Hierarchically Symmetric Transfer and Flexible Charge Matching in Five $[M(phen)_3]^{2+}$ Directed Iodoargentates with 1- to 3-D Framework

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Supporting Information (SI)

Table S1. Crystallographic data and refinement parameters of **1-5**.

Compound	**1-293K**	**2-100K**	**2-293K**
CCDC code	922390	1013715	1415302
Temperature	293(2) K	100(2) K	293(2) K
Empirical formula	$C_{40}H_{30}N_8CoAg_3I_5$	$C_{72}H_{50}N_{12}OCo_2Ag_{11}I_{15}$	$C_{144}H_{100}Co_4N_{24}O_2Ag_{24}I_{33}$
Formula weight	1639.76	4307.17	9210.77
Crystal size (mm)	0.25 × 0.12 × 0.08	0.20 × 0.11 × 0.09	0.19 × 0.13 × 0.06
Crystal system,	Monoclinic	Hexagonal	Hexagonal
space group	$P2_1/c$	$P6_3/m$	$P6_3/m$
a (Å)	15.3138(7)	14.8002(16)	14.8402(4)
b (Å)	23.0323(6)	14.8002(16)	14.8402(4)
c (Å)	14.3495(6)	24.789(3)	24.9918(8)
α (°)	90	90	90
β (°)	115.858(5)	90	90
γ (°)	90	120	120
Volume (Å^3)	4554.5(4)	4702.4(11)	4766.6(2)
Z	4	2	1
D_c (g cm^{-3})	2.391	3.042	3.209
F(000)	3036	3880	4133
μ (mm^{-1})	5.057	7.547	8.132
Reflections collected	18473	10059	10820
Unique reflections	8945	3168	3209
R_{int}	0.0280	0.0441	0.0299
Goodness-of-fit on F^2	1.021	1.288	1.156
R_1/wR_2, $[I\geq 2\sigma(I)]^{a,b}$	0.0484, 0.0965	0.1329, 0.2941	0.0724, 0.2319
R_1/wR_2, (all data)	0.0759, 0.1101	0.1406, 0.2981	0.0901, 0.2486
$\Delta\rho_{max}/\Delta\rho_{min}$ (e Å^{-3})	1.895, -1.896	3.343, -9.947	2.365, -4.083
3-293K	**4-100K**	**4-293K**	**5-293K**
1414140	1013716	1415303	1414141
293(2) K	100(2) K	293(2) K	293(2) K
$C_{144}H_{100}Cu_4N_{24}O_2Ag_{24}I_{33}$	$C_{72}H_{78}N_{12}Co_2O_{15}Ag_{13}I_{17}$	$C_{72}H_{78}N_{12}Co_2O_{15}Ag_{14}I_{17}$	$C_{72}H_{78}N_{12}Cd_2O_{15}Ag_{14}I_{17}$
2393.47	5028.93	5136.8	5243.74
0.22 × 0.18 × 0.06	0.25 × 0.23 × 0.07	0.20 × 0.19 × 0.15	0.30 × 0.28 × 0.20
Hexagonal	Cubic	Cubic	Cubic
$P6_3/m$	$P2_13$	$I2_13$	$I2_13$

14.868(3)	22.7105(5)	22.8119(3)	22.9931(2)
14.868(3)	22.7105(5)	22.8119(3)	22.9931(2)
25.012(4)	22.7105(5)	22.8119(3)	22.9931(2)
90	90	90	90
90	90	90	90
120	90	90	90
4788.2(14)	11713.4(8)	11870.9(5)	12156.05(18)
1	4	4	4
3.201	2.852	2.874	2.865
4141	9120	9308	9476
8.193	6.929	6.998	6.910
10452	11489	5377	5893
3225	6113	3339	3402
0.0590	0.0534	0.0281	0.0264
1.033	1.056	1.103	1.077
0.1696, 0.3761	0.0675, 0.1574	0.0740, 0.2075	0.0820, 0.2293
0.2204, 0.4104	0.1182, 0.1784	0.1064, 0.2366	0.1121, 0.2676
2.874, -4.242	3.597, -1.739	2.678, -4.314	3.292, -4.318

[a] $R_1 = \sum||F_o|-|F_c||/\sum|F_o|$, [b] $wR_2 = [\sum w(F_o^2-F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$

Table. S2 Selected bond lengths (Å) and angles (°) for **1**-**5**.

