Table S1. Selective bond lengths and angles of **1**.

Mn(1)-O(6)#1	2.168(3)	Mn(2)-O(49)	2.043(4)
Mn(1)-O(6)	2.168(3)	Mn(2)-O(33)	2.096(4)
Mn(1)-O(1)	2.202(4)	Mn(2)-O(48)	2.171(4)
Mn(1)-O(1)#1	2.202(4)	Mn(2)-O(57)	2.230(4)
Mn(1)-O(2)	2.209(3)	Mn(2)-O(23)	2.230(4)
Mn(1)-O(2)#1	2.209(3)	O(6)#1-Mn(1)-O(6)	180.0
Mn(3)-O(9)#2	2.163(3)	O(6)#1-Mn(1)-O(1)	84.53(13)
Mn(3)-O(9)	2.163(3)	O(6)-Mn(1)-O(1)	95.47(13)
Mn(3)-O(12)#2	2.222(3)	O(6)#1-Mn(1)-O(1)#1	95.47(13)
Mn(2)-O(8)	2.304(4)	O(6)-Mn(1)-O(1)#1	84.53(13)
Pb(1)-O(4)	2.361(4)	O(1)-Mn(1)-O(1)#1	180.00(15)
Pb(1)-O(8)	2.363(3)	O(49)-Mn(2)-O(48)	95.98(18)
Pb(1)-O(23)	2.507(4)	O(33)-Mn(2)-O(48)	99.45(17)
Pb(1)-O(51)	2.662(5)	O(49)-Mn(2)-O(57)	92.28(18)
O(4)-Pb(1)-O(8)	79.12(13)	O(33)-Mn(2)-O(57)	98.03(17)
O(4)-Pb(1)-O(23)	87.46(13)	O(48)-Mn(2)-O(57)	160.54(17)
O(8)-Pb(1)-O(23)	72.78(12)	O(49)-Mn(2)-O(23)	174.30(16)
O(4)-Pb(1)-O(51)	160.79(15)	O(33)-Mn(2)-O(23)	94.46(15)
O(8)-Pb(1)-O(51)	82.52(14)	O(48)-Mn(2)-O(23)	85.53(15)
O(23)-Pb(1)-O(51)	81.73(13)	O(57)-Mn(2)-O(23)	84.65(15)
O(6)#1-Mn(1)-O(2)	84.14(13)	O(49)-Mn(2)-O(8)	95.65(15)
O(6)-Mn(1)-O(2)	95.86(13)	O(9)#2-Mn(3)-O(7)	81.84(13)
O(1)-Mn(1)-O(2)	98.26(12)	O(9)-Mn(3)-O(7)	98.16(13)
O(1)#1-Mn(1)-O(2)	81.74(12)	O(12)#2-Mn(3)-O(7)	84.02(13)
O(6)#1-Mn(1)-O(2)#1	95.86(13)	O(12)-Mn(3)-O(7)	95.98(13)
O(6)-Mn(1)-O(2)#1	84.14(13)	O(9)#2-Mn(3)-O(7)#2	98.16(13)
O(1)-Mn(1)-O(2)#1	81.74(12)	O(9)-Mn(3)-O(7)#2	81.84(13)
O(1)#1-Mn(1)-O(2)#1	98.26(12)	O(12)#2-Mn(3)-O(7)#2	95.98(13)
O(2)-Mn(1)-O(2)#1	180.00(17)	O(12)-Mn(3)-O(7)#2	84.02(13)
O(49)-Mn(2)-O(33)	90.71(16)	O(7)-Mn(3)-O(7)#2	180.00(5)
O(33)-Mn(2)-O(8)	173.48(14)	O(9)#2-Mn(3)-O(12)	85.80(13)
O(48)-Mn(2)-O(8)	78.51(15)	O(9)-Mn(3)-O(12)	94.20(13)
O(57)-Mn(2)-O(8)	83.18(15)	O(9)#2-Mn(3)-O(12)#2	94.21(13)
O(23)-Mn(2)-O(8)	79.24(13)	O(9)-Mn(3)-O(12)#2	85.80(13)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y+1,-z+1 #2 -x,-y,-z #3 -x,-y+2,-z+1

Table S2. Redox potentials of crystal-CPEs in the 1.0 M H_2SO_4 solutions. Scan rate 140 $mV \cdot s^{-1}$, Potentials (V) vs. SCE.

