Electronic Supplementary Information

High-connected strategy of polyoxometalates towards model of core-shell nanostructure

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Materials and general methods. All chemicals were commercially purchased and used as supplied. Elemental analyses of C, H, and N were performed using an EA1110 elemental analyzer. The IR spectrum was recorded in the range 4000-400cm^{-1} on a Nicolet 360 spectrometer with a pressed KBr pellet. The TG-DTA analysis was carried out by Universal Analysis 2000 thermogravimetric analyzer (TGA) in N_2 with a heating rate of 10 °C /min. Crystal data were collected on a Bruker X8 APEX II-CCD single crystal X-ray diffractometer with Cu Kα radiation (λ = 0.71073Å).

Synthesis of FUNSOM-3. A mixture of $H_3PW_{12}O_{40}\cdot xH_2O$ (0.30 g, 0.1 mmol), $Cu(OAc)_2\cdot H_2O$ (0.20 g, 1.0 mmol) and mt (0.04 g, 0.4 mmol) was dissolved in 10 ml distilled water at room temperature. The pH value of the mixture was adjusted to about 2.0 with 1.0 M HCl. The suspension was placed in a Teflonw-lined autoclave and then kept under autogenous pressure at 160 □ for 3 days. After slowly cooling to room temperature, slightly orange block crystals were filtered and washed with distilled water (48% yield, based on W). Elemental analyses calc. for FUNSOM-3: C, 2.82; H, 0.47; N, 6.58 %; Found: C, 2.80; H, 0.46; N, 6.54 %. IR (KBr pellet, cm^{-1}): 1618, 1378, 1288, 1180, 1084, 988, 892, 798.

Synthesis of FUNSOM-4. A mixture of $H_4SiW_{12}O_{40}\cdot xH_2O$ (0.30 g, 0.10 mmol), AgOAc (0.17 g, 1.0 mmol) and mmt (0.05 g, 0.4 mmol) was dissolved in 10 mL distilled water at room temperature. When the pH was adjusted to about 1.3 with 1.0 M HCl, the suspension was placed in a Teflonw-lined autoclave and kept under autogenous pressure at 160 □ for 3 days. After slowly cooling to room temperature, light yellow block crystals were filtered and washed with distilled water (Yield 39 % based on W). Elemental analyses calc. for FUNSOM-4: C, 2.27; H, 0.38; N, 5.30 %; Found: C, 2.31; H, 0.37; N, 5.28 %. IR (KBr pellet, cm^{-1}): 1618, 1378, 1173, 1014, 978, 922, 786.

Synthesis of FUNSOM-5. It was prepared in a manner similar to that for FUNSOM-4, but the $H_3PW_{12}O_{40}\cdot xH_2O$ (0.30 g, 0.1 mmol) was used instead of $H_4SiW_{12}O_{40}\cdot xH_2O$. About 1.0 ml 1.0 M Na_2S was added to the mixture and then the pH was adjusted to about 1.4 with 1.0 M HCl. After cooling to room temperature, orange block crystals were filtered and washed with distilled water (Yield 45 % based on W). Elemental analyses calc. for FUNSOM-5: C, 2.35; H, 0.46; N, 5.49 %; Found: C, 2.39; H, 0.48; N, 5.51 %. IR (KBr pellet, cm^{-1}): 1620, 1378, 1175, 1080, 983, 891, 802.

Table S1. Crystal Data and Structural Refinements for FUNSOM 3-5.

	FUNSOM-3	FUNSOM-4	FUNSOM-5
formula	$Cu_3C_8N_{16}H_{16}PW_{12}O_{40}$	$Ag_8C_8S_4N_{16}H_{16}SiW_{12}O_{42}$	$Ag_6C_8S_6H_{19}N_{16}PW_{12}O_{42}$
M	3404.07	4233.83	4088.09

crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	16.9285(16)	10.0393(12)	9.9493(12)
b (Å)	14.9877(14)	13.9688(16)	14.0796(17)
c (Å)	19.0063(18)	19.893(2)	19.906(2)
β (deg)	93.066(2)	102.369(2)	101.585(2)
V (Å^3)	4815.4(8)	2725.0(6)	2731.7(6)
Z	4	2	2
Dc (g/cm^3)	4.695	5.155	4.962
μ (mm^{-1})	29.976	28.293	27.613
F(000)	5944.0	3700.0	3578.0
collcd reflns	33970	19690	19021
unique reflns	9422	4739	4764
no. of param	726	432	430
R_{int}	0.0386	0.0560	0.0427
GOF	1.077	1.305	0.999
R_1[a] [I >2σ(I)]	0.0397	0.0761	0.0436
wR_2[b] (all data)	0.1272(9422)	0.1511(4739)	0.1101(4764)

[a]R1 = $\sum||F_o|-|F_c||/\sum|F_o|$; [b]wR2 = $\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

Table S2. Selected bond distances (Å) and angles (°) for FUNSOM 3-5.

