(Supplementary information)

Construction of (3,6)-connected Polyoxometalate-Based Metal-Organic Frameworks (POMOFs) from Triangular Carboxylate and Dimerized Zn_4-ε-Keggin

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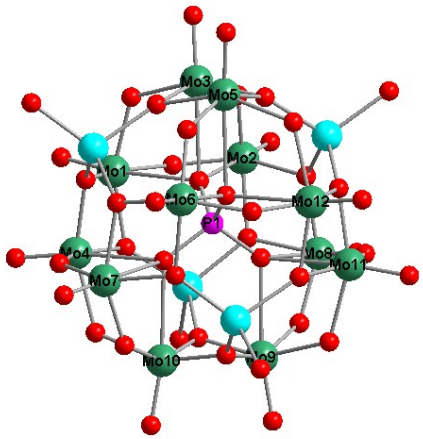
Contents:

Table S1. Crystal data and structure refinement for **1**−**2**.

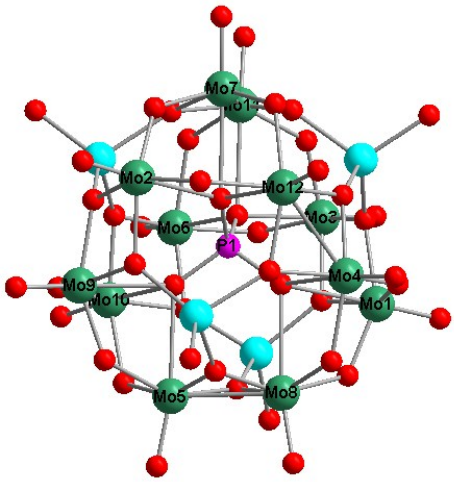
Compound	**1**	**2**
Empirical formula	$C_{69}H_{125}N_3PMo_{12}O_{46}Zn_4$	$C_{114}H_{204}N_6P_2Mo_{24}O_{93}Zn_8$
Formula weight	3176.45	6034.29
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	16.3103(15)	17.257(4)
b (Å)	28.272(3)	21.715(4)
c (Å)	23.888(2)	24.743(6)
ß	108.481(3)	98.940(7)
Volume (Å ^{3})	10447.4(17)	9160(3)
Z	4	2
D $_{calc}$ (Mg/m^3)	2.019	2.188
Absorption coefficient (mm^{-1})	2.384	2.714
F (000)	6268	5904
Reflns collected	114225	84825
Unique reflns	24065	16054
R(int)	0.0407	0.0492
θ range (deg)	2.00 to 27.59 deg.	2.31 to 25.00 deg.
Goodness-of-fit on F^2	1.028	1.035
Final *R* indices [$I>2\sigma(I)$]	*R1= 0.0385, wR2 = 0.0952*	*R1 = 0.0399, wR2 = 0.1003*
R indices (all data)	*R1= 0.0502, wR2 = 0.1018*	*R1 = 0.0521, wR2 = 0.1055*
Data / restraints / parameters	*24065/ 34 / 1201*	*16054 / 161 / 1108*
Largest diff. peak and hole	*1.315 and -1.846 e.A^-3*	*1.741 and -1.044 e.A^-3*

Table S2. Ball and stick representations with partial atomic labeling scheme, selected bond distances (Å) and valence bond calculations of two Keggin building blocks in compounds **1**−**2**.

Compound 1 $[TBA]_3[H_3PMo_{12}O_{40}][Zn_4L^2]$		
		
		ε-Keggin block
	Distances	BVS in the asymmetric unit:
Mo(1)		Σ(Mo1) = 5.1 =>**Mo^{V}**
Mo(1)-O(20)	1.668(3)	
Mo(1)-O(42)	1.949(3)	
Mo(1)-O(27)	1.973(3)	
Mo(1)-O(34)	2.005(3)	
Mo(1)-O(31)	2.014(3)	
Mo(1)-Mo(4)	2.6144(5)	
Mo(2)		Σ(Mo2) =5.9 =>**Mo^{VI}**
Mo(2)-O(18)	1.684(3)	
Mo(2)-O(26)	1.814(3)	
Mo(2)-O(31)	1.814(3)	
Mo(2)-O(35)	2.013(3)	
Mo(2)-O(23)	2.029(3)	
Mo(2)-Mo(8)	3.1859(5)	
Mo(3)		Σ(Mo3) =5.1 =>**Mo^{V}**
Mo(3)-O(28)	1.671(3)	
Mo(3)-O(39)	1.949(3)	
Mo(3)-O(41)	1.962(3)	
Mo(3)-O(34)	2.013(3)	
Mo(3)-O(26)	2.026(3)	

Mo(3)-Mo(5)	2.6169(5)	
Mo(4)		∑(Mo4) =5.1 =>**Mo^{V}**
Mo(4)-O(14)	1.663(3)	
Mo(4)-O(42)	1.951(3)	
Mo(4)-O(27)	1.971(3)	
Mo(4)-O(21)	1.993(3)	
Mo(4)-O(30)	2.066(3)	∑(O30) =1.3 => **OH**
Mo(5)		∑(Mo5) =5.1 =>**Mo^{V}**
Mo(5)-O(29)	1.663(3)	
Mo(5)-O(41)	1.957(3)	
Mo(5)-O(39)	1.959(3)	
Mo(5)-O(15)	2.001(3)	
Mo(5)-O(19)	2.070(3)	∑(O19) =1.3 => **OH**
Mo(6)		∑(Mo6) =5.9 =>**Mo^{VI}**
Mo(6)-O(44)	1.676(3)	
Mo(6)-O(15)	1.813(3)	
Mo(6)-O(12)	1.832(3)	
Mo(6)-O(40)	2.002(3)	
Mo(6)-O(38)	2.007(3)	
Mo(6)-Mo(7)	3.1772(5)	
Mo(7)		∑(Mo7) =5.9 =>**Mo^{VI}**
Mo(7)-O(45)	1.674(3)	
Mo(7)-O(21)	1.813(3)	
Mo(7)-O(43)	1.829(3)	
Mo(7)-O(40)	2.003(3)	
Mo(7)-O(38)	2.011(3)	
Mo(8)		∑(Mo8) =5.9 =>**Mo^{VI}**
Mo(8)-O(13)	1.679(3)	
Mo(8)-O(16)	1.823(3)	
Mo(8)-O(25)	1.831(3)	
Mo(8)-O(35)	2.001(3)	

