Electronic Supplementary Information

Selective Gas Sorption in a [2+3] 'Propeller' Cage Crystal

Shan Jiang, John Bacsa, Xiaofeng Wu, James T. A. Jones, Robert Dawson, Abbie Trewin, Dave J. Adams and Andrew I. Cooper[a,]*

Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK

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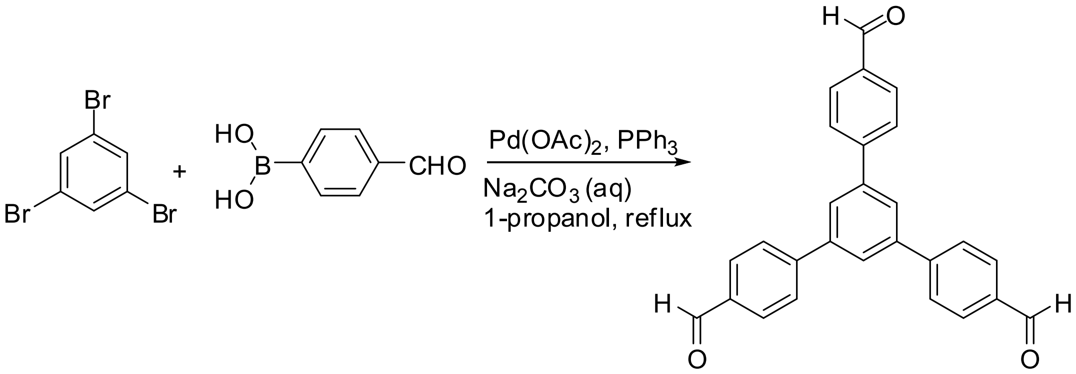
Experimental

Materials. 1,3,5-Tri-(4-formylphenyl) benzenewas prepared by standard literature procedures (see below). All other chemicals were purchased from Sigma-Aldrich and used as received.

Synthesis of 1,3,5-tri-(4-formylphenyl) benzene:



Scheme 1

1,3,5-Tri-(4-formylphenyl) benzene (**1**) was synthesized by a Suzuki coupling reactionand was scaled up by using ChemSpeed SLT106 system to perform multiple parallel reactions.

Synthesis procedure: An oven-dried 150 mL, two-necked round-bottom Radley flask equipped with a magnetic stir bar was flushed with N_2 gas and cooled to room temperature under a N_2 flow. Tribromobenzene (1 g, 3.18 mmol), 4-formylphenylboronic acid (1.72 g, 11.5 mmol), $Pd(OAc)_2$ (3 mg, 0.013 mmol), and PPh_3 (6 mg, 0.026 mmol) were added. After degassing this mixture three times, 1-propanol (20 mL) was added under N_2. The solution was left stirring at 50 °C until all of the solids dissolved. Once the clear solution turned to pale yellow (*ca.* 15 min), a solution of Na_2CO_3 (2M, 6 mL) and water (5 mL) were added under N_2. The resulting mixture was then heated to reflux for 2 h under N_2. The nitrogen sources were removed after reflux and another portion of water (20 mL) was added. The reaction mixture was left under stirring, open to the air for 5 h at room temperature. The mixture was then extracted with chloroform (30 mL) and the organic layers were washed with a 2% solution of $NaHCO_3$ (25 mL). A spoonful of activated charcoal was added into the organic solution and the mixture was stirred for 30 min at room temperature. The suspension was filtered through celite under reduced pressure. Evaporation of the solvent gave the crude product. The pure product was obtained after column chromatography with 70 % yield, or recrystallized from THF with 65 % yield.

^{1}H NMR ($CDCl_3$, 400MHz) δ 10.11 (s, 3H, -CHO), 8.04-7.87 (m, 15H, -ArH) ppm.^{13}C NMR ($CDCl_3$) δ 191.76, 146.29, 141.60, 135.76, 130.44, 127.98, 126.48ppm.IR (KBr pellet, ν)3050 (w), 2811 (w), 2724 (w), 2351 (w), 1689 (s), 1600 (s), 1561 (s), 1392 (m), 1209 (s), 1167 (s), 857 (m), 815(m), 790 (s), 648 (w), 601 (w), 561(w) cm^{-1}.Accurate mass calculated for $C_{27}H_{18}O_3$: 390.13. Found: 391 $[M+H]^+$. Elemental analysis as $C_{27}H_{18}O_3$ (Calculated: C 83.06, H 4.65. Found: C 83.14, H 4.67). Melting point 230 – 232 °C (literature value 231 – 232 °C).[1]

[2+3] propeller cage (CC6) synthesis: Methanol (20 mL) was added to 1,3,5-tri-(4-formylphenyl) benzene (50 mg, 0.128mmol) in a sample vial at room temperature. A solution of 1,5-pentanediamine (20 mg, 0.192 mmol) in MeOH (20 mL) was added slowly. The reaction was left covered for 3-4 days without stirring. The products were observed to crystallize from solution after a week. The crystals were separated carefully from the sample vial using a spatula and washed with MeOH and air dried to give the solvated of [2+3] cage. The crystals suitable for X-ray crystallography were removed directly from the sample vial. To desolvate [2+3] cage, a sample was heated to 100 ˚C under dynamic vacuum for 12 hours. The yield after desolvation was 45 %.

^{1}H NMR ($CDCl_3$, 400MHz) δ 8.16 (s, 6H, CH=N), 7.51-7.28 (m, 30H, -ArH), 3.68(m, 12H,-NCH), 1.77(m, 12H, -CH_2), 1.32(m, 6H, -CH_2) ppm.^{13}C NMR ($CDCl_3$) δ 160.95, 142.13, 141.12, 134.97, 128.10, 126.82, 124.40 ppm. IR (KBr pellet, ν) 3345 (m), 2939 (m), 2840(m), 1640(s), 1600(m), 1560(w), 1457(w), 1378(w), 1304(w), 1220(w), 1018(w), 925(w), 819(s), 617(w), 531(m)cm^{-1}.Accurate mass calculated for $C_{69}H_{66}O_6$: 978.53. Found: 979.49 $[M+H]^+$ and 1001.48 $[M+Na]^+$.

Characterization and Analysis

NMR. Solution ^{1}H NMR spectra were recorded at 400.13 MHz using a BrukerAvance 400 NMR spectrometer. ^{13}C NMR spectra were recorded at 100.6 MHz.

Thermogravimetric Analysis. TGA analysis was carried out using a Q5000IR analyzer (TA instruments) with an automated vertical overhead thermobalance. The samples were heated at the rate of 5 °C /min.

