

A series of novel Anderson-type Polyoxometalate-based Mn^{II} Complexes constructed from pyridyl-derivatives: Assembly, structures, electrochemical and photocatalytic properties

Xiuli Wang,* Junjun Sun, Hongyan Lin, Zhihan Chang, Guocheng Liu, Xiang Wang

Table. S1. Selected bond distances (Å) and angles (°) for the title complexes.

Complex 1			
Mn(1)-N(1)	2.279(4)	O(1)-Mn(1)	2.189(4)
O(2)-Mn(1)	2.157(4)	O(2W)-Mn(1)	2.154(4)
O(3W)-Mn(1)	2.121(4)	Mn(1)-N(4)	2.259(4)
O(3W)-Mn(1)-O(2W)	94.73(19)	O(3W)-Mn(1)-O(2)	90.38(18)
O(2W)-Mn(1)-O(2)	174.67(17)	O(3W)-Mn(1)-O(1)	85.70(15)
O(2W)-Mn(1)-O(1)	96.41(17)	O(2)-Mn(1)-O(1)	82.44(15)
O(3W)-Mn(1)-N(4)	169.91(16)	O(2W)-Mn(1)-N(4)	87.89(16)
O(2)-Mn(1)-N(4)	87.33(15)	O(1)-Mn(1)-N(4)	103.72(15)
O(3W)-Mn(1)-N(1)	93.58(16)	O(2W)-Mn(1)-N(1)	92.34(18)
O(2)-Mn(1)-N(1)	88.84(16)	O(1)-Mn(1)-N(1)	171.25(17)
N(4)-Mn(1)-N(1)	76.56(16)		
Complex 2			
Mn(1)-O(2)	2.131(12)	Mn(1)-O(1)	2.138(11)
Mn(1)-O(4)#1	2.138(12)	Mn(1)-O(10)	2.195(12)
Mn(1)-O(1W)	2.250(12)	Mn(1)-N(1)	2.266(14)
O(2)-Mn(1)-O(1)	90.6(5)	O(2)-Mn(1)-O(4)#1	173.1(5)
O(1)-Mn(1)-O(4)#1	85.5(5)	O(2)-Mn(1)-O(10)	78.7(5)
O(1)-Mn(1)-O(10)	163.9(5)	O(4)#1-Mn(1)-O(10)	104.0(5)
O(2)-Mn(1)-O(1W)	90.6(5)	O(1)-Mn(1)-O(1W)	86.9(5)
O(4)#1-Mn(1)-O(1W)	83.5(4)	O(10)-Mn(1)-O(1W)	81.4(4)
O(2)-Mn(1)-N(1)	100.5(5)	O(1)-Mn(1)-N(1)	113.9(5)
O(4)#1-Mn(1)-N(1)	86.2(5)	O(10)-Mn(1)-N(1)	80.2(5)
O(1W)-Mn(1)-N(1)	156.0(5)		
Complex 3			
Mn(1)-O(1)	2.114(2)	Mn(1)-O(13)#2	2.143(2)
Mn(1)-O(3W)	2.186(2)	Mn(1)-O(2W)	2.191(2)
Mn(1)-O(2)	2.203(2)	Mn(1)-O(1W)	2.207(2)
O(1)-Mn(1)-O(13)#2	94.26(10)	O(1)-Mn(1)-O(3W)	88.65(10)
O(13)#2-Mn(1)-O(3W)	176.73(10)	O(1)-Mn(1)-O(2W)	177.26(10)
O(13)#2-Mn(1)-O(2W)	88.32(9)	O(3W)-Mn(1)-O(2W)	88.80(9)
O(1)-Mn(1)-O(2)	87.61(10)	O(13)#2-Mn(1)-O(2)	90.19(10)

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

O(3W)-Mn(1)-O(2)	88.43(10)	O(2W)-Mn(1)-O(2)	93.30(9)
O(1)-Mn(1)-O(1W)	90.23(9)	O(13)#2-Mn(1)-O(1W)	87.89(9)
O(3W)-Mn(1)-O(1W)	93.60(9)	O(2W)-Mn(1)-O(1W)	88.95(9)
O(2)-Mn(1)-O(1W)	177.00(9)		

