Supplementary Material (ESI) for CrystEngComm

Controllable self-assembly of four new metal-organic frameworks based on different phosphomolybdate clusters by altering molar ratio of H_3PO_4 and Na_2MoO_4

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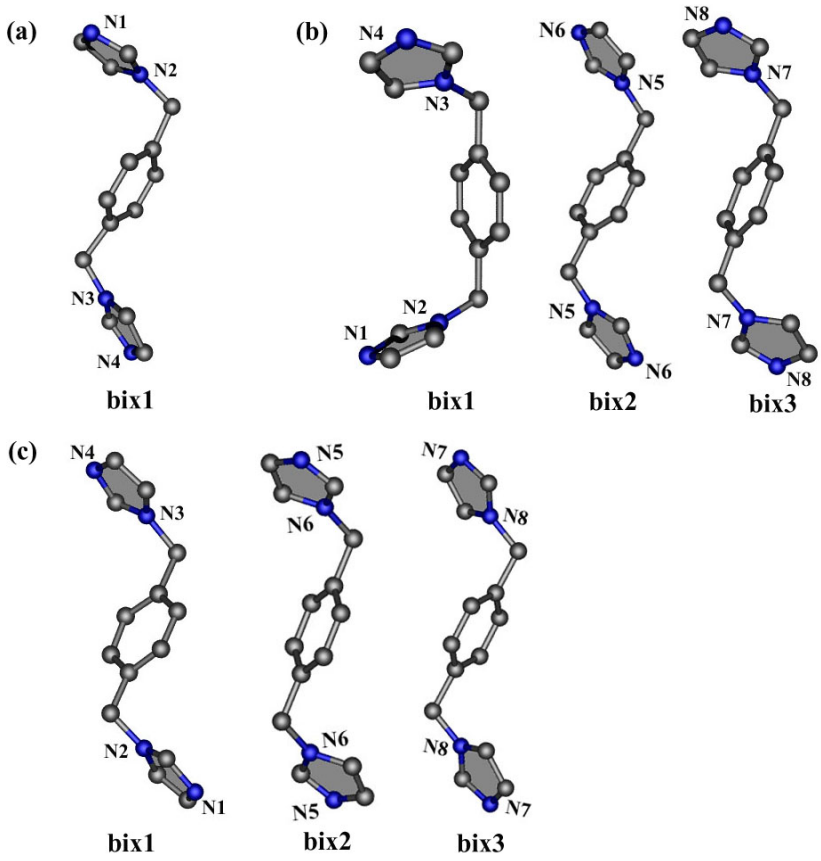

Fig. S1. The detailed conformations of bix ligands in compounds **1**-**3**.

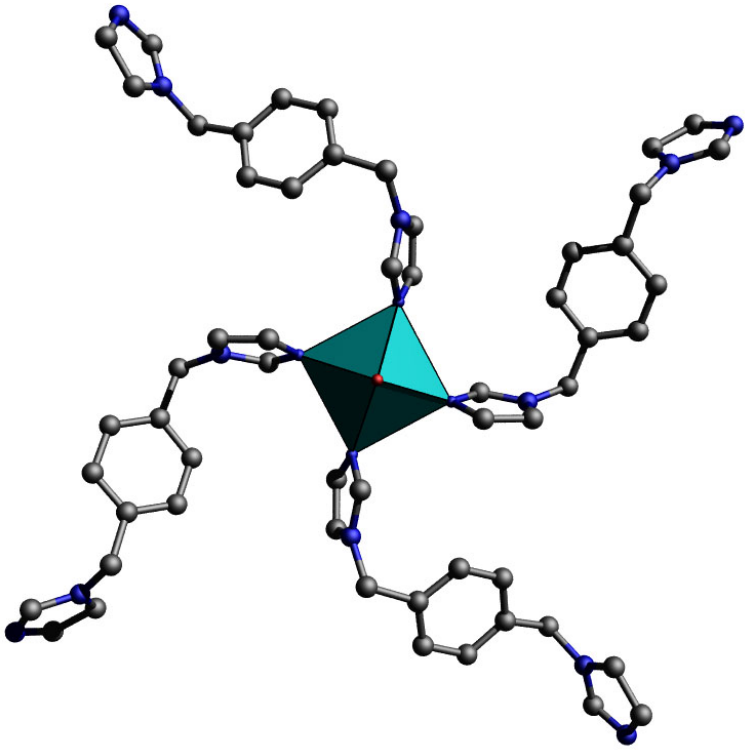

Fig. S2. Polyhedral and ball-and-stick representation of the propeller-shaped structures of the $[CoH(bix)_4]^{3+}$ complex fragments in compound **1**.

