

A functional zeolite analogue assembled from metalloporphyrins

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The assembly of molecular building blocks with metal ions generating microporous network solids has been the focus of intense activity^{1–12}. Because of their potential applications associated with channels and cavities, such materials have been examined for size- and shape-selective catalysis, separations, sensors, molecular recognition and nanoscale reactors. Within this context, assemblies of robust and chemically versatile porphyrin and metalloporphyrin building blocks remain rare. Supramolecular architectures of porphyrin solids based on weak van der Waals interactions^{13,14}, hydrogen bonding^{15,16} and metal-ligand coordination networks^{17–23} have been reported. Although there are frequent allusions to zeolite-like microporosity from crystallography and loss of initial guest solvent molecules, evidence of functional microporous behaviour is scarce. We have demonstrated repeatable sorption–desorption with high selectivity on the basis of size, shape and functional group of the sorbate by a microporous metalloporphyrin solid in analogy to zeolites.

A functional microporous material based on the supramolecular assembly of carboxylate-substituted porphyrins with cobalt ions is reported. Using carboxylic acid-substituted tetraphenylporphyrins as the organic building block, we have pursued the synthesis of novel microporous materials. Porphyrins possess high thermal stability relative to other organic molecules, and are characterized by an approximate two-dimensional square geometry. Metalloporphyrins have been found to be excellent oxidation catalysts for hydroxylation of

