Supporting Information

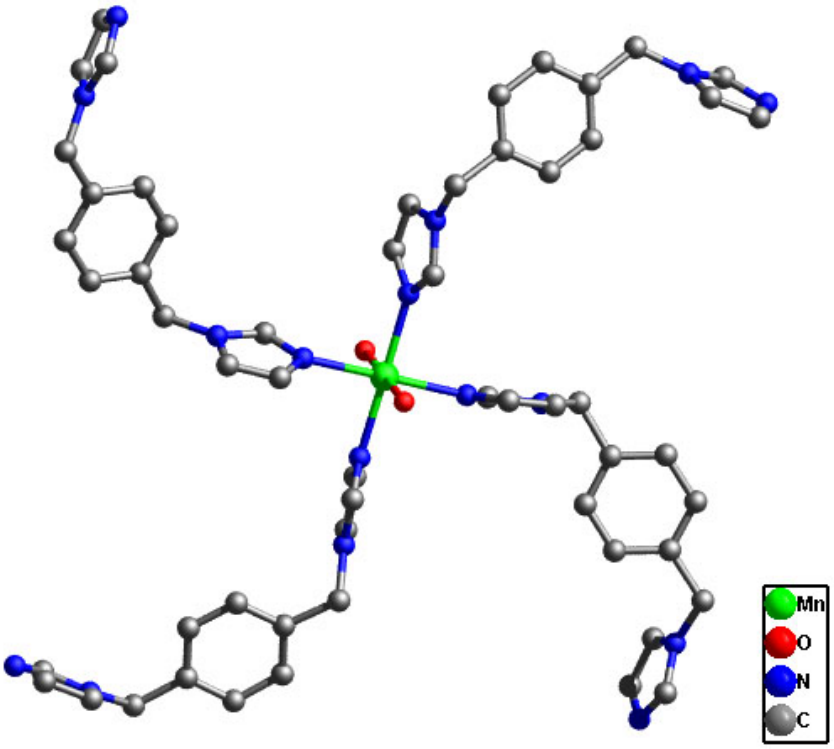

Fig. S1. Ball-and-stick representation of the propeller-shaped structures of the $[MnH(bix)_4]^{3+}$ complex fragments in compound **1.** (all of the hydrogen atoms are omitted for clarity).

