High Capacity Gas Storage by a 4,8-Connected Metal-Organic Polyhedral Framework

Chenrong Tan, Sihai Yang, Xiang Lin, Alexander J. Blake, William Lewis, Neil R. Champness* and Martin Schröder*

School of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD (UK)
Fax: +44 115 9513563; Tel: +44 115 9513491; E-mail: M.Schroder@nottingham.ac.uk, Neil.Champness@nottingham.ac.uk
1. Experimental section.

1.1 Materials and Measurements.

All reagents and solvents were purchased from commercial suppliers and used without further purification. Nuclear magnetic resonance (NMR) spectra were collected on a Bruker DPX300 NMR spectrometer. Mass spectra (MS) were measured on a LC-TOF spectrometer in ESI model. Elemental analyses (C, H, and N) were carried out on a CE-440 elemental analyzer. Thermal gravimetric analyses (TGA) were performed under nitrogen flow (100 ml/min) with a heating rate of 5 °C/min using a TA SDT-600 thermogravimetric analyzer. Fourier transform infrared spectroscopy (FTIR) spectra were recorded using a Nicolet Avatar 360 FT-IR spectrophotometer in the 4000–400 cm⁻¹. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 4-50° on a Philips X’pert diffractometer using Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 40mA.

1.2 Synthesis of H₈L.

To a mixture of 4,4’,4”’,4”’”-tetrabromotetraphenyl methane (0.636g, 1.0mmol), 3,5-di(ethoxycarbonyl)phenylboronic acid (1.6 g, 6.0 mmol) and Cs₂CO₃(1.792 g, 3.0 mmol) in EtOH (40 cm³) under N₂ was added Pd(PPh₃)₄ (0.023 g, 0.02 mmol). The mixture heated with stirring at 80°C for 3 days under N₂. The resultant mixture was evaporated to dryness, extracted with CHCl₃ and dried over MgSO₄. The solution was evaporated to dryness and the crude product was washed with EtOH and hydrolysed by heating in aqueous 2M NaOH at 100°C overnight. The solution was filtered and the filtrate acidified with 36% HCl (Scheme 1s) to precipitate the product as a white solid. The product was collected and dried. Yield: 0.72 g 74%. Elemental analyses (% calc/found) for H₈L (C₅₇H₃₆O₁₆): C 70.08/70.18, H: 3.71/3.63. ¹H NMR (300MHz, DMSO-D6): 8.45(s, 4H), 8.40(s, 8H), 7.75(d, 8H), 7.40(d, 8H). MS (ESI) M/Z (%) = 975.89 [M-1] (100%).
1.3 Preparation of metal complex NOTT-140.

H$_8$L (10.0 mg, 0.01024 mmol) and Cu(NO$_3$)$_2$·2.5H$_2$O (25.0 mg, 0.1075 mmol) were mixed and dispersed in DMF/1,4-dioxane/H$_2$O (7 ml, 3:3:1 v/v/v) in a pressure tube. The resulting blue-green slurry turned clear upon addition of five drops of 10% HCl solution. The pressure tube was sealed and heated at 80°C for 3 days. The blue crystalline product was washed DMF and dried briefly in air. Yield: 17.3 mg (75%).

Elemental analysis (% calc/found) for C$_{91}$H$_{130}$Cu$_4$N$_{10}$O$_{40}$: C 48.40/48.44; H 5.80/5.84; N 6.20/6.20. IR (KBr) cm$^{-1}$: v= 3422(s), 2928(m), 1654(vs), 1570(s), 1509(m), 1415(m), 1370(s), 1300(w), 1104(m), 1017(w), 923(w), 827(m), 773(m), 666(w).
1.4. X-ray single crystal diffraction.

Crystal data for NOTT-140: C_{91}H_{130}Cu_{4}N_{10}O_{40}, M = 2258.21, tetragonal, space group \textit{P4/nnc}, a = b = 18.900(3) Å, c = 33.561(7) Å, V = 11988(3) Å³, Z = 4, T = 120(2) K, F_{000} = 4728, d = 1.251 g cm^{-3}, \mu = 0.779 mm^{-1}, 51240 reflections measured, 3660 unique (R_{int} = 0.194) which were used in all calculations. Final R_{1} = 0.046, wR_{2} = 0.077, Goof = 1.00, maximum \Delta F peak 0.24 e Å^{-3}. The final formula was calculated from the SQUEEZE results combined with elemental analysis data and TGA data.

Single crystal X-ray diffraction data for NOTT-140 were collected at 120(2) K on Beamline I19 at Diamond Light Source. The crystal structure was solved by direct methods and refined by difference Fourier techniques and using the SHELXTL software package.\textsuperscript{1} Hydrogen atoms on the ligand were placed geometrically and refined using a riding model. The hydrogen atoms of coordinated water molecules could not be located, but are included in the formula. The unit cell includes a large region of disordered solvent molecules, which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE\textsuperscript{2} to calculate the contribution to the diffraction from the solvent regions and thereby producing a set of solvent-free diffraction intensities. The final formula was calculated from elemental analysis data combined with TGA analysis: the contents of the solvent region are therefore included in the unit cell contents but not in the refinement model. Details are included in CIF format as part of the Supplementary Information.
2. Views for X-ray crystal structure for NOTT-140.

