Hysteretic sorption of light gases by a porous metal–organic framework containing tris(*para*-carboxylated) triphenylphosphine oxide†‡

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The porous metal–organic framework (MOF) PCM-4, based on tris(*para*-carboxylated) triphenylphosphine oxide, contains atypical, polar organic substituents; the material exhibits a hysteretic sorption of Ar, N_2 and O_2, and demonstrates the advantage of ligands of this type.

The intensive current interest in the rational design of porous metal–organic frameworks (MOFs) has shown how various organic 'linkers' may be tethered to metal (oxide/hydroxide) 'nodes' to form new functional materials.[1] Examples that retain structural integrity and porosity upon removal of a guest solvent have the potential for applications in gas storage/separation,[2] catalysis[3] and polymerization,[4] amongst others. Linear organic linkers, such as 4,4′-bipyridine, 1,4-benzene dicarboxylate, *etc.*,[5] have provided successful routes to large families of porous networks with tunable pore dimensions. Gas sorption studies using various probe gases and limited neutron scattering data[6] have begun to elucidate relationships between framework composition and gas uptake characteristics. New generations of porous MOFs employ more exotic organic groups, which afford novel framework topologies that contain more polar organic substituents[7] and/or unsaturated metal sites[8] to enhance gas storage and guest selectivity.

We are presently interested in preparing functional coordination polymers using carboxylated aromatic phosphines and their derivatives, with an emphasis on exploiting the inherent tripodal geometry and variable oxidation states of phosphorus. The chemistry of 3,3′,3″-phosphanotriylbenzenecarboxylic acid,[9] $\{P(C_6H_4\text{-}p\text{-}CO_2H)_3\}$ ($ptbcH_3$), has resulted in the formation of several metal(II)–phosphine phases[10] and a highly porous phosphine oxide material, presented here. $H[(Zn_3OH(OH_2)_3)(potbc)_2]\cdot 3DMF\cdot 3H_2O$, hereafter referred to as PCM-4 (Phosphine Coordination Material), was synthesized by the addition of stoichiometric amounts of H_2O_2 to mixtures of $Zn(OAc)_2$ and $ptbcH_3$.§ This promoted *in situ* formation of the corresponding phosphine oxide $\{P(=O)(C_6H_4\text{-}p\text{-}CO_2H)_3\}$ (potbc), with concomitant ligand deprotonation and coordination by the metal precursor (see ESI†). Interestingly, PCM-4 could not be obtained directly using $potbcH_3$ under similar conditions.

PCM-4 has primitive cubic crystallographic symmetry‡ and is based on two closely tethered, interpenetrated, 3-D square grids (Class IIa),[11] which are so arranged due to the influence of unusual P=O-mediated inter-network interactions. This results in the presence of large void spaces, formed as a result of the 3-D pore structure, with square openings that measure 11.2 Å along the diagonal. In contrast, interpenetration usually results in minimized voids and restricted porosity.[12] Individual frameworks are based on six-connected Zn_3OH and three-connected P(=O) nodes. Each μ_3-OH-bridged Zn_3 triangle is capped by three bridging carboxylates below the Zn_3O plane, with three terminal carboxylates and three μ_2-OH_2 molecules coordinated above the plane, resulting in pseudo-octahedral Zn centers (Fig. 1A). The *C*3-symmetric building block is linked to twelve other adjacent clusters, resulting in a net that is related to pyrite (pyr) with a $(6^{12}\cdot 8^3)(6^3)_2$ topology (Fig. 1B).[13] This type of net has been previously observed in MOF-150, which is comprised of the related 4,4′,4″-tricarboxytriphenylamine ligand tethered to Zn_4O nodes.[14] In PCM-4, the phosphine oxide-*O* forms close inter-network interactions with adjacent Zn_3 clusters *via* $P{=}O\cdots Zn_3$ ($Zn\cdots O$ = 2.75(1) Å; P–O = 1.49(2) Å) and $P{=}O\cdots HOH$ ($O\cdots H$ = 1.57 Å; P–O = 1.52(2) Å) contacts (Fig. 1C); these inter-molecular distances are significantly shorter than the corresponding sums of their van der Waals radii ($Zn\cdots O$ = 2.9; $O\cdots H$ = 2.7 Å),[15] while P=O distances fall in the conventional range expected for polar $P^{\delta+}$–$O^{\delta-}$ bond character, as reported for $Me_3P(=O)$.[16] The solid-state ^{31}P-NMR spectrum of PCM-4 reveals two distinct P-environments, which are further complicated due to varying degrees of solvation (δ 36.1–25.7). In contrast, the spectrum of dehydrated PCM-4 reveals only a single broad peak *ca.* δ 35.6 (see ESI†). The extended structure of PCM-4 has intersecting channels aligned parallel to the a, b and c axes (Fig. 1D).

