ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Surfactant-assisted Synthesis and Electrochemical Properties of

Unprecedented Polyoxometalate-constituting Metal-Organic

Nanocaged Framework

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Section 1 The basic strategies for constructing POM-based cage structure

Ligands	Metal	Units		POMs-based MOFs		Ref.
	Ag	14 Å×12 Å	(µ _{1,4})		POM- containing double ring	1
	Ag	7.6Å×3.2Å	(µ _{1,2})		POM- Connecting ring	1
About 60 degrees	Ag	8.8Å×7.7Å	(µ _{1,2})		POM- Connecting ring	2
like mode (μ _{1,2})	Cu	(15.5Å×15.5Å)	(μ _{1,2}) or (μ _{1,4})		POM- containing triple ring	4
	Cu	15.5Å×15.5Å	(μ _{1,2}) or (μ _{1,4})		POM- containing double ring	5
About 150 degrees Pyrazole-like modes (μ _{1,4})	Zn	10.4Å×10.4Å	(µ _{1,4})		POM- Containing cage	6
1,2,4-triazole	Zn	0 10.1Å×10.1Å 0	(μ _{1,2}) + (μ _{1,4})		POM- constituting cage	This wor k

 Table S1 Structural summary of representative POMOFs using 1,2,4-triazole ligand.



Scheme S1 The potential coordination modes of 1,2,4-triazole ligand (μ_1 , $\mu_{1,2}$, $\mu_{1,4}$ and $\mu_{1,2,4}$).



Scheme S2 The design strategy for POM-constituting molecular cage.

Section 2 Experimental Section

I. Materials and General Methods

All reagents were commercially purchased and used as received, unless otherwise noted. Elemental analyses for C, H, N were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The IR spectrum was obtained on an Alpha Centaurt FT/IR spectrometer with KBr pellet in the 400-4000 cm⁻¹ region. The XRPD patterns were obtained with a Rigaku D/max 2500V PC diffractometer with Cu-Kα radiation, the scanning rate is 4°/s, 20 ranging from 5-50°. The thermogravimetric analyses (TGA) were carried out on a Perkin-Elmer-7 thermal analyzer at a heating rate of 10 °C·min⁻¹. The simulated PXRD pattern was obtained based on the single-crystal data by diffraction crystal module of the Mercury (Hg) program version 3.3 available free of charge via the Internet at <u>http://www.iucr.org/</u>. SEM images were taken using Phenom ProX with an accelerating voltage of 15 kV. XPS analyses were performed on thermo ESCALAB 250 spectrometer with an Mg–Ka achromatic X-ray source.

II. Synthesis schemes and method for Zn-POMCF and Zn-MOF

Synthesis of $[Zn_{12}(trz)_{12}(0H)_8][VW_{12}O_{40}]$ -4H₂O (Zn-POMCF): A surfactant aqueous solution was prepared by adding 40 mg PEG 1500 in 10 ml of water assisted by ultrasound. Then H₄SiW₁₂O₄₀·xH₂O (300 mg, 0.104 mmol) or H₃PW₁₂O₄₀·xH₂O (300 mg, 0.104 mmol), ZnNO₃·6H₂O (200 mg, 0.672 mmol), trz ligand (80 mg, 1.158 mmol), NH₄VO₃ (36mg, 0.308 mmol) was following dispersed into the surfactant aqueous solution and the pH value of mixture was adjusted to 4.0 with 1M NaOH. Solution was mixed under vigorous stirring for approximately 30 min, transferred and sealed in a 23 mL Teflon lined stainless-steel container maintaining at 170 °C for 3 days then cooled to room temperature at a rate of 10°C·h⁻¹. The light-yellow block crystals suitable for X-ray crystallography were obtained, and then washed with distilled water and air-dried (yield: 36% based on Zn). Elemental analysis: Anal. calcd for C₂₄H₄₀N₃₆Zn₁₂VW₁₂O₅₂ (4706.5): C 6.13, H 0.86, N 10.71%; Found C 6.12, H 0.91, N 10.68%. IR (Figure S11a, KBr pellets, v/cm⁻¹): 3446 (VS), 1620 (S), 1512 (S), 1425 (M), 1387 (W), 1328 (M), 1273 (S), 1208 (W), 1166 (S), 1090 (S), 1004 (M), 917 (S), 798 (VS), 657 (S).

