

Recent developments in robust microporous porphyrin solids

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Dedicated to Professor Hisanobu Ogoshi on the occasion of his 70th birthday

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ABSTRACT: A review of the recent literature is presented which assesses the development of robust microporous porphyrin framework solids and their potential to perform selective sorption or heterogeneous shape- or size-selective catalysis. The review focuses only on those porphyrin solids whose porosity is robust, i.e. whose framework remains after the removal of solvates, as determined by thermal gravimetric analysis (TGA), X-ray powder diffraction (XRD), or gas adsorption studies. Eleven such robust porphyrin framework solids are presented. Copyright © 2004 Society of Porphyrins & Phthalocyanines.

KEYWORDS: porphyrin solids, metal-organic frameworks, microporous solids, robust, catalysis.

INTRODUCTION

The thermal and chemical stability of metalloporphyrins make them attractive building blocks for the molecular engineering of microporous (i.e. pores with diameters less than 20 Å) framework solids [1-2]. Since the early 1990s, the synthesis of porphyrin framework solids has had major contributions from Robson [3, 4], Strouse [5-9], Goldberg [10-12], and Suslick [1, 2, 13-15]. Although there are many single crystal structures of porphyrinic solids that contain pores filled with disordered solvates, very few of these are stable to the removal of solvates. Nonetheless, the well known homogeneous catalysis capabilities of metalloporphyrins [16, 17], especially for oxidation reactions, make porphyrin solids enticing targets for applications as heterogeneous catalysts. Selective sorption of small molecules and size- or shape-selective heterogeneous catalysis [18, 19] are clear goals for research on porphyrin framework solids, but only recently have successes come within

range, and to date, no example of a catalytic porphyrin framework solid has been reported.

Kosal and Suslick thoroughly reviewed the topic of microporous porphyrin and metalloporphyrin materials in 2000 [1-2], and illustrated the diversity of open framework porphyrin structures that could be obtained through van der Waals interactions, hydrogen bonding, and metal-organic coordination bonds. The non-interpenetrating and interpenetrating structures presented were one-, two-, or three-dimensional in nature. In this paper, we review the most recent literature on porphyrin framework solids, in order to assess the potential of robust microporous porphyrin framework solids as selective sorbents or as heterogeneous shape- or size-selective catalysts. We focus only on *robust* (i.e. frameworks that remain intact after removal of solvates) microporous porphyrin framework solids reported since 1999. To be considered "robust," the reported solids must have been evaluated by thermal gravimetric analysis (TGA), X-ray powder diffraction (XRD), or gas adsorption studies to show that the framework retains microporosity upon evacuation. There were eleven such robust porphyrin framework solids, and they are

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presented below.

RECENT DEVELOPMENTS IN MICROPOROUS PORPHYRIN SOLIDS

In a novel coordination motif, Zubieta and coworkers [20] report a three-dimensional framework structure of copper(II) tetra-4-pyridylporphyrins that coordinate to $[\text{Cu}_2\text{Mo}_3\text{O}_{11}]$ chains. These chains run perpendicular to the porphyrin planes as shown in Fig. 1. This framework was synthesized under hydrothermal conditions with the starting materials of MoO_3 , copper nitrate, and free-base tetra-4-pyridylporphyrin. Successive weight percent losses from TGA studies of the compound were reported in the ranges of 230–250 °C, 470–480 °C, and 500–550 °C and were attributed to losses of the pyridyl functional groups on the porphyrin. Another weight percent loss between 575–650 °C was attributed to the porphyrin ring. These assignments are somewhat surprising, since TGA of porphyrin solids typically show an onset of decomposition at ~400 °C. In any case, the maximum temperature at which this structure was stable is 230 °C. The amount of disordered water molecules that must exist in the channels of the structure was not quantified, and no further assessment of the stability of this structure was reported.

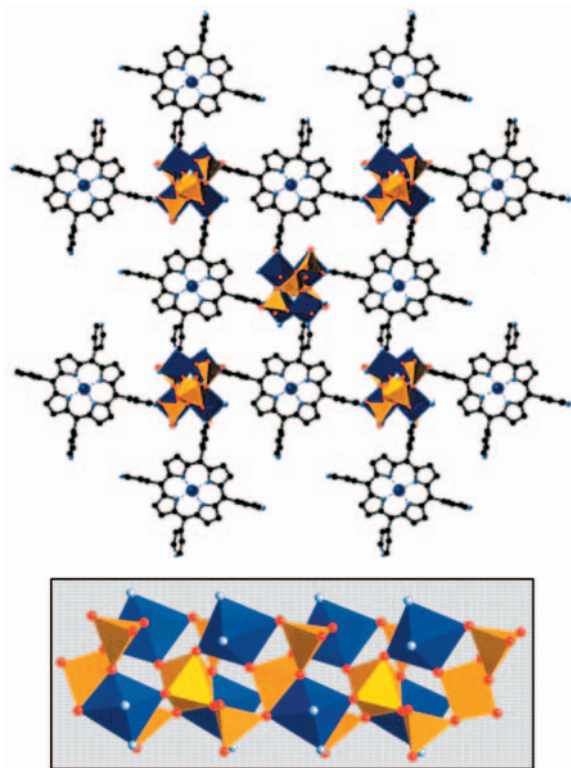


Fig. 1. A neutral 3D framework composed of copper (II) tetra-4-pyridylporphyrins coordinated to $[\text{Cu}_2\text{Mo}_3\text{O}_{11}]$ chains. The $[\text{Cu}_2\text{Mo}_3\text{O}_{11}]$ chains, illustrated in the inset, are perpendicular to the plane of the porphyrins

This same paper also reported another hydrothermally synthesized framework with iron metalloporphyrin. As shown in Fig. 2, this three-dimensional cationic framework contains iron tetra-4-pyridylporphyrins with two coordination modes. Each iron in the porphyrin core is axially coordinated to the pyridyl groups of two neighboring porphyrins, while the remaining pyridyl groups are octahedrally coordinated to iron ions. The positive charge of the framework is balanced by the alternating incorporation of $[\text{Mo}_6\text{O}_{19}]^{2-}$ clusters. For this framework, the authors indicate that 19 molecules of water exist per cavity based on TGA data and density measurements, but no TGA data is presented to assess the stability of the framework. The framework reportedly can absorb 15 weight percent water vapor in a Type I isotherm indicating microporosity, but no details are given. Both of the three-dimensional porphyrin frameworks reported by Zubieta are intriguing but the question of robustness requires further exploration.

