Electronic Supplementary Material (ESI)

Iodoargentates/ iodobismuthate-based Materials Hybridized by Lanthanide Complexes: Photocurrent Responses and Thermochromic Behaviors

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Supporting information

Computation Methods

Table cation:

Figure cation:

in 5

Fig. S9 (a) Thermochromic behavior of 6; (b) ESR spectrum of before/after heating and after cooling down in 6

Fig. S10 Thermogrevimetric curves for 1 and 5

Computation Methods

DFT calculations were carried out using the Gaussian 09 program package.[1] During the calculations, the DMF have been replaced by H_2O in order to cut the computational cost without significantly affecting its electronic properties. A Ag_6I_9 unit was used to simulate the $(Ag_{12}I_{18})_n^{6n-}$ chain. The calculations were performed by using spin restricted DFT wave functions B3LYP. The 6-31g(d) basis set was used for C, N, O and H atoms, while cep-4g basis set was employed for the Ag and I atom, and sdd basis set was applied in La center.

Table S1 Selected Bond Lengths (Å) for 1-3

1							
La(1)-O(1)	2.45(3)	La(1)-O(2)	2.42(3)	La(1)-O(3)	2.50(3)	La(1)-O(4)	2.50(5)
La(1)-O(5)	2.44(4)	La(1)-O(6)	2.42(4)	La(1)-O(7)	2.49(4)	La(1)-O(8)	2.49(4)
Ag(1)-I(1)	2.898(6)	Ag(1)-I(1)#1	2.886(6)	Ag(1)-I(2)	2.796(8)	Ag(1)-I(3)	2.934(7)
Ag(2)-I(1)	2.912(6)	Ag(2)-I(3)	2.833(6)	Ag(2)-I(4)	2.953(6)	Ag(2)-I(5)	2.817(7)
Ag(3)-I(2)	2.791(7)	Ag(3)-I(3)	2.932(7)	Ag(3)-I(4)	2.927(6)	Ag(3)-I(6)	2.804(6)
Ag(4)-I(4)	2.946(6)	Ag(4)-I(6)	2.805(6)	Ag(4)-I(9)	2.838(6)	Ag(4)-I(8)	2.916(6)
Ag(5)-I(4)	2.986(6)	Ag(5)-I(5)	2.788(6)	Ag(5)-I(7)	2.826(6)	Ag(5)-I(9)	2.890(6)
Ag(6)-I(7)	2.824(6)	Ag(6)-I(8)#2	2.881(6)	Ag(6)-I(8)	2.893(6)	Ag(6)-I(9)	2.994(6)
Ag(1)-Ag(1)#1	3.168(10)	Ag(1)-Ag(2)	3.341(7)	Ag(1)-Ag(3)	3.290(7)	Ag(2)-Ag(3)	3.246(7)
Ag(2)-Ag(5)	3.267(7)	Ag(3)-Ag(4)	3.309(7)	Ag(4)-Ag(5)	3.184(7)	Ag(4)-Ag(6)	3.270(7)
Ag(5)-Ag(6)	3.091(6)	Ag(6)-Ag(6)#2	3.143(9)				
Symmetry codes: #1 –x,-y+2,-z+1; #2 –x,-y+1,-z+2							
2							
Nd(1)-O(1)	2.39(2)	Nd(1)-O(2)	2.43(3)	Nd(1)-O(3)	2.44(2)	Nd(1)-O(4)	2.39(3)
Nd(1)-O(5)	2.41(3)	Nd(1)-O(6)	2.51(3)	Nd(1)-O(7)	2.49(2)	Nd(1)-O(8)	2.36(3)
Ag(1)-I(1)	2.993(5)	Ag(1)-I(2)	2.889(5)	Ag(1)-I(6)	2.786(4)	Ag(1)-I(9)	2.824(5)
Ag(2)-I(1)	2.949(4)	Ag(2)-I(2)	2.845(4)	Ag(2)-I(3)	2.809(4)	Ag(2)-I(5)	2.918(5)
Ag(3)-I(1)	2.925(4)	Ag(3)-I(3)	2.804(4)	Ag(3)-I(4)	2.932(5)	Ag(3)-I(8)	2.799(5)
Ag(4)-I(2)	2.995(5)	Ag(4)-I(5)	2.889(4)	Ag(4)-I(5)#1	2.890(4)	Ag(4)-I(9)	2.823(5)
Ag(5)-I(4)	2.938(5)	Ag(5)-I(7)	2.899(5)	Ag(5)-I(7)#2	2.886(5)	Ag(5)-I(8)	2.794(5)
Ag(6)-I(1)	2.952(5)	Ag(6)-I(4)	2.838(5)	Ag(6)-I(6)	2.817(5)	Ag(6)-I(7)	2.924(5)
Ag(1)-Ag(2)	3.170(5)	Ag(1)-Ag(4)	3.106(4)	Ag(1)-Ag(6)	3.283(5)	Ag(2)-Ag(3)	3.333(5)
Ag(2)-Ag(4)	3.277(5)	Ag(3)-Ag(6)	3.227(5)	Ag(3)-Ag(5)	3.287(5)	Ag(4)-Ag(4)#1	3.125(6)
Ag(5)-Ag(5)#2	3.132(7)	Ag(5)-Ag(6)	3.372(5)				
Symmetry codes: #1 -x+1,-y+2,-z; #2 -x+1,-y+1,-z+1							