Synthesis of [Zn₂(trz)₄] (Zn-MOF): A surfactant aqueous solution was prepared by adding 40 mg PEG 1500 in 10 ml of water assisted by ultrasound. Then ZnNO₃·6H₂O (200 mg, 0.672 mmol), trz ligand (80 mg, 1.158 mmol) was following dispersed into the surfactant aqueous solution and the pH value of mixture was adjusted to 4.0 with 1M NaOH. Solution was mixed under vigorous stirring for approximately 30 min, transferred and sealed in a 23 mL Teflon lined stainless-steel container maintaining at 170 °C for 3 days then cooled to room temperature at a rate of 10°C·h⁻¹. The colourless block crystals suitable for X-ray crystallography were obtained, and then washed with distilled water and air-dried (yield: 48% based on Zn). Elemental analysis: Anal. calcd for $C_8H_8N_{12}Zn_2$ (402.99): C 23.84, H 2.00, N 41.71%; Found C 23.83, H 2.09, N 41.70%. IR (Figure S11b, KBr pellets, v/cm⁻¹): 3446 (VS), 3122 (S), 2488 (W), 2423 (W), 1762 (W), 1632 (W), 1507 (VS), 1458 (VS), 1382 (VS), 1312 (VS), 1279 (VS), 1214 (W), 1160 (S), 1079 (S), 1008 (S), 889 (M), 813 (W), 661 (S). Synthesis of (n-Bu₄N)₄[VW₁₂O₄₀]: The (n-Bu₄N)₄[VW₁₂O₄₀] were synthesized according to the previous report.⁷ Typically, to a solution of 8.3 g Na_2WO_4 ·2H₂O and 2.9 g NH_4VO_3 in 35 ml of warm water was added 400 ml of CH₃CN. To the mixture consisting of two liquid-layers was added dropwise 65 ml of conc. HCl with continuous stirring. The resultant turbid solution was

heated at 70 °C for 24 h. After cooling to room temperature, the precipitate was filtered off. To the filtrate was added 15 g of n-Bu₄NBr to precipitate a white salt. The salt was collected by filtration, and washed with water and ethanol, and air-dried.

Unit (mg)	SiW ₁₂ /PW ₁₂	Zn(NO ₃) ₂	1,2,4-trz	NH_4VO_3 or $NaVO_3$	surfactant*	Product
No.1	300	200	80	36	0	No crystal
No.2	300	200	80	0	PEG	No crystal
No.3	300	200	80	36	PEG	Zn-POMCF
No.4	300	200	80	0	SDBS	No crystal
No.5	300	200	80	36	PVP	No crystal
No.6	300	200	80	36	SDBS	Zn-POMCF
No.7	0	200	80	0	PEG	Zn-MOF
No.8	0	200	80	0	SDBS	No crystal
No.9	0	200	80	0	PVP	No crystal

Table S2 the synthesis strategies for crystalline hybrids.

* PEG = Polyethylene glycol 1500; SDBS = sodium dodecyl benzene sulfonate; PVP = polyvinylpyrrolidone

III Cell Assembly and Electrochemical Measurements:

The crystal water of all the as prepared powders was removed before used as the electrode material. Electrochemical lithium-storage properties of the synthesized materials were measured by using CR2025 coin-type test cells assembled in a argon-filled glovebox (the oxygen and water concentration maintained below 1 ppm). To fabricate the working electrode, a slurry with appropriate viscosity consisting of 70 wt % active materials, 20 wt% Super-P carbon and 10 wt% polyvinylidene fluoride (PVDF) binder dissolved in 1-methyl-2-pyrrolidinone was casted on the copper foil, drying at 80°C under vacuum for 24 h. The loading mass of electroactive materials in electrode slurry is about 1.5 mg. The metallic lithium foil as the counter electrode, and 1.0 M LiPF₆ in ethylene carbonate/diethyl carbonate (1:1 v/v) as the electrolyte. Galvanostatic charge/discharge cycles were performed on a LAND 2001A instrument (Wuhan, China) and electrochemical workstation (Princeton Applied Research, PARSTAT 2273, Germany) to record the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) of batteries at constant ambient temperature, respectively.

