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Design and synthesis of aryl-functionalized carbazole-based porous coordination cages

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List of Contents

Experimental Section

General Considerations

All reagents, with the exception of specified solvents, were purchased from commercial vendors and used without further purification. Methanol and N,N-dimethylformamide were obtained from a solvent drying system and stored in a glove box under 3 Å and 4 Å sieves, respectively. Anhydrous ethanol was stored in a glove box under 4 Å sieves. Fresh bottles of N,N-dimethylacetamide and N,N'-dimethylpropyleneurea were degassed with N_2 and stored in a glove box under 4 Å sieves for at least 72 hours before use. Air-sensitive materials were handled in an N_2 glovebox utilizing the solvents described above. 9-isopropyl-cdc and $Cr_2(OAc)_4$ were synthesized as previously reported.[1,2] All gas adsorption measurements were performed on a Micromeritics 3Flex gas adsorption analyser using 4.0 purity gases. Prior to measurements, samples were considered activated when their outgas rate under static vacuum was ≤ 2 μbar/min. For CO_2 or N_2 degas screening, the sample was heated at the specified temperature under dynamic vacuum. For full BET measurements, the sample was heated at the optimal activation temperature under dynamic vacuum.

Note: Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the products identified are necessarily the best available for the purpose.

Single-crystal X-ray diffraction

X-ray structural analysis for $Cu_{12}(^{i}Pr\text{-}cdc)_{12}$, $Cu_{12}(phenyl\text{-}cdc)_{12}$, $Mo_{12}(phenyl\text{-}cdc)_{12}$, $Mo_{12}(^{i}Pr\text{-}phenyl\text{-}cdc)_{12}$, $Mo_{12}(biphenyl\text{-}cdc)_{12}$, $Cu_{12}(carbazolyl\text{-}phenyl\text{-}cdc)_{12}$, $Cu_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$, and $Cr_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$: 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-Kα radiation (λ = 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 unit-cell dimensions, equivalent reflections and systematic absences in the diffraction data are consistent with *Cc*, and *C*2/*c* for $Mo_{12}(phenyl\text{-}cdc)_{12}$ and $Cr_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$; uniquely with $P2_1/c$ for $Cu_{12}(phenyl\text{-}cdc)_{12}$ and $Mo_{12}(biphenyl\text{-}cdc)_{12}$; uniquely with $P2_1/n$ for $Cu_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$; and with *R*3 and *R*-3 for $Cu_{12}(^{i}Pr\text{-}cdc)_{12}$, $Mo_{12}(^{i}Pr\text{-}phenyl\text{-}cdc)_{12}$ and $Cu_{12}(carbazolyl\text{-}phenyl\text{-}cdc)_{12}$. Refinement in the centrosymmetric space group options yielded chemically reasonable and computationally stable results of refinement. The data were treated with multi-scan absorption corrections.[3] Structures were solved using intrinsic phasing methods[4] and refined with full-matrix, least-squares procedures on F^2.[5] The compound molecule is located at an inversion center for $Mo_{12}(phenyl\text{-}cdc)_{12}$, $Cu_{12}(phenyl\text{-}cdc)_{12}$, $Mo_{12}(biphenyl\text{-}cdc)_{12}$, $Cu_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$ and $Cr_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$; and at a three-fold rotoinversion axis in $Cu_{12}(^{i}Pr\text{-}cdc)_{12}$, $Mo_{12}(^{i}Pr\text{-}phenyl\text{-}cdc)_{12}$ and $Cu_{12}(carbazolyl\text{-}phenyl\text{-}cdc)_{12}$.

The disordered cell contents of highly porous 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 located moieties, and high residuals in the structural model.[6] The formulas reported herein reflect only the

atoms that were discretely modeled. Presumably disordered solvent molecules and non-locatable parts of moieties were treated as diffused contributions using Squeeze.[7] Non-crystallographic symmetry restraints were applied to one symmetry unique ligand in $Cu_{12}(^{i}Pr\text{-}cdc)_{12}$ and $Mo_{12}(biphenyl\text{-}cdc)_{12}$. Two phenyl groups and an entire ligand were found disordered in $Cu_{12}(phenyl\text{-}cdc)_{12}$ in two positions with refined site occupancies of 56/44, 64/36 and 52/48, respectively. Three of six symmetry-unique *p*-bromo-phenyl groups, which were treated as idealized rigid groups based on the structure of bromobenzene[8], in $Cr_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$ were found disordered in two positions each with refined site occupancies of 82/18, 66/34, and 57/43. Chemically equivalent atoms in the disordered contributions were constrained with equal atomic displacement parameters. Phenyl groups were constrained to have idealized hexagonal geometry in $Cu_{12}(phenyl\text{-}cdc)_{12}$, $Mo_{12}(^{i}Pr\text{-}phenyl\text{-}cdc)_{12}$, $Mo_{12}(biphenyl\text{-}cdc)_{12}$ and $Cu_{12}(carbazolyl\text{-}phenyl\text{-}cdc)_{12}$. The C_{aryl}-$C_{carboxylate}$ bond distances were constrained to 1.504(14) Å in $Cu_{12}(carbazolyl\text{-}phenyl\text{-}cdc)_{12}$ and $Cu_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$, and treated to non-crystallographic symmetry restraints in $Mo_{12}(biphenyl\text{-}cdc)_{12}$. Two C_{aryl}-C_{aryl} bond distances in $Cu_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$ were constrained to 1.384(13) Å.

TwinRotMat analysis in Platon yielded several potential two-fold axis twin laws for $Cu_{12}(Br\text{-}phenyl\text{-}cdc)_{12}$. We selected (1 1 0) [1 1 0], since it had the highest number of overlaps and highest predicted reduction in the R-value and the rotation matrix is consistent our initial observations that the monoclinic unit cell mimicked a tetragonal cell, i.e. *a* is similar to *b* and ß close to 90°.

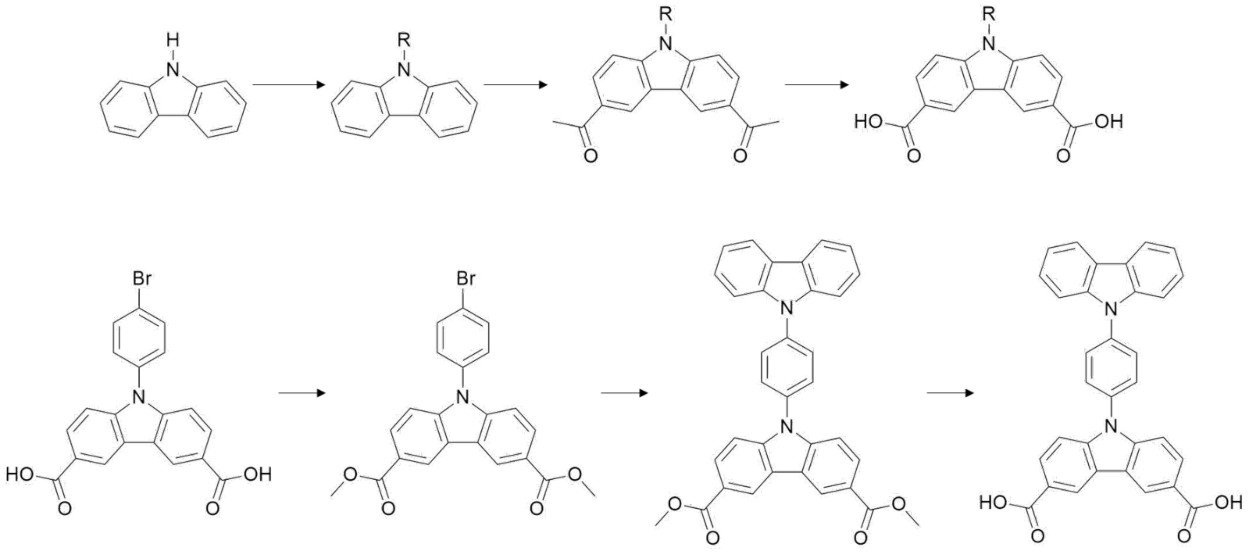
Rigid bond restraints on anisotropic displacement parameters were applied. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were treated as idealized contributions with geometrically calculated positions and with U_{iso} equal to 1.2 U_{eq} (1.5 U_{eq} for methyl) of the attached atom. Atomic scattering factors are contained in the SHELXTL program library. The structures have been deposited at the Cambridge Structural Database under the following CCDC depositary numbers: 1833902, 1941343-1941347, 1950221, 1961488.

Powder Diffraction as a function of Temperature

Powder diffraction data was collected at 17-BM at APS where ʎ= 0.45411 Å. Methanol exchanged Cu_{12}(phenyl-cdc)$_{12}$ was loaded into a capillary inside of a glove box. The capillary was connected to a sealable valve with a rubber o-ring and metal ferrule. This setup was connected to a gas manifold that had a vacuum pump and digital pressure readout attached. The sample was pumped down on until the digital readout showed no change in pressure. The sample was then heated at a rate of 2.5 K/min with powder diffractions scans taken every 7 mins.

Pawley refinements were performed using Topas academic edition. Initially, the space group and unit cell from the crystal structure were used to fit the 298 K evacuated sample. The fit had multiple missing peaks demonstrating that the structure undergoes an initial phase change upon desolation that does not fit the solvated structure. (Figure S60) Unit cell searches were performed on the Cu_{12}(phenyl-cdc)$_{12}$ powder diffraction data at three temperatures, 298 K, 400 K, and 500 K to find a new unit cell. Triclinic, monoclinic, and orthorhombic were all searched for matches in the unit cell. The best results found correlated with a doubling of the A and B axis of the solvated structure's cell. This unit cell was able to fit all three different temperatures with slight distortions in the parameters. (Table S1)

Ligand Synthesis



Scheme 1. Representative synthesis route for the alkyl and aryl functionalized ligands described here (top). Synthesis of 9-(4'-carbazolylphenyl)-cdc (bottom)

Synthesis of 9-methyl-carbazole.[9] Potassium hydroxide (4.2 g, 75 mmol) was suspended in 20 mL of DMF. To this mixture 9H-carbazole (2 g, 12 mmol) was added and the resulting solution was allowed to stir at RT for 0.5 h. Iodomethane (1.1 mL, 18 mmol) was added to the solution and the reaction mixture was allowed to continue stirring at RT for 12 h. The reaction mixture was added to 100 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 2.1 g, 95 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.15 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.47 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.24 – 7.16 (m, 2H), 3.88 (s, 3H).

Synthesis of 3,6-diacetyl-9-methyl-carbazole.[10] 9-methyl-carbazole (6.5 g, 36 mmol) was dissolved in 80 mL of DCM. In a separate flask $AlCl_3$ (14.3 g, 107 mmol) and acetyl chloride (13 mL, 183 mmol) were suspended in 25 mL of DCM. The 9-methyl-carbazole solution was added to the $AlCl_3$ suspension via an addition funnel. The reaction mixture was allowed to stir at RT for 4 h. The reaction mixture was added to 1 L DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 9.1 g, 95 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.04 (s, 2H), 8.17 – 8.10 (m, 2H), 7.74 (d, *J* = 8.6 Hz, 2H), 3.96 (s, 3H), 2.71 (s, 6H).

Synthesis of 9-methyl-cdc.[10] 3,6-diacetyl-9-methyl-carbazole (8.0 g, 30 mmol) was dissolved in 100 mL of chloroform. To this solution 20 mL of Aliquat-336 was added. 120 mL of 10 % NaOCl $_{(aq)}$ solution was added via an addition funnel to the 9-methyl-3,6-diacetyl-carbazole solution. The reaction mixture was set to stir at 65 °C for 12 h. The reaction mixture was allowed to cool and 350 mL of saturated Na_2SO_3 $_{(aq)}$ solution was added. The resulting mixture was added to a separatory funnel and the aqueous layer was collected. The aqueous layer was acidified to pH = 3, precipitated solids were collected via vacuum filtration (Yield: 7.7 g, 95 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.87 (d, *J* = 1.6 Hz, 2H), 8.12 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 3.97 (s, 3H).

Synthesis of 9-ethyl-carbazole.[9] Potassium hydroxide (4.2 g, 75 mmol) was suspended in 20 mL of DMF. To this mixture 9H-carbazole (2 g, 12 mmol) was added and the resulting solution was allowed to stir at RT for 0.5 h. Iodoethane (1.5 mL, 18 mmol) was added to the solution and the reaction mixture was allowed to continue stirring at RT for 12 h. The reaction mixture was added to 100 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 2.2 g, 96 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.15 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.45 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.24 – 7.15 (m, 2H), 4.44 (q, *J* = 7.1 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).

Synthesis of 3,6-diacetyl-9-ethyl-carbazole.[10] 9-ethyl-carbazole (5.3 g, 27 mmol) was dissolved in 60 mL of DCM. In a separate flask $AlCl_3$ (11.1 g, 83 mmol) and acetyl chloride (9.8 mL, 138 mmol) were suspended in 25 mL of DCM. The 9-ethyl-carbazole solution was added to the $AlCl_3$ suspension via an addition funnel. The reaction mixture was allowed to stir at RT for 4 h. The reaction mixture was added to 1 L DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 6.4 g, 85 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.06 (d, *J* = 1.7 Hz, 2H), 8.13 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 4.54 (q, *J* = 7.2 Hz, 2H), 2.71 (s, 6H), 1.34 (t, *J* = 7.1 Hz, 3H).

Synthesis of 9-ethyl-cdc.[10] 3,6-diacetyl-9-ethyl-carbazole (6.7 g, 24 mmol) was dissolved in 100 mL of chloroform. To this solution 20 mL of Aliquat-336 was added. 120 mL of 10 % NaOCl $_{(aq)}$ solution was added via an addition funnel to the 9-ethyl-3,6-diacetyl-carbazole solution. The reaction mixture was set to stir at 65 °C for 12 h. The reaction mixture was allowed to cool and 350 mL of saturated Na_2SO_3 $_{(aq)}$ solution was added. The resulting mixture was added to a separatory funnel and the aqueous layer was collected. The aqueous layer was acidified to pH = 3, precipitated solids were collected via vacuum filtration. (Yield: 5.1 g, 75 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.87

(d, *J* = 1.6 Hz, 2H), 8.12 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 4.53 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H).

Synthesis of 9-propyl-carbazole.[9] Potassium hydroxide (4.2 g, 75 mmol) was suspended in 20 mL of DMF. To this mixture 9H-carbazole (2 g, 12 mmol) was added and the resulting solution was allowed to stir at RT for 0.5 h. 1-iodopropane (1.8 mL, 18 mmol) was added to the solution and the reaction mixture was allowed to continue stirring at RT for 12 h. The reaction mixture was added to 100 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 2.4 g, 96 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.14 (dt, *J* = 7.8, 0.9 Hz, 2H), 7.60 (d, *J* = 8.2 Hz, 2H), 7.44 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 2H), 7.21 – 7.15 (m, 2H), 4.35 (t, *J* = 7.0 Hz, 2H), 1.79 (h, *J* = 7.3 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

Synthesis of 3,6-diacetyl-9-propyl-carbazole.[10] 9-propyl-carbazole (2.3 g, 11 mmol) was dissolved in 30 mL of DCM. In a separate flask $AlCl_3$ (4.4 g, 33 mmol) and acetyl chloride (3.9 mL, 55 mmol) were suspended in 25 mL of DCM. The 9-propyl-carbazole solution was added to the $AlCl_3$ suspension via an addition funnel. The reaction mixture was allowed to stir at RT for 4 h. The reaction mixture was added to 800 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 2.7 g, 84 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.07 (d, *J* = 1.7 Hz, 2H), 8.12 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.79 (d, *J* = 8.7 Hz, 2H), 4.47 (t, *J* = 7.0 Hz, 2H), 2.71 (s, 6H), 1.82 (q, *J* = 7.2 Hz, 2H), 0.86 (t, *J* = 7.4 Hz, 3H).

Synthesis of 9-propyl-cdc.[10] 3,6-diacetyl-9-propyl-carbazole (2.9 g, 10 mmol) was dissolved in 30 mL chloroform. To this solution 5 mL of Aliquat-336 was added. 30 mL of 10 % $NaOCl_{(aq)}$ solution was added via an addition funnel to the 9-propyl-3,6-diacetyl-carbazole solution. The reaction mixture was set to stir at 65 °C for 12 h. The reaction mixture was allowed to cool and 75 mL of saturated $Na_2SO_{3\ (aq)}$ solution was added. The resulting mixture was added to a separatory funnel and the aqueous layer was collected. The aqueous layer was acidified to pH = 3, precipitated solids were collected via vacuum filtration. (Yield: 2.4 g, 80 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.87 (d, *J* = 1.7 Hz, 2H), 8.11 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.76 (d, *J* = 8.7 Hz, 2H), 4.46 (t, *J* = 7.1 Hz, 2H), 1.83 (q, *J* = 7.2 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H).

Synthesis of 9-butyl-carbazole.[9] Potassium hydroxide (4.2 g, 75 mmol) was suspended in 20 mL of DMF. To this mixture 9H-carbazole (2 g, 12 mmol) was added and the resulting solution was allowed to stir at RT for 0.5 h. 1-iodobutane (2 mL, 18 mmol) was added to the solution and the reaction mixture was allowed to continue stirring at RT for 12 h. The reaction mixture was added to 100 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 2.4 g, 89 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.15 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.45 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 2H), 4.39 (t, *J* = 7.0 Hz, 2H), 1.80 – 1.68 (m, 2H), 1.36 – 1.22 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H).

Synthesis of 3,6-diacetyl-9-butyl-carbazole.[10] 9-butyl-carbazole (6.0 g, 27 mmol) was dissolved in 80 mL of DCM. In a separate flask $AlCl_3$ (10.9 g, 82 mmol) and acetyl chloride

(9.7 mL, 137 mmol) were suspended in 25 mL of DCM. The 9-butyl-carbazole solution was added to the $AlCl_3$ suspension via an addition funnel. The reaction mixture was allowed to stir at RT for 4 h. The reaction mixture was added to 800 mL of DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 7.5 g, 90 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.06 (d, *J* = 1.7 Hz, 2H), 8.12 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.77 (d, *J* = 8.7 Hz, 2H), 4.50 (t, *J* = 7.0 Hz, 2H), 2.71 (s, 6H), 1.77 (dq, *J* = 10.2, 7.1 Hz, 2H), 1.35 – 1.21 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H).

Synthesis of 9-butyl-cdc.[10] 3,6-diacetyl-9-butyl-carbazole (7.7 g, 25 mmol) was dissolved in 100 mL of chloroform. To this solution 10 mL of Aliquat-336 was added. 120 mL of 10 % $NaOCl_{(aq)}$ solution was added via an addition funnel to the 9-butyl-3,6-diacetyl-carbazole solution. The reaction mixture was set to stir at 65 °C for 12 h. The reaction mixture was allowed to cool and 350 mL of saturated $Na_2SO_{3\ (aq)}$ solution was added. The resulting mixture was added to a separatory funnel and the aqueous layer was collected. The aqueous layer was acidified to pH = 3, precipitated solids were collected via vacuum filtration. (Yield: 5.9 g, 76 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.87 (d, *J* = 1.6 Hz, 2H), 8.11 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.75 (d, *J* = 8.6 Hz, 2H), 4.48 (t, *J* = 7.1 Hz, 2H), 1.78 (p, *J* = 7.4 Hz, 2H), 1.31 (h, *J* = 7.5 Hz, 2H), 0.88 (t, *J* = 7.4 Hz, 3H).

Synthesis of 3,6-diacetyl-9-phenyl-carbazole.[11,12] 9-phenyl-carbazole (10.0 g, 41 mmol) was dissolved in 50 mL of DCM. In a separate flask $AlCl_3$ (16.4 g, 123 mmol) and acetyl chloride (14.6 mL, 205 mmol) were suspended in 25 mL of DCM. The 9-phenyl-carbazole solution was added to the $AlCl_3$ suspension via an addition funnel. The reaction mixture was allowed to stir at RT for 4 hrs. The reaction mixture was added to 500 mL of DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 12.1 g, 90 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.20 – 9.15 (m, 2H), 8.10 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.75 – 7.60 (m, 5H), 7.43 (d, *J* = 8.7 Hz, 2H), 2.73 (s, 6H).

Synthesis of 9-phenyl-cdc.[11,12] NaOH (72 g, 1.8 mol) was slowly added to 300 mL of DI H_2O. The prepared NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 30 mL of Br_2 were added via an addition funnel. The prepared NaOBr solution was allowed to stir at 0 °C for an additional 30 mins. 3,6-diacetyl-9-phenyl-carbazole (13.1 g, 40 mmol) was dissolved in 300 mL of 1,4-dioxane. The prepared NaOBr solution was added via an addition funnel to the 3,6-diacetyl-9-phenyl-carbazole solution. The reaction mixture was set to stir at 50 °C for 12 hrs. The reaction mix was allowed to cool to RT and 400 mL of saturated Na_2SO_3 (aq) solution was added. The reaction mix was acidified to pH = 2, precipitated solids were collected via vacuum filtration. (Yield: 11.1 g, 90 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.98 (d, *J* = 1.6 Hz, 2H), 8.09 (dd, *J* = 8.7, 1.6 Hz, 2H), 7.75 – 7.60 (m, 5H), 7.43 (d, *J* = 8.6 Hz, 2H).

Synthesis of 9-(4'-^{i}Prphenyl)-carbazole.[13] 9H-carbazole (585 mg, 3.5 mmol), 1-Iodo-4-isopropylbenzene (630 µL, 3.9 mmol), potassium carbonate (2.0 g, 14.4 mmol), copper iodide (76 mg, 0.4 mmol), N,N'-dimethylethylenediamine (120 µL, 1.1 mmol) and 20 mL of 1,4-dioxane were added to a 40 mL scintillation vial. The scintillation vial was placed on a 110 °C hot plate in a 20 mL aluminum block for 3 days. The reaction mix was allowed to cool and removed from the glovebox. The reaction mix was added to 100 mL DI H_2O,

precipitated solids were collected via vacuum filtration. (Yield: 849 mg, 85 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.25 (dd, *J* = 7.8, 1.1 Hz, 2H), 7.54 (s, 4H), 7.43 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 2H), 7.28 (ddd, *J* = 7.9, 6.9, 1.2 Hz, 2H), 3.05 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 6H).

Synthesis of 3,6-diacetyl-9-(4'-*i*Prphenyl)-carbazole.[11,12] Solid 9-(4'-^{i}Pr-phenyl)-carbazole (856 mg, 3 mmol) was slowly added to a suspension of $AlCl_3$ (1.2 g, 9 mmol) and acetyl chloride (1.1 mL, 15 mmol) in 25 mL of DCM. This mixture was allowed to stir at RT for 4 hrs, then added to 250 mL DI H_2O. The reaction flask was washed with acetone which was poured into the DI H_2O/DCM mixture, precipitated solids were collected via vacuum filtration. (Yield: 1 g, 91 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.16 (d, *J* = 1.7 Hz, 2H), 8.09 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.58 (d, *J* = 2.6 Hz, 4H), 7.42 (d, *J* = 8.7 Hz, 2H), 3.06 (h, *J* = 6.9 Hz, 1H), 2.72 (s, 6H), 1.32 (d, *J* = 6.9 Hz, 6H).