Compound **1**-293K			
Ag(1)-I(1)	2.6992(11)	Ag(1)-I(5)#1	3.0165(12)
Ag(1)-I(2)	3.0075(11)	Ag(1)-I(6)#1	3.0639(12)
Ag(2)-I(6)#1	2.8515(10)	Ag(2)-I(4)	2.7383(11)
Ag(2)-I(5)#1	3.0460(13)	Ag(2)-I(2)	2.9633(11)
Ag(3)-I(5)	2.8524(10)	Ag(3)-I(2)	2.8847(10)
Ag(3)-I(4)	2.8537(10)	Ag(3)-I(6)	2.9349(9)
Ag(1)-Ag(2)	2.8720(12)		
I(1)-Ag(1)-I(2)	107.11(4)	I(1)-Ag(1)-I(5)#1	129.52(4)
I(2)-Ag(1)-I(5)#1	95.27(3)	I(2)-Ag(1)-I(6)#1	105.28(3)
I(1)-Ag(1)-I(6)#1	124.97(4)	I(5)#1-Ag(1)-I(6)#1	89.49(3)
I(4)-Ag(2)-I(5)#1	133.14(5)	I(4)-Ag(2)-I(6)#1	116.60(4)
I(6)#1-Ag(2)-I(5)#1	93.02(3)	I(4)-Ag(2)-I(2)	104.44(3)
I(2)-Ag(2)-I(5)#1	95.57(3)	I(6)#1-Ag(2)-I(2)	112.17(4)
I(5)-Ag(3)-I(2)	121.02(3)	I(5)-Ag(3)-I(6)	95.39(3)
I(4)-Ag(3)-I(2)	103.57(3)	I(4)-Ag(3)-I(6)	122.64(3)
I(5)-Ag(3)-I(4)	115.53(3)	I(2)-Ag(3)-I(6)	98.76(3)
Compound **2**-100K			
Ag(1)-I(1)	2.799(6)	Ag(3)-I(5)#3	3.014(5)
Ag(1)-I(2)	2.862(5)	Ag(3)-I(4)	2.837(5)
Ag(1)-I(3)#1	2.936(4)	Ag(3)-I(5)	2.861(5)
Ag(1)-I(2)#1	2.862(5)	Ag(2B)-I(3)	2.925(12)

