

Supplementary Material (ESI) for *CrystEngComm*
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A series of polyoxometalate-based hybrid complexes constructed by a tripodal ligand containing mixed N/O donors

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Table S1. Selected bond distances (Å) and angles (°) for complexes 1–6.

Complex 1			
Cd(1)–N(4)	2.139(5)	Cd(1)–N(5)	2.133(5)
N(5)–Cd(1)–N(4)	178.9(2)		
Symmetry codes: ¹ 1–X,1–Y,1–Z; ² –X,1–Y,1–Z; ³ 1–X,–Y,1–Z			
Complex 2			
Co(1)–N(1) ³	2.124(4)	Co(1)–O(3)	2.047(4)
Co(1)–O(6) ²	2.100(4)	Co(1)–O(4)	2.075(4)
Co(1)–O(5)	2.056(4)	Co(1)–O(1)	2.143(4)
O(3)–Co(1)–O(4)	93.08(17)	O(5)–Co(1)–O(4)	89.61(16)
O(3)–Co(1)–O(1)	87.13(16)	O(5)–Co(1)–O(1)	84.68(15)
O(3)–Co(1)–N(1) ³	102.59(17)	O(5)–Co(1)–N(1) ³	85.58(16)
O(4)–Co(1)–O(6) ²	178.23(17)	O(3)–Co(1)–O(6) ²	87.64(16)
O(4)–Co(1)–O(1)	92.17(18)	O(3)–Co(1)–O(5)	171.47(16)
O(4)–Co(1)–N(1) ³	88.13(18)	C(3)–N(1)–Co(1) ⁴	114.2(4)
N(1) ³ –Co(1)–O(1)	170.25(17)	O(5)–Co(1)–O(6) ²	89.91(15)
Mo(4)–O(5)–Co(1)	145.9(2)	C(1)–N(1)–Co(1) ⁴	132.6(4)
O(6) ² –Co(1)–N(1) ³	90.14(17)	O(6) ² –Co(1)–O(1)	89.48(16)
Symmetry codes: ¹ 1–X,1–Y,2–Z; ² –X,1–Y,1–Z; ³ +X,1+Y,+Z			
Complex 3			
Cu(05)–O(17)	2.072(5)	Cu(05)–O(2) ²	2.178(4)
Cu(05)–N(2)	2.097(6)	Cu(05)–O(3)	2.043(4)
Cu(05)–O(4)	2.110(4)	Cu(05)–O(5) ³	2.140(4)
Mo(1)–O(5)–Cu(05) ³	171.7(3)	O(3)–Cu(05)–O(4)	168.70(18)
O(4)–Cu(05)–O(2) ²	82.26(17)	O(3)–Cu(05)–O(5) ³	87.42(18)
O(5) ³ –Cu(05)–O(2) ²	87.22(18)	O(3)–Cu(05)–O(2) ²	86.99(18)
Mo(1)–O(4)–Cu(05)	146.4(3)	O(3)–Cu(05)–O(17)	95.04(19)
N(2)–Cu(05)–O(2) ²	167.95(19)	O(3)–Cu(05)–N(2)	104.8(2)
C(5)–N(2)–Cu(05)	115.2(5)	O(17)–Cu(05)–O(4)	88.77(19)
C(1)–O(2)–Cu(05) ⁴	134.9(4)	O(17)–Cu(05)–O(5) ³	177.25(19)
C(6)–N(2)–Cu(05)	133.5(5)	O(17)–Cu(05)–O(2) ²	91.7(2)

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O(4)–Cu(05)–O(5) ³	88.59(18)	O(17)–Cu(05)–N(2)	89.9(2)
N(2)–Cu(05)–O(5) ³	90.6(2)	N(2)–Cu(05)–O(4)	85.84(19)

