Electronic Supplementary Information for:

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

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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 N₂ and stored in a glove box under 4 Å sieves for at least 72 hours before use. Air-sensitive materials were handled in an N₂ glovebox utilizing the solvents described above. 9-isopropyl-cdc and Cr₂(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 CO₂ or N₂ 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 Cu₁₂(Pr-cdc)₁₂, Cu₁₂(phenyl-cdc)₁₂, Mo₁₂(phenyl-cdc)₁₂, Mo₁₂(Pr-phenyl-cdc)₁₂, Mo₁₂(biphenyl-cdc)₁₂, Cu₁₂(carbazoyl-phenyl-cdc)₁₂, Cu₁₂(Br-phenyl-cdc)₁₂, and Cr₁₂(Pr-phenyl-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 C2/c for Mo₁₂(phenyl-cdc)₁₂ and Cr₁₂(Br-phenyl-cdc)₁₂; uniquely with P2₁/c for Cu₁₂(phenyl-cdc)₁₂ and Mo₁₂(biphenyl-cdc)₁₂; uniquely with P2₁/n for Cu₁₂(Br-phenyl-cdc)₁₂; and with R3 and R-3 for Cu₁₂(Pr-cdc)₁₂, Mo₁₂(Pr-phenyl-cdc)₁₂ and Cu₁₂(carbazoyl-phenyl-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 methods⁴ and refined with full-matrix, least-squares procedures on F².⁵ The compound molecule is located at an inversion center for Mo₁₂(phenyl-cdc)₁₂, Cu₁₂(phenyl-cdc)₁₂, Mo₁₂(biphenyl-cdc)₁₂, Cu₁₂(Br-phenyl-cdc)₁₂ and Cr₁₂(Br-phenyl-cdc)₁₂; and at a three-fold rotoinversion axis in Cu₁₂(Pr-cdc)₁₂, Mo₁₂(Pr-phenyl-cdc)₁₂ and Cu₁₂(carbazoyl-phenyl-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. Non-crystallographic symmetry restraints were applied to one symmetry unique ligand in Cu$_{12}$(iPr-cdc)$_{12}$ and Mo$_{12}$(biphenyl-cdc)$_{12}$. Two phenyl groups and an entire ligand were found disordered in Cu$_{12}$(phenyl-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-phenyl-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-cdc)$_{12}$, Mo$_{12}$(Pr-phenyl-cdc)$_{12}$, Mo$_{12}$(biphenyl-cdc)$_{12}$ and Cu$_{12}$(carbazolyl-phenyl-cdc)$_{12}$. The $C_{aryl}-C_{carboxylate}$ bond distances were constrained to 1.504(14) Å in Cu$_{12}$(carbazolyl-phenyl-cdc)$_{12}$ and Cu$_{12}$(Br-phenyl-cdc)$_{12}$, and treated to non-crystallographic symmetry restraints in Mo$_{12}$(biphenyl-cdc)$_{12}$. Two $C_{aryl}-C_{aryl}$ bond distances in Cu$_{12}$(Br-phenyl-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-phenyl-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 $\beta$ 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 \( \lambda = 0.45411 \) Å. Methanol exchanged \( \text{Cu}_{12}(\text{phenyl-cdc})_{12} \) 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 desorption that does not fit the solvated structure. (Figure S60) Unit cell searches were performed on the \( \text{Cu}_{12}(\text{phenyl-cdc})_{12} \) 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 2.1 g, 95 %) ¹H NMR (400 MHz, DMSO-d₆) \( \delta = 8.15 \) (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 AlCl₃ (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 AlCl₃ 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 9.1 g, 95 %) ¹H NMR (400 MHz, DMSO-d₆) 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 Na₂SO₃ (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 %) ¹H NMR (400 MHz, DMSO-d₆) 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 2.2 g, 96 %) ¹H NMR (400 MHz, DMSO-d₆) 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 AlCl₃ (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 AlCl₃ 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 6.4 g, 85 %) ¹H NMR (400 MHz, DMSO-d₆) 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 Na₂SO₃ (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 %) ¹H NMR (400 MHz, DMSO-d₆) 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.** 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 2.4 g, 96 %) ¹H NMR (400 MHz, DMSO-d₆) 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-diacyethyl-9-propyl-carbazole.** 9-propyl-carbazole (2.3 g, 11 mmol) was dissolved in 30 mL of DCM. In a separate flask AlCl₃ (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 AlCl₃ 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 2.7 g, 84 %) ¹H NMR (400 MHz, DMSO-d₆) 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.** 3,6-diacyethyl-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-diacyethyl-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 Na₂SO₃ (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 %) ¹H NMR (400 MHz, DMSO-d₆) 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.** 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 2.4 g, 89 %) ¹H NMR (400 MHz, DMSO-d₆) 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-diacyethyl-9-butyl-carbazole.** 9-butyl-carbazole (6.0 g, 27 mmol) was dissolved in 80 mL of DCM. In a separate flask AlCl₃ (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 AlCl₃ 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 7.5 g, 90 %) ¹H NMR (400 MHz, DMSO-d₆) 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 50 °C for 12 h. The reaction mixture was allowed to cool and 350 mL of saturated Na₂SO₃ (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 %) ¹H NMR (400 MHz, DMSO-d₆) 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 AlCl₃ (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 AlCl₃ 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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 12.1 g, 90 %) ¹H NMR (400 MHz, DMSO-d₆) 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 H₂O. The prepared NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 30 mL of Br₂ 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 Na₂SO₃ (aq) solution was added. The reaction mix was acidified to pH = 2, precipitated solids were collected via vacuum filtration. (Yield: 11.1 g, 90 %) ¹H NMR (400 MHz, DMSO-d₆) 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'-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'-dimethylenelethyleneamine (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 H₂O,
