Supporting Information for

Homochiral Silver-Based Coordination Polymers Exhibiting Temperature-Dependent Photoluminescence Behavior

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1. Materials and General Procedures.

All of the chemicals are commercial available and used without further purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectrum was recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. The CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10^{o}C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. All fluorescence measurements were carried out on a LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). All UV/Vis absorption spectrum were recorded on a Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). ^{1}H and ^{13}C NMR experiments were carried out on a MERCURYplus 400 spectrometer operating at resonance frequencies of 400 MHz.

X-ray Crystallography. Single-crystal XRD data for the compounds was collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 123K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved using direct method, and refined by full-matrix least-squares on F2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). Some bond lengths involving tert-butyl groups and guest molecules were constrained to be reasonable values. In all compounds, the guest molecules and H-atoms were refined isotropically, while all other atoms were refined anisotropically. Crystal data and details of the data collection are given in Table S1, while the selected bond distances and angles are presented in Tables S2-S4.

2. Synthesis of compounds 1-3

Synthesis of Ag**L**(ClO_4) **(1):** A solution of $AgClO_4$ (20.7 mg, 0.10 mmol) in CH_3CN (5 mL) was added into a solution of **L** (41.7 mg, 0.05 mmol) in i-PrOH (1 mL). The solution was stirred for 10 minutes and then was allowed to stand at room temperature. After two days, yellow flake-like crystals of **1** were collected. Yield: 41.6 mg (80.2%). Elemental analysis (%) Calcd for $C_{52}H_{58}AgClN_4O_{10}$: C 59.92, H 5.61, Cl 3.40, N 5.38. Found: C 59.12, H 5.64, Cl, 3.37; N, 5.35. IR (KBr): 3472 (w), 2948 (s), 2915 (s), 2572 (w), 1630 (s), 1451 (s), 1408 (m), 1356 (m), 1279 (w), 1286 (m), 1227 (m), 1166 (m), 1090 (s), 954 (s), 842 (m), 783 (w), 627 (m), 508 (w) cm^{-1}. Elemental analysis showed **1** has the formula [Ag**L**(ClO_4)]; this is consistent with the TGA result.

Synthesis of Ag**L**(BF_4) **(2):** A solution of $AgBF_4$ (19.5 mg, 0.10 mmol) in CH_3CN (2 ml) and 2-BuOH (3 ml) was carefully layered on to a solution of **L** (41.7 mg, 0.05 mmol) in THF (5 mL) in a test tube. The tube was covered with parafilm and the solvents were allowed to diffuse slowly over three days to afford yellow rodlike crystals of **2.** Yield: 38.6 mg (77.9%). Elemental analysis (%) Calcd for $C_{52}H_{58}AgBF_4N_4O_6$: C 60.65, H 5.68, N 5.44. Found: C 59.97, H 5.66, N 5.42. IR (KBr): 3445 (w), 2954 (s), 2921 (s), 2576 (w), 1773 (m), 1655 (m), 1622 (s), 1435 (s), 1393 (m), 1375 (m), 1290 (m), 1275 (m), 1232 (m), 1172 (s), 1063 (s), 1039 (s), 973 (m), 937 (w), 828 (m), 632 (w), 523 (w) cm^{-1}. Elemental analysis showed **2** has the formula [Ag**L**(BF_4)]; this is consistent with the TGA result.

Synthesis of Ag**L**(NO_3) **(3):** A solution of $AgNO_3$ (17.0 mg, 0.10 mmol) in CH_3CN (5 mL) was carefully layered on to a solution of **L** (41.7 mg, 0.05 mmol) in CH_2Cl_2 (5 mL) in a test tube. The tube was covered with parafilm and the solvents were allowed to diffuse slowly over four days to afford yellow rodlike crystals of **3**. Yield: 37.7 mg (78.2%). Calcd for $C_{52}H_{58}AgN_5O_9$: C 62.15, H 5.82, N 6.97. Found: C 61.96, H 5.80, N 6.92. Found: C 61.96, H 5.80, N 6.92. IR (KBr): 3436 (w), 2954 (m), 2909 (m), 1605 (w), 1441 (s), 1384 (s), 1284 (m), 1226 (w), 1189 (w), 1159 (m), 1080(w), 1011 (m), 957 (m), 860 (w), 825 (m), 776 (w), 632 (w), 616 (w), 500 (w) cm^{-1}. Elemental analysis showed **3** has the formula [Ag**L**(NO_3)]; this is consistent with the TGA result.

3. Anion exchange for compounds 1 and 2.

A 100 mg portion of $NaNO_3$ (or $AgBF_4$) was dissolved in water (5 mL), to which 30 mg of well-ground complex **1** was added; this mixture was stirred for 24 h at room temperature in the dark. The solid was isolated by filtration, washed with water several times, and dried. The FT-IR spectrum and the powder pattern X-ray diffraction pattern of the exchanged solid of complex **1** were recorded.