Symmetry codes: ¹1-X,-Y,2-Z; ²+X,-1+Y,+Z; ³2-X,-Y,1-Z

Complex 4

Fe(1)–O(3)	2.060(7)	N(4)–Fe(1) ⁴	2.127(9)
Fe(1)–O(2)	2.148(8)	O(4)–Fe(1) ²	2.097(7)
Fe(1)–O(5)	2.064(7)	Fe(1)–O(4) ²	2.097(7)
Fe(1)–O(6)	2.084(8)	Mo(1)–O(4)–Fe(1) ²	174.9(4)
O(3)–Fe(1)–O(2)	84.6(3)	O(3)–Fe(1)–O(4) ²	90.6(3)
O(3)–Fe(1)–O(5)	171.2(3)	O(3)–Fe(1)–N(4) ³	85.5(3)
O(3)–Fe(1)–O(6)	89.1(3)	O(5)–Fe(1)–O(2)	86.9(3)
O(5)–Fe(1)–O(6)	93.1(3)	O(4) ² –Fe(1)–N(4) ³	90.4(3)
O(5)–Fe(1)–O(4) ²	87.3(3)	N(4) ³ –Fe(1)–O(2)	170.1(3)
C(13)–N(4)–Fe(1) ⁴	115.4(7)	O(5)–Fe(1)–N(4) ³	103.0(3)
C(13)–N(4)–C(12)	103.9(9)	O(6)–Fe(1)–O(2)	91.4(3)
C(12)–N(4)–Fe(1) ⁴	134.0(8)	O(6)–Fe(1)–O(4) ²	178.7(3)
Mo(1)–O(3)–Fe(1)	145.4(4)	O(6)–Fe(1)–N(4) ³	88.3(4)
C(1)–O(2)–Fe(1)	132.8(7)	O(4) ² –Fe(1)–O(2)	89.9(3)

Symmetry codes: ¹1-X,1-Y,1-Z; ²-X,1-Y,1-Z; ³1-X,-Y,1-Z

Complex 5

Ni(1)–O(13)	2.0256(18)	Ni(1)–O(12) ³	2.0716(19)
Ni(1)–O(16) ²	2.1015(19)	Ni(1)–O(14)	2.047(2)
Ni(1)–N(4)	2.085(2)	Ni(1)–O(15)	2.0311(19)
O(13)–Ni(1)–O(15)	172.72(8)	O(14)–Ni(1)–N(4)	88.00(10)
O(13)–Ni(1)–N(4)	85.89(8)	O(15)–Ni(1)–O(16) ²	86.71(8)
O(12) ³ –Ni(1)–O(16) ²	89.67(8)	O(15)–Ni(1)–O(12) ³	87.25(8)
O(12) ³ –Ni(1)–N(4)	90.53(9)	O(15)–Ni(1)–O(14)	93.17(9)
O(14)–Ni(1)–O(16) ²	91.77(9)	O(15)–Ni(1)–N(4)	101.01(9)
O(14)–Ni(1)–O(12) ³	178.52(9)	N(4)–Ni(1)–O(16) ²	172.27(8)
C(7)–O(16)–Ni(1) ⁴	131.73(17)	Mo(4)–O(13)–Ni(1)	144.90(11)
Mo(4)–O(12)–Ni(1) ³	173.51(12)	O(13)–Ni(1)–O(16) ²	86.38(7)
C(13)–N(4)–Ni(1)	133.1(2)	O(13)–Ni(1)–O(12) ³	90.40(8)
C(11)–N(4)–Ni(1)	114.61(19)	O(13)–Ni(1)–O(14)	89.36(8)

Symmetry codes: ¹1-X,2-Y,-Z; ²+X,1+Y,+Z; ³-X,2-Y,1-Z

Complex 6

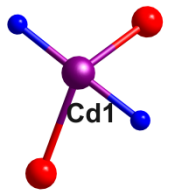
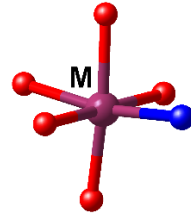
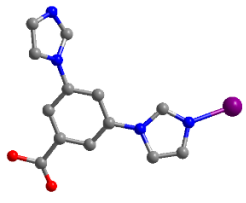
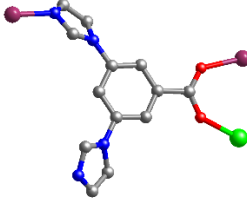
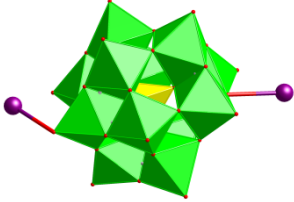
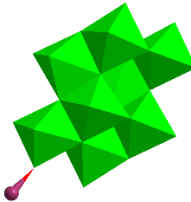
Zn(1)–O(13)	2.093(2)	Zn(1)–O(16) ²	2.166(2)
Zn(1)–O(12) ³	2.156(2)	Zn(1)–O(15)	2.043(2)
Zn(1)–N(1)	2.098(3)	Zn(1)–O(14)	2.081(3)
O(12) ³ –Zn(1)–O(16) ²	87.17(10)	O(14)–Zn(1)–O(16) ²	92.44(11)

