ELECTRONIC SUPPLEMENTARY INFORMATION

Highly Porous and Robust Scandium-based Metal-Organic Frameworks for Hydrogen Storage

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1. Experimental Section

1.1 Materials and Measurements

All reagents and solvents were used as received from commercial suppliers without further purification. Elemental microanalyses for C, H and N were carried out on a CE-440 elemental analyser at the University of Nottingham. Powder X-ray diffraction (PXRD) data were collected under both ambient and *in-situ* conditions on a Bruker AXS D8 Advance diffractometer operated at 40 kV and 40 mA (Cu $K\alpha_1$, λ= 1.5406 Å), with a heating rate of 2 °C/min and step size of 0.04 °/2θ. An MRI TCP-20 with PtRh strip heater was used for the *in-situ* variable temperature PXRD experiments. Thermogravimetric analysis (TGA) was performed under N_2 at a scan rate of 2 °C/min using a TA Universal Analysis 2000 system.

1.2 Synthesis of $\{[Sc_2(BPTC)(OH)_2] \cdot (H_2O)_{1.25}\}_\infty$ NOTT-400

Scandium triflate (0.030g, 0.061 mmol) and H_4BPTC (0.010 g, 0.030 mmol) were mixed in THF (4.0 ml), DMF (3.0 ml), water (1.0 ml) and HCl (36.5 %, 2 drops). The resultant slurry mixture was stirred until complete dissolution occurred. The solution was then placed in a pressure tube and heated in an oil bath to 75 °C for 72 h. The tube was cooled down to room temperature at a rate of 0.1 °C/min, and the colourless crystalline product was separated by filtration, washed with DMF (5.00 ml) and dried in air. Yield: 67.6 % (based on ligand). Elemental analysis corresponds to $Sc_2C_{16}H_{10.5}O_{11.25}$ %: Cal: C, 40.66; H: 2.24; found: C, 40.67; H, 2.26.

1.3 Synthesis of $\{[Sc(TDA)(OH)] \cdot (H_2O)_{2.6}\}_\infty$ NOTT-401

Scandium triflate (0.057 g, 0.116 mmol) and thiophene-2,6-dicarboxylic acid, H_2TDA, (0.01 g, 0.058 mmol) were dispersed in THF (4.0 ml), DMF (3.0 ml), H_2O (1.0 ml) and HCl (36.5 %, 2 drops) and sealed in a pressure tube. The clear solution was heated at 90 °C in an oil bath for 72 h. The tube was cooled to room temperature over a period of 12 h and the colourless crystalline product separated by filtration, washed with DMF (5.00 ml) and dried in air. Yield: 71.1 % (based on ligand). Elemental analysis data corresponds to $ScO_{7.6}C_6H_{8.2}S$%: Cal: C, 25.84; H, 2.75; found: C, 25.82; H, 2.72.

