

## Sorption and catalysis by robust microporous metalloporphyrin framework solids

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**ABSTRACT:** Two isostructural metalloporphyrin framework solids have been synthesized. Both frameworks contains manganese(III) metal complexes of *trans*-dicarboxylateporphyrins whose peripheralcarboxylates coordinate the edges of tetrahedral  $Zn_4O^{+6}$  clusters; the two metalloporphyrins explored are Mn(III) and Co(II). The cubic interpenetrated frameworks have 72% free volume and  $4 \times 7 \text{ \AA}$  averaged size pores. The evacuated frameworks are robust and retain a structure open to the sorption of substrates with medium polarity. The manganese porphyrin framework catalyzes the hydroxylation of cyclic and linear alkanes with iodosylbenzene as oxidant in a size- and polarity-selective manner. In addition, the catalysis was found to occur *within the pores*, making this a rare case of porphyrin framework solid with interior catalysis.

**KEYWORDS:** framework solid, metalloporphyrin, hydroxylation, size selective catalysis, size selective sorption, nanoporous.

### INTRODUCTION

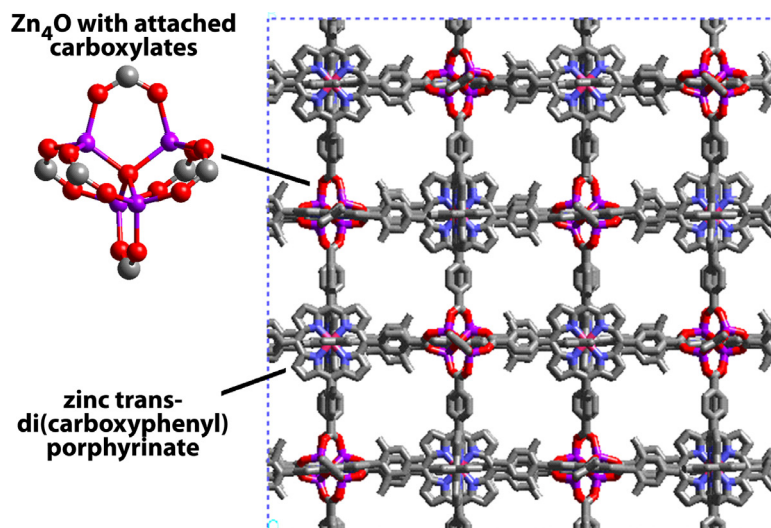
The rational design of porous solids has been greatly advanced by the linkage of molecular “building-blocks” through various metal ion or cluster coordination frameworks [1–14]. Having channels and pores similar to those found in zeolitic materials, these metal organic framework (MOF) solids have the 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, [15–19] they are attractive as linker building blocks for the development of microporous (*i.e.* pores with diameters less than  $20 \text{ \AA}$ ) framework solids that might serve as heterogeneous catalysts. Since the early 1990s, [2, 3, 20–31] much work

has been done to develop porphyrin framework solids, with more recent contributions from Hupp, Paz, Huang, van der Voort, and others [4, 11, 19, 32]. Many single-crystal structures of porphyrinic solids contain pores filled with disordered solvates, but very few are stable to the removal of solvates. In addition, even though the creation of a size- or shape-selective heterogeneous catalyst is often cited as the potential application of this research, to date very few catalytic porphyrin framework solids have been reported [3, 32–36].

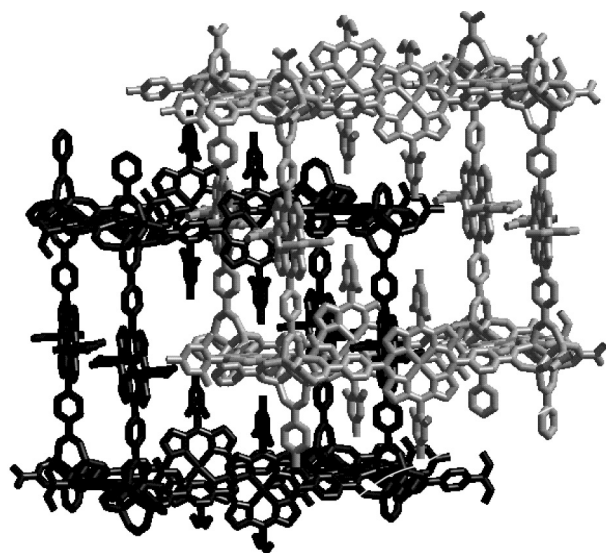
We have previously reported [37] a robust microporous framework solid made up of zinc *trans*-bis(carboxyphenyl) porphyrins linked to  $Zn_4O$  clusters; the linker specifically is 5,15-di(*p*-hydroxycarbonylphenyl)-10,20-di(2',4',6'-trimethylphenyl)porphyrinatozinc(II). This precursor (shown in Figs 1 and 2) has been dubbed Porphyrinic Illinois Zeolite Analog #4 (PIZA-4) and builds upon Yaghi's discovery [38] of porous  $Zn_4O$  bridged arene-dicarboxylate metal-organic framework solids. PIZA-4 has an interpenetrated cubic framework with 74% free volume, contains  $4 \times 7 \text{ \AA}$  averaged pores down each axis, does not collapse upon evacuation of the crystallization

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**Fig. 1.** Crystal structure of interpenetrated PIZA-4 with view down cubic axis. Hydrogens are omitted for clarity. Enlargement shows coordination of six carboxylates from the metalloporphyrins to the  $Zn_4O$  tetrahedral cluster. The metalloporphyrin groups are  $Zn(\text{CarMesP})$ , i.e. 5,15-di(*p*-hydroxycarbonylphenyl)-10,20-di(2',4',6'-trimethylphenyl)porphyrinatozinc(II)



**Fig. 2.** Representation of the two interpenetrating frameworks of PIZA-4; a symmetric interpenetration of the frameworks is shown

solvates, and re-sorbs solvates of medium polarity. In this paper, we expand upon this work and introduce two isostructural frameworks that contain more versatile metal ions (Mn and Co porphyrinate complexes) that function as heterogeneous catalysts for hydroxylation of alkanes. From the observed shape selectivity, we have shown that the catalysis occurs within the pores of these microporous solids.

## EXPERIMENTAL

All chemicals were purchased from Aldrich or Fisher and used without further purification.  $^1\text{H}$  NMR spectra

were recorded on either a Varian Unity 400 MHz or 500 MHz spectrometer at 20 °C. UV-Visible spectra were recorded on a Hitachi U-3300 spectrometer. The University of Illinois Microanalytical Laboratory carried out the elemental analyses. Fast atom bombardment (FAB) mass spectra were recorded using a VG ZAB-SE spectrometer in The School of Chemical Sciences Mass Spectrometry Laboratory at the University of Illinois.

### 5,15-di(4-hydroxycarbonylphenyl)-10,20-di(2',4',6'-trimethylphenyl)porphyrin, $H_2\text{CarMesP}$

This free-base porphyrin was synthesized following the procedure outlined by Paterno [37, 39]. An equimolar mixture of *meso*-mesityldipyromethane and methyl 4-formylbenzoate in chloroform was treated with boron trifluoride diethyl etherate. The resulting porphyrin was oxidized with DDQ, isolated, and de-methylated by treating it with 5% KOH and refluxing in THF. Yield: 8.5%. UV-vis (dmsO, nm): 420 (Soret), 515, 550, 591, 647.  $^1\text{H}$  NMR (dmsO- $d_6$ , 20 °C):  $\delta$  13.3 (bs, 1H, COOH), 8.79 (d,  $J = 4.4$  Hz, 4H,  $\beta$ -pyrrole), 8.65 (d,  $J = 4.8$  Hz, 4H,  $\beta$ -pyrrole), 8.34 (s, 3H, ArH), 7.34 (s, 4H, mesityl ArH), 2.57 (s, 6H, *p*-ArCH<sub>3</sub>), 1.74 (s, 12H, *o*-ArCH<sub>3</sub>), -2.78 (bs, 2H, inner pyrrole). FAB-MS ( $MH^+$ , amu): 787.4 (Calcd. for  $C_{52}H_{40}N_4O_4$ : 786.3). EA:  $C_{52}H_{42}N_4O_4$ . Calculated C, 79.37; H, 5.38; N, 7.12. Found C, 78.94; H, 5.41; N, 6.79.