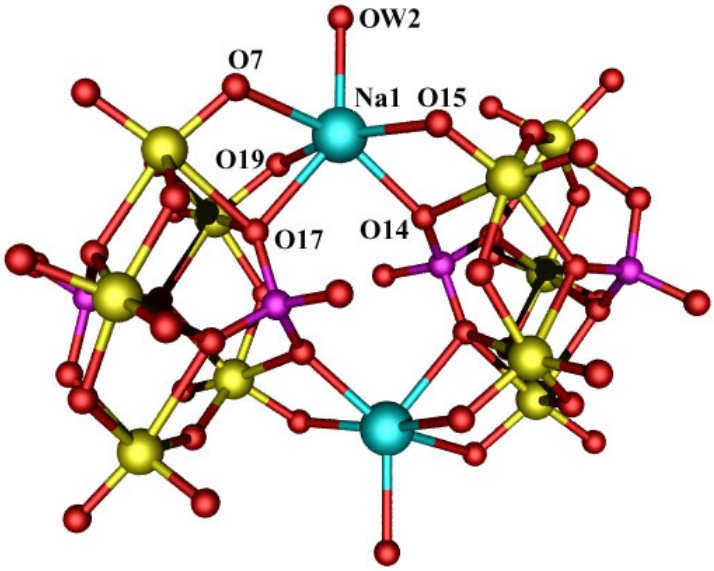

Fig. S3. Ball-and-stick representation of a centrosymmetric dimer $Na_2(P_2Mo_5)_2$ in compound **2**.

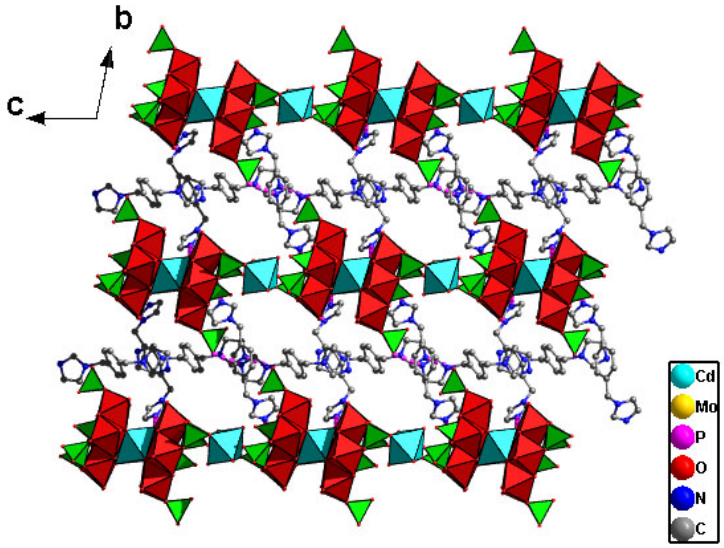

Fig. S4. Polyhedral and ball-and-stick representation of the 2D supramolecular layer in **3** along (1,0,0) axis.

