Electronic Supplementary Information

Two Rare Indium-based Porous Metal-Metalloporphyrin Frameworks Exhibiting Interesting CO_2 Uptake

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Synthesis of MMPF-7:

A mixture of tcpp (0.005g), $In(NO_3)_3{\cdot}xH_2O$ (0.006g), 1 drop of concentrated nitric aicd (con. HNO_3), 1.0 mL dimethylformamide (DMF) and 1.0 mL acetonitrile (MeCN) was put in a 4 mL vial and heated to 85 ^oC for 48 hours. The resulting dark colored block crystals were obtained (yield: 55% based on tcpp). The sample was scaled up into hundreds of milligrams using multiple vials. IR (cm^{-1}):1659(w); 1604(s); 1505(m); 1384(vs); 1278(w); 1178(w); 1099(w); 1017(m); 962(m); 873(m); 799(m); 774(s); 714(vs); 491(vs). Elemental analysis: Formula based upon TGA plot: $(In_{1.29}C_{48}H_{25.42}O_{8.57}N_4)$ $(C_2H_8N)_{0.71}(CH_3CN)_{1.33}(C_3H_7NO)_{2.50}$, Calculated: C, 58.97; H, 4.37; N, 9.86 %; Elemental Analysis: C, 58.73; H, 4.39; N 9.90 %.

Synthesis of MMPF-8:

A mixture of tcbpp (0.001g), $In(NO_3)_3{\cdot}xH_2O$ (0.005g), 1 drop of concentrated hydrochloric acid (con. HCl), 0.1 mL water (H_2O), 0.25 mL methanol (MeOH) and 0.5 mL dimethylformamide (DMF) was sealed in a Pyrex tube under vacuum and heated to 85 ^oC for 48 hours. The resulting dark colored block crystals were obtained (yield: 65% based on the tcbpp). The sample was scaled up into hundreds of milligrams using multiple tubes. IR (cm^{-1}): 1650(w); 1604(s); 1520(w); 1378(vs); 1206(w); 1177(w); 1100(w); 1005(vs); 873(w); 850(w); 780(vs); 716(m); 666(m); 522(w); 427(s). Elemental analysis: Formula based upon TGA plot: $(In_2C_{72}H_{40}N_4O_{10})$ $(C_3H_7NO)_{12}$, Calculated: C, 58.22; H, 5.61; N, 10.06 %; Elemental Analysis: C, 58.01; H, 5.63; N 10.02 %.

General methods:

Commercially available reagents were purchased as high purity from Fisher Scientific or Frontier Scientific and used without further purification.5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (tcpp) was purchased from Frontier Scientific. 5,10,15,20-tetrakis (4-carboxybiphenyl)porphyrin (tcbpp) was synthesized as the literature reported.[1] Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res from 30^{o}C to 800 ^oC at the speed of 10 ^oC/min.

Gas Adsorption Experiments:

Gas adsorption isotherms of MMPF-7 and MMPF-8 were collected using the surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples were washed with methanol, and then activated with supercritical CO_2 in a Tousimis Samdri PVT-3D critical point dryer. CO_2 gas adsorption isotherms were collected at 273K using a water-ice bath and at 295K with a water bath. The N_2 isotherm of MMPF-8 was measured at 77K using a liquid nitrogen bath.