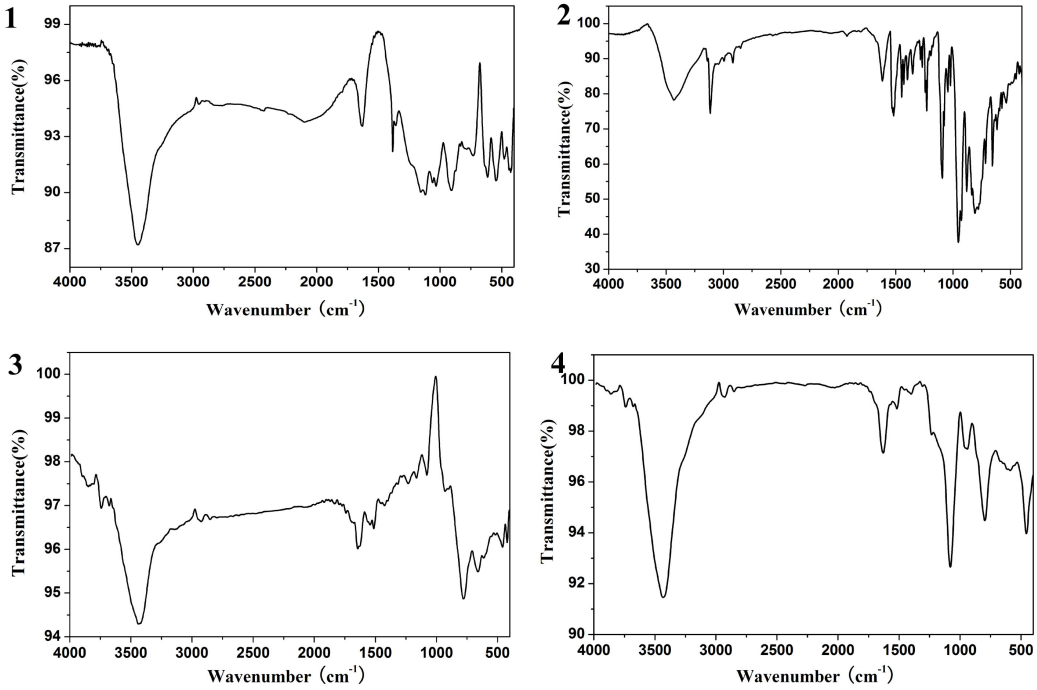

Fig. S2. The IR spectra of compounds **1-4**.

The TG analysis

	Temperature	first weight loss	Temperature	second weight loss
Compound 1	45°C to 125°C	1.20% (calcd 1.28%)	150 to 358 °C	33.65% (calcd 33.78%)
Compound 2	180°C to 240°C	1.19% (calcd 1.25%)	260 to 580 °C	33.26% (calcd 33.15%)
Compound 3	160˚C to 200˚C	2.35% (calcd 2.48%)	210˚C to 480˚C	32.87% (calcd 32.76%)
Compound 4	100˚C to 150˚C	2.28% (calcd 2.37%)	200˚C to 350˚C	31.25% (calcd 31.37%)