Mo(8)-O(23)	2.002(3)	
Mo(9)		∑(Mo9) =5.1 =>**Mo^{V}**
Mo(9)-O(11)	1.672(3)	
Mo(9)-O(36)	1.940(3)	
Mo(9)-O(32)	1.951(3)	
Mo(9)-O(25)	2.003(3)	
Mo(9)-O(17)	2.074(3)	∑(O17) =1.3 => **OH**
Mo(9)-Mo(10)	2.6024(6)	
Mo(10)		∑(Mo10) =5.2 =>**Mo^{V}**
Mo(10)-O(46)	1.668(3)	
Mo(10)-O(36)	1.950(3)	
Mo(10)-O(32)	1.958(3)	
Mo(10)-O(43)	1.982(3)	
Mo(10)-O(30)	2.054(3)	
Mo(11)		∑(Mo11) =5.1 =>**Mo^{V}**
Mo(11)-O(24)	1.662(3)	
Mo(11)-O(37)	1.944(3)	
Mo(11)-O(33)	1.955(3)	
Mo(11)-O(16)	1.994(3)	
Mo(11)-O(17)	2.077(3)	
Mo(11)-Mo(12)	2.5977(6)	
Mo(12)		∑(Mo12) =5.3 =>**Mo^{V}**
Mo(12)-O(22)	1.667(3)	
Mo(12)-O(33)	1.946(3)	
Mo(12)-O(37)	1.955(3)	
Mo(12)-O(12)	2.005(3)	
Mo(12)-O(19)	2.067(3)	
Mo(12)-O(2)	2.513(3)	
3 OH, 8 Mo^{V} and 4 Mo^{VI} {ε-$H_3PMo^{V}_8Mo^{VI}_4O_{40}$}$^{8-}$		
Compound 2 $[TPA]_3[H_3PMo_{12}O_{40}][Zn_4L^1]\cdot 0.5H_2O$		



		ε-Keggin block
	Distances	BVS in the asymmetric unit:
Mo(1)		∑(Mo1) = 5.9 =>**Mo^{VI}**
Mo(1)-O(10)	1.679(4)	
Mo(1)-O(24)	1.813(4)	
Mo(1)-O(29)	1.819(4)	
Mo(1)-O(36)	2.016(4)	
Mo(1)-O(39)	2.019(4)	
Mo(1)-Mo(3)	3.1932(9)	
Mo(2)		∑(Mo2) =5.9 =>**Mo^{VI}**
Mo(2)-O(11)	1.684(4)	
Mo(2)-O(21)	1.806(4)	
Mo(2)-O(17)	1.832(4)	
Mo(2)-O(33)	2.001(4)	
Mo(2)-O(42)	2.003(4)	
Mo(2)-Mo(9)	3.1837(9)	
Mo(3)		∑(Mo3) =5.9 =>**Mo^{VI}**
Mo(3)-O(8)	1.685(4)	
Mo(3)-O(35)	1.816(4)	
Mo(3)-O(19)	1.826(4)	
Mo(3)-O(36)	1.990(4)	
Mo(3)-O(39)	1.999(4)	

Mo(4)		∑(Mo4) =5.1 =>**Mo^{V}**
Mo(4)-O(22)	1.669(4)	
Mo(4)-O(30)	1.950(4)	
Mo(4)-O(38)	1.957(4)	
Mo(4)-O(23)	2.007(4)	
Mo(4)-O(24)	2.015(4)	
Mo(4)-Mo(12)	2.6087(10)	
Mo(5)		∑(Mo5) =5.2 =>**Mo^{V}**
Mo(5)-O(16)	1.655(4)	
Mo(5)-O(34)	1.945(4)	
Mo(5)-O(41)	1.961(4)	
Mo(5)-O(9)	1.991(4)	
Mo(5)-O(18)	2.081(4)	∑(O18) =1.3 => **OH**
Mo(5)-Mo(8)	2.6029(8)	
Mo(6)		∑(Mo6) =5.1 =>**Mo^{V}**
Mo(6)-O(15)	1.661(5)	
Mo(6)-O(37)	1.955(4)	
Mo(6)-O(40)	1.956(4)	
Mo(6)-O(35)	1.998(4)	
Mo(6)-O(32)	2.070(4)	∑(O32) =1.3 => **OH**
Mo(6)-Mo(10)	2.6098(9)	
Mo(7)		∑(Mo7) =5.1 =>**Mo^{V}**
Mo(7)-O(12)	1.669(5)	
Mo(7)-O(26)	1.951(4)	
Mo(7)-O(28)	1.956(4)	
Mo(7)-O(17)	1.995(4)	
Mo(7)-O(31)	2.068(4)	∑(O31) =1.3 => **OH**
Mo(7)-Mo(11)	2.6116(9)	
Mo(8)		∑(Mo8) =5.2 =>**Mo^{V}**
Mo(8)-O(27)	1.662(4)	
Mo(8)-O(34)	1.948(4)	

Mo(8)-O(41)	1.956(4)	
Mo(8)-O(23)	2.007(4)	
Mo(8)-O(29)	2.021(4)	
Mo(9)		∑(Mo9) =5.9 =>**Mo^{VI}**
Mo(9)-O(20)	1.678(4)	
Mo(9)-O(9)	1.814(4)	
Mo(9)-O(25)	1.821(4)	
Mo(9)-O(42)	2.011(4)	
Mo(9)-O(33)	2.014(17)	
Mo(10)		∑(Mo10) =5.1 =>**Mo^{V}**
Mo(10)-O(14)	1.664(4)	
Mo(10)-O(37)	1.951(4)	
Mo(10)-O(40)	1.958(4)	
Mo(10)-O(25)	1.999(4)	
Mo(10)-O(18)	2.071(4)	
Mo(11)		∑(Mo11) =5.2 =>**Mo^{V}**
Mo(11)-O(13)	1.662(5)	
Mo(11)-O(26)	1.952(4)	
Mo(11)-O(28)	1.952(4)	
Mo(11)-O(19)	1.988(4)	
Mo(11)-O(32)	2.067(4)	
Mo(12)		∑(Mo12) =5.1 =>**Mo^{V}**
Mo(12)-O(7)	1.659(4)	
Mo(12)-O(30)	1.948(4)	
Mo(12)-O(38)	1.951(4)	
Mo(12)-O(21)	2.008(4)	
Mo(12)-O(31)	2.091(4)	
		3 OH, 8 Mo^{V} and 4 Mo^{VI} {ε-$H_3PMo^{V}_8Mo^{VI}_4O_{40}$}$^{8-}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for compounds **1**−**2**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Compound 1