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

Table S2a. Selected hydrogen-bonding geometry (Å, °) for complex **1**

D-H...A	D-H	H...A	D...A	D-H...A
C(3)-H(3A)...O(12)	0.93	2.27	3.1603	160

Table S2b. Selected hydrogen-bonding geometry (Å, °) for complex **2**

D-H...A	D-H	H...A	D...A	D-H...A
N(3)-H(3b)...O(25)	0.86	2.46	3.1930	143

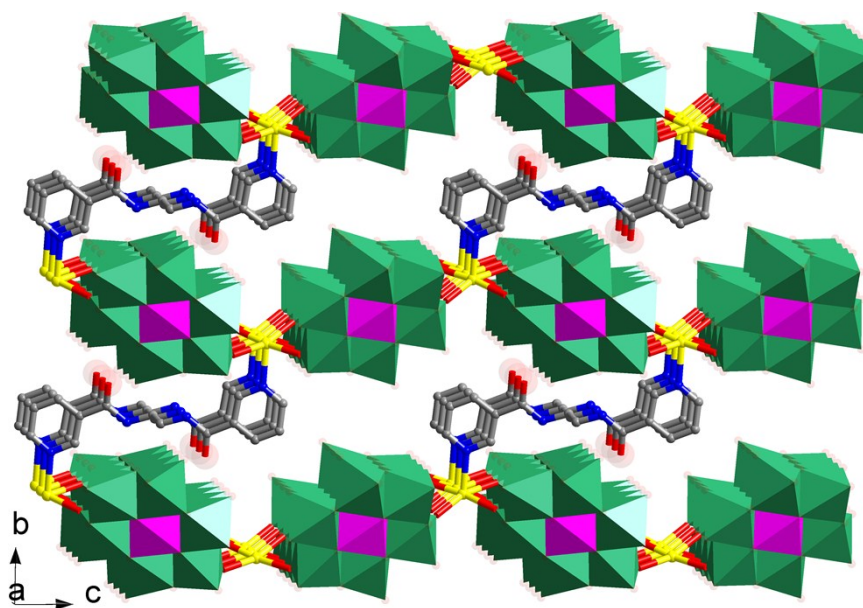


Fig. S1. Representation of the 3D framework of **2**.