Powder X-ray Diffraction. Powder X-ray diffraction data were collected on a PANalyticalX'pert pro multi-purpose diffractometer (MPD) in transmission Debye-Scherrer geometry operating with a Cu anode at 40 kV 40 mA. Samples were ground and mounted as loose powder onto a transparent film and spun at 2s/rotation. PXRD patterns were collected in 2 one hour scans with a step size of 0.013 degrees 2θ and scan time of 115 s/step over 5 – 50 deg 2θ. The incident X-ray beam was conditioned with 0.04 rad Soller slits and an anti-scatter slit of 1/2 deg. The diffracted beam passed through an automatic antiscatter slit (5 mm), 0.04 rad Soller slits and Ni filter before processing by the PIXcel detector operating in scanning mode. The data were also measured on a Bruker D8 advance diffractometer using monochromatic Cu Kα_1 radiation (λ = 1.54056 Å). Samples were mounted in 1.0 mm diameter special glass capillaries and recorded over 3 - 40 2θ.

Gas Sorption Analysis. All samples were tested with gases of the following purities: hydrogen (99.9995% - BOC gases), carbon dioxide (SCF grade – BOC gases) and methane (ultrahigh purity -BOC). Surface areas and pore size distributions were measured by nitrogen adsorption and desorption at 77.3 K using a Micromeritics ASAP 2020 volumetric adsorption analyzer. Samples were degassed at offline at 120 °C for 15 h under vacuum (10^{-5} bar) before analysis, followed by degassing on the analysis port under vacuum, also at 80 °C. Carbon dioxide isotherms were measured at 273 and 293K using a Micromeritics 2020 volumetric adsorption analyzer using the same degassing procedure.

Fourier Transform Infrared Spectroscopy (FTIR).IR spectra were collected on a Bruker Tensor 27 spectrometer. Samples were analyzed as KBr disks for 16 scans with a resolution of 4 cm^{-1}. Spectra were recorded in transmission mode.

Atomistic Simulations

Molecular models were generated from X-ray crystallographic data structure using Materials Studio 5.0 (Accelrys).Connolly surfaces were calculated by rolling a probe molecule across the substrate, the interface taken from the contact point of the probe molecule.[2]

X-Ray Crystallography

Data collection and refinement for solvated **CC6**:

Single crystal X-ray data were collected a Bruker APEX diffractometer, with 1.5 kW graphite monochromated Mo radiation. The detector to crystal distance was 60 mm and the temperature of the crystal 100K. Exposure times of 20 s per frame and scan widths of 0.3º were used throughout the data collection. The data collection was performed using three ω scans with different φ values yielding data in the range 1.3 to 25.7° with an average completeness of 97%. The frames were integrated with the SAINT v6.45a (Bruker (2005). SAINT V6.45a, BRUKER AXS Inc., Madison, WI, USA). A mult-scan absorption correction was carried out using the program SADABS V2008-1 (Bruker (2008). SAINT V6.45a, BRUKER AXS Inc., Madison, WI, USA). The structure was solved and refined with X-SEED (*J. Supramol. Chem.* **2001**, 1, 189-191), a graphical interface to SHELX (Sheldrick, G.M. (2008). ActaCryst. A64, 112-122).

The crystal structure is built from nearly planar 2+3 cage molecules. Two of the three aminopentyl linker molecules are disordered, and this disorder could be modeled effectively by splitting each of these atoms into 2 distinct sites and restraining the equivalent 1,2 and 1,3 bond distances to be similar. The site occupancies were free to refine but the populations refined to approximately 50% for each component.

Description of the crystal structure:

The cage molecule has pseudo 3-fold symmetry. The 3-fold symmetry of the triphenyl substituted phenyl ring is broken (Figure **S1 B**):

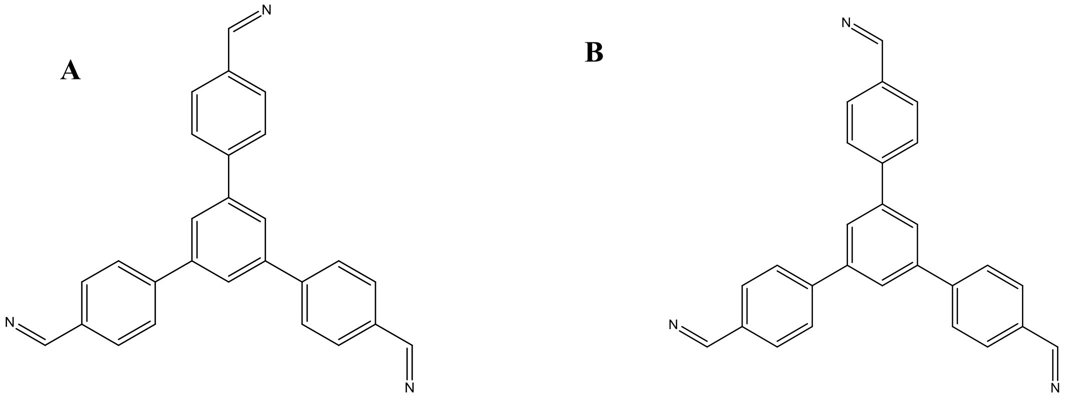
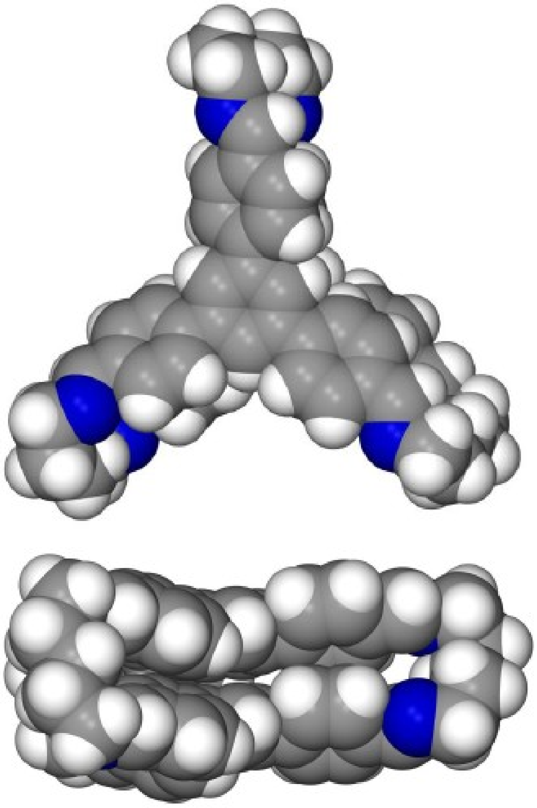


Figure S1. A) and **B)**. Three fold symmetrical and non-three fold symmetrical version, where the top C=N bond has been rotated by 120 degrees in **B**, hence breaking the symmetry.

