

Supporting Information for:

Mechanochemical Synthesis of Porous Molecular Assemblies

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Experimental Procedures

Reagents were obtained from commercial vendors and used as received. During the isolation and solvent exchange steps, all materials retain better crystallinity/higher surface areas if they are not allowed to completely dry.

Synthesis of 5-Tert-butylamide-1,3-benzenedicarboxylic Acid (5-HN(CO)Bu-1,3-H₂bdc). 5-aminoisophthalic acid (0.9455 g, 5.219 mmol) and trimethyl acetyl chloride (1.0356 g, 8.5885 mmol) were added to a 100 mL RBF with 40 mL of THF and stirred at 50 °C for 12 hours. Solution became homogeneous and was dried under vacuum at 50 °C, until tan precipitate was leftover. 20 mL of CHCl₃ was added to the precipitate and stirred until powder was fully dispersed. Precipitate was filtered and dried using vacuum filtration to yield 91 % of product. ¹H-NMR (400MHz, DMSO): δ = 13.22 (s, 2H, OH), 9.61 (s, 1H, NH), 8.54 (s, 2H, CH arom), 8.15 (s, 1H, CH arom), 1.23 (s, 6H, CH₃).

Synthesis of 5-Pentoxo-1,3-benzenedicarboxylic Acid. Dimethyl 5-hydroxyisophthalate (5.32 g, 25.3 mmol), potassium carbonate (5.51 g, 39.9 mmol), and pentyl iodide (3.7 mL, 28.3 mmol) were added to a 50 mL RBF with 20 mL of acetone and stirred at 40 °C for 12 hours. A colorless precipitate was separated via vacuum filtration. Potassium hydroxide (0.617 g, 11.0 mmol) in 20 mL of H₂O was added to the filtrate and stirred for 12 hours at 50 °C. The solution was concentrated to remove the acetone, then acidified to a pH of 1. The tan precipitate was isolated via vacuum filtration. Precipitate was thoroughly washed with CHCl₃ and dried to yield 87 % of product. Further purification was made by washing product with CHCl₃. ¹H-NMR (400 MHz, DMSO): δ = 13.30 (s, 2H, OH), 8.05 (s, 1H, CH arom), 7.61 (s, 2H, CH arom), 4.05 (q, 2H, CH₂), 1.72 (sextet, 2H, CH₂), 1.37 (sextet, 2H, CH₂), 1.36 (sextet, 2H, CH₂), 0.88 (t, 3H, CH₃).

Synthesis of $\text{Cu}_{24}(\text{tBu-amide-bdc})_{24}$. a) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.1561 g, 0.7821 mmol) and 5- $\text{HN}(\text{CO})\text{Bu}$ -1,3-benzenedicarboxylic acid (5- $\text{HN}(\text{CO})\text{Bu}$ -1,3- H_2bdc) (0.2427 g, 0.9150 mmol) were added to a 65 mL steel vial with two 1 mm diameter steel ball bearings. The resulting mixture was milled for 90 minutes and 10-15 mL of MeOH was added to the steel vial and transferred to a 20 mL scintillation glass vial. The vial was centrifuged and solvent was decanted to leave behind crystalline powder.

b) $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.1007 g, 0.5045 mmol) and 5-tertbutylamide-1,3-benzenedicarboxylic acid (5- $\text{HN}(\text{CO})\text{Bu}$ -1,3- H_2bdc) (0.1548 g, 0.5836 mmol) were added to a 20 mL scintillation vial with 19.8141 mL of dimethylformamide. The homogenous solution was left uncapped for 7 days, yielding very large blue crystals which were characterized with single crystal x-ray diffraction.

Synthesis of $\text{Cu}(\text{OPent-bdc})$ hexagonal sheet. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.210 g, 1.05 mmol) and 5-Pentoxo-1,3-benzenedicarboxylic acid (5- OPent -1,3- H_2bdc) (0.296 g, 1.16 mmol) were added to a 65 mL steel vial with two 1 mm diameter steel ball bearings. The resulting mixture was milled for 24 minutes and 10-15 mL of THF were added to the steel vial and transferred to a 20 mL scintillation glass vial. The vial was centrifuged and solvent was decanted to leave behind crystalline powder. Ether washes followed to remove THF.

