Supplementary Material (ESI) for Faraday Discussions

Electronic Supplementary Information

Pore with Gate: Modulating Hydrogen Storage in Metal Organic Framework Materials *via* Cation Exchange

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1. Experimental methods.

1.1 Materials and measurements

All reagents and solvents were used as received from commercial suppliers without further purification. Analyses for C, H, and N were carried out on a CE-440 elemental analyzer. Thermogravimetric analyses (TGA) were performed under a N_2 atmosphere (100 ml/min) using a TA SDT-600 thermogravimetric analyzer with a heating rate of 2 °C/min. The IR spectra were recorded using a Bruker TENSER 27 FT-IR spectrophotometer in KBr mode. Analyses for Li and In were carried out using an ICP-MAS analyzer. Calibration curves for ICP-MAS were prepared by dilution of commercially available standards with the sample dissolved in concentrated HNO_3, and diluted to an appropriate concentration for measurement. Powder X-ray diffraction (PXRD) data were collected over the 2θ range 4-50^o on a Bruker Advanced D8 diffractometer using Cu-Kα radiation ($\lambda = 1.54056$ Å, 40 kV/40mA).

1.2 Single crystal X-ray diffraction studies

X-ray diffraction data of single crystals of NOTT-210, NOTT-211 and NOTT-213 were collected at 293(2) K on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire-3 CCD detector. X-ray diffraction data of single crystals of NOTT-212 were collected at 120(2) K on Station 9.8 of the Synchrotron Radiation Source at STFC Daresbury Laboratory. The structures were solved by direct methods and developed by difference Fourier techniques using the SHELXTL software package.[1] The hydrogen atoms on the ligands were placed geometrically and refined using a riding model. Geometric restraints were applied to the phenyl ring and the carboxylate group of the organic ligand. The unit cell volume includes a large region of disordered solvents 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 formula was calculated from the SQUEEZE results combined with elemental analysis and TGA data: the contents of the solvent/cation region are therefore represented in the unit cell contents but were not included in the refinement model. Single crystal data and refinement results are summarised in Table S1.

Table S1. Summary of X-ray single crystal structural data.

	NOTT-210-solv	NOTT-211-solv	NOTT-212-solv	NOTT-213-solv
Formula	$C_{30}H_{40}InN_3O_{14}$	$C_{32}H_{38}InN_3O_{12}$	$C_{30}H_{36}F_4InN_3O_{14}$	$C_{34}H_{38}InN_3O_{12}$
Formula weight	781.47	771.47	853.44	795.48
Temperature (K)	293	293	120	293
Wavelength (Å)	0.71073	0.71073	0.6943/synchrotron	0.71073
Space group	$P4_2/mmc$	$P4_2/mmc$	$I4_1/acd$	$P4_2/mmc$
a, b (Å)	9.9532(3)	9.9617(4)	19.807(5)	9.9617(4)
c (Å)	26.701(1)	26.747(2)	53.454(9)	26.747(2)
V (Å^3)	2645.1(2)	2654.3(3)	20971(8)	2654.3(3)
Z	2	2	16	2
D_{calc} (g/cm^3)	0.981	0.965	1.081	0.993
μ	0.493	0.488	0.513	0.489
$F(000)$	804	792	6944	812
Diffraction number Total/unique/R_{int}	1073/24345/0.090	1084/8753/0.130	3732/61209/0.054	1085/24009/0.093
R_1 [$F > 4\sigma(F)$] /wR_2 [all F^2]	0.062/0.174	0.081/0.187	0.055/0.177	0.046/0.105
GOF	1.01	1.01	1.05	1.01
Difference map extrema (e Å^{-3})	-0.49 – 0.35	-0.34 – 1.11	-0.77 – 0.30	-0.26 – 0.62
CCDC deposition number	799919	799920	799921	799922