precipitated solids were collected via vacuum filtration. (Yield: 849 mg, 85 %) $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 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'-Prphenyl)-carbazole.**$^{11,12}$ Solid 9-(4'-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$_2$O. The reaction flask was washed with acetone which was poured into the DI H$_2$O/DCM mixture, precipitated solids were collected via vacuum filtration. (Yield: 1 g, 91 %) $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 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'-Prphenyl)-cadc.**$^{11,12}$ NaOH (6 g, 150 mmol) was slowly added to 30 mL DI H$_2$O. 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'-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'-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$_2$SO$_3$ (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$_6$) $\delta$ = 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'-dimethylethlenediamine (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$_2$O, precipitated solids were collected via vacuum filtration. (Yield: 935 mg, 85 %) $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 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$_2$O. The reaction flask was washed with acetone which was poured into the DI H$_2$O/DCM mixture, precipitated solids were collected via vacuum filtration. (Yield: 1.1 g, 92 %) $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ = 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.\textsuperscript{11,12} NaOH (6 g, 150 mmol) was slowly added to 30 mL DI H\textsubscript{2}O. The NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 3 mL of Br\textsubscript{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-diacytetyl-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-diacytetyl-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\textsubscript{2}SO\textsubscript{3} (aq) solution was added. The reaction mix was acidified to pH = 2, precipitated solids were collected via vacuum filtration. (Yield: 905 mg, 75 %) \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}) \( \delta = 8.91 \) (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-diacytetyl-9-(4'-bromophenyl)-carbazole.\textsuperscript{11,12} 9-(4'-bromophenyl)-carbazole (10.0 g, 31 mmol) was dissolved in 50 mL of DCM. In a separate flask AlCl\textsubscript{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\textsubscript{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\textsubscript{2}O, precipitated solids were collected via vacuum filtration. (Yield: 10.7 g, 85 %) \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}) \( \delta = 9.18 \) (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.\textsuperscript{11,12} NaOH (58 g, 1.445 mol) was slowly added to 250 mL DI H\textsubscript{2}O. The prepared NaOH solution was allowed to stir at 0 °C for 30 mins. To the cold NaOH solution 25 mL of Br\textsubscript{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-diacytetyl-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-diacytetyl-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\textsubscript{2}SO\textsubscript{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 %) \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}) \( \delta = 8.98 \) (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.\textsuperscript{14} 9-(4'-bromophenyl)-cdc (6.2 g, 15 mmol) and K\textsubscript{2}CO\textsubscript{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\textsubscript{2}O, precipitated solids were collected via vacuum filtration. (Yield: 5.9 g, 89 %) \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d}\textsubscript{6}) \( \delta = 9.06 \) (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.\textsuperscript{13} Dimethyl 9-(4'-bromophenyl)-cdc (1.5 g, 3.4 mmol), 9H-carbazole (652 mg, 3.9 mmol), potassium carbonate (2.0 g,
copper iodide (65 mg, 0.34 mmol), N,N'-dimethylethlenediamine (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 H₂O, precipitated solids were collected via vacuum filtration. (Yield: 1.3 g, 72 %) ¹H NMR (400 MHz, DMSO-d₆) 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 H₂O. The reaction mixture was acidified to pH = 1, precipitated solids were collected via vacuum filtration. (Yield: 1.6 g, 94 %) ¹H NMR (400 MHz, DMSO-d₆) 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 Cu₁₂(iPr-cdc)₁₂. 9-iPr-cdc (59.5 mg, 0.2 mmol) and Cu(NO₃)₂•2.5 H₂O (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 Cu₁₂(phenyl-cdc)₁₂. 9-phenyl-cdc (66.3 mg, 0.2 mmol) and Cu(NO₃)₂•2.5 H₂O (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 Cu₁₂(Br-phenyl-cdc)₁₂. 9-(4'-bromophenyl)-cdc (102.6 mg, 0.25 mmol) was dissolved in 7.5 mL of DMA. Cu(NO₃)₂•2.5 H₂O (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$_2$O (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 μL 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. The 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$_{12}$('Prphenyl-cdc)$_{12}$. 9-(4'-'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.