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O(15)–Zn(1)–O(13)	169.21(10)	O(14)–Zn(1)–N(1)	89.55(12)
O(15)–Zn(1)–O(12) ³	87.35(10)	N(1)–Zn(1)–O(12) ³	90.44(11)
O(15)–Zn(1)–O(16) ²	86.77(10)	N(1)–Zn(1)–O(16) ²	168.54(10)
O(15)–Zn(1)–O(14)	94.69(11)	Mo(01)–O(13)–Zn(1)	146.38(14)
O(15)–Zn(1)–N(1)	104.32(11)	Mo(01)–O(12)–Zn(1) ³	172.34(15)
O(14)–Zn(1)–O(13)	89.20(10)	C(8)–O(16)–Zn(1) ⁴	133.9(2)
O(14)–Zn(1)–O(12) ³	177.90(10)	O(13)–Zn(1)–O(12) ³	88.71(9)
O(13)–Zn(1)–O(16) ²	83.00(9)	C(1)–N(1)–Zn(1)	115.0(2)
O(13)–Zn(1)–N(1)	85.74(10)	C(2)–N(1)–Zn(1)	132.6(2)

Symmetry codes: ¹1-X,2-Y,-Z; ²+X,1+Y,+Z; ³-X,2-Y,1-Z

Table S2. The coordination modes of TMs, ligands and polyanions in complexes 1–6.

Complex	1	2-6
TMs		
Ligand		
Polyanions		

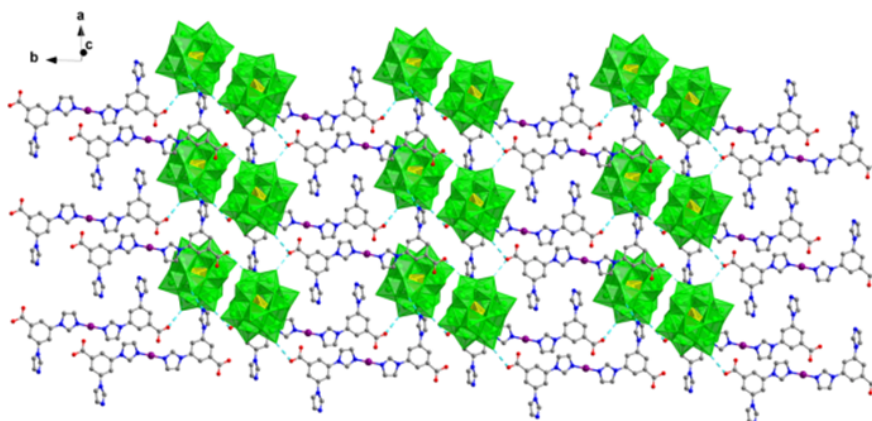


Fig. S1. View of the 2D supramolecular structure of complex 1.

