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A Highly Tunable Metal-Organic Frameworks

with Open Metal Centers

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Experimental

PPF-1: A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (8.9 mg, 0.03 mmol), meso-Tetra(4-carboxyphenyl)porphryin (7.9 mg. 0.01 mmol), pyrazine (1.6 mg, 0.02 mmol), N,N-diethylformamide (1.5 mL) and ethanol (0.5 mL) was added to a small capped vial, heated at 80°C for 24 hours, and then cooled to room temperature over 9 hours. The resulting dark red, square plate single crystals were isolated by filtration, washed with DEF and dried at room temperature. Yield: 7.0 mg (57% based on starting metal salt). The product loses solvent in air and is insoluble in common organic solvents. In spite of the necessity of pyrazine to grow crystals suitable for single crystal structure analysis, all characterization of PPF-1 indicates the pyrazine does not incorporate into the structure. Elemental analysis: % Found (% Calc.), for $Zn_2(ZnTCPP) \cdot 3H_2O \cdot 2DEF$: C 56.26 (56.30), H 3.96 (4.23), N 7.07 (6.79). FT-IR (KBr pellet): 3431(w), 2926(w), 2362(w), 1658(w), 1603(s), 1399(s), 1204(w), 1171(w), 1100(w),1061(w), 994(m), 870(w), 835(w), 775(m), 712(m), 660(w).

PPF-1Co: A mixture of $Co(NO_3)_2 \cdot 6H_2O$ (8.7 mg, 0.03 mmol), meso-Tetra(4-carboxyphenyl)porphryin (7.9 mg. 0.01 mmol), N,N-dimethylformamide (1.5 mL) and ethanol (0.5 mL) was added to a small capped vial. The vial contents were sonicated to mix, then 20 μL of .1 M HNO_3 (diluted in EtOH), was added to the vial. The mixture was sonicated one more time, heated at 80°C for 24 hours, and then cooled to room temperature over 9 hours. The resulting dark red, square plate single crystals were isolated by filtration, washed with DMF and dried at room temperature. Yield: 2.3 mg (17% based on starting porphyrin). Elemental analysis: % Found (% Calc.), for $Co_2(CoTCPP) \cdot 2H_2O \cdot 4.75DEF$: C 55.63 (55.51), H 4.72 (4.73), N 9.12 (9.10).

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Crystal data for PPF 1, Zn_2(ZnTCPP)·3H_2O·2DEF, at 120 K

$C_{48}H_{30}N_4O_{11}Zn_3$, *Fw* = 1034.87, tetragonal, *I4/mmm*, *a*=*b*=16.6814(10) Å, *c*=17.4944(15) Å, $\alpha = \beta = \gamma = 90°$, *V* = 4868.2(6) Å ^{3}, *Z* = 2, crystal size = 0.23×0.22×0.04 mm^3, F(000) = 1048, ρ_{calcd} = 0.706 mg/m^3, μ ($Mo_{K\alpha}$)= 0.764mm^{-1}; $2\theta_{max}$ = 56.52°, total number of reflections 1393 (R_{int} = 0.0369), 70 parameters, The final R_1 = 0.0629, wR_2 = 0.1713 [$I > 2\sigma(I)$]; R_1 = 0.0650, wR_2 = 0.1743 (all data), GOF on F^2= 1.149;

Crystal data for PPF 1, Zn_2(ZnTCPP)·3H_2O·2DEF, at 296 K

$C_{48}H_{30}N_4O_{11}Zn_3$, *Fw* = 1034.87, tetragonal, *I4/mmm*, *a* = *b* = 16.6940(10) Å, *c* = 18.5799(15) Å, $\alpha = \beta = \gamma = 90°$, *V* = 5718.0(6) Å ^{3}, *Z* = 2, crystal size = 0.39×0.33×0.05 mm^3, F(000) = 1048, ρ_{calcd} = 0.664 mg/m^3, μ ($Mo_{K\alpha}$)= 0.718mm^{-1}; $2\theta_{max}$ = 52.12°, total number of reflections 1496 (R_{int} = 0.0665), 98 parameters, The final R_1 = 0.0481, wR_2 = 0.1283 [$I > 2\sigma(I)$]; R_1 = 0.0647, wR_2 = 0.1373 (all data), GOF on F^2= 1.036.

