Electronic Supplementary Information (ESI)

Synthesis and Characterization of Two Metallo-Hydrogen-Bonded Organic Frameworks with Diverse Structures and Properties

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General information

Methanol (MeOH), acetonitrile (CH_3CN), *N*,*N*-dimethyl formamide (DMF), tetrahydrofuran (THF), trifluoro acetic acid (TFA), hexamethylenetetramine(HMTA), 4-hydroxybenzoic acid methyl ester, acetone, dichloromethane (DCM), K_3PO_4, $Cu(NO_3)_2$, $CDCl_3$, Deuterium Oxide were obtained from commercial suppliers and used without further purification, Methyl 3,5-diformyl-4-hydroxybenzoate was synthesized according to the literature.[1, 2]

^1H NMR spectra were recorded on a Bruker Avance 400 spectrometer (400.1 MHz for ^1H NMR). Powder X-ray diffraction (PXRD) data were collected on a Rigaku MiniFlex 600 diffractometer working with Cu Kα radiation, and the recording speed was 3 °min^{-1} over the 2ϑ range of 4−40 ° at room temperature. To collect the PXRD patterns at different temperatures, the sample was heated in air to the anticipated temperature and maintained for 30 min. Then, the PXRD patterns were collected at room temperature. Crystal structure data were collected on a SuperNova diffractometer equipped with a copper micro-focus X-ray sources (λ = 1.54184 Å). Fourier transform infrared (FT-IR) spectra of the samples were recorded on KBr pellets in the 400−4000 cm^{-1} range using a VERTEX70 spectrometer. Elemental analyses (C, H, N) were performed on an Elementar Vario MICRO elemental analyzer. The thermo gravimetric analyses (TGA) were recorded on a NETZSCH STA 449C unit at a heating rate of 10 $^oC \cdot min^{-1}$ under nitrogen atmosphere. Gas adsorption measurements were performed using a Micromeritics ASAP 2020 surface area and pore size analyser. Before sorption experiments, the as-synthesized **MHOF-PO_4-1** was frozen in refrigerator for 1 day, then the sample was dried in a lyophilizer for 1 day; the as-synthesized **MHOF-PO_4-2** was exchanged with CH_3CN for 1 day, for each 4 hours fresh solvent was exchanged, then the sample was exchanged with DCM for 3 days, fresh DCM was exchanged every day. Both the samples were degassed under reduced pressure (< 10^{-2} Pa) at room temperature for 10 hours. UHP grade gas was used for gas sorption measurement. Water vapor adsorption measurements were performed with an IGA-100B analyser (Hiden, UK) over the 0-30 mbar range at 298 K. Before sorption experiments, the samples were degassed under reduced pressure (< 10^{-2} Pa) at 60 ^oC for 10 hours.

Synthetic procedure

Synthesis of the ligand

4.16 g (20 mmol) Methyl 3,5-diformyl-4-hydroxybenzoate was dissolved in 80 mL CH_3CN, light yellow precipitate formed after 2.28 g (20 mmol) cyclohexane diamine in 30 mL methanol was added at 0 ^oC with vigorous stir, filtered and washed with methanol after reacted for 12 hours. 4.9 g compound **1** was collected after dried in vacuum (yield 85%). ^1H NMR (400 MHz, Chloroform-*d*) δ 14.99 (s, 3H, OH-benzene), 8.67 (s, 3H, CH=N), 8.44 (d, *J* = 2.2 Hz, 3H, benzene), 8.27 (s, 3H, CH=N), 7.89 (d, *J* = 2.2 Hz, 3H, benzene), 3.83 (s, 9H, -CH_3), 3.61–3.49 (m, 3H, -CH-N cyclohexane), 3.34 (q, *J* = 8.9 Hz, 3H, -CH-N cyclohexane), 2.03 – 1.40 (m, 24H, –CH_2- of cyclohexane); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.48 (-CO_2-), 166.22 (CH=N), 163.90 (CH=N), 155.87 (benzene-OH), 136.42 (benzene), 131.51 (benzene), 124.52 (benzene), 118.77 (benzene), 117.57 (benzene), 74.90 (-CH-N cyclohexane), 71.66 (-CH-N cyclohexane), 51.84(CH_3-CO_2), 33.16, 32.96, 24.35 and 24.14 (–CH_2- of cyclohexane).