### Manganese(III) 5,15-di(*p*-hydroxycarbonylphenyl)-10,20-di(2',4',6'-trimethylphenyl)porphyrinate chloride, $Mn(\text{CarMesP})(\text{Cl})$

$Mn(\text{CarMesP})(\text{Cl})$  was prepared by refluxing  $H_2$ - $(\text{CarMesP})$  in DMF with 7 equivalents  $MnCl_2 \cdot 4H_2O$  using

the Adler method [40]. Yield: 91%. UV-vis (DMF, nm): 469 (Soret), 573. FAB-MS ( $MH^+$ , amu): 839.2 (Calcd. for  $MnC_{52}H_{40}N_4O_4$ : 839.2). EA:  $C_{52}H_{40}N_4O_4MnCl$ . Calculated C, 71.35; H, 4.61; N, 6.40. Found C, 71.49; H, 4.32; N, 6.35.

**Cobalt(II) 5,15-di(*p*-hydroxycarbonylphenyl)-10,20-di(2',4',6'-trimethylphenyl)porphyrinate, Co(CarMesP)**

The Co(CarMesP) was prepared by refluxing  $H_2$ (CarMesP) in DMF with 5 equivalents  $CoCl_2 \cdot 6H_2O$  using the Adler method [40]. Yield: 94%. UV-vis (DMF, nm): 431 (Soret), 541. FAB-MS ( $MH^+$ , amu): 844.2 (Calcd. for  $CoC_{52}H_{40}N_4O_4$ : 843.2). EA:  $C_{52}H_{40}N_4O_4Co \cdot H_2O$ . Calculated C, 72.47; H, 4.91; N, 6.50. Found C, 72.39; H, 4.49; N, 6.55.

**PIZA-5 ( $[Mn(CarMesP)Cl]_3Zn_4O \cdot Solvate_x$ )**

Cubic purplish-black crystals (0.20–0.50 mm edges) were obtained by slow triethylamine vapor diffusion into a DMF solution of 3.5 mM Mn(CarMesP)(Cl) and 4.7 mM  $Zn(NO_3)_2$ . The  $Zn(NO_3)_2$  stock solution was prepared by dissolving 25 mg ZnO into 1 mL of 1 M  $HNO_3$ . The addition of this acidic solution to the porphyrin solution ensured that the porphyrin's carboxylic acid groups remained in acid form until the triethylamine diffused in to perform the deprotonation. Crystals were obtained on a small-scale by placing the porphyrin solution and the triethylamine solution into a closed 20 mL scintillation vial. For the porphyrin solution, approximately 100  $\mu$ L was placed in an open 6  $\times$  40 mm test tube. For the triethylamine solution, 100  $\mu$ L of 2% triethylamine in DMF was placed in a 8 mm ID  $\times$  35 mm vial capped with a rubber septum, which had a 25G 5/8 inch needle inserted. Crystals appeared after approximately two weeks. Yield: 75%. EA:  $C_{156}H_{132}N_{13}O_{25}Mn_3Zn_4Cl_2 = [Mn(CarMesP)]_3Cl_2(NO_3)Zn_4O \cdot 9H_2O$ . Calculated C, 60.71; H, 4.31; N, 5.90; Zn, 8.48; Mn, 5.34; Cl, 2.30. Found C, 60.72; H, 3.95; N, 6.01; Zn, 8.30; Mn, 5.35; Cl, 2.40.

**PIZA-6 ( $[Co(CarMesP)]_3Zn_4O \cdot Solvate_x$ )**

In a similar manner, cubic purplish-red crystals (0.05–0.10 mm edges) were obtained by slow triethylamine vapor diffusion into a solution of 3.4 mM Co(CarMesP) and 4.5 mM  $Zn(NO_3)_2$  in 50/50 vol.% DMF/chlorobenzene. Crystals appeared after approximately two weeks. Yield: 70%. EA:  $C_{156}H_{136}N_{12}O_{24}Co_3Zn_4 = [Co(CarMesP)]_3Zn_4O \cdot 11H_2O$ . Calculated C, 62.43; H, 4.57; N, 5.60; Zn, 8.72; Co, 5.89; Cl, 0.00. Found C, 62.02; H, 4.21; N, 5.91; Zn, 9.18; Co, 5.73; Cl, 0.46.

**Crystallographic study of PIZA-5**

A 0.40 mm  $\times$  0.40 mm  $\times$  0.20 mm purple prism-shaped crystal was carefully transferred *via* mother

liquor to a 0.40 mm X-ray diffraction capillary tube. Diffraction data from this crystal was collected on a Siemens/P4 HiStar instrument at room temperature, using a Cu rotating-anode as radiation source with a graphite monochromator. The X-ray structure of PIZA-5 was solved by direct methods [41] in the cubic  $Fd\bar{3}$  space group ( $R_1 = 0.1652$ ,  $wR_2 = 0.4124$ ). Highly porous solids, such as zeolites, inherently give limited quality overall refinements due to the disorder of the solvates; nonetheless, useful framework information can be obtained even from a structure with high  $R$  values, [1] especially when the components of the bridges are relative rigid groups (*e.g.* phenyl rings, compact metal oxide clusters, and in this case porphyrins). The  $Zn_4O$  clusters of the host framework were well ordered; however, the porphyrin links suffered from libration in addition to modeled solvate disorder. The crystal examined did not diffract beyond 1.3 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 non-isomorphous subgroups cascading down to  $F^1$  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 [42]. 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  $F^2$ . Final refinement parameters are given in Supporting Information, Table S1.

**Thermal Gravimetric Analyses (TGA)**

Thermal gravimetric analyses were performed on a Perkin-Elmer TGA7/DSC7 instrument. For the TGA sorption measurements of the various solvates, the following procedure was used. First, the solid was evacuated in a 150 °C vacuum oven for one day. Then the sample was covered in approximately 5 mL of a particular solvate to be assessed for sorption. After one day of sorption, the solid was separated from the solvate *via* filtration through a medium frit, washed with 2 mL *n*-pentane, and quickly transferred to the TGA pan. The sample was then heated from 25 to 250 °C at 10 °C/min under a nitrogen environment (20 mL nitrogen/min. at  $t = 1$  min.), while monitoring the weight loss. The weight percent losses for each solvent were corrected by subtracting 2.5 wt.% for PIZA-5 and 3.0 wt.% for PIZA-6 due to surface water sorption as suggested by TGA measurements on the evacuated solids.

## Catalytic studies

Catalytic oxidation reactions were performed at room temperature in a 2 mL closed glass vial equipped with a magnetic stirrer. In a standard experiment, solid catalyst and iodobenzene (15 molar ratio to the catalyst) were suspended in 0.200 mL of solvent (acetonitrile or acetonitrile/dichloromethane mixture). The substrates were purchased from Aldrich in their highest purity and run through a neutral alumina column prior to use. The substrate (2000 molar ratio) was then added and the oxidation reaction was carried out for two hours (unless stated otherwise) under magnetic stirring. To eliminate the excess of iodobenzene, sodium sulfite was added and the products of the reaction were separated from the solid catalyst by exhaustive washing and centrifugation of the solid with an acetonitrile-dichloromethane-methanol mixture (1:1:1 volume ratio). The extracted solution was analyzed by a gas chromatography-mass spectrometer (GC-MS) equipped with an HP 6890 Series GC System and an HP 5973 Mass Selective Detector. An Agilent DB-35MS column was used (29.5 m  $\times$  247  $\mu$ m  $\times$  0.25  $\mu$ m). The amount of the products was determined by using 1-octanol as the internal standard. Each reaction was performed twice and the product mixture was analyzed three times by GC-MS. Control reactions without catalyst were performed for each substrate. Iodobenzene (PhIO) was prepared through the hydrolysis of iodobenzene diacetate following the methods described by Saltzman and Sharefkin [43]. The purity was measured by iodometric assay and found to be 97.0% [44].

