Electronic Supplementary Information

A Pillar-Free, Highly Porous Metalloporphyrinic Framework Exhibiting Eclipsed Porphyrin Arrays

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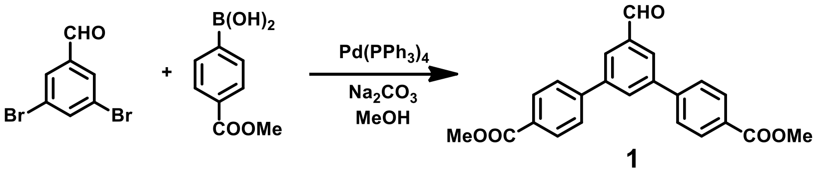
Section S1 *Materials and General Procedures*

All solvents and reagents were purchased and commercially available and, unless otherwise noted, used without further purification. NMR was performed on either a Bruker FT-NMR spectrometer (400 MHz) or a Bruker FT-NMR spectrometer (300 MHz). Thermogravimetric Analysis (TGA) was performed on a Perkin Elmer STA 6000 Thermogravimetric Analyzer, heated from 30°C to 1000°C at a rate of 2.7°C/minute under N_2 atmosphere. Infrared spectroscopy was performed on a Nicolet Avatar 360 FT-IR. To prevent preferential orientation, powder X-ray diffraction (PXRD) data was collected using the spinning capillary method as previously demonstrated by Hupp[1] and Choe[2]. PXRD data was taken with a Bruker AXS DA X-ray diffractometer with a GADDS area detector. The copper target X-ray tube was set to 40 kV and 40 mA. Gas adsorption isotherms of UNLPF-1 were collected using the surface area analyzer ASAP-2020. N_2 gas adsorption isotherms were measured at 77 K using a liquid N_2; Low-pressure CO_2 adsorption isotherms were measured at 273 K using an ice water.

Section S2 *Synthesis*

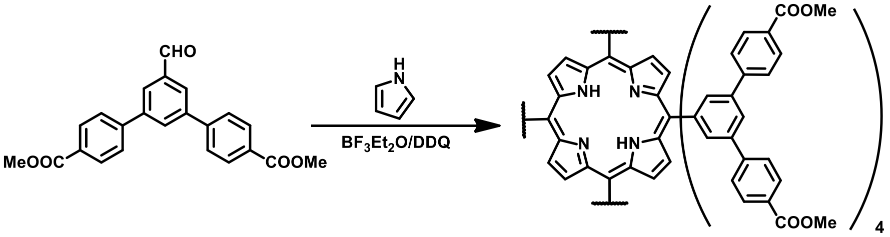
S2.1 Synthesis of 3,5-bis[(4-methoxycarbonyl)phenyl]benzaldehyde (**1**)



1

A solution of 3,5-dibromobenzaldehyde (2.95 g, 11.18 mmol), and 4-methoxycarbonyl-benzene boronic acid (5.05 g, 28.06 mmol) in 300 mL of MeOH was degassed for 30 min. To this solution, sodium carbonate (11.890 g, 0.11 mol) and tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$, 0.4863 g, 0.42 mmol) were added and the reaction was refluxed under Ar at 80˚C for 18 hrs. The solid white precipitate was collected by vacuum filtration and washed with MeOH. The dried crude product was then extracted with dichloromethane (3 x 50 mL) and dried over $MgSO_4$. The product was then dried in vacuo resulting in a solid white powder, 3.68 g,(yield: 88%) of 3,5-bis[(4-methoxy-carbonyl)phenyl]-benzaldehyde. ^{1}H NMR ($CDCl_3$): 10.21 (*s*, 1H), 8.39 (*t*, 2H, J = 1.6 Hz), 8.16 (*d*, 2H, J= 1.7 Hz), 8.14 (*t*, 1H, J= 1.2 Hz), 8.13 (*m*, 2H), 7.91 (*dt*, 2H, J = 7.8 Hz, 1.6 Hz), 7.62 (*t*, 2H, J = 7.7 Hz), 4.0 (*s*, 6 H). HR-ESI MS [$M^{+}\cdot$] : 374.1167 (3.4 ppm)