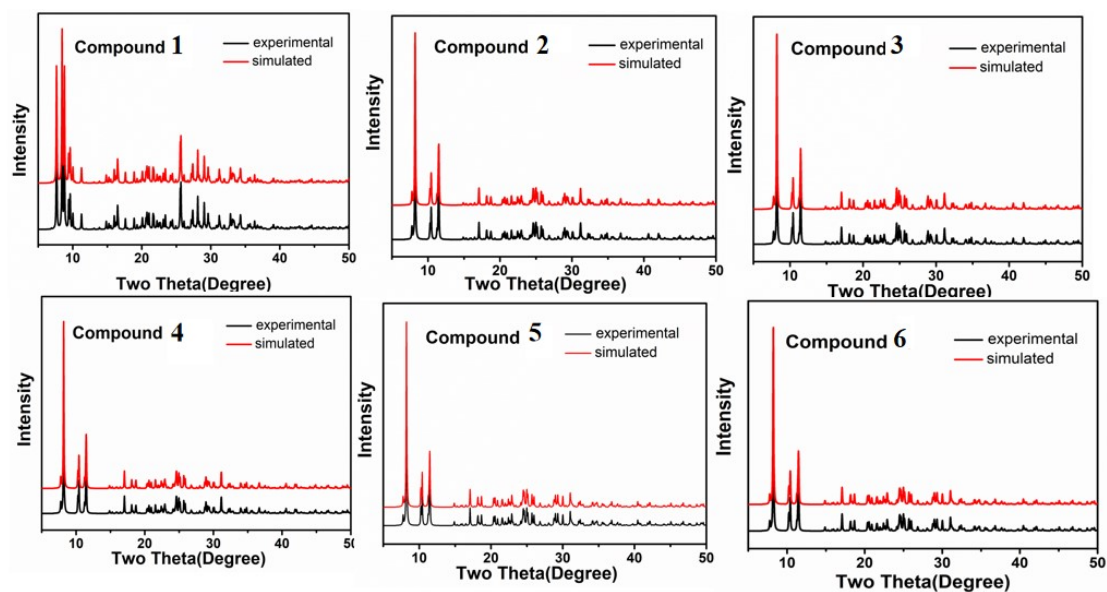


Fig. S2. The PXRD patterns of complexes 1–6.

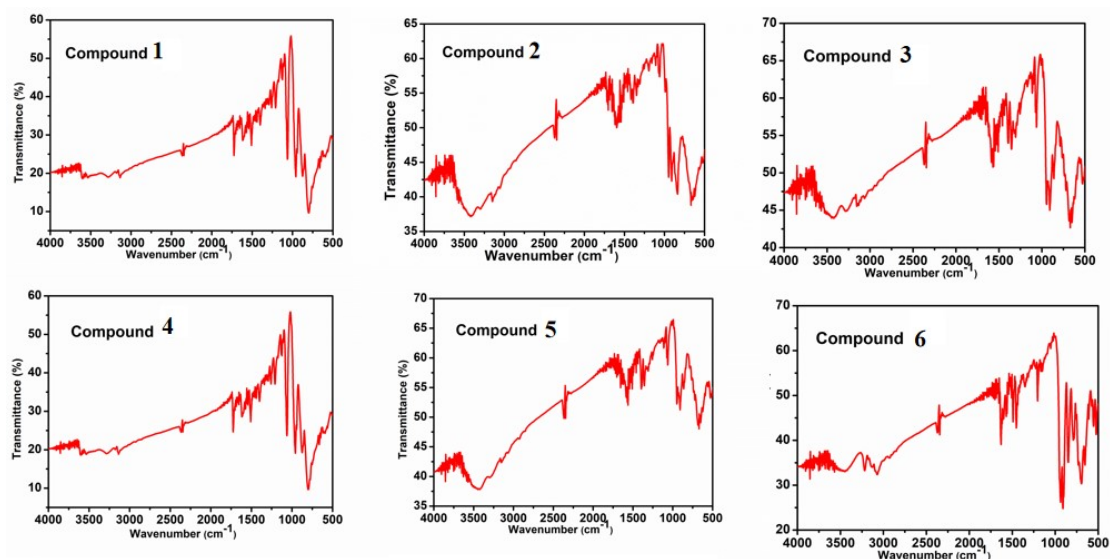


Fig. S3. The IR spectra of complexes 1–6.

Table S3. The IR Spectra data of complexes 1–6.

	$\nu(\text{Mo}-\text{O}_a)$	$\nu(\text{Mo}-\text{O}_d)$	$\nu(\text{Mo}-\text{O}_{b/c}-\text{Mo})$	$\nu(\text{Mo}-\text{O}_b)$	$\nu(\text{Mo}-\text{O}_t)$	$\nu(\text{P}-\text{O})$	Ligand
1	–	959	876, 799	–	–	1057	1192–1736
2	823	–	–	934	669	–	1192–1736
3	893	–	–	941	663	–	1192–1736
4	802	–	–	949	669	–	1192–1736
5	900	–	–	956	641	–	1192–1736

