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Influence of N-donor Site in 5-(x-pyridyl)-1H-tetrazole Ligands (x = 2, 4) on Assembly of Polyoxometalates-based Compounds Modified by Multinuclear Metal Clusters and Infinite Chains

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Table. S1. Selected bond lengths (Å) and bond angles (°) for compounds **1**–**4**.

Cu(1)-N(2)	1.940(8)	Cu(1)-N(7)	1.959(8)
Cu(1)-N(1)	2.029(8)	Cu(1)-N(6)	2.036(9)
O(1W)-Cu(3)	1.921(7)	O(1W)-Cu(4)	1.965(7)
O(2W)-Cu(2)	1.995(7)	N(9)-Cu(2)	2.215(9)
N(11)-Cu(2)	2.027(9)	N(12)-Cu(2)	1.994(9)
N(13)-Cu(3)	2.009(8)	N(14)-Cu(4)	2.014(9)
N(16)-Cu(3)	2.052(8)	N(17)-Cu(3)	1.991(8)
N(18)-Cu(2)	1.972(9)	Cu(3)-N(4)#2	2.325(10)
Cu(4)-O(1W)#3	1.965(7)	Cu(4)-N(14)#3	2.014(9)
N(2)-Cu(1)-N(7)	170.8(4)	N(2)-Cu(1)-N(1)	81.3(3)
N(7)-Cu(1)-N(1)	99.0(3)	N(2)-Cu(1)-N(6)	97.6(4)
N(7)-Cu(1)-N(6)	80.9(3)	N(1)-Cu(1)-N(6)	173.0(4)
Cu(3)-O(1W)-Cu(4)	119.5(4)	C(2)-N(1)-Cu(1)	114.3(7)
C(4)-N(1)-Cu(1)	127.1(7)	C(1)-N(2)-Cu(1)	115.4(7)
N(3)-N(2)-Cu(1)	138.8(7)	N(3)-N(4)-Cu(3)#2	114.8(7)
N(5)-N(4)-Cu(3)#2	133.8(7)	C(8)-N(6)-Cu(1)	114.1(7)
C(12)-N(6)-Cu(1)	128.0(8)	C(7)-N(7)-Cu(1)	115.6(7)
N(8)-N(7)-Cu(1)	139.5(7)	N(8)-N(9)-Cu(2)	121.4(6)
C(18)-N(11)-Cu(2)	125.0(8)	C(14)-N(11)-Cu(2)	115.8(7)

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N(13)-N(12)-Cu(2)	138.1(6)	C(13)-N(12)-Cu(2)	114.4(7)
N(12)-N(13)-Cu(3)	128.3(6)	N(14)-N(13)-Cu(3)	122.4(7)
N(13)-N(14)-Cu(4)	118.4(6)	N(15)-N(14)-Cu(4)	129.7(7)
C(24)-N(16)-Cu(3)	128.6(8)	C(20)-N(16)-Cu(3)	113.8(7)
C(19)-N(17)-Cu(3)	113.1(7)	N(18)-N(17)-Cu(3)	140.1(7)
N(19)-N(18)-Cu(2)	124.4(7)	N(17)-N(18)-Cu(2)	126.4(7)
N(18)-Cu(2)-O(2W)	92.6(4)	N(18)-Cu(2)-N(12)	93.7(4)
O(2W)-Cu(2)-N(12)	163.6(3)	N(18)-Cu(2)-N(11)	173.6(4)
O(2W)-Cu(2)-N(11)	93.4(4)	N(12)-Cu(2)-N(11)	79.9(4)
N(18)-Cu(2)-N(9)	90.2(4)	O(2W)-Cu(2)-N(9)	97.1(3)
N(12)-Cu(2)-N(9)	98.0(3)	N(11)-Cu(2)-N(9)	91.2(3)
O(1W)-Cu(3)-N(17)	173.9(3)	O(1W)-Cu(3)-N(13)	88.8(3)
N(17)-Cu(3)-N(13)	91.4(3)	O(1W)-Cu(3)-N(16)	98.3(3)
N(17)-Cu(3)-N(16)	80.5(3)	N(13)-Cu(3)-N(16)	167.0(3)
O(1W)-Cu(3)-N(4)#2	93.5(3)	N(17)-Cu(3)-N(4)#2	92.5(3)
N(13)-Cu(3)-N(4)#2	90.7(3)	N(16)-Cu(3)-N(4)#2	99.7(4)
O(1W)-Cu(4)-O(1W)#3	180.0(1)	O(1W)-Cu(4)-N(14)	89.7(3)
O(1W)#3-Cu(4)-N(14)	90.3(3)	O(1W)-Cu(4)-N(14)#3	90.3(3)
O(1W)#3-Cu(4)-N(14)#3	89.7(3)	N(14)-Cu(4)-N(14)#3	180.0(2)

Symmetry codes for **1**: #1 -x+2,-y-2,-z+2 #2 -x+3,-y-1,-z+1 #3 -x+4,-y-1,-z

Cu(1)-N(3)#1	1.974(7)	Cu(1)-N(1)	1.990(7)
Cu(1)-N(2)	2.001(7)	Cu(1)-O(1W)	2.012(7)
Cu(1)-N(7)	2.253(6)	N(9)-Cu(2)#3	1.984(6)
N(10)-Cu(2)	2.005(6)	N(11)-Cu(3)	2.012(7)
N(12)-Cu(3)	2.037(6)	N(14)-Cu(2)	2.014(7)
Cu(2)-N(9)#3	1.984(6)	Cu(3)-N(11)#4	2.012(7)
Cu(3)-N(12)#4	2.037(6)	N(3)#1-Cu(1)-N(1)	174.3(3)
N(3)#1-Cu(1)-N(2)	93.9(3)	N(1)-Cu(1)-N(2)	80.8(3)
N(3)#1-Cu(1)-O(1W)	90.9(3)	N(1)-Cu(1)-O(1W)	92.0(3)