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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'-iPrphenyl)-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'-carbazoylphenyl)-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$_{12}$(iPr-cdc)$_{12}$. H-atoms omitted for clarity.

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

**Figure S16.** Crystal structure of \( \text{Mo}_{12}(\text{phenyl-cdc})_{12} \). H-atoms omitted for clarity.
Figure S17. Crystal structure of Mo$_{12}$(Prphenyl-cdc)$_{12}$. H-atoms omitted for clarity.

Figure S18. Crystal structure of Mo$_{12}$(biphenyl-cdc)$_{12}$. H-atoms omitted for clarity.
Figure S19. CO$_2$ adsorption in Cu$_{12}$(Pr-cdc)$_{12}$ at 195 K.

Figure S20. CO$_2$ adsorption in Cu$_{12}$(phenyl-cdc)$_{12}$ at 195 K. Filled and open symbols represent adsorption and desorption, respectively.
Figure S21. N\textsubscript{2} adsorption in Cu\textsubscript{12}(Br-phenyl-cdc)\textsubscript{12} at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

Figure S22. N\textsubscript{2} adsorption in Cu\textsubscript{12}(carbazolyl-phenyl-cdc)\textsubscript{12} at 77 K. Filled and open symbols represent adsorption and desorption, respectively.
Figure S23. $\text{N}_2$ adsorption in $\text{Cr}_{12}(\text{phenyl-cdc})_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

Figure S24. $\text{N}_2$ adsorption in $\text{Cr}_{12}(\text{Br-phenyl-cdc})_{12}$ at 77 K. Filled and open symbols represent adsorption and desorption, respectively.
Figure S25. N\textsubscript{2} adsorption in Mo\textsubscript{12}(phenyl-cdc)\textsubscript{12} at 77 K. Filled and open symbols represent adsorption and desorption, respectively.

Figure S26. N\textsubscript{2} adsorption in Mo\textsubscript{12}(iPrphenyl-cdc)\textsubscript{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$_{12}$([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$_{12}$([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 $n \cdot (1 - P/P_0)$ 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 $P/P_0/(n \cdot (1 - P/P_0))$ 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 $n \cdot (1 - P/P_0)$ 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 $P/P_0 / (n \cdot (1 - P/P_0))$ 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 $n(1-P_0/P)$ vs $P_0/P$ of Cr$_{12}$(Br-phenyl-cdc)$_{12}$. According to the first BET consistency criterion, the BET linear fit can be determined via the maximum $P_0/P$, which is indicated by the dashed line.