## Diffuse reflectance UV-visible spectroscopy

The control linker porphyrin, Mn(CarMesP)(Cl), and pre-catalysis PIZA-5 were evacuated in a 150 °C vacuum oven for 24 h. Post-catalysis PIZA-5 was removed from the reaction mixture (mostly acetonitrile and alkane) and allowed to dry on a glass slide. Approximately 5 mg of each solid sample was suspended in 1 mL of Nujol. This suspension was then smeared on a glass slide, covered with a thin glass slip, and measured with a Hitachi U-3300 UV-Visible instrument containing a diffuse reflectance integrating sphere attachment. Barium sulfate was used as the reference.

## X-ray Powder Diffraction (XRD)

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 re-solvated directly in the capillary tube *via* a syringe.

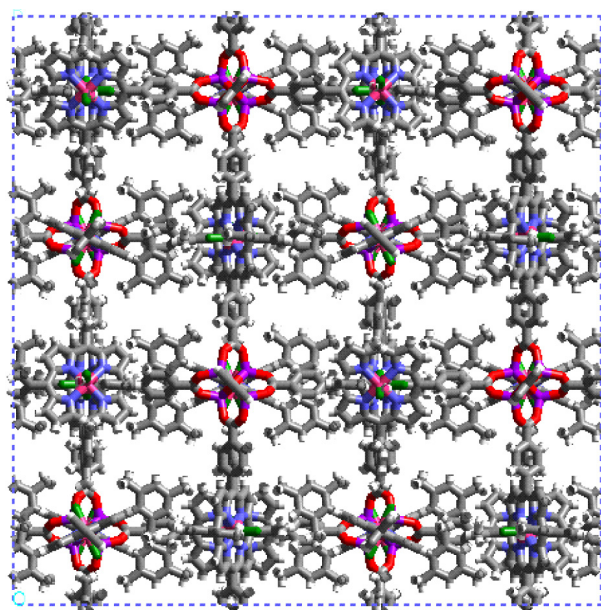
## RESULTS AND DISCUSSION

### Structural characterizations of PIZA-5 and PIZA-6

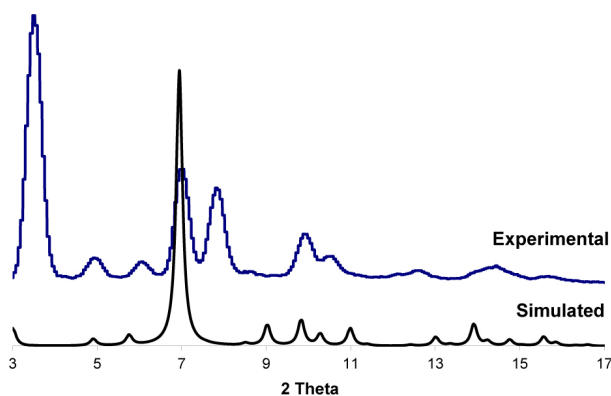
#### Structure of a manganese porphyrin framework solid (PIZA-5)

The structural model of the solid contains an interpenetrated cubic framework of manganese(III) *trans*-dicarboxylateporphyrins that coordinate the edges of tetrahedral  $Zn_4O^{+6}$  clusters as shown in Fig. 2. This framework is isostructural to that of PIZA-4 ( $[Zn(CarMesP)(Cl)]_3Zn_4O$ ) [37], the only difference being that the zinc metalloporphyrin has been replaced by a manganese porphyrin. The manganese in the porphyrins has an oxidation state of III as demonstrated by the attached chloride found in the crystal structure and by the visible spectrum. The X-ray structure framework formula is  $[Mn(CarMesP)(Cl)]_3Zn_4O \cdot Solvate_x$ , having a ratio of three metalloporphyrins (each with a 2- charge) for every one  $Zn_4O^{+6}$  cluster, making it a charge-neutral framework.

The interpenetrated framework of PIZA-5 is largely open space with 72% free volume (calculated for a 1.4 Å probe radius, *i.e.* a water molecule, using Cerius<sup>2</sup> version 4.8) and has a similar pore structure to that of PIZA-4. In the solvated crystal, the pores are filled with disordered DMF (*N,N*-dimethylformamide). The large free volume found from modeling of the crystal structure was confirmed by thermal gravimetric analysis (TGA) measurements on the as-synthesized solvated crystal. A measured weight loss of 34% (up to 250 °C) is equivalent to 330 DMF molecules occupying each unit cell, which corresponds to solvate occupation of 105% ( $\pm 6\%$ ) of the calculated accessible free volume.



**Fig. 3.** Crystal structure of interpenetrated PIZA-5 with view down cubic axis



**Fig. 4.** Experimental and simulated XRD patterns of powders of PIZA-5; simulated using the centered structure found in the single crystal x-ray structure

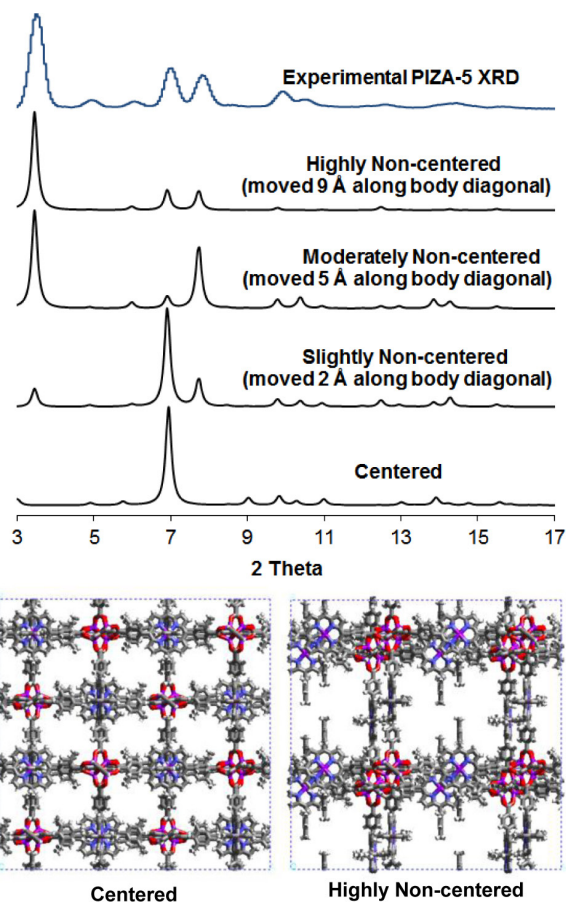
The XRD powder pattern was simulated from the single crystal structure. Unlike PIZA-4, the simulated pattern for PIZA-5 did not match that of the experimental PIZA-5 XRD powder pattern for the solvated crystals, as illustrated in Fig. 4. Since the interpenetrated frameworks are not chemically connected, we reasoned that upon removal of solvates, the two frameworks might well move towards one another to minimize their collective van der Waals energy. To this end, we ran XRD simulations on a PIZA-5 model where the two frameworks were changed from centered (symmetric) positions to increasing non-centered by moving one framework along the cubic body diagonal with respect to the other. These simulations, shown in Fig. 5, indicate that non-centered frameworks result in a simulated XRD that matches very closely the experimental XRD. Therefore, the bulk sample is dominated by microcrystalline solid containing interpenetrated frameworks that are non-centered with respect to one another; as discussed later, this may be due to partial loss of solvates in the powder.