IV X-ray Crystallographic Study:

Crystallographic data for as-prepared compounds were collected on Bruker SMART-CCD diffractometer with monochromatic Mo-K α radiation ($\lambda = 0.71069$ Å) at 296 K. The structures were solved by the direct method and refined full-matrix last squares on F² through the SHELXTL and OLEX software package. All non-hydrogen atoms were refined anostropically and the 'ISOR' command was used to refine some APD problems. The positions of hydrogen atoms on carbon atoms were calculated theoretically. The crystal data for two compounds are summarized in Table S3. The selected bond lengths and bond angles are given in Table S5-6. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC Numbers 1583784 for **Zn-POMCF** and 1851043 for **Zn-MOF**.

Compounds	Zn-POMCF	Zn-MOF
Formula	$C_{24}H_{40}N_{36}Zn_{12}VW_{12}O_{52}$	$C_8H_8N_{12}Zn_2$
Fw	4706.5	403.0
Т (К)	293	296

Table S3 Crystal Data and Structure Refinements for the compounds.

space group	I 4/m	P n m a
<i>a</i> (Å)	18.795	7.613
b (Å)	18.795	9.982
<i>c</i> (Å)	12.808	17.506
α (°)	90	90
β(°)	90	90
γ (°)	90	90
V (Å ³)	4524.3	1330.4
Ζ	8	8
D_c (g·cm ⁻³)	3.496	1.972
μ (mm ⁻¹)	18.501	3.622
F(000)	4294.0	768.0
Theta range for data collection	1.532 to 24.995	2.327 to 27.621
Largest diff. peak and hole(e.Å-3)	4.964 and -6.207	3.332 and -0.940
Reflections collected	11519	7601
Independent reflections	2094	1621
R _{int}	0.0406	0.0284
Final $R1^a$, $wR2^b$ [$I > \sigma(I)$]	0.0585, 0.1714	0.0570, 0.1604
Final R1 ^a , wR2 ^b (all data)	0.0651, 0.1760	0.0650, 0.1681
GOF on F ²	1.083	1.061

 ${}^{o}R_{1} = \sum / / F_{o} |-|F_{c} / / \sum |F_{o}| {}^{b}wR_{2} = \{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}] \}^{1/2}$

Section 3 Supplementary Structural Information

Fig. S1 The images of single crystals for Zn-POMCF (left) and Zn-MOF (right) under optical microscope.

Fig. S2 a) Ball/stick/polyhedral view of the crystallographic unit (left) and the coordination pattern of the $[VW_{12}O_{40}]^{4-}$ polyanion (right). All of the hydrogen atoms and water molecules were omitted for clarity; b) Ball/stick view of the coordination patterns of two crystallographic independent Zn²⁺ ions and two trz ligands.

Fig. S3 Ball/ stick view of the position of $[(\mu_3-OH)]$, $[(\mu_2-OH)]$ and free water molecules in the structure, and which are omitted in the following description.

Fig. S4 Ball/stick view of the accessible diameters confined by $[Zn_8(trz)_8]^{8+}$ of $[Zn_{12}(trz)_{12}]^{12+}$ macrocycle.

Fig. S5 a) Ball/ stick view of the 3D metal-organic framework constructed by $[Zn_{12}(trz)_{12}]^{12+}$ macrocycle along different directions; b) Ball/ stick view of the connection mode between adjacent $[Zn_{12}(trz)_{12}]^{12+}$ macrocycles.

Fig. S6 Ball/ stick view of the whole 3D metal-organic framework containing two kinds of tunnels (labeled A and B), the H atoms and water molecules were omitted for clarity.

Fig. S7 Schematic illustration of the topology of **Zn-POMCF** along [0,0,1] direction. The dark blue nodes represent $[Zn_3(trz)_3]$ fragment, and the red nodes symbolize POM polyanions.

Fig. S8 Ball/stick view of whole 3D framework (a) constructed by propeller-like [Zn₂(trz)₆] chain (b) and [Zn(trz)₄] fragment (c).

Section 4 Supplementary Physical Characterizations

Fig. S9 The IR curves of Zn-POMCF (up) and Zn-MOF (below), respectively.