Synthesis of 9-(4'-*i*Prphenyl)-cdc.[11,12] NaOH (6 g, 150 mmol) was slowly added to 30 mL DI H_2O. The NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 3 mL of Br_2 were added via an addition funnel. The prepared NaOBr solution was allowed to stir at 0 °C for an additional 30 mins. 3,6-diacetyl-9-(4'-^{i}Pr-phenyl)-carbazole (1.1 g, 3 mmol) was dissolved in 30 mL of 1,4-dioxane in a separate flask. The prepared NaOBr solution was added via an addition funnel to the 3,6-diacetyl-9-(4'-^{i}Pr-phenyl)-carbazole solution. The reaction mixture was set to stir at 50 °C for 12 hrs. The reaction mixture was allowed to cool to RT and 60 mL of saturated Na_2SO_3 (aq) solution was added. The reaction mix was acidified to pH = 2, precipitated solids were collected via vacuum filtration. (Yield: 1 g, 91 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.97 (d, *J* = 1.7 Hz, 2H), 8.09 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.59 (s, 4H), 7.42 (d, *J* = 8.8 Hz, 2H), 3.07 (p, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 6H).

Synthesis of 9-biphenyl-carbazole.[13] 9H-carbazole (585 mg, 3.5 mmol), 4-Iodobiphenyl (1.1 g, 3.9 mmol), potassium carbonate (2.0 g, 14.4 mmol), copper iodide (76 mg, 0.4 mmol), N,N'-dimethylethylenediamine (120 µL, 1.1 mmol) and 20 mL of 1,4-dioxane were added to a 40 mL scintillation vial. The scintillation vial was placed on a 110 °C hot plate in a 20 mL aluminum block for 3 days. The reaction mix was allowed to cool and removed from the glovebox. The reaction mix was added to 100 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 935 mg, 85 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.28 (d, *J* = 7.8 Hz, 2H), 8.00 – 7.96 (m, 2H), 7.84 – 7.79 (m, 2H), 7.76 – 7.71 (m, 2H), 7.55 (t, *J* = 7.7 Hz, 2H), 7.50 – 7.43 (m, 5H), 7.32 (ddd, *J* = 8.0, 4.8, 3.3 Hz, 2H).

Synthesis of 3,6-diacetyl-9-biphenylcarbazole.[11,12] Solid 9-biphenyl-carbazole (958 mg, 3 mmol) was slowly added to a suspension of $AlCl_3$ (1.2 g, 9 mmol) and acetyl chloride (1.1 mL, 15 mmol) in 25 mL of DCM. This mixture was allowed to stir at RT for 4 hrs. The reaction mixture was then poured into 250 mL DI H_2O. The reaction flask was washed with acetone which was poured into the DI H_2O/DCM mixture, precipitated solids were collected via vacuum filtration. (Yield: 1.1 g, 92 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.18 (d, *J* = 1.7 Hz, 2H), 8.11 (dd, *J* = 8.7, 1.7 Hz, 2H), 8.02 – 7.96 (m, 2H), 7.85 – 7.78 (m, 2H), 7.77 – 7.72 (m, 2H), 7.68 – 7.51 (m, 2H), 7.55 – 7.35 (m, 5H), 2.73 (s, 6H).

Synthesis of 9-biphenyl-cdc.[11,12] NaOH (6 g, 150 mmol) was slowly added to 30 mL DI H_2O. The NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 3 mL of Br_2 were added via an addition funnel. The prepared NaOBr solution was allowed to stir at 0 °C for an additional 30 mins. 3,6-diacetyl-9-biphenyl-carbazole (1.2 g, 3 mmol) was dissolved in 30 mL of 1,4-dioxane in a separate flask. The prepared NaOBr solution was added via an addition funnel to the 3,6-diacetyl-9-biphenyl-carbazole solution. The reaction mixture was set to stir at 50 °C for 12 hrs. The reaction mixture was allowed to cool to RT and 60 mL of saturated Na_2SO_3 (aq) solution was added. The reaction mix was acidified to pH = 2, precipitated solids were collected via vacuum filtration. (Yield: 905 mg, 75 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.91 (d, *J* = 1.6 Hz, 2H), 8.09 (dd, *J* = 8.6, 1.6 Hz, 2H), 7.99 (d, *J* = 8.5 Hz, 2H), 7.85 – 7.73 (m, 5H), 7.55 (t, *J* = 7.6 Hz, 2H), 7.47 – 7.43 (m, 2H).

Synthesis of 3,6-diacetyl-9-(4'-bromophenyl)-carbazole.[11,12] 9-(4'-bromophenyl)-carbazole (10.0 g, 31 mmol) was dissolved in 50 mL of DCM. In a separate flask $AlCl_3$ (12.4 g, 93 mmol) and acetyl chloride (11 mL, 155 mmol) were suspended in 25 mL DCM. The 9-(4'-bromophenyl)-carbazole solution was added to the $AlCl_3$ suspension via an addition funnel. The reaction mixture was allowed to stir at RT for 4 h. The reaction mixture was then added to 250 mL of DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 10.7 g, 85 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.18 (d, *J* = 1.6 Hz, 2H), 8.11 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.96 – 7.88 (m, 2H), 7.71 – 7.64 (m, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 2.73 (s, 6H).

Synthesis of 9-(4'-bromophenyl)-cdc.[11,12] NaOH (58 g, 1.445 mol) was slowly added to 250 mL DI H_2O. The prepared NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 25 mL of Br_2 were added via an addition funnel. The prepared NaOBr solution was allowed to stir at 0 °C for an additional 30 mins. 3,6-diacetyl-9-(4'-bromophenyl)-carbazole (11.8 g, 29 mmol) was dissolved in 250 mL of 1,4-dioxane. The prepared NaOBr solution was added via an addition funnel to the 3,6-diacetyl-9-(4'-bromophenyl)-carbazole. The reaction mixture was set to stir at 100 °C for 12 hrs. the reaction mix was allowed to cool to RT and 400 mL of saturated Na_2SO_3 (aq) solution was added. The reaction mix was acidified to pH = 1, precipitated solids were collected via vacuum filtration. (Yield: 10.0 g, 84 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 8.98 (d, *J* = 1.6 Hz, 2H), 8.09 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.96 – 7.88 (m, 2H), 7.71 – 7.64 (m, 2H), 7.46 (d, *J* = 8.7 Hz, 2H).

Synthesis of Dimethyl 9-(4'-bromophenyl)-cdc.[14] 9-(4'-bromophenyl)-cdc (6.2 g, 15 mmol) and K_2CO_3 (10.4 g, 75 mmol) were suspended in 450 mL DMF and stirred at RT for 12 h. Iodomethane (2 mL, 32 mmol) was added and the reaction mixture stirred at RT for 24 h. The reaction mixture was added to 500 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 5.9 g, 89 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.06 (d, *J* = 1.6 Hz, 2H), 8.10 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.96 – 7.88 (m, 2H), 7.71 – 7.64 (m, 2H), 7.47 (d, *J* = 8.7 Hz, 2H), 3.92 (s, 6H).

Synthesis of Dimethyl 9-(4'-carbazolylphenyl)-cdc.[13] Dimethyl 9-(4'-bromophenyl)-cdc (1.5 g, 3.4 mmol), 9H-carbazole (652 mg, 3.9 mmol), potassium carbonate (2.0 g,

14.4 mmol), copper iodide (65 mg, 0.34 mmol), N,N'-dimethylethylenediamine (120 µL, 1.1 mmol) and 20 mL of 1,4-Dioxane were added to a 40 mL scintillation vial. The scintillation vial was placed on a 110 °C hot plate in a 20 mL aluminum block for 3 days. The reaction mix was allowed to cool and removed from the glovebox. The reaction mix was added to 100 mL DI H_2O, precipitated solids were collected via vacuum filtration. (Yield: 1.3 g, 72 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 9.10 (d, *J* = 1.7 Hz, 2H), 8.31 (d, *J* = 7.8 Hz, 2H), 8.16 (dd, *J* = 8.7, 1.7 Hz, 2H), 7.98 (s, 4H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.63 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 2H), 3.94 (s, 6H).

Synthesis of 9-(4'-carbazolylphenyl)-cdc. Dimethyl 9-(4'-carbazolyolphenyl)-cdc (1.8 g, 3.5 mmol) was dissolved in 100 mL 1,4-Dioxane. To this solution 100 mL of 2M NaOH $_{(aq)}$ solution was added. The resulting solution was heated to 100 °C for 12 h. The reaction mixture was allowed to cool and added to 500 mL DI H_2O. The reaction mixture was acidified to pH = 1, precipitated solids were collected via vacuum filtration. (Yield: 1.6 g, 94 %) ^{1}H NMR (400 MHz, DMSO-d_6) δ = 12.9 (s, 2H), 9.03 (d, *J* = 1.6 Hz, 2H), 8.30 (d, *J* = 7.8 Hz, 2H), 8.16 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.99 (s, 4H), 7.68 (d, *J* = 8.7 Hz, 2H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.52 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 2H), 7.40 – 7.31 (m, 2H).

Cage Synthesis

Synthesis of Cu_{12}(^{i}Pr-cdc)$_{12}$. 9-iPr-cdc (59.5 mg, 0.2 mmol) and $Cu(NO_3)_2$•2.5 H_2O (46.5 mg, 0.2 mmol) were dissolved in 2 mL of DMA. To this solution 1 mL of DMF was added and the solution was heated at 80 °C for 1 h. Concurrently, quinuclidine hydrochloride (22.1 mg, 0.15 mmol) was dissolved in 1.5 mL of DMF and heated at 80 °C for 1 h. The two hot solutions were mixed and continued heating at 80 °C for 12 h. The reaction was removed from heat, allowed to cool to RT, the mother liquor decanted and the crystals collected. The crystals were rinsed with 100 °C DMA and then washed with DMA for 12 h, the DMA was then decanted and replaced for fresh DMA 3 times. The crystals were then washed 3 times with MeOH. Optimal material was obtained after activation at 50 °C under dynamic vacuum.

Synthesis of Cu_{12}(phenyl-cdc)$_{12}$. 9-phenyl-cdc (66.3 mg, 0.2 mmol) and $Cu(NO_3)_2$•2.5 H_2O (46.5 mg, 0.2 mmol) were sonicated and dissolved in 15 mL of DMA. The solution was heated at 100 °C for 12 h. The reaction was removed from heat, allowed to cool to RT, the mother liquor decanted and the crystals collected. The crystals were washed with DMA for 12 h, the DMA was then decanted and replaced for fresh DMA 3 times. The crystals were then washed 3 times with MeOH. Optimal material was obtained after activation at 50 °C under dynamic vacuum.

Synthesis of Cu_{12}(Br-phenyl-cdc)$_{12}$. 9-(4'-bromophenyl)-cdc (102.6 mg, 0.25 mmol) was dissolved in 7.5 mL of DMA. $Cu(NO_3)_2$•2.5 H_2O (58.1 mg, 0.25 mmol) was dissolved in 7.5 mL of DMA. The solutions were mixed at room temperature and 250 µL of pyridine was added. The resulting solution was heated at 100 °C for 2 d. The reaction was removed from heat and allowed to cool to RT. The cooled

solution was then divided into 5 mL portions and MeOH was diffused into the solutions to obtain crystals. The mother liquor was then decanted and the crystals collected. The crystals were washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 100 °C under dynamic vacuum.

Synthesis of Cu_{12}(carbazolyl-phenyl-cdc)$_{12}$. 9-(4'-carbazolylphenyl)-cdc (19.9 mg, 0.04 mmol) and $Cu(NO_3)_2$•2.5 H_2O (9.3 mg, 0.04 mmol) were sonicated and dissolved in 3 mL of DMA. To this solution 100 µL DMSO was added. The resulting solution was heated at 100 °C for 12 h. The reaction was removed from heat and allowed to slowly cool to RT, the mother liquor decanted and the crystals collected. The crystals were washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 75 °C under dynamic vacuum.

Synthesis of Cr_{12}(phenyl-cdc)$_{12}$. 9-phenyl-cdc (16.6 mg, 0.05 mmol) was suspended in 1.5 mL of DMF. $Cr_2(OAc)_4$ (17.0 mg, 0.05 mmol) was suspended in 1.5 mL of DMF. The suspensions were heated at 100 °C for 12 h to dissolve solids. The resulting solutions were removed from heat, allowed to cool to RT and then mixed. The reaction mixture was then allowed to stand at RT for 12 h. The mother liquor was decanted and the powder was collected. The powder was washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 75 °C under dynamic vacuum.

Synthesis of Cr_{12}(Br-phenyl-cdc)$_{12}$. 9-(4'-bromophenyl)-cdc (20.5 mg, 0.05 mmol) was suspended in 1.5 mL of DMPU. $Cr_2(OAc)_4$ (17.0 mg, 0.05 mmol) was suspended in 1.5 mL of DMPU. The suspensions were heated at 90 °C for 12 h to dissolve solids. The resulting solutions were removed from heat, allowed to cool to RT, mixed and 100 uL of pyridine was added. The reaction mixture was then returned to heat for an additional 12 h. The reaction was removed from heat and allowed to cool to RT. This solution was split between two vials and EtOH was vapor diffused into the solutions to obtain crystals. The mother liquor was then decanted and the crystals collected. The crystals were then washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 50 °C under dynamic vacuum.

Synthesis of Mo_{12}(phenyl-cdc)$_{12}$. 9-phenyl-cdc (82.8 mg, 0.25 mmol) was suspended in 7.5 mL of DMPU. $Mo_2(OAc)_4$ (53.5 mg, 0.125 mmol) was suspended in 7.5 mL of DMPU. The suspensions were heated at 100 °C for 12 h to dissolve solids. The resulting solutions were removed from heat, allowed to cool to RT and then mixed. The resulting solution was then returned to heat for an additional 12 h. The reaction was removed from heat, allowed to cool to RT, the mother liquor decanted and the crystals collected. The crystals were washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 75 °C under dynamic vacuum.

Synthesis of Mo_{12}(Br-phenyl-cdc)$_{12}$. 9-(4'-bromophenyl)-cdc (51.3 mg, 0.125 mmol) was suspended in 5 mL DMPU. $Mo_2(OAc)_4$ (26.8 mg, 0.0625 mmol) was suspended in 5 mL DMPU. The suspensions were heated at 100 °C for 12 h to dissolve solids. The resulting solutions were removed from heat, allowed to cool to RT, mixed and 100 µL pyridine was added. The reaction mixture was then returned to heat for an additional 12 h. The reaction was removed from heat and allowed to cool to RT. This solution was split between two vials and 15 mL of MeOH was added to each vial. The mother liquor was decanted and the resulting powder collected. The powder was washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 75 °C under dynamic vacuum.

Synthesis of Mo_{12}(^{i}Prphenyl-cdc)$_{12}$. 9-(4'-^{i}Prphenyl)-cdc (93.4 mg, 0.25 mmol) was suspended in 7.5 mL DMF. $Mo_2(OAc)_4$ (53.5 mg, 0.125 mmol) was suspended in 7.5 mL of DMF. The suspensions were heated at 100 °C for 12 h to dissolve solids. The resulting solutions were removed from heat, allowed to cool to RT and then mixed. The reaction mixture was then returned to heat for an additional 12 h. The reaction was removed from heat, allowed to cool to RT, the mother liquor decanted and the crystals collected. The crystals were washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 75 °C under dynamic vacuum.

Synthesis of Mo_{12}(biphenyl-cdc)$_{12}$. 9-biphenyl-cdc (73.3 mg, 0.18 mmol) was suspended in 5 mL of DMPU. $Mo_2(OAc)_4$ (38.5 mg, 0.09 mmol) was suspended in 4.75 mL of DMPU. The suspensions were heated at 100 °C for 12 h to dissolve solids. The resulting solutions were removed from heat, allowed to cool to RT and then mixed. The reaction mixture was returned to heat for an additional 12 h. The reaction was removed from heat, allowed to cool to RT, the mother liquor decanted and the crystals collected. The crystals were washed with MeOH for 12 h, the MeOH was then decanted and replaced for fresh MeOH 5 times. Optimal material was obtained after activation at 75 °C under dynamic vacuum.

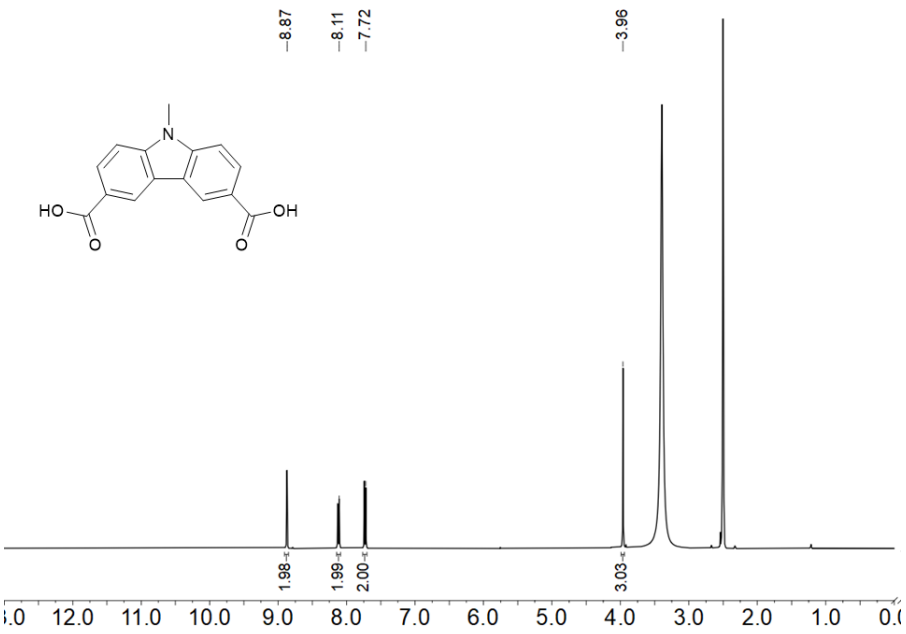


Figure S1. NMR spectra of 9-methyl-cdc.

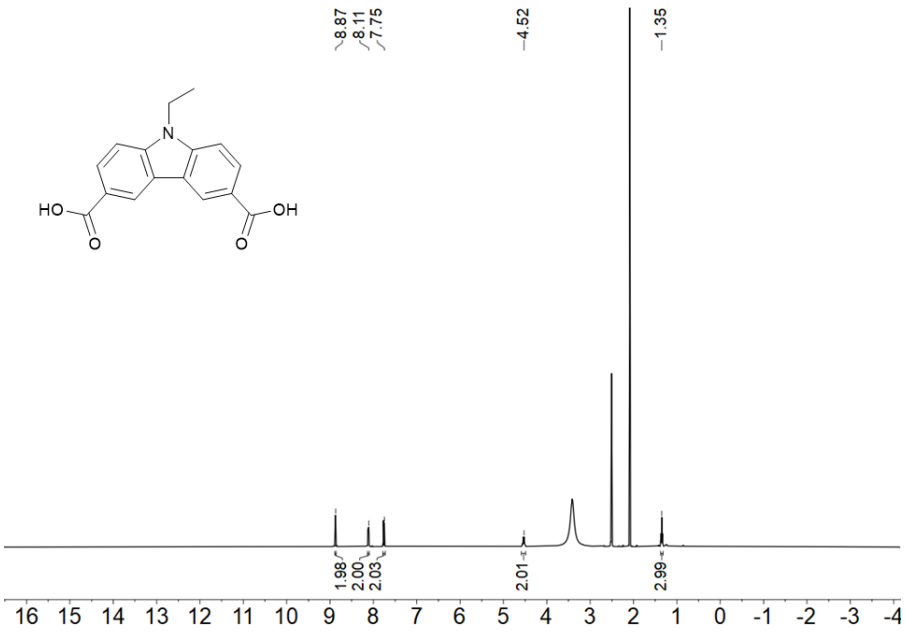


Figure S2. NMR spectra of 9-ethyl-cdc.

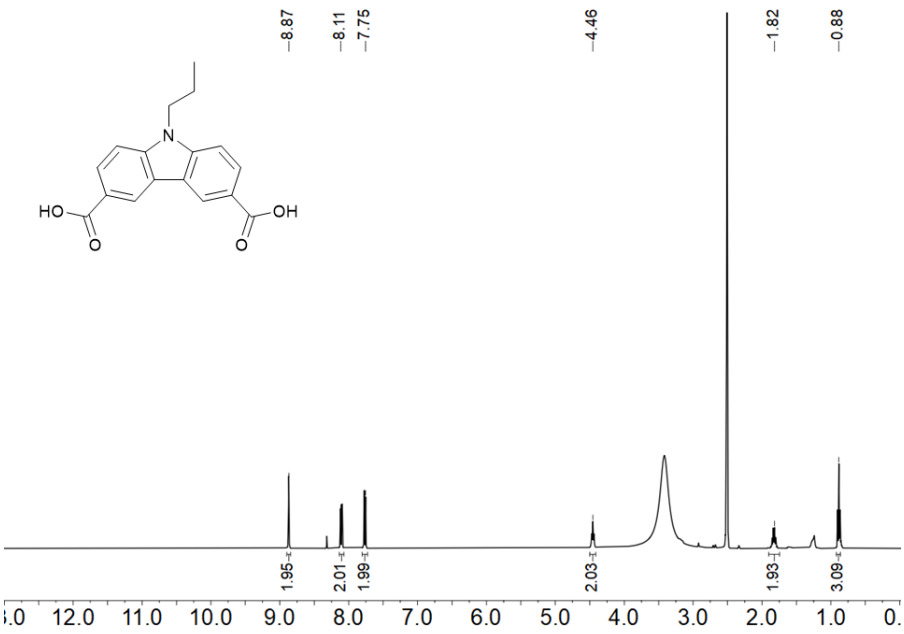


Figure S3. NMR spectra of 9-propyl-cdc.

