

Electronic Supplementary Material for

Encapsulation of Polyoxometalates within Layered Metal-Organic Frameworks with Topological and Pore Control

Zhi He,^{†a} Qingqing Pang,^{†a} Damien Rankine,^b Christopher J. Sumbly,^b Lijuan Zhang,^{*c}
Christian J. Doonan^{*b} and Qiaowei Li^{*a}

^a*Department of Chemistry, Fudan University, 220 Handan Road, Shanghai 200433, China. Email: qwli@fudan.edu.cn*

^b*School of Chemistry and Physics, The University of Adelaide, SA 5005, Australia. Email: christian.doonan@adelaide.edu.au*

^c*Laboratory of Advanced Materials, Fudan University, 2205 Songhu Road, Shanghai 200433, China. Email: zhanglijuan@fudan.edu.cn*

[†]These authors contributed equally to this work.

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1 Synthesis and Activation of Metal-Organic Frameworks (MOFs).

All chemicals were purchased from commercial suppliers and used as received without further purifications.

Cu₆(*m*-BDC)₆(H₂O)₆·H₃[P(W₃O₁₀)₄] (structure **a**, *m*-H₂BDC = 1,3-benzenedicarboxylic acid): A solid mixture of Cu(NO₃)₂·3H₂O (20 mg, 0.083 mmol), *m*-H₂BDC (14 mg, 0.084 mmol), and H₃[P(W₃O₁₀)₄] (100 mg, 0.035 mmol) was dissolved in a solution mixture of 0.75 mL *N,N*-dimethylformamide (DMF), 0.75 mL ethanol, and 0.5 mL H₂O in a 4-mL vial. The vial was capped tightly and placed in an oven at 85 °C for 24 hours. Blue crystals were collected (yield: 66% based on cupric nitrate). FT-IR: (KBr 4000-450 cm⁻¹): 3442(s), 3175(w), 1626(s), 1575(w), 1466(w), 1448(w), 1385(vs), 1275(w), 1163(w), 1101(s), 1059(s), 1015(w), 883(s), 958(s), 817(vs), 749(w), 724(w), 663(w), 595(w), 491(w). Formula: C₄₈H₃₉Cu₆O₇₀PW₁₂. Elemental Analysis: Found (%) C = 12.76, H = 1.03; Calc. (%) C = 13.24, H = 0.90.

Activation of structure a with heating (structure **a1**, Cu₆(*m*-BDC)₆·H₃[P(W₃O₁₀)₄]): After solvent exchange with acetone for nine times over three days, the crystals of structure **a** were fully activated in vacuum at 180 °C over 8 hours. Dark green crystals were collected and kept in a nitrogen filled vial.

Cu(*m*-BDC)(H₂O) (structure **b**): Cu(*m*-BDC)(H₂O) was synthesized by methods previously reported on literature¹ with modifications. A solid mixture of Cu(NO₃)₂·3H₂O (20 mg, 0.083 mmol) and *m*-H₂BDC (14 mg, 0.084 mmol) was dissolved in a solution mixture of 0.75 mL DMF, 0.75 mL ethanol, and 0.5 mL H₂O in a 4-mL vial. The vial was capped tightly and placed in an oven at 85 °C for 24 hours. Blue crystals of Cu(*m*-BDC)(H₂O) were collected.

Cu(*m*-TBDC)(DMF) (structure **c**): A solid mixture of Cu(NO₃)₂·3H₂O (4.9 mg, 0.020 mmol) and 5'-methyl-1,1':3',1''-terphenyl-4,4''-dicarboxylic acid (*m*-H₂TBDC, 6.7 mg, 0.020 mmol) was dissolved in a solution mixture of 188 μL DMF, 188 μL ethanol, and 125 μL H₂O in a 4-mL vial. The vial was capped tightly and placed in an oven at 85 °C for 3 hours. Blue crystals were collected. When POM was present in the solution, the same structure **c** was obtained. Yield: 77%

based on cupric nitrate). FT-IR: (KBr 4000-450 cm^{-1}): 3412(s), 3060(w), 1697(w), 1665(s), 1612(s), 1560(w), 1402(vs), 1254(w), 1185(w), 1103(w), 1017(w), 848(s), 808(w), 781(vs), 709(w), 676(w), 553(w), 517(s). Formula: $\text{C}_{24}\text{H}_{21}\text{CuNO}_5$. Elemental Analysis: Found (%) C = 60.72, H = 4.19, N = 2.86; Calc. (%) C = 61.73, H = 4.53, N = 3.00.

