Electronic Supplementary Information (ESI) for

The conformational behavior of multivalent tris (imidazolium) cyclophanes in the hybrids with metal (pseudo)halides or polyoxometalates

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1. Synthesis

{[$CuBr_3$]$_{1.5}$· L1·(CH_3CN)} (**1a**) Acetonitrile and water solution of L1 ·Br_3(0.0084 g, 0.01 mmol) was added to a stirring colorless solution of CuBr (0.0014 g, 0.01 mmol) dissolved in 1.5 mL DMF in the presence of excess KBr (0.0060 g, 0.05 mmol). The resulting mixture was stirred for 5 min and filtered. Then the solution was slowly evaporated in a vial at room temperature. The colorless prismatic crystals of **1a** suitable for X-ray analysis were obtained in 9% yield after a week. The product was not soluble in common solvents. IR(KBr): 3441.64(s), 1634.55(w), 1560.93(m), 1463.02(w), 1341.07(w), 1194.37(w), 1124.65(m), 1030.86(w), 927.97(w), 758.61(w), 575.60(w),564.95(w)cm^{-1}.The prismatic crystals suitable for X-ray analysis were obtained after aweek.

{L1·[CuI_3] 2$I_{0.5}$·(H_2O)} (**1b**) Acetonitrile and water solution of L1·3PF_6^- (0.1043 g, 0.01 mmol) was added to a stirring colorless solution of CuI (0.0019 g, 0.01 mmol) dissolved in 1.5 mL acetonitrile in the presence of excess KI (0.0083 g, 0.05 mmol). The resulting mixture was stirred for 5 min and filtered. Then the solution was slowly evaporated in a vial at room temperature. The colorless prismatic crystals of **1b** suitable for X-ray analysis were obtained in about 15% yield after a week. The product was not soluble in common solvents. IR(KBr): 3456.10(m), 3155.54(w), 1701.02 (w), 1610.48(m), 1561.96(s), 1486.19(m), 1452.35(m), 1340.52(m), 1267.67(w), 1234.15(m), 1189.77(m), 1130.36(m), 842.44(s), 753.40(s), 592.25(w), 558.06(s)cm^{-1}.

{L2·[PbI_5]} (2a)1.5 mL acetonitrile and 6 drops of water solution of L2 ·Br_3(0.0071 g, 0.01 mmol) was added to a stirring colorless solution of PbI_2 (0.0046 g, 0.01 mmol) dissolved in 1.5 mL DMF solution in the presence of excess KI (0.0083 g, 0.05 mmol). The resulting yellow mixture was stirred for 5 min and filtered. Then the solution was slowly evaporated in a vial at room temperature. The light yellow prismatic crystals of **2a**suitable for X-ray analysis were obtained in about 10% yield after a week. The product was not soluble in common solvents. IR(KBr): 3444.73(w), 1660.51(w), 1561.24(w), 1449.87(w), 1319.20(w), 1180.13(w), 1131.97(s), 805.38(m), 749.70(m), 613.55(m) 578.04(w) cm^{-1}.

{$(L2)_2$·[$Cu_2I_5]_2$} (2b) 1.5 mL acetonitrile and 6 drops of water solution of L2 ·Br_3(0.0071 g, 0.01 mmol) was added to a stirring colorless solution of CuI (0.0019 g, 0.01 mmol) dissolved in 1.5 mL acetonitrile solution in the presence of excess KI (0.0083 g, 0.05 mmol). The resulting yellow mixture was stirred for 5 min and filtered. Then the solution was slowly evaporated in a vial at room temperature. The prismatic crystals of **2b**suitable for X-ray analysis were obtained in about 15% yield after a week. The product was not soluble in common solvents. IR(KBr): 3486.48(s), 3099.56(m), 1615.11(w), 1564.69(w), 1320.97(w), 1130.15(s), 809.23 (m), 751.13(m), 614.33(m) cm^{-1}.

{L3·$Ag(SCN)_4$·(CH_3CN) ·$2H_2O$} (3a) Acetonitrile and water solution of L3·Br_3(0.0076g, 0.01 mmol) was added to a stirring colorless solution of AgSCN (0.0016 g, 0.01 mmol) dissolved in 1.5 mL acetonitrile solution in the presence of excess KSCN (0.0083 g, 0.05 mmol). The resulting mixture was stirred for 5 min and filtered. Then the solution was slowly evaporated in a vial at room temperature. The colorless crystals of **3a** suitable for X-ray analysis were obtained after a week in about 12% yield. IR(KBr): 3415.23(m), 3136.41 (m), 3106.72 (m), 2083.44(s), 2056.83(s), 1567.06(s), 1313.97(m), 1227.27(w), 1128.42(s), 1027.37(w), 918.16(w), 817.85(s), 804.13(s), 739.32(m), 615.63(s), 562.96(w) cm^{-1}.

{L3·[HgI_4] ·I} (3b) The procedure was similar to the synthesis of compound **3a**, except that$HgI_2$was used instead of AgSCN,and KI was replaced by KSCN. Light yellow precipitation appeared and maintained 3 days at 80 °C under the solvent

thermal condition and then drop to 30 °C in 24 hours. The light yellow crystal of **3b** was obtained after a week in a 9% yield. The product was not soluble in common solvents. IR(KBr): 3449.36(m), 3128.98(vs), 3096.91(vs), 1563.11(s), 1444.72(m), 1381.97(w), 1310.24(s), 1230.01(w), 1125.79(s), 813.63(vs), 802.13(vs), 735.57(s), 720.70(vs), 613.69(s) cm^{-1}.

The synthesisof**4:** $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$(0.062 g, 0.05 mmol), L2·Br_3(0.1071 g, 0.15 mmol), $CuCl_2\cdot 2H_2O$ and 10 mL H_2O were mixed well at room temperature, the mixture was stirred with small magnets for 1 hour. Then the mixture was sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 130 °C under autogenously pressure for 4 days. After slow cooling to roomtemperature with therate 10 °C h^{-1}, purple crystals were precipitated from the bottom of the kettle in a 40% yield. IR(KBr): 3443.78(m), 1636.96(w), 1563.19(w), 1457.67(w), 1316.60(w), 1145.67(m), 936.52(m), 911.29(s), 822.68(m), 795.07(m), 750.44(m), 681.60(m), 615.78(m), 571.00(m) cm^{-1}.

Table S1. Solubility test of compounds **1a-4** in common solvents.

	CH_3OH	C_2H_5OH	H_2O	CH_3CN	THF	CH_2Cl_2	$CH_3CH_2OCH_2CH_3$	CH_3COCH_3	DMF
1a	×	×	×	×	×	×	×	×	slightly soluble
1b	×	×	×	×	×	×	×	×	slightly soluble
2a	×	×	×	×	×	×	×	×	slightly soluble
2b	×	×	×	×	×	×	×	×	slightly soluble
3a	×	×	×	×	×	×	×	×	slightly soluble
3b	×	×	×	×	×	×	×	×	slightly soluble
4	×	×	×	×	×	×	×	×	×

'×'----- insoluble.

Table S2. Crystal data and structure refinement of compounds **L1-L3 and 1a-4**.

Compound	**L1**·I_3	**L2**·I_3	**L3**·Br_2·I	**1a**
Formula	$C_{39}H_{42}I_3N_7$	$C_{30}H_{39}I_3N_6O_3$	$C_{33}H_{43}Br_2IN_6O_2$	$C_{41}H_{46}N_8(CuBr_3)_{1.5}$
Formula weight	989.49	912.37C	842.45	1105.55
Crystal system	monoclinic	Monoclinic	Monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1$	$P2_1/m$	$P2_1/c$
a/Å	13.34926(19)	8.7246(3)	10.0714(5)	15.9746(2)
b/Å	16.7927(2)	18.8111(5)	17.5006(5)	35.1240(5)
c/Å	36.5631 (6)	11.1783(4)	10.6518(6)	16.4115(2)
α(°)	90.00	90	90	90
β(°)	90.0824(13)	111.852(5)	115.604(7)	90
γ(°)	90.00	99.191(3)	90.00	90
V/Å^3	8196.4 (2)	1702.76 (11)	1693.09(16)	9208.4(2)
Z	8	2	2	4
ρ/Mg cm^{-3}	1.604	1.779	1.653	1.595
μ/mm^{-1}	2.323	2.792	3.345	5.769
F(000)	3872.0	888.0	844.0	4392.0
Crystal size/mm^3	0.24 × 0.18× 0.11	0.13× 0.12× 0.10	0.14 × 0.11× 0.10	0.18 × 0.15×0.08
T/K	293(2)	293(2)	293(2)	293(2)
Reflections collected	37281	7242	7436	23151
data/restrains/ parameters	16019/0/898	5278/10/394	3569/2/217	8214/0/518
GOF on F^2	1.039	1.000	1.033	1.089
Final R indices [I>2σ (I)]	R_1 = 0.0659, wR_2 = 0.1829	R_1 = 0.0426, wR_2 = 0.0637	R1= 0.0534, wR2= 0.1080	R1=0.1134, wR2= 0.2688
R indices (all data)	R_1 = 0.0944, wR_2 = 0.2035	R_1 = 0.0583, wR_2 = 0.0713	R_1 =0.0846, wR_2 = 0.1223	R_1 = 0.1191, wR_2 = 0.2713
Largest diff. peak	2.63	0.51	0.62	1.41
hole(eÅ^{-3})	-3.16	-0.60	-0.58	-1.02
Compound	**1b**	**2a**	**2b**	**3a**
Formula	$C_{39}H_{44}CuI_4N_7O$	$C_{30}H_{33}I_5N_6Pb$	$C_{60}H_{69}Cu_4I_{10}N_{12}O_2$	$C_{39}H_{46}AgN_{11}O_2S_4$