In a report that presents a new bonding mode for zinc tetra(*p*-carboxyphenyl)porphyrins, Goldberg and coworkers [21] describe an open framework that contains bilayers of coordinated porphyrins, axially linked by bipyridyl ligands as shown in Fig. 3. The two-dimensional bilayers consist of zinc tetra(*p*-carboxyphenyl)porphyrins that are both hydrogen bonded and coordinated to a sodium ion pair as indicated in Fig. 3. One of the four carboxylic acid groups on each porphyrin is deprotonated during synthesis to form a charge-neutral framework. This structure contains $8 \times 12.5 \text{ \AA}$ and $8 \times 10 \text{ \AA}$ pores down

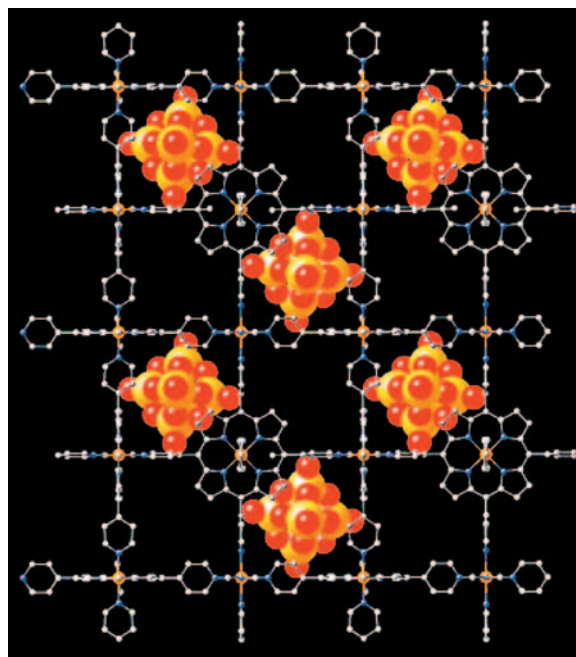


Fig. 2. A cationic 3D framework composed of iron tetra-4-pyridylporphyrins with $[\text{Mo}_6\text{O}_{19}]^{2-}$ clusters incorporated for charge balance

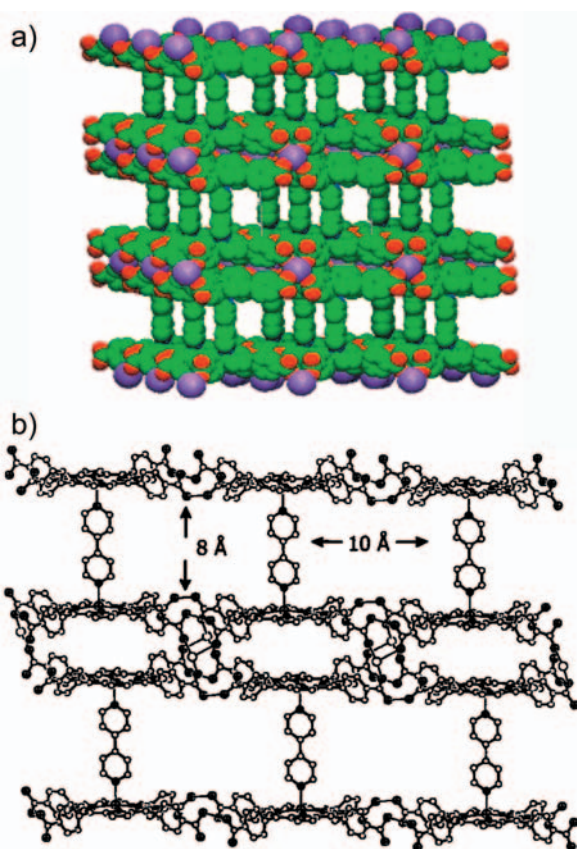


Fig. 3. a) A 3D framework composed of zinc tetra(*p*-carboxyphenyl)porphyrin/sodium ion pair bilayers, axially coordinated by bipyridyl ligands. b) Bilayers are formed from both hydrogen bonding and coordination to sodium ion pairs, which are in turn separated by coordination of bipyridyl ligands to the porphyrins' metal centers

the crystallographic *a* and *b* axes and has a large void volume of 58%. TGA measurements indicate a 32% weight loss between 50 to 150 °C, corresponding to 32 methanol solvates. Goldberg claims that there is “no apparent phase transition or damage to the crystal morphology” after heating to 150 °C, but no XRD data was presented. Further heating to 400 °C results in a 13.5% weight loss that was attributed to the loss of ethyl benzoate, bridging bipyridyl ligands, and carboxylate groups. The stability of this framework was reported to be the subject of further investigations. A brief mention of “simple exchange experiments” was reported later [11], which suggests that the lattice may reversibly sorb common organic solvents, but no data were presented.