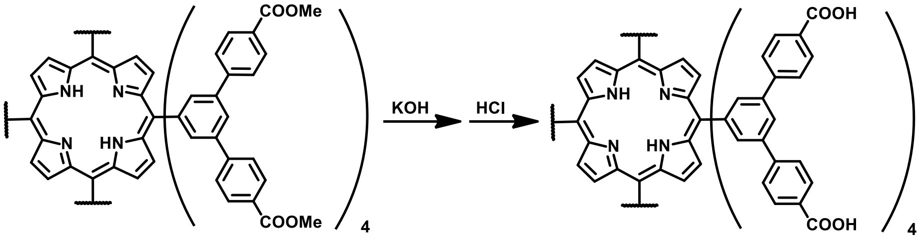
S2.2 Synthesis of tetrakis 3,5-bis[(4-methoxycarbonyl)phenyl]phenyl porphine (**2**)



1 **2**

A solution of 3,5-bis[(4-methoxycarbonyl)phenyl]benzaldehyde (1.8611 g, 5 mmol), and pyrrole (342 µL, 5 mmol) in 500 mL of dichloromethane was degassed for 30 min. $BF_3{\cdot}Et_2O$ was added via syringe (62.8 µL, 2.56 mmol) and the reaction shaded from ambient light and stirred under Ar at room temperature for 8 hrs. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (0.8526g, 3.76 mmol) was added and the reaction was allowed to continue stirring at room temperature for 12 hrs. The crude product was dried onto silica and washed with methanol to remove impurities. The product was then purified via column chromatography and eluted with dichloromethane. The crude product was then dried in vacuo and then taken up in 50 mL of MeOH to remove further impurities. The product was then collected by vacuum filtration which resulted in a shiny purple solid (0.72 g, yield: 34.3%) of tetrakis 3,5-bis[(4-methoxycarbonyl)phenyl]phenyl porphine. ^{1}H NMR ($CDCl_3$): 9.09 (*s*, 8H), 8.60 (*d*, 8H, J = 1.7 Hz), 8.37 (*t*, 4H, *J* = 1.7 Hz), 8.18 (*d*, 16H, J = 8.5 Hz), 8.02 (*d*, 16 H, J = 8.5 Hz), 3.91 (*s*, 24H), −2.67 (*s*, 2H). MALDI MS: $[M+H]^+$:1687.6

S2.3 Synthesis of tetrakis 3,5-bis[(4-carboxy)phenyl]phenyl porphine (**OCP-3**) (**3**)



2 **3**

A solution of tetrakis 3,5-bis[(4-methoxycarbonyl)phenyl]phenyl porphine (0.72 g, 0.43 mmol) and potassium hydroxide (0.577 g, 10.32 mmol) in THF/H_2O (v/v 1:1) was refluxed at 80˚C for 3 days. THF was then removed in vacuo and the resultant aqueous solution was acidified to a pH of 1 with hydrochloric acid. The product was collected by vacuum filtration, resulting in a dark purple solid (0.67 g, yield: 96%) of tetrakis 3,5-bis[(4-carboxy)phenyl]phenyl porphine. ^{1}H NMR (d-DMSO): 13.00 (*s*, 8H), 9.09 (s, 8H), 8.66 (*s*, 8H), 8.56 (*s*, 4H), 8.21 (*d*, 16H, J = 8.7 Hz), 8.10 (*d*, 16H, J = 8.6 Hz), −2.74 (*s*, 2H). HR-ESI MS: $[M-3H]^{3-}$: 523.7973 (0.38 ppm), $[M-4H]^{4-}$: 392.5963 (0.25 ppm)