	x	y	z	U(eq)
Mo(1)	4509(1)	6008(1)	4997(1)	16(1)
Mo(2)	5740(1)	6625(1)	6196(1)	15(1)
Mo(3)	6156(1)	5446(1)	6108(1)	15(1)
Mo(4)	2894(1)	5778(1)	4820(1)	18(1)
Mo(5)	5818(1)	4799(1)	6787(1)	17(1)
Mo(6)	3752(1)	4441(1)	6654(1)	16(1)
Mo(7)	2258(1)	4941(1)	5637(1)	16(1)
Mo(8)	4794(1)	6911(1)	7127(1)	17(1)
Mo(9)	2682(1)	6567(1)	6821(1)	22(1)
Mo(10)	1837(1)	6093(1)	5882(1)	21(1)
Mo(11)	4401(1)	6016(1)	7971(1)	22(1)
Mo(12)	4775(1)	5138(1)	7846(1)	21(1)
Zn(1)	2546(1)	5297(1)	7089(1)	24(1)
Zn(2)	3507(1)	6884(1)	5650(1)	21(1)
Zn(3)	6282(1)	5965(1)	7495(1)	21(1)
Zn(4)	4204(1)	4763(1)	5350(1)	16(1)
P(1)	4135(1)	5735(1)	6411(1)	14(1)
O(1)	4044(2)	6119(1)	6855(1)	19(1)
O(2)	4451(2)	5272(1)	6757(1)	19(1)
O(3)	4798(2)	5885(1)	6098(1)	17(1)
O(4)	3240(2)	5668(1)	5937(1)	18(1)
O(5)	2884(2)	7469(1)	5355(2)	34(1)
O(6)	1891(3)	7000(1)	4749(2)	42(1)
O(7)	-2851(2)	9707(1)	3390(2)	37(1)
O(8)	7374(2)	6025(1)	8120(1)	32(1)
O(9)	-2082(3)	10813(1)	6972(2)	42(1)
O(10)	1839(2)	5119(1)	7561(2)	37(1)
O(11)	1886(2)	6907(1)	6897(2)	34(1)
O(12)	4041(2)	4592(1)	7438(1)	26(1)
O(13)	5265(2)	7441(1)	7317(2)	33(1)
O(14)	2494(2)	5826(1)	4090(1)	27(1)
O(15)	4846(2)	4336(1)	6649(1)	22(1)
O(16)	4935(2)	6621(1)	7833(1)	26(1)
O(17)	3223(2)	6368(1)	7697(1)	25(1)
O(18)	6369(2)	7107(1)	6256(2)	30(1)
O(19)	5797(2)	4827(1)	7648(1)	20(1)
O(20)	4473(2)	6111(1)	4302(1)	24(1)
O(21)	2370(2)	5169(1)	4955(1)	21(1)
O(22)	5026(2)	4955(1)	8544(1)	34(1)
O(23)	4631(2)	6910(1)	6260(1)	21(1)
O(24)	4582(2)	6035(1)	8696(2)	35(1)
O(25)	3642(2)	7039(1)	6967(1)	25(1)

O(26)	6485(2)	6135(1)	6278(1)	21(1)
O(27)	3532(2)	6369(1)	5101(1)	20(1)
O(28)	7082(2)	5228(1)	6057(1)	24(1)
O(29)	6651(2)	4434(1)	6883(1)	27(1)
O(30)	1902(2)	6104(1)	5037(1)	22(1)
O(31)	5200(2)	6570(1)	5409(1)	21(1)
O(32)	2224(2)	5924(1)	6719(1)	24(1)
O(33)	3672(2)	5462(1)	7683(1)	24(1)
O(34)	5620(2)	5644(1)	5261(1)	16(1)
O(35)	5776(2)	6527(1)	7038(1)	21(1)
O(36)	2642(2)	6621(1)	6003(1)	21(1)
O(37)	5413(2)	5724(1)	7854(1)	21(1)
O(38)	3415(2)	4626(1)	5800(1)	19(1)
O(39)	5331(2)	4925(1)	5939(1)	16(1)
O(40)	2709(2)	4853(1)	6514(1)	22(1)
O(41)	6299(2)	5437(1)	6955(1)	18(1)
O(42)	3946(2)	5400(1)	4994(1)	17(1)
O(43)	1558(2)	5411(1)	5754(1)	25(1)
O(44)	3325(2)	3898(1)	6622(2)	29(1)
O(45)	1586(2)	4482(1)	5413(2)	30(1)
O(46)	858(2)	6331(1)	5750(2)	36(1)

Compound 2

	x	y	z	U(eq)
Mo(1)	1287(1)	3068(1)	1191(1)	24(1)
Mo(2)	-2655(1)	4177(1)	418(1)	25(1)
Mo(3)	246(1)	1915(1)	1433(1)	23(1)
Mo(4)	391(1)	4484(1)	1141(1)	26(1)
Mo(5)	-352(1)	3403(1)	-804(1)	27(1)
Mo(6)	-1219(1)	1505(1)	399(1)	29(1)
Mo(7)	-2220(1)	3341(1)	1603(1)	30(1)
Mo(8)	778(1)	3774(1)	-54(1)	26(1)
Mo(9)	-2289(1)	3537(1)	-672(1)	25(1)
Mo(10)	-1503(1)	2084(1)	-535(1)	29(1)
Mo(11)	-1635(1)	2229(1)	1639(1)	30(1)
Mo(12)	-1048(1)	4642(1)	1314(1)	28(1)
Zn(1)	-102(1)	3312(1)	2048(1)	30(1)
Zn(2)	-2862(1)	2578(1)	333(1)	32(1)
Zn(3)	549(1)	2154(1)	84(1)	28(1)
Zn(4)	1009(1)	5287(1)	126(1)	27(1)
P(1)	-861(1)	3174(1)	590(1)	23(1)

O(1)	1321(3)	1744(2)	-264(2)	39(1)
O(2)	733(3)	1986(2)	-1110(2)	44(1)
O(3)	-3866(3)	2173(2)	241(2)	42(1)
O(4)	-3328(3)	1367(2)	725(2)	46(1)
O(5)	265(3)	3477(2)	2796(2)	43(1)
O(6)	-621(3)	4222(2)	2809(2)	43(1)
O(7)	-955(3)	5310(2)	1643(2)	40(1)
O(8)	936(3)	1477(2)	1810(2)	39(1)
O(9)	-1448(2)	3703(2)	-1006(2)	31(1)
O(10)	2163(3)	2833(2)	1519(2)	39(1)
O(11)	-3483(3)	4553(2)	159(2)	40(1)
O(12)	-2801(3)	3288(2)	2081(2)	41(1)
O(13)	-2066(3)	1916(2)	2128(2)	44(1)
O(14)	-1774(3)	1495(2)	-953(2)	42(1)
O(15)	-1435(3)	787(2)	200(2)	43(1)
O(16)	25(3)	3543(2)	-1368(2)	38(1)
O(17)	-2930(2)	3778(2)	1013(2)	32(1)
O(18)	-775(3)	2521(2)	-1005(2)	33(1)
O(19)	-544(3)	1924(2)	1846(2)	31(1)
O(20)	-3046(3)	3814(2)	-1112(2)	43(1)
O(21)	-2057(3)	4762(2)	799(2)	32(1)
O(22)	805(3)	5114(2)	1447(2)	38(1)
O(23)	915(2)	4485(2)	471(2)	26(1)
O(24)	1183(2)	3841(2)	1446(2)	31(1)
O(25)	-2317(3)	2712(2)	-807(2)	34(1)
O(26)	-1201(2)	3013(2)	1930(2)	29(1)
O(27)	1421(3)	3989(2)	-452(2)	36(1)
O(28)	-2454(2)	2627(2)	1123(2)	32(1)
O(29)	1489(2)	3285(2)	516(2)	29(1)
O(30)	-206(3)	4114(2)	1666(2)	30(1)
O(31)	-1709(3)	4182(2)	1829(2)	33(1)
O(32)	-1781(3)	1515(2)	1080(2)	32(1)
O(33)	-2007(2)	4270(2)	-181(2)	29(1)
O(34)	429(2)	2955(2)	-302(2)	28(1)
O(35)	-226(2)	1379(2)	922(2)	31(1)
O(36)	546(2)	2764(2)	1687(2)	30(1)
O(37)	-525(2)	1825(2)	-89(2)	31(1)
O(38)	-561(2)	4743(2)	659(2)	28(1)
O(39)	827(2)	2270(2)	868(2)	30(1)
O(40)	-2108(2)	2007(2)	69(2)	31(1)
O(41)	-226(2)	4151(2)	-355(2)	27(1)
O(42)	-2784(2)	3384(2)	0(2)	31(1)
O(43)	-858(2)	2533(2)	869(2)	26(1)
O(44)	-1132(2)	3086(2)	-32(2)	28(1)

