Electronic Supplementary Information

Quest for Highly Porous Metal-Metalloporphyrin Framework based upon a Custom-Designed Octatopic Porphyrin Ligand

Xi-Sen Wang,[a] Matthew Chrzanowski,[a] Chungsik Kim,[a] Wen-Yang Gao,[a] Lukasz Wojtas,[a] Yu-Sheng Chen,[b] X. Peter Zhang,[a] and Shengqian Ma[a,]*

[a] *Department of Chemistry, University of South Florida, 4202 E. Fowler Avenue, Tampa, FL 33620 USA. Fax: +1 813-974-3203; Tel: +1 813-974-5217; E-mail: sqma@usf.edu*

[b] *ChemMatCARS, Center for Advanced Radiation Sources, The University of Chicago, 9700 S. Cass Avenue, Argonne, IL 60439 USA*

General methods.

Commercially available reagents were purchased as high purity from Fisher Scientific or Frontier Scientific and used without further purification. Tetrakis(3,5-dicarboxyphenyl)porphine (H_{10}tdcpp) was synthesized by the literature.[1,2] Solvents were purified according to standard methods and stored in the presence of molecular sieve. Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res.

Synthesis of MMPF-2:

A mixture of H_{10}tdcpp (0.001 g), $Co(NO_3)_2 \cdot 6H_2O$ (0.003 g), and 1.0 mL mixture solvent (DMA(dimethylacetamide):MeOH:H_2O = 4:1:1) was sealed in a Pyrex tube under vacuum and heated to 115 °C for 24 hours. The resulting dark red block crystals were washed with DMA to give pure MMPF-2 $\{[Co_3(OH)(H_2O)_4](Co\text{-}Htdcpp)_3\} \cdot (H_2O)_{20} \cdot (CH_3OH)_{22} \cdot (C_4H_9NO)_{25}$ (yield: 60% based on tdcpp). Anal. Calc. for MMPF-2: C, 47.53; H, 6.18; N, 7.38; Found: C, 48.99; H, 6.08; N, 7.58.

Single-Crystal X-Ray Diffraction Studies of MMPF-2:

The X-ray diffraction data were collected using synchrotron radiation, λ = 0.40663 Å, at Advanced Photon Source, Argonne National Laboratory. Indexing was performed using APEX2[3] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01[4]. Absorption correction was performed by multi-scan method implemented in SADABS.5 Space groups were determined using XPREP implemented in APEX2.[3] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F2) contained in APEX2[3] and WinGX v1.70.01[6-9] programs packages. Despite of using synchrotron source and trying several crystals from different batches, diffraction experiment resulted in low quality diffraction data (lack of high angle reflections). This can be attributed to the presence of the ligand / solvent disorder and to the presence of bad quality, multiply twinned crystals. Due to the low resolution of the data, C, N, O atoms were refined with isotropic displacement parameters and disordered ligand moiety was refined using

distance restraints. Hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). The contribution of disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in Platon program.[10,11] Crystal data and refinement conditions are shown in Table S2. The framework is neutral: μ-OH- is located in the center of Co-trimer and the negative charge is balanced by H+ cations, located between O3…O3′ carboxylate oxygen atoms. Crystal data and refinement conditions are shown in Table S2. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: CCDC 840130, this data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

The MMPF-2 structure has been solved and refined in P4/mbm space group. There are six porphyrin moieties and 30 Co cations in the unit cell. There are two independent porphyrin moieties in the structure with Co1 and Co4 core metals. Both porphyrin moieties are located on symmetry elements so that Co1 atom is located at a site with mmm symmetry (d Wyckoff position) and Co4 is located at site with m.2m symmetry (g Wyckoff position). Consequently there is 1/8 of Co1-porphyrin moiety and ¼ of Co4-porphyrin moiety in the asymmetric unit. N1 and N2 nitrogen atoms of Co1-porphyrin are located on 2-fold axis and two mirror planes (2.mm and m.2m site symmetries respectively) while N3 and N4 nitrogen atoms of Co4-porphyrin are located on a mirror plane (..m and m.. site symmetries respectively).