1.4 X-Ray Crystallography

Single crystal diffraction data for NOTT-400 were collected on Station 9.8 of the Synchrotron Radiation Source at STFC Daresbury Laboratory. Diffraction data for NOTT-401 were collected on Beamline I19 at the Diamond Light Source. The details for data collection are included in CIF files in the Supplementary Information. Structures were solved by direct methods and developed by difference Fourier techniques using the SHELXTL software package.[1] The hydrogen atoms on the ligand were placed geometrically and refined using a riding model. The unit cell volumes include a large region of disordered solvent which could not be modelled as discrete atomic sites. We employed PLATON/SQUEEZE[2] to calculate the contribution to the diffraction from the solvent region and thereby produced a set of solvent-free diffraction intensities. The final formulae were calculated from the SQUEEZE[2] results combined with elemental analytical data.
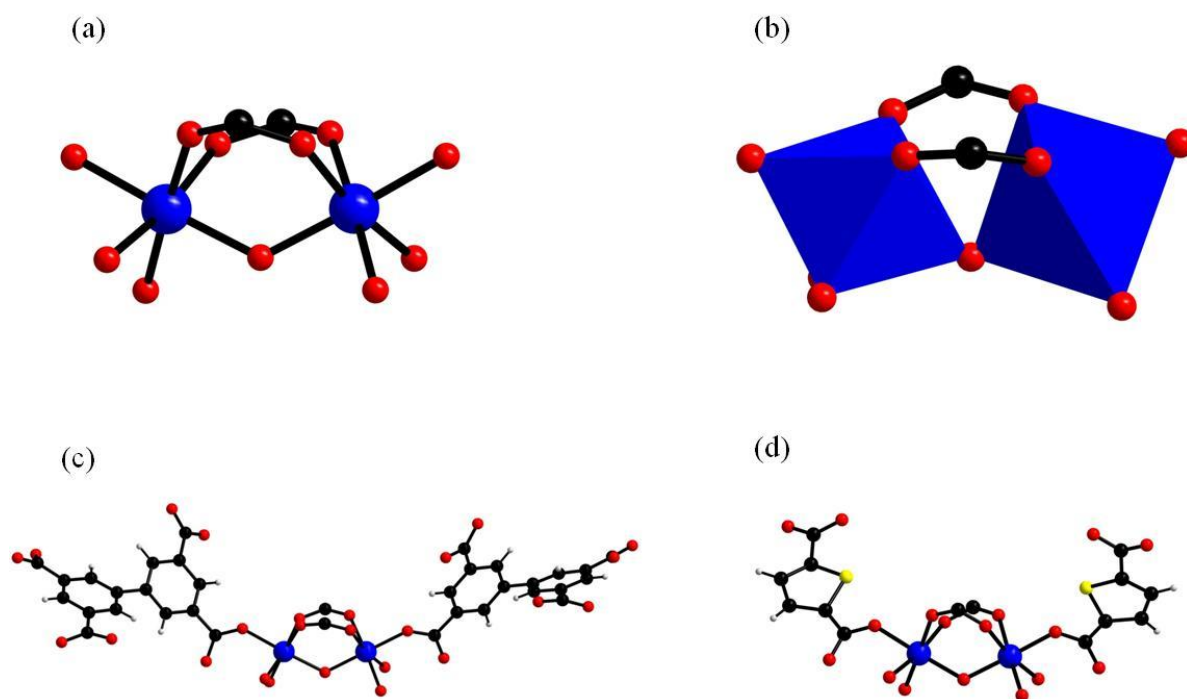

Figure S1: (a) The binuclear building block comprising two Sc(III) centres each with approximately octahedral geometry; (b) a polyhedral representation of the two Sc(III) octahedra sharing a μ_2-hydroxo group; (c) the binuclear building block of NOTT-400 showing the ligand [BPTC]$^{4-}$ coordinated to Sc(III) centres and (d) the building block of NOTT-401 showing the ligand [TDA]$^{2-}$ coordinated to Sc(III) centres (Sc blue, S yellow, O red, C black, H small grey spheres).

1.5 Nitrogen and hydrogen adsorption isotherms.

N_2 and H_2 isotherms were recorded on an IGA system (Hidden 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 grade (99.9995 %) H_2 was purchased from BOC and purified further using calcium aluminosilicate and activated carbon adsorbents to remove trace amounts of water and other impurities before introducing into the IGA system. The density of H_2 at 77 K in the buoyancy correction was calculated by the Redlich-Kwong-Soave equation of state of H_2 incorporated in the IGASWIN software of the IGA system. The surface area was calculated using the BET method based on adsorption data in the partial pressure (P/Po) range 0.06 to 0.22. The pore size distribution (PSD) was determined by applying the Dubinin-Astakhov analysis to the N_2 adsorption data analysis to the isotherm data.
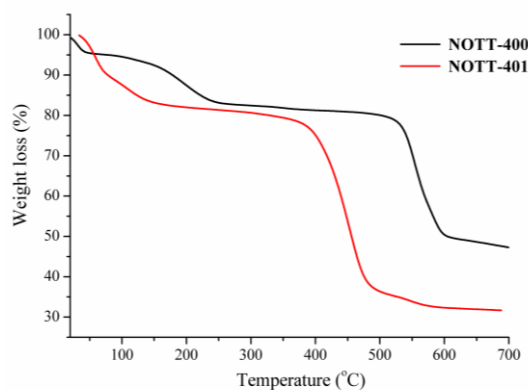
2. TGA plots

