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## *Cis*-decalin oxidation as a stereochemical probe of *in-MOF* versus *on-MOF* catalysis

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Development of catalyst-controlled C–H hydroxylation could provide direct access to valuable synthetic targets, such as primary metabolites. Here, we report a new family of porous materials, comprised of 2-dimensional metalloporphyrin layers and flexible aliphatic linkers, and demonstrate C–H hydroxylation activity. We demonstrate that the stereochemistry of *cis*-decalin oxidation provides a useful tool for differentiating *catalysis in* from *catalysis on* porous materials, which is critical to leveraging the potential of porous materials for catalyst-controlled oxidation chemistry.

Enzymatic C–H oxidation during xenobiotic metabolism and biosynthesis is accomplished with *catalyst-controlled* selectivity within substrate-adaptive enzyme active sites.<sup>1</sup> In contrast, most synthetic C–H hydroxylation methods proceed with *substrate-controlled* selectivity at either the weakest or the most sterically unencumbered C–H bond.<sup>2</sup> The development of strategies for catalyst-controlled C–H hydroxylation could provide direct entry into complex functional molecules, such as metabolites.<sup>3</sup> We are interested in utilizing flexible metal-organic frameworks (MOFs) as catalyst platforms to achieve oxidation selectivities that are challenging to access in solution-phase chemistry.

MOFs are a class of materials comprised of metal nodes and organic linking elements that typically display rigid 3dimensional structure and network porosity.<sup>4</sup> Porphyrinic MOFs, in which metallopophyrins are incorporated as linking elements, have garnered intense interest due to the potential use of these materials as biomimetic heterogeneous oxidation catalysts.<sup>5</sup> Among the challenges to developing efficient oxidation catalysis based on porphyrinic materials are: 1) generating large-pore, non-interpenetrating materials that support substrate diffusion,<sup>5a,6</sup> 2) controlling M–L binding to access materials with open metal sites,<sup>7</sup> and 3) accessing robust frameworks that maintain structure during guest removal or exchange.<sup>8</sup> Even with these criteria met, it remains a substantial challenge to differentiate catalysis *on materials* (*i.e.* catalyst sites on the exterior of crystallites) from catalysis *in materials*. We are interested in porphyrinic materials that feature flexible organic linkers as platforms for catalyst-controlled oxidation of organic molecules based on the contention that network flexibility<sup>9</sup> may provide substrate-specific reaction environments in which to accomplish catalysis. Critical to development of catalysts for these applications is determining if catalysis is accomplished inside catalyst pores or on the surface of catalyst particles. Here we report the synthesis of a new family of porphyrinic materials and present a stereochemical test based on *cis*-decalin oxidation to differentiate catalysis *in materials* from catalysis *on materials*.

Solvothermal combination of 5,10,15,20-tetrakis(4carboxyphenyl)porphyrin iron chloride (Fe(tcpp)Cl), 1,3-di(1H-1,2,4-triazol-1-yl)propane (btp), and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O in N,N'diethylacetamide (DEA) and ethanol (EtOH) at 80 °C affords a dark-purple crystalline material with the empirical formula  $[Zn_2(Fe(tcpp))(btp)(NO_3)]_n$  (**Fe(btp)**, Figure 1). The chemical composition of Fe(btp) was evaluated by: 1) elemental analysis; 2) acid digestion followed by UV-vis and <sup>1</sup>H NMR analyses to define the Fe(tcpp) and btp content, respectively (Figures S1 and S2); 3) ICP-MS analysis of an acid-digested sample to establish the Fe:Zn ratio (Table S1); and 4) diffuse reflectance UV-vis spectroscopy (Figure S1). Elemental analysis and IR spectroscopy (Figure S3) indicate that the chloride counterions of the Fe(tcpp)Cl starting material are replaced by nitrate ions during solvothermal synthesis of Fe(btp). The average Fe(tcpp):btp ratio of acid-digested samples is 0.8, which indicates the presence of some ligand absences from the ideal  $[Zn_2(Fe(tcpp))(btp)(NO_3)]_n$  empirical formula.

A wide variety of network topologies are available for layered porphyrinic materials.<sup>7b,10</sup> For example, while PPF-5, which is a layered material comprised of Ni(tcpp), 4,4'-bypyridine (bpy), and dizinc tetracarboxylate nodes features an AA stacking motif in which dizinc sites are connected by bpy, PPF-3, which is a layered material comprised of Fe(tcpp), bpy, and dizinc tetracarboxylate nodes features an AB stacking

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stacking model.