Synthesis of $\text{Cu}_{24}(\text{H-bdc})_{24}$ cage. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.160 g, 0.081 mmol) and 1,3-benzenedicarboxylic acid (1,3- H_2bdc) (0.146 g, 8.79 mmol) were added to a 65 mL steel vial with two 1 mm diameter steel ball bearings. The resulting mixture was milled for 78 minutes and 10-15 mL of EtOH were added to the steel vial and transferred to a 20 mL scintillation glass vial. The vial was centrifuged and solvent was decanted to leave behind crystalline powder.

Synthesis of $\text{Cu}(\text{NH}_2\text{-bdc})$ material. $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$ (0.250 g, 1.25 mmol) and 5- NH_2 -1,3-benzenedicarboxylic acid (5- NH_2 -1,3- H_2bdc) (0.250 g, 1.37 mmol) were added to a 65 mL steel vial with two 1 mm diameter steel ball bearings. The resulting mixture was milled for 30 minutes and 10-15 mL of MeOH were added to the steel vial and transferred to a 20 mL scintillation glass vial. The vial was centrifuged and solvent was decanted to leave behind crystalline powder.

Nuclear Magnetic Resonance Spectra

tbutyl amide Ligand dried.1.fid
PROTON_16 DMSO /opt/topspin gtaggart 10

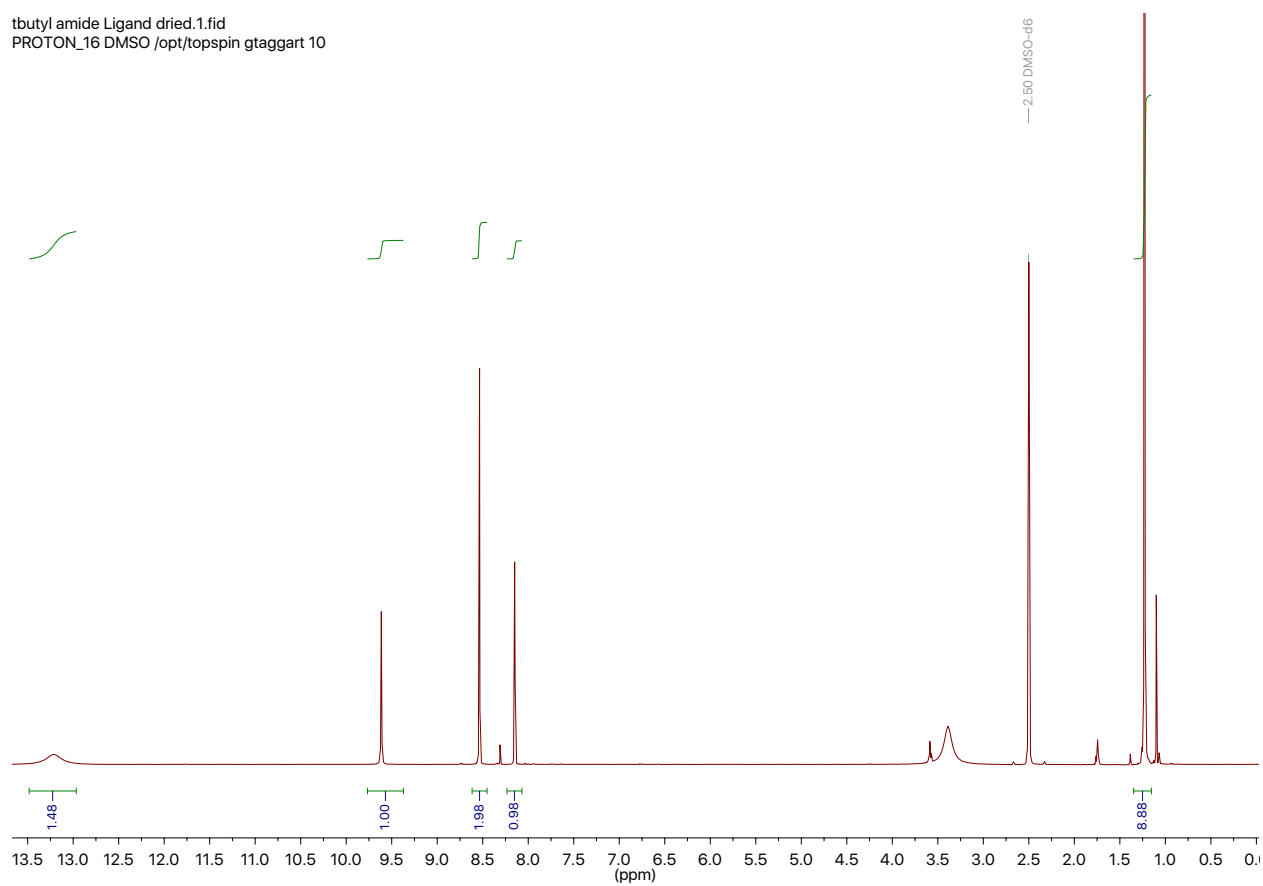


Figure S1. NMR spectra of 5-Tert-butylamide-1,3-benzenedicarboxylic acid [5-HN(CO)^tBu-H₂-bdc].

Powder X-ray Diffraction Details

X-ray powder diffraction patterns were taken at room temperature on a Rigaku MiniFlex powder diffractometer and Bruker D8 XRD using filtered Cu K α radiation.

Powder X-ray Diffraction Patterns

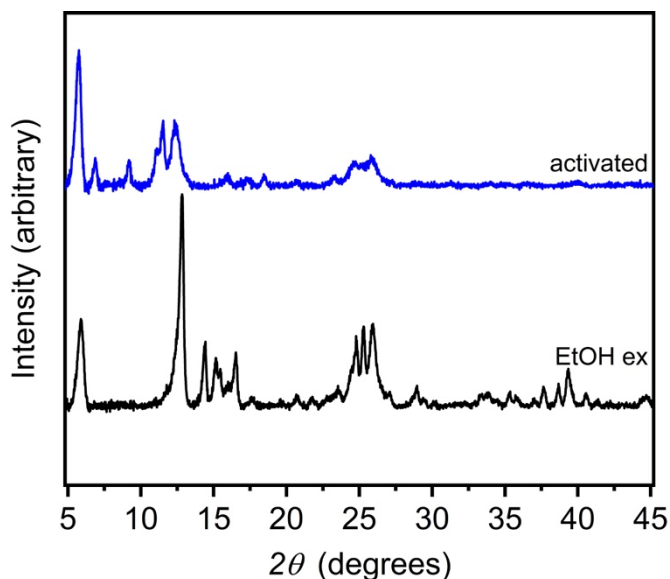


Figure S2. Powder X-ray diffraction patterns for Cu(NH₂-bdc) mechanochemically-synthesized material, solvent exchanged with ethanol (black) as compared to activated material (blue).

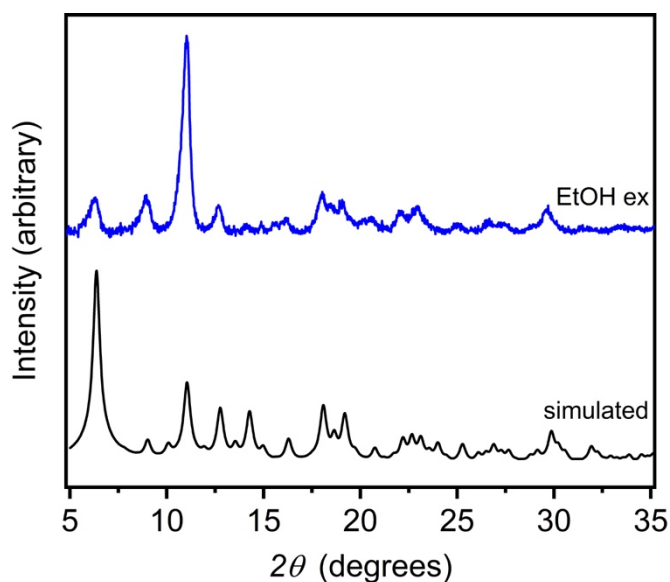


Figure S3. Powder X-ray diffraction patterns for Cu₂₄(H-bdc)₂₄ synthesized cage solvent exchanged with ethanol as compared to simulated pattern from published results.¹