A 100 mg portion of $NaNO_3$ (or $Zn(ClO_4)_2$) was dissolved in water (5 mL), to which 30 mg of well-ground complex **2** was added; this mixture was stirred for 24 h at room temperature in the dark. The solid was isolated by filtration, washed with water several times, and dried. The FT-IR spectrum and the powder pattern X-ray diffraction pattern of the exchanged solid of complex 2 were recorded.

4. Table S1. Crystal data and structure refinement for **1-3**

Identification code	**1**	**2**	**3**
Empirical formula	$C_{106}H_{112}Ag_2Cl_2N_9O_{23}$	$C_{116}H_{112}Ag_2B_2F_8N_8O_{16}$	$C_{29}H_{25.5}Ag_{0.5}N_4O_{4.5}$
Formula weight	2166.69	2263.50	555.97
Temperature (K)	123	123	123
Wavelength (Å)	1.54178	1.54178	1.54178
Crystal system	monoclinic	monoclinic	hexagonal
Space group	*C*2	*C*2	$P6_522$
Unit cell dimensions	a = 51.6398(14) Å b = 13.6915(4) Å c = 17.5930(5) Å alpha = 90º beta = 102.8280(1)º gamma= 90º	a = 31.6945(7) Å b = 18.9206(5) Å c = 23.8228(5) Å alpha = 90º beta = 109.8150(10)º gamma = 90 º	a = 18.7958(3) Å b = 18.7958(3) Å c = 29.6903(8) Å alpha= 90º beta = 90º gamma= 120º
Volume ($Å^3$), Z	12128.3(6), 4	13440.2(5), 4	9083.8(3), 12
Density (calculated) (mg/m^3)	1.187	1.119	1.220
Absorption coefficient (mm^{-1})	3.530	2.893	3.142
F(000)	4492	4672	3444
θ range for data collection (º)	3.42 to 50.00	5.03 to 52.50	3.10 to 59.95
Limiting indices	-51≤ h≤ 49, -13≤ k≤ 10, -17≤ l≤ 17	-32≤ h≤ 32, -17≤ k≤ 19, -24≤ I≤ 24	-18 ≤ h ≤ 21, -20 ≤ k ≤ 19, -29≤ I ≤ 31
Reflections collected	28808	16824	28020
Independent reflections	9509 [R(int) = 0.0336]	9706 [R(int) = 0.0355]	4296 [R(int) = 0.0315]
Completeness to theta	50.00/95.4 %	52.50/95.0 %	59.95/94.2 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	9509 / 71 / 1106	9706 / 121/1048	4296 / 47 / 291
Goodness-of-fit on F^2	1.038	1.042	1.082
Final R indices [I>2sigma(I)]	R1 = 0.0756, wR2 = 0.1996	R1 = 0.0730, wR2 = 0.1995	R1 = 0.0666, wR2 = 0.1817
R indices (all data)	R1 = 0.0783, wR2 = 0.2040	R1 = 0.0868, wR2 = 0.2132	R1 = 0.0681, wR2 = 0.1838
Absolute structure parameter	0.029(10)	0.031(10)	0.03(3)
Largest diff. peak and hole ($e.Å^{-3}$)	1.654 and -0.863	0.759 and -1.413	0.922 and -0.389

5.1 Table S2. Selected bond lengths [Å] and angles [°] for **1.**

Ag(2)-N(4)#1	2.132(15)
Ag(2)-N(4)#2	2.132(15)
Ag(2)-O(13)	2.748(11)
Ag(2)-O(13)#1	2.748(11)
Ag(2)-Ag(1)	3.167(2)
Ag(2)-Ag(1) #3	3.167(2)
Ag(4)-N(8)#4	2.157(15)
Ag(4)-N(8)#5	2.157(14)
Ag(4)-Ag(3)	3.195(2)
Ag(4)-Ag(3)#6	3.195(2)
N(1)-Ag(1)	2.181(5)
N(1)-Ag(1)#3	2.225(6)
N(4)-Ag(2)#7	2.132(4)
N(5)-Ag(3)#6	2.152(9)
N(5)-Ag(3)	2.249(9)
N(8)-Ag(4)#8	2.157(3)
O(17)-Ag(3)	2.436(11)
O(13)-Ag(1)	1.851(11)
O(13)-Ag(1)#3	2.522(11)
Ag(1)-Ag(1)#3	0.787(4)
Ag(1)-N(1)#3	2.225(6)
Ag(1)-O(13)#3	2.522(11)
Ag(3)-Ag(3)#6	0.594(8)
Ag(3)-N(5)#6	2.152(9)
N(4)#1-Ag(2)-N(4)#2	177(4)
N(4)#1-Ag(2)-O(13)	91(2)
N(4)#2-Ag(2)-O(13)	86.8(9)
N(4)#1-Ag(2)-O(13)#3	86.8(8)
N(4)#2-Ag(2)-O(13)#3	91(3)
O(13)-Ag(2)-O(13)#3	85.4(5)
N(4)#1-Ag(2)-Ag(1)	89(2)
N(4)#2-Ag(2)-Ag(1)	88(2)
O(13)-Ag(2)-Ag(1)	35.6(2)
O(13)#3-Ag(2)-Ag(1)	49.9(2)
N(4)#1-Ag(2)-Ag(1)#3	87.7(19)
N(4)#2-Ag(2)-Ag(1)#3	89(2)
O(13)-Ag(2)-Ag(1)#3	49.9(2)
O(13)#3-Ag(2)-Ag(1)#3	35.6(2)
Ag(1)-Ag(2)-Ag(1)#3	14.28(7)
N(8)#4-Ag(4)-N(8)#5	174(3)
N(8)#4-Ag(4)-Ag(3)	86.3(19)
N(8)#5-Ag(4)-Ag(3)	87.4(14)