CPE	Peaks	IV	I	II	III	V	Conversion% of Fe(III)
1	E_{pa}	-0.1369	-0.0112	0.2662	0.4068	0.1210	66.9%, 90 min;
	E_{pc}		-0.0391	0.2244	0.3631		74.7%, 150 min
	$1/2E_p$		-0.0252	0.2453	0.3850		50 °C
	ΔE_p		0.0279	0.0418	0.0437		This work
2	E_{pa}	-0.1430	-0.0260	0.3037	0.4348	0.1300	36.8%, 90 min;
	E_{pc}		-0.0120	0.2285	0.3723		60.6%, 150 min
	$1/2E_p$		-0.0190	0.2661	0.4036		50 °C
	ΔE_p		0.0140	0.0752	0.0625		This work
3	E_{pa}	-0.1322	-0.0213	0.3037	0.4318	0.1370	52.5%, 90 min;
	E_{pc}		-0.0182	0.2224	0.3662		66.9%, 150 min
	$1/2E_p$		-0.0198	0.2631	0.3990		50 °C
	ΔE_p		0.0031	0.0813	0.0656		This work
4	E_{pa}	-0.1431	-0.0215	0.2861	0.4224	0.1310	44.9%, 90 min;
	E_{pc}		-0.0203	0.2308	0.3752		69.8%, 150 min
	$1/2E_p$		-0.0209	0.2585	0.3988		50 °C
	ΔE_p		0.0012	0.0553	0.0472		This work
5	E_{pa}	-0.1799	-0.0511	0.2037	0.3637		53.6%, 90 min;
	E_{pc}		-0.0712	0.1890	0.3274		71.2%, 150 min
	$1/2E_p$		-0.0612	0.1964	0.3456		50 °C
	ΔE_p		0.0201	0.0147	0.0363		Ref. 21
6	E_{pa}	-0.2095	-0.0714	0.1837	0.3258		45.3%, 90 min;
	E_{pc}		-0.1171	0.1548	0.2775		63.1% 150 min
	$1/2E_p$		-0.0943	0.1693	0.3017		55 °C
	ΔE_p		0.0457	0.0289	0.0483		Ref. 22
7	E_{pa}	-0.1870	-0.0327	0.2159	0.3594		63.0%, 150 min
	E_{pc}		-0.0910	0.1819	0.3112		50 °C
	$1/2E_p$		-0.0619	0.1989	0.3353		Our data
	ΔE_p		0.0583	0.0340	0.0482		
8	E_{pa}	-0.1987	-0.0700	0.1795	0.3261		48.4%, 90 min;
	E_{pc}		-0.1166	0.1524	0.2798		77.3%, 150 min
	$1/2E_p$		-0.0933	0.1660	0.3030		55 °C
	ΔE_p		0.0466	0.0271	0.0463		Ref. 22

5 Mn_2-{$Mn(P_4Mo_6)_2$}[21]: $Na(H_2O)_2(Hbpp)_3[Na_2(bpp)][Mn_2(H_2O)_5]\{Mn[Mo_{12}O_{24}(OH)_6(HPO_4)_6(H_2PO_4)(PO_4)]\}\cdot(HPO_4)\cdot 2H_2O$;

6 {$Ni(P_4Mo_6)_2$}[22]: $(H_2bpp)_6\{Ni[Mo_6O_{13}(OH)_2(HPO_4)_3(H_2PO_4)]_2\}_2\cdot 13H_2O$;

7 Co_2-{$Co(P_4Mo_6)_2$}[8]: $(H_2bpp)_6[Co(H_2O)_2]_4\{Co[Mo_6O_{12}(OH)_3(HPO_4)_2(H_2PO_4)(PO_4)]_2\}_2\cdot 2(HPO_4)\cdot 12H_2O$;

8 Cd_2-{$Cd(P_4Mo_6)_2$}[22]: $(H_2bpp)_2[Cd(H_2O)Cd(H_2O)_2]_2\{Cd[Mo_6O_{12}(OH)_3(HPO_4)_2(PO_4)_2]_2\}\cdot 8H_2O$

References see the text.

Elements	mass%	atomic%	Elements	mass%	atomic%
C K	23.78	43.24	Mn K	2.47	0.98
O K	32.15	43.89	Mo L	28.60	6.51
P K	6.68	4.71	Pb M	6.32	0.67
gross	100%				

Elements	mass%	atomic%	Elements	mass%	atomic%
C K	22.08	40.35	Ni K	2.92	1.09
O K	34.14	46.84	Mo L	29.49	6.75
P K	6.25	4.43	Pb M	5.11	0.54
gross	100%				

Elements	mass%	atomic%	Elements	mass%	atomic%
C K	20.59	38.35	Co K	2.51	0.95
O K	34.60	48.38	Mo L	29.70	6.93
P K	6.57	4.75	Pb M	6.03	0.65

Elements	mass%	atomic%	Elements	mass%	atomic%
C K	29.16	51.36	Mo L	25.24	5.57
O K	28.75	38.01	Cd L	3.66	0.69
P K	5.22	3.56	Pb M	7.96	0.81