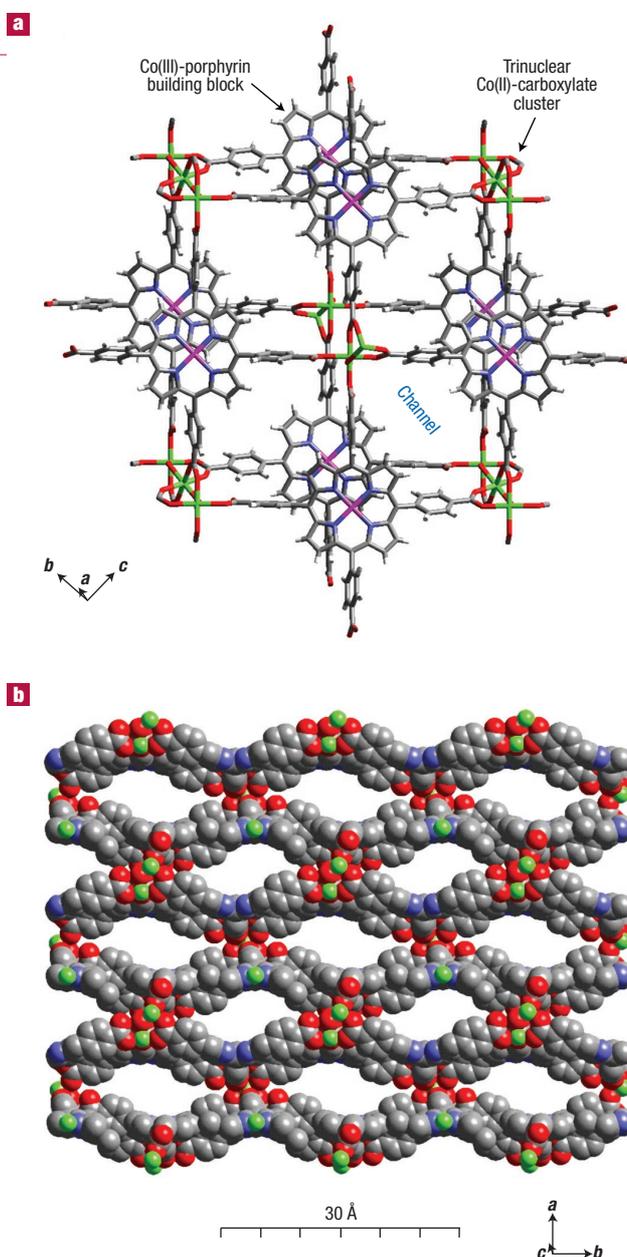


Figure 1 Molecular diagrams of the PIZA-1 network. Grey colouring indicates carbon atoms, red oxygen, blue nitrogen, green Co(II) ions in trinuclear clusters, and purple Co(III) ions. **a**, PIZA-1 structure viewed along the *a* axis showing connectivity leading to formation of $30.8 \times 30.8 \times 10.0$ Å internal voids at the intersection of tri-directional channels. Along the crystallographic *a* axis, four channels of dimensions 13.8×6.8 Å per unit cell are observed. Trinuclear Co(II)-carboxylate clusters link the eight Co(III)-metalloporphyrin building blocks. Single crystal data for PIZA-1: $[\text{CoT}(\text{p-CO}_2)\text{PPCo}_{1.5}(\text{C}_5\text{H}_5\text{N})_3(\text{H}_2\text{O})] \cdot 11\text{C}_5\text{H}_5\text{N}$ at 198(2) K: monoclinic, $P2_1/n$ (No. 14), $a = 18.879(3)$ Å, $b = 23.554(4)$ Å, $c = 23.655(4)$ Å, $\beta = 103.253(4)^\circ$, $Z = 4$, volume = $10,234(4)$ Å³, R_1 (unweighted, based on F_0) = 4.42, wR_2 (weighted) = 10.41. **b**, Space filling view of the PIZA-1 network along *b* or *c* axes. The plane of the ruffled porphyrin macrocycles is perpendicular to the plane of the paper, therefore the porphyrins are effectively viewed along the narrowest edge of their approximate square geometry. Spheres represent 70% van der Waals radii.

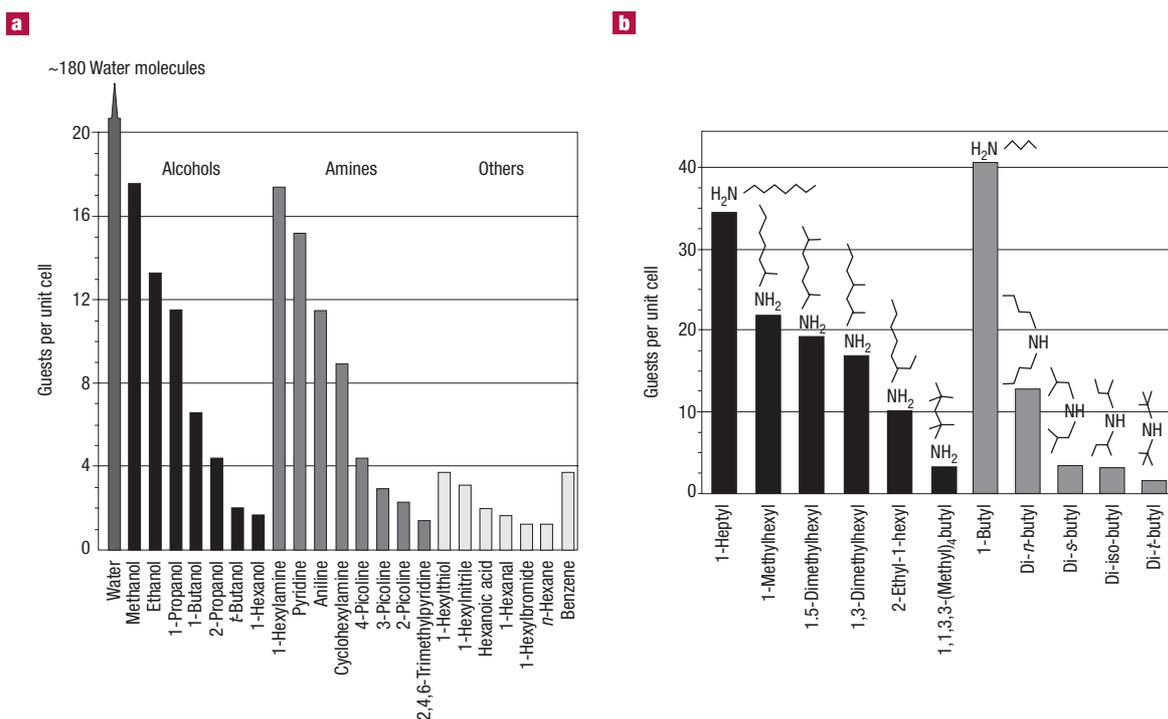


Figure 2 Size-, shape-, and functional-group selectivity as probed by thermal desorption of guest molecules. **a**, Selectivity observed in a variety of chemical groups.