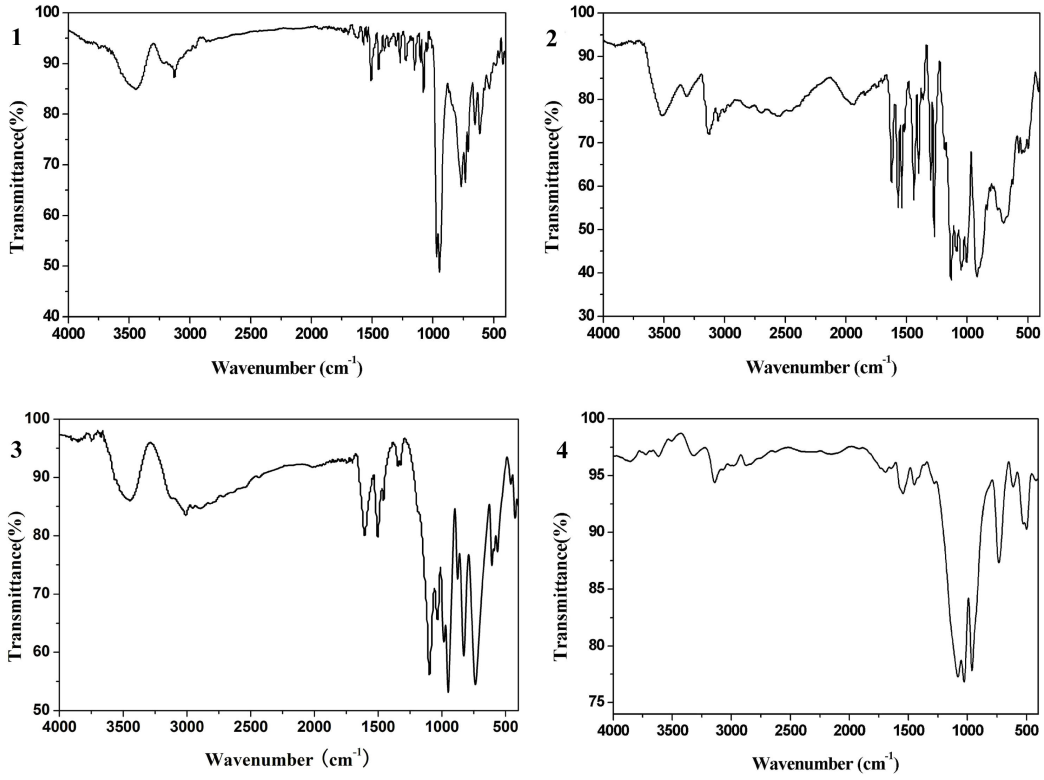

Fig. S5. The IR spectra of compounds **1-4**.

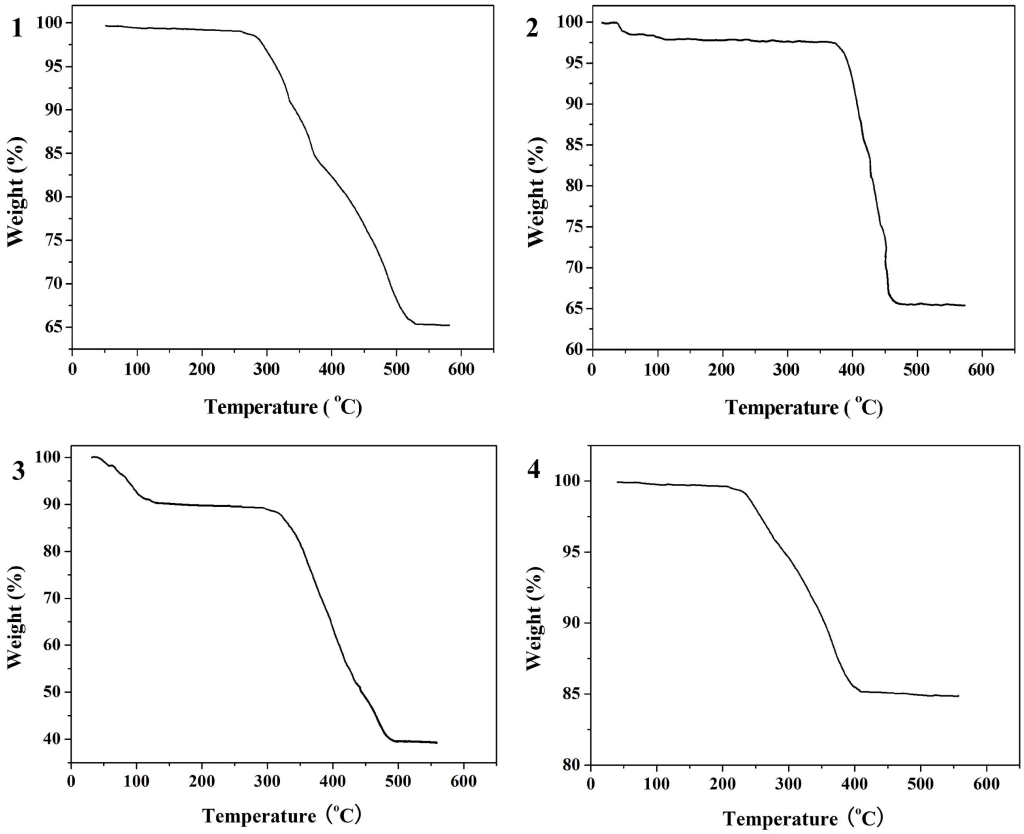

Fig. S6. The TG curves of compounds **1-4**.