Goldberg reports another porphyrin framework composed of two-dimensional layers of manganese(III) tetraphenylporphyrins that are coordinated to free-base tetra-4-pyridylporphyrins in the arrangement shown in Fig. 4 [11]. These two-dimensional layers stack on top of one another through π - π interactions to form 4.5 Å channels perpendicular to the porphyrins' faces and have a void volume of approximately

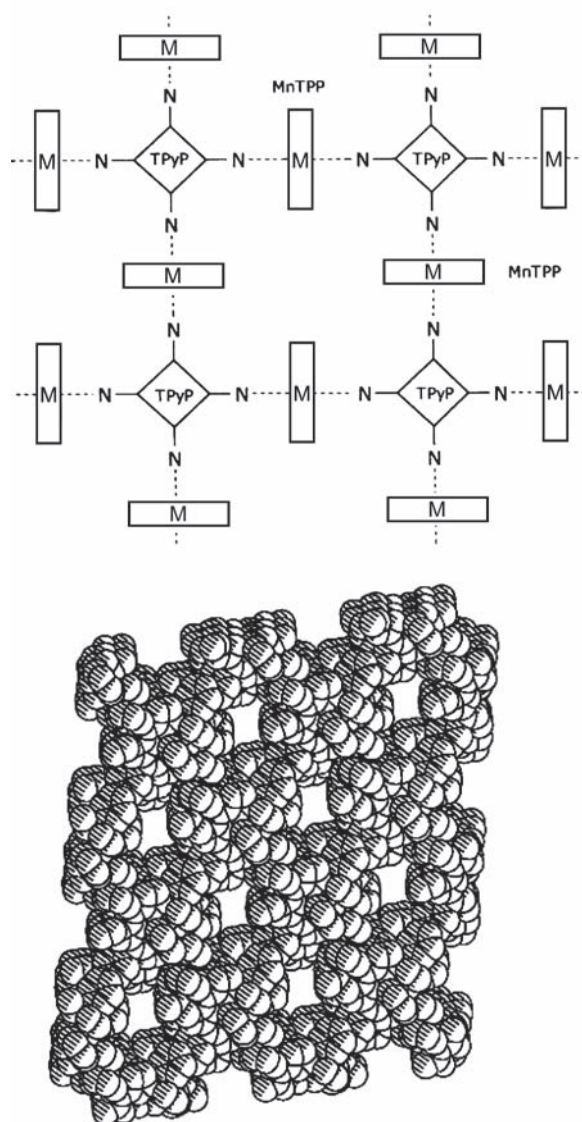


Fig. 4. Mixed 2D stacked layers of free base tetra-4-pyridylporphyrins coordinated to the metal centers of manganese (III) tetraphenylporphyrins. Top view shows the connectivity in the 2D layer. Bottom view illustrates the pores formed through layer stacking. Perchlorate counterions have been removed for clarity

50%. This material was characterized by TGA and a 32.5% weight loss occurred from 80 to 150 °C, corresponding to ten nitrobenzene solvates per every three porphyrins. No other weight loss was observed until 300 °C, which was taken to mean that the original framework structure was preserved. However, neither XRD data or gas adsorption studies were carried out to confirm this claim.

A crystal structure of tin(IV) tetratolylporphyrin phenolate complexes reported by Langford and coworkers [22] has helical channels that pitch every 10 Å to create 5.5 Å diameter cylindrical pores down the the crystallographic *c* axis, as shown in Fig. 5. The porphyrins pack tightly and interact through

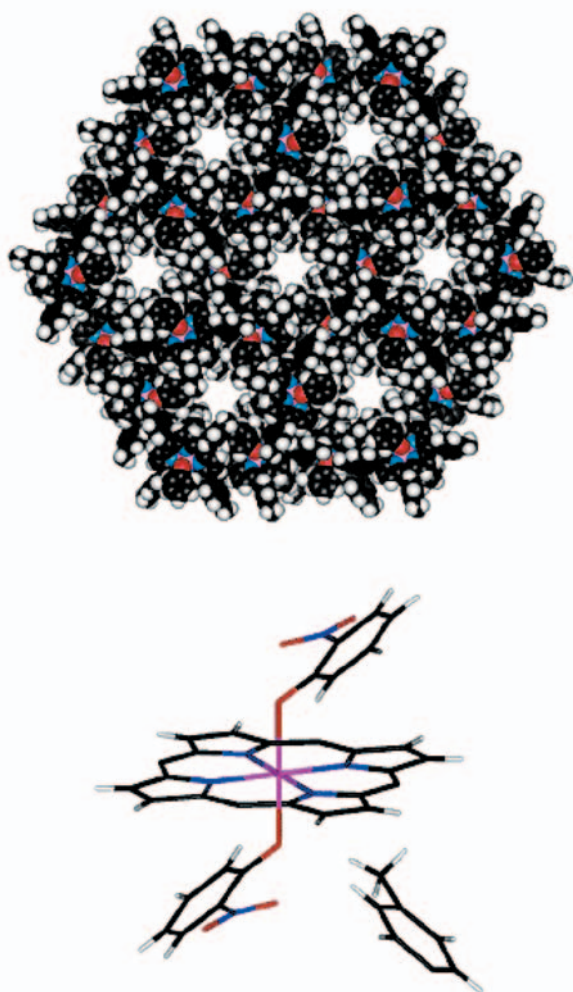


Fig. 5. Crystal structure of tin (IV) tetratolyl porphyrin phenolates. Top view shows 5.5 Å pores down the crystallographic c axis. Bottom view illustrates the hydrogen bonding between two hydrogen atoms of the tolyl group to the oxygen atom of the phenolate ligand

weak nonclassical hydrogen bonding between two hydrogen atoms of a tolyl group and an oxygen atom on a phenolate ligated to a neighboring porphyrin (Fig. 5). TGA and differential scanning calorimetry (DSC) measurements on this system indicate that minimal weight loss or phase change occurs up to 200 °C. No other tests were done to assess the microporosity of the de-solvated structure.