6	906	–	–	934	691	–	1192–1736
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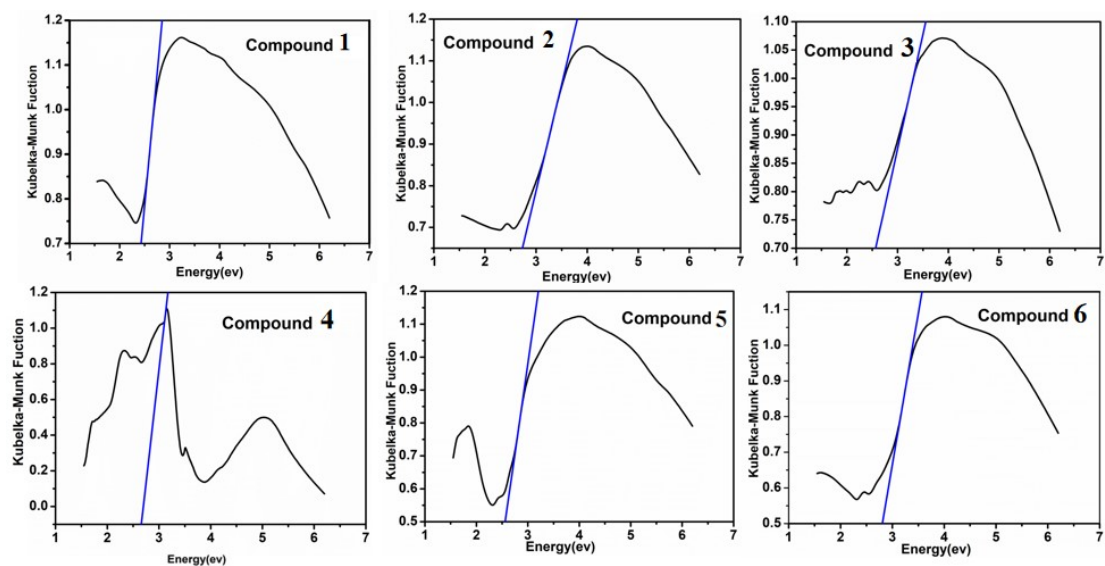


Fig. S4. The Diffuse reflection spectra of complexes 1–6.

Table S4. Experimental data for detecting Cr(VI), Fe(III), and H₂O₂ using 1–, 2– CPEs as amperometric sensors.

CPE	substance	Response time	Concentration range	Sensitivity	Correlation coefficient	Detection limit
1	Cr(VI)	2.1s	4×10^{-3} – 9.2×10^{-2} mM	2.53366 $\mu\text{A mM}^{-1}$	0.99687	5.3×10^{-4} M
2	Cr(VI)	1.8s	4×10^{-3} – 9.2×10^{-2} mM	45.1197 $\mu\text{A mM}^{-1}$	0.99957	2.3×10^{-3} M
1	Fe(III)	2.2s	4×10^{-3} – 9.2×10^{-2} mM	8.10058 $\mu\text{A mM}^{-1}$	0.99633	2.3×10^{-4} M
2	Fe(III)	2.3s	4×10^{-3} – 9.2×10^{-2} mM	74.1925 $\mu\text{A mM}^{-1}$	0.99980	1.2×10^{-3} M
1	H ₂ O ₂	2.7s	4×10^{-3} – 9.2×10^{-2} mM	8.06275 $\mu\text{A mM}^{-1}$	0.99868	1.0×10^{-3} M
2	H ₂ O ₂	2.5s	4×10^{-3} – 9.2×10^{-2} mM	54.20066 $\mu\text{A mM}^{-1}$	0.99986	9.0×10^{-4} M

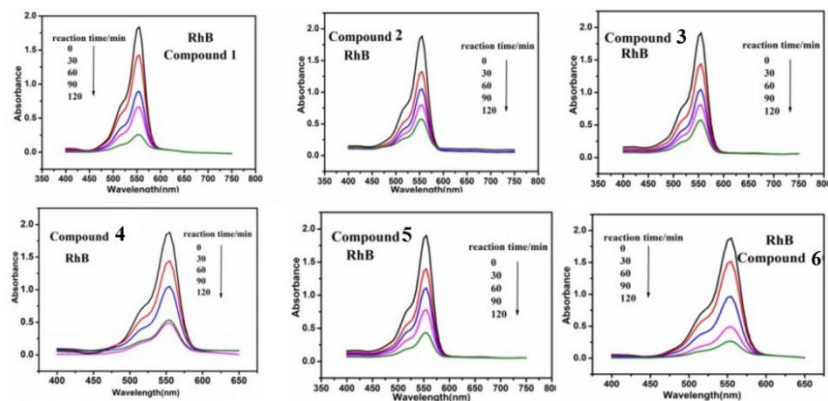


Fig. S5. The UV-vis absorption spectra of aqueous RhB under UV light irradiation in the present of complexes 1–6.