3							
Sm(1)-O(1)	2.41(4)	Sm(1)-O(2)	2.36(6)	Sm(1)-O(3)	2.38(5)	Sm(1)-O(4)	2.41(7)
Sm(1)-O(5)	2.37(5)	Sm(1)-O(6)	2.41(4)	Sm(1)-O(7)	2.35(5)	Sm(1)-O(8)	2.39(6)
Ag(1)- I(2)	2.977(9)	Ag(1)-I(7)	2.886(10)	Ag(1)-I(7)#2	2.877(10)	Ag(1)-I(8)	2.813(9)
Ag(2)- I(1)	2.910(8)	Ag(2)-I(3)	2.794(8)	Ag(2)-I(4)	2.932(10)	Ag(2)-I(9)	2.777(11)
Ag(3)- I(1)	2.945(9)	Ag(3)-I(2)	2.827(11)	Ag(3)-I(3)	2.787(9)	Ag(3)-I(7)	2.911(8)
Ag(4)-I(1)	2.973(11)	Ag(4)- I(2)	2.874(9)	Ag(4)-I(6)	2.786(8)	Ag(4)-I(8)	2.812(8)
Ag(5)- I(1)	2.952(9)	Ag(5)-I(4)	2.825(8)	Ag(5)-I(5)	2.909(10)	Ag(5)-I(6)	2.796(11)
Ag(6)-I(4)	2.916(11)	Ag(6)-I(5)	2.894(8)	Ag(6)-I(5)#1	2.869(8)	Ag(6)-I(9)	2.788(11)
Ag(1)-Ag(1)#2	3.133(12)	Ag(1)-Ag(3)	3.248(11)	Ag(1)-Ag(4)	3.102(9)	Ag(2)-Ag(5)	3.224(10)
Ag(2)-Ag(3)	3.316(11)	Ag(3)-Ag(4)	3.169(10)	Ag(2)-Ag(6)	3.289(10)	Ag(4)-Ag(5)	3.269(10)
Ag(5)-Ag(6)	3.357(11)	Ag(6)-Ag(6)#1	3.123(14)				
Symmetry codes: #1 -x+1,-y+2,-z+1; #2 -x+1,-y+3,-z							

Table S2 Selected Bond Lengths (Å) for 4-6

4							
La-O(1)	2.503(17)	La-O(2)	2.434(19)	La-O(3)	2.505(17)	La-O(4)	2.48(2)
La-O(5)	2.534(16)	La-O(6)	2.43(2)	La-O(7)	2.501(15)	La-O(8)	2.531(19)
Bi(1)-I(3)	3.278(2)	Bi(1)-I(4)	3.331(2)	Bi(1)-I(5)	2.939(2)	Bi(1)-I(6)	2.939(2)
Bi(1)-I(7)	3.226(3)	Bi(1)-I(8)	2.927(2)	Bi(2)-I(1)	2.945(2)	Bi(2)-I(2)	2.993(2)
Bi(2)-I(7)	3.144(2)	Bi(2)-I(3)	3.257(2)	Bi(2)-I(4)	3.221(2)	Bi(2)-I(9)	2.946(3)
α-5							
Pr(1)-O(1)	2.392(10)	Pr(1)-O(2)	2.293(14)	Pr(1)-O(3)	2.336(10)	Pr(1)-O(4)	2.389(11)
Pr(1)-O(5)	2.400(9)	Pr(1)-O(6)	2.278(13)	Pr(1)-O(7)	2.328(11)	Pr(1)-O(8)	2.326(13)
Bi(1)-I(1)	2.9557(14)	Bi(1)-I(2)	2.9436(14)	Bi(1)-I(3)	2.9376(15)	Bi(1)-I(4)	3.3375(14)
Bi(1)-I(5)	3.2310(15)	Bi(1)-I(6)	3.2569(14)	Bi(2)-I(4)	3.2145(14)	Bi(2)-I(5)	3.1544(14)
Bi(2)-I(6)	3.2662(15)	Bi(2)-I(8)	2.9991(13)	Bi(2)-I(9)	2.9600(16)	Bi(2)-I(7)	2.9601(15)
β-5							
Pr(1)-O(1)	2.385(11)	Pr(1)-O(2)	2.327(12)	Pr(1)-O(3)	2.343(11)	Pr(1)-O(4)	2.289(12)
Pr(1)-O(5)	2.386(10)	Pr(1)-O(6)	2.366(11)	Pr(1)-O(7)	2.345(11)	Pr(1)-O(8)	2.298(13)
Bi(1)-I(1)	2.9318(13)	Bi(1)-I(2)	2.9275(14)	Bi(1)-I(3)	2.9442(13)	Bi(1)-I(4)	3.2195(13)
Bi(1)-I(5)	3.3169(13)	Bi(1)-I(6)	3.2508(13)	Bi(2)-I(4)	3.1371(13)	Bi(2)-I(5)	3.1973(12)
Bi(2)-I(6)	3.2553(14)	Bi(2)-I(7)	2.9524(13)	Bi(2)-I(8)	2.9456(14)	Bi(2)-I(9)	2.9921(13)
6							
Er(1)-O(1)	2.484(8)	Er(1)-O(2)	2.476(10)	Er(1)-O(3)	2.389(9)	Er(1)-O(4)	2.459(10)
Er(1)-O(5)	2.445(9)	Er(1)-O(6)	2.475(8)	Er(1)-O(7)#1	2.384(11)	Er(1)-O(8)#2	2.439(8)
Bi(1)-I(1)	2.9926(11)	Bi(1)-I(2)	3.2093(10)	Bi(1)-I(4)	3.2470(11)	Bi(1)-I(5)	2.9494(10)
Bi(1)-I(6)	3.1426(11)	Bi(1)-I(9)	2.9471(12)	Bi(2)-I(2)	3.3268(10)	Bi(2)-I(3)	2.9457(11)
Bi(2)-I(4)	3.2704(11)	Bi(2)-I(6)	3.2208(11)	Bi(2)-I(7)	2.9299(11)	Bi(2)-I(8)	2.9210(11)

Table S3 Hydrogen bridging details of 1-3

Compound	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry codes
1	C(7)-H(7C)···O(2)	0.96	2.36	2.77(14)	105	

	C(12)-H(12)···O(2)	0.92	2.43	3.10(11)	130	
	C(25)-H(25A)···O(8)	0.96	2.55	2.90(15)	101	
	C(20)-H(20B)···O(1)	0.97	2.58	3.53(8)	167	1+x,y,z
	C(2)-H(2)···I(3)	0.93	3.03	3.90(4)	156	-x,1-y,1-z
	C(17)-H(17C)···I(9)	0.96	3.04	3.94(12)	156	-x,1-y,1-z
	C(10)-H(10A)···O(3)	0.96	2.38	2.79(6)	105	
	C(10)-H(10C)···I(4)	0.96	3.04	3.99(6)	171	x,-1+y,z
	C(13)-H(13A)···O(4)	0.95	2.27	2.71(6)	107	
2	C(18)-H(18A)···O(6)	0.96	2.24	2.68(4)	107	
	C(21)-H(21A)···O(7)	0.96	2.43	2.82(6)	103	
	C(24)-H(24A)···O(8)	0.96	2.54	2.90(9)	102	
	C(26)-H(26A)···O(5)	0.95	2.24	2.65(9)	104	
	C(7)-H(7B)···O(2)	0.96	2.49	3.44(14)	172	1+x,y,z
	C(9)-H(9)···O(5)	0.94	2.54	3.07(10)	116	
	C(16)-H(16C)···O(1)	0.96	2.29	2.76(12)	109	
3	C(22)-H(22B)···I(9)	0.97	3.02	3.95(7)	160	1-x,2-y,1-z
	C(24)-H(24)···O(7)	0.92	2.53	3.05(19)	116	
	C(25)-H(25C)···O(4)	0.93	2.09	2.5(4)	107	
	C(26)-H(26C)···O(7)	0.95	2.39	2.76(19)	103	