Ag(1)-I(3)	2.936(4)	Ag(2B)-I(1)#2	2.595(18)
Ag(2)-I(3)	2.834(7)	Ag(2B)-I(3)#1	2.925(12)
Ag(2)-I(5)#3	3.259(10)	Ag(3B)-I(5)	2.668(13)
Ag(2)-I(1)#2	2.811(10)	Ag(3B)-I(3)#1	2.852(8)
Ag(2)-I(3)#1	2.834(7)	Ag(3B)-I(5)#3	2.684(13)
Ag(3)-I(3)	2.850(5)	Ag(3B)-I(3)	2.852(8)
Ag(1)-Ag(2)	3.213(11)	Ag(1)-Ag(2B)	2.97(2)
Ag(3)-Ag(3)#4	3.045(8)	Ag(3)-Ag(3)#3	3.045(8)
Ag(2B)-Ag(3B)	3.15(2)		
I(1)-Ag(1)-I(2)#1	113.56(18)	I(1)-Ag(1)-I(2)	113.56(18)
I(2)#1-Ag(1)-I(3)	109.7(2)	I(1)-Ag(1)-I(3)	116.58(12)
I(1)-Ag(1)-I(3)#1	116.58(12)	I(2)-Ag(1)-I(3)	99.3(2)
I(2)-Ag(1)-I(3)#1	109.7(2)	I(2)#1-Ag(1)-I(3)#1	99.3(2)
I(5)#3-Ag(3B)-I(3)	105.8(3)	I(3)-Ag(1)-I(3)#1	99.01(17)
I(3)#1-Ag(3B)-I(3)	103.0(4)		
Compound **3**-293K			
Ag(1)-I(6)	2.114(7)	Ag(3)-I(5)	2.876(3)
Ag(1)-I(2)#5	3.035(3)	Ag(2)-I(4)#6	2.807(6)
Ag(2)-I(6)	2.517(17)	Ag(2)-I(3)#2	2.837(4)
Ag(2)-I(2)#5	3.262(5)	Ag(2')-I(3)#2	2.853(5)
Ag(2')-I(4)#6	2.685(8)	Ag(2')-I(6)	3.007(17)
Ag(3)-I(3)#2	2.9389(19)	Ag(3)-I(5)	2.876(3)
Ag(1)-Ag(1)#5	3.133(4)	Ag(3)-Ag(2)	3.308(5)
Ag(1)-Ag(1)#1	3.133(4)	Ag(3)-Ag(2')	2.920(7)
I(6)-Ag(1)-I(3)	69.0(3)	I(6)-Ag(1)-I(2)#5	56.8(3)
I(6)-Ag(1)-I(2)	66.7(4)	I(3)-Ag(1)-I(2)#5	99.51(11)
I(3)-Ag(1)-I(2)	109.94(8)	I(2)-Ag(1)-I(2)#5	98.37(9)
I(6)-Ag(1)-I(1)	165.6(3)	I(1)-Ag(1)-I(2)#5	109.46(8)
I(3)-Ag(1)-I(1)	121.17(10)	I(2)-Ag(1)-I(1)	114.72(11)
I(6)-Ag(2)-I(4)#6	160.9(3)	I(3)-Ag(2)-I(3)#2	103.04(18)
I(6)-Ag(2)-I(3)	64.44(17)	I(6)-Ag(2)-I(2)#5	51.1(3)
I(4)#6-Ag(2)-I(3)	123.67(11)	I(4)#6-Ag(2)-I(2)#5	109.83(15)
I(6)-Ag(2)-I(3)#2	64.44(17)	I(3)-Ag(2)-I(2)#5	94.45(12)
I(4)#6-Ag(2)-I(3)#2	123.67(11)	I(3)#2-Ag(2)-I(2)#5	94.45(12)
I(4)-Ag(3)-I(5)	113.80(9)	I(4)-Ag(3)-I(3)	117.91(9)
I(4)-Ag(3)-I(3)#2	117.91(9)	I(5)-Ag(3)-I(3)	103.32(9)
I(5)-Ag(3)-I(3)#2	103.32(9)	I(3)#2-Ag(3)-I(3)	98.17(8)
Compound **4**-100K			
Ag(1)-I(2)#1	2.9004(6)	Ag(1)-I(2)#2	2.9004(6)
Ag(1)-I(2)	2.9004(6)	Ag(1)-I(1)	2.9352(14)
Ag(2)-I(5)	2.7832(9)	Ag(2)-I(4)	2.8556(9)
Ag(2)-I(2)#1	2.8488(9)	Ag(2)-I(2)	2.8917(9)
Ag(3)-I(3)	2.7818(9)	Ag(3)-I(2)	2.9017(9)
Ag(3)-I(1)	2.8642(7)	Ag(3)-I(4)	2.9207(8)