#### **Structure of a cobalt porphyrin framework solid (PIZA-6)**

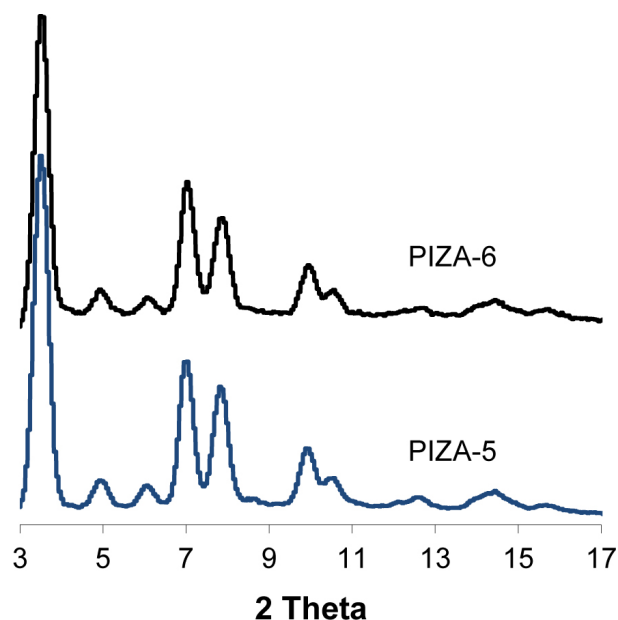
Due to small crystal size, attempts at finding single crystals that diffracted X-rays well were unsuccessful for PIZA-6. An experimental XRD pattern of PIZA-6 solvated microcrystals matched that of the experimental XRD pattern for PIZA-5 as shown in Fig. 6. Because of this similarity, we concluded that PIZA-6 also consisted of interpenetrated frameworks that were non-centered with respect to one another comparable to PIZA-5 solvated powders.

#### **The robust nature of PIZA-5 and PIZA-6: Evacuation and refilling of pores**

In order to confirm the empirical formula of the frameworks of evacuated PIZA-5 and PIZA-6, the solvates were completely removed by heating the solid at



**Fig. 5.** Comparison between the experimental PIZA-5 powder XRD and simulations. The non-centered simulations have one of the interpenetrated frameworks 2 Å, 5 Å, or 9 Å (along the unit cell cube body diagonal) with respect to the other framework. No significant non-bonding contacts are developed between the interpenetrated frameworks during these shifts

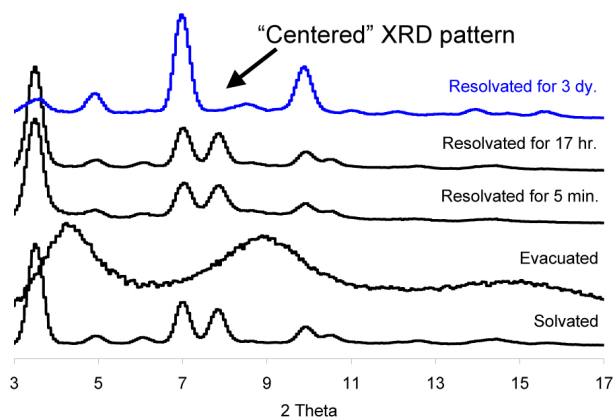


**Fig. 6.** Experimental XRD patterns of PIZA-5 and PIZA-6 powders

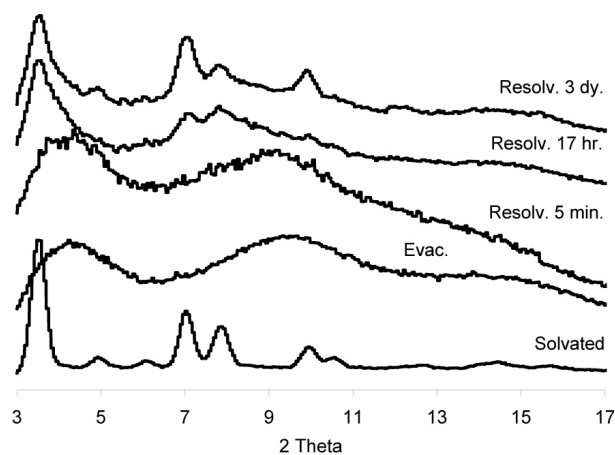
150 °C under vacuum (confirmed by the measurement of total weight loss from TGA studies). Elemental analysis of the evacuated PIZA-5 solid confirmed a similar formula expected from the X-ray crystal structure, with a difference between the formula derived from elemental analysis and that of the single crystal structure matching the replacement of a third of the chloride axial ligands with a nitrate ion. The presence of nitrate in a bulk sample of evacuated PIZA-5 was confirmed by FT-IR ( $\nu = 1385 \text{ cm}^{-1}$ ). Elemental analysis of the evacuated PIZA-6 solid confirmed the expected formula for the framework without solvate. The water in the calculated formulas is from sorption from the atmosphere onto the surface of the solid prior to elemental analysis.

The evacuated PIZA-5 solid reversibly re-sorbs  $\approx 358$  DMF molecules per unit cell (*i.e.* 37% weight loss up to 250 °C), which corresponds to  $114 \pm 13\%$  of the accessible free volume calculated from the single-crystal x-ray structure. In the same fashion, the evacuated PIZA-6 solid reversibly re-sorbs  $\approx 351$  DMF molecules per unit cell (36% weight loss up to 250 °C), which corresponds to  $111 \pm 13\%$  of the accessible free volume calculated from the single-crystal model. These two findings indicate that the pores remain available for re-sorption of solvate in both PIZA-5 and PIZA-6.

As shown in Fig. 7, the XRD peaks for evacuated PIZA-5 powder are broadened and shifted when compared to the initial solvated sample, but still show substantial long-range order. The evacuated PIZA-5 powder was re-exposed to liquid DMF to induce refilling of its pores. The solid was completely insoluble ( $< \mu\text{M}$ ) and did not redissolve, so dissolution/recrystallization does not occur. Nevertheless, upon re-solvation, the original XRD powder pattern for PIZA-5 returns within a few minutes (Fig. 7) and is unchanged during the next 17 h. After 3 d of re-solvation, however, a surprising result was observed. The XRD pattern had changed dramatically to that expected for the fully centered state of the interpenetrated frameworks, similar to the simulated PIZA-5 XRD pattern (see Fig. 5) produced



**Fig. 7.** Experimental XRD patterns of evacuated and re-solvated PIZA-5



**Fig. 8.** Evacuated and re-solvated XRD patterns of PIZA-6

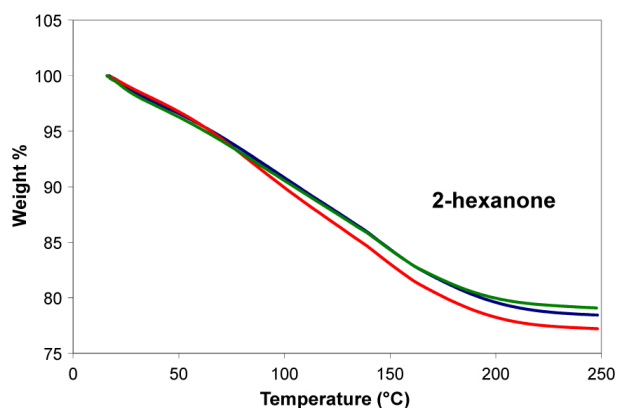
from the single-crystal data. This result confirms our initial hypothesis that the interpenetrated frameworks can be found in both the non-centered and centered states.

As shown in Fig. 8, the XRD peaks for evacuated PIZA-6 powder are broadened and shifted when compared to the initial solvated sample, but still show substantial long-range order, similar to evacuated PIZA-5. The evacuated PIZA-6 powder was soaked in 50/50 vol.% DMF/chlorobenzene to induce refilling of the evacuated pores. The solid was insoluble ( $< \mu\text{M}$ ) and did not redissolve. Upon re-solvation, the original XRD powder pattern for PIZA-6 returns but somewhat more slowly compared to the re-solvation of PIZA-5. After 17 h and 3 d of re-solvation, the same XRD powder pattern is observed, and the “centered” case did not appear. The “centered” case has been observed however for freshly prepared PIZA-6, indicating that the crystallization conditions can affect how centered the frameworks are when the crystals are harvested.