FUNSOM-3			
Cu(1)-N(1)	1.934(12)	N(14)#1-Cu(1)-N(5)	101.4(5)
Cu(1)-N(14)#1	1.938(14)	N(1)-Cu(1)-O(1)	92.0(4)
Cu(1)-N(5)	2.131(15)	N(14)#1-Cu(1)-O(1)	92.4(4)
Cu(1)-O(1)	2.425(8)	N(5)-Cu(1)-O(1)	85.3(4)
Cu(2)-N(9)	1.887(12)	N(9)-Cu(2)-N(2)	169.3(6)
Cu(2)-N(2)	1.885(12)	N(10)-Cu(3)-N(13)	135.0(5)
Cu(3)-N(10)	1.954(10)	N(10)-Cu(3)-N(6)#2	121.2(5)
Cu(3)-N(13)	2.038(12)	N(13)-Cu(3)-N(6)#2	103.0(5)
Cu(3)-N(6)#2	2.057(13)	N(10)-Cu(3)-O(2)	96.1(4)
Cu(3)-O(2)	2.417(9)	N(13)-Cu(3)-O(2)	92.8(4)
N(1)-Cu(1)-N(5)	111.4(5)	N(6)#2-Cu(3)-O(2)	88.6(4)
FUNSOM-4			
Ag(1)-N(1)	2.28(2)	S(1)-Ag(2)-S(2)	139.9(3)
Ag(1)-O(5)	2.45(2)	O(1W)-Ag(2)-Ag(2)#2	68.6(7)
Ag(1)-S(2)	2.559(8)	S(1)-Ag(2)-Ag(2)#2	117.7(2)
Ag(1)-Ag(2)	3.107(4)	S(2)-Ag(2)-Ag(2)#2	82.9(2)
Ag(2)-O(1W)	2.41(3)	O(1W)-Ag(2)-Ag(1)	150.4(6)
Ag(2)-S(1)	2.419(8)	S(1)-Ag(2)-Ag(1)	89.2(2)
Ag(2)-S(2)	2.505(8)	S(2)-Ag(2)-Ag(1)	52.9(2)
Ag(2)-Ag(2)#2	3.027(6)	Ag(2)#2-Ag(2)-Ag(1)	95.78(16)
Ag(3)-N(5)	2.26(3)	N(5)-Ag(3)-S(2)#3	156.5(7)
Ag(3)-S(2)#3	2.479(7)	N(5)-Ag(3)-O(2)#4	93.8(9)

Ag(3)-O(2)#4	2.50(3)	S(2)#3-Ag(3)-O(2)#4	102.2(6)
Ag(3)-S(1)#5	2.718(8)	N(5)-Ag(3)-S(1)#5	93.3(6)
Ag(3)-Ag(3)#3	3.180(5)	S(2)#3-Ag(3)-S(1)#5	104.7(3)
Ag(4)-N(2)#6	2.26(3)	O(2)#4-Ag(3)-S(1)#5	86.1(7)
Ag(4)-N(6)	2.35(3)	N(5)-Ag(3)-Ag(3)#3	80.2(6)
Ag(4)-O(3)#7	2.56(3)	S(2)#3-Ag(3)-Ag(3)#3	85.2(2)
Ag(4)-S(1)#5	2.651(7)	O(2)#4-Ag(3)-Ag(3)#3	81.5(7)
N(1)-Ag(1)-O(5)	96.3(9)	S(1)#5-Ag(3)-Ag(3)#3	165.6(2)
N(1)-Ag(1)-S(2)	131.9(6)	N(2)#6-Ag(4)-N(6)	133.6(9)
O(5)-Ag(1)-S(2)	98.5(6)	N(2)#6-Ag(4)-O(3)#7	83.2(10)
N(1)-Ag(1)-Ag(2)	81.1(6)	N(6)-Ag(4)-O(3)#7	134.3(9)
O(5)-Ag(1)-Ag(2)	116.1(6)	N(2)#6-Ag(4)-S(1)#5	123.9(7)
S(2)-Ag(1)-Ag(2)	51.36(19)	N(6)-Ag(4)-S(1)#5	91.5(7)
O(1W)-Ag(2)-S(1)	120.2(7)	O(3)#7-Ag(4)-S(1)#5	83.7(7)
O(1W)-Ag(2)-S(2)	98.9(7)		
FUNSOM-5			
Ag(1)-N(1)	2.244(15)	N(1)-Ag(1)-S(2)#3	96.2(4)
Ag(1)-S(1)#2	2.462(4)	S(1)#2-Ag(1)-S(2)#3	104.63(15)
Ag(1)-O(6)	2.571(13)	O(6)-Ag(1)-S(2)#3	83.9(3)
Ag(1)-S(2)#3	2.719(4)	N(1)-Ag(1)-Ag(1)#2	79.1(4)
Ag(1)-Ag(1)#2	3.278(3)	S(1)#2-Ag(1)-Ag(1)#2	84.11(12)
Ag(2)-N(6)	2.287(14)	O(6)-Ag(1)-Ag(1)#2	81.9(3)
Ag(2)-N(2)	2.351(15)	S(2)#3-Ag(1)-Ag(1)#2	164.84(12)
Ag(2)-S(2)#3	2.630(4)	N(6)-Ag(2)-N(2)	132.1(5)
Ag(3)-N(5)	2.234(14)	N(6)-Ag(2)-S(2)#3	123.5(4)
Ag(3)-S(1)#4	2.480(5)	N(2)-Ag(2)-S(2)#3	96.2(4)
Ag(3)-O(3)#5	2.517(13)	N(5)-Ag(3)-S(1)#4	142.5(4)
N(1)-Ag(1)-S(1)#2	154.7(4)	N(5)-Ag(3)-O(3)#5	90.5(5)
N(1)-Ag(1)-O(6)	92.7(5)	S(1)#4-Ag(3)-O(3)#5	100.1(4)
S(1)#2-Ag(1)-O(6)	103.5(3)		