N(2)-Cu(1)-O(1W)	142.1(3)	N(3)#1-Cu(1)-N(7)	100.0(2)
N(1)-Cu(1)-N(7)	83.5(2)	N(2)-Cu(1)-N(7)	104.7(2)
O(1W)-Cu(1)-N(7)	111.4(3)	C(2)-N(1)-Cu(1)	115.8(5)
C(6)-N(1)-Cu(1)	125.9(6)	C(1)-N(2)-Cu(1)	112.7(5)
N(3)-N(2)-Cu(1)	141.9(5)	N(4)-N(3)-Cu(1)#1	126.2(5)
N(2)-N(3)-Cu(1)#1	123.7(5)	C(12)-N(6)-Cu(2)	126.7(6)
C(8)-N(6)-Cu(2)	114.7(5)	N(8)-N(7)-Cu(1)	112.1(4)
C(7)-N(7)-Cu(1)	139.5(5)	N(8)-N(9)-Cu(2)#3	126.1(5)
N(10)-N(9)-Cu(2)#3	124.9(4)	C(7)-N(10)-Cu(2)	113.0(5)
N(9)-N(10)-Cu(2)	141.2(5)	C(18)-N(11)-Cu(3)	126.7(6)
C(14)-N(11)-Cu(3)	114.3(6)	C(13)-N(12)-Cu(3)	110.6(5)
N(13)-N(12)-Cu(3)	142.4(6)	N(13)-N(14)-Cu(2)	132.0(6)
N(15)-N(14)-Cu(2)	115.3(5)	N(9)#3-Cu(2)-N(10)	93.7(2)
N(9)#3-Cu(2)-N(14)	92.5(2)	N(10)-Cu(2)-N(14)	173.5(3)
N(9)#3-Cu(2)-N(6)	174.3(2)	N(10)-Cu(2)-N(6)	80.7(3)
N(14)-Cu(2)-N(6)	93.1(3)	N(11)#4-Cu(3)-N(11)	180.0(1)
N(11)#4-Cu(3)-N(12)	98.2(3)	N(11)-Cu(3)-N(12)	81.8(3)
N(11)#4-Cu(3)-N(12)#4	81.8(3)	N(11)-Cu(3)-N(12)#4	98.2(3)
N(12)-Cu(3)-N(12)#4	180.0(1)		

Symmetry codes for **2**: #1 -x-1,-y+1,-z #2 -x-2,-y,-z-1 #3 -x-1,-y,-z #4 -x-2,-y-1,-z

Ag(1)-N(6)	2.162(7)	Ag(1)-N(7)	2.176(7)
Ag(1)-Ag(2)	3.1280(11)	N(2)-Ag(3)	2.287(7)
Ag(2)-N(5)	2.183(7)	Ag(2)-N(8)	2.280(7)
Ag(2)-O(5)	2.474(7)	Ag(3)-N(10)	2.215(7)
Ag(3)-N(9)#5	2.327(7)	N(9)-Ag(3)#7	2.327(7)
N(6)-Ag(1)-N(7)	162.4(3)	N(6)-Ag(1)-Ag(2)	94.9(2)
N(7)-Ag(1)-Ag(2)	67.53(19)	N(3)-N(2)-Ag(3)	121.7(6)
C(1)-N(2)-Ag(3)	132.3(6)	N(5)-Ag(2)-N(8)	157.3(3)

N(5)-Ag(2)-O(5)	108.5(3)	N(8)-Ag(2)-O(5)	94.0(3)
N(5)-Ag(2)-Ag(1)	93.6(2)	N(8)-Ag(2)-Ag(1)	64.12(18)
O(5)-Ag(2)-Ag(1)	157.63(18)	N(10)-Ag(3)-N(2)	127.0(3)
N(10)-Ag(3)-N(9)#5	130.9(3)	N(2)-Ag(3)-N(9)#5	101.5(3)
N(3)#6-N(5)-Ag(2)	125.0(6)	N(4)-N(5)-Ag(2)	122.8(6)
C(8)-N(6)-Ag(1)	119.5(6)	C(7)-N(6)-Ag(1)	123.8(6)
N(10)-N(7)-Ag(1)	135.4(6)	N(8)-N(7)-Ag(1)	113.4(5)
N(7)-N(8)-Ag(2)	113.2(5)	N(9)-N(8)-Ag(2)	137.8(6)
C(9)-N(9)-Ag(3)#7	120.5(6)	N(8)-N(9)-Ag(3)#7	132.4(5)
N(7)-N(10)-Ag(3)	130.0(5)	C(9)-N(10)-Ag(3)	124.6(6)

Symmetry codes for **3**: #1 -x,-y-1,-z-2 #2 x+1,-y-1/2,z+1/2 #3 x-1,y,z #4 x+1,y,z #5 x,-y-1/2,z+1/2 #6 x-1,-y-1/2,z-1/2 #7 x,-y-1/2,z-1/2