N(8)#4-Ag(4)-Ag(3)#6	87.4(16)
N(8)#5-Ag(4)-Ag(3)#6	86.3(16)
Ag(3)-Ag(4)-Ag(3)#6	10.67(15)
C(1)-N(1)-Ag(1)	127.5(4)
C(5)-N(1)-Ag(1)	111.6(4)
C(1)-N(1)-Ag(1)#3	107.1(4)
C(5)-N(1)-Ag(1)#3	131.0(4)
Ag(1)-N(1)-Ag(1)#3	20.56(11)
C(51)-N(4)-Ag(2)#7	115.8(3)
C(50)-N(4)-Ag(2)#7	124.1(3)
C(53)-N(5)-Ag(3)#6	111.8(4)
C(57)-N(5)-Ag(3)#6	126.8(4)
C(53)-N(5)-Ag(3)	125.4(4)
C(57)-N(5)-Ag(3)	111.7(4)
Ag(3)#6-N(5)-Ag(3)	15.3(2)
C(102)-N(8)-Ag(4)#8	119.9(2)
C(103)-N(8)-Ag(4)#8	119.9(3)
Cl(2)-O(17)-Ag(3)	141.5(7)
Cl(1)-O(13)-Ag(1)	143.8(8)
Cl(1)-O(13)-Ag(1)#3	154.7(8)
Ag(1)-O(13)-Ag(1)#3	10.95(12)
Cl(1)-O(13)-Ag(2)	131.1(7)
Ag(1)-O(13)-Ag(2)	84.7(4)
Ag(1)#3-O(13)-Ag(2)	73.7(3)
Ag(1)#3-Ag(1)-O(13)	142.5(3)
Ag(1)#3-Ag(1)-N(1)	82.9(6)
O(13)-Ag(1)-N(1)	98.8(4)
Ag(1)#3-Ag(1)-N(1)#3	76.6(6)
O(13)-Ag(1)-N(1)#3	108.5(4)
N(1)-Ag(1)-N(1)#3	152.6(3)
Ag(1)#3-Ag(1)-O(13)#3	26.5(3)
O(13)-Ag(1)-O(13)#3	116.1(6)
N(1)-Ag(1)-O(13)#3	89.4(3)
N(1)#3-Ag(1)-O(13)#3	80.3(3)
Ag(1)#3-Ag(1)-Ag(2)	82.86(4)
O(13)-Ag(1)-Ag(2)	59.8(3)
N(1)-Ag(1)-Ag(2)	98.1(2)
N(1)#3-Ag(1)-Ag(2)	97.1(2)
O(13)#3-Ag(1)-Ag(2)	56.4(3)
Ag(3)#6-Ag(3)-N(5)#6	91.6(17)
Ag(3)#6-Ag(3)-N(5)	73.1(16)
N(5)#6-Ag(3)-N(5)	155.0(3)
Ag(3)#6-Ag(3)-O(17)	163.1(5)
N(5)#6-Ag(3)-O(17)	94.6(4)

N(5)-Ag(3)-O(17)	105.8(5)
Ag(3)#6-Ag(3)-Ag(4)	84.67(7)
N(5)#6-Ag(3)-Ag(4)	100.2(3)
N(5)-Ag(3)-Ag(4)	98.0(3)
O(17)-Ag(3)-Ag(4)	78.8(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y-1/2,-z+1 #2 x-1/2,y-1/2,z #3 -x,y,-z+1 #4 x+1/2,y-1/2,z
#5 -x+1/2,y-1/2,-z #6 -x+1,y,-z #7 x+1/2,y+1/2,z #8 x-1/2,y+1/2,z

