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Hydrogen adsorption in microporous organic framework polymer†

Saad Makhseed* and Jacob Samuel

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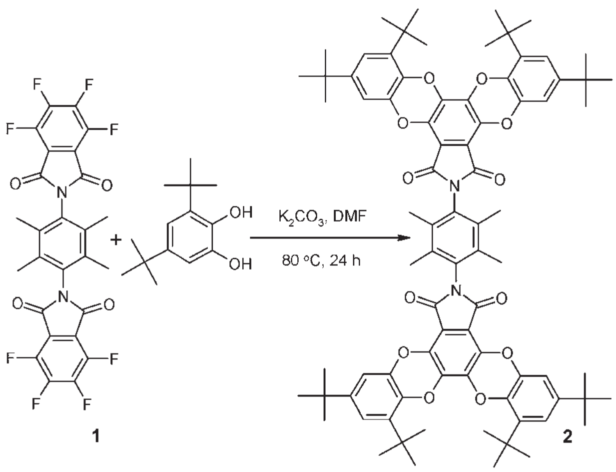
A microporous organic framework polymer (OFP) based on a polyimide framework exhibits a high surface area (1159 m^2 g^{-1}) and shows a reversible H_2 storage capacity of 3.94 wt% at 10 bar and 77 K, the highest yet reported for an organic polymer.

Efficient hydrogen storage has been identified as one of the most challenging tasks to accomplish the goals for hydrogen economy, encompassing problems related to ease of storage and release, transportation, and safety issues.[1] In particular, materials are required to meet the ambitious US Department of Energy (DOE) targets for volumetric and gravimetric storage in vehicular applications.[2,3] The major criteria in the development of new hydrogen storage materials are improved energy storage density, using readily available elements, low heat of adsorption, low cost, low weight, high stability against O_2 and moisture for long cycle life.[4] Thus extensive efforts are on-going to design and develop efficient hydrogen storage materials to compete with conventional liquefaction and compression methods. For this purpose many materials have been explored including carbon nanotubes (CNTs),[5] activated carbons,[6] zeolites,[7] metal hydrides[8] and metal organic frameworks (MOFs).[9–11] The current target set by the DOE requires the development of a storage system able to absorb 6 wt% of hydrogen by the year 2010.

Recently several studies have focussed on organic polymers of intrinsic microporosity (PIMs).[12,13] The storage capacity of PIMs is in the range 0.95–1.63 wt% H_2 at 1 bar and 77 K with a maximum uptake of 2.9 wt% at 10 bar for a triptycene-based PIM (Trip-PIM). These values are promising for a new class of materials but fall far short of realistic values for a practical hydrogen storage material. These organic polymers are composed of light elements, which offer an advantage over metal organic frameworks (MOFs), zeolites and other microporous materials for onboard storage.[12] Hyper-crosslinked polymers (HCPs) represent another class of high surface area organic microporous materials.[14–16] The most important one is the so-called Davankov-type resins prepared by extensive crosslinking of polystyrene. The HCPs prepared by Cooper and co-workers exhibit hydrogen adsorption around 0.89–1.69 wt% at 1.13 bar and 77 K and a maximum uptake of 3.68 wt% at 15 bar.[14] Recently, the group of Svec[16] has developed hyper-crosslinked polyanilines with a surface area exceeding 630 m^2 g^{-1} and the best of these materials afforded 2.2 wt% at 30 bar.