Formula weight	1197.95	1319.31	2513.43	936.98
Crystal system	monoclinic	Triclinic	Monoclinic	orthorhombic
Space group	$P2_1/c$	P-1	$P2_1/c$	Pnnm
a/Å	16.6035(5)	8.7292(4)	8.6659(3)	20.7409(5)
b/Å	14.3351(3)	13.9897(6)	43.0938(10)	17.1057(3)
c/Å	17.8354(3)	15.3377(7)	22.4966(6)	11.6678(2)
α(°)	90	90.287(3)	90.00	90.00
β(°)	95.774(2)	98.190(4)	112.628(4)	90.00
γ(°)	90	99.191(3)	90.00	90.00
V/Å^3	4223.53(16)	1829.38 (13)	7754.6(4)	4139.61(14)
Z	4	2	4	2
ρ/Mg cm^{-3}	1.884	2.395	2.153	1.503
μ/mm^{-1}	3.480	8.859	32.858	6.196
F(000)	2304	1204	4700	1936.0
Crystal size/mm^3	0.28× 0.21×0.09	0.23× 0.12× 0.05	0.19× 0.16× 0.06	0.32 × 0.13× 0.02
T/K	293(2)	293(2)	293(2)	293(2)
Reflections collected	19145	14965	13509	10590
data/restrains/ parameters	8609/0/483	7435/0/382	13509/12/813	3902/12/300
GOF on F^2	1.021	1.026	1.070	1.098
Final R indices [I>2σ (I)]	R1=0.0501, wR2= 0.1127	R1 = 0.0438, wR2 = 0.1017	R1 = 0.0795, wR2 = 0.2294	R1 = 0.0682, wR2 = 0.1866
R indices (all data)	R_1 = 0.0820, wR_2 = 0.1306	R1 = 0.0627, wR2 = 0.1125	R1 = 0.0844, wR2 = 0.2373	R1 =0.0769, wR2 = 0.1931
Largest diff. peak	1.09	1.17	2.62	1.12
hole(eÅ^{-3})	-0.85	-2.16	-1.40	-0.44

Compound	**3b**	**4**
Formula	$C_{33}H_{39}HgI_5N_6$	$C_{120}H_{162}Mo_{20}N_{24}O_{81}$
Formula weight	1354.79	5155.53
Crystal system	monoclinic	Orthorhombic
Space group	$P2_1/c$	$Cmc2_1$
a/Å	10.7081(3)	11.3449(3)

b/Å	16.2105(3)	20.7592(6)
c/Å	27.4270(8)	17.6129(6)
α(o)	90.00	90
β(o)	125.510(4)	90
γ(o)	90.00	90
V/Å^3	3875.4(2)	4148.0(2)
Z	4	1
ρ/Mg cm^{-3}	2.322	2.064
μ/mm^{-1}	7.986	12.817
F(000)	2496.0	2538.0
Crystal size/mm^3	0.20× 0.18× 0.15	0.30× 0.09× 0.03
T/K	293(2)	293(2)
Reflections collected	18683	7783
data/restrains/ parameters	7907/0/412	2926/13/315
GOF on F^2	1.041	1.053
Final R indices [I>2σ (I)]	R1=0.0350, wR2= 0.0764	R1 = 0.0348, wR2 = 0.0879
R indices (all data)	R1 = 0.0463, wR2 = 0.0819	R1 = 0.0387, wR2 = 0.0926
Largest diff. peak	1.33	0.55
hole(eÅ^{-3})	-0.95	-0.73

Table S3. Selected bond lengths (Å) and bond angles (°) for **1a**-**4**.

Compound **1a**					
Br(1)-Cu(1)	2.336(3)	Br(2)-Cu(1)	2.399(3)	Br(3)-Cu(1)	2.380(3)
Br(4)-Cu(2)	2.380(6)	Br(5)-Cu(2)	2.423(6)	Br(6)-Cu(2)	2.386(6)
Br(1)-Cu(1)-Br(2)	126.69(11)	Br(1)-Cu(1)-Br(3)	123.45(11)	Br(3)-Cu(1)-Br(2)	109.82(11)
Br(4)-Cu(2)-Br(5)	120.0(2)	Br(4)-Cu(2)-Br(6)	124.3(3)	Br(6)-Cu(2)-Br(5)	115.6(2)
Compound **1b**					
Cu(1)-I(1)	2.5953(14)	Cu(1)-I(2)	2.5491(11)	Cu(1)-I(3)	2.5636(13)
I(2)-Cu(1)-I(1)	115.45(5)	I(2)-Cu(1)-I(3)	123.38(4)	I(3)-Cu(1)-I(1)	120.91(5)
Compound **2a**					

I(1)-Pb(1)	3.1403(7)	I(2)-Pb(1)	3.2293(8)	I(3)-Pb(1)	3.2158(8)
I(4)-Pb(1)	3.2732(8)	I(5)-Pb(1)	2.9616(9)		
I(1)-Pb(1)-I(2)a	84.655(19)	I(1)-Pb(1)-I(3)	133.61(2)	I(1)-Pb(1)-I(4)	91.048(19)
I(2)-Pb(1)-I(4)	171.459(19)	I(3)-Pb(1)-I(2)	98.695(19)	I(3)-Pb(1)-I(4)	89.618(19)
I(5)-Pb(1)-I(1)	114.20(2)	I(5)-Pb(1)-I(2)	86.61(2)	I(5)-Pb(1)-I(3)	112.19(2)
I(5)-Pb(1)-I(4)	88.42(2)				
Compound **2b**					
Cu(1) -Cu(2)	2.476(5)	Cu(1) -I(1)	2.493(3)	Cu(1) -I(2)	2.655(4)
Cu(1) -I(3)	2.966(5)	Cu(1) -I(4)	2.756(5)	Cu(2) -I(2)	2.904(5)
Cu(2) -I(3)	2.675(4)	Cu(2) -I(4)	2.817(4)	Cu(2) -I(5)	2.546(4)
Cu(3) -Cu(4)	2.468(5)	Cu(3) -I(6)	2.508(4)	Cu(3) -I(7)	2.709(4)
Cu(3) -I(8)	2.869(6)	Cu(3) -I(9)	2.717(4)	Cu(4) -I(7)	2.818(5)
Cu(4) -I(8)	2.663(4)	Cu(4) -I(9)	2.877(5)	Cu(4) -I(10)	2.540(3)
Cu(2) -Cu(1)-I(1)	163.2(3)	Cu(2) -Cu(1)-I(2)	68.83(15)	Cu(2) -Cu(1)-I(3)	58.05(14)
Cu(2) -Cu(1)-I(4)	64.90(14)	I(1) -Cu(1)-I(2)	123.68(18)	I(1) -Cu(1)-I(3)	106.18(16)
I(1) -Cu(1)-I(4)	118.67(16)	I(2) -Cu(1)-I(3)	101.36(14)	I(2) -Cu(1)-I(4)	100.02(14)
I(4) -Cu(1)-I(3)	104.28(14)	Cu(1) -Cu(2)-I(2)	58.51(15)	Cu(1) -Cu(2)-I(3)	70.18(15)
Cu(1) -Cu(2)-I(4)	62.37(14)	Cu(1) -Cu(2)-I(5)	172.2(2)	I(3) -Cu(2)-I(2)	102.50(15)
I(3) -Cu(2)-I(4)	110.72(14)	I(4) -Cu(2)-I(2)	92.90(12)	I(5) -Cu(2)-I(2)	114.95(17)
I(5) -Cu(2)-I(3)	116.79(15)	I(5) -Cu(2)-I(4)	115.80(16)	Cu(1) -I(2)-Cu(2)	52.67(11)
Cu(2) -I(3)-Cu(1)	51.76(11)	Cu(1) -I(4)-Cu(2)	52.73(11)	Cu(4) -Cu(3)-I(6)	169.7(3)
Cu(4) -Cu(3)-I(7)	65.77(15)	Cu(4) -Cu(3)-I(8)	59.30(15)	Cu(4) -Cu(3)-I(9)	67.19(15)
I(6) -Cu(3)-I(7)	111.81(16)	I(6) -Cu(3)-I(8)	112.69(18)	I(6) -Cu(3)-I(9)	112.34(17)
I(7) -Cu(3)-I(8)	99.75(15)	I(7) -Cu(3)-I(9)	106.87(14)	I(9) -Cu(3)-I(8)	100.59(14)
Cu(3)-Cu(4)-I(7)	61.23(14)	Cu(3)-Cu(4)-I(8)	67.86(16)	Cu(3)-Cu(4)-I(9)	60.53(15)
Cu(3)-Cu(4)-I(10)	171.0(3)	I(7) -Cu(4)-I(9)	99.86(14)	I(8) -Cu(4)-I(7)	102.18(14)
I(8) -Cu(4)-I(9)	101.71(14)	I(10) -Cu(4)-I(7)	118.20(17)	I(10) -Cu(4)-I(8)	120.02(17)
I(10) -Cu(4)-I(9)	111.87(17)	Cu(3) -I(7)-Cu(4)	53.01(12)	Cu(4) -I(8)-Cu(3)	52.84(11)
Cu(3) -I(9)-Cu(4)	52.27(11)				
Compound **3a**					
Ag(1)-S(1)	2.618(3)	Ag(1)-S(2)	2.618(2)	Ag(1)-S(3)	2.607(2)
Ag(1)-S(3)#1	2.607(2)	S(3)-Ag(1)-S(1)	115.33(7)	S(3) #1-Ag(1)-S(1)	115.33(7)
S(1)-Ag(1)-S(2)	91.56(8)	S(3)-Ag(1)-S(2)	116.48(6)	S(3)-Ag(1)-S(3)#1	102.41(12)
S(3) #1-Ag(1)-S(2)	116.48(6)	C(2)-S(2)-Ag(1)	105.3(3)	C(3)-S(3)-Ag(1)	95.0(3)
C(1)-S(1)-Ag(1)	107.2(3)				
Compound **3b**					
Hg(1)-I(1)	2.7997(5)	Hg(1)-I(2)	2.7843(5)	Hg(1)-I(3)	2.8112(5)
Hg(1)-I(4)	2.7980(5)	I(2)-Hg(1)-I(1)	115.401(16)	I(2)-Hg(1)-I(3)	106.457(17)
I(1)-Hg(1)-I(3)	110.154(16)	I(4)-Hg(1)-I(1)	103.392(16)	I(4)-Hg(1)-I(3)	109.318(15)
I(2)-Hg(1)-I(4)	112.071(16)				
Compound **4**					
Mo(1)-Mo(2)	3.1646(11)	Mo(1)-O(1)	1.706(6)	Mo(1)-O(2)	1.686(8)

