Electronic Supplementary Material (ESI) for Dalton Transactions.

(Supplementary information)

The First Tritopic Bridging Ligand 1,3,5-tris(4-carboxyphenyl)-benzene (H_3BTB) Functionalized Porous Polyoxometalate-Based Metal-Organic Framework (POMOF): From Design, Sythesis to Electrocatalytic Properties

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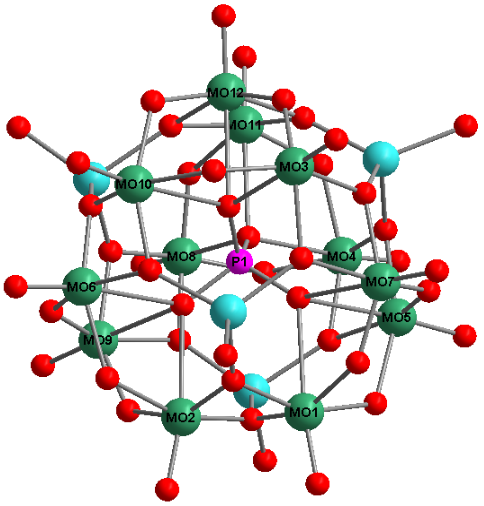
Experimental General Information

X-ray Crystallographic Study. Single-crystal X-ray diffraction analysis data was collected on a Bruker Smart Apex CCD diffractometer with Mo Kα monochromated radiation (λ=0.71073 Å) at room temperature. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the SHELXTL package. Anisotropic thermal parameters were used to refine all Mo, Zn, P, O (except disordered O22 and O90) atoms. All the C atoms in the BTB^{3-} ligand were anisotropically refined. Part of C and N atoms were isotropically refined to avoid resulting in the "non positive defines". Therefore, isotropic non-H atoms in main residue were reported with 29 in checkcif. After locating and refining the hybrid POM and TBA, the difference Fourier map showed many peaks of very low electronic density, suggesting an extensive disordered of the water solvent molecules. Thus, the solvent molecules reside in those regions of diffuse electron density were treated by the PLATON/SQUEEZE procedure,[14] which suggested a unit cell accessible volume of 1407.3 $Å^3$ (about 12.2%), which could accommodate about 35 water molecules per formula unit. The structure was then refined again using the generated solvent-free diffraction data. Sensible restraints (including DFIX, ISOR, SIMU, DELU) were used confine the C–N and C–C bond with similar lengths, and to confine the thermal parameters as well as Hirshfeld differences. The hydrogen atoms attached to carbon positions were placed in geometrically calculated positions. Hydrogen atoms attached to the disordered C atoms and the bridging oxygen atoms (O19, O21, O24, O62, O66 and O86) were not located but included in the structural formula because of the charge balance requirements. Improved data was gotten by deleting all the solvent water and TBA molecules and then applied PLATON/SQUEEZE. The crystal data and structure refinement results of compound **1** are summarized in Table S1. Selected bond lengths and angles are listed in Tables S2 and S3, respectively. Crystallographic data for the structure reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC numbers 1011903 and 1028529 for SQUEEZED water, and SQUEEZED water and TBA, respectively.

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

Compound **1**	**1a** (squeezed water)	**1a′** (squeezed water and TBA)
Empirical formula	$C_{150}H_{252}N_6P_2Mo_{24}O_{92}Zn_8$ $\cdot(\sim 35H_2O)$	$(TBA)_6C_{54}H_{30}P_2Mo_{24}O_{92}Zn_8$ $\cdot(\sim 35H_2O)$
Formula weight	6499.02	5038.24
Temperature (K)	296(2)	296(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	*P-1*	*P-1*
a (Å)	15.745(2)	15.745(2)
b (Å)	26.506(4)	26.506(4)
c (Å)	27.765(4)	27.765(4)
a	86.976(4)	86.976(4)
β	84.139(4)	84.139(4)
γ	88.302(4)	88.302(4)
Volume (Å ^{3})	11507(3)	11507(3)
Z	2	2
D $_{calc}$ (mg/m^3)	1.876	1.454
Absorption coefficient (mm^{-1})	2.167	2.144
F (000)	6416	4736
Reflns collected	218677	218702
Unique reflns	39866	39866
R(int)	0.0791	0.0870
θ range (deg)	1.476to 25.00 deg.	0.738 to 25.00
Goodness-of-fit on F^2	1.037	1.091
Final *R* indices [$I>2\sigma(I)$]	R_1 =0.0882,wR_2=0.2129	*R1 = 0.0726, wR2 = 0.2043*
R indices (all data)	R_1 =0.1209,wR_2=0.2279	*R1 = 0.1020, wR2 = 0.2162*
Data / restraints / parameters	*39866 / 133 / 2400*	*39866/ 71 / 1615*
Largest diff. peak and hole	*1.282 and -1.102 e.A^-3*	*1.539and -1.128e.A^-3*
Total potential solvent area Vol Å ^{3} per Unit Cell Vol 11507.0 Å ^{3}	*1407.3*	*6866.7*
	12.2%	*59.7%*
CCDC number	1011903	1028529

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 compound **1**.

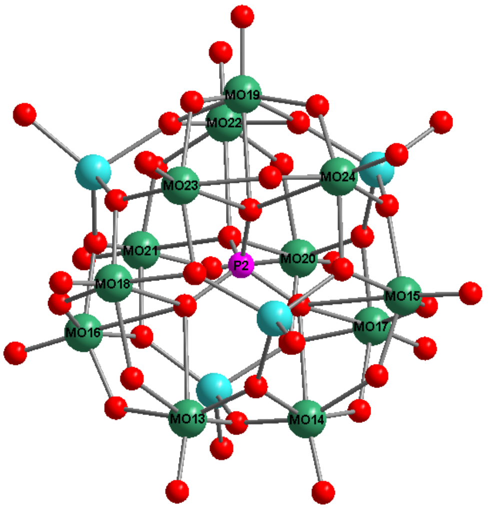


Keggin block-1

	Distances	BVS in the asymmetric unit:
Mo(1)		Σ(Mo1) = 5.1 **=>Mo$^{\mathrm{V}}$**
Mo(1)-O(9)	1.673(8)	
Mo(1)-O(15)	1.951(7)	
Mo(1)-O(17)	1.973(9)	
Mo(1)-O(35)	1.996(8)	
Mo(1)-O(21)	2.051(8)	Σ(O21) =1.3 **=> OH**
Mo(1)-Mo(2)	2.609(2)	
Mo(2)		Σ(Mo2) =5.1 **=>Mo$^{\mathrm{V}}$**
Mo(2)-O(5)	1.655(7)	
Mo(2)-O(15)	1.942(7)	
Mo(2)-O(17)	1.952(8)	
Mo(2)-O(31)	1.992(8)	
Mo(2)-O(24)	2.052(18)	Σ(O24) =1.3 **=> OH**
Mo(2)-Mo(1)	2.609(2)	
Mo(3)		Σ(Mo3) =5.8 **=>Mo$^{\mathrm{VI}}$**
Mo(3)-O(33)	1.703(8)	
Mo(3)-O(18)	1.813(7)	
Mo(3)-O(28)	1.823(7)	

Mo(3)-O(11)	2.013(8)	
Mo(3)-O(8)	2.019(7)	
Mo(3)-Mo(7)	3.176(2)	
Mo(4)		Σ(Mo4) =5.2 =>**Mo^{V}**
Mo(4)-O(39)	1.678(8)	
Mo(4)-O(27)	1.959(7)	
Mo(4)-O(14)	1.953(7)	
Mo(4)-O(26)	1.996(7)	
Mo(4)-O(19)	2.034(8)	Σ(O19) =1.3 => **OH**
Mo(4)-Mo(5)	2.591(2)	
Mo(5)		Σ(Mo5) =5.1 =>**Mo^{V}**
Mo(5)-O(29)	1.670(7)	
Mo(5)-O(14)	1.936(7)	
Mo(5)-O(27)	1.958(7)	
Mo(5)-O(34)	2.007(8)	
Mo(5)-O(21)	2.097(8)	
Mo(5)-Mo(4)	2.591(3)	
Mo(6)		Σ(Mo6) =5.1 =>**Mo^{V}**
Mo(6)-O(32)	1.650(8)	
Mo(6)-O(12)	1.952(7)	
Mo(6)-O(7)	1.945(7)	
Mo(6)-O(23)	1.992(8)	
Mo(6)-O(24)	2.071(7)	
Mo(6)-Mo(10)	2.616(2)	
Mo(7)		Σ(Mo7) =5.9 =>**Mo^{VI}**
Mo(7)-O(30)	1.710(8)	
Mo(7)-O(34)	1.840(8)	
Mo(7)-O(35)	1.831(8)	
Mo(7)-O(8)	1.982(7)	
Mo(7)-O(11)	2.013(7)	
Mo(7)-Mo(3)	3.177(3)	
Mo(8)		Σ(Mo8) =5.7 =>**Mo^{VI}**

