

Supporting Information

Mo-based crystal POMOFs with high electrochemical capacitor performance

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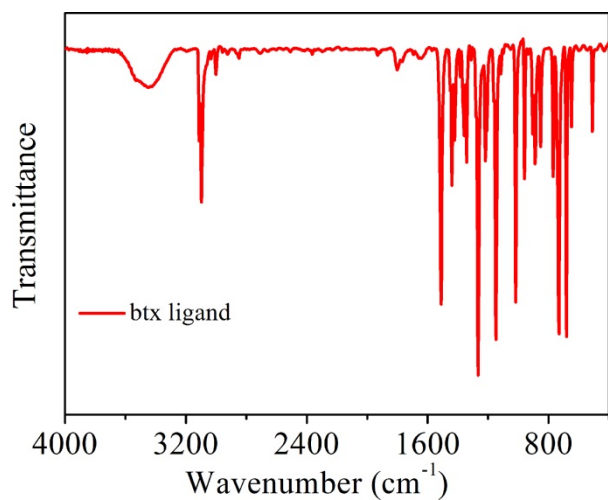


Figure S1. The IR spectrum of ligand of 1,4-bis(triazol-1-ylmethyl) benzene (btx).

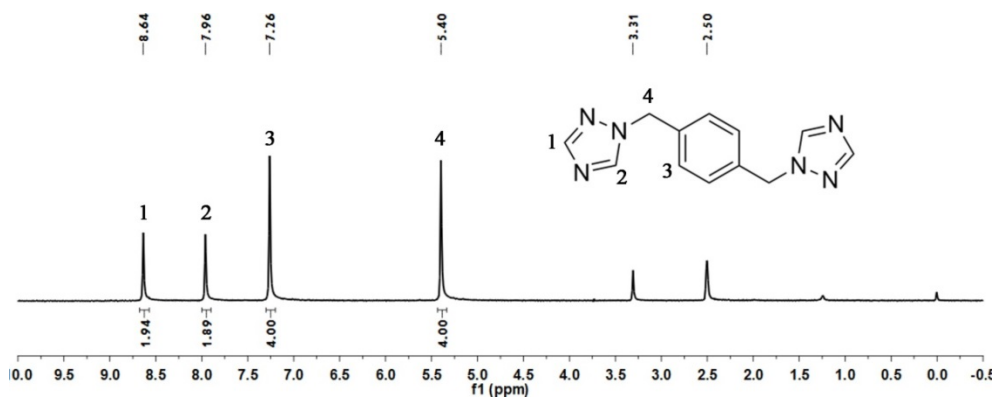


Figure S2. The ^1H NMR of ligand of 1,4-bis(triazol-1-ylmethyl) benzene (btx).

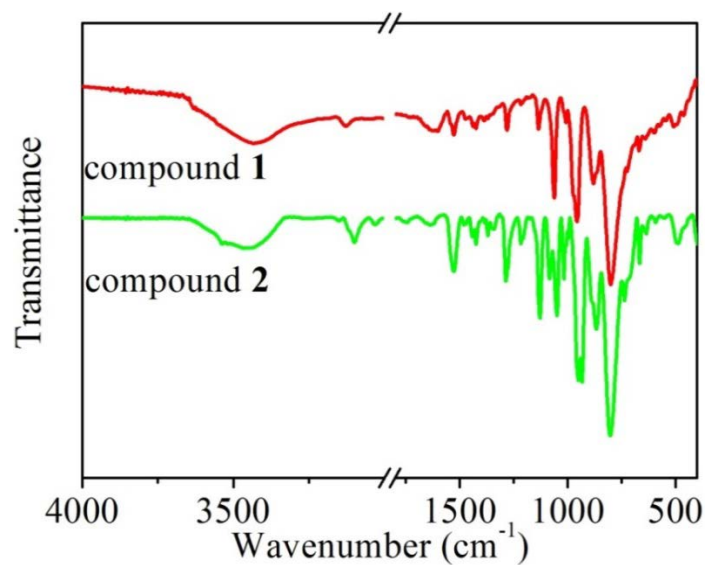


Figure S3. The IR spectra of compounds **1** (red line) and **2** (green line).