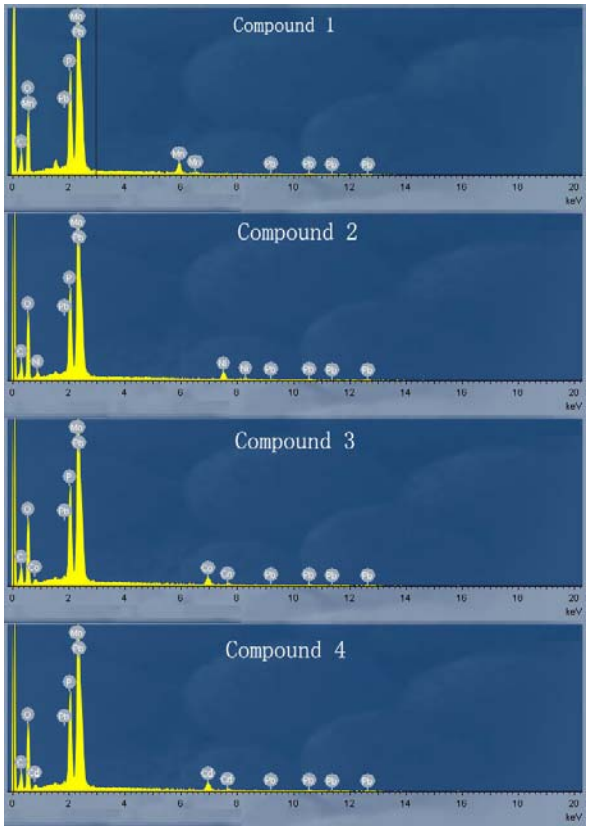

Fig. S1. The EDS of compounds **2-4**.

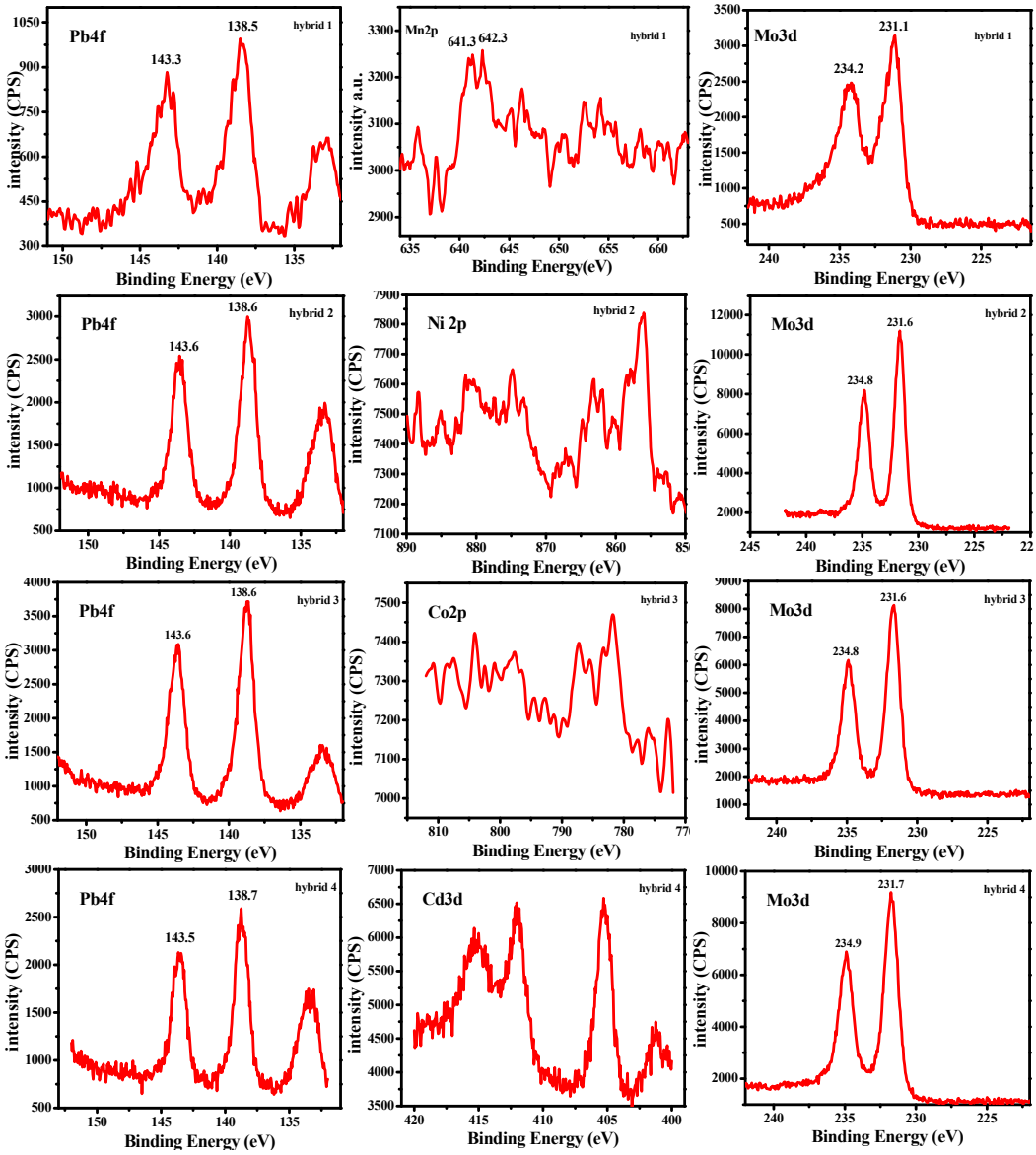

Fig. S2. X-Ray photoelectron spectroscopy of compounds **1-4**.

