Supporting Information

Using a flexible bis(pyrazol) ligand to construct four new Keggin-based compounds: syntheses, structures and properties

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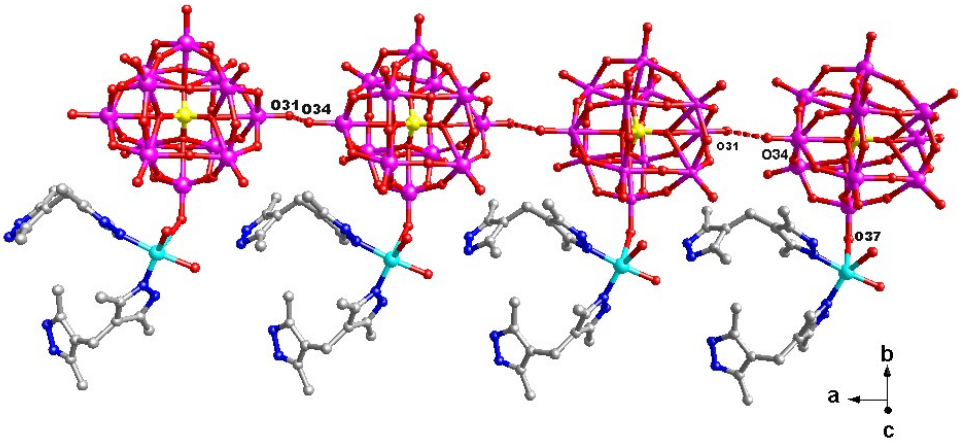

Fig. S1. The 1D supramolecular chain of compound **1** through hydrogen bonding interactions (O31···O34 = 3.238 Å).

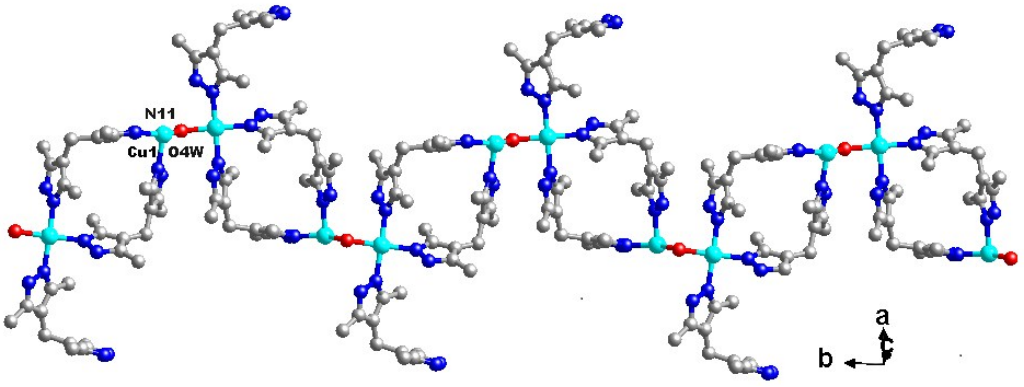

Fig. S2. The 1D cycle-connecting-cycle chain of **3** with type-I H_2bdpm hanging up and down.

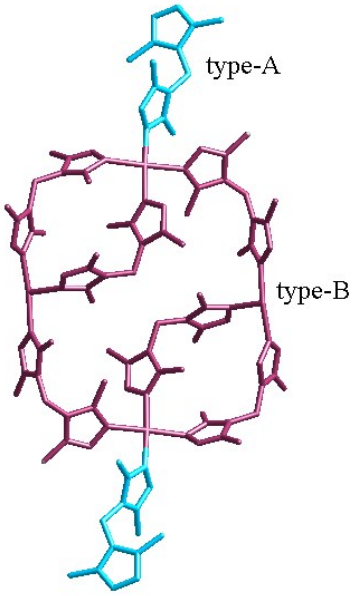

Fig. S3. Two functions of the H_2bdpm: linking mode (blue, type-A) and cyclization mode (purple, type-B).