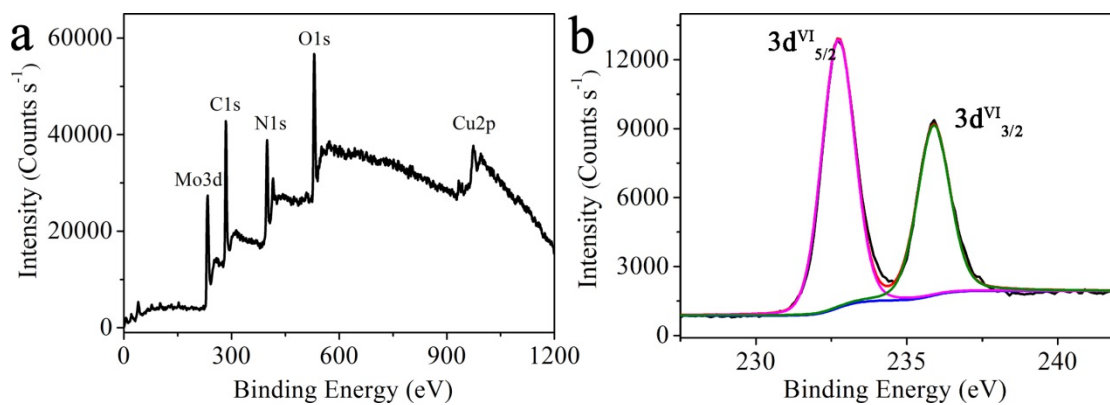


Figure S4. The XPS survey spectrum of **1** and high-resolution XPS spectrum of Mo (3d).

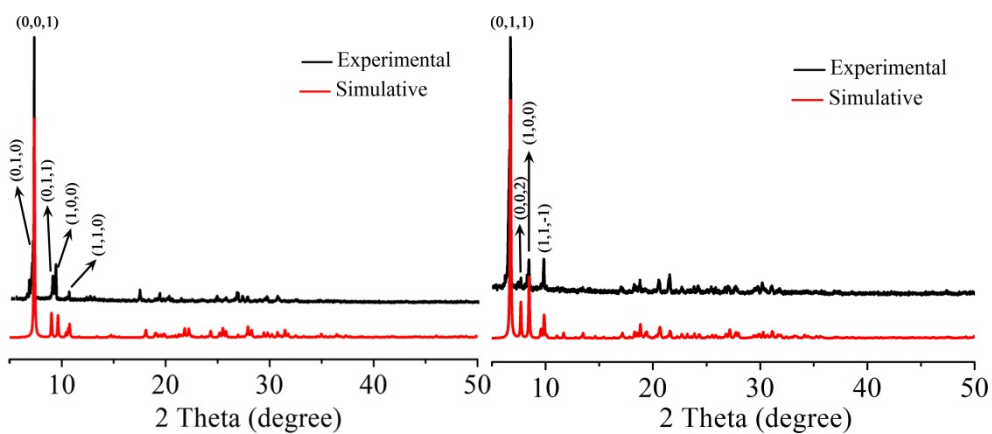


Figure S5. Experimental (black lines) and simulative (red lines) powder X-ray diffraction patterns of compounds **1** and **2**.

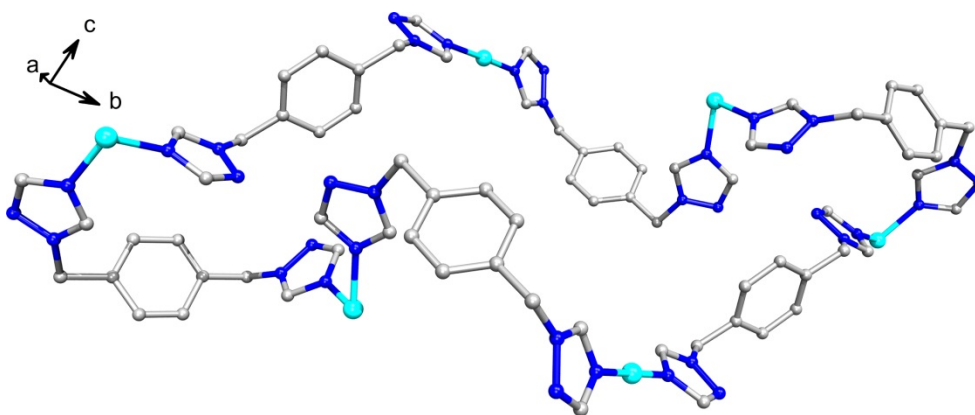


Figure S6. Six Cu(II) cations and six btx ligands are included in 78-membered macrocycle Cu-MOF square lattices.