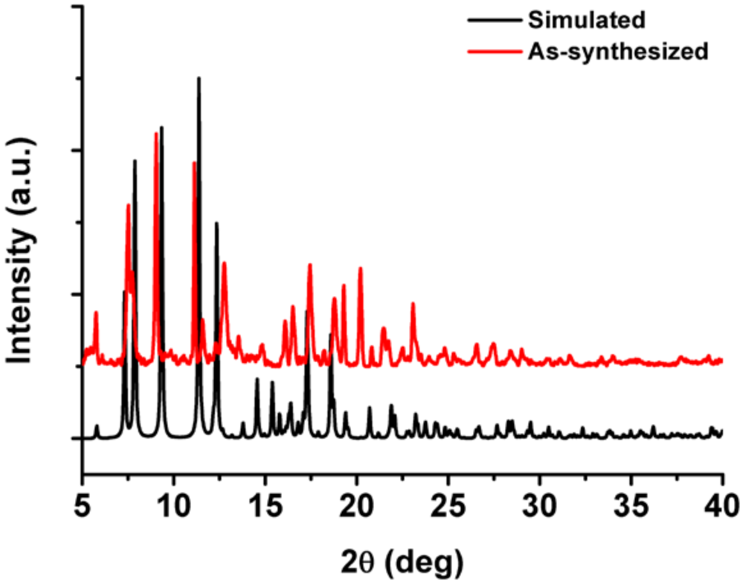


Fig. S1 Powder X-ray diffraction patterns of MMPF-7.

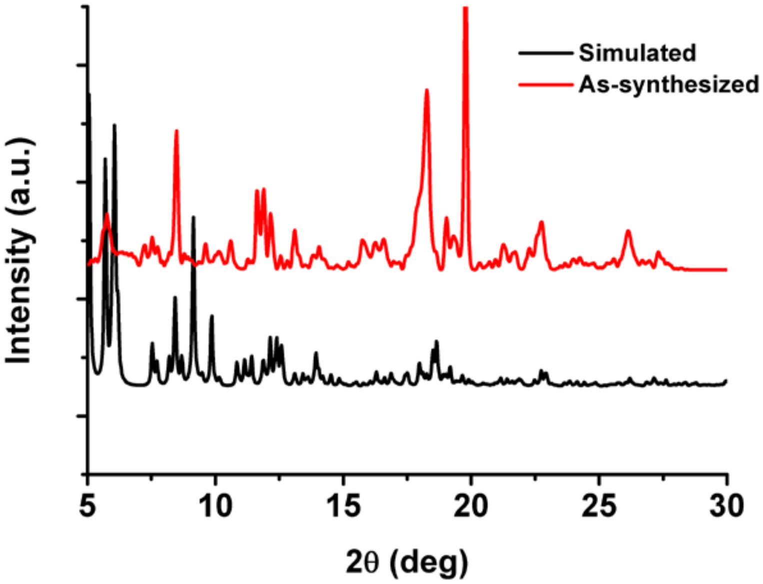


Fig. S2 Powder X-ray diffraction patterns of MMPF-8.

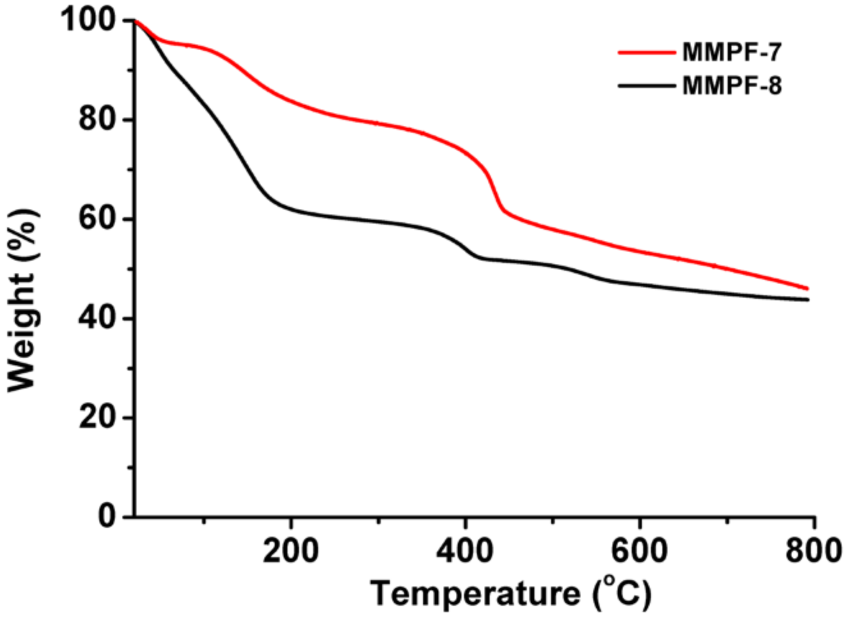


Fig. S3 TGA plots of MMPF-7 and MMPF-8.

