

Crystal Engineering of a Microporous, Catalytically Active *fcu* Topology MOF Using a Custom-Designed Metalloporphyrin Linker**

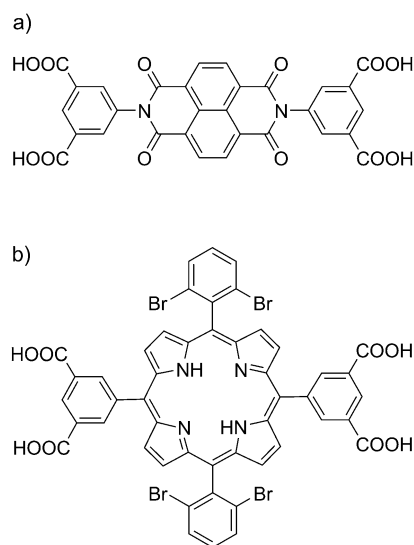
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A major driving force behind the recent surge of interest in metal–organic frameworks (MOFs)^[1] lies with their amenability to design using crystal engineering^[2a–d] strategies. In particular, MOFs with specific composition and topology can be targeted by judicious selection of organic linkers and metal-based molecular building blocks^[2e–g] (MBBs) that serve as nodes.^[2] Furthermore, their modular nature means that prototypical MOFs can serve as blueprints or platforms for a plethora of derivatives with controlled pore size and surface area, as exemplified by the practice of “reticular synthesis”.^[3] Such features make MOFs stand out over traditional porous materials, and afford them with potential for use in gas storage,^[4] separation,^[5] CO₂ capture,^[6] sensor,^[7] catalysis,^[8] and other areas.^[9]

High-symmetry MOFs based upon high-connectivity polyhedral cage MBBs that are in effect supermolecular building blocks (SBBs) can provide exquisite control over structure because of their high connectivity and also afford the features of confined nanospace^[10] and extra-large surface area.^[11] Such MOFs have afforded superior performance in the context of gas storage for hydrogen, methane, CO₂, and other gas molecules.^[4,6,11,12] The nature of the nanospace in SBB-based MOFs is such that they can encapsulate catalytically active species, for example, organometallics,^[13] polyoxometallates,^[14] metalloporphyrins (porph@MOMs),^[15] and enzymes.^[16] Along with encapsulation of catalysts, it is possible to generate porphyrin-walled MOFs by custom-designing metalloporphyrin moieties so that they can serve as vertices and/or edges and/or faces. In principle, the metal

clusters residing on the vertices could also contribute as active sites to achieve an even higher density of active sites than that of porph@MOMs.^[15] Polyhedral MOFs are therefore attractive targets as catalyst supports for heterogeneous catalysis. However, although metallosalens and metalloporphyrins have been utilized as linkers for catalytically active MOFs^[17] and polyhedral cage-containing metal–metalloporphyrin frameworks exist,^[18] MOFs sustained by catalytically active metalloporphyrin linkers and catalytically active MBBs remain unexplored.

Herein, we report such a MOF that based upon a previously reported *fcu* topology net built from 12-connected cubohectahedral SBBs of formula [Co₂(μ₂-H₂O)(H₂O)₄]₆-(bdc)₁₂ and benzoimidophenanthroline tetracarboxylate (bipa-tc) linkers (Scheme 1 a), *fcu*-MOF-1.^[19] The new com-



Scheme 1. The ligands that serve as linkers in *fcu*-MOF-1 and MMPF-3: a) benzoimidophenanthroline tetracarboxylic acid (H₄bipa-tc) and b) 5,15-bis(3,5-dicarboxyphenyl)-10,20-bis(2,6-dibromophenyl)porphyrin (H₄dcdbp).