Figure 2S: TGA analysis of compounds NOTT-400 and NOTT-401.
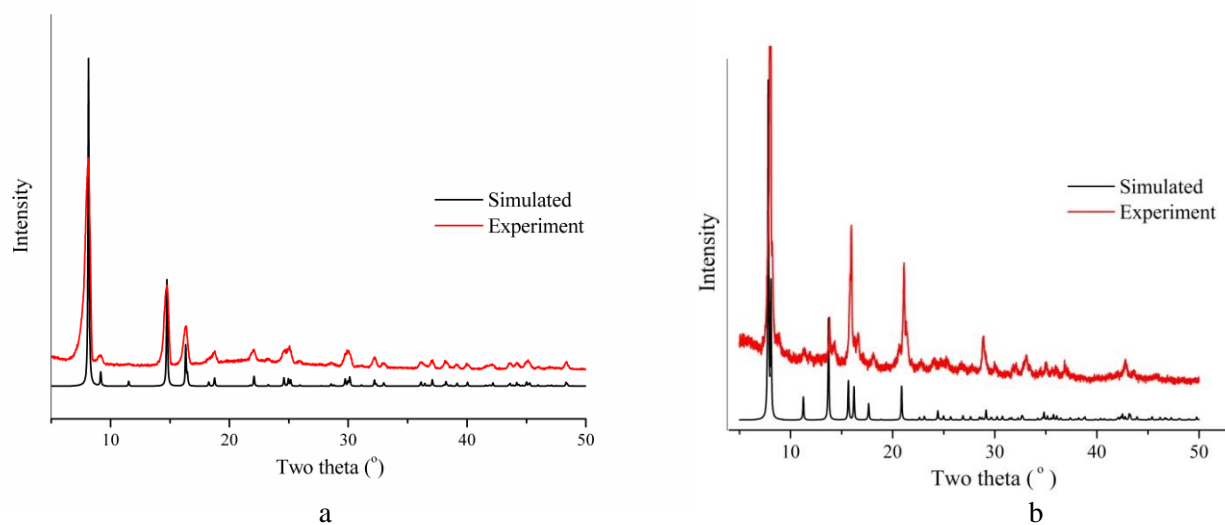
3. PXRD Patterns

a
b

Figure 3S: Experimental PXRD data and simulated pattern derived from the single crystal structures of (a) NOTT-400 and (b) NOTT-401.
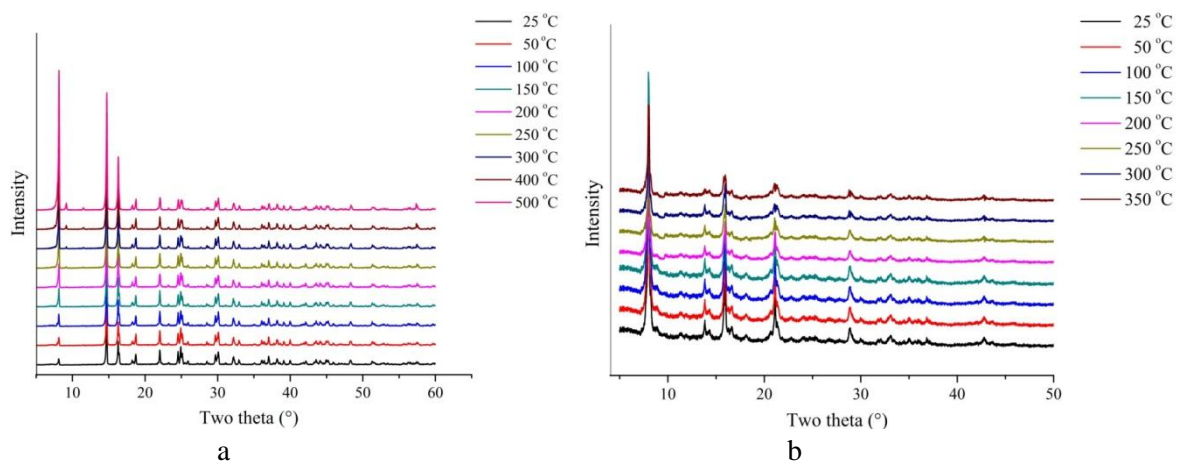