Fig. S10 The PXRD patterns of **Zn-POMCF**: simulated pattern (below) and as-synthesized sample (up), respectively. The PXRD patterns of **Zn-MOF**: simulated pattern (below), as-synthesized sample (middle) and **Zn-MOF** immersed in electrolyte for 24h (up), respectively.

Fig. S11 The TG curves of Zn-POMCF (left) and Zn-MOF (right), respectively.

Fig. S12 The EDS spectrum, the SEM image and the elemental mapping images of **Zn-POMCF** (up) and **Zn-MOF** (below).

	Element Number	Element Symbol	Element Name	Atomic Conc.	Weight Conc.
	8	0	Oxygen	41.54	22.98
	7	Ν	Nitrogen	25.01	12.11
Zn-POIVICF	6	С	Carbon	21.71	9.02
	74	W	Tungsten	7.31	46.47
	30	Zn	Zinc	3.26	7.37
	23	V	Vanadium	1.16	2.05
	Element	Element	Element	Atomic	Weight
	Number	Symbol	Name	Conc.	Conc.
Zn-MOF	7	Ν	Nitrogen	55.57	37.15
	6	С	Carbon	29.76	17.06
	30	Zn	Zinc	14.67	45.79

Table S4 EDS element contents in Zn-POMCF and Zn-MOF.

Fig. S13 N2 adsorption-desorption isotherms and the corresponding pore size distribution of **Zn-POMCF** (a) and **Zn-MOF** (b).

Fig. 14 PXRD patterns of **Zn-POMCF**: (a) the as-synthesized sample soaked in aqueous solutions with different pH values at room temperature for 24 h and (b) immersed in electrolyte and other organic solvents at room temperature for 24 h. "Sim": simulated pattern, and "Exp": as-synthesized sample.

Fig. S15 IR patterns of **Zn-POMCF**: the synthesized sample soaked in aqueous solutions with different pH values at room temperature for 12 h.

Fig. S16 SEMs of **Zn-POMCF** (a, b) and **Zn-MOF** (c, d): the as-synthesized sample immersed in electrolyte at room temperature for 24 h.

Fig. S17 XPS spectra of **Zn-POMCF** before and after discharged at 0.01 V. (a, c and e): As synthesized powders, (a) Survey scan. (b) W 4f. (c) Zn 2p. (b, d and f): Discharged at 0.01 V, (b) Survey scan. (d) W 4f. (f) Zn 2p. The cells were disassembled in the glove box after discharged at a constant current of 100 mAg⁻¹ to 0.01 V. The working electrode was washed with acetonitrile before vacuum drying for 12 h at room temperature. Then it will have to be scraped off the Cu foil for XPS tests.

Fig. S18 XPS spectra of **Zn-MOF** before and after discharged at 0.01 V. (a and c): As synthesized powders, (a) Survey scan. (b) Zn 2p. (b and d): Discharged at 0.01 V, (b) Survey scan. (d) Zn 2p. The cells were disassembled in the glove box after discharged at a constant current of 100 mAg⁻¹ to 0.01 V. The working electrode was washed with acetonitrile before vacuum drying for 12 h at room temperature. Then it will have to be scraped off the Cu foil for XPS tests.

The XPS analysis and calculation of the theoretical capacities: According to XPS results, the W 4f spectrum shows two main peaks at 37.1 eV and 35.1 eV ascribed to W⁶⁺ 4f_{5/2} and W⁶⁺ 4f_{7/2} before the discharge of the cell. However, after discharging to 0.01 V, the existence of W⁴⁺ can be discovered in the binding energy of 37.3 eV (Fig. S17c and d). This result indicates that the W⁶⁺ is reduced to the W⁴⁺ during the intercalation. As showed in Figs. S7e and f, two peaks of Zn 2p3/2 and Zn 2p 1/2 at 1021.5 eV and 1044.5 eV in Zn 2p prove the existence of Zn²⁺, while the shifting and separation of the binding energy indicate the partial production of Zn⁰ after discharging to 0.01 V. Both valence changes of Mo and Zn demonstrate the redox reaction of **Zn-POMCF** in LIBs.