To confirm the permanent porosity of PCM-4, crystalline samples were studied by thermogravimetric analysis (TGA). The observed two-step desolvation corresponds to initial removal of $3H_2O$ (25–75 °C), followed by 3DMF (→210 °C), which results in a combined 21% mass loss. This value is in good agreement with a void space of 5340 $Å^3$ containing 158 e^- per PCM-4 formula unit, as calculated using the SQUEEZE utility in PLATON.[17] The framework remains stable to above 350 °C, as confirmed by TGA on a pre-desolvated sample of PCM-4 (evacuated at 190 °C for 12 h) (Fig. 2).

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‡ Crystal data for PCM-4: $C_{42}H_{31}O_{18}P_2Zn_3$; MW = 1081.72, cubic, space group *Pa*-3, a = 22.9079(10) Å, V = 12021.4(8) $Å^3$, Z = 8, ρ = 1.195 g cm^{-3}, $\mu(Mo_{K\alpha})$ = 1.297 mm^{-1}, R_1 = 0.104 (0.129), 10121 measured reflections, (2601 independent reflections, $I > 2\sigma(I)$), wR_2 = 0.291 (0.368) (all data), R_{int} = 0.0943, GOF = 1.013 (1.289) (data before the application of SQUEEZE). CCDC 682285. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b802809e

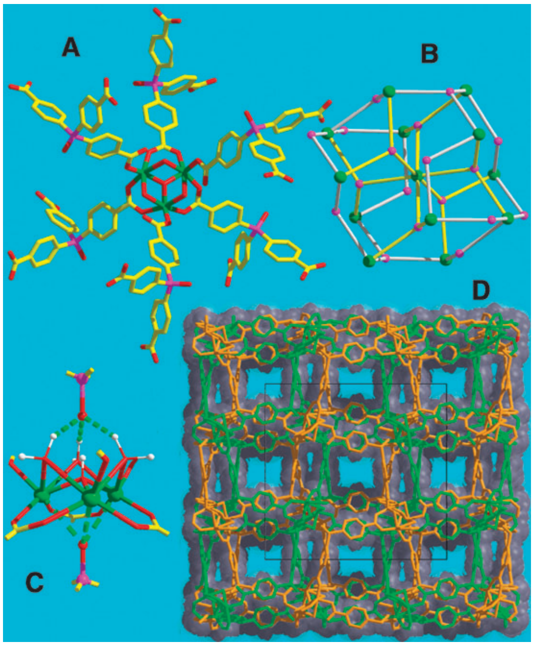

Fig. 1 (A) The six-connected building block of PCM-4, consisting of six potbc^{3-} ligands around a Zn_3OH cluster (Zn = green; P = pink; O = red; C = yellow); (B) extended schematic representation of the same building block, depicting 6^9 topology; (C) close-range inter-network P=O contacts above and below the plane of a Zn_3OH cluster (dashed green lines); (D) the interpenetrated porous network in PCM-4, with superimposed space-filling representation.

Adsorption studies using CO_2 on PCM-4 at 196 K revealed a reversible type-I isotherm, as expected for microporous materials, thus confirming definite adsorption inside the pores after de-gassing at 473 K (see ESI†). Fitting the CO_2 isotherm to the BET model gave an estimated surface area of 540 $m^2\ g^{-1}$, which is typical for microporous zeolites. The micropore volume of PCM-4 was estimated to be 0.26 ml g^{-1} under the same conditions, using the Dubinin–Radushkevich equation.[18]

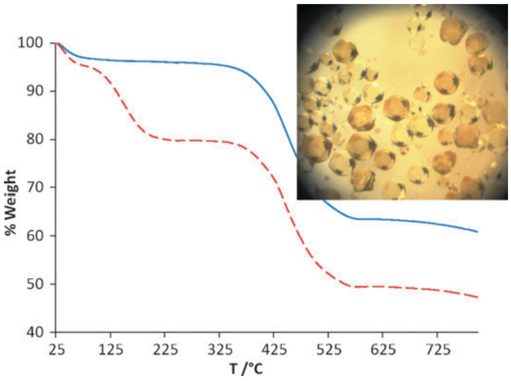

Fig. 2 TGA data for PCM-4. As-synthesized sample (red line); dehydrated sample (blue line). Inset: light microscope image of cuboctahedral crystals of PCM-4.

