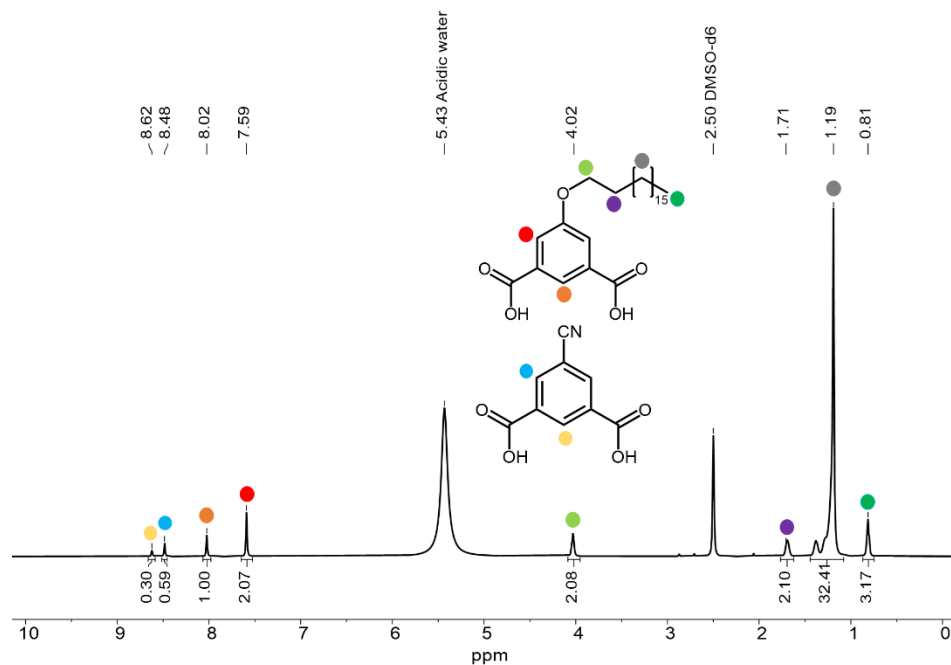


**Figure S20.**  $^1\text{H-NMR}$  spectrum of DCl digested  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{20}(\text{5-OH-bdc})_4$  cage resulting from grinding of  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  and 5-OH-1,3-benzenedicarboxylic acid in 1:4 equivalent ratio.

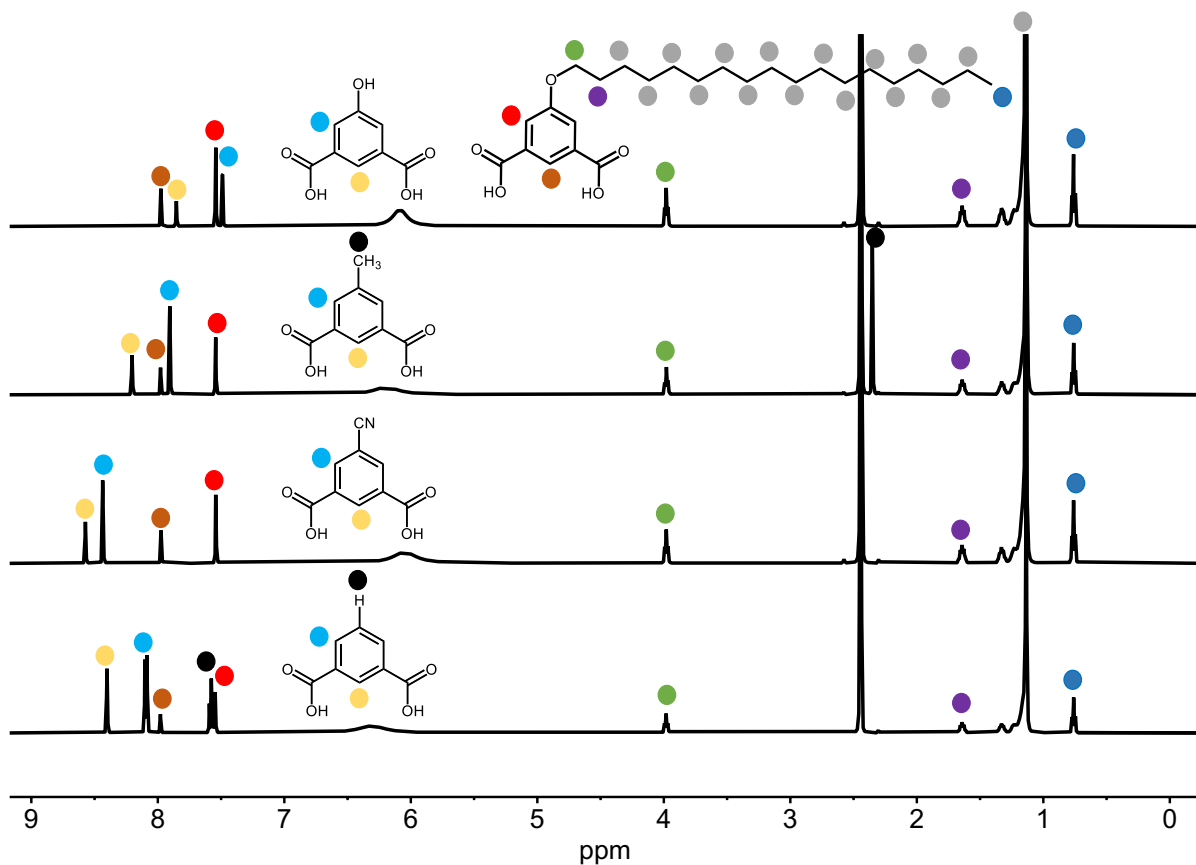




**Figure S21.** <sup>1</sup>H-NMR spectrum of DCI digested Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>16</sub>(5-CH<sub>3</sub>-bdc)<sub>8</sub> attained from mechanochemical grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and 5-CH<sub>3</sub>-1,3-benzenedicarboxylic acid ligand in 1:8 equivalent ratio.



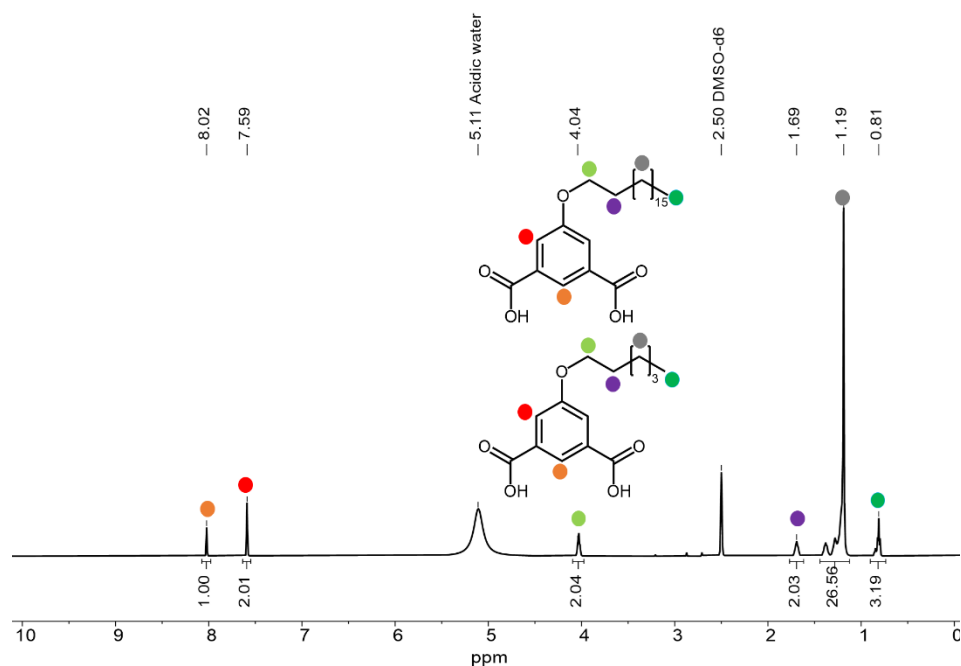
**Figure S22.** <sup>1</sup>H-NMR spectrum of DCI digested Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>16</sub>(5-CN-bdc)<sub>8</sub> obtained from grinding of 1:8 equivalent Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and 5-CN-1,3-benzenedicarboxylic acid.



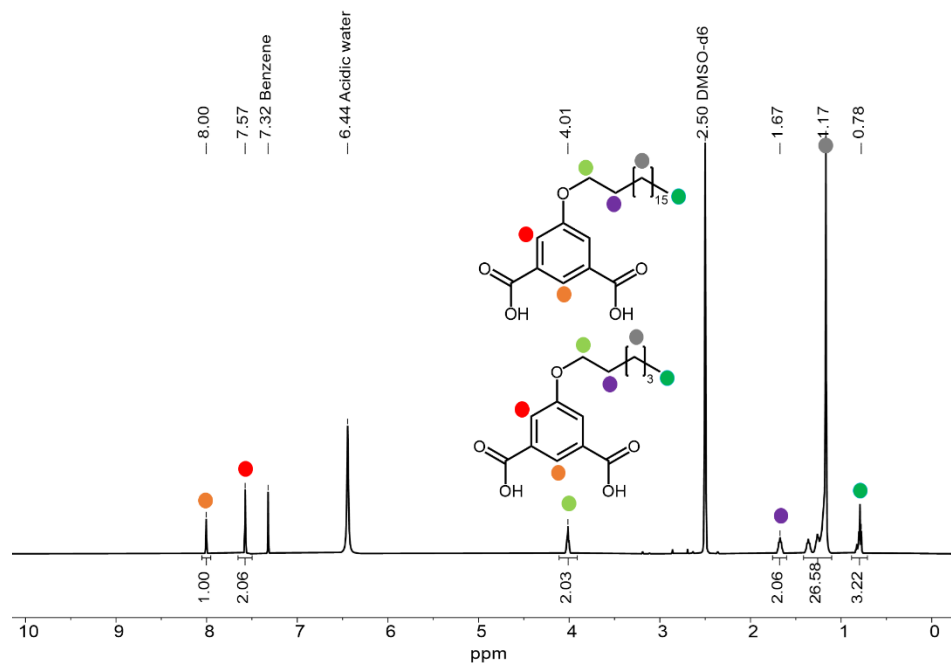
**Figure S23.**  $^1\text{H-NMR}$  spectrum of mechanochemically ground (DCI digested)  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{12}(\text{R-bdc})_{12}$  cages obtained from the grinding of  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$  and corresponding R-bdc ligands in 1:24 equivalent ratio.