1.3 Gas adsorption isotherms

H_2 and N_2 isotherms (pressure range 0-1.0 bar, measured with a high resolution pressure transducer) were recorded at 77 K (liquid nitrogen) or 87 K (liquid argon) 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%) H_2 and N_2 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 80-120 °C and 10^{-10} bar for 1 day to give desolvated samples. In a typical procedure, 50-100 mg of dry sample was used for the measurements. The densities of desolvated samples used in buoyancy corrections were 1.60-1.80 g cm^{-3} for complexes in this study. This was estimated from the crystallographic density of the desolvated sample and PLATON/SQUEEZE[28] result. The density of bulk 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 density of liquid H_2 at the boiling point (0.0708 g cm^{-3}) was used for the adsorbate buoyancy correction. Pore size distribution (PSD) data were obtained by applying Dubinin-Astakhov analysis of the N_2 isotherms at 77 K. The analyses were carried out with IGASwin V1.03.181, and the constants for N_2 were: sorbate phase density = 0.808 g/cc; surface tension = 8.85 mN/m; DA interaction constant = 2.96 $kJnm^3/mol$.

1.4 Inelastic neutron scattering

The rotational transitions of adsorbed H_2 molecules can be observed using inelastic neutron spectroscopy (INS). INS spectra were recorded on the TOSCA spectrometer at the ISIS Facility of the Rutherford Appleton Laboratory (UK) for energy transfers between ~2 and 500 meV. In this region TOSCA has a high resolution of ~2% ~E/E, corresponding to ~0.3 meV, facilitating the observation of individual excitations. The sample was loaded with *para*-hydrogen (H_2), which was prepared in a separate cryostat using a magnetic catalyst and low-temperature H_2. The amount of H_2 loaded was determined volumetrically *via* calculation from the calibrated pipe volume and the gas pressure.

Using an argon glove box, the desolvated NOTT-209 sample was loaded into a cylindrical vanadium sample container with an annealed copper vacuum seal and connected to a gas handling system. The sample was degassed at 10^{-5} Pa and 60-120 °C to remove any remaining trace guest solvent molecules. The temperature during data collection was controlled using a helium cryostat (± 0.5 ^{o}C). H_2 gas was loaded and unloaded at various stages during the experiments, and the amounts monitored. Each loading of H_2 was performed at 50 K in order to make sure that H_2 was present in the gas phase when not adsorbed and also to ensure sufficient mobility of H_2 inside the crystalline NOTT-209 structure. Subsequently, the temperature was reduced to below 15 K in order to perform the scattering measurement with as far as possible reduced thermal motion for the H_2. Background spectra (sample can plus NOTT-209) were subtracted to obtain the spectra of adsorbed dihydrogen.

2. Synthesis of complexes

Synthesis of $[H_2ppz][In_2(L^6)_2](DMF)_{3.5}(H_2O)_5$ (NOTT-200-solv).

H_4L^6 (0.015 g, 0.031 mmol), $In(NO_3)_3$ (0.009 g, 0.031 mmol) and piperazine (0.015g, 0.18 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-200-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.035 g (70%). Elemental analysis (% calc/found): $In_2O_{24.5}C_{70.5}H_{74.5}N_{5.5}$ (In: 14.17/13.68; C 52.25/52.19; H 4.63/4.45; N 4.75/4.65). Selected IR: ν (cm^{-1}) = 3630(w), 3015(w), 2946(w), 2811(w), 2324(w), 1718(s), 1572(m), 1435(m), 1365(vs), 1251(m), 1021(m), 918(m), 826(m), 776(s), 751(s), 663(w).

Synthesis of $[Li_{1.5}(H_3O)_{0.5}][In_2(L^6)_2](H_2O)_{11}$ (NOTT-201-solv).

To prepare the Li^+-exchanged sample NOTT-201-solv, crystals of as-synthesized NOTT-200-solv were immersed in a saturated solution of LiCl in distilled water/acetone (1:1 v/v) at room temperature. The crystals were soaked for 10 days and the LiCl solution refreshed three times daily. Upon decanting the metal chloride solutions, the cation-exchanged crystals of NOTT-201-solv were rinsed and soaked in distilled water/acetone (1:1 v/v) for 3 days to remove residual free LiCl. Elemental analysis (% calc/found): $In_2O_{27.5}C_{56}H_{51.5}Li_{1.5}$ (In: 16.35/15.93; Li: 0.74/0.72; C 47.62/47.89; H 3.76/3.70; N 0.0/0.0). Selected IR: ν (cm^{-1}) = 3621(w), 3031(w), 2947(w), 2161(m), 1700(m), 1617(s), 1560(s), 1362(vs), 1248(m), 1076(m), 916(m), 857(m), 774(s), 754(s), 661(w).