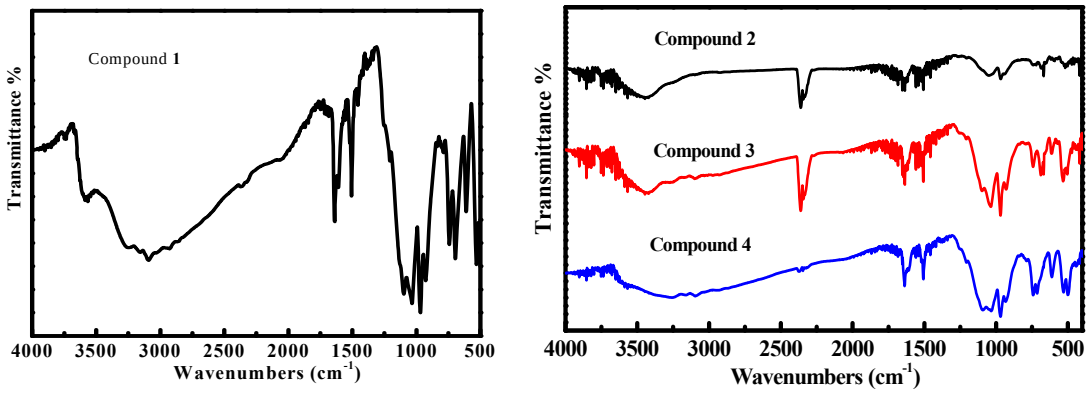

Fig. S3. IR spectra of compounds **1-4**.