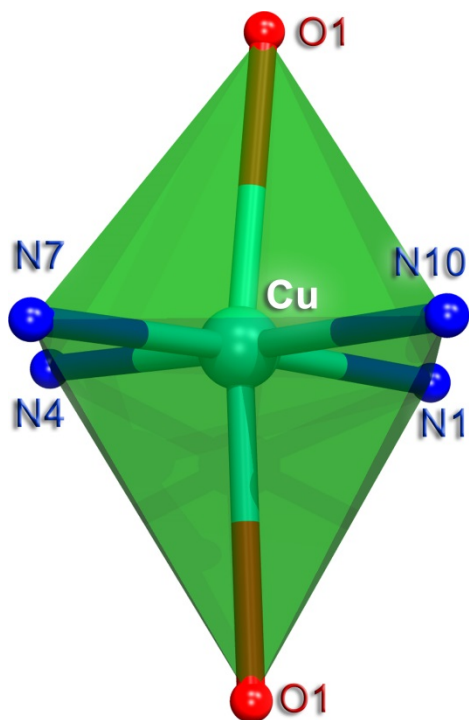


Figure S7. The distorted octahedron geometry of Cu(II) cation in compound **2**.

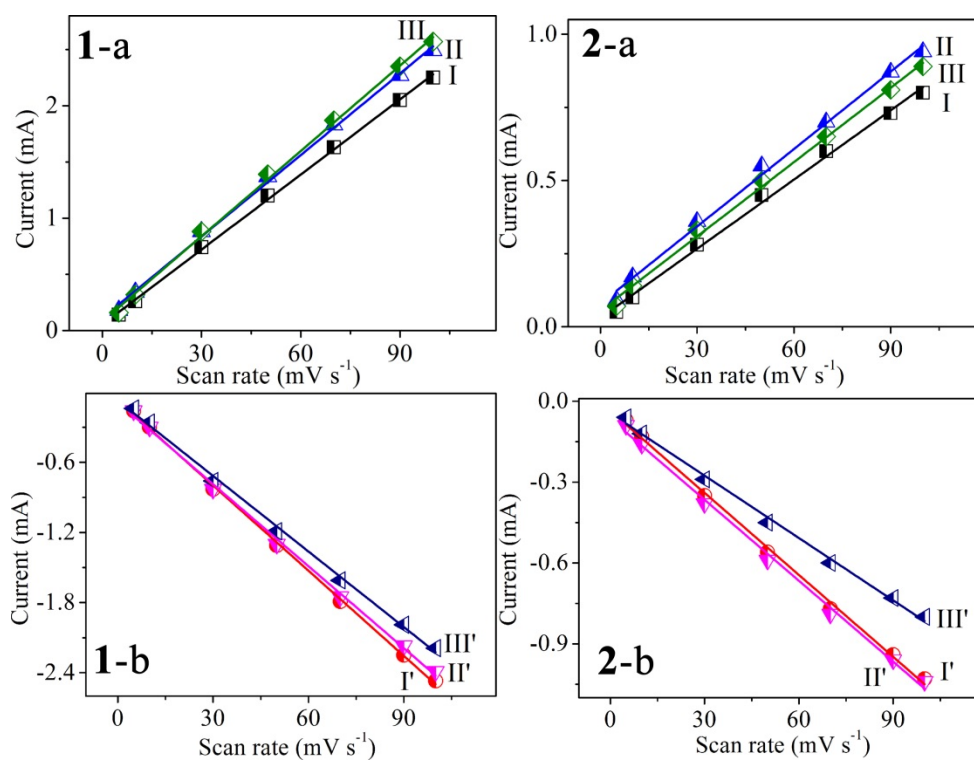


Figure S8. The plots of cathodic peak currents for **1**- and **2**-based electrodes vs. scan rates.