Synthesis of $[Me_2NH_2][In(L^1)](DMF)(CH_3CN)(H_2O)_4$ (NOTT-204-solv).

H_4L^1 (0.015 g, 0.045 mmol) and $In(NO_3)_3$ (0.014 g, 0.045 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3.0 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and the colourless octahedral crystalline product separated by filtration, washed with DMF and dried in air. Yield: 0.023 g (70%). Elemental analysis (% calc/found): $InO_{13}C_{23}H_{32}N_3$ (C 41.0/39.0, H 4.8/4.4, N 6.3/7.1). Selected IR: ν (cm^{-1}) = 3443(w), 2926(w), 1650(vs), 1569(m), 1490(w), 1410(s), 1384(vs), 1253(m), 1094(m), 1060(m), 907(w), 856(w), 773(m), 747(s), 659(m).

Synthesis of $[Li_{0.5}(H_3O)_{0.5}][In(L^1)](H_2O)_5(C_3H_6O)_{0.5}$ (NOTT-205-solv).

To prepare the Li^+-doped sample NOTT-205-solv, crystals of as-synthesized NOTT-204-solv were immersed in a concentrated solution of LiCl in distilled water/acetone (1:1 v/v). The crystals were soaked for 10 days and the LiCl solution refreshed every day. Upon decanting the metal chloride solutions, the cation-exchanged crystals of NOTT-205-solv were rinsed and soaked in distilled water/acetone (1:1 v/v) for 3 days to remove residual free LiCl from the pores of NOTT-205-solv. Elemental analysis (% calc/found): $InO_{14}C_{17.5}H_{20.5}Li_{0.5}$ (C 36.6/34.9, H 3.6/2.9, N 0.0/0.0). Selected IR: ν (cm^{-1}) = 3469(w), 2927(w), 1703(m), 1612(m), 1552(m), 1418(s), 1364(vs), 1229(m), 1090(m), 992(m), 913(w), 782(m), 710(m), 657(m).

Synthesis of $[(Me_2NH_2)(H_3O)][In_2(L^7)_2](DMF)_4(H_2O)_5$ (NOTT-206-solv).

H_4L^7 (0.015 g, 0.029 mmol) and $In(NO_3)_3$ (0.0089 g, 0.029 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-206-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.039 g (80%). Elemental analysis (% calc/found): $In_2O_{26}C_{74}H_{81}N_5$ (In 13.62/13.25; C 52.71/52.69; H 4.84/4.51; N 4.15/4.07). Selected IR: ν (cm^{-1}) = 3620(m), 3009(m), 2956(w), 2801(w), 2326(w), 1720(s), 1435(m), 1360(vs), 1250(m), 1011(m), 918(m), 777(s), 663(w).

Synthesis of $[Li_{1.2}(H_3O)_{0.8}][In_2(L^7)_2](H_2O)_{14}$ (NOTT-207-solv).

To prepare the Li^+-exchanged sample NOTT-207-solv, crystals of as-synthesized NOTT-206-solv were immersed in a saturated solution of LiCl in distilled water/acetone (1:1 v/v) at room temperature. The crystals were soaked for 10 days and the LiCl solution refreshed three times daily. Upon decanting the metal chloride solutions, the cation-exchanged crystals of NOTT-207-solv were rinsed and soaked in distilled water/acetone (1:1 v/v) for 3 days to remove residual free LiCl. Elemental analysis (% calc/found): $In_2O_{30.8}C_{60}H_{62.4}Li_{1.2}$ (In 15.16/14.76; C 47.59/47.55; H 4.15/4.27; Li 0.55/0.53; N 0.0/0.0). Selected IR: ν (cm^{-1}) = 3629(w), 3011(w), 2957(w), 2162(m), 1705(m), 1617(s), 1566(s), 1383 (vs), 1077(m), 916(m), 774(s), 656(w).