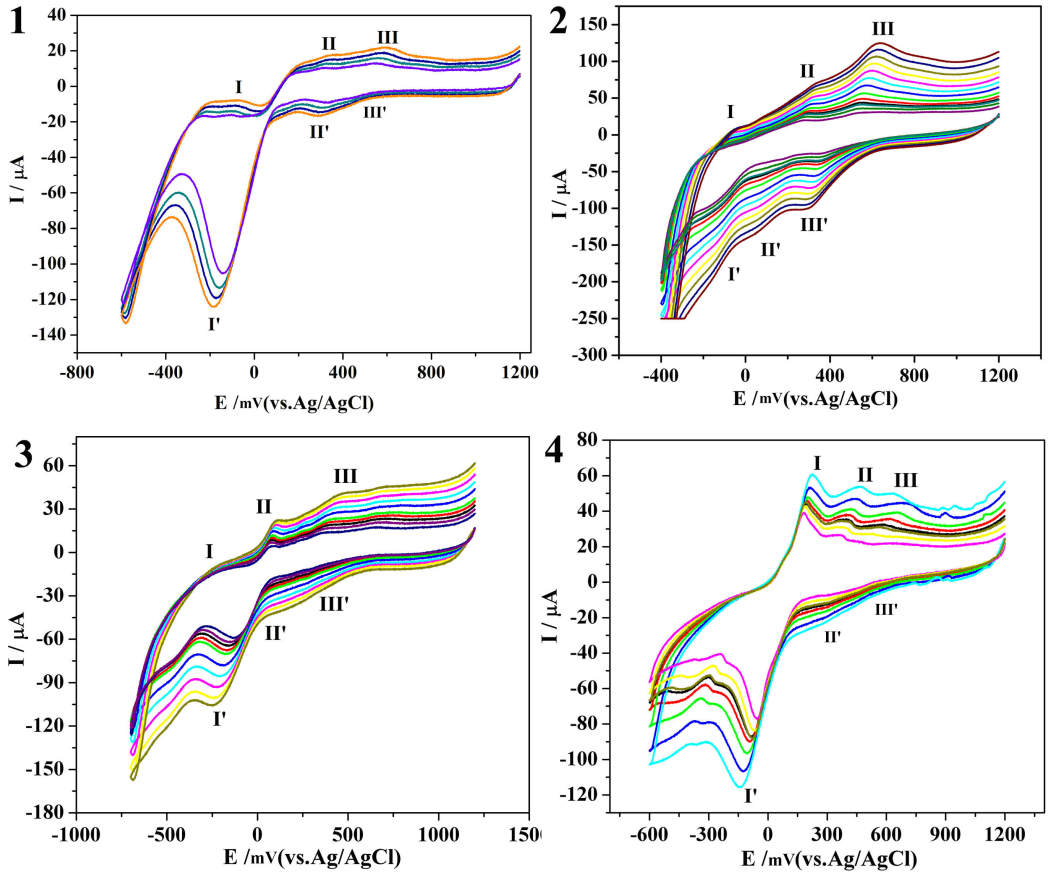

Fig. S3. The cyclic voltammograms of compounds **1-4** in 1M H_2SO_4 at different scan rates.

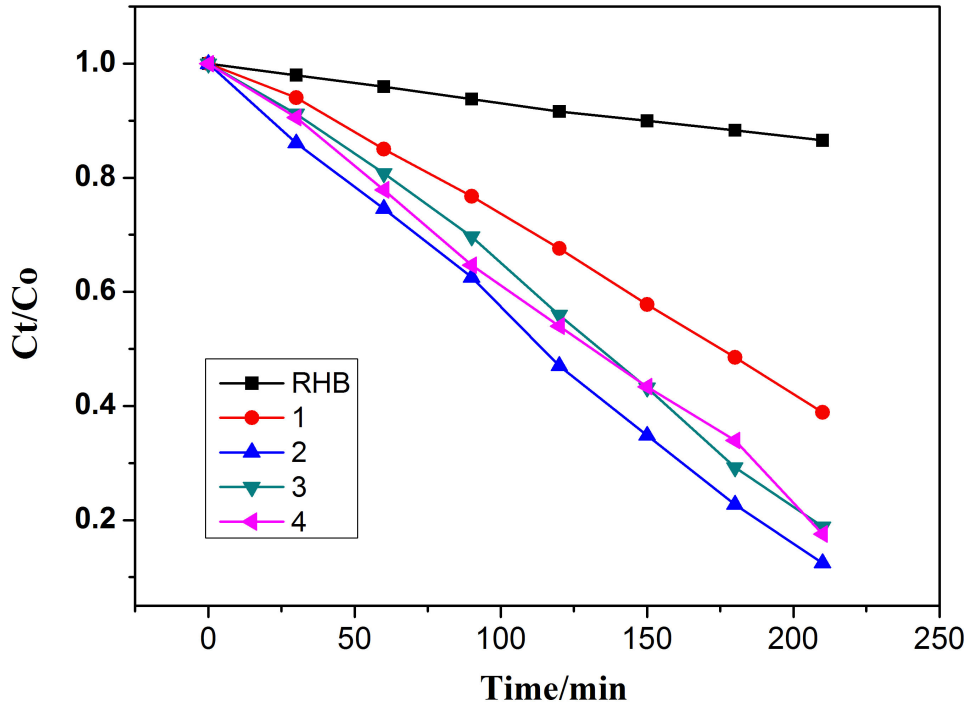

Fig. S4. Changes in C_t/C_0 plot of RhB solutions (2×10^{-5} mol L^{-1}) versus reaction time in the presence of 5 mg compounds **1-4**.