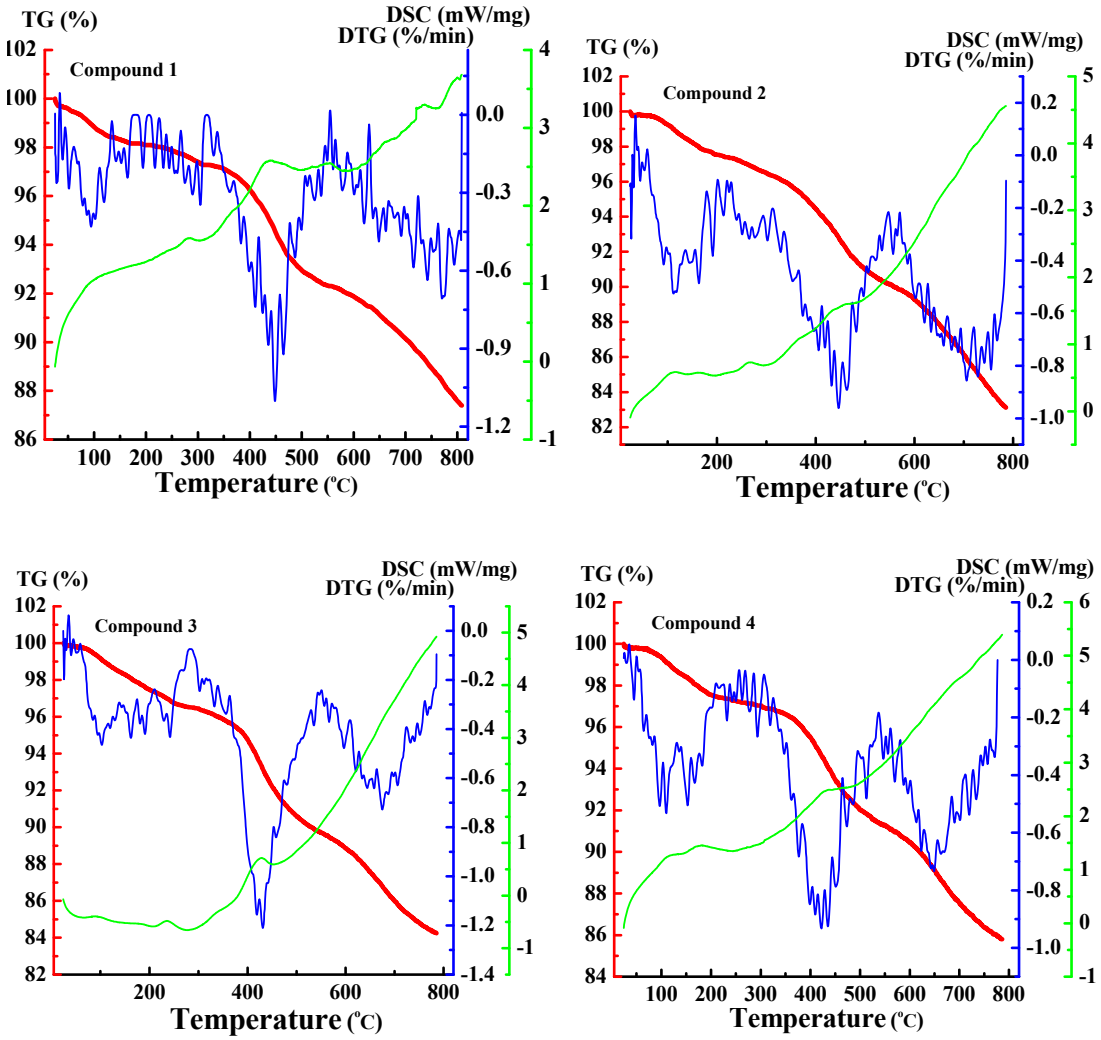

Fig. S4. TG and DSC curves of compounds **1-4**

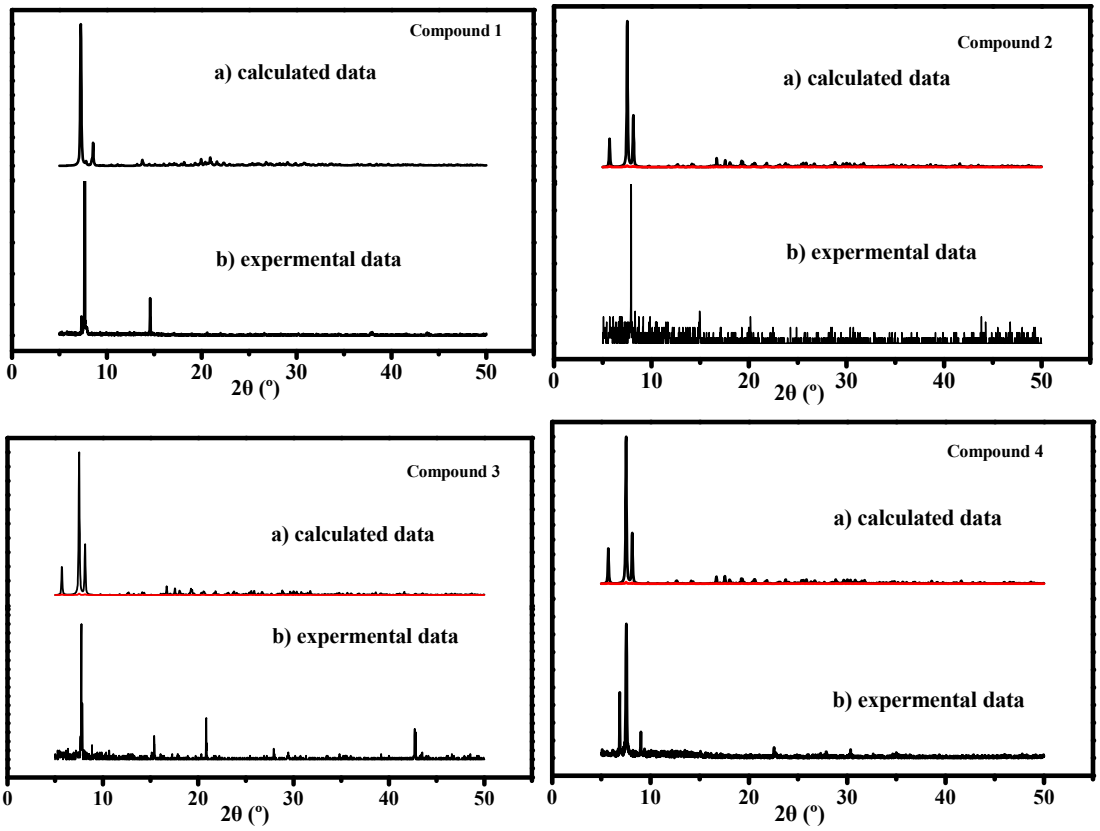

Fig. S5. XRD curves of compounds **1-4**

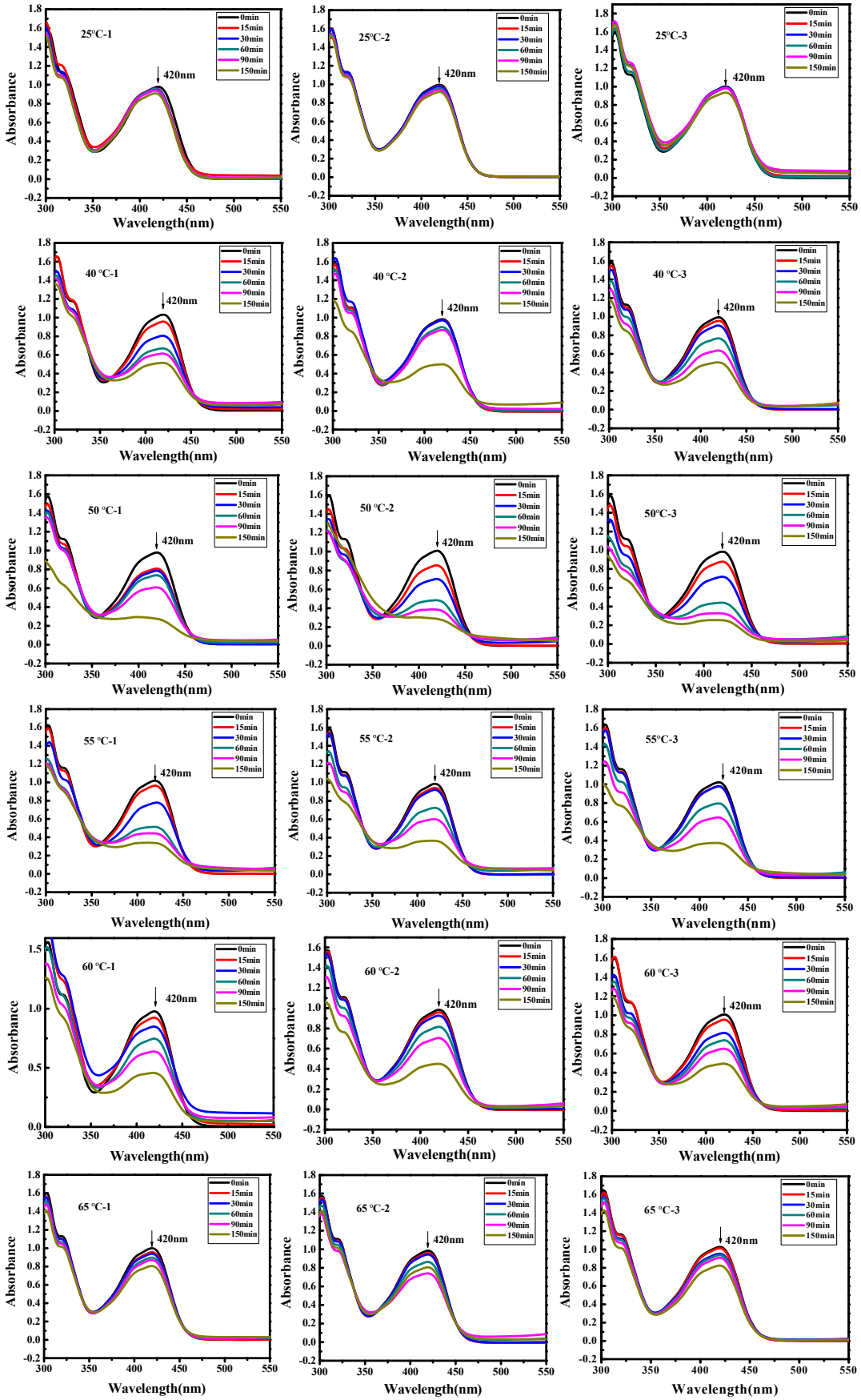