X-ray diffraction data was recorded on a Bruker SMART Apex CCD system with graphite-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073Å) at 120(2) K and 296(2) K, respectively. The crystal structures are solved by direct methods (SHELXTL[1]) and all non-hyrogen atoms refined anisotropically by full-matrix least-squares techniques on F^2 (SHELXTL[1]). The SQUEEZE subroutine[2] in the PLATON software package was applied to mask the electron density in the cavities. CCDC 62596 and 62597 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

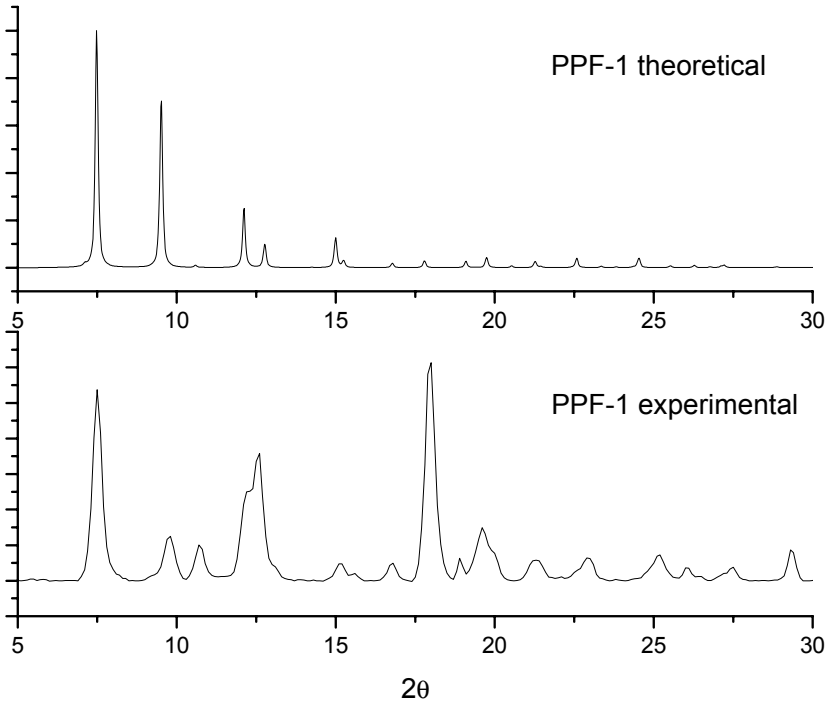

Figure S1. Powder X-ray diffraction patterns for a) simulated and b) as-synthesized PPF-1.

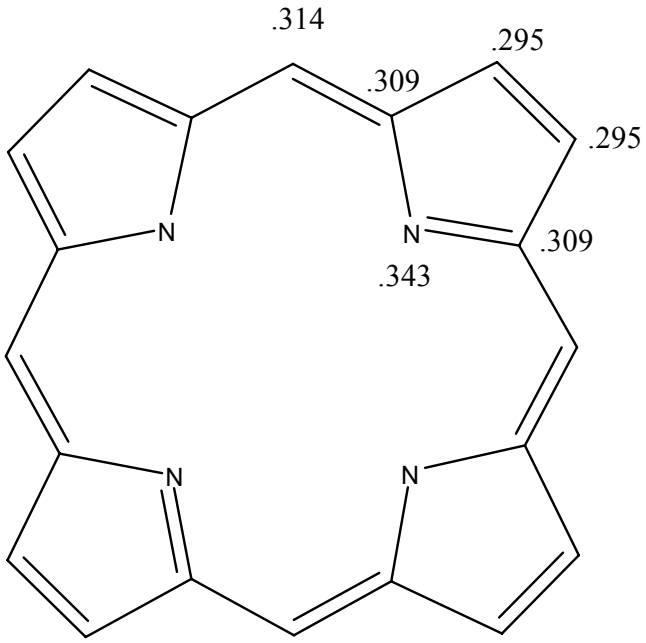

Figure S2. Diagram of porphyrin macrocycle at 296 K. The numbers indicate elevation (in Å) from the porphyrin basal plane at 120 K. Note there is four-fold symmetry in the crystal that matches the symmetry of the molecule.