### 4.3 Solvent assisted inter-cage linker exchange (SALE)

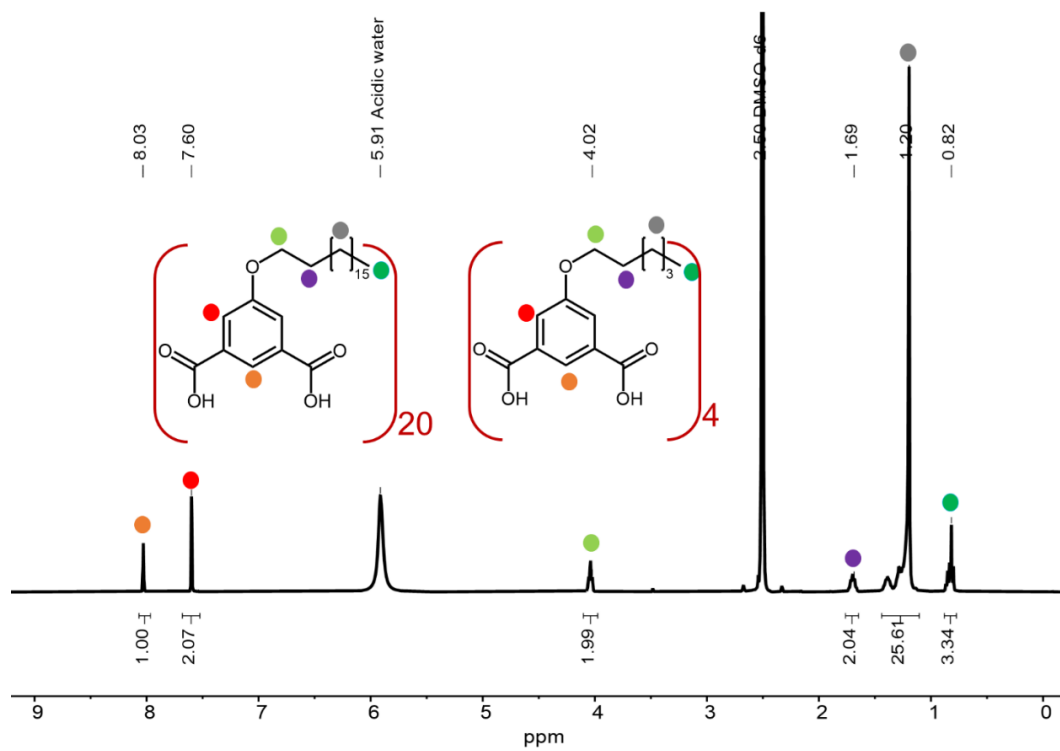
An equimolar (1:1) mixture of  $\text{Cu}_{24}(5\text{-hexoxy-bdc})_{24}$  and  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{24}$  cage was allowed to stir nonstop in benzene for 7 days to facilitate inter-cage ligand exchange. The stirred solution was then subjected to UV-vis absorbance measurement every 24 hours to observe the solubility change of the cages due to intercage ligand exchange. The intermediate filtrates of the stirred solution (2 days and 4 days) were characterized by  $^1\text{H-NMR}$  identifying the filtrate as a mixed ligand cage of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{20}(5\text{-hexoxy-bdc})_4$  effectively contributing to the increased absorbance. The final benzene-stirred insoluble solid (after 7 days) corresponds to a mixed ligand cage of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_4(5\text{-hexoxy-bdc})_{20}$ .



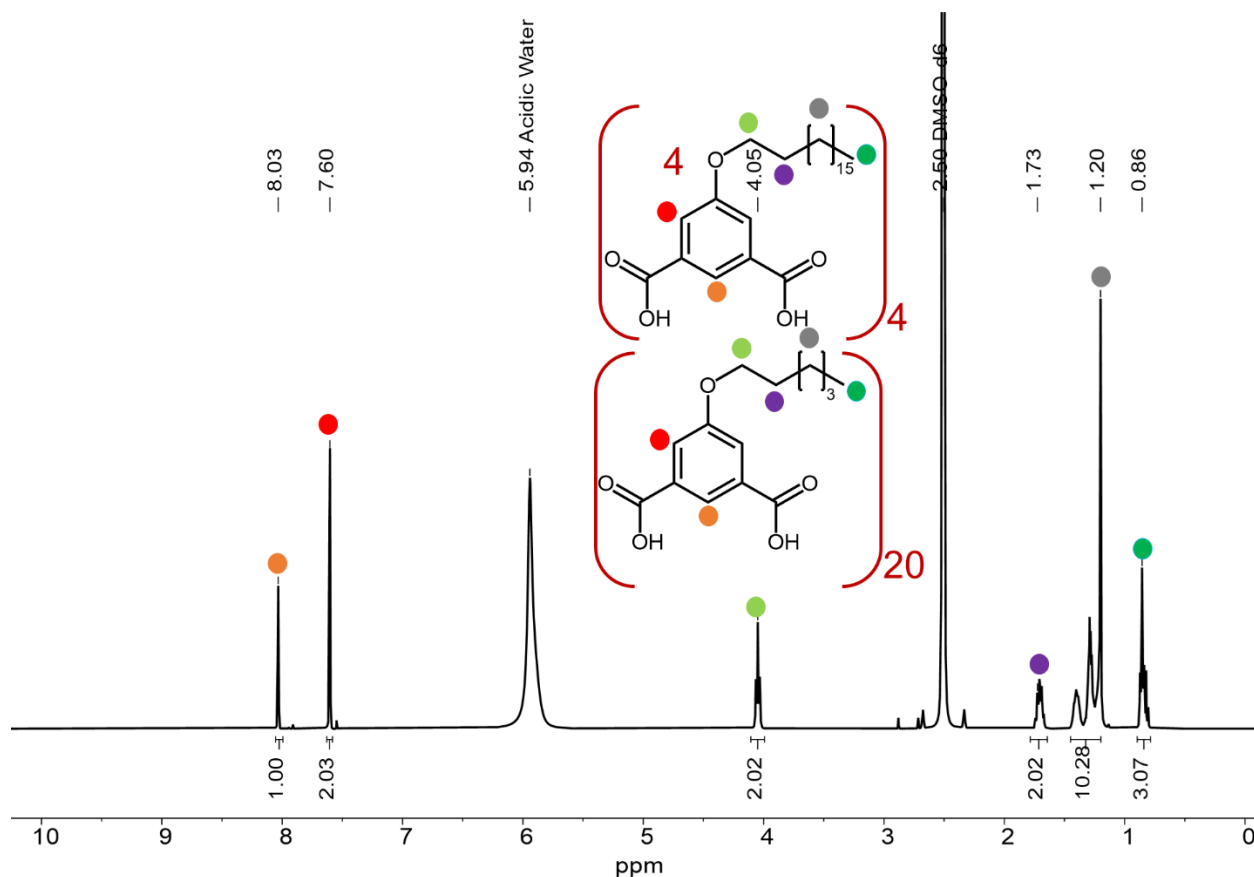
**Figure S24.** <sup>1</sup>H-NMR spectrum of DCI digested benzene soluble Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>20</sub>(5-hexoxy-bdc)<sub>4</sub> in DMSO-d<sub>6</sub> resulting from 2 days stirring of Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> mixture in benzene.



**Figure S25.** <sup>1</sup>H-NMR spectrum of DCI digested benzene soluble Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>20</sub>(5-hexoxy-bdc)<sub>4</sub> resulting from 4 days stirring of Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> mixture in benzene.



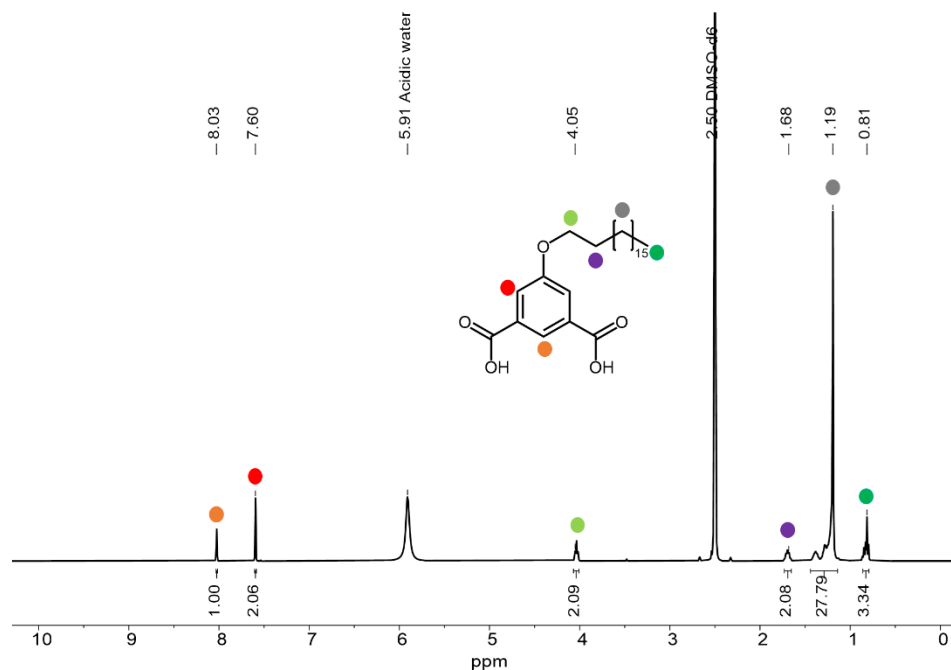
**Figure S26.** <sup>1</sup>H-NMR spectrum of DCl digested benzene-soluble Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>20</sub>(5-hexoxy-bdc)<sub>4</sub> cage resulting from 7 days stirring of Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> in benzene.



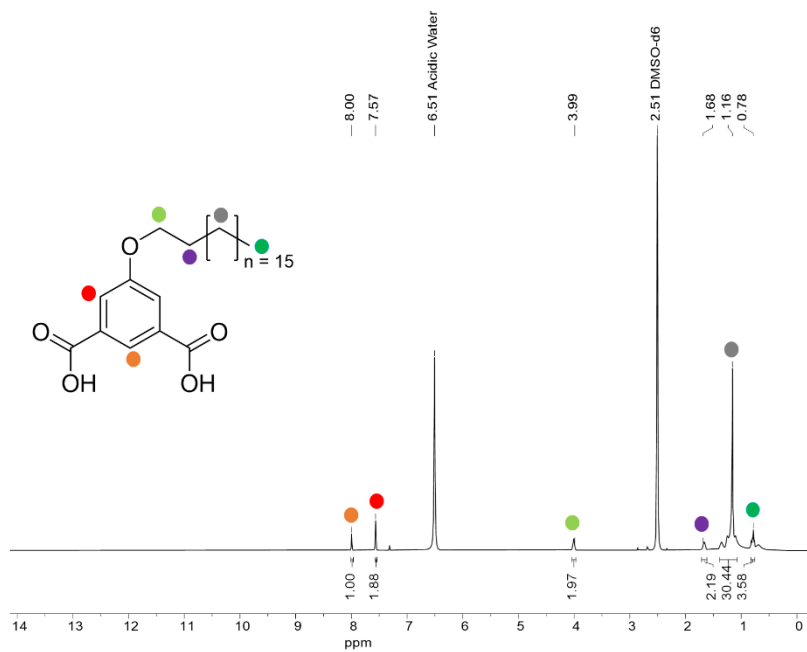
**Figure S27.**  $^1\text{H-NMR}$  spectrum of DCI digested  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_4(\text{5-hexoxy-bdc})_{20}$  obtained from benzene stirring of  $\text{Cu}_{24}(\text{5-hexoxy-bdc})_{24}$  and  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  mixture for 7 days.