5.2. Table S3. Selected bond lengths [Å] and angles [º] for **2**.

Ag(1)-N(1)	2.143(4)
Ag(1)-N(8)#1	2.143(16)
Ag(1)-Ag(2)	3.0976(13)
Ag(2)-N(4)#2	2.14(2)
Ag(2)-N(5)	2.162(4)
N(4)-Ag(2)#3	2.137(5)
N(8)-Ag(1)#1	2.143(4)
N(1)-Ag(1)-N(8)#1	173.3(17)
N(1)-Ag(1)-Ag(2)	106.1(2)
N(8)#1-Ag(1)-Ag(2)	78(3)
N(4)#2-Ag(2)-N(5)	172(3)
N(4)#2-Ag(2)-Ag(1)	81(3)
N(5)-Ag(2)-Ag(1)	107.0(2)
C(1)-N(1)-Ag(1)	117.6(3)
C(5)-N(1)-Ag(1)	122.3(3)
C(51)-N(4)-Ag(2)#3	119.2(2)
C(50)-N(4)-Ag(2)#3	120.0(3)
C(53)-N(5)-Ag(2)	116.8(3)
C(57)-N(5)-Ag(2)	121.6(3)
C(102)-N(8)-Ag(1)#1	118.8(3)
C(103)-N(8)-Ag(1)#1	120.9(3)

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

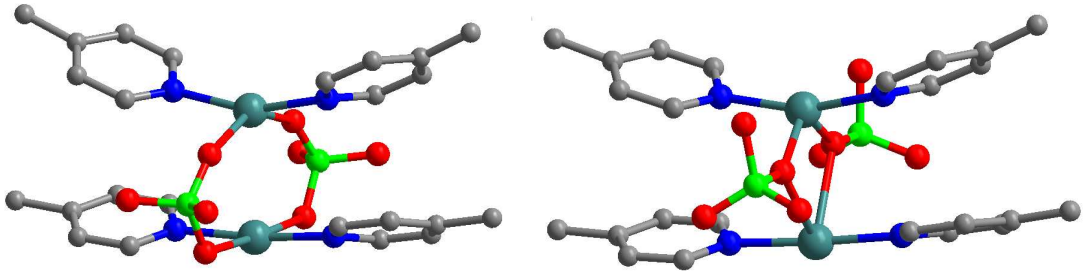
5.3. Table S4. Selected bond lengths [Å] and angles [º] for **3.**

Ag(1)-N(1)#1	2.135(5)
Ag(1)-N(1)	2.135(5)

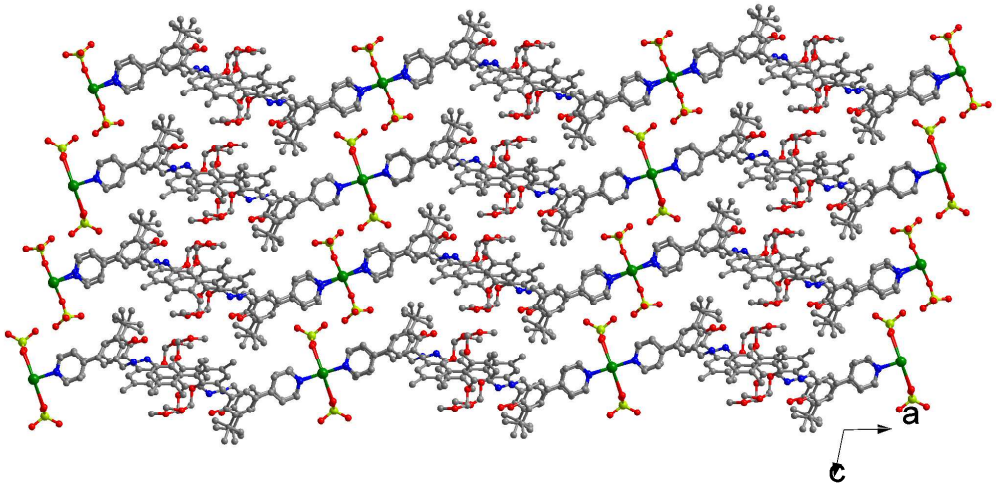
N(1)#1-Ag(1)-N(1)	173.3(5)
C(1)-N(1)-Ag(1)	117.7(4)
C(5)-N(1)-Ag(1)	121.7(4)

Symmetry transformations used to generate equivalent atoms:
#1 x-y+1,-y+2,-z+2 #2 x,x-y+1,-z+17/6 #3 –x, -x+y,-z+4/3

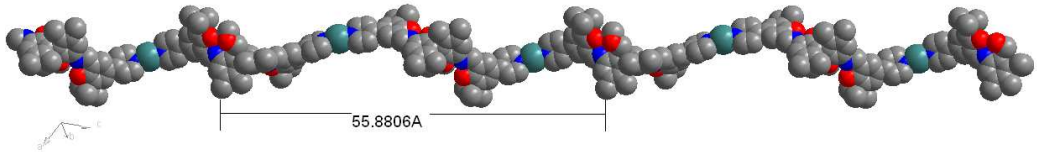
6.1. Figure S1. Coordination environments of the Ag (connected with monodentate and bidentate ClO_4^- anions) in **1**.