Ag(4)-I(7)#3	2.7733(8)	Ag(4)-I(3)	2.8624(9)
Ag(4)-I(7)	2.7999(9)	Ag(4)-I(4)	2.9723(9)
Ag(5)-I(6)	2.7991(8)	Ag(5')-I(7)	2.768(4)
Ag(5)-I(7)	2.8215(9)	Ag(5')-I(6)	2.772(4)
Ag(5)-I(5)	2.8291(9)	Ag(5')-I(5)	2.805(3)
Ag(5)-I(4)	3.0537(9)	Ag(5')-I(4)#4	3.096(4)
Ag(1)-Ag(2)#1	3.0670(8)	Ag(1)-Ag(3)	3.2247(9)
Ag(1)-Ag(2)	3.0670(8)	Ag(1)-Ag(3)#1	3.2247(9)
Ag(1)-Ag(2)#2	3.0670(8)	Ag(1)-Ag(3)#2	3.2247(9)
Ag(2)-Ag(5)	2.9193(10)	Ag(2)-Ag(3)	3.2537(10)
Ag(3)-Ag(4)	2.9790(9)	Ag(4)-Ag(5)	3.2631(10)
I(2)#1-Ag(1)-I(2)	111.13(2)	I(2)#1-Ag(1)-I(1)	107.76(2)
I(2)#1-Ag(1)-I(2)#2	111.13(2)	I(2)-Ag(1)-I(1)	107.76(2)
I(2)-Ag(1)-I(2)#2	111.13(2)	I(2)#2-Ag(1)-I(1)	107.76(2)
I(5)-Ag(2)-I(2)#1	105.75(3)	I(5)-Ag(2)-I(2)	109.26(3)
I(5)-Ag(2)-I(4)	116.19(3)	I(2)#1-Ag(2)-I(2)	112.90(3)
I(2)#1-Ag(2)-I(4)	102.41(3)	I(4)-Ag(2)-I(2)	110.20(3)
I(3)-Ag(3)-I(4)	113.12(3)	I(3)-Ag(3)-I(1)	115.99(3)
I(1)-Ag(3)-I(4)	99.82(2)	I(3)-Ag(3)-I(2)	109.57(3)
I(2)-Ag(3)-I(4)	108.11(3)	I(1)-Ag(3)-I(2)	109.68(3)
I(7)#3-Ag(4)-I(7)	123.04(3)	I(7)#3-Ag(4)-I(4)	99.95(3)
I(7)#3-Ag(4)-I(3)	105.32(3)	I(7)-Ag(4)-I(4)	109.09(3)
I(7)-Ag(4)-I(3)	109.34(3)	I(3)-Ag(4)-I(4)	109.29(3)
I(7)-Ag(5)-I(4)	106.29(3)	I(6)-Ag(5)-I(7)	115.94(3)
I(5)-Ag(5)-I(4)	108.86(3)	I(7)-Ag(5)-I(5)	110.31(3)
I(6)-Ag(5)-I(5)	117.12(3)	I(6)-Ag(5)-I(4)	96.65(3)
I(7)-Ag(5')-I(6)	118.65(13)	I(7)-Ag(5')-I(4)#4	97.13(11)
I(7)-Ag(5')-I(5)	112.63(13)	I(6)-Ag(5')-I(4)#4	96.26(11)
I(6)-Ag(5')-I(5)	118.85(13)	I(5)-Ag(5')-I(4)#4	108.41(12)
Compound **5**-293K			
Ag(1)-I(3)#8	2.8872(11)	Ag(1)-I(4)	2.966(3)
Ag(1)-I(3)#5	2.8872(11)	Ag(2)-I(1)	2.8964(16)
Ag(2)-I(3)#8	2.8741(16)	Ag(2)-I(2)	2.8006(16)
Ag(3)-I(1)	3.0269(19)	Ag(3) -I(2)	2.7692(19)
Ag(3)-I(4)#1	2.8379(18)	Ag(3')-I(4)#1	2.809(2)
Ag(3)-I(3)#9	2.8758(19)	Ag(3')-I(1)#10	3.027(3)
Ag(3')-I(3)#9	2.796(3)	Ag(1)-Ag(2)#8	3.1058(16)
Ag(1)-Ag(2)#5	3.1058(16)	Ag(1)-Ag(3)#1	3.178(2)
Ag(1)-Ag(3)#4	3.178(2)	Ag(2)-Ag(3)	2.926(2)
Ag(2)-Ag(3)#1	3.346(2)	Ag(2)-Ag(1)	3.1058(16)
Ag(3)-Ag(2)#1	3.346(2)	Ag(3)-Ag(1)#1	3.178(2)
I(3)#8-Ag(1)-I(3)	110.58(6)	I(3)#8-Ag(1)-I(4)	108.34(6)
I(3)#8-Ag(1)-I(3)#5	110.58(6)	I(3)-Ag(1)-I(4)	108.34(6)
I(3)-Ag(1)-I(3)#5	110.58(6)	I(3)#5-Ag(1)-I(4)	108.34(6)

I(2)-Ag(2)-I(3)	107.97(5)	I(2)-Ag(2)-I(1)	113.58(5)
I(2)-Ag(2)-I(3)#8	112.31(5)	I(3)-Ag(2)-I(1)	101.58(5)
I(3)-Ag(2)-I(3)#8	111.47(5)	I(3)#8-Ag(2)-I(1)	109.44(5)
I(2)-Ag(3)-I(1)	110.58(6)	I(3)#9-Ag(3)-I(1)	105.87(6)
I(4)#1-Ag(3)-I(1)	98.74(5)		