#### 4.4 Mechanochemical grinding of $\text{Cu}_{24}(\text{hexoxy-bdc})_{24}$ and $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$

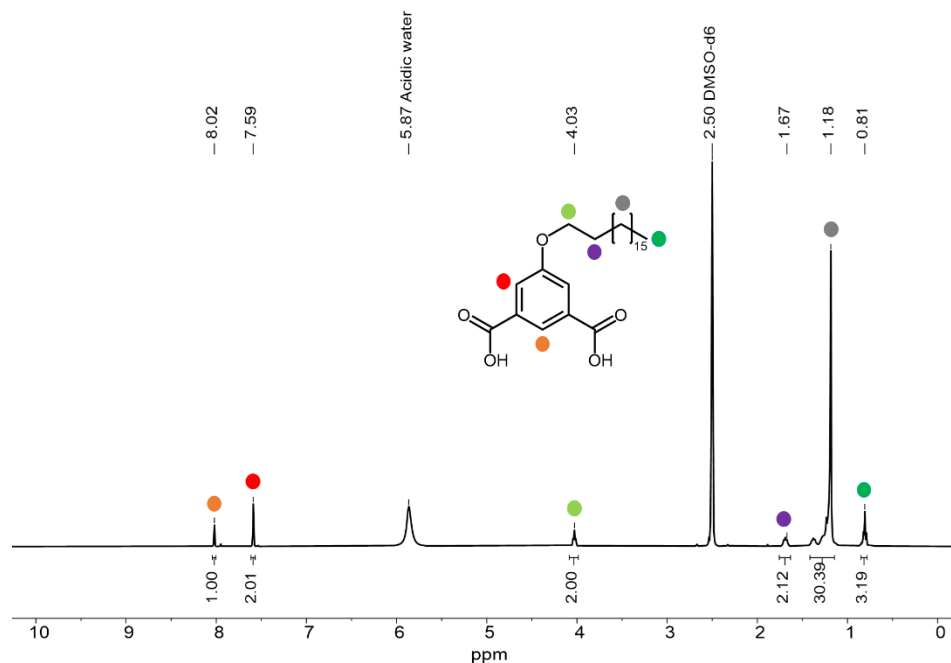
A series of activated  $\text{Cu}_{24}(\text{5-hexoxy-bdc})_{24}$  and  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$  cages was mechanochemically ground in 1:0.5, 1:1, 1:2, and 1:5 ratio for 10 minutes followed by rapid benzene wash to remove the non-exchanged soluble  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_{24}$ . Then, both the insoluble solid and benzene-washed filtrate were vacuumed off and activated for  $^1\text{H-NMR}$  analysis. The obtained insoluble solids are nothing but a mechanochemically exchanged mixed ligand cages,  $\text{Cu}_{24}(\text{5-octadecoxy-bdc})_n(\text{5-hexoxy-bdc})_{(24-n)}$ , containing both hexoxy-bdc and octadecoxy-bdc ligands distributed in corresponding cage ratios.



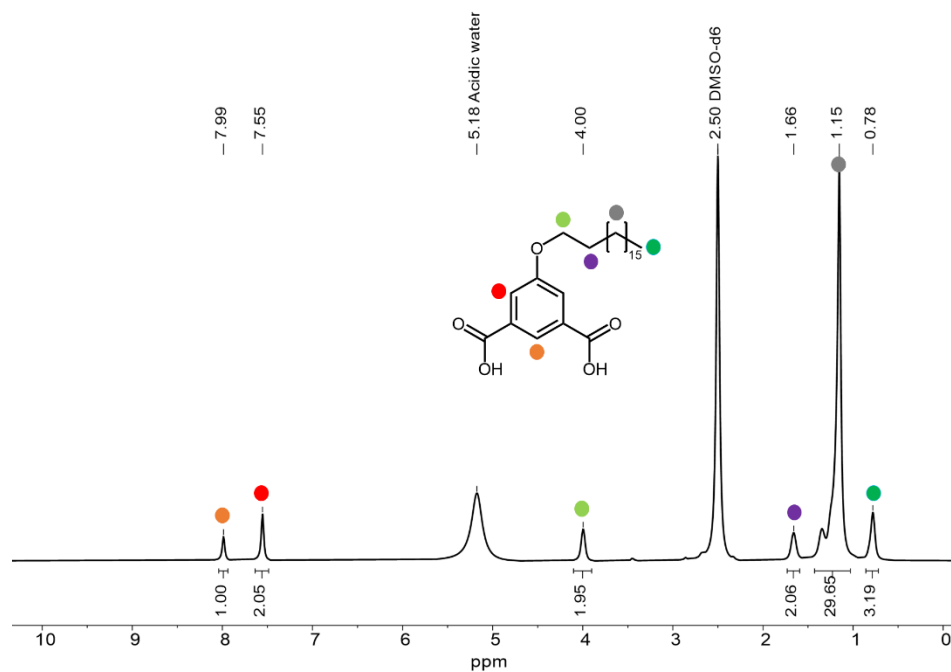
**Figure S28.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene wash obtained from the grinding of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cu}_{24}(5\text{-hexoxy-bdc})_{24}$  in a 1:2 ratio in  $\text{DMSO-d}_6$ .



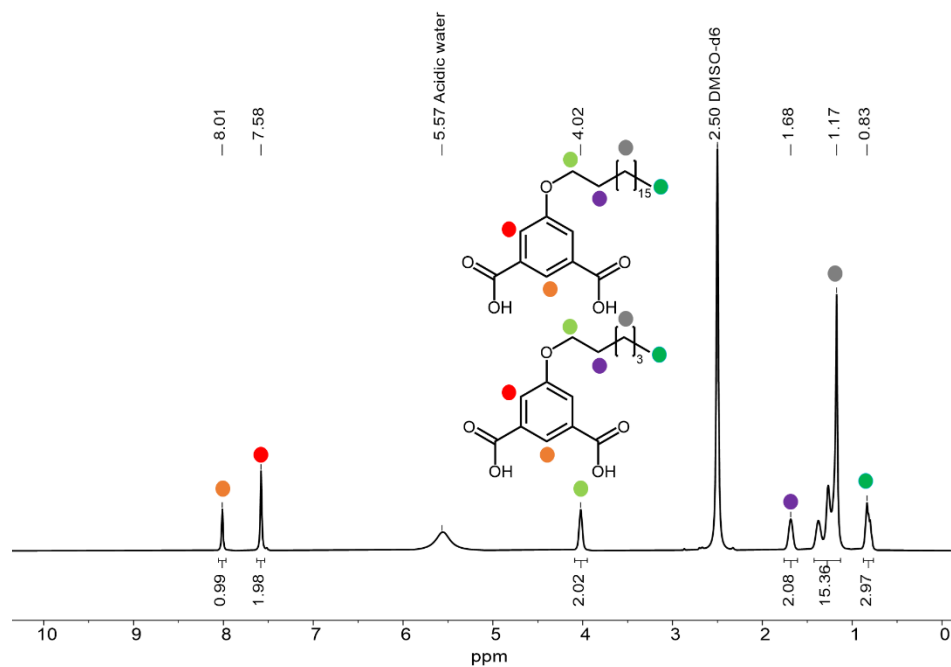
**Figure S29.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene wash in  $\text{DMSO-d}_6$  resulting from a 1:1 grinding of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cu}_{24}(5\text{-hexoxy-bdc})_{24}$  cage.



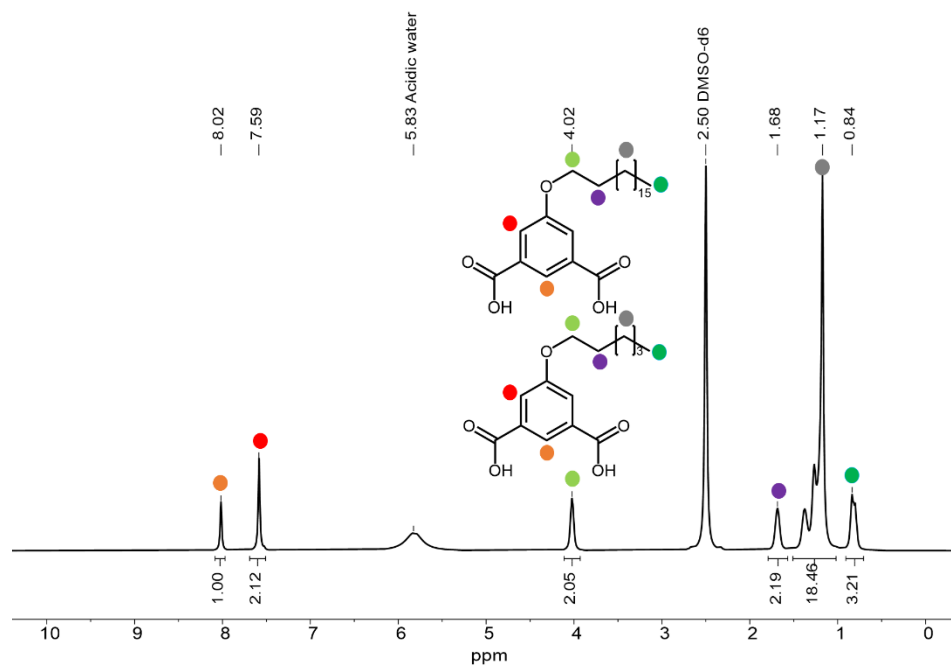
**Figure S30.**  $^1\text{H-NMR}$  spectrum of DCl digested benzene wash in  $\text{DMSO-d}_6$  obtained from 2:1 grinding of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cu}_{24}(5\text{-hexoxy-bdc})_{24}$ .



**Figure S31.**  $^1\text{H-NMR}$  spectrum of DCl digested benzene wash in  $\text{DMSO-d}_6$  obtained from 5:1 grinding of  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cu}_{24}(5\text{-hexoxy-bdc})_{24}$ .