Table S4 Hydrogen bridging details of 4-6

Compound	D–H···A	D–H/Å	H···A/Å	D···A/Å	∠(D–H···A)/º	Symmetry codes
	C(1)-H(1)···O(7)	0.93	2.54	3.23(5)	132	
	C(6)-H(6)···I(6)	0.93	3.03	3.81(3)	143	1+x,1/2-y,1/2+z
	C(9)-H(9)···O(3)	0.93	2.52	3.26(4)	137	
	C(20)-H(20A)···O(4)	0.96	2.48	2.86(8)	103	
4	C(22)-H(22C)···O(6)	0.96	2.36	2.78(6)	106	
	C(23)-H(23C)···I(1)	0.96	2.96	3.82(6)	148	
	C(24)-H(24)···O(5)	0.93	2.48	3.03(4)	118	
	C(26)-H(26C)···O(7)	0.96	2.38	2.76(4)	103	
	C(27)-H(27)···O(2)	0.94	2.60	3.14(5)	117	
	C(6)-H(6)···O(3)	0.93	2.35	3.068(18)	133	
	C(10)-H(10)···O(7)	0.93	2.52	3.197(18)	130	
	C(13)-H(13B)···O(2)	0.96	2.36	2.75(3)	104	
α-**5**	C(14)-H(14)···O(1)	0.93	2.38	2.886(18)	114	
	C(17)-H(17)···O(6)	0.93	2.41	2.96(2)	118	
	C(23)-H(23)···O(5)	0.93	2.42	2.894(19)	112	
	C(1)-H(1)···I(3)	0.93	3.00	3.767(16)	141	
	C(6)-H(6)···O(7)	0.93	2.30	3.034(19)	136	1+x,y,z
	C(10)-H(10)···O(3)	0.93	2.44	3.156(19)	133	
β-**5**	C(14)-H(14)···O(5)	0.93	2.40	2.883(19)	113	
	C(18)-H(18C)···O(4)	0.96	2.46	2.79(3)	100	
	C(20)-H(20)···O(4)	0.93	2.44	2.97(2)	117	

	C(22)-H(22C)···O(6)	0.96	2.44	2.77(5)	100	
	C(23)-H(23)···O(1)	0.93	2.35	2.861(19)	115	
	C(27)-H(27B)···I(8)	0.96	3.04	3.99(3)	172	-1+x,y,z
6	C(1)-H(1)···O(8)	0.93	2.42	3.158(15)	137	-1+x,y,-1+z
	C(6)-H(6)···I(3)	0.93	3.03	3.775(12)	138	-1+x,y,-1+z
	C(7)-H(7)···O(5)	0.93	2.49	3.229(16)	136	-1+x,y,z
	C(11)-H(11)···O(3)	0.93	2.52	3.076(19)	118	
	C(12)-H(12A)···O(2)	0.96	2.38	2.73(4)	101	
	C(19)-H(19C)···O(4)	0.96	2.39	2.79(3)	105	
	C(20)-H(20)···O(1)	0.93	2.55	3.018(15)	112	
	C(24)-H(24A)···O(7)	0.96	2.44	2.78(3)	100	
	C(26)-H(26)···O(6)	0.93	2.49	2.998(15)	115	1+x,y,1+z
	C(27)-H(27C)···O(8)	0.96	2.38	2.769(16)	104	

Table S5. π–π stacking interactions in 4-6 (lengths in Å and angles in °)

Compound	Cg(I)···Cg(J)	Symmetry code	Dist. Centroids	Dihedral angle	CgI_Perp dist.	CgJ_Perp dist.
4	Cg(1)→Cg(1)	1-x,1-y,1-z	3.712(15)	0	3.624(10)	3.624(10)
	Cg(1)→Cg(2)	-x,1-y,1-z	3.712(15)	0.0(12)	3.624(10)	3.624(10)
	Ring Cg(1): N(5)→C(6)→C(4)→C(8) →C(9)→					
	Ring Cg(2): C(4)→C(5)→C(6) →N(5)→C(8)→C(9)→					
***α*-5**	Cg(1)→Cg(2)	x,1/2-y,-1/2+z	3.645(3)	4.3(3)	3.2450(19)	3.1126(19)
	Ring Cg(1): C(9)→C(10)→C(11)→C(12)→;Ring Cg(2): C(5)→C(6)→C(7)→C(8)→					
***β*-5**	Cg(1)→Cg(2)	-1+x,y,z	3.556(6)	3.6(6)	3.253(4)	3.158(4)
	Cg(3)→Cg(4)	x,1+y,z	3.578(6)	2.9(6)	3.248(4)	3.170(4)
	Ring Cg(1): C(13)→C(14)→C(15)→C(16)→;Ring Cg(2): C(1)→C(2)→C(3)→C(4)→					
	Ring Cg(3): C(9)→C(10)→C(11)→C(12)→;Ring Cg(4): C(5)→C(6)→C(7)→C(8)→					
6	Cg(1)→Cg(2)	-1+x,1/2-y,-1/2+z	3.675(3)	4.3(3)	3.1292(19)	3.2559(19)
	Cg(1)→Cg(3)	x,1/2-y,1/2+z	3.644(3)	4.3(3)	3.1123(19)	3.2448(19)
	Ring Cg(1): C(9)→C(10)→C(11)→C(12)→;Ring Cg(2): C(5)→C(6)→C(7)→C(8)→					
	Ring Cg(3): N(2) →C(22)→C(23)→C(24)→C(25)→C(26)→;					