Ag(1)-N(4)	2.319(11)	Ag(1)-N(7)#2	2.357(10)
Ag(1)-N(5)	2.369(10)	Ag(2)-N(2)	2.221(11)
Ag(2)-N(12)#3	2.229(12)	Ag(2)-N(13)#2	2.321(11)
N(7)-Ag(1)#4	2.357(10)	N(12)-Ag(2)#5	2.229(12)
N(13)-Ag(2)#4	2.321(11)	N(4)-Ag(1)-N(7)#2	104.3(4)
N(4)-Ag(1)-N(5)	113.3(4)	N(7)#2-Ag(1)-N(5)	106.2(4)
N(2)-Ag(2)-N(12)#3	136.3(4)	N(2)-Ag(2)-N(13)#2	110.2(4)
N(12)#3-Ag(2)-N(13)#2	111.3(4)	N(4)-N(2)-Ag(2)	124.8(9)
N(1)-N(2)-Ag(2)	123.9(9)	N(2)-N(4)-Ag(1)	121.9(8)
N(3)-N(4)-Ag(1)	128.8(9)	N(13)-N(5)-Ag(1)	117.1(8)
C(1)-N(5)-Ag(1)	136.4(8)	N(13)-N(7)-Ag(1)#4	123.9(8)
N(12)-N(7)-Ag(1)#4	127.1(8)	C(1)-N(12)-Ag(2)#5	133.4(8)
N(7)-N(12)-Ag(2)#5	119.9(8)	N(7)-N(13)-Ag(2)#4	119.8(8)
N(5)-N(13)-Ag(2)#4	129.6(8)		

Symmetry codes for **4**: #1 -x,y,-z+3/2 #2 -x+1/2,y-1/2,-z+3/2 #3 x,y-1,z #4 -x+1/2,y+1/2,-z+3/2 #5 x,y+1,z

Table S2. Hydrogen-bonding geometries (Å, °) of compounds **1** and **4**

	D–H···A	D–H	H···A	D···A	D–H···A
Compound **1**	C10–H10A···O19	0.929	2.533	3.400	155.41
Compound **4**	C9–H9A···O18	0.930	3.019	3.066	84.12

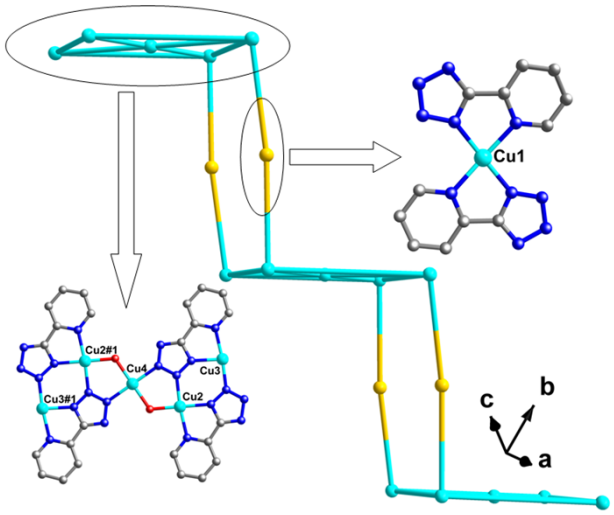
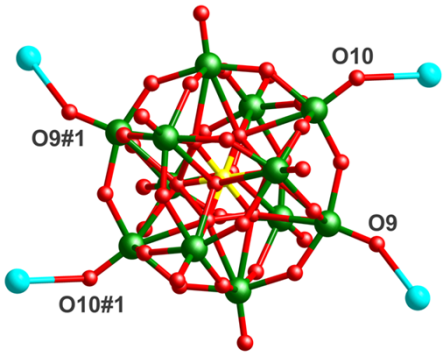
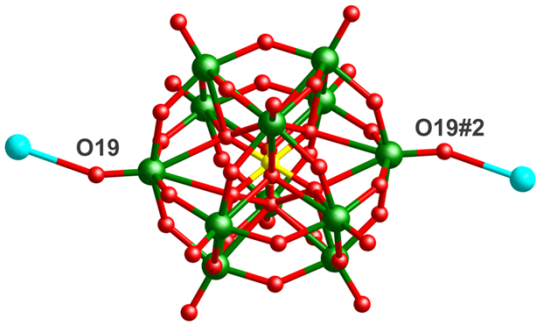


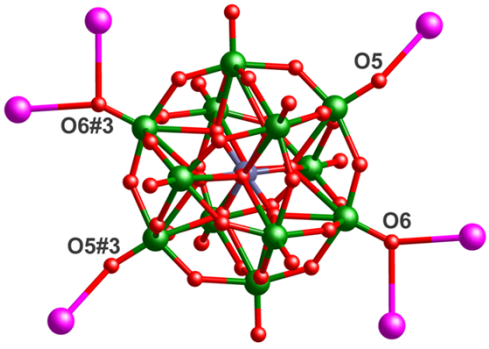
Fig. S1. The penta-nuclear clusters and mono-nuclear Cu^{II} subunits for construction of the 1D stair-like Cu-2-ptz chain in **1**. Symmetry codes: #1 4-x, -1-y, -z



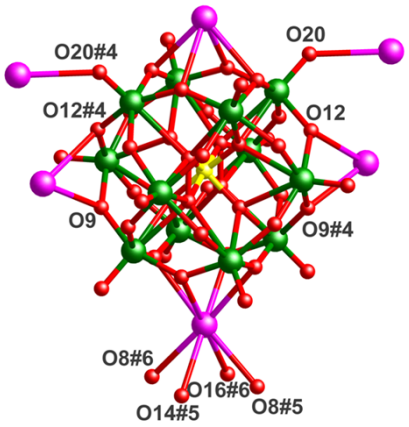
Compound 1



Compound 2



Compound 3



Compound 4

Fig. S2. The coordination modes of Keggin anions in the title compounds. Symmetry codes: #1 2-x, -2-y, 2-z; #2 -2-x, -y, -1-z; #3 -x, -1-y, -2-z; #4 -x, y, -1.5-z; #5 -x, 1+y, 1.5-z; #6 x, 1+y, z.