Mo(8)-O(36)	1. 675(8)	
Mo(8)-O(26)	1.810(7)	
Mo(8)-O(25)	1.818(8)	
Mo(8)-O(13)	1.995(7)	
Mo(8)-O(10)	2.035(7)	
Mo(8)-Mo(9)	3.182(2)	
Mo(9)		Σ(Mo9) =5.7 **=>Mo**$^{\mathbf{VI}}$
Mo(9)-O(38)	1.684(8)	
Mo(9)-O(23)	1.823(7)	
Mo(9)-O(31)	1.837(7)	
Mo(9)-O(10)	2.024(7)	
Mo(9)-O(13)	2.014(7)	
Mo(9)-Mo(8)	3.182(2)	
Mo(10)		Σ(Mo10) =5.3 **=>Mo**$^{\mathbf{V}}$
Mo(10)-O(22)	1.668(7)	
Mo(10)-O(22A)	1.64(4)	
Mo(10)-O(12)	1.934(16)	
Mo(10)-O(7)	1.950(7)	
Mo(10)-O(16)	2.019(6)	
Mo(10)-O(28)	2.040(7)	
Mo(10)-Mo(6)	2.616(2)	
Mo(11)		Σ(Mo11) =5.1 **=>Mo**$^{\mathbf{V}}$
Mo(11)-O(37)	1.658(8)	
Mo(11)-O(20)	1.956(6)	
Mo(11)-O(6)	1.969(7)	
Mo(11)-O(25)	2.001(8)	
Mo(11)-O(19)	2.098(7)	
Mo(11)-Mo(12)	2.614(2)	
Mo(12)		Σ(Mo12) =5.2 **=>Mo**$^{\mathbf{V}}$
Mo(12)-O(40)	1.658(7)	
Mo(12)-O(20)	1.942(7)	
Mo(12)-O(6)	1.979(6)	
Mo(12)-O(18)	2.000(7)	
Mo(12)-O(16)	2.011(6)	

Mo(12)-Mo(11)	2.612(2)	
		3OH, 8 Mo^{V} and 4 Mo^{VI}
		**Keggin block-2**
Mo(13)		∑(Mo13) =5.5 =>**Mo^{V}**
Mo(13)-O(81)	1.643(9)	
Mo(13)-O(72)	1.932(7)	
Mo(13)-O(60)	1.964(8)	
Mo(13)-O(67)	2.004(8)	
Mo(13)-O(66)	2.057(18)	∑(O66) =1.2 => **OH**
Mo(13)-Mo(14)	2.604(4)	
Mo(14)		∑(Mo14) =5.0 =>**Mo^{V}**
Mo(14)-O(85)	1.658(9)	
Mo(14)-O(72)	1.937(8)	
Mo(14)-O(74)	1.959(8)	
Mo(14)-O(60)	1.974(7)	
Mo(14)-O(86)	2.104(8)	∑(O86) =1.3 => **OH**
Mo(14)-Mo(13)	2.604(4)	
Mo(15)		∑(Mo15) =5.9 =>**Mo^{VI}**
Mo(15)-O(51)	1.676(7)	
Mo(15)-O(57)	1.816(8)	
Mo(15)-O(74)	1.838(8)	
Mo(15)-O(63)	1.992(7)	
Mo(15)-O(58)	2.014(8)	
Mo(15)-Mo(24)	3.178(2)	
Mo(16)		∑(Mo16) =5.8 =>**Mo^{VI}**
Mo(16)-O(78)	1.688(7)	
Mo(16)-O(71)	1.816(7)	

Mo(16)-O(67)	1.855(8)	
Mo(16)-O(82)	2.004(7)	
Mo(16)-O(56)	2.012(7)	
Mo(16)-Mo(21)	3.180(2)	
Mo(17)		∑(Mo17) =5.1 =>**Mo**^{V}
Mo(17)-O(84)	1.652(7)	
Mo(17)-O(53)	1.956(7)	
Mo(17)-O(59)	1.955(7)	
Mo(17)-O(57)	1.991(8)	
Mo(17)-O(86)	2.036(8)	
Mo(17)-Mo(20)	2.604(2)	
Mo(18)		∑(Mo18) =5.1 =>**Mo**^{V}
Mo(18)-O(80)	1.662(8)	
Mo(18)-O(68)	1.952(6)	
Mo(18)-O(55)	1.949(6)	
Mo(18)-O(71)	2.008(7)	
Mo(18)-O(66)	2.086(8)	
Mo(18)-Mo(23)	2.617(3)	
Mo(19)		∑(Mo19) =5.2 =>**Mo**^{V}
Mo(19)-O(76)	1.654(8)	
Mo(19)-O(70)	1.943(6)	
Mo(19)-O(52)	1.942(7)	
Mo(19)-O(64)	2.011(7)	
Mo(19)-O(54)	1.998(7)	
Mo(19)-Mo(22)	2.615(3)	
Mo(20)		∑(Mo20) =5.3 =>**Mo**^{V}
Mo(20)-O(83)	1.660(8)	
Mo(20)-O(59)	1.945(8)	
Mo(20)-O(61)	1.991(7)	
Mo(20)-O(53)	1.945(7)	
Mo(20)-O(62)	2.052(8)	∑(O62) =1.3 **=> OH**
Mo(20)-Mo(17)	2.602(3)	
Mo(21)		∑(Mo21) =5.7 =>**Mo**^{VI}
Mo(21)-O(77)	1.685(8)	
Mo(21)-O(79)	1.824(8)	
Mo(21)-O(61)	1.820(7)	
Mo(21)-O(56)	2.011(7)	

Mo(21)-O(82)	2.022(7)	
Mo(16)-Mo(21)	3.183(3)	
Mo(22)		$\sum$(Mo22) =5.3 =>**Mo^{V}**
Mo(22)-O(69)	1.657(8)	
Mo(22)-O(52)	1.943(6)	
Mo(22)-O(70)	1.946(7)	
Mo(22)-O(79)	1.991(7)	
Mo(22)-O(62)	2.072(7)	
Mo(22)-Mo(19)	2.613(3)	
Mo(23)		$\sum$(Mo23) =5.2 =>**Mo^{V}**
Mo(23)-O(73)	1.649(8)	
Mo(23)-O(68)	1.937(7)	
Mo(23)-O(55)	1.970(6)	
Mo(23)-O(65)	2.014(7)	
Mo(23)-O(54)	2.032(7)	
Mo(23)-Mo(18)	2.617(3)	
Mo(24)		$\sum$(Mo24) =5.8 =>**Mo^{VI}**
Mo(24)-O(75)	1.686(8)	
Mo(24)-O(65)	1.811(6)	
Mo(24)-O(64)	1.845(7)	
Mo(24)-O(63)	2.000(7)	
Mo(24)-O(58)	2.021(7)	
Mo(24)-Mo(15)	3.175(3)	
3OH, 8 Mo^{V} and 4 Mo^{VI}		

The examination of the Mo···Mo distances have proved to be the best criterion to assess the oxidation degree of the Mo ions, accordingly the Mo^{V}···Mo^{V} distances are equal to ~2.6 Å while Mo^{VI}···Mo^{VI} distances are quite longer (~3.2 Å).[1] As a result, four Mo^{V}—Mo^{V} pairs and two Mo^{VI}—Mo^{VI} pairs were observed. The presence of eight Mo^{V} and four Mo^{VI} ions, as well as three protonated briding oxygen atoms have further been identifed by valence bond calculation (Table S2). The ε-Keggin core is stablized by four tetrahedral coordinated Zn^{II} ions capping the four hexangular windows of the POM, and the entity of {ε-$H_3PMo^{V}_8Mo^{VI}_4O_{40}Zn_4$} is thus formed which maintains the overall tetrahedral symmetry (Figure S1). The P–O bond distances in the central PO_4 tetrahedron lie in the expected range of 1.534(7)–1.564(7) Å. The Zn–O bond distances are in the range of 1.892(9)–2.011(8) Å. The remaining charges are compensated by the counter-cations. According to the valence calculation results, the structural formula of **1** is confirmed to be, $[TBA]_6[H_3PMo^{V}_8Mo^{VI}_4O_{40}]_2[Zn_8(BTB)_2]$ (TBA= $C_{16}H_{36}N$, BTB= $C_{27}H_{15}O_6$, total empirical formula=$C_{150}H_{252}O_{92}N_6P_2Mo_{24}Zn_8$).