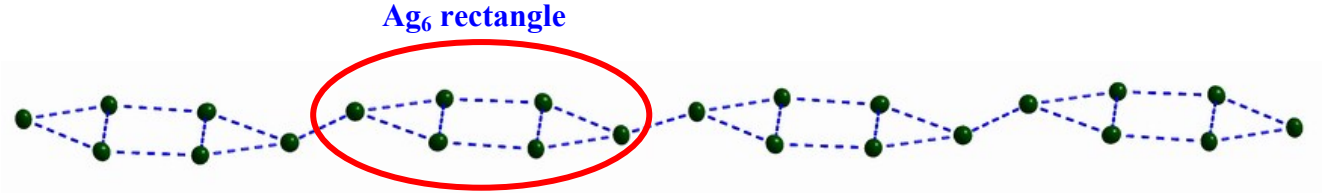
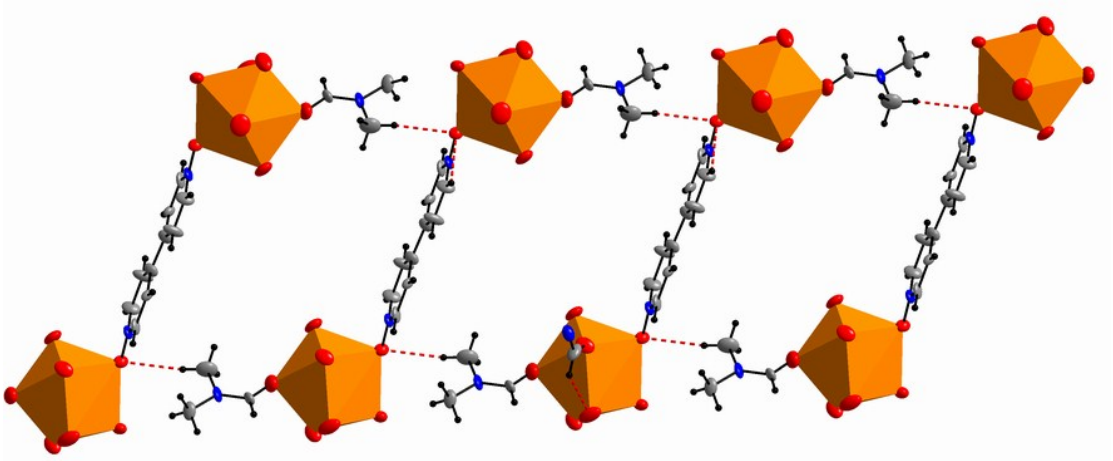
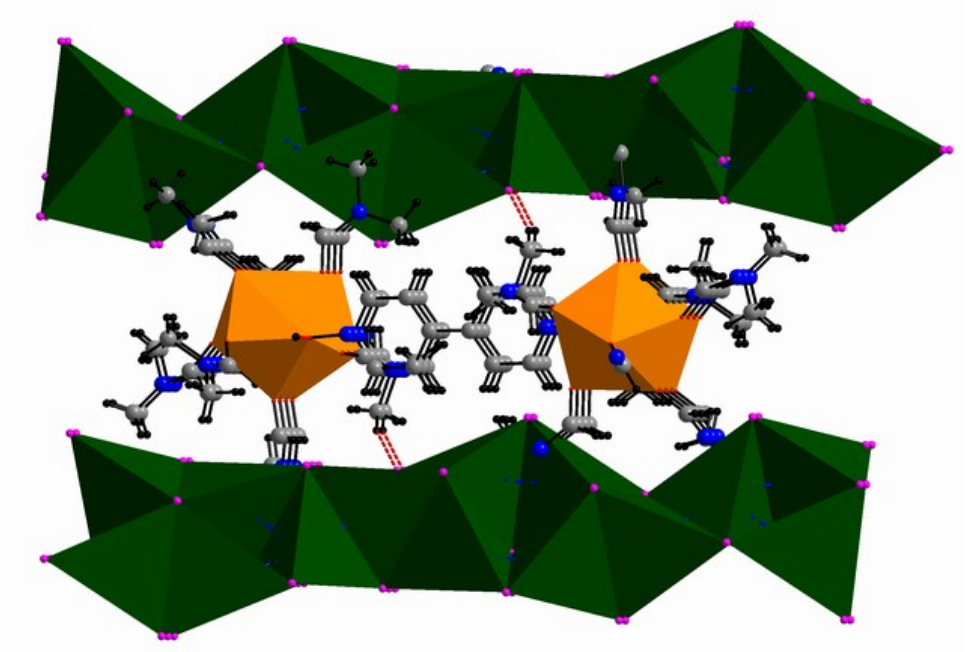


Fig. S1 Structure of Ag_6 rectangle and the silver-chain based on argentophilicity interactions

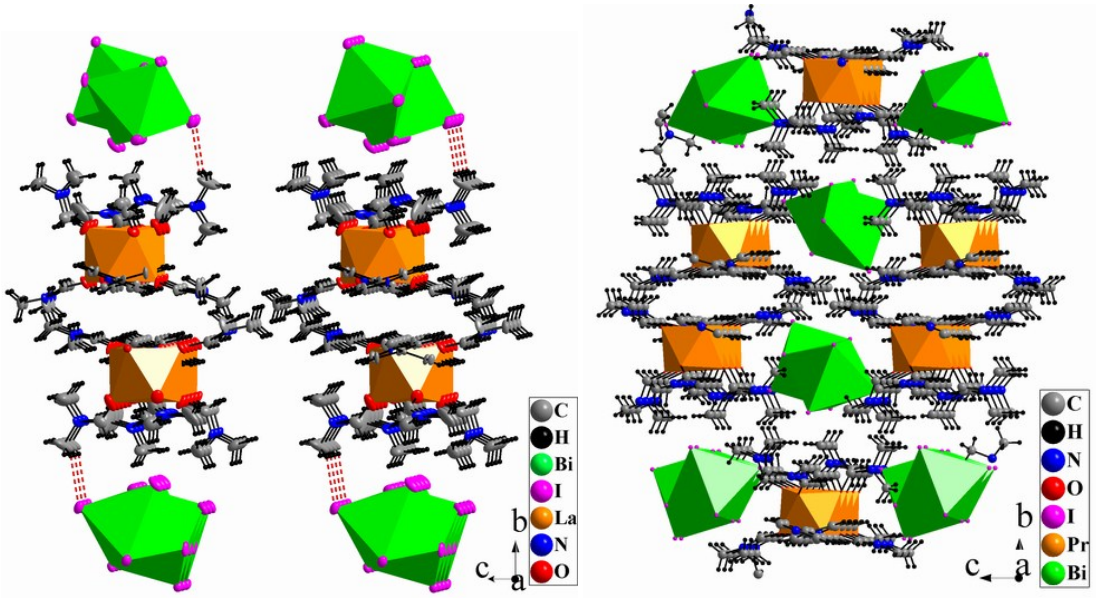


(a)