In order to demonstrate which section does contribute more for capacitance performance, the parent POM (**PMo@TBAB**) and the bare MOF particle (**Cu-MOF**) were prepared, and then **PMo@TBAB** and **Cu-MOF** were used as electrode materials to measure the capacitance performance, as shown in Figure S9.

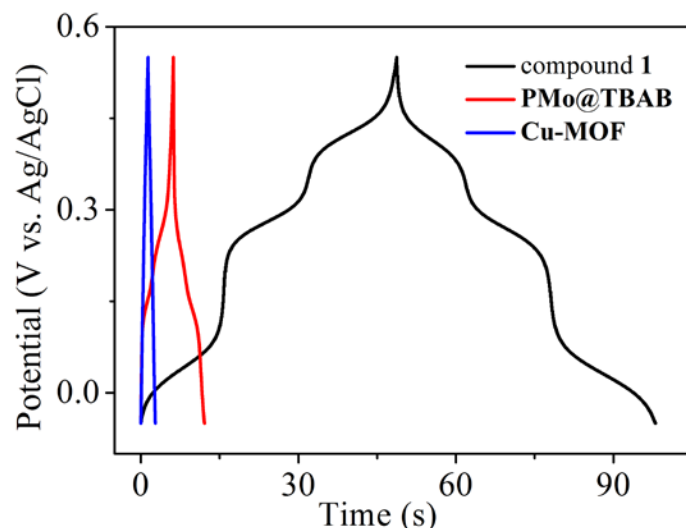


Figure S9. The comparison of capacitance performance of compound **1**, **PMo@TBAB** and **Cu-MOF**.

Synthesis of PMo@TBAB: Firstly, a solution of 0.1160 g (0.06 mmol) of PMo_{12} dissolving in 20 mL of distilled water was added to the solution of 5 mL of distilled water containing 0.0580 g (0.18 mmol) of tetrabutylammonium bromide (TBAB) under stirring, and a resulting suspension was filtrated, and the precipitate was collected, washed with distilled water three times, and dried in the oven at 80 °C for 5 h, then **PMo@TBAB** was obtained. Then **PMo@TBAB** was characterized by IR spectrum (Figure S9-1).

Synthesis of Cu-MOF: **Cu-MOF** was prepared by an identical synthesis method with compound **1** except that the POMs had not been added into the reaction system and the green color powder was collected, washed with distilled water three times, and dried in the oven at 80 °C for 5 h, then **Cu-MOF** can be obtained. Then **Cu-MOF** was characterized by IR spectrum (Figure S9-2).

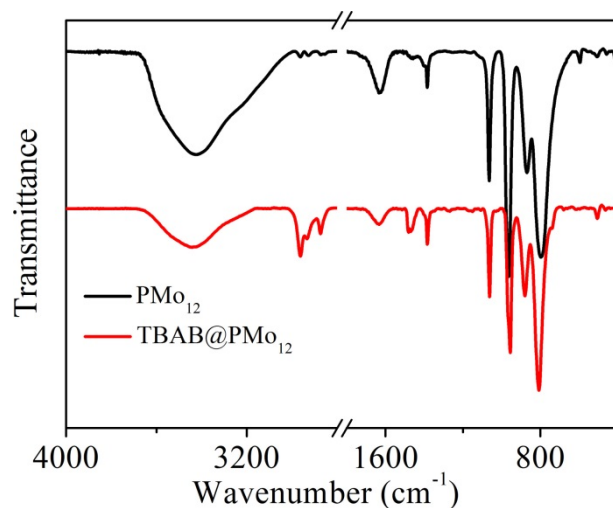


Figure S9-1. The IR spectra of PMo_{12} and TBAB@PMo_{12} .