McKeown and coworkers [23] took a much different approach in the development of a robust microporous porphyrin solid. Instead of utilizing the normal coordination schemes of hydrogen bonding or metal-ligand coordination, they utilized covalent bonds to make a true polymer from the monomeric units of *meso*-tetrakis(pentafluorophenyl)porphyrin and 5,5',6,6'-tetrahydroxy-3,3,3',3'-tetramethyl-1,1'-spirobisindane (a dicatchol). The polymerization reaction is shown in Scheme 1. In order to remove the *N*-methylpyrrolidone solvent, the resulting polymer was Soxhlet extracted with methanol, acetone, and

THF over several days and then dried in a vacuum oven. TGA studies of this evacuated polymer showed only a 3% weight loss up to 350 °C, which was attributed to adsorbed water. The elemental analysis of this evacuated solid matches well with the expected formula.

Although these polymers are not crystalline, unlike the other examples presented in this review, the resulting evacuated polymer is obviously microporous as indicated by the Type I nitrogen isotherm shown in Fig. 6. The evacuated polymer must have a robust structural "framework" since it is able to maintain its void volume and have high BET surface areas of 1000 m²/g. An iron porphyrin analog polymer was also created and shown to have a similar surface area, making this solid a potential heterogeneous catalysis. The catalytic and adsorption properties of these amorphous solids remain to be explored.

Reed and coworkers [24] reported the use of C₆₀ fullerenes as pillars to separate two-dimensional layers of *meso*-tetra-4-pyridylporphyrins that are coordinated to lead nitrate units. The two-dimensional porphyrin layer, shown in Fig. 7, is the same as those found in a closed-packed layer structure reported earlier by Rogers [25]. In Reed's structure, the fullerenes separate the layers through close interactions with the core of the free-base porphyrin as shown in Fig. 7. The void volume of this structure is estimated to be 52% and is filled with the crystallization solvent 1,1,2,2-tetrachloroethane. TGA studies indicate that 80% of these solvates can be removed by heating the solid at 250 °C under vacuum. XRD results of this semi-evacuated solid suggest that crystallinity remains, but the original powder pattern is shifted. The solid can be fully evacuated when heated above 300 °C, but an amorphous material results.

An interpenetrated 3D network of zinc tetra-4-pyridylporphyrin coordinated to both silver ions and the zinc centers of the porphyrins was prepared by Ciani and co-workers [26]. A view of the network down the crystallographic c axis shows an open structure that has 55% void volume (Fig. 8). Interpenetrating 2D layers of zinc tetra-4-pyridylporphyrins coordinated to silver ions interpenetrate one another perpendicularly in a

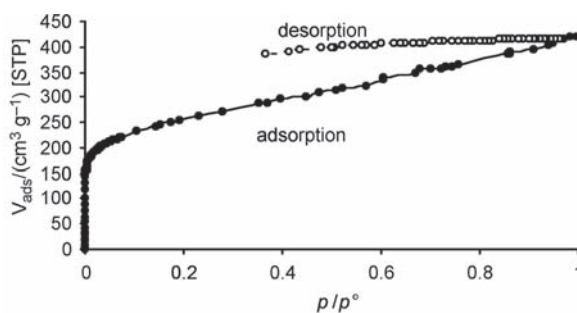
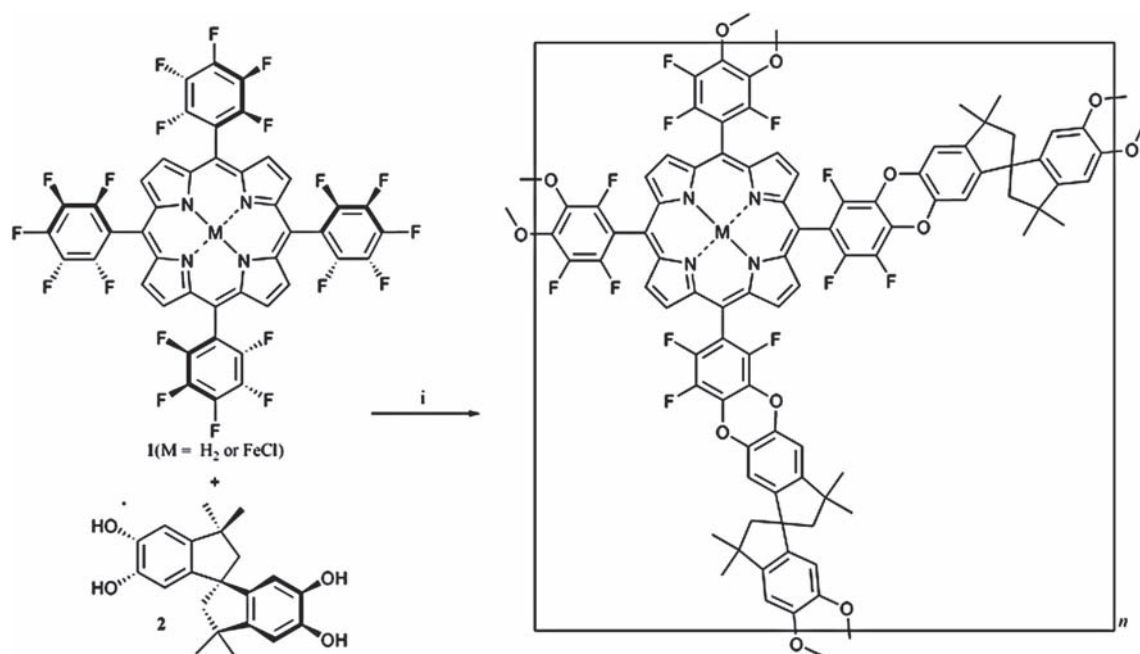