compound, MMPF-3 (MMPF denotes metal–metalloporphyrin framework), was prepared solvothermally from a novel porphyrin ligand that is an analogue of bipa-tc, 5,15-bis(3,5-dicarboxyphenyl)-10,20-bis(2,6-dibromophenyl)porphyrin (dcdbp, Scheme 1 b),^[20] and Co(NO₃)₂. Cube-shaped, dark-red crystals of MMPF-3, [Co₂(μ₂-H₂O)(H₂O)₄](Co-dcdbp)-(H₂O)₆·(C₂H₅OH)₁₂·(DMF)₁₂, (as determined by x-ray crystallography, elemental analysis, and thermogravimetric analysis) were thereby harvested. Single-crystal X-ray diffraction

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studies were conducted at the Advanced Photon Source, Argonne National Laboratory and revealed that MMPF-3 crystallizes in the same space group, $P\bar{a}3$, as **fcu**-MOF-1, with $a = 38.805(3)$ Å, $(39.288(2)$ Å in **fcu**-MOF-1). As expected, MMPF-3 is based upon $\text{Co}_2(\mu_2\text{-H}_2\text{O})(\text{H}_2\text{O})_4(\text{COO})_4$ MBBs (Supporting Information, Figure S2) that afford the cubohe-mioctahedral SBBs that serve as 12-connected nodes (Figure 1a) in the resulting **fcu** topology network (Supporting Information, Figure S3).

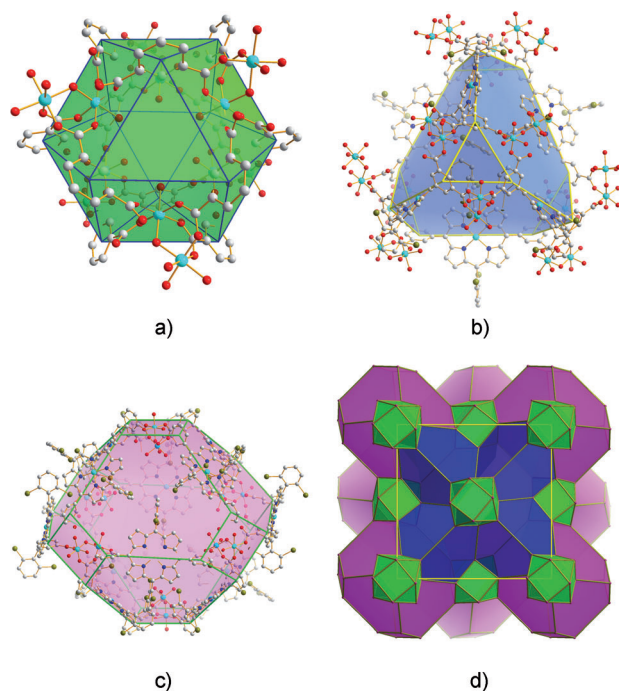


Figure 1. The three types of polyhedral cages present in MMPF-3: a) cubohe-mioctahedron, b) truncated tetrahedron, and c) truncated octahedron. d) 3D structure of MMPF-3 illustrating how its polyhedral cages are connected. See also the Supporting Information, Figure S3, which highlights how MMPF-3 is formed by linking the 12 vertices of the cubohe-mioctahedral cage.

fcu-MOF-1 was targeted as a blueprint because it exhibits three types of polyhedral cage: a cubohe-mioctahedron with a window size of ca. 5.9 Å and inner dimensions of about 7.3 Å (atom-to-atom distance); a truncated tetrahedron in which six linkers form the edges of the tetrahedron (2,6-dibromophenyl moieties occupy the inner space of the cage, Figure 1b); a truncated octahedron, with a window size of about 9.2 Å (atom to atom distance) and a cavity with an internal volume of about 4000 Å³ (Figure 1c). In the truncated octahedral cage, twelve bipa-tc linkers form the main edges of the octahedron. Furthermore, the SBBs occupy the vertices in such a manner that one Co^{II} cation of each $\text{Co}_2(\mu_2\text{-H}_2\text{O})(\text{H}_2\text{O})_4(\text{COO})_4$ MBB orients towards the center of the cage. The equivalent nanoscopic polyhedron in MMPF-3 possesses twelve cobalt centers that orient towards the center of the cage and therefore exhibits eighteen metal centers with a density of about 5 Co/nm³. The three types of polyhedral cage are interconnected (Figure 1d), and MMPF-3 possesses

a solvent-accessible volume of 60% as calculated from PLATON.^[20]