Table S1. Selected bond lengths (Å) for compound **1.**

Mo(1)-O(1)	1.686(6)	Mo(2)-O(3)	1.679(7)
Mo(1)-O(9)	1.806(6)	Mo(2)-O(6)	1.802(6)
Mo(1)-O(5)	1.817(6)	Mo(2)-O(7)	1.811(6)
Mo(1)-O(8)	2.057(6)	Mo(2)-O(8)	2.053(6)
Mo(1)-O(11)	2.065(6)	Mo(2)-O(11)#1	2.072(6)
Mo(1)-O(4)	2.395(6)	Mo(2)-O(4)	2.457(6)
V(2)-O(2)	1.616(6)	Mn(1)-N(1)	2.167(9)
V(2)-O(7)#2	1.902(6)	Mn(1)-N(1)#1	2.167(9)
V(2)-O(9)#3	1.902(6)	Mn(1)-N(1)#4	2.167(9)
V(2)-O(6)	1.939(6)	Mn(1)-N(1)#5	2.167(9)
V(2)-O(5)	1.940(6)	Mn(1)-O(10)#5	2.193(9)
V(1)-O(10)	1.634(9)	Mn(1)-O(10)	2.193(9)
V(1)-O(11)	1.896(6)	P(1)-O(4)#1	1.533(6)
V(1)-O(11)#1	1.896(6)	P(1)-O(4)#3	1.533(6)
V(1)-O(8)	1.970(6)	P(1)-O(4)	1.533(6)
V(1)-O(8)#1	1.970(6)	P(1)-O(4)#2	1.533(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+0,-y-1/2,z+0 #2 -y-1/4,x-1/4,-z+3/4 #3 y+1/4,-x-1/4,-z+3/4

#4 -y-1/4,x-1/4,-z+7/4 #5 y+1/4,-x-1/4,-z+7/4

Table S2. Selected bond lengths (Å) for compound **2**.

P(1)-O(9)#1	1.532(3)	P(1)-O(9)#2	1.532(3)
P(1)-O(9)	1.532(3)	P(1)-O(9)#3	1.532(3)
Zn(1)-N(1)	2.124(4)	Zn(1)-N(1)#5	2.124(4)
Zn(1)-O(1)	2.209(4)	Zn(1)-N(1)#4	2.124(4)
Zn(1)-O(1)#5	2.209(4)	Zn(1)-N(1)#2	2.124(4)
V(1)-O(1)	1.624(4)	V(1)-O(3)	1.981(3)
V(1)-O(10)#2	1.897(3)	V(1)-O(3)#2	1.981(3)
V(1)-O(10)	1.897(3)	Mo(1)-O(8)	1.678(3)
Mo(3)-O(2)	1.619(3)	Mo(1)-O(7)	1.813(3)
Mo(3)-O(7)#3	1.907(3)	Mo(1)-O(6)	1.816(3)
Mo(3)-O(4)#3	1.913(3)	Mo(1)-O(3)	2.043(3)
Mo(3)-O(6)	1.937(3)	Mo(1)-O(10)	2.054(3)
Mo(3)-O(11)#2	1.950(3)	Mo(1)-O(9)#2	2.457(3)
Mo(3)-O(9)#2	2.477(3)	Mo(2)-O(10)	2.048(3)
Mo(2)-O(5)	1.686(3)	Mo(2)-O(3)#2	2.056(3)
Mo(2)-O(4)	1.802(3)	Mo(2)-O(9)	2.394(3)
Mo(2)-O(11)	1.812(3)		

Symmetry transformations used to generate equivalent atoms:

#1 y+1/4,-x+3/4,-z-1/4 #2 -x+1,-y+1/2, z+0 #3 -y+3/4,x-1/4,-z-1/4

#4 -y+3/4,x-1/4,-z+3/4 #5 y+1/4,-x+3/4,-z+3/4

Table S3. Selected bond lengths (Å) for compound **3**.