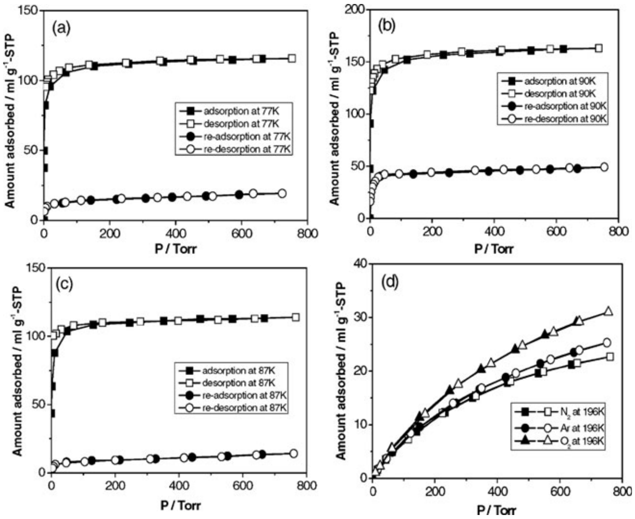

Fig. 3 Cyclic adsorption–desorption isotherms of selected gases at low temperatures in PCM-4 de-gassed at 473 K for 2 h under vacuum: (a) nitrogen at 77 K, (b) oxygen at 90 K, (c) argon at 87 K, and (d) all three gases at 196 K.

A striking feature observed in the isotherms of N_2 (77 K), Ar (87 K) and O_2 (90 K) was irreversible sorption (Fig. 3). Specifically, the Ar isotherms revealed a marked hysteresis loop between adsorption and desorption isotherms, which was accompanied by only partial desorption, even when the pressure was reduced to 1×10^{-4} Torr. After evacuation at 87 K, the re-adsorption isotherm of Ar at 87 K resulted in a very low uptake, indicative of a confinement effect of Ar in the pores (Fig. 3c). It is worth noting that sorption isotherms of this cycle are completely regenerated when de-gassed above 298 K. Moreover, in spite of the confinement effect, the desorption of Ar is quickly equilibrated within 10 min, regardless of sorption pressure, indicating relatively fast desorption of the physisorbed Ar molecules (see ESI†). According to sorption kinetics, the rate of re-adsorption of Ar in PCM-4 containing trapped Ar molecules is faster than that of the first adsorption in fresh PCM-4, indicating that physisorption occurs on the external surface (see ESI†). Temperature-programmed desorption (TPD) analysis of Ar (see ESI†) further supports the observed Ar-trapping behavior; the Ar-TPD profile indicates that desorption occurs at temperatures between at 90 and 210 K. Moreover, the desorbed amount obtained (98 ml g^{-1} or 4.3 mmol g^{-1}) is in close agreement with the sorption amount (100 ml g^{-1}-STP) strongly trapped in the pores at 87 K. The hysteretic sorption of O_2 and N_2 was similarly confirmed by TPD analysis. Additionally, the desorbed amounts of O_2 (5.0 mmol g^{-1}) and N_2 (4.3 mmol g^{-1}) are relatively well matched with their sorption amounts trapped in the pores; 4.3 mmol g^{-1} at 90 K (O_2) and 3.8 mmol g^{-1} at 77 K (N_2), respectively.