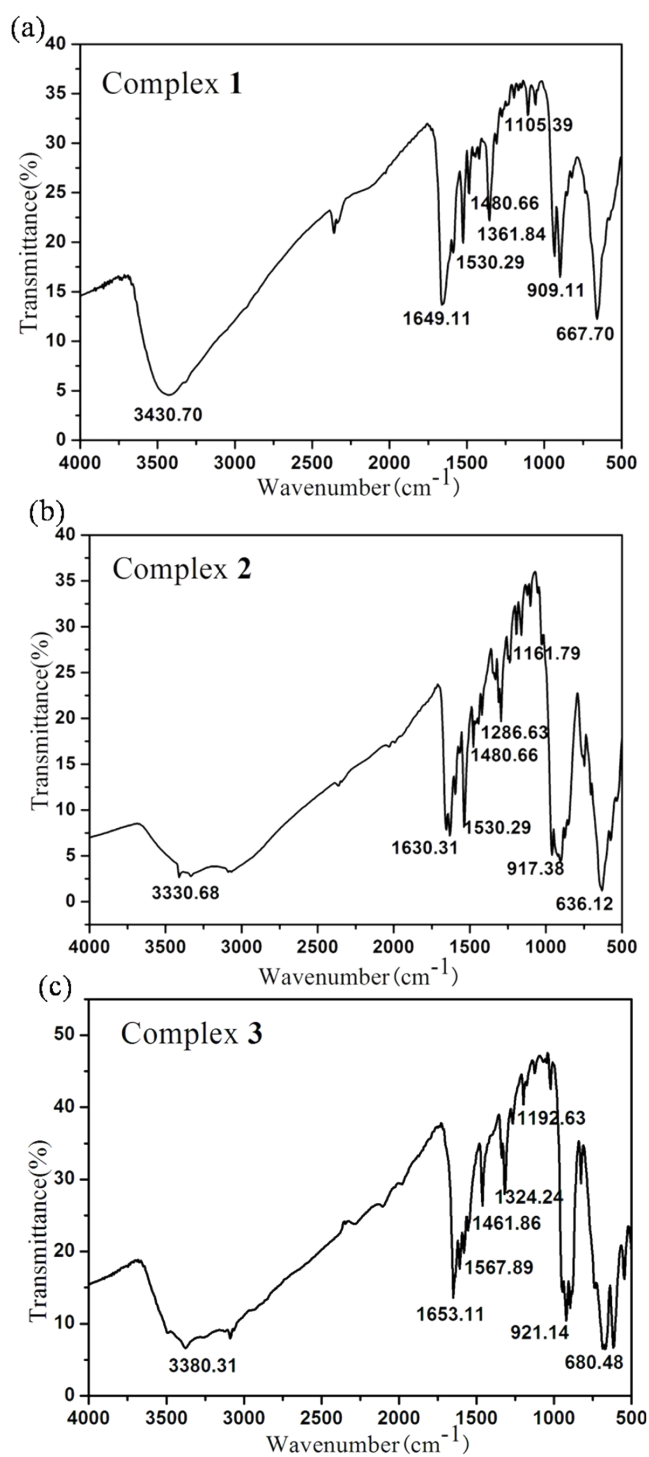


Fig. S2. The IR spectra of the title complexes.