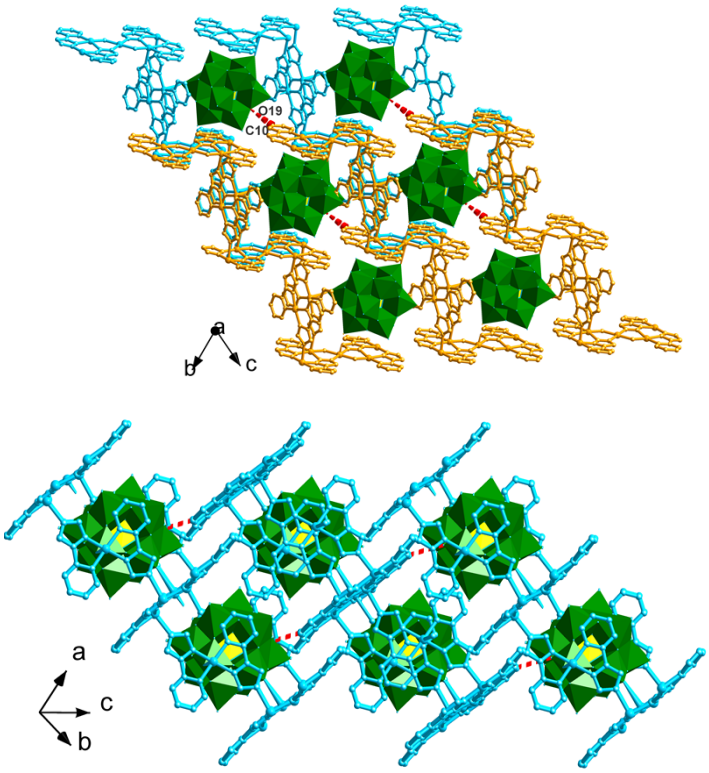


Fig. S3. The 3D supramolecular framework of **1** with C–H···O (C(10)–H(10A)···O(19) = 3.400 Å) hydrogen-bonding interactions.

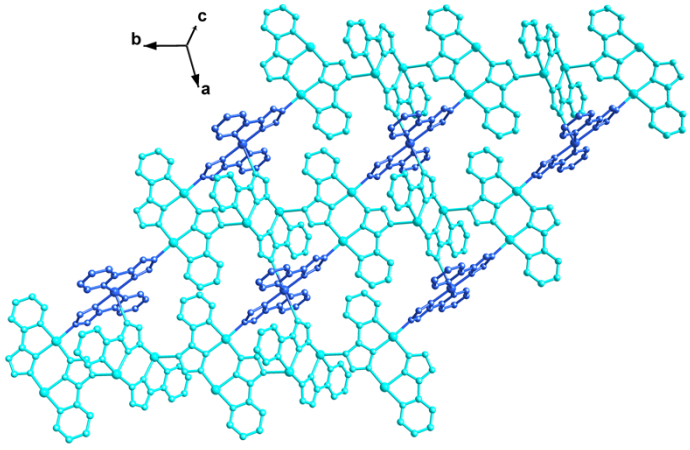


Fig. S4. The 2D layer of compound **2**.

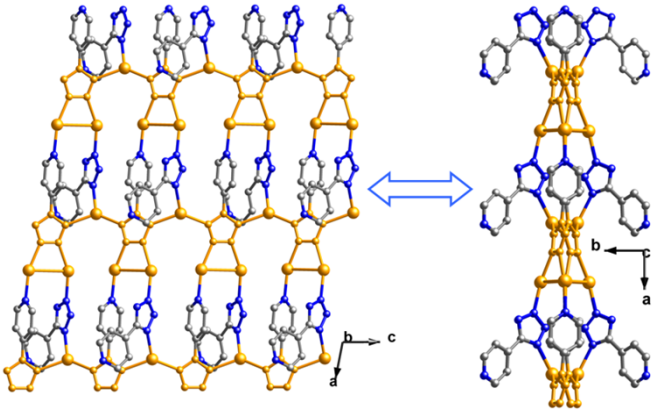


Fig. S5. The 2D layer of compound **3** viewed along *b*- and *c*-axis.

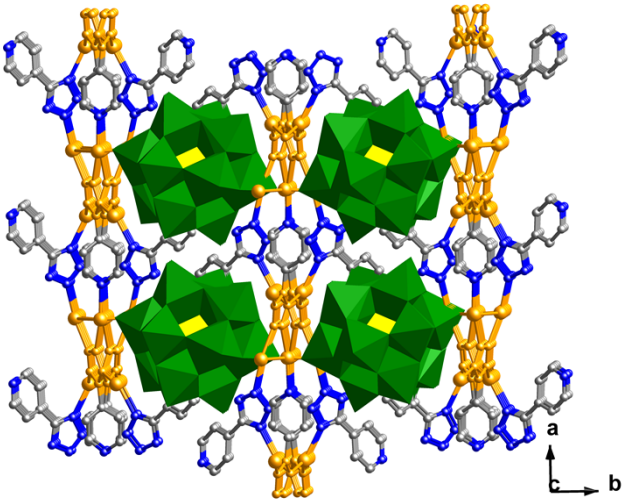


Fig. S6. The 3D structure of compound **3**.

