

Supporting information for

pH-Dependent syntheses of copper-quinoxaline-polyoxotungatate
hybrids: variable role of Keggin-type polyanion in different pH
conditions

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Table S1 The selected bond distances and angles for compounds 1–4.

Compound 1			
Distances (Å)			
W(1)-O(29)	1.72(8)	W(1)-O(20)	1.91(5)
W(1)-O(5)	1.91(5)	W(1)-O(10)	1.92(8)
W(1)-O(11)	1.95(3)	W(1)-O(1)	2.45(6)
W(2)-O(30)	1.71(3)	W(2)-O(21)	1.91(4)
W(2)-O(12)	1.91(7)	W(2)-O(6)	1.92(1)
W(2)-O(5)	1.93(8)	W(2)-O(1)	2.46(4)
W(3)-O(31)	1.72(1)	W(3)-O(22)	1.90(2)
W(3)-O(13)	1.92(4)	W(3)-O(6)	1.92(1)
W(3)-O(7)	1.92(1)	W(3)-O(2)	2.44(5)
W(4)-O(32)	1.71(4)	W(4)-O(23)	1.86(9)
W(4)-O(7)	1.91(4)	W(4)-O(8)	1.92(6)
W(4)-O(14)	1.95(1)	W(4)-O(2)	2.45(1)
W(5)-O(33)	1.72(4)	W(5)-O(8)	1.92(3)
W(5)-O(9)	1.92(4)	W(5)-O(24)	1.93(3)
W(5)-O(15)	1.94(9)	W(5)-O(3)	2.43(3)
W(6)-O(34)	1.71(2)	W(6)-O(10)	1.90(7)
W(6)-O(9)	1.92(1)	W(6)-O(16)	1.92(1)
W(6)-O(25)	1.94(6)	W(6)-O(3)	2.44(9)
W(7)-O(35)	1.67(7)	W(7)-O(19)	1.91(7)
W(7)-O(17)	1.92(3)	W(7)-O(12)	1.92(6)
W(7)-O(11)	1.94(6)	W(7)-O(1)	2.48(2)
W(8)-O(36)	1.71(7)	W(8)-O(17)	1.93(4)
W(8)-O(18)	1.92(7)	W(8)-O(13)	1.94(2)
W(8)-O(14)	1.97(1)	W(8)-O(2)	2.46(2)
W(9)-O(37)	1.68(4)	W(9)-O(19)	1.91(3)
W(9)-O(18)	1.91(4)	W(9)-O(16)	1.92(9)
W(9)-O(15)	1.93(3)	W(9)-O(3)	2.43(8)
W(10)-O(38)	1.71(2)	W(10)-O(25)	1.88(3)
W(10)-O(20)	1.91(5)	W(10)-O(26)	1.92(3)
W(10)-O(28)	1.92(9)	W(10)-O(4)	2.46(1)
W(11)-O(39)	1.72(9)	W(11)-O(21)	1.90(8)
W(11)-O(22)	1.92(4)	W(11)-O(26)	1.92(8)
W(11)-O(27)	1.94(8)	W(11)-O(4)	2.45(7)
W(12)-O(40)	1.69(2)	W(12)-O(27)	1.89(1)
W(12)-O(24)	1.91(4)	W(12)-O(28)	1.93(9)
W(12)-O(23)	1.94(4)	W(12)-O(4)	2.46(2)
O(1)-P(1)	1.52(5)	O(2)-P(1)	1.54(8)
O(3)-P(1)	1.54(8)	O(4)-P(1)	1.52(6)
Angles (deg)			
O(20)-W(1)-O(5)	90.6(4)	O(5)-W(1)-O(10)	154.6(4)
O(21)-W(2)-O(6)	85.4(4)	O(30)-W(2)-O(12)	101.0(4)

O(31)-W(3)-O(22)	102.5(4)	O(13)-W(3)-O(7)	87.5(4)
O(32)-W(4)-O(7)	102.5(4)	O(32)-W(4)-O(14)	100.9(4)
O(33)-W(5)-O(9)	102.5(4)	O(33)-W(5)-O(15)	100.8(4)
O(10)-W(6)-O(9)	154.9(3)	O(9)-W(6)-O(25)	88.1(4)
O(35)-W(7)-O(17)	103.5(4)	O(19)-W(7)-O(1)	81.2(3)
O(36)-W(8)-O(18)	101.3(4)	O(36)-W(8)-O(14)	100.3(4)
O(37)-W(9)-O(19)	103.9(5)	O(37)-W(9)-O(15)	101.7(5)
O(38)-W(10)-O(26)	101.7(4)	O(25)-W(10)-O(4)	82.1(3)
O(21)-W(11)-O(26)	90.1(4)	O(26)-W(11)-O(27)	85.7(4)
O(27)-W(12)-O(28)	87.9(3)	O(27)-W(12)-O(4)	72.2(3)
O(1)-P(1)-O(4)	109.7(5)	O(1)-P(1)-O(3)	109.4(5)
O(4)-P(1)-O(3)	109.5(4)	O(1)-P(1)-O(2)	109.2(5)