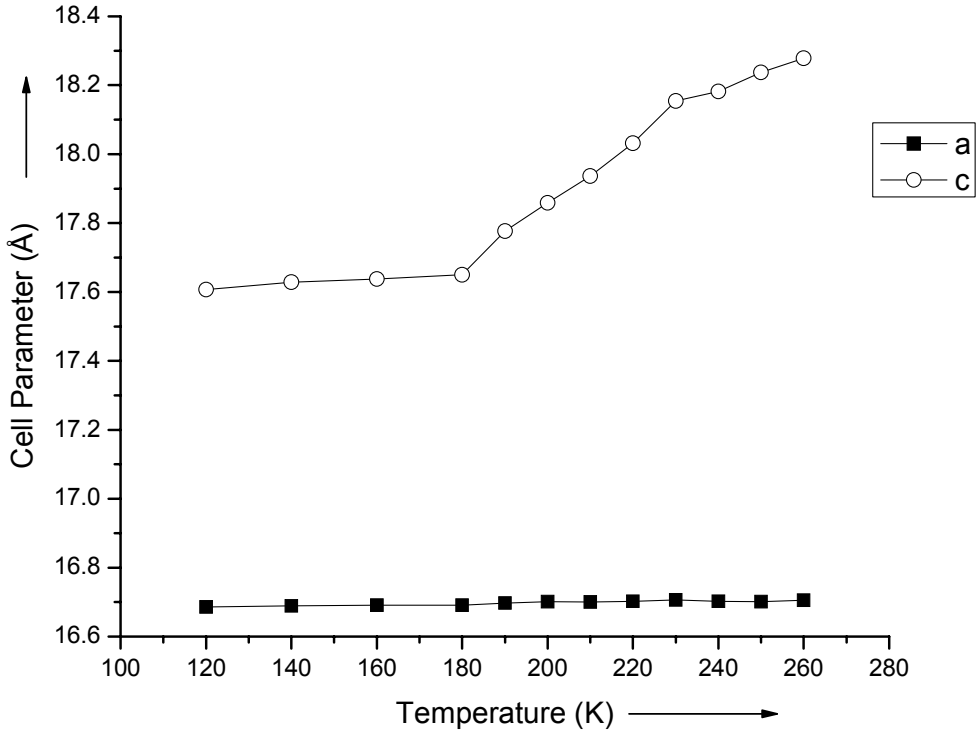

Figure S3. Change in unit cell parameters of PPF-1 as a function of temperature. The *a* parameter stays constant while the *c* parameter begins to change drastically at 180 K.

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Table S1. Temperature dependent single crystal unit cell measurements for PPF-1.

Temp (K)	*a* parameter (Å)	*c* parameter (Å)	Cell volume (Å^3)
120	16.6863(8)	17.6070(14)	4902.4(5)
140	16.6892(9)	17.6283(15)	4910.0(6)
160	16.6907(9)	17.6376(16)	4913.5(6)
180	16.691(3)	17.650(4)	4917.3(15)
190	16.697(3)	17.777(4)	4955.9(15)
200	16.701(2)	17.859(3)	4981.6(13)
210	16.7001(15)	17.936(2)	5002.4(9)
220	16.702(2)	18.032(3)	5029.9(11)
230	16.706(3)	18.154(5)	5067(2)
240	16.702(5)	18.182(7)	5072(3)
250	16.701(5)	18.237(7)	5087(3)
260	16.705(6)	18.278(9)	5101(4)

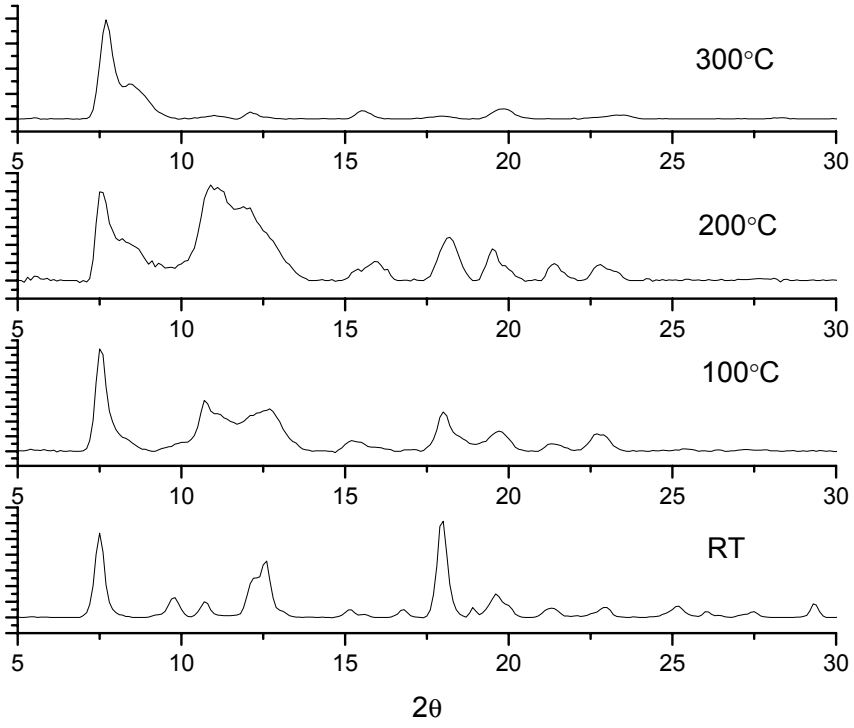

Figure S4. Temperature dependent X-ray powder patterns for PPF-1. Prominent peaks show that the 2D framework remains intact at 300°C