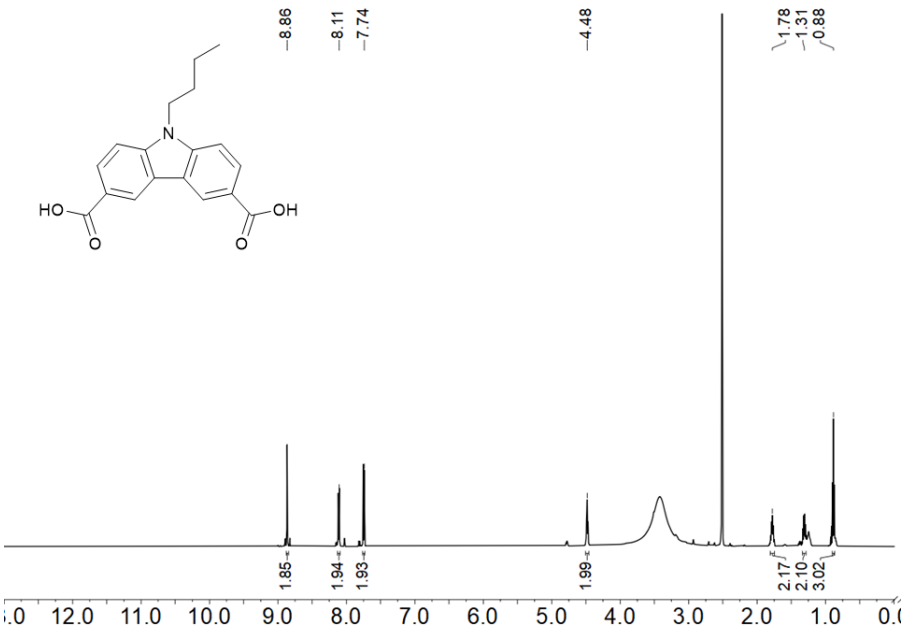


Figure S4. NMR spectra of 9-butyl-cdc.

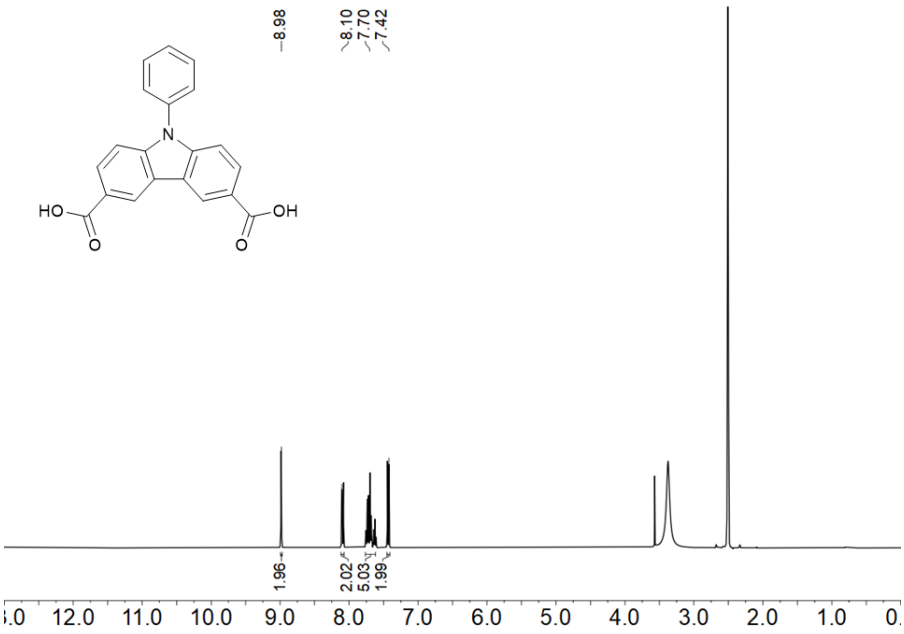


Figure S5. NMR spectra of 9-phenyl-cdc.

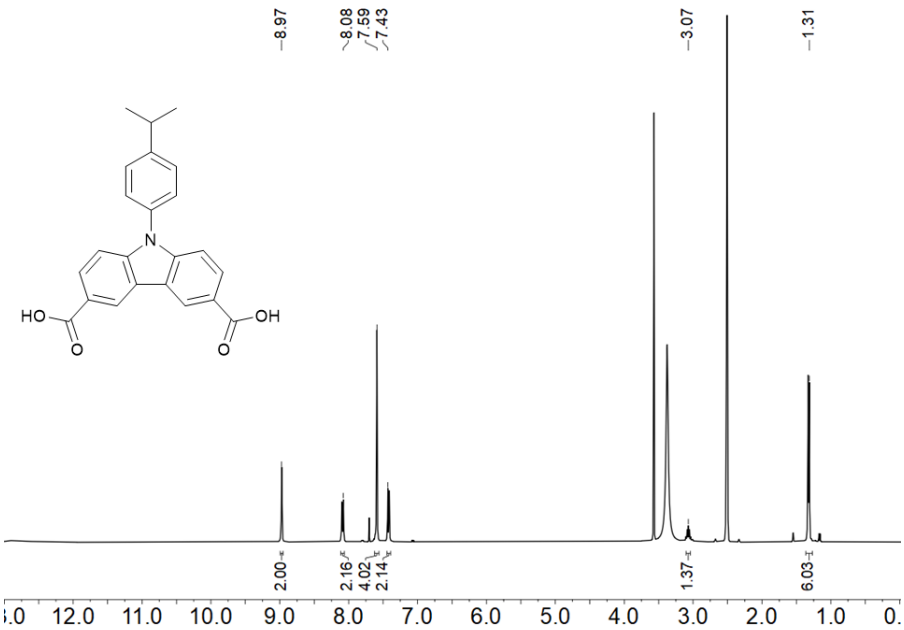


Figure S6. NMR spectra of 9-(4'-^{i}Prphenyl)-cdc.

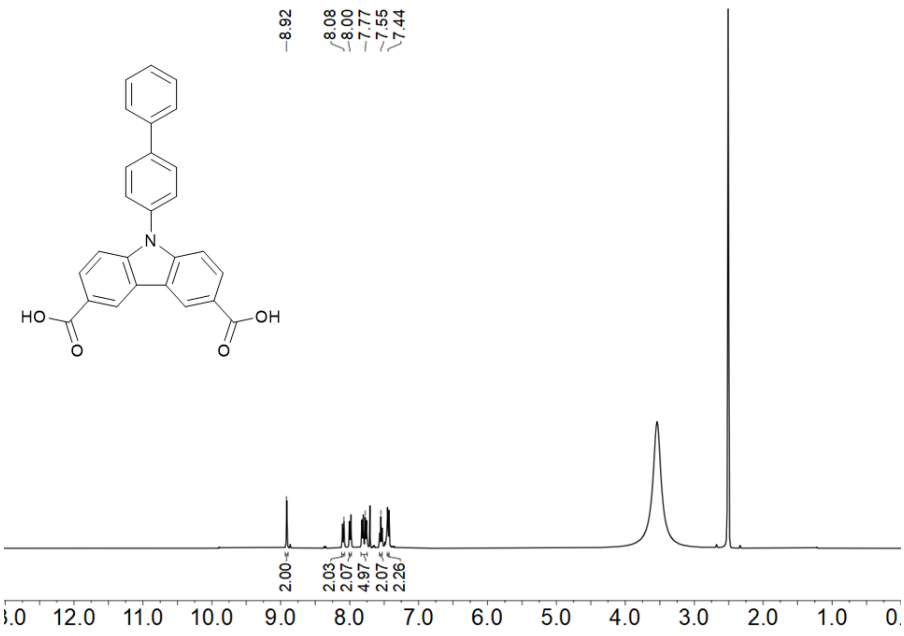


Figure S7. NMR spectra of 9-biphenyl-cdc.

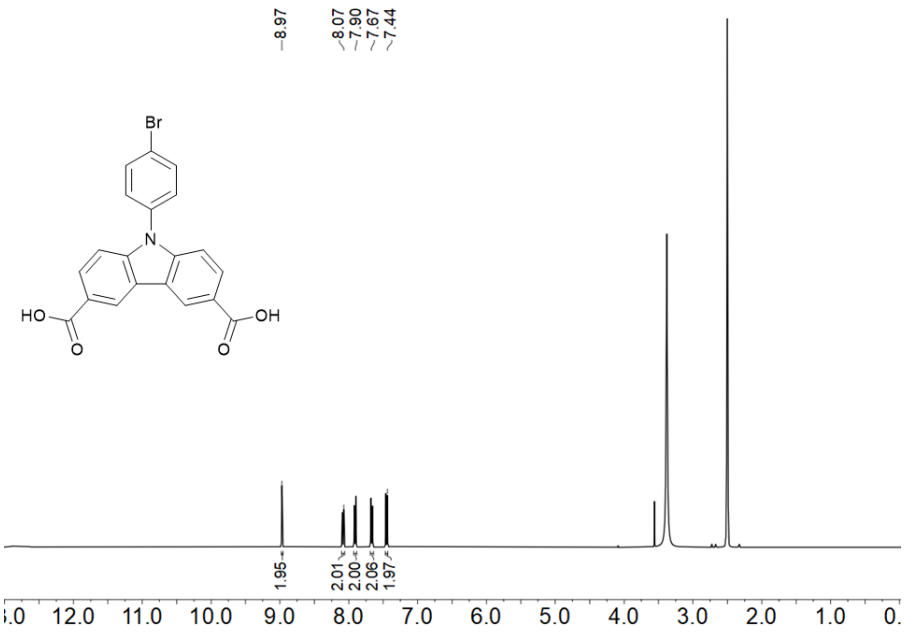


Figure S8. NMR spectra of 9-(4’-bromophenyl)-cdc.

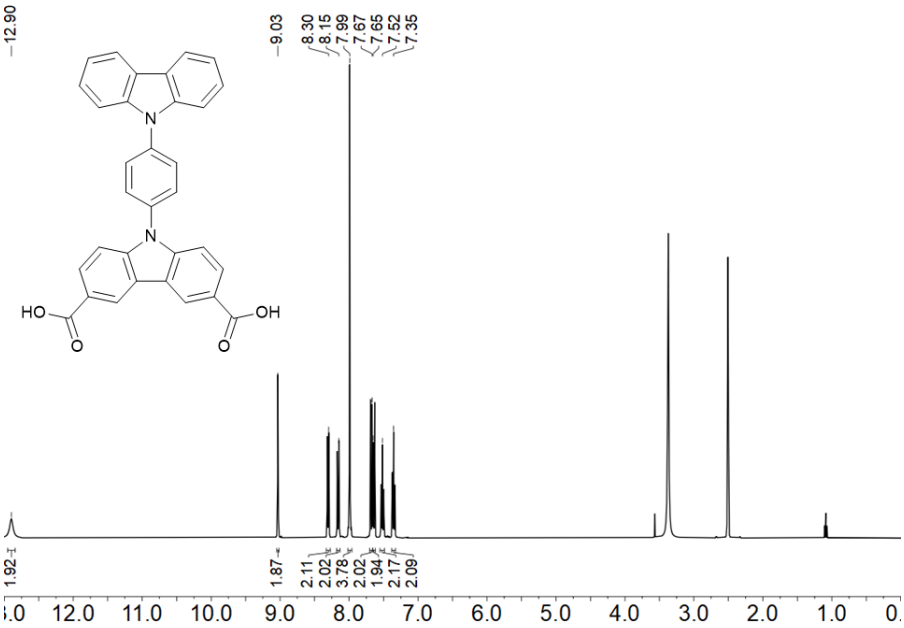


Figure S9. NMR spectra of 9-(4'-carbazolylphenyl)-cdc.

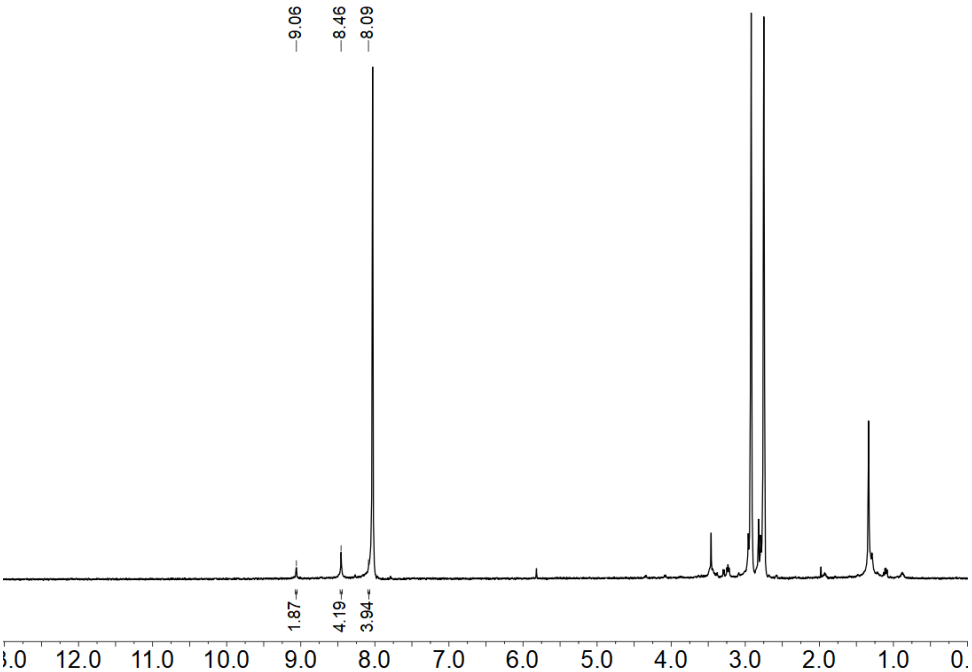


Figure S10. NMR spectra of Mo_{12}(Br-phenyl-cdc)$_{12}$. NMR was prepared by dissolving ~10 mg of cage in 750 µL DMF-d_7.

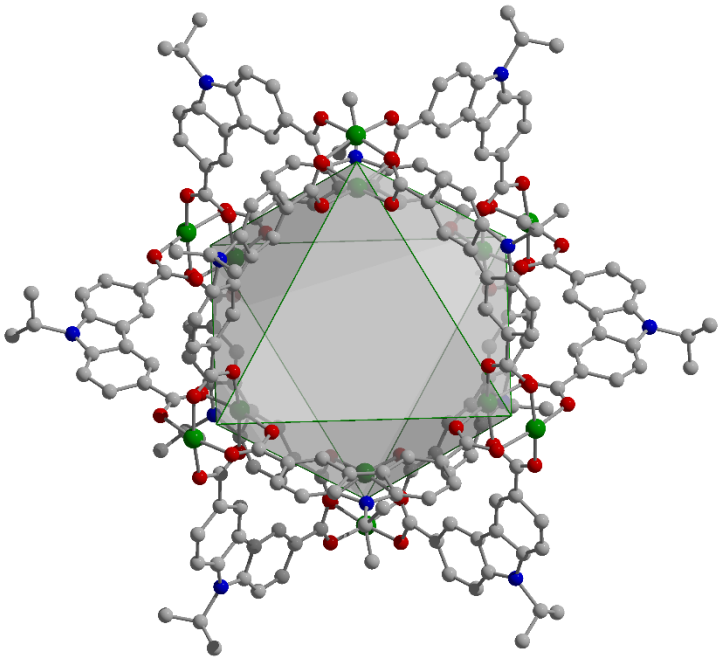


Figure S11. Crystal structure of $Cu_{12}(^{i}Pr\text{-}cdc)_{12}$. H-atoms omitted for clarity.

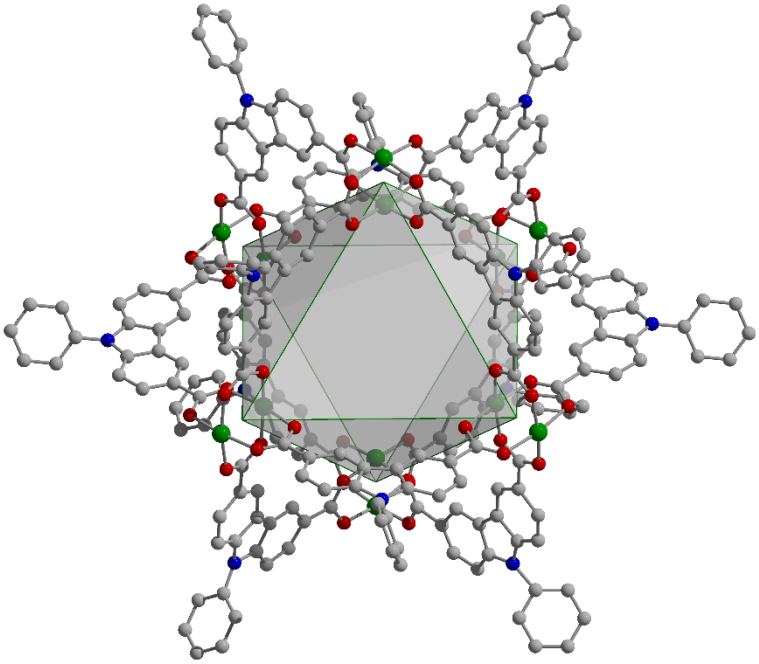


Figure S12. Crystal structure of the $Cu_{12}(phenyl\text{-}cdc)_{12}$. H-atoms omitted for clarity.

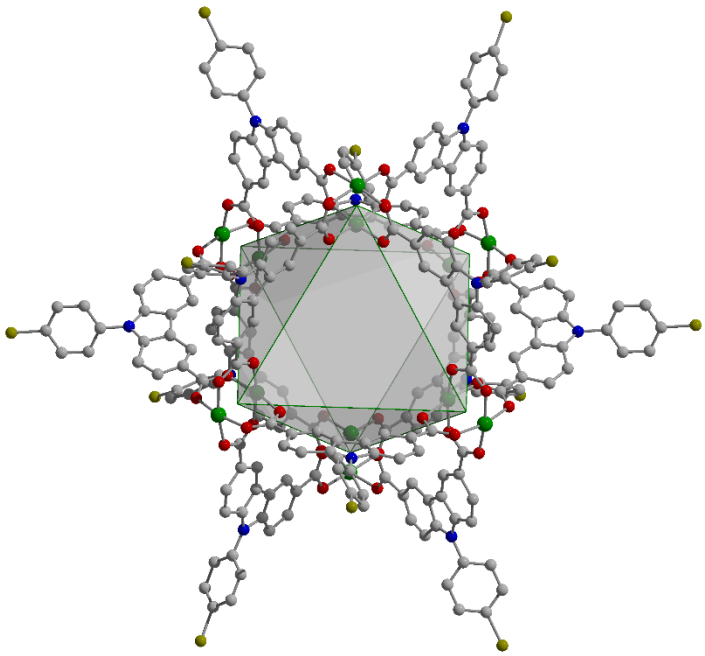


Figure S13. Crystal structure of Cu_{12}(Br-phenyl-cdc)$_{12}$. H-atoms omitted for clarity.

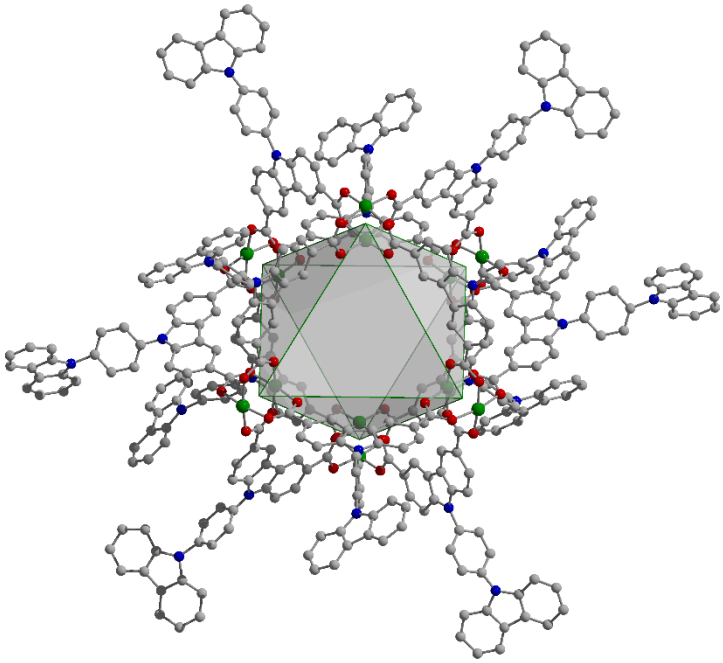


Figure S14. Crystal structure of Cu_{12}(carbazolyl-phenyl)-cdc)$_{12}$. H-atoms omitted for clarity.

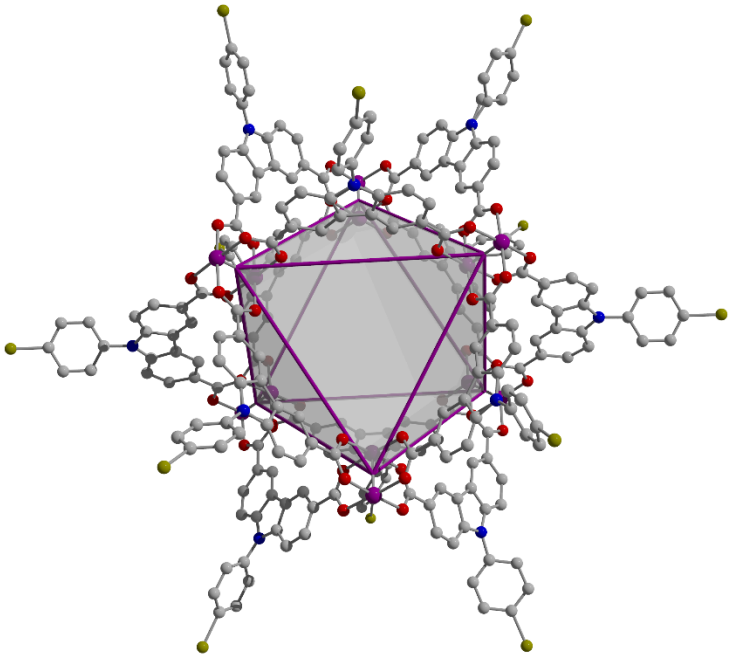


Figure S15. Crystal structure of Cr_{12}(Br-phenyl-cdc)$_{12}$. H-atoms omitted for clarity.

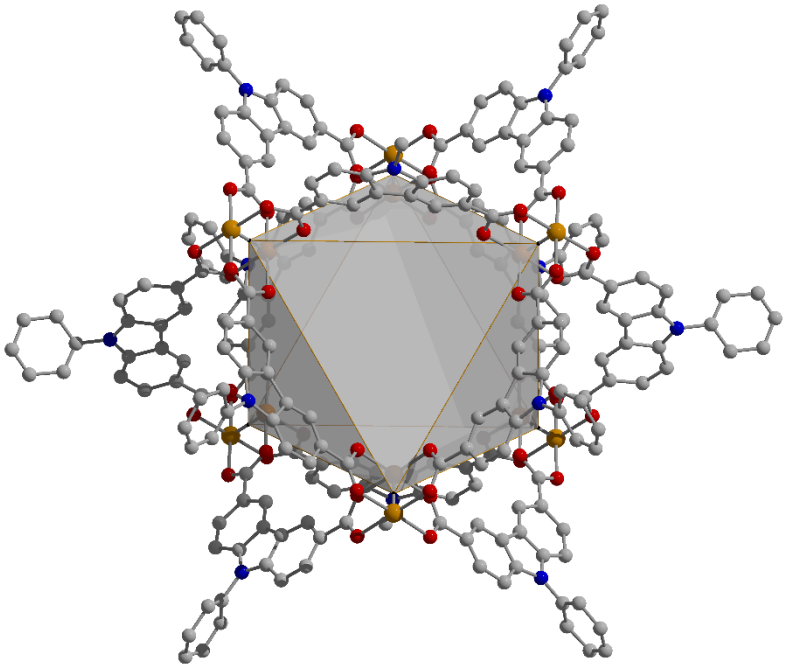


Figure S16. Crystal structure of Mo_{12}(phenyl-cdc)$_{12}$. H-atoms omitted for clarity.