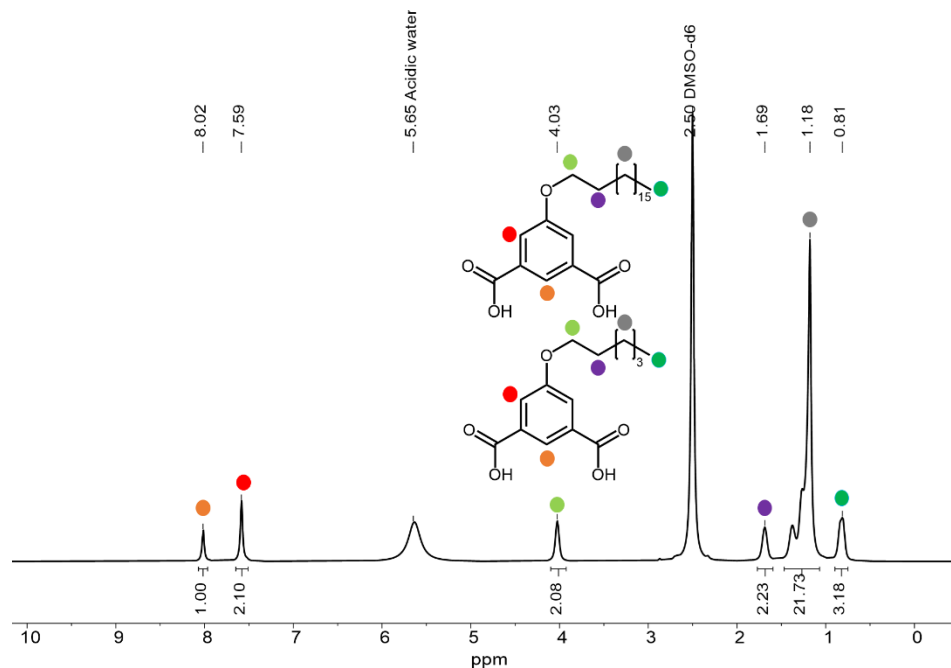


**Figure S32.** <sup>1</sup>H-NMR spectrum of DCI digested Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>9</sub>(5-hexoxy-bdc)<sub>15</sub> in DMSO-d<sub>6</sub> obtained from grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> cage in a 1:2 ratio.

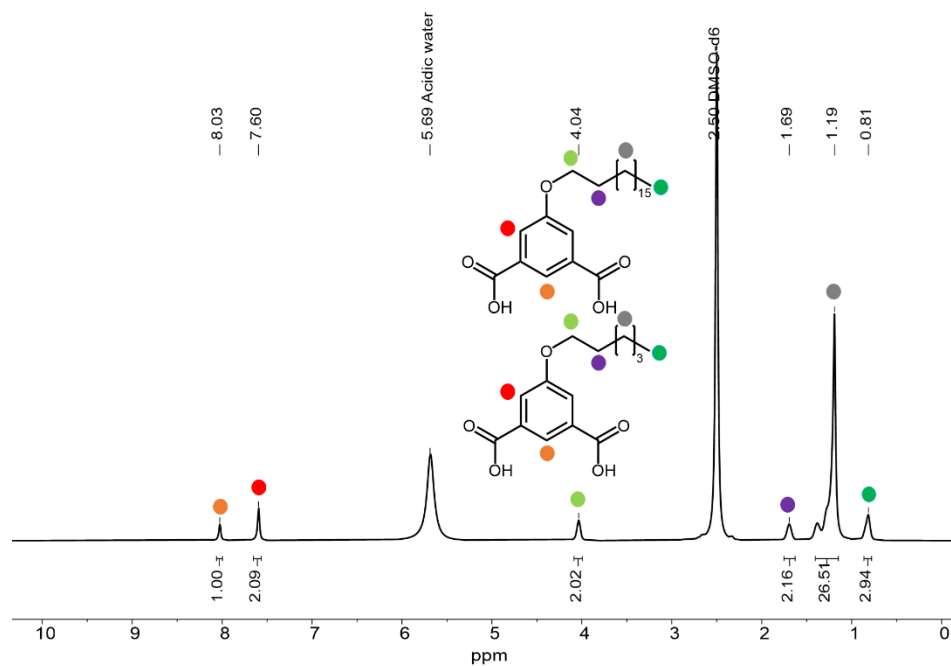


**Figure S33.** <sup>1</sup>H-NMR spectrum of DCI digested Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>13</sub>(5-hexoxy-bdc)<sub>11</sub> in DMSO-d<sub>6</sub> obtained from 1:1 grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub>.





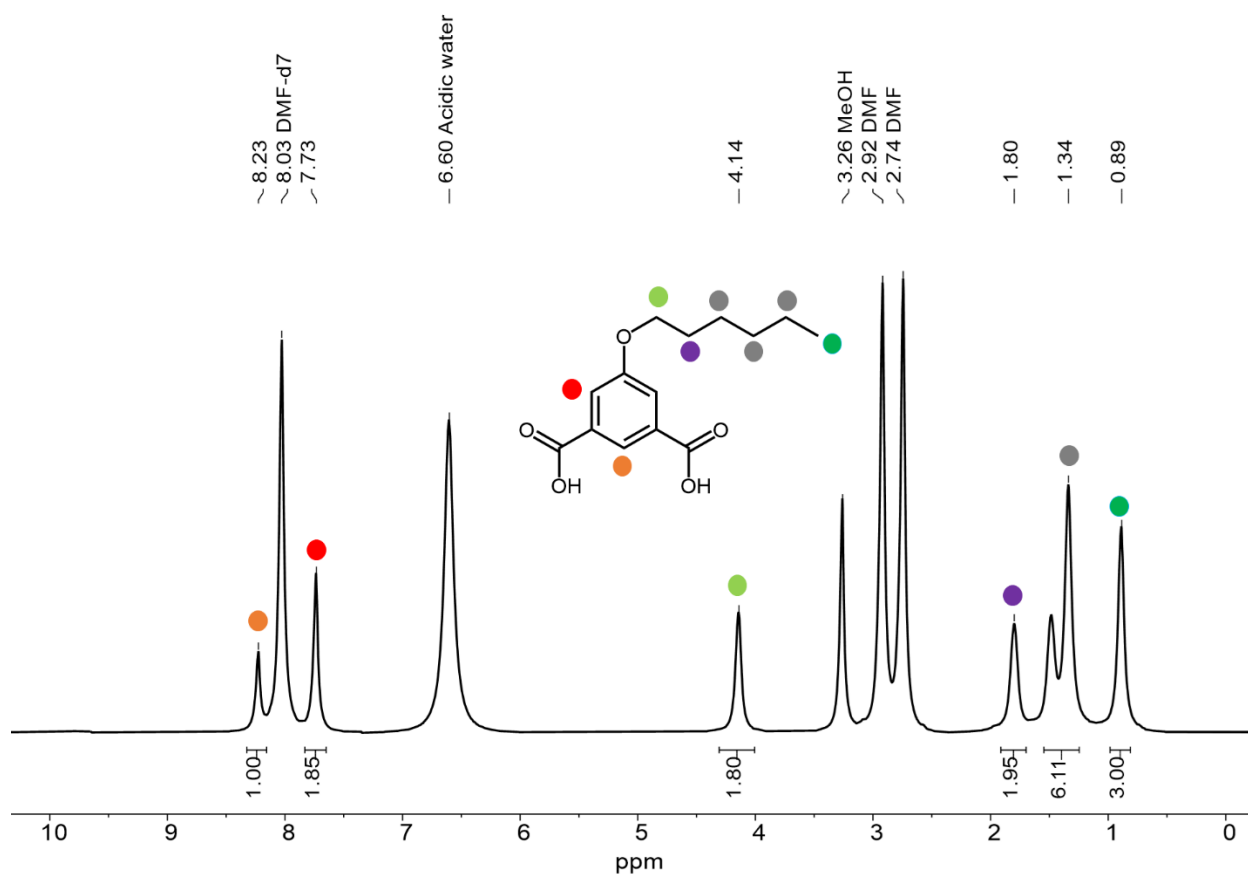
**Figure S34.** <sup>1</sup>H-NMR spectrum of DCl digested Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>16</sub>(5-hexoxy-bdc)<sub>8</sub> in DMSO-d<sub>6</sub> resulting from 2:1 grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub>.



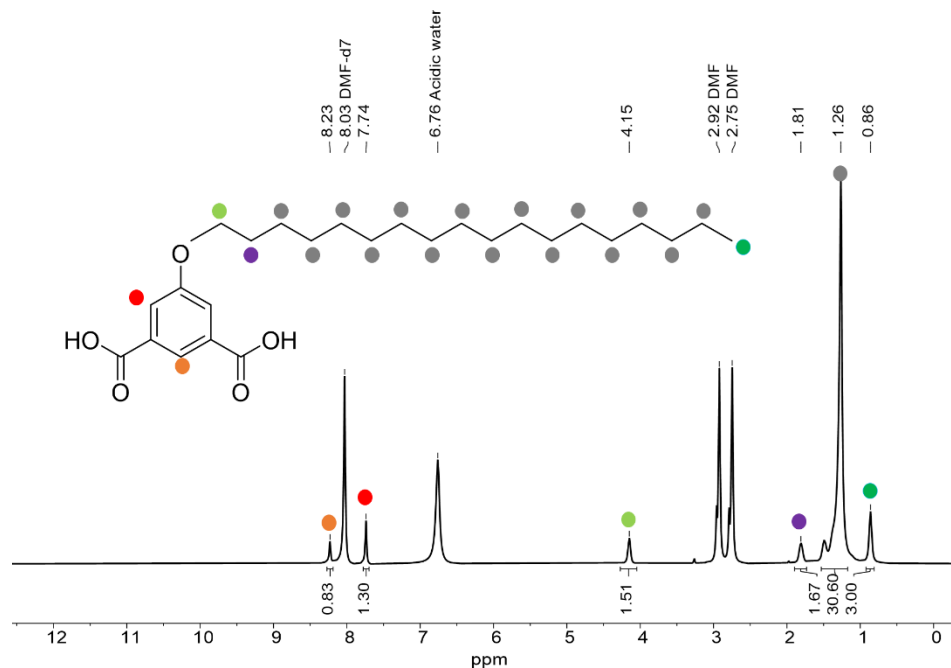
**Figure S35.** <sup>1</sup>H-NMR spectrum of DCl digested Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>20</sub>(5-hexoxy-bdc)<sub>4</sub> in DMSO-d<sub>6</sub> obtained from 5:1 grinding of Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> and Cu<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub>.