Synthesis of $[H_2ppz][In_2(L^8)_2](DMF)_4(H_2O)_{5.5}$ (NOTT-208-solv).

H_4L^8 (0.015 g, 0.027 mmol), piperazine (0.015 g, 0.18 mmol) and $In(NO_3)_3$ (0.0081 g, 0.027 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-208-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.022 g (90%). Elemental analysis (% calc/found): $In_2O_{25.5}C_{84}H_{87}N_6$ (In 12.63/12.26; C 55.49/55.53; H 4.82/5.03; N 4.62/4.76). Selected IR: ν (cm^{-1}) = 3622(m), 3016 (m), 2950(w), 2800(w), 2336 (w), 1727(s), 1440(m), 1360(vs), 1252(m), 1011(m), 912(m), 770(s), 668(w).

Synthesis of $[Li_{1.4}(H_3O)_{0.6}][In_2(L^8)_2](Ace)_4(H_2O)_{11}$ (NOTT-209-solv).

To prepare the Li^+-exchanged sample NOTT-209-solv, crystals of as-synthesized NOTT-208-solv were immersed in a saturated solution of LiCl in distilled water/acetone (1:1 v/v) at room temperature. The crystals were soaked for 10 days and the LiCl solution refreshed three times daily. Upon decanting the metal chloride solutions, the cation-exchanged crystals of NOTT-209-solv were rinsed and soaked in distilled water/acetone (1:1 v/v) for 3 days to remove residual free LiCl. Elemental analysis (% calc/found): $In_2O_{31.6}C_{80}H_{83.8}Li_{1.4}$ (In 12.83/12.55; C 53.67/53.86; H 4.72/4.73; Li 0.54/0.52; N 0.0/0.0). Selected IR: ν (cm^{-1}) = 3634(w), 3010(w), 2967(w), 2152(m), 1700(m), 1610(s), 1552(s), 1380 (vs), 1070(m), 926(m), 775(s), 656(w).

Synthesis of $[Me_2NH_2][InL^2](DMF)_2(H_2O)_4$ (NOTT-210-solv).

H_4L^2 (0.015 g, 0.037 mmol) and $In(NO_3)_3$ (0.011 g, 0.037 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-210-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.023 g (80%). Elemental analysis (% calc/found): $InO_{14}C_{30}H_{40}N_3$ (C 46.11/45.22; H 5.16/5.03; N 5.38/4.76). Selected IR: ν (cm^{-1}) = 3421(m), 3021(w), 2947(w), 1701(m), 1617(s), 1555(s), 1363(vs), 1248(m), 920(m), 820(m), 754(s).

Synthesis of $[Me_2NH_2][InL^3](DMF)_2(H_2O)_2$ (NOTT-211-solv).

H_4L^3 (0.015 g, 0.035 mmol) and $In(NO_3)_3$ (0.010 g, 0.035 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-211-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.024 g (90%). Elemental analysis (% calc/found): $InO_{12}C_{32}H_{38}N_3$ (C 49.82/48.22; H 4.96/5.06; N 5.45/5.20). Selected IR: ν (cm^{-1}) = 3431(m), 3041(w), 2962(w), 1708(m), 1612(s), 1555(s), 1367(vs), 1268(m), 910(m), 810(m), 755(s).

Synthesis of $[Me_2NH_2][InL^4](DMF)_2(H_2O)_4$ (NOTT-212-solv).

H_4L^4 (0.015 g, 0.024 mmol) and $In(NO_3)_3$ (0.007 g, 0.024 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-212-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.014 g (70%). Elemental analysis (% calc/found): $InO_{14}C_{30}H_{36}F_4N_3$ (C 42.22/41.00; H 4.25/4.20; N 4.92/5.10). Selected IR: ν (cm^{-1}) = 3441(m), 2962(w), 1700(m), 1615(s), 1565(s), 1368(vs), 1269(m), 910(m), 812(m), 753(s).