a
b

Figure 4S: *In situ* PXRD patterns for (a) NOTT-400 and (b) NOTT-401. Samples held for 5 mins at each temperature
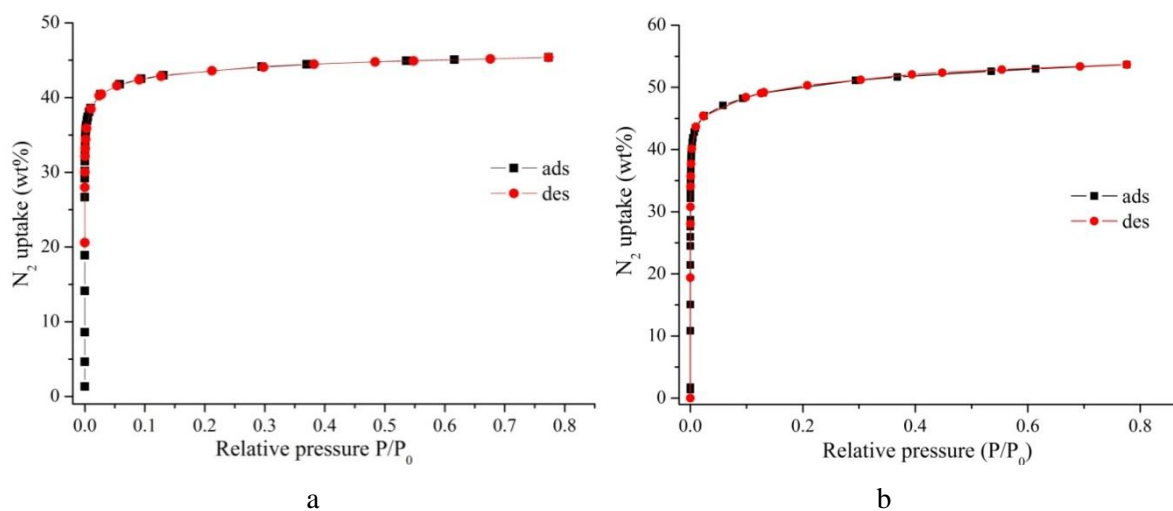
4. Nitrogen adsorption isotherms

Figure 5S: N$_2$ sorption isotherms for (a) desolvated NOTT-400a and (b) desolvated NOTT-401a at 77 K.
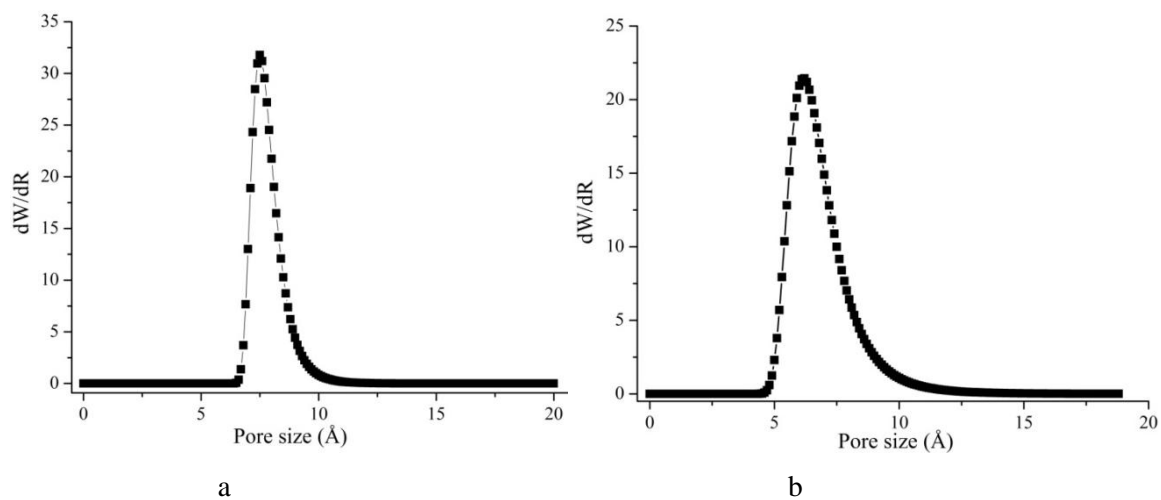
5. Pore Size Distribution Analysis

Figure 6S: Pore size distribution for (a) desolvated NOTT-400a and (b) desolvated NOTT-401a (b).