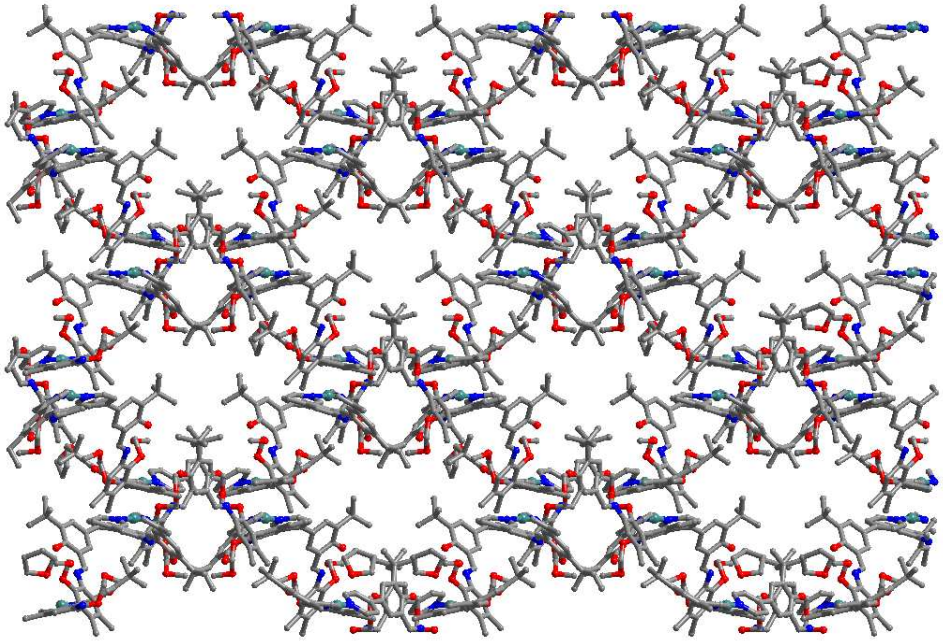
6.2. Figure S2. A view of 3D structure of **1** along the *b*-axis.



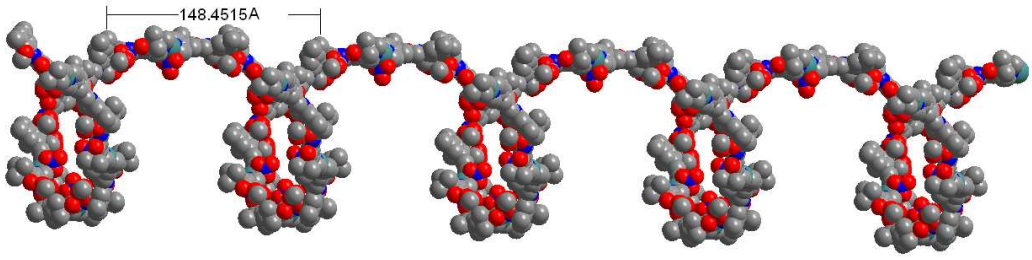
7.1. Figure S3. The space-filling representation of a 1D 2_1 helix chain in **2**



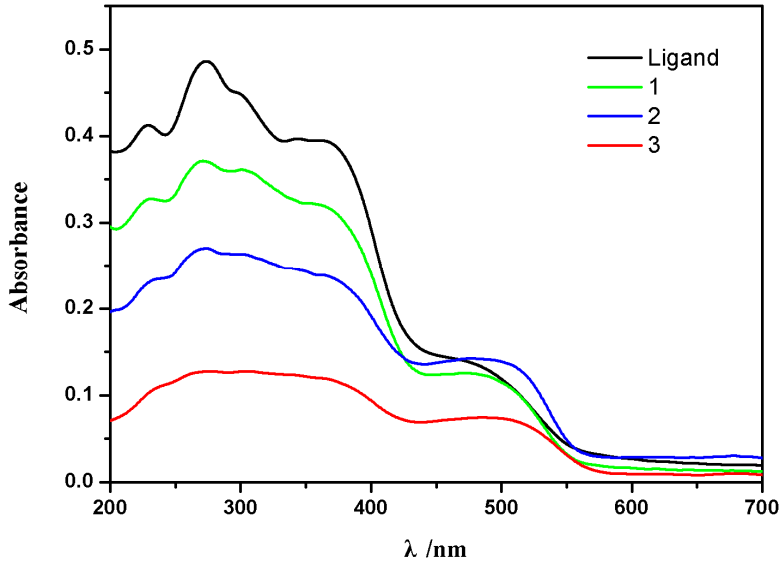
7.2. Figure S4. A view of 3D structure of **2** along the *c*-axis