That MMPF-3 exhibits permanent porosity was confirmed by CO₂ adsorption at 273 K, which revealed a surface area of about 750 m²g⁻¹ using NLDFT analysis (Supporting Information, Figure S5).^[21] Given the high density of cobalt metal centers in the truncated octahedral cages of MMPF-3, we evaluated its catalytic performance in the context of epoxidation of *trans*-stilbene, which has recently been studied in cobalt-based MOFs.^[22] We conducted assays for the epoxidation of *trans*-stilbene using *tert*-butyl hydroperoxide (tbhp) as oxidant in acetonitrile at 60°C. Control experiments were conducted for homogeneous cobalt(II)-metalated dcdbp (Co(dcdbp)), **fcu**-MOF-1, and a blank under the same conditions. As revealed by Figure 2 and Table 1, MMPF-3 demonstrated the most efficient catalytic activity for epoxidation of *trans*-stilbene of the compounds studied in terms of both yield (95.7% over 24 h) and selectivity (87.1% epoxide product). This compares favorably to the corresponding values for homogeneous Co(dcdbp) (60.4% yield, 67.0% epoxide), **fcu**-MOF-1 (47.1% yield, 76.7% epoxide), and the blank (9.0%

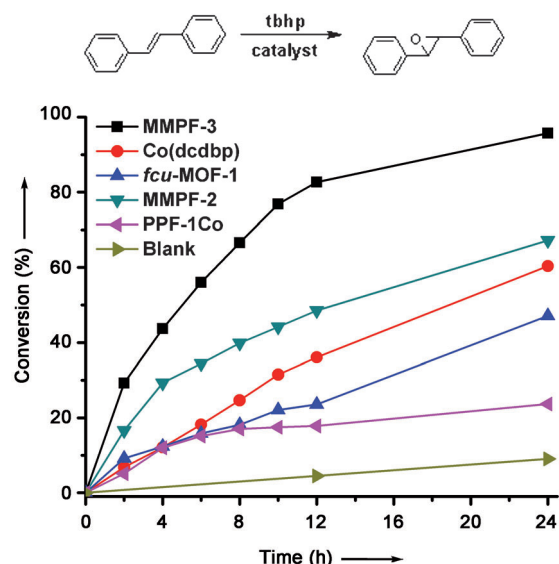


Figure 2. Kinetic traces of *trans*-stilbene epoxidation catalyzed by heterogeneous MMPF-3, homogenous Co(dcdbp), **fcu**-MOF-1, PPF-1Co, and in the absence of catalyst (the molar ratio of *trans*-stilbene/tbhp/catalyst was 1000:1500:1 for all of the catalytic assays).

Table 1: The epoxidation of *trans*-stilbene catalyzed by MMPF-3 and related catalysts.^[a]

Catalyst	Conversion [%] ^[b]	Epoxide [%]	TOF ^[c] [h ⁻¹]
MMPF-3	95.7	87.1	69
Co(dcdbp)	60.4	67.0	30
fcu -MOF-1	47.1	76.7	20
MMPF-2	67.2	58.0	40
PPF-1Co	23.7	30.1	15
blank	9.0	55.8	n.a.
MMPF-3 ^[d]	94.4	83.9	64

[a] *trans*-Stilbene (1 mmol), tbhp (1.5 mmol), catalyst (0.001 mmol), acetonitrile (5.0 mL) were stirred at 60°C for 24 h. [b] After 24 h. [c] Average over 12 h (n.a. = not applicable). [d] The eighth cycle.