Although, to the best of our knowledge, there has been no previous report of Ar-trapping in porous MOFs, analogous confinement effects of light gases in MOFs have been already reported.[19] For example, Zhao *et al.* have shown that it is possible to confine H_2 in a nanoporous MOF from a strong hysteresis of H_2 at 77 K, if access to the porosity is controlled dynamically by openings in the porous structure.[19c] In contrast to the trapping behaviors of light gases at 77–90 K in PCM-4, N_2, Ar and O_2 sorption was nearly reversible at 196 K in PCM-4, indicative of temperature-dependent gas trapping. Maji *et al.* reported that the interaction between the cavity surface of MOFs and gas molecules are important in strong gas sorption, and moreover, the structural flexibility[20b] contributes to the sorption behavior, even if a doubly-interpenetrated structure occurs in the compound.[20] Likewise, the unusual phenomenon and observed reproducibility of gas sorption in PCM-4 upon repeated loading and unloading cycles in the range 77–298 K may be primarily ascribed to cooperative phenomena, wherein the guest adsorbate induces reversible distortions in the framework and pore structure, leading to effective trapping at low temperature. Dipolar host–guest interactions within the pores may also play a role in Ar-trapping. For example, solid acids have been shown to interact with Ar, as determined by low-temperature TPD studies.[21] The enthalpy of Ar desorption was calculated with the Arrhenius equation using the Ar-TPD profiles, obtained according to the different ramping rate (see ESI†). Consequently, relatively strong adsorption of Ar (desorption enthalpy = 16.1 kJ mol^{-1}) in PCM-4 at low temperature is conceivable, *via* interactions with acidic (unsaturated) Zn(II) sites present in the dehydrated material. However, such polar host–guest interactions cannot be solely responsible for Ar-trapping, as the amount of Zn(II) sites (2.8 mmol g^{-1}) is slightly larger than half of the total amount of desorbed gas. The saturation value of Ar adsorbed in PCM-4 is much higher than common examples of solid acids (<1 mmol g^{-1}).[21] Further studies are needed to elucidate the specific sorption sites and unusual mechanisms of light gases in PCM-4. It was noted in this work that the material is sufficiently stable and robust that a whole series of reproducible sorption measurements could be performed without changing the sample.

In summary, an unusual porous MOF PCM-4, based on tris(*para*-carboxylated) triphenylphosphine oxide, has been developed as an example of advanced porous coordination materials that contain atypical, polar organic substituents. P=O groups undergo inter-framework interactions with adjacent Zn_3 clusters, leading to the formation of interpenetrated nets with large void spaces. The material is highly stable when desolvated, and exhibits a curious hysteretic adsorption of Ar, N_2 and O_2, which has been cooperatively confirmed by temperature-programmed desorption (TPD) studies. The results herein offer promise for the synthesis of other interesting new functional materials using phosphine-based ligands.

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Notes and references

§ 3,3′,3″-Phosphanotriylbenzenecarboxylic acid, $\{P(C_6H_5\text{-}p\text{-}CO_2H)_3\}$, (40 mg, 0.10 mmol)[9] was dissolved in DMF : H_2O : EtOH (1 : 1 : 1, 2.5 cm^3), to which was added H_2O_2 solution (10 mg, 100 vols). The mixture was shaken and a second solution of zinc(II) acetate hydrate (33 mg, 0.15 mmol) in DMF (2.5 cm^3) was quickly added. The opaque suspension was heated in a 20 cm^3 sealed glass vial at 80 °C (graphite thermal bath) for 3–5 d. The resulting crystalline solid was washed several times with EtOH, sonicated for 5–10 min and decanted; this procedure was repeated, if required, until the supernatant remained clear. PCM-4 was dried by evaporation in air. The above reaction was also scaled-up to give reproducible syntheses on a 16× scale (average yield 33 mg, 46% based on Zn). Anal. found: C, 45.38; H, 4.09; N, 3.94; P, 3.97. $C_{54}H_{60}N_4O_{25}P_2Zn_3$ requires: C, 45.57; H, 4.25; N, 3.93; P, 4.35%. ^{31}P-NMR (solid-state, 161.9 MHz) δ 36.12, 33.33, 26.82 and 25.73. ν_{max} (KBr/cm^{-1}): 3410 br s, 2960 m, 2931 m, 1654 m, 1610 s, 1551 s, 1535 m, 1498 m, 1396 br s, 1308 w, 1168 m, 1137 w, 1112 m, 1017 m, 865 w, 847 w, 775 m, 739 s, 700 m, 670 w, 663 w and 634 w. PCM-4 after dehydration in a vacuum at 180 °C for 5 h: found: C, 47.34; H, 3.11; N, 0.12%. ^{31}P-NMR (solid-state, 161.9 MHz) δ 35.65 (br).

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