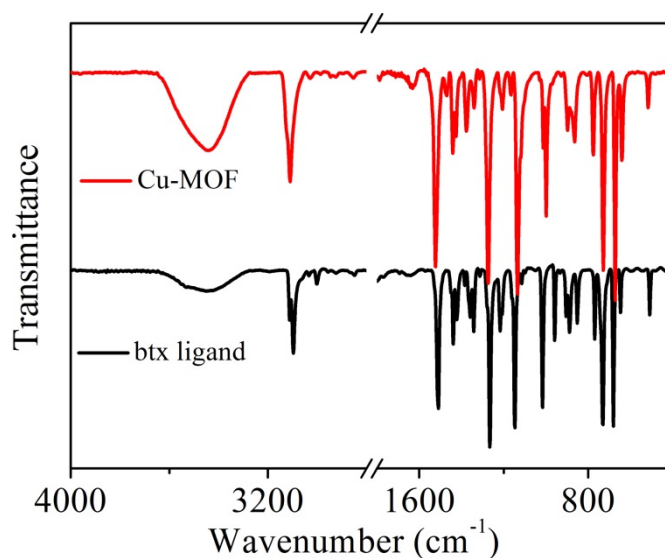


Figure S9-2. The IR spectra of btx ligand and Cu-MOF .

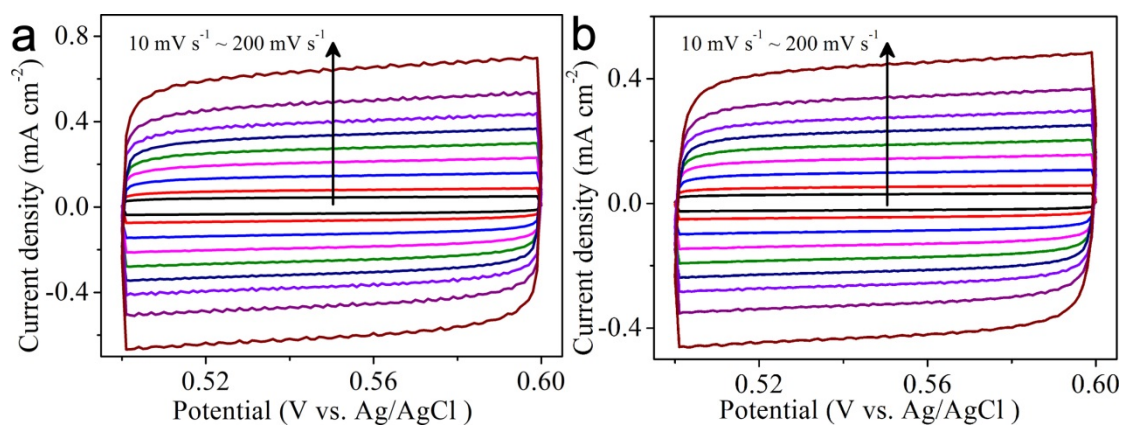


Figure S10. CV curves of **1** (a) and **2** (b) at different scan rates of 10, 20, 40, 60, 80, 100, 120, 150 and 200 mV s^{-1} .

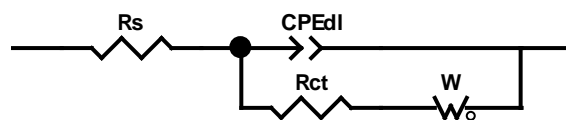


Figure S11. The proposed equivalent circuit for the electrochemical capacitor (R_s reflects the resistance of electrolyte and R_{ct} reflects the charge-transfer process).