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PXRD and SCXRD data.

motif, in which dizinc sites are bound to metalloporphyrin

sites.<sup>10</sup> We have used a combination of single-crystal X-ray

diffraction (SCXRD), powder X-ray diffraction (PXRD), and

modeling to confirm that Fe(btp) features AA-stacking of

porphyrinic layers and is isostructural with PPF-5. SCXRD

analysis confirmed the 2-D porphyrinic layers in Fe(btp) are

connected by dizinc tetracarboxylates and indicated AA stacking of the 2-D layers with alignment of the dizinc units

along the crystallographic *c*-axis. Interlayer connectivity, however, could not be established by SCXRD due to severe

disordering in the crystallographic c-axis (see Figure S4 for SCXRD data). PXRD was collected for Fe(btp) and is displayed

in Figure 1. We constructed a model based on the 2-D layers

determined by SCXRD and the layer-to-layer spacing set at

15.28 Å, which was calculated from the first main peak at  $2\Theta$  =

5.781° in the measured PXRD pattern. The measured PXRD

data are in good agreement with the structure model

presented in Figure 1d and 1e. The PXRD data for Fe(btp)

display a strong [00/] preferred orientation, which is common

for layered porphyrinic materials<sup>10</sup> and consistent with the

plate morphology of Fe(btp) crystallites. We also simulated the

PXRD pattern expected of AB stacking (Figure S5) and the observed PXRD is most well-matched to the presented AA

The assignment of AA stacking is further bolstered by conversion of **Fe(btp)** to  $[Zn_2(Fe(tcpp))(bpy)(NO_3)]_n$  (**Fe(bpy)**)

via post-synthetic linker exchange<sup>11</sup> chemistry (Figure 2).

Fe(btp) is unstable in fresh DEA; <sup>1</sup>H NMR analysis of the

solvent indicated leaching of btp from the material and PXRD

indicated amorphization of the network. In contrast, Fe(btp) is

solutions of bpy resulted in the isolation of an isostructural layered material Fe(bpy). Similar to Fe(btp), interlayer connectivity of Fe(bpy) could not be resolved by SCXRD (Figure S6), but the PXRD pattern measured for Fe(bpy) indicates that Fe(bpy) is an AA-stacked material isostructural with PPF-5 (Figure 2).<sup>10</sup> Additionally, the unit cell parameters of **Fe(bpy)** (a = b = 16.70 Å, c = 14.05 Å;  $P_4/m$ ) are similar to those of PPF-5  $(a = b = 16.65 \text{ Å}, c = 14.05 \text{ Å}; P_4/mmm)$  but dissimilar to those of PPF-3 (a = b = 16.63 Å, c = 25.08 Å;  $I_4/mmm$ ). We have extended similar post-synthetic linker exchange chemistry to the preparation of two additional isoreticular frameworks - $[Zn_2(Fe(tcpp))(bpe)(NO_3)]_n$  (Fe(bpe)) and  $[Zn_2(Fe(tcpp))(bpp)-$ (NO<sub>3</sub>)]<sub>n</sub> (Fe(bpp)) - which are based on 1,2-bis(4pyridyl)ethane (bpe) and 1,3-bis(4-pyridyl)propane (bpp) linkers, respectively. The obtained isoreticular family of materials displays linker-dependent layer-to-layer spacing (14.04 Å (Fe(bpy)), 15.28 Å (Fe(btp)), 16.39 Å (Fe(bpe)), and 16.45 Å (Fe(bpp); Figure S7). Characterization data is collected in Figures S8–S10 and Tables S1 and S2. The original report of PPF-5 explored the solvothermal

chemistry of Zn(NO<sub>3</sub>)<sub>2</sub>, Fe(tcpp), and bpy and showed the evolution of PPF-3, which features an AB stacking motif.<sup>10</sup> We were interested in the observation that linker exchange from Fe(btp) provides access to an AA stacking motif (PPF-5 topology), and specifically were interested in addressing whether templating provided access to network topologies not accessible by direct synthesis. To address this issue, we have carefully examined the impact of bpy loading on the reaction outcome and have found that Fe(bpy) is obtained from





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**Figure 2.** Comparison of the PXRD pattern of **Fe(bpy)** with the simulated and experimental PXRD patterns for PPF-3 and PPF-5 materials, which feature AB- and AA-stacking motifs, respectively.

solvothermal synthesis at low bpy loading, while PPF-3 is obtained at higher loading (Figure S11). Similar stoichiometrydependent phase isolation was observed when btp loading was varied in **Fe(btp)** syntheses (Figure S12).