Compound 2

Distances (Å)

Cu(1)-N(1)	1.99(1)	Cu(1)-N(2)	2.01(4)
Cu(1)-N(3)	2.03(8)		

Angles (deg)

N(1)-Cu(1)-N(2)	131.5(3)	N(1)-Cu(1)-N(3)	123.3(3)
N(2)-Cu(1)-N(3)	105.0(3)		

Compound 3^a

Distances (Å)

Cu(1)-N(1)	1.92(2)	Cu(2)-N(3)	1.96(7)
Cu(1)-O(23)	2.43(4)	Cu(2)-N(2)	1.20(2)
Cu(1)-O(22) ^{#1}	2.77(9)	Cu(2)-N(5)	2.03(8)
		Cu(2)-O(14)	2.79(5)

Angles (deg)

N(1)-Cu(1)-N(1) ^{#2}	169.0(6)	N(3)-Cu(2)-N(2)	135.7(5)
N(1)-Cu(1)-O(23)	95.5(3)	N(3)-Cu(2)-N(5)	116.9(5)
N(1) ^{#2} -Cu(1)-O(23)	95.5(3)	N(2)-Cu(2)-N(5)	107.4(4)
N(1)-Cu(1)-O(22) ^{#2}	91.9(3)	N(3)-Cu(2)-O(14)	84.2(4)
O(23)-Cu(1)-O(22) ^{#2}	84.5 (9)	N(2)-Cu(2)-O(14)	79.3(4)

^aSymmetry codes for 3: #1: x,-y+3/2,z-1/2; #2: -x+3/2,-y+3/2,z.

Compound 4^b

Distances (Å)

Cu(1)-N(2)	1.93(5)	W(4)-O(13)	2.03(7)
Cu(1)-N(1)	1.92(8)	Cu(2) ^{#3} -O(13)	2.03(7)
Cu(1)-O(1)	2.42(4)	W(4)-O(10)	1.94(4)
Cu(2) ^{#1} -O(5)	1.93(9)	Cu(2)-O(6) ^{#1}	2.40(2)

Angles (deg)

N(2)-Cu(1)-N(1)	175.0(6)	N(2)-Cu(1)-O(1)	82.8(5)
N(1)-Cu(1)-O(1)	101.7(5)	O(10)-Cu(2)-O(10) ^{#3}	87.9(7)
O(5) ^{#1} -Cu(2)-O(10)	158.4(7)	O(5) ^{#1} -Cu(2)-O(13)	101.9(5)
O(5) ^{#1} -Cu(2)-O(5) ^{#2}	89.5(8)	O(10)-Cu(2)-O(13)	99.6(4)

^bSymmetry codes for **4**: #1: -x,-y,-z+1; #2: -x,y,-z+1; #3: -x,-y,-z+2.

Figure S1. The 2D 6^3 topological layer in **2**.

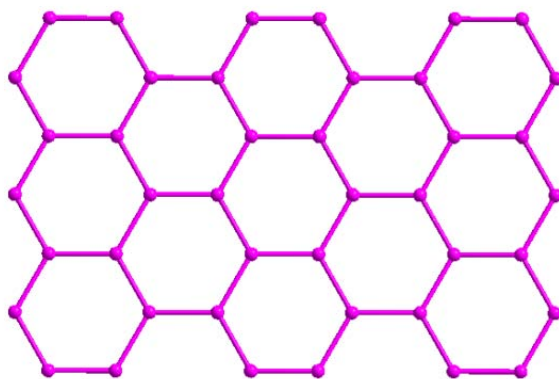


Figure S2. A view along the *c*-axis showing the stacking of **2**. The different layers are represented with different colors.