The theoretical capacities were calculated according to equation S1:

Q = nF/3.6M = 96500n/3.6M equation S1

Where Q is the reversible charging–discharging capacity, n is the number of electrons passed during the redox reaction, and M is the molecular weight.

(1) Calculation of the theoretical capacities of POMs:

When Li⁺ intercalate/deintercalate into the structure of VW_{12} , we based on the redox reactions of W atoms which are due to the intercalation mechanism for Li storage (equations S2) and the XPS results in Fig. 17.

If twelve W⁶⁺ are all reduced to W⁴⁺, maximum of n = 24, $Q_{POM} = 224$ mAh g⁻¹.

(2) Calculation of the theoretical capacities of MOFs:

Redox reactions where Zn²⁺ transformed into Zn occurred in Zn-based POMOFs because of the intercalation mechanism for Li storage, which has been confirmed by Lan et.al.^{8,9} On the other hand, possible lithiation/delithiation sites for coordination with Li such as the N atoms in trz ligands of POMOF.

As seen in Schematic S1, one Li⁺ maybe coordinate with one trz ligand, thus, in $Zn_3(trz)_3$, n = 9, $Q_{MOF} = 612$ mA h g⁻¹. However, further investigations are necessary to understand the exact mechanism in this case.

(3) Calculation of the theoretical capacities of POMOFs:

The molecular formula of **Zn-POMCF** is $[Zn_{12}(trz)_{12}][VW_{12}O_{40}]$. And based on the discussions above, here the maximum of n = 36 + 24 = 60, $Q_{Zn-POMCF} = 360$ mAh g⁻¹.

Fig. S20 Nyquist plots for Zn-POMCF (a) and Zn-MOF (b) (the static time more than 6 hours).

Fig. 21 Nyquist plots of fresh cell prolonged storage for **Zn-POMCF** (the high frequency intercept at the Zre-axis corresponds to the electrolyte resistance, the semicircle corresponds to SEI film resistance and charge-transfer resistance.

Fig. 22 Nyquist plots of Zn-POMCF electrode of the cell during the second charge process.

Fig. 23 Nyquist plots of Zn-POMCF electrode of the cell during the 201th times charge process.