Crystal and Refinement Data

$(C_{138}H_{132}N_{12})$, $6(CH_4O)$
$M = 2150.81$
colourless prism,
$0.50 \times 0.20 \times 0.05$ mm^3
orthorhombic, space group $Pca2_1$
$a = 26.055(4)$
$b = 15.571(2)$
$c = 14.686(2)$ Å
$V = 5958.3(14)$ Å^3,
$Z = 2$,
$D_c = 1.199$ g/cm^3
$T = 100(2)$K
19523 reflections collected, 10077 unique
$R_{int} = 0.0423$
Final $GooF = 0.949$
$R1 = 0.0556$
$wR2 = 0.1160$
780 parameters, 439 restraints
$\mu = 0.073$ mm^{-1}



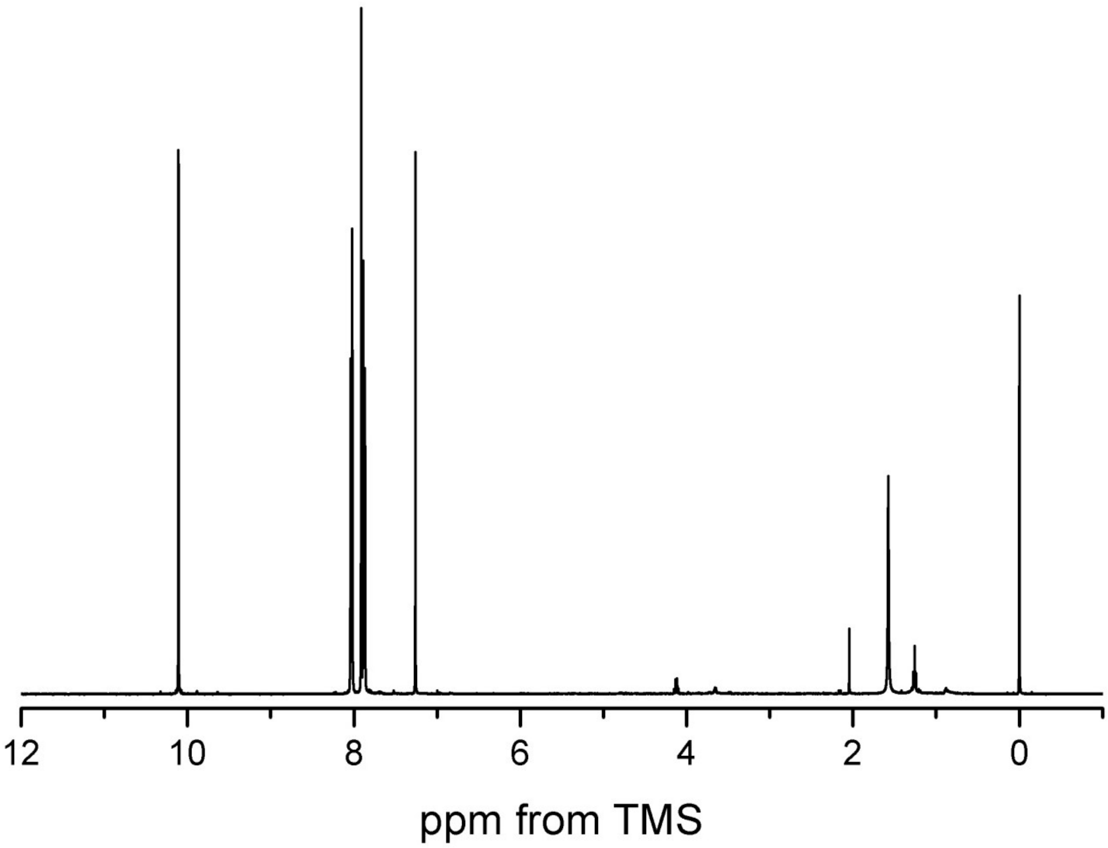


Figure S2.^{1}H NMR ($CDCl_3$) spectra for 1,3,5-tri-(4-formylphenyl) benzene

(δ 4.12 , 2.05 , 1.06 is EtOAc solvent ; δ 1.6 is H_2O solvent)

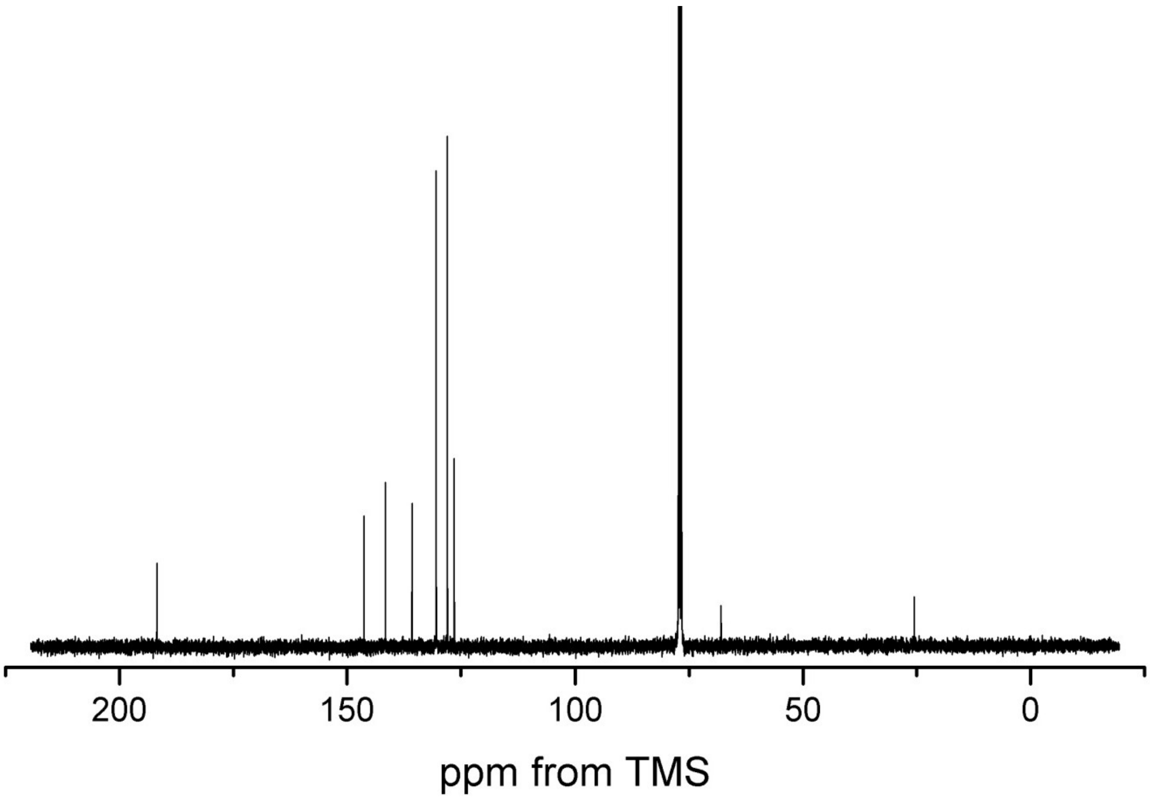


Figure S3. ^{13}C NMR ($CDCl_3$) spectra for 1, 3, 5-tri-(4-formylphenyl) benzene