6. Derivation of the isosteric heats of H_2 adsorption.

Gravimetric H_2 adsorption was measured from 0-20 bar at 77K and 87K for desolvated NOTT-400a and NOTT-401a. All data were strictly corrected for the buoyancy of system, samples and absorbates. All the H_2 sorption isotherms show good reversibility and absence of hysteresis (Figures 7S). The H_2 adsorption kinetic data confirm that equilibrium is achieved within *ca.* 3 mins of the isotherm pressure step. These suggest a typical H_2 adsorption and exclude any significant effect due to the presence of impurities.
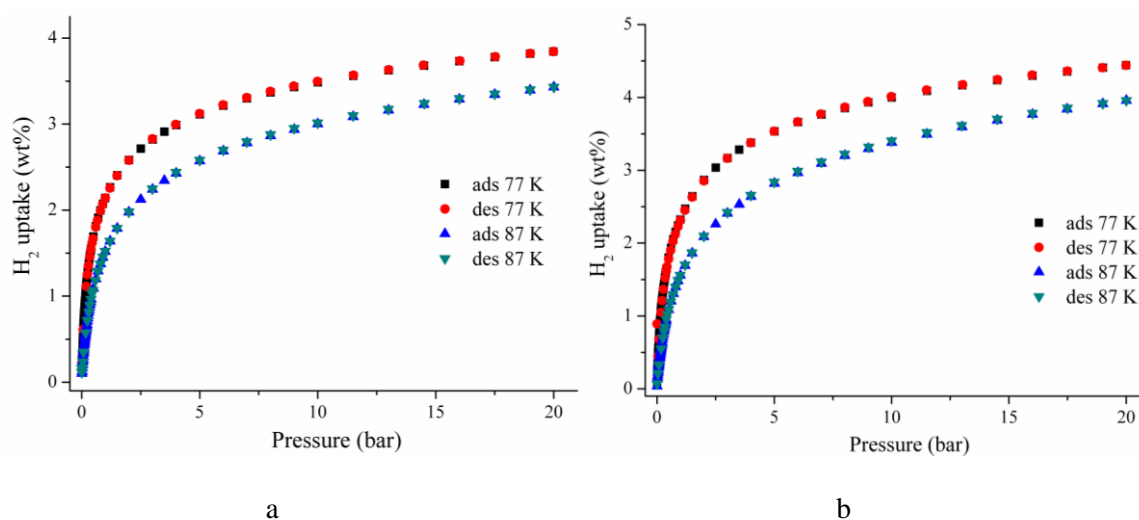

a
b

Figure 7S: H_2 isotherms for (a) desolvated NOTT-400a and (b) desolvated NOTT-401at 77 and 87 K.

The isosteric heats of H_2 adsorption were determined by fitting a virial-type equation to both 77 and 87 K adsorption isotherms. The $\ln(n/p)$ values for a given amount adsorbed (*n*) were calculated from the linear regressions from the virial equation analysis using the following virial equation:[3, 4]

$$ln(n/p) = A_0 + A_1n + A_2n^2\ldots \qquad (1)$$

where *p* is pressure, *n* is amount adsorbed and A_0, A_1 etc. are virial coefficients. A_0 is related to adsorbate-adsorbent interactions, while A_1 describes adsorbate-adsorbate interactions.[4] Henry's Law constant (K_H) is equal to $exp(A_0)$, and at low surface coverage, A_2 and higher terms can be ignored. A plot of $ln(n/p)$ versus *n* should give a straight line at low surface coverage.

Simulation of H_2 adsorption data at 77 and 87 K for NOTT-400a and NOTT-401a between 50 and 400 mbar using equation (1) are presented in Figures 8S and 9S, respectively. All the regression coefficients

were larger than 0.998, showing that the model fits the data very well. The virial method based on equation (1) is preferred at low pressure because the linearity in the low pressure part of the isotherm provides direct confirmation of the accuracy of the interpolations. The isosteric heats of adsorption for H_2 on desolvated NOTT-400a and NOTT-401b were calculated as a function of surface coverage. The estimated error in the measured isosteric enthalpies is 0.1 kJ/mol.
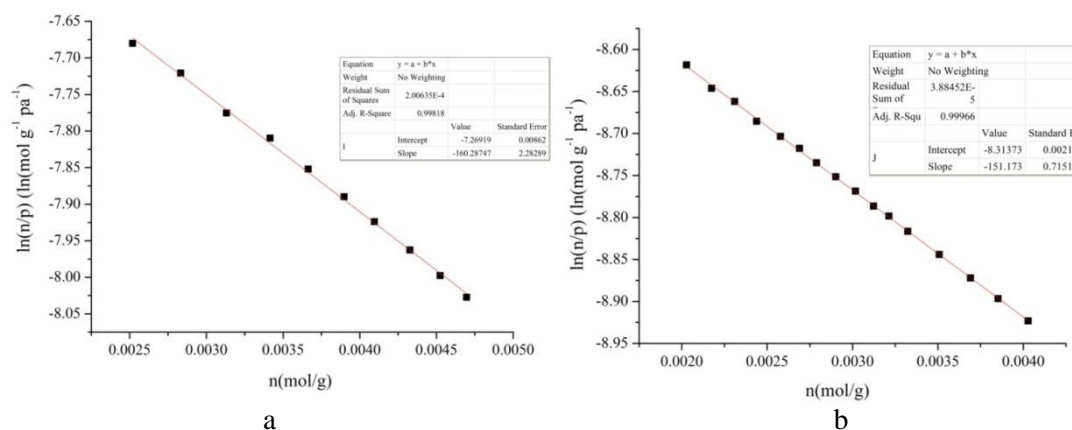