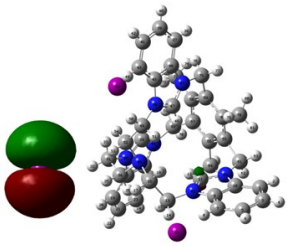
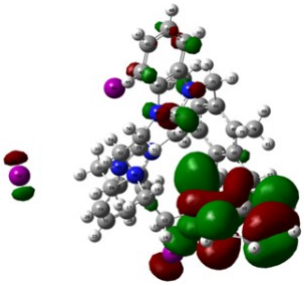
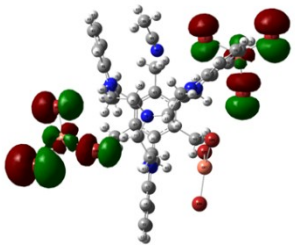
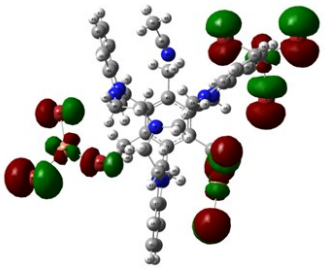
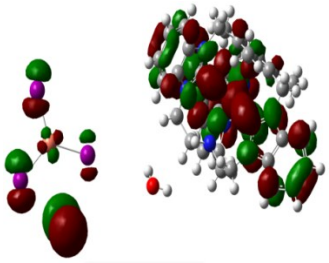
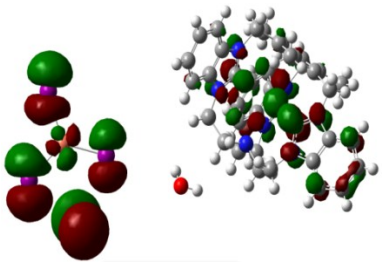
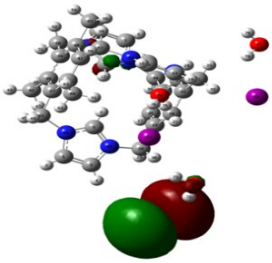
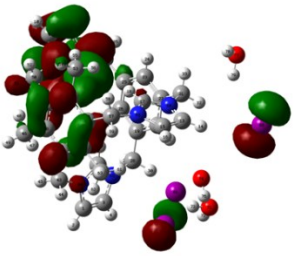
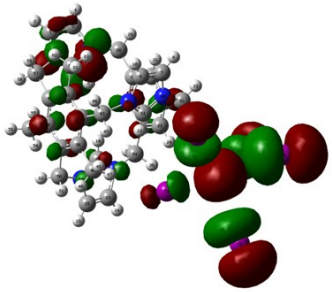
Mo(1)-O(3)	1.927(5)	Mo(1)-O(4)	1.934(7)	Mo(1)-O(8)	2.272(7)
Mo(1)-O(11)	2.458(7)	Mo(2)-O(4)	1.913(7)	Mo(2)-O(5)	1.708(8)
Mo(2)-O(6)	1.722(7)	Mo(2)-O(7)	1.931(5)	Mo(2)-O(8)	2.349(7)
Mo(2)-O(11)	2.382(7)	Mo(3)-O(8)#2	1.825(6)	Mo(3)-O(8)	1.825(6)
Mo(3)-O(9)	1.704(15)	Mo(3)-O(10)	1.731(15)	O(3)-Mo(1)#2	1.927(5)
O(7)-Mo(2)#2	1.930(5)	O(11)-Mo(1)#2	2.458(7)	O(11)-Mo(2)#2	2.382(7)
O(1)-Mo(1)-Mo(2)	114.8(3)	O(1)-Mo(1)-O(3)	99.3(4)	O(1)-Mo(1)-O(4)	97.9(3)
O(1)-Mo(1)-O(8)	160.1(3)	O(1)-Mo(1)-O(11)	88.0(3)	O(2)-Mo(1)-Mo(2)	124.3(3)
O(2)-Mo(1)-O(1)	105.1(4)	O(2)-Mo(1)-O(3)	102.7(4)	O(2)-Mo(1)-O(4)	105.7(4)
O(2)-Mo(1)-O(8)	94.3(3)	O(2)-Mo(1)-O(11)	166.9(4)	O(3)-Mo(1)-Mo(2)	107.1(3)
O(3)-Mo(1)-O(4)	141.4(4)	O(3)-Mo(1)-O(8)	80.5(3)	O(3)-Mo(1)-O(11)	73.2(3)
O(4)-Mo(1)-Mo(2)	34.5(2)	O(4)-Mo(1)-O(8)	72.0(3)	O(4)-Mo(1)-O(11)	73.2(3)
O(8)-Mo(1)-Mo(2)	47.79(18)	O(8)-Mo(1)-O(11)	72.8(3)	O(11)-Mo(1)-Mo(2)	48.13(17)
O(4)-Mo(2)-Mo(1)	34.9(2)	O(4)-Mo(2)-O(7)	141.5(4)	O(4)-Mo(2)-O(8)	70.5(3)
O(4)-Mo(2)-O(11)	75.3(3)	O(5)-Mo(2)-Mo(1)	118.7(3)	O(5)-Mo(2)-O(4)	99.4(4)
O(5)-Mo(2)-O(6)	105.5(4)	O(5)-Mo(2)-O(7)	101.9(4)	O(5)-Mo(2)-O(8)	163.2(3)
O(5)-Mo(2)-O(11)	91.7(4)	O(6)-Mo(2)-Mo(1)	120.1(3)	O(6)-Mo(2)-O(4)	103.8(3)
O(6)-Mo(2)-O(7)	100.9(3)	O(6)-Mo(2)-O(8)	90.2(3)	O(6)-Mo(2)-O(11)	162.5(3)
O(7)-Mo(2)-Mo(1)	106.7(3)	O(7)-Mo(2)-O(8)	80.4(4)	O(7)-Mo(2)-O(11)	72.3(3)
O(8)-Mo(2)-Mo(1)	45.78(16)	O(8)-Mo(2)-O(11)	72.9(3)	O(11)-Mo(2)-Mo(1)	50.21(19)
O(8)#2-Mo(3)-O(8)	107.2(4)	O(9)-Mo(3)-O(8)	111.2(4)	O(9)-Mo(3)-O(8)#2	111.2(4)
O(9)-Mo(3)-O(10)	108.2(8)	O(10)-Mo(3)-O(8)#2	109.5(4)	O(10)-Mo(3)-O(8)	109.5(4)
Mo(1)-O(3)-Mo(1)#2	121.9(5)	Mo(2)-O(4)-Mo(1)	110.7(3)	Mo(2)#2-O(7)-Mo(2)	120.5(5)
Mo(1)-O(8)-Mo(2)	86.4(2)	Mo(3)-O(8)-Mo(1)	120.1(3)	Mo(3)-O(8)-Mo(2)	120.3(4)
Mo(1)-O(11)-Mo(1)#2	86.5(3)	Mo(2)#2-O(11)-Mo(1)#2	81.66(12)	Mo(2)-O(11)-Mo(1)#2	145.0(4)
Mo(2)#2-O(11)-Mo(1)	145.0(4)	Mo(2)-O(11)-Mo(1)	81.66(12)	Mo(2)-O(11)-Mo(2)#2	89.4(3)