By comparison, ~180 water molecules are sorbed in 24-h exposure (105 ml H₂O per 100 g solid). Before guest exposure, solids were degassed for 24 h at 275 °C in vacuo. 10 mg of the solid was placed in 2 ml freshly distilled solvent for 24 h. The solids were isolated by suction filtration and washed with 4 ml of 1-pentane. TGA: 10 °C min⁻¹ under N₂. **b**, Comparison of linear, unsubstituted 1-heptylamine and substituted alkyl amine isomers further demonstrates the shape-selective sorption behaviour of PIZA-1 (black columns). Size- and shape-selectivity within the butylamine series at near-saturation exposure levels (grey columns). As the hydrophilic amine group is more sterically congested, sorption is observed to decline.

alkanes and epoxidation of alkenes²⁴. Porous metalloporphyrin networks have the potential to act as size- and shape-selective catalysts. Here, we report the synthesis, characterization—including single-crystal X-ray structure—and selective absorption properties of a novel metalloporphyrin network [CoT(*p*-CO₂)PPCo_{1,5}] (designated PIZA-1 for porphyrinic Illinois zeolite analogue no. 1) with large, refillable tri-directional channels exhibiting extraordinary hydrophilic character. The void volume of the stable, thermally robust, solvate-free material is calculated to be 74% of the total unit cell volume. Size, shape and functional-group-selective sorption indicate a marked preference for water and amines. This organic zeolite analogue also demonstrated remarkable ability as a molecular sieve for the removal of water from common organic solvents. Lining the walls of the channel are functionalized sites that are potential locations for catalytic reactions. This work combines the metal–organic framework paradigm with the materials chemistry of porphyrin networks to create functional molecular recognition.

The compound PIZA-1 was prepared solvothermally by heating a mixture of freebase porphyrin acid and cobalt chloride (see Supplementary Information). Single-crystal X-ray structure analysis revealed a neutral network solid composed of ruffled cobalt(III) porphyrin cores—in which the pyrrole rings are alternately displaced above and below the porphyrin plane by ± 0.591 Å—connected by bridging trinuclear Co(II)-carboxylate clusters (Fig. 1a). The neutrality of the framework in this network material, and the consequent absence of permanent counterions is noteworthy.

The extended structure reveals a single, independent network with large, bi-directional oval-shaped channels (9 × 7 Å, determined on the

basis of the van der Waals radii of atoms lining the pore) along the crystallographic *b* and *c* axes (Fig. 1b) and another set of channels (14 × 7 Å) along the crystallographic *a* axis. Fifty six pyridine molecules per unit cell (12 coordinated ligands and 44 disordered solvate guests) have been crystallographically determined. The oval shape of the channels along the crystallographic *b* and *c* axis is due to ruffling of the metalloporphyrin macrocycles when coordinated to the bridging trinuclear Co(II)-carboxylate clusters.

The large internal cavities of PIZA-1 are a direct consequence of the trinuclear Co(II)-carboxylate cluster forcing the substantial ruffling of the porphyrin building blocks. The linear trinuclear metal-carboxylate cluster of PIZA-1, similar to that previously observed in molecular species^{25,26}, can be contrasted with the bent trinuclear M(II)-carboxylate clusters (where M = Co, Mn) of isostructural three-dimensional frameworks (PIZA-2 and PIZA-3) with planar metalloporphyrin macrocycles showing lower void volumes (unpublished results, M.E.K., J.H.C., S.R.W. and K.S.S.). The major difference between the linear trinuclear clusters of PIZA-1 and bent trinuclear clusters is the presence of axially coordinating, nitrogenous Lewis bases.