$\text{Cu}_4(m\text{-NTBDC})_4(\text{H}_2\text{O})_4 \cdot \text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4]$ (structure **d**): A solid mixture of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (5.2 mg, 0.022 mmol), 5'-diethylaminomethyl-1,1':3',1''-terephthalic acid (*m*- H_2NTBDC , 4.8 mg, 0.012 mmol), and $\text{H}_3[\text{P}(\text{W}_3\text{O}_{10})_4]$ (5.5 mg, 0.0019 mmol) was dissolved in a solution mixture of 188 μL DMF, 188 μL ethanol, and 125 μL H_2O in a 4-mL vial. The vial was capped tightly and placed in an oven at 85 $^\circ\text{C}$ for 22 hours. Blue crystals were collected.

2 Single Crystal Structure Determinations.

Crystals of **a**, **c** and **d** coated with Paratone oil on a Cryloop pin were mounted on a Bruker SMART Apex II single-crystal x-ray diffractometer equipped with a CCD area detector and operated at 1500 W power (50 kV, 30 mA) to generate Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The crystal structures were solved by Direct Methods and refined on F^2 by full-matrix least-squares using the Shelx^{tl}-97² program systems. Details of crystal data, data collection, structure solution, and refinement are given in Table S1, S2, and S3. CCDC 943144-943146 contains the crystallographic data for these structures. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal data and structure refinement for structure **a**.

Identification code	a	
Empirical formula	C48 H36 Cu6 O70 P W12	
Formula weight	4351.18	
Temperature	296(2) K	
Wavelength	0.71073 \AA	
Crystal system	Trigonal	
Space group	$P\bar{3}$	
Unit cell dimensions	a = 18.7659(11) \AA	$\alpha = 90.00^\circ$
	b = 18.7659(11) \AA	$\beta = 90.00^\circ$
	c = 11.3114(13) \AA	$\gamma = 120.00^\circ$
Volume	3449.7(5) \AA^3	

Z	1
Density (calculated)	2.094 Mg/m ³
Absorption coefficient	10.944 mm ⁻¹
F(000)	1961
Crystal size	0.35 x 0.30 x 0.05 mm ³
Theta range for data collection	1.80 to 27.51°
Index ranges	-23<=h<=24, -24<=k<=24, -14<=l<=13
Reflections collected	28318
Independent reflections	5213 [R(int) = 0.0639]
Completeness to theta = 27.51°	98.0 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	5213 / 14 / 213
Goodness-of-fit on <i>F</i> ²	1.187
Final R indices [I>2sigma(I)]	R1 = 0.1045, wR2 = 0.3207
R indices (all data)	R1 = 0.1406, wR2 = 0.3418
Largest diff. peak and hole	6.603 and -3.999 e.Å ⁻³

Table S2. Crystal data and structure refinement for structure **c**.

Identification code	c	
Empirical formula	C ₂₄ H ₂₁ Cu N O ₅	
Formula weight	466.96	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>C</i> 2/ <i>c</i>	
Unit cell dimensions	a = 29.26(4) Å	α = 90.00°
	b = 9.821(14) Å	β = 113.821(17)°
	c = 18.95(3) Å	γ = 90.00°
Volume	4981(13) Å ³	
Z	8	
Density (calculated)	1.245 Mg/m ³	
Absorption coefficient	0.908 mm ⁻¹	
F(000)	1928	
Crystal size	0.30 x 0.05 x 0.05 mm ³	
Theta range for data collection	2.21 to 24.81°	
Index ranges	-34<=h<=34, -11<=k<=10, -21<=l<=14	
Reflections collected	11170	
Independent reflections	4211 [R(int) = 0.0925]	
Completeness to theta = 24.81°	97.8 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	4211 / 0 / 293	

Goodness-of-fit on F^2	0.707
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0582, wR2 = 0.2105
R indices (all data)	R1 = 0.1020, wR2 = 0.2320
Largest diff. peak and hole	1.033 and -0.435 e.Å ⁻³

Table S3. Crystal data and structure refinement for structure **d**.

