

Porphyrin Network Materials: Chemical Exploration in the Supramolecular Solid-State

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Rational design of solid-state materials from molecular building blocks possessing desired physical and chemical characteristics remains among the most challenging tasks for the synthetic chemist. Recently, there has been intense activity focusing on this research area, including the assembly of a wide range of organic molecules, inorganic metal clusters, and coordination complexes into extended networks.¹⁻⁷ Motivated by potential applications associated with channels and cavities, such materials have been explored for size- and shape-selective catalysis, separations, sensors, molecular recognition and nano-scale reactors. Within this context, assemblies of robust and chemically versatile porphyrin and metalloporphyrin building blocks remain rare. Using *meso*-tetrapyrrolyl and *meso*-tetracyanophenyl metalloporphyrins, Robson and coworkers reported cationic network solids with large extended channels (10–15 Å) occupied by non-coordinated anions and solvent molecules.⁸ Supramolecular architectures of porphyrin solids with hydrogen bonded or metal-ligand coordination networks have been reported over the past few years.⁹⁻¹² Although allusions to zeolite-like microporosity based on crystallography and loss of initial guest solvent molecules have appeared in the literature, evidence of functional microporous behavior is scarce.

Using *p*-carboxylic acid tetraphenyl porphyrin molecules as the organic building block, the synthesis of novel microporous materials has been pursued for this work. Porphyrins possess high thermal stability relative to other organic molecules and are characterized by an approximate two-dimensional square geometry. Metalloporphyrins have demonstrated utility as excellent oxidation catalysts for hydroxylation of alkanes and epoxidation of alkenes.¹³ Porous metalloporphyrin networks have the potential to act as size- and shape-selective catalysts. The solvothermal synthesis, characterization, and selective sorption properties of a 3-dimensional metalloporphyrin network solid, [CoT(*p*-CO₂)PPCo_{1.5}], named PIZA-1 for Porphyrinic Illinois Zeolite Analogue 1, have been investigated (Figure 1).

Synthesized via the self-assembly of *p*-carboxy tetraphenyl porphyrins with metal ions, the extended structure reveals a single, independent, neutral network with large, bi-directional oval-shaped channels (9 x 7 Å) along the crystallographic *b*- and *c*-axes (Figure 2) and another set of channels (14 x 7 Å) along the *a*-axis. At the intersection of channels, an internal chamber (31 x 31 x 10 Å) is realized. Channel-shape is attributable to ruffling of the metalloporphyrin macrocycles when coordinated to the bridging trinuclear Co(II)-carboxylate clusters. 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 indicates a preference for water and amines. This organic zeolite analogue also demonstrates remarkable ability as a molecular sieve for removal of water from common organic solvents. By powder X-ray

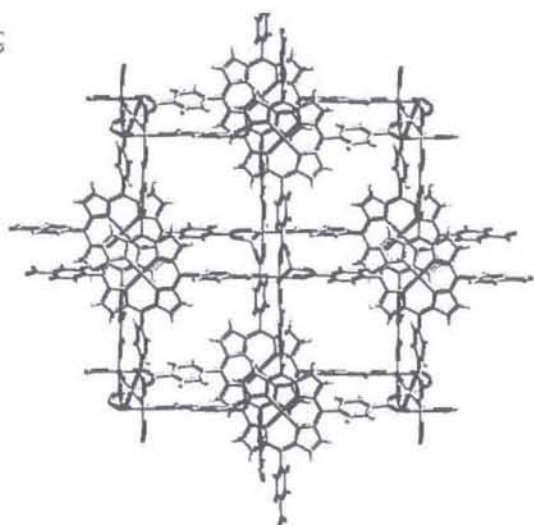


Figure 1

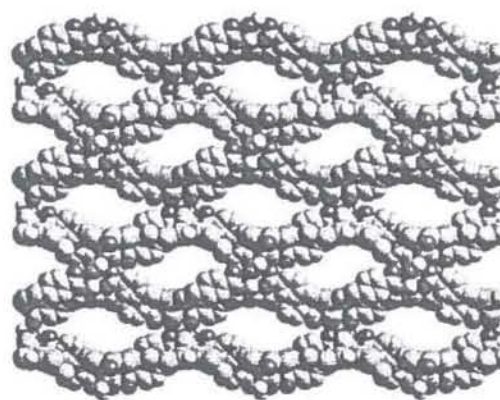


Figure 2

diffraction and BET gas adsorption studies, this material has been shown to maintain its porous structure as a guest-free solid when heated under vacuum to 250°C. Using thermal gravimetric analysis (TGA), selectivity with regard to hydrophilicity of guest species, guest size and guest shape has been investigated (Figure 3, 24-hour exposure to guests). PIZA-1 demonstrates extremely high capacity for repeated selective sorption of water. In comparison to 4Å molecular sieves, PIZA-1 exhibits higher capacity and faster response for the selective adsorption of water from benzene, toluene and tetrahydrofuran solutions (Figure 4). Molecular modeling of sorbed guests corroborates experimental results.

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,^{14,15} can be contrasted with the bent trinuclear M(II)-carboxylate clusters (M = Co, Mn) of isostructural 3-dimensional frameworks: PIZA-2 and PIZA-3. Containing near-planar metalloporphyrin macrocycles, PIZA-2 and -3 manifest lower void volumes (56%). The difference is the presence of terminal coordinating, nitrogenous Lewis bases in the linear trinuclear clusters.

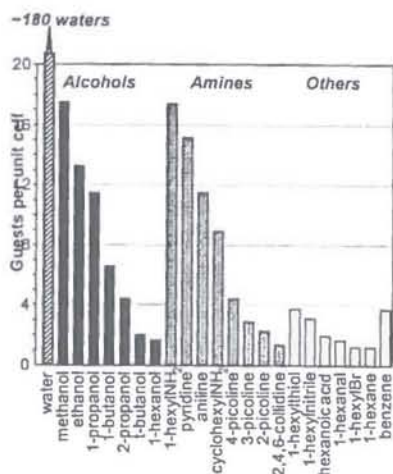


Figure 3

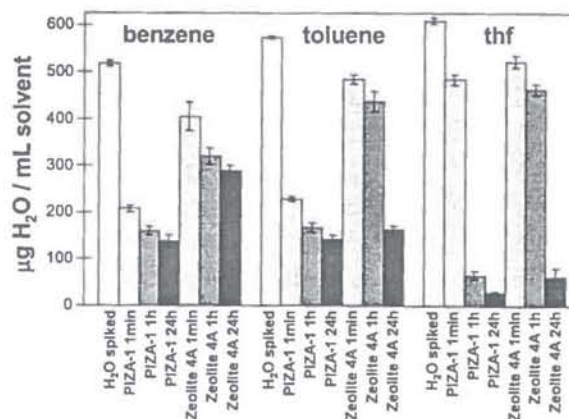


Figure 4

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