5. The Selected bonds lengths and angles for Zn-POMCF and Zn-MOF

W(2)-O(5)	1.693(11)	V(1)-O(1)#3	1.65(2)
W(2)-O(6)	1.870(16)	V(1)-O(1)#1	1.65(2)
W(2)-O(3)	1.875(15)	V(1)-O(1)#7	1.65(2)
W(2)-O(2)	1.888(17)	V(1)-O(1)#4	1.65(2)
W(2)-O(2)#1	1.892(17)	V(1)-O(1)#2	1.65(2)
W(2)-O(1)	2.340(19)	V(1)-O(1)#8	1.65(2)
W(2)-O(1)#1	2.375(17)	V(1)-O(1)	1.65(2)
W(1)-O(4)#2	1.66(2)	O(2W)-Zn(1)#5	2.366(11)
W(1)-O(3)#3	1.875(15)	N(1)-C(2)	1.33(2)
W(1)-O(3)#2	1.875(15)	N(1)-C(2)#5	1.33(2)
W(1)-O(6)#4	1.883(15)	N(1)-Zn(2)#9	1.95(2)
W(1)-O(6)	1.883(15)	O(4)-W(1)#8	1.66(2)
W(1)-O(1)	2.361(19)	O(3W)-Zn(1)#5	2.086(9)
W(1)-O(1)#4	2.361(19)	N(2)-C(1)#10	1.31(2)
Zn(2)-N(1)#2	1.95(2)	N(2)-N(3)	1.364(19)
Zn(2)-N(2)	1.963(15)	N(3)-C(3)	1.31(2)
Zn(2)-N(2)#5	1.964(15)	N(4)-C(3)#11	1.33(2)
Zn(2)-O(3W)	1.967(14)	N(4)-C(1)	1.37(2)
Zn(1)-O(3W)	2.086(9)	N(5)-C(2)	1.28(2)
Zn(1)-N(3)	2.090(13)	N(5)-N(5)#5	1.33(3)
Zn(1)-N(4)	2.091(14)	O(2)-W(2)#2	1.892(17)
Zn(1)-N(5)	2.108(13)	O(1)-W(2)#2	2.375(17)
Zn(1)-O(5)	2.209(11)	O(3)-W(1)#8	1.875(15)
Zn(1)-O(2W)	2.366(11)	C(1)-N(2)#11	1.31(2)
V(1)-O(1)#6	1.65(2)	C(3)-N(4)#10	1.33(2)
N(1)#2-Zn(2)-N(2)	117.8(5)	O(5)-W(2)-O(6)	100.4(8)
N(1)#2-Zn(2)-N(2)#5	117.8(5)	O(5)-W(2)-O(3)	98.8(8)
N(2)-Zn(2)-N(2)#5	115.8(9)	O(6)-W(2)-O(3)	87.7(8)
N(1)#2-Zn(2)-O(3W)	104.7(7)	O(5)-W(2)-O(2)	103.4(7)
N(2)-Zn(2)-O(3W)	97.4(4)	O(6)-W(2)-O(2)	89.6(7)
N(2)#5-Zn(2)-O(3W)	97.4(4)	O(3)-W(2)-O(2)	157.7(9)
O(3W)-Zn(1)-N(3)	90.2(5)	O(5)-W(2)-O(2)#1	100.9(7)
O(3W)-Zn(1)-N(4)	168.9(5)	O(6)-W(2)-O(2)#1	158.7(9)
N(3)-Zn(1)-N(4)	93.0(5)	O(3)-W(2)-O(2)#1	88.2(7)
O(3W)-Zn(1)-N(5)	83.2(5)	O(2)-W(2)-O(2)#1	86.3(10)
N(3)-Zn(1)-N(5)	171.6(5)	O(5)-W(2)-O(1)	158.3(7)
N(4)-Zn(1)-N(5)	92.6(5)	O(6)-W(2)-O(1)	63.7(8)
O(3W)-Zn(1)-O(5)	91.2(5)	O(3)-W(2)-O(1)	95.3(9)
N(3)-Zn(1)-O(5)	94.2(5)	O(2)-W(2)-O(1)	63.9(7)

Table S5 Selected bonds lengths (Å) and angles (°) for Zn-POMCF.