S2.4 Synthesis of UNLPF-1

A solution of OCP-3 (8 mg) and $Zn(NO_3)_2\cdot 6H_2O$ (11 mg) in N,N'-dimethylformamide (6 mL) and acetic acid (0.2 mL) was heated at 80°C for 72 hrs. The resulting dark red block crystals were washed with pure ethanol and collected by vacuum filtration to give pure UNLPF-1 $\{[Zn_2(H_2O)_2]_2\cdot[(ZnOCP\text{-}3)(H_2O)_2]\}$ (yield: 72% based on OCP-3). Elemental Analysis Calcd (%) for $C_{103}H_{85}Zn_5N_5O_{22}$ (UNLPF-1) = $\{[Zn_2(H_2O)_2]_2\cdot[(ZnOCP\text{-}3)(H_2O)_2]\}\cdot(C_3H_7NO)\cdot(H_2O)_6$: C 56.65, H 3.92, N 3.21; Found: C 56.36, H 4.01, N 3.15. FT-IR: *v* = 1579.49 cm^{-1} (s), 1540.92 cm^{-1}(m), 1380.85 cm^{-1}(s), 779.14 cm^{-1}(s).

Section S3 ^{1}*H NMR Data*

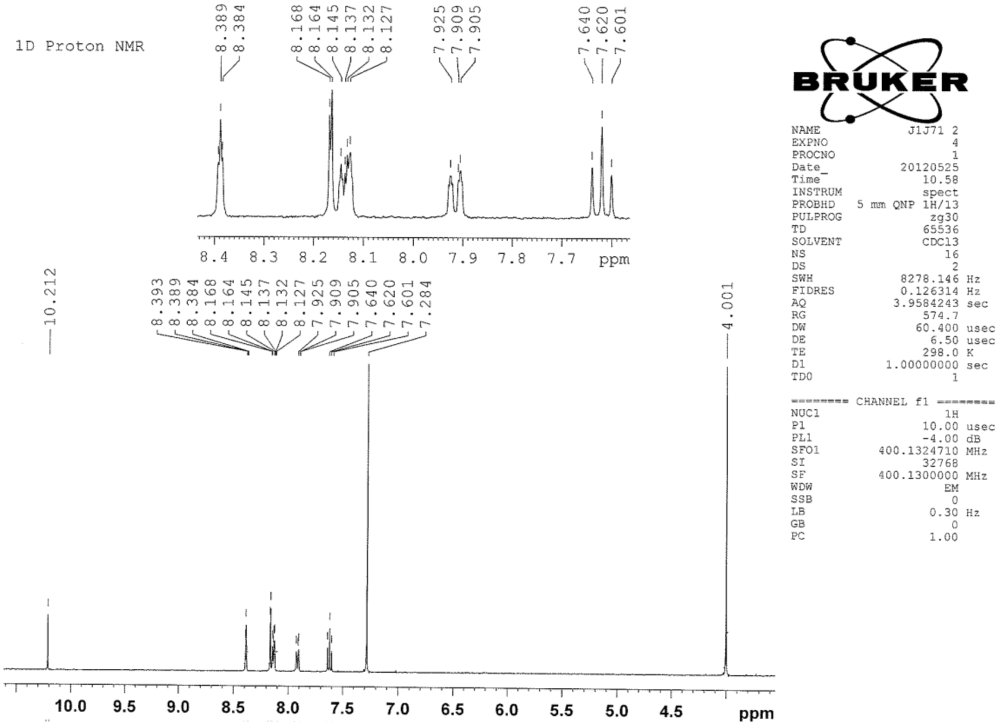


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Figure S1. ^{1}H NMR spectrum for 3,5-bis[(4-methoxycarbonyl)phenyl]benzaldehyde (**1**)