Our research focussed on a novel approach to create microporous polymer frameworks with high volumetric capacity. Control of microporosity is an important issue related to the hydrogen adsorption. The best systems were known to be PIMs. PIMs typically have rigid backbones (ladder-like sequences) and incorporate sites of contortion (spiro-centres) that force the backbone to twist and turn. Here we describe a novel polyimide that incorporates the features of a PIM. We also demonstrate that polyimide networks can be considered as "intrinsically microporous". The possibility of the preparation of a framework material was confirmed by making a model compound **2** (see ESI†) directly from a reaction between four molar equivalents of di-*tert*-butyl catechol with 1,4-bis(4,5,6,7-tetrafluorophthalimido)-2,3,5,6-tetramethylbenzene **1** (Scheme 1).‡ The reaction product was characterised by mass spectrometry, NMR and elemental analyses which indicate that all the eight F atoms were replaced by four catechol units. This highly efficient nucleophilic aromatic substitution reaction (yield >90%) is clearly suitable for the preparation of the target organic framework polymer. The polymer framework **OFP-3** (Scheme 2) was synthesised by the polycondensation of **1** with the commercially available spirobiscatechol(5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirbisindane) at 80 °C.§ The crude product was precipitated in deionised water followed by washing with a variety of solvents (methanol, acetone and THF) and then dried under vacuum. The high yield of product (95%) was attributed to the efficiency of the framework formation. The insoluble yellow fluorescent powder was characterised by IR, solid-state ^{13}C NMR, elemental and XPS analyses. The IR spectroscopic analysis confirms the structural identification of **OFP-3** by the appearance of a new dibenzodioxane link



Scheme 1 Synthesis of model compound **2**.

Department of Chemistry, Kuwait University, PO Box 5969, Safat, 13060, Kuwait. E-mail: smakhseed@kuc01.kuniv.edu.kw; Fax: 9654816482; Tel: 9654985538

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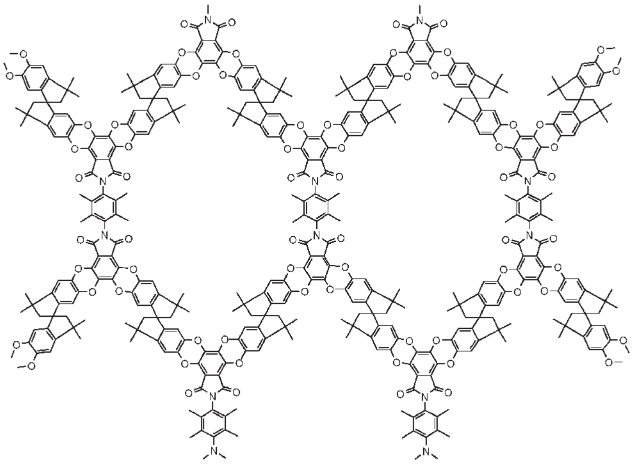

Scheme 2 Representation of the idealised structure of the organic framework polymer (**OFP-3**).

related band and the absence of bands corresponding to fluorinated aromatics as supported by the XPS analysis (<1% residual fluorine). In comparison with the monomers and precursor molecules the solid-state ^{13}C NMR spectrum seems to confirm the proposed structure of **OFP-3** from the expected signal position as well as the relative signal intensities. Thermogravimetric analysis (TGA) shows that material exhibits good thermal stability, with only a 5% mass loss up to 312 °C, corresponding to the evaporation of the entrapped solvents.

Nitrogen adsorption measurements (Fig. 1) give a BET surface area of 1159 $m^2 g^{-1}$ for **OFP-3** which is higher than the trip-PIM[13] but less than the HCPs.[14,15] The adsorption–desorption isotherms clearly exhibit pronounced hysteresis up to low partial pressure which is typically observed for microporous materials. The high surface area of **OFP-3** may be due to its rigid nonlinear architecture. The rigidity arises from the restricted rotation as a result of the dioxane linkage formation and the nonlinearity created by the spirobiscatechol. In addition the four methyl substituents hinder the rotation about C–N bond of the imide groups. In particular, the polymer constrained by a fixed network structure freezes any possible structural relaxations leading to creation of microporous structure.