(1) L. M. Rodriguez-Albelo, G. Rousseau, P. Mialane, J. Marrot, C. Mellot-Draznieks, A. R. Ruiz-Salvador, S.-W. Li, R.-J. Liu, G.-J. Zhang, B. Keita and A. Dolbecq, *Dalton Trans.*, 2012, **41**, 9989.

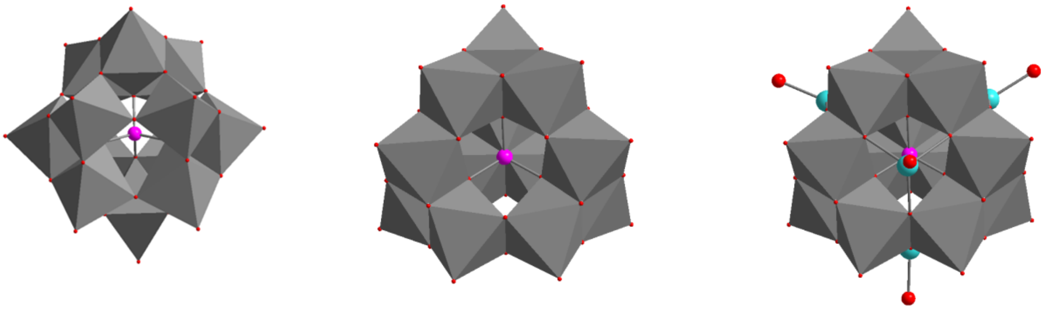
Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å x 10^3) for compound **1**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Mo(1)	12795(1)	3458(1)	3086(1)	41(1)
Mo(2)	11939(1)	3976(1)	3755(1)	39(1)
Mo(3)	15680(1)	3251(1)	4132(1)	30(1)
Mo(4)	14999(1)	4937(1)	2516(1)	38(1)
Mo(5)	14579(1)	4023(1)	2377(1)	39(1)
Mo(6)	12866(1)	4245(1)	4843(1)	31(1)
Mo(7)	14852(1)	3022(1)	3173(1)	33(1)
Mo(8)	13963(1)	5682(1)	3371(1)	31(1)
Mo(9)	12380(1)	5188(1)	4011(1)	31(1)
Mo(10)	14432(1)	3939(1)	4954(1)	26(1)
Mo(11)	15939(1)	5206(1)	3601(1)	30(1)
Mo(12)	16180(1)	4482(1)	4253(1)	27(1)
Mo(13)	7822(1)	8322(1)	1018(1)	42(1)
Mo(14)	7009(1)	8012(1)	1840(1)	42(1)
Mo(15)	4829(1)	8057(1)	2082(1)	33(1)
Mo(16)	7947(1)	9555(1)	607(1)	34(1)
Mo(17)	5943(1)	8912(1)	2634(1)	38(1)
Mo(18)	6651(1)	8813(1)	34(1)	32(1)
Mo(19)	3949(1)	9755(1)	930(1)	27(1)
Mo(20)	5986(1)	9870(1)	2374(1)	35(1)
Mo(21)	7004(1)	10353(1)	1306(1)	31(1)
Mo(22)	4814(1)	10364(1)	1395(1)	30(1)
Mo(23)	4981(1)	8867(1)	163(1)	28(1)
Mo(24)	3788(1)	8483(1)	1220(1)	29(1)
Zn(1)	13479(1)	3071(1)	4245(1)	37(1)
Zn(2)	12761(1)	4832(1)	2817(1)	43(1)
Zn(3)	16380(1)	3976(1)	3077(1)	37(1)
Zn(4)	14270(1)	5283(1)	4573(1)	26(1)
Zn(5)	6015(1)	10087(1)	268(1)	30(1)
Zn(6)	3987(1)	9292(1)	2154(1)	35(1)
Zn(7)	5685(1)	7842(1)	893(1)	38(1)
Zn(8)	7889(1)	9278(1)	1855(1)	41(1)
P(1)	14221(2)	4284(1)	3668(1)	26(1)

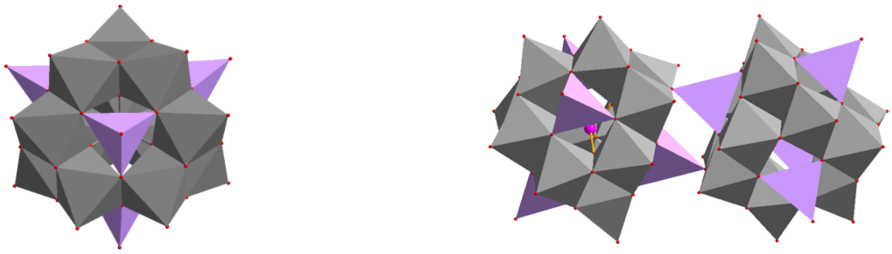
P(2)	5906(2)	9105(1)	1304(1)	28(1)
O(1)	13316(4)	4379(3)	3921(2)	29(2)
O(2)	14588(4)	4771(3)	3417(2)	27(2)
O(3)	14809(4)	4079(3)	4059(2)	27(2)
O(4)	14158(4)	3896(3)	3275(2)	32(2)
O(5)	10966(5)	3769(3)	3723(3)	55(2)
O(6)	16382(4)	4508(2)	3537(2)	27(2)
O(7)	13917(4)	4610(2)	4855(2)	29(2)
O(8)	14609(5)	3009(3)	3888(3)	40(2)
O(9)	12001(5)	3131(3)	2907(3)	56(2)
O(10)	13544(4)	5471(3)	4068(2)	30(2)
O(11)	15826(4)	3385(3)	3407(3)	33(2)
O(12)	13486(4)	3610(3)	4711(2)	31(2)
O(13)	12916(4)	5289(3)	3324(2)	36(2)
O(14)	15574(5)	4284(3)	2626(3)	37(2)
O(15)	12697(5)	3388(3)	3792(3)	36(2)
O(16)	15569(4)	4282(2)	4904(2)	27(2)
O(17)	12387(5)	4169(3)	3091(3)	52(2)
O(18)	16443(4)	3745(3)	4181(3)	35(2)
O(19)	15977(5)	5210(3)	2844(3)	41(2)
O(20)	15418(4)	5072(3)	4264(2)	28(2)
O(21)	13380(5)	3690(3)	2421(3)	46(2)
O(22)	14298(5)	3800(3)	5550(2)	19(2)
O(22A)	14790(20)	3807(13)	5482(13)	11(8)
O(23)	12400(4)	4918(3)	4628(3)	36(2)
O(24)	11912(4)	3938(3)	4496(3)	40(2)
O(25)	15020(5)	5741(3)	3569(3)	39(2)
O(26)	14314(5)	5537(3)	2751(2)	40(2)
O(27)	13884(5)	4639(3)	2485(3)	39(2)
O(28)	15090(4)	3307(2)	4724(2)	32(2)
O(29)	14801(6)	4025(3)	1775(2)	50(2)
O(30)	15325(5)	2440(3)	3093(3)	53(2)
O(31)	11699(5)	4716(3)	3792(3)	42(2)
O(32)	12426(5)	4177(3)	5407(3)	48(2)
O(33)	16252(5)	2701(3)	4199(3)	48(2)
O(34)	15081(5)	3348(3)	2574(3)	48(2)
O(35)	13717(5)	2928(3)	3124(3)	45(2)
O(36)	13609(6)	6282(3)	3313(3)	53(2)
O(37)	16779(5)	5558(3)	3643(3)	43(2)
O(38)	11736(5)	5703(3)	4072(3)	51(2)
O(39)	15336(6)	5126(3)	1944(3)	51(2)
O(40)	17089(5)	4665(3)	4433(3)	42(2)
O(41)	12889(6)	2473(3)	4446(3)	61(3)
O(42)	11826(7)	2956(4)	4763(4)	83(4)