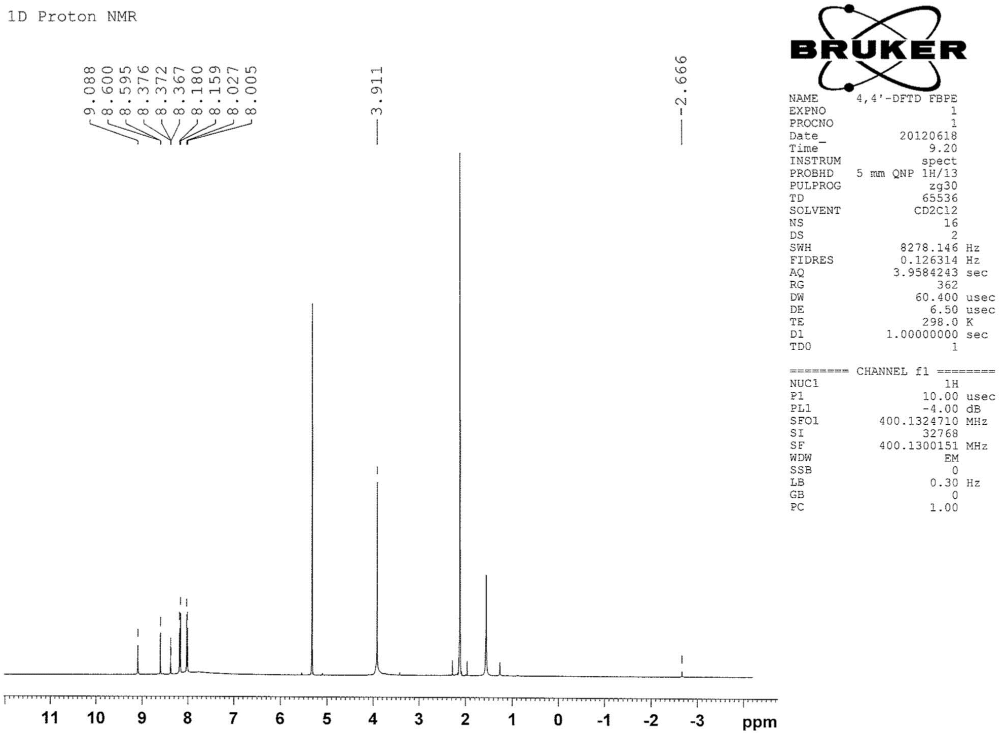

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Figure S2. ^{1}H NMR spectrum for of tetrakis 3,5-bis[(4-methoxycarbonyl)phenyl]phenyl porphine (**2**)