#### 4. 5 Mechanochemical grinding of Cr<sub>24</sub>(hexoxy-bdc)<sub>24</sub> and Cr<sub>24</sub>(octadecoxy-bdc)<sub>24</sub>

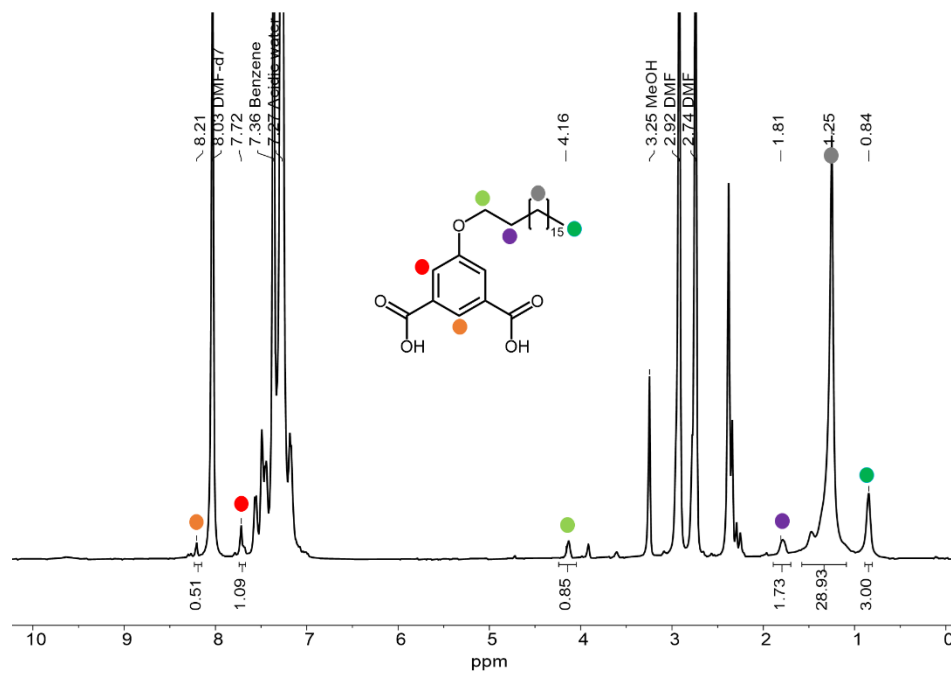
Identical series of activated cages also prepared for Cr<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> and Cr<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> in 1:0.5, 1:1, 1:2, and 1:5 for mechanochemically grinding. The mixture was ground for 10 minutes followed by a rapid benzene wash to remove the non-exchanged soluble Cu<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub>. Both the insoluble solid and benzene-washed filtrate were then vacuumed dried and activated for <sup>1</sup>H-NMR analysis. The solid is a mechanochemically exchanged mixed ligand cage containing both hexoxy-bdc and octadecoxy-bdc ligands whereas the filtrate is most likely a non-exchanged Cr<sub>24</sub>(5-octadecoxy-bdc)<sub>24</sub> cage.



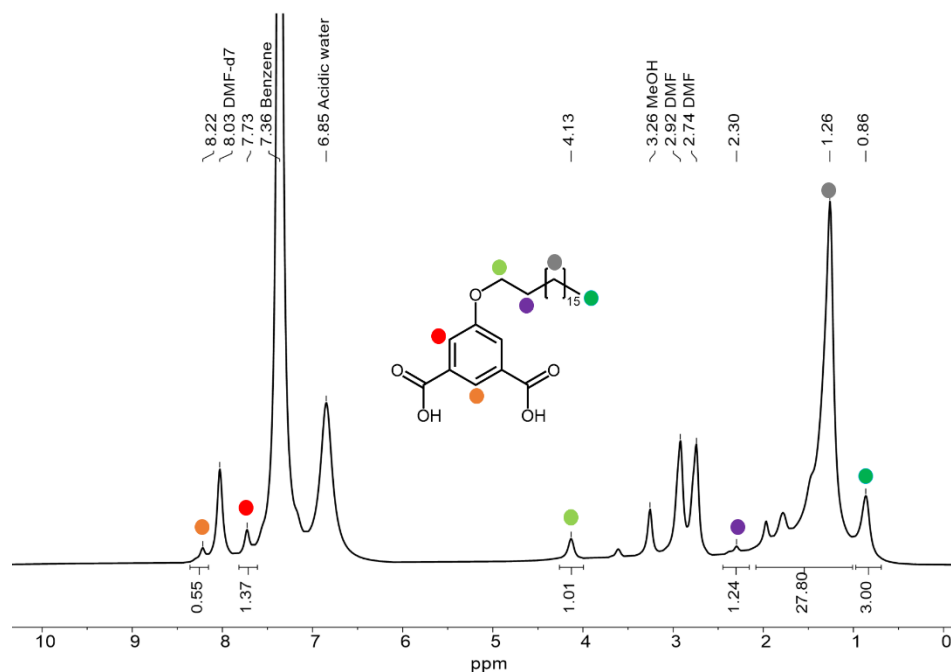
**Figure S36.** <sup>1</sup>H-NMR spectrum of DCI digested Cr<sub>24</sub>(5-hexoxy-bdc)<sub>24</sub> in DMF-d<sub>7</sub>.



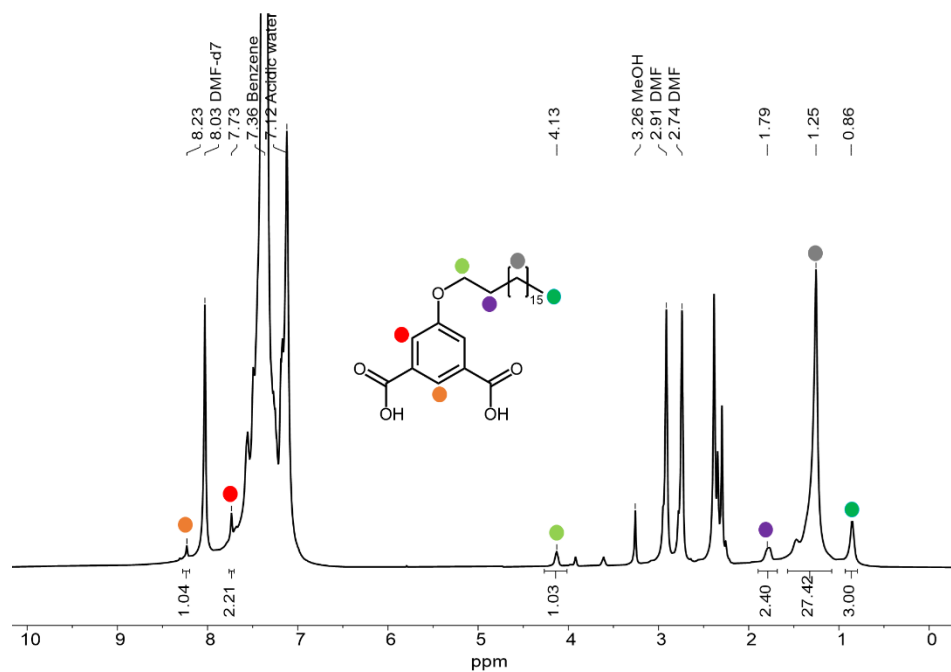
**Figure S37.**  $^1\text{H-NMR}$  spectrum of DCI digested  $\text{Cr}_{24}(5\text{-octadecoxy-bdc})_{24}$  in  $\text{DMF-d}_7$ .



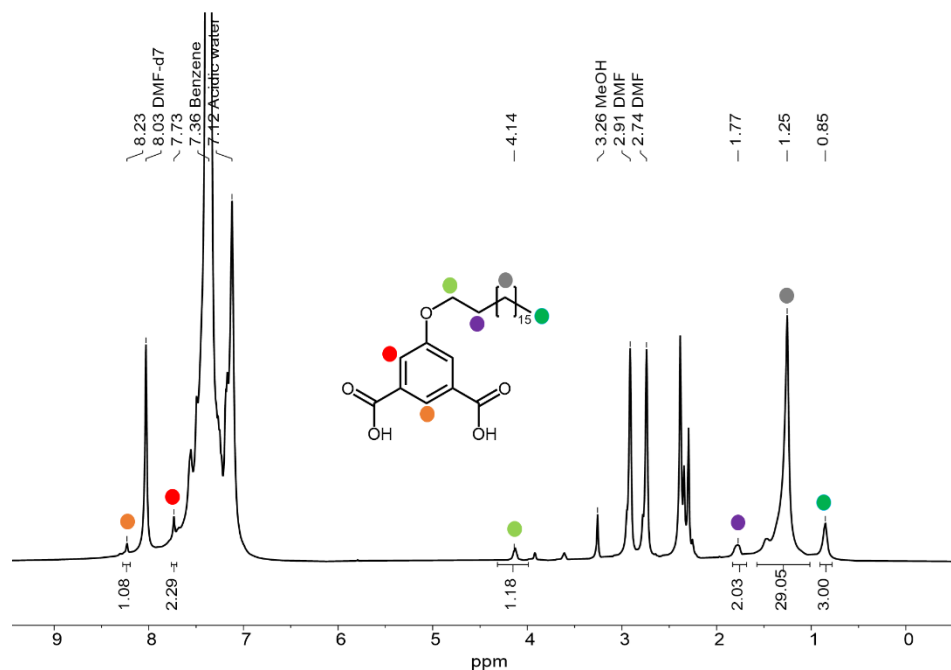
**Figure S38.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene wash in  $\text{DMF-d}_7$  obtained from the grinding of  $\text{Cr}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(5\text{-hexoxy-bdc})_{24}$  in 1:2 ratio.



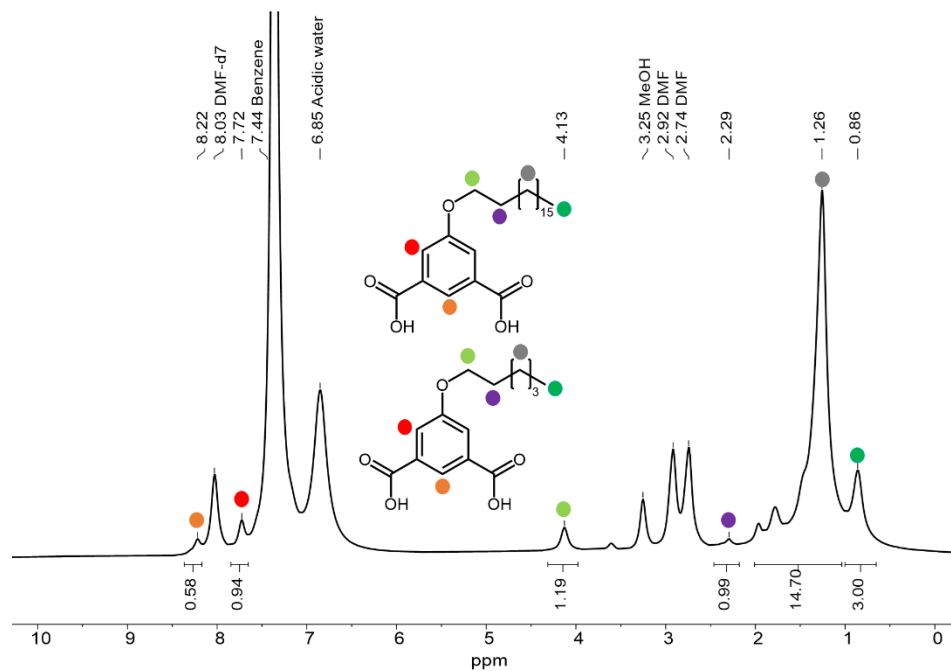
**Figure S39.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene wash in  $\text{DMF-d}_7$  resulting from 1:1 grinding of  $\text{Cr}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(5\text{-hexoxy-bdc})_{24}$  cage.