Heat of Adsorption (Q_{st}) Calculations.

The virial equation of the form given in Equation (1) was employed to calculate the enthalpies of adsorption for CO_2 on MMPF-7 and MMPF-8.

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

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 $a_0 \ldots a_m$ were then used to calculate the isosteric heat of adsorption by the following expression:

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

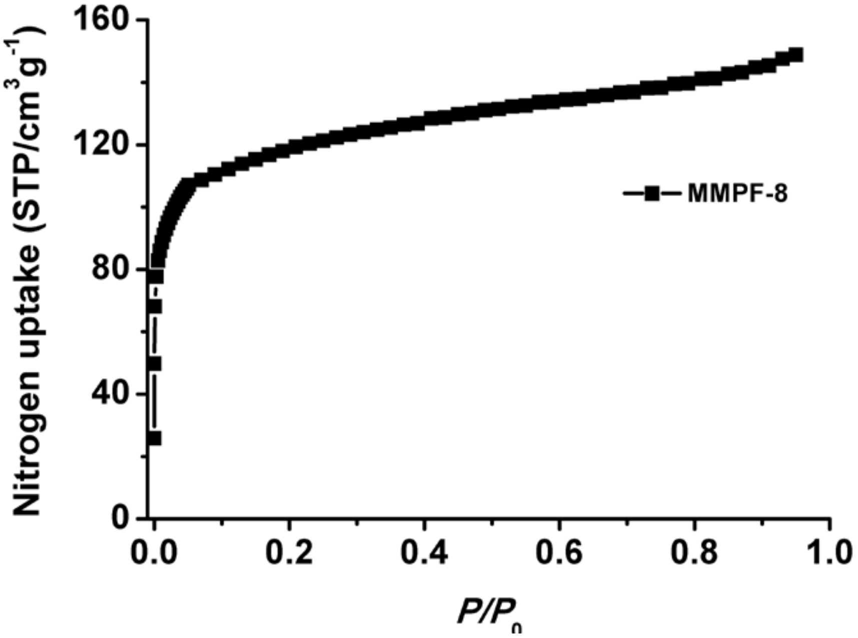
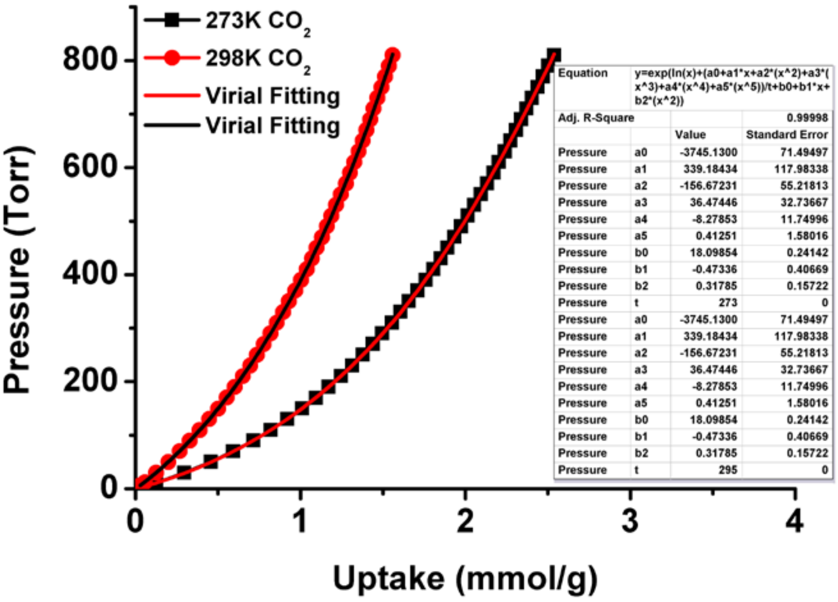
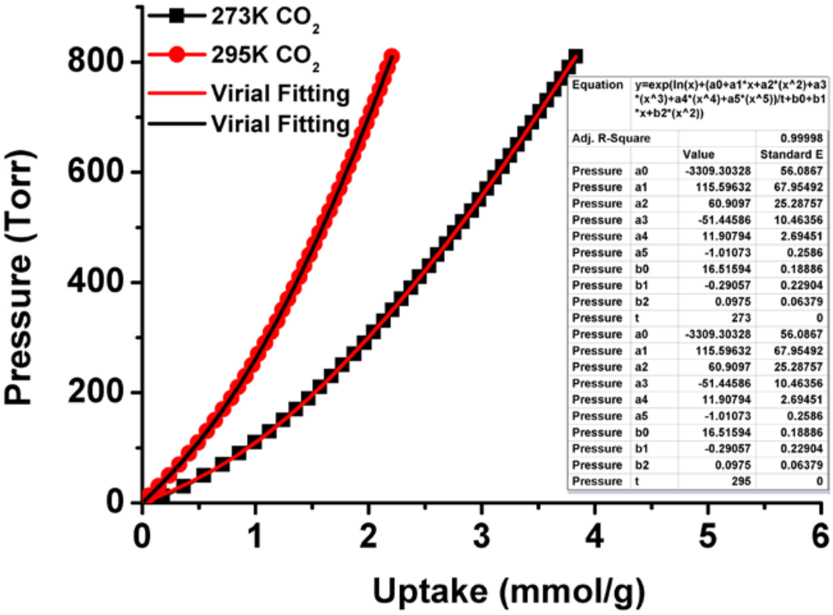