N(4)-Zn(1)-O(5)	99.2(5)	O(2)#1-W(2)-O(1)	95.9(7)
N(5)-Zn(1)-O(5)	91.0(5)	O(5)-W(2)-O(1)#1	154.2(7)
O(3W)-Zn(1)-O(2W)	76.9(5)	O(6)-W(2)-O(1)#1	96.6(9)
N(3)-Zn(1)-O(2W)	91.6(6)	O(3)-W(2)-O(1)#1	62.5(8)
N(4)-Zn(1)-O(2W)	92.4(5)	O(2)-W(2)-O(1)#1	95.9(7)
N(5)-Zn(1)-O(2W)	82.0(6)	O(2)#1-W(2)-O(1)#1	63.1(7)
O(5)-Zn(1)-O(2W)	166.7(4)	O(1)-W(2)-O(1)#1	47.4(9)
O(1)#6-V(1)-O(1)#3	70.2(6)	O(4)#2-W(1)-O(3)#3	99.4(9)
O(1)#6-V(1)-O(1)#1	109.8(6)	O(4)#2-W(1)-O(3)#2	99.4(9)
O(1)#3-V(1)-O(1)#1	180	O(3)#3-W(1)-O(3)#2	88.0(11)
O(1)#6-V(1)-O(1)#7	71.3(13)	O(4)#2-W(1)-O(6)#4	102.5(9)
O(1)#3-V(1)-O(1)#7	109.8(6)	O(3)#3-W(1)-O(6)#4	88.1(7)
O(1)#1-V(1)-O(1)#7	70.2(6)	O(3)#2-W(1)-O(6)#4	158.2(10)
O(1)#6-V(1)-O(1)#4	108.7(13)	O(4)#2-W(1)-O(6)	102.5(9)
O(1)#3-V(1)-O(1)#4	70.2(6)	O(3)#3-W(1)-O(6)	158.2(10)
O(1)#1-V(1)-O(1)#4	109.8(6)	O(3)#2-W(1)-O(6)	88.1(7)
O(1)#7-V(1)-O(1)#4	180	O(6)#4-W(1)-O(6)	87.7(11)
O(1)#6-V(1)-O(1)#2	109.8(6)	O(4)#2-W(1)-O(1)	155.9(5)
O(1)#3-V(1)-O(1)#2	71.3(13)	O(3)#3-W(1)-O(1)	96.2(9)
O(1)#1-V(1)-O(1)#2	108.7(13)	O(3)#2-W(1)-O(1)	62.8(7)
O(1)#7-V(1)-O(1)#2	70.2(6)	O(6)#4-W(1)-O(1)	96.3(9)
O(1)#4-V(1)-O(1)#2	109.8(6)	O(6)-W(1)-O(1)	63.1(8)
O(1)#6-V(1)-O(1)#8	70.2(6)	O(4)#2-W(1)-O(1)#4	155.9(5)
O(1)#3-V(1)-O(1)#8	108.7(13)	O(3)#3-W(1)-O(1)#4	62.8(7)
O(1)#1-V(1)-O(1)#8	71.3(13)	O(3)#2-W(1)-O(1)#4	96.2(9)
O(1)#7-V(1)-O(1)#8	109.8(6)	O(6)#4-W(1)-O(1)#4	63.1(8)
O(1)#4-V(1)-O(1)#8	70.2(6)	O(6)-W(1)-O(1)#4	96.3(9)
O(1)#2-V(1)-O(1)#8	180	O(1)-W(1)-O(1)#4	48.0(9)
O(1)#6-V(1)-O(1)	180	C(2)-N(5)-Zn(1)	136.2(12)
O(1)#3-V(1)-O(1)	109.8(6)	N(5)#5-N(5)-Zn(1)	117.6(4)
O(1)#1-V(1)-O(1)	70.2(6)	W(2)-O(2)-W(2)#2	136.4(11)
O(1)#7-V(1)-O(1)	108.7(13)	V(1)-O(1)-W(2)	122.2(9)
O(1)#4-V(1)-O(1)	71.3(13)	V(1)-O(1)-W(1)	120.3(9)
O(1)#2-V(1)-O(1)	70.2(6)	W(2)-O(1)-W(1)	95.9(7)
O(1)#8-V(1)-O(1)	109.8(6)	V(1)-O(1)-W(2)#2	120.3(9)
C(2)-N(1)-C(2)#5	100.6(19)	W(2)-O(1)-W(2)#2	96.2(7)
C(2)-N(1)-Zn(2)#9	129.6(9)	W(1)-O(1)-W(2)#2	95.7(7)
C(2)#5-N(1)-Zn(2)#9	129.6(9)	W(2)-O(3)-W(1)#8	138.9(12)
Zn(2)-O(3W)-Zn(1)	112.9(5)	W(2)-O(5)-Zn(1)	164.7(8)
Zn(2)-O(3W)-Zn(1)#5	112.9(5)	N(2)#11-C(1)-N(4)	111.7(15)
Zn(1)-O(3W)-Zn(1)#5	104.1(6)	N(5)-C(2)-N(1)	113.5(15)
C(1)#10-N(2)-N(3)	106.7(14)	N(3)-C(3)-N(4)#10	113.8(14)
C(1)#10-N(2)-Zn(2)	134.8(12)	W(2)-O(6)-W(1)	137.0(12)

N(3)-N(2)-Zn(2)	118.2(10)	N(2)-N(3)-Zn(1)	121.3(10)
C(3)-N(3)-N(2)	105.6(13)	C(3)#11-N(4)-C(1)	102.1(13)
C(3)-N(3)-Zn(1)	133.0(11)	C(3)#11-N(4)-Zn(1)	131.7(11)
C(2)-N(5)-N(5)#5	106.1(10)	C(1)-N(4)-Zn(1)	126.1(11)

Symmetry transformations used to generate equivalent atoms: #1= y,-x+2, z; #2= -y+2, x, z; #3 =-y+2, x, -z+1; #4= x, y, -z+1; #5= x, y, -z; #6= -x+2, -y+2, -z+1; #7= -x+2, -y+2, z; #8= y, -x+2, -z+1; #9= y, -x+2, -z; #10= y-1/2, -x+3/2, -z+1/2; #11= -y+3/2, x+1/2, -z+1/2