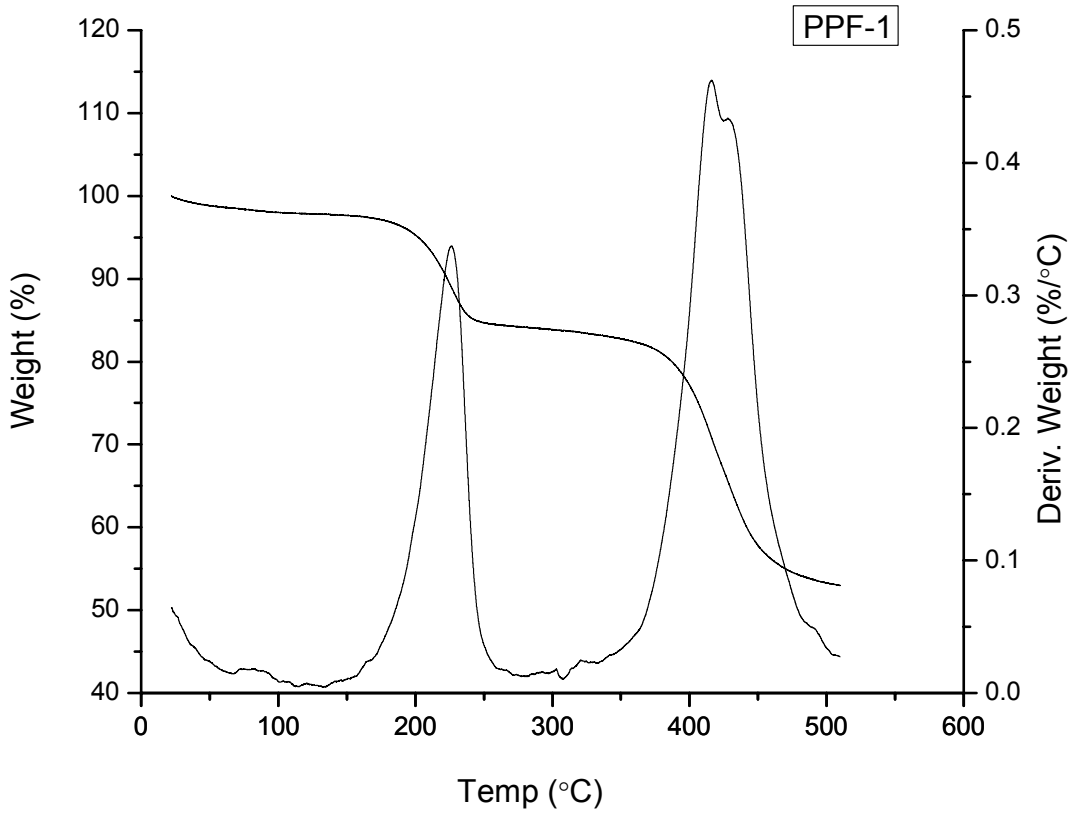

Figure S5. Thermogravimetric analysis plot of PPF-1. The solvent loss corresponds to 3 H_2O and 2 DEF molecules (theoretical: 20.7%, experimental 20.0%)

N_2 adsorption measurement: The pore structures were determined by the adsorption N_2 at 77K using volumetric equipment (Micromeretics ASAP2010). The as-synthesized samples (weight ~50 mg) was placed in the quartz tube and dried under high vacuum at 573 K for two days prior to the adsorption measurement. High purity N_2 gas (99.999%) was used. Elemental analysis after activation shows Zn_2(ZnTCPP). % Found (%Calc.), C 57.61 (58.77), H 2.75 (2.46), N 5.52 (5.71)

Table S2. Data for adsorption-desorption of N_2 in PPF-1 at 77K.

P/P0	Pressure (mmHg)	Amount adsorbed (cm^3/g)
0.0025	0.000003481	12.7087
0.00222	0.000003098	25.4189
0.00195	0.000002722	38.1318
0.00208	0.000002903	50.845
0.00272	0.000003786	63.5548
0.00605	0.000008434	76.2638
0.05891	0.000082163	88.8714
0.42231	0.000589128	100.8814
0.48015	0.000669879	101.8158
0.7814	0.001090312	105.186
1.27626	0.001781037	108.7677
2.19196	0.003059201	112.6568
3.53301	0.004931258	116.1012
5.37295	0.007499216	119.1244
8.95278	0.012495191	122.7776
14.56536	0.02032791	126.2185
23.68979	0.033061245	129.4907
38.68479	0.053986438	132.5105
64.44337	0.089932803	135.4614
103.9978	0.145129279	138.1806
168.10039	0.234582236	141.0173
271.21518	0.378469946	144.1394
307.17722	0.428649089	145.2474
313.93295	0.438067274	145.5602
335.42279	0.468049702	146.1534
356.13574	0.496947451	146.703
377.42343	0.526641117	147.2505
398.65921	0.556266885	147.7715
419.83932	0.585814369	148.267
440.93674	0.61523947	148.745
475.32321	0.663212081	149.4721
509.62701	0.711068347	150.2253

