

Supplementary Material (ESI) for CrystEngComm

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Four Octamolybdate Complexes Constructed from a Quinoline-imidazole-monoamide Ligand: Structures, Electrochemical, Photocatalytic and Magnetic Properties

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Table. S1. Selected bond distances (\AA) and angles ($^\circ$) for complexes **1-4**.

Complex 1			
Co(1)-O(1)	2.1569(18)	Co(1)-O(2)	2.0979(19)
Co(1)-N(3)	2.071(2)		
O(1)#1-Co(1)-O(1)	180.00(9)	O(2)-Co(1)-O(1)#1	89.79(8)
O(2)#1-Co(1)-O(2)	180.0	O(2)-Co(1)-O(1)	90.21(8)
N(3)-Co(1)-O(1)#1	100.78(8)	N(3)-Co(1)-O(1)	79.22(8)
N(3)-Co(1)-O(2)#1	91.91(8)	N(3)-Co(1)-O(2)	88.09(8)
N(3)#1-Co(1)-N(3)	180.0		
Symmetry code for 1: #1 -x+1,-y,-z+1			
Complex 2			
Ni(1)-O(1)	2.087(3)	Ni(1)-N(3)	2.027(3)
Ni(1)-O(13)	2.110(3)		
O(1)#1-Ni(1)-O(1)	180.0	O(1)#1-Ni(1)-O(13)	89.41(12)
N(3)-Ni(1)-O(1)	88.69(13)	O(13)-Ni(1)-O(1)	90.59(12)
N(3)-Ni(1)-O(1)#1	91.31(13)	N(3)#1-Ni(1)-N(3)	180.0
O(13)-Ni(1)-N(3)	80.87(12)	O(13)-Ni(1)-N(3)#1	99.13(12)
O(13)#1-Ni(1)-O(13)	180.00(14)		
Symmetry code for 2: #1 -x+1,-y,-z+1			
Complex 3			
Zn(1)-O(2)	2.173(4)	Zn(1)-N(3)	2.032(4)
Zn(1)-O(1)	2.169(4)		
O(2)-Zn(1)-O(2)#1	180.0	O(11)#1-Zn(1)-O(2)	89.93(15)
O(11)-Zn(1)-O(2)	90.07(15)	O(11)-Zn(1)-O(11)#1	180.0
N(3)-Zn(1)-O(2)#1	88.24(15)	N(3)-Zn(1)-O(2)	91.76(15)
N(3)#1-Zn(1)-O(11)	99.89(15)	N(3)-Zn(1)-O(11)	80.11(15)
N(3)-Zn(1)-N(3)#1	180.0		
Symmetry code for 3: #1 -x+1,-y+1,-z			
Complex 4			
Cu(1)-O(1W)#1	1.971(4)	Cu(1)-O(1W)	1.955(4)
Cu(1)-O(1)	2.001(4)	Cu(1)-O(2)	2.373(4)
Cu1-Cu1#1	2.863	Cu(1)-N(1)	1.953(5)
O(1W)-Cu(1)-O(1W)#1	86.34(17)	O(1W)#1-Cu(1)-O(1)	166.83(17)
O(1W)-Cu(1)-O(1)	92.32(16)	O(1W)-Cu(1)-O(2)	86.13(16)

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O(1W)#1-Cu(1)-O(2)	86.58(16)	O(1)-Cu(1)-O(2)	106.42(16)
N(1)-Cu(1)-O(1W)#1	100.56(18)	N(1)-Cu(1)-O(1W)	169.4(2)
N(1)-Cu(1)-O(1)	82.78(18)	N(1)-Cu(1)-O(2)	86.24(19)
Cu(1)-O(1W)-Cu(1)#1	93.66(16)		
Symmetry code for 4 : #1 -x+1,-y+2,-z+1			