Symmetry code for FUNSOM-3: #1 -x+3/2, y+1/2, -z+3/2; #2 -x+3/2, y-1/2, -z+3/2; FUNSOM-4: #2 -x, -y, -z+1; #3 -x+1, -y, -z+1; #4 x+1/2, -y+1/2, z+1/2; #5 x+1, y, z; #6 -x+1/2, y-1/2, -z+1/2; #7 -x+1, -y, -z; FUNSOM-5: #2 -x, -y+1, -z+2; #3 -x+1/2, y+1/2, -z+3/2; #4 -x-1/2, y-1/2, -z+3/2; #5 x, y-1, z.

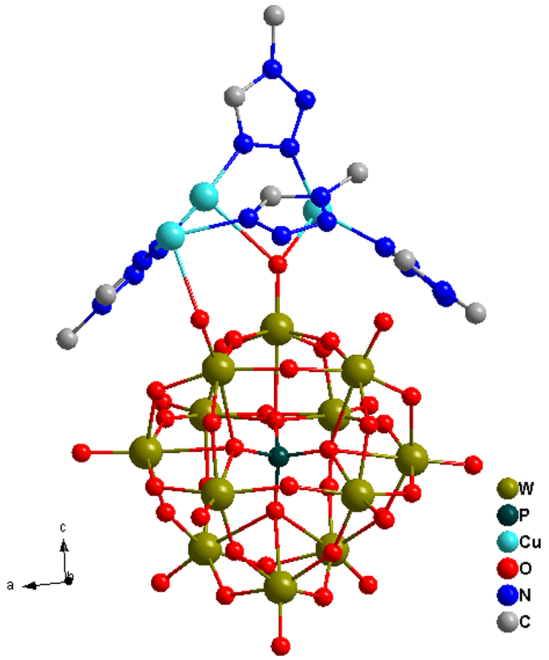


Fig. S1. Ball-stick view of the asymmetric unit of FUNSOM-3. All H atoms are omitted for clarity.

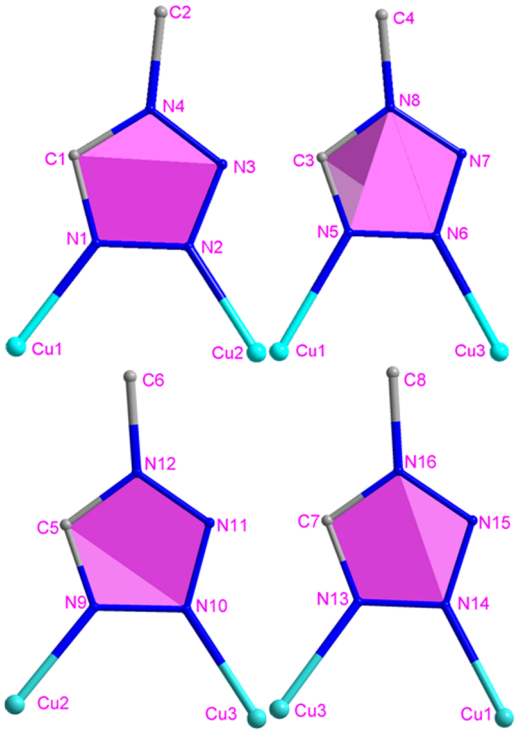


Fig. S2. Coordination details of four kinds of mt ligands in FUNSOM-3.

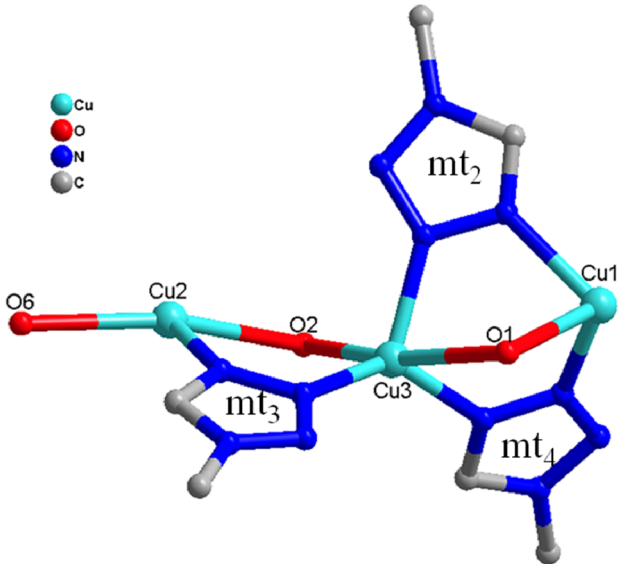


Fig. S3. The coordination detail of SBU[a].

