

## Supporting Information For:

### Design and Synthesis of porous Nickel (II) and Cobalt (II) Cages

Eric J. Gosselin, Casey A. Rowland, Krista P. Balto, Glenn P. A. Yap, Eric D. Bloch\*

Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716,  
United States

\*edb@udel.edu

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## Experimental Section

General Considerations. All reagents were obtained from commercial vendors and used without purification, excluding solvents. Methanol was obtained from a solvent drying system and stored in a glove box under 3Å sieves. Thermogravimetric analyses (TGA) were carried out from 50 °C to 600 °C at a 2 °C min<sup>-1</sup> heating rate with a TA Q5000 SA under a nitrogen environment. All adsorption measurements were obtained on a Micromeritics 3Flex. Infrared spectroscopy was performed on a material using a Bruker Tensor 27 instrument. <sup>1</sup>H-NMR spectra were taken on a AV 400 spectrometer equipped with a cryogenic QNP probe.

### *Synthetic Techniques*

**Synthesis of nickel MOF.** Ni(acetate)<sub>2</sub>·4H<sub>2</sub>O (1.0 g, 4 mmol) and methanol (10 mL) were added to a 20 mL scintillation vial. Once the metal salt had dissolved, N,N'-dimethylacetamide (10 mL) was added to the solution. Benzene-1,3-dicarboxylic acid (H<sub>2</sub>BDC) (0.666 g, 4 mmol), methanol (10 mL) and N,N'-dimethylacetamide (10 mL) were added to a 20 mL scintillation vial. 1-azabicyclo[2.2.2]octane (ABCO) (1.126 g, 10 mmol), methanol (20 mL) and N,N'-dimethylacetamide (20 mL) were added to a 100 mL VWR glass jar. Nickel solution (1 mL), ligand solution (1 mL) and ABCO solution (2 mL) were pipetted into twenty 4 mL scintillation vials and sealed with a Teflon lined caps. The resulting solution was then heated in an oven at 373 K for 14 days. Dark green crystals were isolated by removing light green precipitate and excess solvent. Solvent exchange was completed by soaking the product in heated DMA at 298 K for three days with the solvent replaced every 24 hours. The DMA washed crystals were isolated by pipetting off excess DMA solvent and soaked in tetrahydrofuran at 298 K for three days with the solvent replaced every 24 hours. Activated material was obtained by evacuation at 423 K.

**Synthesis of Ni(Me-bdc).** Ni(acetate)<sub>2</sub>·4H<sub>2</sub>O (0.250 g, 1 mmol) and methanol (15 mL) were added to a 20 mL scintillation vial. 5-methyl benzene-1,3-dicarboxylic acid (Me-BDC) (0.540 g, 3 mmol) and methanol (15 mL) were added to a 20 mL scintillation vial. Ligand solution (5 mL) was added to the metal salt solution. The combined solution (10 mL) and N,N'-dimethylacetamide (10 mL) were added to a new 20 mL scintillation vial and sealed with a Teflon lined cap. The resulting solution was then heated in an oven at 373 K for 14 days. Dark green crystals were isolated by carefully removing light green precipitate and excess solvent.

**Synthesis of Co(Me-bdc).** Cobalt(II) chloride·6 H<sub>2</sub>O (0.131 g, 1.0 mmol), 5-methyl benzene-1,3-dicarboxylic acid (0.725g, 0.4 mmol) and N,N'-dimethylformamide (12 mL) were combined in a 20 mL scintillation vial. The resulting stock solution (2 mL), methanol (2 mL) and pyridine (0.08 mL) were combined in a 7 mL scintillation vial and sealed with a Teflon cap. The resulting solution was heated in an oven at 373 K overnight. Dark blue/green crystals were collected by removing excess solvent.

**Synthesis of Ni(OEt-bdc).** Ni(acetate)<sub>2</sub>·4H<sub>2</sub>O (0.995 g, 4 mmol) and methanol (20 mL) were added to a 100 mL VWR glass jar. Once the metal salt had dissolved, N,N'-dimethylacetamide (20 mL) was added to the solution. 5-ethoxy benzene-1,3-dicarboxylic acid (0.810 g, 3.8 mmol), methanol (20 mL) and N,N'-dimethylacetamide (20 mL) were added to a 100 mL VWR glass vial.

Metal solution (2 mL) and Ligand solution (2 mL) were added to twenty 4 mL scintillation vials. The resulting solution was then heated on a dry hot bath in an aluminum block at 373 K for 14 days. Dark green crystals were isolated by carefully removing light green precipitate and excess solvent.

**Synthesis of Co(OEt-bdc).** Cobalt(II) nitrate·6 H<sub>2</sub>O (0.107 g, 0.57 mmol), 5-ethoxy benzene-1,3-dicarboxylic acid (0.838 g, 0.4 mmol) and N,N'-dimethylformamide (12 mL) were combined in a 20 mL scintillation vial. The resulting stock solution (2 mL), methanol (2 mL) and pyridine (0.08 mL) were combined in a 7 mL scintillation vial and sealed with a Teflon cap. The resulting solution was heated in an oven at 373 K for six hours. Dark blue/green crystals were collected by removing pink precipitate and excess solvent.

**Synthesis of Ni(<sup>t</sup>Bu-bdc).** Ni(acetate)<sub>2</sub>·4H<sub>2</sub>O (1.97 g, 7.9 mmol) and methanol (20 mL) were added to a 100 mL VWR glass jar. 5-tertbutyl-benzene-1,3-dicarboxylic acid (1.959 g, 8.8 mmol) and methanol (20 mL) were added to a 100 mL VWR glass jar. Once ligand and metal were dissolved in their respective solutions, N,N'-dimethylacetamide (20 mL) was added to each solution. The resulting nickel solution (2 mL) was added to a 4 mL scintillation vial. Ligand solution (2 mL) was then added to the vial. The resulting solution was then heated in an oven at 373 K for 14 days. Dark green crystals were seen on the sides of the vials and were isolated by carefully removing light green precipitate and excess solvent.

**Synthesis of Ni<sub>24</sub>(OH-bdc)<sub>24</sub>.** Ni(acetate)<sub>2</sub>·4H<sub>2</sub>O (0.250 g, 1 mmol) and methanol (15 mL) were added to a 20 mL scintillation vial. 5-hydroxy benzene-1,3-dicarboxylic acid (OH-BDC) (0.546 g, 3 mmol) and methanol (15 mL) were added to a 20 mL scintillation vial. Ligand solution (5 mL) was added to the metal salt solution. The combined solution (10 mL) and N,N'-dimethylacetamide (10 mL) were added to a new 20 mL scintillation vial and sealed with a Teflon lined cap. The resulting solution was then heated in an oven at 373 K for 14 days. Dark green crystals were isolated by carefully removing light green precipitate and excess solvent. Solvent exchange was completed by soaking the product in heated DMA at 298 K for three days with the solvent replaced every 24 hours. The DMA washed crystals were isolated by pipetting off excess DMA solvent and soaked in tetrahydrofuran at 298 K for three days with the solvent replaced every 24 hours. Activated material was obtained by evacuation at 298 K.

**Synthesis of Co(H-cdc).** Cobalt (II) nitrate·6 H<sub>2</sub>O (0.048 g, 0.16 mmol) and N,N'-dimethylacetamide (20 mL) were combined in a 20 mL scintillation vial. 9-H-carbazole-3,6-dicarboxylic acid (9-H-cdc) (0.128 g, 0.5 mmol) and DMA (20 mL) were combined in a separate 20 mL scintillation vial. 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.056 g, 0.5 mmol) and DMA (20 mL) were combined in a 20 mL scintillation vial. The resulting cobalt solution (1.5 mL), the resulting 9-H-cdc solution (1.5 mL) were combined into a 7 mL scintillation vial and sealed with a Teflon cap. The resulting solution was heated on a dry bath in an aluminum block at 343 K for one hour. DABCO solution (1 mL) was added to the hot reaction mixture. The solution was then heated for an additional 20 hours on the 343 K dry hot bath. The vials were removed from heat and allowed to cool to room temperature. Dark blue/green crystals were collected by removing brown precipitate and excess solvent.



**Synthesis of Ni<sub>12</sub>(<sup>i</sup>pr-cdc)<sub>12</sub>.** Ni(Acetate)<sub>2</sub>·4H<sub>2</sub>O (0.500 g, 2 mmol) and methanol (20 mL) were added to a 100 mL VWR glass jar. Once the metal salt had dissolved, N,N'-dimethylacetamide (20 mL) was added to the solution. 9-isopropyl-carbazole-3,6-dicarboxylic acid (0.148 g, 0.5 mmol) and N,N'-dimethylacetamide (20 mL) were added to a 20 mL scintillation vial. Metal solution (1 mL), ligand solution (2 mL) and a 50:50 mixture of N,N'-dimethylacetamide and methanol (1 mL) were added to ten 4 mL scintillation vials and sealed with a Teflon lined cap. The resulting solution was then heated in an oven at 373 K for 14 days. The as-synthesized crystals were washed in fresh DMA over the course of three days with the solvent being exchanged every 12 hours. DMA washed crystals were isolated and washed with benzene for three days with the solvent being replaced every 12 hours. Activated material was obtained by evacuation at 373 K.

**Synthesis of Co<sub>12</sub>(<sup>i</sup>pr-cdc)<sub>12</sub>.** Cobalt(II) nitrate·6 H<sub>2</sub>O (0.048 g, 0.26 mmol) and N,N'-dimethylacetamide (DMA) (20 mL) were combined in a 20 mL scintillation vial. 9-isopropyl-carbazole-3,6-dicarboxylic acid (0.148 g, 0.5 mmol) and N,N'-dimethylacetamide were combined in a 20 mL scintillation vial. The vial was placed on a shaker table for five hours to dissolve most of the ligand. 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.056 g, 0.5 mmol) and DMA (20 mL) were combined in a 20 mL scintillation vial. Cobalt stock solution (1 mL), ligand stock solution (1 mL), DMA (1 mL) and pyridine (0.08 mL) were added to a 4 mL scintillation vial and sealed with a Teflon cap. The resulting solution was heated on a dry hot bath in an aluminum block at 358 K for one hour. DABCO solution (1 mL) was added to the hot reaction mixture. The solution was then heated for an additional 20 hours on the 358 K dry hot bath. The vials were removed from heat and allowed to cool to room temperature. Dark blue/green crystals were collected by removing brown precipitate and excess solvent. The as-synthesized crystals were washed in fresh DMA over the course of three days with the solvent being removed every 12 hours. DMA washed crystals were isolated and washed with benzene for three days with the solvent being replaced every 12 hours. Activated material was obtained by evacuation at 473 K.

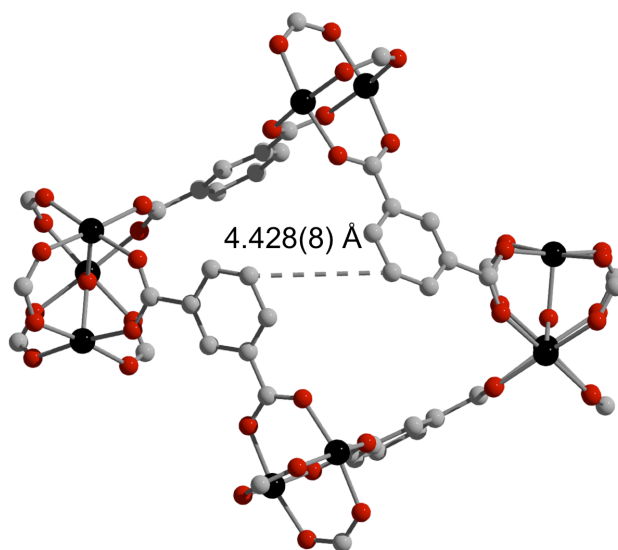
**Synthesis of 9-isopropyl-carbazole.** Carbazole (5 g, 0.03 mol), potassium hydroxide (10.5 g, 187 mmol) and N,N'-dimethylformamide (50 mL) were added to a 100 mL round bottom flask. The resulting solution was stirred at room temperature for 30 minutes. To this mixture isopropyl iodide (9 mL, 0.09 mol) was added. The resulting solution was then heated at 358 K overnight. The mixture was allowed to cool to room temperature and then poured into a round bottom flask containing DI water (250 mL). The precipitated solids were collected via vacuum filtration and washed with DI water. No further purification was done prior to the following synthesis.