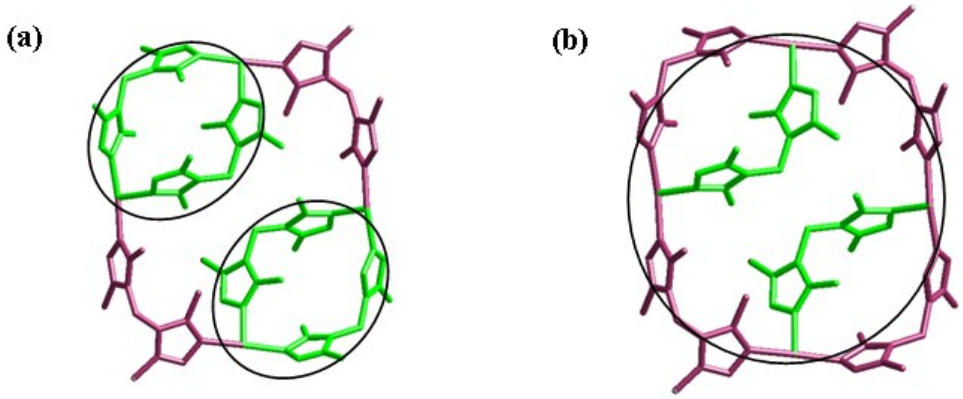

Fig. S4. (a) The bi-nuclear $[Cu_2(H_2bdpm)_2]^{4+}$ cycle (green) in nested cycle subunit. (b) The tetra-nuclear cycle (purple) in nested cycle subunit.

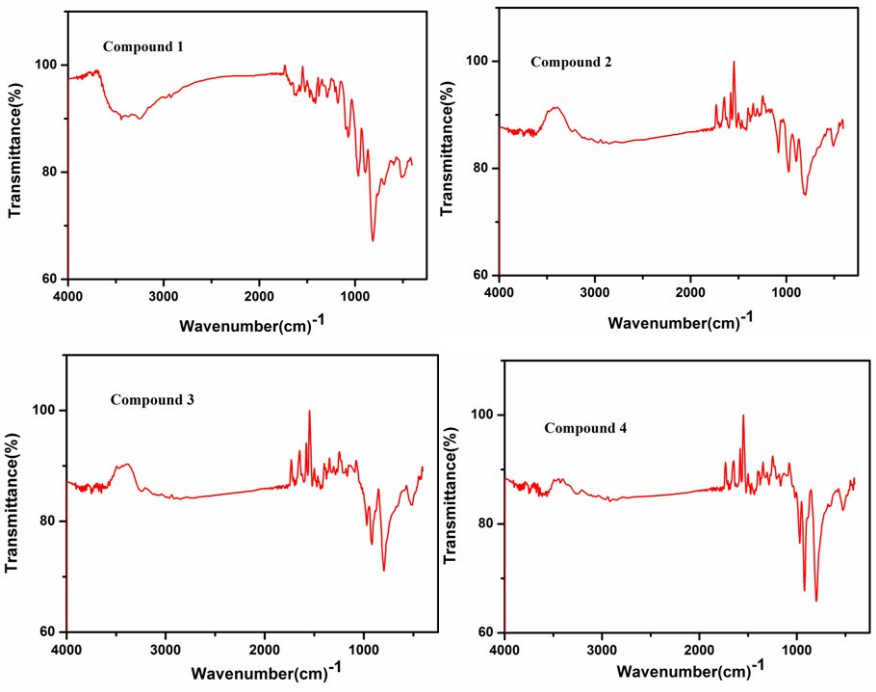

Fig. S5. The IR spectra of compounds **1**, **2**, **3** and **4**.