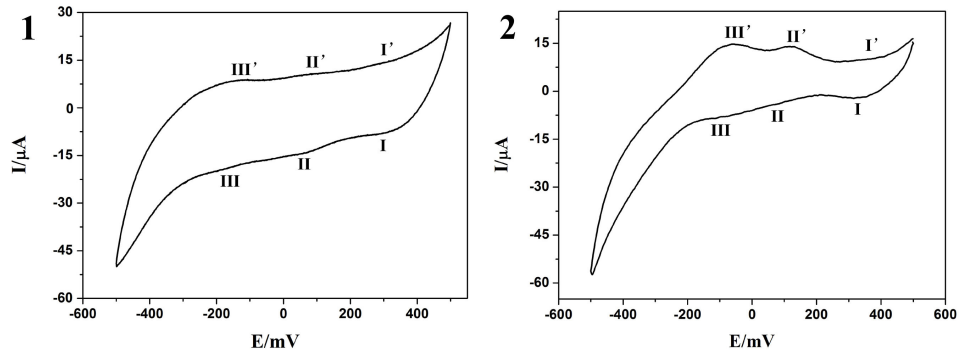

Fig. S7. The electrochemical properties of compounds **1** and **2**.

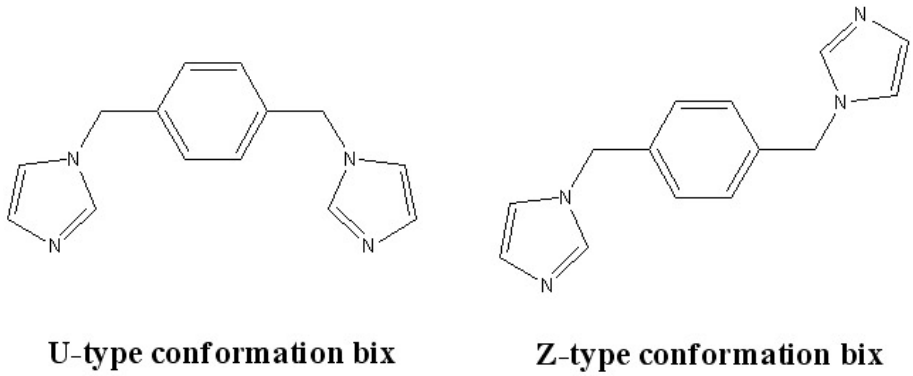

Fig. S8. The scheme view of two conformations of bix ligands.