O(45)	-1421(2)	3606(2)	848(2)	27(1)
O(46)	-30(2)	3463(2)	679(2)	26(1)

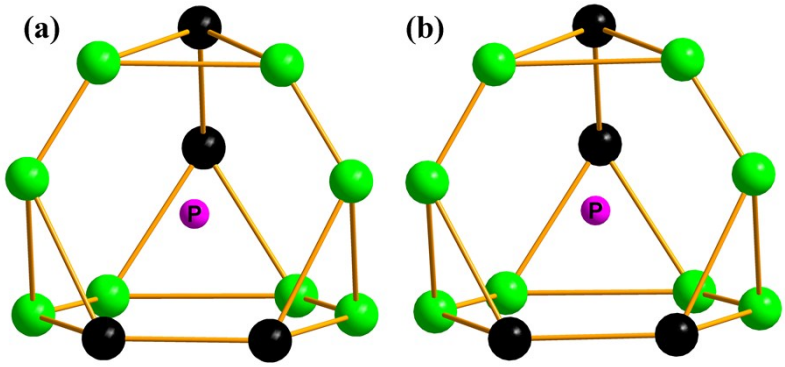


Figure S1. Representations of the disposition of the twelve Mo atoms: the {ε-$H_3PMo^{V}_8Mo^{VI}_4O_{40}\}^{8-}$ polyoxoanion in compounds **1** (a) and **2** (b), respectively.

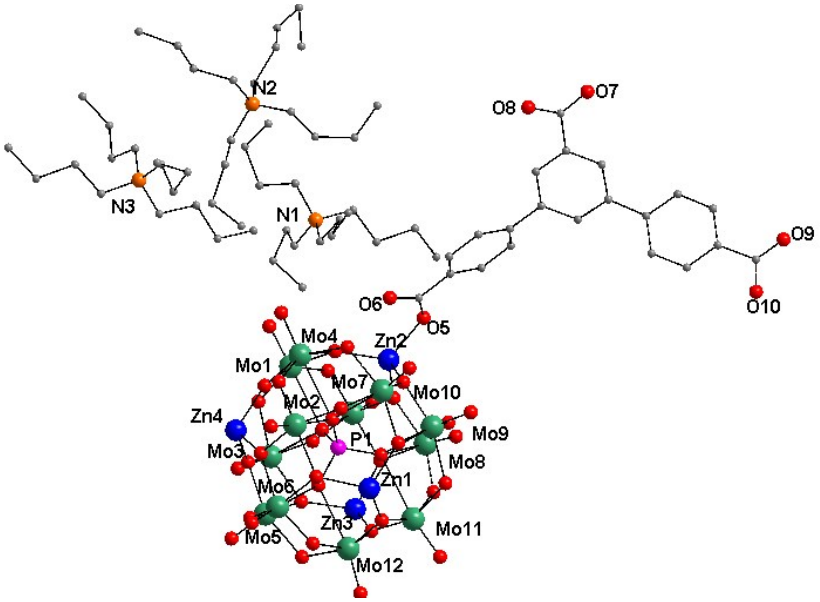


Figure S2. Ball-and-stick representation of the asymmetric unit of compound **1**. Hydrogen atoms are omitted for clarity.

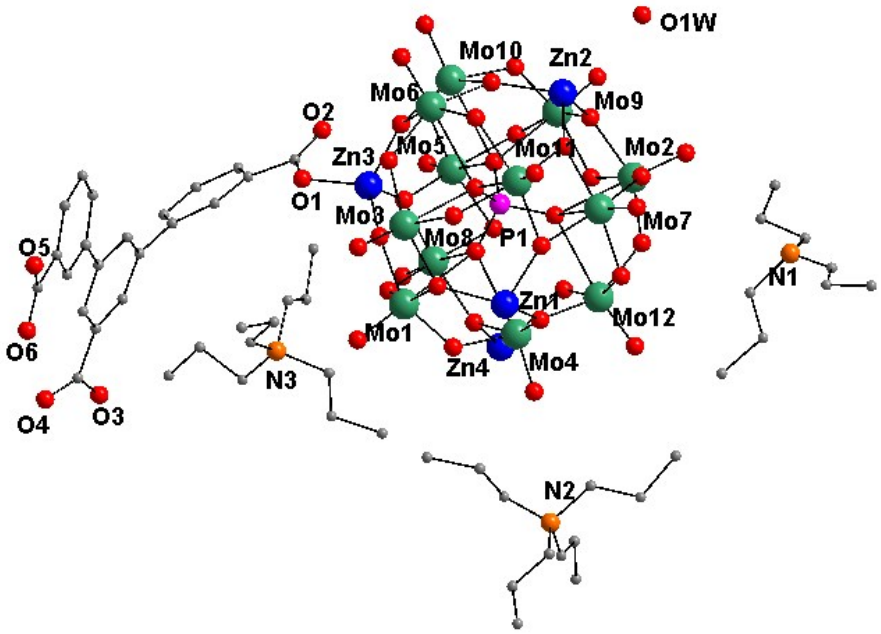


Figure S3. Ball-and-stick representation of the asymmetric unit of compound **2**. Hydrogen atoms are omitted for clarity.

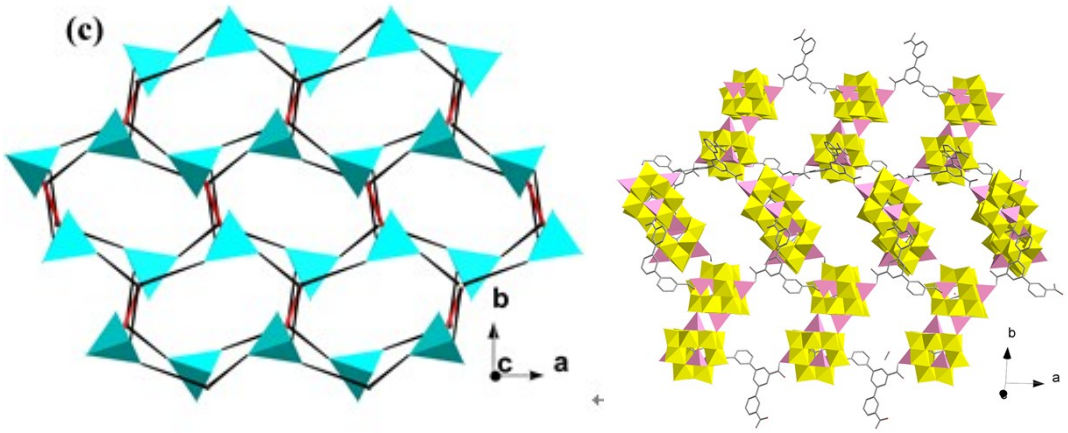


Figure S4. Polyhedral representation of compound **2** in *ab* planes.