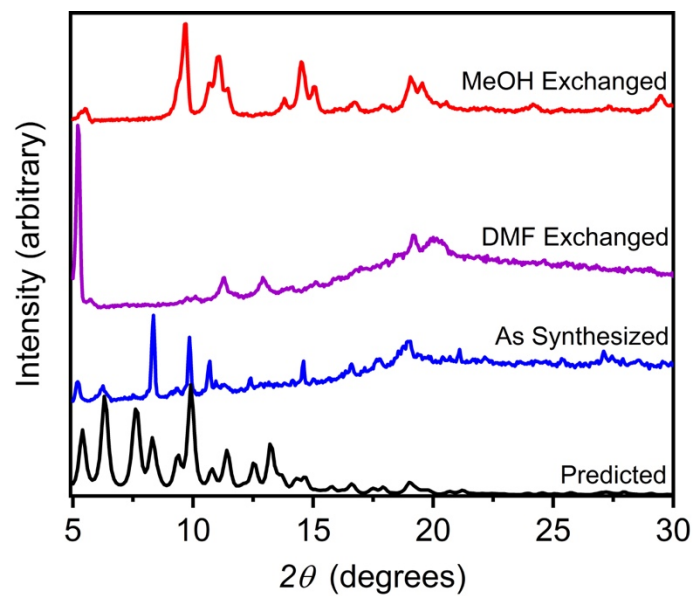


Figure S4. Powder X-ray diffraction patterns for $\text{Cu}_{24}(\text{'Bu-amide-bdc})_{24}$ cage synthesized solvothermally, solvent exchanged with DMF, and solvent exchanged with methanol.

