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A Robust Microporous Zinc Porphyrin Framework Solid

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A robust microporous zinc(II) metalloporphyrin framework solid has been synthesized. The proposed structural model developed from X-ray single crystal data has an interpenetrated three-dimensional framework of zinc *trans*-biscarboxylate tetraarylporphyrins whose carboxylates coordinate the six edges of tetrahedral Zn_4O^{6+} clusters, maintaining a charge-neutral framework. This cubic framework has 74% free volume and 4 × 7 Å pores. N_2 adsorption gives a type I isotherm with a surface area of 800 m^2/g, which is greater than that of a typical zeolite. Experimental evidence indicates that the interpenetrated frameworks of the evacuated solid remain intact and retain a microporous structure. This is a versatile framework system: alteration of the metal in the porphyrin may create a catalytically active solid, and modification of the 10-, 20-substituents of the porphyrin can provide control over both the polarity and the size of the pores.

The rational design of porous solids has been greatly advanced by the linkage of molecular “building-blocks” in various coordination or organometallic frameworks.[1−5] Having channels and pores analogous to those found in zeolites and their analogues, these framework solids have the potential to perform shape-selective separations, chemical sensing, and catalysis. Since metalloporphyrins are effective catalysts for the hydroxylation and epoxidation of alkanes and alkenes under homogeneous conditions,[6−8] our group has been interested in synthesizing porous metalloporphyrin frameworks that could serve as heterogeneous catalysts. We report here a precursor to such a potential catalyst: a robust microporous framework solid made up of zinc *trans*-bis(carboxyphenyl)porphyrins linked by Zn_4O clusters.

We and other groups have previously developed metalloporphyrin framework and network solids.[9−14] In particular, one of our solids, PIZA-1,[15] has been shown to be an efficient and shape-selective sorbent.[1] PIZA-1, which contains cobalt tetra-*p*-carboxyphenylporphyrin complexes linked by carboxylate coordination to cobalt trinuclear clusters, has extremely high affinities for polar substrates such as water, amines, and alcohols. Since it would be advantageous to also have framework solids that sorb nonpolar substrates (e.g., alkanes and alkenes, upon which further oxidation chemistry could be done), we set out to make a less polar porphyrin framework solid.

Building upon Yaghi’s recent discovery[16] of porous Zn_4O bridged arene−dicarboxylate metal−organic framework solids, we have now synthesized a Zn_4O framework with zinc(II) *trans*-biscarboxylatetetraarylporphyrin bridges, which we designate PIZA-4.[15] This solid was obtained by slow triethylamine vapor diffusion into a solution of 3.4 mM Zn(p-CO_2)P_2Mes_2P and 4.5 mM $Zn(NO_3)_2$ in 50/50 vol % DMF/chlorobenzene.

The X-ray structure of PIZA-4 was solved by direct methods[17] in the cubic $Fd\bar{3}$ space group (R1 = 0.1922, wR2 = 0.4629).[18] The proposed structural model of the solid contains an interpenetrated cubic framework of zinc(II) *trans*-carboxylateporphyrins that coordinate the edges of tetrahedral Zn_4O^{6+} clusters as shown in Figure 1. Highly porous solids

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(15) Abbreviations: CoT(p-CO_2)PPC$o_{1.5}$ designated PIZA-1 for porphyrinic Illinois zeolite analogue 1; T(p-CO_2)PP, 5,10,15,20-tetra(p-carboxyphenylporphyrinate(−2); (p-CO_2)P_2Mes_2P, 5,15-di(p-carboxyphenyl)-10,20-di(2′,4′,6′-trimethylphenyl)porphyrinate(−2); PIZA-4, [Zn(p-CO_2)$P_2Mes_2P]_3Zn_4O$.

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(17) Structure was solved and refined using SHELX97 (Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997).

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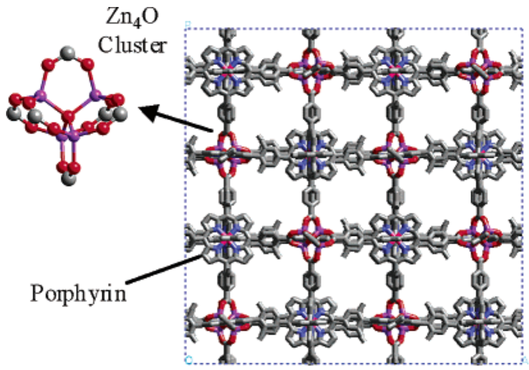

Figure 1. Crystal structure of interpenetrated PIZA-4 looking down the cubic axis. Hydrogens are omitted for clarity. Enlargement shows coordination of six carboxylates from the porphyrins to the Zn_4O tetrahedral cluster.

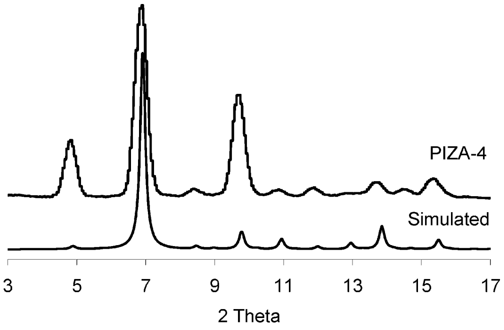

Figure 2. XRD pattern of solvated PIZA-4. Simulated XRD pattern was calculated from crystal structure shown in Figure 1.