It should be noted that in the XRD evacuation and re-solvation studies of PIZA-5 and PIZA-6, the evacuated state was achieved through a gentle procedure: the solvates were swapped by a liquid-solid exchange (chloroform for DMF) and then the solids were placed under vacuum at room temperature for one day. By using this evacuation procedure, we were able to see the return of the original XRD pattern upon re-solvation. A crystalline XRD pattern with defined peaks still appears upon re-solvation if the PIZA-5 or PIZA-6 samples were evacuated in a single step at 150 °C under vacuum, but the peak positions are shifted irregularly. These frameworks evacuated under harsher conditions still remain insoluble and exhibit crystalline XRD patterns, suggesting that the frameworks remained chemically intact.

### Sorption properties of PIZA-4, PIZA-5 and PIZA-6

In order to explore the sorption properties and determine the polarity of the pores in evacuated PIZA-4,

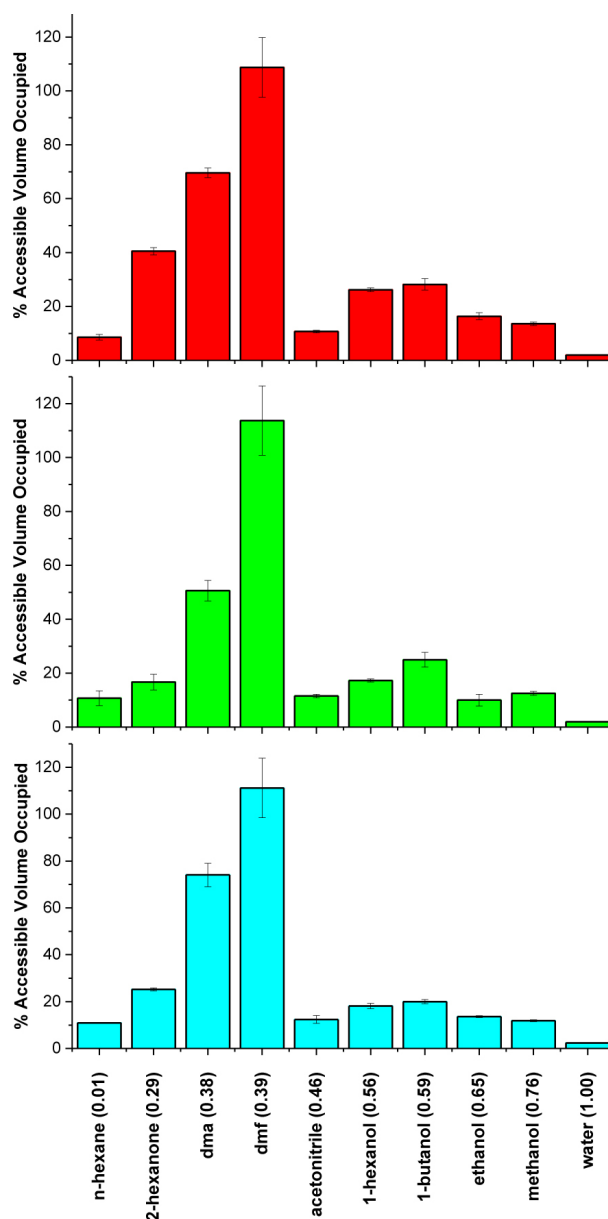


**Fig. 9.** Weight percent loss from PIZA-4 re-solvated with 2-hexanone

PIZA-5, and PIZA-6, we re-solvated evacuated samples by soaking for 24 h in different liquids with varying polarity. After exposure to each liquid, a TGA measurement was carried out to determine the weight percent loss from the re-solvated solid. This process was repeated three times for each solvent on the same solid sample and was found to be reproducible as indicated by the example shown in Fig. 9 for the sorption of 2-hexanone into PIZA-4. The measured weight percent loss below 250 °C measured the amount of solvent sorbed into the framework. The weight percent losses were then converted into “percent accessible volume occupied” values (Tables S2–S4). These values give an indication of how “full” the PIZA-4 framework is after resolution by each liquid, compared to the amount that can theoretically fit based on Cerius<sup>2</sup> modeling of both the solvate and of the framework’s pores.

Results calculated from TGA data (Fig. 10) indicate that PIZA-4, PIZA-5, and PIZA-6 have similar selectivity towards sorption of liquids with medium polarity. This result makes sense due to the fact that the only difference between the three interpenetrated frameworks is the metal incorporated into the metalloporphyrin. Because these frameworks selectively sorb substrates of medium polarity, it suggests that the frameworks also have medium polarity, which implies that a relatively wide range of potential substrates for catalytic reactions may be sorbable.

One important oxidation reaction for metalloporphyrins is the hydroxylation of alkanes. Since the porphyrinic frameworks are potential catalysts, it is important to assess whether the framework has a preference for the sorption of a reactant or its more polar product. For example, in the hydroxylation of cyclic hydrocarbons, one would prefer a framework that would prefer the substrate cyclic alkanes over the product, cyclic alcohols. This would prevent catalyst poisoning (kinetic inhibition) by sorption of product during its production by giving preferential sorption of substrate and expulsion of product. To explore this concept, we examined the



**Fig. 10.** Comparison of sorption characteristics for the framework solids,  $[M(\text{CarMesP})(\text{Cl})]_3\text{Zn}_4\text{O}$ , where (top)  $M=\text{Zn}$  for PIZA-4, (middle)  $M=\text{Mn}$  for PIZA-5, and (bottom)  $M=\text{Co}$  for PIZA-6:  $E_T^N$  solvent polarity values are provided in parentheses to indicate the polarity of each solvent accessed [45]

sorption characteristics of PIZA-5 with a series of cyclic alkanes and their respective cyclic alcohols.

PIZA-5 (evacuated 24 h at 150 °C under vacuum) was re-solvated for 24 h with a series of cyclic alkanes (cyclopentane to cyclooctane) and their corresponding alcohols. By performing TGA measurements on the re-solvated PIZA-5 framework, it was found that PIZA-5 is slightly selective (*i.e.* 1.5-fold) toward the sorption of cyclopentanol (and perhaps cyclooctanol) compared to their respective alkanes (Fig. 11). This finding suggests that the hydroxylation product of the reaction with cyclopentane would get stored in the framework

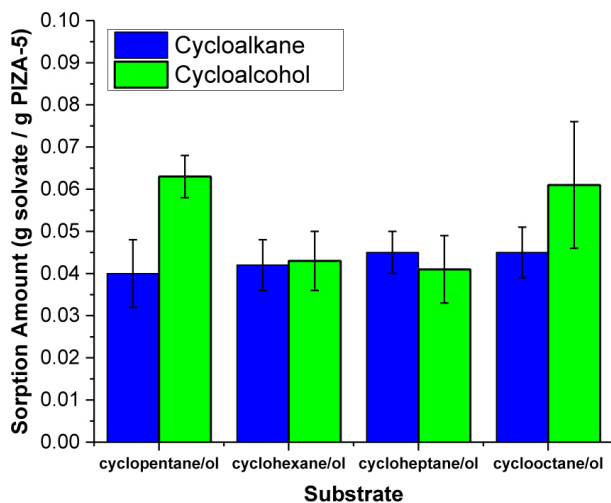


Fig. 11. Sorption of cyclic alkanes and cyclic alcohols into PIZA-5

somewhat more than substrate and could inhibit catalysis to some extent as the product is preferentially sorbed into the framework. In contrast, PIZA-5 is non-selective toward the sorption of cyclohexanol and cycloheptanol compared to their respective alkanes. With cyclohexane and cycloheptane as substrates, catalysis in PIZA-5 would be much less likely to be inhibited by the hydroxylation products.