(δ 26 , 68 are THF solvent)

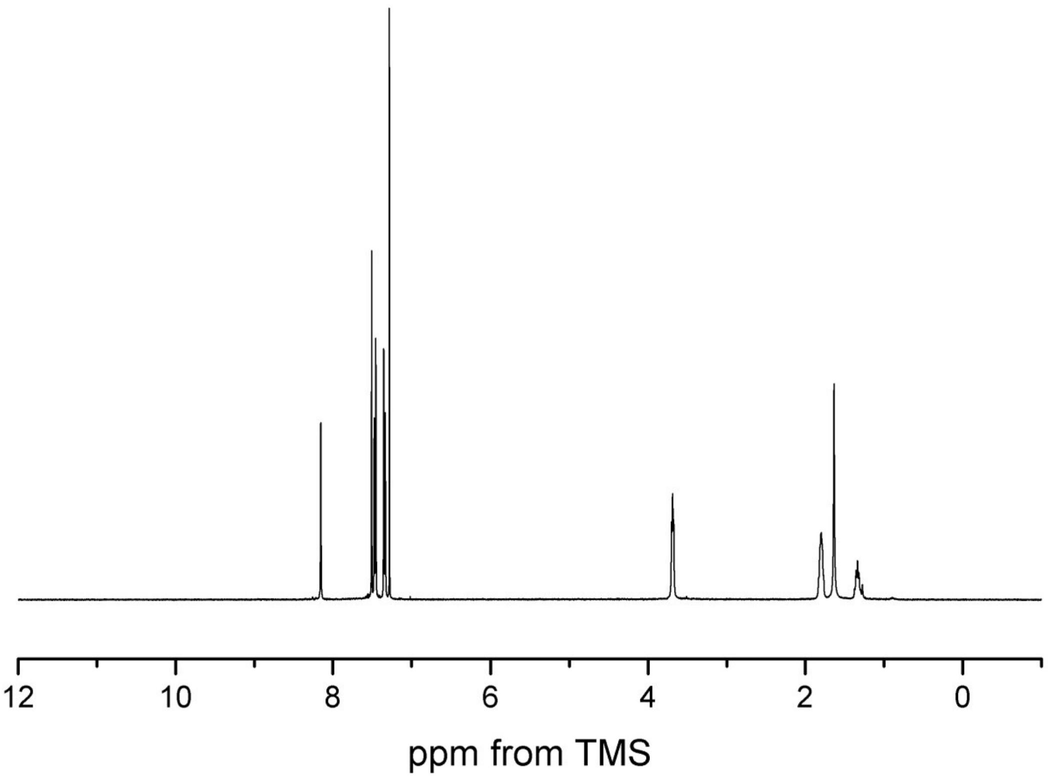


Figure S4. ^{1}H NMR ($CDCl_3$) spectra for [2+3] propeller cage **CC6** after gas sorption (δ 1.6 is H_2O)