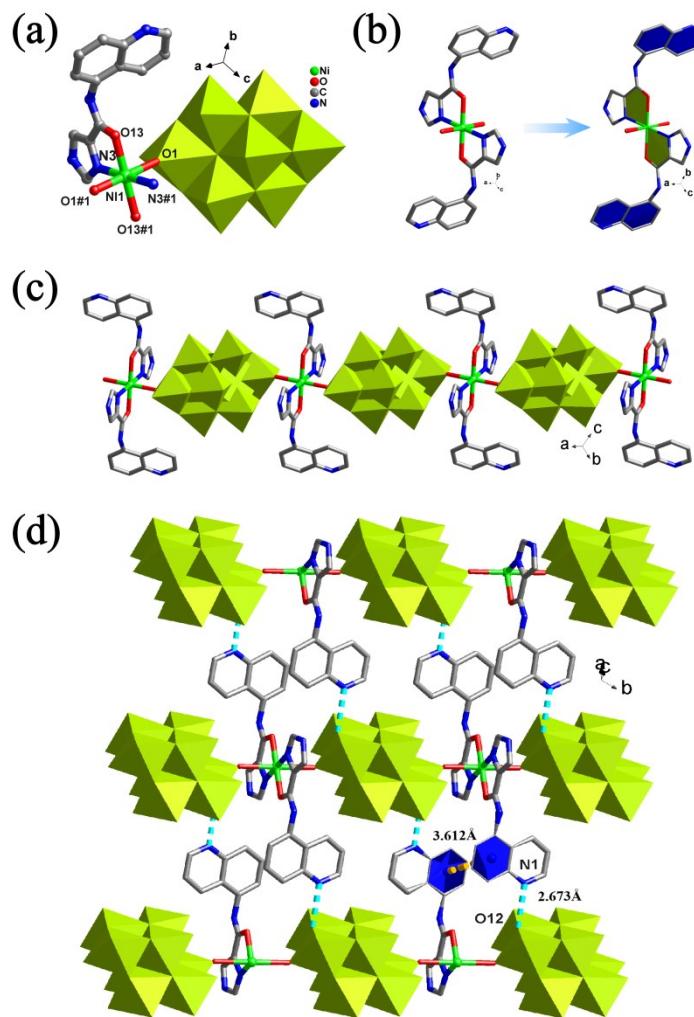


Fig. S1 Structural motives in **2**: (a) the coordination mode of metal center and polyoxoanion. Symmetry code: #1: -x+1,-y,-z+1; (b) the mononuclear unit $[\text{Ni}(\text{HL})_2]^{4+}$; (c) the 1D long chain fragment; (d) the 2D supramolecular layer.

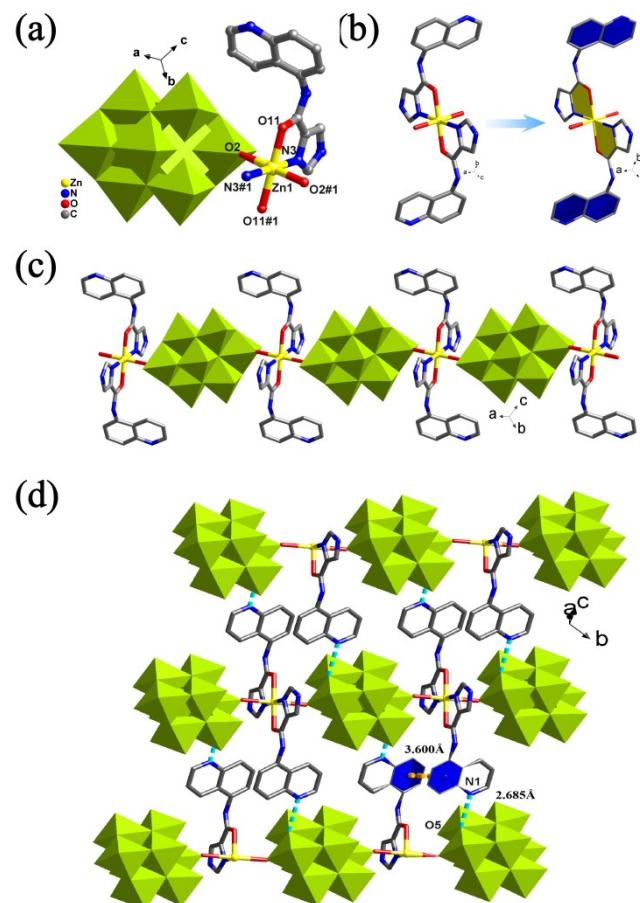


Fig. S2 Structural motives in **3**: (a) the coordination mode of metal center and polyoxoanion. Symmetry code: #1: $-x+1, -y+1, -z$; (b) the mononuclear unit $[Zn(HL)_2]^{4+}$; (c) the 1D chain fragment; (d) the 2D supramolecular layer.