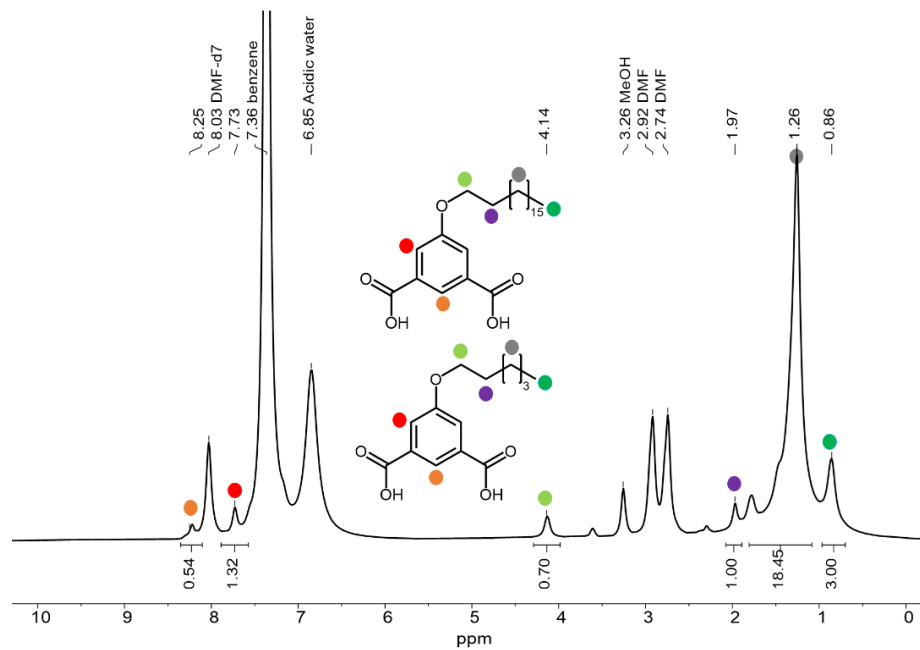
**Figure S40.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene wash in  $\text{DMF-d}_7$  obtained from 2:1 grinding of  $\text{Cr}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(5\text{-hexoxy-bdc})_{24}$ .



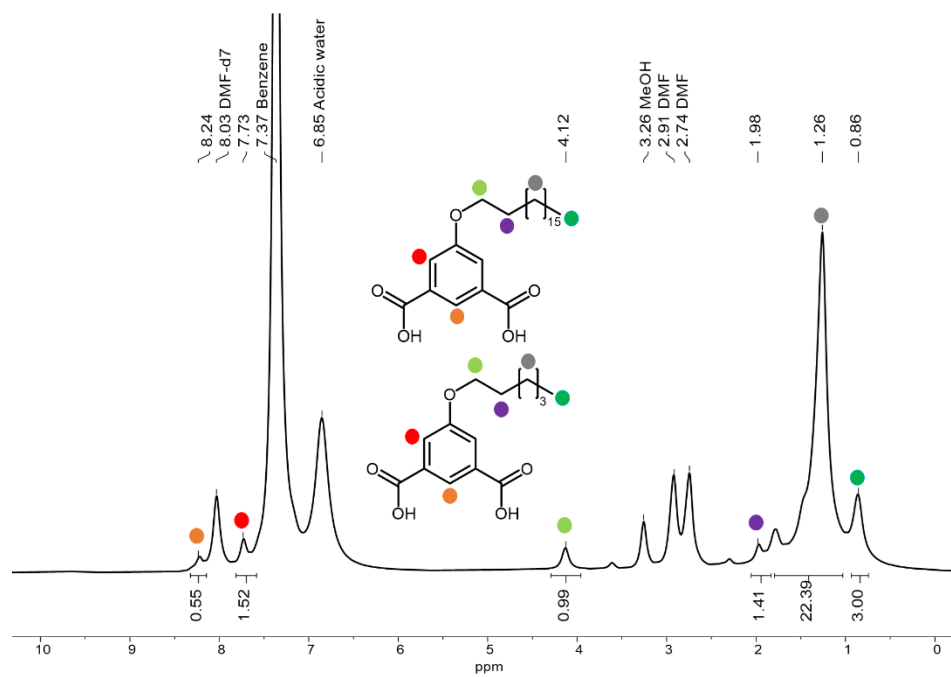
**Figure S41.**  $^1\text{H-NMR}$  spectrum of DCI digested benzene wash in  $\text{DMF-d}_7$  obtained from 5:1 grinding of  $\text{Cr}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(5\text{-hexoxy-bdc})_{24}$  cage.



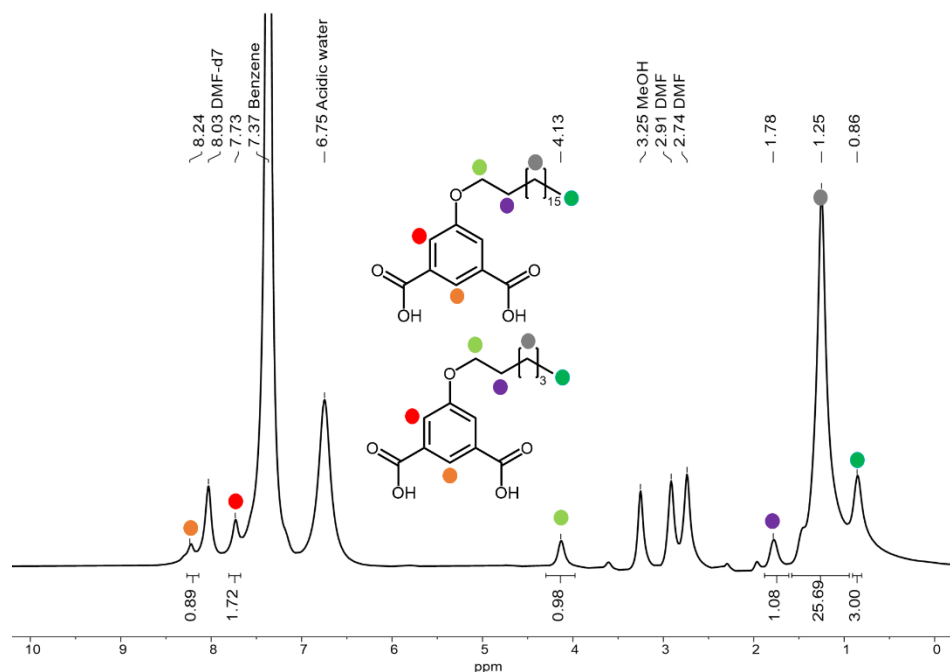
**Figure S42.**  $^1\text{H-NMR}$  spectrum of DCI digested  $\text{Cu}_{24}(5\text{-octadecoxy-bdc})_9(5\text{-hexoxy-bdc})_{15}$  in  $\text{DMF-d}_7$  obtained from grinding of  $\text{Cr}_{24}(5\text{-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(5\text{-hexoxy-bdc})_{24}$  cage in 1:2.



**Figure S43.**  $^1\text{H-NMR}$  spectrum of DCI digested  $\text{Cr}_{24}(\text{5-octadecoxy-bdc})_{12}(\text{5-hexoxy-bdc})_{12}$  in  $\text{DMF-d}_7$  obtained from 1:1 grinding of  $\text{Cr}_{24}(\text{5-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(\text{5-hexoxy-bdc})_{24}$ .



**Figure S44.**  $^1\text{H-NMR}$  spectrum of DCI digested  $\text{Cr}_{24}(\text{5-octadecoxy-bdc})_{16}(\text{5-hexoxy-bdc})_8$  in  $\text{DMF-d}_7$  resulting from 2:1 grinding of  $\text{Cr}_{24}(\text{5-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(\text{5-hexoxy-bdc})_{24}$  cage.



**Figure S45.**  $^1\text{H-NMR}$  spectrum of DCI digested  $\text{Cr}_{24}(\text{5-octadecoxy-bdc})_{20}(\text{5-hexoxy-bdc})_4$  in  $\text{DMF-d}_7$  obtained from 5:1 grinding of  $\text{Cr}_{24}(\text{5-octadecoxy-bdc})_{24}$  and  $\text{Cr}_{24}(\text{5-hexoxy-bdc})_{24}$ .

**Table 1:** No. of experimentally obtained integrated protons of benzene washed insoluble solid and corresponding filtrate of mechanochemically ground  $\text{Cu}_{24}(\text{hexoxy-bdc})_{24}$  and  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$ ; and  $\text{Cr}_{24}(\text{hexoxy-bdc})_{24}$  and  $\text{Cr}_{24}(\text{octadecoxy-bdc})_{24}$  cages in ratio of 1:0.5, 1:1, 1:2, 1:5.

$\text{M}_{24}(\text{hexoxy-bdc})_{24} :$ $\text{M}_{24}(\text{octadecoxy-bdc})_{24}$ $\text{M} = \text{Cu, Cr}$	$\text{Cu}^{2+}$ cage		$\text{Cr}^{2+}$ cage	
	Insoluble solid; $\text{Cu}_{24}(\text{octadecoxy-bdc})_n(\text{hexoxy-bdc})_{(24-n)}$	Filtrate $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$	Insoluble solid $\text{Cr}_{24}(\text{octadecoxy-bdc})_n(\text{hexoxy-bdc})_{(24-n)}$	Filtrate $\text{Cr}_{24}(\text{octadecoxy-bdc})_{24}$
1:0.5	22	35	22	36
1:1	26	37	25	35
1:2	29	37	29	35
1:5	33	37	33	36

**Table 2:** Statistical distribution of hexoxy-bdc and octadecoxy-bdc ligands in mixed ligand cage upon distribution on different ratios and corresponding no. of theoretical protons.