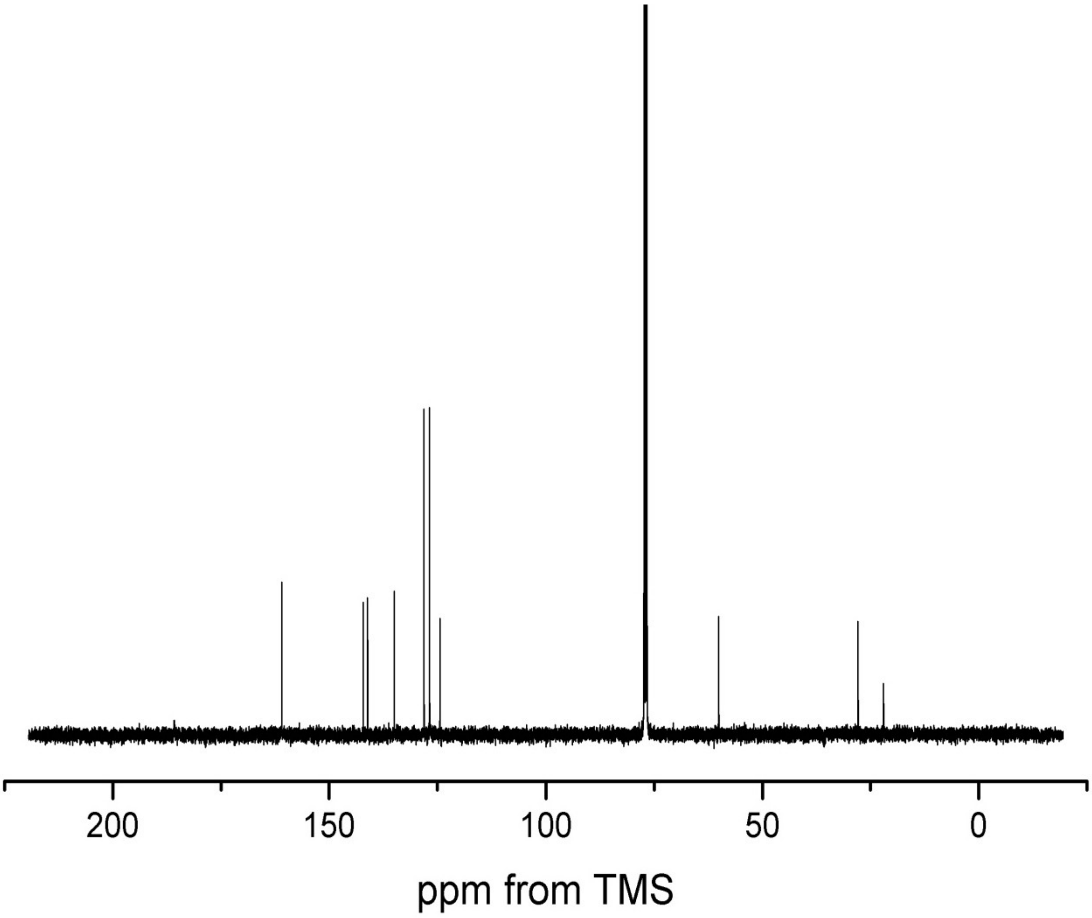


Figure S5. ^{13}C NMR ($CDCl_3$) spectra for [2+3] propeller cage, **CC6**

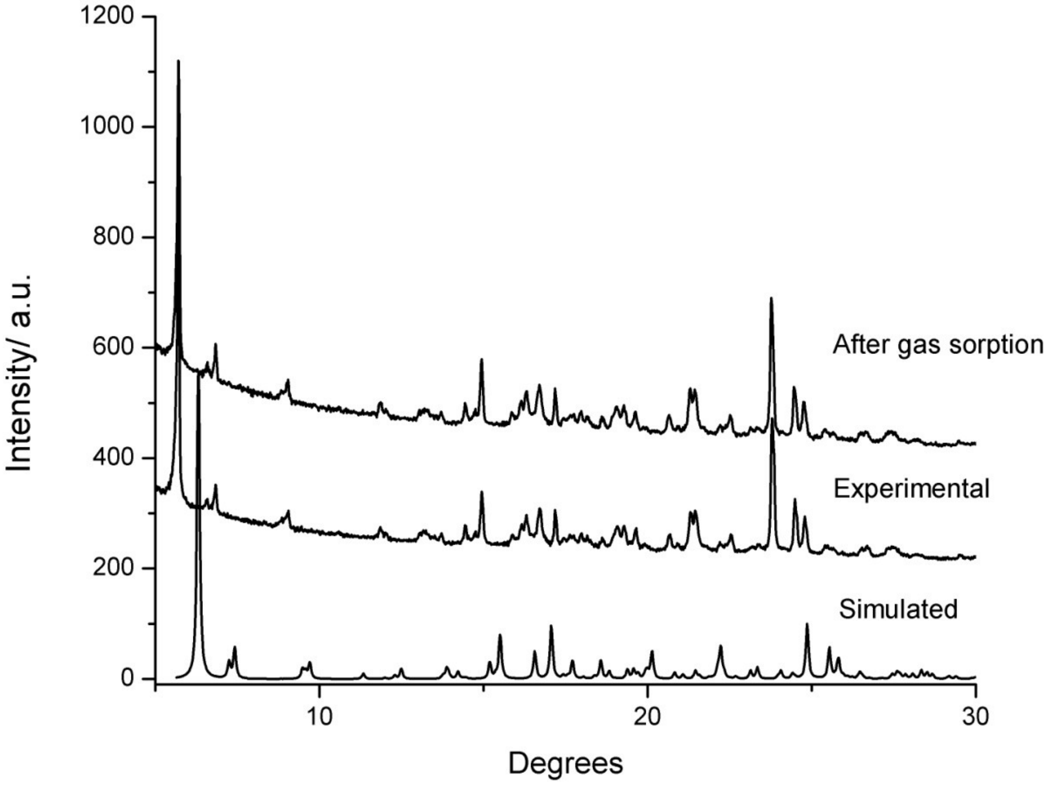


Figure S6. Powder X-ray diffraction patterns for **CC6** recorded for the bulk sample as-synthesized before (middle) and after (top) gas sorption. The simulated PXRD from the single crystal structure for **CC6** is shown as a comparison (bottom). Note that the experimental PXRD data were collected at ambient temperature while the single crystal X-ray data used to produce the simulated pattern were collected at cryogenic temperatures; this leads to a shift in peak positions between the experimental and calculated datasets.

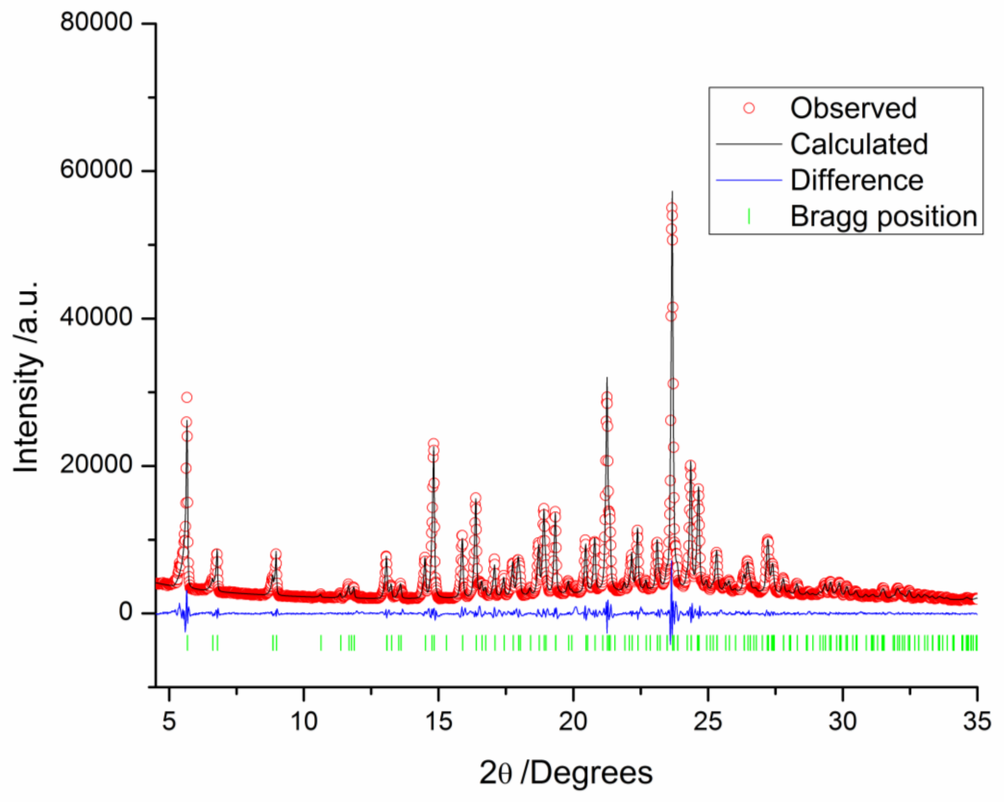


Figure S7. Le Bail fitting for **CC6.** Orthorhombic, Pca21 *a* = 26.00(1) Å, *b* = 15.545(1) Å, *c* = 15.0133(8) Å, *V* = 6068(7) Å^3. Agreement factors R_{wp}= 5.63 %, R_{exp} = 1.46 %, R_p = 4.02 %, *GoF* = 3.85.