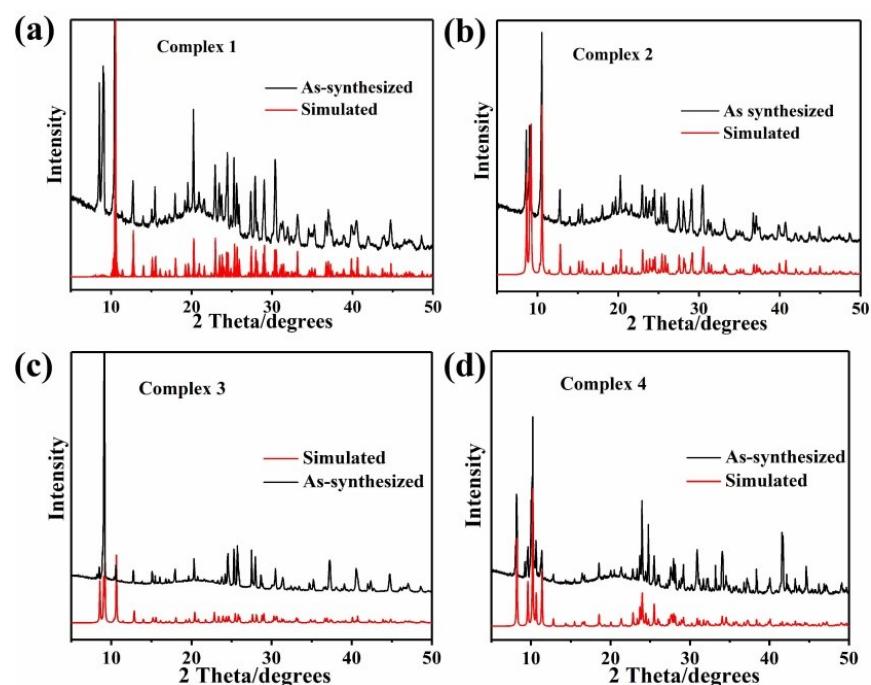


Fig. S3 PXRD patterns of complexes 1-4.

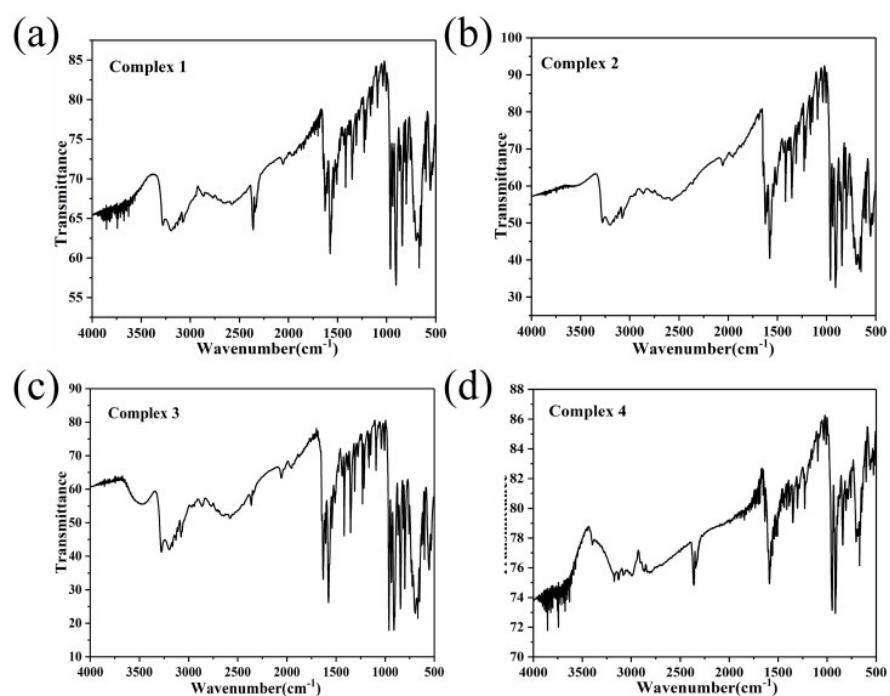


Fig. S4 The IR spectra of complexes 1-4.