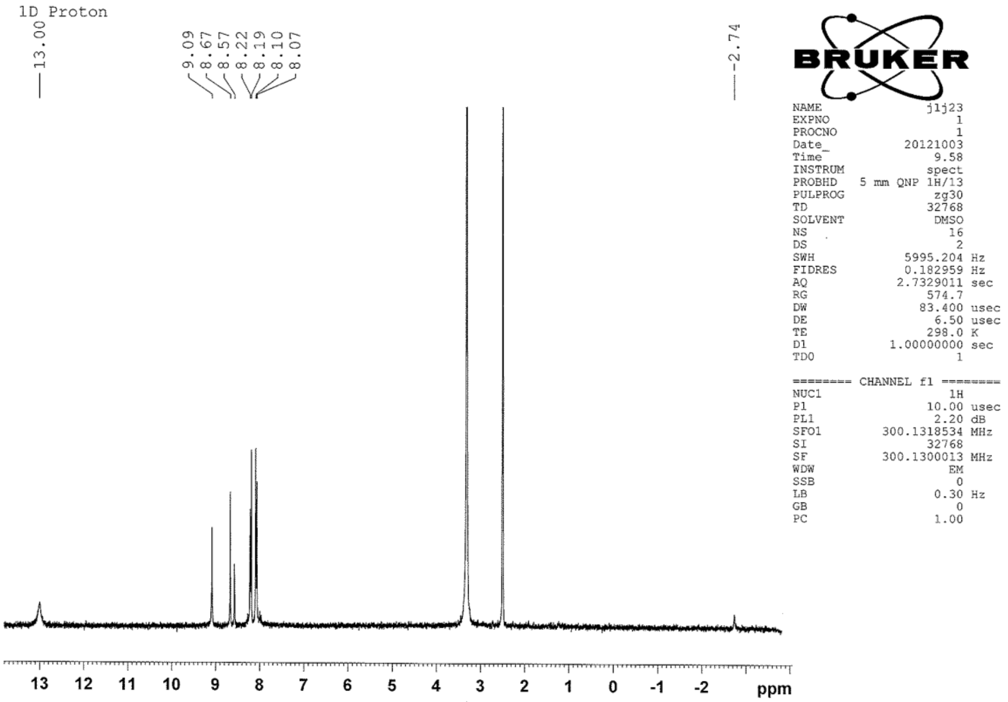

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Figure S3. ^{1}H NMR spectrum for of tetrakis 3,5-bis[(4-carboxy)phenyl]phenyl porphine (**OCP-3**) (**3**)

Section S3 *Crystallographic Data*

Single crystal X-ray diffraction data was collected using synchrotron radiation, λ = 0.49594 Å, at the Advanced Photon Source, Chicago, IL. 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 F^2) contained in APEX2 and WinGXv1.70.00.[6] C,N,O atoms were refined with anisotropic displacement parameters and H atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: $U_{iso}(H) = 1.2U_{eq}(\text{-CH})$. The contribution of disordered solvent molecules was treated as diffuse using the SQUEEZE procedure implemented in PLATON.[7] Crystal data and refinement conditions are shown in Table S1.

Table S1 *Crystal data and structure refinement for UNLPF-1*

Identification	UNLPF-1
empirical formula	$C_{100}H_{66}Zn_5N_4O_{22}$
empirical formula (with solvent)	$\{[Zn_2(H_2O)_2]_2\cdot[(ZnOCP\text{-}3)(H_2O)_2]\}\cdot(C_3H_7NO)\cdot(H_2O)_6$ = $C_{103}H_{85}Zn_5N_5O_{22}$
formula weight (g·mol^{-1})	2002.51 (2183.69 including solvent)
temperature (K)	100(2) K
wavelength (Å)	0.49594
crystal system, space group	tetragonal, *I*4/*mcm*
a (Å)	30.701(4)
b (Å)	30.701(4)
c (Å)	28.957(5)
α (deg)	90
β (deg)	90
γ (deg)	90
volume (Å^3)	27294.0
Z, density (calcd) (Mg·m^{-3})	4, 0.432
abs coefficient (mm^{-1})	0.196
F(000)	3504
crystal size (mm^3)	0.03 x 0.03 x 0.03 mm
θ range (deg)	0.93 to 14.38 deg
reflections collected/unique	95600 / 3788 [R_{int} = 0.1807]
completeness to θ (%)	99.1%
refinement method	Full-matrix least-squares on F^2
data / restraints / parameters	3788 / 158 / 160
goodness-of-fit on F^2	0.991
final *R* indices [I>2sigma(I)]	R_1 = 0.0659, wR_2 = 0.1605
largest diff. peak and hole (e.A^{-3})	0.284 and −0.329

Section S4 *Powder X-Ray Diffraction Data*

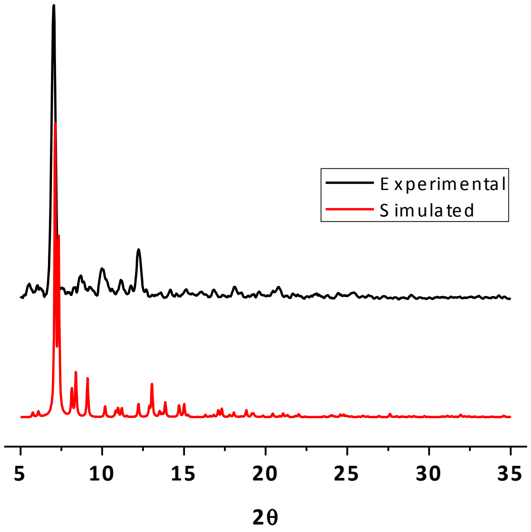

Figure S4. Experimental X-ray powder diffraction pattern for UNLPF-1 (black) and simulated powder pattern (red).