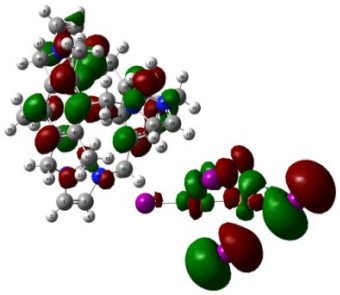
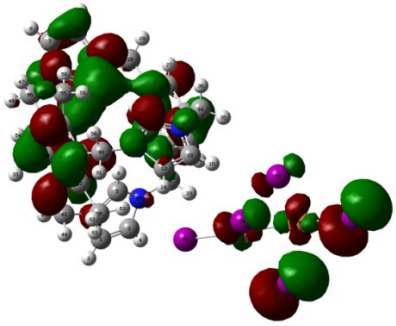
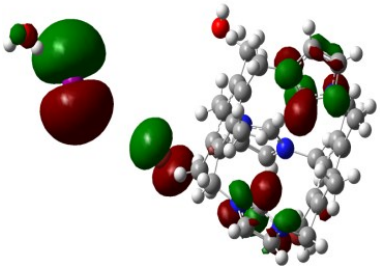
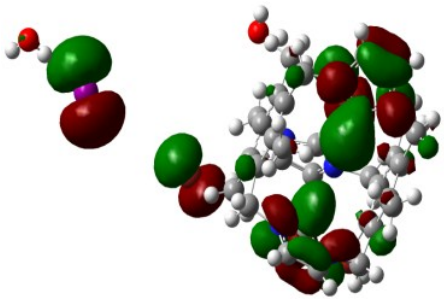
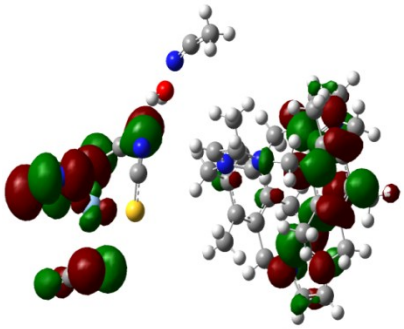
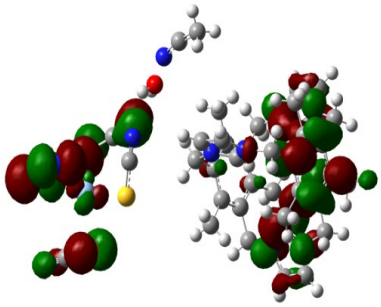
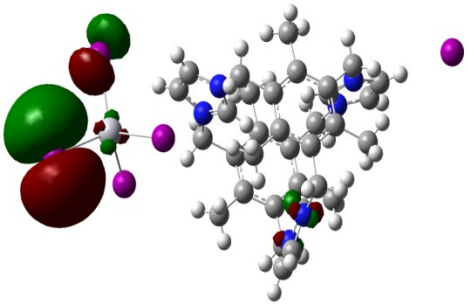
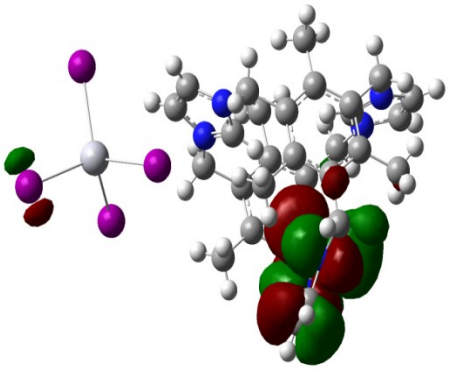
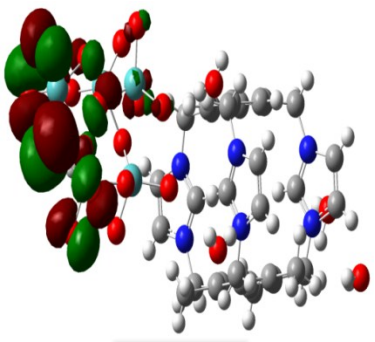
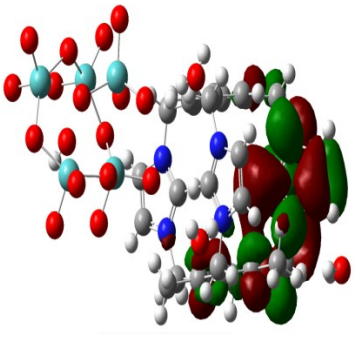
Table S4. Comparison of some important conformational parameters of **L1-3** and **1a-4**.

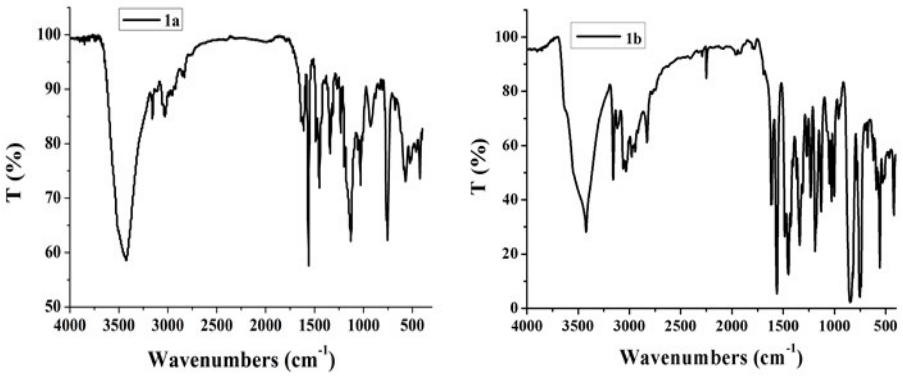
	The vertical height of the cages (Å)	Dihedral angles between imidazole rings (º)	Distances between the 2-C (Å)	Refs
L1 • I_3	5.14(type A) 5.03 (type B)	17.03 , 77.25, 88.73 24.53, 70.44, 85.04	4.476, 4.246, 4.186 4.249, 4.257, 4.413	this article
{L1 • $[CuBr_3]_{1.5}$ • (CH_3CN)}**1a**	4.91 (type B)	45.49, 19.70, 64.93	4.231, 4.160, 4.486	this article
{L1 • $[CuI_3]$ • $2I_{0.5}$ • (H_2O)}**1b**	5.02 (type B)	33.27, 64.63, 82.14	4.234, 4.278, 4.367	this article
L2 • Br_3	5.14	31.6, 76.0, 44.4	4.548, 4.716, 4.613	26a
L2 • I_3	5.15	32.24, 77.99,45.89	4.606, 4.549, 4.659	this article
{L2 • $[PbI_5]$} **2a**	5.15	13.12, 42.67,54.82	4.525, 4.902, 4.638	this article
{$(L2)_2$ • $[Cu_2I_5]_2$ • $4H_2O$}**2b**	5.19 5.14	37.54, 26.78, 63.81 19.67, 51.86, 70.96	4.528, 4.867, 4.704 4.620, 4.587, 5.433	this article
L3 • Br_3 • 2 H_2O	5.15	54.0, 99.1, 153.2	4.70,4.71,4.51	26b-c
L3 • Br_2 • I	5.18	36.52, 56.60, 86.88	4.67, 4.56, 4.66	this article
{L3 • $Ag(SCN)_4$ • (CH_3CN) • 2 H_2O} **3a**	5.09	52.41, 75.18, 52.41	4.59, 4.55, 4.55	this article

{L3 • $[HgI_4]$ ·I }**3b**	5.08	37.35, 60.04,82.60	4.74, 4.66, 4.56	this article
{L2 • $[HMo_5O_{17}]$ • $(H_2O)_{3.25}$}**4**	5.21	7.89, 7.89, 15.78	4.553, 4.553, 5.105	this article

Table S5. The results of the computational studies of compounds **1a-4**.