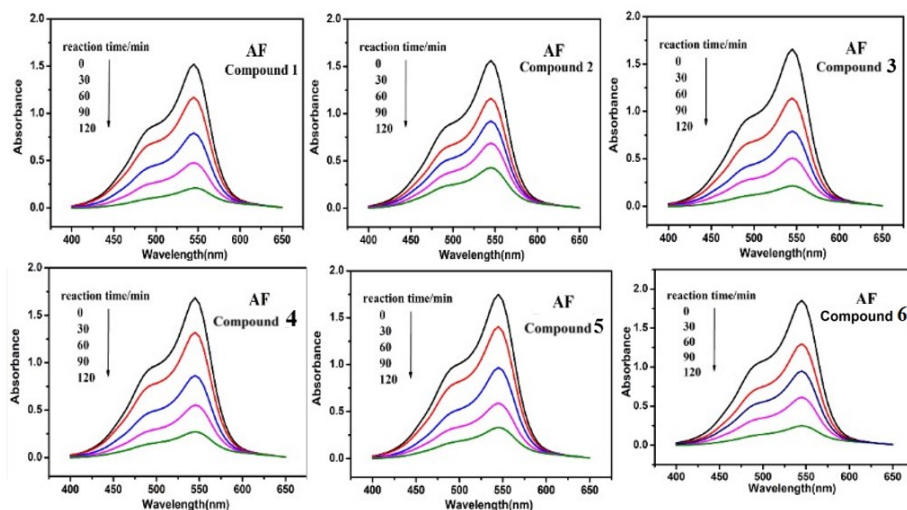


Fig. S6. The UV-vis absorption spectra of aqueous AF under UV light irradiation in the present of complexes 1–6.

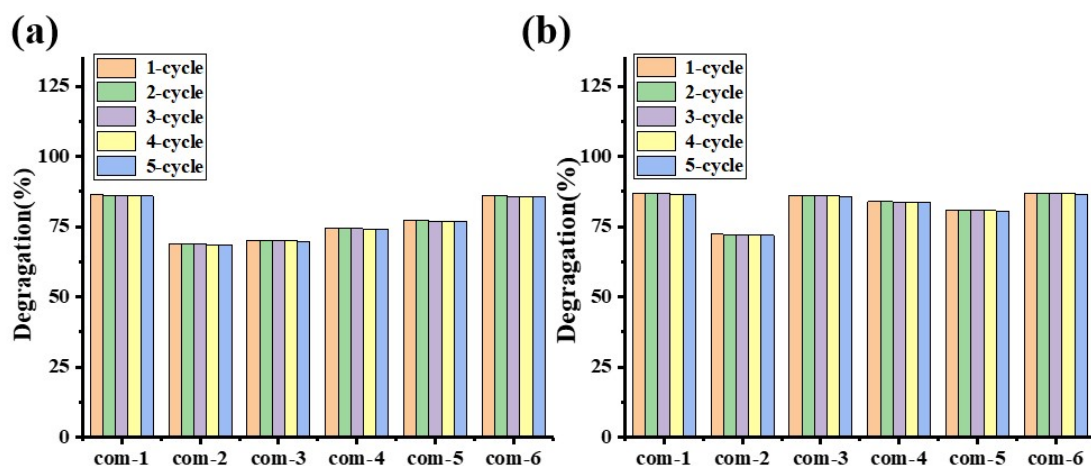


Fig. S7. Degradation rates of complexes 1–6 as catalysts in cyclic test.