Symmetry code: for **1**: #1 x, -y+3/2, z-1/2; #2 x, -y+3/2, z+1/2; for **2**: #1 x, y, -z+3/2; #2 -y+1, x-y, z; #3 -x+y, -x, z; #4 -y, x-y, z; #5 -x+y+1, -x+1, z; #6 -y, x-y, -z+3/2; #7 -y+1, x-y+1, z; #8 -x+y, -x+1, z; for **3**: #1 -x+y, -x, z; #2 x, y, -z+1/2; #3 -x+y, -x, -z+1/2; #4 -y+1, x-y+1, z; #5 -y, x-y, z; #6 -x+y, -x+1, z; for **4**: #1 z, x, y; #2 y, z, x; #3 -z+1/2, -x, y+1/2; #4 -y, z-1/2, -x+1/2; #5 -z+1/2, -x+1, y-1/2; #6 -y+1, z+1/2, -x+1/2; for 5: #1 -x+2, -y+1/2, z+0; #2 -y+1, -z+1/2, x-1; #3 y+1, z, x-1; #4 -z+1, -x+3/2, y+0; #5 y+1/2, -z+1/2, -x+1; #6 z, x-1, y+1; #7 y+1, z-1, x; #8 -z+1, x-1/2, -y+1/2; #9 z+1, -x+1, -y+1/2; #10 z+1, x-1, y;

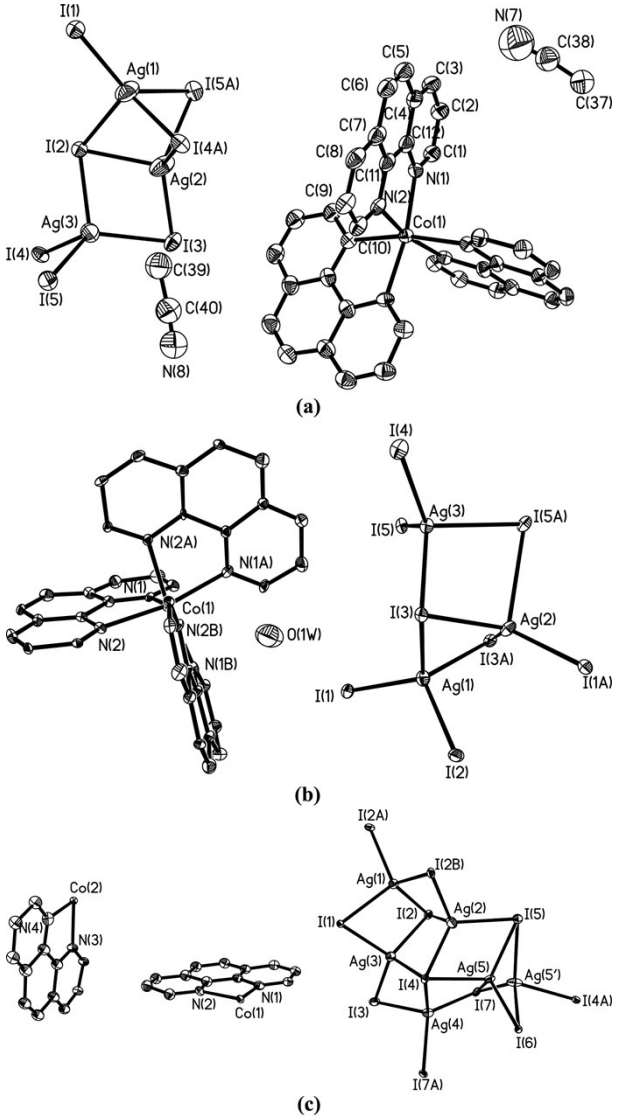


Figure. S1 The asymmetric unit diagram of **1**(a) **2** (b) and **4** (c).

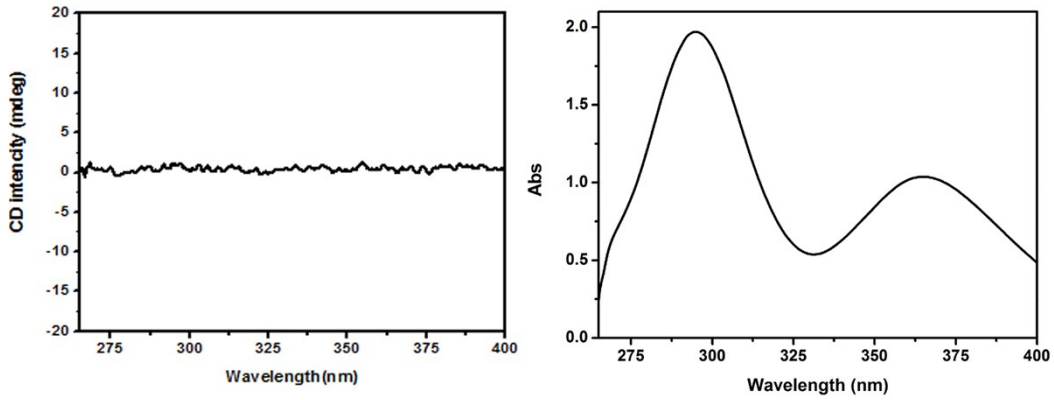


Figure S2. The CD spectra of compound **4** in the DMSO solution.