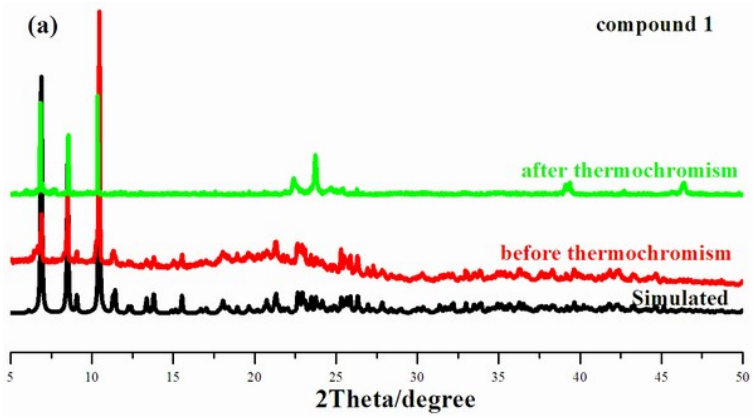
(b)

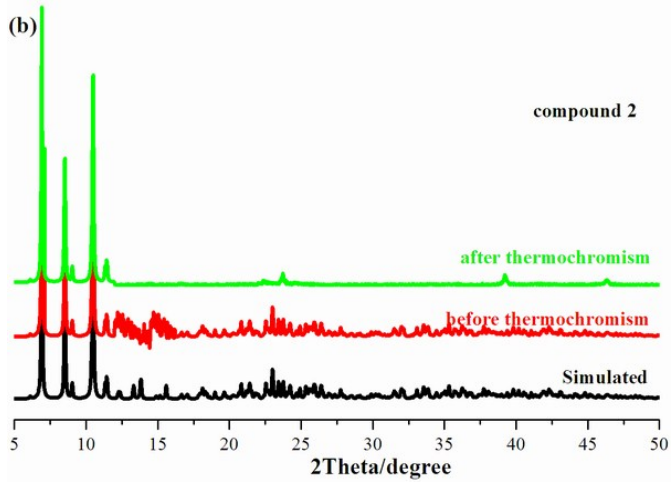
Fig. S2 (a) the 1-D $[Ln_2(dpdo)(DMF)_{14}]_n^{6n+}$ chain bridged by hydrogen bonds (other coordinated DMF were omitted for clarity); (b) 3-D network based on hydrogen bonds between $[Ln_2(dpdo)(DMF)_{14}]_n^{6n+}$ chain and $(Ag_{12}I_{18})_n^{6n-}$chains of 3

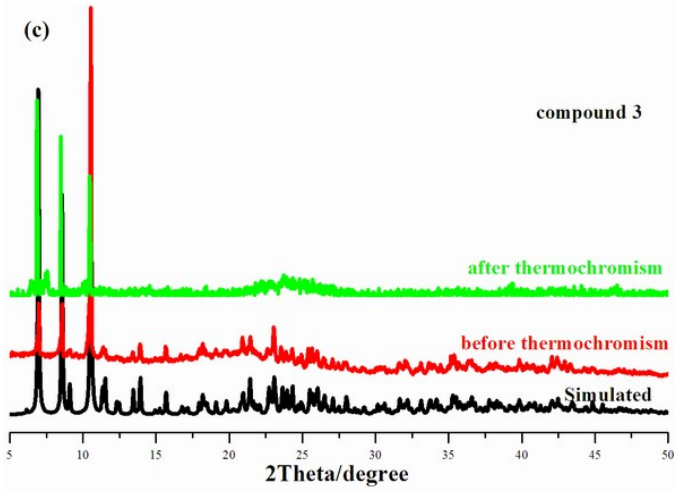


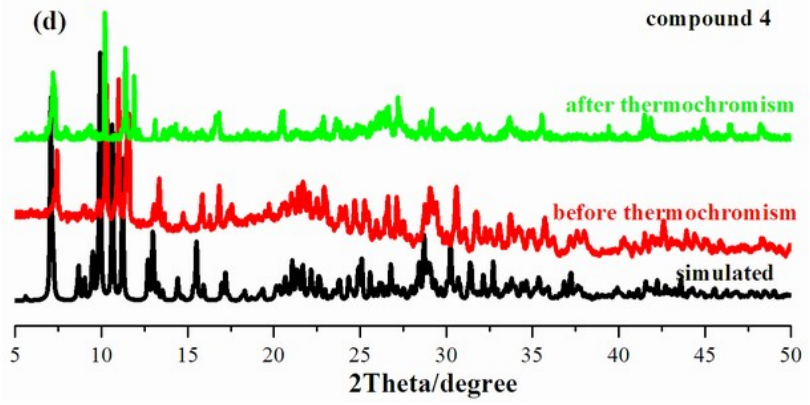
(a) (b)

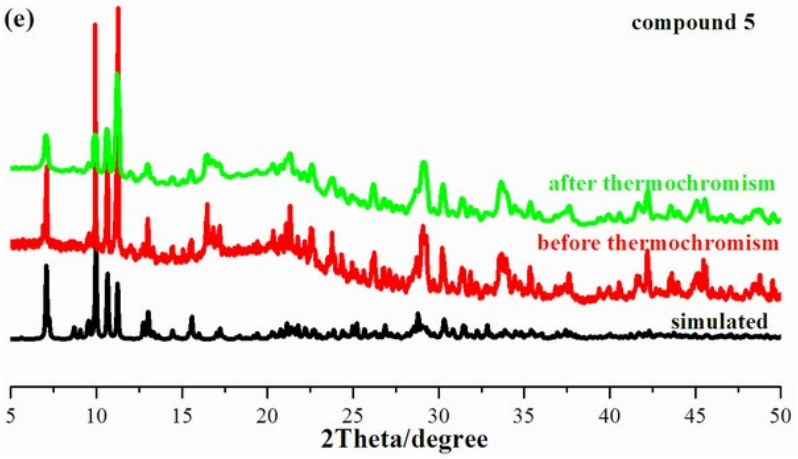
Fig. S3 Packing diagram of 4, 6 (a) and 5 (b)