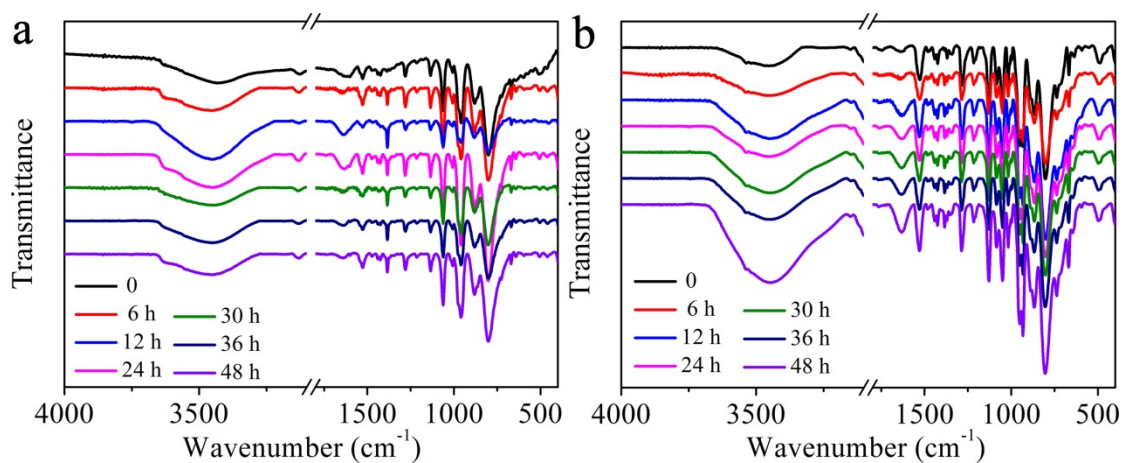


Figure S12. FTIR spectra of compounds **1** and **2** immersed in H_2SO_4 for 0, 6, 12, 24, 30, 36 and 48 h, respectively.

Table S1. Selected bond lengths (Å) and angles (°) for compound **1**.

Compound 1					
P-O(1A)	1.485(6)	Mo(1)-O(2B)	2.448(6)	N(3)-C(1)	1.314(7)
P-O(1A)#1	1.485(6)	Cu-N(1)	1.882(5)	N(3)-N(2)	1.351(7)
P-O(1B)#1	1.505(6)	Cu-N(1)#2	1.882(5)	N(3)-C(3)	1.467(7)
P-O(1B)	1.505(6)	Mo(3)-O(7)	1.653(4)	C(4)-C(6)	1.369(8)
P-O(2A)#1	1.541(6)	Mo(3)-O(9)	1.816(5)	C(4)-C(5)	1.379(8)
P-O(2A)	1.541(6)	Mo(3)-O(4)	1.826(4)	C(4)-C(3)	1.507(8)
P-O(2B)	1.578(6)	Mo(3)-O(8)	1.969(5)	C(5)-C(6)#3	1.389(9)
P-O(2B)#1	1.578(6)	Mo(3)-O(6)	2.005(5)	C(6)-C(5)#3	1.389(9)
Mo(1)-O(1)	1.647(4)	Mo(3)-O(2A)	2.424(6)	N(4)-C(9)	1.447(15)
Mo(1)-O(12)#1	1.828(5)	Mo(3)-O(1B)	2.491(6)	N(4)-C(11)	1.480(14)
Mo(1)-O(2)	1.832(5)	N(1)-C(1)	1.320(7)	N(4)-C(7)	1.827(17)
Mo(1)-O(3)	1.961(5)	N(1)-C(2)	1.356(8)	C(7)-C(8)	1.267(18)
Mo(1)-O(4)	1.969(4)	C(2)-N(2)	1.313(8)	C(11)-C(12)	1.436(16)
O(1A)-P-O(1A)#1	180.000(1)	O(1)-Mo(1)-O(12)#1	102.9(3)		
O(1A)-P-O(1B)#1	66.8(3)	O(1)-Mo(1)-O(2)	102.3(3)		
O(1A)#1-P-O(1B)#1	113.2(3)	O(12)#1-Mo(1)-O(2)	93.8(3)		
O(1A)-P-O(1B)	113.2(3)	O(1)-Mo(1)-O(3)	101.2(3)		
O(1A)#1-P-O(1B)	66.8(3)	O(12)#1-Mo(1)-O(3)	87.8(2)		
O(1B)#1-P-O(1B)	180.0(5)	O(2)-Mo(1)-O(3)	155.5(3)		
O(1A)-P-O(2A)#1	111.5(3)	O(1)-Mo(1)-O(4)	101.3(2)		
O(1A)#1-P-O(2A)#1	68.5(3)	N(4)-C(9)-C(10)	111.4(11)		
O(1B)#1-P-O(2A)#1	70.3(3)	N(1)-Cu-N(1)#2	180.000(1)		
O(1B)-P-O(2A)#1	109.7(3)	C(1)-N(1)-C(2)	103.3(5)		
O(1A)-P-O(2A)	68.5(3)	N(3)-C(3)-C(4)	111.9(5)		
O(1A)#1-P-O(2A)	111.5(3)	C(4)-C(5)-C(6)#3	120.5(6)		
O(1B)#1-P-O(2A)	109.7(3)	C(4)-C(6)-C(5)#3	120.1(6)		
Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1; #2 -x+1,-y+1,-z+2; #3 -x+2,-y,-z+2					

Table S2. Selected bond lengths (Å) and angles (°) for compound **2**.