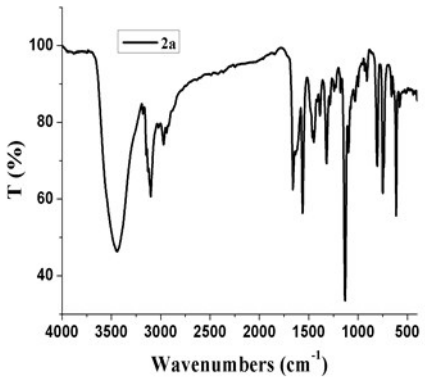
Compound	HOMO	LUMO	The energy band gap (eV)
L1·I_3			0.31
1a			0.22
1b			0.22
L2·I_3			0.30
2a			0.33

2b			0.33
L3·Br_2 ·I			0.27
3a			0.26
3b			0.28
4			0.28

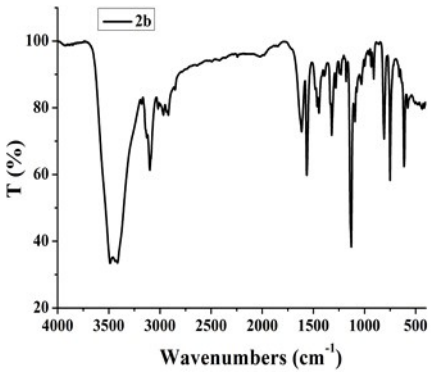


(1a)

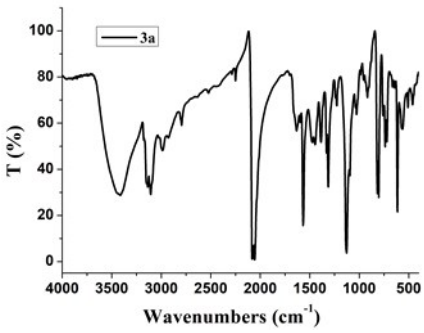
(1b)



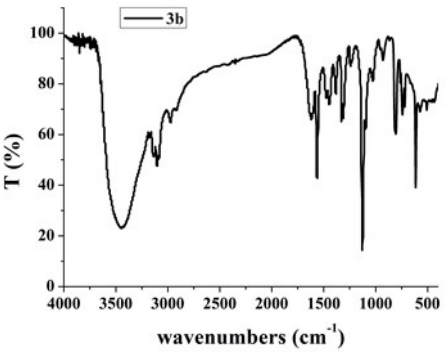
(2a)



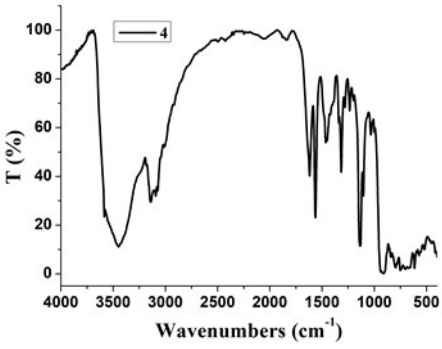
(2b)



(3a)



(3b)



(4)

Fig. S1. IR spectra of complexes **1a-4**.

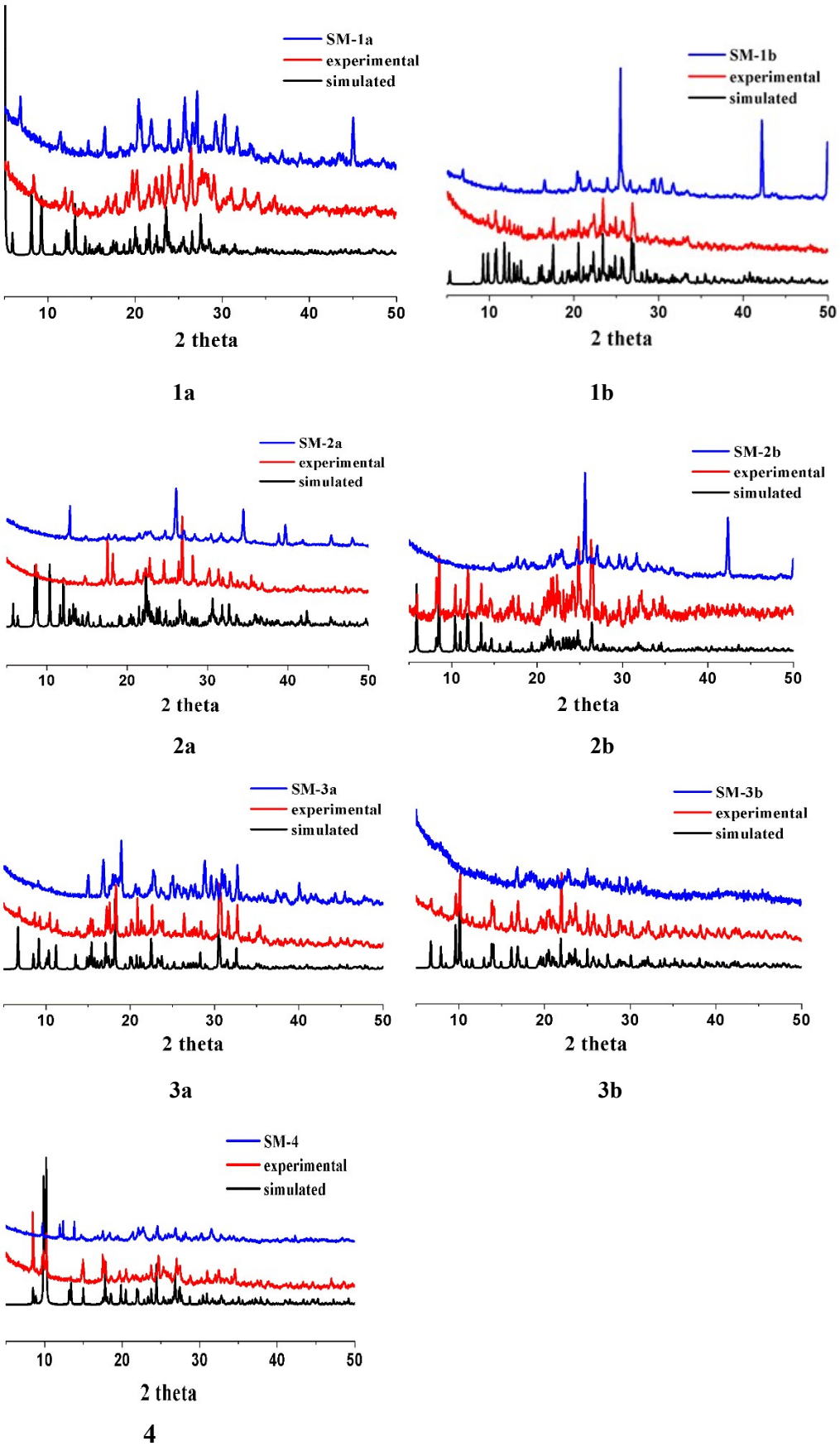


Fig.S2. Power X-ray Diffraction (PXRD) *of* complexes **1a-4** and their start materials(SM).

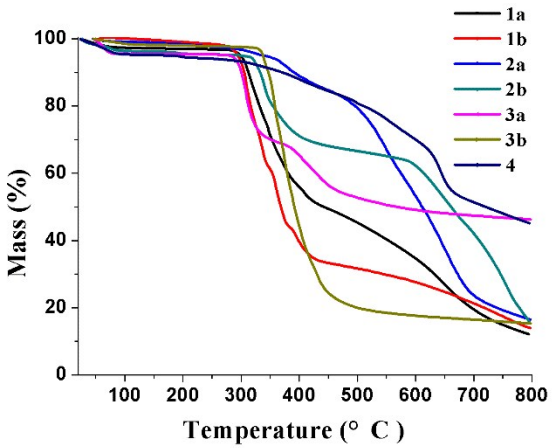
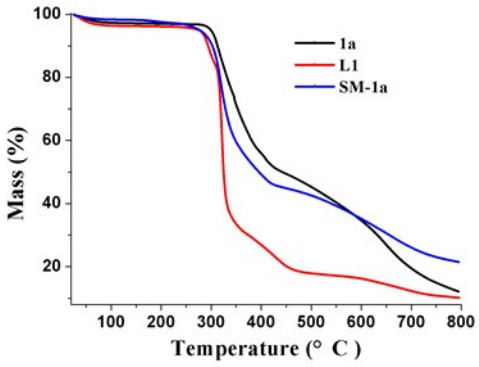
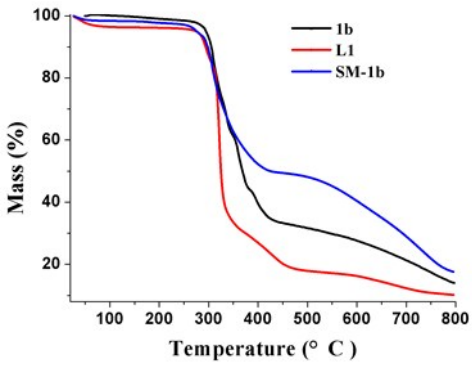


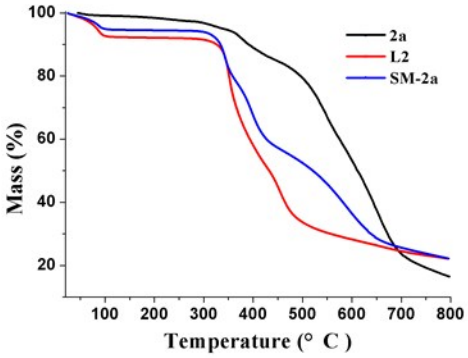
Fig. S3. The TG curves of compounds**1a-4** under nitrogen conditions.