Section S5 *FT-IR Data*

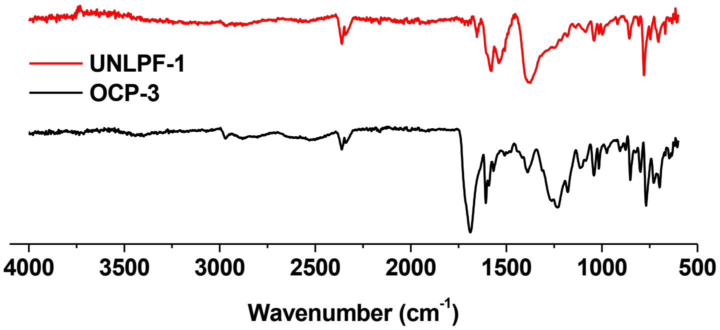

Figure S5. FT-IR spectra for OCP-3 (black) and UNLPF-1 (red).

Section S6 *Thermal Gravimetric Analysis*

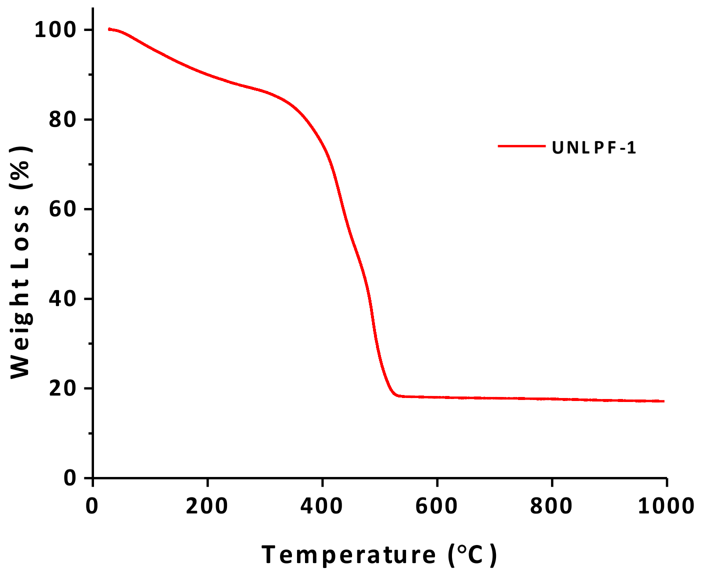

Figure S6. Thermogravimetric Analysis Data for UNLPF-1

Section S7 *Additional Information*

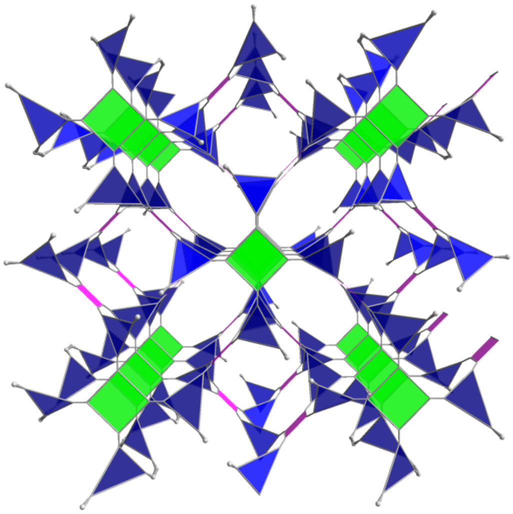

Figure S7. Trinodal (3,4,4)-connected net, where 4-connected porphyrin cores are green squares, 3-connected terphenyl arms are blue triangles, and 4-connected paddlewheel SBUs are pink squares.