Fig. S6. UV absorption spectra of three-times cycle experiments with catalyst **1**.

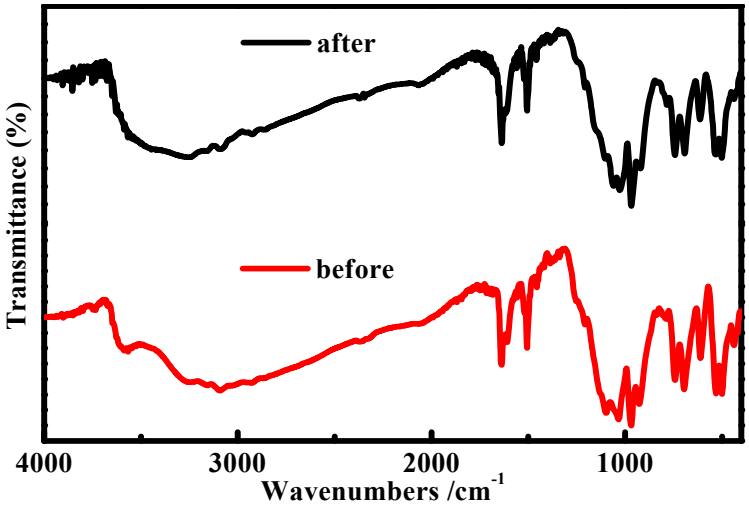

Fig. S7. IR spectra of **1**: after degradation (black line); before degradation (red line).