Fig. 6. Type I nitrogen gas isotherm of the evacuated microporous porphyrin polymer



Scheme 1. Polymerization reaction between porphyrin and dicatechol

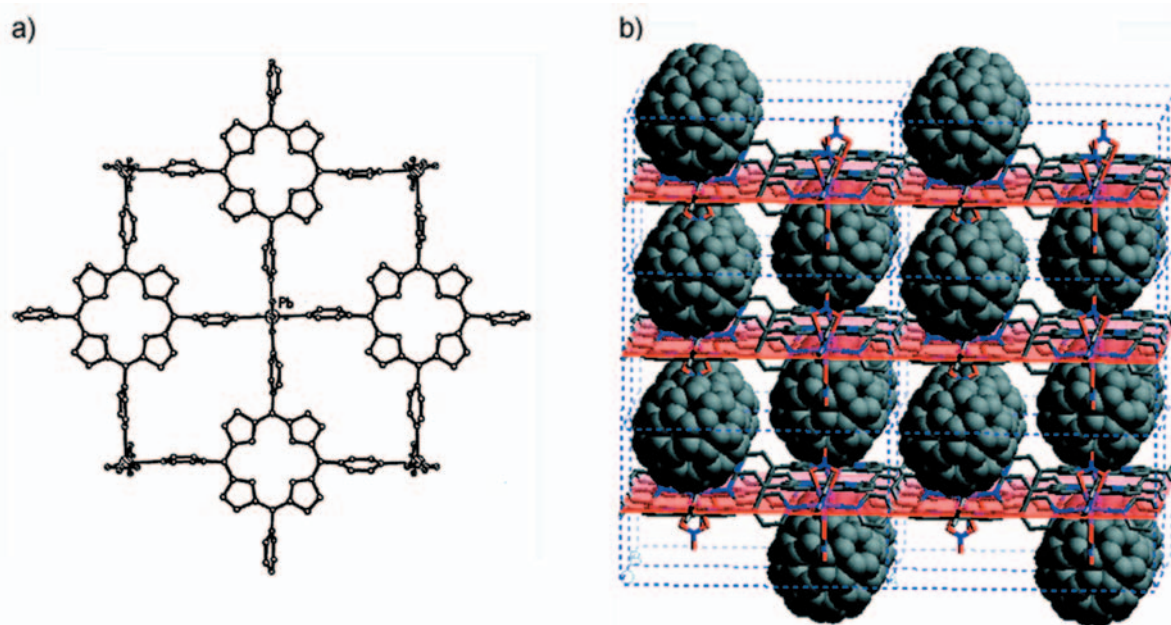


Fig. 7. a) 2D porphyrin layer formed from coordination of pyridyl groups to lead nitrate units. b) Fullerenes act as pillars to separate the 2D porphyrin layers

bilayer fashion and run parallel to the crystallographic *c* axis shown in Fig. 8. These bilayers are then further coordinated through the interaction of the pyridyl groups (of porphyrins perpendicular to the *c* axis) to the zinc centers of the porphyrins in the bilayers.

Thermogravimetric analysis showed a continuous weight decrease from 40 to 400 °C, corresponding to the sequential loss of the crystallographically determined solvates: water, trichloroethane, and *N,N'*-dimethylacetamide. No further decomposition

was found until 500 °C. XRD patterns of the solid as it was heated slowly to 130 °C indicated a loss in crystallinity and a collapse of the network upon initial evacuation of the solvates. If this solid was immersed in the crystallization solvent mixture, however, the original XRD pattern returned. This result suggests that the microporosity only exists when the solid is solvated.

A solvothermally synthesized framework, dubbed PIZA-1 (Porphyrinic Illinois Zeolite Analogue-1), of

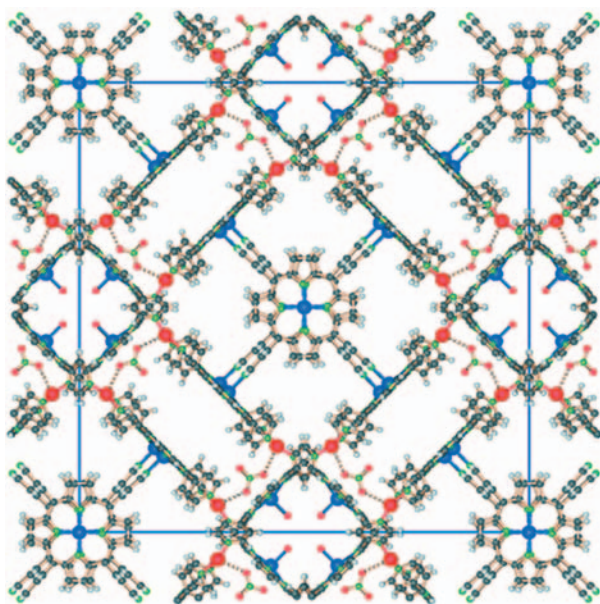


Fig. 8. A 3D interpenetrated network composed of zinc tetra-4-pyridylporphyrins and silver ions. View is down the crystallographic *c* axis

ruffled cobalt(III) tetra(*p*-carboxyphenyl)porphyrins coordinated in three dimensions to linear trinuclear cobalt (II) clusters was reported by Suslick and coworkers [13]. The crystal structure indicates that there are $7 \times 14 \text{ \AA}$ channels down the crystallographic *a* axis and $7 \times 9 \text{ \AA}$ channels down both the *b* and *c* axes, creating a open framework with an impressive void volume of 74%. The molecular diagrams in Fig. 9 illustrate these channels which contain disordered pyridine and water molecules in the as-synthesized state.