Thermal gravimetric analysis (TGA) indicated a significant (60%) weight loss attributable to loosely held solvate molecules and coordinated pyridine and water molecules (see Supplementary Information). The integrity and robustness of PIZA-1 was confirmed by powder X-ray diffraction studies on the solvate-filled and evacuated framework solids. Further proof of the stability of the evacuated material was obtained by means of a series of nitrogen adsorption studies on microcrystalline material. PIZA-1 is thermally stable in

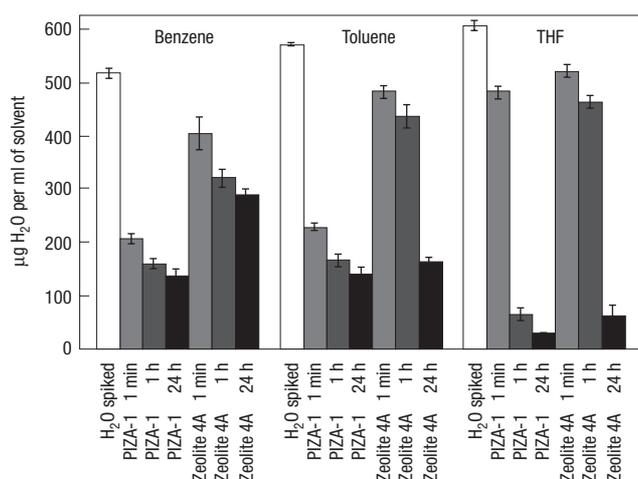


Figure 3 Selective adsorption of water from benzene, toluene and tetrahydrofuran (THF) solutions, determined by Karl–Fischer coulometric titration. Organic solvents were saturated with water under N_2 , 50 mg of PIZA-1 or 50 mg of Zeolite 4A, pre-treated and ground, were stirred in a flask under N_2 . On the basis of thermal desorption: 1-min exposure should correspond to 0.67 ml H_2O adsorbed per gram of solid; 50 mg PIZA-1 has the capacity to adsorb 0.034 ml H_2O . Zeolite 4A: 0.22 g H_2O per gram.

vacuum to >250 °C for five days, and decomposition begins during TGA at ~ 375 °C.

Molecular modelling of the evacuated network of PIZA-1 revealed a large calculated occupiable and accessible void volume of 47.9% (4,905 Å³ per unit cell) for a 1.40 Å probe radius (that is, the van der Waals radii for a water molecule)^{27,28}. Comparative calculations done using the same methods for the molecular sieve, Zeolite 4A, resulted in smaller occupiable volumes for all physically meaningful probe radii (for example, 27.2% for a 1.40 Å probe radius).

Selectivity with regard to the hydrophilicity of guest species, size and shape was probed by gravimetrically monitoring the thermal desorption of a variety of guests (Fig. 2a,b) from the fully desolvated network. The host network solid, PIZA-1, was exposed to guests for time periods ranging from one minute to one week. The guests that were incorporated to the greatest extent were water, amines and alcohols. PIZA-1 demonstrated extremely high capacity for repeated selective adsorption of water. A single evacuated sample was allowed to adsorb water for one hour before analytical desorption. The procedure was repeated ten times on the same sample to confirm the robustness and stability of PIZA-1 to multiple cycles of guest removal and adsorption. The network adsorbed an average of 162 (with a standard deviation of 9) water molecules per unit cell (78 ml H_2O per 100 g solid host). The sorption of water was also rapid: a one-minute exposure correlated to 156 guest water molecules per unit cell. For 24-h, one-week and three-week exposures, PIZA-1 sorbed 180 (105 ml water per 100 g solid host), 233 (112 ml water per 100 g) and 277 (162 ml water per 100 g) guest water molecules per unit cell, respectively. By comparison, zeolites commonly used as desiccants do not have nearly as large a capacity: Zeolite 4A and ALPO₄-18 molecular sieves (of pore size 3.8×3.8 Å) absorb 22 ml water per 100 g desiccant²⁹ and 32.8 ml water per 100 g solid³⁰, respectively.

Sorption of amines was also substantial, and provided a platform to explore further selectivity by PIZA-1. For the series of linear alkyl amines ($C_nH_{2n+1}NH_2$), chain length makes a substantial impact on the extent of sorption. Short-chain alkyl amines ($n = 4, 5$ or 6) were adsorbed to the greatest extent. As chain length increases ($n = 7, 8, 10$) a progressive

decrease in sorption was observed. As indicated by thermal desorption, PIZA-1 sorbs three 1-hexylamine guest molecules per unit cell (1-min exposure), 18 guest molecules per unit cell (24-hour exposure) and 35 guest molecules per unit cell (one-week exposure). At low exposure (<30 min) the sorption of pyridine, aniline and 1-hexylamine guests correlates to the available cobalt coordination sites (10.6 pyridine, 10.3 aniline and 10.4 1-hexylamine molecules per unit cell).