**Synthesis of 9-isopropyl-3,6-diacetyl carbazole.** 9-isopropyl carbazole from the above reaction was added to a 250 mL round bottom flask and dissolved in DCM (100 mL). The resulting solution was stirred at room temperature until all solid dissolved. DCM (25 mL), aluminum (III) chloride (14 g, 0.105 mol) and acetyl chloride (12.5 mL, 0.175 mol) were added to another 250 mL round bottom flask. The resulting solution flask was fitted with an addition funnel filled with the 9-isopropyl carbazole/DCM solution. The addition funnel was connected to a water bubbler. 9-isopropyl carbazole solution was added dropwise over 45 minutes. The resulting solution was then allowed to stir at room temperature for four hours before being poured into ice cold DI water (1

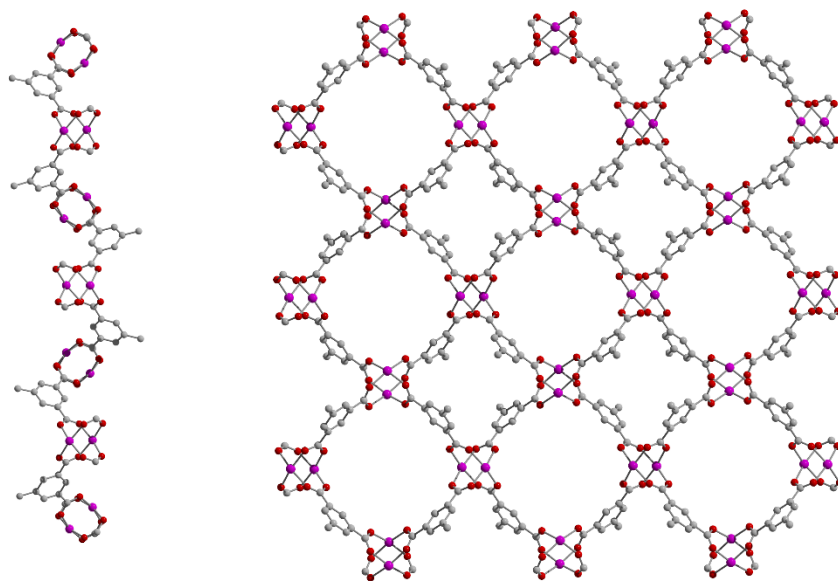
L). The precipitated solids were collected via vacuum filtration and washed with DI water. No further purification was done prior to the following synthesis.

**Synthesis of 9-isopropyl-carbazole-3,6-dicarboxylic acid.** 9-isopropyl-3,6-diacetyl carbazole from the above reaction, chloroform (100 mL) and Aliquat-336 (10 mL) were combined in a 500 mL round bottom flask. The flask was fitted with an addition funnel filled with 10 % NaOCl (aq) solution (125 mL). The NaOCl solution was added dropwise over 30 minutes. The resulting solution was set to reflux at 338 K for 18 hours. The resulting solution and Na<sub>2</sub>SO<sub>3</sub> (400 mL) were added to a 1 liter separating funnel. The chloroform layer was removed and discarded. The aqueous layer was acidified to pH = 2 using conc. HCl (aq) solution. The precipitated solids were collected via vacuum filtration and washed thoroughly with DI water.

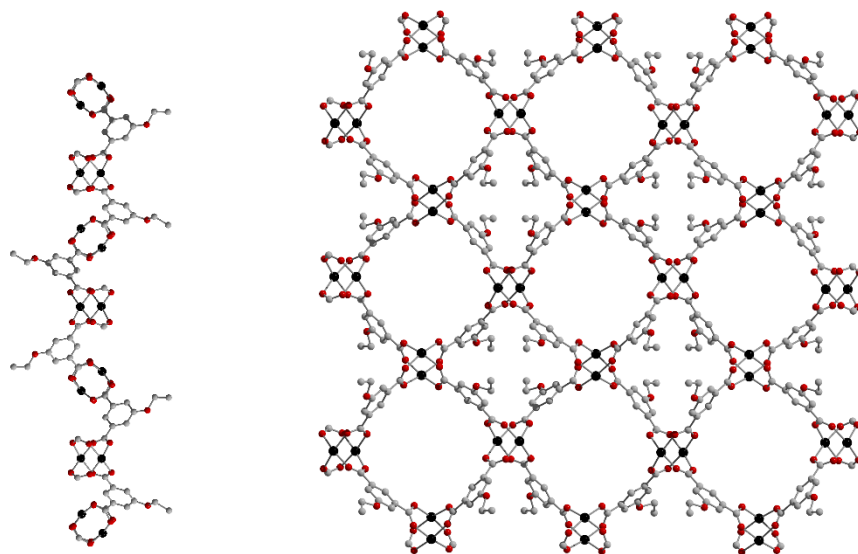
## Structures of Materials



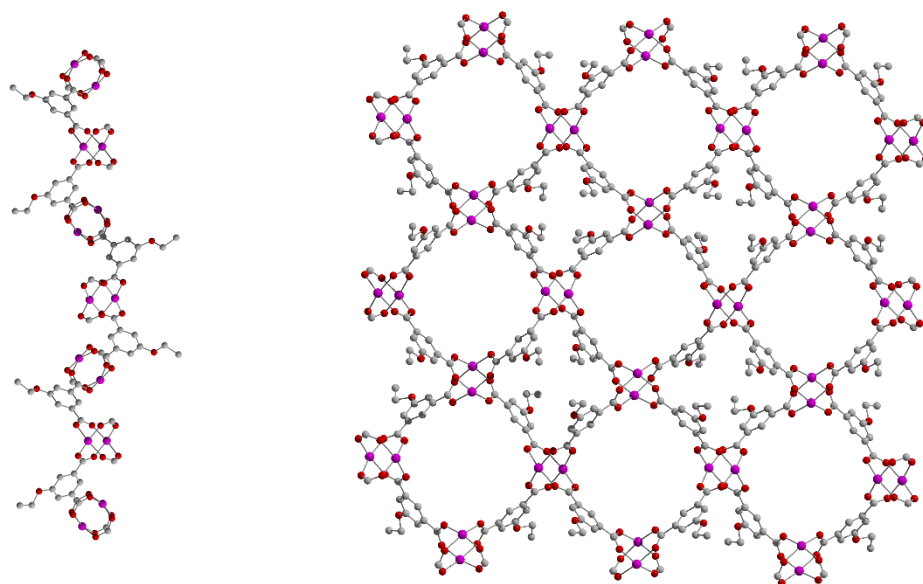
**Figure S1.** Small pore within the nickel MOF showing an intermolecular distance of 4.428(8) Å between two ligands.



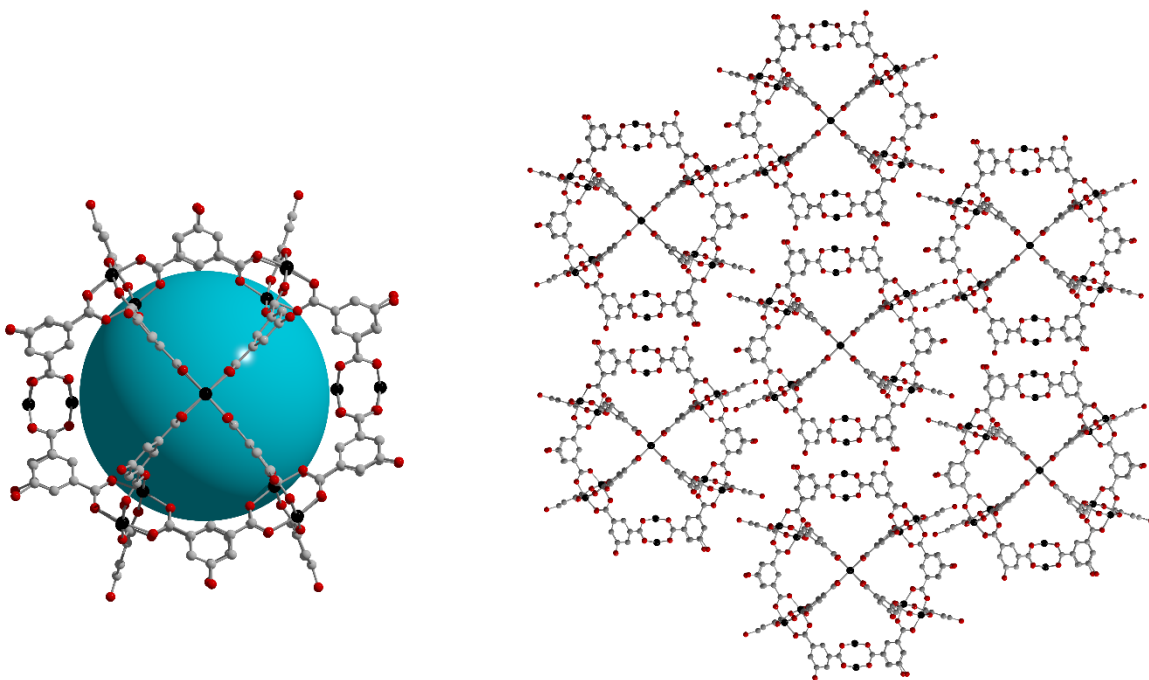
**Figure S2.** (Left) Co(Me-bdc) tetragonal sheet structure, b-axis. (Right) Co(Me-bdc) tetragonal sheet structure, c-axis. Pink, red and gray represent cobalt, oxygen and carbon respectively.



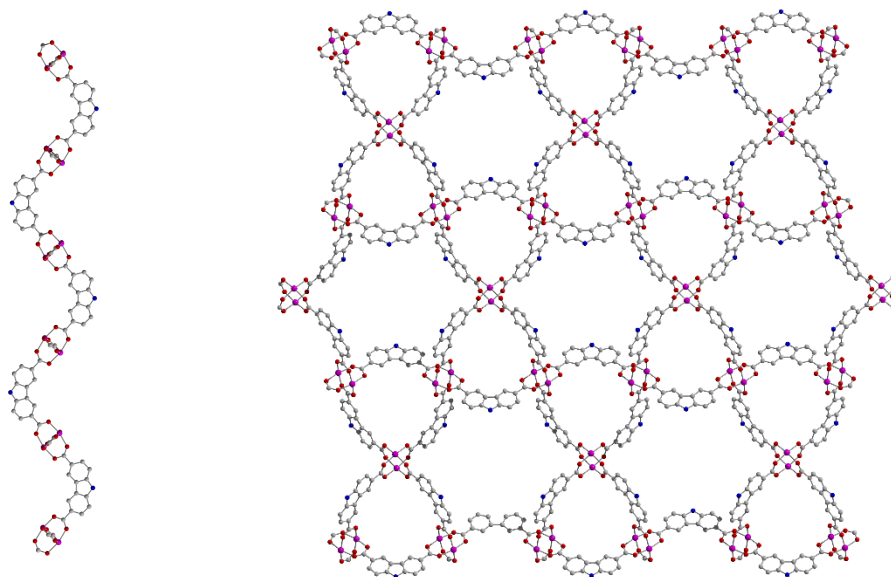
**Figure S3.** (Left) Ni(OEt-bdc) tetragonal sheet structure, b-axis. (Right) Ni(OEt-bdc) tetragonal sheet structure, c-axis. Black, red and gray represent nickel, oxygen and carbon respectively.