Thermal Gravimetric Analysis Plots

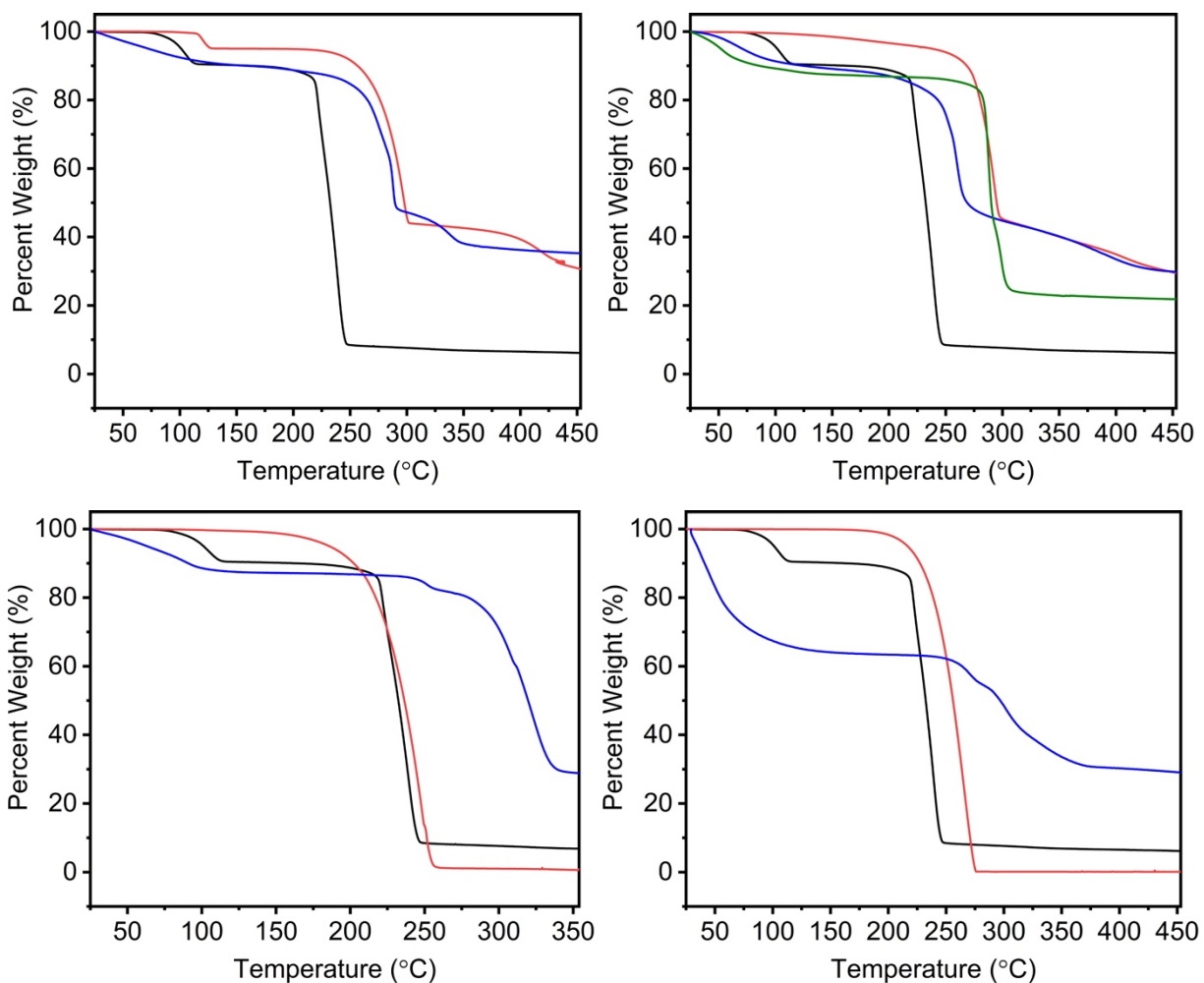


Figure S5. TGA plots for Cu_X-bdc materials [(-NH₂ (upper left), 'Bu-amide- (upper right), -OPent (lower left), and -H (lower right). Black line is copper acetate, red is ligand, blue is ball milled porous material, and green is solvothermally synthesized material.

Infrared Spectra

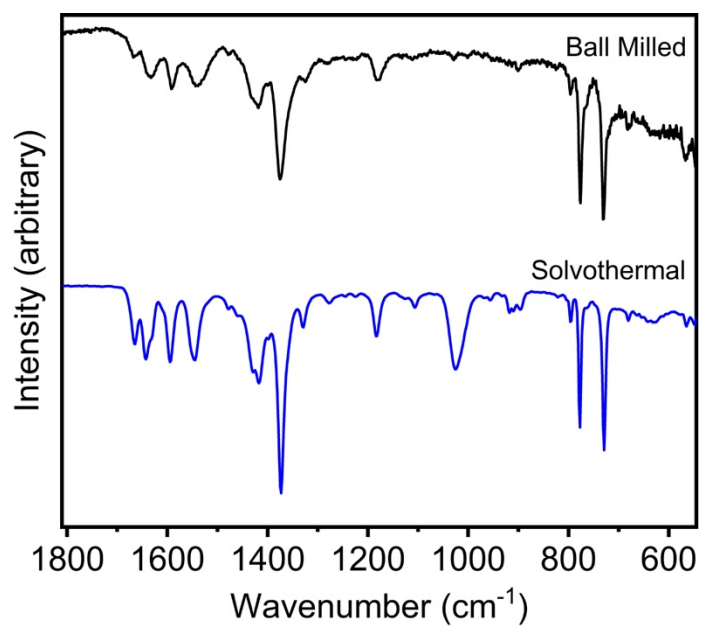


Figure S6. Infrared spectra of methanol washed $\text{Cu}_{24}(\text{tBu-amide-bdc})_{24}$.