Gas Adsorption Experiments.

Gas adsorption isotherms of MMPF-2 were collected using the surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples were soaked with methanol, and then were activated using the Supercritical CO_2 Dryer according to the procedures reported in the literature.[12] N_2, Ar, and O_2 gas adsorption isotherms were measured at 77 K or 87K using a liquid N_2 or Ar bath, respectively, and CO_2 gas adsorption isotherms were measured at 273 K and 298 K using an ice-water bath and 298 K water bath respectively.

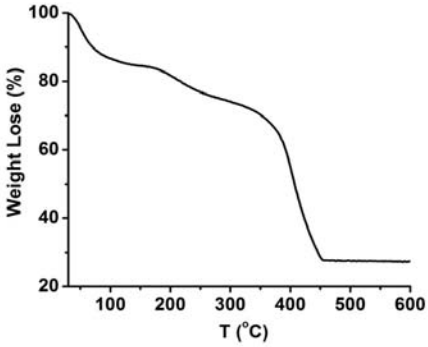


Fig. S1. TGA plot of MMPF-2.

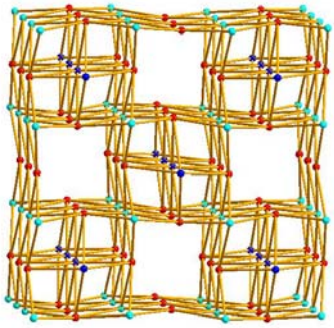


Fig. S2. *msq* topology of MMPF-2.

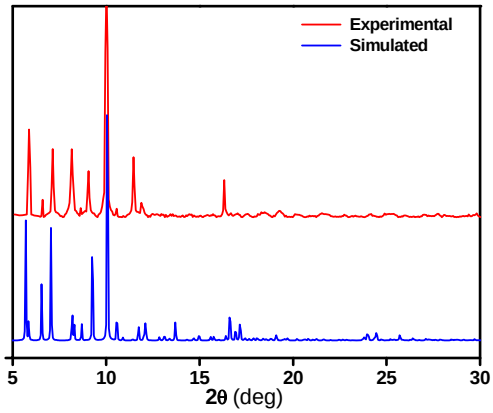


Fig. S3. Powder X-Ray patterns of MMPF-2.

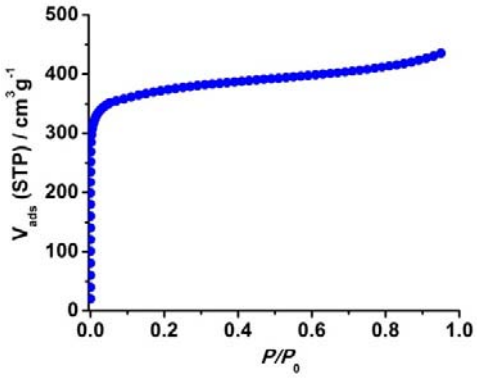


Fig. S4. N_2 adsorption isotherm of MMPF-2 at 77K (Langmuir surface area (P/P_0 = 0.9): 2005 m^2/g; BET surface area (P/P_0 = 0.02~0.2): 1420 m^2/g).

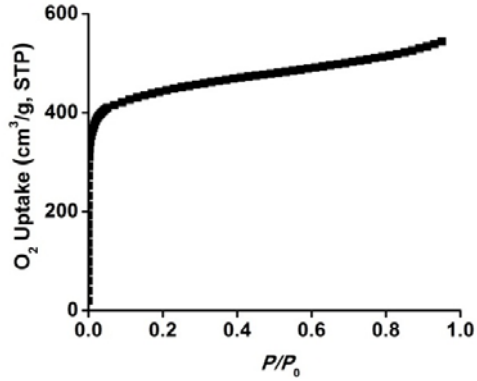


Fig. S5. O_2 adsorption isotherm of MMPF-2 at 87K (Langmuir surface area (P/P_0 = 0.9): 2041 m^2/g; BET surface area (P/P_0 = 0.02~0.2): 1406 m^2/g).