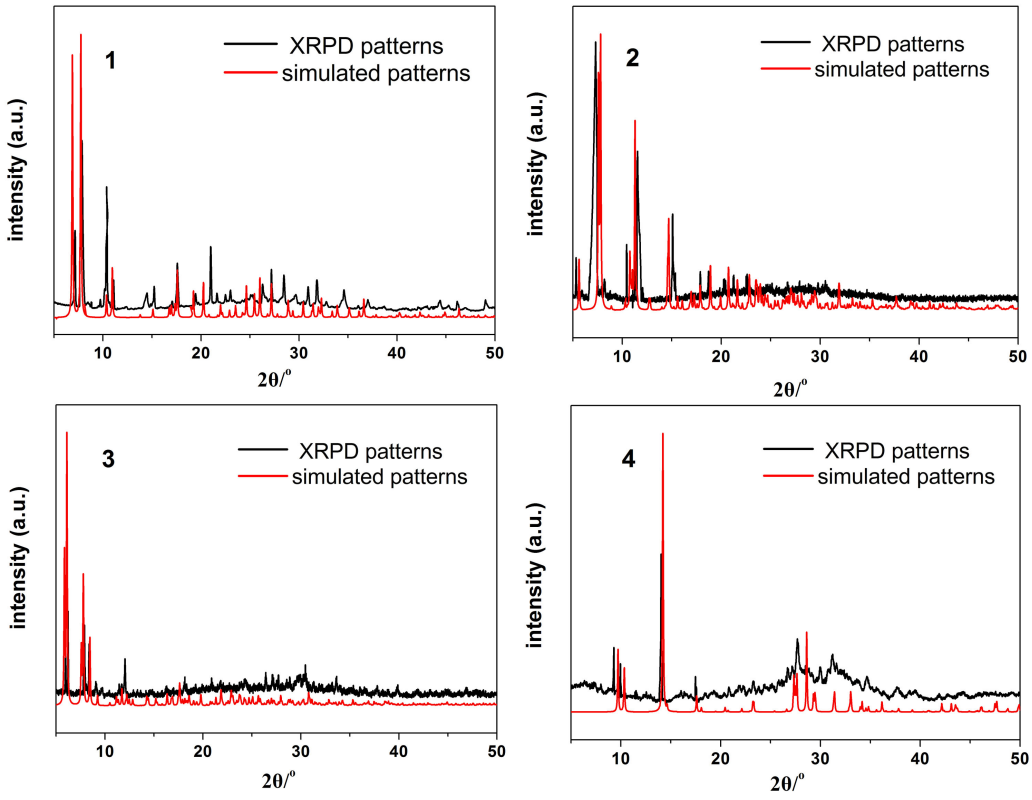

Fig. S9. XRPD patterns and simulated patterns for compounds **1-4**.

Table S1. Selected bond lengths (Å) for compound **1**.

Mo(1)-O(4)	1.689(3)	Mo(2)-O(6)	1.683(3)
Mo(1)-O(9)	1.808(3)	Mo(2)-O(3)	1.808(3)
Mo(1)-O(1)	1.814(3)	Mo(2)-O(8)	1.818(3)
Mo(1)-O(7)#1	2.052(3)	Mo(2)-O(7)	2.052(3)
Mo(1)-O(5)	2.057(3)	Mo(2)-O(5)	2.056(3)
Mo(1)-O(10)	2.437(3)	Mo(2)-O(10)	2.440(3)
V(1)-O(11)	1.608(3)	V(2)-O(2)	1.628(4)
V(1)-O(9)#3	1.922(3)	V(2)-O(7)#1	1.893(3)
V(1)-O(8)#2	1.930(3)	V(2)-O(7)	1.893(3)
V(1)-O(3)	1.937(3)	V(2)-O(5)#1	1.967(3)
V(1)-O(1)	1.944(3)	V(2)-O(5)	1.967(3)
P(1)-O(10)#1	1.531(2)	Co(1)-O(2)#4	2.122(4)
P(1)-O(10)#2	1.531(2)	Co(1)-O(2)	2.122(4)
P(1)-O(10)	1.531(3)	Co(1)-N(1)#1	2.125(4)
P(1)-O(10)#3	1.531(3)	Co(1)-N(1)	2.125(4)
Co(1)-N(1)#4	2.125(4)	Co(1)-N(1)#5	2.125(4)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+3/2,z+0 #2 -y+5/4,x+1/4,-z+1/4 #3 y-1/4,-x+5/4,-z+1/4

#4 y-1/4,-x+5/4,-z+5/4 #5 -y+5/4,x+1/4,-z+5/4

Table S2. Selected bond lengths (Å) for compound **2**.

Na(1)-OW2B	2.315(13)	Mo(1)-O(9)	1.692(5)
Na(1)-O(14)#1	2.348(4)	Mo(1)-O(19)	1.719(4)
Na(1)-O(19)	2.385(5)	Mo(1)-O(22)	1.903(4)
Na(1)-O(15)#1	2.388(5)	Mo(1)-O(23)	1.948(4)
Na(1)-OW2A	2.404(12)	Mo(1)-O(16)	2.146(4)
Na(1)-O(7)	2.468(5)	Mo(1)-O(17)	2.468(4)
Na(1)-O(17)	2.518(5)	Mo(2)-O(2)	1.700(5)
Mo(3)-O(8)	1.706(4)	Mo(2)-O(15)	1.719(4)
Mo(3)-O(7)	1.713(5)	Mo(2)-O(10)	1.889(4)
Mo(3)-O(18)	1.894(5)	Mo(2)-O(23)	1.945(4)
Mo(3)-O(22)	1.924(4)	Mo(2)-O(14)	2.281(4)
Mo(3)-O(20)	2.284(4)	Mo(2)-O(16)	2.309(4)
Mo(3)-O(17)	2.343(4)	Mo(5)-O(3)	1.697(5)
Mo(4)-O(4)	1.699(5)	Mo(5)-O(1)	1.700(6)
Mo(4)-O(6)	1.701(4)	Mo(5)-O(10)	1.921(4)
Mo(4)-O(21)	1.917(5)	Mo(5)-O(21)	1.927(5)
Mo(4)-O(18)	1.935(4)	Mo(5)-O(11)	2.270(5)
Mo(4)-O(13)	2.238(4)	Mo(5)-O(13)	2.410(4)
Mo(4)-O(20)	2.344(4)	P(1)-O(14)	1.504(4)
P(2)-O(5)	1.511(5)	P(1)-O(13)	1.536(4)
P(2)-O(11)	1.517(5)	P(1)-O(17)	1.537(4)
P(2)-O(20)	1.553(4)	P(1)-O(12)	1.562(4)
P(2)-O(16)	1.562(4)		