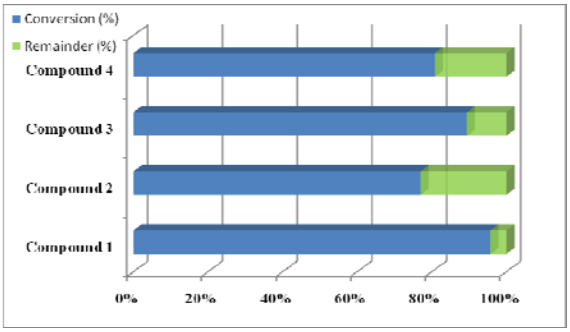

Fig. S8. The reduction rates of Fe (III) catalyzed by compounds **1-4** at 270 min, 50°C.

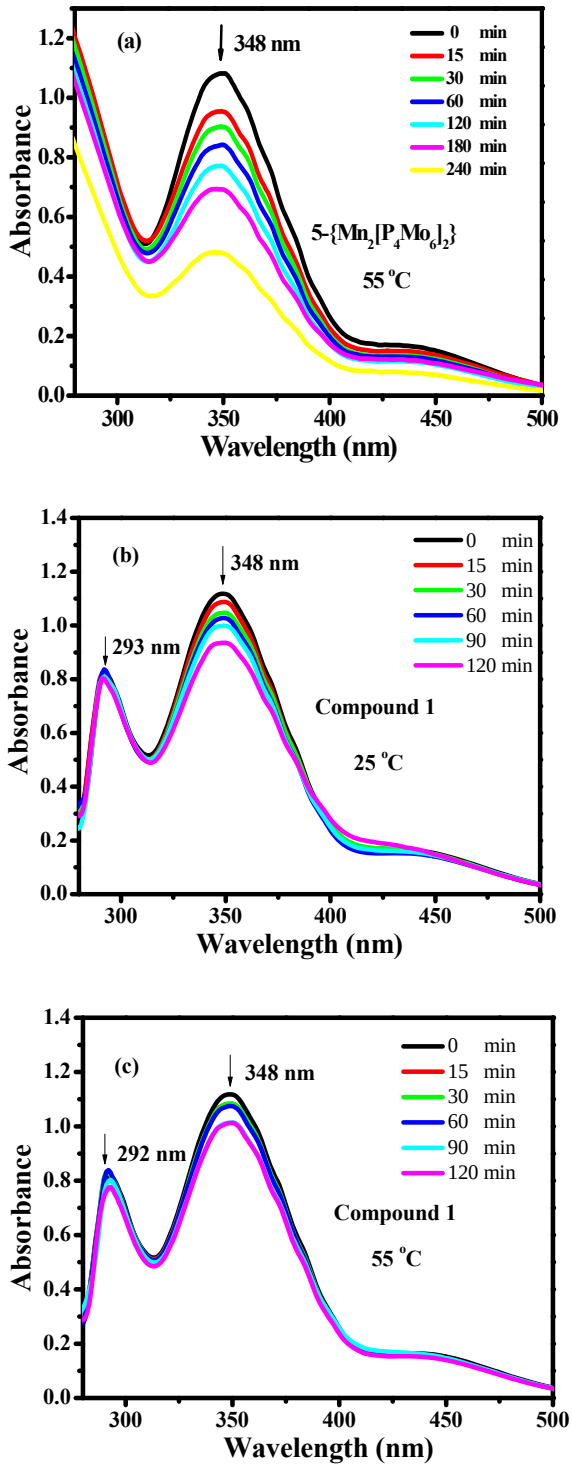

Fig. S9. (a) UV spectra of catalytic reduction of Cr(VI) by the reported compound[7] at 55 °C; (b) UV spectra of catalytic reduction of Cr(VI) by compound **1** at 25 °C; (c) UV spectra of catalytic reduction of Cr(IV) by compound **1** at 55 °C. The other reaction conditions are same for these experiments. Ref. [7] sees the text.