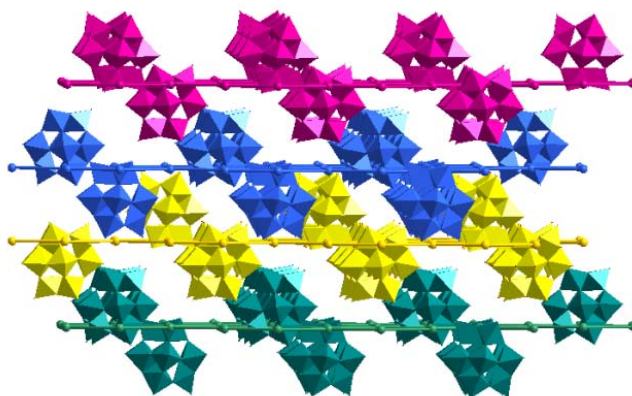


Figure S3. The PW12 clusters link with four adjacent 1D zigzag chains. The green ball represents PW12 cluster and the pink chains represent the 1D metal-organic zigzag chain.

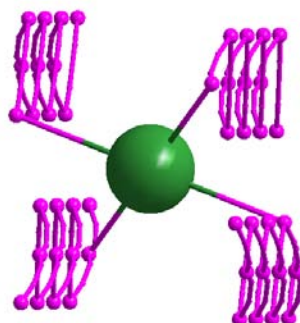


Figure S4. View of coordination detail of $\text{HPCu}^{\text{II}}\text{W}_{11}\text{O}_{39}^{4-}$ clusters in **4**.

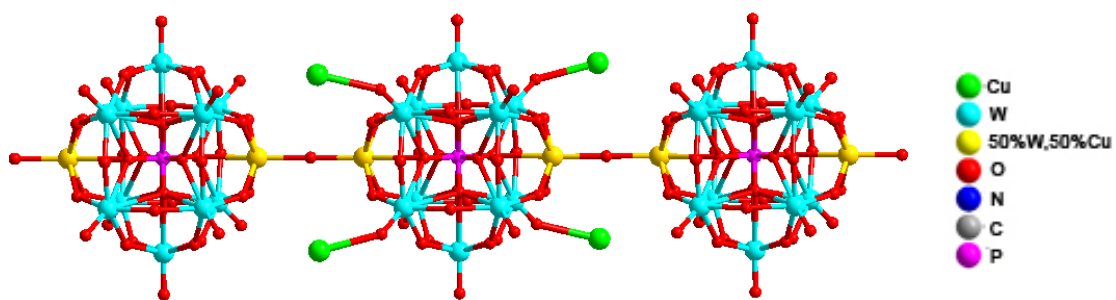


Figure S5. The side view of the “sandwich-like” layer in **4**.

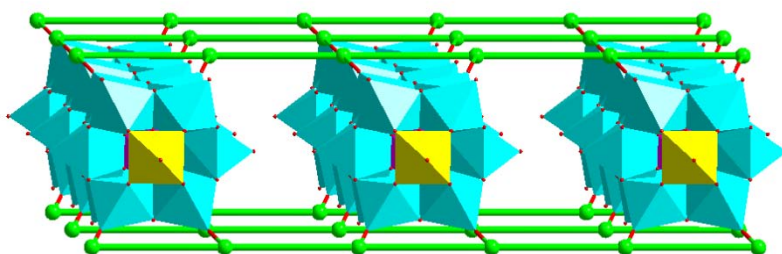


Fig. S6 IR spectra of compounds **1–4**.