$M_{24}(\text{hexoxy-bdc})_{24} :$ $M_{24}(\text{octadecoxy-bdc})_{24}$	$M_{24}(\text{octadecoxy-bdc})_n(\text{hexoxy-bdc})_{(24-n)}$	
	Statistical ligand distribution	Theoretical no. of H
1:0.5	$M_{24}(\text{octadecoxy-bdc})_8(\text{hexoxy-bdc})_{16}$	21
1:1	$M_{24}(\text{octadecoxy-bdc})_{12}(\text{hexoxy-bdc})_{12}$	25
1:2	$M_{24}(\text{octadecoxy-bdc})_{16}(\text{hexoxy-bdc})_8$	29
1:5	$M_{24}(\text{octadecoxy-bdc})_{20}(\text{hexoxy-bdc})_4$	33

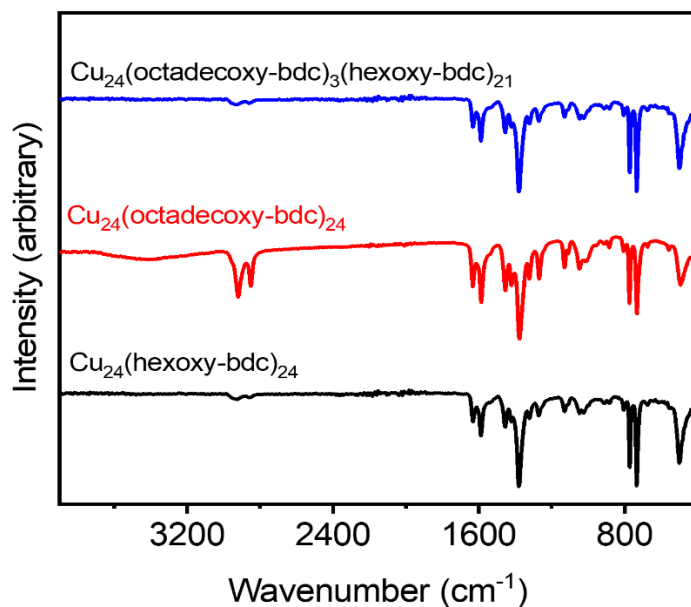
$$\text{Theoretical no. of H} = \frac{(\text{no. of hexoxy - bdc ligands} * \text{no. of H per chain}) + (\text{no. of octadecoxy - bdc ligands} * \text{no. of H per chain})}{\text{total no. of ligands} = 24}$$

**Table 3:** No of theoretical and experimental protons for Cu(II) and Cr(II) mixed ligand cages distributed in different ratios.

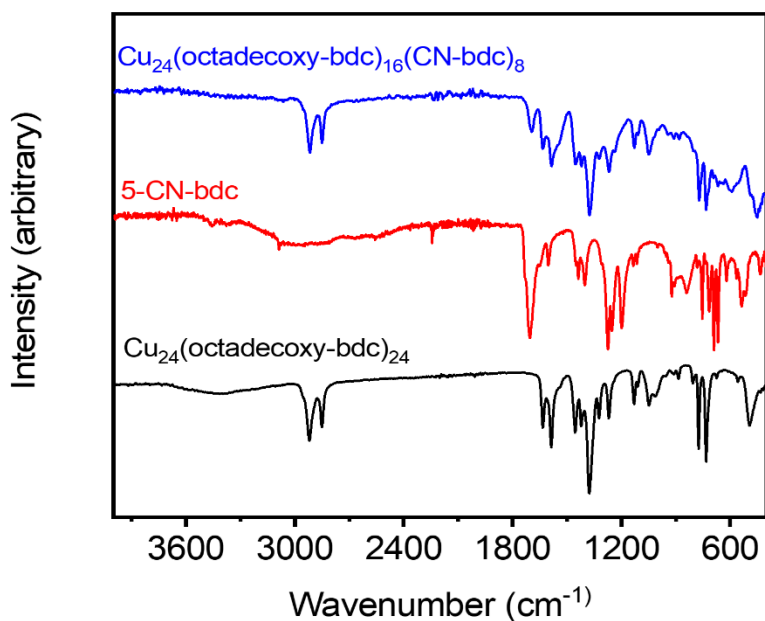
$M_{24}(\text{hexoxy-bdc})_{24} :$ $M_{24}(\text{octadecoxy-bdc})_{24}$ $M = \text{Cu}^{2+}, \text{Cr}^{2+}$	$M_{24}(\text{octadecoxy-bdc})_n(\text{hexoxy-bdc})_{(24-n)}$		
	Theoretical	Experimental	
		Cu <sup>2+</sup> cage	Cr <sup>2+</sup> cage
1:0.5	21	22	22
1:1	25	26	25
1:2	29	29	29
1:5	33	33	33



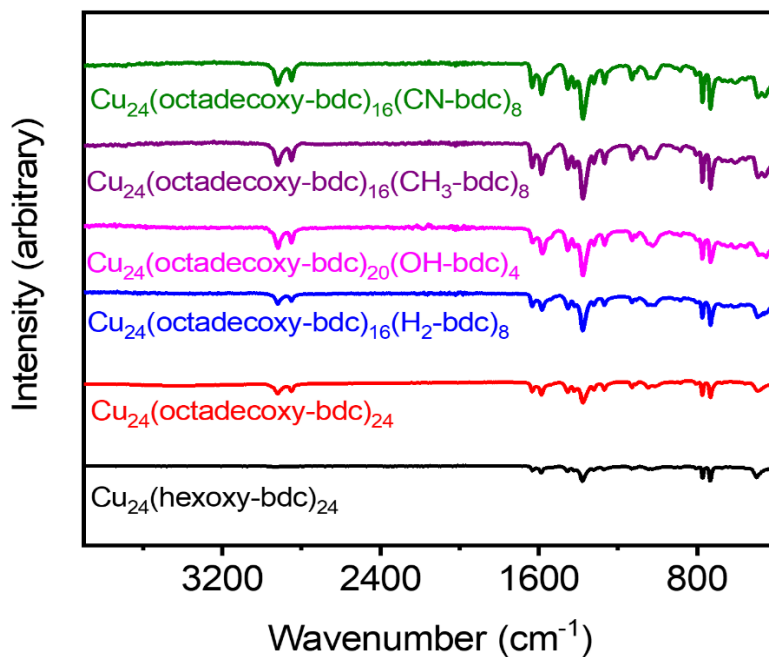
## 5. Infrared Spectra



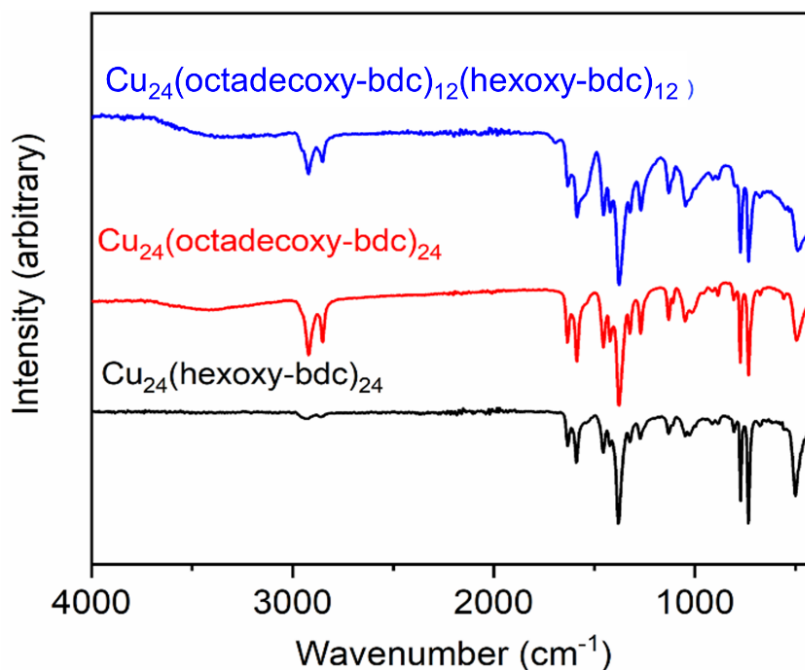
**Figure S46.** Infrared spectrum of Cu<sub>24</sub>(octadecoxy-bdc)<sub>3</sub>(hexoxy-bdc)<sub>21</sub> cage obtained from sequential grinding of Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage and free hexoxy-bdc ligand (blue), Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage (red), and Cu<sub>24</sub>(hexoxy-bdc)<sub>24</sub> cage (black)



**Figure S47.** Infrared spectrum of activated Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> cage (black), CN-bdc ligand (red), and mechanochemically obtained mixed ligand Cu<sub>24</sub>(octadecoxy-bdc)<sub>16</sub>(CN-bdc)<sub>8</sub> cage (blue).

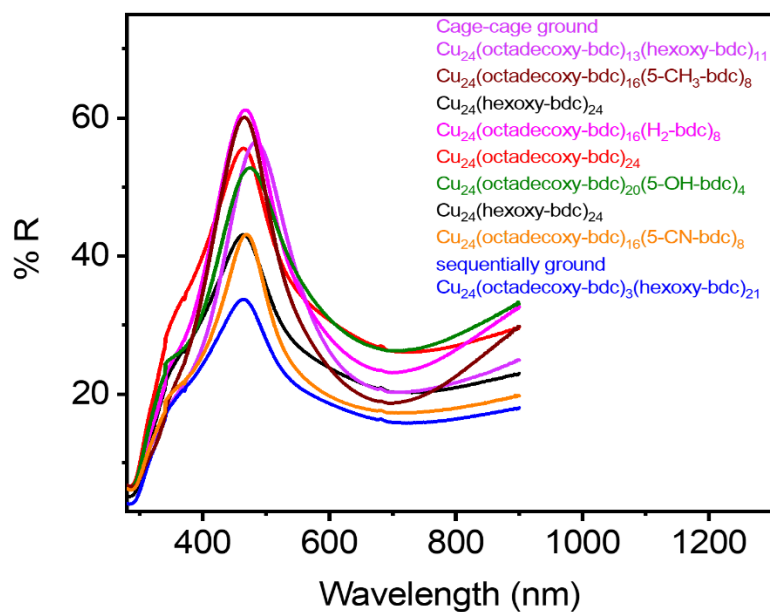


**Figure S48.** Infrared spectrum of  $\text{Cu}_{24}(\text{octadecoxy-bdc})_n(\text{R-bdc})_{24-n}$  cages obtained from mechanochemical grinding of  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$  cage and different R-bdc ligands.



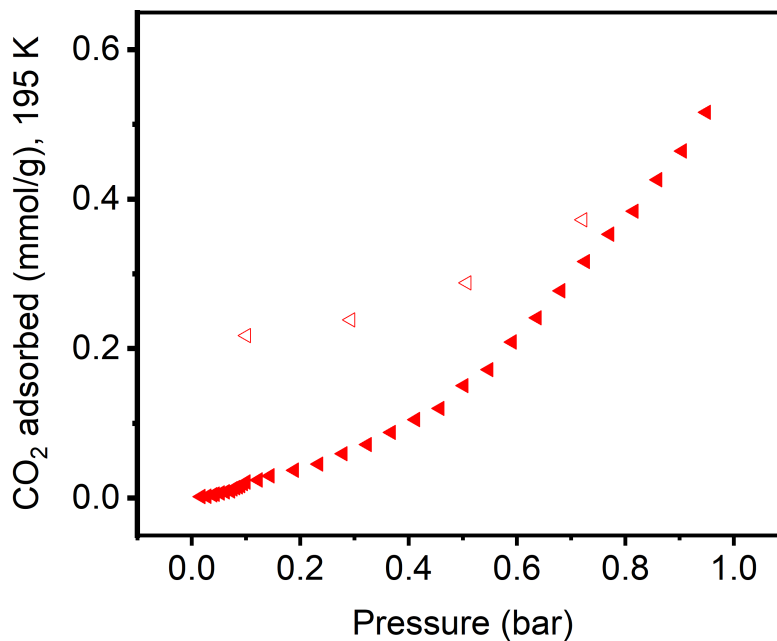
**Figure S49.** Infrared spectrum of  $\text{Cu}_{24}(\text{hexoxy-bdc})_{24}$  cage (black),  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$  cage (red) and mechanochemically obtained mixed ligand  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{12}(\text{hexoxy-bdc})_{12}$  cage (blue).