O(43)	17383(5)	4674(4)	2511(3)	57(3)
O(44)	17330(5)	3831(4)	2594(3)	59(3)
O(45)	12015(6)	5078(3)	2339(3)	52(2)
O(46)	12386(6)	4371(3)	1957(3)	53(2)
O(47)	6685(4)	8996(3)	934(2)	30(2)
O(48)	5915(4)	8714(3)	1737(2)	31(2)
O(49)	5921(4)	9652(3)	1487(2)	31(2)
O(50)	5073(4)	9068(3)	1052(2)	29(2)
O(51)	4155(5)	7609(3)	2317(3)	52(2)
O(52)	4969(5)	10139(3)	736(2)	30(2)
O(53)	5057(4)	9396(2)	2447(2)	31(2)
O(54)	4139(4)	9454(3)	281(2)	32(2)
O(55)	5855(4)	9390(3)	81(3)	29(2)
O(56)	6994(4)	10078(3)	646(2)	33(2)
O(57)	5056(5)	8398(3)	2603(3)	42(2)
O(58)	4020(5)	8623(3)	1902(3)	38(2)
O(59)	6859(5)	9336(3)	2324(3)	39(2)
O(60)	6780(5)	7929(3)	1163(3)	42(2)
O(61)	6853(5)	10279(3)	1965(2)	35(2)
O(62)	5076(5)	10351(3)	2112(2)	36(2)
O(63)	4748(5)	8011(3)	1375(2)	33(2)
O(64)	3318(4)	9128(3)	1173(3)	34(2)
O(65)	4136(4)	8436(3)	582(2)	29(2)
O(66)	7548(5)	8309(3)	305(3)	43(2)
O(67)	8457(4)	8955(3)	818(3)	45(2)
O(68)	5799(4)	8350(2)	346(2)	27(2)
O(69)	4183(5)	10875(3)	1381(3)	45(2)
O(70)	4067(4)	9808(3)	1615(2)	26(2)
O(71)	7538(4)	9335(3)	69(3)	37(2)
O(72)	7781(5)	8563(3)	1665(3)	40(2)
O(73)	4743(4)	8720(3)	-377(3)	41(2)
O(74)	5876(5)	7729(3)	2009(3)	42(2)
O(75)	2949(5)	8098(3)	1323(3)	45(2)
O(76)	3132(5)	10140(3)	833(3)	43(2)
O(77)	7706(5)	10824(3)	1205(3)	49(2)
O(78)	8795(5)	9895(3)	373(3)	49(2)
O(79)	5965(5)	10658(3)	1242(2)	35(2)
O(80)	6808(5)	8667(3)	-544(3)	48(2)
O(81)	8614(6)	7903(4)	984(3)	58(3)
O(82)	7816(4)	9747(3)	1300(2)	33(2)
O(83)	6026(6)	10124(3)	2905(3)	57(2)
O(84)	5977(5)	8925(3)	3226(3)	47(2)
O(85)	7621(6)	7517(4)	1978(4)	62(3)
O(86)	6816(5)	8338(3)	2518(3)	44(2)

O(87)	3104(5)	9482(3)	2641(3)	50(2)
O(88)	3771(5)	10171(4)	2787(3)	56(3)
O(89)	5514(6)	7190(3)	676(3)	51(2)
O(90)	5174(13)	6743(8)	107(7)	64(5)
O(90A)	5328(12)	6955(7)	-93(7)	56(5)
O(91)	8232(6)	8707(4)	2759(3)	64(3)
O(92)	8702(5)	9380(3)	2309(3)	52(2)



α-Keggin naked ε-Keggin Zn_4^{II} capped ε-Keggin



four-capped ε-Keggin core the dimer of the capping POM

Figure S1. Representations of α and ε isomers of Keggin, the four-capped ε-Keggin core as well as the dimer of the capping POM. Grey octahedron: MoO_6, Purple tetrahedron: ZnO_4; Pink sphere: P, Blue sphere: Zn, Red sphere: oxygen.

As is well known, the Keggin $\{XM_{12}O_{40}\}$ (heteroatom X, most commonly P or Si; transition metal M, most commonly W or Mo) structure is the most archetypal POM structure which is built from the association of four M_3O_{13} groups around a central XO_4 tetrahedron (Fig. S1).[2] There are five theoretically possible isomers of the Keggin structure derevied formally from the successive 60° rotations around the C_3 axes of the M_3O_{13} units, which is designated by the prefixes α, β, γ, δ and ε.[3]

(2) M. T. Pope, *Heteropoly and Isopoly Oxometalates*; Springer: Berlin, 1983.

(3) L. C. W. Baker and J. S. Figgis, *J. Am. Chem. Soc.*, 1970, **92**, 3794.

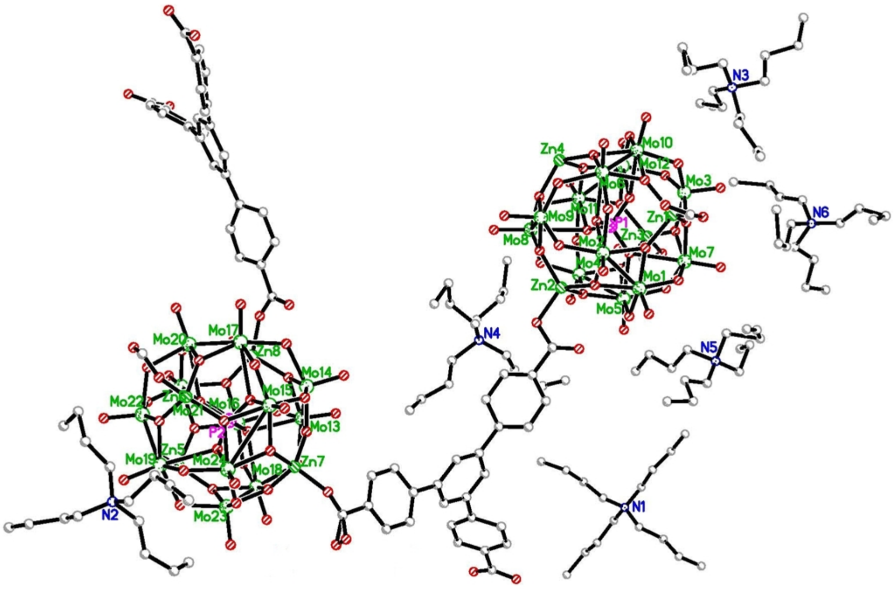
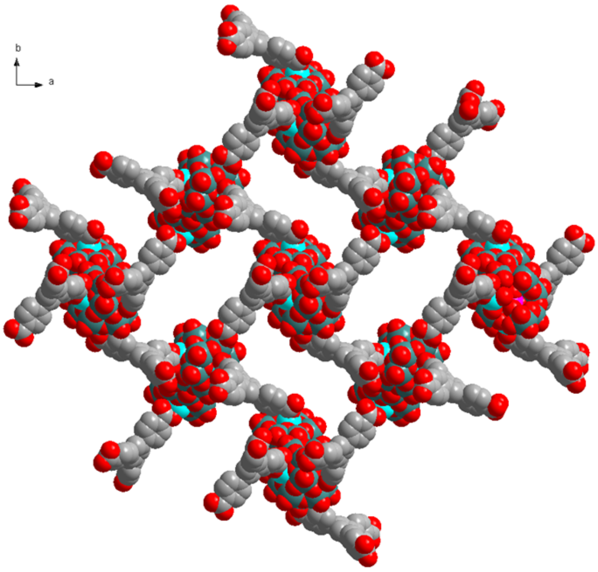


Figure S2. Ball-and-stick representation of the asymmetric unit of compound **1**. Hydrogen atoms are omitted for clarity.