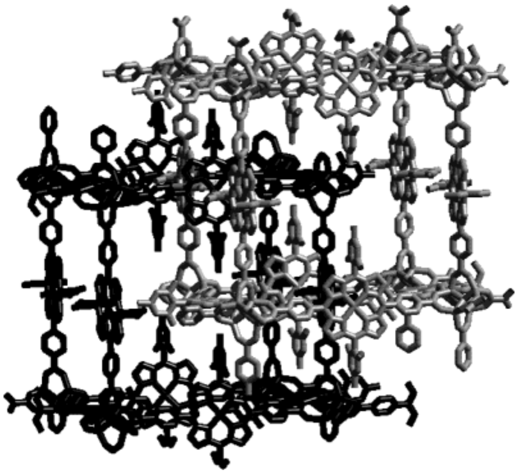

Figure 3. Representation that illustrates the two interpenetrating frameworks of PIZA-4. One framework is shaded darker.

are inherently likely to give limited quality overall refinements, as is well-known for zeolites, etc. Nonetheless, useful framework information can be obtained from a structure with high *R* values.[2] In addition, further characterization (XRD, TGA, EA (elemental analysis), and N_2 isotherm measurement) all supports the proposed structural model developed from the single crystal data. The XRD powder pattern was simulated from the single crystal structure and was found to match that of the experimental PIZA-4 XRD powder pattern[19] (Figure 2 and Table S1).

As mentioned earlier, PIZA-4 has an interpenetrated structure that is illustrated in Figure 3. Even with this interpenetration, the framework solid is largely open with 74% free volume (calculated for a 1.4 Å probe radius using Cerius[2] version 4.8) and 4 × 7 Å pores down each axis (van der Waals surface distance). In the solvated crystal, the pores are filled with disordered solvate. This large free volume was confirmed by TGA measurements on the as-synthesized solvated crystal (Table S2). A measured weight loss of 32% (up to 250 °C) is equivalent to 134 DMF and 102 chlorobenzene molecules occupying each unit cell, which corresponds to 100% of the calculated accessible free volume being occupied.

In order to evaluate the robustness of evacuated PIZA-4, the solvates were completely removed by heating the solid at 150 °C under vacuum, as confirmed by TGA.[20] Elemental analysis of the evacuated solid confirmed the expected formula for the framework without solvates.[21] To determine the nature of evacuated PIZA-4, we characterized it with nitrogen isotherm measurements, XRD, and TGA.

Reversible type I N_2 isotherms (Figure S1) at 77 K were measured for desolvated PIZA-4 solids and are consistent with microporosity (i.e., pores with diameters less than 20 Å that still exist in the evacuated state). A Langmuir surface area of 800 m^2/g, calculated from the isotherm data, is greater than the 500 m^2/g for a typical zeolite. The evacuated solid also reversibly resorbs 241 DMF molecules per unit cell, which corresponds to 94% of the accessible free volume calculated from the single crystal model (Table S3). These two findings indicate that the pores remain open and available for resorption of solvate.

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(18) Crystal data for PIZA-4: cubic $Fd\bar{3}$, $a = 51.1237(12)$ Å, $V = 133619(5)$ Å^3, $Z = 16$, calculated density = 0.561 g/cm^3, R1 = 0.1922, wR2 = 0.4629, Cu Kα (1.54178 Å), $\mu = 0.768$ mm^{-1}. In the single crystal structure, the Zn_4O clusters of the host framework were well ordered; however, the porphyrin links suffered from considerable libration in addition to modeled and suspected solvate disorder. No crystals examined diffracted beyond 1.5 Å resolution, most likely due to the large amount of disordered solvate in the host framework. All efforts to refine more complex disordered models as well as efforts to refine discrete framework models in nonisomorphous subgroups cascading down to F1 failed to improve the model chemically. Benzoate, pyrrole, and mesityl moieties were refined as rigid idealized groups. Positions for solvate atoms were so severely disordered that no discrete model for solvate molecules surfaced in difference Fourier maps. The proposed structural model was refined with contributions from the solvate molecules removed from the diffraction data using the bypass procedure in PLATON.[23] The electron count from the "squeeze" model converged in good agreement with the number of solvate molecules predicted by TGA results on the as-synthesized solvated crystals. The space group choice was confirmed by successful convergence of the full-matrix least-squares refinement on F^2.

(19) X-ray powder diffraction patterns were collected on the same instrument used for single crystal measurements for 300 s with a 15 cm sample-to-detector distance. Solvated crystals used for XRD measurements were not crushed, but rather gently transferred along with mother liquor into a 1.0 mm X-ray capillary tube. Evacuated crystals were also not crushed prior to placement in a 1.0 mm X-ray capillary tube. The evacuated samples were resolvated directly in the capillary tube via a syringe.