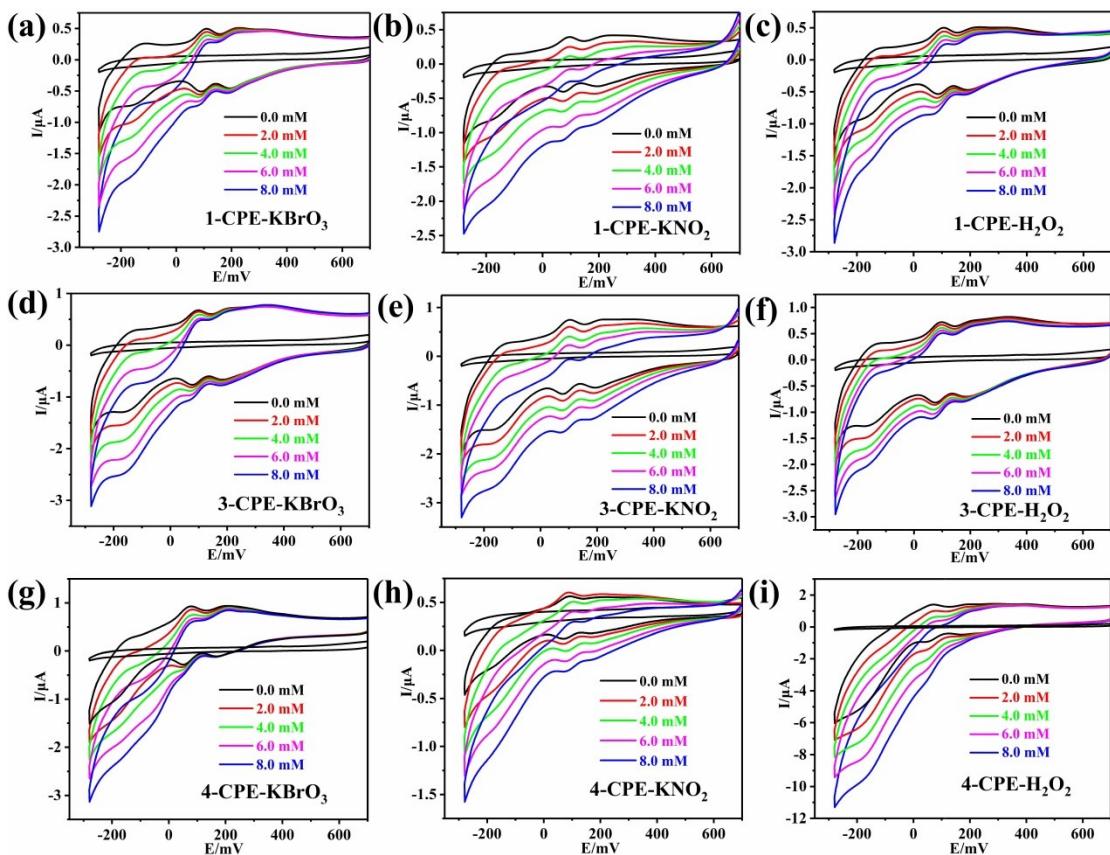


Fig. S5 (a-c) Cyclic voltammograms of the 1-CPE in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ aqueous solution (Scan rate: 60 mV·s⁻¹) containing 0, 2, 4, 6 and 8 mM bromate, nitrite, H₂O₂; (d-f) Cyclic voltammograms of the 3-CPE in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ aqueous solution (Scan rate: 60 mV·s⁻¹) containing 0, 2, 4, 6 and 8 mM bromate, nitrite, H₂O₂; (g-i) Cyclic voltammograms of the 4-CPE in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ aqueous solution (Scan rate: 60 mV·s⁻¹) containing 0, 2, 4, 6 and 8 mM bromate, nitrite, H₂O₂.

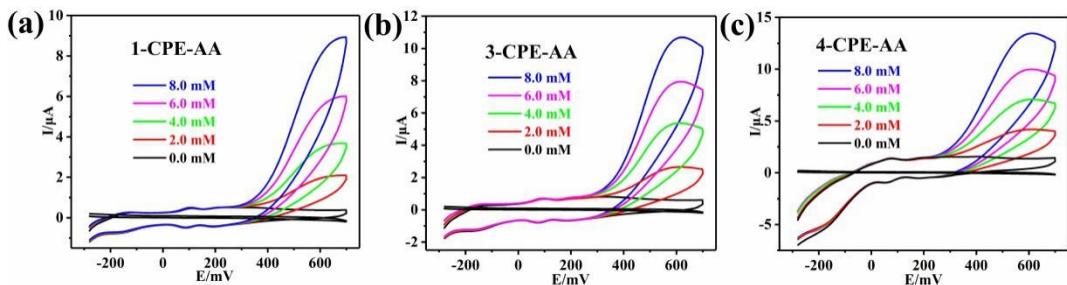


Fig. S6 Cyclic voltammograms of the 1-CPE (a), 3-CPE (b) and 4-CPE (c) in 0.1 M H₂SO₄ + 0.5 M Na₂SO₄ aqueous solution (Scan rate: 60 mV·s⁻¹) containing 0, 2, 4, 6 and 8 mM AA.