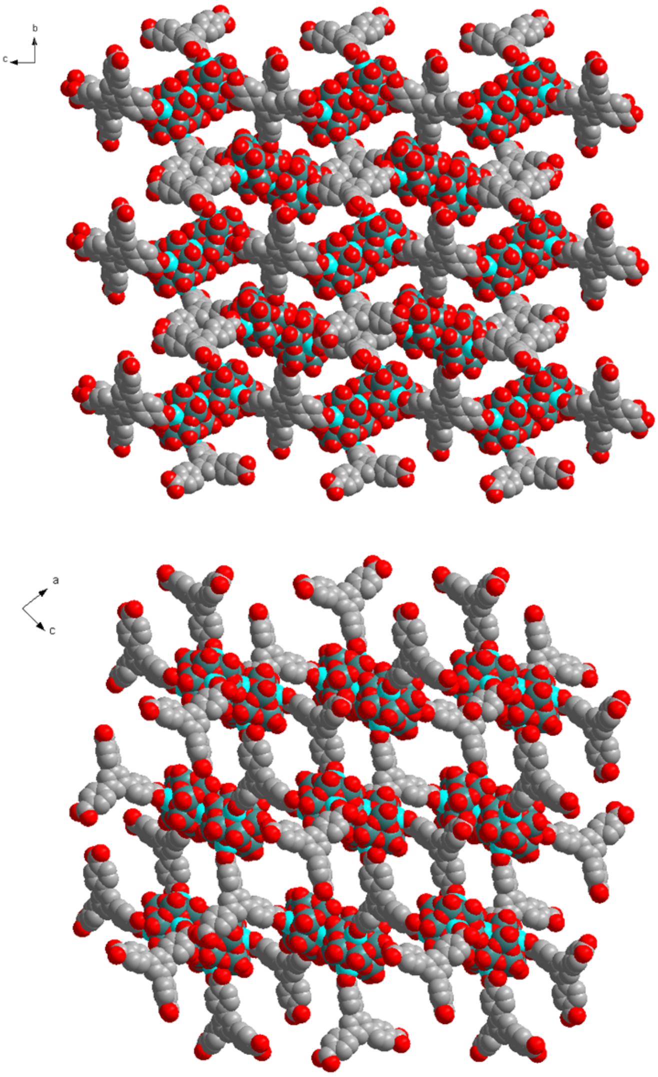
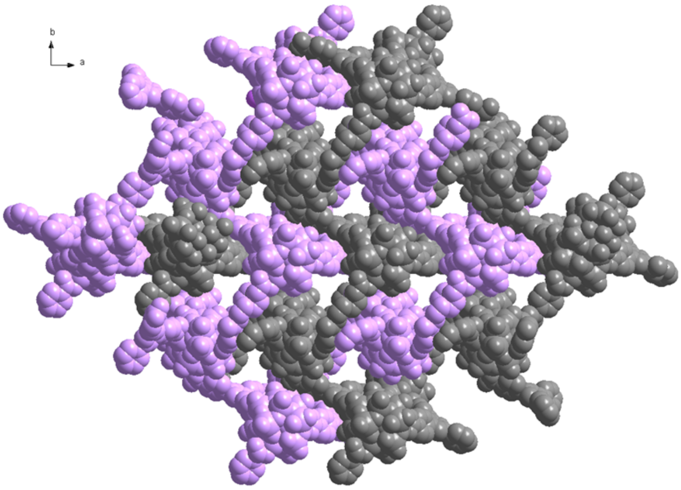


Figure S3. Space-filling representations of the channels in *ab*, *bc* and *ac* planes, respectively for the single 3D framework of **1**.

(a)



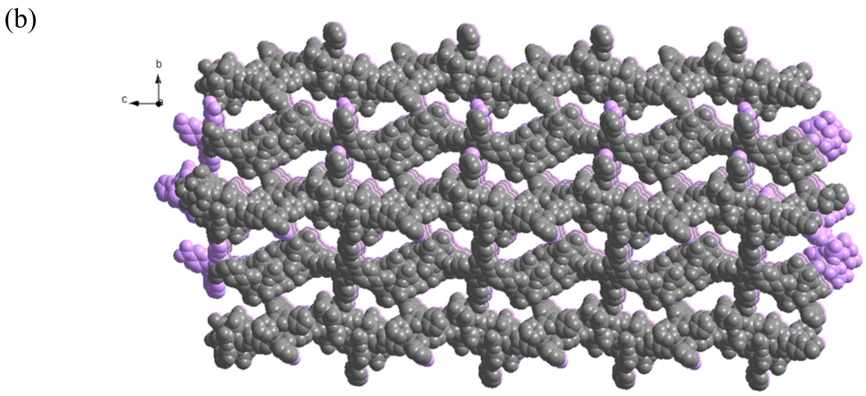


Figure S4. Space-filling representations of the channels in *ab* (a) and *bc* (b) planes in the 2-fold interpenetrating 3D framework of **1**.

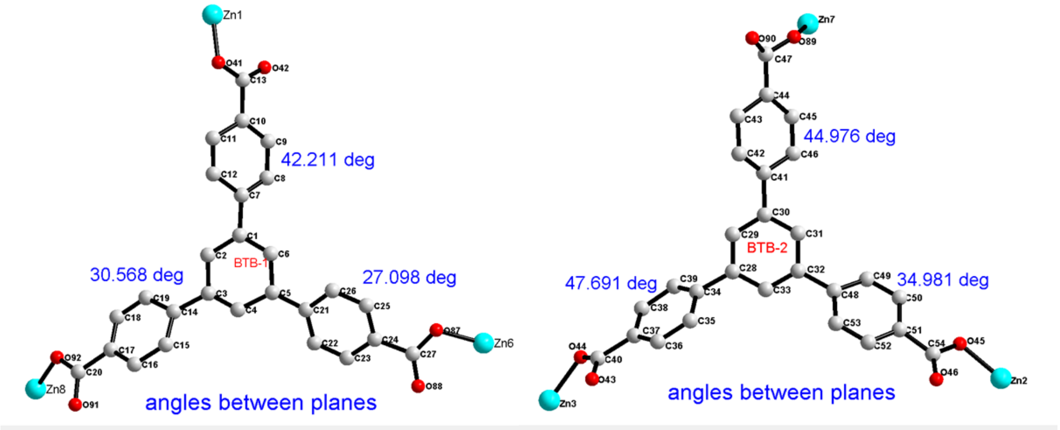


Figure S5. Ball-and-stick representations of the coordiantion modes and angles between planes in two BTB ligands.

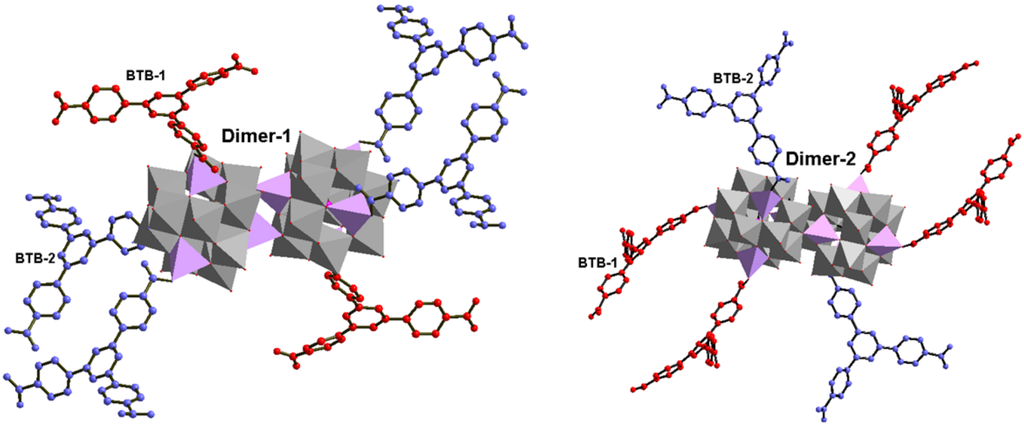


Figure S6. Representations of the connections of POM-Metal-ligand in two types of POM dimers.