Isosteric Heat of Adsorption (*Qst*) Calculations.

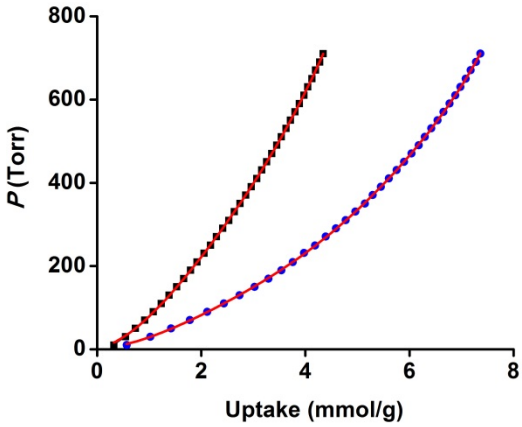
The virial equation of the form given in Equation (1)[13] was employed to calculate the enthalpies of adsorption for CO2 on MMPF-2.

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

where P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m and n represent the number of coefficients required to adequately describe the isotherms. The equation was fitted by

using the the least-squares method; m and n were gradually increased until the contribution of *a* and *b* coefficients toward the overall fitting is statistically trivial, as determined by the t-test. The values of the virial coefficients *a0…am* were then used to calculate the isosteric heat of adsorption by the following expression:

$$Q_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2)$$



Equation	y=exp(ln(x)+(a0+a1*x+a2*(x^2)+a3*(x^3)+a4*(x^4)+a5*(x^5))/(t+b0+b1*x+b2*(x^2))		
Adj. R-Square			0.99996
		Value	Standard Error
F	a0	-3615.28967	90.51245
F	a1	400.31828	56.69051
F	a2	-145.04836	14.11283
F	a3	27.14743	4.1941
F	a4	-2.83821	0.67536
F	a5	0.11649	0.03946
F	b0	15.75176	0.29115
F	b1	-0.25046	0.17205
F	b2	0.06531	0.02395
F	t	298	0
H	a0	-3615.28967	90.51245
H	a1	400.31828	56.69051
H	a2	-145.04836	14.11283
H	a3	27.14743	4.1941
H	a4	-2.83821	0.67536
H	a5	0.11649	0.03946
H	b0	15.75176	0.29115
H	b1	-0.25046	0.17205
H	b2	0.06531	0.02395
H	t	273	0

Fig. S6. Nonlinear curve fitting of CO_2 adsorption isotherms for MMPF-2 at two 273 K and 298 K.