The evacuated PIZA-1 framework is robust as evidenced by XRD and nitrogen adsorption studies. The framework was found to be thermally stable up to $375 \text{ }^\circ\text{C}$ through TGA studies. The evacuated PIZA-1 is selective towards the adsorption of highly polar guests. PIZA-1 has the remarkable ability, as shown in Fig. 10, to reversibly sorb water with larger capacity, greater affinity, and faster speed than the standard Zeolite 4A dessicant. In addition, size- and shape-selective adsorption was demonstrated through sorption studies on a series of amines and alcohols. PIZA-1 represents a significant advance in the development of robust microporous porphyrins solids that use only metal-organic coordinations to connect the three-dimensional structure.

Two other porphyrin frameworks have been reported by Kosal and Suslick [27] and were named PIZA-2 and PIZA-3. PIZA-2 contains cobalt(III) tetra(*p*-carboxyphenyl)porphyrins that coordinate to a bent trinuclear cobalt cluster. PIZA-3 is isostructural to PIZA-2, but instead contains manganese(III) tetra(*p*-carboxyphenyl)porphyrins and a bent trinuclear manganese cluster. A molecular diagram

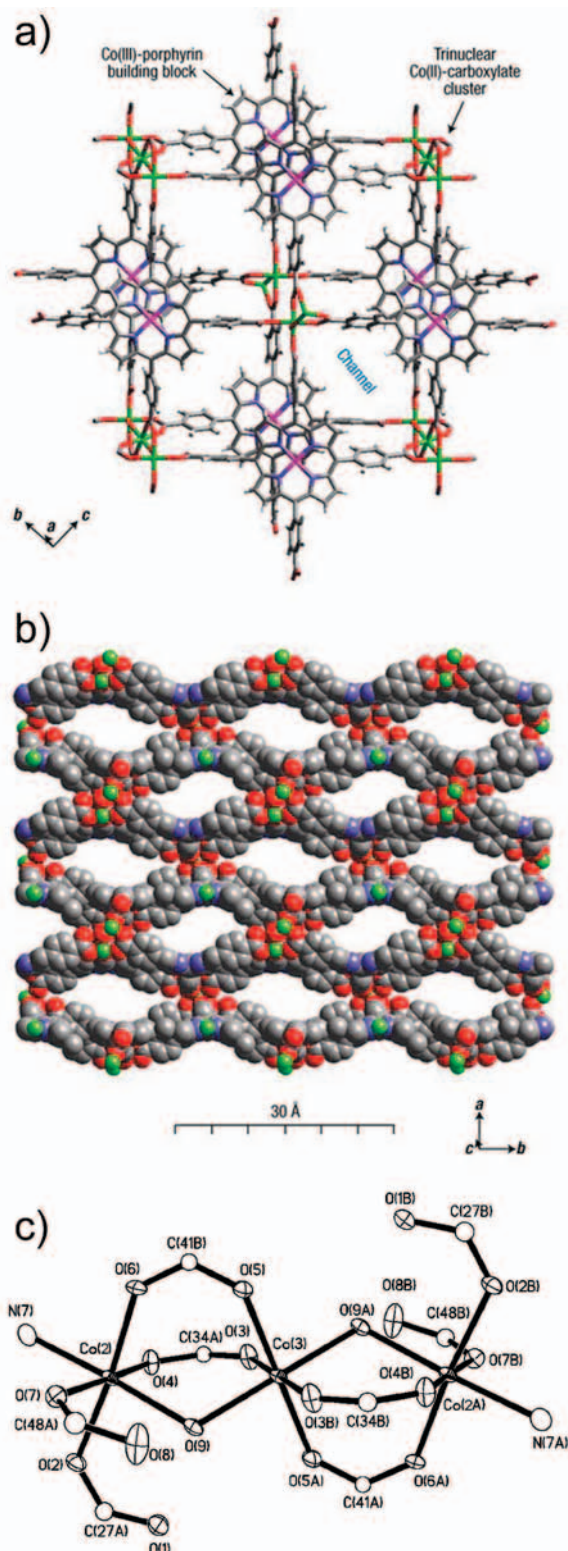


Fig. 9. Molecular diagrams of PIZA-1 (Co(III) tetra(*p*-carboxyphenyl)porphyrins coordinated in three dimensions to linear trinuclear cobalt (II) clusters). a) Top view shows the $7 \times 14 \text{ \AA}$ channels down the crystallographic *a* axis; b) bottom view shows the $7 \times 9 \text{ \AA}$ channels down the *c* (and *b*) axis; c) enlarged ORTEP of the trinuclear cobalt cluster that bridges the porphyrins

of the PIZA-3 framework is shown in Fig. 11. There are alternating $5 \times 9 \text{ \AA}$ and $7 \times 8 \text{ \AA}$ pores down the crystallographic a axis and $3 \times 5 \text{ \AA}$ pores down the c axis, creating an open framework with 56% void volume. Characterization of the stability, sorption, and catalytic properties of these two frameworks is ongoing.