544.01508	0.759033321	150.9795
578.39789	0.806997344	151.7964
612.78375	0.854955774	152.6579
647.08313	0.902800905	153.616
681.36047	0.950614304	154.9067
714.45953	0.996679565	160.0625
668.70715	0.932835123	156.0576
633.14661	0.883219615	154.9552
598.64124	0.835068406	154.0541
578.44769	0.806891275	153.5274
544.0545	0.758899627	152.7082
509.72775	0.711010002	151.8742
475.34732	0.663039625	151.0312
440.97101	0.615083353	150.1577
398.64825	0.556038426	149.0706
356.57208	0.497345025	147.3061
334.93909	0.467166588	146.2746
313.85516	0.43775007	145.692
293.02307	0.408690238	145.1091
271.70233	0.37894948	144.5098
232.64429	0.324467608	143.3641
193.53453	0.269918667	142.0664
167.36388	0.233416571	141.0867
103.56588	0.144436735	137.9399
63.62405	0.088730572	135.0172
39.47141	0.055046549	132.2037
24.9379	0.034777503	129.3723
15.08216	0.021032385	126.0253
9.31008	0.012982693	122.6507
5.68199	0.007923084	119.1976
3.49151	0.004868477	115.8314
2.04073	0.002845371	112.1098
1.27093	0.00177191	108.78
0.85022	0.001185247	105.7593

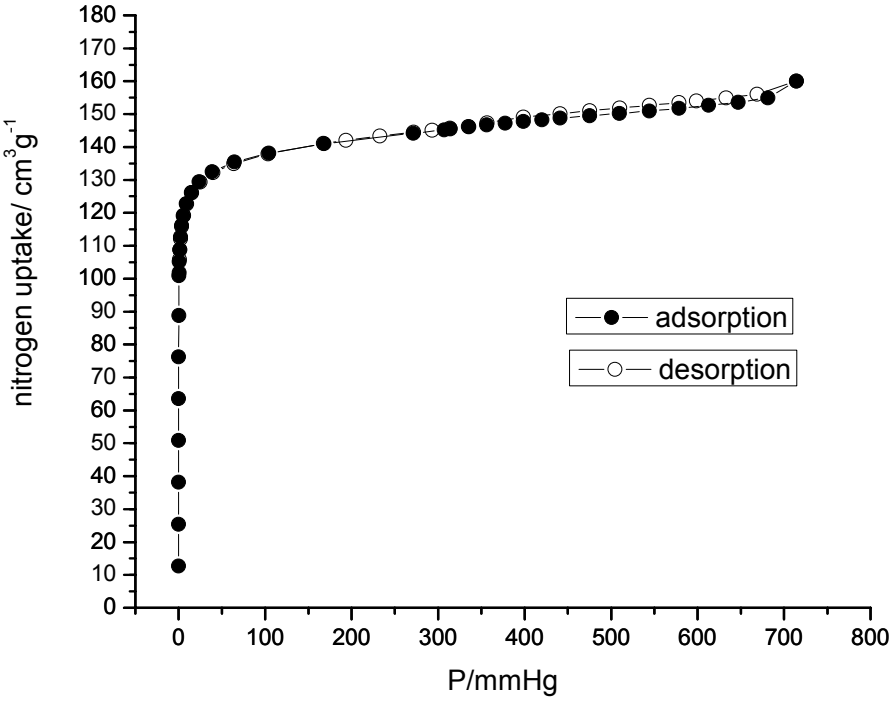

Figure S6. Nitrogen adsorption-desorption isotherm of PPF-1 at 77 K obtained with N_2 gas in the pressure range after activating at 300°C for 48 hours.

H_2 adsorption measurement. Low pressure hydrogen adsorption was determined using a Micromeritics ASAP 2010 volumetric adsorption apparatus using the same activation conditions as above. UHP H_2 gas was used. High pressure adsorption was done on a BELSORP HP apparatus.

Table S3. Data for adsorption-desorption of H_2 in PPF-1 at 77K.

P/P0	Pressure (mmHg)	Amount adsorbed (cm^3/g)
0.0000390	3.81015	7.3914
0.000169	16.5299	25.2751
0.000309	30.19813	38.2625
0.000525	51.31472	51.8157
0.000794	77.54267	62.9484
0.001237	120.8499	74.7611
0.001741	170.001	83.4487
0.002146	209.5636	88.5339
0.002563	250.2703	92.7093
0.003229	315.3682	97.8856
0.004073	397.7583	102.832
0.00503	491.2585	107.0747
0.006314	616.6143	111.3513
0.007676	749.6435	114.7757
0.006216	607.0527	111.2205
0.004947	483.1633	106.8823
0.003042	297.0924	96.8568
0.001926	188.1318	86.1175
0.001182	115.3934	73.5411
0.000728	71.06616	60.416
0.000424	41.36953	45.8567
0.000262	25.55005	33.9251
0.000168	16.3705	24.5284
9.96E-05	9.72577	15.9575