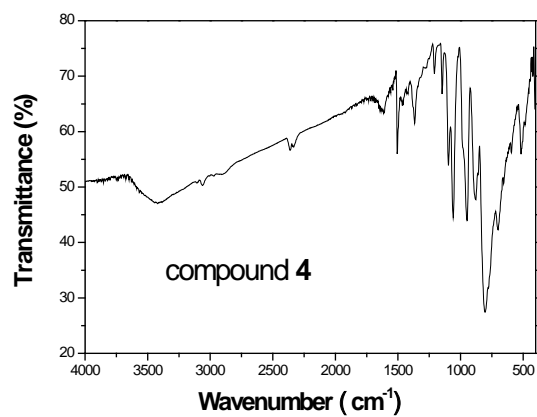
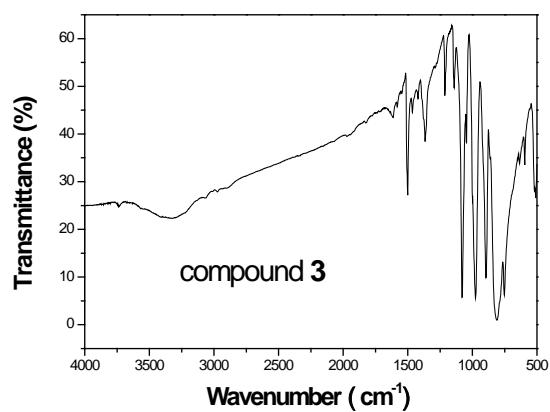
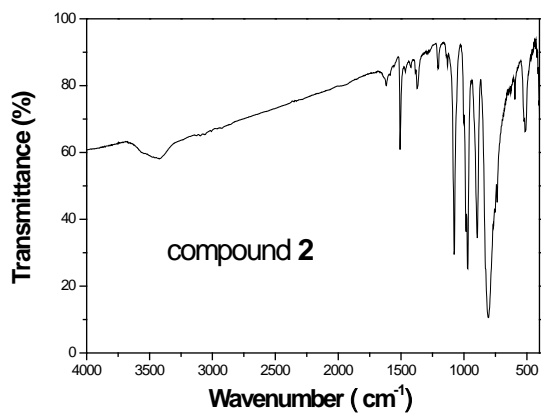
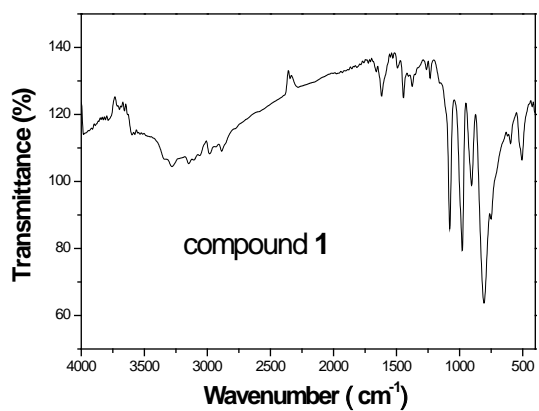


Fig. S7 TG curves of compounds 2–4.

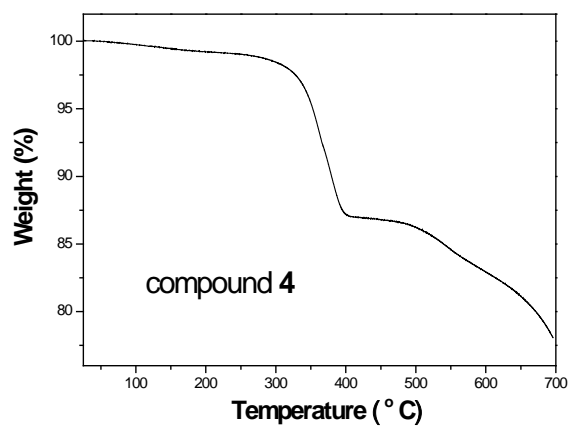
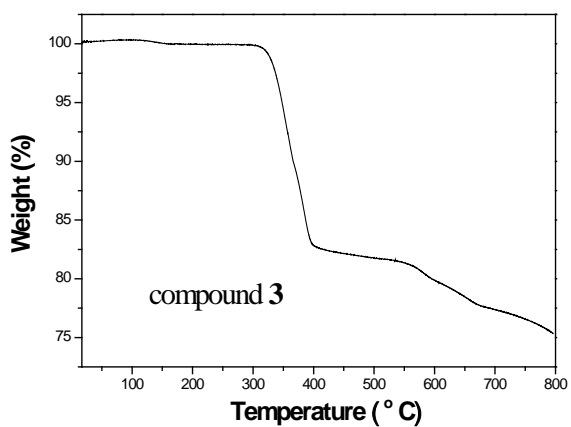
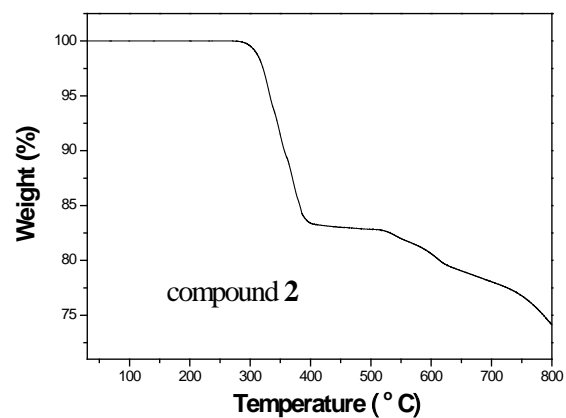


Fig. S8 The XPRD patterns of compounds 2–4.