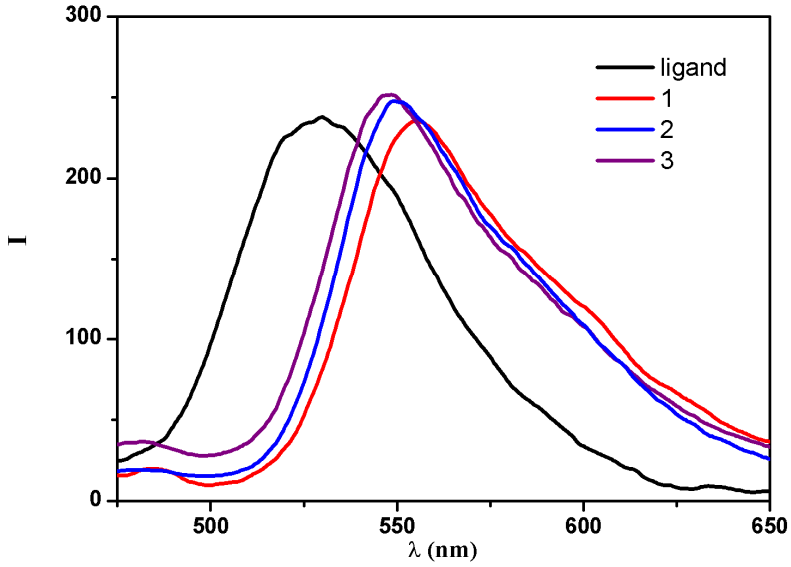
8. Figure S5. Space-filling representations of a 1D 6_5 helix chain in **3**



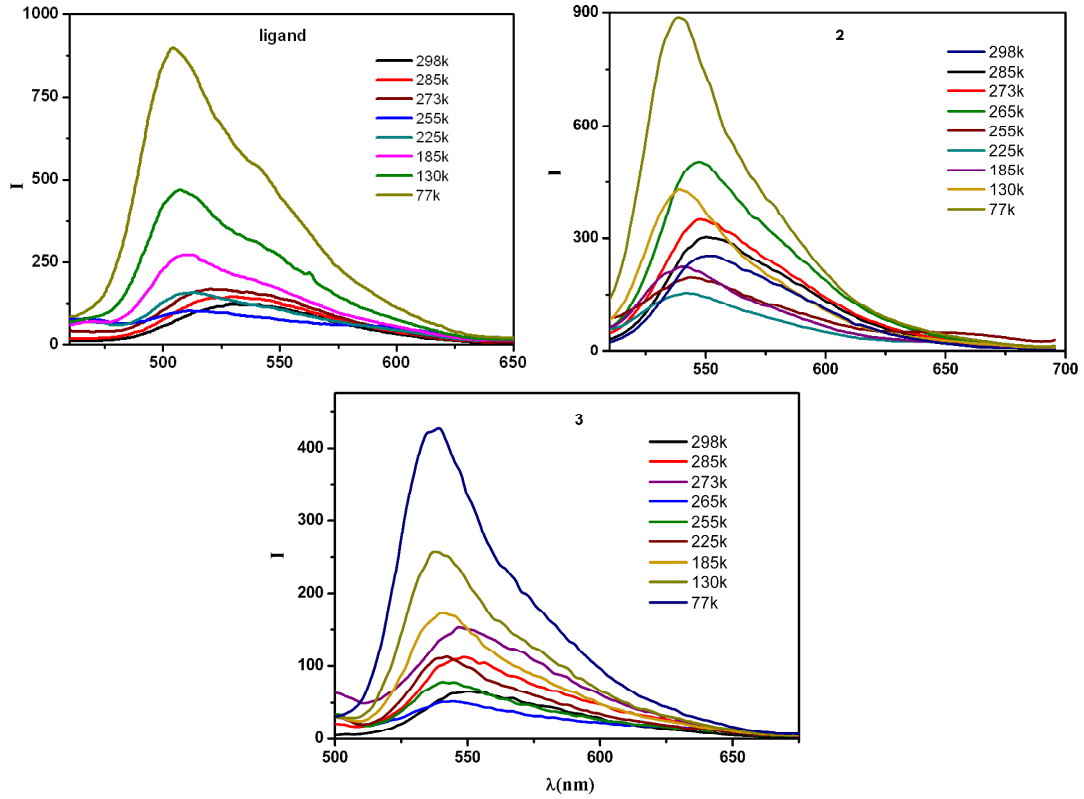
9. Figure S6. UV/Vis spectra of **1-3** and **L** in the solid state at room temperature.