Cu(1)-N(1)#1	2.038(7)	Cu(1)-N(1)#3	2.038(7)
Cu(1)-N(1)#2	2.038(7)	Cu(1)-O(1)#3	2.353(8)
Cu(1)-N(1)	2.038(7)	Cu(1)-O(1)	2.353(8)
Mo(1)-O(8)	1.695(6)	Mo(2)-O(7)	1.680(6)
Mo(1)-O(4)	1.793(6)	Mo(2)-O(2)	1.803(6)
Mo(1)-O(6)	1.813(6)	Mo(2)-O(5)	1.805(6)
Mo(1)-O(10)	2.042(5)	Mo(2)-O(9)	2.051(6)
Mo(1)-O(9)	2.057(6)	Mo(2)-O(10)#1	2.051(5)
Mo(1)-O(3)	2.398(6)	Mo(2)-O(3)	2.454(6)
Mo(3)-O(11)	1.607(6)	Mo(3)-O(5)	1.943(6)
Mo(3)-O(2)#4	1.909(6)	Mo(3)-O(6)	1.957(6)
Mo(3)-O(4)#5	1.915(6)	Mo(3)-O(3)	2.475(5)
V(1)-O(1)	1.599(8)	P(1)-O(3)#4	1.539(6)
V(1)-O(10)	1.902(5)	P(1)-O(3)#1	1.539(6)
V(1)-O(10)#1	1.902(5)	P(1)-O(3)	1.539(6)
V(1)-O(9)	1.979(5)	P(1)-O(3)#5	1.539(6)
V(1)-O(9)#1	1.979(5)	O(2)-V(2)#5	1.909(6)
O(4)-Mo(3)#4	1.915(6)	O(2)-Mo(3)#5	1.909(6)
O(10)-Mo(2)#1	2.051(5)	O(4)-V(2)#4	1.915(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+0,-y+1/2,z+0 #2 -y+1/4,x+1/4,-z+1/4 #3 y-1/4,-x+1/4,-z+1/4

#4 -y+1/4,x+1/4,-z+5/4 #5 y-1/4,-x+1/4,-z+5/4

Table S4. Selected bond lengths (Å) for compound **4**.

Mo(1)-O(10)	1.643(8)	Mo(2)-O(12)	1.654(8)
Mo(1)-O(9)	1.847(9)	Mo(2)-O(6)	1.845(8)
Mo(1)-O(15)	1.858(8)	Mo(2)-O(11)	1.846(9)
Mo(1)-O(13)	1.926(8)	Mo(2)-O(17)	1.925(8)
Mo(1)-O(6)	1.931(8)	Mo(2)-O(16)	1.951(9)
Mo(1)-O(21)	2.435(13)	Mo(2)-O(2)	2.403(13)
Mo(1)-O(2)	2.454(13)	Mo(2)-O(1)	2.407(14)
Mo(3)-O(5)	1.650(8)	Mo(4)-O(4)	1.649(8)
Mo(3)-O(19)	1.837(9)	Mo(4)-O(14)	1.791(8)
Mo(3)-O(17)#1	1.847(9)	Mo(4)-O(16)#1	1.862(9)
Mo(3)-O(18)	1.951(10)	Mo(4)-O(9)	1.928(9)
Mo(3)-O(15)#1	1.957(9)	Mo(4)-O(8)	1.990(9)
Mo(3)-O(20)	2.417(12)	Mo(4)-O(21)	2.424(12)
Mo(3)-O(2)#1	2.495(13)	Mo(4)-O(1)#1	2.464(14)
Mo(5)-O(3)	1.651(8)	Mo(6)-O(7)	1.659(7)
Mo(5)-O(22)	1.811(10)	Mo(6)-O(8)#1	1.825(9)
Mo(5)-O(13)	1.863(9)	Mo(6)-O(18)	1.843(11)
Mo(5)-O(19)	1.935(9)	Mo(6)-O(11)	1.962(10)
Mo(5)-O(14)	1.997(9)	Mo(6)-O(22)	1.980(10)
Mo(5)-O(20)	2.431(13)	Mo(6)-O(20)	2.433(12)
Mo(5)-O(21)	2.496(13)	Mo(6)-O(1)	2.500(13)
Cu(1)-N(1)#2	1.873(9)	Cu(2)-N(4)	1.876(10)
Cu(1)-N(1)	1.873(9)	Cu(2)-N(5)	1.879(10)
P(1)-O(1)	1.529(13)	P(1)-O(21)#1	1.538(13)
P(1)-O(1)#1	1.529(13)	P(1)-O(21)	1.538(13)
P(1)-O(2)	1.535(13)	P(1)-O(20)	1.581(12)
P(1)-O(2)#1	1.535(13)	P(1)-O(20)#1	1.581(12)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y,-z #2 -x+1,-y+1,-z

Table S5. The bond valence sum calculations for V and Mo atoms in compounds **1-4**.