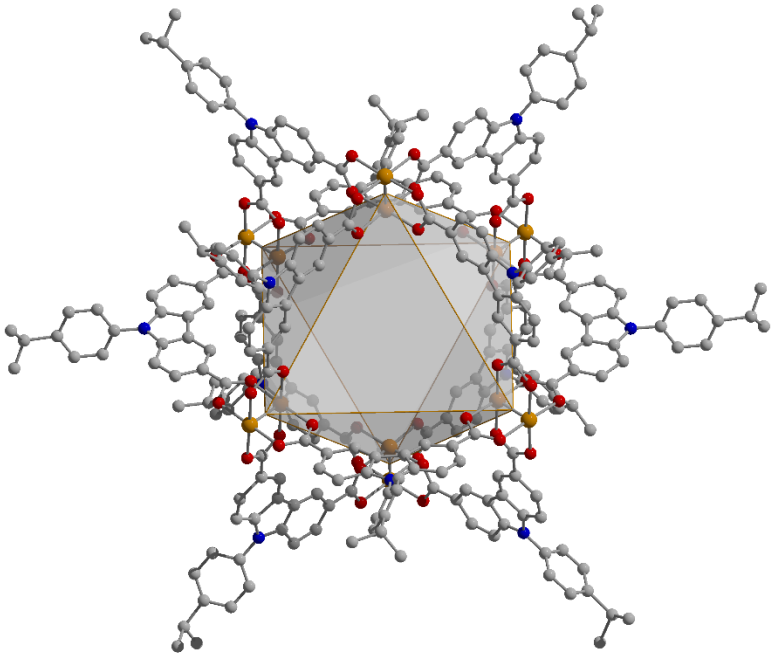


Figure S17. Crystal structure of $Mo_{12}(^{i}Prphenyl\text{-}cdc)_{12}$. H-atoms omitted for clarity.

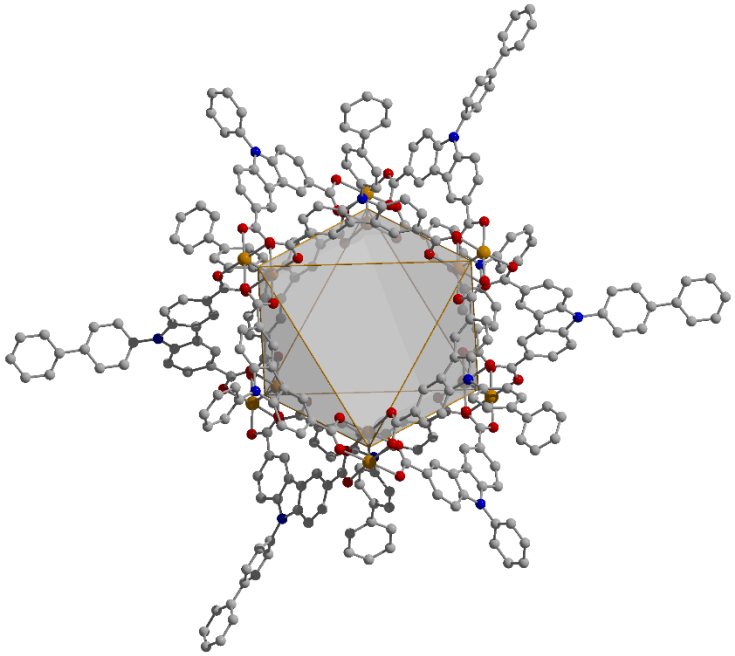


Figure S18. Crystal structure of $Mo_{12}(biphenyl\text{-}cdc)_{12}$. H-atoms omitted for clarity.

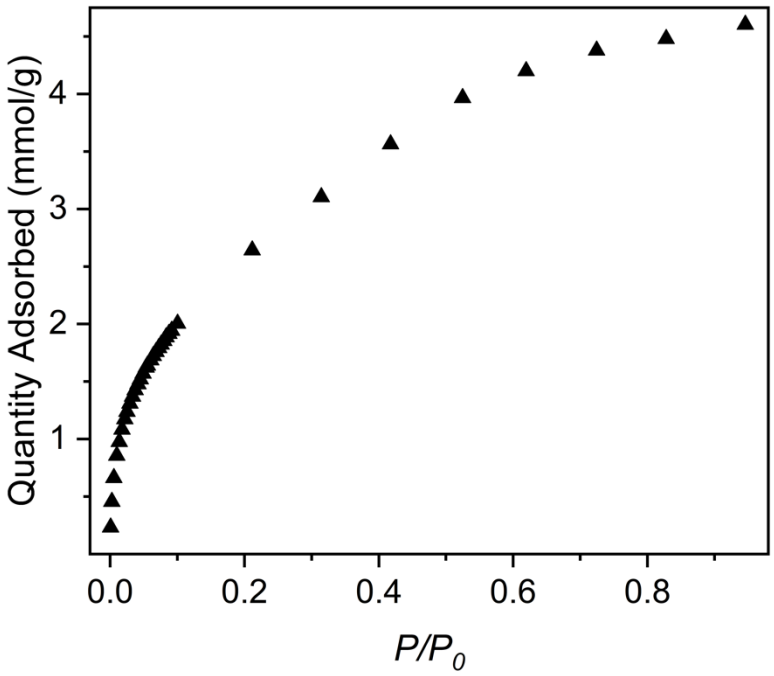


Figure S19. CO_2 adsorption in $Cu_{12}(^{i}Pr\text{-}cdc)_{12}$ at 195 K.

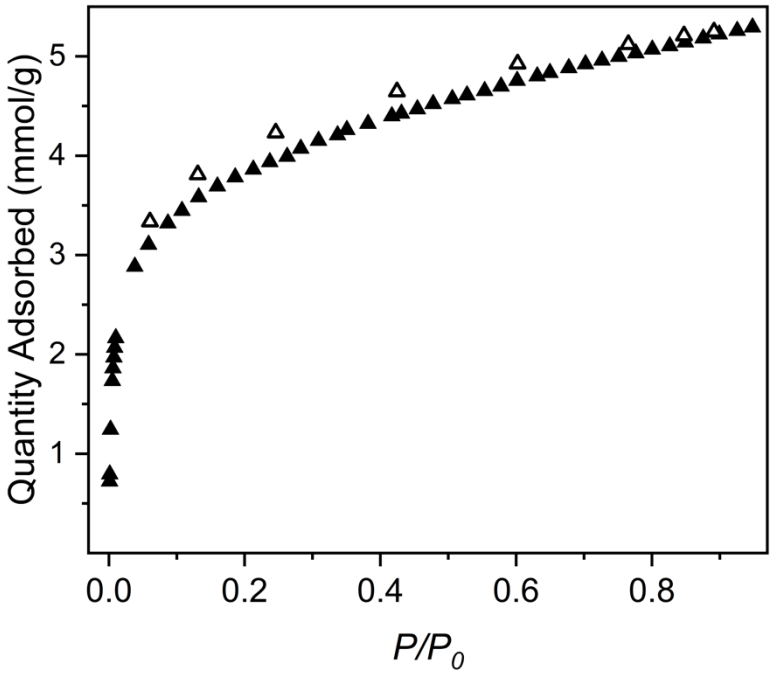


Figure S20. CO_2 adsorption in $Cu_{12}(phenyl\text{-}cdc)_{12}$ at 195 K. Filled and open symbols represent adsorption and desorption, respectively.

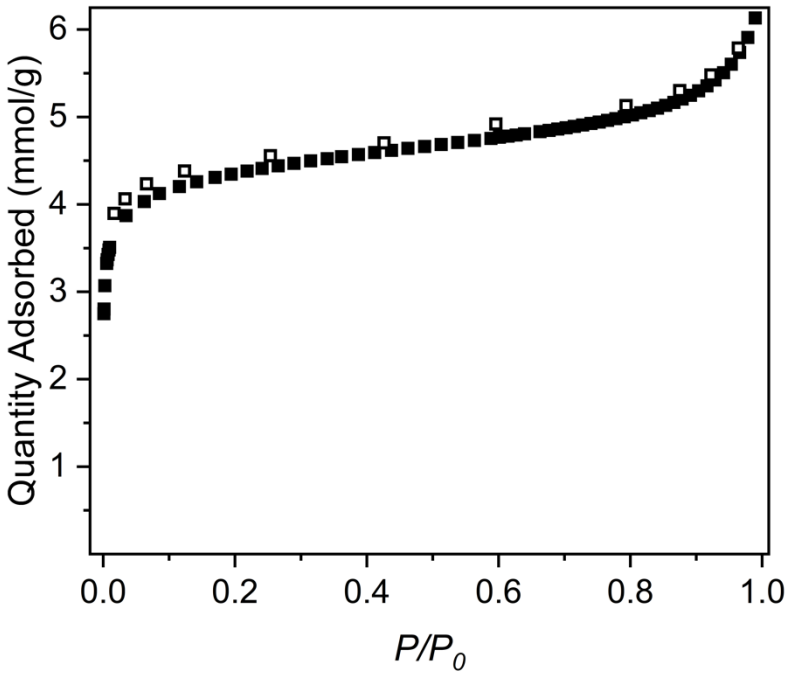


Figure S21. N_2 adsorption in Cu_{12}(Br-phenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

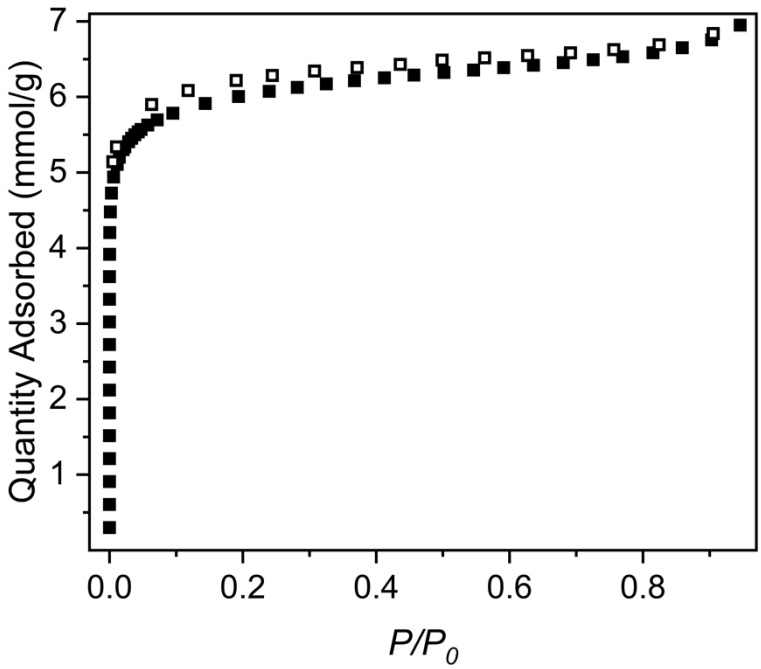


Figure S22. N_2 adsorption in Cu_{12}(carbazolyl-phenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

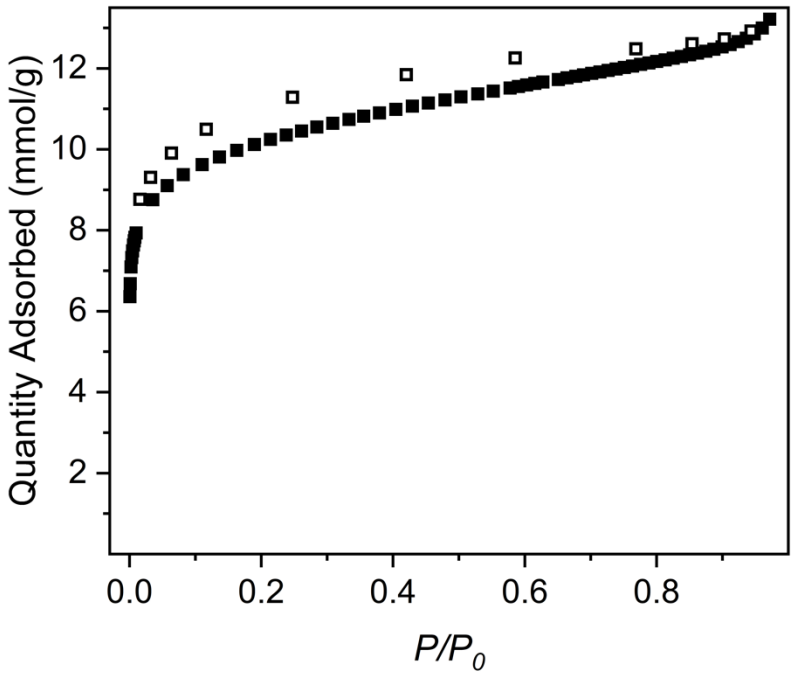


Figure S23. N_2 adsorption in Cr_{12}(phenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

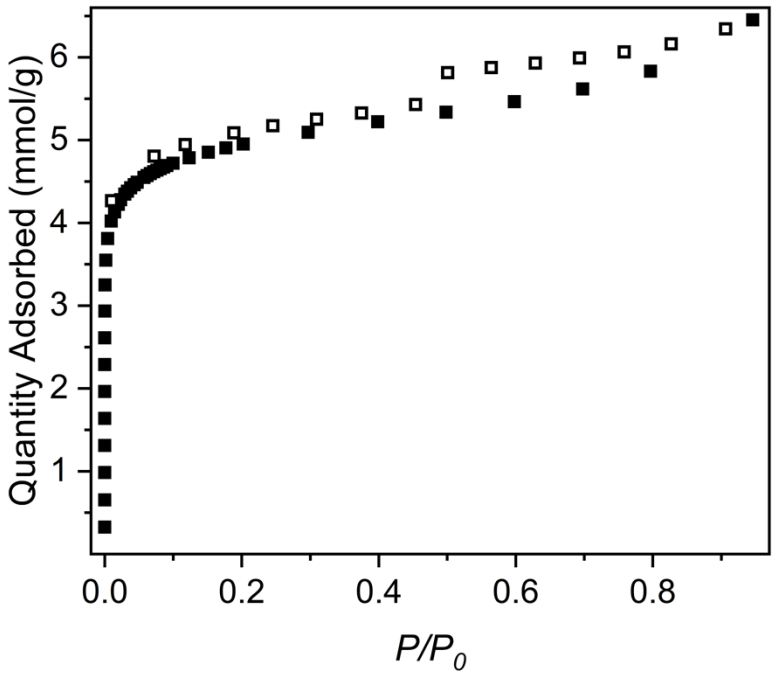


Figure S24. N_2 adsorption in Cr_{12}(Br-phenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

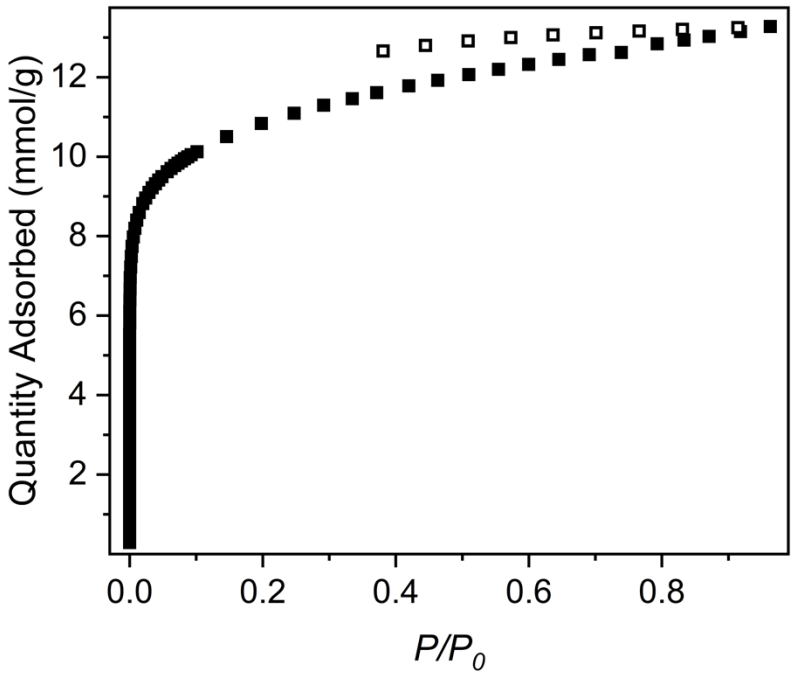


Figure S25. N_2 adsorption in Mo_{12}(phenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

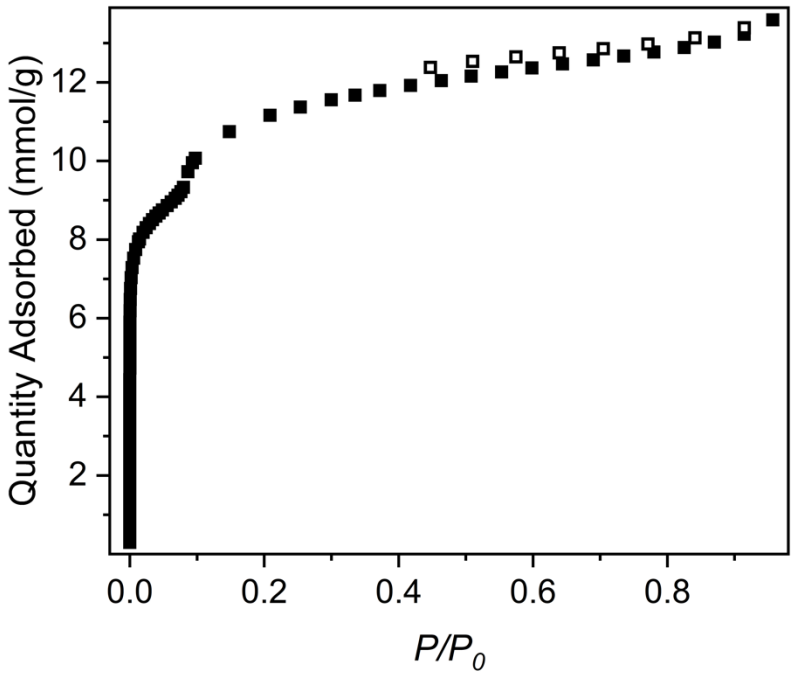


Figure S26. N2 adsorption in Mo_{12}(^{i}Prphenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

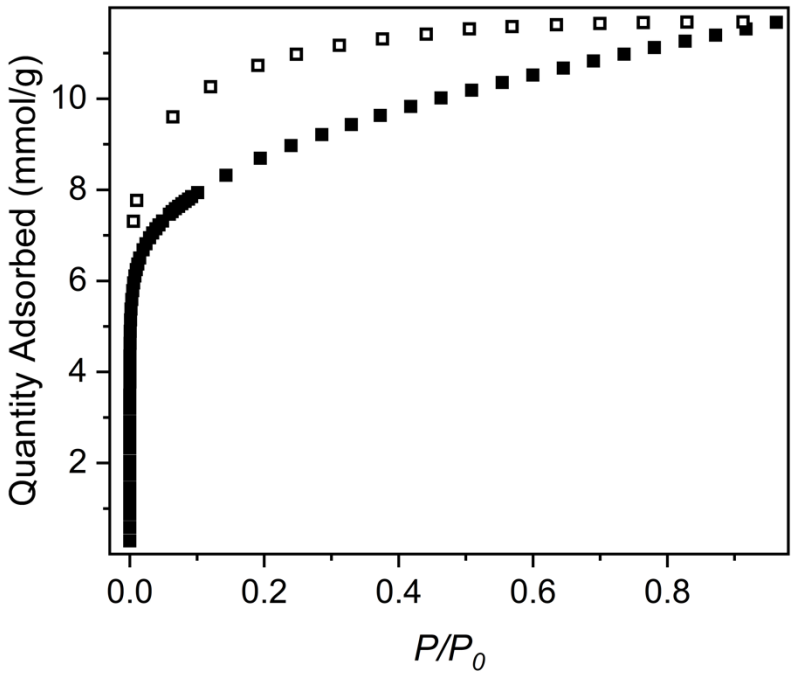


Figure S27. N_2 adsorption in Mo_{12}(biphenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

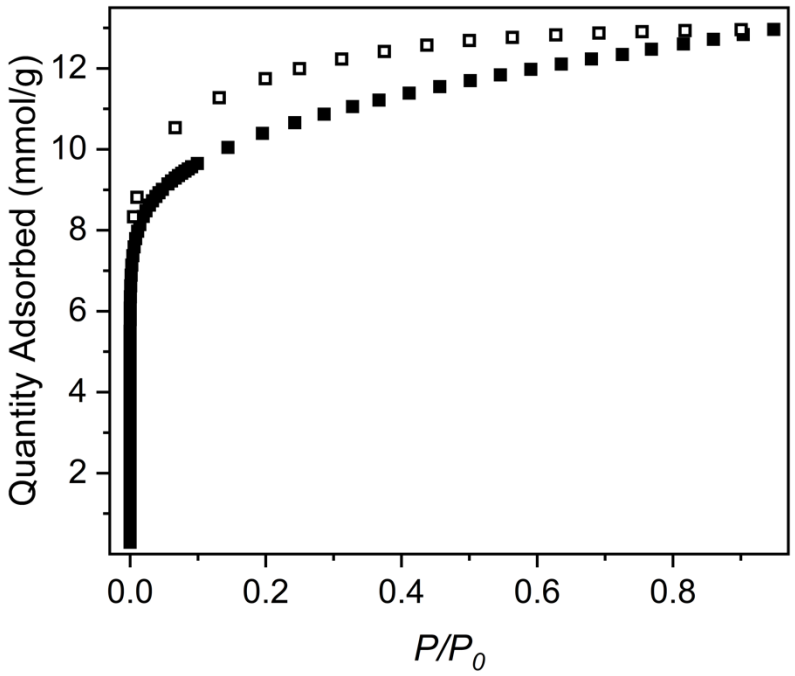


Figure S28. N_2 adsorption in Mo_{12}(Br-phenyl-cdc)$_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

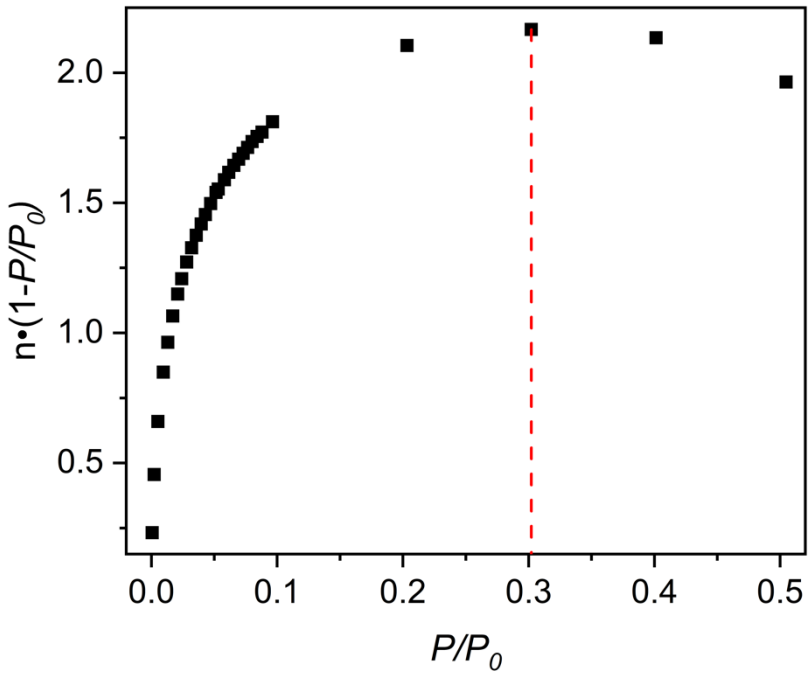


Figure S29. Plot of n•(1-*P/P*$_0$) vs *P/P*$_0$ of Cu$_{12}$(*i*Pr-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum *P/P*$_0$, which is indicated by the dashed line.