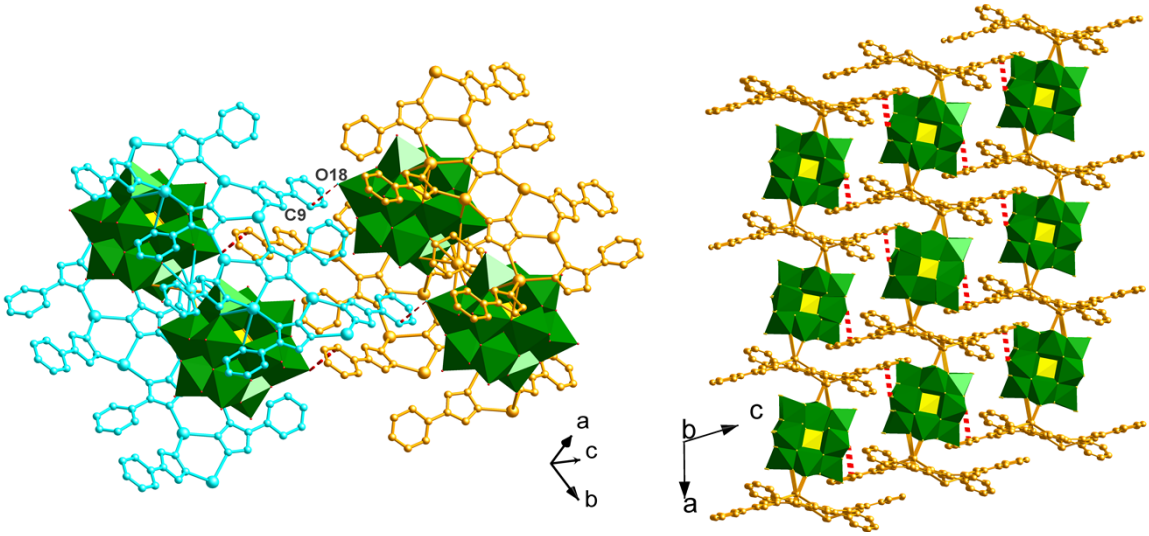


Fig. S7. The 3D supramolecular framework of **4** with C–H···O (C(9)–H(9A)···O(18) = 3.066 Å) hydrogen-bonding interactions.

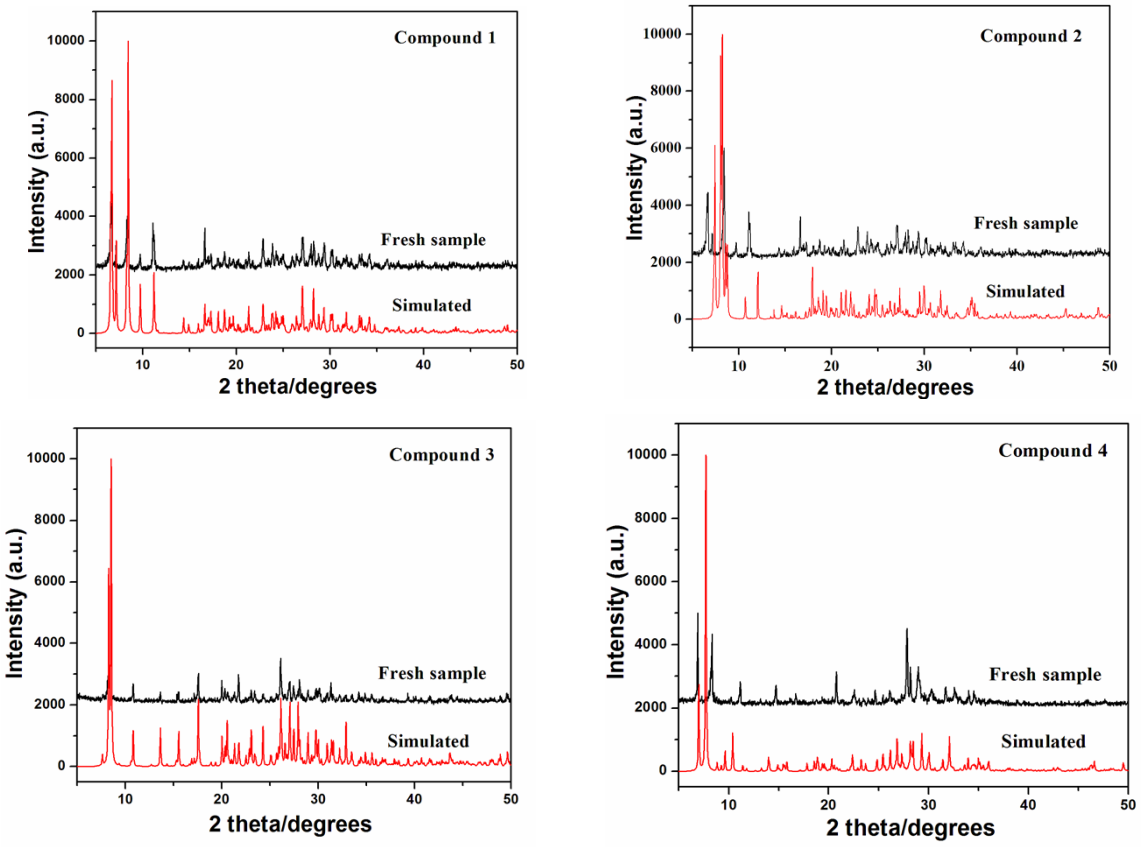


Fig. S8. The PXRD patterns of compounds **1**–**4**.