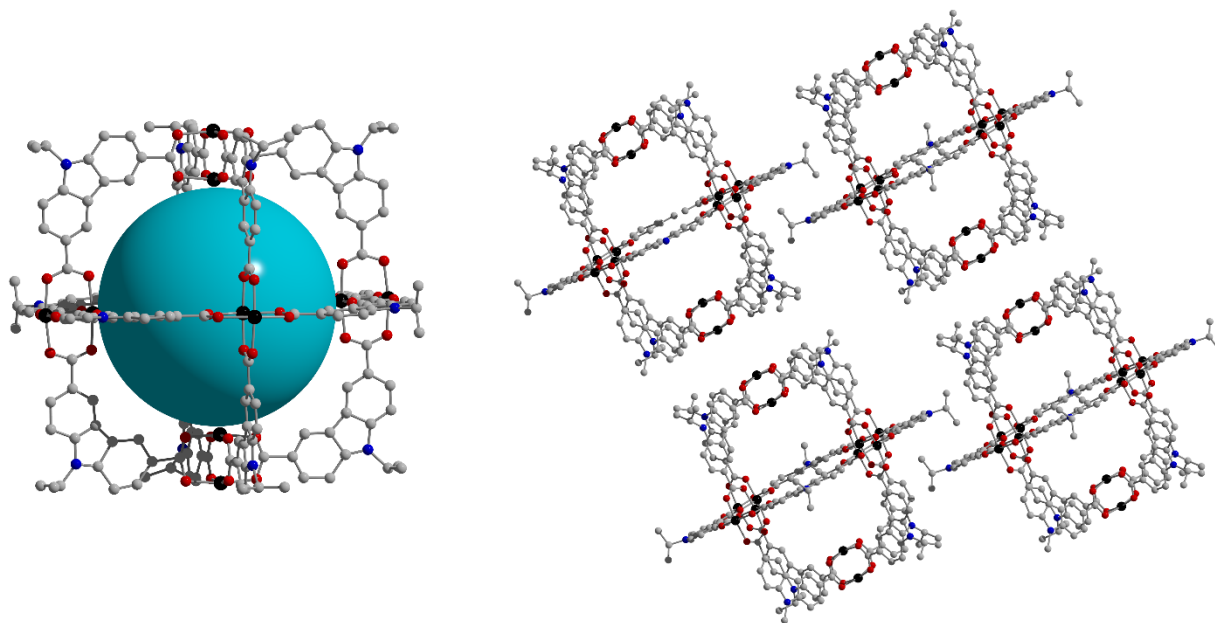
**Figure S4.** (Left) Co(OEt-bdc) tetragonal sheet structure, b-axis. (Right) Co(OEt-bdc) tetragonal sheet structure, c-axis. Pink, red and gray represent cobalt, oxygen and carbon respectively.



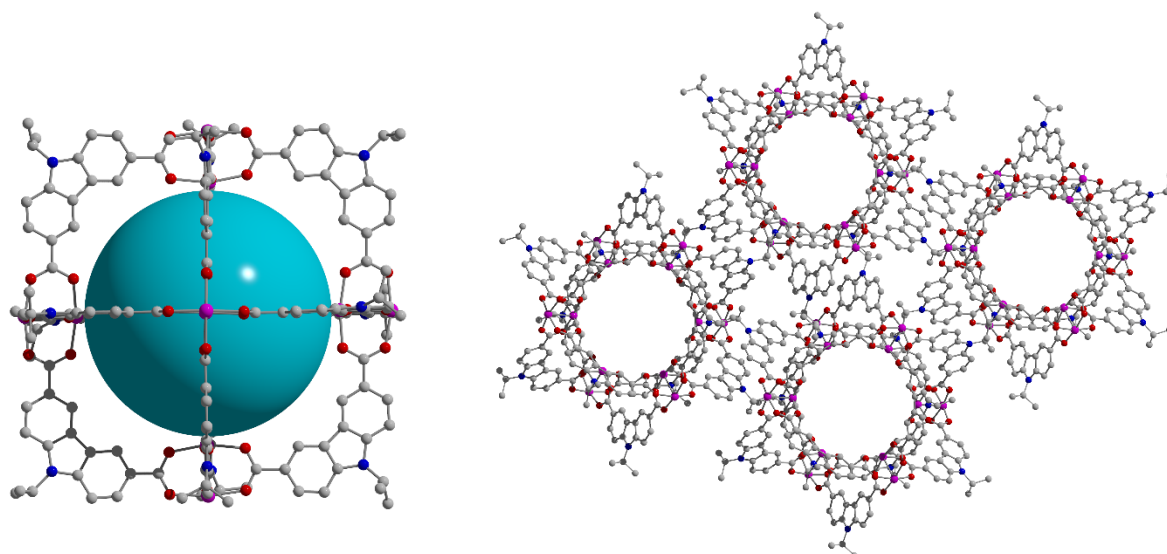
**Figure S5.** (Left)  $\text{Ni}_{24}(\text{OH-bdc})_{24}$  Cage structure. (Right) Corresponding packing structure of the cages. Black, red and gray represent nickel, oxygen and carbon respectively.



**Figure S6.** (Left)  $\text{Co}(\text{H-cdc})$  hexagonal sheet structure, b-axis. (Right)  $\text{Co}(\text{H-cdc})$  hexagonal sheet structure, c-axis. Pink, red, gray and blue represent cobalt, oxygen, carbon and nitrogen respectively.

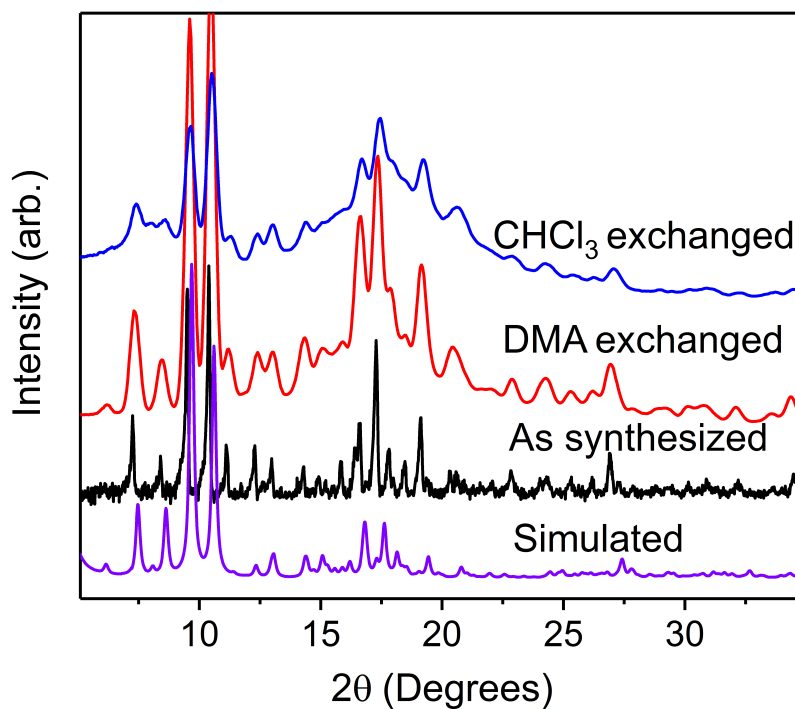


**Figure S7.** (Left)  $\text{Ni}_{12}(\text{iPr-cdc})_{12}$  Cage structure. (Right) Corresponding packing structure of the cages. Black, red, gray and blue represent nickel, oxygen, carbon and nitrogen respectively.

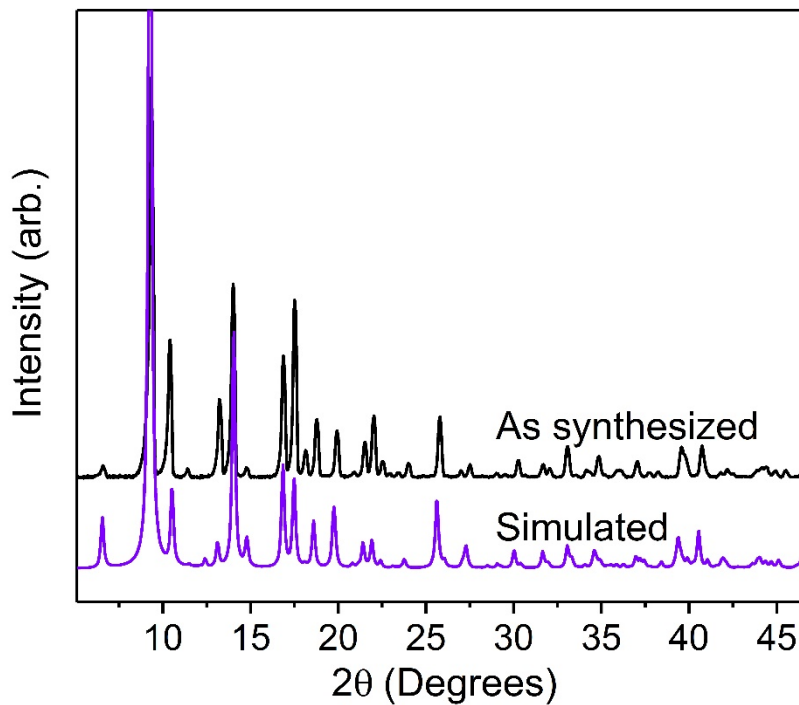


**Figure S8.** (Left)  $\text{Co}_{12}(\text{iPr-cdc})_{12}$  Cage. (Right) Corresponding packing structure of the cages, Pink, red, blue and gray represent cobalt, oxygen, carbon and nitrogen respectively.

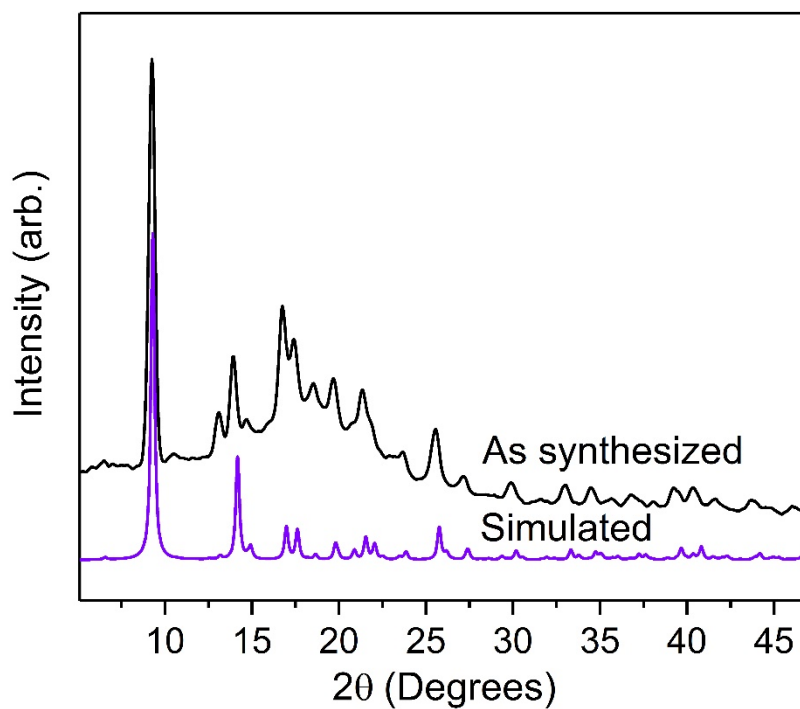
## Powder X-ray Diffraction Plots



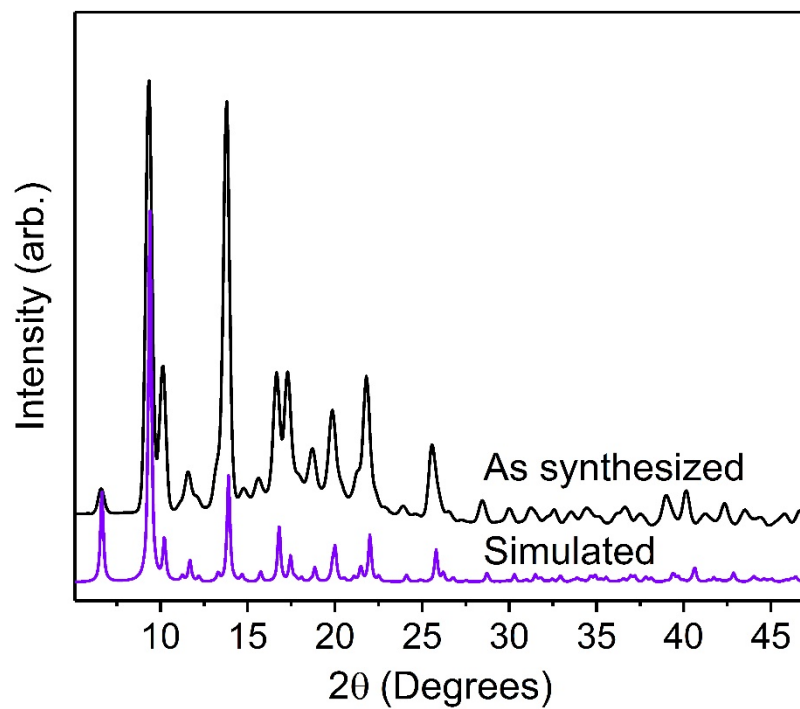
**Figure S9.** Powder X-ray diffraction pattern of the nickel MOF simulated (purple), after synthesis (black), DMA exchanged (red) and chloroform exchanged (blue).