Fe(btp) undergoes amorphization upon removal of volatile solvent guest molecules (Figure S13). Thermogravimetric analysis (TGA) measured under  $N_2$  flow reveals ~50% weight loss between 23-150 °C (Figure S14) and IR spectroscopy shows that this mass loss is associated with removal of DEA (Figure S3). Gas sorption isotherms (up to 1 bar of pressure) were measured for the desolvated solid (Fe(btp)<sub>act</sub>) with N<sub>2</sub> and  $CO_2$  at 77 K and 195 K, respectively, and indicate that Fe(btp)<sub>act</sub> has very low accessible internal surface area (i.e. 89  $m^2/g$  based on CO<sub>2</sub> isotherm as compared to theoretical surface area of 3580 m<sup>2</sup>/g, Figure S15). Network structure, as probed by PXRD analysis, did not return after soaking Fe(btp)<sub>act</sub> in DEA and EtOH (Figure S13). Additionally, in situ PXRD experiments carried out at the Advanced Photon Source (APS) while sequentially subjecting Fe(btp)<sub>act</sub> to vacuum and then to high pressure gas (up to 100 bar CH<sub>4</sub> or 30 bar CO<sub>2</sub> pressure) indicate that the vacuum-induced phase transition of Fe(btp) to Fe(btp)<sub>act</sub> is irreversible (Figures S16 and S17).

For application to oxidation catalysis, porosity in the absence of solvent is not required, only maintenance of porosity during guest exchange is necessary.<sup>12</sup> The layered materials presented here readily participate in guest exchange. Soaking **Fe(btp)** in a CH<sub>3</sub>CN solution of fluorescent dye rhodamine  $6G^{13}$  results in the intercalation of dye into the material (30 wt%), as evidenced by UV-vis analysis of both the soaking liquid and the digested solids (Table S3 and Figure S18). The ability for solution-phase guest exchange reactions to proceed demonstrates that the porosity of our materials is maintained in the presence of suitable guests. In contrast, no dye uptake is observed with **Fe(btp)**<sub>act</sub>.

We selected *cis*-decalin as a substrate for hydroxylation catalysis using our layered materials for two reasons. First, *cis*-decalin presents multiple chemically and stereochemically distinct C–H bonds. Second, *cis*-decalin provides a stereochemical probe during oxidation: Hydrogen-atom



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**Figure 3.** Epimerization of *cis*-decalin-derived radicals provides a mechanism to generate both *cis*- and *trans*-1 during radical hydroxylation.

abstraction (HAA) from C9 generates a tertiary radical that can undergo epimerization (Figure 3).<sup>14</sup> The ratio of *cis*- and *trans*decahydronaphthalen-9-ol (1) provides information regarding the rate of hydroxylation relative to epimerization. The modest preference for stereoretention during oxidation catalyzed by soluble metalloporphyrins has been rationalized as arising from radical rebound within a solvent cage.<sup>15</sup>

Treatment of Fe(btp) with cis-decalin and 2-tertbutylsulfonyliodosylbenzene,<sup>16</sup> a common soluble oxygenatom transfer reagent, results in a >100:1 mixture of cis- and trans-1 (Figure 4, entry 1). Fe(btp) could be recycled without loss of activity or selectivity. Removal of Fe(btp) and addition of oxidant to the filtrate does not result in cis-decalin oxidation indicating that Fe(btp) functions as a heterogeneous catalyst. Molecular catalysts Fe(tpp)Cl and Fe(tmp)Cl afforded 3.3:1 and 8.5:1 mixtures, respectively (entries 7 and 8; tpp: 5,10,15,20tetraphenylporphyrin; tmp: 5,10,15,20-tetrakis(4-methoxycarbonylphenyl)porphyrin). Similarly, catalysis with Fe(btp)act, which does not exhibit dye-uptake activity (Table S3), results in a 4:1 mixture of cis- and trans-1 (Entry 3). The availability of both porous (Fe(btp)) and non-porous (Fe(btp)<sub>act</sub>) materials with the same chemical composition allows direct examination of the selectivity of oxidation inside the porous material as compared with at exposed particle surfaces.