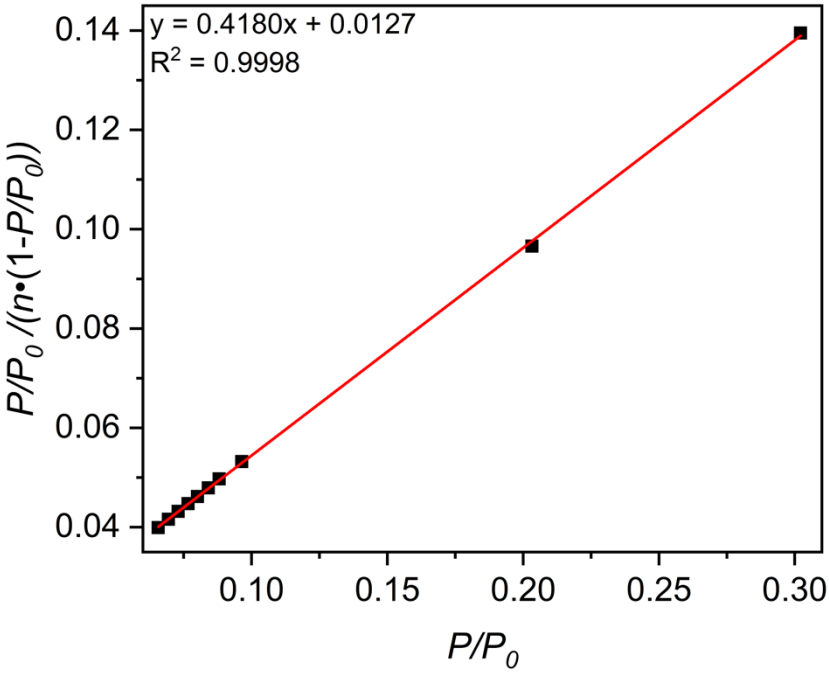


Figure S30. Plot of *P/P*$_0$ /(n•(1-*P/P*$_0$)) vs *P/P*$_0$ of Cu$_{12}$(*i*Pr-cdc)$_{12}$ to determine the BET surface area. The slope of the line for *P/P*$_0$ < 0.302 is 0.4180 with a y-intercept of 0.0127. These values satisfy the second BET consistency criterion and yield a BET surface area of 205 m^2/g.

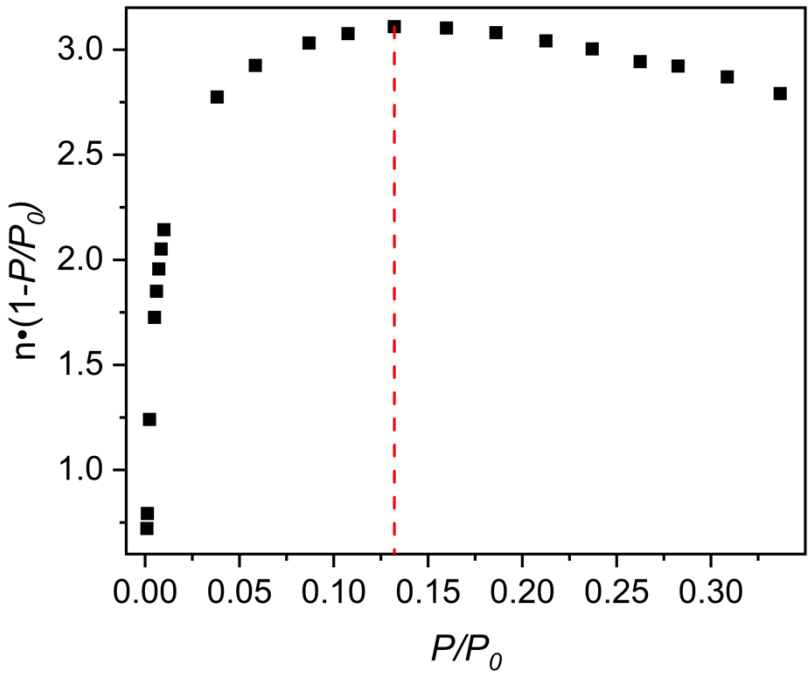


Figure S31. Plot of n•(1-*P/P*$_0$) vs *P/P*$_0$ of Cu_{12}(phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum *P/P*$_0$, which is indicated by the dashed line.

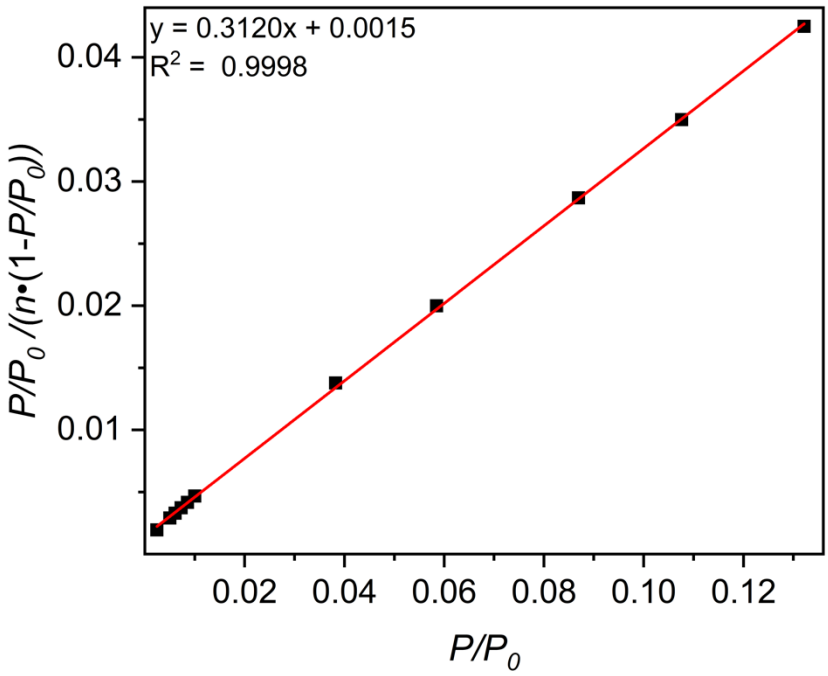


Figure S32. Plot of *P/P*$_0$ /(n•(1-*P/P*$_0$)) vs *P/P*$_0$ of Cu_{12}(phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for *P/P*$_0$ < 0.132 is 0.3120 with a y-intercept of 0.0015. These values satisfy the second BET consistency criterion and yield a BET surface area of 313 m^2/g.

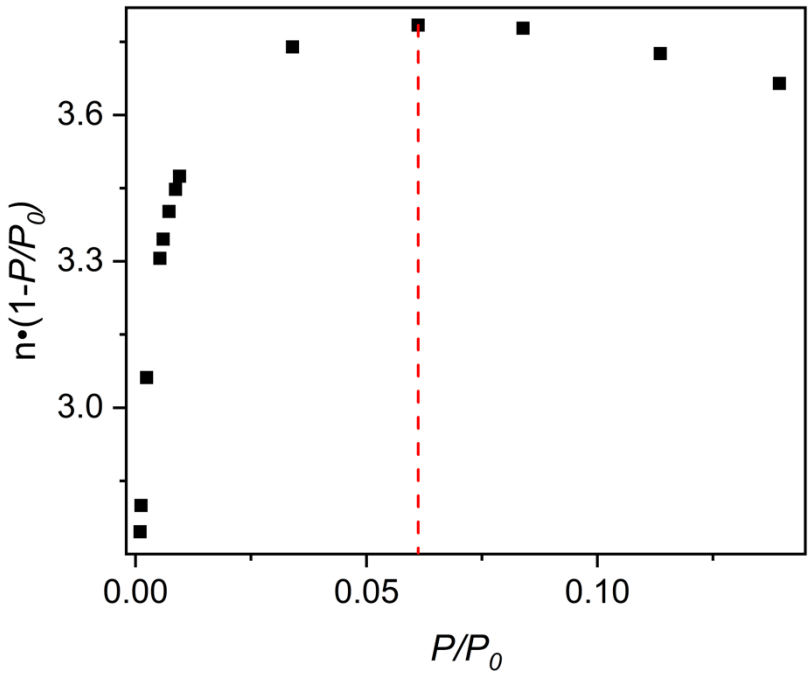


Figure S33. Plot of n•(1-P/P_0) vs P/P_0 of Cu_{12}(Br-phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

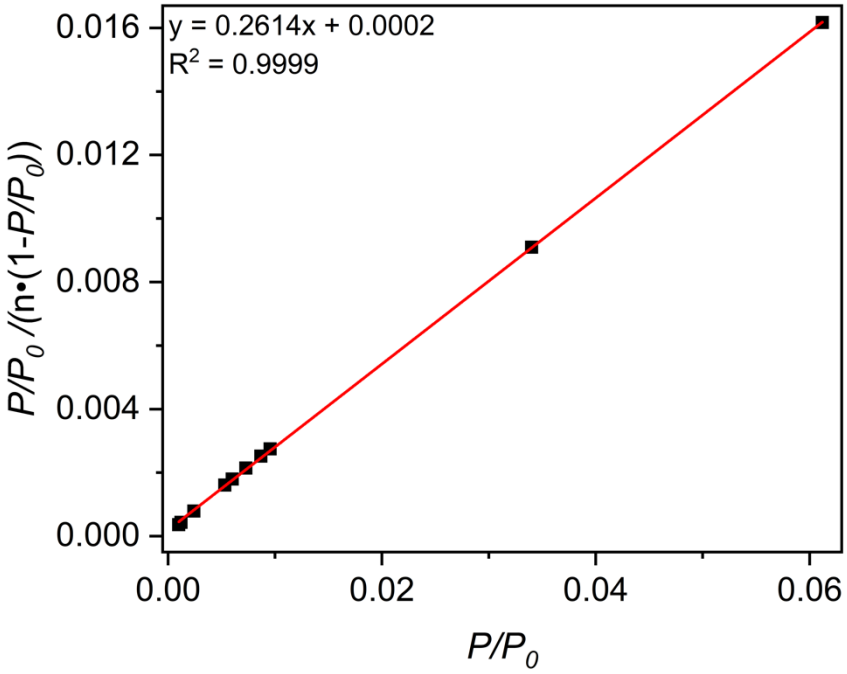


Figure S34. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of Cu_{12}(Br-phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for $P/P_0 < 0.061$ is 0.2614 with a y-intercept of 0.0002. These values satisfy the second BET consistency criterion and yield a BET surface area of 373 m^2/g.

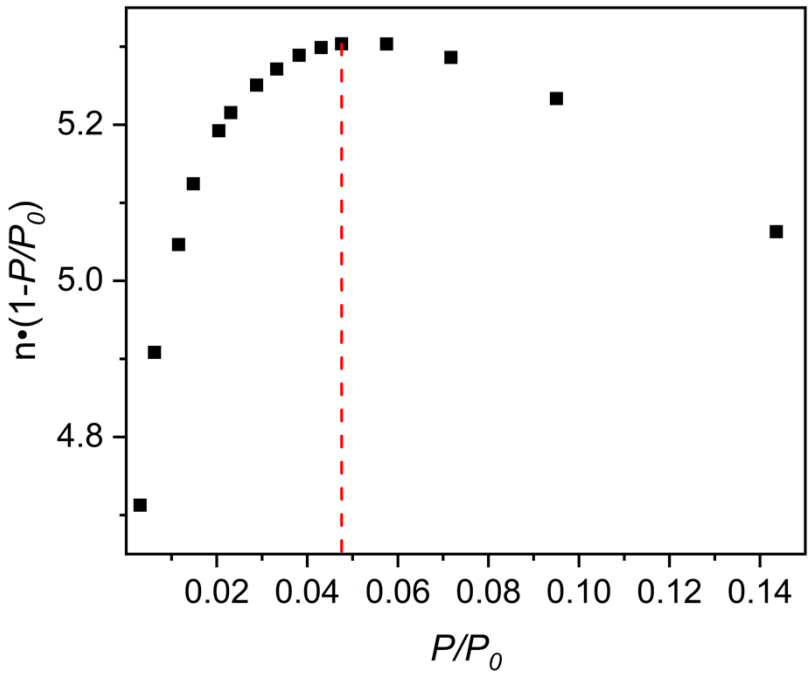


Figure S35. Plot of n•(1-P/P_0) vs P/P_0 of Cu_{12}(carbazolyl-phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

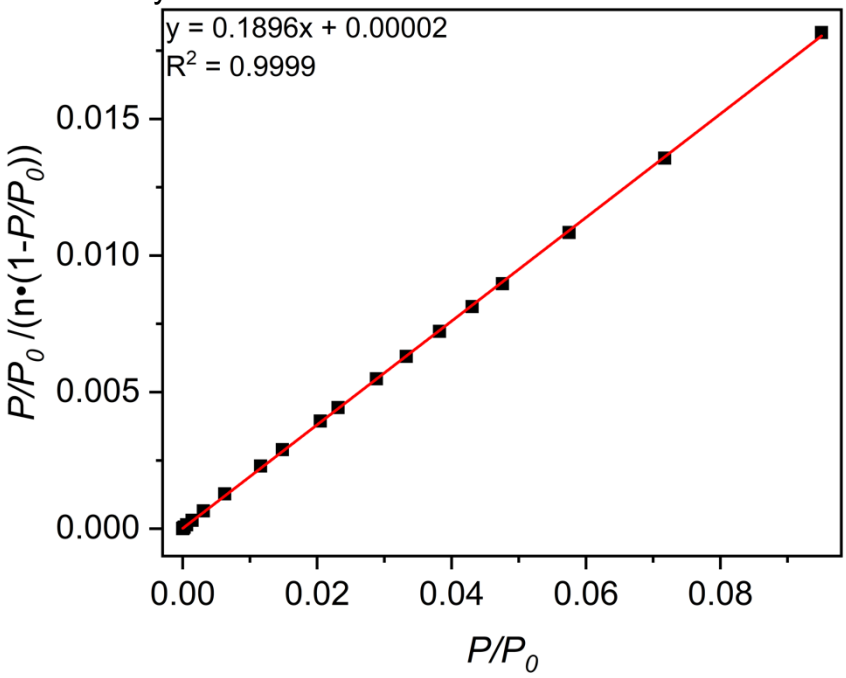


Figure S36. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of Cu_{12}(carbazolyl-phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for $P/P_0 < 0.476$ is 0.1896 with a y-intercept of 0.00002. These values satisfy the second BET consistency criterion and yield a BET surface area of 515 m^2/g.

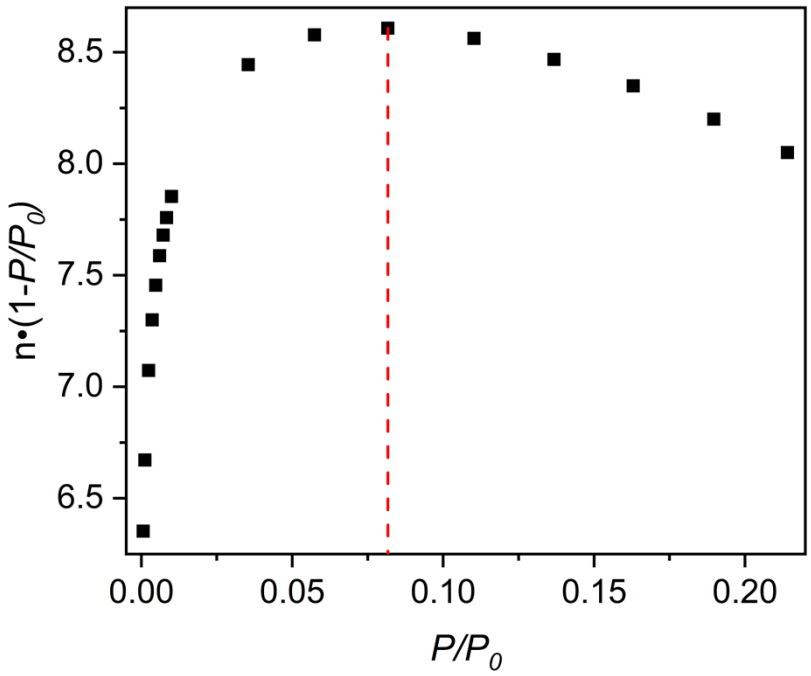


Figure S37. Plot of n•(1-P/P_0) vs P/P_0 of Cr_{12}(phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

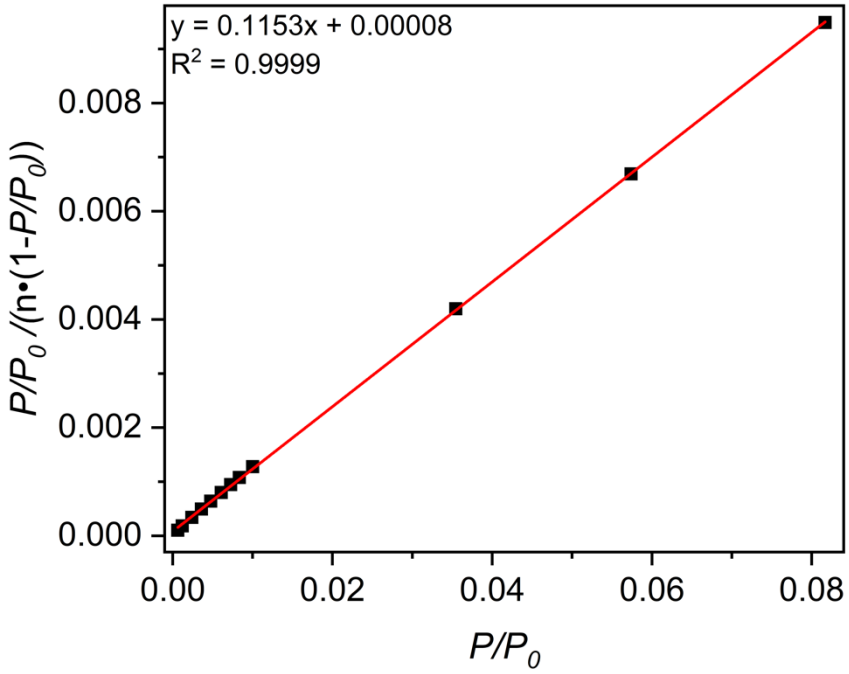


Figure S38. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of Cr_{12}(phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for $P/P_0 < 0.082$ is 0.1153 with a y-intercept of 0.00008. These values satisfy the second BET consistency criterion and yield a BET surface area of 846 m^2/g.

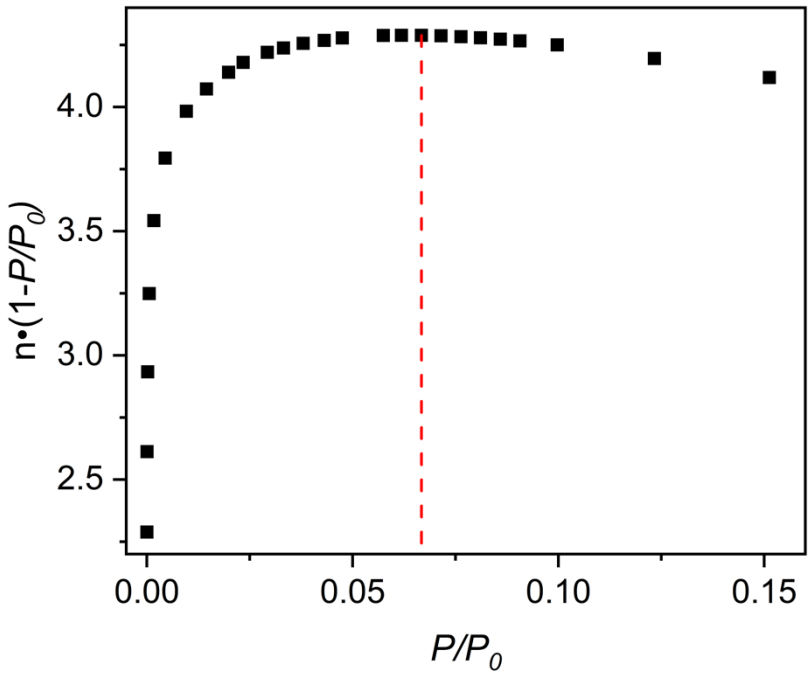


Figure S39. Plot of n•(1-P/P_0) vs P/P_0 of Cr_{12}(Br-phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

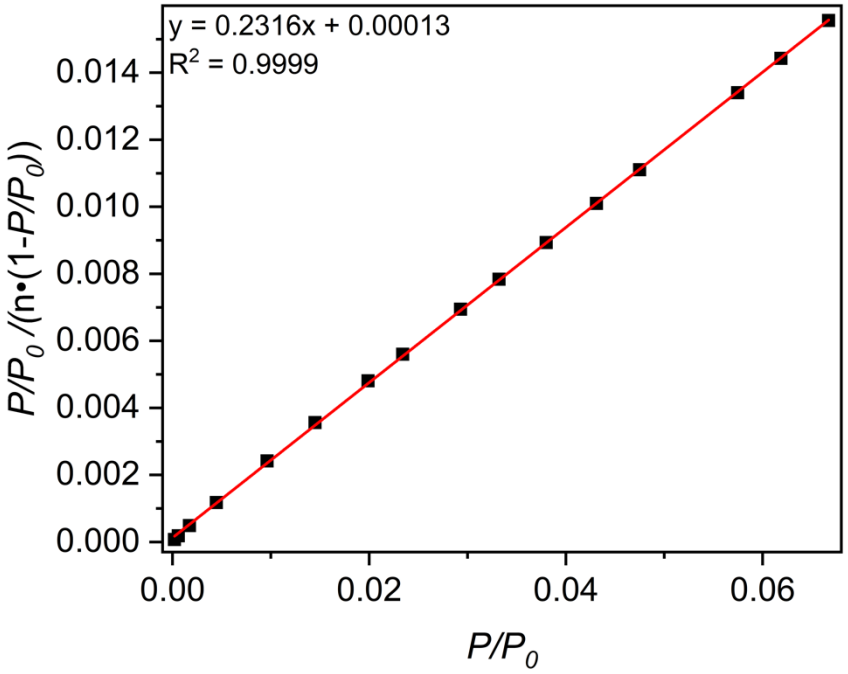


Figure S40. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of Cr_{12}(Br-phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for $P/P_0 < 0.067$ is 0.2316 with a y-intercept of 0.00013. These values satisfy the second BET consistency criterion and yield a BET surface area of 421 m^2/g.