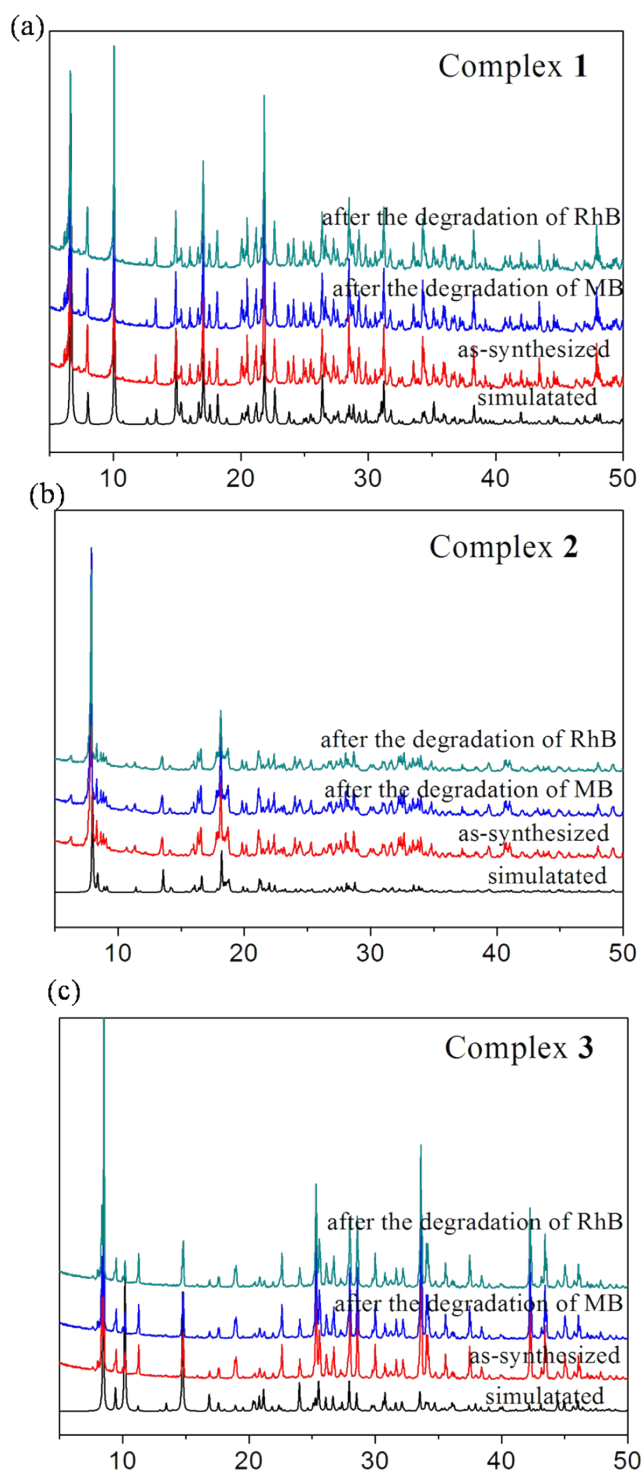


Fig. S3. Powder X-ray diffraction patterns of the title complexes.

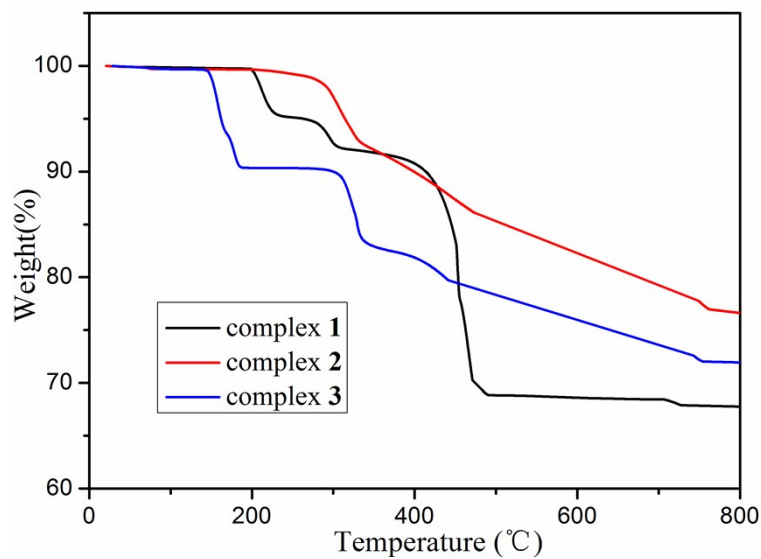


Fig. S4. The TGA curves of the title complexes.