Figure 8S: Virial fitting plot for the adsorption of H_2 on NOTT-400a at 77 K (a) and 87 K (b).
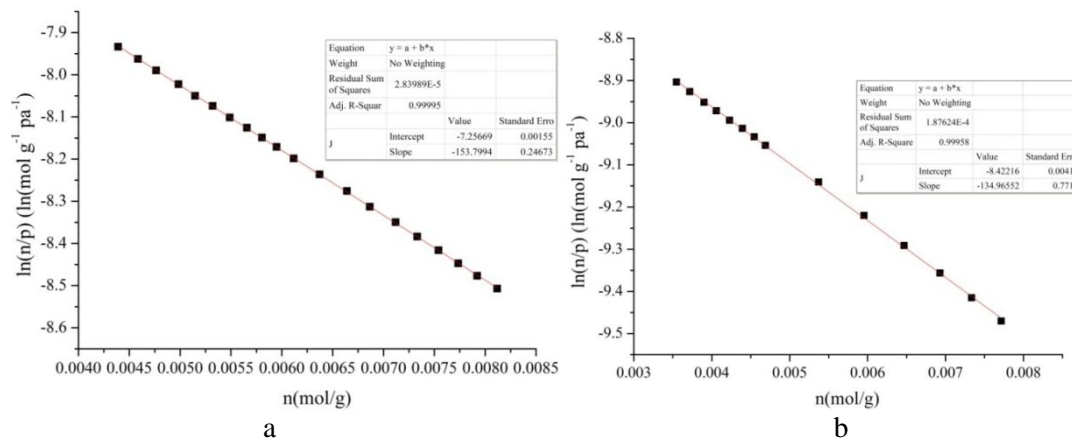

Figure 9S: Virial fitting plot for the adsorption of H_2 on NOTT-400a at 77 K (a) and 87 K (b).
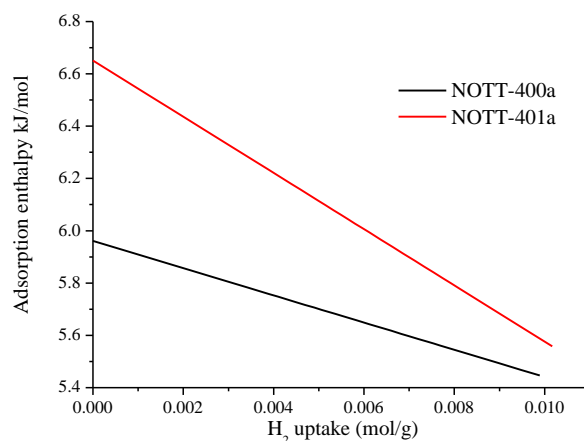
Figure 10S: Variation of adsorption enthalpy at low loading for NOTT-400a and NOTT-401a.

References:
1. G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112.
2. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; P.v.d. Sluis and A. L. Spek, *Acta Crystallogr.*, *Sect. A*, 1990, **46**, 194.
3. X. Zhao, S. Villar-Rodil, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2006, **110**, 9947; X. Zhao, B. Xiao, A. J. Fletcher and K. M. Thomas, *J. Phys. Chem. B*, 2005, **109**, 8880; I. P. Okoye, M. Benham and K. M. Thomas, *Langmuir*, 1997, **13**, 4054; C. R. Reid, I. P. OKoye and K. M. Thomas, *Langmuir*, 1998, **14**, 2415; C. R. Reid and K. M. Thomas, *Langmuir*, 1999, **15**, 3206; C. R. Reid and K. M. Thomas, *J. Phys. Chem. B*, 2001, **105**, 10619.
4. J. H. Cole, D. H. Everett, C. T. Marshall, A. R. Paniego, J. C. Powl and Rodrigue.F, *J. Chem. Soc., Faraday Trans. I*, 1974, **70**, 2154.