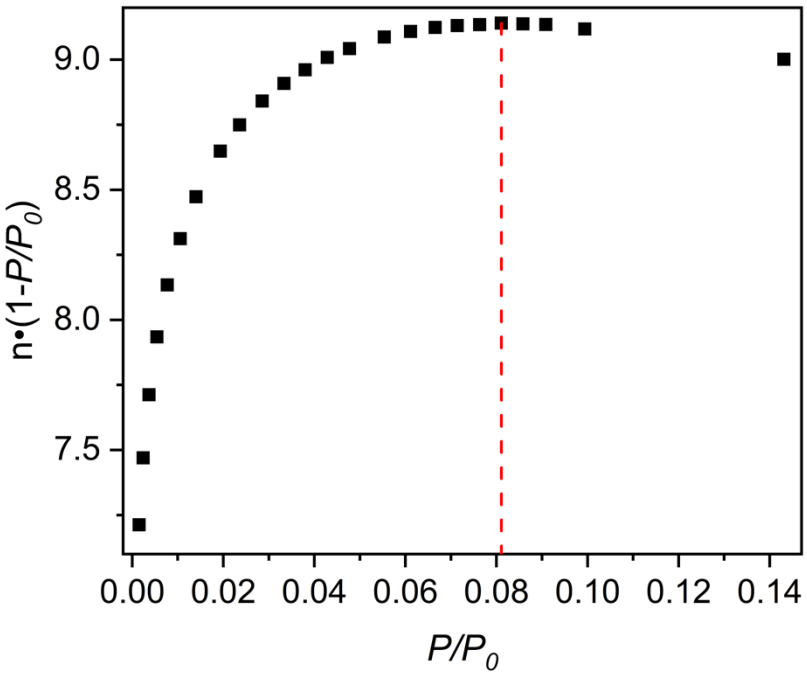


Figure S41. Plot of n•(1-P/P_0) vs P/P_0 of Mo_{12}(phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

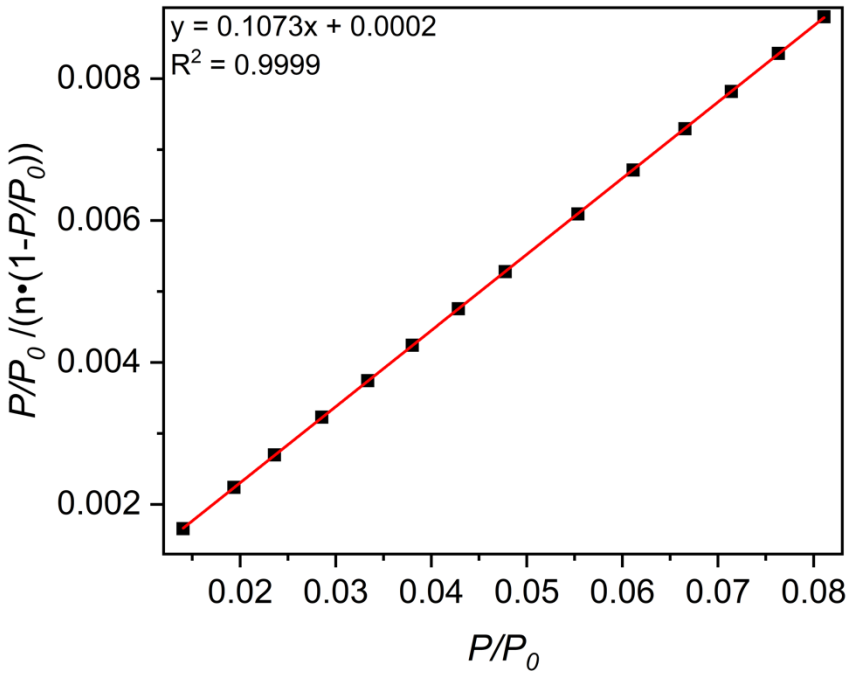


Figure S42. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of Mo_{12}(phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for P/P_0 < 0.081 is 0.1073 with a y-intercept of 0.0002. These values satisfy the second BET consistency criterion and yield a BET surface area of 909 m^2/g.

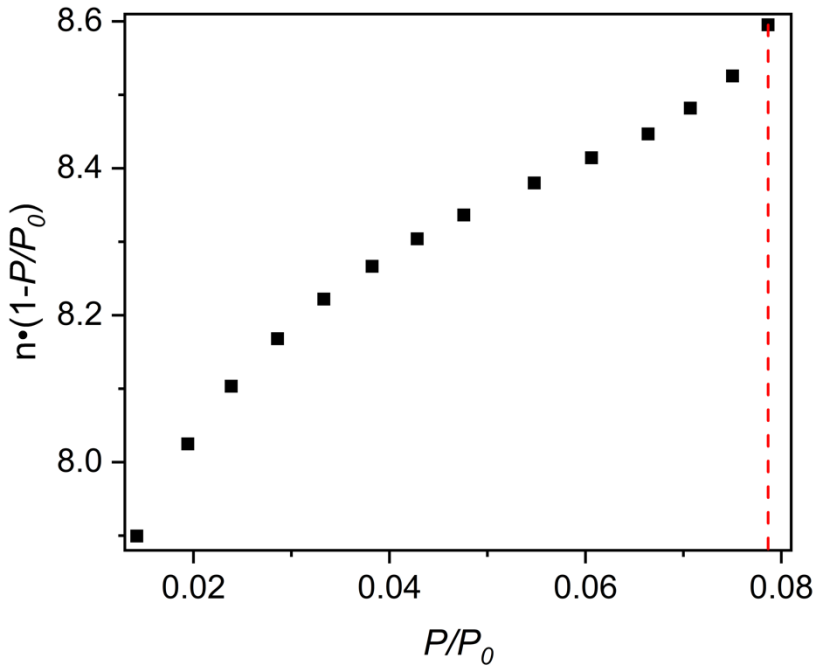


Figure S43. Plot of n•(1-P/P_0) vs P/P_0 of $Mo_{12}(^{i}Prphenyl\text{-}cdc)_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

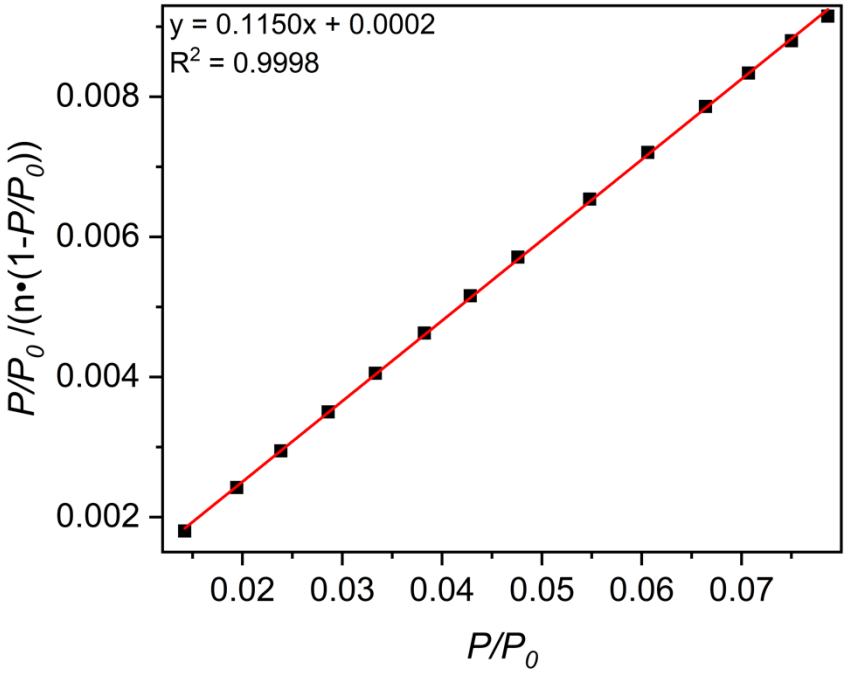


Figure S44. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of $Mo_{12}(^{i}Prphenyl\text{-}cdc)_{12}$ to determine the BET surface area. The slope of the line for $P/P_0 < 0.079$ is 0.1150 with a y-intercept of 0.0002. These values satisfy the second BET consistency criterion and yield a BET surface area of 849 m^2/g.

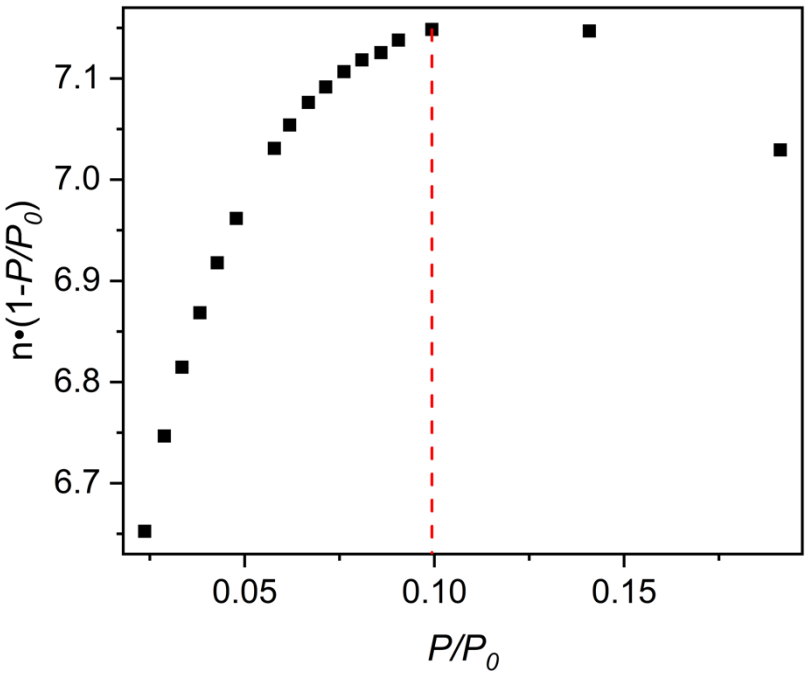


Figure S45. Plot of n•(1-*P/P*$_0$) vs *P/P*$_0$ of Mo_{12}(biphenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum *P/P*$_0$, which is indicated by the dashed line.

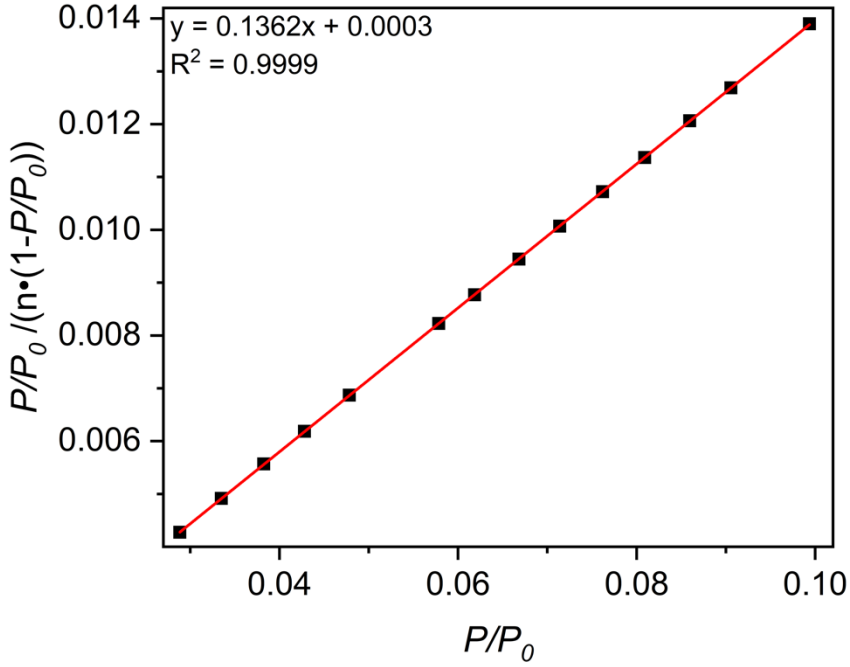


Figure S46. Plot of *P/P*$_0$ /(n•(1-*P/P*$_0$)) vs *P/P*$_0$ of Mo_{12}(biphenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for *P/P*$_0$ < 0.099 is 0.1362 with a y-intercept of 0.0003. These values satisfy the second BET consistency criterion and yield a BET surface area of 716 m^2/g.

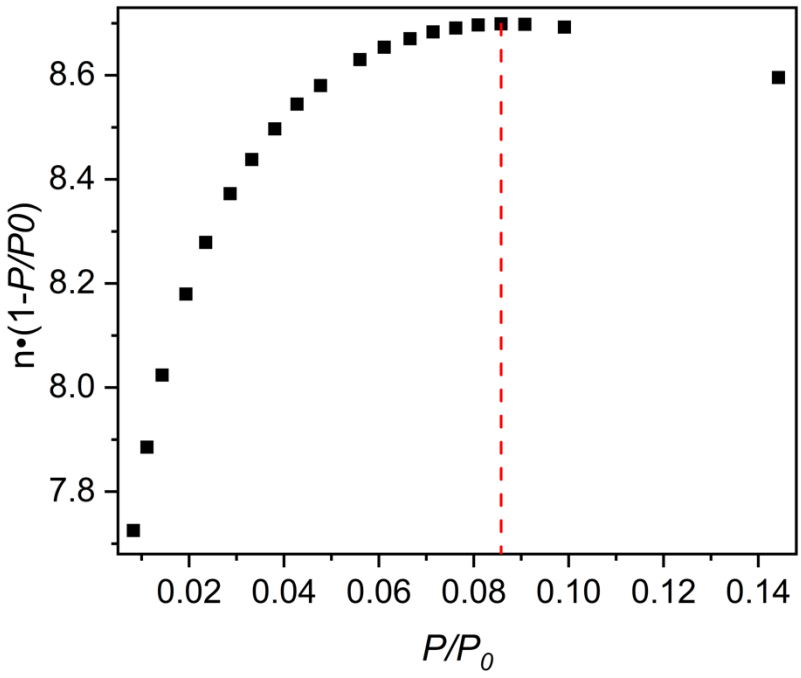


Figure S47. Plot of n•(1-P/P_0) vs P/P_0 of Mo_{12}(Br-phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum P/P_0, which is indicated by the dashed line.

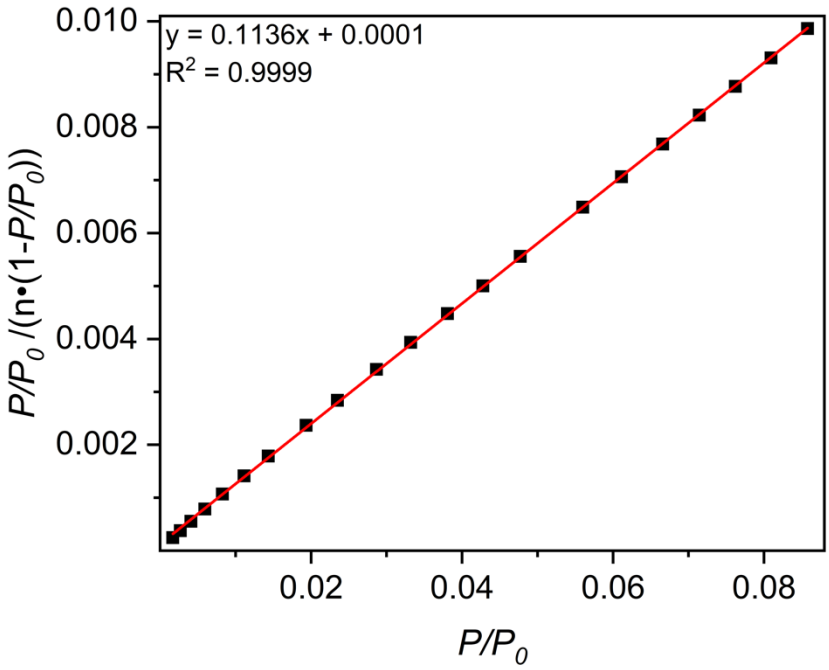


Figure S48. Plot of P/P_0 /(n•(1-P/P_0)) vs P/P_0 of Mo_{12}(Br-phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for P/P_0 < 0.081 is 0.1136 with a y-intercept of 0.0001. These values satisfy the second BET consistency criterion and yield a BET surface area of 859 m^2/g.

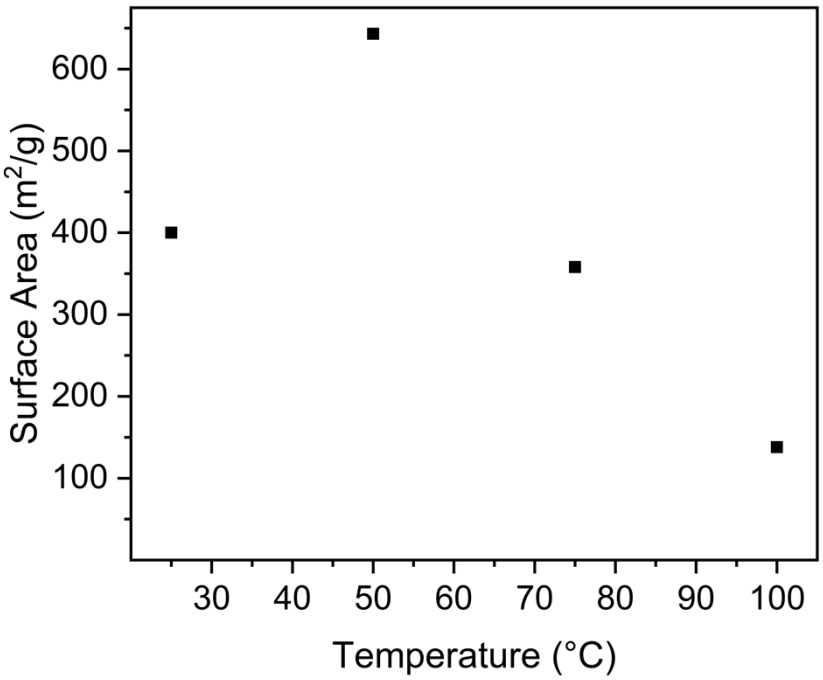


Figure S49. $Cu_{12}(cdc)_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

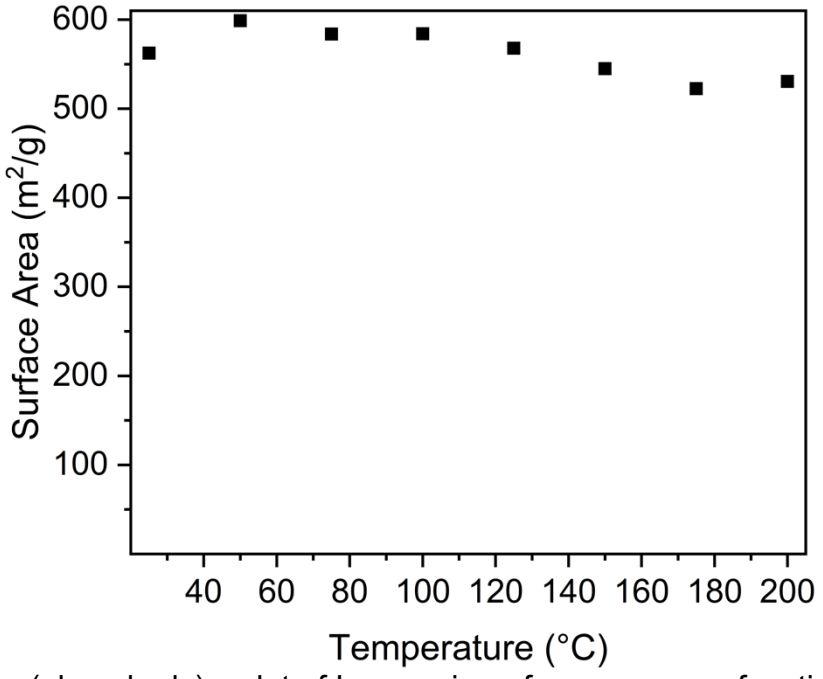


Figure S50. $Cu_{12}(phenyl\text{-}cdc)_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 195 K CO_2 isotherm was run to determine the Langmuir surface area.