**Figure S10.** Powder X-ray diffraction of Ni(Me-bdc) sheets simulated (purple) and after synthesis (black).

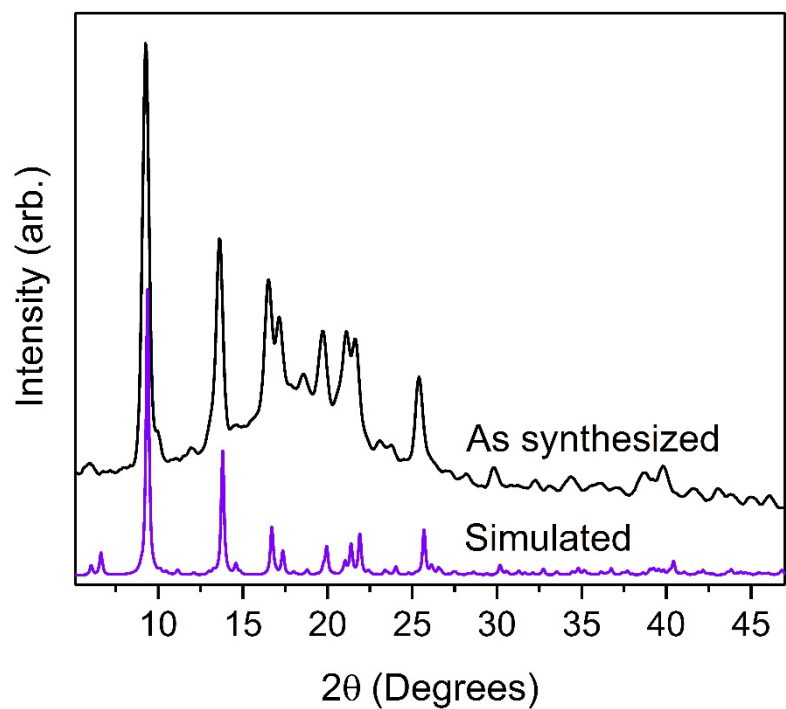


**Figure S11.** Powder X-ray diffraction of Co(Me-bdc) sheets simulated (purple) and after synthesis (black).

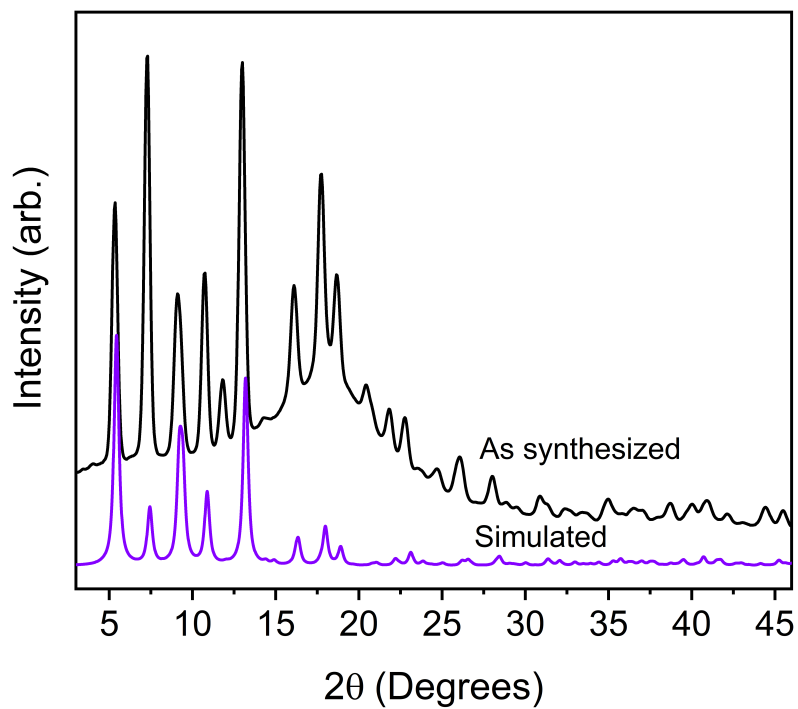


**Figure S12.** Powder X-ray diffraction of Ni(OEt-bdc) sheets simulated (purple) and after synthesis (black).

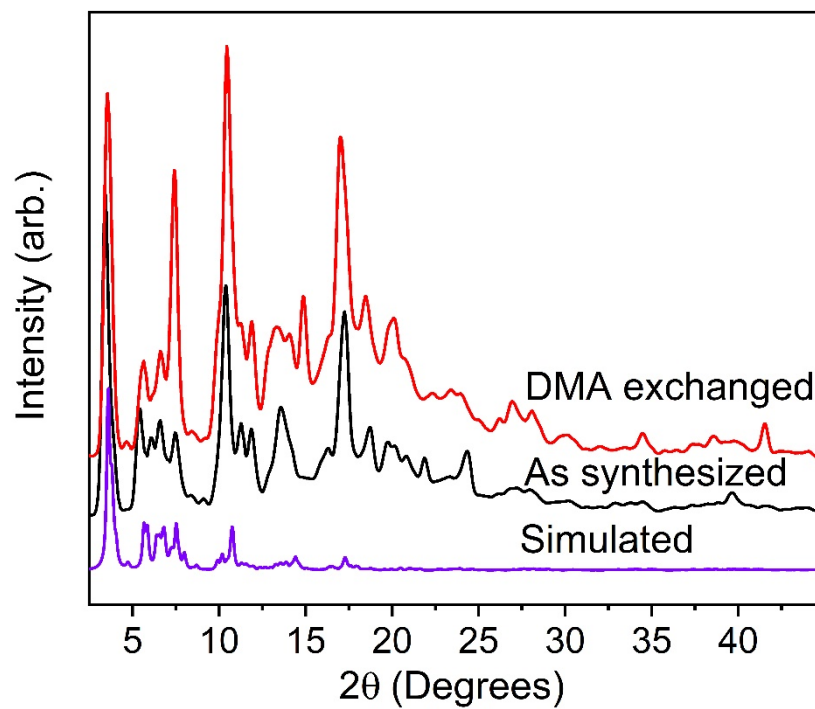




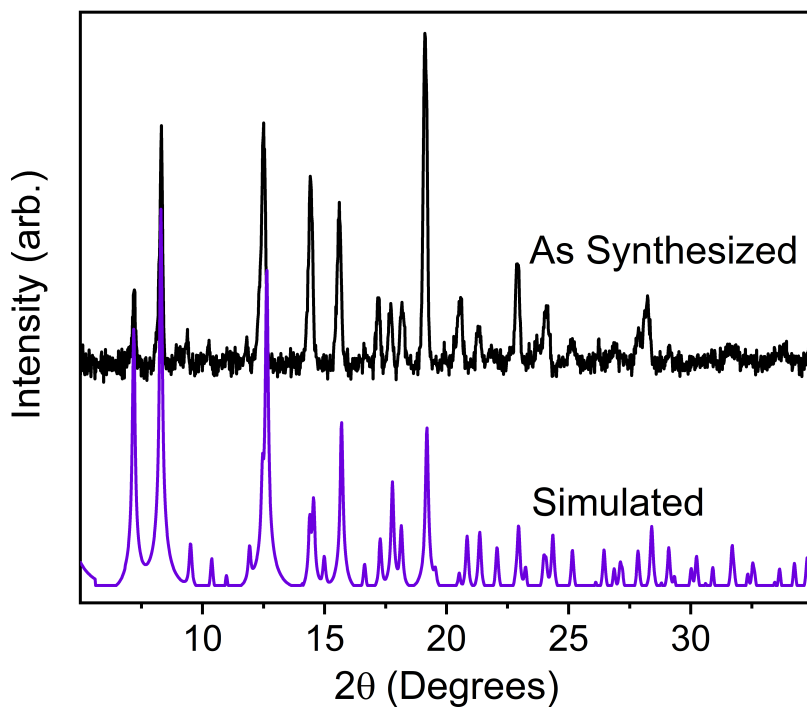
**Figure S13.** Powder X-ray diffraction of Co(OEt-bdc) sheets simulated (purple) and after synthesis (black).



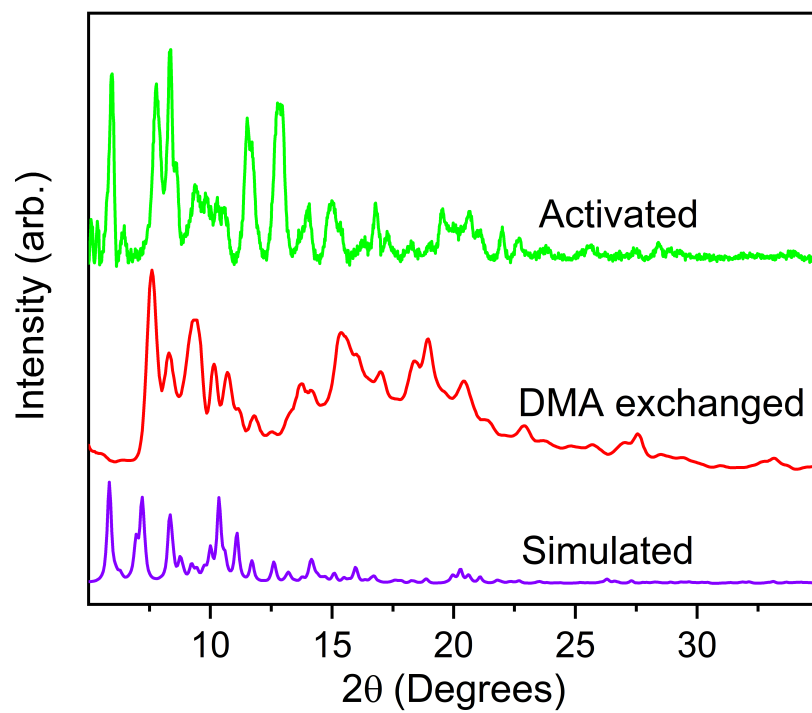
**Figure S14.** Powder X-ray diffraction of Ni(<sup>t</sup>Bu-bdc) sheets simulated (purple) and after synthesis (black).



**Figure S15.** Powder X-ray diffraction pattern of  $\text{Ni}_{24}(\text{OH-bdc})_{24}$  simulated (purple), after synthesis (black) and DMA exchanged (red).