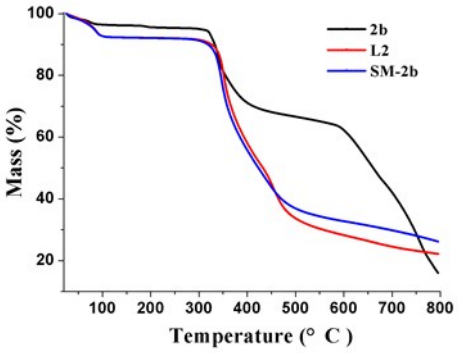
(**1a**)



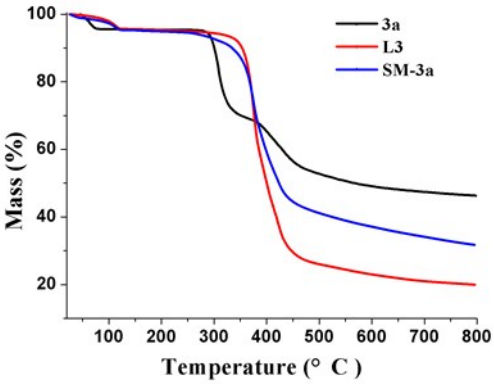
(**1b**)



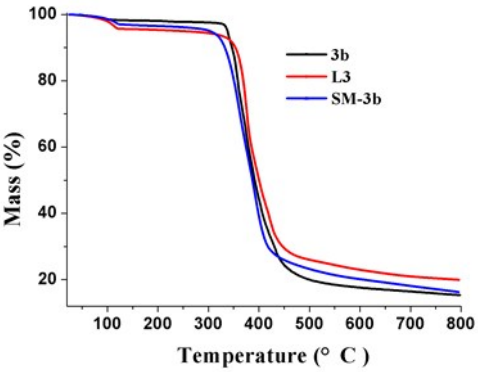
(**2a**)



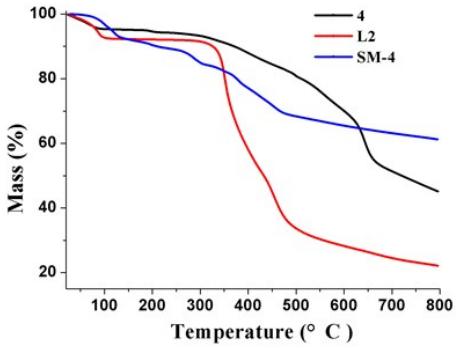
(**2b**)



(**3a**)



(**3b**)



(**4**)

Fig. S4. The TG curves of compoundsL1, L2, L3, **1a-4** and their starting materials (**SM-1a-4**)

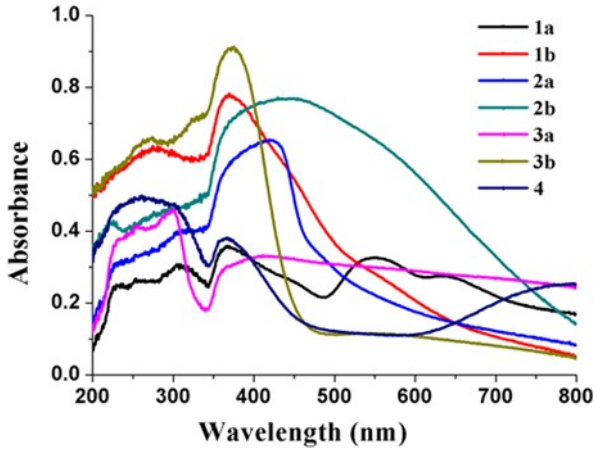


Fig. S5. The UV-Vis absorption of compounds 1a-4.

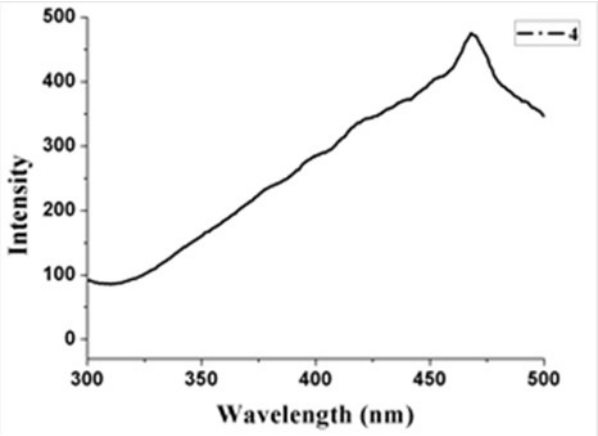
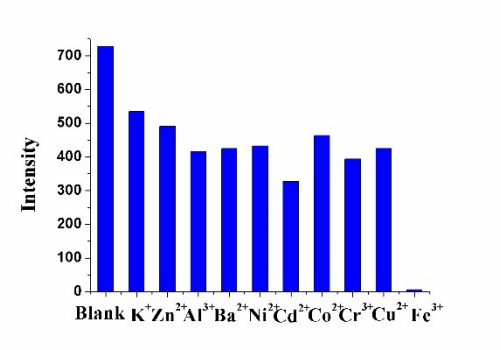
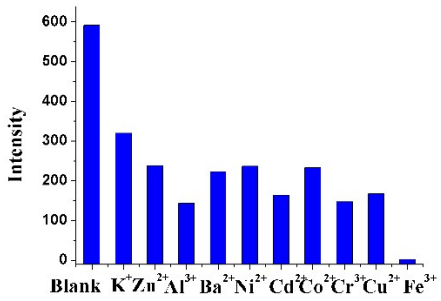


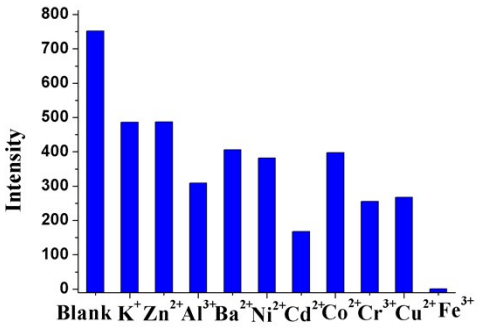
Fig. S6. The fluorescence spectra of **4** in solid state (Ex= 409 nm).