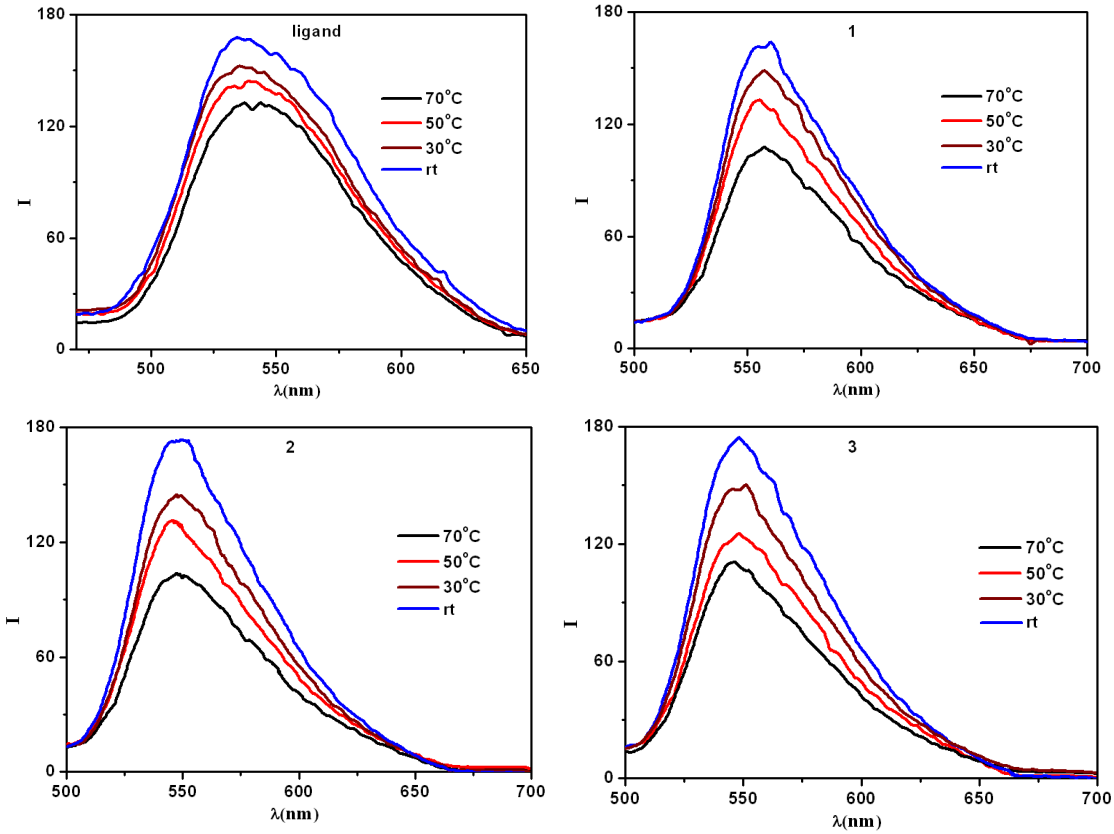


10. Figure S7. PL spectra of **1-3** and **L** in the solid state at room temperature.

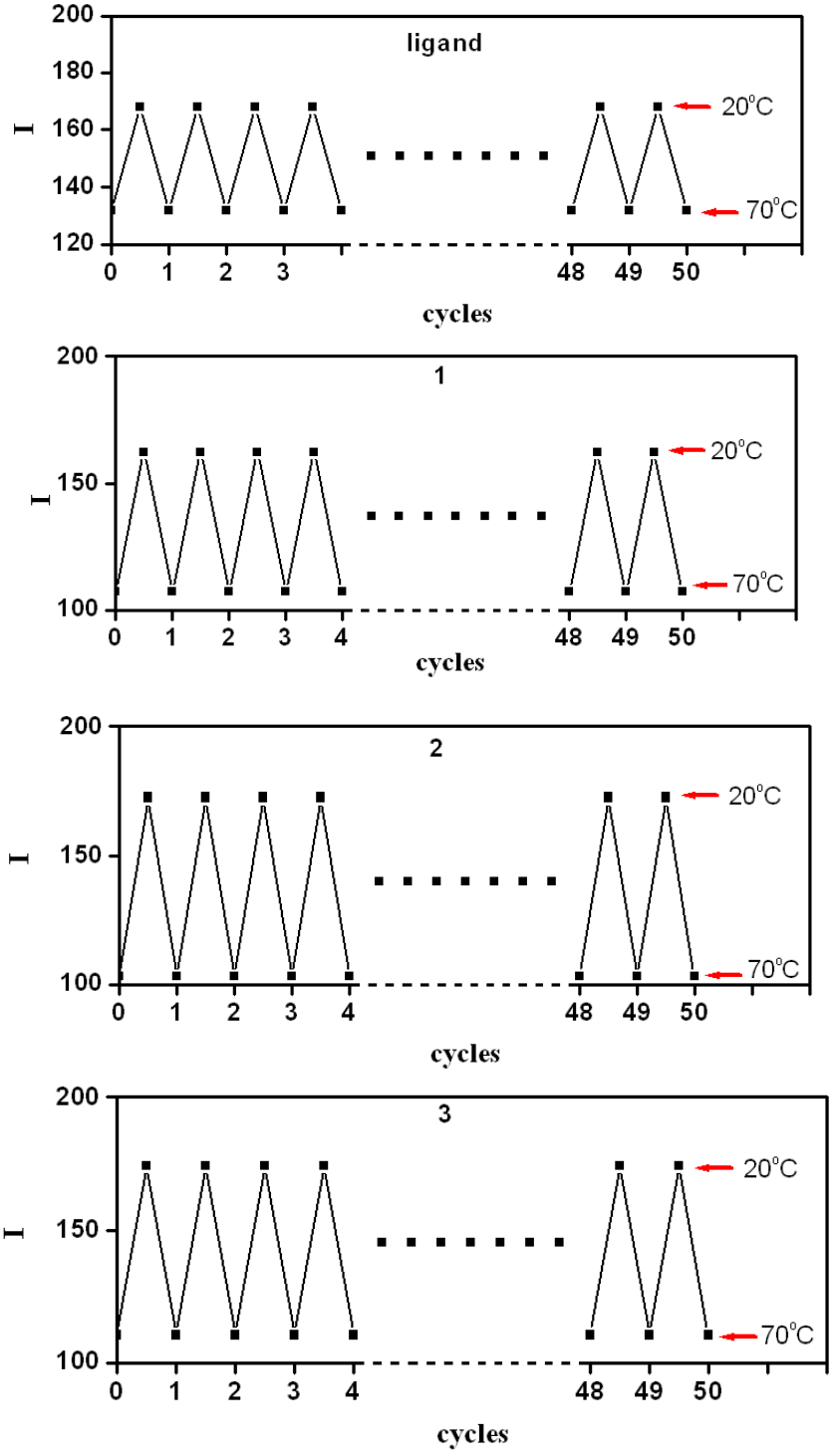