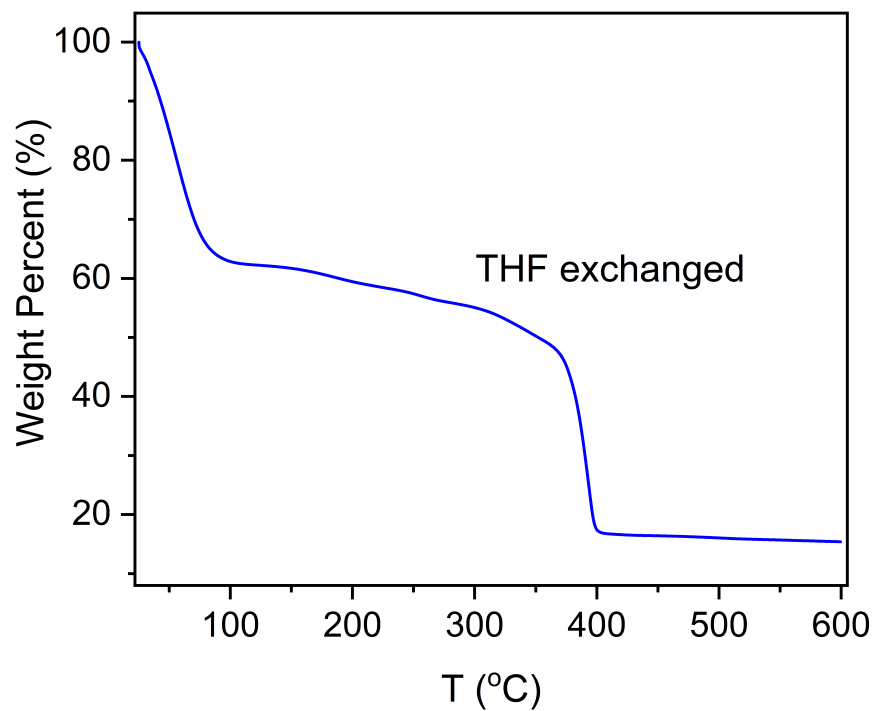


**Figure S16.** Powder X-ray diffraction pattern of  $\text{Co}(\text{H-cdc})$  sheets simulated (purple) and after synthesis (black).

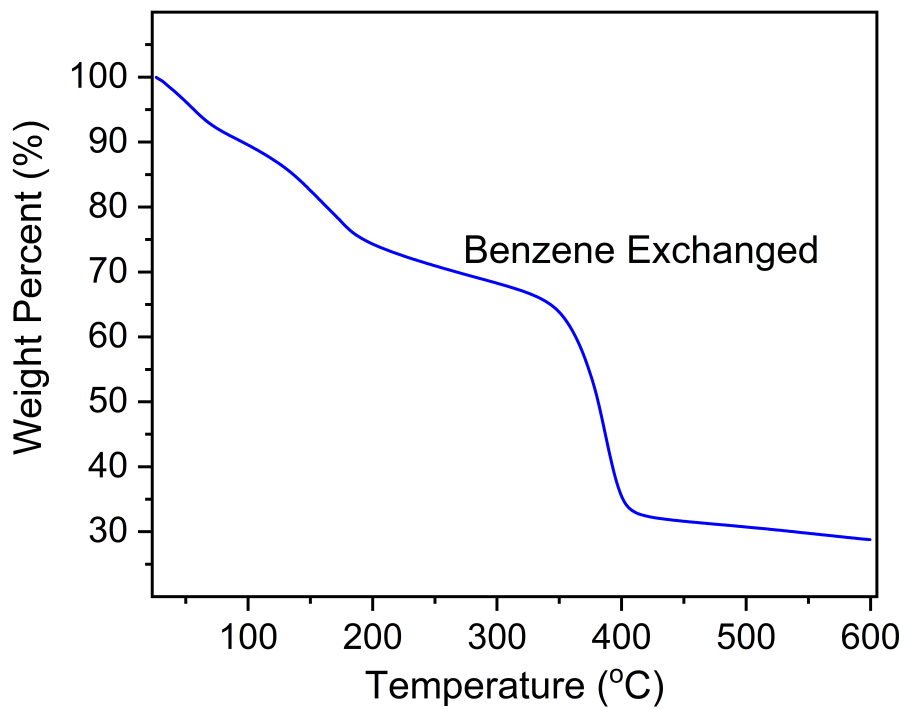


**Figure S17.** Powder X-ray diffraction pattern of  $\text{Ni}_{12}(\text{iPr-cdc})_{12}$  simulated (purple), DMA exchanged (red) and activated sample (green).

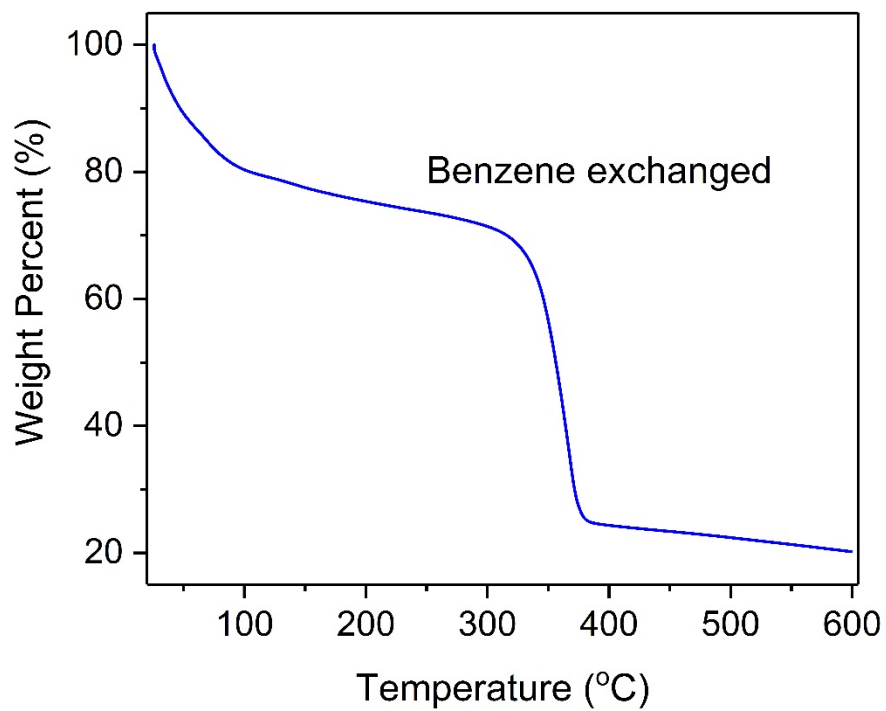
### Thermal Gravimetric Analysis



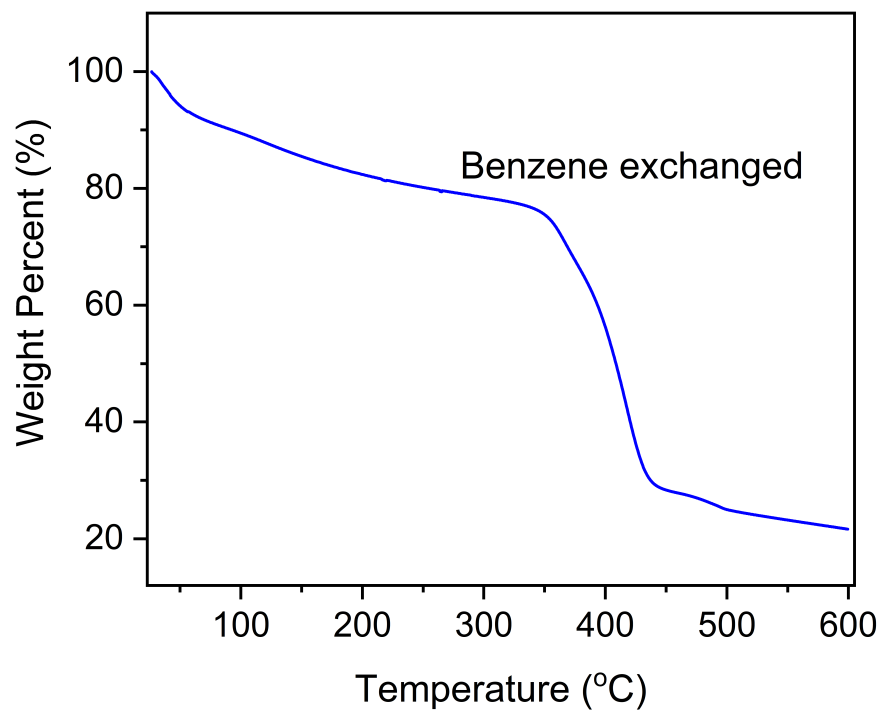
**Figure S18.** Thermogravimetric analysis of tetrahydrofuran exchanged nickel MOF from 25 °C to 600 °C at a ramp rate of two degrees per minute.



**Figure S19.** Thermogravimetric analysis of benzene exchanged  $\text{Ni}_{24}(\text{OH-bdc})_{24}$  cage from 25 °C to 600 °C at a ramp rate of two degrees per minute.

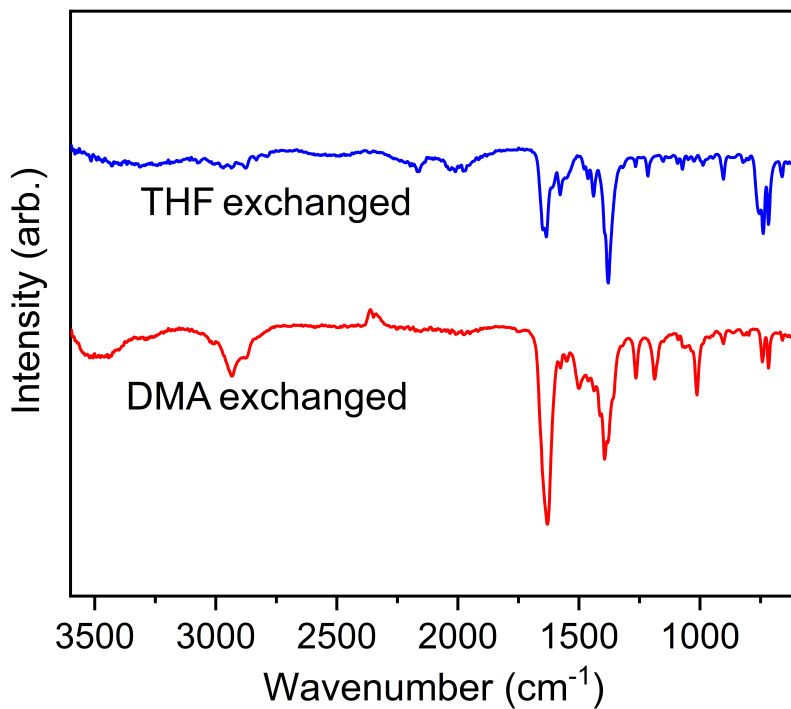


**Figure S20.** Thermogravimetric analysis of benzene exchanged  $\text{Ni}_{12}(\text{iPr-cdc})_{12}$  cage from 25  $^{\circ}\text{C}$  to 600  $^{\circ}\text{C}$  at a ramp rate of two degrees per minute.