(c)
compound 3
after thermochromism
before thermochromism
Simulated
5
10
15
20
25
30
35
40
45
50
2Theta/degree


(d)
compound 4
after thermochromism
before thermochromism
simulated
5
10
15
20
25
30
35
40
45
50
2Theta/degree


(e)
compound 5
after thermochromism
before thermochromism
simulated
5
10
15
20
25
30
35
40
45
50
2Theta/degree

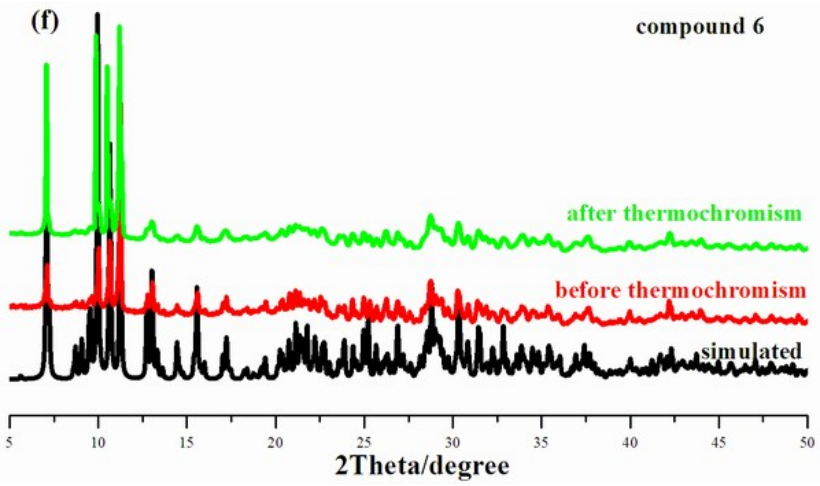
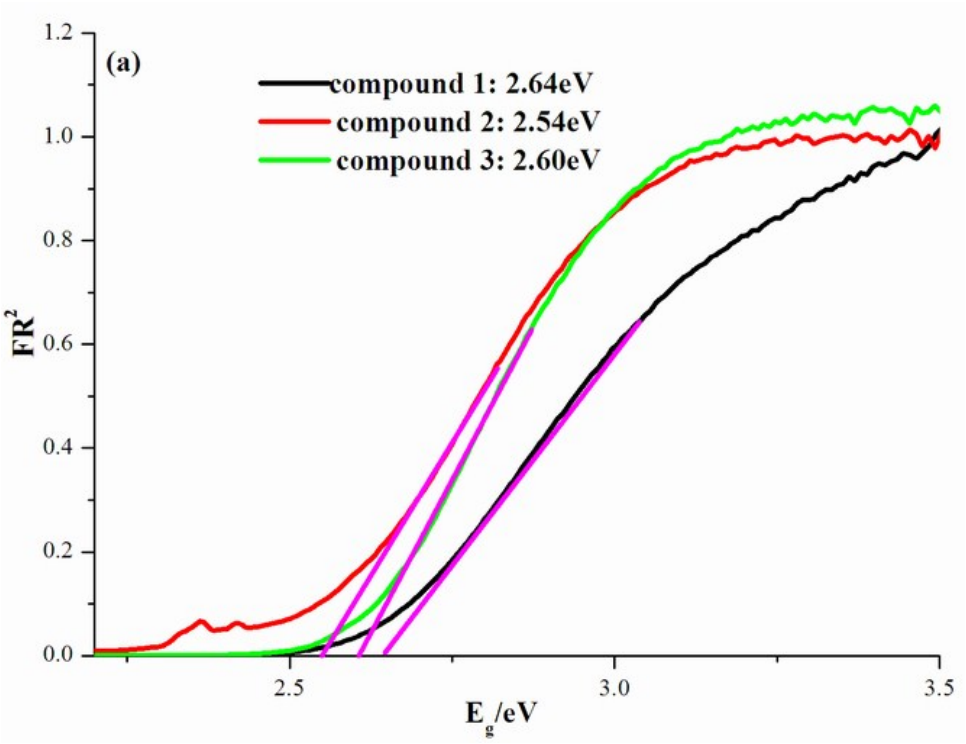


Fig. S4 Powder X-ray diffraction (PXRD) patterns before and after thermochromism for compounds 1-6