### Catalytic properties of PIZA-5

#### Kinetic studies of cyclohexane hydroxylation with PIZA-5 and iodosylbenzene

To examine catalytic oxidation reactions with PIZA-5 ( $[\text{Mn}(\text{CarMesP})\text{Cl}]_3\text{Zn}_4\text{O}$ ), a kinetic study of cyclohexane hydroxylation was undertaken with the catalyst, using iodosylbenzene (PhIO) as the oxidant (PIZA-5/PhIO/cyclohexane = 1/10/2500). Aliquots were removed from the reaction mixture at regular intervals and analyzed by GC-MS. The turnover numbers for cyclohexanol and percent yield of iodobenzene are plotted against reaction time in Fig. 12. After two hours, the concentrations of cyclohexanol and iodobenzene leveled off. At this time, the turnover number for the reaction, both for alcohol production and for release of iodobenzene) is  $1.0 \pm 0.1$  mol product/mol porphyrin. After 24 h, another 15 equivalents of fresh iodosylbenzene were added. The turnover number was then measured at 48 h and was  $2.2 \pm 0.1$  mol product/mol porphyrin, showing that PIZA-5 is able to continue catalysis with fresh oxidant, albeit considerably more slowly than the initial rates of oxidation.

Since the turnover number increased with additional oxidant, another kinetic study was performed with a much larger excess of oxidant (PIZA-5/PhIO/cyclohexane = 1/500/6000), as shown in Fig. 12c. Aliquots from the reaction mixture were taken at intervals to access the

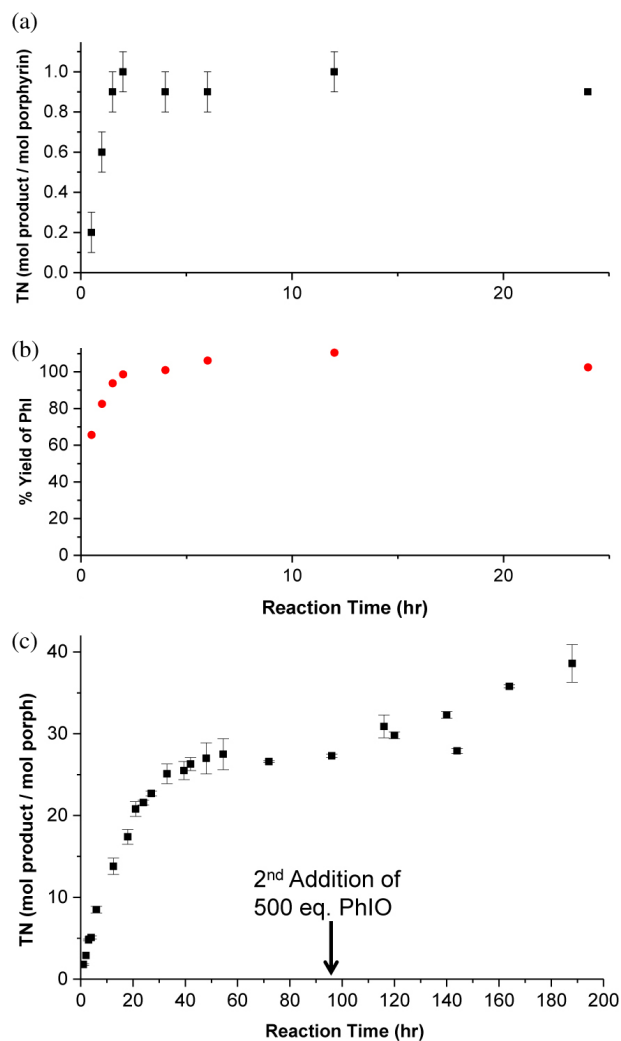


Fig. 12. Kinetic studies of catalytic oxidation of cyclohexane by PIZA-5/PhIO. (a) Turnover numbers vs. reaction time for PIZA-5/PhIO/cyclohexane (1/10/2500). (b) Yield of iodobenzene vs. reaction time for PIZA-5/PhIO/cyclohexane (1/10/2500); (c) Second kinetic study with larger excess of oxidant and substrate: PIZA-5/PhIO/cyclohexane (1/500/6000). As indicated, a second dosage of 500 equivalents PhIO was added at 96 h

turnover number over an eight-day period. The turnover number levels off at 27 mol product/mol porphyrin after 40 h of reaction, which indicates that the PIZA-5 catalytic sites have become blocked and further catalysis becomes quite slow; the addition of a second addition of 500 equivalents of fresh PhIO after 96 h of reaction confirms this inhibition and does not increase the turnover number substantially.

Typical turnover numbers of 2 to 12 mol product/mol catalyst are reported for the homogeneous phase hydroxylation of cyclohexane with manganese(III) tetraphenylporphyrins using a variety of oxidants and reaction times [46–50]. The PIZA-5 turnover numbers obtained in the kinetic studies are somewhat better (30 to 40), but on the same order of magnitude, making



this heterogeneous system comparable. If the phenyl groups of the porphyrins in PIZA-5 were chlorinated or fluorinated, the turnover number might be increased further, as seen in the homogeneous systems [48, 50]. The turnover numbers may also be improved in PIZA-5 by altering the mesityl groups to substituents that are more aliphatic, making the framework less polar and more amenable to sorption of alkanes.

#### Catalysis in the pores of PIZA-5 ([Mn(CarMesP)Cl]<sub>3</sub>Zn<sub>4</sub>O)

An extraction experiment was performed on a spent PIZA-5 solid to determine if product was being stored in the pores. After 48 h of reaction, an aliquot was taken from the product mixture of PIZA-5/PhIO/cyclohexane (1/25/1700) and analyzed by GC-MS. Then after performing an extraction procedure on the spent PIZA-5 solid with an acetonitrile/dichloromethane/methanol (1:1:1 volume ratio) mixture and placing the washings with the original product mixture, a second aliquot was removed and analyzed. The turnover number of  $6.6 \pm 0.1$  mol cyclohexanol/mol PIZA-5 was calculated for the non-extracted aliquot. In comparison, a turnover number of  $11.3 \pm 0.6$  mol cyclohexanol/mol PIZA-5 was calculated for the extracted aliquot. The difference in these turnover numbers indicates that there is significant product trapped inside the pores (*i.e.* nearly half of the total). According to a Cerius<sup>2</sup> (version 4.8) model of cyclohexanol and the accessible volume in PIZA-5, the maximum amount of cyclohexanol that can be stored is 15.4 mol cyclohexanol/mol PIZA-5. The experimental extracted amount of 4.7 mol cyclohexanol/mol PIZA-5 fits within this limit. Also, if PIZA-5 is assumed to be made up of 20 micron cubes (supported by optical microscopy studies), only  $\sim 10^{-4}$  mol of cyclohexanol/mol PIZA-5 would be able to adsorb as a monolayer onto the external surface of PIZA-5, further indicating that the cyclohexanol must be coming from within the pores.

An additional experiment was completed to determine if the extracted PIZA-5 would be catalytically active again. In an initial trial with PIZA-5/PhIO/cyclohexane (1/17/3000) where the product was extracted, the turnover number was  $7.9 \pm 0.9$  mol cyclohexanol/mol PIZA-5. The extracted catalyst from this initial run was then re-used under the same conditions. The turnover number for the recycled catalyst was  $8.1 \pm 0.6$  mol cyclohexanol/mol PIZA-5. The similarity in the turnover numbers indicates that the removal of the stored cyclohexanol allows PIZA-5 to be regenerated as a catalyst.