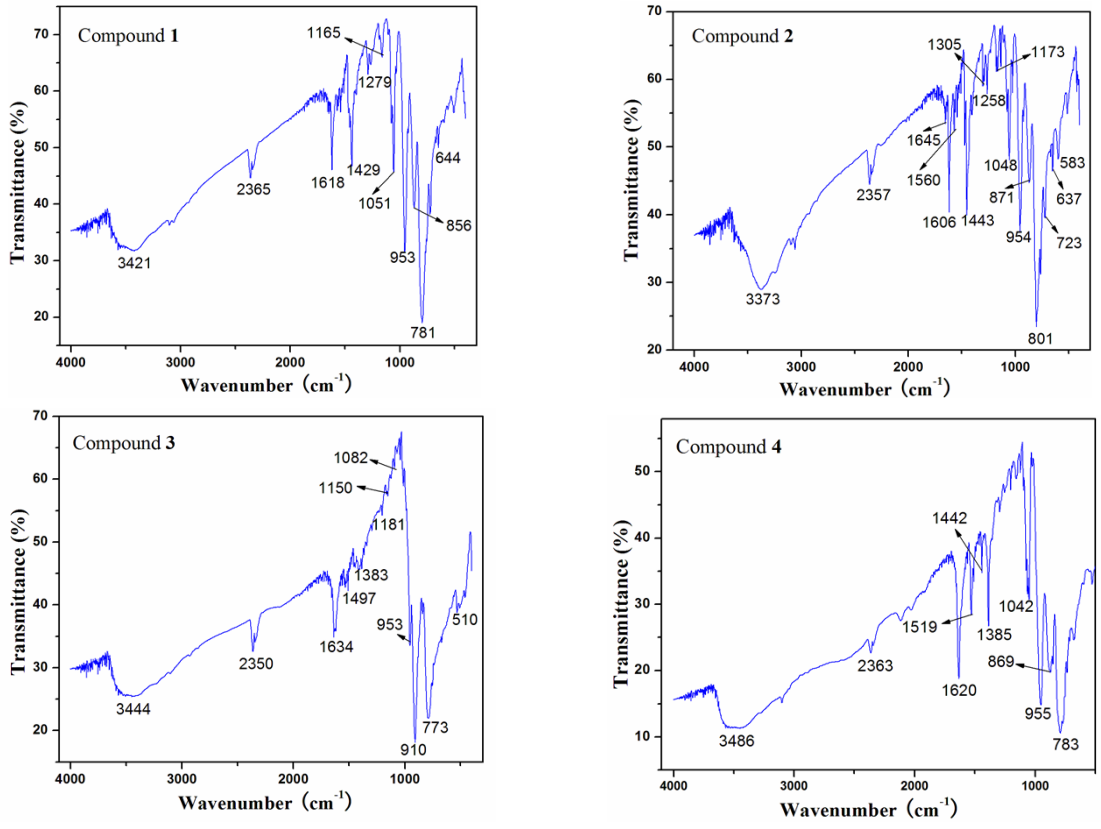


Fig. S9. The IR spectra of compounds **1**–**4**.

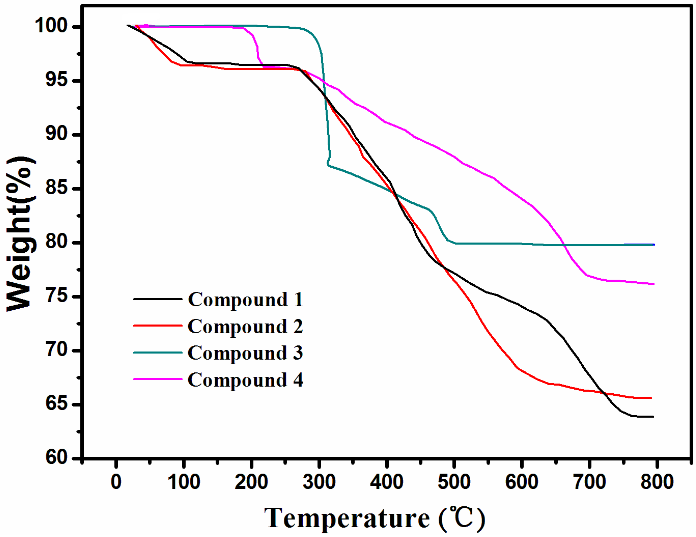


Fig. S10. The TGA curves of the compounds **1**–**4**.