4 g compound **1** was suspended in 100 mL solution of MeOH/THF (4:6) and stirred in ice water bath, 24 eqiv $NaBH_4$ was added portionwise, stirred for 12 hours. The reaction was quenched by adding 5 mL H_2O, and the mixture was evaporated to dryness, then 100 mL H_2O was added, the white precipitate was filtered and washed with water, then the precipitate was dried in vacuum as compound **2** with quantitative yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 6H, benzene), 5.50 (b, 9H, OH and NH), 3.89 – 3.75 (m, 12H, CH_2-NH), 3.80 (s, 9H, CH_3), 2.55 (s, 6H, CH-NH of cyclohexane), 2.02-1.29 (m, 24H, -CH_2- of cyclohexane). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.50 (-CO_2-), 130.45 (benzene), 124.62 (benzene-CH_2), 115.43 (benzene-CO_2Me), 59.21 (CH-NH), 51.44 (CH_3-CO_2), 46.13 (CH_2-NH of cyclohexane), 30.62 and 24.95 (-CH_2- of cyclohexane).

2 g compound **2** was dissolved in 60 mL 4mol/L HCl aqueous solution, and refluxed at 85^{o}C overnight. After cooled down to room temperature, the mixture was evaporated to dry as **L·6HCl** with quantitative yield. ^{1}H NMR (400 MHz, Deuterium Oxide) δ 7.92 (s, 6H, bezene), 4.27 (dd, *J* = 72.1, 13.2 Hz, 12H, CH_2-NH), 3.58 (s, 6H, CH-NH of cyclohexane), 2.28-1.33 (m, 24H, -CH_2- of cyclohexane). ^{13}C NMR (101 MHz, Deuterium Oxide) δ 168.67 (-CO_2H), 158.47 (benzene-OH), 135.14 (benzene), 122.81 (benzene-CH_2), 119.58 (benzene-CO_2Me), 57.33 (-CH-NH), 44.57 (CH_2-NH of cyclohexane), 25.70 and 21.61 (-CH_2- of cyclohexane).

MHOF-PO_4-1: 40 mg K_3PO_4, 100 mg $Cu(NO_3)_2$ and 100 mg **L·6HCl** was charged into a 20mL vial, then 10 mL H_2O was added, the mixture was sonicated for 3 min and heated in a 65 ^{o}C oven for 2 days, after washed with water, dark green crystal was harvested with a yield of 72%. Elemental analysis for $LCu_3PO_4 \cdot 12H_2O$ calculated (%): N=6.34, C=40.72, H=6.18; found (%): N=7.22, C=40.36, H=5.45.

MHOF-PO_4-2: 30 mg **MHOF-PO_4-1** was added into an 8 mL vial, after added 1.5 mL DMF and 1.5 mL H_2O, 20 µL HBF_4 (40 %wt aqueous solution) was added subsequently, the vial was capped and sonicated for 5 min, then the vial was put into a 100 ^{o}C oven for 5 days. The upper solution was decanted after took the vial out of the oven immediately, then the crystal was washed with CH_3CN and acetone for three times, dark green needle like crystal was harvested with a yield of 78%. Elemental analysis for $LCu_3PO_4 \cdot 13H_2O$ calculated (%): N=6.24, C=40.13, H=6.17; found (%): N=6.19, C=39.45, H=6.11.