Compound **1**			
Mo1	6.006	V1	4.199
Mo2	6.031	V2	4.565
Compound **2**			
Mo1	6.016	V1	4.189
Mo2	6.058	V2	4.510
Mo3	6.189		
Compound **3**			
Mo1	6.059	Mo3	6.103
Mo2	6.146	V1	4.246
Compound **4**			
Mo1	6.466	Mo4	6.470
Mo2	6.430	Mo5	6.343
Mo3	6.364	Mo6	6.288

Table S6. Hydrogen bonds for compounds **1**-**4**.

Compound **1**			
Donor---H....Acceptor	D - H	H...A	D...A
N(9) --H(9A)..O(3)	0.86	2.10	2.915(14)
N(9)--H(9A)..O(40)	0.86	2.59	3.120(15)
C(3)--H(3B)..O(3)	0.97	2.39	3.278(16)
C(4)--H(4A)..O(8)	0.93	2.60	3.524(18)
C(11)--H(11A)..O(8)	0.93	2.59	3.504(15)
C(17)--H(17A)..N(8)	0.93	2.59	2.895(15)
C(17)--H(17A)..O(10)	0.93	2.50	3.380(15)
C(34)--H(34A)..O(3)	0.93	2.60	3.316(15)
C(74)--H(74A)..O(21)	0.97	2.48	3.438(17)
Compound **2**			
Donor---H....Acceptor	D - H	H...A	D...A
N(5)--H(5A)..O(5)	0.86	2.05	2.870(12)
C(2)--H(2B)..O(7)	0.97	2.46	3.425(13)
C(3)--H(3A)..O(5)	0.93	2.56	3.293(11)
C(18)--H(18A)..N(4)	0.93	2.59	2.901(11)
C(18)--H(18A)..O(8)	0.93	2.47	3.348(11)
C(21)--H(21A)..O(2)	0.93	2.57	3.487(11)
C(23)--H(23A)..O(5)	0.97	2.38	3.273(10)
Compound **3**			
Donor---H....Acceptor	D - H	H...A	D...A
C(2)--H(2A)..O(2)	0.97	2.49	3.444(11)
C(6)--H(6A)..O(1)	0.93	2.58	3.089(10)
C(12)--H(12A) .O(7)	0.93	2.45	3.342(12)
C(14)--H(14A) .O(11)	0.93	2.57	3.488(10)
C(26)--H(26B)..O(8)	0.97	2.36	3.270(11)
Compound **4**			
Donor---H....Acceptor	D - H	H...A	D...A
C(3)--H(3B)..O(6)	0.97	2.56	3.39(2)
C(3)--H(3B)..O(12)	0.97	2.51	3.39(2)
C(4)--H(4A)..N(2)	0.93	2.55	2.86(2)
C(6)--H(6A)..O(11)	0.93	2.56	3.38(2)
C(6)--H(6A)..O(22)	0.93	2.53	3.258(18)
C(10)--H(10A)..O(5)	0.93	2.39	3.174(17)
C(11)--H(11A)..O(3)	0.93	2.50	3.289(19)
C(11)--H(11A)..O(13)	0.93	2.53	3.37(2)
C(13)--H(13A)..O(6)	0.93	2.57	3.496(19)
C(14)--H(14A)..O(9)	0.93	2.37	3.239(18)
C(23)--H(23A)..O(17)	0.93	2.47	3.34(2)

C(25)--H(25B)..O(16)	0.97	2.58	3.510(18)
C(26)--H(26A)..O(3)	0.93	2.25	3.017(16)
C(27)--H(27A)..Ow(1)	0.93	2.54	3.345(18)
C(27)--H(27A)..O(12)	0.93	2.36	2.939(19)
C(28)--H(28A)..Ow(1)	0.93	1.87	2.783(19)