Lattice constants from single crystal data measured at 100 K: *a* = 26.055 (4), *b* = 15.571(2), *c* = 14.686(2) Å, *V* = 5958.3(14) Å^3

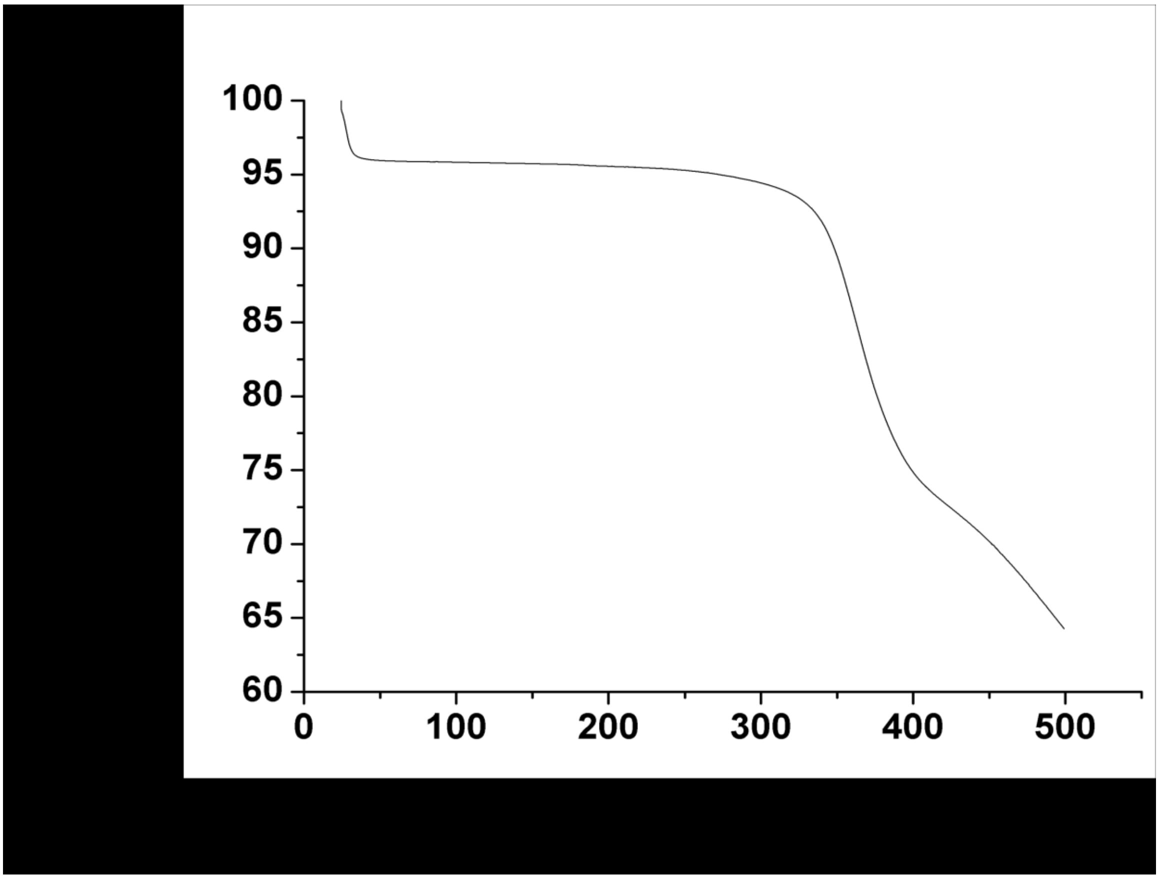


Figure S8. Thermogravimetric (TGA) data for [2+3] propeller cage **CC6**. The heating rate wass 5 °C min^{-1} under a nitrogen flow. The onset of decomposition for **CC6** occurs at approximately 350 ˚C.

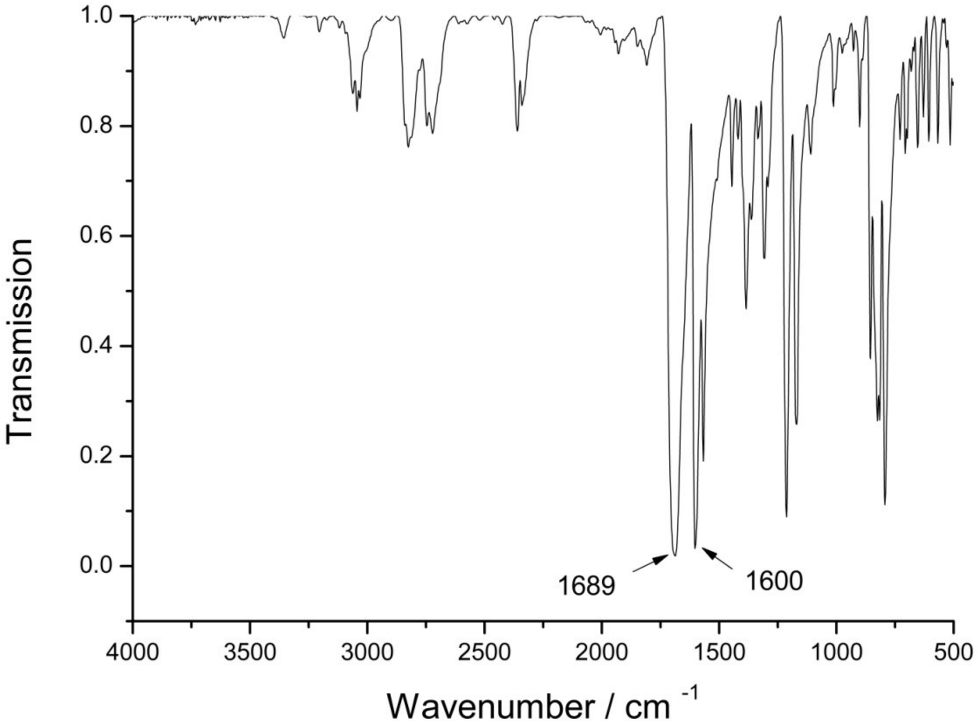


Figure S9. FTIR spectroscopy for 1,3,5-tri-(4-formylphenyl)benzene showing a strong C=O stretch at 1689 cm^{-1} and **H-C**=O stretch at 2820-2710 cm^{-1}.

