Supporting Information

Fabrication and Electrochemical Performance of Unprecedented POM-Based Metal-Carbene Frameworks

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Experimental Section

All chemical materials were commercially purchased and used without further purification. The Elemental analyses(C, H, and N) were measured by the Perkin-Elmer 2400 CHN elemental analyzer. The FT-IR was obtained from the Alpha Centaurt FT/IR spectrometer with KBr pellets. The power X-ray diffraction (PXRD) patterns were scanned by the Rigaku D/MAX 2500 V XRD diffractometer with Cu-Kα radiation. The TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Galvanostatic charge/discharge cycles were performed on a LAND 2001A Battery Tester between 0.01 and 3.00 V at various current densities. Cyclic voltammetry measurements were carried out on an electrochemical workstation (CHI750D) in the potential range of 0.01 - 3.00 V vs. Li^+/Li at a scan rate of 0.1 mV s^{-1}.

Synthesis of [Cu$_{10}$(H$_3$trz)$_4$(Htrz)$_4$] (HPW$_{12}$O$_{40}$) (1). $H_3PW_{12}O_{40}$ (300 mg, 0.15 mmol), $Cu(CH_3COO)_2$ (150 mg, 0.75 mmol) and 1,2,4-trz ligand (80 mg, 1.16 mmol) were dissolved in distilled water (10 mL) with stirring for 30 min at room temperature, and pH value was adjusted to *ca.* 1.5 by 1 M HCl. The resulting solution was transferred and sealed in a 20 mL Teflon-lined stainless steel reactor and heated at 180 °C for 5 days. After the autoclave was cooled to room temperature at 10 ºC·h^{-1}, the black block crystals of **1** were obtained, and then washed with distilled water and air-dried (yield: 46% based on Cu). Elemental analysis: Anal. calcd for $C_{16}H_{17}Cu_{10}N_{24}O_{40}PW_{12}$ (4058.08): C 4.75, H 0.42 and N 8.28 %; Found C 4.70, H 0.51 and N 8.26 %. IR (KBr pellet, cm^{-1}): 3434 (*m*), 3106 (*w*), 1633 (*m*), 1484 (*m*), 1284 (*m*), 1164 (*m*), 1056 (*s*), 941 (*s*), 804 (*vs*), 653 (*s*), 514 (*m*).

Synthesis of [Cu$_{10}$(H$_3$trz)$_4$(Htrz)$_4$] (H$_2$SiW$_{12}$O$_{40}$) (2). The preparation of **2** was similar to **1**, except that the $H_3PW_{12}O_{40}$ was replaced by $H_4SiW_{12}O_{40}$. The black block crystals of **2** (yield: 43% based on Cu) were successfully isolated. Elemental analysis: Anal. calcd for $C_{16}H_{18}Cu_{10}N_{24}O_{40}SiW_{12}$ (4056.21): C 4.74, H 0.45 and N 8.26%; Found C 4.71, H 0.49 and N 8.21%. IR (KBr pellet, cm^{-1}): 3434 (*m*), 3104 (*w*), 1484 (*m*), 1284 (*m*), 1164 (*m*), 929 (*m*), 887 (*s*), 792 (*vs*), 653 (s), 530 (*m*).

X-ray Crystallographic Measurements. Crystallographic data for **1** and **2** were collected on the Bruker SMART-CCD diffractmeter with Mo-Kα radiation (λ =