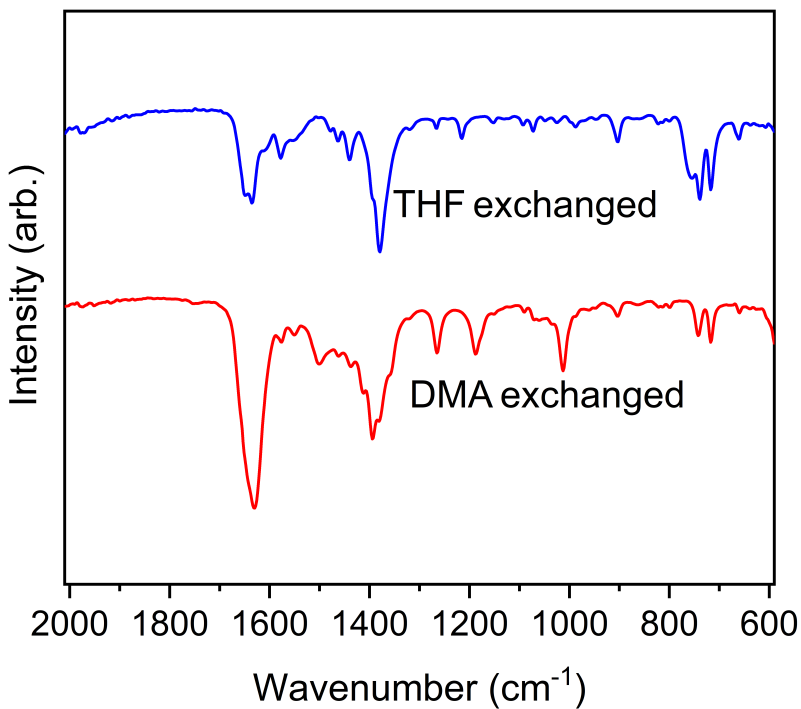


**Figure S21.** Thermogravimetric analysis of benzene exchanged  $\text{Co}_{12}(\text{iPr-cdc})_{12}$  cage from 25  $^{\circ}\text{C}$  to 600  $^{\circ}\text{C}$  at a ramp rate of two degrees per minute.

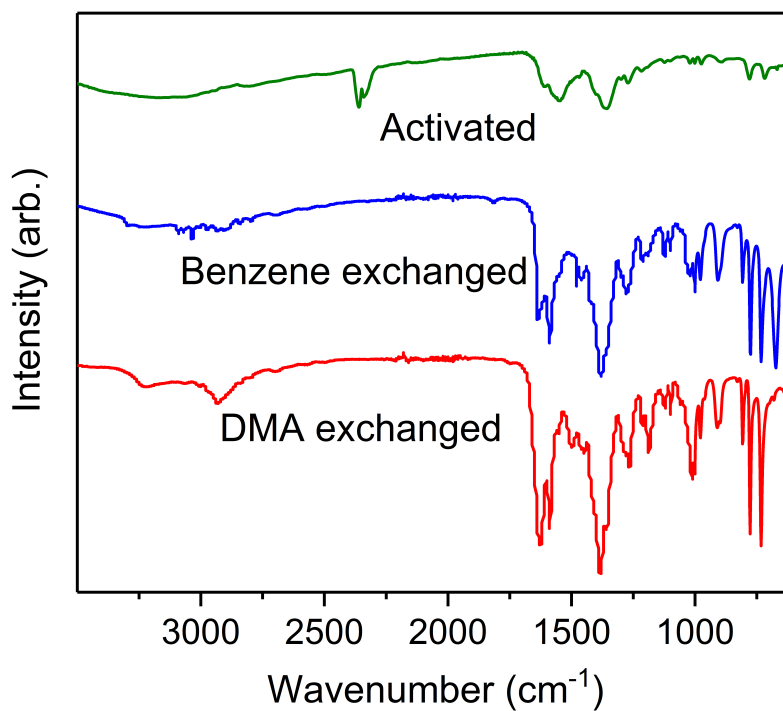
## Infrared Spectroscopy



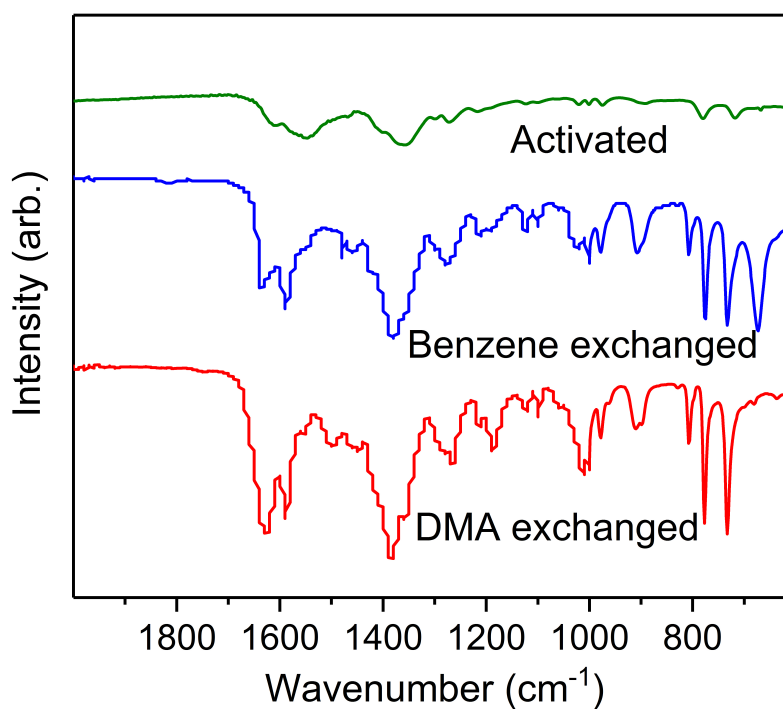
**Figure S22.** Infrared spectra of the nickel MOF DMA exchanged (red) and tetrahydrofuran exchanged (blue) from 600 cm<sup>-1</sup> to 3500 cm<sup>-1</sup>.



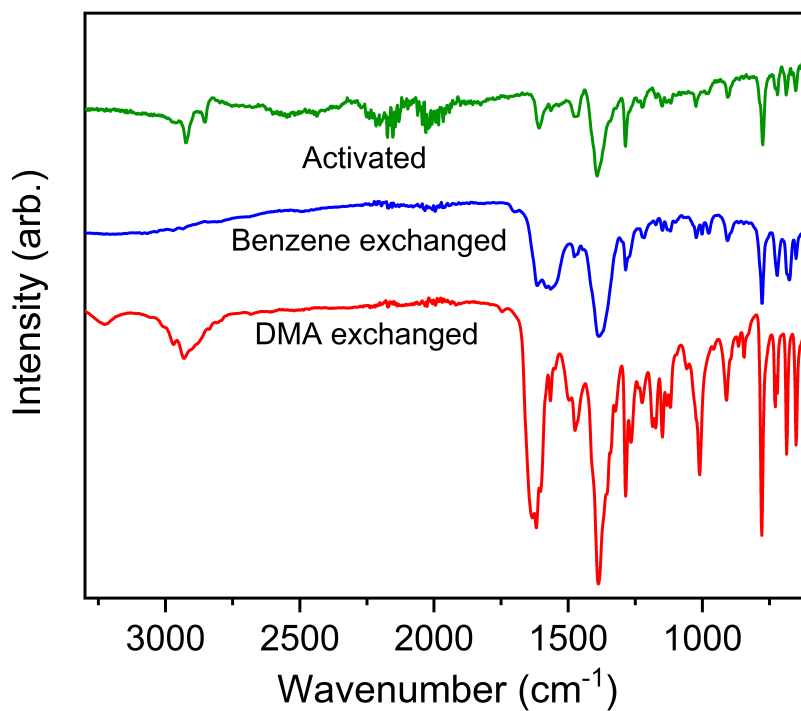
**Figure S23.** Infrared spectroscopy of the nickel MOF DMA exchanged (red) and tetrahydrofuran exchanged (blue) from 600 cm<sup>-1</sup> to 2000 cm<sup>-1</sup>.



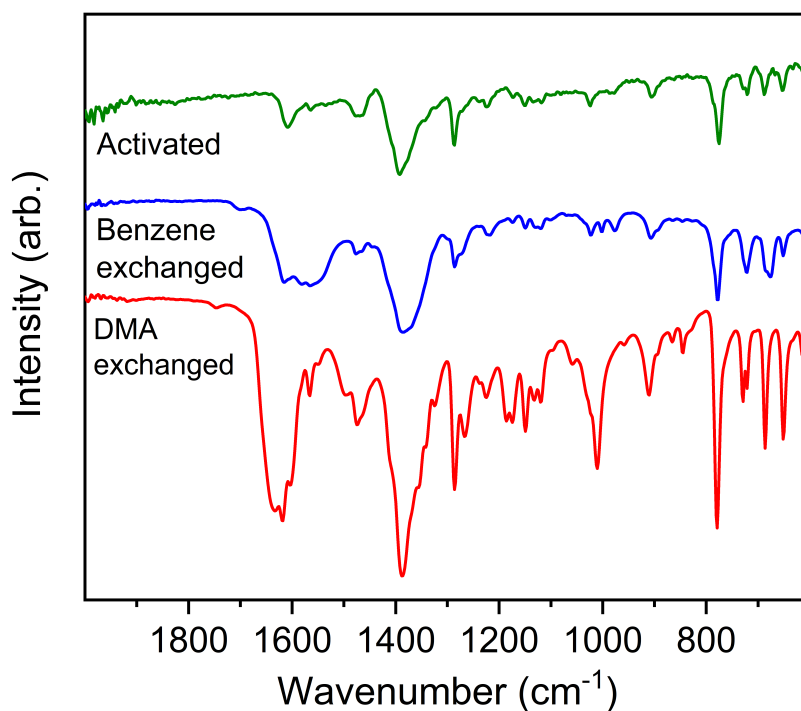
**Figure S24.** Infrared spectroscopy of  $\text{Ni}_{24}(\text{OH-bdc})_{24}$  cage DMA exchanged (red), benzene exchanged (blue) and activated (green) from  $600 \text{ cm}^{-1}$  to  $3300 \text{ cm}^{-1}$ .



**Figure S25.** Infrared spectroscopy of  $\text{Ni}_{24}(\text{OH-bdc})_{24}$  cage DMA exchanged (red), benzene exchanged (blue) and activated (green) from  $600 \text{ cm}^{-1}$  to  $2000 \text{ cm}^{-1}$ .

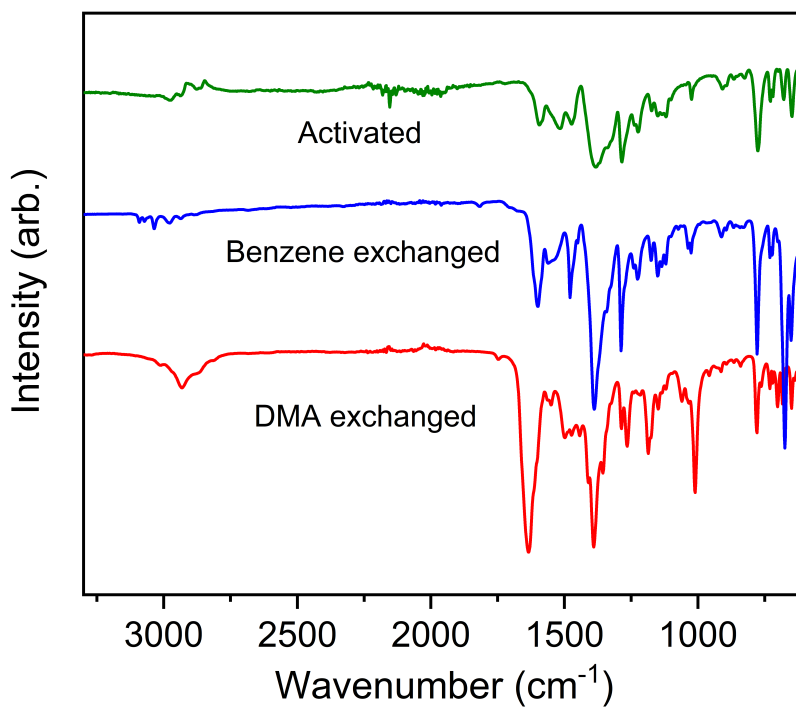


**Figure S26.** Infrared spectroscopy of  $\text{Ni}_{12}(\text{iPr-cdc})_{12}$  cage DMA exchanged (red), benzene exchanged (blue) and activated (green) from  $600 \text{ cm}^{-1}$  to  $3300 \text{ cm}^{-1}$ .