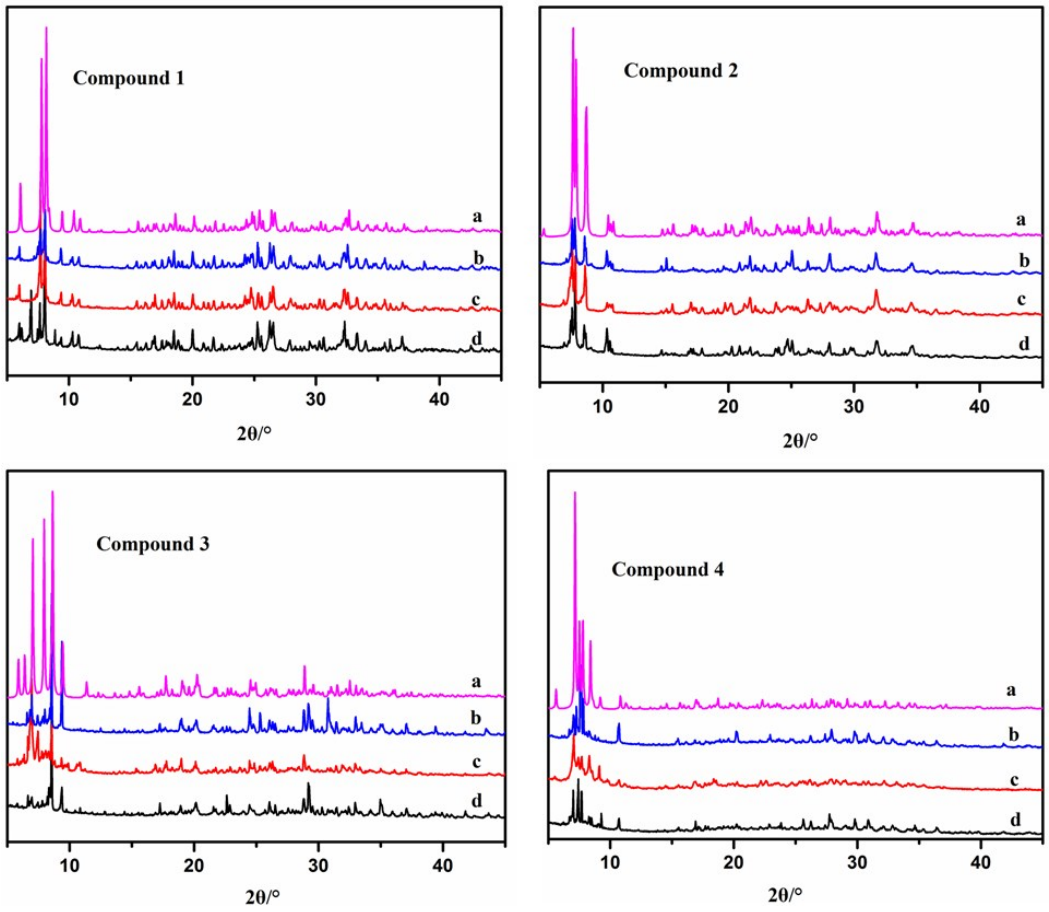

Fig. S6. The simulative (a), experimental (b) and recycled after photocatalysis (c for MB and d for RhB) powder X-ray diffraction patterns for compounds **1**–**4**.

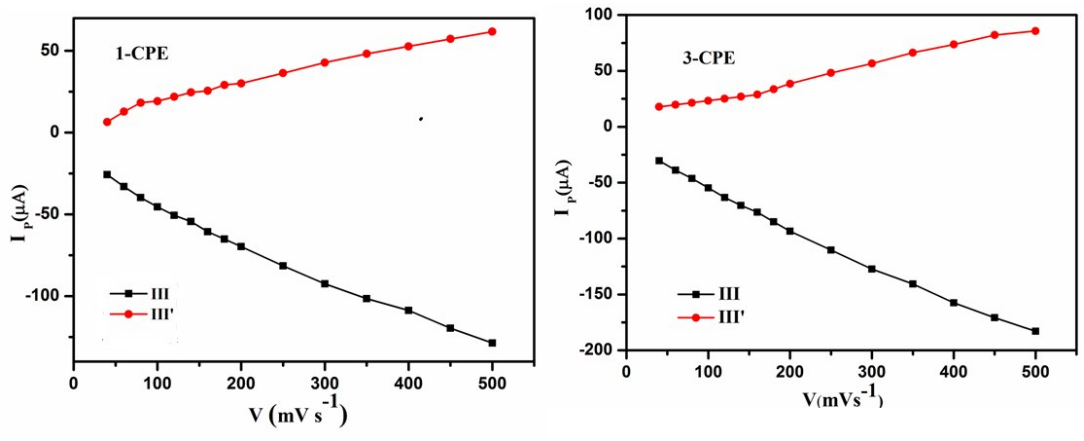

Fig. S7. The dependence of anodic peak (III) and cathodic peak (III') currents of **1**– and **3**–CPE on scan rates.