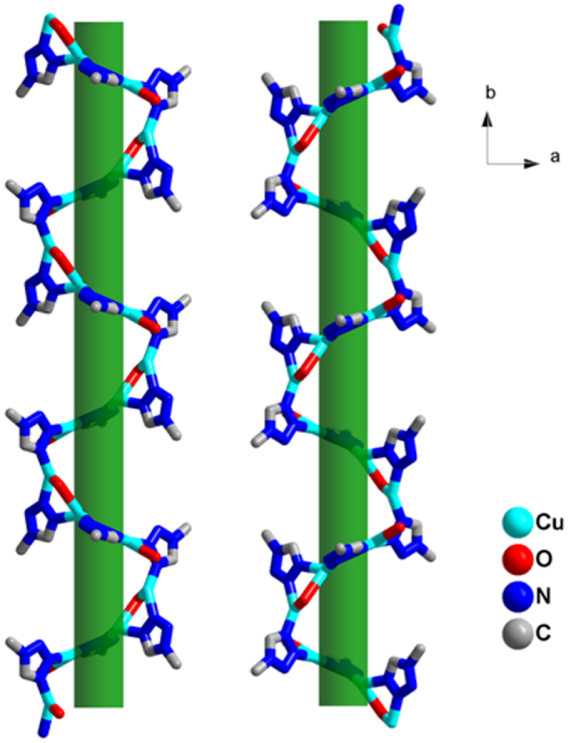


Fig. S4. View of the left- and right-handed helical chains in FUNSOM-3.

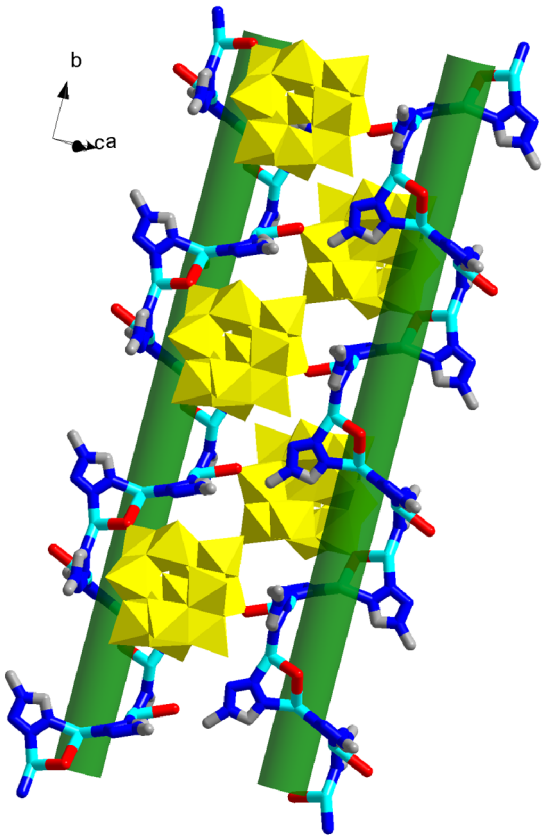


Fig. S5. The meso-helical structure constructed by left-/right-handed helical chains and $[PW_{12}O_{40}]^{3-}$ anions.

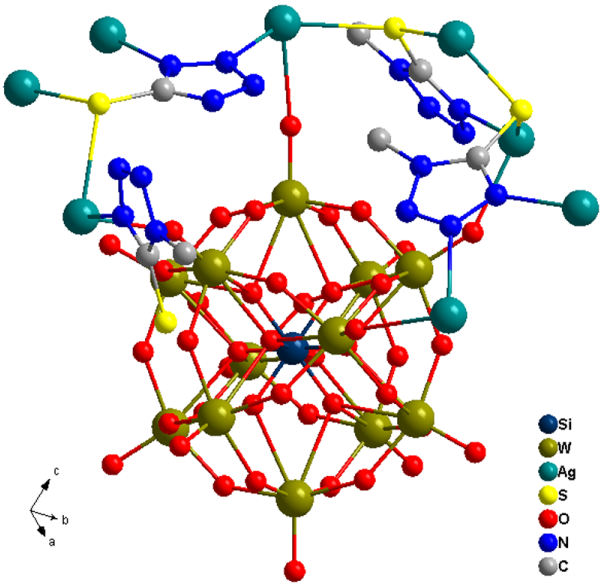


Fig. S6. Ball-stick view of the asymmetric unit of FUNSOM-4. All H atoms and coordinated water molecules are omitted for clarity.

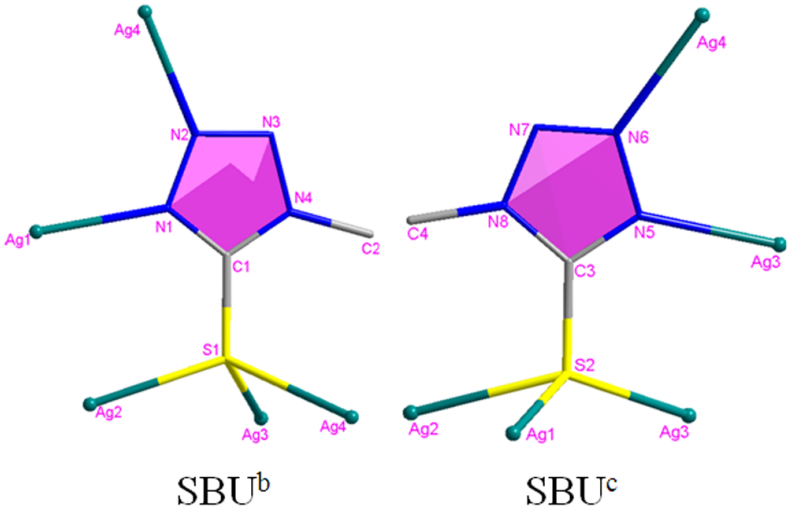


Fig. S7. Coordination modes of two kinds of mmt ligands in FUNSOM-4.