Table S2 *Density of Open Metal Sites and Solvent Accessibilities of Selected Metalloporphyrinic Frameworks*

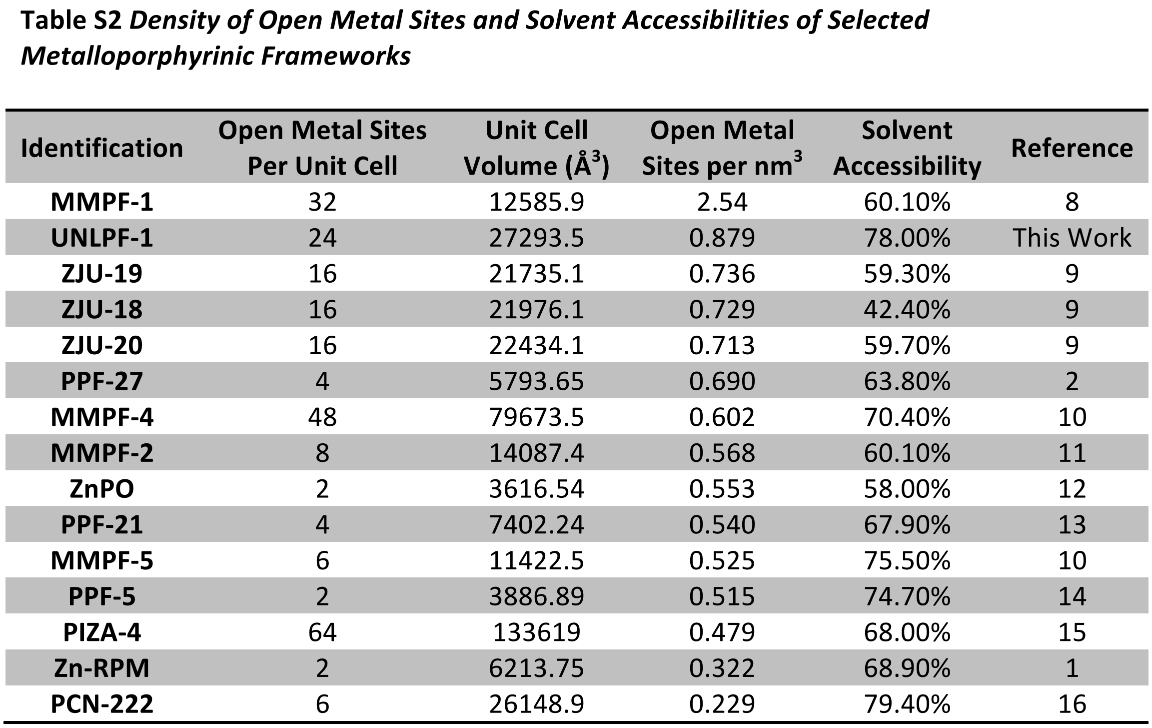

Table S2 ***Density of Open Metal Sites and Solvent Accessibilities of Selected Metalloporphyrinic Frameworks***

Identification	Open Metal Sites Per Unit Cell	Unit Cell Volume (Å^3)	Open Metal Sites per nm^3	Solvent Accessibility	Reference
MMPF-1	32	12585.9	2.54	60.10%	8
UNLPF-1	24	27293.5	0.879	78.00%	This Work
ZJU-19	16	21735.1	0.736	59.30%	9
ZJU-18	16	21976.1	0.729	42.40%	9
ZJU-20	16	22434.1	0.713	59.70%	9
PPF-27	4	5793.65	0.690	63.80%	2
MMPF-4	48	79673.5	0.602	70.40%	10
MMPF-2	8	14087.4	0.568	60.10%	11
ZnPO	2	3616.54	0.553	58.00%	12
PPF-21	4	7402.24	0.540	67.90%	13
MMPF-5	6	11422.5	0.525	75.50%	10
PPF-5	2	3886.89	0.515	74.70%	14
PIZA-4	64	133619	0.479	68.00%	15
Zn-RPM	2	6213.75	0.322	68.90%	1
PCN-222	6	26148.9	0.229	79.40%	16

Section S8 *References*

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