![Figure S1: View of the packing diagram for NOTT-140 viewed along crystallographic a-axis. (Cu: blue, O: red, C: grey, H and water molecules are omitted for clarity, void for cage A: purple, void for cage B: orange).]
Figure S2: View of the packing of the octahedral and cuboctahedral cages in the framework structure for NOTT-140.

3. TGA plot and powder X-ray diffraction for NOTT-140.

The unco-ordinated solvent molecules in NOTT-140 can be readily exchanged for acetone and/or removed by heating at 100°C either under a flow of N₂ gas or in vacuo. TGA measurements show that the as-synthesised sample loses solvent slowly between 20 and 100°C (Figure S3). The weight loss of 48.0% from NOTT-140 correlates with solvent loss based upon 2.5 DMF, 0.25 1,4-dioxane and 2 water molecules per copper. The volatility of crystallization solvents in the samples contributes to the discrepancies between room temperature and 300°C. Powder X-ray diffraction confirms the phase purity for the bulk materials (Figure S4).
Figure S3: TGA plot of NOTT-140

Figure S4: Comparison of PXRD patterns of simulated, as-synthesised and activated samples for NOTT-140.

H₂, CO₂ and CH₄ isotherms (0-20 bar) were recorded at 77 K (liquid nitrogen) or 87 K (liquid argon) or 283 and 293 K using a temperature-programmed water bath on an IGA-003 system (Hiden Isochema, Warrington, UK) at the University of Nottingham under ultra high vacuum in a clean system with a diaphragm and turbo pumping system. Ultra-pure plus grade (99.9995%) H₂, CO₂ and CH₄ were purchased from BOC and purified further using calcium aluminosilicate and activated carbon adsorbents to remove trace amounts of water and other impurities before introduction into the IGA system. Powder samples were loaded into the IGA and degassed at 100 °C and 10⁻¹⁰ bar for 1 day to give the desolvated samples. In a typical procedure, ~80 mg of dry sample was used for the measurements. The density of desolvated sample used in buoyancy corrections was 1.70 g cm⁻³ for the complex in this study. This was estimated from the crystallographic density of the desolvated sample and PLATON/SQUEEZE² result. The density of bulk H₂ at 77 K in the buoyancy correction was calculated by the Redlich-Kwong-Soave equation of state of H₂ incorporated in the IGASWIN software of the IGA system. The density of liquid H₂ at the boiling point (0.0708 g cm⁻³) was used for the adsorbate buoyancy correction.

N₂ and Ar adsorption data were recorded at 77K (liquid nitrogen) or 87K (liquid argon) (Figure S5) on an Autosorb-1c instrument at the University of Nottingham under ultra high vacuum in a clean system with a diaphragm and turbo pumping system. Ultra-pure research grade (99.9999%) N₂ and high-purity (99.999%) Ar were purchased from BOC. The BET surface areas and pore size distribution was calculated by using the software (version 1.60) integrated in the instrumentation. Pore size distribution (PSD) data and cumulative pore volume were determined by analysis of the Ar isotherm at 87 K using a non-local density functional theory (NLDFT) implementing a hybrid kernel based on a zeolite/silica model containing cylindrical and spherical pores as implemented in the Autosorb1 software package (Figure S6).³
Figure S5: Gas sorption isotherms for NOTT-140; N₂ at 77 K, Ar at 87 K and H₂ at 77 K up to 1.0 bar.

Figure S6: Pore size distribution (left axis, red curve) and cumulative pore volume (right axis, blue curve) for NOTT-140, calculated from a NLDFT fit to the Ar adsorption data.
5. Analysis of isosteric adsorption enthalpy.

The isosteric heat of adsorption $Q_{st}$ was determined by Virial Method equation (1) from H$_2$ adsorption isotherms at 77 K and 87 K, CO$_2$ adsorption isotherms at 283 K and 293 K AND CH$_4$ adsorption isotherms at 283 K and 293 K (Figure S7).

$$\ln(p) = \ln(n) + \frac{1}{T} \sum_{i=0}^{m} a_i n^i + \sum_{j=0}^{n} b_j n^j$$  \hspace{1cm} (1)

where $p$ is the pressure expressed in mbar, $n$ is the amount adsorbed in mmol/g, $T$ is the temperature in K, $a_i$ and $b_j$ are virial coefficients, and $m$, $n$ represent the number of coefficients. The values of the virial coefficients $a_0$ through $a_m$ were then used to calculate the isosteric heat of adsorption using equation (2). $Q_{st}$ is the coverage-dependent isosteric heat of adsorption and $R$ is the universal gas constant.

$$Q_{st} = -R \sum_{i=0}^{m} a_i n^i$$  \hspace{1cm} (2)

Isosteric adsorption enthalpies for H$_2$, CH$_4$ and CO$_2$ isotherms are shown in Figure S8.

Figure S7: Virial expression fitting graphs of (a) H$_2$ at 77 K (red) and 87 K (blue), (b) CH$_4$ and (c) CO$_2$ at 283 K (red) and 293 K (blue) adsorption data for NOTT-140. (a): fitting error=0.011, $R^2$=1.00, (b): fitting error=0.0079, $R^2$=1.00, (c): fitting error=0.014, $R^2$=1.00.
Figure S8: Isosteric heats of H₂, CH₄ and CO₂ adsorption for NOTT-140.

Figure S9: Gas sorption isotherms for NOTT-140. N₂ at 77 K, Ar at 87 K and H₂ at 77 K up to 1.0 bar.
References