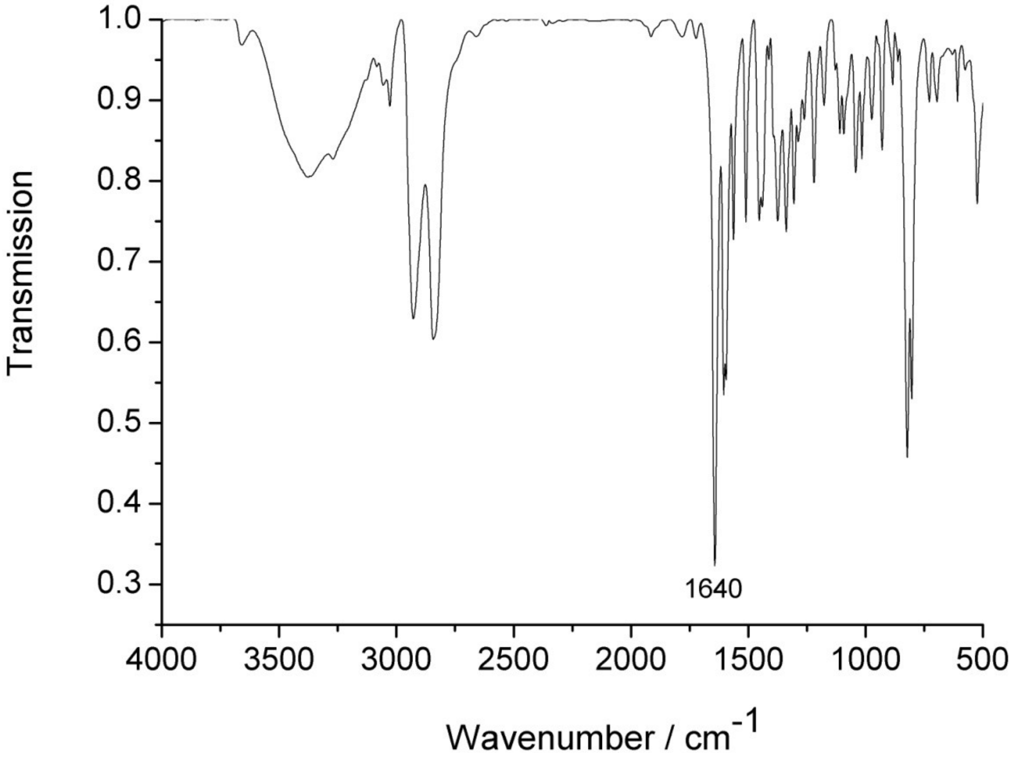


Figure S10. FTIR spectroscopy for **CC6** showing a strong imine stretch at 1640 cm^{-1}.

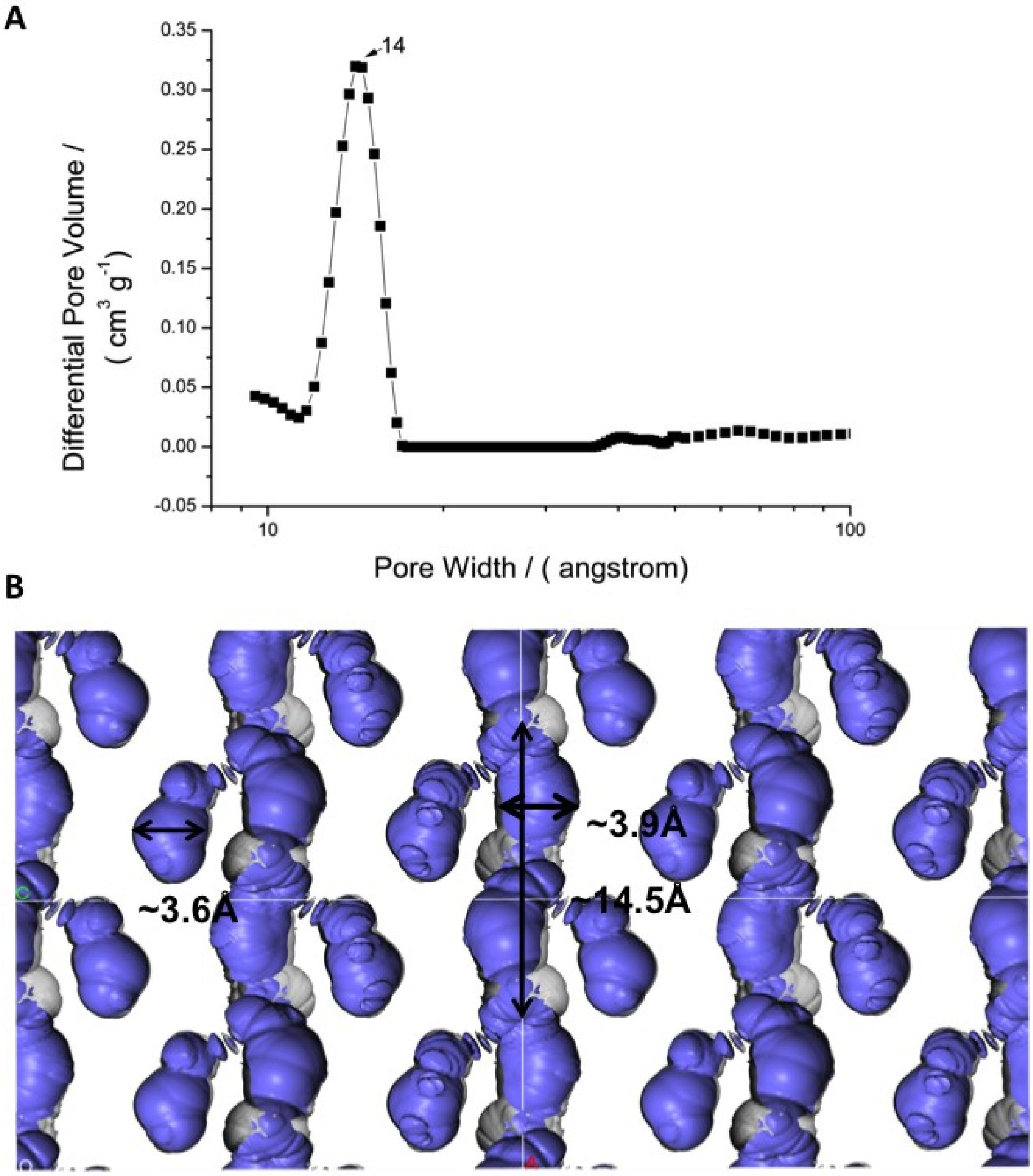


Figure S11. **(A)** Pore size distributions as calculated by application of non-local density functional theory (NL-DFT) analysis to N_2 adsorption isotherms obtained at 77 K. (B) The diameter of the 1-D pore channels based Connolly surfaces was calculated using a probe radius of 1.82 Å to be ~ 3.9 Å. The diameter of side pores is ~ 3.6 Å. An approximate pore channel length of 14.5 Å can be defined as the distance between two necks in the continuous 1-D channels; this is consistent with the measured pore size distribution of 14 Å based on the N_2 isotherm.