Identification code	d
Empirical formula	C118 H142 Cu4 N10 O88 P W12
Formula weight	5599.75
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2/n$
Unit cell dimensions	a = 18.0410(38) Å $\alpha = 90.00^\circ$ b = 27.8300(58) Å $\beta = 106.695(3)^\circ$ c = 24.1272(51) Å $\gamma = 90.00^\circ$
Volume	11603(4) Å ³
Z	2
Density (calculated)	1.602 Mg/m ³
Absorption coefficient	6.353 mm ⁻¹
F(000)	5286
Crystal size	0.15 x 0.12 x 0.12 mm ³
Theta range for data collection	1.14 to 25.50°
Index ranges	-19 ≤ h ≤ 21, -33 ≤ k ≤ 33, -25 ≤ l ≤ 29
Reflections collected	50340
Independent reflections	21540 [R(int) = 0.0530]
Completeness to theta = 25.50°	99.6 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21540 / 28 / 937
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2\sigma(I)$]	R1 = 0.0673, wR2 = 0.2236
R indices (all data)	R1 = 0.1178, wR2 = 0.2716
Largest diff. peak and hole	2.920 and -3.272 e.Å ⁻³

3 X-ray Powder Diffraction of the MOFs.

Powder X-ray diffraction (PXRD) was carried out with a Bruker AXS D8 Advance X-ray Powder Diffractometer operated at 1,600 W power (40 kV, 40 mA) using Cu $K\alpha$ radiation. Simulated PXRD pattern was calculated using Mercury 3.0 from the corresponding single-crystal structural data.

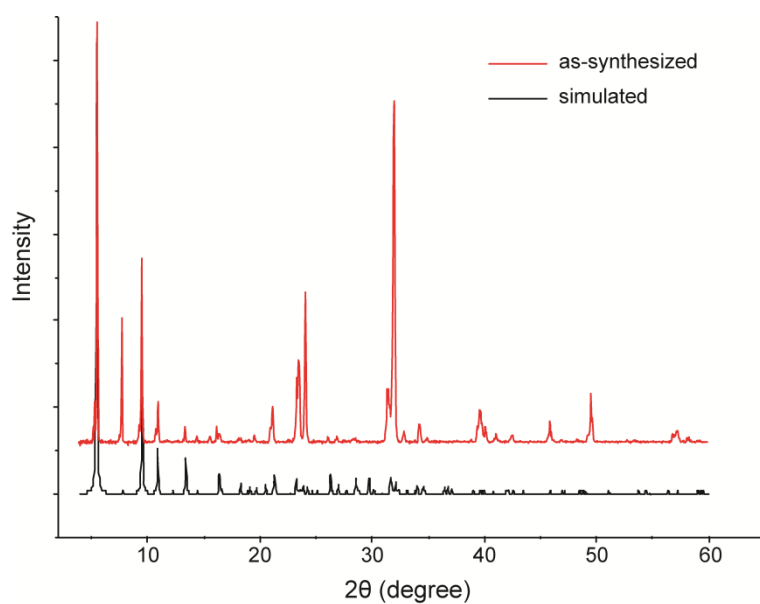


Figure S1. XRD patterns for the as-synthesized structure **a**, compared with simulated pattern calculated from single crystal data.