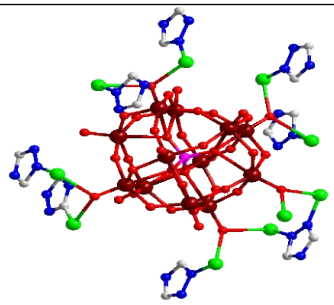
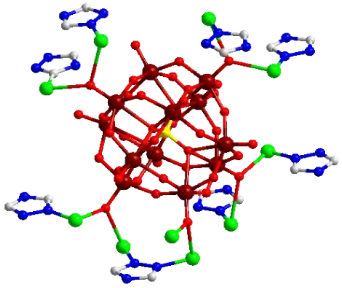
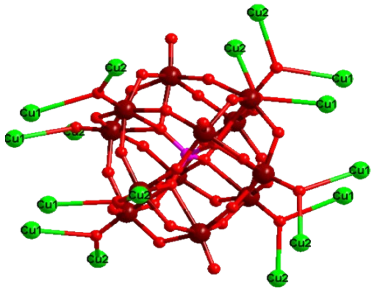
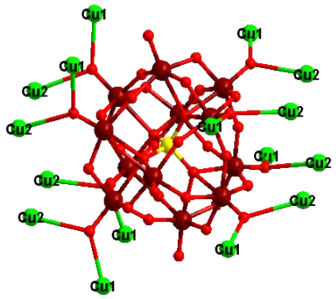
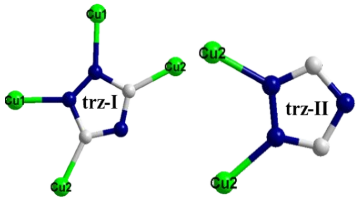
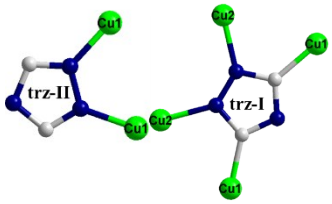
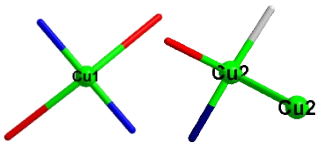
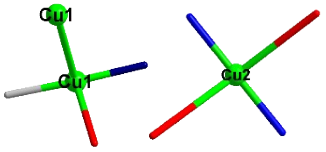
0.71073 Å) at room temperature. The structures of **1** and **2** were resolved and refined by the direct method and refined full-matrix last squares on F^2 through the *SHELXTL* and *WINGX* software package.[1] All non-hydrogen atoms were refined anostropically and the some ADP and NDP error atoms in **1** and **2** were refined through the ISOR, DELU and SIMU command. The crystal data and selected bond lengths and angles of **1** and **2** are listed in Tables S2-S4 (Supporting information). The CCDC reference numbers of **1** and **2** are 1515264 and 1515265, respectively.

Battery analyses. The mixture of the samples (**1/2**/$(NBu_4)_3[PW_{12}O_{40}]$/$(NBu_4)_4[SiW_{12}O_{40}]$), Super-P carbon and poly-vinylidene fluoride (PVDF) at a weight ratio 7:2:1 was passed on the pure Cu foil and followed by drying in vacuum at 50°C for 24 h. The loading mass of electroactive materials in electrode slurry is ~2 $mg \cdot cm^{-2}$. The testing coin cells were assembled in an argon-filled glovebox with the working electrode as-fabricated, metallic lithium foil as the counter electrode, and 1.0 M $LiPF_6$ in ethylene carbonate/diethyl carbonate (1:1 v/v) as the electrolyte.

References

[1] (*a*) G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Refinement, University of Göttingen, Germany.* 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Solution, University of Göttingen, Germany*. 1997.

Table S1. Structural information of POMs and Cu ions and asymmetric unit of compounds **1** and **2**.

Compound **1**	Compound **2**
	
$[Cu_{10}(H_3trz)_4(Htrz)_4](HPW_{12}O_{40})$	$[Cu_{10}(H_3trz)_4(Htrz)_4](H_2SiW_{12}O_{40})$
	
	
	