Synthesis of $[Me_2NH_2][InL^5](DMF)_2(H_2O)_2$ (NOTT-213-solv).

H_4L^5 (0.015 g, 0.033 mmol) and $In(NO_3)_3$ (0.010 g, 0.033 mmol) were mixed and dispersed in a mixture of DMF/CH_3CN (3 ml, 2:1 v/v). The resulting white slurry turned clear upon addition of two drops of 6M HNO_3 solution. The solution was then heated to 90°C for 1 day and colourless octahedral crystals of NOTT-213-solv were separated by filtration, washed with DMF and dried in air. Yield: 0.023 g (90%). Elemental analysis (% calc/found): $InO_{12}C_{34}H_{36}N_3$ (C 51.47/51.00; H 4.57/4.40; N 5.30/5.12). Selected IR: ν (cm^{-1}) = 3450(m), 3051(w), 2962(w), 1705(m), 1620(s), 1555(s), 1368(vs), 1270(m), 920(m), 810(m), 755(s).

3. TGA plots for NOTT-210, NOTT-211, NOTT-212 and NOTT-213

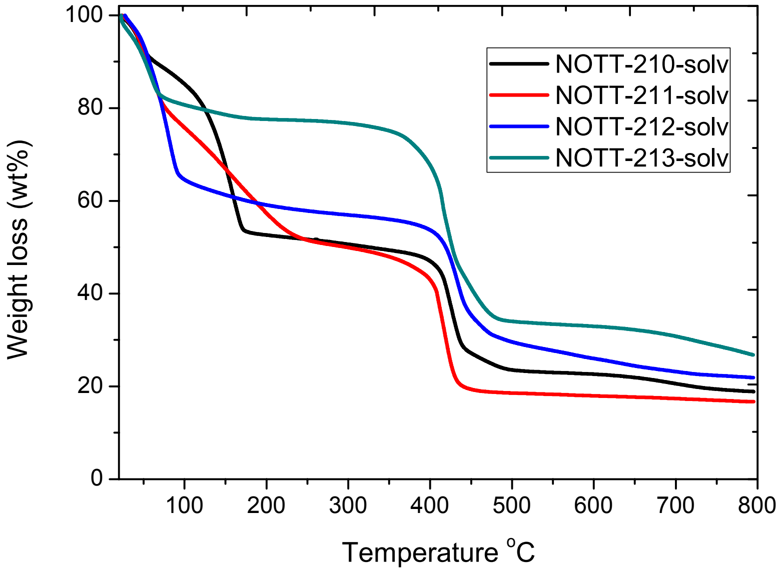
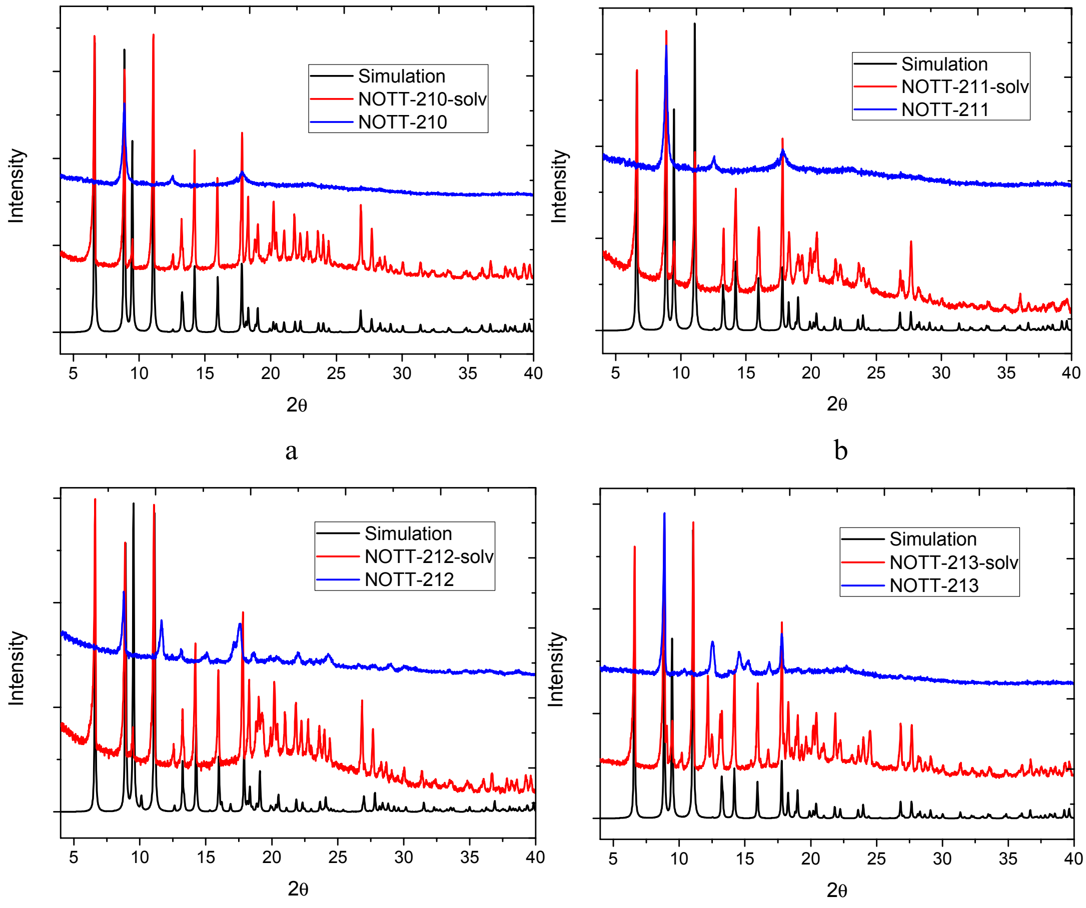