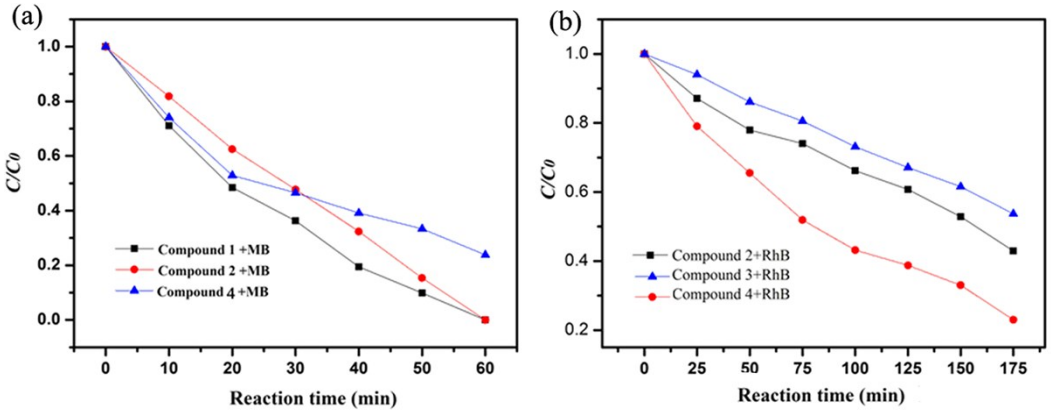

Fig. S8. Photocatalytic decomposition rates of MB (a) and RhB (b) solutions under UV irradiation with the use of compounds **1**, **2**, **3** and **4**.

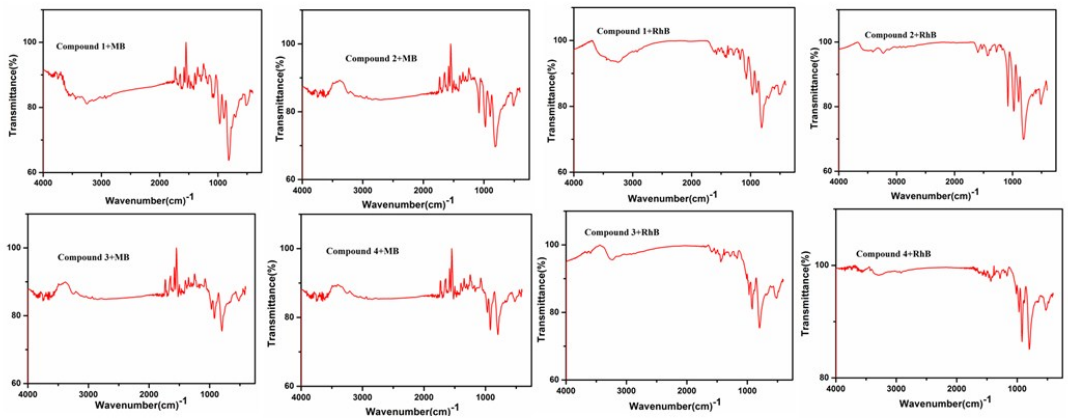

Fig. S9. The IR spectra for recycled catalysts **1**–**4** after photocatalysis.