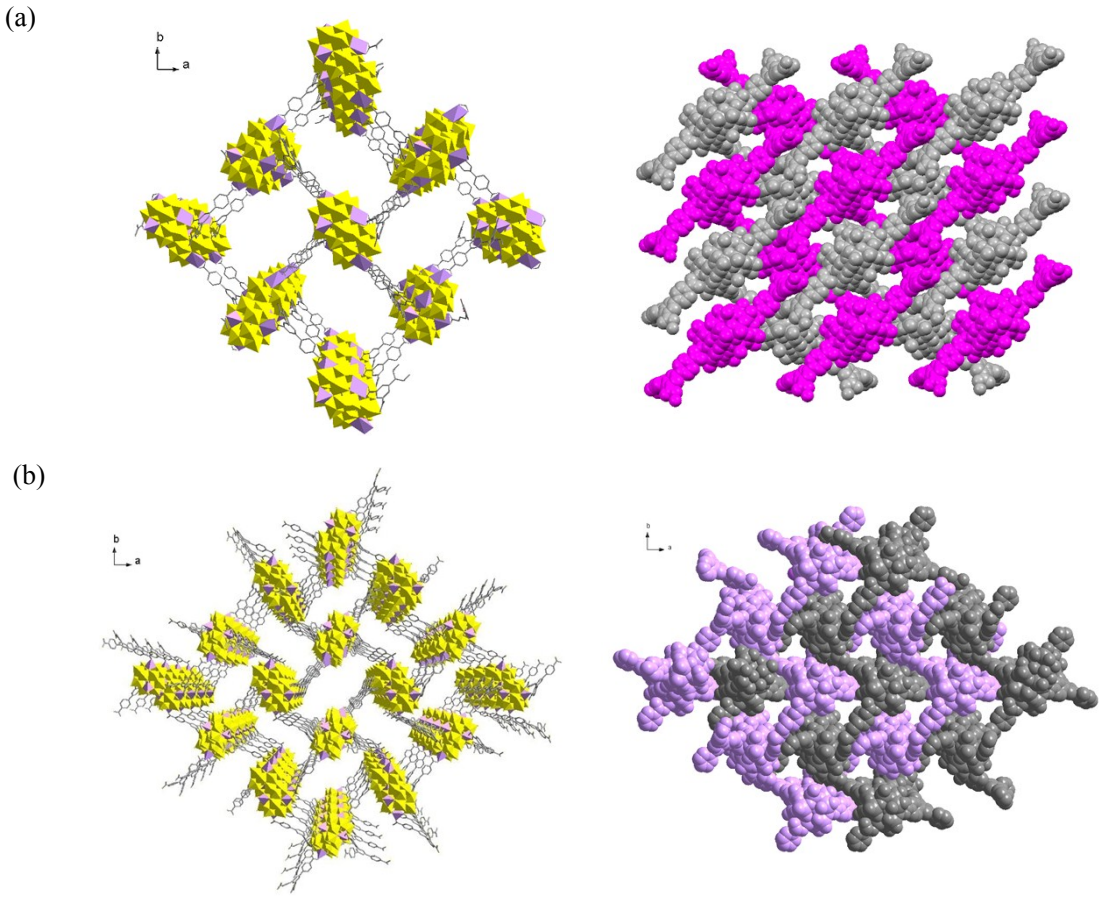


Figure S5. Comparisons of the 3D frameworks of compound **1** (a) and compound YZU-100 (**b**) in our previous work.

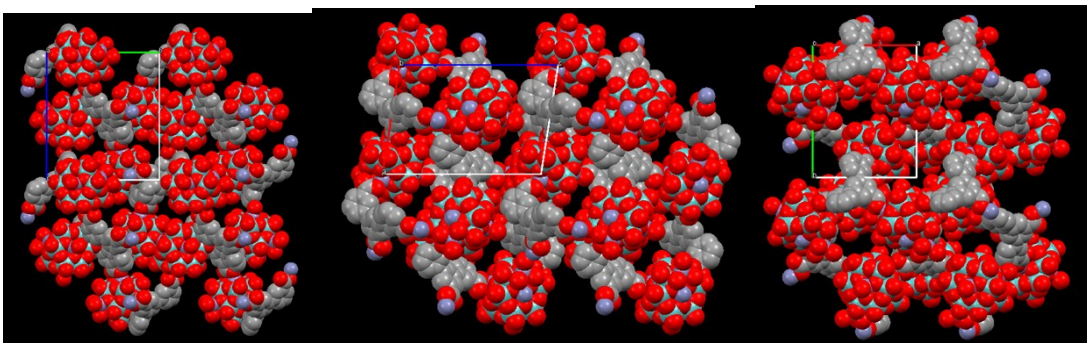


Figure S6. Space-filling representations of compound **2** in the *bc*, *ac* and *ab* plane, respectively.

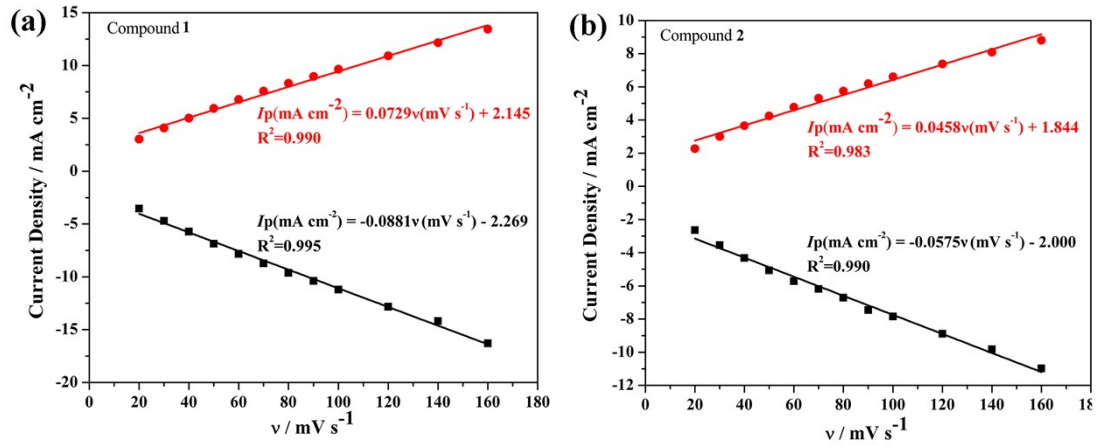


Figure S7. The dependence of cathodic and anodic peak currents of the II-II' waves as a function of the scan rate for GCEs of **1**–**2**.