Crystallographic data

Table S1. Crystal data and structure refinement for **MHOF-PO$_4$-1** and **MHOF-PO$_4$-2**

Compound name	**MHOF-PO$_4$-1**	**MHOF-PO$_4$-2**
Empirical formula	$C_{45}H_{69}Cu_3N_6O_{19}P$	$C_{45}H_{63}Cu_3N_6O_{16}P$
Formula weight	1219.65	1165.60
Temperature (K)	100.00(3)	155.00(7)
Wavelength (Å)	1.54184	1.54184
Crystal system	Cubic	Hexagonal
Space group	$F4_132$	$P6_3$
Unit cell dimensions (Å)	a = 37.4254(2)	a =19.7940(2) c = 9.02850(10)
Volume (Å^3)	52420.3(8)	3063.47(7)
Z	32	2
Calculated density (g/cm^3)	1.236	1.264
Absorption coefficient (mm^{-1})	1.904	1.977
F(000)	20320	1210
Reflections collected	15912	22875
Independent reflections	4330	3924
Goodness-of-fit on F^2	0.992	1.084
Final R indices [I>2σ(I)]	R1 = 0.0538, wR2 = 0.1547	R1 = 0.0199, wR2 = 0.0536
R indices (all data)	R1 = 0.0651, wR2 = 0.1632	R1 = 0.0228, wR2 = 0.0541
Absolute structure parameter	0.025(19)	0.004(7)