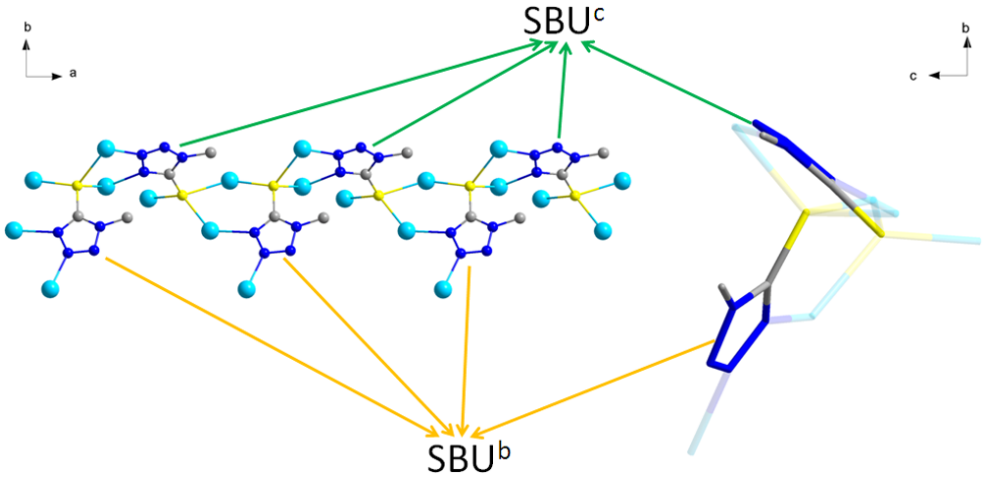


Fig. S8. The 1D chain constructed by SBU^b & SBU^c units view along c-axes (left) and a-axes (right) in FUNSOM-4.

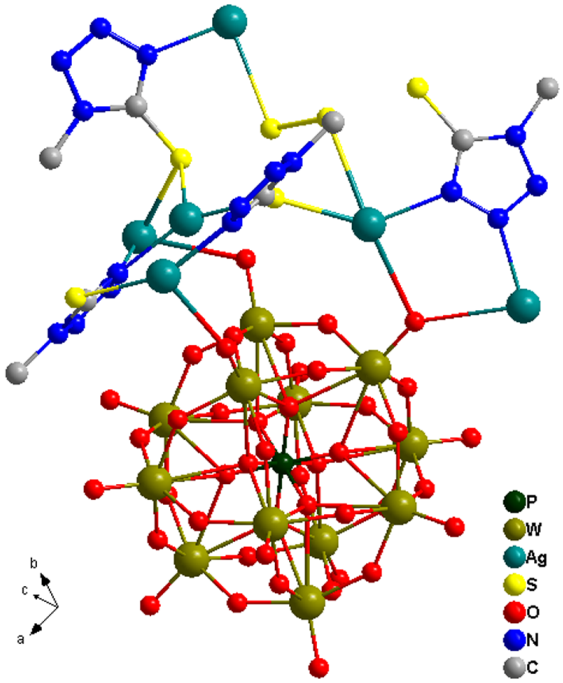


Fig. S9. Ball-stick view of the asymmetric unit of FUNSOM-5. All H atoms and lattice water molecules are omitted for clarity.

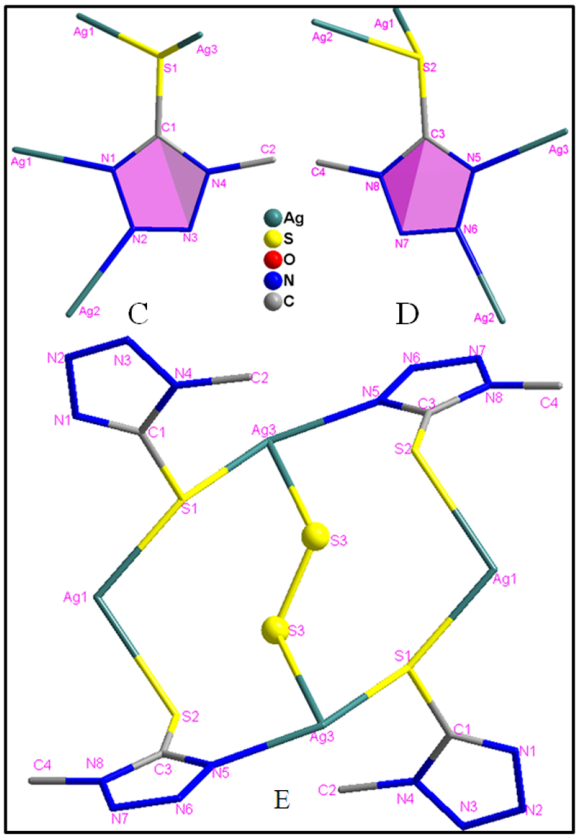


Fig. S10. Coordination details of SBU^{d} (a), SBU^{e} (b) and S_2^{2-} unit (c) within FUNSOM-5.