Fig. 2 shows the micropore size distribution for **OFP-3** as calculated by the Horvath–Kawazoe (HK) method. The HK method is suitable for microporous materials and its equation relates the adsorption potential with the micropore size and allows each amount adsorbed at a relative pressure to be expressed in terms of the width of a slit shaped pore. Our analysis shows maximum pore size in the range of 0.5–0.6 nm. The small pore diameter is especially advantageous for H_2 storage. X-Ray diffraction revealed that **OFP-3** is an amorphous material. High-resolution transmission electron microscopy (HRTEM) was employed for the spatial mapping of the pores. The framework organization leads to worm hole type pore structures.

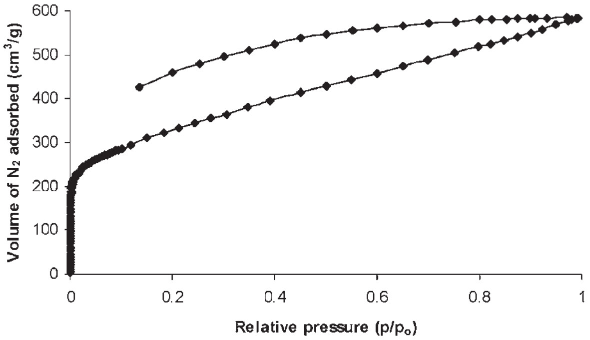

Fig. 1 N_2 adsorption–desorption isotherms at 77 K for **OFP-3**.

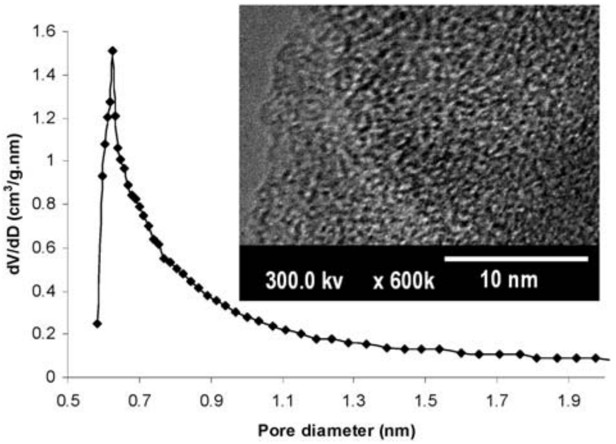

Fig. 2 Pore size distribution for **OFP-3**, calculated by the Horvath–Kawazoe (HK) method showing the abundance of sub-nanometer pores (inset is the HRTEM image).

Hydrogen adsorption–desorption isotherms were measured at 77 K using a ASAP 2020 and 99.999% pure H_2 over the pressure range 0–10 bar (these measurements were carried out at Micromeritics Analytical Laboratory, USA). The framework polymer afforded a hydrogen storage capacity of 1.56 wt% at 1 bar which is comparable with the other reported microporous polymers.[12–16] However, at 10 bar **OFP-3** adsorbs nearly 3.94% by weight of material (Fig. 3). In addition the shape of the isotherm indicates that adsorption has not reached saturation and further significant hydrogen uptake could occur at higher pressures. This level of uptake is higher than all the reported organic polymers and some MOFs. Moreover small micropores such as that indicated for **OFP-3** can adsorb hydrogen effectively.[12] These ultramicropores allow the dihydrogen molecule to interact with multiple

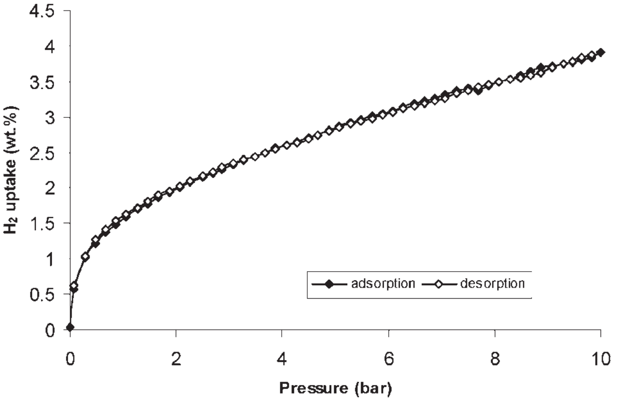

Fig. 3 Hydrogen adsorption–desorption isotherm for **OFP-3** at 77 K. There is no significant hysteresis observed during desorption.