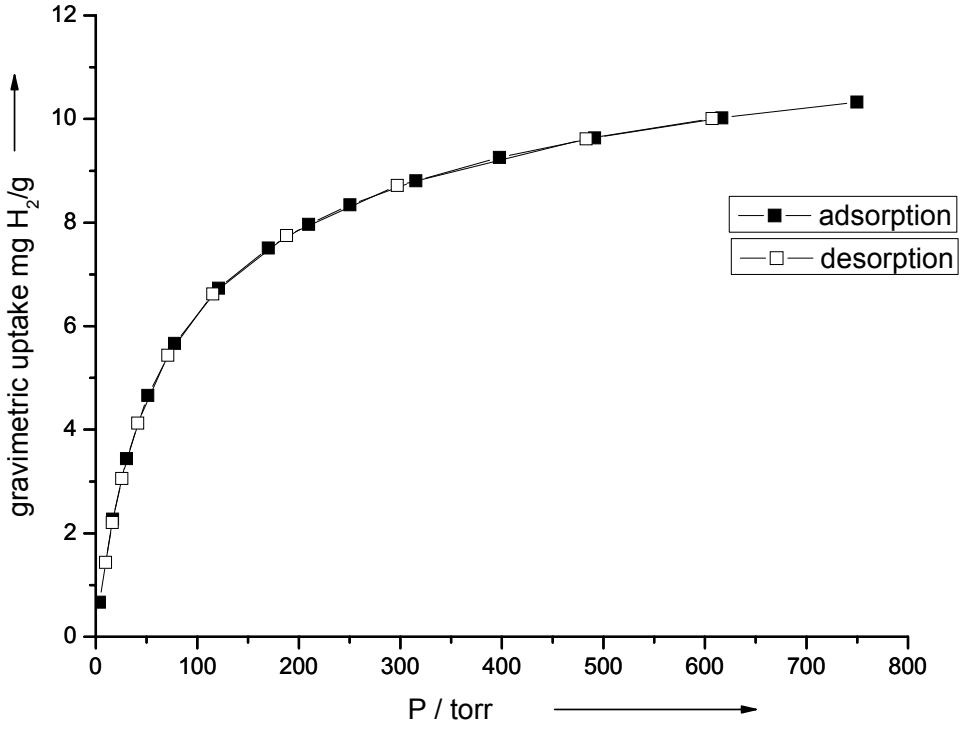

Figure S7. Hydrogen adsorption isotherm for PPF1 volumetrically at 77 K. The volumetric data have been converted by a factor of 0.09 mgH_2/cm^3 (STP).

Table S3. Data for adsorption-desorption of H_2 in PPF-1 at 87K.

P/P0	Pressure (mmHg)	Amount adsorbed (cm^3/g)
0.0000496	4.84214	6.5507
0.000125	12.25397	13.5474
0.000207	20.26418	19.273
0.000347	33.92825	26.7887
0.000485	47.36506	32.5536
0.000809	79.05803	42.5831
0.001305	127.4766	52.631
0.001834	179.1622	59.686
0.002608	254.6675	66.3311
0.003297	322.0038	70.1344
0.005117	499.8047	75.2276
0.006548	639.5126	76.5165
0.007898	771.3732	76.5367
0.006206	606.1166	76.4192
0.004881	476.6624	74.734
0.003144	307.0586	69.2008
0.001953	190.697	60.6016
0.001292	126.1419	51.8936
0.000728	71.05581	39.9328
0.000407	39.7462	29.1564
0.00026	25.40073	21.6882
0.000165	16.10071	15.717
0.000102	9.96241	10.8036

Calculating Hydrogen Enthalpies[3]

The following virial type expression was used to fit the data taken at 77 K and 87 K:

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

Where P is the pressure in torr, N is the amount adsorbed in mmol/g, T is temperature in K, a_i and b_i are virial coefficients.

The heat of adsorption Q_{st} can be calculated by

$$Q_{st} = -R \sum_{i=o}^{m} a_i N^i$$

Where R is the ideal gas constant.

Table S4. Data for high pressure adsorption-desorption of H_2 in PPF-1 at 77K.

Pressure (bar)	Amount adsorbed (wt %)
0.03198	0.28267
0.08557	0.49604
0.15692	0.64617
0.24278	0.74147
0.33457	0.81083
0.4303	0.8645
0.52603	0.90648
0.62077	0.93789
0.71552	0.96453
0.8073	0.9873
0.89415	1.01259
0.97409	1.03068
1.05601	1.04382
1.39156	1.09512
1.73698	1.1331
2.08241	1.16577
2.41796	1.18755
2.76339	1.20438
3.10881	1.22814
3.4641	1.24443
3.80952	1.25676
4.15495	1.27134
4.50037	1.28268
4.84579	1.29141
5.19122	1.30896
5.84259	1.32876
6.48409	1.35693
7.13546	1.3725
7.77696	1.38834
8.41846	1.42038
9.05996	1.44828
9.70146	1.47573
10.36269	1.50552
10.95485	1.53441
11.64569	1.56312
12.23785	1.58886
12.92869	1.62261
13.52085	1.65447
14.113	1.68255
14.80385	1.71045
15.396	1.73295
15.98816	1.76697
16.58031	1.80054
17.27116	1.84905
17.86331	1.88154