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y,-z+1

Table S3. Selected bond lengths (Å) for compound **3**.

Cd(1)-O(21)	2.264(10)	Cd(2)-O(7)#2	2.061(12)
Cd(1)-O(21)#1	2.264(10)	Cd(2)-O(7)	2.061(12)
Cd(1)-O(27)#1	2.276(10)	Cd(2)-O(2W)	2.186(11)
Cd(1)-O(27)	2.276(10)	Cd(2)-O(2W)#2	2.186(11)
Cd(1)-O(26)	2.310(9)	Cd(2)-O(1W)#2	2.224(14)
Cd(1)-O(26)#1	2.310(9)	Cd(2)-O(1W)	2.224(14)
Mo(1)-O(30)	1.676(11)	Mo(2)-O(14)	1.665(11)
Mo(1)-O(26)	1.936(10)	Mo(2)-O(16)	1.922(12)
Mo(1)-O(23)	1.948(11)	Mo(2)-O(21)	1.971(9)
Mo(1)-O(4)	2.037(12)	Mo(2)-O(8)	2.074(11)
Mo(1)-O(24)	2.138(10)	Mo(2)-O(5)	2.128(11)
Mo(1)-O(25)	2.289(9)	Mo(2)-O(22)	2.236(11)
Mo(3)-O(6)	1.661(12)	Mo(4)-O(17)	1.654(12)
Mo(3)-O(26)	1.952(10)	Mo(4)-O(18)	1.937(11)
Mo(3)-O(23)	1.954(11)	Mo(4)-O(27)	1.994(10)
Mo(3)-O(10)	2.041(11)	Mo(4)-O(15)	2.051(10)
Mo(3)-O(20)	2.085(11)	Mo(4)-O(20)	2.115(10)
Mo(3)-O(19)	2.286(9)	Mo(4)-O(19)	2.314(11)
Mo(5)-O(9)	1.660(12)	Mo(6)-O(13)	1.705(11)
Mo(5)-O(16)	1.925(11)	Mo(6)-O(18)	1.918(11)
Mo(5)-O(21)	1.969(12)	Mo(6)-O(27)	1.976(10)
Mo(5)-O(11)	2.081(11)	Mo(6)-O(12)	2.073(11)
Mo(5)-O(24)	2.140(10)	Mo(6)-O(5)	2.118(12)
Mo(5)-O(25)	2.278(11)	Mo(6)-O(22)	2.250(11)
P(1)-O(29)	1.492(14)	P(3)-O(2)	1.506(11)
P(1)-O(4)	1.516(13)	P(3)-O(19)	1.538(11)
P(1)-O(11)	1.522(11)	P(3)-O(25)	1.546(11)
P(1)-O(28)	1.570(17)	P(3)-O(22)	1.582(10)
P(2)-O(7)	1.506(11)	P(4)-O(3)	1.499(11)
P(2)-O(15)	1.536(11)	P(4)-O(8)	1.512(12)
P(2)-O(10)	1.538(12)	P(4)-O(12)	1.518(13)
P(2)-O(1)	1.559(12)	P(4)-O(31)	1.569(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z #2 -x,-y+1,-z+1

Table S4. Selected bond lengths (Å) for compound **4**.