Compound **1:**	$Ip(mA\ cm^{-2}) = 0.0729\times v\ (mV\ s^{-1}) + 2.145$	$R^2=0.990$
	$Ip(mA\ cm^{-2}) = -0.0881\times v\ (mV\ s^{-1}) - 2.269$	$R^2=0.995$
Compound **2:**	$Ip(mA\ cm^{-2}) = 0.0458\times v\ (mV\ s^{-1}) + 1.844$	$R^2=0.983$
	$Ip(mA\ cm^{-2}) = -0.0575\times v\ (mV\ s^{-1}) - 2.000$	$R^2=0.990$

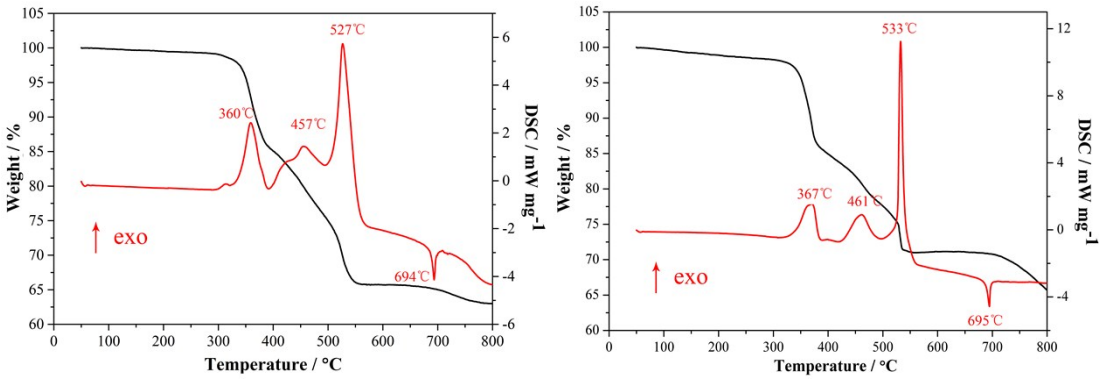
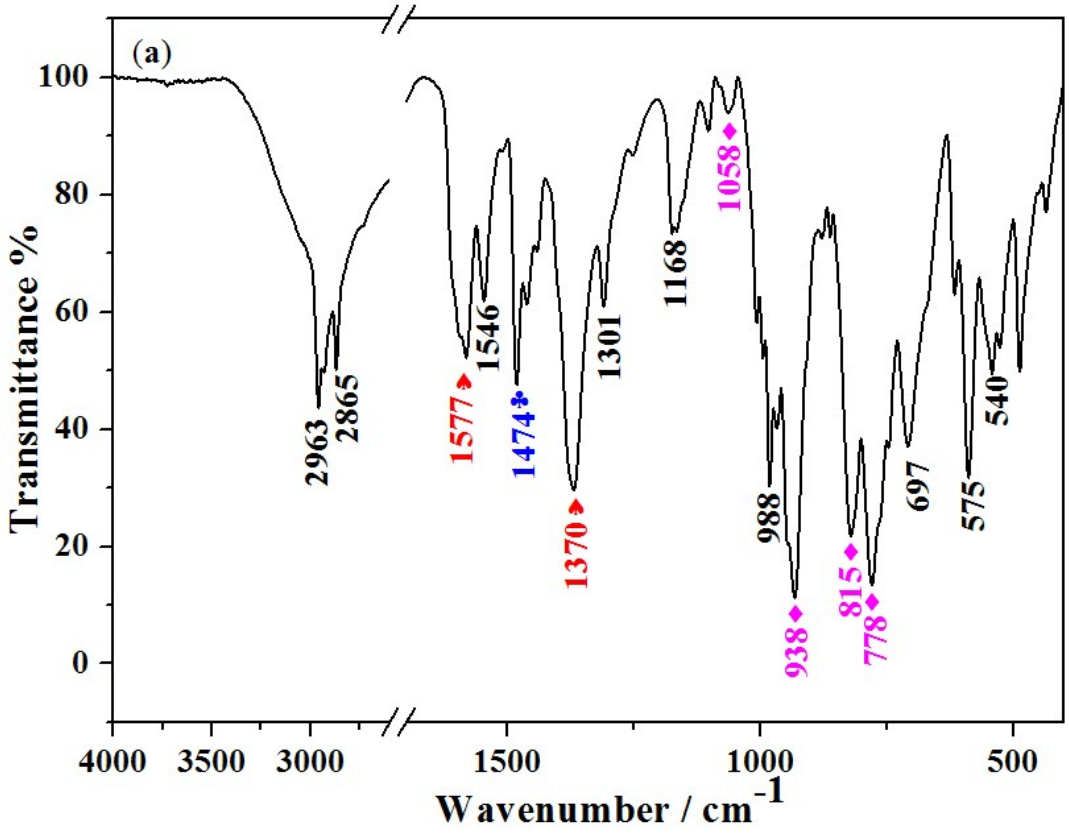


Figure S8. TGA/DSC data recorded in air for compounds **1** (left) and **2** (right).

Compound 1 (YZU-105)	$[TBA]_3[H_3PMo_{12}O_{40}][Zn_4L^2]$	
Mr=3177.0	$[C_{48}H_{111}N_3][H_3PMo_{12}O_{40}][Zn_4C_{21}H_{11}O_6]$	
	$C_{69}H_{125}N_3PMo_{12}O_{46}Zn_4$	
3(TBA), (730.43)	23.0% (Cal.)	34.3%(Cal.), 34.5%(Exp.), 580℃
(L^2), (359.31)	11.3% (Cal.)	
Compound 2 (YZU-106)	$[TPA]_3[H_3PMo_{12}O_{40}][Zn_4L^2]\cdot 0.5H_2O$	
	$[C_{36}H_{87}N_3][H_3PMo_{12}O_{40}][Zn_4C_{21}H_{11}O_6]\cdot 0.5H_2O$	
Mr=3017.2	$C_{57}H_{102}N_3PMo_{12}O_{46.5}Zn_4$	
$0.5H_2O$	0.3% (Cal.)	30.8% (Cal.), 29.6 %(Exp.), 580℃
3(TPA), (562.11)	18.6% (Cal.)	
(L^2), (359.31)	11.9% (Cal.)	

Thermogravimetric Analyses. Thermogravimetric analyses of compounds **1**–**2** were carried out in air atmosphere with a heating rate of 5 °C min^{-1} in the temperature range from 50 to 800 °C. The TGA curve for **1** exhibit three distinct weight losses in the range of 50–580 °C. The observed total weight loss of 34.5% is in good agreement the calculated value of 34.3%, which is attributed to the loss of three TBA and one ligand molecule. Two moderate exothermic peaks at 360 and 457 °C indicate the oxidation processes for the TBA. A sharp exothermic peak at 527 °C indicates the oxidation process for the L^2 ligand molecule. The last endothermic peak at 694 °C is attributed to the melting point peak of MoO_3. For compound **2**, four consecutive weight losses were observed in the range of 50–580 °C. The observed total weight loss of 29.6% (cal. 30.8%) is attributed to the loss of one half water, three TPA and one ligand molecule. Two moderate exothermic peaks at 367 and 461 °C indicate the oxidation processes for the TPA. A sharp exothermic peak at 533 °C indicates the oxidation process for the L^1 ligand molecule. The last endothermic peak at 695 °C is attributed to the melting point peak of MoO_3.