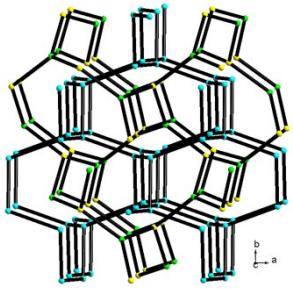
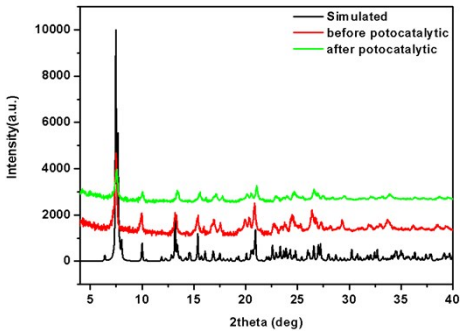
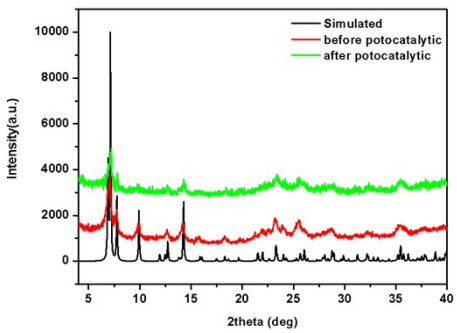


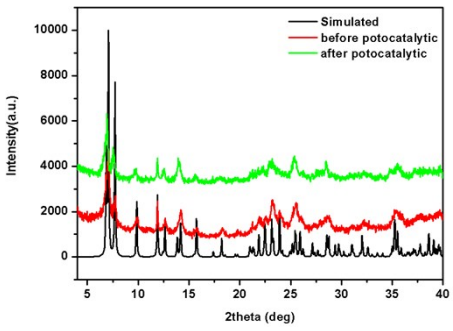
Figure S3. View of the two different (10, 3) topological network of the 3-D $[Ag_{13}I_{17}]_n^{4n-}$ framework and cationic supramolecular 3-D network of $[Co(phen)_3]^{2+}$ with contrary four-fold interpenetration helical chains which reveals obvious image relationship. (The cyan, yellow and green dots represent the unit $[Co(phen)_3]^{2+}$, Ag_6I_{13} and Ag_7I_{13} cores respectively. The black lines represent the contrary four-fold helical chains.)