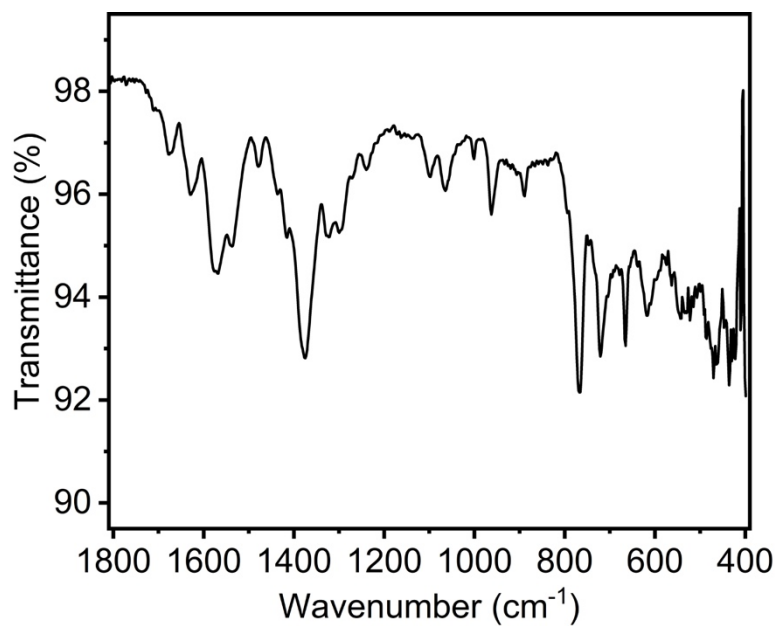


Figure S7. Infrared spectra of ethanol washed $\text{Cu}(\text{NH}_2\text{-bdc})$.

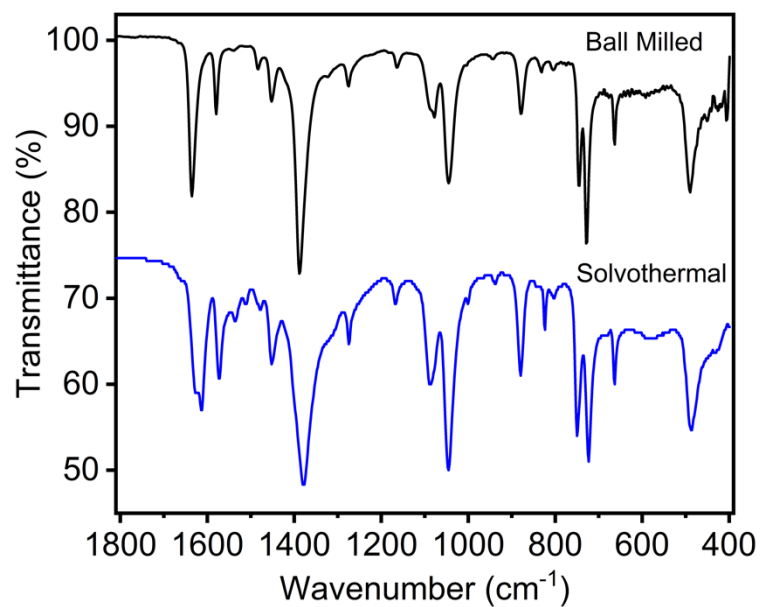


Figure S8. Infrared spectra of ethanol washed $\text{Cu}_{24}(\text{H-bdc})_{24}$.

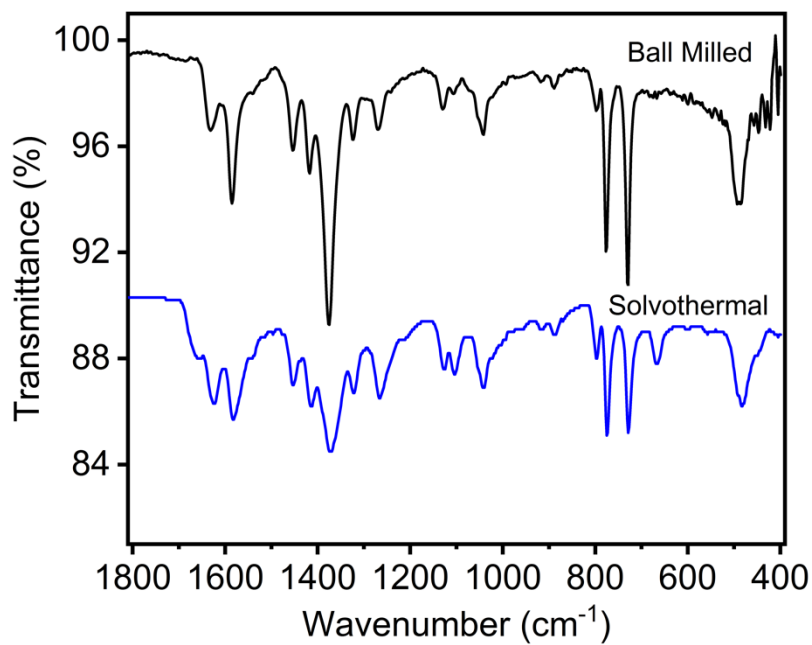


Figure S9. Infrared spectra of methanol washed $\text{Cu}(\text{OPent-bdc})$ hexagonal material.