Crystal structure

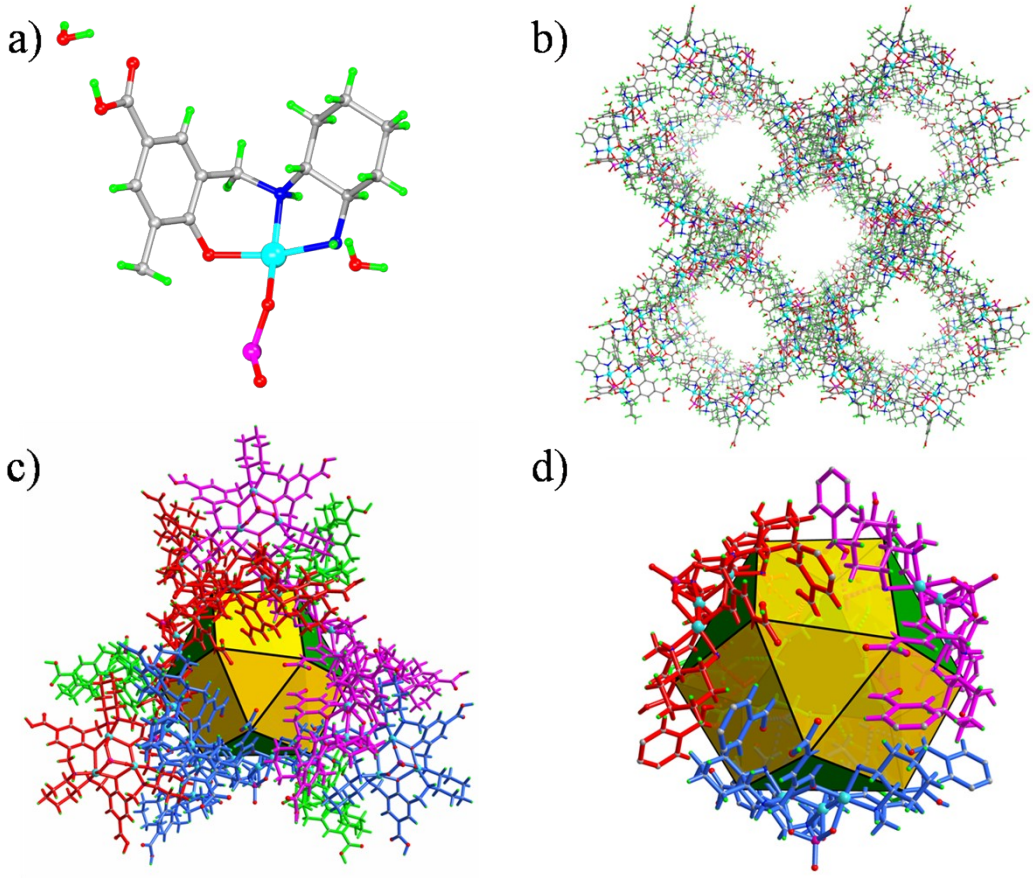

Figure s1. (a)The asymmetric unit and (b) one single network of **MHOF-PO$_4$-1**; (c) the 4-fold interpenetrated framework and (d) pseudo-cuboctahedral cage in **MHOF-PO$_4$-1**.

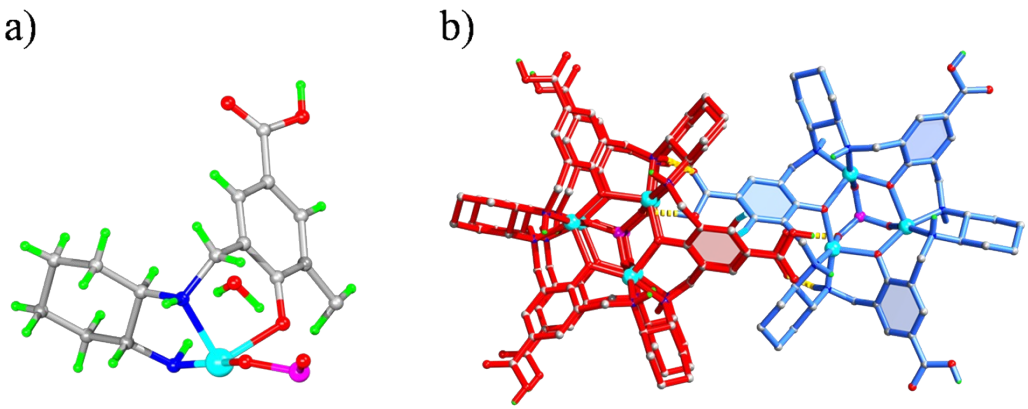

Figure s2. a) Asymmetric unit and b) H-bonded linkage between complexes in **MHOF-PO$_4$-2**.