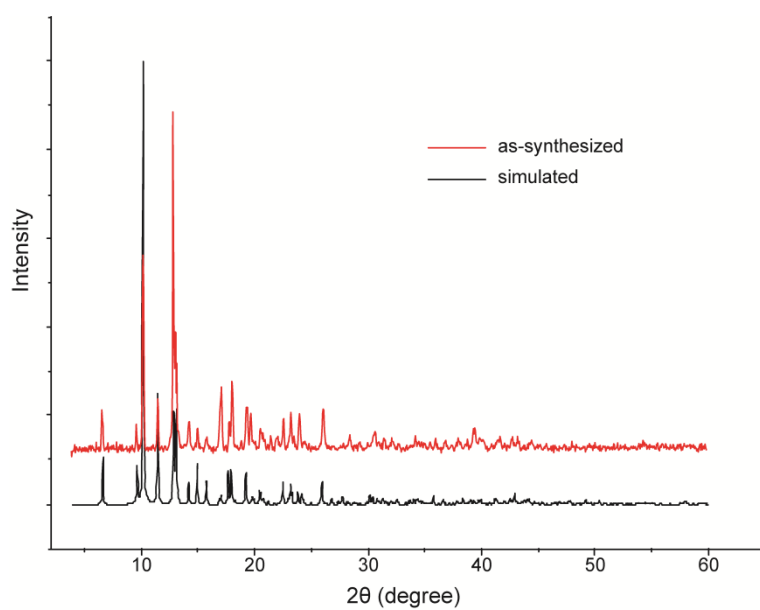


Figure S2. XRD patterns for the as-synthesized structure **c**, compared with simulated pattern calculated from single crystal data.

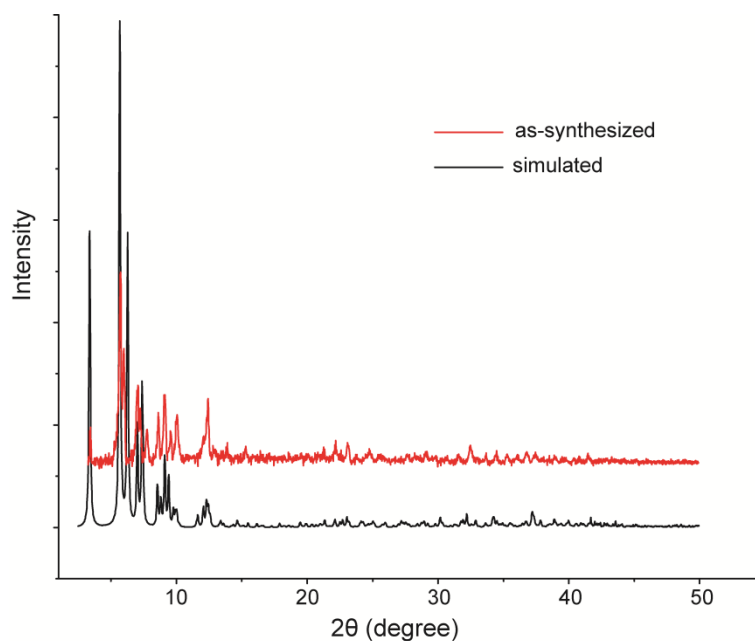


Figure S3. XRD patterns for the as-synthesized structure **d**, compared with simulated pattern calculated from single crystal data.

4 N₂ Adsorption Isotherm for structure a1.

N₂ adsorption and desorption measurements were performed on a Micromeritics ASAP 2020 system. Ultra-high purity N₂ (99.999 %) was purchased and used as received. Prior to measurements, sample was activated by the heating method described above. Low pressure N₂ adsorption isotherm was measured at 77 K.

The specific surface area for N₂ was calculated using the Brunauer-Emmet-Teller (BET) model in linear range determined from the consistency criteria ($0.05 < P/P_0 < 0.3$). The resulting BET surface area is 70.4 m² g⁻¹ and the Langmuir surface area is 109.5 m² g⁻¹.