* Htrz = trz-I and H_3trz= trz-II, trz = 1,2,4-triazole

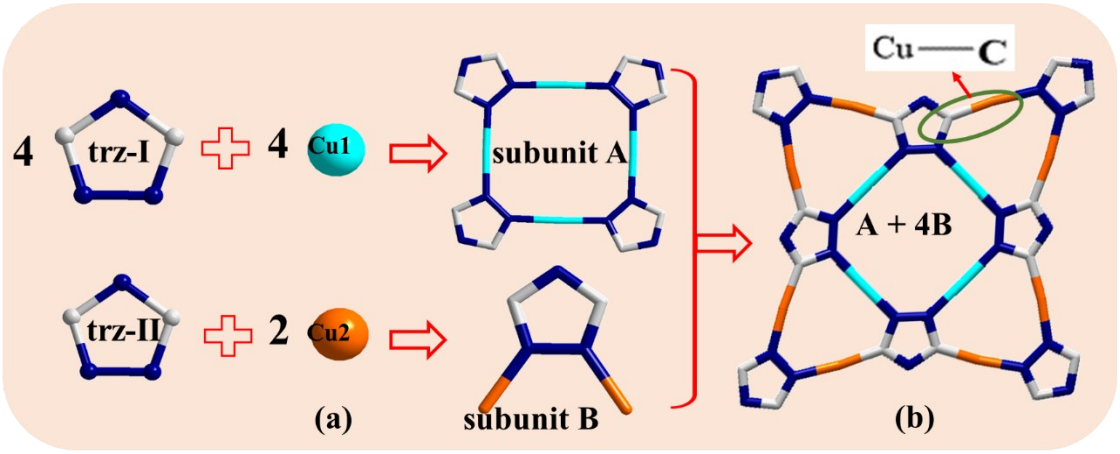


Figure S1. Representation of the $[Cu_{12}(trz)_8]^{4+}$ metallmacrocycles generated by the subunit A subunits B copper-carbon bonds in compounds **1** and **2**.

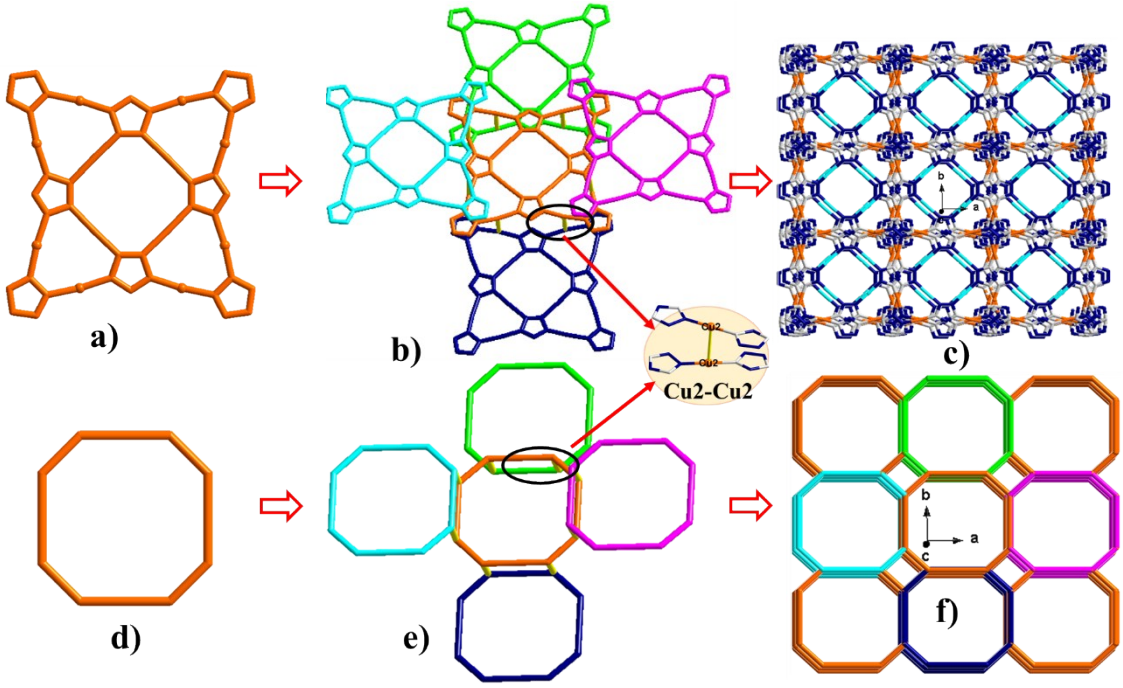


Figure S2. Ball/stick and topology representation of each $[Cu_{12}(trz)_8]^{4+}$ metallmacrocycles connecting the surrounding five $[Cu_{12}(trz)_8]^{4+}$ metallmacrocycles to construct the 3D metal-organic frameworks *via* the Cu2-Cu2 interaction.