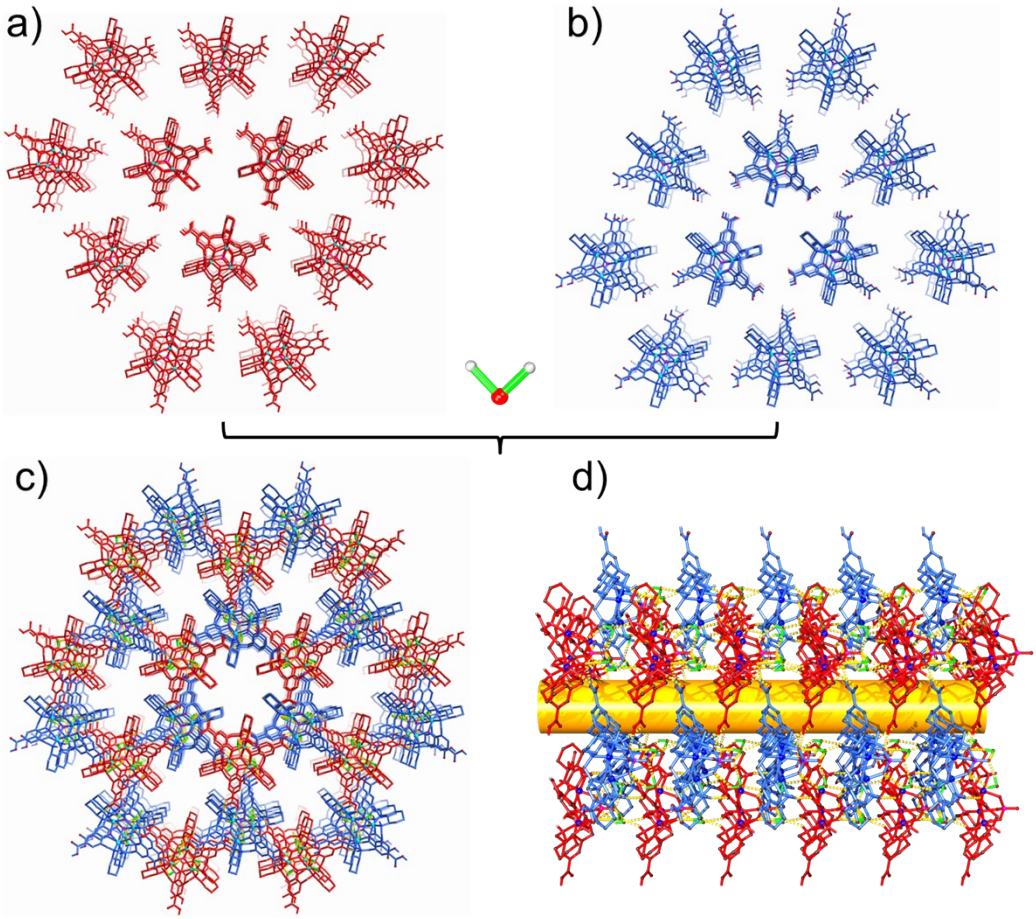

Figure s3. (a) and (b) the two different layer in **MHOF-PO$_4$-2**, (c) the 3-peridoc packing of **MHOF-PO$_4$-2** along c direction, and (d) The 1D channel along c direction in **MHOF-PO$_4$-2**.

FT-IR spectrum

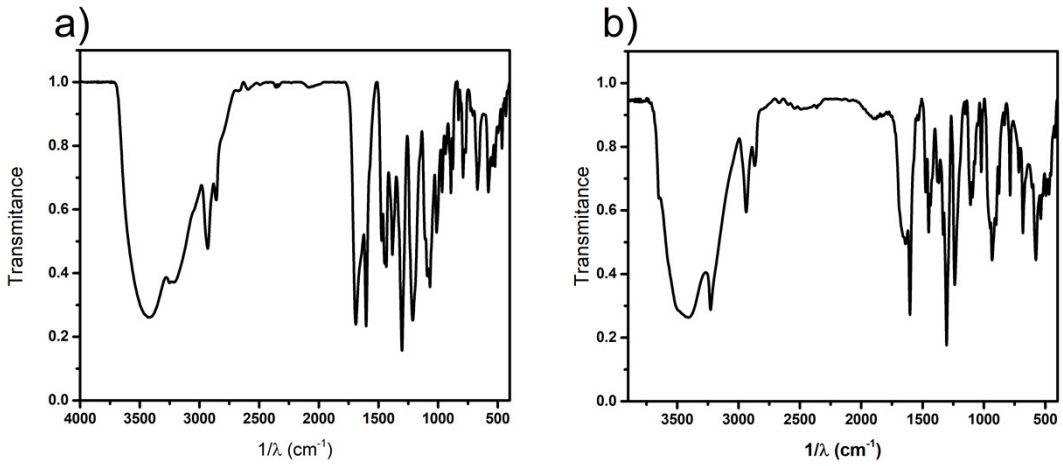

Figure s4. FT-IR spectrum of a) **MHOF-PO$_4$-1** and b) **MHOF-PO$_4$-2**.