Fig. S4 Nitrogen isotherm of MMPF-8 at 77K.



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			0.99998
		Value	Standard Error
Pressure	a0	-3745.1300	71.49497
Pressure	a1	339.18434	117.98338
Pressure	a2	-156.67231	55.21813
Pressure	a3	36.47446	32.73667
Pressure	a4	-8.27853	11.74996
Pressure	a5	0.41251	1.58016
Pressure	b0	18.09854	0.24142
Pressure	b1	-0.47336	0.40669
Pressure	b2	0.31785	0.15722
Pressure	t	273	0
Pressure	a0	-3745.1300	71.49497
Pressure	a1	339.18434	117.98338
Pressure	a2	-156.67231	55.21813
Pressure	a3	36.47446	32.73667
Pressure	a4	-8.27853	11.74996
Pressure	a5	0.41251	1.58016
Pressure	b0	18.09854	0.24142
Pressure	b1	-0.47336	0.40669
Pressure	b2	0.31785	0.15722
Pressure	t	295	0

Fig. S5 The plots of virial equation of MMPF-7.



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			0.99998
		Value	Standard E
Pressure	a0	-3309.30328	56.0867
Pressure	a1	115.59632	67.95492
Pressure	a2	60.9097	25.28757
Pressure	a3	-51.44586	10.46356
Pressure	a4	11.90794	2.69451
Pressure	a5	-1.01073	0.2586
Pressure	b0	16.51594	0.18886
Pressure	b1	-0.29057	0.22904
Pressure	b2	0.0975	0.06379
Pressure	t	273	0
Pressure	a0	-3309.30328	56.0867
Pressure	a1	115.59632	67.95492
Pressure	a2	60.9097	25.28757
Pressure	a3	-51.44586	10.46356
Pressure	a4	11.90794	2.69451
Pressure	a5	-1.01073	0.2586
Pressure	b0	16.51594	0.18886
Pressure	b1	-0.29057	0.22904
Pressure	b2	0.0975	0.06379
Pressure	t	295	0

Fig. S6 The plots of virial equation of MMPF-8.