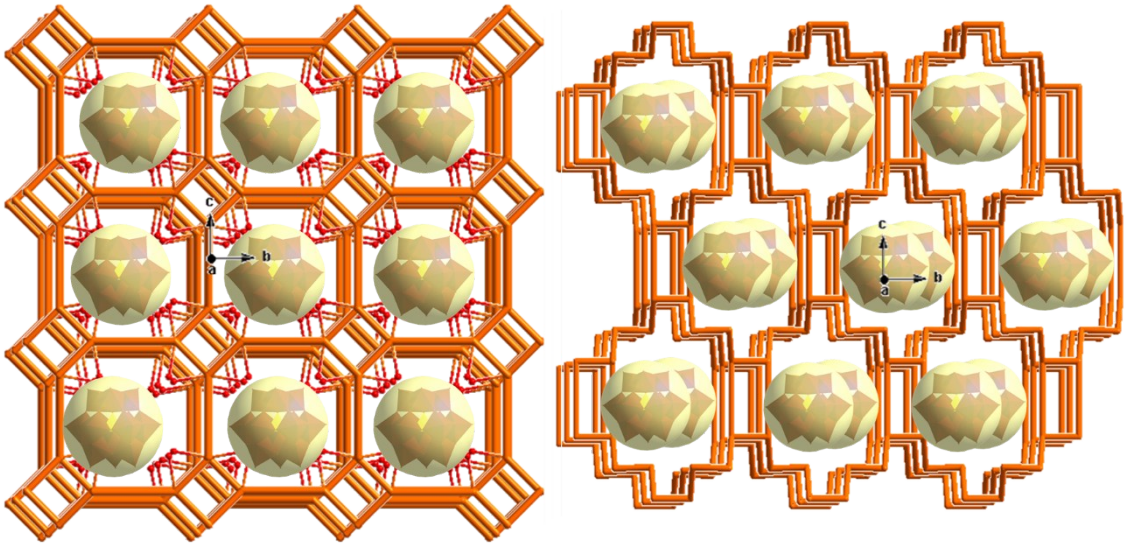


Figure S3. Combined ball-stick and topological representation of the POM clusters inserted into the 3D metal-organic carbene frameworks *via* the Cu-O interaction compound **1** and **2**.