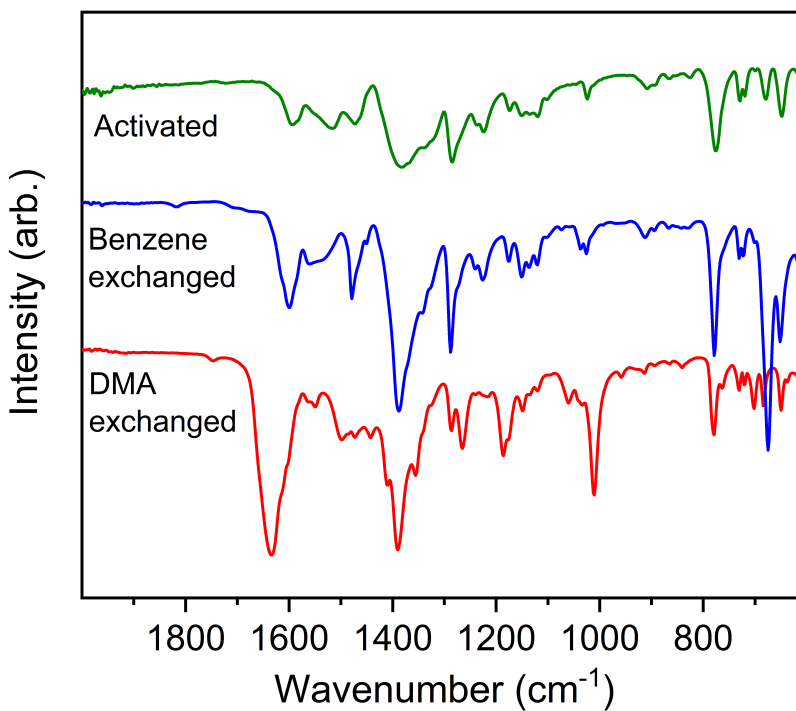


**Figure S27.** Infrared spectroscopy of  $\text{Ni}_{12}(\text{iPr-cdc})_{12}$  cage DMA exchanged (red), benzene exchanged (blue) and activated (green) from  $600 \text{ cm}^{-1}$  to  $2000 \text{ cm}^{-1}$ .



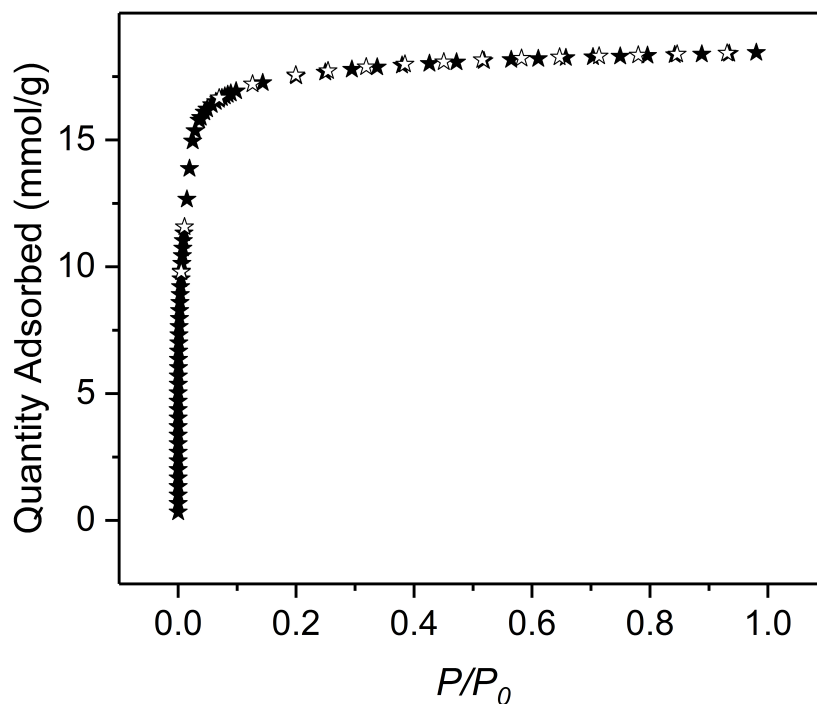


**Figure S28.** Infrared spectroscopy of  $\text{Co}_{12}(\text{iPr-cdc})_{12}$  cage DMA exchanged (red), benzene exchanged (blue) and activated (green) from  $600 \text{ cm}^{-1}$  to  $3300 \text{ cm}^{-1}$ .

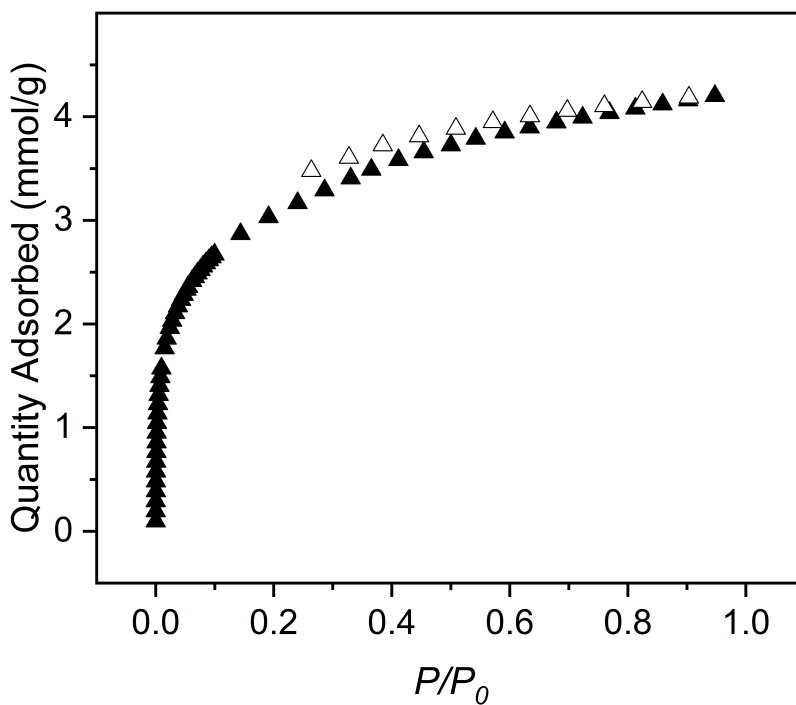


**Figure S29.** Infrared spectroscopy of  $\text{Co}_{12}(\text{iPr-cdc})_{12}$  cage DMA exchanged (red), benzene exchanged (blue) and activated (green) from  $600 \text{ cm}^{-1}$  to  $2000 \text{ cm}^{-1}$ .

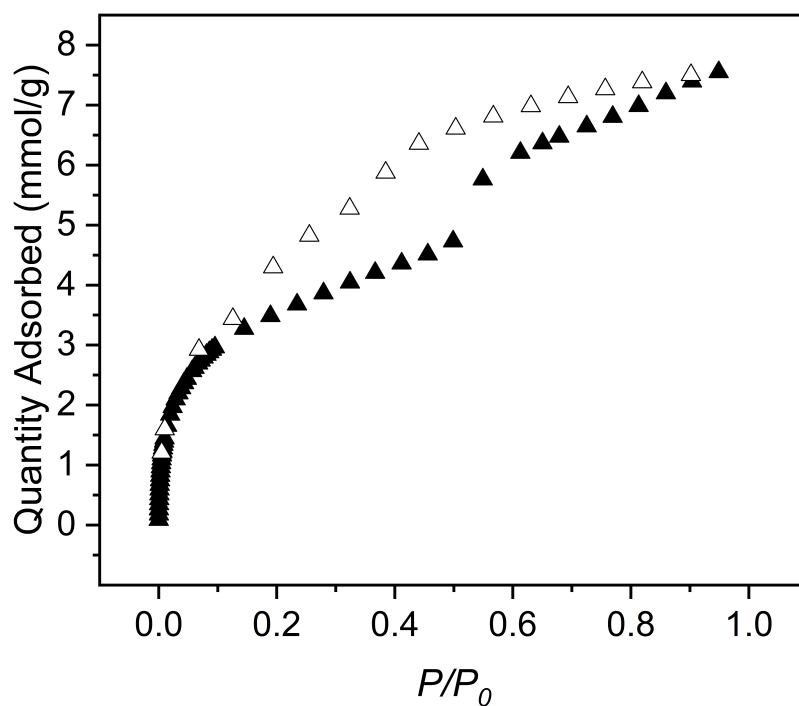
## Gas Adsorption



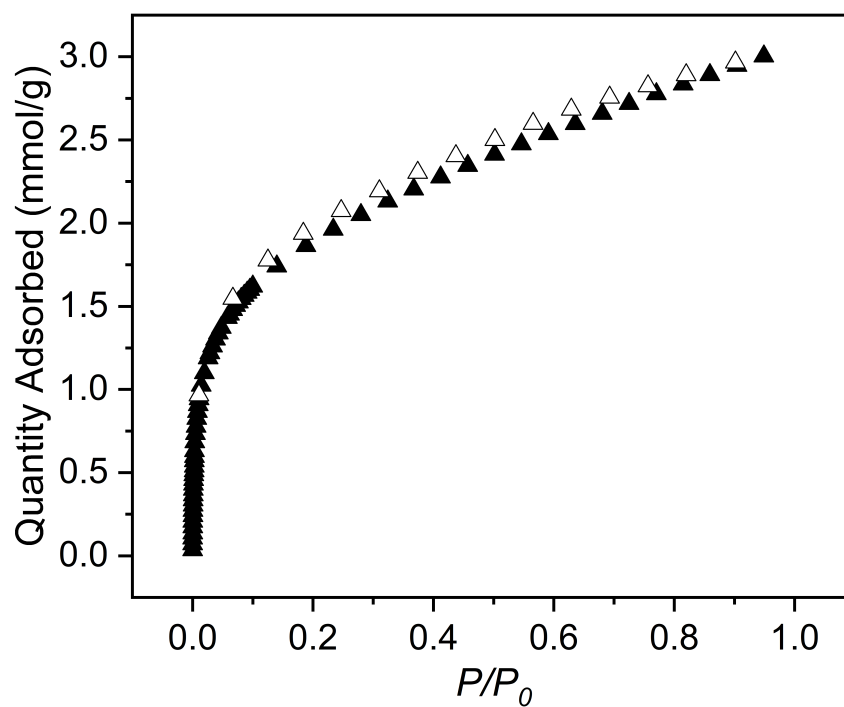
**Figure S30.** N<sub>2</sub> adsorption isotherm at 77 K for the nickel MOF.