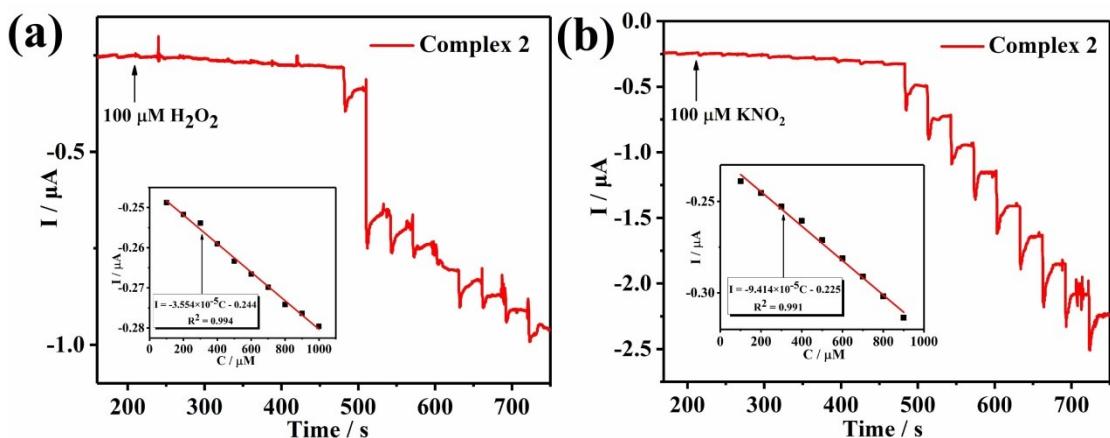


Fig. S7 Current response of **2**-CPE with successive addition of H_2O_2 (a) potassium nitrite (b) into stirring $0.1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at -0.2 V per 30 s interval (Inset: the plot of response current vs concentrations of substrate).

Supplementary Material (ESI) for CrystEngComm

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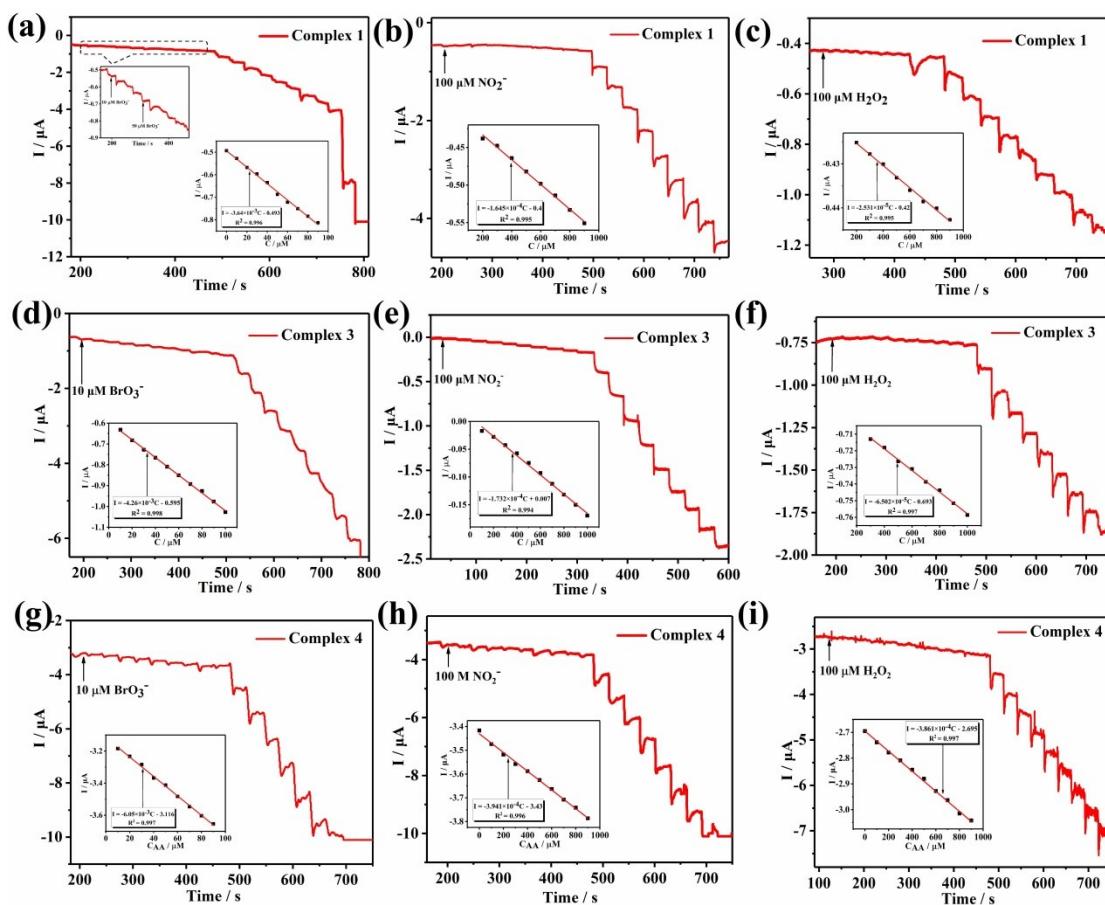


Fig. S8 (a-c) Current response of 1-CPE with successive addition of potassium bromate, potassium nitrite, and H_2O_2 into stirring $0.1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at -0.2 V per 30 s interval (Inset: the plot of response current vs concentrations of substrate); (d-f) Current response of 3-CPE with successive addition of potassium bromate, potassium nitrite, and H_2O_2 into stirring $0.1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at -0.2 V per 30 s interval (Inset: the plot of response current vs concentrations of substrate); (g-i) Current response of 4-CPE with successive addition of potassium bromate, potassium nitrite, and H_2O_2 into stirring $0.1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at -0.2 V per 30 s interval (Inset: the plot of response current vs concentrations of substrate).