Intensity
Blank K+ Zn2+ Al3+ Ba2+ Ni2+ Cd2+ Co2+ Cr3+ Cu2+ Fe3+

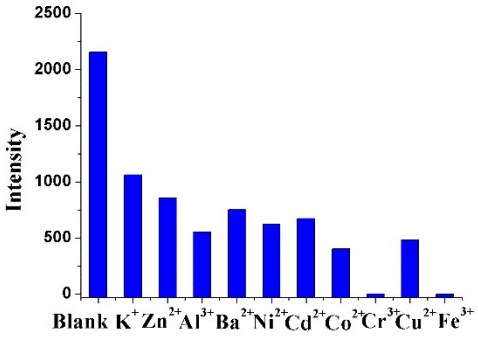
a


Intensity
Blank K+ Zn2+ Al3+ Ba2+ Ni2+ Cd2+ Co2+ Cr3+ Cu2+ Fe3+

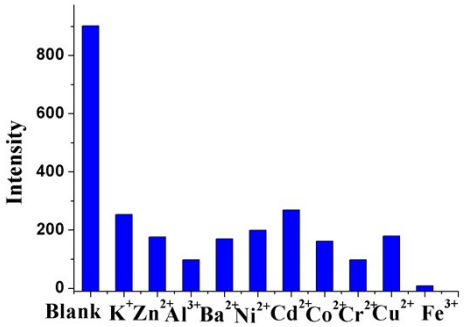
b


Intensity
Blank K+ Zn2+ Al3+ Ba2+ Ni2+ Cd2+ Co2+ Cr3+ Cu2+ Fe3+

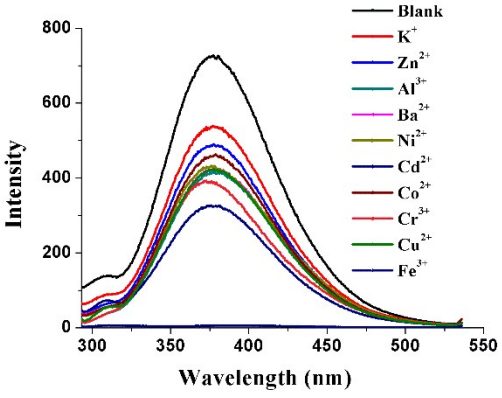
c


Intensity
Blank K+ Zn2+ Al3+ Ba2+ Ni2+ Cd2+ Co2+ Cr3+ Cu2+ Fe3+

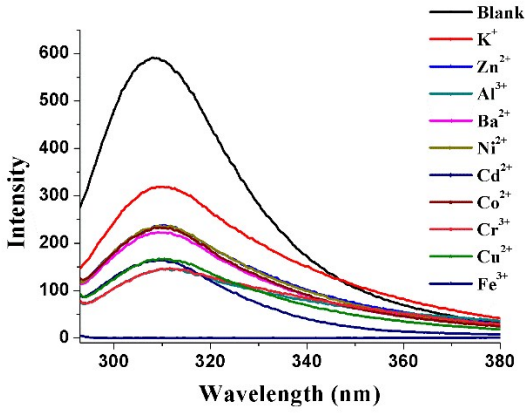
d


Intensity
Blank K+ Zn2+ Al3+ Ba2+ Ni2+ Cd2+ Co2+ Cr3+ Cu2+ Fe3+

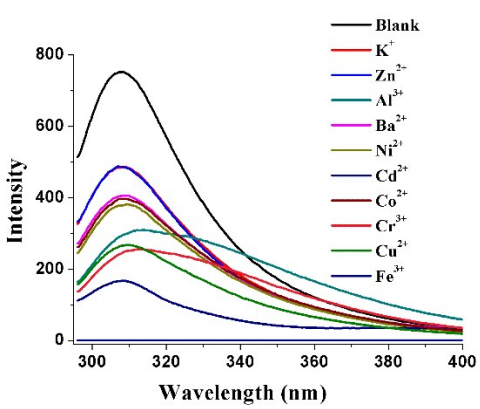
e


Intensity
Wavelength (nm)
Blank
K+
Zn2+
Al3+
Ba2+
Ni2+
Cd2+
Co2+
Cr3+
Cu2+
Fe3+

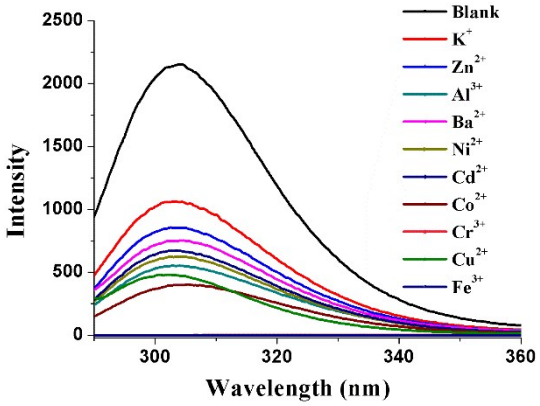
a


Intensity
Wavelength (nm)
Blank
K+
Zn2+
Al3+
Ba2+
Ni2+
Cd2+
Co2+
Cr3+
Cu2+
Fe3+

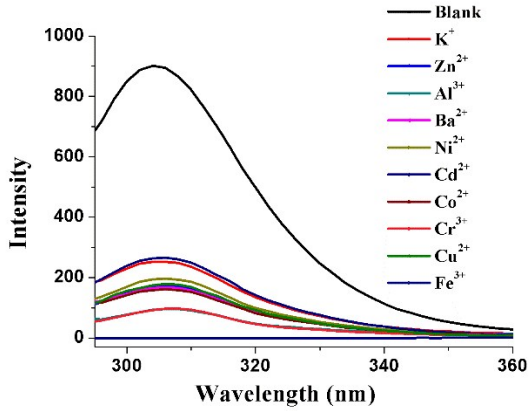
b


Blank
K+
Zn2+
Al3+
Ba2+
Ni2+
Cd2+
Co2+
Cr3+
Cu2+
Fe3+
Intensity
Wavelength (nm)

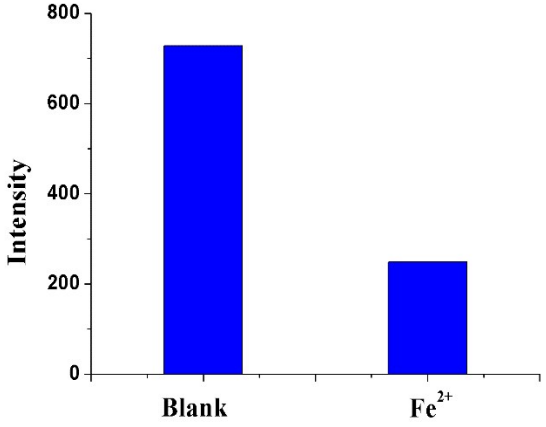
c


Blank
K+
Zn2+
Al3+
Ba2+
Ni2+
Cd2+
Co2+
Cr3+
Cu2+
Fe3+
Intensity
Wavelength (nm)

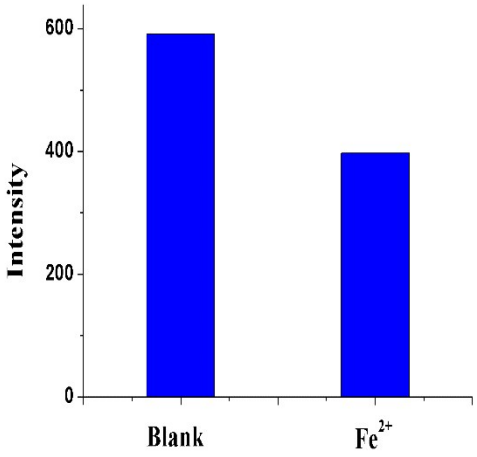
d


Blank
K+
Zn2+
Al3+
Ba2-
Ni2+
Cd2+
Co2+
Cr3+
Cu2+
Fe3+
Intensity
Wavelength (nm)

e


Intensity
Blank
Fe2+

(1b)


Intensity
Blank
Fe2+

(2a)

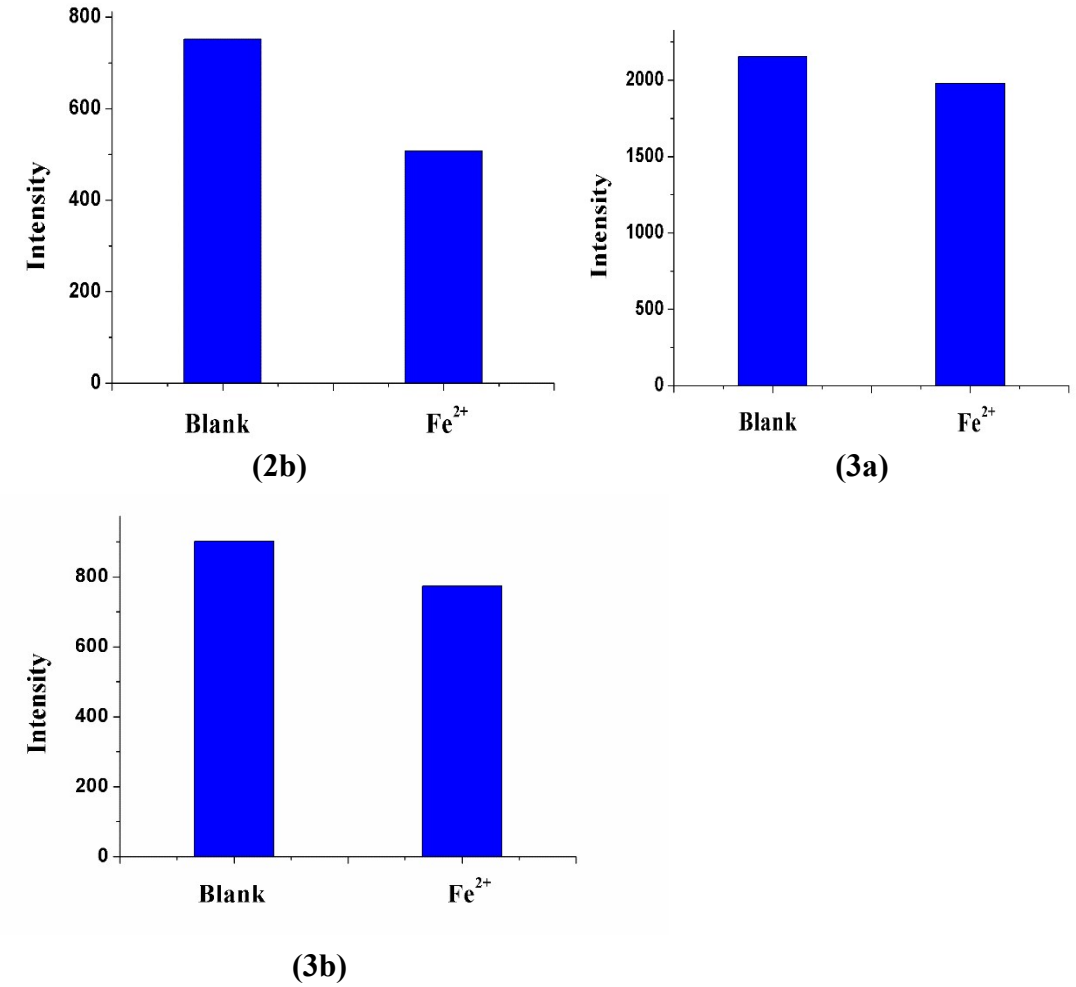
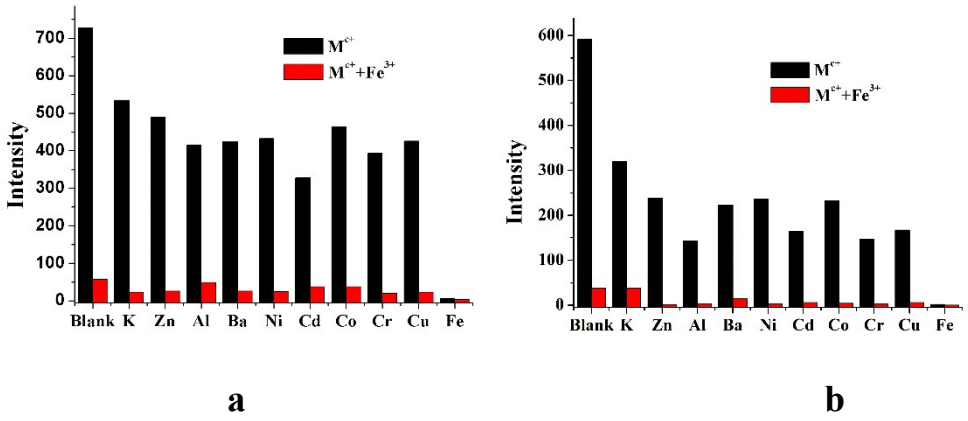