Finally, a robust microporous zinc porphyrin framework solid has been developed by Smithenry and Suslick [28]. Building upon Yaghi's recent report [29] of porous Zn_4O bridged arene-dicarboxylate framework solids, a Zn_4O framework with zinc (II) *trans*-biscarboxylate tetraarylporphyrin bridges has been synthesized. The structural model of the

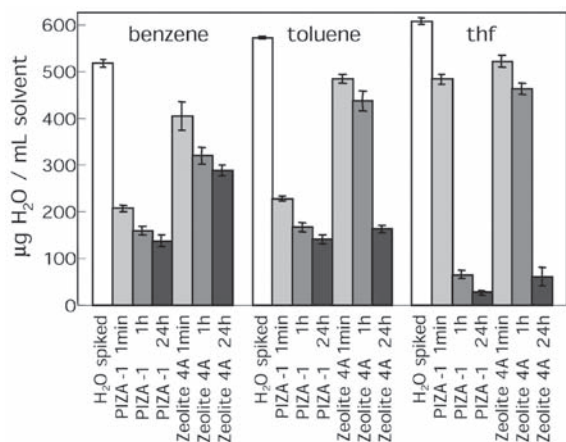


Fig. 10. Selective water adsorption into the nanoporous porphyrin solid, PIZA-1 from benzene, toluene and tetrahydrofuran (thf) solutions, In a comparison to 4A molecular sieves, the Co-porphyrin network solid has a higher capacity, an higher affinity, and a faster response

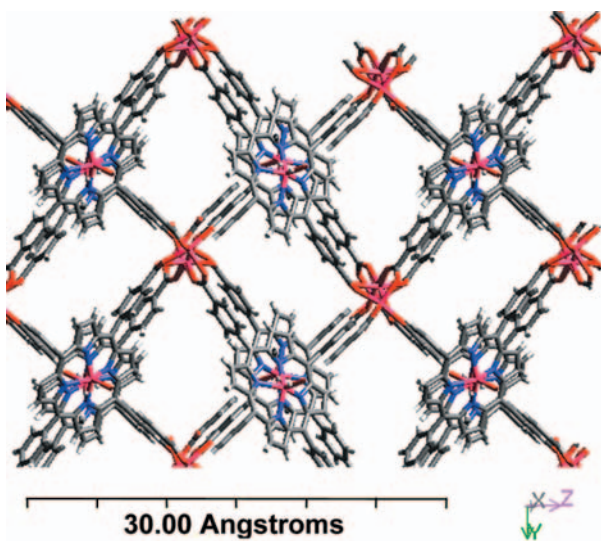


Fig. 11. Molecular diagram of PIZA-3 (Mn(III) tetra(*p*-carboxyphenyl)porphyrin coordinated to a bent trinuclear cobalt cluster) illustrating alternating pores; view down the crystallographic a axis

solid, which we designate PIZA-4, contains an interpenetrated cubic framework of zinc (II) *trans*-carboxylateporphyrins that coordinate the edges of tetrahedral Zn_4O clusters as shown in Fig. 12. The interpenetrated framework solid is largely open with 74% free volume and $4 \times 7 \text{ \AA}$ averaged pores down each axis. In order to evaluate the robustness of evacuated PIZA-4, the solvates were completely removed by heating the solid at $150 \text{ }^\circ\text{C}$ under vacuum, as confirmed by TGA (Fig. 13). The minimal weight loss up to $400 \text{ }^\circ\text{C}$ indicates the stability of this framework. Elemental analysis of the evacuated solid confirmed the expected formula for the framework without solvate.

To determine the nature of evacuated PIZA-4, reversible Type I N_2 isotherms (Fig. 14) at 77K were measured for the de-solvated PIZA-4 solids and are consistent with microporosity. A Langmuir surface area of $800 \text{ m}^2/\text{g}$, calculated from the isotherm data, compares favorably to the $\sim 500 \text{ m}^2/\text{g}$ for a typical

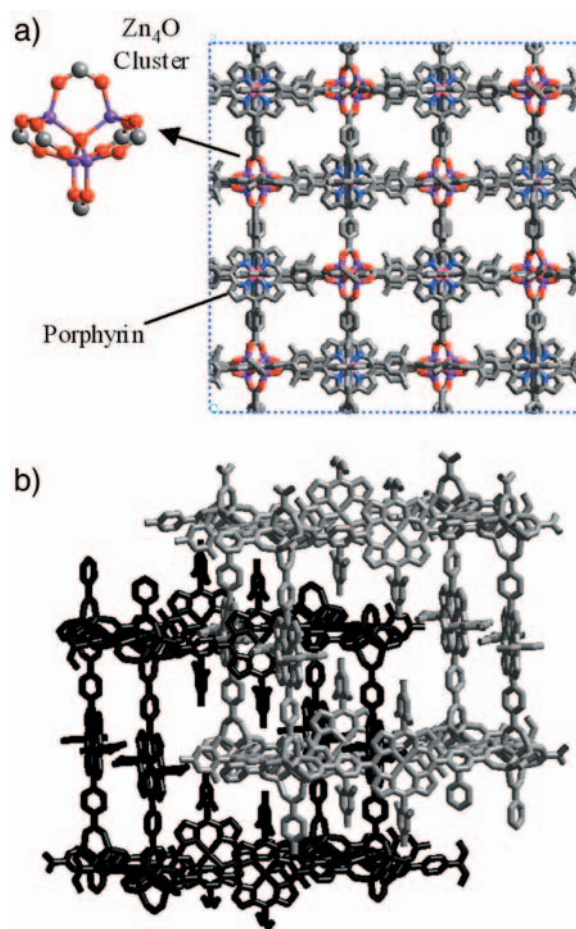


Fig. 12. a) Average view of the crystal structure of PIZA-4 (interpenetrated cubic framework of Zn(II) *trans*-carboxylateporphyrins coordinating to tetrahedral Zn_4O clusters). Enlargement shows coordination of six carboxylates from the porphyrins to the Zn_4O tetrahedral cluster. b) Representation of the two interpenetrating frameworks of PIZA-4