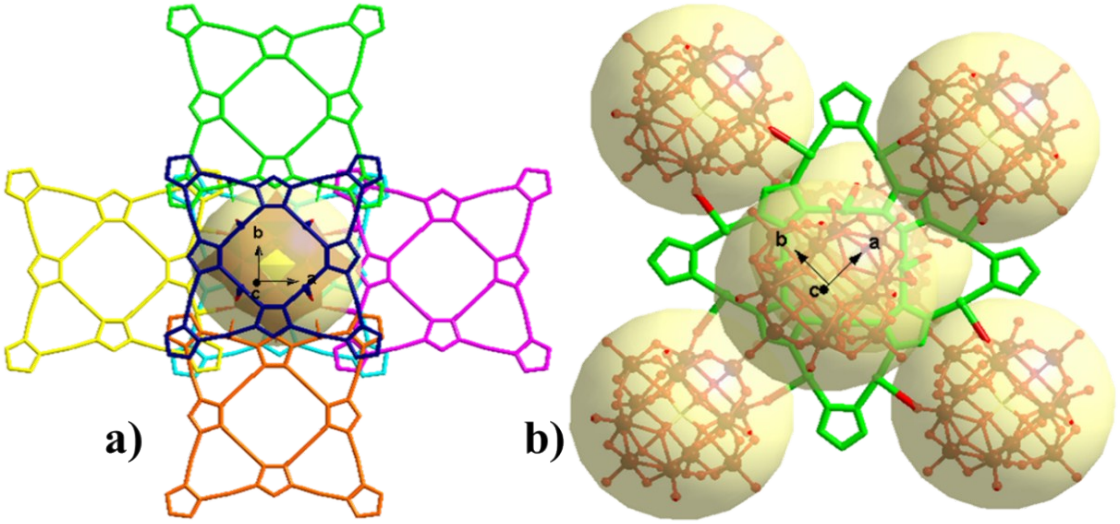


Figure S4. The Combined ball-stick representation of (a) each POM clusters surrounded by six $[Cu_{12}(trz)_8]^{4+}$ metallmacrocycles and (b) each $[Cu_{12}(trz)_8]^{4+}$ metallmacrocycles also surrounded by six POM clusters.

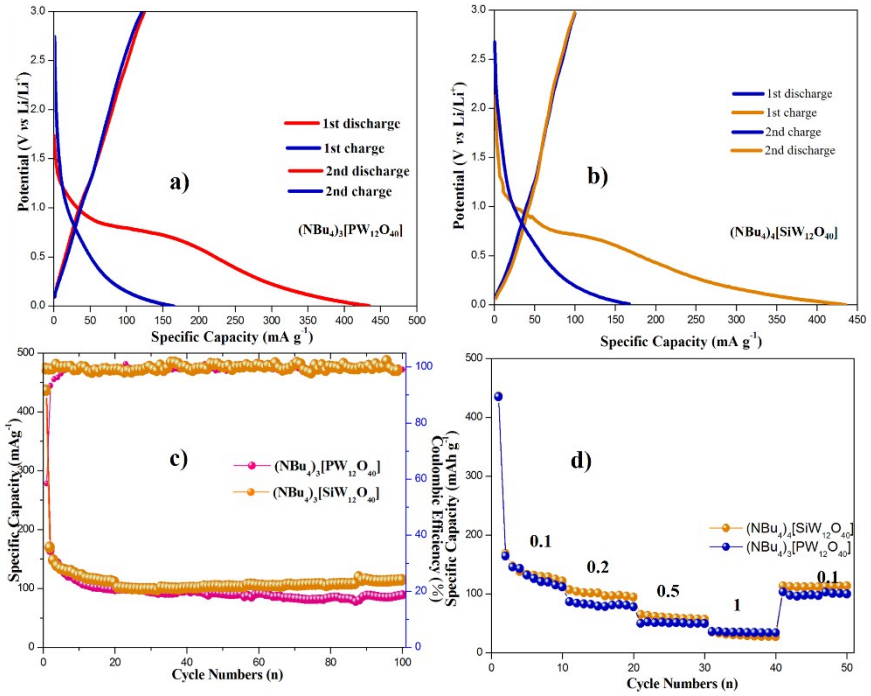


Figure S5. The charge-discharge curves of (a) $(NBu_4)_3[PW_{12}O_{40}]$ and (b) $(NBu_4)_4[SiW_{12}O_{40}]$ anodes during the initial two cycles at a current density100 $mA \cdot g^{-1}$. (c) The discharge capacity and the coulombic efficiency of $(NBu_4)_3[PW_{12}O_{40}]$ and $(NBu_4)_4[SiW_{12}O_{40}]$ anodes at a current density 100 $mA \cdot g^{-1}$; (d) Rate performance of $(NBu_4)_3[PW_{12}O_{40}]$ and $(NBu_4)_4[SiW_{12}O_{40}]$ anodes at current densities of 100 $mA \cdot g^{-1}$ to 1 $A \cdot g^{-1}$.