Single-Crystal X-ray Diffraction for MMPF-7 and MMPF-8

The X-ray diffraction data for MMPF-8 were collected using synchrotron radiation, λ = 0.41328 Å, at Advanced Photon Source, Argonne National Lab, Chicago. The X-ray diffraction data for MMPF-7 were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2*[2] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01.[3] Absorption correction was performed by multi-scan method implemented in SADABS.[4] Space groups were determined using XPREP implemented in APEX2.[2] Structures were solved using SHELXS-97 (direct methods) and refined using SHELXL-97 (full-matrix least-squares on F^2) contained in WinGX[5,6,7,8] and OLEX2 programs.[9]

MMPF-7

All non-H atoms were found in the difference Fourier map and all (except disordered O1) were refined anisotropically. The position in the center of porphyrin core is partially occupied by In2 atom with refined occupancy of 0.284(2). The contribution of heavily disordered solvent molecules / counterions was treated as diffuse using Squeeze procedure implemented in Platon program.[10, 11] 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). Crystal data and refinement conditions are shown in Table S1.

MMPF-8

All non-H atoms were found in the difference Fourier map and were refined anisotropically. Despite the fact that synchrotron radiation have been used, diffraction data were observed only up to 1.05 Å resolution which could be attributed to solvent disorder. All atoms have been refined using restraints (DFIX, DANG, FLAT, DELU, SIMU, ISOR) and constraints for benzene rings (AFIX 66) in order to obtain chemically feasible model which would otherwise be distorted due to the lower resolution of diffraction data. The contribution of heavily disordered solvent molecules was treated as diffuse using Squeeze procedure implemented in Platon program.[9,10] 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). Crystals has been racemic twin with BASF = 0.25(1). Crystal data and refinement conditions are shown in Table S2.

Table S1. Crystal data and structure refinement for **MMPF-7**

Identification code	MMPF-7
Empirical formula	$C_{49.42}H_{31.10}In_{1.29}N_{4.71}O_{8.57}$
Formula weight	976.11
Temperature	228(2) K
Crystal system, space group	Monoclinic, *C*2/*c*
Unit cell dimensions	*a* = 7.6333(3) Å *alpha* = 90 deg.
	b = 24.1332(11) Å *beta* = 93.505(3) deg.
	c = 30.5291(14) Å *gamma* = 90 deg.
Volume	5613.4(4) Å^3
Z, Calculated density	4, 1.155 Mg/m^3
Absorption coefficient	4.698 mm^-1
F(000)	1969.0
Crystal size	0.1 x 0.1 x 0.1 mm
Theta range for data collection	2.90 to 65.07 deg.
Limiting indices	-8<=h<=8, -26<=k<=27, -35<=l<=24
Reflections collected / unique	11445 / 4517 [*R*(int) = 0.0615]
Data / restraints / parameters	4517 / 0 / 287
Goodness-of-fit on F^2	0.951
Final R indices [I>2sigma(I)]	*R*1 = 0.0547, w*R*2 = 0.1305
R indices (all data)	*R*1 = 0.0812, w*R*2 = 0.1396
Largest diff. peak and hole	0.923 and -0.593 e. Å^-3

Table S2. Crystal data and structure refinement for **MMPF-8**

Identification code	MMPF-8
Empirical formula	$C_{83.25}H_{66.25}In_2N_{7.75}O_{13.75}$
Formula weight	1624.83
Temperature	100(2) K
Crystal system, space group	Monoclinic, *Cc*
Unit cell dimensions	*a* = 41.982(3) Å *alpha* = 90 deg.
	b = 21.5588(12) Å *beta* = 92.6350(10) deg.
	c = 43.755(2) Å *gamma* = 90 deg.
Volume	39560(4) Å^3
Z, Calculated density	16, 1.091 Mg/m^3
Absorption coefficient	0.608 mm^-1
F(000)	13248.0
Crystal size	0.21 x 0.16 x 0.14 mm
Theta range for data collection	1.01 to 11.35 deg.
Limiting indices	-38<=h<=39, -19<=k<=20, -41<=l<=41
Reflections collected / unique	147776 / 34753 [R(int) = 0.0941]
Data / restraints / parameters	34753 / 2063 / 2786
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	*R*1 = 0.0699, w*R*2 = 0.1770
R indices (all data)	*R*1 = 0.1043, w*R*2 = 0.1891
Largest diff. peak and hole	0.421 and -0.456 e. Å^-3

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