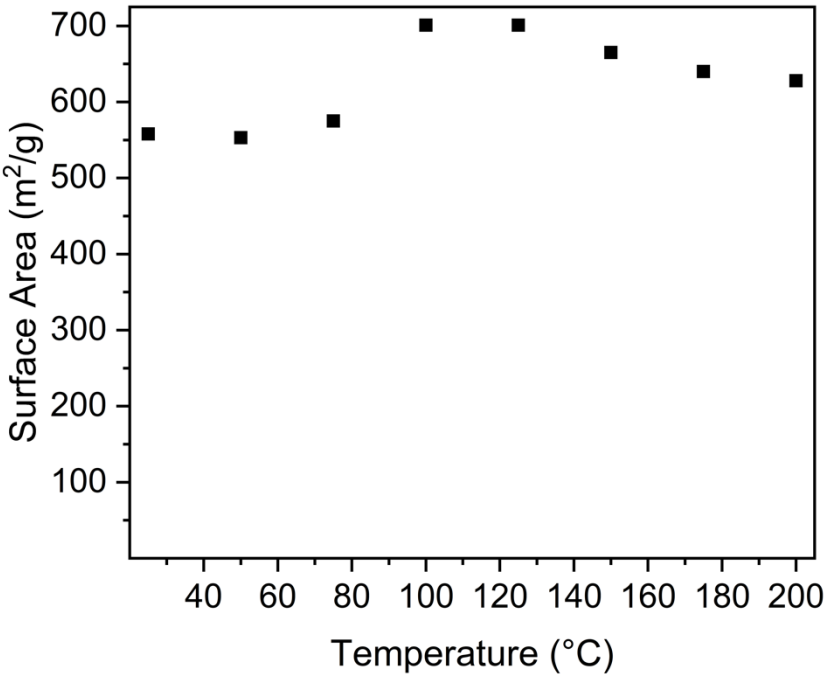


Figure S51. Cu_{12}(Br-phenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

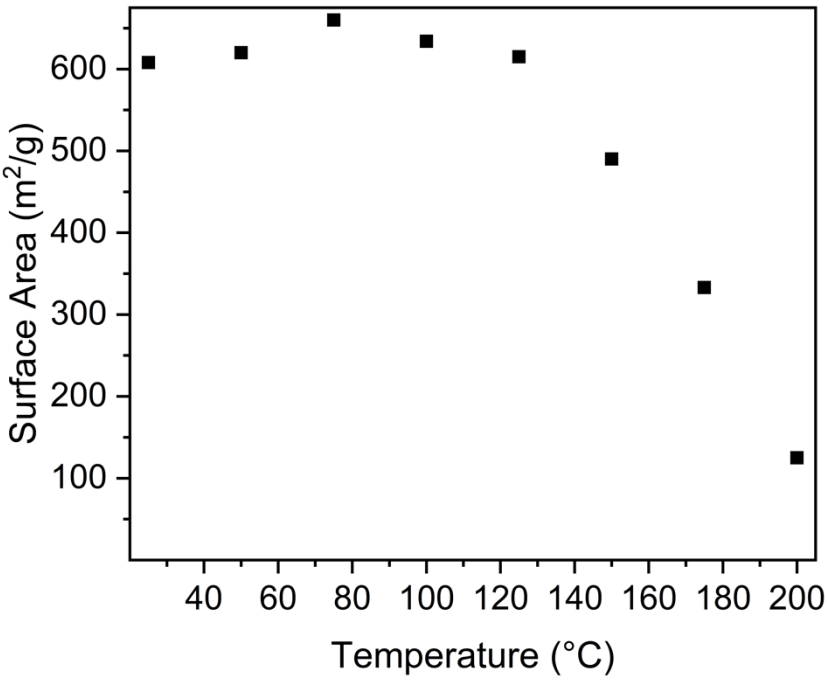


Figure S52. Cu_{12}(carbazolyl-phenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

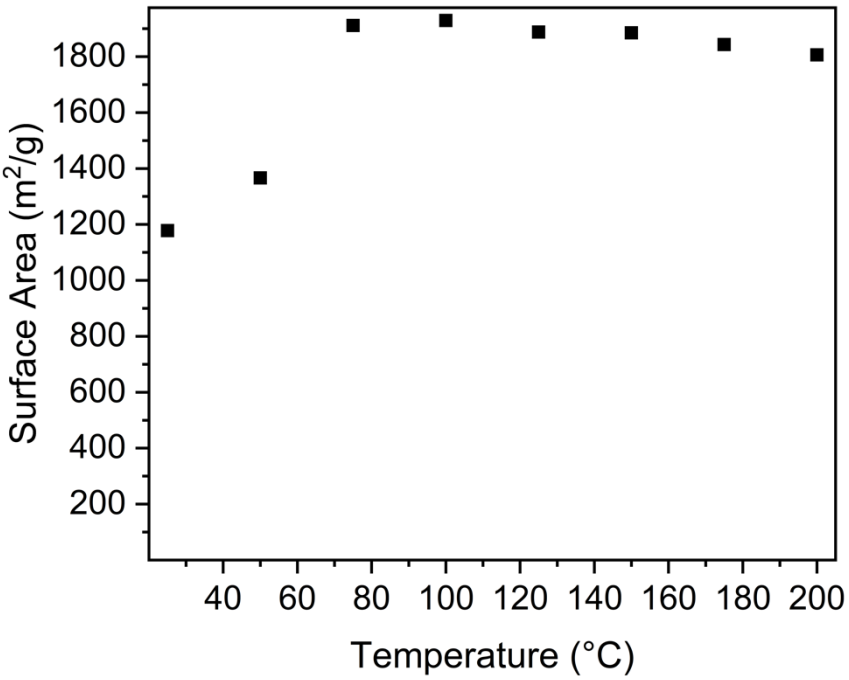


Figure S53. $Cr_{12}(cdc)_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

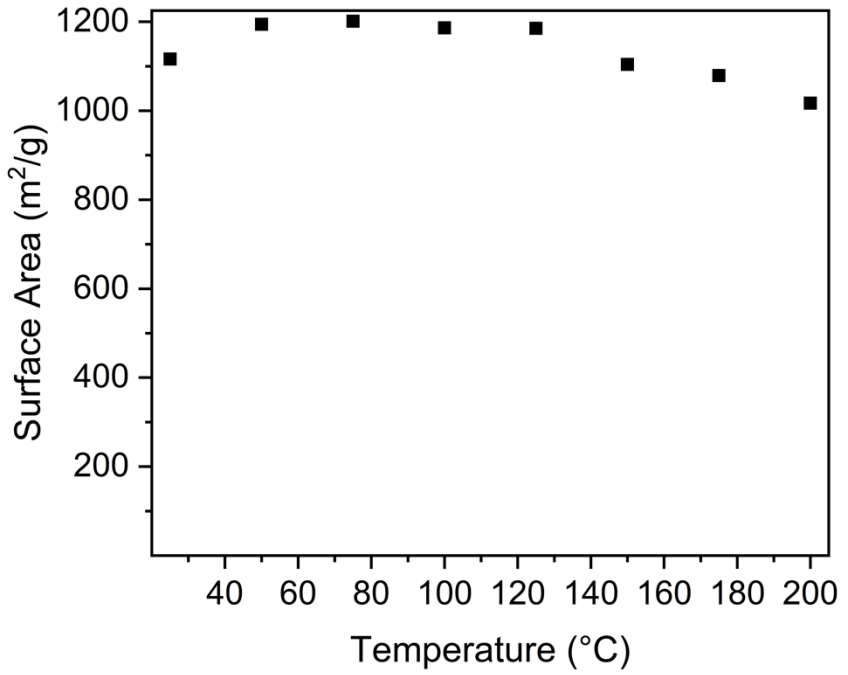


Figure S54. $Cr_{12}(phenyl\text{-}cdc)_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

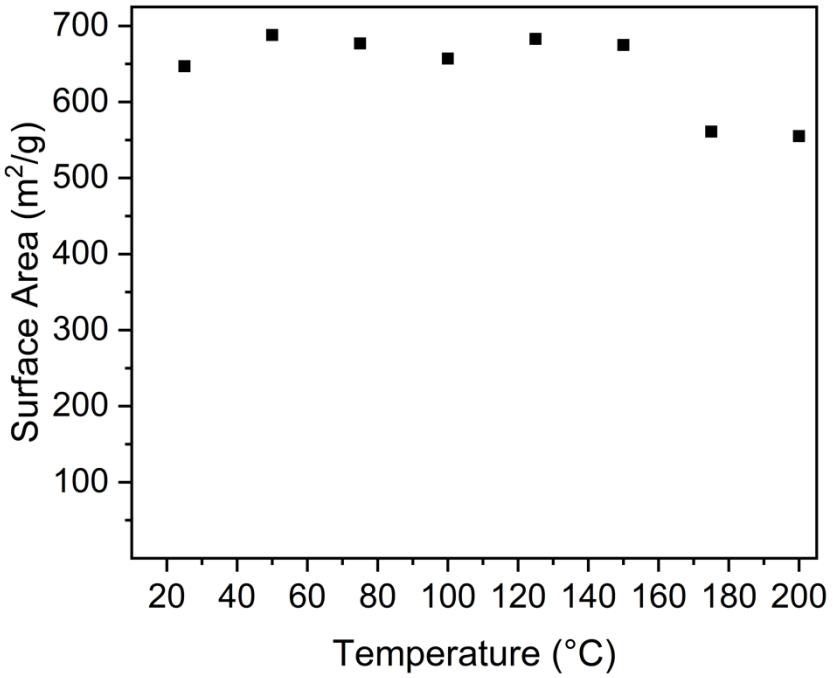


Figure S55. Cr_{12}(Br-phenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

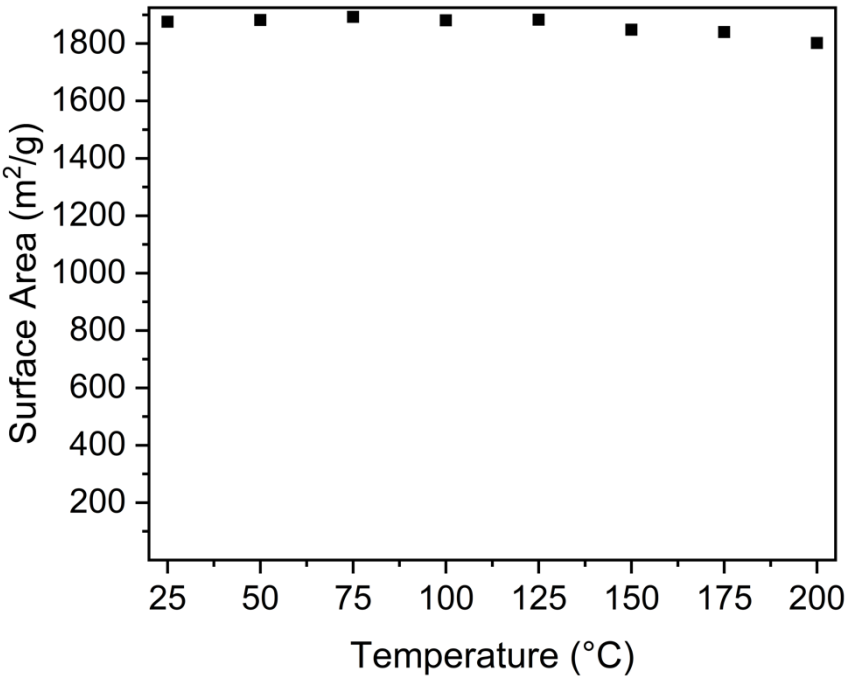


Figure S56. $Mo_{12}(cdc)_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

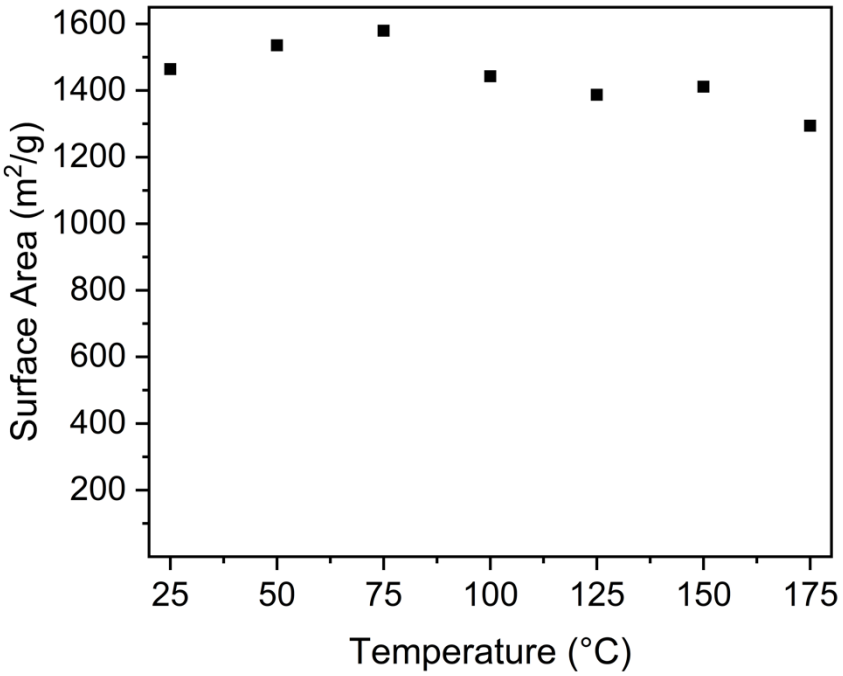


Figure S57. Mo_{12}(phenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

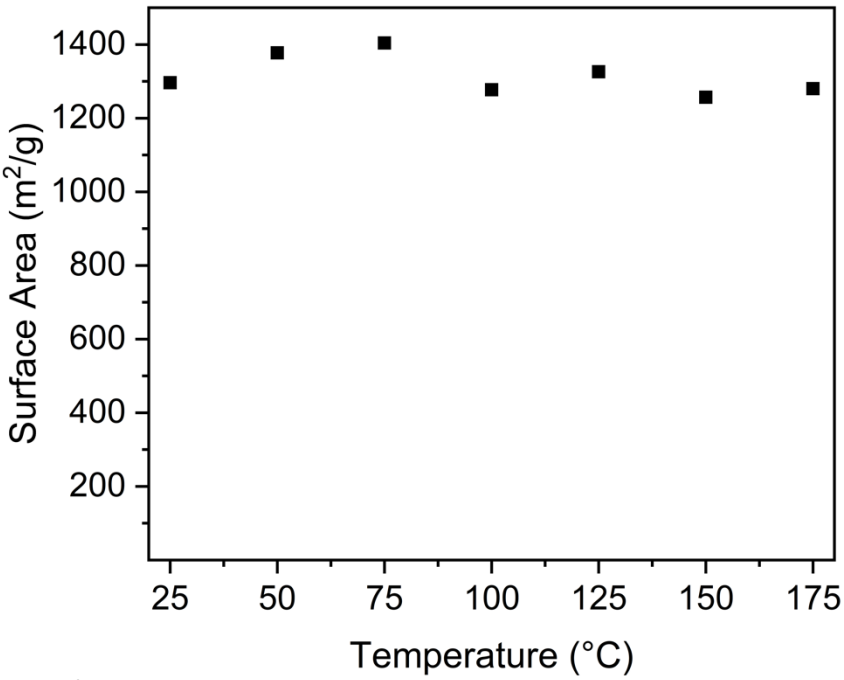


Figure S58. Mo_{12}(^{i}Prphenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

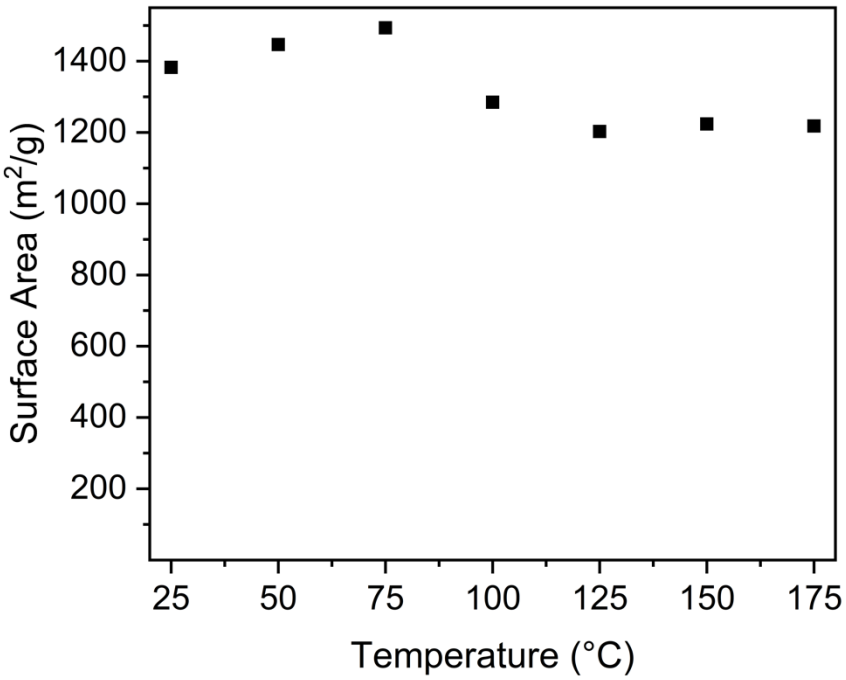


Figure S59. Mo_{12}(biphenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

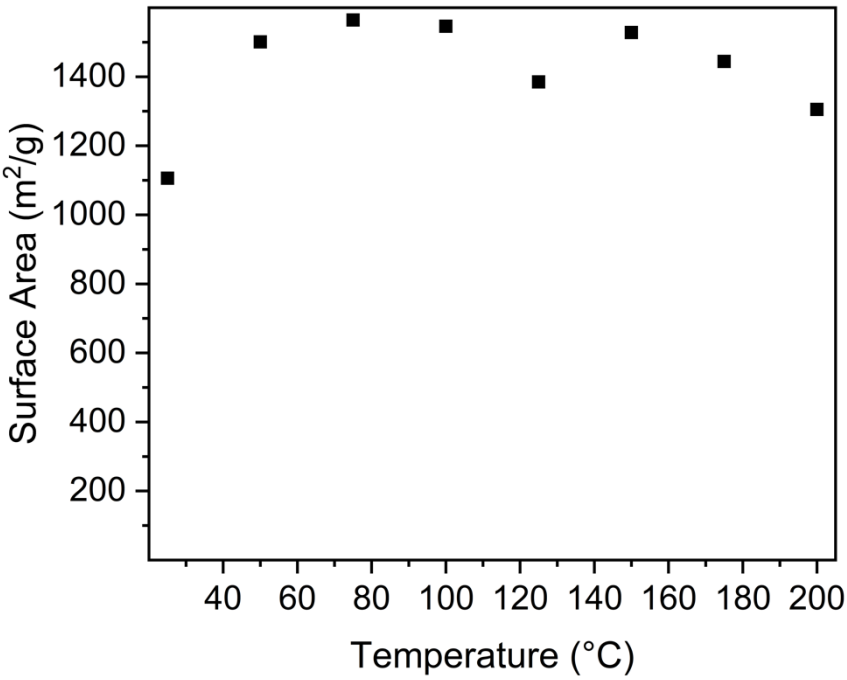


Figure S60. Mo_{12}(Br-phenyl-cdc)$_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K N_2 isotherm was run to determine the Langmuir surface area.

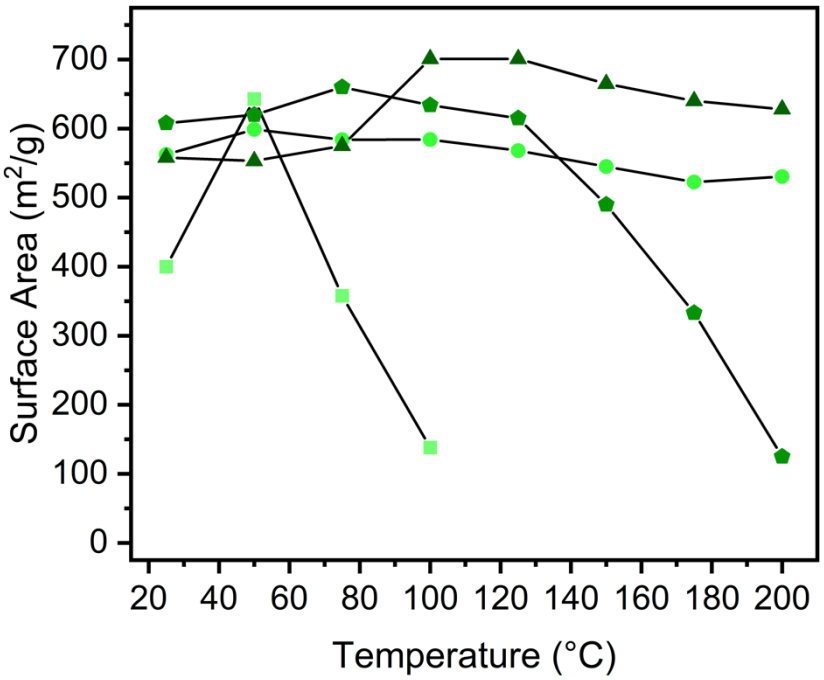


Figure S61. Degas surveys for the copper cages where Langmuir surface areas are plotted as a function of activation temperature and square, circles, triangles, and pentagons represent 9H, 9-phenyl, 9-bromophenyl and 9-carbazolylphenyl functionalization, respectively.

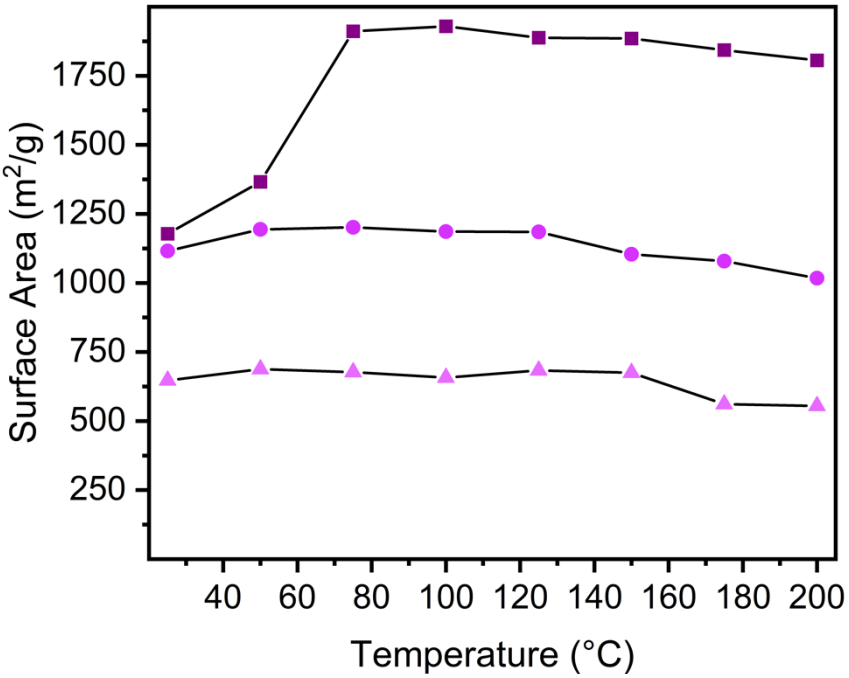


Figure S62. Degas surveys for the chromium cages where Langmuir surface areas are plotted as a function of activation temperature and square, circles, and triangles represent 9H, 9-phenyl, and 9-bromophenyl functionalization, respectively.

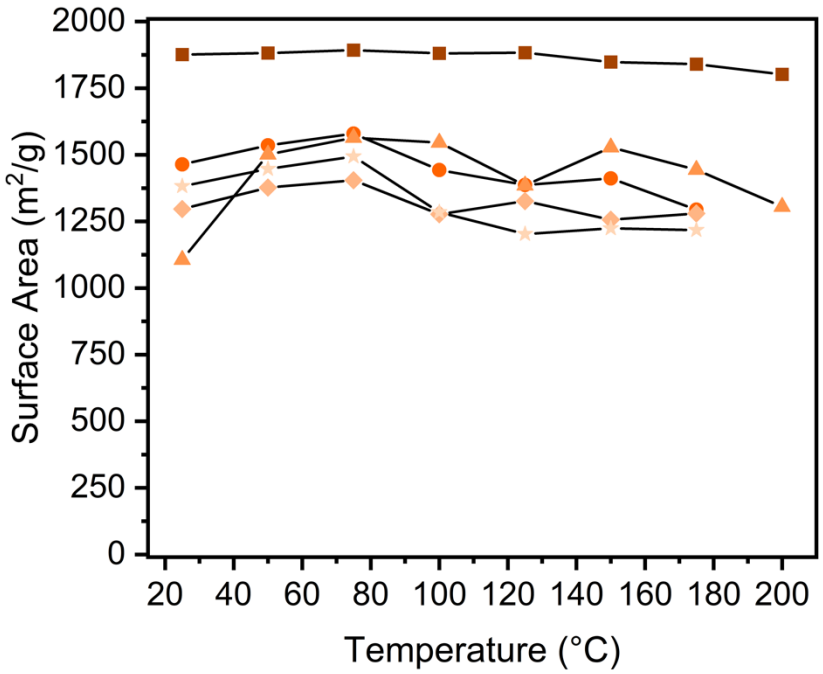


Figure S63. Degas surveys for the molybdenum cages where Langmuir surface areas are plotted as a function of activation temperature and square, circles, triangles, stars, and diamonds represent 9H, 9-phenyl, 9-bromophenyl, 9-biphenyl and 9-^{i}Prphenyl functionalization, respectively.