Table 1 Comparison of surface area and hydrogen uptake (wt%) at 77 K of organic framework polymer (**OFP-3**) with selected other high performance materials

Material	$S_{BET}/m^2\ g^{-1}$	H_2 uptake (1 bar)	H_2 uptake (10 bar)	Ref.
OFP-3	1159	1.56	3.94	—
Trip-PIM	1065	1.65	2.71	13
HCP	1466	1.28	2.75	14
IRMOF-8	1818	1.50	3.6	9
HKUST-1	2175	2.54	3.6	10
MOF-505	1670	2.59	3.7	11
Carbon AX-21	2421	2.40	4.0	17

portions of the framework thereby increasing the interaction energy. In addition, the adsorption is completely reversible and there is no significant hysteresis which is consistent with the physisorption of hydrogen on a microporous material.

The reproducibility of the hydrogen adsorption was also confirmed. The comparison of hydrogen adsorption in other microporous materials is summarised in Table 1. On comparing various organic polymers and MOFs we observed that the storage capacity is only poorly correlated to the BET surface area. However in order to attain good storage capacity it will be necessary to design materials with greater accessible surface area and microporosity.

This study demonstrates the viability of the concept of synthesising novel microporous organic framework structures. Furthermore this type of material performs well in comparison with other microporous organic materials, carbons and MOFs having higher or similar surface area. Further studies are in progress to increase the uptake of hydrogen at the same conditions.

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Notes and references

‡ 1,4-Bis(4,5,6,7-tetrafluorophthalimido)-2,3,5,6-tetramethylbenzene **1**: Tetrafluorophthalic anhydride was added to a stirred solution of 2,3,5,6-tetramethyl-1,4-phenylenediamine in glacial acetic acid and refluxed for 12 h. The white solid obtained was further refluxed in acetic anhydride for 12 h. After cooling, the precipitated product was filtered off and washed with petroleum ether to give a light yellow solid. Yield 70%; mp > 300 °C; ^{1}H NMR (DMSO-d_6, 400 MHz, 25 °C) δ 2.08 (s, 12 H); ^{13}C NMR (100 MHz) (DMSO-d_6) δ 166.22, 145.90, 143.24, 134.25, 130.25, 113.53, 15.64; IR (KBr), ν/cm^{-1}: 1792 and 1731 (imide), 1511 and 1499 (C=C), 945 (C–F). Calc. (%) for $C_{26}H_{12}F_8N_2O_4$ (568.38): C, 54.94; H, 2.13; N, 4.93. Found: C, 54.92; H, 2.17; N, 5.16; MS (EI): m/z (%) 568 ($M^{+\bullet}$, 100).

§ **OFP-3**: A mixture of monomer **1** (0.752 g, 1.3 mmol) and spirobiscatechol (0.901 g, 2.6 mmol) in dry DMF (100 ml) and K_2CO_3 (2.15 g, 15.6 mmol) was stirred at 80 °C for 24 h. After cooling, the reaction mixture was poured into deionised water and the solid product collected by filtration and washed with methanol. The insoluble polymer was then purified by refluxing in methanol, acetone and THF. The obtained yellow fluorescent powder was dried in a vacuum oven at 100 °C for 12 h (1.5 g, yield 95%). ^{13}C CP/MAS NMR (75 MHz, 25 °C) δ/ppm: 161.70, 147.80, 140.28, 136.80, 132.80, 111.16, 57.76, 42.99, 29.66, 14.09. IR (KBr) ν/cm^{-1}: 1773 and 1722 (imide), 1460 (C=C). Calc. (%) for the proposed repeat unit $C_{68}H_{52}N_2O_{12}$ (1088): C, 75.00; H, 4.77; N, 2.57. Found: C, 73.87; H, 4.83; N, 2.65.

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