yield, 55.8% epoxide). The average turnover frequency (TOF) in the first 12 hour was 69 h^{-1} for MMPF-3, almost 3.5 times faster than that of **fcu**-MOF-1. We attribute the enhancement of catalytic performance in MMPF-3 versus **fcu**-MOF-1 to the higher density of active cobalt centers in the former and/or cooperative interactions between the active centers.^[17m] We also determined the catalytic activity for the 3D-channel cobalt-based porphyrin MOF MMPF-2, which was recently reported by our group,^[23] and the 2D-channel MOF PPF-1Co that is based upon cobalt-metalated tetrakis(4-carboxyphenyl)porphyrin and $\text{Co}_2(\text{COO})_4(\text{H}_2\text{O})_2$ MBBs.^[24] Figure 2 reveals that MMPF-2 converts 67.2% of substrate after 24 h (Table 1), whereas PPF-1Co converts only 23.7% (Table 1). We attribute the reduced catalytic activity in these two porphyrin-based MOFs to misalignment (that is, not oriented directly towards the channel center) or non-alignment (oriented parallel to the channels) of the cobalt centers, respectively. No detectable leaching of active site or cobalt metal in the reaction solution was observed after removal of MMPF-3 by filtration, and MMPF-3 can be reused for eight cycles without significant drop in its catalytic activity (Table 1). Our results therefore highlight how appropriately designed polyhedral cages can serve as efficient nanoreactors. However, it should be noted that several factors, for example, amount of catalyst, oxidant, solvent, reaction temperature, and time, can profoundly influence performance (for example conversion, epoxide selectivity, TOF) in catalytic epoxidation of *trans*-stilbene.^[25] We are currently investigating these factors in the context of MMPF-3 and are also studying epoxidation of different olefin substrates with various molecular sizes and shapes to assess whether or not size- and shape-selectivity can be effected. These studies will be reported separately in the near future.

In summary, polyhedral cage-based nanoreactors that exhibit a high density of about five catalytically active cobalt centers per nm^3 have been generated in MMPF-3 by decoration of a previously known 12-connected MOF, **fcu**-MOF-1, with a custom-designed Co^{II} metalloporphyrin ligand. MMPF-3 exhibits permanent microporosity and demonstrates superior performance in the context of both selectivity and overall conversion in catalytic epoxidation of *trans*-stilbene when compared to the parent **fcu**-MOF-1 and two other cobalt-porphyrin MOFs. The crystal engineering approach for the generation of polyhedral cage-based nanoreactors with a high density of catalytically active centers is expected to be a broadly applicable approach for the development of new classes of highly efficient heterogeneous catalytic systems for epoxidation and related reactions.

Experimental Section

Synthesis of MMPF-3: A mixture of 5,15-bis(3,5-dicarboxyphenyl)-10,20-bis(2,6-dibromophenyl)porphyrin (dcdbp) (2.0 mg), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (8.0 mg) and 1.2 mL mixed solvent (0.5 mL *N,N*-dimethylformamide (DMF), 0.5 mL ethanol, and 0.2 mL H_2O) was sealed in a Pyrex tube under vacuum and heated at 85°C for 48 h. The resulting dark red crystals were washed with DMF three times to give MMPF-3 as pure crystals with formula of $[\text{Co}_2(\mu_2\text{-H}_2\text{O})(\text{H}_2\text{O})_4](\text{Co-dcdbp})(\text{H}_2\text{O})_6(\text{C}_2\text{H}_5\text{OH})_{12}(\text{DMF})_{12}$ (yield: 70% based on dcdbp). Elemental Analysis calcd (%) for MMPF-3: C 44.65, H 6.87, N 7.71;

found: C 45.99, H 6.58, N, 7.85. The reaction was amplified to hundreds of milligrams quantity using multiple tubes.

Crystal Data for MMPF-3: $\text{C}_{48}\text{H}_{20}\text{Br}_4\text{N}_4\text{O}_{14}\text{Co}_3$, $M_r = 1373.11$, cubic, $P\bar{a}3$, $a = 38.805(3)$, $V = 58434(7) \text{ \AA}^3$, $Z = 24$, $T = 100(2) \text{ K}$, $\rho_{\text{calcd}} = 0.936 \text{ g cm}^{-3}$, $R_1 (I > 2\sigma(I)) = 0.1142$, ωR_2 (all data) = 0.3275. CCDC 891567 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Full experimental details for ligand synthesis, structure drawings, TGA plots, and gas sorption isotherms are presented in the Supporting Information.

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