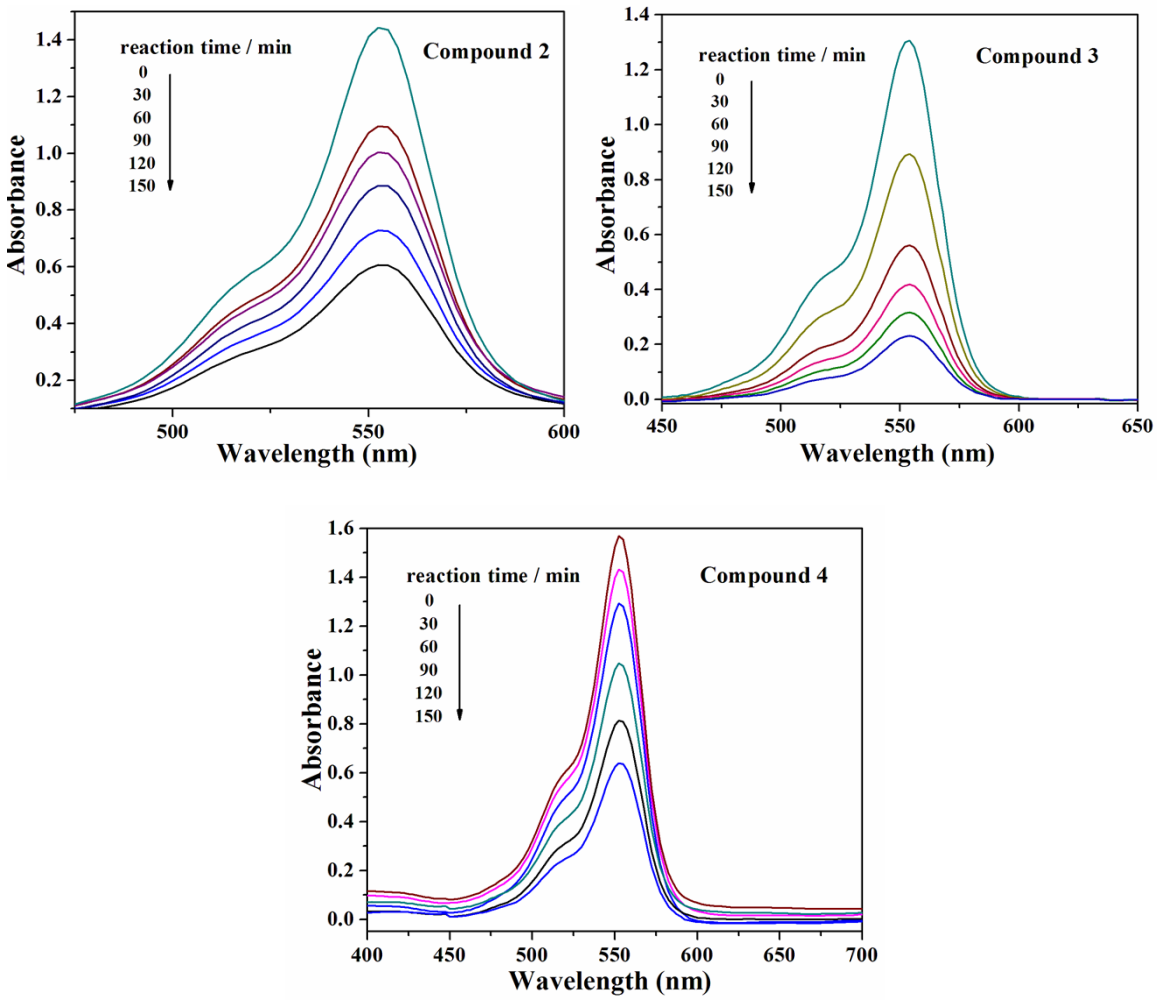


Fig. S11. Absorption spectra of the RhB solution during the decomposition reaction under UV irradiation with the presence of compounds **2**–**4**.

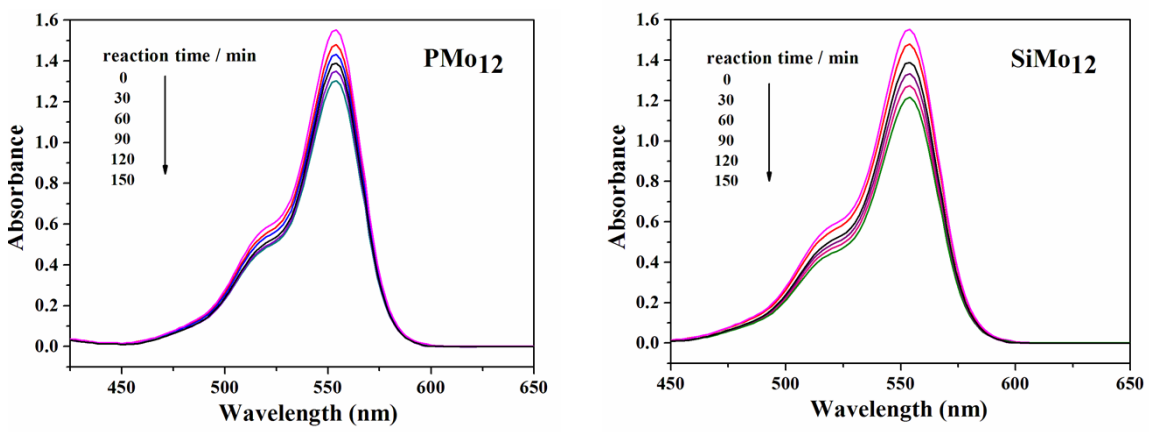


Fig. S12. Absorption spectra of the RhB solution during the decomposition reaction under UV irradiation with the presence of parent POM (PMo_{12} and $SiMo_{12}$).

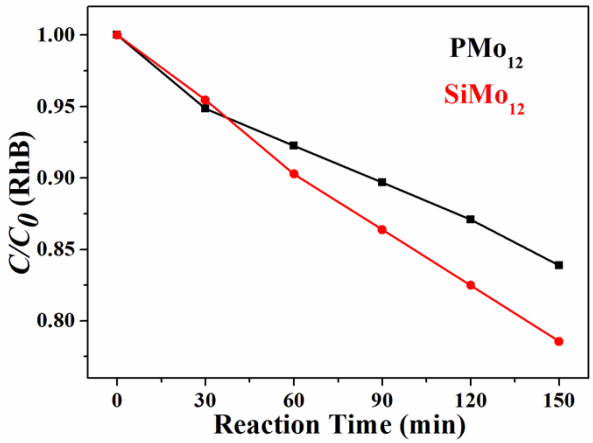


Fig. S13. Photocatalytic decomposition rate of MB solution under UV irradiation with the use of parent POMs. (Black: PMo_{12} and Red: $SiMo_{12}$).