TGA data

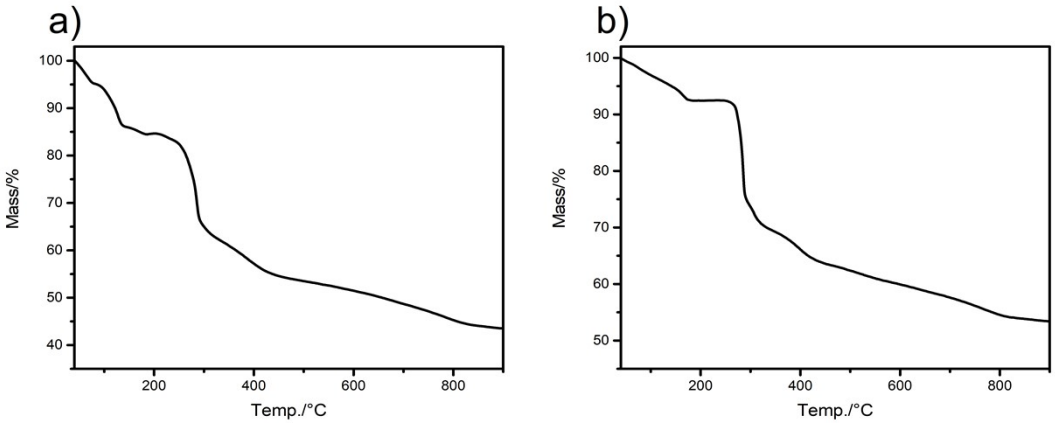

Figure s5. TGA curve of a) **MHOF-PO$_4$-1** and b) **MHOF-PO$_4$-2**.

Water adsorption cycles

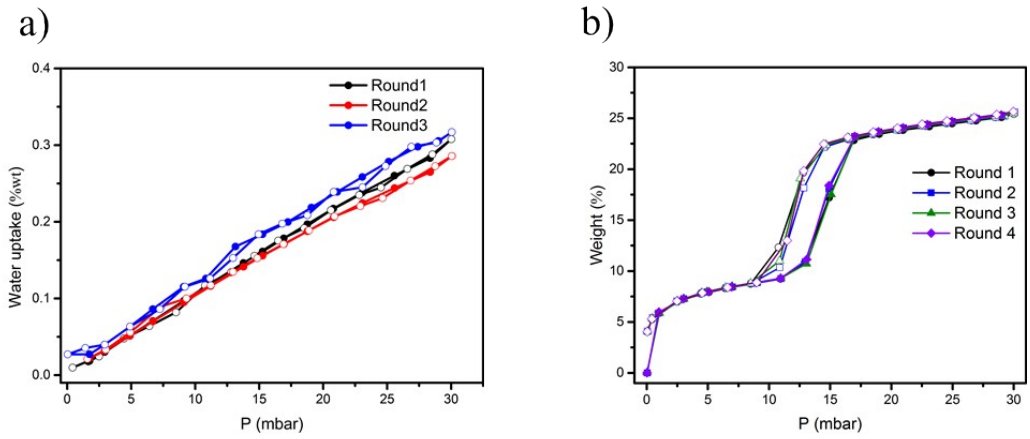

Figure s6. Water adsorption cycles of a) **MHOF-PO$_4$-1** and b) **MHOF-PO$_4$-2**.