#### Hydroxylation of cyclic alkanes with PIZA-5 and iodobenzene

To probe the size selectivity of PIZA-5 ([Mn(CarMesP)Cl]<sub>3</sub>Zn<sub>4</sub>O) as a nanoporous oxidation catalyst, we examined the hydroxylation of a series of cyclic alkane substrates under solid-liquid conditions (PIZA-5/PhIO/

cyclic alkane = 1/15/2000). The reactions were run for two hours and quenched with sodium sulfite. Then the catalyst was extracted and the resulting product mixture was analyzed by gas chromatography-mass spectrometry (GC-MS). The turnover numbers and percent yield of iodobenzene are shown in Table S5. Cyclopentane, cyclohexane, and cycloheptane gave a product mixture with the alcohol as the major product, while cyclooctane produced only cyclooctanone. Control reactions done for each substrate without PIZA-5 resulted in no product, except for cyclodecane (which produced only small amounts of cyclodecanone in the control without increase in the presence of PIZA-5).

The total turnover numbers (TN) of these oxidation experiments are plotted in Fig. 13 and indicate that PIZA-5 is selective towards the oxidation of cyclohexane and cycloheptane over the other substrates. As expected from Cerius<sup>2</sup> modeling studies that show that cyclodecane and cyclododecane are larger than the pores estimated from the XRD structure, PIZA-5 showed no activity towards the oxidation of cyclodecane and cyclododecane. Control reactions were performed using the precursor porphyrin (insoluble in acetonitrile like the framework), Mn(CarMesP)(Cl), under the same conditions. Since the precursor porphyrin solid should not be microporous, catalysis would only occur on the exposed external surface. Thus, this control should give an indication of the amount of catalysis that occurs on the external surface of PIZA-5. As shown in Fig. 14, oxidation reactions using the non-porous insoluble control porphyrin have turnover numbers that are very small compared to those using PIZA-5 as catalyst. These low turnover numbers indicate that the catalysis occurring on the external surface of

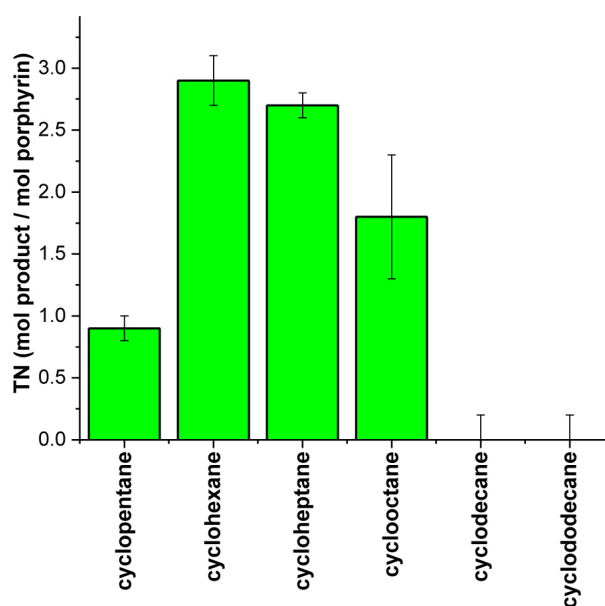
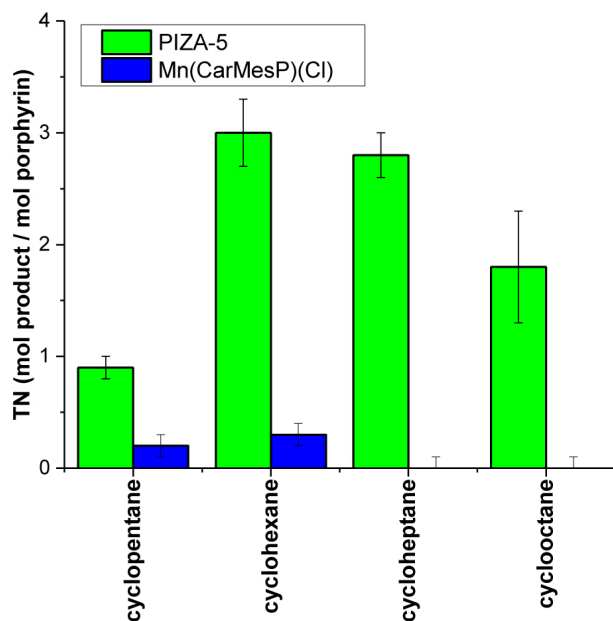


Fig. 13. Turnover numbers for PIZA-5/PhIO/cyclic alkanes (1/15/2000) after 2 h



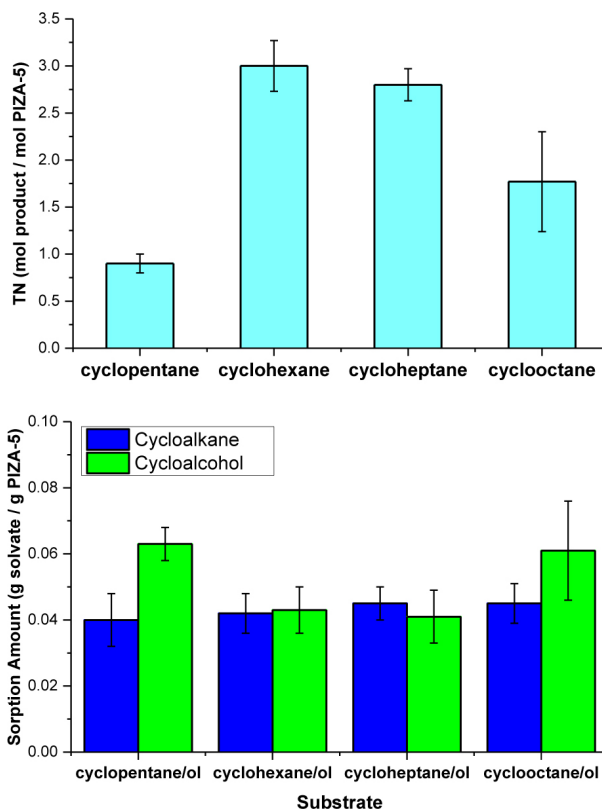
**Fig. 14.** Comparison of TNs of cyclic alkanes using PIZA-5 and the non-porous solid control, Mn(CarMesP)(Cl). (Porphyrin/PhIO/cyclic alkane = 1/5/700)

PIZA-5 is small in comparison to the catalysis occurring in the pores.

As shown in Fig. 15, the sorption of cyclic alkanes and cyclic alcohols into PIZA-5 is compared with turnover numbers for the oxidation of cyclic alkanes with PIZA-5. Since PIZA-5 is selective toward sorption of cyclopentanol compared to cyclopentane, the product cyclopentanol is likely stored in the framework and inhibits further reaction. This phenomenon may be similar for cyclooctane, although the sorption error bars for cyclooctane and cyclooctanol overlap. In contrast, since PIZA-5 is non-selective toward the sorption of cyclohexanol and cycloheptanol compared to their respective alkanes, its activity is less inhibited by these hydroxylation products. Therefore, the turnover numbers for a particular substrate are correlated to how selective the PIZA-5 framework is towards the sorption of reactant over the product. In other words, the control that the framework of PIZA-5 shows over catalytic activity reflects both *size-* and *polarity-selectivity*.