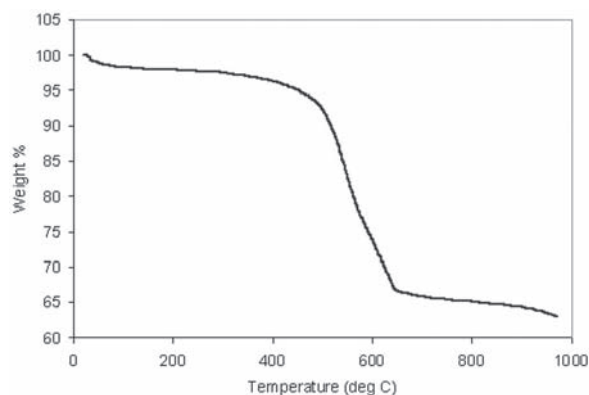


Fig. 13. TGA of evacuated PIZA-4. Minimal weight loss occurs up to 400 °C at which point the porphyrin starts to decompose

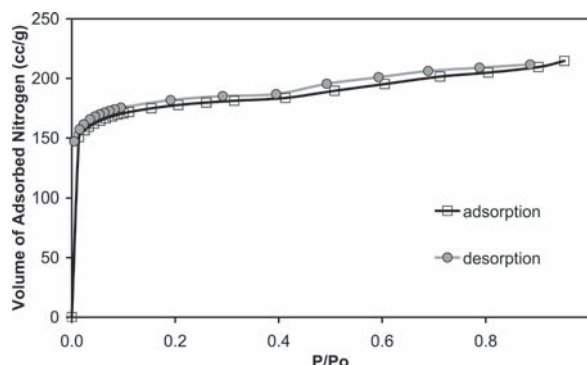


Fig. 14. Reversible Type I nitrogen gas isotherm for evacuated PIZA-4, indicating microporosity

zeolite. The evacuated solid also reversibly re-sorbs 241 N,N-dimethylformamide molecules per unit cell, which corresponds to 94% of the assessible free volume calculated from the single crystal model. These two findings indicate that the pores remain open and available for re-sorption of solvate.

As shown in Fig. 15, the XRD peaks for evacuated PIZA-4 powder are broadened and shifted when compared to the initial solvated sample, but still show substantial long-range order. Re-exposure of the evacuated PIZA-4 powder to N,N-dimethylformamide/chlorobenzene resolves the solid and the original XRD powder pattern for PIZA-4 returns within a few minutes (Fig. 15). Because the solid is completely insoluble ($<\mu\text{M}$), the resolution does not involve dissolution/recrystallization, but rather a direct diffusion of solvates back into the pores of the framework solid.

The PIZA-4 framework has been characterized fully by XRD, TGA, and gas and solvate adsorption studies, showing that the evacuated framework is robust and microporous. Results from TGA analysis of solvate desorption (Fig. 16) indicate that PIZA-4 is selective towards adsorption of substrates with medium polarity, which is in striking contrast to the

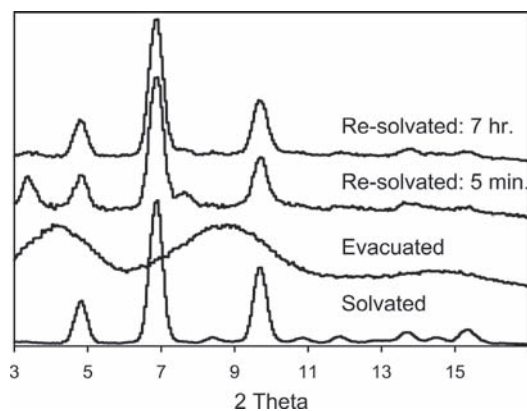


Fig. 15. XRD patterns of evacuated and re-solvated PIZA-4

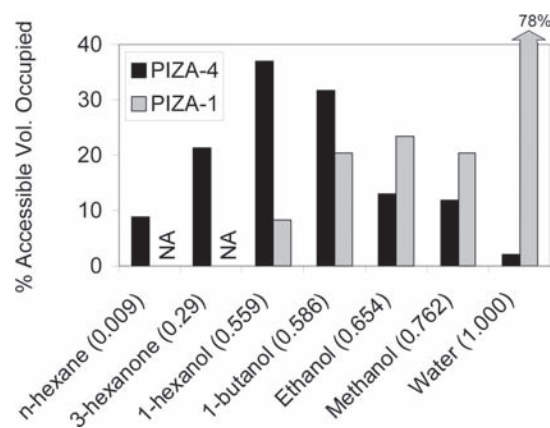


Fig. 16. PIZA-4 and PIZA-1 sorption data for substrates of increasing polarity. E_T^N solvent polarity values given in parentheses (3-hexanone value approximated from that of 2-hexanone) [30]

very polar pores of PIZA-1. PIZA-5 and PIZA-6 have also been synthesized and are isostructural to PIZA-4 and contain manganese and cobalt *trans*-biscarboxylatetraarylporphyrins, respectively [31]. As will be reported elsewhere, PIZA-5 represents the successful realization of a heterogeneous catalytic metalloporphyrin framework where size- and polarity-selective catalysis occurs in the pores.

CONCLUSION

In this review, we have assessed the current state of the development of robust microporous porphyrin framework solids that have the potential to perform selective small-molecule sorption or heterogeneous catalysis with size- or shape-selectivity. In spite of the large number of framework solid state structures, there remain only a very few examples where the solids are *robust* and retain their microporosity after loss of solvates. A single-crystal X-ray structure is simply insufficient to justify claims of porosity for

framework solids; the absence of characterization data from XRD after evacuation, thermal gravimetric analysis, and gas sorption studies in most such reports make such claims of porosity optimistic, at best.

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