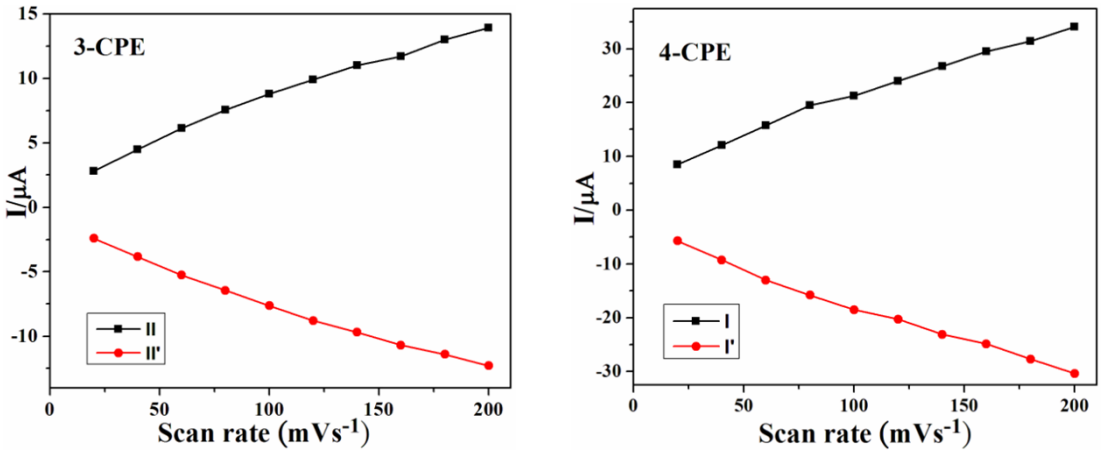


Fig. S14. The dependence of anodic peak (II) and cathodic peak (II') currents for **3**–CPE and anodic peak (I) and cathodic peak (I') currents for **4**–CPE on scan rates.

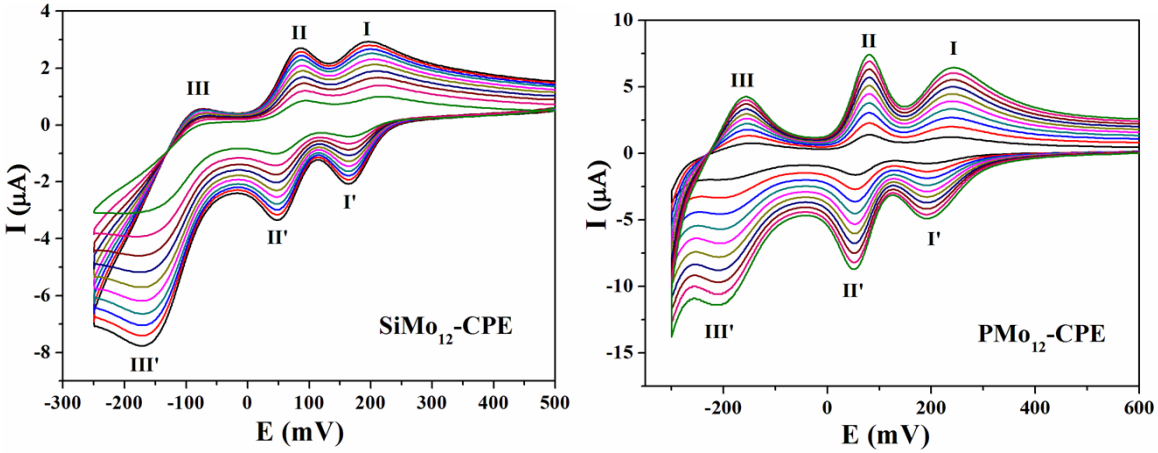


Fig. S15. Cyclic voltammograms of the **$SiMo_{12}$**– and **PMo_{12}**–CPEs in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 20, 40, 60, 80, 100, 120, 140, 160, 180 and 200 mVs^{-1}, respectively).

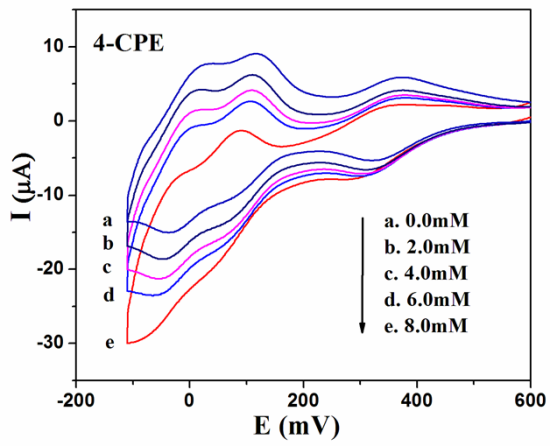


Fig. S16. Cyclic voltammograms of the **4**–CPE in 0.1 M H_2SO_4 +0.5 M Na_2SO_4 aqueous solution containing 0.0–8.0 mM KNO_2. Scan rate: 200$mV \cdot s^{-1}$.