CO_2 and C_2H_2 uptake

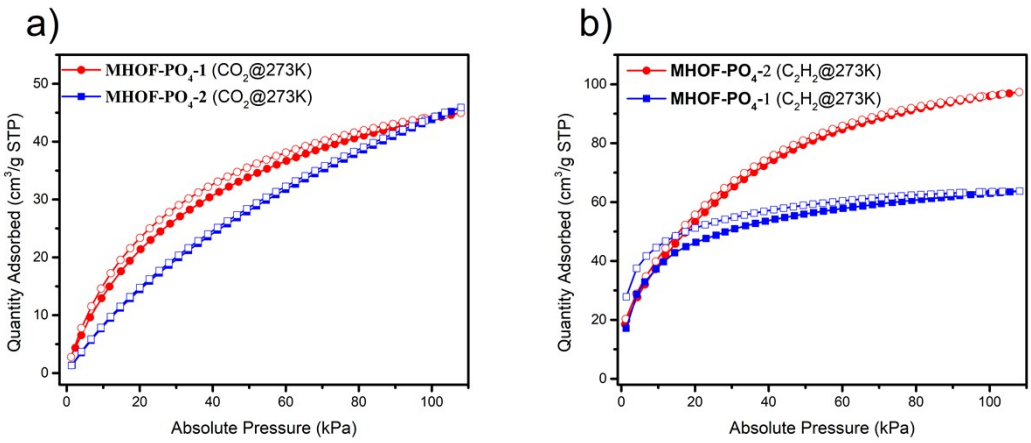

Figure s7. CO_2 (273 K) and C_2H_2 (273 K) uptake of a) **MHOF-PO$_4$-1** and b) **MHOF-PO$_4$-2**.

Reference:

1. L. F. Lindoy, G. V. Meehan and N. Svenstrup, *Synthesis-Stuttgart*, 1998, **1998**, 1029-1032.
2. T. Routasalo, J. Helaja, J. Kavakka and A. M. P. Koskinen, *Eur. J. Org. Chem.*, 2008, **2008**, 3190-3199.

Table S2. Part of bond lengths [Å] and angles [deg] for **MHOF-PO_4-1.**

Cu(21)-O(20)	1.949(4)	P(23)-O(22)-Cu(21)	124.4(3)
Cu(21)-O(22)	1.984(4)	C(7)-O(20)-Cu(21)	113.2(3)
Cu(21)-N(11)	2.015(5)	C(17)-N(18)-C(19)	116.0(4)
Cu(21)-N(18)	2.022(5)	C(17)-N(18)-Cu(21)	108.7(4)
P(23)-O(22)	1.520(4)	C(19)-N(18)-Cu(21)	112.3(4)
P(23)-O(24)	1.585(8)	C(12)-N(11)-C(10)	115.4(5)
O(20)-C(7)	1.335(7)	C(12)-N(11)-Cu(21)	103.9(4)
O(2)-C(3)	1.319(8)	C(10)-N(11)-Cu(21)	113.5(4)
O(1)-C(3)	1.238(8)	C(9)-C(8)-C(7)	120.3(6)
N(18)-C(17)	1.486(7)	C(9)-C(8)-C(10)	122.2(6)
N(18)-C(19)	1.488(7)	C(7)-C(8)-C(10)	117.4(5)
N(11)-C(12)	1.474(8)	C(6)-C(5)-C(4)	122.4(6)
N(11)-C(10)	1.500(8)	C(5)-C(6)-C(7)	119.4(6)
C(8)-C(7)	1.402(9)	O(20)-C(7)-C(8)	119.8(5)
C(8)-C(10)	1.477(9)	O(20)-C(7)-C(6)	121.1(5)
C(8)-C(9)	1.382(9)	C(8)-C(7)-C(6)	119.2(6)
C(5)-C(6)	1.360(8)	C(5)-C(4)-C(9)	118.0(5)
C(5)-C(4)	1.400(9)	C(5)-C(4)-C(3)	122.5(5)
C(6)-C(7)	1.419(8)	C(9)-C(4)-C(3)	119.5(5)
C(4)-C(9)	1.408(8)	O(1)-C(3)-O(2)	122.7(6)
C(4)-C(3)	1.479(8)	O(1)-C(3)-C(4)	123.1(6)
C(12)-C(13)	1.489(9)	O(2)-C(3)-C(4)	114.2(5)
C(12)-C(17)	1.516(8)	C(8)-C(9)-C(4)	120.6(6)
C(17)-C(16)	1.540(8)	N(11)-C(12)-C(13)	117.0(6)
C(16)-C(15)	1.516(9)	N(11)-C(12)-C(17)	104.3(5)
C(13)-C(14)	1.524(10)	C(13)-C(12)-C(17)	111.0(5)
C(15)-C(14)	1.516(10)	N(18)-C(17)-C(12)	109.6(5)
O(20)-Cu(21)-O(22)	91.04(18)	N(18)-C(17)-C(16)	110.7(5)
O(20)-Cu(21)-N(11)	92.15(19)	C(12)-C(17)-C(16)	111.3(5)
O(22)-Cu(21)-N(11)	162.1(2)	C(8)-C(10)-N(11)	113.8(5)
O(20)-Cu(21)-N(18)	163.06(18)	C(15)-C(16)-C(17)	110.1(6)
O(22)-Cu(21)-N(18)	88.22(19)	C(12)-C(13)-C(14)	110.7(6)
N(11)-Cu(21)-N(18)	83.6(2)	C(14)-C(15)-C(16)	111.1(6)
O(22)-P(23)-O(24)	106.48(18)	C(15)-C(14)-C(13)	111.7(6)