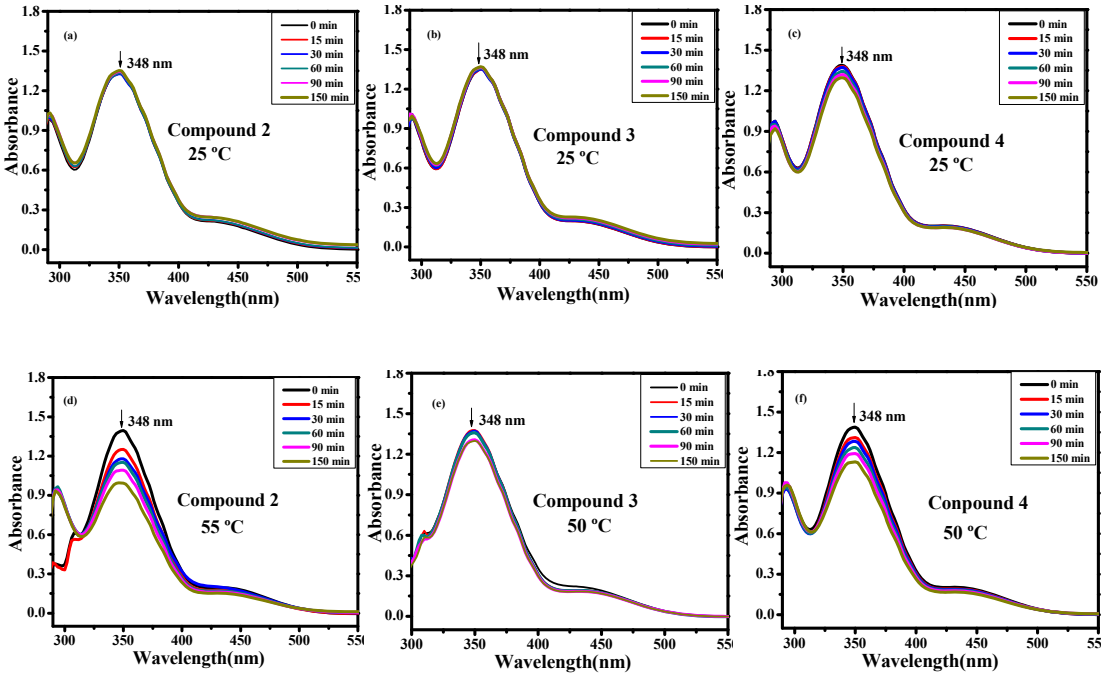

Fig. S10. (a-c) UV spectra of catalytic reduction of Cr (VI) by compounds **2-4** at 25 °C; (d-f) UV spectra of catalytic reduction of Cr (VI) by compounds **2-4** at 55 °C.

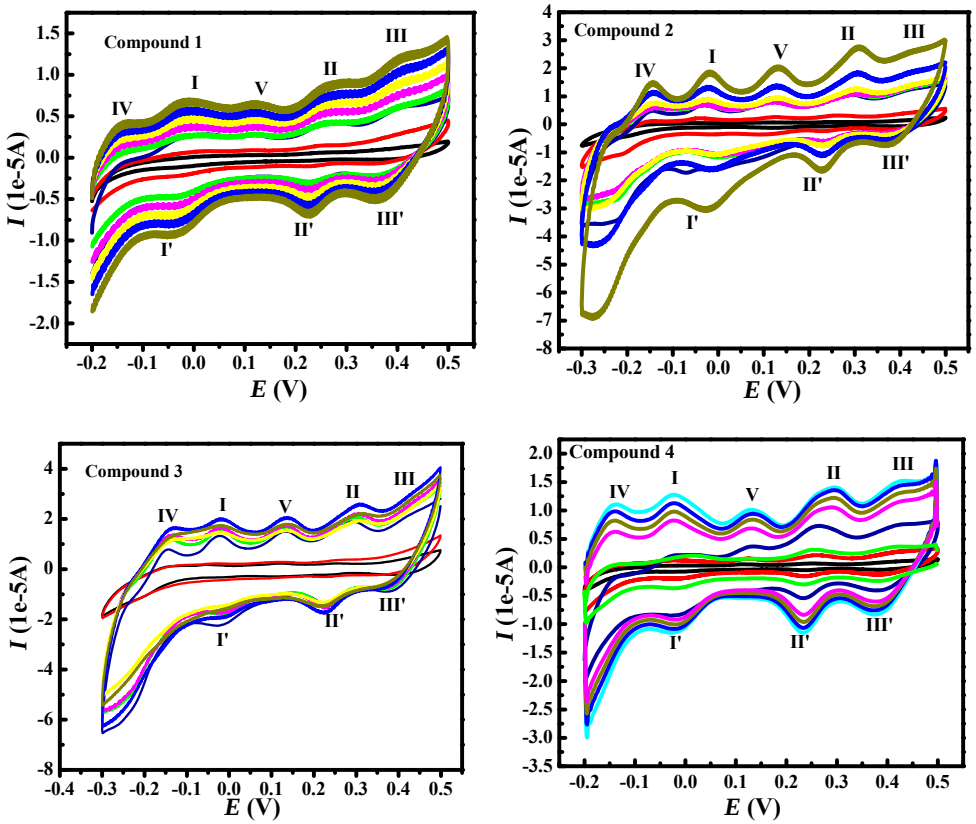

Fig. S11. Cyclic voltammograms of (a) 1-CPE, (b) 2-CPE, (c) 3-CPE, and (d) 4-CPE in the 1.0 M H_2SO_4 solution at different scan rates (from inner to outer: 20, 50, 80, 110, 140, 170, and 200 mV·s^{-1}). Potentials vs. SCE.