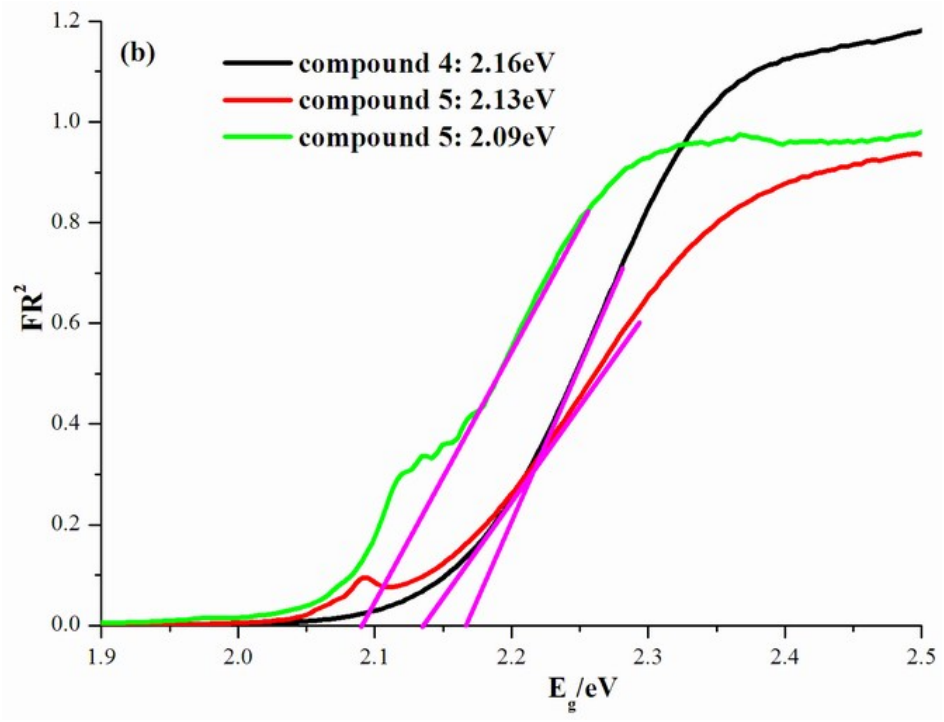
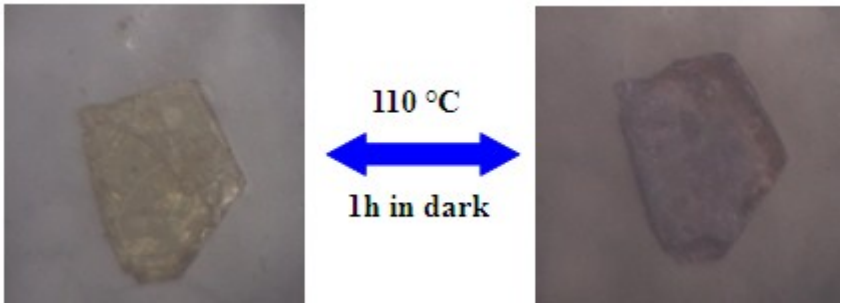
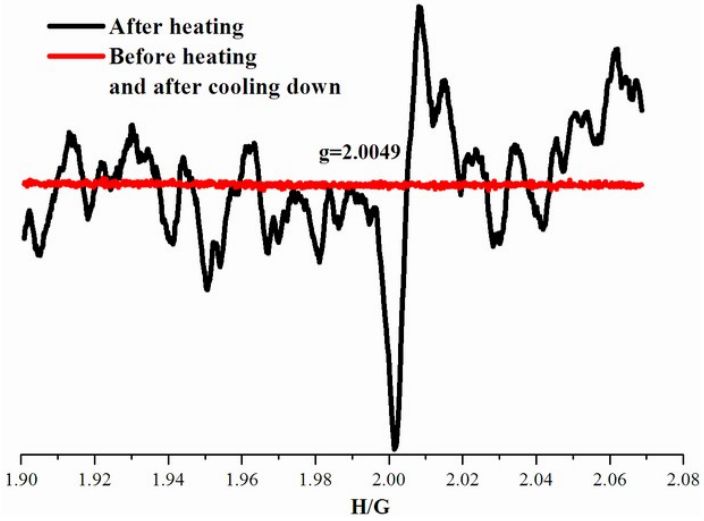


Fig. S5 Diffuse reflectance spectra of 1-3 (a) and 4-6 (b) in Kubelka-Munk unit

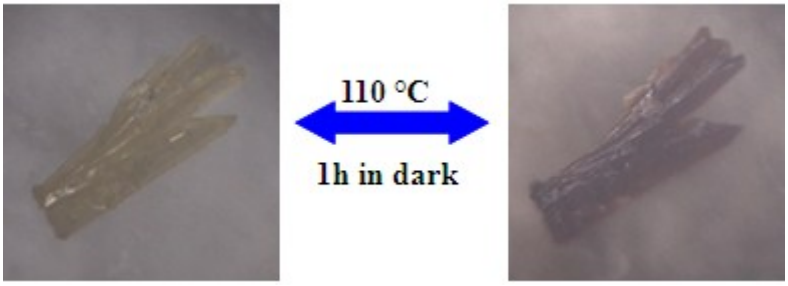


(a)

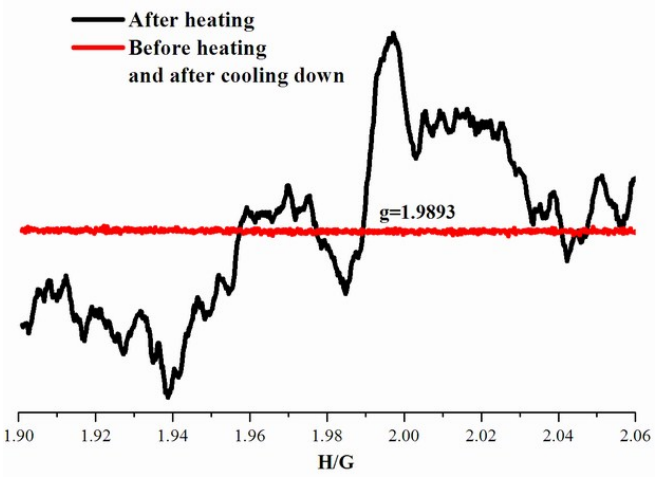


(b)

Fig. S6 Thermochromic behavior (a); ESR spectrum of before/after heating and after cooling down in 2 (b)

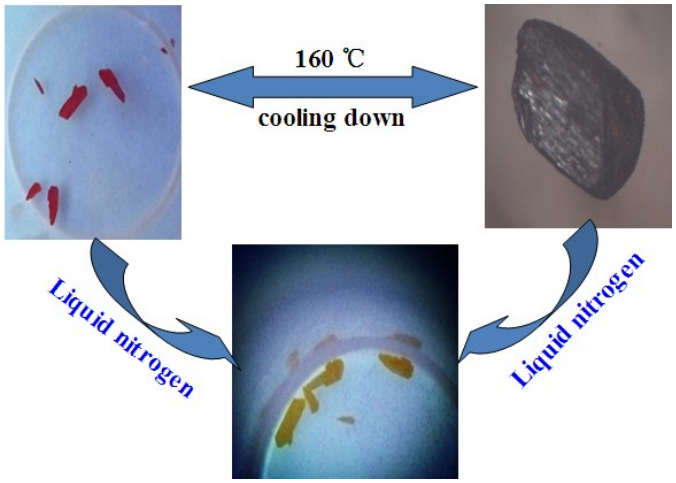


(a)