Compound 2					
P-O(1B)	1.454(10)	Mo(1)-O(2B)	2.420(9)	C(17)-C(18)#5	1.371(14)
P-O(1B)#1	1.454(10)	Mo(1)-O(1A)	2.441(9)	C(17)-H(17)	0.9300
P-O(1A)#1	1.510(11)	Cu-N(4)	1.978(7)	C(18)-C(17)#5	1.371(14)
P-O(1A)	1.510(11)	Cu-N(10)	1.984(7)	C(18)-H(18)	0.9300
P-O(2B)#1	1.520(9)	Cu-N(1)	2.018(7)	C(22)-C(23)	1.361(13)
P-O(2B)	1.520(9)	Cu-N(7)	2.044(7)	C(23)-C(24)#6	1.361(15)
P-O(2A)#1	1.601(10)	Cu-O(1)	2.364(6)	C(23)-H(23)	0.9300
P-O(2A)	1.601(10)	C(3)-N(3)	1.467(12)	C(24)-C(23)#6	1.361(15)
Mo(1)-O(1)	1.672(6)	C(3)-C(10)#3	1.513(14)	C(24)-H(24)	0.9300
Mo(1)-O(4)	1.808(7)	C(3)-H(3A)	0.9700	N(2)-N(3)	1.326(11)
Mo(1)-O(5)	1.831(8)	C(3)-H(3B)	0.9700	N(5)-N(6)	1.316(11)
Mo(1)-O(3)	1.972(7)	C(10)-C(11)	1.377(13)	N(8)-N(9)	1.346(11)
Mo(1)-O(2)	1.980(8)	C(10)-C(3)#4	1.513(13)	N(11)-N(12)	1.344(10)
O(1)-Mo(1)-O(4)	102.1(4)	Mo(3)-O(7)-Mo(2)	135.3(4)		
O(1)-Mo(1)-O(5)	104.2(4)	Mo(3)-O(8)-Mo(3)#2	180.00(5)		
O(4)-Mo(1)-O(5)	94.9(4)	N(3)-C(3)-C(10)#3	112.2(8)		
O(1)-Mo(1)-O(3)	96.8(3)	N(3)-C(3)-H(3A)	109.2		
O(4)-Mo(1)-O(3)	87.5(3)	C(11)-C(10)-C(9)	117.1(10)		
O(5)-Mo(1)-O(3)	157.8(4)	C(11)-C(10)-C(3)#4	121.1(8)		
O(1)-Mo(1)-O(2)	98.8(4)	C(9)-C(10)-C(3)#4	121.7(9)		
O(4)-Mo(1)-O(2)	157.8(4)	C(18)#5-C(17)-H(17)	118.4		
O(5)-Mo(1)-O(2)	87.1(3)	C(17)#5-C(18)-C(16)	119.7(10)		
O(3)-Mo(1)-O(2)	82.6(3)	C(17)#5-C(18)-H(18)	120.2		
O(1)-Mo(1)-O(2B)	158.6(4)	C(24)#6-C(23)-C(22)	120.4(10)		
O(4)-Mo(1)-O(2B)	97.2(4)	C(24)#6-C(23)-H(23)	119.8		
O(5)-Mo(1)-O(2B)	64.6(4)	C(22)-C(24)-C(23)#6	121.6(10)		
Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z; #2 -x, -y+1, -z; #3 -x+1, y+1/2, -z+1/2; #4 -x+1, y-1/2, -z+1/2; #5 -x+1, -y, -z; #6 -x, -y, -z					

Table S3. Summary of the typical MOF-based and POM-based supercapacitor electrodes at 3-electrode configuration.