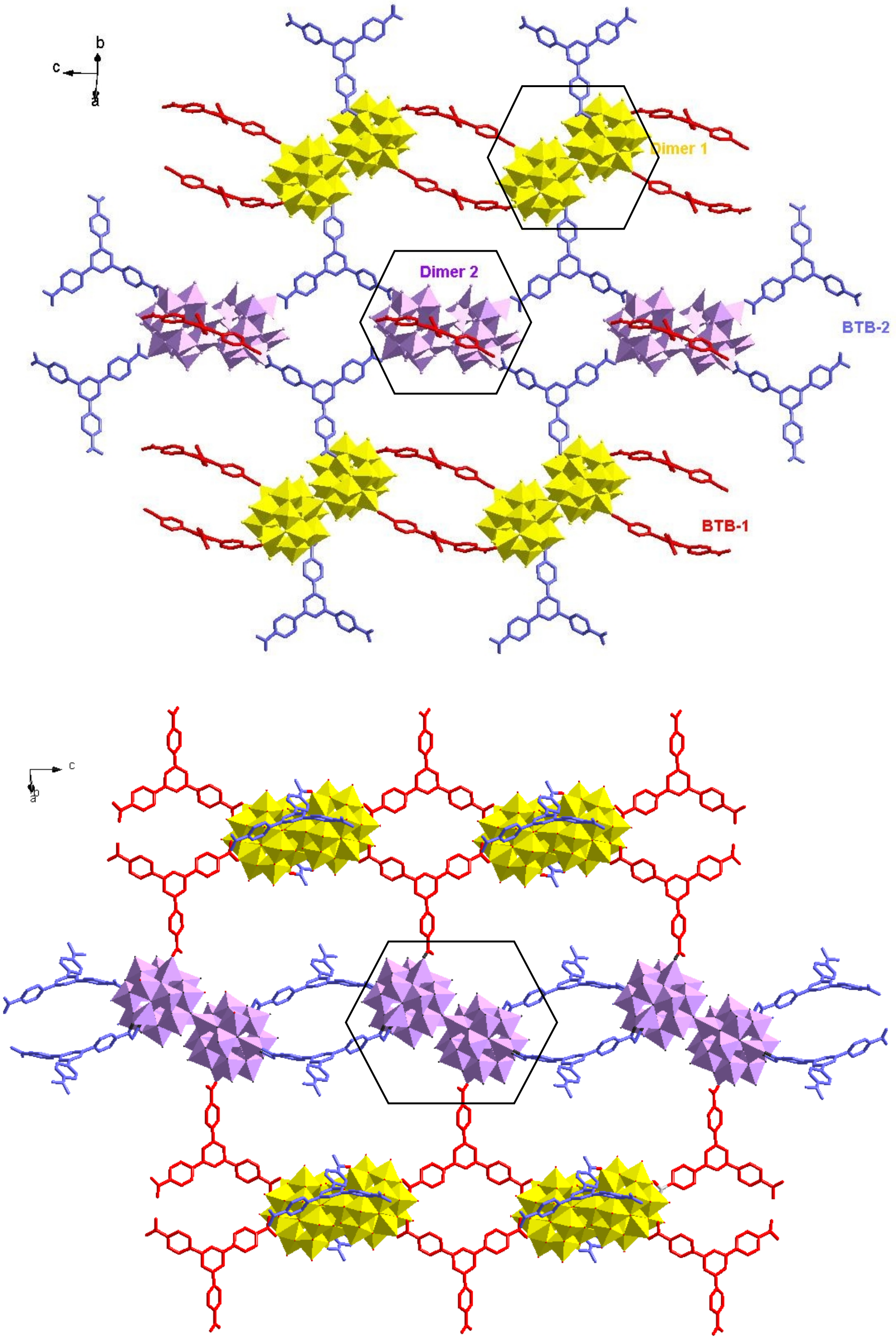
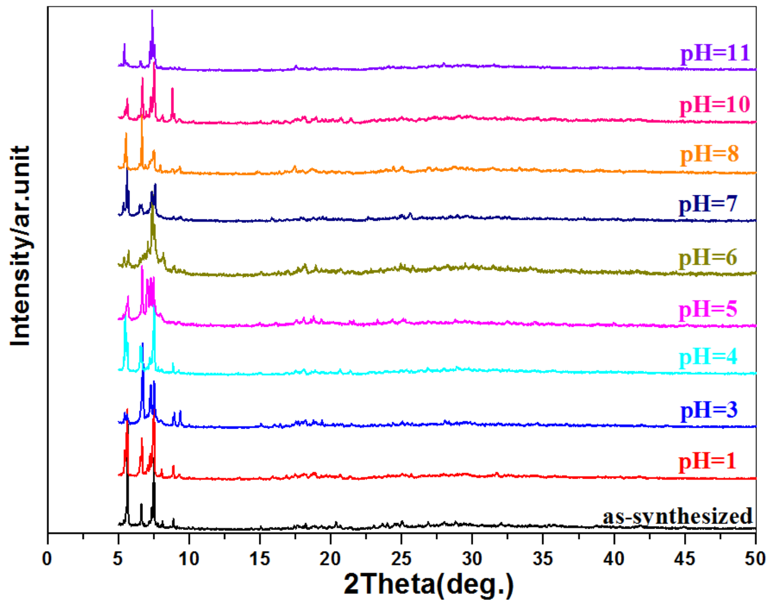
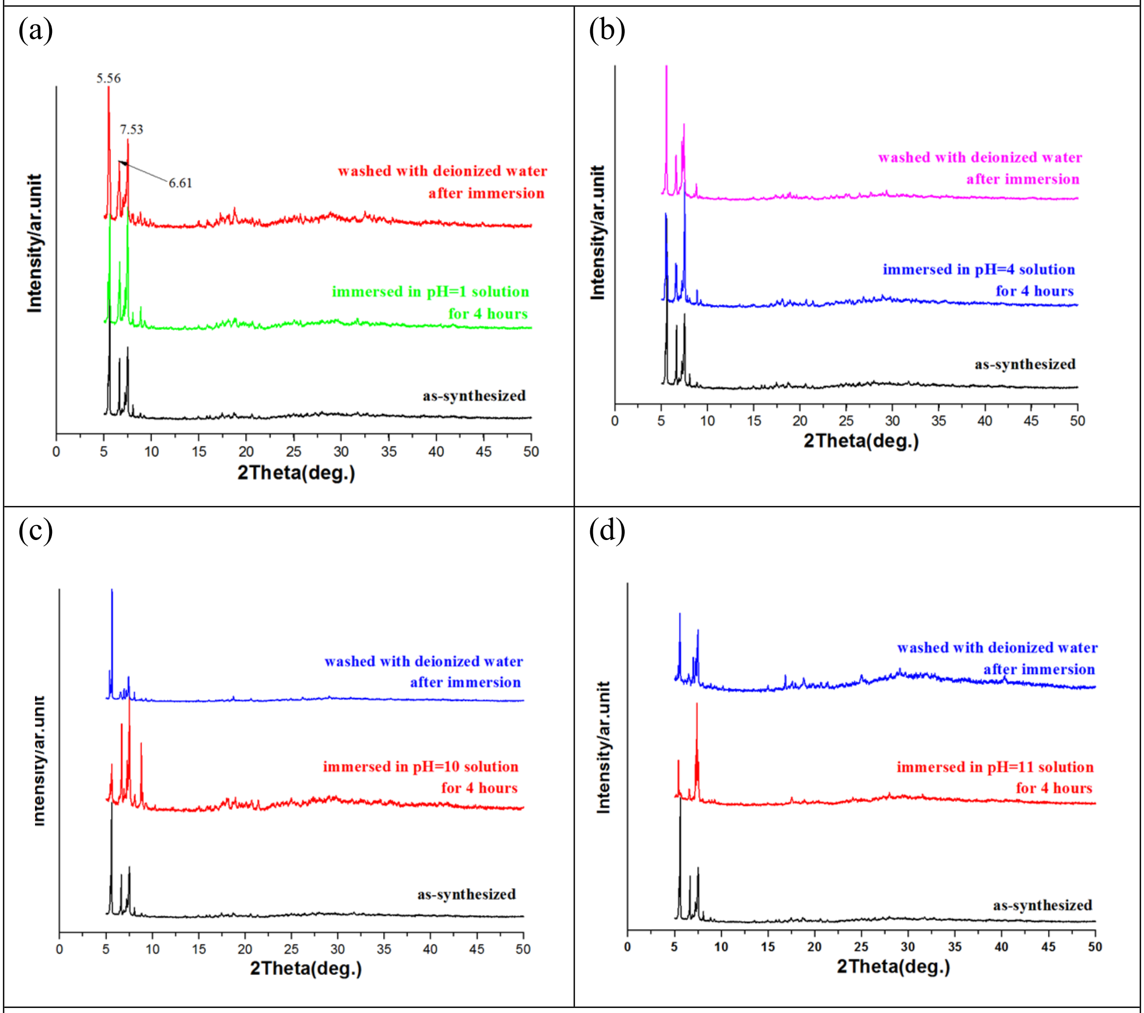


Figure S7. Representations of the connections between different BTB molecules and Dimers in a horizonal plane (a) and in a vertical plane (b) based on Dimer 1.