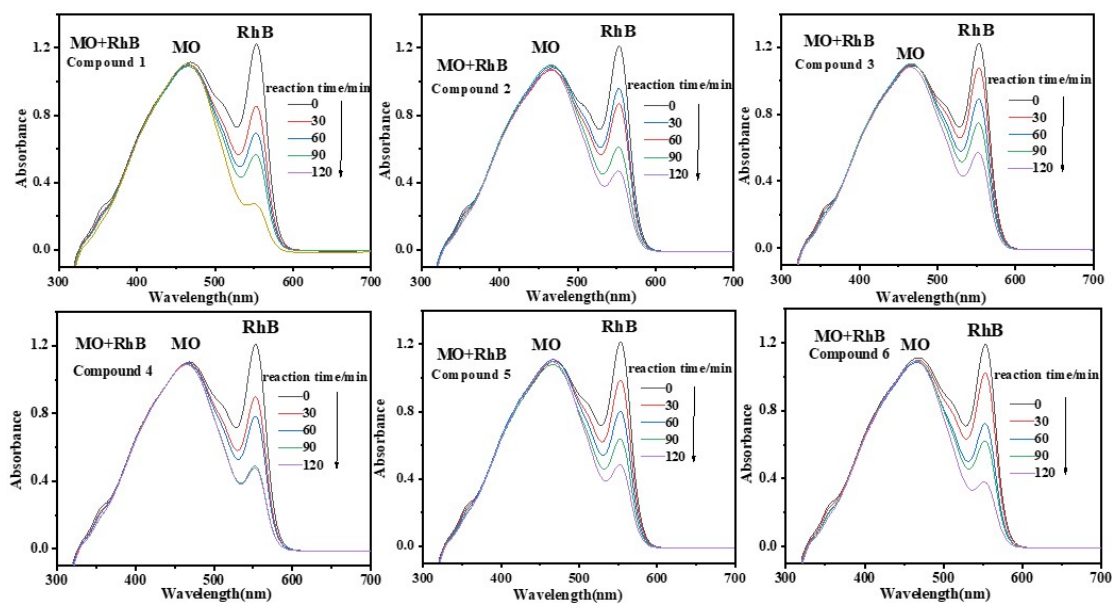


Fig. S8. The UV-vis absorption spectra of aqueous MO+RhB under UV light irradiation in the presence of complexes 1–6.

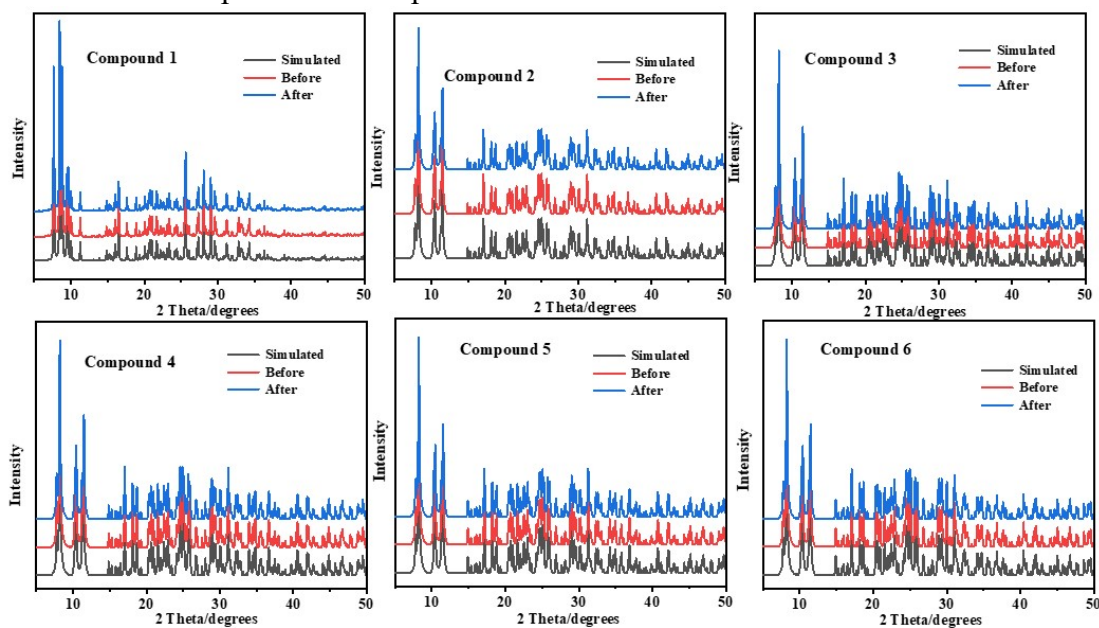


Fig. S9. The PXRD patterns of complexes 1–6 (Before and after photocatalysis of RhB).