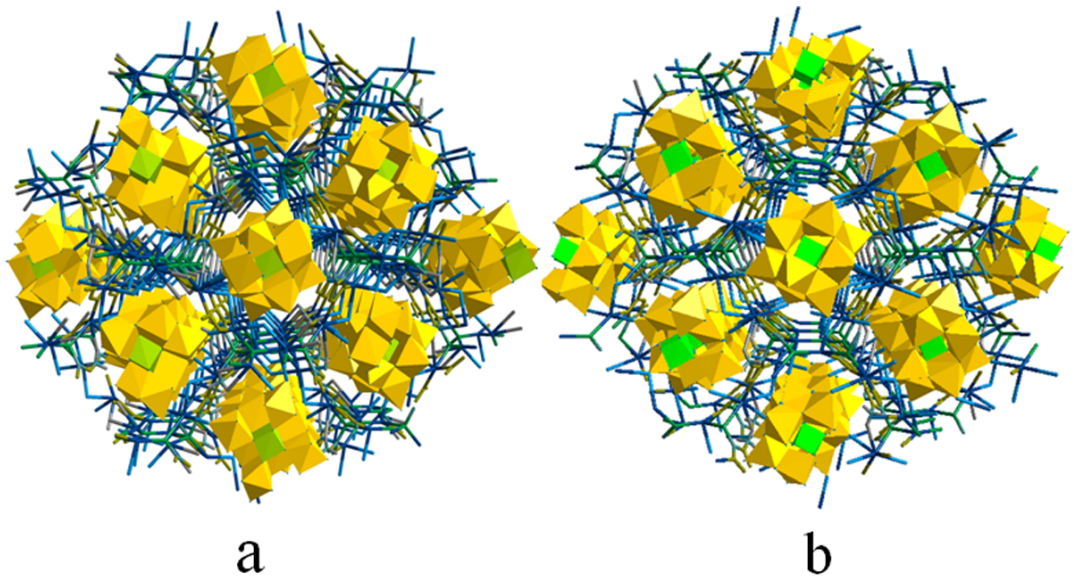


Fig. S11. Perspective view of the FUNSOM-4 (a) & FUNSOM-5 (b) along the a-axis. The POMs act as high-connected templates locating in the straight channels of the 3D metal-organic framework.

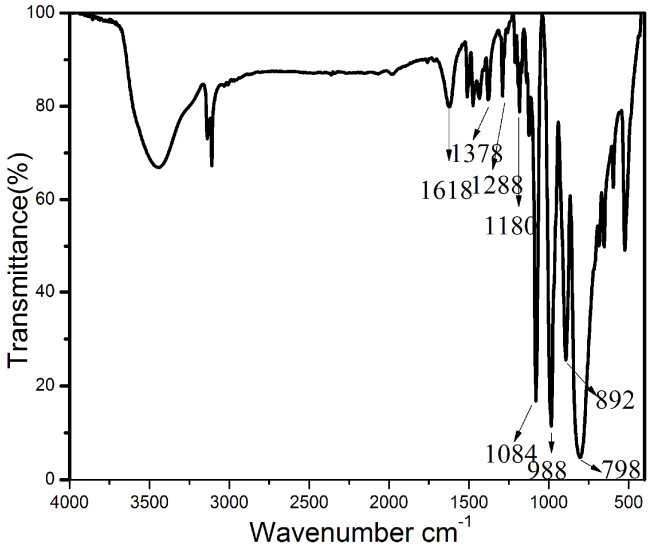


Fig. S12. IR spectra of FUNSOM-3. The characteristic bands at 798, 892, 988, and 1084 cm^{-1} are attributed to ν (W-Ot), ν (W-Ob-W), ν (W-Oc-W), and ν (P-O), respectively. The bands in the range of 1180–1618 cm^{-1} are assigned to the vibrations of mt ligand.

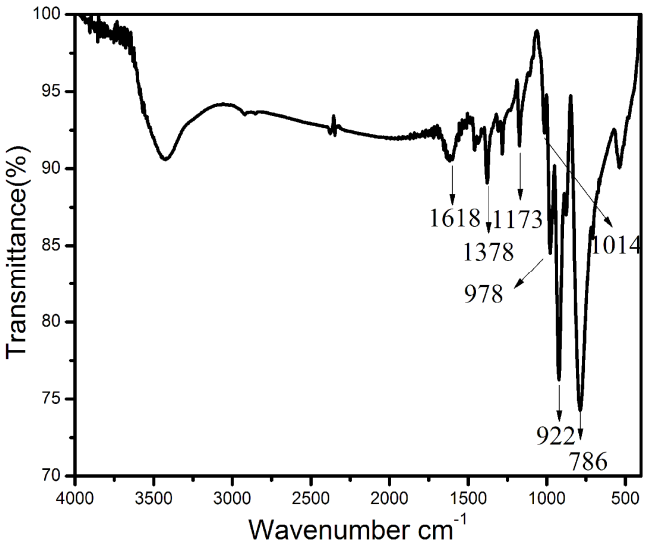


Fig. S13. IR spectra of FUNSOM-4. The characteristic bands at 786, 922, and 978 cm^{-1} are attributed to *v* (W-Ot), *v* (W-Ob-W), *v* (W-Oc-W), and *v* (Si-O), respectively. The bands in the range of 1173–1618 cm^{-1} are assigned to the vibrations of mmt ligand.

