

ROBUST MICROPOROUS METALLOPORPHYRIN FRAMEWORK SOLIDS

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Metalloporphyrins, which are thermally and chemically stable, have known catalytic properties in the homogeneous phase.¹⁻³ These features make metalloporphyrins attractive as building blocks for microporous framework solids. Since the early 1990s, much work has been done to develop porphyrin framework solids with major contributions from Robson,^{4,5} Strouse,⁶⁻¹⁰ Goldberg,¹¹⁻¹³ and Suslick.¹⁴⁻¹⁶ However, even though size- or shape-selective heterogeneous catalysis is often cited as the potential application of this research, no example of a catalytic porphyrin framework solid has been reported in the literature to date.¹⁷⁻¹⁹ In fact, only a few of the reported porphyrin frameworks are stable to removal of the crystallization solvent.

We have been interested in creating a heterogeneous metalloporphyrin metal-organic framework catalyst that could transform substrates in a size-, shape-, polarity-, or regio-selective manner. Building upon Yaghi's recent discovery²⁰ of porous Zn_4O bridged arene-dicarboxylate metal-organic framework solids, three robust metalloporphyrin framework solids with large void volumes (>70%) and 4 x 7 Å pores have been successfully synthesized and characterized.²¹ The proposed structural model for these frameworks, developed from X-ray single crystal data, has an interpenetrated three-dimensional framework of trans-biscarboxylate tetraarylmetalloporphyrins whose carboxylates coordinate the six edges of tetrahedral Zn_4O^{6+} clusters, maintaining a charge-neutral framework (Figures 1 and 2). The three interpenetrated frameworks vary only in the incorporated porphyrin metal (zinc, manganese, and cobalt) and have been dubbed Porphyrin Illinois Zeolite Analogues (PIZA-4, PIZA-5, and PIZA-6, respectively). Experimental evidence indicates that the interpenetrated frameworks of the evacuated solid remain intact and retain a microporous structure after removal of the large amount of disordered solvates (Figures 3 and 4). These microporous frameworks are selective towards the entry of substrates having medium polarity.

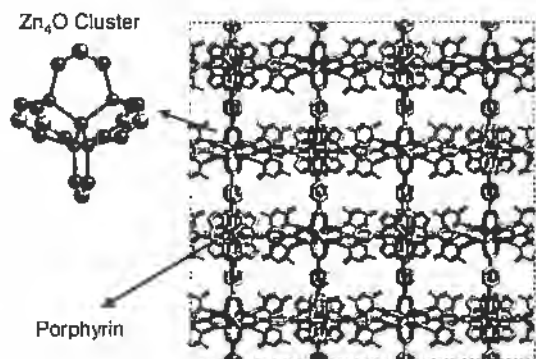


Figure 1. Crystal structure of interpenetrated PIZA-4. Enlargement shows coordination of carboxylates from the porphyrins to the Zn_4O tetrahedral cluster.

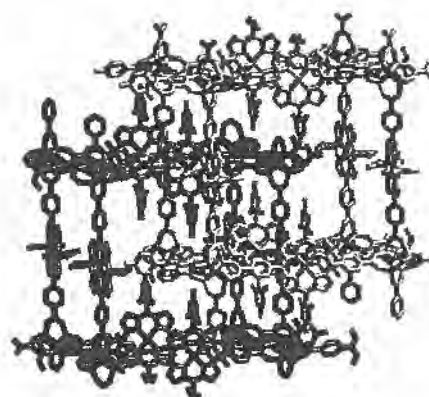


Figure 2. Representation of the two interpenetrating frameworks of PIZA-4. One framework is shaded darker.

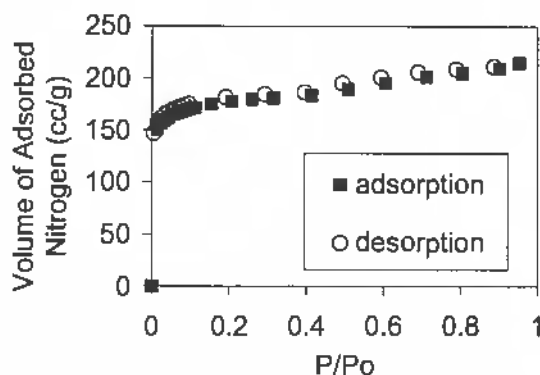


Figure 3. Reversible Type I nitrogen isotherm for PIZA-4.

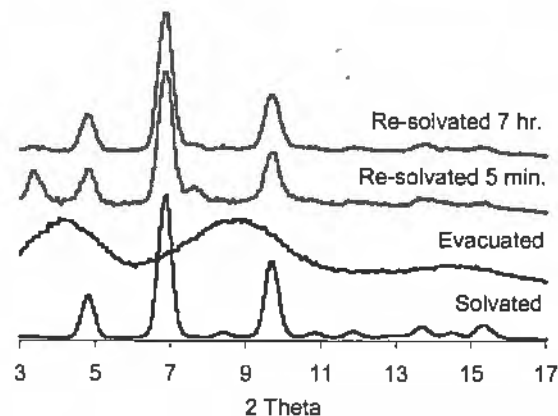


Figure 4. XRD patterns of evacuated and re-solvated PIZA-4.

The manganese porphyrin framework, PIZA-5, has been shown to catalyze the hydroxylation of cyclic and linear alkanes under liquid-solid conditions, using iodosylbenzene as oxidant. This framework is novel as the catalysis occurs in the pores. Another impressive feature of PIZA-5 is that it hydroxylates cyclic and linear alkanes in a size- and polarity-selective manner. The cobalt porphyrin framework, PIZA-6, was not found to be an effective catalyst under liquid-solid conditions, using iodosylbenzene as oxidant.

Both PIZA-5 and PIZA-6 should be further tested under gas-solid phase conditions using molecular oxygen as the oxidant so that higher reaction temperatures can be assessed. In addition, alteration of the mesityl groups could make the overall framework less polar, more amenable to alkane sorption, and thus more catalytically active.

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