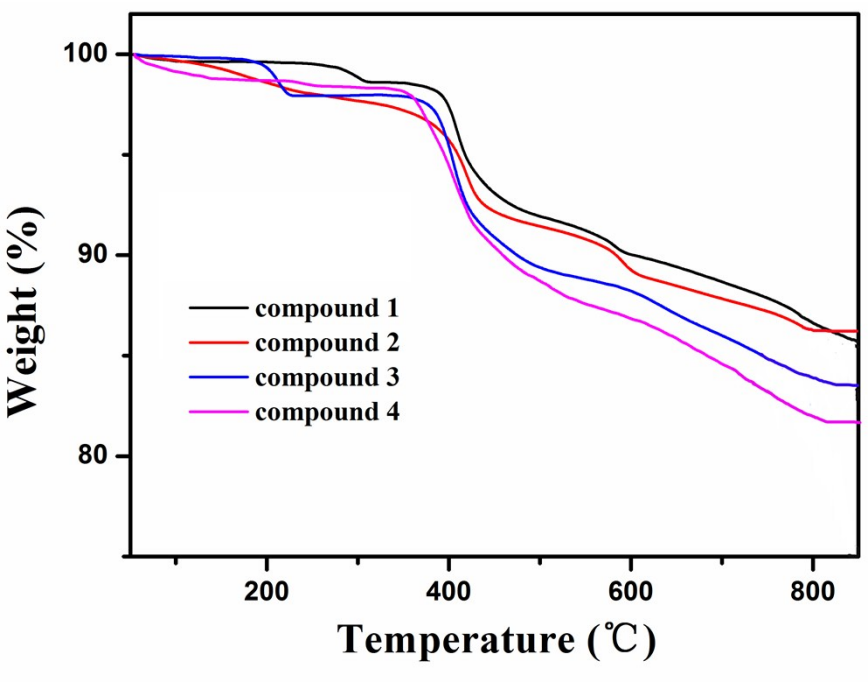

Fig. S10. The TG curves for compounds **1**–**4**.

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

Compound **1**			
Cu(1)-N(2)	1.924(11)	Cu(1)-O(1W)	1.942(9)
Cu(1)-N(5)	1.955(12)	Cu(1)-O(2W)	1.962(10)
Cu(1)-O(37)	2.553(10)	N(6)-N(5)-Cu(1)	123.8(9)
N(2)-Cu(1)-O(1W)	90.7(4)	N(2)-Cu(1)-N(5)	92.8(5)
O(1W)-Cu(1)-N(5)	174.5(5)	N(2)-Cu(1)-O(2W)	150.6(5)
O(1W)-Cu(1)-O(2W)	86.8(4)	N(5)-Cu(1)-O(2W)	92.2(5)
C(3)-N(2)-Cu(1)	130.5(9)	N(1)-N(2)-Cu(1)	125.3(9)
C(12)-N(5)-Cu(1)	130.2(10)		
Compound 2			
Cu(1)-O(10)	2.93(2)	Cu(1)-O(22)	3.01(2)
Cu(1)-O(42)	3.30(2)	Cu(1)-N(1)	1.86(2)
Cu(1)-N(5)	1.87(2)	O(10)-Cu(1)-O(22)	54.5(6)
O(10)-Cu(1)-O(42)	98.1(6)	O(22)-Cu(1)-O(42)	146.1(6)
N(1)-Cu(1)-O(10)	80.1(9)	N(1)-Cu(1)-O(22)	106.8(8)

N(1)-Cu(1)-O(42)	84.5(8)	N(1)-Cu(1)-N(5)	170.5(11)
N(5)-Cu(1)-O(10)	108.1(10)	N(5)-Cu(1)-O(22)	75.4(9)
N(5)-Cu(1)-O(42)	98.9(9)	W(1)#1-O(10)-Cu(1)	115.1(10)
W(2)-O(10)-Cu(1)	100.7(9)	W(2)-O(22)-Cu(1)	103.5(9)
W(8)-O(42)-Cu(1)	137.6(12)	N(2)-N(1)-Cu(1)	124.0(16)
C(3)-N(1)-Cu(1)	129.9(19)	N(6)-N(5)-Cu(1)	123.1(18)
C(14)-N(5)-Cu(1)	126(2)		