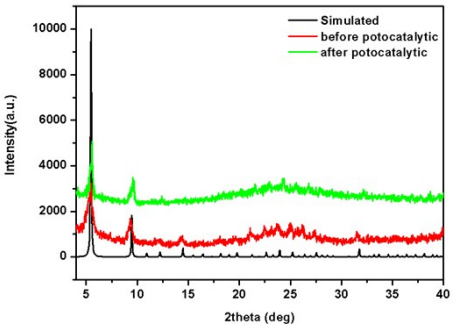
Compound **1**



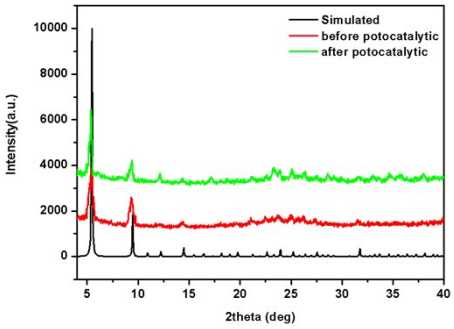
Compound **2**



Compound **3**

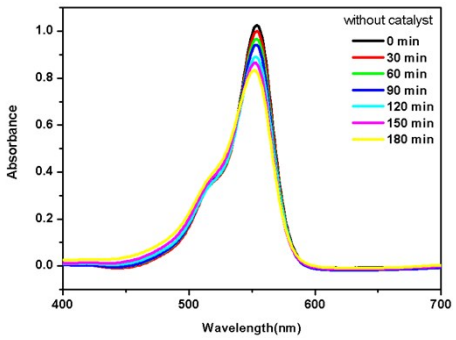


Compound **4**

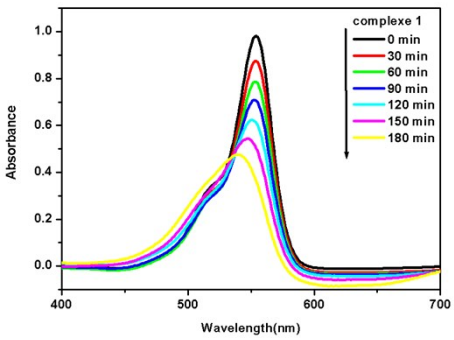


Compound **5**

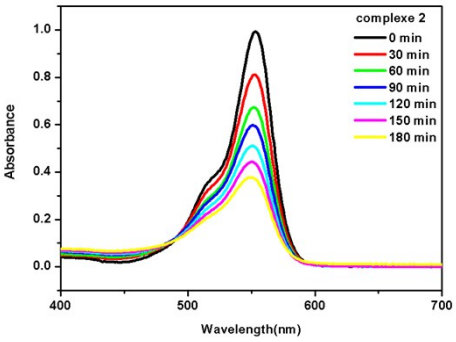
Figure S4. Experimental XRD patterns of compound **1-5** exposed in air (red), after potocatalytic (green) and simulation patterns of compound **1 -5** (black).