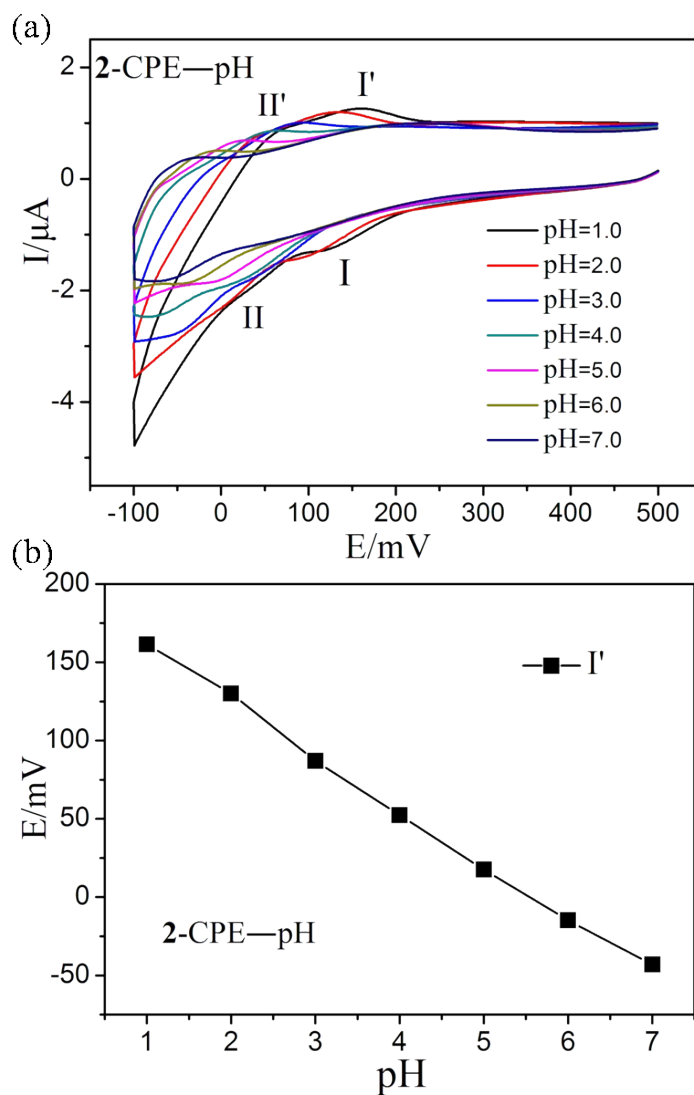


Fig. S5. (a) Cyclic voltammograms of 2-CPE at different pH values (Scan rate: $40 \text{ mV} \cdot \text{s}^{-1}$); (b) Variation of anodic peak potential of the Mo^{VI} -based wave (I') with different pH for 2-CPE

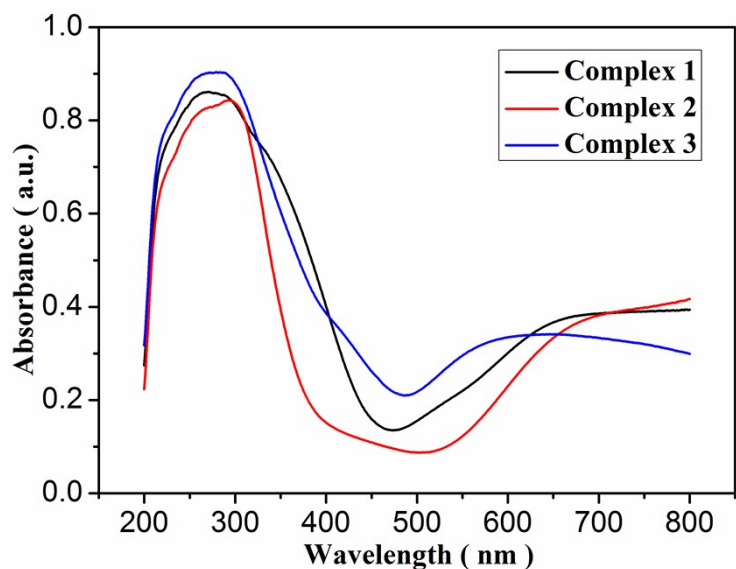


Fig. S6. The diffuse reflection spectra of complexes 1-3 in the crystalline state.