#### Hydroxylation of linear alkanes with PIZA-5 and iodosylbenzene

To explore potential regioselectivity, the hydroxylation of a series of linear alkanes was studied with PIZA-5 ([Mn(CarMesP)Cl]<sub>3</sub>Zn<sub>4</sub>O) under liquid-solid conditions (PIZA-5/PhIO/alkane = 1/15/2000). The reactions were run for two hours and quenched with sodium sulfite. The catalyst was extracted and the resulting product mixture was analyzed by GC-MS. As shown in Table S6, only *n*-hexane, *n*-heptane, and *n*-octane were hydroxylated. The alcohols produced for these substrates were in the



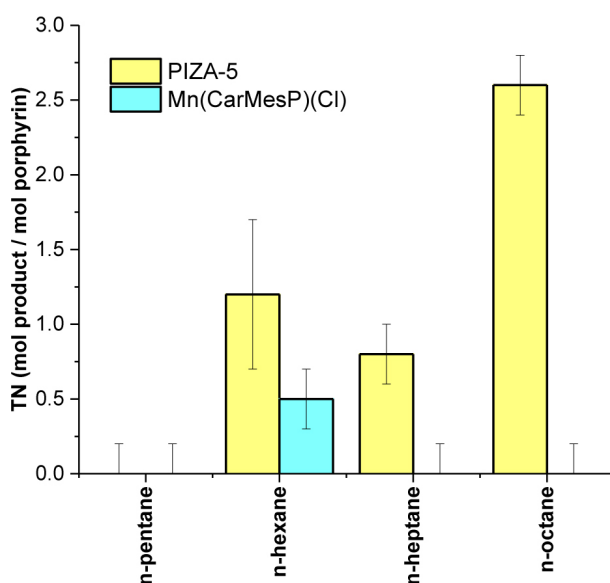
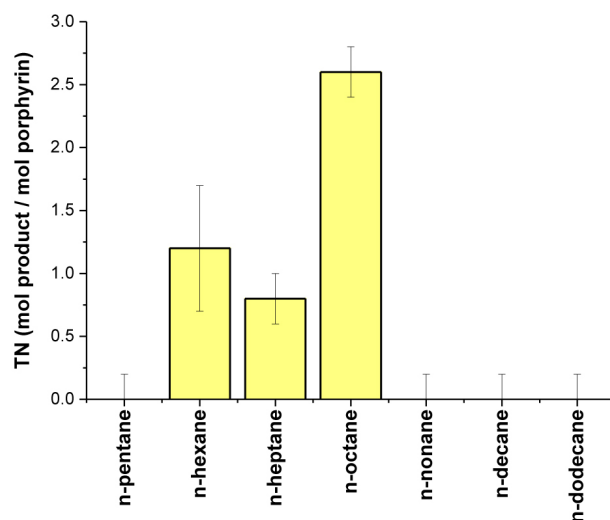
**Fig. 15.** Comparison of the catalytic turnover numbers (upper) and sorption data (lower) for PIZA-5 with various cycloalkanes

expected statistical proportion based on the number of available hydrogens on the linear alkanes and no production of terminal alcohols (1-ols) or aldehydes was observed, indicating no significant regioselective oxidation. Control reactions without PIZA-5 under the same conditions were done for each substrate and resulted in no product.

The turnover results of these oxidation experiments are plotted in Fig. 16 and appear to indicate that PIZA-5 is selective for oxidation of linear alkanes with six to eight carbons, with a preference for *n*-octane. As with the cyclic alkane series, the results of the control reactions (Fig. 16) using the precursor porphyrin, Mn(CarMesP)(Cl) (which is insoluble in the chosen reaction solvents) as catalyst, suggest that the amount of catalytic activity from the external surface of PIZA-5 is small in comparison to that which occurs in the pores. As suggested by the earlier conclusion that PIZA-5 can act in a polarity-selective manner, the selective oxidation of *n*-octane may occur because the octanol molecules produced are less polar than the smaller alcohols, and are expelled from the framework more easily.

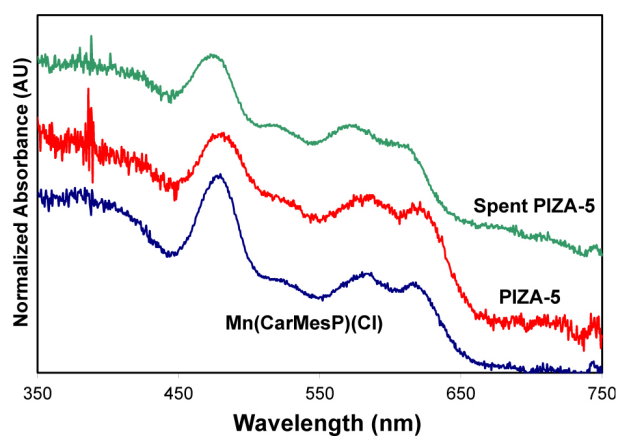
#### Hydroxylation of cyclic and linear alkanes with PIZA-6 and iodosylbenzene

The evacuated PIZA-6 framework solid ([Co(CarMesP)Cl]<sub>3</sub>Zn<sub>4</sub>O) was also tested as a liquid-solid



**Fig. 16.** Turnover numbers for oxidation of linear alkanes by PIZA-5. Upper: PIZA-5/PhIO/linear alkanes (1/15/2000) at 2 h. Lower: Comparison of PIZA-5 with nonporous solid insoluble control porphyrin, Mn(CarMesP)(Cl)

phase heterogeneous catalyst in the oxidation of alkanes with iodobenzene. The reaction conditions of PIZA-6/PhIO/alkane (1/15/2000) were used with acetonitrile as solvent, similar to those used for the PIZA-5 catalysis trials. Of the four cyclic alkanes tested (cyclopentane through cyclooctane), only cycloheptane was oxidized into cycloheptanol by PIZA-6. The turnover number was very low for this substrate ( $0.3 \pm 0.1$  mol product/mol porphyrin) with 100% conversion of the iodobenzene to iodobenzene. None of the other cyclic alkanes were converted. In addition, the PIZA-6/PhIO system did not oxidize any of the linear alkanes tested (*n*-pentane to *n*-octane). These findings suggest that PIZA-6 is not an effective catalyst for hydroxylating alkanes in the liquid-solid phase using iodobenzene.



**Fig. 17.** Diffuse reflectance UV-visible spectra of the soluble porphyrin linker Mn(CarMesP)(Cl), PIZA-5 before oxidation catalysis, and PIZA-5 after catalysis. Spectra have been normalized to the Soret peak at  $\sim 477$  nm and offset for clarity

### Stability of PIZA-5 to oxidation conditions

The PIZA-5 and PIZA-6 solids were stable to all of the oxidation conditions explored. To the un-aided eye, the solids appeared to be the same at the end of the reactions. No discoloration of the solid occurred and only minimal coloration ( $< \mu\text{M}$ ) of the solvent solution was observed. Since the solvent did not pick up color from the solid, this indicates that the solid was not dissolving or decomposing, as free porphyrins or porphyrin decomposition products would quickly color the solution.

PIZA-5 ( $[\text{Mn}(\text{CarMesP})\text{Cl}]_3\text{Zn}_4\text{O}$ ) was analyzed before and after catalysis by diffuse reflectance UV-Visible spectroscopy. For comparison, the linker porphyrin was also analyzed as a control. The results of this semi-quantitative experiment are shown in Fig. 17. Similar spectra are observed for PIZA-5 before and after catalysis with large excesses of iodobenzene and are similar to those found for the control porphyrin without oxidation, indicating that PIZA-5 is stable to our oxidation conditions.

## CONCLUSIONS

Two robust metalloporphyrin framework solids, PIZA-5 and PIZA-6, were synthesized and are isostructural to the previously reported PIZA-4. PIZA-5 contains manganese (III) porphyrinate as linkers between  $\text{Zn}_4\text{O}$  clusters while PIZA-6 has a cobalt(II) porphyrinate. The cubic interpenetrated frameworks have 72% free volume and  $4 \times 7 \text{ \AA}$  pores. Experimental evidence shows that the evacuated frameworks are robust and retain a structure open to sorption of substrates with medium polarity and are capable of re-sorption of solvates. The heterogeneous catalytic activity of the PIZA-5/PhIO system is similar to, but more rapid than, that found in homogeneous conditions with the analogous soluble Mn(III) porphyrin complex.

In addition, the sorption and catalysis by PIZA-5 showed size and polarity selectivity among a range of cyclo- and *n*-alkanes (C<sub>5</sub> to C<sub>12</sub>) and corresponding alcohols that demonstrate that the catalytic reactions occur *inside the pores of the framework solid*, making PIZA-5 a rare case of a catalytic porphyrin framework solid.

### Acknowledgments

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### Supporting information

PIZA-5 crystallographic data, TGA sorption data, and product tables. This material is available free of charge via the Internet.

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