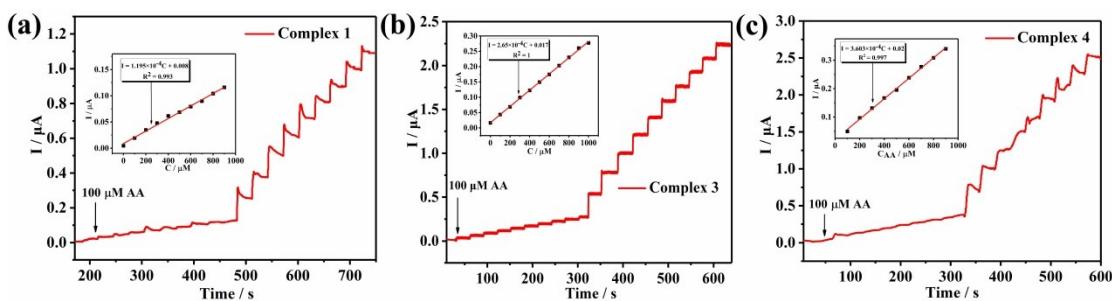


Fig. S9 Current response of 1-CPE (a), 3-CPE (b) and 4-CPE (c) with successive addition of AA into stirring $0.1 \text{ M H}_2\text{SO}_4 + 0.5 \text{ M Na}_2\text{SO}_4$ aqueous solution at 0.2 V per 30 s interval (Inset: the plot of response current vs concentrations of substrate).

Table. S2 Parameters for potassium bromate, potassium nitrite, H₂O₂ and AA determination using 1-4 CPEs

Material		1-CPE	2-CPE	3-CPE	4-CPE
Detection limit ($\mu\text{mol L}^{-1}$)	BrO ₃ ⁻	15	1.67	45	33
	NO ₂ ⁻	348	37	1114	510
	H ₂ O ₂	2263	98	6134	520
	AA	330	6	230	87
Linear Range ($\mu\text{mol L}^{-1}$)	BrO ₃ ⁻	10-812	10-795	10-848	10-665
	NO ₂ ⁻	100-8000	100-8000	100-8000	100-8000
	H ₂ O ₂	100-8000	100-8000	100-8000	100-8000
	AA	100-8000	100-8000	100-8000	100-8000
Sensitivity ($\mu\text{A cm}^{-2} \text{mM}^{-1}$)	BrO ₃ ⁻	3.64×10^{-3}	2.09×10^{-3}	4.26×10^{-3}	6.05×10^{-3}
	NO ₂ ⁻	1.645×10^{-4}	9.414×10^{-5}	1.732×10^{-4}	3.941×10^{-4}
	H ₂ O ₂	2.531×10^{-5}	3.554×10^{-5}	6.502×10^{-5}	3.861×10^{-4}
	AA	1.195×10^{-4}	2.382×10^{-5}	2.65×10^{-4}	3.603×10^{-4}