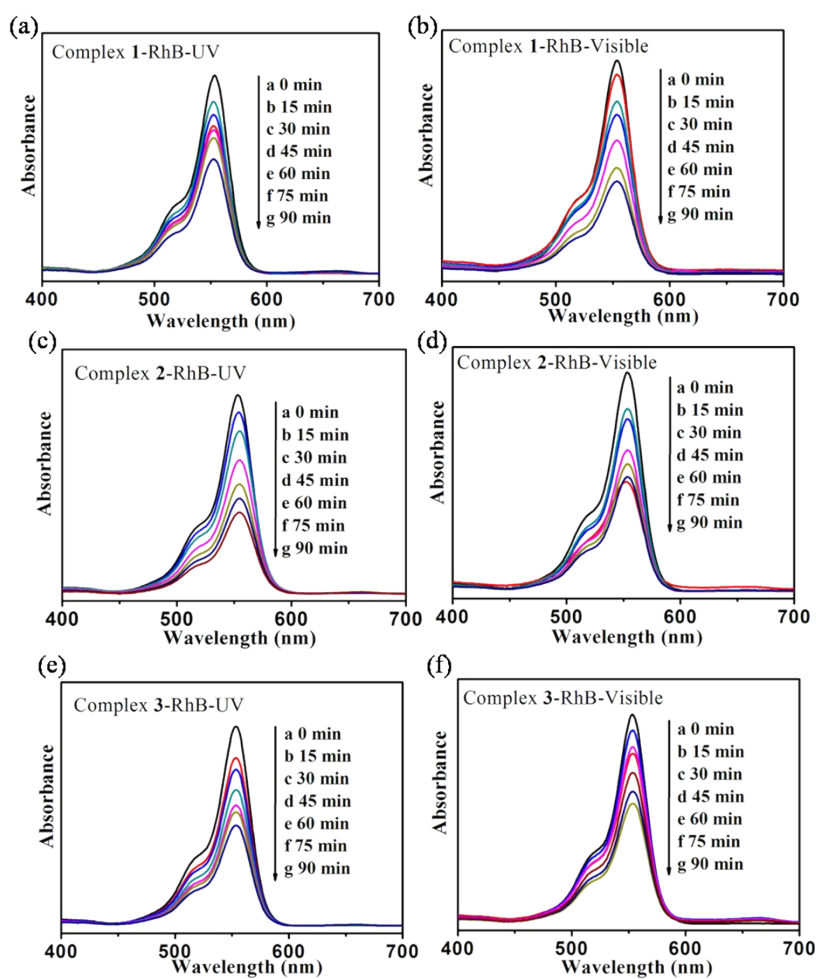


Fig. S7. Absorption spectra of the RhB solution during the decomposition reaction under UV and visible light irradiation at the presence of the title complexes.

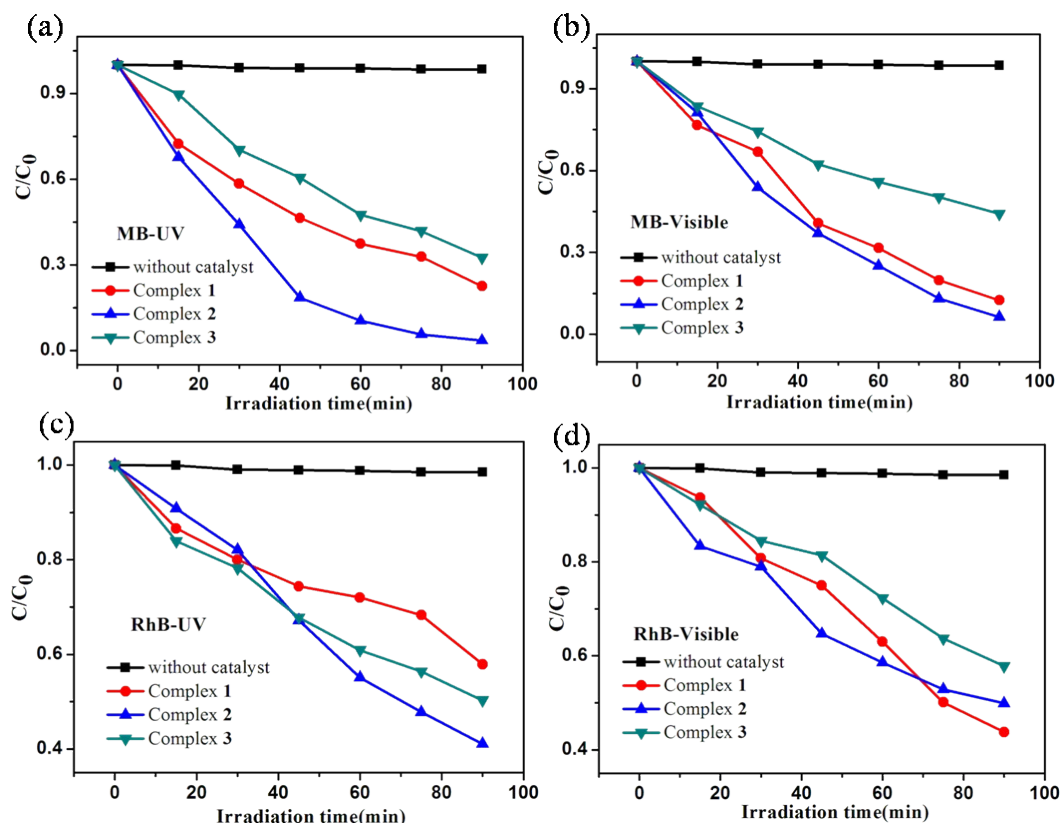


Fig. S8 Photocatalytic decomposition rate of MB (a-b) and RhB (c-d) solution with the use of title complexes.