Gas Adsorption Measurements

All gas adsorption measurements were obtained with a Micromeritics 3Flex gas adsorption analyzer. The 3Flex tubes were evacuated on the Smartvac system after being heating in the oven to remove water. Once cooled and evacuated, the sealed tubes were weighed and then brought into the glove box. The Cu_X-bdc samples were loaded into the tubes, sealed, removed from the glove box, and degassed at room temperature for 12h. Each sample was considered activated when the static outgas rate was less than 2 μ bar/min. Once fully activated, the tube was weighed to determine an accurate mass of the sample. N₂ adsorption isotherm measurements of Cu_X-bdc samples were surveyed from 25 °C to 200 °C in increments of 25 °C. Once maximum surface area was achieved, new samples were then loaded and heated to their corresponding optimal temperature at a ramp rate of 1 °C/min. Surface areas and pore volumes were measured via N₂ isotherm in a 77 K liquid nitrogen bath and calculated using the Micromeritics software.

N₂ Full Isotherms

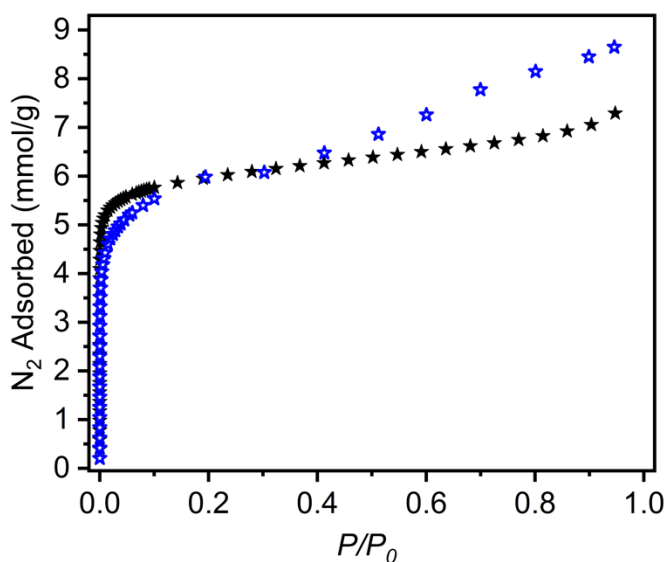


Figure S10. Nitrogen uptake of the solvothermally synthesized (black) and ball milled (blue) Cu₂₄(^tBu-amide-bdc).

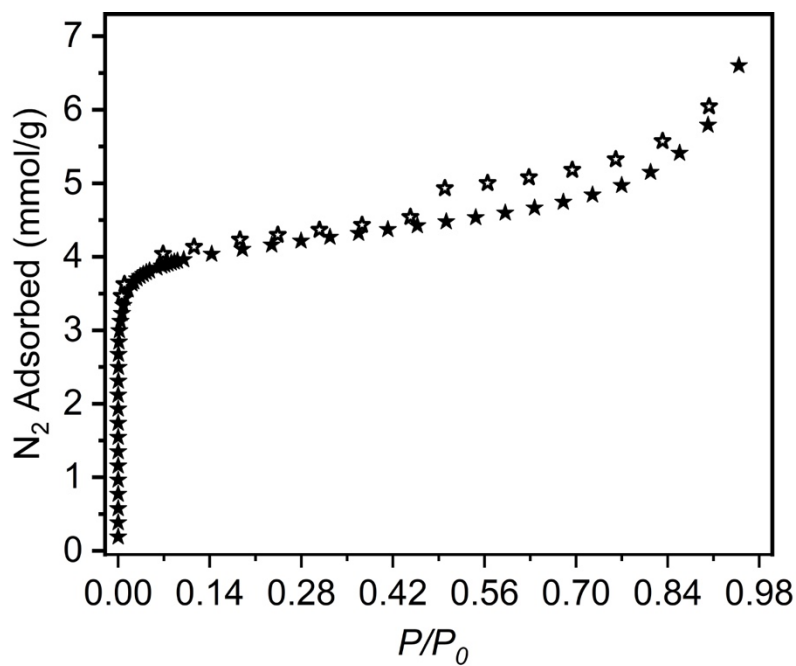


Figure S11. Nitrogen uptake of the solvothermally synthesized Cu(NH₂-bdc). Filled data points denote adsorption and open data points denote desorption.