(20) TGA of the evacuated solid shows minimal weight loss up to 400 °C, indicating that all of the solvates have been removed by the evacuation procedure.

(21) Elemental analysis of PIZA-4: $C_{156}H_{130}N_{12}O_{21}Zn_7 = [Zn(p\text{-}CO_2)P_2\text{-}Mes_2P]_3Zn_4O{\cdot}8H_2O$. Calcd: C, 63.16; H, 4.42; N, 5.67; Zn, 15.43. Found: C, 63.29; H, 4.19; N, 5.56; Zn, 15.12. The water in the EA is from sorption from the atmosphere onto the surface of the solid prior to EA. The eight molecules of water included in the formula are in fair agreement with the TGA weight loss measured for the evacuated solid after 12 h of exposure to ambient atmosphere.

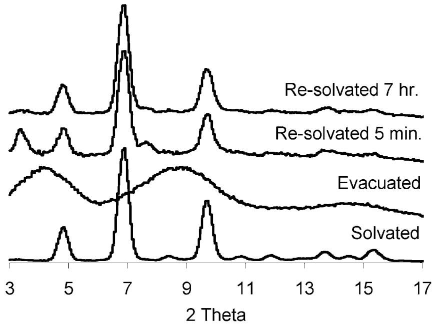

Figure 4. XRD patterns of evacuated and resolvated PIZA-4.

As shown in Figure 4, 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. The evacuated PIZA-4 powder was re-exposed to DMF/chlorobenzene to induce resolvation. The solid was insoluble ($<\mu$M) and did not redissolve. Upon resolvation, the original XRD powder pattern (along with two new peaks) for PIZA-4 returns within a few minutes (Figure 4). The new peaks at 2θ of 3.4° and 7.6° diminish with time and are much reduced after 7 h of resolvation. We believe this is due to an interesting phenomenon in these interpenetrated frameworks: the interpenetrated frameworks are centered with respect to one another in the presence of solvate, but upon desolvation the interpenetrated frameworks move toward one another, introducing an asymmetry that goes away again upon resolvation. This asymmetry probably arises from van der Waals forces between the two interpenetrated frameworks in the absence of solvates.

An XRD simulation was done for a model where one of the interpenetrated frameworks was pushed 2 Å “off-center” on the cubic body diagonal with respect to the other. This nonsymmetric, noncentered interpenetrated framework model matches the new peaks found in the XRD (Figure S2). We propose that the chemically intact frameworks are noncentered initially, and return with time to a centered configuration after resolvation. Since the dominant XRD pattern upon initial resolvation is that of the centered frameworks, this suggests that only minimal structural change from the evacuated state must occur to incorporate the reintroduced solvates. Since resolvation acts to center the two interpenetrated frameworks, removal of the solvates has the opposite effect. This movement would likely cause inter- and intraframework (lattice strain) disorder and broaden the XRD peaks in the evacuated pattern.[24]

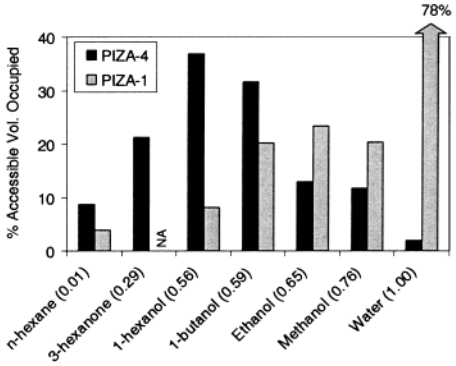

Figure 5. PIZA-4 and PIZA-1 sorption data for substrates of increasing polarity. E_T^N solvent polarity values given in parentheses (3-hexanone value approximated from that of 2-hexanone).[22] n.a. = not available.

We explored the adsorption properties and determined the polarity of the pores in evacuated PIZA-4 by resolvation with solvents of varying polarity for 1 day (Table S3). Results calculated from TGA data (Figure 5) indicate that PIZA-4 is selective toward adsorption of substrates with medium polarity, which is in striking contrast to the very polar pores of PIZA-1.[1] Further control is possible through alteration of the non-carboxylate phenyl groups of the porphyrins; the 10-, 20-mesityl groups in the current solid provide a means to control the shape and moderate polarity of the solids’ pore structure.

In summary, we have synthesized and characterized a novel microporous zinc porphyrin framework solid that contains a large free volume. The framework solid is robust to >400 °C and remains intact even after removal of solvates, as confirmed by XRD, N_2 adsorption isotherm, and TGA studies. Due to the microporosity of the evacuated solid, modification of the metalloporphyrins in the framework could lead to a series of exciting shape- and polarity-selective heterogeneous catalysts.

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Supporting Information Available: Crystallographic data (p75tsag2p), TGA sorption data, nitrogen isotherms, XRD simulations, indexed XRD, and crystal structure views for PIZA-4. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) An addition of 5% lattice strain to the noncentered simulated XRD gives a pattern with two broad maxima similar in shape, but not position, to the evacuated pattern. The proposed model for the evacuated case requires further development.