Table S3. Part of bond lengths [Å] and angles [deg] for **MHOF-PO_4-2.**

O(1)-P(2)	1.515(3)	C(6)-N(5)-Cu(4)	113.79(14)
P(2)-O(3)	1.5460(14)	N(5)-C(6)-C(7)	112.54(18)
O(3)-Cu(4)	1.9906(15)	C(8)-C(7)-C(12)	120.1(2)
Cu(4)-O(16)	1.9605(14)	C(8)-C(7)-C(6)	122.02(19)
Cu(4)-N(5)	2.0183(19)	C(12)-C(7)-C(6)	117.85(19)
N(5)-C(6)	1.487(3)	C(7)-C(8)-C(9)	120.7(2)
C(6)-C(7)	1.495(3)	C(10)-C(9)-C(8)	119.05(19)
C(7)-C(8)	1.383(3)	C(10)-C(9)-C(13)	119.64(19)
C(7)-C(12)	1.410(3)	C(8)-C(9)-C(13)	121.27(19)
C(8)-C(9)	1.396(3)	C(9)-C(10)-C(11)	121.73(19)
C(9)-C(10)	1.395(3)	C(10)-C(11)-C(12)	118.3(2)
C(9)-C(13)	1.481(3)	C(10)-C(11)-C(17)	119.88(19)
C(10)-C(11)	1.398(3)	C(12)-C(11)-C(17)	121.72(17)
C(11)-C(12)	1.414(3)	O(16)-C(12)-C(7)	119.04(19)
C(11)-C(17)	1.503(3)	O(16)-C(12)-C(11)	121.06(19)
C(12)-O(16)	1.336(2)	C(7)-C(12)-C(11)	119.91(18)
C(13)-O(14)	1.229(3)	O(14)-C(13)-O(15)	123.1(2)
C(13)-O(15)	1.312(3)	O(14)-C(13)-C(9)	123.5(2)
C(17)-N(18)	1.480(3)	O(15)-C(13)-C(9)	113.36(19)
N(18)-C(19)	1.486(3)	C(12)-O(16)-Cu(4)	114.03(12)
C(19)-C(20)	1.510(4)	N(18)-C(17)-C(11)	113.45(18)
C(19)-C(24)	1.527(3)	C(17)-N(18)-C(19)	113.93(17)
C(20)-C(21)	1.519(5)	N(18)-C(19)-C(20)	113.9(2)
C(21)-C(22)	1.540(5)	N(18)-C(19)-C(24)	108.31(18)
C(22)-C(23)	1.501(5)	C(20)-C(19)-C(24)	110.8(2)
C(23)-C(24)	1.529(4)	C(19)-C(20)-C(21)	111.3(3)
O(1)-P(2)-O(3)	110.25(6)	C(20)-C(21)-C(22)	110.9(3)
P(2)-O(3)-Cu(4)	128.66(9)	C(23)-C(22)-C(21)	111.9(3)
O(16)-Cu(4)-O(3)	90.01(6)	C(22)-C(23)-C(24)	111.1(4)
O(16)-Cu(4)-N(5)	92.33(7)	C(19)-C(24)-C(23)	109.7(2)
O(3)-Cu(4)-N(5)	163.12(7)		