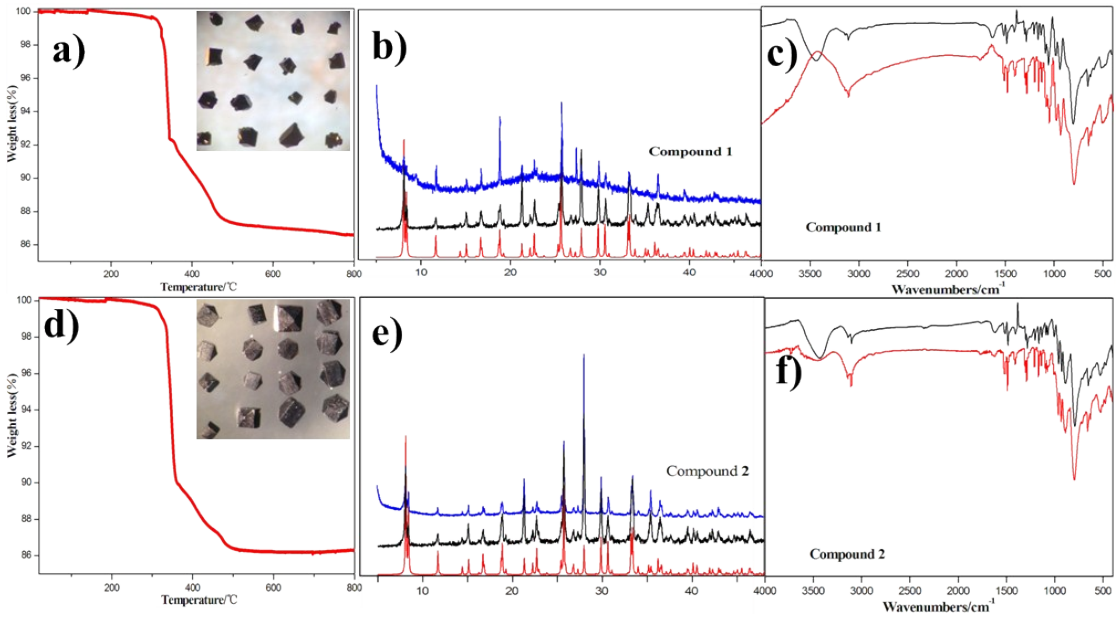


Figure S6. The TG curve of (a) **1** and (d) **2**; the simulative (red), experimental (room temperature, black) and experimental (heated, blue) PXRD patterns for (b) **1** and (e) **2**; the room temperature (black) and heated (red) IR spectra of (c) **1** and (f) **2**, respectively.

Table S2. Crystallographic data and structural refinements for **1** and **2**.

Compounds	Compound **1**	Compound **2**
Chemical formula	$C_{16}H_{17}Cu_{10}N_{24}O_{40}PW_{12}$	$C_{16}H_{18}Cu_{10}N_{24}O_{40}SiW_{12}$
CCDC no.	1515264	1515265
Formula weight	4058.08	4056.21
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	tetragonal	tetragonal
Space group	*I41/amd*	*I41/amd*
a(Å)	21.0740(19)	21.0434(8)
b(Å)	21.0740(19)	21.0434(8)
c(Å)	12.766(2)	12.7594(9)
α(°)	90	90
β(°)	90	90
γ(°)	90	90
V(Å^3) / Z	5669.6(14)/4	5650.2(6)/ 4
Density (g·cm^{-3})	4.744	4.756
Abs coeff. (mm^{-1})	30.210	30.224
F(000)	7140.0	7136.0
Data collect θ range	1.87-25.00 °	1.867 - 25.000°
Reflns collected	13238	13568
Independent reflns	1334	1327
Rint	0.0636	0.0356
Data/restraints/parameters	1334/ 24/ 95	1327/ 0/ 131
Goodness-of-fit on F^2	1.116	1.162
Final R indices [I > 2δ(I)]	R_1 = 0.0414, wR_2 = 0.1070	R_1 = 0.0221, wR_2 = 0.0575
R indices (all data)	R_1 = 0.0501, wR_2 = 0.1176	R_1 = 0.0235, wR_2 = 0.0581
Largest diff. peak and hole(e.Å^{-3})	12.801 and -2.354	3.386 and -1.167

$R_1 = \Sigma(||F_0|-|F_c||)/\Sigma|F_0|$, $wR_2 = \Sigma w(|F_0|^2-|F_c|^2)^2/\Sigma w\,(|F_0|^2)^2]^{1/2}$

Table S3. Bond lengths [Å] and angles [°] for compound **1**.