18.45547	1.92222
19.04762	1.95111
19.63977	1.99395
20.23193	2.02509
19.54108	1.97865
18.94893	1.94193
18.25808	1.91421
17.56723	1.87038
16.87639	1.85463
16.28423	1.80477
15.59339	1.7847
14.90254	1.74852
14.31039	1.71405
13.61954	1.67544
12.92869	1.64799
12.33654	1.62891
11.64569	1.60371
11.05354	1.60362
10.36269	1.57716
9.78041	1.54404
9.16852	1.53207
8.47767	1.51092
7.78682	1.48968
7.10585	1.46304
6.44461	1.44837
5.80311	1.42533
5.16161	1.40859
4.52998	1.39203
4.19442	1.38186
3.87861	1.3725
3.55292	1.36575
3.23711	1.34784
2.97064	1.34055
2.72391	1.32903
2.47718	1.31778
2.04293	1.29501
1.64816	1.26477
1.283	1.23084
0.97508	1.19133
0.78954	1.15578
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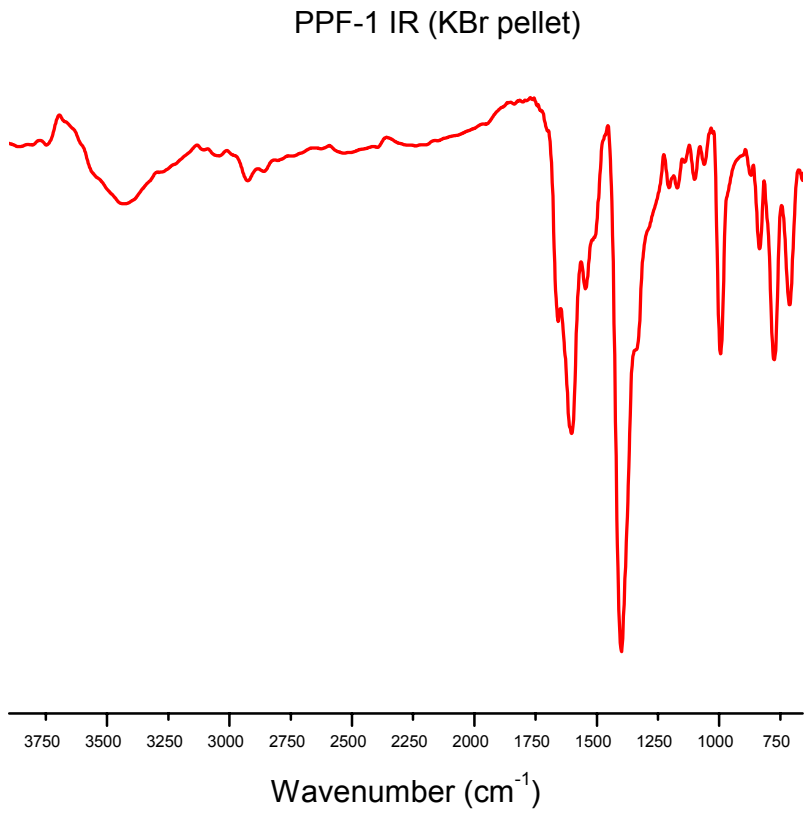

Figure S8. Infrared spectra of compound PPF-1

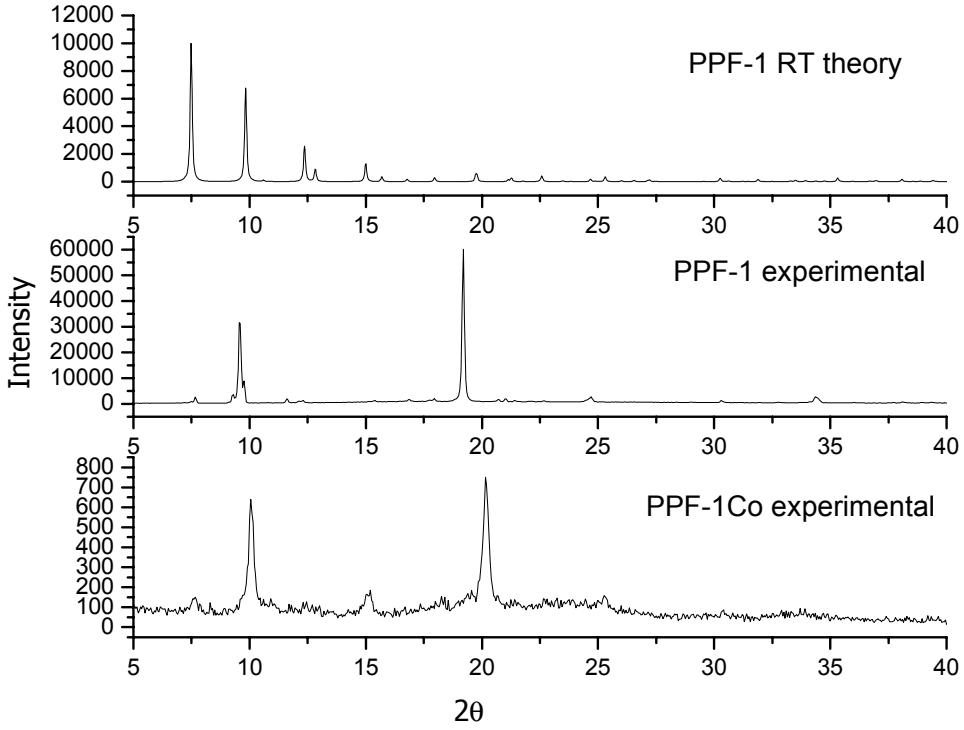

Figure S9. Powder pattern of PPF-1Co compared to theoretical and experimental powder pattern of PPF-1.