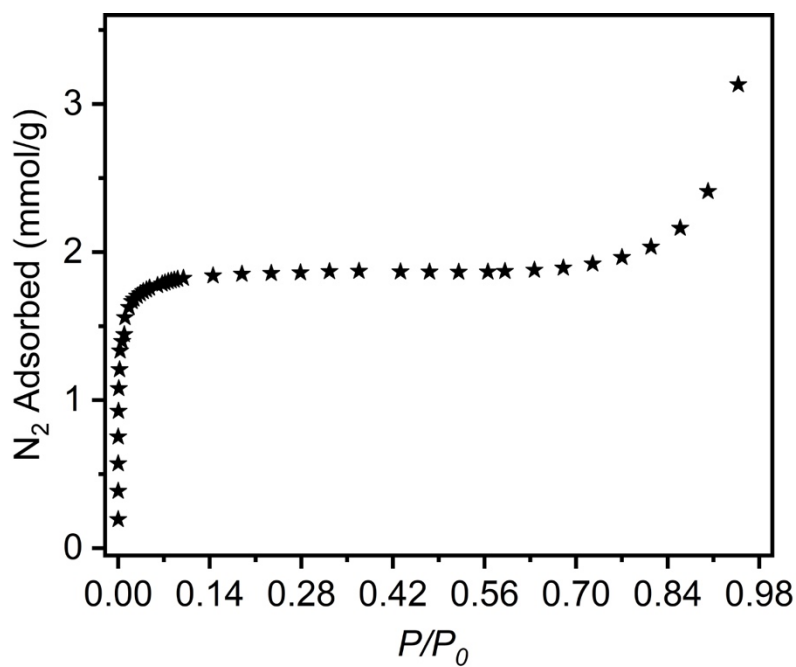


Figure S12. Nitrogen uptake of the solvothermally synthesized Cu₂₄(H-bdc)₂₄. Filled data points denote adsorption and open data points denote desorption.

Crystallographic Information

X-ray structural analysis for **Cu₂₄(^tBu-amide-bdc)₂₄**: Crystals were mounted using viscous oil onto a plastic mesh and cooled to the data collection temperature. Data were collected on a Bruker-AXS APEX II DUO CCD diffractometer with Cu-K α radiation ($\lambda = 1.54178$ Å) focused with Goebel mirrors. Unit cell parameters were obtained from 36 data frames, 0.5° ω , from three different sections of the Ewald sphere. The systematic absences in the diffraction data are consistent with $I4$, $I-4$, and $I4/m$. Refinement in the centrosymmetric space group option, $I4/m$, yielded chemically reasonable and computationally stable results of refinement. The data were treated with multi-scan absorption corrections.¹ Structures were solved using intrinsic phasing methods² and refined with full-matrix, least-squares procedures on F^2 .³ The compound molecule is located at an inversion center.

The disordered contents of highly porous metal-organic framework (MOF) and metal-organic polyhedra (MOP) complexes result in diffraction data that are limited in coverage and resolution. As a result, it is common to have multiple restraints and constraints, incompletely identified moieties, and high residuals in the structural model.⁴ The data-set was treated as two-component twinned at (0 1 0).⁵ The formulas reported herein reflect only the atoms that were discretely modeled. Presumably disordered solvent molecules were treated as diffused contributions.⁶ The best-fitting t-butyl group was restrained to have similar 1,2 and 1,3 distances and was used as a model to geometrically restrain the remaining t-butyl groups. Phenyl groups were constrained to have idealized hexagonal geometry. Global rigid bond restraints on displacement parameters were applied. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2 U_{eq} (1.5 U_{eq} for methyl) of the attached atom. Atomic scattering factors are contained in the SHELXTL program library.³ The structures have been deposited at the Cambridge Structural Database under the following CCDC depositary number: **1835131**.

References:

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- 4) Sheldrick, G. M. Crystal structure refinement with SHELXL *Acta Cryst.* **2015**, C71, 3-8.
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- 6) Spek, A. L. Structure validation in chemical crystallography. *Acta Cryst.* **2009**, D65, 148-155.
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