Based on the hypothesis that metalloporphyrin sites housed within **Fe(btp)** accomplish highly stereospecific oxidation while metalloporphyrin sites on the surface of catalyst particles accomplish oxidation in low stereospecificity, we evaluated the selectivity that was achieved using ground samples of our porous materials. Grinding **Fe(btp)** reduces the particle size and thus, for a given catalyst loading, increases the proportion of catalyst sites on the exterior surface of particles. Examination of the impact of grinding on catalyst performance has been pursued previously to probe the activity of the exterior surface of catalyst materials.<sup>17</sup>

As-synthesized samples of **Fe(btp)** exhibit a broad particle size distribution, with many crystallites exhibiting larger than 100  $\mu$ m edges. Ground samples of **Fe(btp)** showed narrower particle size distribution centered at ~10  $\mu$ m (SEM images are collected in Figures S19 and S20). Whereas as-synthesized **Fe(btp)** affords a >100:1 mixture of *cis*- and *trans*-1, oxidation with a ground sample of **Fe(btp)** provides a 50:1 mixture (Entry 2). Importantly, grinding has no impact on dye uptake capacity indicating that while grinding diminishes the average crystallite

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Figure 4. Oxidation of cis-decalin affords a catalystdependent mixture of *cis*- and *trans*-1.

size, it has no impact on material porosity (Table S3). A similar trend is observed when Fe(bpy) is used as an oxidation catalyst. As synthesized samples afford a 53:1 mixture of cisand trans-1 while ground samples afford a 37:1 ratio (Entries 4 and 5).

The collected data is consistent with rapid hydroxylation of radical intermediates inside our porous materials. Relatively slow hydroxylation of radical intermediates by surface-bound catalysts provides opportunity for loss of stereospecificity during oxidation. These observations suggest that our porous materials effectively function as tight solvent cages and prevent stereochemical scrambling during hydroxylation chemistry. Further, the observed relationship between the outer surface area of catalyst particles and reaction stereospecificity provides a useful tool to differentiate catalysis in from catalysis on these porous materials.

In summary, we have prepared a new isoreticular family of layered porphyrinic materials with substrate-accessible unsaturated Fe porphyrin sites. We have shown that these materials affect highly stereospecific oxidation of cis-decalin while hydroxylation with homogeneous and non-porous analogs proceeds with low stereospecificity. Oxidation stereospecificity provides a chemical probe for differentiating catalysis in versus catalysis on these porous materials. Accomplishing catalysis in materials is a critical prerequisite to utilizing pore structure to control chemical selectivity. We anticipate that use of cis-decalin oxidation specifically, and other stereochemical probes generally, may provide useful tools for evaluating the locus of catalysis with porous materials.