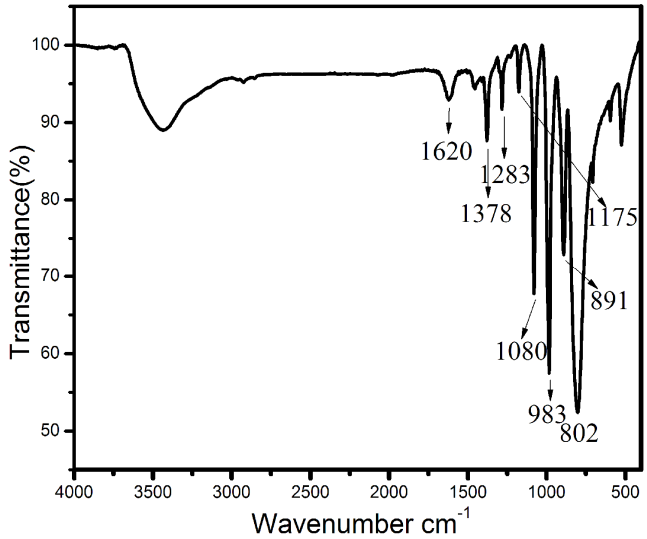


Fig. S14. IR spectra of FUNSOM-5. The characteristic bands at 802, 891, 983, and 1080 cm^{-1} are attributed to *v* (W-Ot), *v* (W-Ob-W), *v* (W-Oc-W), and *v* (P-O), respectively. The bands in the range of 1175–1620 cm^{-1} are assigned to the vibrations of mmt ligand.

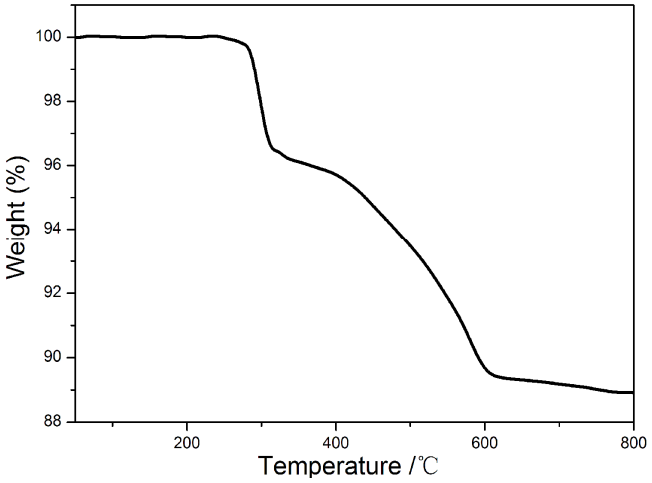


Fig. S15. TG curve of FUNSOM-3. The weight loss of 9.93% (calcd, 9.41%) from 250 to 600 ℃ corresponds to the loss of the mt ligand.

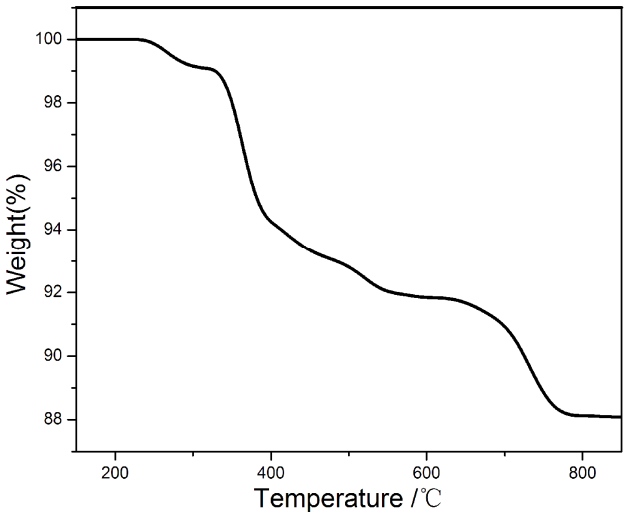


Fig. S16. TG curve of FUNSOM-4. The TG curve indicates that coordinated water molecules are eliminated from the network (calcd, 0.85%; found, 0.99%) when the temperature increased from 250 to about 350 °C, after which removal of the organic components occurred (350-800 °C). The total weight loss was consistent with the calculated values (calcd, 11.64%; found, 11.75%).