Compound 1			
Bonds	Lengths	Bonds	Lengths
C(1)-Cu(2)	1.885(10)	O(7)-W(2)#2	2.424(6)
N(1)-Cu(2)	1.901(11)	O(7)-W(2)	2.424(6)
N(2)-Cu(1)	1.968(14)	O(7)-W(1)	2.428(6)
O(2)-W(2)	1.914(8)	P(1)-O(7)#4	1.546(10)
O(2)-W(1)	1.934(8)	P(1)-O(7)#5	1.546(9)

O(3)-W(2)#3	1.914(8)	P(1)-O(7)#3	1.546(10)
O(3)-W(1)	1.924(8)	O(1)-W(1)	1.687(6)
O(5)-W(2)	1.718(6)	O(4)-W(2)#6	1.908(6)
O(6)-W(2)#2	1.912(7)	O(4)-W(2)	1.908(6)
O(6)-W(2)	1.912(7)	Cu(1)-N(2)#1	1.968(14)
O(7)-P(1)	1.546	Cu(2)-Cu(2)#7	3.002(4)
W(1)-O(2)#2	1.934(8)	W(1)-O(3)#2	1.924(8)
Bonds	Angles	Bonds	Angles
O(7)#4-P(1)-O(7)#5	109.7(9)	O(3)#2-W(1)-O(7)	83.6(3)
O(7)#4-P(1)-O(7)	109.7(3)	O(2)#2-W(1)-O(7)	72.9(3)
O(7)#5-P(1)-O(7)	109.1(2)	O(2)-W(1)-O(7)	72.9(3)
O(7)#4-P(1)-O(7)#3	109.1(7)	O(5)-W(2)-O(4)	101.3(3)
O(7)#5-P(1)-O(7)#3	109.7(9)	O(5)-W(2)-O(6)	102.8(3)
O(7)-P(1)-O(7)#3	109.7(3)	O(4)-W(2)-O(6)	88.7(3)
N(2)#1-Cu(1)-N(2)	177.7(9)	O(5)-W(2)-O(3)#3	101.3(3)
C(1)-Cu(2)-N(1)	171.9(5)	O(4)-W(2)-O(3)#3	85.5(3)
C(1)-Cu(2)-Cu(2)#7	91.7(3)	O(6)-W(2)-O(3)#3	155.9(3)
N(1)-Cu(2)-Cu(2)#7	93.1(4)	O(5)-W(2)-O(2)	101.5(3)
O(1)-W(1)-O(3)	102.2(3)	O(4)-W(2)-O(2)	157.0(3)
O(1)-W(1)-O(3)#2	102.2(3)	O(6)-W(2)-O(2)	88.6(3)
O(3)-W(1)-O(3)#2	86.7(5)	O(3)#3-W(2)-O(2)	87.7(4)
O(1)-W(1)-O(2)#2	101.5(3)	O(5)-W(2)-O(7)	173.0(4)
O(3)-W(1)-O(2)#2	156.3(4)	O(4)-W(2)-O(7)	84.2(2)
O(3)#2-W(1)-O(2)#2	88.0(4)	O(6)-W(2)-O(7)	72.7(2)
O(1)-W(1)-O(2)	101.5(3)	O(3)#3-W(2)-O(7)	83.4(3)
O(3)-W(1)-O(2)	88.0(4)	O(2)-W(2)-O(7)	73.2(3)
O(3)#2-W(1)-O(2)	156.3(4)	O(1)-W(1)-O(7)	172.0(3)
O(2)#2-W(1)-O(2)	87.6(5)	O(3)-W(1)-O(7)	83.6(3)

#1 y+1/4,x-1/4,-z+1/4; #2 -x+1,y,z; #3 -y+3/4,-x+3/4,-z+5/4; #4 y+1/4,x-1/4,-z+5/4; #5 -x+1,-y+1/2,z; #6 x,-y+1/2,z; #7 x,-y,-z

Table S4. Bond lengths [Å] and angles [°] for compound **2**.