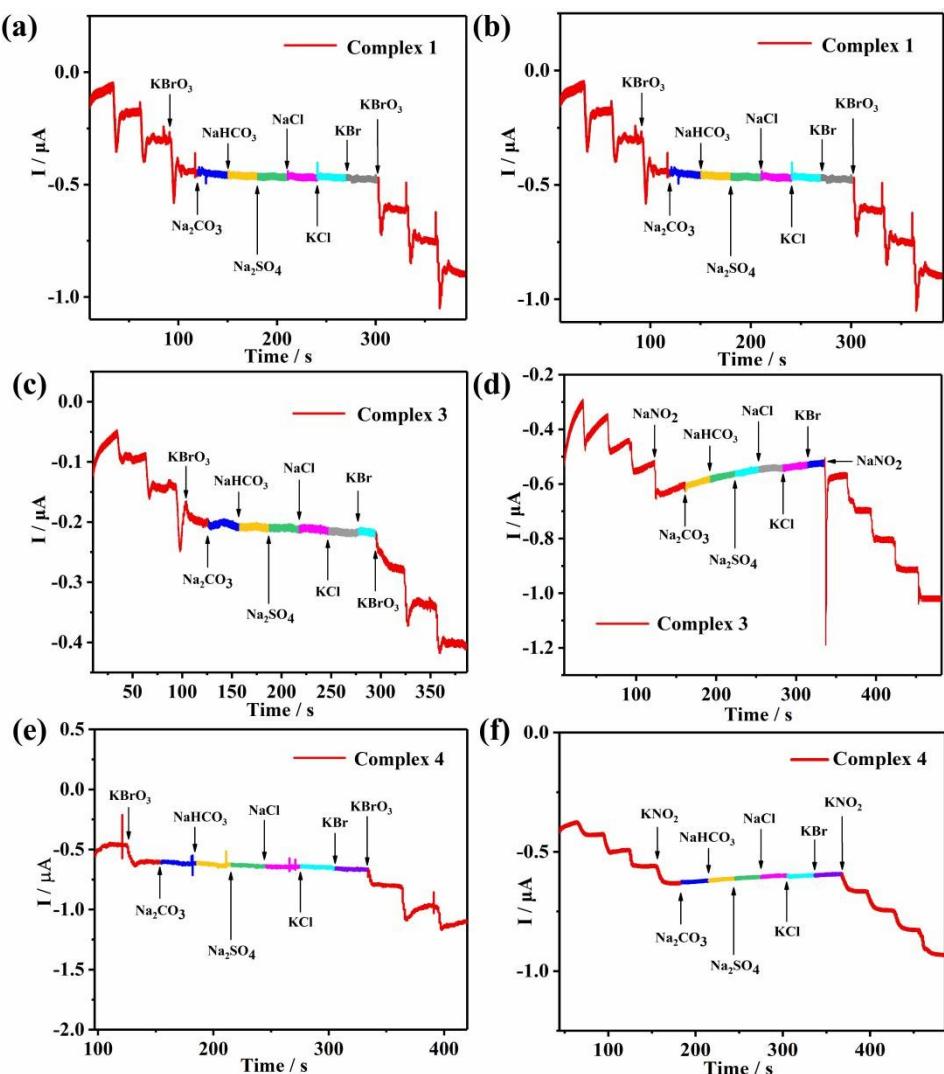


Fig. S10 Current response for potassium bromate (a), potassium nitrite (b) and potential interference substances on 1-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 ; Current response for potassium bromate (c), potassium nitrite (d) and potential interference substances on 3-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 ; Current response for potassium bromate (e), potassium nitrite (f) and potential interference substances on 4-CPE in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 .

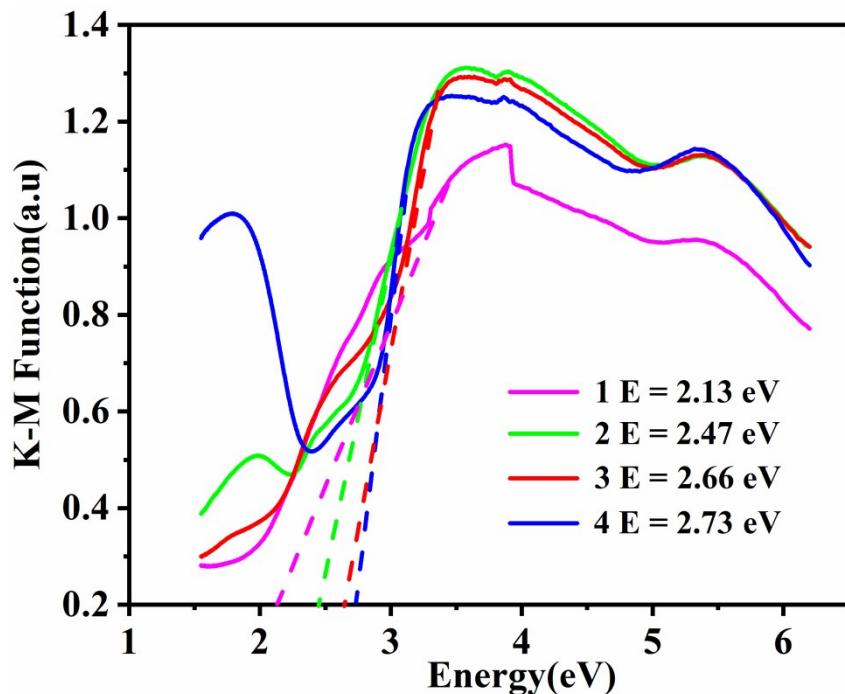


Fig. S11 Diffuse reflection spectra of Kubelka–Munk (K–M) function versus energy (eV) of complexes **1–4**.