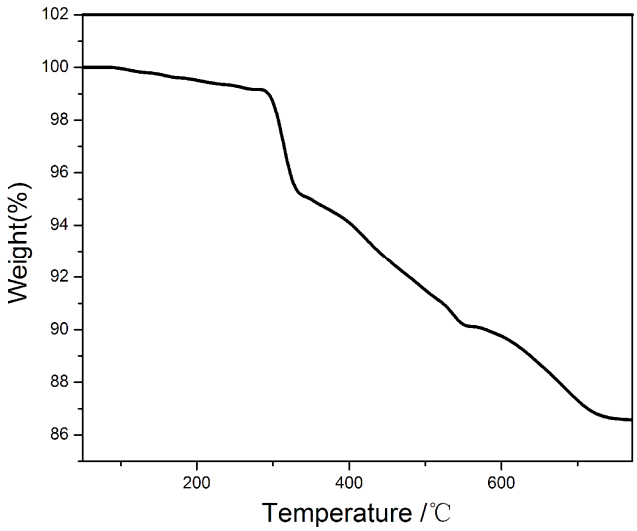
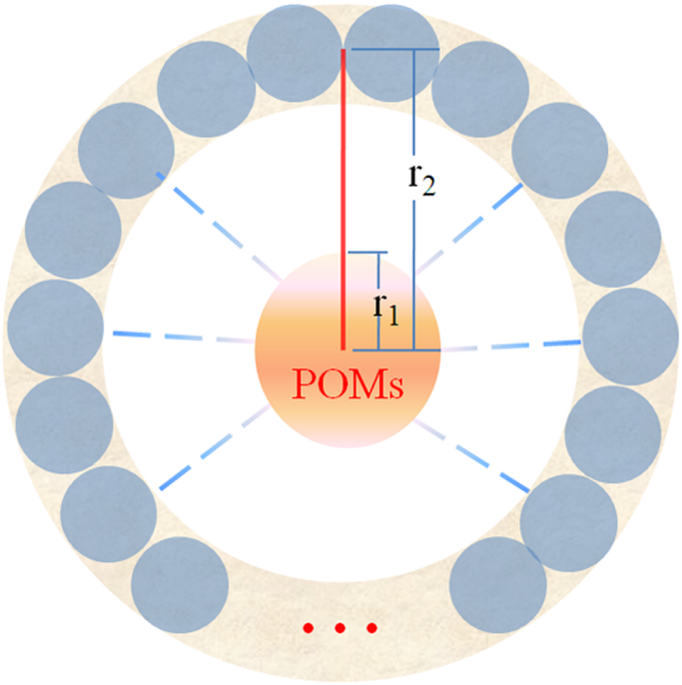
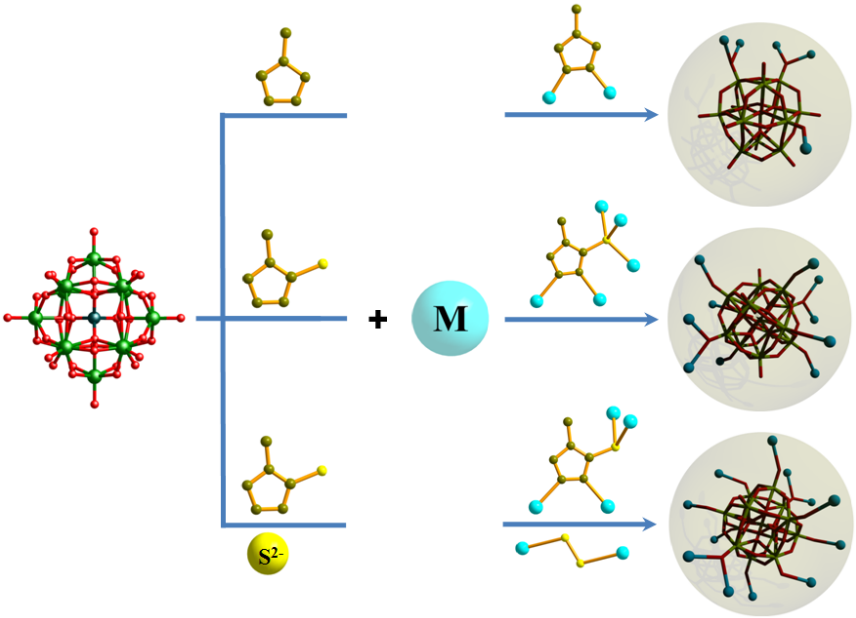


Fig. S17. TG curve of FUNSOM-5. The TG curve indicates that water molecules are eliminated from the network (calcd, 0.88%; found, 0.85%) when the temperature increased from room temperature to about 300 °C, after which removal of the organic components occurred (300-800 °C). The total weight loss was consistent with the calculated values (calcd, 13.44%; found, 13.73%).



Scheme S1. Scheme view of the mathematical analysis. Assuming that the Ag atoms (r_{Ag} = 0.72 Å) connected with POMs (r_{POM} = 5.225 Å) through Ag-O bonds ($r_{Ag\text{-}O}$ = 2.5Å) and the Ag atoms are averagely dispersed on the surface of the Keggin-type polyanions. The distance between two Ag atoms is the same as that in the Ag unit cell (r_{AgU} = 3.545 Å). The distance between the centre of the shell layer and POMs was select as r_2 ($r_2 = r_{POM} + r_{Ag\text{-}O} + r_{Ag}$ = 8.445 Å). It's no difficult to understand that the shell is constituted by those Ag atoms. Thus, the probable number (N) of the Ag atoms connected to POMs can be calculated: $N = 4\pi r_2^2/\pi r_{AgU}^2 = 23$.



Scheme S2. Formation of the high-connected POMs showing the key structural components of sulfur atoms, which are introduced following the two major steps: 1) addition the sulfhydryl into the organic ligand, thus the ligand mt was changed to mmt; 2) introduction free S^{2-} anions into the reaction system from inorganic salt Na_2S.