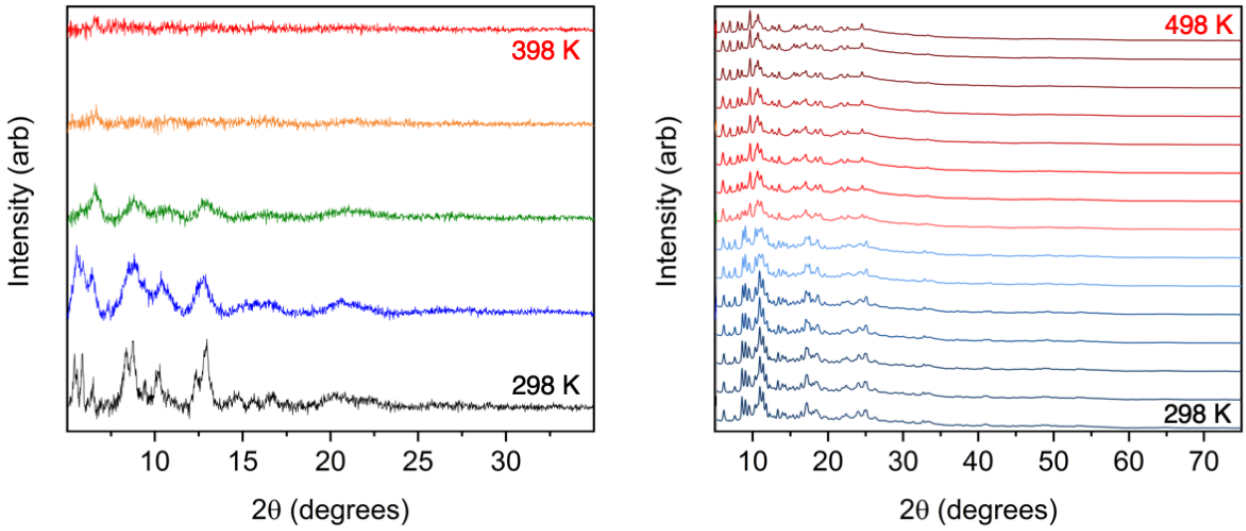


Figure S64. PXRD patterns of $Cu_{12}(cdc)_{12}$ (left) and Cu_{12}(phenyl-cdc)$_{12}$ (right) plotted as a function of activation temperature.

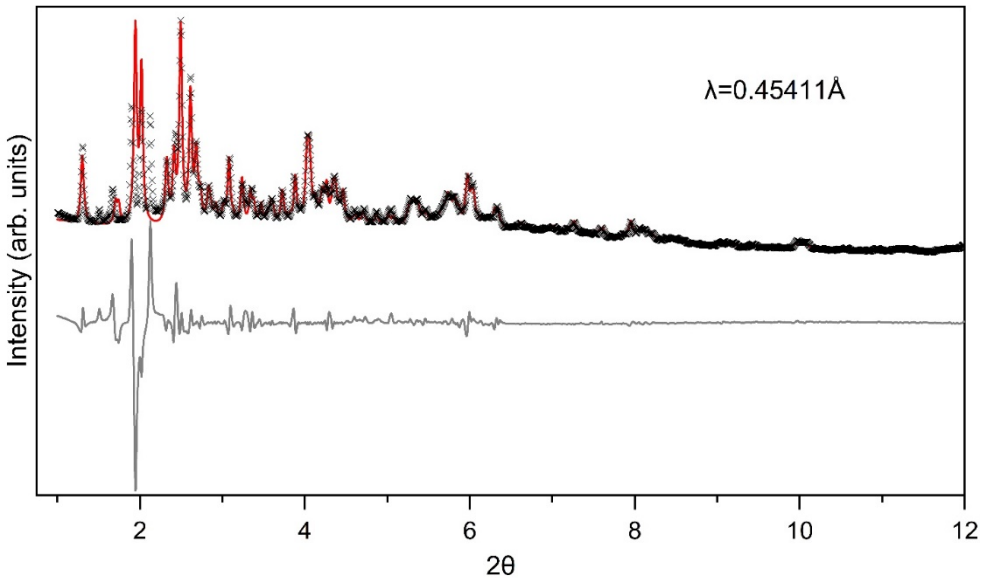


Figure S65. Pawley refinement of room temperature evacuated Cu_{12}(phenyl-cdc)$_{12}$ based on a refined unit cell from the as synthesized crystal structure of space group $P2_1/c$. The black X's, red line and grey line represent the experimental data, the Pawley fit and the difference curve between the experimental and fit data respectively. The unit cell parameters used for the fit were a=20.11, b= 22.33, c= 39.20, and β= 99.58. The fit statistics were R_p= 4.91 %, R_{wp}= 13.59 %, and GoF= 10.79.

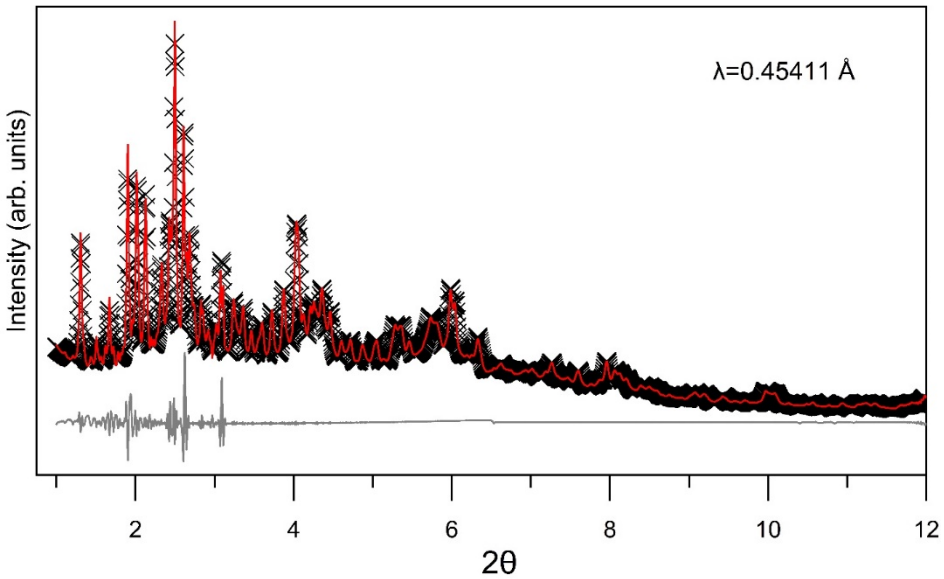


Figure S66. Pawley refinement of room temperature evacuated Cu_{12}(phenyl-cdc)$_{12}$ based on a doubling of the A and B axis of the unit cell of the as synthesized crystal structure of space group $P2_1/c$. The black X's, red line and grey line represent the experimental data, the Pawley fit and the difference curve between the experimental and fit data respectively. The unit cell parameters used for the fit were a=39.50 Å b=82.44 Å c=27.26 Å β=100.82° . The fit statistics were R_p=1.39 %, R_{wp}=3.07 %, GoF=1.36.

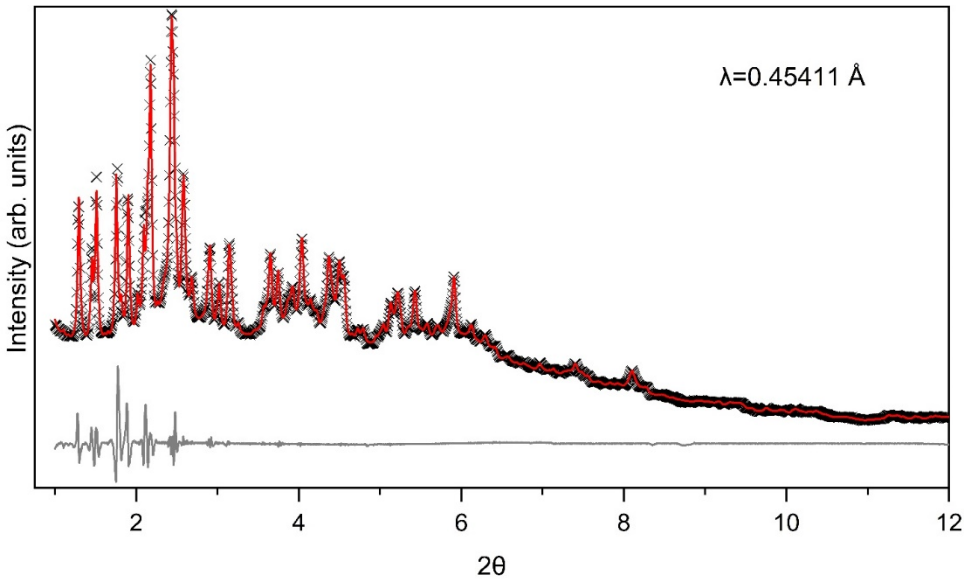


Figure S67. Pawley refinement of 400 K heated and evacuated Cu_{12}(phenyl-cdc)$_{12}$ sample based on a doubling of the A and B axis of the unit cell of the as synthesized crystal structure of space group $P2_1/c$. The black X's, red line and grey line represent the experimental data, the Pawley fit and the difference curve between the experimental and fit data respectively. The unit cell parameters used for the fit were a= 39.94 Å, b= 82.49 Å, c= 28.56 Å, and β= 97.98°. The fit statistics were R_p= 1.14 %, R_{wp}= 2.88 %, GoF= 1.17.

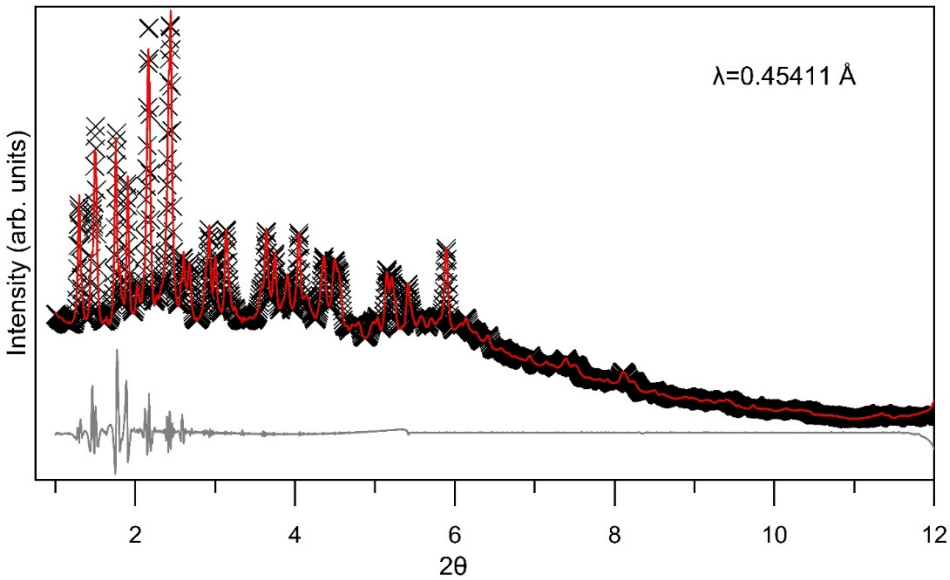


Figure S68. Pawley refinement of 500 K heated and evacuated Cu_{12}(phenyl-cdc)$_{12}$ sample based on a doubling of the A and B axis of the unit cell of the as synthesized crystal structure of space group $P2_1/c$. The black X's, red line and grey line represent the experimental data, the Pawley fit and the difference curve between the experimental and fit data respectively. The unit cell parameters used for the fit were a= 39.16 Å, b= 80.25 Å, c= 27.78 Å and β=97.42°. The fit statistics were R_p= 1.28 %, R_{wp}= 3.14 %, GoF= 1.24.

	298 K	400 K	500 K
a axis (Å)	39.50	39.94	39.16
b axis (Å)	82.44	82.49	80.25
c axis (Å)	27.26	28.56	27.78
β (°)	100.82	97.98	97.42
R_p (%)	1.39	1.14	1.28
R_{wp} (%)	3.07	2.88	3.14
GoF	1.36	1.17	1.24

Table S1. Tabulated unit cell parameters and fit statistics from Pawley refinements at three different temperatures of space group $P2_1/c$.

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Structure factors have been supplied for datablock(s) eric160_a_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Mo12(phenyl-cdc)12

Bond precision: C-C = 0.0344 A Wavelength=1.54178

Cell: a=59.221(4) b=23.4873(15) c=41.898(2)
alpha=90 beta=125.318(3) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	47552(5)	47551(5)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C240 H146 Mo12 N16 O54, 2(C) [+ solvent]	?
Sum formula	C242 H146 Mo12 N16 O54 [+ solvent]	C242 H146 Mo12 N16 O54
Mr	5293.04	5293.02
Dx,g cm-3	0.739	0.739
Z	4	4
Mu (mm-1)	2.828	2.828
F000	10584.0	10584.0
F000’	10609.47	
h,k,lmax	54,21,38	53,21,38
Nref	18907	18700
Tmin,Tmax		0.480,0.751
Tmin’		

Correction method= # Reported T Limits: Tmin=0.480 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 0.989 Theta(max)= 44.695

R(reflections)= 0.0929(10264) wR2(reflections)= 0.3044(18700)

S = 1.000 Npar= 1461

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Structure factors have been supplied for datablock(s) eric177_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Mo12(iPrphenyl-cdc)12

```
Bond precision:  C-C = 0.0269 A          Wavelength=1.54178

Cell:             a=26.357(6)     b=26.357(6)     c=56.276(13)
                  alpha=90        beta=90         gamma=120
Temperature:      200 K
```

	Calculated	Reported
Volume	33857(20)	33857(17)
Space group	R -3	R -3 :h
Hall group	-R 3	-R 3
Moiety formula	C276 H204 Mo12 N12 O48, 12(O) [+ solvent]	?
Sum formula	C276 H204 Mo12 N12 O60 [+ solvent]	C276 H204 Mo12 N12 O60
Mr	5799.79	5799.78
Dx,g cm-3	0.853	0.853
Z	3	3
Mu (mm-1)	3.017	3.017
F000	8784.0	8784.0
F000’	8805.37	
h,k,lmax	21,21,45	21,21,45
Nref	4249	4176
Tmin,Tmax	0.650,0.778	0.600,0.719
Tmin’	0.589	

```
Correction method= # Reported T Limits: Tmin=0.600 Tmax=0.719
AbsCorr = MULTI-SCAN

Data completeness= 0.983          Theta(max)= 38.861

R(reflections)= 0.0905( 3407)     wR2(reflections)= 0.2651( 4176)

S = 1.092                 Npar= 521
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Structure factors have been supplied for datablock(s) eric183_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Mo12(biphenyl-cdc)12

Bond precision: C-C = 0.0409 A Wavelength=1.54178

Cell: a=19.686(3) b=27.191(3) c=39.897(5)
alpha=90 beta=93.427(3) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	21318(5)	21318(5)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C288 H160 Mo12 N12 O48 [+ solvent]	?
Sum formula	C288 H160 Mo12 N12 O48 [+ solvent]	C312 H180 Mo12 N12 O48
Mr	5707.57	6015.95
Dx,g cm-3	0.889	0.937
Z	2	2
Mu (mm-1)	3.170	3.190
F000	5720.0	6048.0
F000’	5733.50	
h,k,lmax	14,20,30	14,20,30
Nref	9856	9413
Tmin,Tmax	0.748,0.850	0.577,0.747
Tmin’	0.741	

Correction method= # Reported T Limits: Tmin=0.577 Tmax=0.747
AbsCorr = MULTI-SCAN

Data completeness= 0.955 Theta(max)= 35.942

R(reflections)= 0.1175(4978) wR2(reflections)= 0.3528(9413)

S = 0.965 Npar= 1501

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Structure factors have been supplied for datablock(s) eric354_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Cr12(Br-phenyl-cdc)12

Bond precision: C-C = 0.0164 A Wavelength=1.54178

Cell: a=42.1022(12) b=27.7671(8) c=37.031(1)
alpha=90 beta=104.5652(14) gamma=90
Temperature: 150 K

	Calculated	Reported
Volume	41900(2)	41900(2)
Space group	C 2/c	C 2/c
Hall group	-C 2yc	-C 2yc
Moiety formula	C240 H120 Br12 Cr12 N12 O60 [+ solvent]	C240 H120 Br12 Cr12 N12 O60
Sum formula	C240 H120 Br12 Cr12 N12 O60 [+ solvent]	C240 H120 Br12 Cr12 N12 O60
Mr	5714.29	5714.39
Dx,g cm-3	0.906	0.906
Z	4	4
Mu (mm-1)	4.193	4.193
F000	11328.0	11328.0
F000’	11318.25	
h,k,lmax	42,27,37	42,27,37
Nref	22018	21909
Tmin,Tmax	0.491,0.605	0.502,0.750
Tmin’	0.415	

Correction method= # Reported T Limits: Tmin=0.502 Tmax=0.750
AbsCorr = MULTI-SCAN

Data completeness= 0.995 Theta(max)= 50.513

R(reflections)= 0.1121(11707) wR2(reflections)= 0.3726(21909)

S = 1.249 Npar= 1444

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Structure factors have been supplied for datablock(s) eric334_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Cu12(Br-phenyl-cdc)12

Bond precision: C-C = 0.0278 A Wavelength=1.54178

Cell: a=26.9417(14) b=26.9492(14) c=35.287(2)
alpha=90 beta=90.249(3) gamma=90
Temperature: 180 K

	Calculated	Reported
Volume	25620(2)	25620(2)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C260 H140 Br12 Cu12 N18 O54 [+ solvent]	C260 H140 Br12 Cu12 N18 O54
Sum formula	C260 H140 Br12 Cu12 N18 O54 [+ solvent]	C260 H140 Br12 Cu12 N18 O54
Mr	6101.31	6101.29
Dx,g cm-3	0.791	0.791
Z	2	2
Mu (mm-1)	1.953	1.953
F000	6052.0	6052.0
F000’	6003.52	
h,k,lmax	27,27,35	26,26,35
Nref	27339	26848
Tmin,Tmax	0.654,0.774	0.572,0.750
Tmin’	0.545	

Correction method= # Reported T Limits: Tmin=0.572 Tmax=0.750
AbsCorr = MULTI-SCAN

Data completeness= 0.982 Theta(max)= 50.864

R(reflections)= 0.1652(19750) wR2(reflections)= 0.4347(26848)

S = 1.658 Npar= 1532

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Structure factors have been supplied for datablock(s) eric307_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Cu12(carbazolylphenyl-cdc)12

Bond precision: C-C = 0.0395 A Wavelength=1.54178

Cell: a=35.9602(19) b=35.9602(19) c=36.207(2)
alpha=90 beta=90 gamma=120
Temperature: 150 K

	Calculated	Reported
Volume	40548(6)	40548(5)
Space group	R -3	R -3 :h
Hall group	-R 3	-R 3
Moiety formula	C384 H216 Cu12 N24 O60 [+ solvent]	C384 H216 Cu12 N24 O60
Sum formula	C384 H216 Cu12 N24 O60 [+ solvent]	C384 H216 Cu12 N24 O60
Mr	6888.41	6888.28
Dx,g cm-3	0.846	0.846
Z	3	3
Mu (mm-1)	0.908	0.908
F000	10548.0	10548.0
F000’	10507.34	
h,k,lmax	29,29,30	29,26,30
Nref	5434	5392
Tmin,Tmax	0.931,0.970	0.592,0.748
Tmin’	0.903	

Correction method= # Reported T Limits: Tmin=0.592 Tmax=0.748
AbsCorr = MULTI-SCAN

Data completeness= 0.992 Theta(max)= 39.922

R(reflections)= 0.1750(2485) wR2(reflections)= 0.5072(5392)

S = 1.697 Npar= 631

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Structure factors have been supplied for datablock(s) eric136_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Cu12(iPr-cdc)12

```
Bond precision:  C-C = 0.0418 A          Wavelength=1.54178

Cell:              a=21.265(2)      b=21.265(2)      c=69.250(8)
                   alpha=90         beta=90          gamma=120
Temperature:       200 K
```

	Calculated	Reported
Volume	27120(7)	27119(6)
Space group	R -3	R -3 :h
Hall group	-R 3	-R 3
Moiety formula	C204 H162 Cu12 N12 O48 [+ solvent]	?
Sum formula	C204 H162 Cu12 N12 O48 [+ solvent]	C204 H162 Cu12 N12 O48
Mr	4312.05	4311.93
Dx,g cm-3	0.792	0.792
Z	3	3
Mu (mm-1)	1.115	1.115
F000	6606.0	6606.0
F000’	6553.33	
h,k,lmax	14,14,48	14,14,46
Nref	2149	2107
Tmin,Tmax	0.834,0.944	0.562,0.750
Tmin’	0.809	

```
Correction method= # Reported T Limits: Tmin=0.562 Tmax=0.750
AbsCorr = MULTI-SCAN

Data completeness= 0.980          Theta(max)= 32.479

R(reflections)= 0.0880( 1021)     wR2(reflections)= 0.2803( 2107)

S = 1.151                 Npar= 419
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Structure factors have been supplied for datablock(s) eric157_sq

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No syntax errors found. CIF dictionary Interpreting this report

Datablock: Cu12(phenyl-cdc)12

Bond precision: C-C = 0.0202 A Wavelength=1.54178

Cell: a=20.2176(8) b=22.8067(8) c=40.8077(14)
alpha=90 beta=100.344(2) gamma=90
Temperature: 200 K

	Calculated	Reported
Volume	18510.5(12)	18510.5(12)
Space group	P 21/c	P 21/c
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C240 H132 Cu12 N12 O60 [+ solvent]	?
Sum formula	C240 H132 Cu12 N12 O60 [+ solvent]	C240 H132 Cu12 N12 O60
Mr	4906.17	4906.05
Dx,g cm-3	0.880	0.880
Z	2	2
Mu (mm-1)	1.163	1.163
F000	4968.0	4968.0
F000’	4935.30	
h,k,lmax	20,22,40	19,22,40
Nref	19587	19280
Tmin,Tmax		0.632,0.751
Tmin’		

Correction method= # Reported T Limits: Tmin=0.632 Tmax=0.751
AbsCorr = MULTI-SCAN

Data completeness= 0.984 Theta(max)= 50.678

R(reflections)= 0.1281(10880) wR2(reflections)= 0.4134(19280)

S = 1.428 Npar= 1453

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