Figure 1s. TGA plots for NOTT-210, NOTT-211, NOTT-212 and NOTT-213.

4. Powder X-Ray diffraction patterns for NOTT-210, NOTT-211, NOTT-212 and NOTT-213.



a

b

c

d

Figure 2s. Comparison of simulated, experimental and desolvated PXRD patterns for NOTT-210-solv (a), NOTT-211-solv (b), NOTT-212-solv (c) and NOTT-213-solv (d).

5. Nitrogen sorption isotherm for NOTT-210.

Framework structures of desolvated NOTT-210, NOTT-211, NOTT-212 and NOTT-213 are not stable on desolvation. Thus, no apparent N_2 adsorption was observed for these four materials (see Fig. 3s for example), and BET areas for these desolvated materials are estimated to be ~20 m^2g^{-1}, which is close to the surface area for powder solid materials.

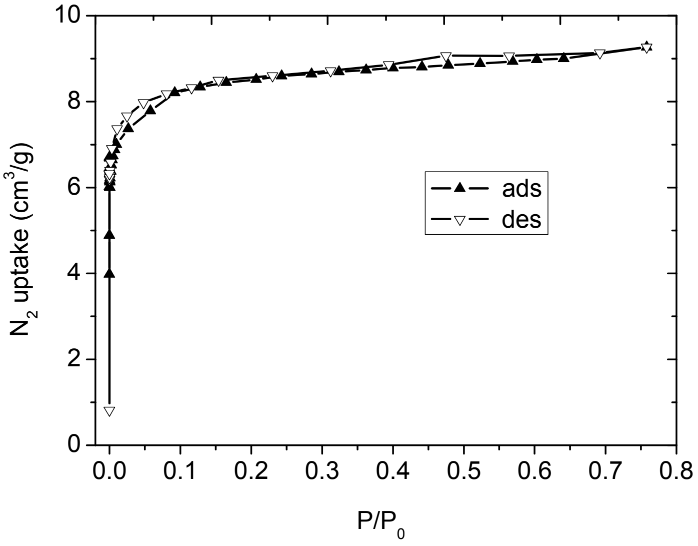


Figure 3s. N_2 sorption isotherms at 77 K for NOTT-210.

References:

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