Mo(1)-O(1)	1.752(4)	Co(1)-O(3)#2	2.067(4)
Mo(1)-O(3)	1.753(4)	Co(1)-O(3)#1	2.067(4)
Mo(1)-O(2)#1	1.794(4)	Co(1)-O(5)#1	2.079(5)
Mo(1)-O(4)	2.095(4)	Co(1)-O(5)#2	2.079(5)
Mo(1)-O(6)#1	2.126(4)	Co(1)-O(1)	2.094(4)
Mo(1)-O(2)	2.201(4)	Co(1)-O(1)#3	2.094(4)
Co(2)-O(7)	1.923(5)	P(1)-O(7)	1.512(5)
Co(2)-O(7)#4	1.923(5)	P(1)-O(5)	1.528(5)
Co(2)-O(7)#5	1.923(5)	P(1)-O(4)	1.545(5)
Co(2)-O(7)#6	1.923(5)	P(1)-O(6)	1.549(5)

Symmetry transformations used to generate equivalent atoms:

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

#4 -y+5/4,x+1/4,-z-3/4 #5 y-1/4,-x+5/4,-z-3/4 #6 -x+1,-y+3/2,z+0

Table S5. Hydrogen bonds for compounds **1**-**3**.

Donor--H...Acceptor [ARU]	D - H	H...A	D...A	D - H...A
Compound **1**				
C(4)--H(4A)..O(6) [ ]	0.97	2.42	3.291(5)	150
C(4) --H(4B)..O(1) [10544.01]	0.97	2.48	3.295(5)	142
C(11)--H(11A)..O(4) [13555.01]	0.97	2.44	3.276(5)	145
[10544.] = 1/4-y,-1/4+x,-1/4+z [13555.] = 1/2-x,1/2-y,1/2-z				
Compound **2**				
C(11)--H(11B)..O(1) [ ]	0.97	2.54	3.434(12)	154
C(2)--H(2A)..Ow(1) [ ]	0.93	1.70	2.571(11)	155
C(3)--H(3A)..O(10) [1455.01]	0.93	2.30	3.166(12)	154
C(4)--H(4A)..O(15) [1455.01]	0.97	2.44	3.320(10)	151
C(27)--H(27A)..O(2) [1455.01]	0.93	2.53	3.363(10)	149
C(6)--H(6A)..O(9) [1465.01]	0.93	2.39	3.249(10)	154
C(23)--H(23A)..O(6) [2655.01]	0.93	2.40	3.307(10)	165
C(18)--H(18A)..O(18) [2656.01]	0.97	2.50	3.451(11)	165
C(18)--H(18B)..O(9) [2756.01]	0.97	2.40	3.337(10)	162
C(15)--H(15A)..O(19) [2756.01]	0.93	2.19	3.045(10)	152
[1455.] = -1+x,y,z [1465.] = -1+x,1+y,z [2655.] = 1-x,-y,-z [2656.] = 1-x,-y,1-z [2756.] = 2-x,-y,1-z				
Compound **3**				
C(3)--H(3A)..O(6) [2556.01]	0.93	2.27	3.13(2)	155
C(1)--H(1A)..O(13) [2566.01]	0.93	2.26	3.08(2)	148
C(22)--H(22A)..O(1W) [2566.01]	0.93	2.51	3.39(3)	156
C(12)--H(12A)..Ow(6) [2656.08]	0.93	2.54	3.43(3)	159
C(17)--H(17A)..O(14) [2665.01]	0.93	2.33	3.25(3)	169
C(14)--H(14A)..O(16) [2666.01]	0.93	2.46	3.35(2)	161
[2556.] = -x,-y,1-z [2566.] = -x,1-y,1-z [2656.] = 1-x,-y,1-z [2665.] = 1-x,1-y,-z [2666.] = 1-x,1-y,1-z				

Table S6. The bond valence sum calculations for V and Mo atoms in compounds **1-4**.

Compound **1**			
Mo1	5.976	V1	4.508
Mo2	5.991	V2	4.131
Compound **2**			
Mo1	6.100	Mo4	6.116
Mo2	6.065	Mo5	6.056
Mo3	6.071		
Compound **3**			
Mo1	4.897	Mo4	4.890
Mo2	4.935	Mo5	4.888
Mo3	4.991	Mo6	4.753
Compound **4**			
Mo1	5.998		