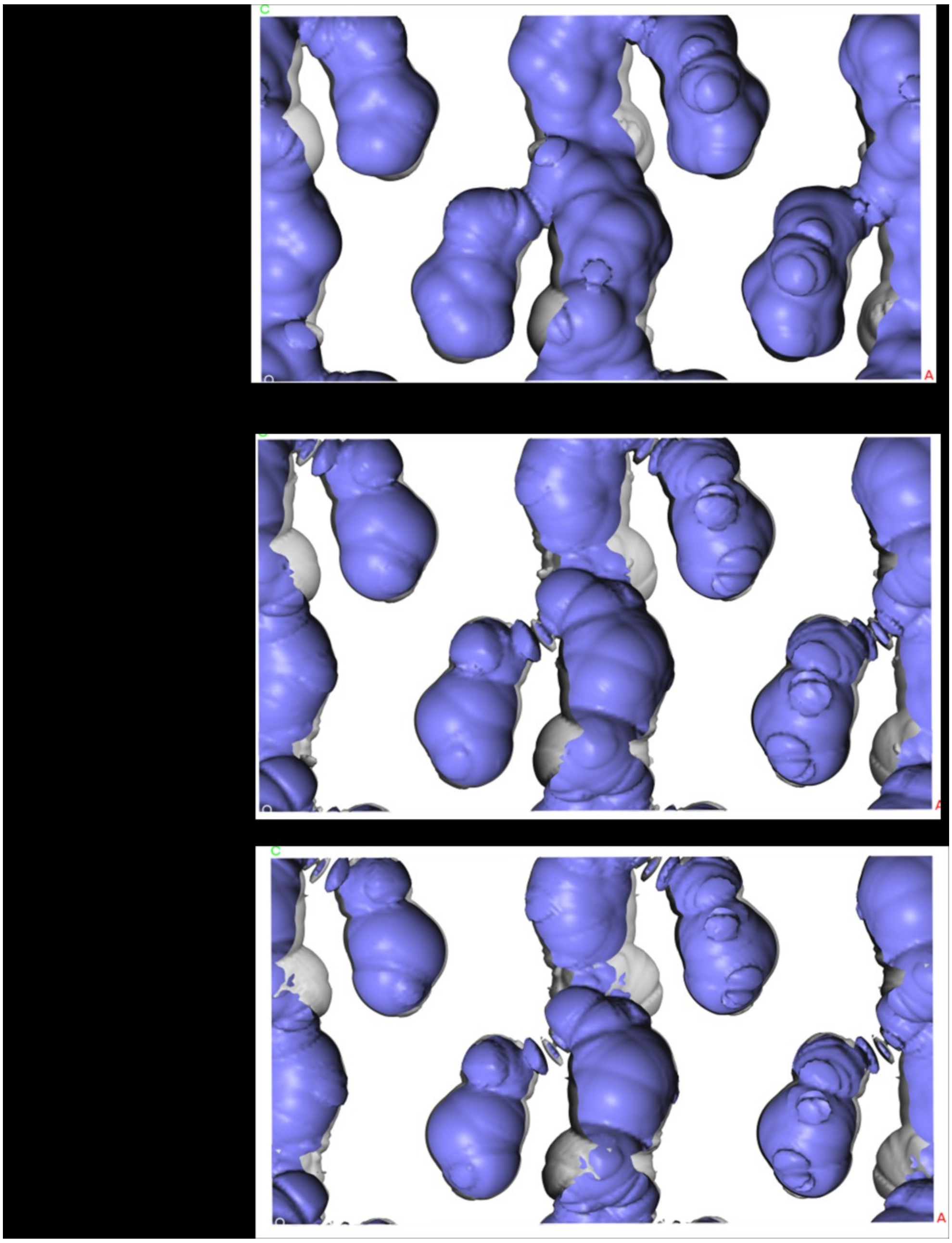


Figure S12 Connolly surfaces generated using probe radii of 1.42 Å, 1.72 Å, and 1.82 Å for H_2 (**top**), CO_2 (**middle**), and N_2 (**bottom**), respectively. The Connolly surface constructed using a H_2 probe radius of 1.42 Å shows a 1-D channel with a fully connected 'side pore' (top). Using a probe radius of 1.72 Å for CO_2, a 1-D channel was observed but a narrow restricted neck to this side pore was observed (middle). The Connolly surface obtained using with a N_2 probe radius of 1.82 Å also demonstrated a narrow, restricted 1-D channel, but in this case the 'side pore' was not connected to the channel (bottom).

Compound	N_2 uptake (cm^3/g)	CO_2 uptake (cm^3/g)	Ideal selectivity (CO_2/N_2)	Reference
CC1β[a]	4.26	33.15	8	2
CC2 [a]	7.17	38.08	5	4
CC3 [a]	4.26	30.91	7	4
CC4 [a]	4.03	33.38	8	
CC5 [a]	4.48	32.48	7	
CC6 [b]	1.79	20.16	11	
ZC1 [c]	0.033	3.32	100	5
ZC2 [c]	0.065	4.35	67	5
ZC3 [c]	0.157	5.58	36	5
ZC4 [c]	0.016	2.27	138	5
ZC2'[c]	0.117	4.56	39	5
ZC13 [c]	0.104	3.95	38	5
ZC14 [c]	0.127	8.01	63	5
ZIF95 [d]	1.68	21.28	13	6
ZIF100 [d]	1.79	19.5	11	6
MIL102 [e]	4.48	47.04	11	7
Post-synthesized MOF 3 [f]	1.12	14.18	13	8
Post-synthesized MOF 4 [f]	3.584	31.36	9	8
Post-synthesized MOF 5 [f]	1.12	15	13	8

[**a**] Measured at 300 K, 1 bar; [**b**] at 300 K, 1.2 bar; [**c**] at 293 K, 1bar; [**d**] at 298 K, 1.13bar; [**e**] at 304 K, 1bar [**f**] at 298 K, 1bar

Table S1. Summary of CO_2uptake, N_2 uptake and ideal selectivity (CO_2/N_2) in selected porous materials

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