No.	Electrode	Current density	Specific capacitance	Ref.
1	HT-RGO-PMO ₁₂ (HT-RGO)	1 A g ⁻¹	276 (215) F g ⁻¹	Phys. Chem. Chem. Phys. 16(2014)20411
2	AC/PMO ₁₂ O ₄₀	2 A g ⁻¹	183 F g ⁻¹	Electrochem. Commun. 24(2012)35.
3	CNTs/PDDA/[P ₂ V-W ₁₇ O ₆₂] ⁸⁻	0.2 A g ⁻¹	82 Fg ⁻¹	J. Solid State Electr. 17(2013)1631
4	HPW/RGO	2 A g ⁻¹	153.8 F g ⁻¹	Compos. Part B-Eng. 121(2017)75
5	PPy-PMO ₁₂ /rGO	2 A g ⁻¹	252 F g ⁻¹	Chem. Commun. 51(2015)12377
6	AC@PMO ₁₂ O ₄₀	1 mV s ⁻¹	223 F g ⁻¹	J. Power Sources 326(2016)569
7	MWCNT-PMO ₁₂	25 mV s ⁻¹	106.9 F cm ⁻³	Electrochem. Commun. 43(2014)60
8	Na ₆ V ₁₀ O ₂₈	2 A g ⁻¹	143 Fg ⁻¹	ChemPhysChem 15(2014)2162
9	PEDOT.[PV ₂ Mo ₁₀ O ₄₀]; PEDOT.[PMO ₁₂ O ₄₀]	100 mV s ⁻¹	70; 140 F g ⁻¹	Electrochim. Acta 49(2004)861
10	Co8-MOF-5	25 mV s ⁻¹	0.49 F g ⁻¹	Mater. Lett. 68(2012)126
11	Cu-CATNWAs	0.5 A g ⁻¹	202 F g ⁻¹	Adv. Funct. Mater. 2017, 1702067

12	ZIF-67	hierarchical flower-like structure	1 A g ⁻¹	188.7 F g ⁻¹	RSC Adv. 5(2015)58772
13	UiO-66		5 mV s ⁻¹	1144 F g ⁻¹	RSC Adv. 5(2015)17601
14	ZIF-67		0.5 A g ⁻¹	168.3 F g ⁻¹	Nano-Micro Lett. 9(2017)43
15	Layered Co-MOF nano sheets	structural	1 A g ⁻¹	2564 F g ⁻¹	Chem-A Eur. J. 23(2017)631
16	ZIF-67-CC		10 mV s ⁻¹	1.47 mF cm ⁻²	J. Am. Chem. Soc 137(2015)4920
17	V ^{IV} (O)(bdc)		0.5 A g ⁻¹	572.1 F g ⁻¹	Small 2018, 1801815
18	N-NFC		1 A g ⁻¹	387.3 F g ⁻¹	Nanoscale 11(2019)2492
19	Cu@BTC-120		1.5 A g ⁻¹	228 F g ⁻¹	Appl. Surf. Sci. 460(2018)33
20	ZIF-8; ZIF-8@ZIF-67	ZIF-67;	2 A g ⁻¹	239; 119; 270 F g ⁻¹	J. Am. Chem. Soc. 137(2015)1572

21	MOF-5	0.05 A g ⁻¹	90 F g ⁻¹	ACS Mater. Interfaces 7(2015)3655
22	[Cu ₂ (C ₁₂ H ₁₂ N ₆) ₄ (P ^{VI} Mo ^V ₃ O ₃₉)]	5 A g ⁻¹	146.7 F g ⁻¹	This work
23	[Cu ^I H ₂ (C ₁₂ H ₁₂ N ₆)(P ^{VI} Mo ₁₂ O ₄₀)]·[(C ₆ H ₁₅ N)(H ₂ O) ₂]	5 A g ⁻¹	239.2 F g ⁻¹	This work

Table S4. The calculated values of R_s and R_{ct} through the proposed equivalent circuit.

Compounds	R _s (Ω)	R _{ct} (Ω)
1	4.93	3.33
2	5.08	6.26