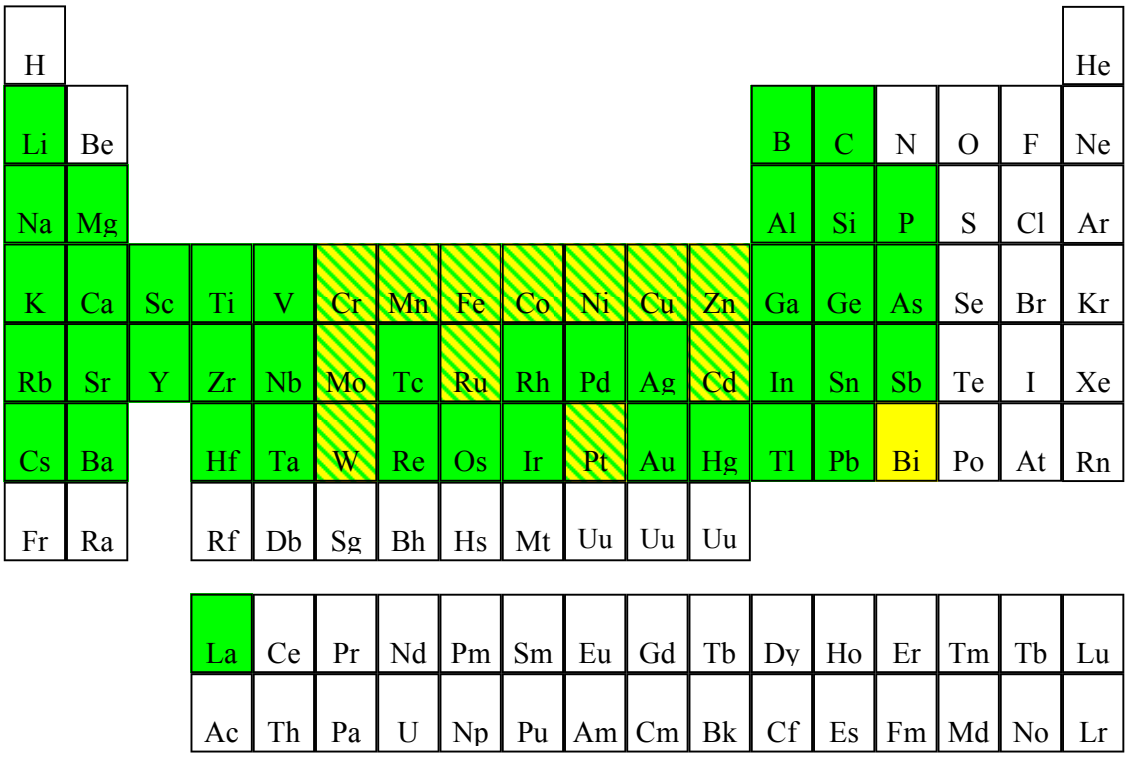

Figure S10. Metals that can be inserted into porphyrin[4] (Green) and metals that can be formed into paddlewheel structures[5] (Yellow) according to the Cambridge Structural Database.

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References

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3. a) L. Czepirski, J. Jagiello, *Chem. Eng. Sci.* **1989**, 44, 797-801; b)M. Dincă, A. F. Yu, J. R. Long, *J. Am. Chem. Soc*. **2006**, 128, 8904-8913.

4 a) J. K. M. Sanders, N. Bampos, Z. Cyde-Watson, S. L. Darling, J. C. Hawley, H-J. Kim, C. C. Mak, S. J. Webb, in *The Porphyrin Handbook, Vol 3* (Eds. K. M. Kadish, K. M. Smith, R. Guilard) Academic Press, San Diego, CA, **2000**, pp. 4; b) Of the various metalloporphyrins, the following MTCPP have been crystallographically characterized. Refcodes of the MTCPPs are: Zn (LOJFUL); Pt (OLEKOF); Pd (OLEKIZ); Ni (GAPKIS); Mn (NEPWAG); Co (KAJPUH); Cu (LOJFOF); Fe (MAQJUJ).

5 For examples of known paddlewheel clusters, see the following Refcodes: Co (BAZBOU); Cr (ACPCRB); Mn (UFIFIY); Fe (KASBEM); Ni (BAZBIO); Cu (AFAVAE); Zn (MANLUJ); Mo (FAFKON); Ru (AACRUB); Cd (YUSBAP); W (FIZBIA); Pt (PAKYUV); Bi (EZOHUW).