Figure S40. Plot of $P_0/(n(1-P_0/P))$ vs $P_0/P$ of Cr$_{12}$(Br-phenyl-cdc)$_{12}$ to determine the BET surface area. The slope of the line for $P_0/P < 0.067$ 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 $n \cdot (1-P/P_0)$ 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 $P/P_0 / (n \cdot (1-P/P_0))$ 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$_{12}$('Prphenyl-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$_{12}$('Prphenyl-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 $n \cdot (1 - P/P_0)$ 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 $P_0/(n \cdot (1 - P/P_0))$ 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 $n \cdot (1 - P/P_0)$ 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 $P/P_0/(n \cdot (1 - P/P_0))$ 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-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. $\text{Cu}_{12}(\text{Br-phenyl-cdc})_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K $\text{N}_2$ isotherm was run to determine the Langmuir surface area.

Figure S52. $\text{Cu}_{12}(\text{carbazolyl-phenyl-cdc})_{12}$ plot of Langmuir surface area as a function of activation temperature. The samples were activated at the specified temperature and then a 77 K $\text{N}_2$ 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-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$_{12}$(iPrphenyl-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-iPrphenyl 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 $\beta=99.58$. 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, $\beta=100.82^\circ$. 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 $\beta=97.98^\circ$. 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 $\beta=97.42^\circ$. The fit statistics were $R_p=1.28\%$, $R_{wp}=3.14\%$, GoF= 1.24.
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<tr>
<td>β (°)</td>
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<tr>
<td>( R_p ) (%)</td>
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<td>1.14</td>
<td>1.28</td>
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<tr>
<td>( R_{wp} ) (%)</td>
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<td>2.88</td>
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<td>GoF</td>
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<td>1.24</td>
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**Table S1.** Tabulated unit cell parameters and fit statistics from Pawley refinements at three different temperatures of space group P2\(_1\)/c.
checkCIF/PLATON report

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

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<td>Hall group</td>
<td>-C 2yc</td>
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<td>MULTI-SCAN</td>
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Data completeness= 0.989            Theta(max)= 44.695
R(reflections)= 0.0929( 10264)      wr2(reflections)= 0.3044( 18700)
S = 1.000                          Npar= 1461
checkCIF/PLATON report

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

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<td>R -3 : h</td>
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<td>Hall group</td>
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<td>-R 3</td>
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Data completeness = 0.983  Theta(max) = 38.861
R(reflections) = 0.0905 (3407)  wR²(reflections) = 0.2651 (4176)
S = 1.092  Npar = 521
checkCIF/PLATON report

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

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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
checkCIF/PLATON report

Structure factors have been supplied for datablock(s) eric354_sq

**THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW procedure for publication, it should not replace the expertise of an experienced crystallographic referee.**

No syntax errors found. CIF dictionary Interpreting this report

**Datablock: Cr12(Br-phenyl-cdc)12**

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

Cell:

\[
\begin{align*}
    & a=42.1022(12) & b=27.7671(8) & c=37.031(1) \\
    & \alpha=90 & \beta=104.5652(14) & \gamma=90 \\
\end{align*}
\]

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 C240 H120 Br12 Cr12 N12
O60 [+] solvent] O60
Sum formula C240 H120 Br12 Cr12 N12 C240 H120 Br12 Cr12 N12
O60 [+] solvent] 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
checkCIF/PLATON report

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 Å  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]
Sum formula  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
**checkCIF/PLATON report**

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 Å  
Wavelength=1.54178

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Temperature: 150 K

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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
checkCIF/PLATON report

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:**

\[a=21.265(2) \quad b=21.265(2) \quad c=69.250(8)\]

\[\alpha=90 \quad \beta=90 \quad \gamma=120\]

**Temperature:**  200 K

**Volume**  Calculated  Reported

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
### Datablock: Cu12(phenyl-cdc)12

**Bond precision:** C-C = 0.0202 Å

**Cell:**
- \( a = 20.2176(8) \) Å
- \( b = 22.8067(8) \) Å
- \( c = 40.8077(14) \) Å
- \( \alpha = 90^\circ \)
- \( \beta = 100.344(2)^\circ \)
- \( \gamma = 90^\circ \)

**Temperature:** 200 K

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<td>-P 2ybc</td>
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</tr>
<tr>
<td>Tmin, Tmax</td>
<td>0.632, 0.751</td>
</tr>
</tbody>
</table>

**Correction method:** # Reported \( T \) Limits: \( T_{\text{min}}=0.632 \) \( T_{\text{max}}=0.751 \)

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
3) Apex3; Bruker AXS Inc.: Madison, WI, 2015.