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### Notes and references

- 1 (a) J. Clardy and C. Walsh, Nature, 2004, 432, 829. (b) B. Meunier, S. P. de Visser and S. Shaik, Chem. Rev., 2004, 104, 3947. (c) L. Que, Jr. and W. B. Tolman, Nature, 2008, 455, 333.
- 2 (a) B. A. Arndtsen, R. G. Bergman, T. A. Mobley and T. H. Peterson, Acc. Chem. Res., 1995, 28, 154. (b) T. Newhouse and P. S. Baran, Angew. Chem. Int. Ed., 2011, 50, 3362.
- (a) K. Zhang, B. M. Shafer, M. D. Demarsil, H. A. Stern and R. 3 Fasan, J. Am. Chem. Soc., 2012, 134, 18695. (b) J. Genovino, S. Lütz, D. Sames and B. B. Touré, J. Am. Chem. Soc., 2013, 135, 12346.
- (a) B. F. Abrahams, B. F. Hoskins and R. Robson, J. Am. Chem. Soc., 1991, 113, 3606. (b) O. M. Yaghi, G. Li and H. Li, Nature, 1995, 378, 703. (c) H. Li, M. Eddaoudi, M. O'Keefe and O. M. Yaghi, Nature, 1999, 402, 276.
- (a) K. S. Suslick, P. Bhyrappa, J. H. Chou, M. E. Kosal, S. 5 Nakagaki, D. W. Smithenry and S. R. Wilson, Acc. Chem. Res., 2005, 38, 283. (b) W.-Y. Gao, M. Chrzanowski and S. Ma, Chem. Soc. Rev., 2014, 43, 5841.
- (a) M. E. Kosal, J.-H. Chou, S. R. Wilson and K. S. Suslick, Nat. 6 Mater., 2002, 1, 118. (b) A. M. Shultz, O. K. Farha, J. T. Hupp and S. T. Nguyen, J. Am. Chem. Soc., 2009, 131, 4204. (c) O. K. Farha, A. M. Shutlz, A. A. Sarjeant, S. T. Nguyen and J. T. Hupp, J. Am. Chem. Soc., 2011, 133, 5652. (d) X.-L. Lv, K. Wang, B. Wang, J. Su, X. Zou, Y. Xie, J.-R. Li and H.-C. Zhou, J. Am. Chem. Soc., 2017, 139, 211.
- (a) E. Y. Choi, P. M. Barron, R. W. Novotny, C. H. Hu, Y. U. 7 Kwon and W. Y. Choe, CrystEngComm, 2008, 10, 824. (b) E.-Y. Choi, P. M. Barron, R. W. Novotny, H.T. Son, C. Hu and W. Choe, Inorg. Chem., 2009, 48, 426. (c) E. Y. Choi, C. A. Wray, C. H. Hu and W. Choe, CrystEngComm, 2009, 11, 535. (d) P. M. Barron, C. A. Wray, C. Hu, Z. Guo and W. Choe, Inorg. Chem., 2010, 49, 10217.
- B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, Nature, 1994, 369, 727.
- (a) C. Serre, F. Millange, C. Thouvenot, M. Noguès, G. Marsolier, D. Louër and G. Ferey, J. Am. Chem. Soc., 2002, 124, 13519. (b) S. Kitagawa, R. Kitaura and S.-I. Noro, Angew. Chem. Int. Ed., 2004, 43, 2334. (c) H. Sato, W. Kosaka, R. Matsuda, A. Hori, Y. Hijikata, R. V. Belosludov, S. Sakaki, M. Takata and S. Kitagawa, Science, 2014, 343, 167. (d) J. A. Mason, J. Oktawiec, M. K. Taylor, M. R. Hudson, J. Rodriguez, J. E. Bachman, M. I. Gonzalez, A. Cervellino, A. Guagliardi, C. M. Brown, P. L. Llewellyn, N. Masciocchi and J. R. Long, Nature, 2015, 527, 357.
- 10 P. M. Barron, H.-T. Son, C. Hu and W. Choe, Cryst. Growth Des., 2009, 9, 1960.
- 11 (a) B. J. Burnett, P. M. Barron, C. Hu and W. Choe, J. Am. Chem. Soc., 2011, 133, 9984. (b) S. Takaishi, E. J. DeMarco, M. J. Pellin, O. K. Farha and J. T. Hupp, Chem. Sci., 2013, 4, 1509.
- 12 L. J. Barbour, Chem. Commun. 2006, 1163.
- 13 L. Ma, J. M. Falkowski, C. Abney and W. Lin, Nat. Chem., 2010, 2, 838.
- 14 (a) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel and L. A. Singer, J. Am. Chem. Soc., 1965, 87, 2590. (b) M. Zhou, D. Balcells, A. R. Parent, R. H. Crabtree and O. Eisenstein, ACS Catal. 2012, 2, 208-218.
- 15 J. T. Groves and T. E. Nemo, J. Am. Chem. Soc., 1983, 105, 6243.
- 16 D. Macikenas, E. Skrzypczak-Jankun and J. D. Protasiewicz, J. Am. Chem. Soc., 1999, 121, 7164.
- (a) K. S. Suslick, P. Bhyrappa, J.-H. Chou, M. E. Kosal, S. 17 Nakagaki, D. W. Smithenry and S. R. Wilson, Acc. Chem. Res. 2005, 38, 283. (b) C. Zou, T. Zhang, M.-H. Xie, L. Yan, G.-Q. Kong, X.-L. Yang, A. Ma and C.-D. Wu, Inorg. Chem. 2013, 52, 3620.

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