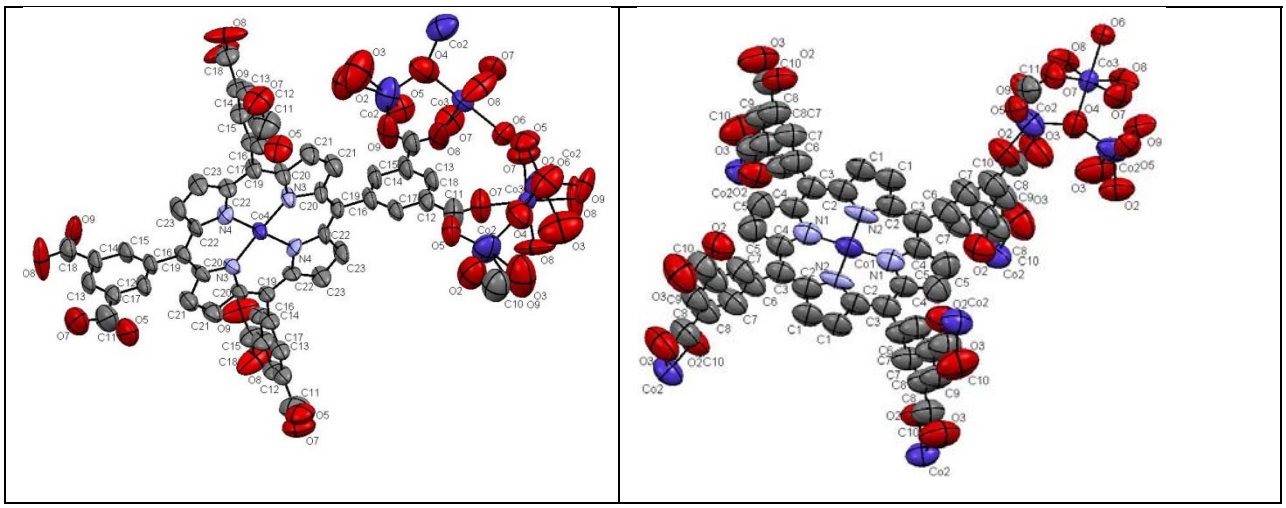


Fig.S7. Coordination and atom numbering scheme for MMPF-2. Atomic displacement ellipsoids are drawn at 50% probability level

Table S1. List of porphyrin-based MOFs with surface area derived from gas sorption measurements.

Compound Name	Surface area (cm^3/g)	Reference
MIL-141-Li	635[a]	59
MIL-141-Na	510 [a]	59
MIL-141-K	810 [a]	59
MIL-141-Ru	820 [a]	59
MIL-141-Cs	860 [a]	59
PIZA-1	125[a]	18，30
PIZA-4	800[b]	23，30
ZnMn-RPM	1000[c]	57
ZnPO-MOF	500[c]	44
$[Cu_2(AcO)_4(CuTPyP)$	1036[b]	33
Zn_4·ZnTCPEP·DABCO	461[a]	60
PPF-1	622[b]	42
MMPF-1	420[d]	54
MMPF-2	**2037[b]**	**This work**

[a] BET surface area; [b] Langmuir surface area; [c] NLDFT surface area derived from CO_2 adsorption at 273K; [d] Langmuir surface area derived from CO_2 adsorption at 195K.

Table S2. Crystal data and structure refinement for MMPF-2

Identification code	275
Empirical formula	C156 H60 Co15 N12 O56
Formula weight	3882.11
Empirical formula including solvents	C278 H425 Co15 N37 O123
	$\{[Co_3(OH)(H_2O)]_4(Co\text{-}Htdcpp)_3\}\cdot(H_2O)_{20}\cdot(CH_3OH)_{22}\cdot(C_4H_9NO)_{25}$
Formula weight including solvents	7130.5
Temperature	100(2) K
Wavelength	0.40663 A
Crystal system, space group	Tetragonal, P4/mbm
Unit cell dimensions	a = 30.163(4) A alpha = 90 deg.
	b = 30.163(4) A beta = 90 deg.
	c = 15.4840(19) A gamma = 90 deg.
Volume	14088(3) A^3
Z, Calculated density	2, 0.915 Mg/m^3 (1.647 Mg/m^3 - solvent
Absorption coefficient	included)
F(000)	0.175 mm^-1
Crystal size	3866 (7482 – solvent included)
Theta range for data collection	0.05 x 0.05 x 0.02 mm
Limiting indices	0.86 to 10.09 deg.
Reflections collected / unique	-26<=h<=25, -26<=k<=26, -13<=l<=12
Completeness to theta = 10.09	55336 / 2586 [R(int) = 0.0906]
Absorption correction	99.4 %
Max. and min. transmission	Semi-empirical from equivalents
Refinement method	0.9965 and 0.9913
Data / restraints / parameters	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	2586 / 265 / 295
Final R indices [I>2sigma(I)]	1.097
R indices (all data)	R1 = 0.0883, wR2 = 0.2566
Largest diff. peak and hole	R1 = 0.1116, wR2 = 0.2791
	0.767 and -0.469 e.A^-3

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Refs. S15-S61 account for all 2D and 3D porphyrin-based MOFs described thus far (94, excluding one new MOF contained in the current report).

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