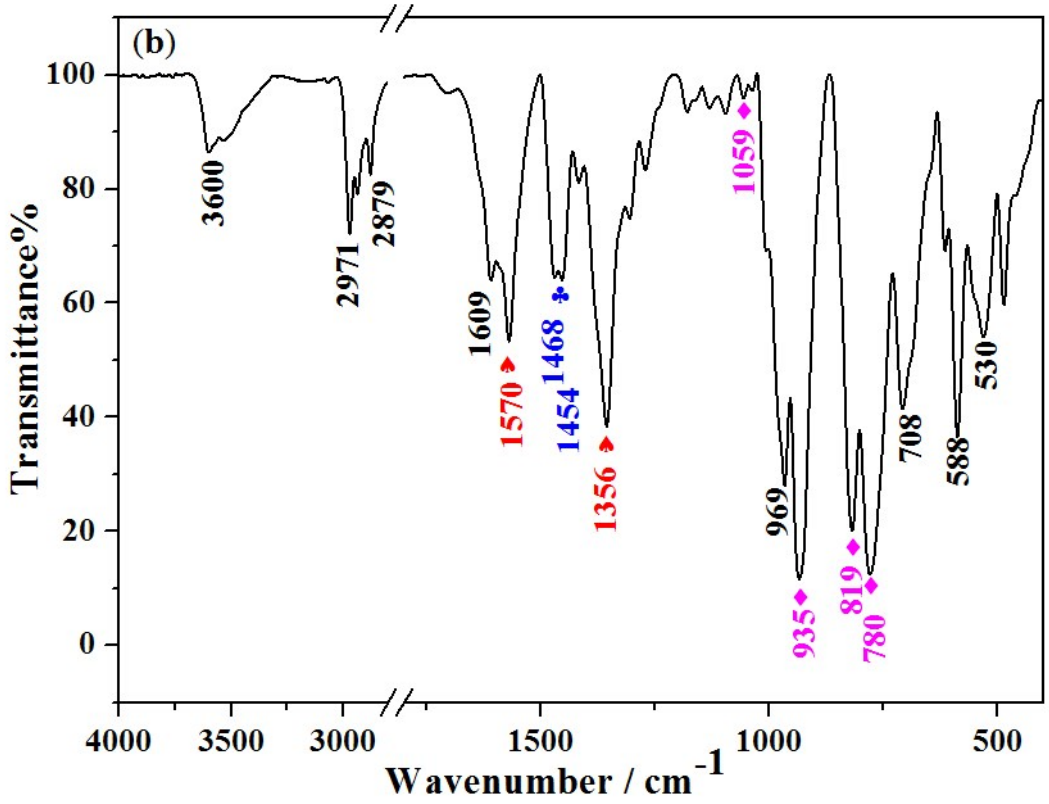


Figure S9. The IR spectra of compounds **1** (a) and **2** (b).

The υ(C–O) vibrations of the carboxylate linker are identified at 1577 (ν_{asym}), 1372 cm^{-1} (ν_{sym}) for **1**, and 1570 (ν_{asym}), 1356 cm^{-1} (ν_{sym}) for **2**. The signature of the TBA cations is found around 1474 cm^{-1} in compound **1**. The TPA ions are identified at 1468 and 1454 cm^{-1} in compound **2**. The characteristic broad peak at 3600 cm^{-1} confirms the existence of water molecule in compound **2**. Moreover, the υ(P–O) and υ(Mo–O$_d$) vibrations of the Keggin skeleton are encountered around 1058 and 938 cm^{-1} in **1**, and 1059 and 935 cm^{-1} in **2**. The υ(Mo–O$_b$–Mo) and υ(Mo–O$_c$–Mo) vibrations are found around 815 and 778 cm^{-1} in **1**, and 819 and 780 cm^{-1} in **2**.

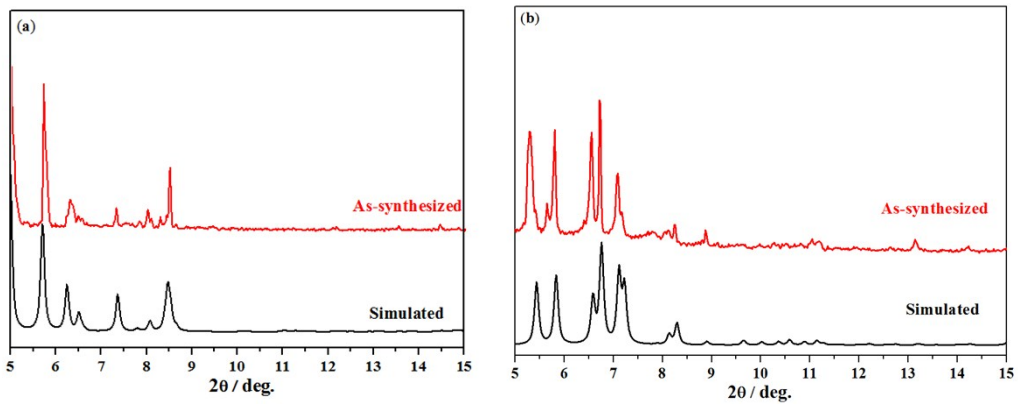


Figure S10. Experimental and simulated powder X-ray diffraction patterns of compounds **1** (a) and **2** (b).

Table S4. Summary for synthesis condition of **YZU 100−106**.

Compound	Formula	Counter cations	Ligand	Synthesis condition		Reference
YZU-103	$[TBA]_9\{[H_3PMo_{12}O_{40}]_2[H_2PMo_{12}O_{40}]\}[Zn_{12}(L^1)_4]$	TBA	L^1	180,3d	pH=3.6	[23]
YZU-104	$[TBA]_3[H_4PMo_{12}O_{40}][Zn_4(HL^2)_2]\cdot 0.5H_2O$	TBA	L^2	200,3d	pH=4.0	[23]
YZU-105	$[TBA]_3[H_3PMo_{12}O_{40}][Zn_4L^2]$	TBA	L^2	180,3d	pH=4.7	This work
YZU-106	$[TPA]_3[H_3PMo_{12}O_{40}][Zn_4L^1]\cdot 0.5H_2O$	TPA	L^1	180,3d	pH=4.2	This work
YZU-100	$[TBA]_6[H_3PMo_{12}O_{40}]_2[Zn_8(BTB)_2]\cdot(\sim 35H_2O)$	TBA	H_3BTB	180,3d	pH=4.9	[20]
YZU-101	$[TBA]_3[H_4PMo^V_8Mo^{VI}_4O_{40}Zn_4][C_7H_6(COO)_2]_2$	TBA	H_2MIP	180,3d	pH=4.9	[17]
YZU-102	$[TBA]_3[H_2PMo^V_8Mo^{VI}_4O_{40}Zn_4][C_7H_6(COO)_2]$	TBA	H_2MIP	180,3d	pH=4.0	[18]