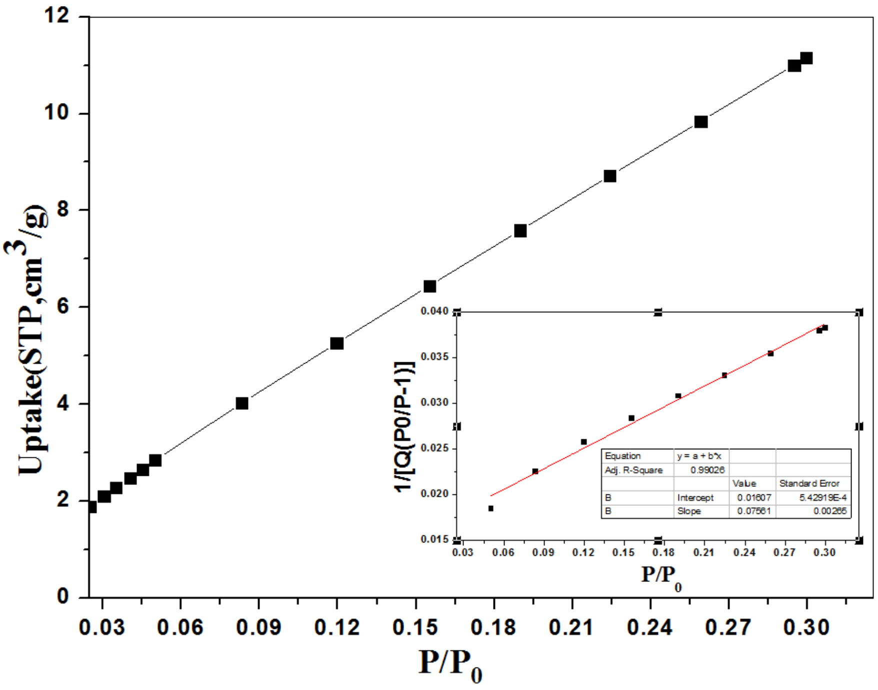
P.S. Samples were immersed at various pH solutions for 4 hours from 1 to 11.



P.S. Samples were immersed at pH=1 (a), 4 (b),10 (c) and 11(d) solutions for 4 hours, and then immersed in deionized water for another 4 hours.

Figure S8. The PXRD spectra of compound **1** under different treatment in aqueous.

When the sample was immersed in pH=11 solution, the solution color gradually changes from colorless to blue, which could be attributed to the partly dissolution of the sample in the basic solution. Although the relative intensity of the stronger diffraction peaks at 2θ = 5.56, 6.61 and 7.53 recovered after suffering further immersion in deionized water, the entire crystallinity became worse and the intensities became weak.



Equation	y = a + b*x		
Adj. R-Square	0.99026		
		Value	Standard Error
B	Intercept	0.01607	5.42919E-4
B	Slope	0.07561	0.00265

Figure S9. N_2 isotherm at 77 K in the range from 0.03 to 0.3. Inset: Plot of the linear region for the BET equation.

The N_2 adsorption isotherm of **1** does not show the microporous character which indicates that the heating treatment for removing the TBA^+ cations inside the channels is failed.

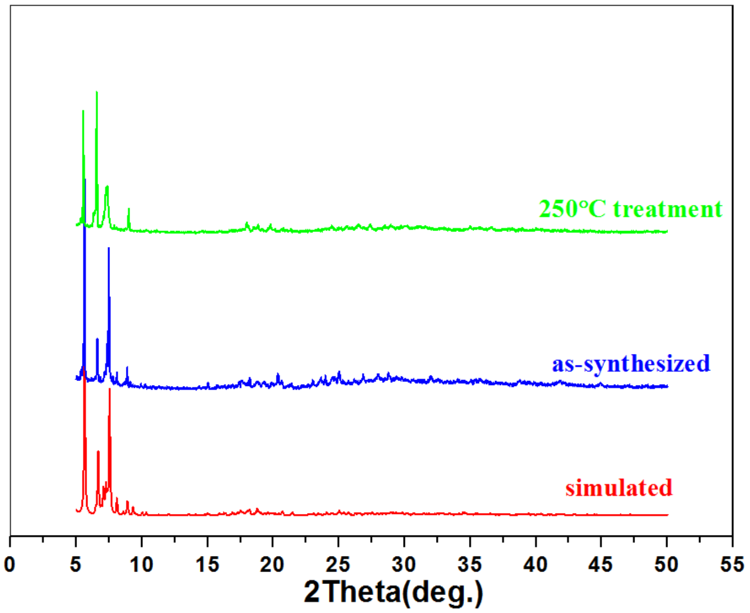


Figure S10. The PXRD patterns of the as-synthesized compound **1** and the sample after treatment at 250 °C overnight under high vacuum.

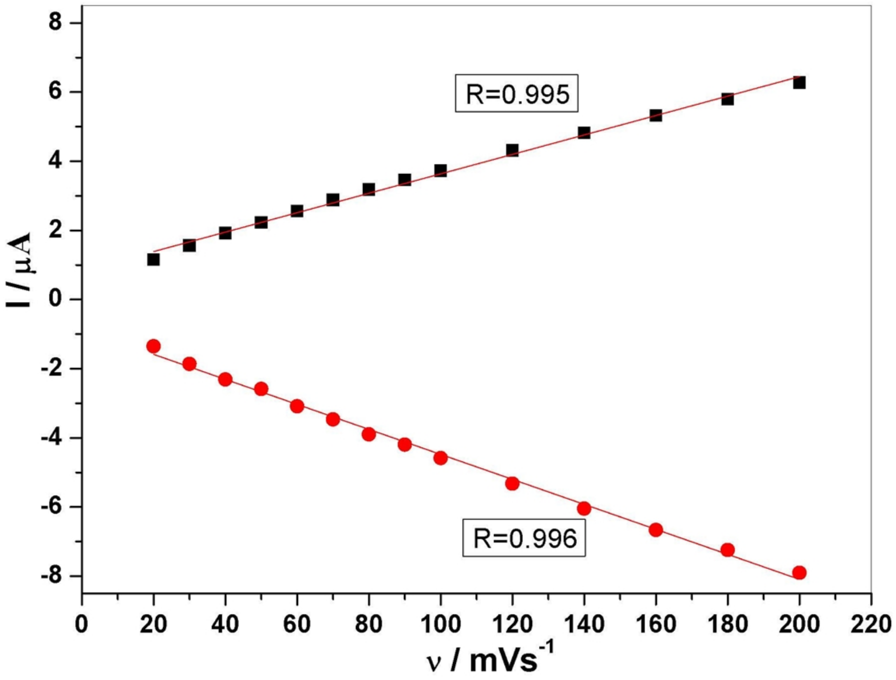


Figure S11. The dependence of cathodic and anodic peak currents of the second redox waves as a function of the scan rate.

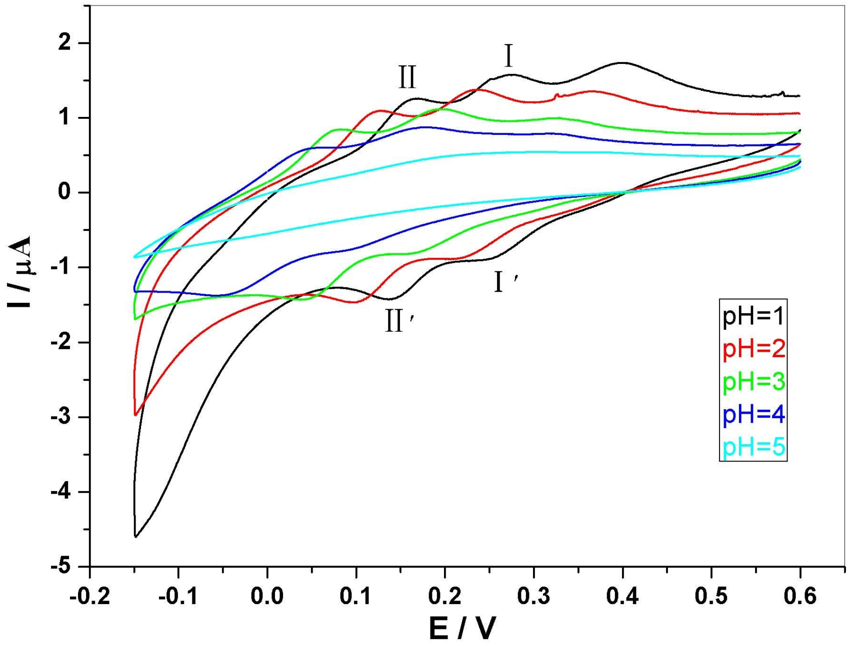


Figure S12. Cyclic voltammograms of **1**-CPE in H_2SO_4 solutions as a function of pH (from pH=1 to 5). Scan rate=80 mV s^{-1}.