Size-selectivity was examined by sorption studies on a series of progressively larger aromatic amines: pyridine $>$ aniline $>$ 3,5-dimethylaniline $>$ 4-*t*-butylpyridine $>$ 2,4,6-trimethylpyridine (Fig. 2a). Size selectivity was also dramatically illustrated by comparing the sorption of cyclohexylamine (8.9 guests per unit cell) to that of dicyclohexylamine (2.3 guests per unit cell).

Shape-selectivity was probed using the picoline series (methyl pyridines, $C_5H_7N(CH_3)$). Steric hindrance paralleled the observed sorption: the least sterically hindered, 4-picoline, was absorbed more than 2-picoline, which was absorbed more than the most sterically hindered, 3-picoline. Shape-selectivity was also investigated by observing the sorption of the isomers of butyl-substituted amines: the least hindered *n*-butylamine was absorbed much more than di-*n*-butylamine, which was absorbed much more than the increasingly sterically hindered di-*iso*-, di-*s*- and di-*t*-butylamines (Fig. 2b). As the bulky organic substituents encroach upon the hydrophilic group, guest sorption declines.

Alcohol guests were also strongly sorbed by PIZA-1 (Fig. 2a). As the hydrophobicity and steric bulk of the alcohols increased, the sorption decreased (methanol $>$ ethanol $>$ propanol $>>$ butanol $>$ hexanol). Direct comparisons between linear and branched alcohols (for example, 1-propanol versus 3-propanol, and 1-butanol versus *t*-butanol) again demonstrated the correlation between increased steric hindrance and decreased sorption.

A series of functionalized *n*-alkanes was explored, including hexyl alcohol, thiol, nitrile, aldehyde, bromide, and hexane itself. None of these showed substantial sorption compared to *n*-hexylamine. The preference observed in the 1-hexyl analogue guests can be attributed in part to its increased hydrophobicity and to its strong coordinating capability. The low absorption of hexanoic acid initially appears anomalous, but probably reflects the strong tendency of carboxylic acids to form large hydrogen-bonded dimers.

It is possible to trick PIZA-1 into sorbing non-polar guests. For example, sorption of *n*-hexane was achieved by successive washings of the solid with progressively higher concentrations of hexane in pyridine (beginning with 50% and concluding with 90% v/v hexane in pyridine). Confirmation of the absorption of hexane was determined via TGA coupled with mass spectrometry (see Supplementary Information). The pyridine probably coordinates to the available functionalized sites; how labile this coordination is has not been determined. We hypothesize that the accessibility of the interior of PIZA-1 requires the presence of a hydrophilic molecule, such as pyridine, in order to maintain the porosity necessary to allow sorption of hydrophobic guests into the channels. The ability to absorb hexane may permit the use of PIZA-1 as a shape-selective oxidative catalyst for alkanes.

No solvent was found to redissolve the PIZA-1 solid (including strong donor solvents such as dimethyl sulphoxide and dimethyl formamide, strong acids such as concentrated sulphuric and hydrochloric acids, and strong bases). The lack of visible colour (determined spectrophotometrically at <0.01 absorbance units) in such solvents correspond to solubilities in the guest liquids of $<1 \times 10^{-8}$ M. The robust PIZA-1 solid remained undissolved throughout all experiments. The sole exception was concentrated aqueous tetra-alkylammonium hydroxide (20–40%), which did dissolve PIZA-1.

PIZA-1 possesses extraordinary properties as a desiccant for the selective drying of common organic solvents (for example, benzene, toluene and tetrahydrofuran). In a comparison to Zeolite 4A, PIZA-1 demonstrated both a higher capacity and faster response for the selective

sorption of water (Fig. 3). PIZA-1 acted as a better desiccant in one hour than Zeolite 4A did in one day.

The results from this work demonstrate the feasibility of porphyrin molecules as building blocks for the rational construction of functional porous solids. We are currently exploring the incorporation of additional catalytically active metals (Mn^{III}, Fe^{III}, Ru^{III} and Cr^{III}) into the porphyrin macrocycle, and their reactivity as size- and shape-selective oxidation catalysts.

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Competing financial interests

The authors declare that they have no competing financial interests.