Zn(1)-N(3)	2.114(7)	Zn(2)-N(6)	1.979(6)
Zn(1)-N(4)#1	2.145(5)	Zn(2)-N(5)	1.991(5)
Zn(1)-N(4)	2.145(5)	Zn(2)-N(5)#2	1.991(5)
Zn(1)-N(1)#1	2.164(5)	Zn(2)-N(7)	2.024(12)
Zn(1)-N(1)	2.164(5)	Zn(2)-N(7)#2	2.024(13)
Zn(1)-N(2)	2.215(7)	N(5)-Zn(2)-N(5)#2	113.7(3)
N(5)-Zn(2)-N(7)	93.3(4)	N(3)-Zn(1)-N(4)#1	94.02(18)
N(5)#2-Zn(2)-N(7)	107.2(4)	N(3)-Zn(1)-N(4)	94.02(18)
N(6)-Zn(2)-N(7)#2	105.8(6)	N(4)#1-Zn(1)-N(4)	89.9(3)
N(5)-Zn(2)-N(7)#2	107.2(4)	N(3)-Zn(1)-N(1)#1	89.95(18)
N(5)#2-Zn(2)-N(7)#2	93.3(4)	N(4)#1-Zn(1)-N(1)#1	175.98(18)
N(7)-Zn(2)-N(7)#2	16.3(6)	N(4)-Zn(1)-N(1)#1	89.25(18)
N(4)#1-Zn(1)-N(2)	90.75(17)	N(3)-Zn(1)-N(1)	89.95(18)
N(4)-Zn(1)-N(2)	90.74(17)	N(4)#1-Zn(1)-N(1)	89.25(18)
N(1)#1-Zn(1)-N(2)	85.35(17)	N(4)-Zn(1)-N(1)	175.98(18)
N(1)-Zn(1)-N(2)	85.35(17)	N(1)#1-Zn(1)-N(1)	91.4(3)
N(6)-Zn(2)-N(5)	116.64(16)	N(3)-Zn(1)-N(2)	173.3(3)
N(6)-Zn(2)-N(5)#2	116.64(16)	N(6)-Zn(2)-N(7)	105.8(6)

Table S6 Selected bonds lengths (Å) and angles (°) for Zn-MOF.

Symmetry transformations used to generate equivalent atoms: #1= x, -y+1/2, z; #2= x, -y+3/2, z; #3= -x-1/2, -y+1, z-1/2; #4= x-1/2, y, -z+3/2; #5= x+1/2, -y+1/2, -z+3/2; #6= -x, -y+1, -z+2; #7= - 1/2, -y+1/2, -z+3/2; #8= x+1/2, y, -z+3/2; #9= -x-1/2, -y+1, z+1/2.

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- [4] Synthesis of [Cu₁₀(trz)₆Cl₂(H2O)][HPW₁₂O₄₀]: A mixture of H₃PW₁₂O₄₀ (300 mg), Cu(CH3COO)₂ (200 mg, 1.10 mmol), 1,2,4-triazole (70 mg, 1.01 mmol) and NH₄VO₃ (36 mg) were dissolved in distilled water (10 mL) with stirring for 1 h at room temperature, and pH value was adjusted to ca. 1.38 by 1 M HCl. The resulting solution was transferred and sealed in a 20 mL Teflon-lined stainless steel reactor and heated at 170 °C for 3 days. After slow cooling to room temperature, we collected the black octahedral blocks. Yield: 32.5 % based on Cu.
- [5] Synthesis of[Cu₁₂(trz)₈Cl][PMo₁₂O₄₀(VO)₂] : A mixture of H₃PMo₁₂O₄₀ (300 mg), 1,2,4-trz (60 mg,), Cu(CH₃COO)₂ (200 mg) and NH₄VO₃ (40mg) were dispersed in 10 mL distilled water at room temperature. The suspension was stirred for about 30 min, and the pH value was then adjusted to about 1.5 using 1.0 M HCl. The suspension was transferred to a Teflon-lined autoclave (20mL) and kept at 170°C for 4 days. After slow cooling to room temperature, we collected the black octahedral blocks. Yield: 51.5 % based on Cu.
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