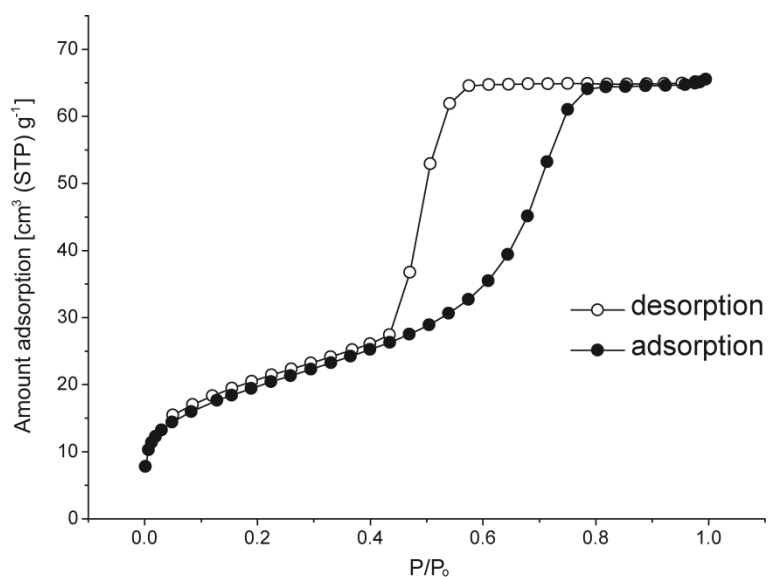


Figure S4. N₂ adsorption isotherms at 77 K for structure **a1**. Closed symbols: adsorption; Open symbols: desorption.

By a simple estimation of the surface area from Materials Studio, structure **d** has a surface area of around 1300 m² g⁻¹ (after removing all the DMF and water molecules in the pores, and water coordinated to Cu(II)). However, due to the fact that structure **d** is a layered MOF structure, structure change is possible after activation and/or during the adsorption. No significant N₂ uptake was observed in the very preliminary test on **d** after activation by 100 °C heating under vacuum.

5 Cyclic Voltammogram of structure **a1**.

The cyclic voltammetry experiment was carried out by using a powder microelectrode. A diameter of 30 μm Pt wire was sealed in a glass tube through a gas burner. After being polished by sandpaper, the Pt wire sealed in the glass was eroded in nitrohydrochloric acid at 100°C for 5 min. Then a groove with ~10 μm in depth was produced. Before electrochemical tests, the prepared powder microelectrode was ground within the material (POM-containing MOF structure **a1**) for several minutes. After this process, several particles of active materials were inserted in the groove mentioned above. The electrolyte was 1 M LiPF₆ in PC. Lithium-metal foils were used as counter and reference electrodes. This experiment was conducted with a scan rate of 0.002 V/S with Solartron Instrument model 1287 controlled by a computer.

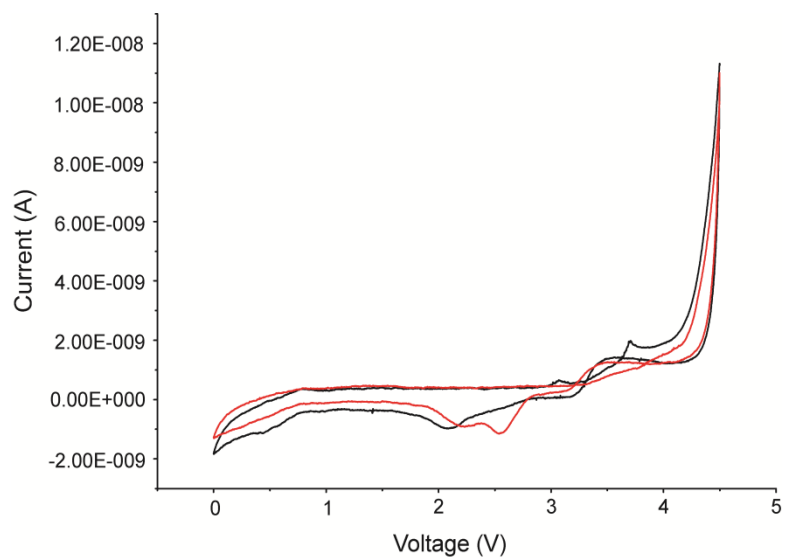


Fig. S5 Cyclic voltammogram at sweep rate of 2 mV/s for microelectrode of structure **a1**. 1st cycle: black; 2nd cycle: red.

References:

- (1) D.-X. Xue, Y.-Y. Lin, X.-N. Cheng and X.-M. Chen, *Cryst. Growth Des.*, 2007, **7**, 1332.
- (2) G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.