Compound 2			
Bonds	Lengths	Bonds	Lengths
C(1)-Cu(1)	1.883(7)	O(5)-Si(1)	1.629(7)
N(1)-Cu(1)	1.890(6)	O(5)-W(1)	2.340(5)
N(4)-Cu(2)	1.967(9)	O(5)-W(1)#5	2.340(5)
O(2)-W(1)#4	1.9081(17)	O(5)-W(2)	2.354(7)
O(2)-W(1)	1.9081(17)	O(6)-W(1)	1.911(5)

O(3)-W(2)	1.701(8)	O(6)-W(2)#6	1.929(5)
O(4)-W(1)	1.921(5)	O(7)-W(1)	1.717(5)
O(4)-W(2)	1.939(5)	O(10)-W(1)	1.910(3)
Si(1)-O(5)#8	1.629(7)	O(10)-W(1)#5	1.910(3)
Cu(1)-Cu(1)#2	2.996(2)	Si(1)-O(5)#6	1.629(7)
Cu(2)-N(4)#9	1.967(9)	Si(1)-O(5)#7	1.629(7)
W(2)-O(6)#6	1.929(5)	W(2)-O(4)#5	1.939(5)

Bonds	Angles	Bonds	Angles
O(5)-Si(1)-O(5)#6	109.9(2)	O(7)-W(1)-O(4)	99.4(2)
O(5)-Si(1)-O(5)#7	108.5(5)	O(2)-W(1)-O(4)	159.0(3)
O(5)#6-Si(1)-O(5)#7	109.9(2)	O(10)-W(1)-O(4)	89.9(3)
O(5)-Si(1)-O(5)#8	109.9(2)	O(6)-W(1)-O(4)	87.6(2)
O(5)#6-Si(1)-O(5)#8	108.5(5)	O(7)-W(1)-O(5)	172.0(2)
O(5)#7-Si(1)-O(5)#8	109.9(2)	O(2)-W(1)-O(5)	85.1(3)
C(1)-Cu(1)-N(1)	171.6(3)	O(10)-W(1)-O(5)	73.7(2)
C(1)-Cu(1)-Cu(1)#2	91.4(2)	O(6)-W(1)-O(5)	84.36(19)
N(1)-Cu(1)-Cu(1)#2	93.1(2)	O(4)-W(1)-O(5)	74.5(2)
N(4)-Cu(2)-N(4)#9	177.7(5)	O(3)-W(2)-O(6)#6	100.9(2)
O(7)-W(1)-O(2)	101.4(3)	O(3)-W(2)-O(6)#10	100.9(2)
O(7)-W(1)-O(10)	101.6(3)	O(6)#6-W(2)-O(6)#10	85.9(3)
O(2)-W(1)-O(10)	89.0(3)	O(3)-W(2)-O(4)	101.0(2)
O(7)-W(1)-O(6)	100.7(2)	O(6)#6-W(2)-O(4)	88.2(2)
O(2)-W(1)-O(6)	85.6(2)	O(6)#10-W(2)-O(4)	158.0(2)
O(10)-W(1)-O(6)	157.7(2)	O(3)-W(2)-O(4)#5	101.0(2)
O(6)#6-W(2)-O(5)	84.52(19)	O(6)#6-W(2)-O(4)#5	158.0(2)
O(6)#10-W(2)-O(5)	84.52(19)	O(6)#10-W(2)-O(4)#5	88.2(2)
O(4)-W(2)-O(5)	73.83(17)	O(4)-W(2)-O(4)#5	89.4(3)
O(4)#5-W(2)-O(5)	73.83(17)	O(3)-W(2)-O(5)	172.6(3)

#1 -x,-y+1,-z; #2 x,-y+1,-z; #3 -y+3/4,-x+3/4,-z+1/4; #4 -x, y, z; #5 x,-y+1/2,z; #6 y-1/4,x+1/4,-z+3/4; #7 -x,-y+1/2,z; #8 -y+1/4,-x+1/4,-z+3/4; #9 y-1/4,x+1/4,-z-1/4; #10 y-1/4,-x+1/4,-z+3/4