Fig.S7. Photoluminescence intensity change of the **1b-3b** (a-e) treated with 0.01 mol/L different metal ions and the fluorescence spectra of detecting metal ions(a-e)excited at 276 nm. And photoluminescence intensity change of the **1b-3b** treated with Fe^{2+}0.01 mol/L.



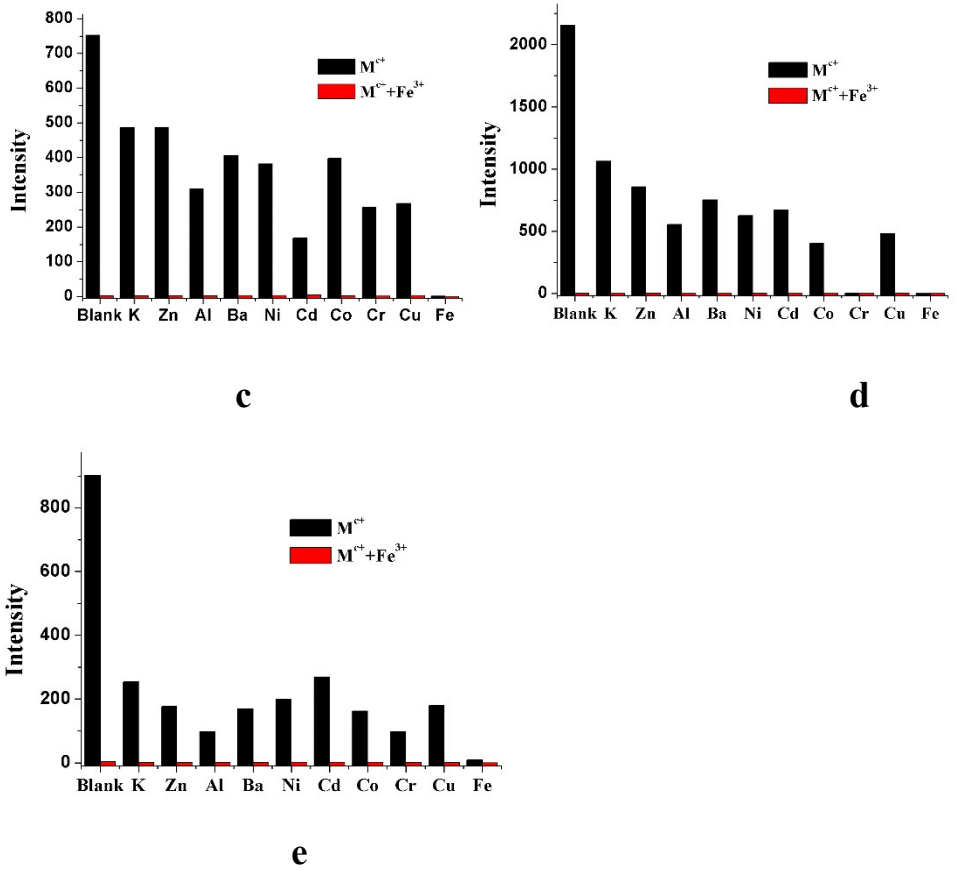
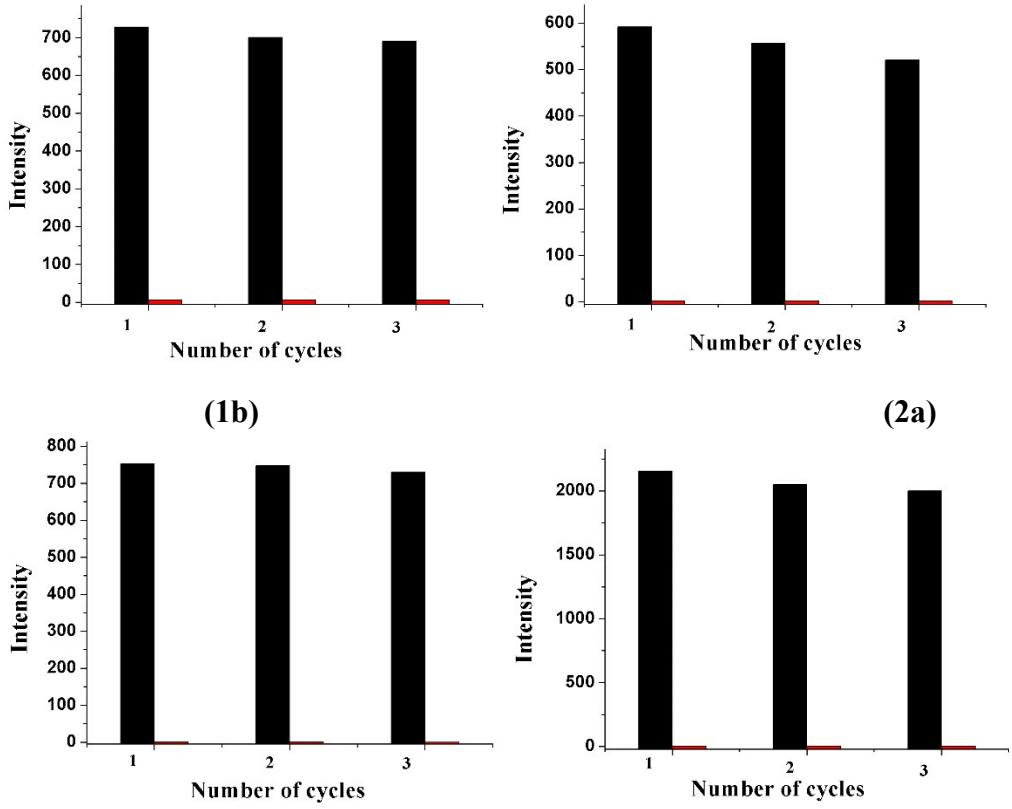
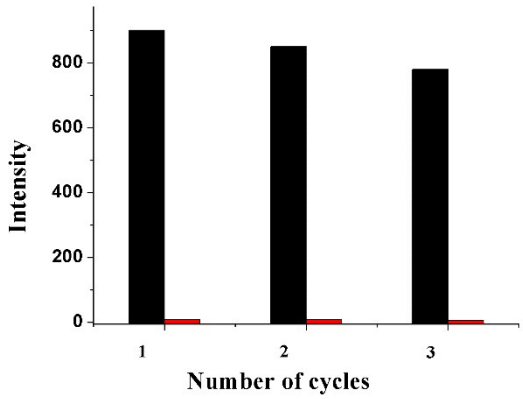


Fig. S8. Fluorescence spectrum of **1b-3b** (a-e) (20 mg) in the presence of various metal ions (0.01 M) and Fe^{3+}(0.005 M) (λ=276 nm).



(2b) **(3a)**



(3b)

Fig. S9. Three cycle tests of compounds **1b-3b** for sensing Fe^{3+} ions.