## 6. UV-visible

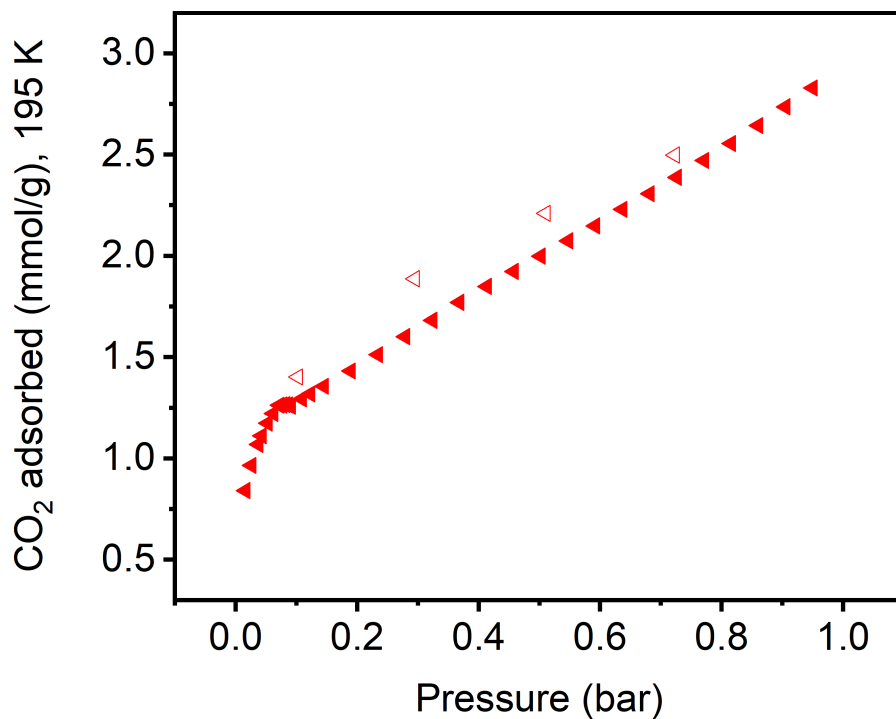


**Figure S50.** Diffuse reflectance of different mixed ligand cages obtained from mechanochemical grinding of different cage-free ligands, R-bdc, showing identical reflectance of parent  $\text{Cu}_{24}(\text{hexoxy-bdc})_{24}$  and  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{24}$  cages.

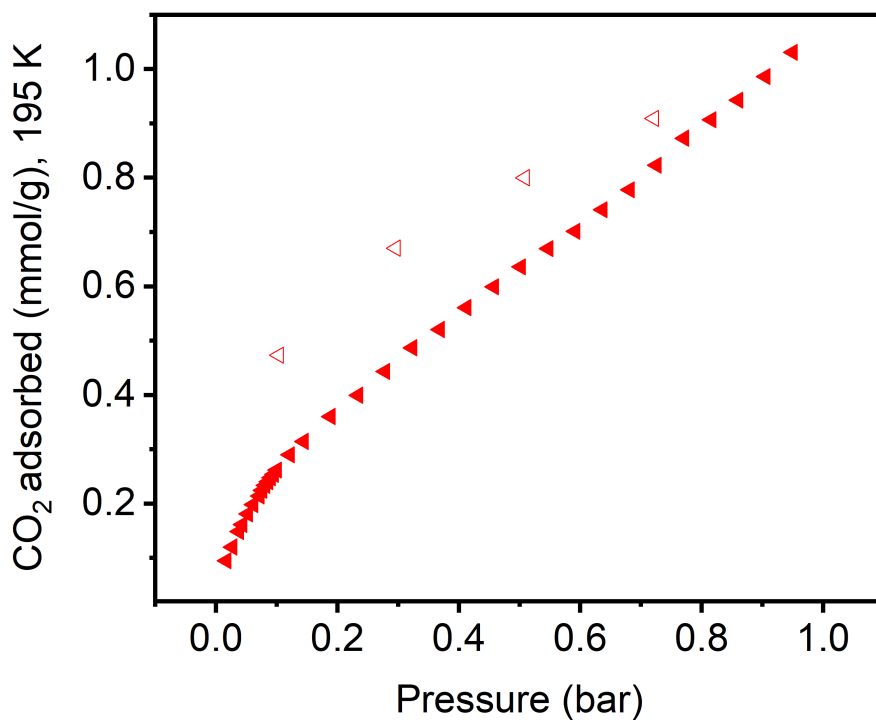
## 7. Gas adsorption measurements



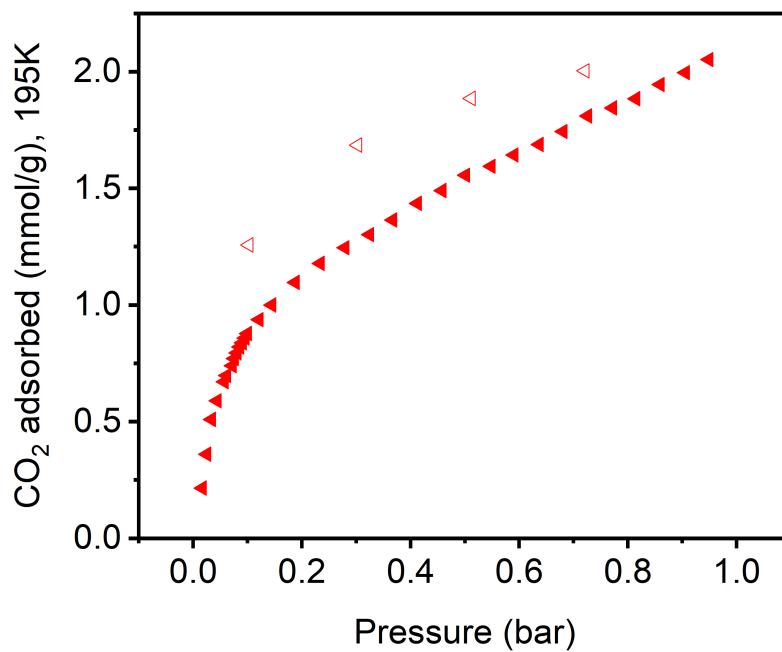
**Figure S51.** Full  $\text{CO}_2$  BET isotherms of mechanochemically obtained mixed ligand  $\text{Cu}_{24}(\text{octadecoxy-bdc})_{16}(\text{CN-bdc})_8$  cage activated at RT. The measured surface area is  $42 \text{ m}^2/\text{g}$  (Lang  $178 \text{ m}^2/\text{g}$ ).



**Figure S52.** Full CO<sub>2</sub> BET isotherms of Cu<sub>24</sub>(octadecoxy-bdc)<sub>12</sub>(hexoxy-bdc)<sub>12</sub> cage obtained from the grinding of Cu<sub>24</sub>(hexoxy-bdc)<sub>24</sub> and octadecoxy-bdc ligand in 1:24 equivalent ratio. The surface area is 135 m<sup>2</sup>/g (Lang 343 m<sup>2</sup>/g)

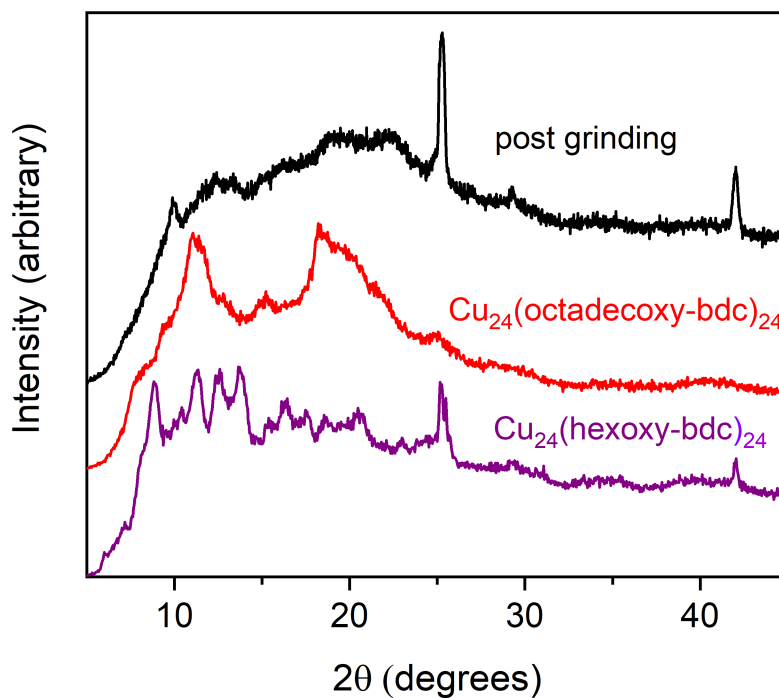


**Figure S53.** Full CO<sub>2</sub> BET isotherms of mechanochemically obtained mixed ligand Cu<sub>24</sub>(octadecoxy-bdc)<sub>13</sub>(hexoxy-bdc)<sub>11</sub> cage activated at RT. The measured surface area is 36 m<sup>2</sup>/g (Lang 167 m<sup>2</sup>/g).



**Figure S54.** Full CO<sub>2</sub> BET isotherms of Cr<sub>24</sub>(octadecoxy-bdc)<sub>13</sub>(hexoxy-bdc)<sub>11</sub> cage obtained from the grinding of Cr<sub>24</sub>(hexoxy-bdc)<sub>24</sub> and Cr<sub>24</sub>(octadecoxy-bdc)<sub>24</sub> in 1:1 ratio. Surface area recorded, 164 m<sup>2</sup>/g (Lang 249 m<sup>2</sup>/g).

### 8. Powder X-ray diffraction



**Figure S55:** PXRD pattern of Cu<sub>24</sub>(hexoxy-bdc)<sub>24</sub>, Cu<sub>24</sub>(octadecoxy-bdc)<sub>24</sub>, and ground insoluble solid (benzene washed) 1:1 cage.

## Reference

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- 1 A. M. Anonio, K. J. Korman, G. P. A. Yap and E. D. Bloch, *Chem. Sci.*, 2020, **11**, 12540-12546.