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

Compound **3**

Cu(1)-O(4W)	1.911(8)	Cu(1)-N(12)	1.960(10)
Cu(1)-N(2)#1	1.995(11)	Cu(1)-O(3W)	2.017(10)
Cu(1)-O(37)	2.451(10)	N(9)-Cu(2)#1	2.000(11)
Cu(2)-O(4W)	1.951(8)	Cu(2)-N(3)	1.965(10)
Cu(2)-N(9)#2	2.000(11)	Cu(2)-N(7)	2.029(10)
N(2)-Cu(1)#2	1.995(11)	N(11)-N(12)-Cu(1)	128.9(9)
O(4W)-Cu(1)-N(12)	156.1(4)	O(4W)-Cu(1)-N(2)#1	89.4(4)
N(12)-Cu(1)-N(2)#1	94.5(5)	N(12)-Cu(1)-O(3W)	87.4(4)
O(4W)-Cu(1)-O(3W)	88.7(4)	N(2)#1-Cu(1)-O(3W)	178.0(4)
O(4W)-Cu(2)-N(3)	177.7(4)	O(4W)-Cu(2)-N(9)#2	89.1(4)
N(3)-Cu(2)-N(9)#2	89.8(4)	O(4W)-Cu(2)-N(7)	90.0(4)
N(3)-Cu(2)-N(7)	91.4(4)	N(9)#2-Cu(2)-N(7)	170.9(4)
C(4)-N(2)-Cu(1)#2	137.0(10)	N(1)-N(2)-Cu(1)#2	117.5(8)
C(8)-N(3)-Cu(2)	132.6(8)	N(4)-N(3)-Cu(2)	121.9(7)
Cu(1)-O(4W)-Cu(2)	124.8(4)	C(12)-N(7)-Cu(2)	134.9(8)
N(8)-N(7)-Cu(2)	118.8(8)	N(10)-N(9)-Cu(2)#1	123.5(8)
C(25)-N(9)-Cu(2)#1	131.9(8)	C(31)-N(12)-Cu(1)	121.9(10)

Symmetry codes: #1 -x-1/2,y+1/2,-z+1/2 #2 -x-1/2,y-1/2,-z+1/2

Compound **4**

Cu(1)-N(4)	2.022(11)	Cu(1)-N(6)	2.019(12)

Cu(1)-N(10)	2.036(11)	Cu(1)-N(12)	2.073(12)
N(1)-Cu(2)#1	2.005(12)	Cu(2)-N(15)	1.978(12)
Cu(2)-N(1)#2	2.005(12)	Cu(2)-N(14)	2.021(12)
Cu(2)-N(7)#3	2.029(12)	Cu(2)-O(30)	2.332(10)
N(7)-Cu(2)#3	2.029(12)	N(6)-Cu(1)-N(4)	176.6(5)
N(6)-Cu(1)-N(10)	88.0(5)	N(4)-Cu(1)-N(10)	89.1(5)
N(4)-Cu(1)-N(12)	89.0(5)	N(6)-Cu(1)-N(12)	93.7(5)
N(10)-Cu(1)-N(12)	178.1(5)	C(3)-N(1)-Cu(2)#1	134.5(10)
N(2)-N(1)-Cu(2)#1	117.7(9)	N(15)-Cu(2)-N(1)#2	152.9(5)
N(15)-Cu(2)-N(14)	87.3(5)	N(1)#2-Cu(2)-N(14)	88.8(5)
N(15)-Cu(2)-N(7)#3	93.5(5)	C(9)-N(4)-Cu(1)	130.7(10)
N(14)-Cu(2)-N(7)#3	169.1(5)	N(1)#2-Cu(2)-N(7)#3	95.3(5)
N(1)#2-Cu(2)-O(30)	92.8(4)	N(15)-Cu(2)-O(30)	113.2(5)
N(7)#3-Cu(2)-O(30)	86.7(4)	N(14)-Cu(2)-O(30)	83.0(4)
N(3)-N(4)-Cu(1)	113.7(9)	C(19)-N(6)-Cu(1)	134.6(10)
N(5)-N(6)-Cu(1)	118.2(9)	C(23)-N(7)-Cu(2)#3	134.8(10)
N(8)-N(7)-Cu(2)#3	120.3(9)	C(29)-N(10)-Cu(1)	130.9(10)
N(9)-N(10)-Cu(1)	121.7(9)	C(42)-N(12)-Cu(1)	137.4(12)
N(11)-N(12)-Cu(1)	109.0(9)	C(34)-N(14)-Cu(2)	134.7(10)
N(13)-N(14)-Cu(2)	116.4(9)	C(15)-N(15)-Cu(2)	128.0(11)
N(16)-N(15)-Cu(2)	124.0(9)	W(9)-O(30)-Cu(2)	137.2(5)
Symmetry codes: #1 -x+3/2,y-1/2,-z+1/2		#2 -x+3/2,y+1/2,-z+1/2	#3 -x+3/2,-y+1/2,-z+1