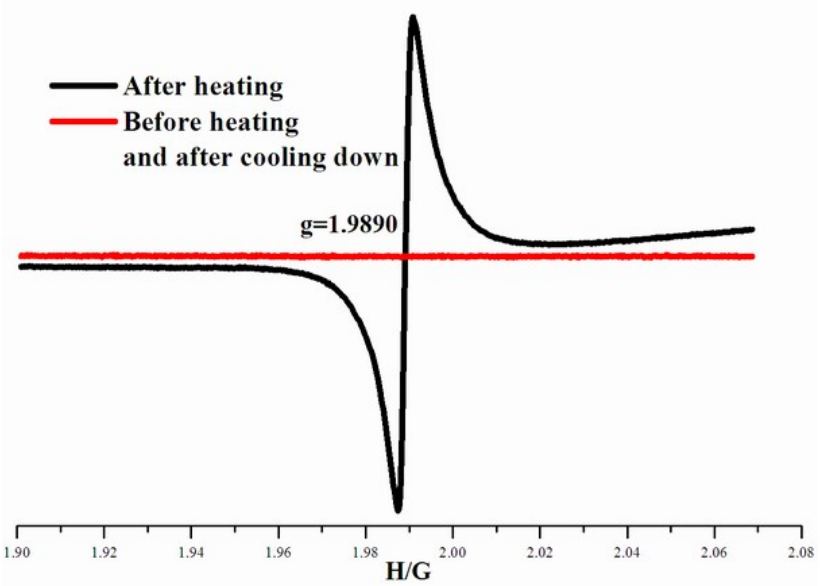


(b)

Fig. S7 Thermochromic behavior (a); ESR spectrum of before/after heating and after cooling down in 3 (b)

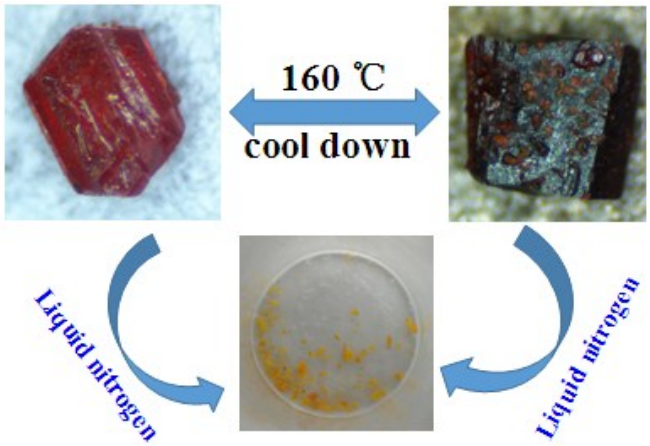


(a)

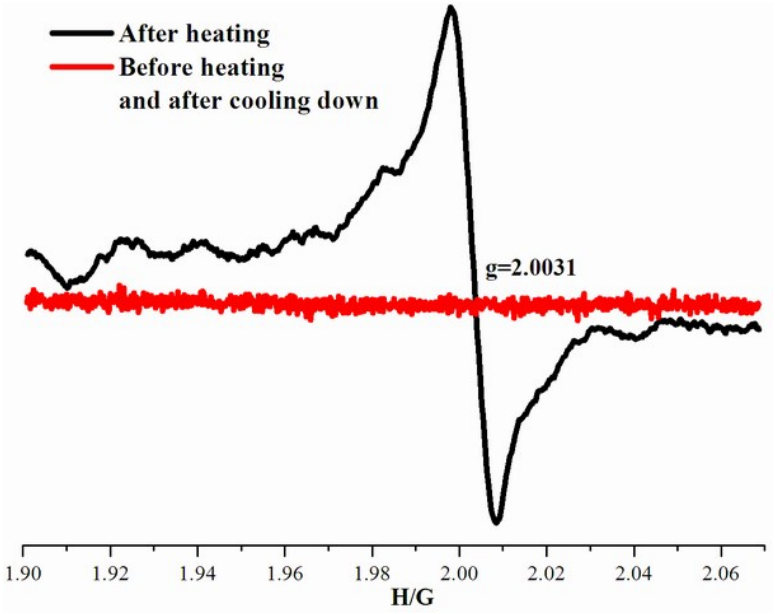


(b)

Fig. S8 (a) Thermochromic behavior of 5; (b) ESR spectrum of before/after heating and after cooling down in 5



(a)



(b)

Fig. S9 (a) Thermochromic behavior of 6; (b) ESR spectrum of before/after heating and after cooling down in 6

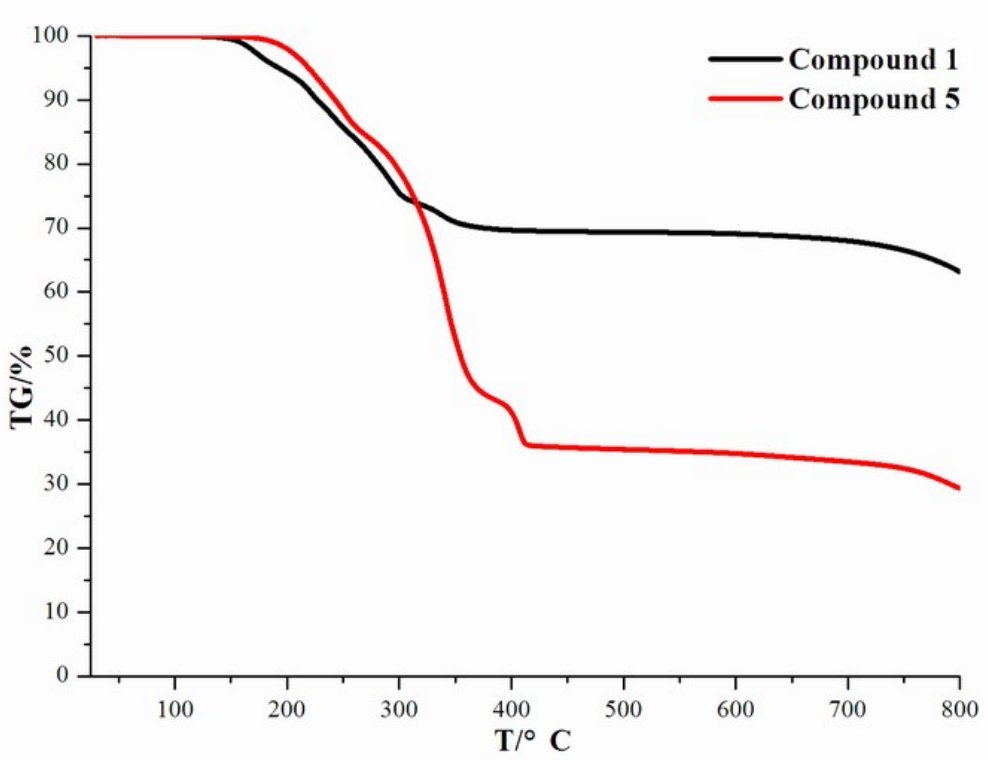


Fig. S10 Thermogrevimetric curves for 1 and 5

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