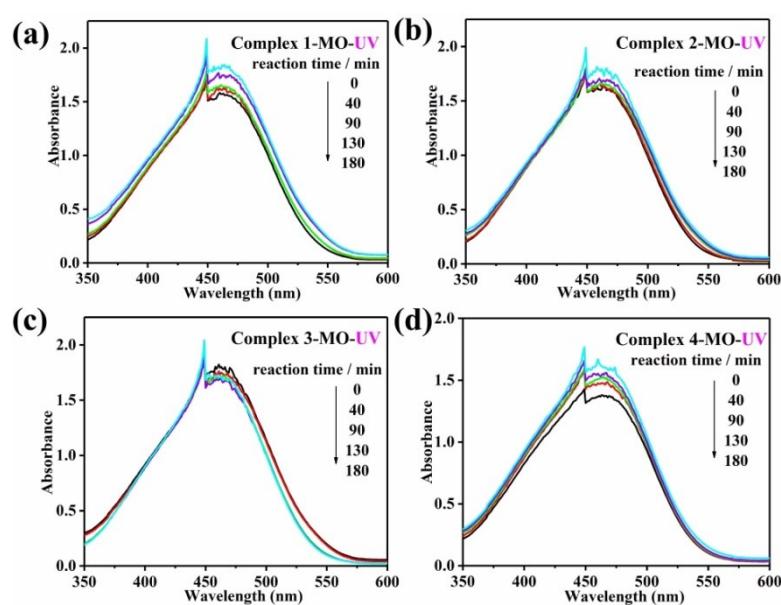


Fig. S12 Photocatalytic reaction of MO solutions within 180 min in the presence of complexes **1–4** under UV irradiation.

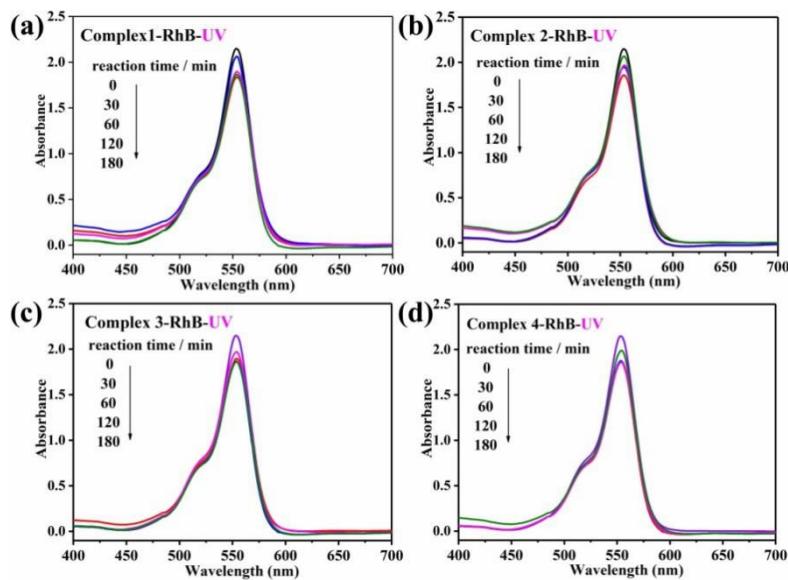


Fig. S13 Photocatalytic reaction of RhB solutions within 180 min in the presence of complexes **1**-**4** under UV irradiation.

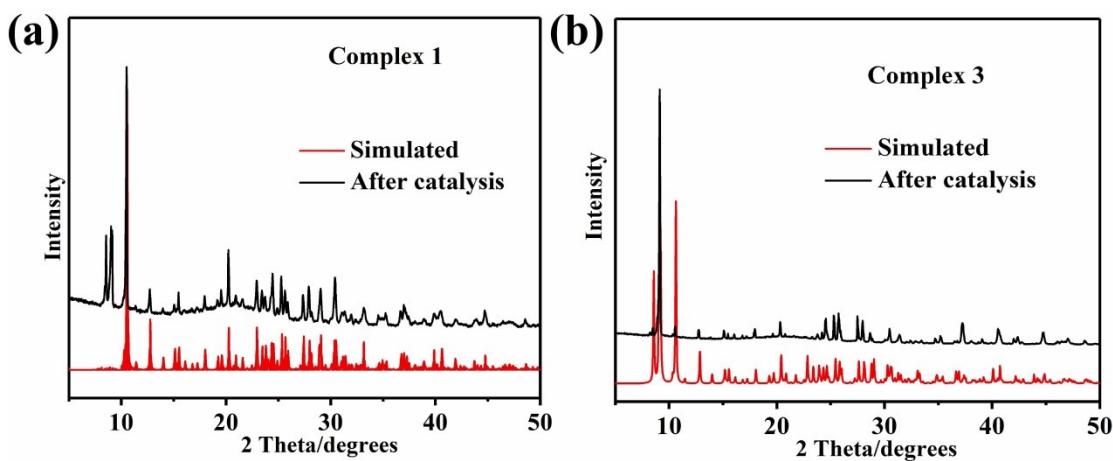


Fig. S14 PXRD patterns of complexes **1** and **3** on MB after catalysis.