Structural illustration for YZU-101:

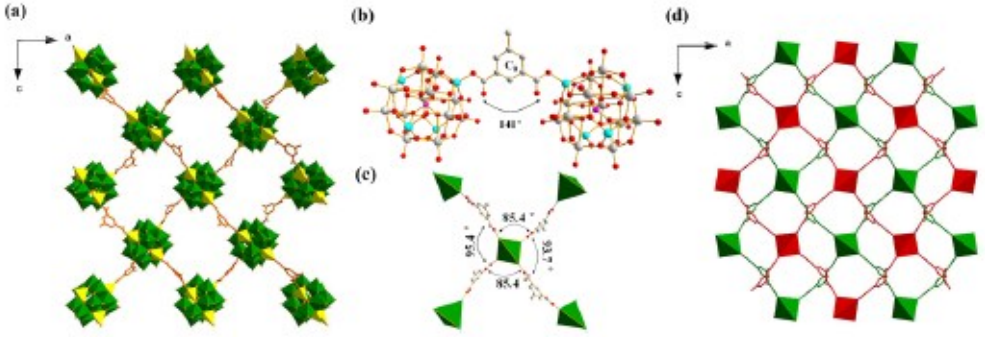


Fig. 2 (a) *Polyhedral* representation of the 2D sheet in the *ac* plane; (**b**) View of the connection mode of the 5-mip linker with the indication of the Zn–C_6–Zn angle; (c) View of the connection mode between adjacent Zn_4-ε-Keggin anions with the indication of the P–P–P angle; Zn_4-ε-Keggin: *green tetrahedron*; (**d**) Schematic view of the staggered arrangment of adjacent layers along the *b* axis

17 B.-X. Dong, L. Chen, S.-Y. Zhang, Y.-C. Wu, H. Tian, J. Ge, L. Song, Y.-L. Teng, W.-L. Liu, *J. Clust. Sci*., 2015, **26**, 1595–1605.

Structural illustration for YZU-102:

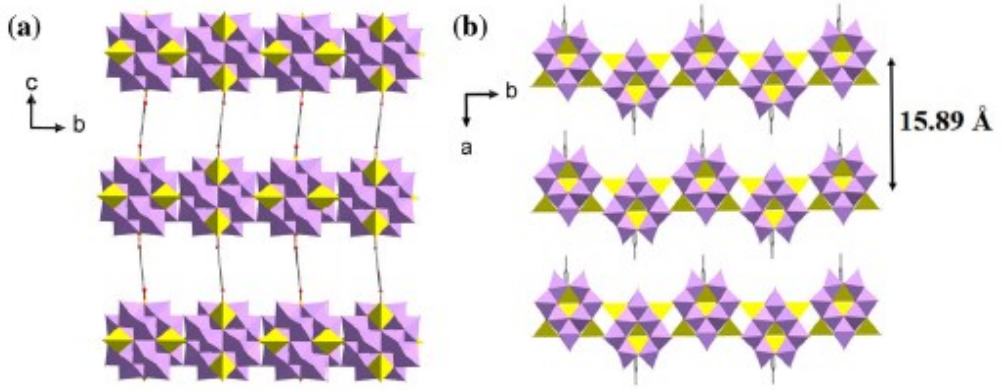


Fig. 2 a Polyhedral presentation of the 2D sheet in the *bc* plane; **b** View of the staggered arrangment of adjacent layers along the *a* axis

18 B.-X. Dong, Y.-C. Wu, H. Tian, C.-B. Liu, W.-L. Liu, Y.-L. Teng, *J. Clust. Sci*., 2016, **27**, 361–371.

Structural illustration for YZU-103:

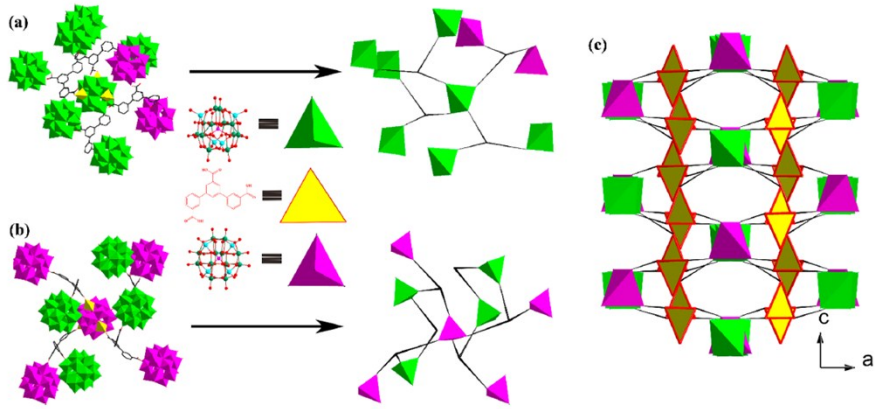


Figure 2. Polyhedral and schematic presentations of the 8-connected Zn_4-ε-Keggin fragment constructed by {ε-Keggin 1} (a) and {ε-Keggin 2} (b); (c) Illustration of the 3D (3,4)-connected framework of **1**.

Structural illustration for YZU-104:

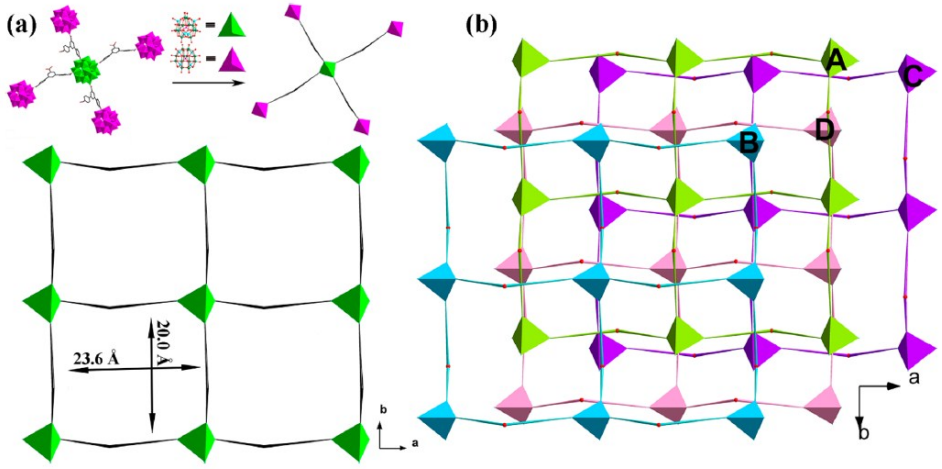


Figure 3. (a) Polyhedral and schematic presentations of the 4-connected Zn_4-ε-Keggin fragment in a 2D 4^4 network of **2**. (b) Schematic presentation of the ABCD stacking style of **2**.

23 B.-X. Dong, F.-Y. Bu, Y.-C. Wu, J. Zhao, Y.-L. Teng, W.-L. Liu and Z.-W. Li**,** *Cryst. Growth Des.*, August 23, 2017, DOI: 10.1021/acs.cgd.7b00825.