**Figure S31.** CO<sub>2</sub> adsorption isotherm at 195 K for Ni<sub>24</sub>(OH-bdc)<sub>24</sub> cage.



**Figure S32.** CO<sub>2</sub> adsorption isotherm at 195 K for Ni<sub>12</sub>(iPr-cdc)<sub>12</sub> cage.



**Figure S33.** CO<sub>2</sub> adsorption isotherm at 195 K for Co<sub>12</sub>(iPr-cdc)<sub>12</sub> cage.

## NMR Spectroscopy

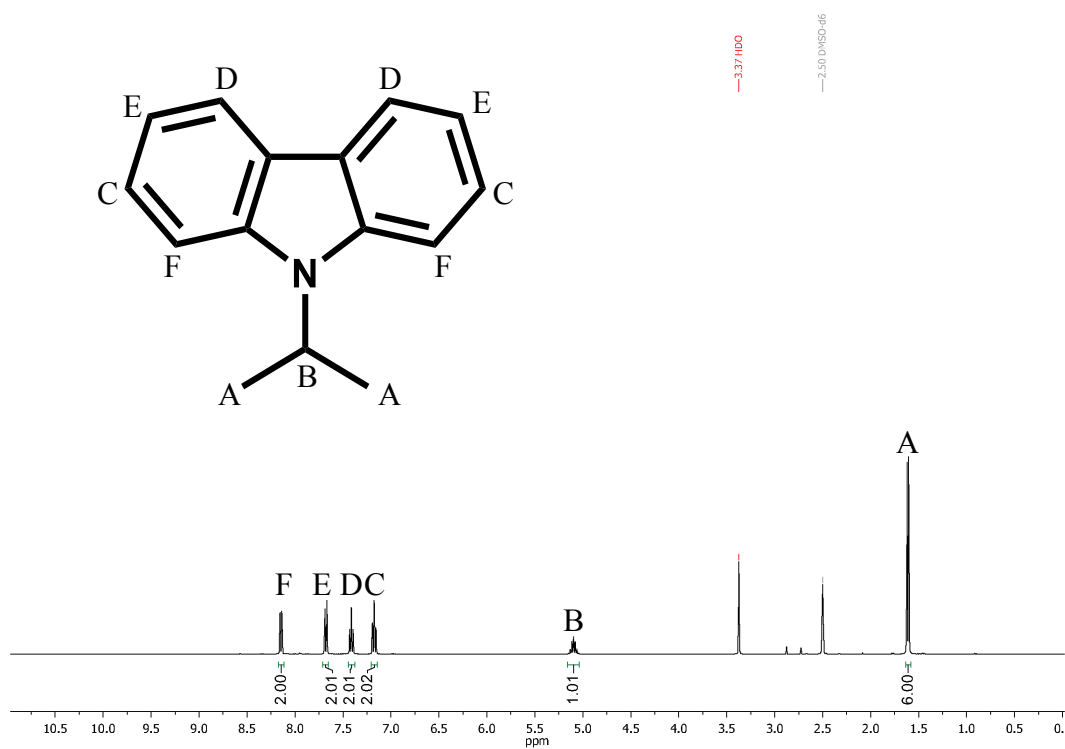


Figure S34. NMR spectrum of 9-isopropyl carbazole

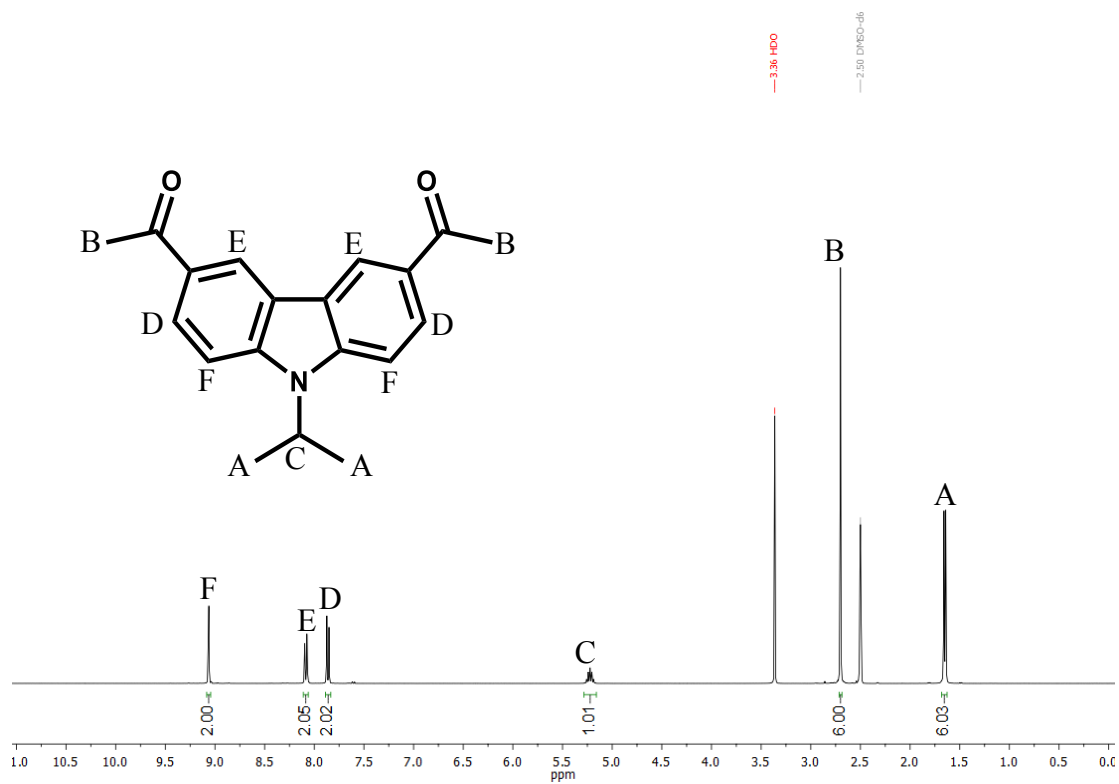
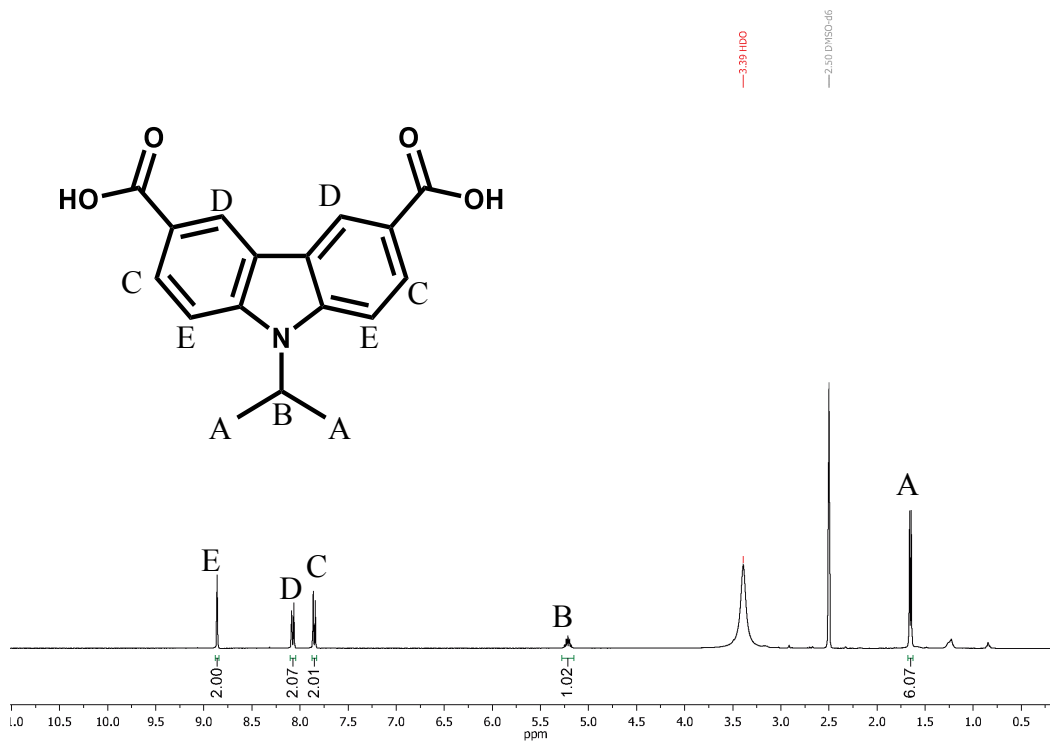


Figure S35. NMR spectrum of 9-isopropyl acetyl carbazole.



**Figure S36.** NMR spectrum of 9-isopropyl-carbazole-3,6-dicarboxylic acid.

## X-ray Crystallography

Metal-organic framework (MOF) complexes often have pores and channels. In similar fashion, cage complexes have accessible spaces between discrete polyhedra as well as inside each polyhedron that could be populated by any combination of solvent molecules, spectator metathesis products, or flexible moieties of the ligands such as alkyl chains. These ambiguous occupancies, together with the usually high temperature crystallization conditions required, conspire to yield highly mosaic or multiple, weakly diffracting crystals. As a result, it is common to have multiple restraints and constraints, incompletely identified moieties, and high residuals in the structural model in attempts to obtain the best information from limited diffraction data coverage and resolution.<sup>1</sup>

Nonetheless, with care to be within the limits of interpretation, these structures still yield valid structural insight. The results herein represent the best of several trials. The formulas reported reflect only the atoms that can be identified and H-atoms with positions that can be calculated. In all cases excluding Co(OPr-bdc) sheets, which appeared not to have significant residual density, the remaining electron density that cannot be localized as atoms was treated as a diffused contribution.<sup>2</sup>

Chemical occupancies in the cage structures are based on the number of complete polyhedra in the unit cell. For MOFs, excluding the reported nickel MOF, the occupancies are calculated on the number of dimetallic paddlewheel monomers in the unit cell. In the case of the nickel MOF, fractional atoms in the formula are avoided by using an occupancy basis unit composed of three dimeric paddlewheels and two trimetallic oxo complexes.

Crystals were mounted onto plastic mesh using viscous oil and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II Duo CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda=0.71073$  Å) for Ni(OEt-bdc) sheets, Co(Me-bdc) sheets, and Ni(Me-bdc) sheets. All other diffraction data were collected with Cu-K $\alpha$  radiation ( $\lambda = 1.54178$  Å) focused with Goebel mirrors. Unit cell parameters were obtained from 60 data frames,  $0.3^\circ \omega$ , from three different sections of the Ewald sphere.

No symmetry higher than triclinic was observed for Ni<sub>24</sub>(OH-bdc)<sub>24</sub> cage and Ni<sub>12</sub>(iPr-cdc)<sub>12</sub> cage, and solution in the centrosymmetric space group option, *P-1*, yielded chemically reasonable and computationally stable results of refinement.

The unit-cell dimensions, equivalent reflections and systematic absences in the diffraction data are consistent with *P-3m1*, *P321*, and *P3m1* for Ni(<sup>t</sup>Bu-bdc) sheets and Co(H-cdc) sheets; with *P6<sub>3</sub>/mcm*, *P6<sub>3</sub>cm*, and *P-6c2* for the nickel MOF; uniquely with *P4/ncc* for Ni(OEt-bdc) sheets; with *I4*, *I-4* and *I4/m* for Co(OEt-bdc) sheets; uniquely with *P4/nmm* for Co(Me-bdc) sheets and Ni(Me-bdc) sheets; with *R-3* for Co<sub>12</sub>(iPr-cdc)<sub>12</sub> cage; and with *P-42<sub>1</sub>m* and *P42<sub>1</sub>2* for Co(OPr-bdc) sheets. In Co(OEt-bdc) sheets and in Co(OPr-bdc) sheets, despite a thorough investigation of the other options, only the noncentrosymmetric space groups *I4* and *P-42<sub>1</sub>m*, respectively, yielded chemically reasonable and computationally stable results of refinement. Inspection with PLATON did not reveal potential overlooked symmetry.<sup>3</sup> In the remaining cases where space group options are available, solution in the centrosymmetric space group option yielded chemically reasonable and computationally stable results of refinement. The data set for Co(OEt-bdc) sheets was treated as an inversion twin with a refined distribution ratio of 67/43. The absolute structure parameter refined to nil in Co(OPr-bdc) sheets indicating the true hand of the data has been determined.<sup>4</sup> The data sets were treated with absorption corrections based on redundant multiscan

data.<sup>5</sup> The structures were solved using intrinsic phasing<sup>6</sup> and refined with full-matrix, least-squares procedures on  $F^2$ .<sup>7</sup>

The isophthalic and DMA ligands in Ni(<sup>t</sup>Bu-bdc) sheets were each found disordered in two positions with refined site occupancies of 72/28 and 75/25, respectively.

All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as idealized contributions. Atomic scattering factors are contained in the SHELXTL program library.<sup>7</sup>

The CIFs have been deposited with the Cambridge Crystallographic Database Centre under depositary numbers Co(Me-bdc) sheets: 1833892; Co(OEt-bdc) sheets: 1833893; Co(OPr-bdc) sheets: 1833894; Co(H-cdc) sheets: 1833895; Ni(Me-bdc) sheets: 1833896; Ni(<sup>t</sup>Bu-bdc) sheets: 1833897; Ni(OEt-bdc) sheets: 1833898; Co<sub>12</sub>(iPr-cdc)<sub>12</sub> cage: 1833899; Ni<sub>24</sub>(OH-bdc)<sub>24</sub>: 1833900; Ni<sub>12</sub>(iPr-cdc)<sub>12</sub> cage: 1833901; nickel MOF: 1833903.

## **References**

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