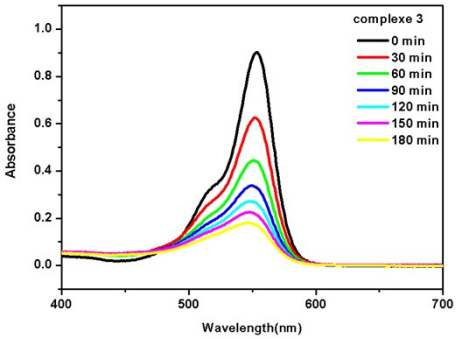
Without catalyst



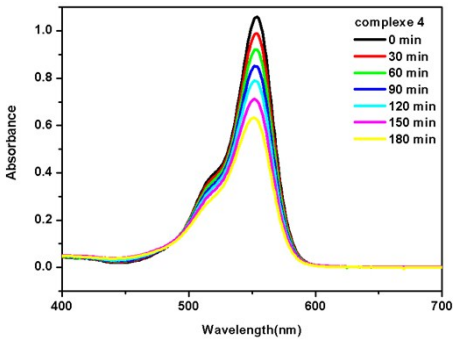
Compound **1**



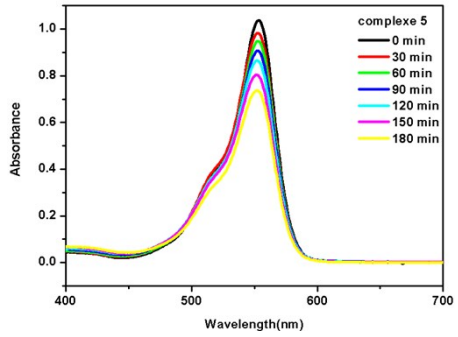
Compound **2**



Compound **3**

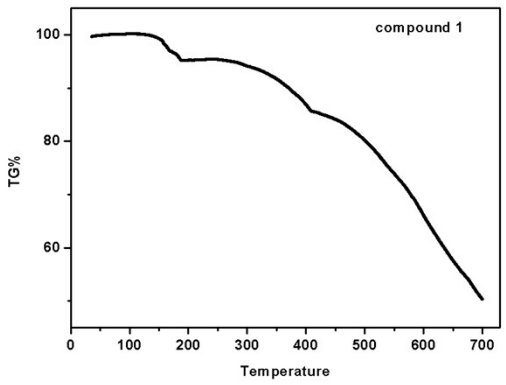


Compound **4**

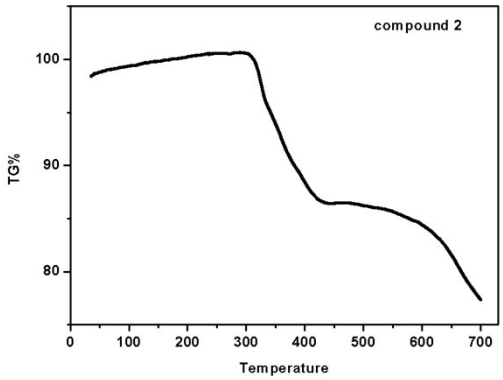


Compound **5**

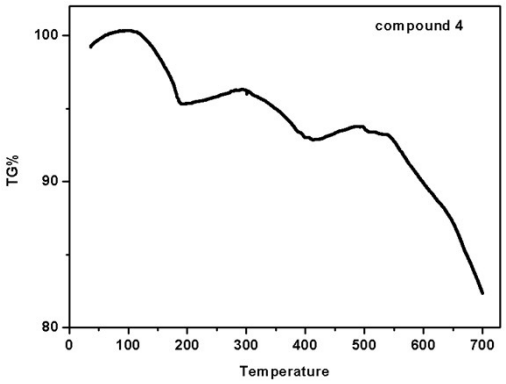
Figure S5. Absorption spectra of the RhB aqueous solution under 175-W Hg-lamp irradiation with no catalyst and compounds **2 – 5**.



Compound **1**

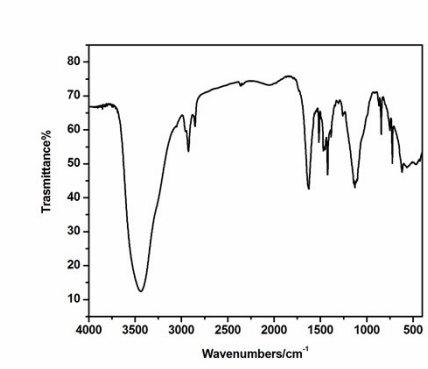


Compound **2**

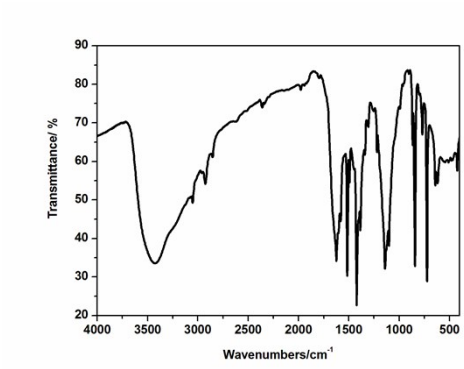


Compound **4**

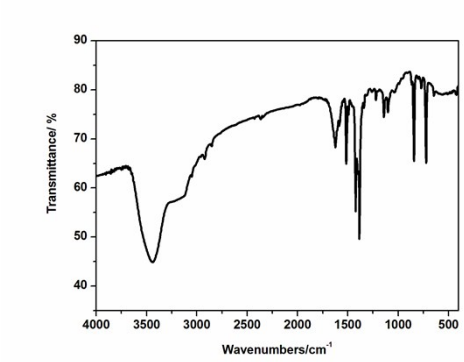
Figure. S6 IR spectra for **1** -5.



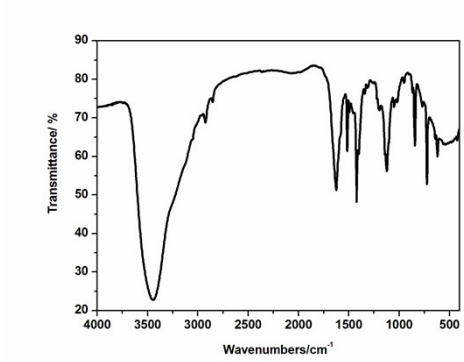
Compound **1**



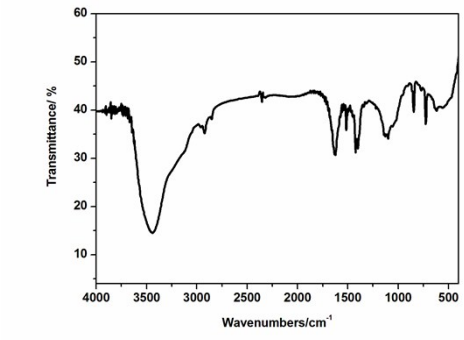
Compound **2**



Compound **3**



Compound **4**



Compound **5**

Figure. S7 IR spectra for **1** -5.