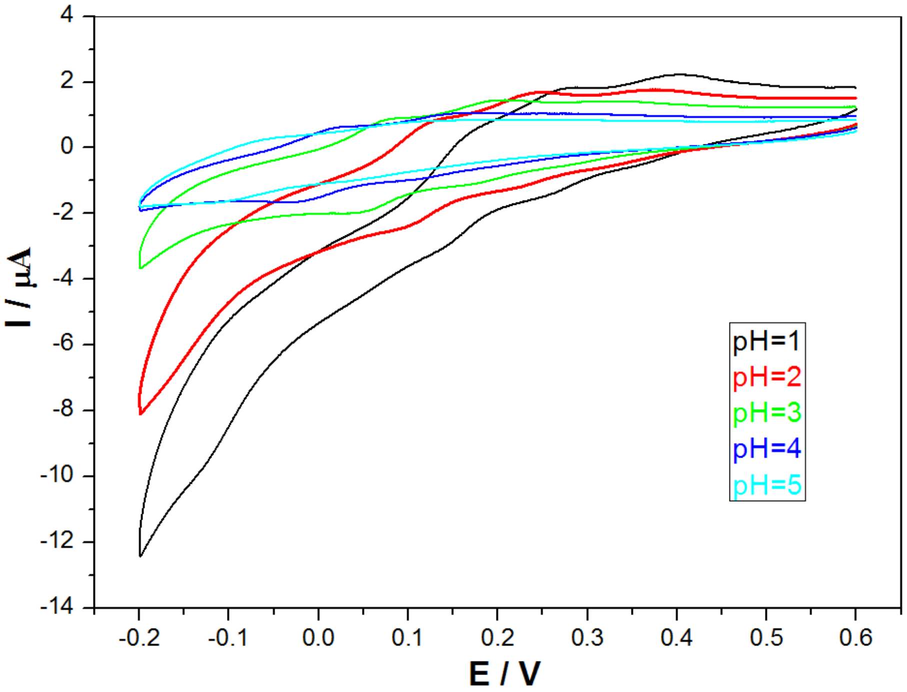


Figure S13. Cyclic voltammograms of **1**-CPE obtained at a scan rate of 80 mV s^{-1} in H_2SO_4 solutions containing 2.0 mM bromate ion over the pH range of 1 to 5.

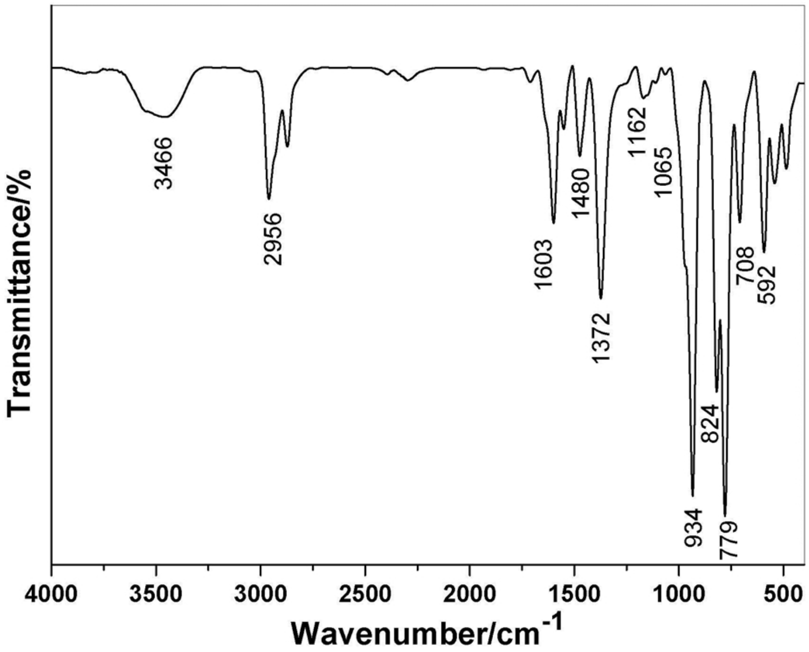


Figure S14. The IR spectrum of compound **1**.

The IR spectrum exhibits the characteristic peaks of the Keggin structure at 779, 824, 934, 1065 cm^{-1} in compound **1**, which are attributed to υ(Mo–O$_c$–Mo), υ(Mo–O$_b$–Mo), υ(Mo–O$_d$) and υ(P–O), respectively. The peak at 1603 cm^{-1} is the characteristic for νC–O vibration in the carboxylate linker. The signatures of the TBA ions and water molecules are identified at 1480 cm^{-1} and 3466 cm^{-1}, respectively.

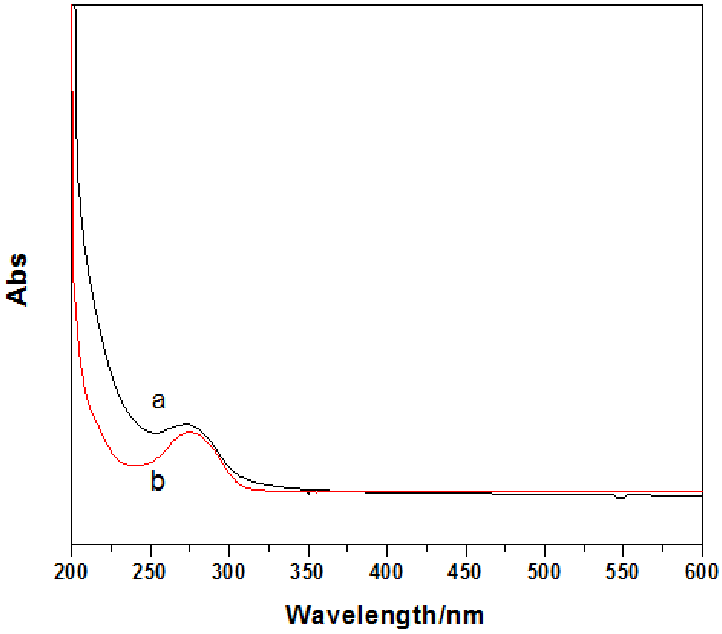


Figure S15. The UV spectra of (a) compound **1** and (b) H_3BTB in methanol solution**.**

Both of the compound **1** and the carboxylate ligand exhibit the same absorption band at 277 nm.

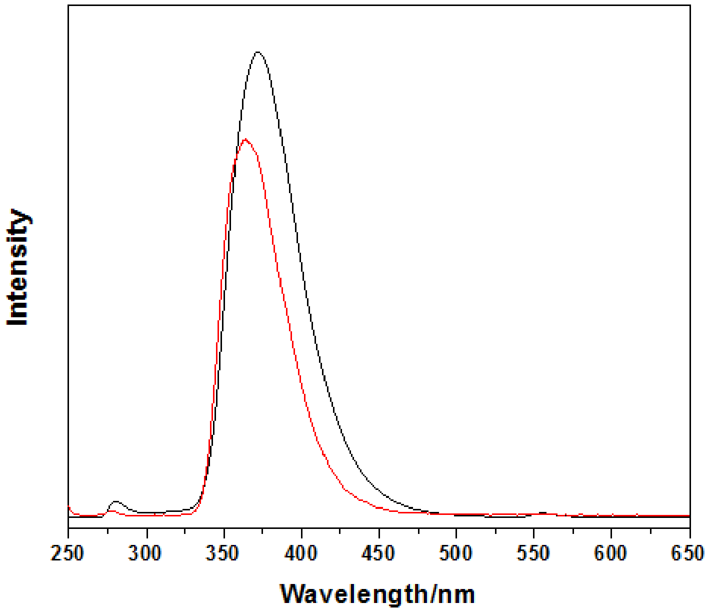


Figure S16. The fluorescence emission spectra of H_3BTB ligand (red line) and compound **1** (black line) in methanol solution.

Upon excitation at 277 nm, free H_3BTB ligand exhibits strong emission at 363.7 nm. In comparison with the free ligand, the emission band for compound **1** is bathochromic and is centered at 372 nm.