11. Figure S8. PL spectra of **1-3** and **L** in the solid state at different temperatures

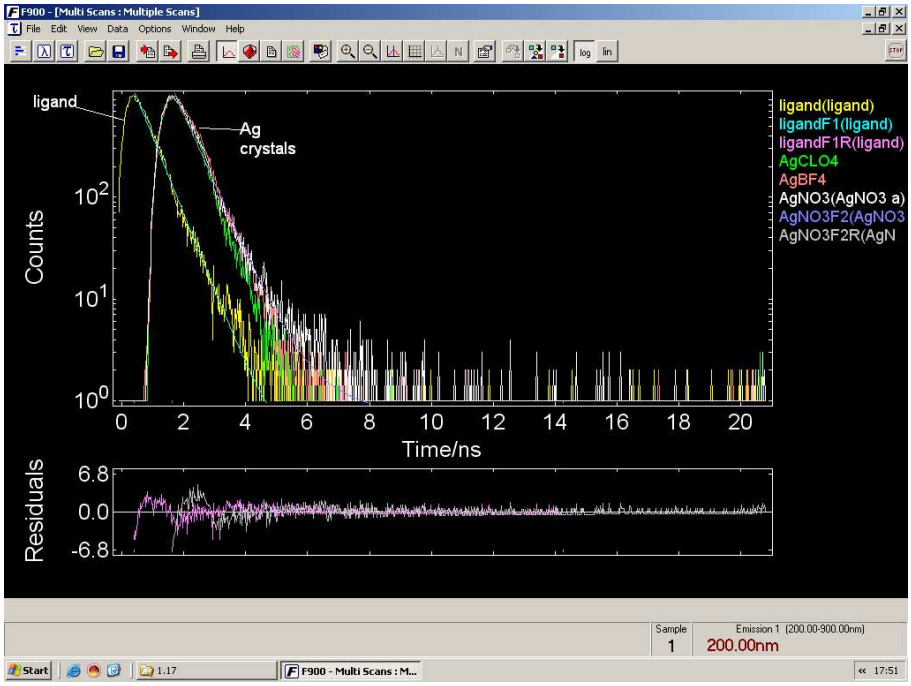




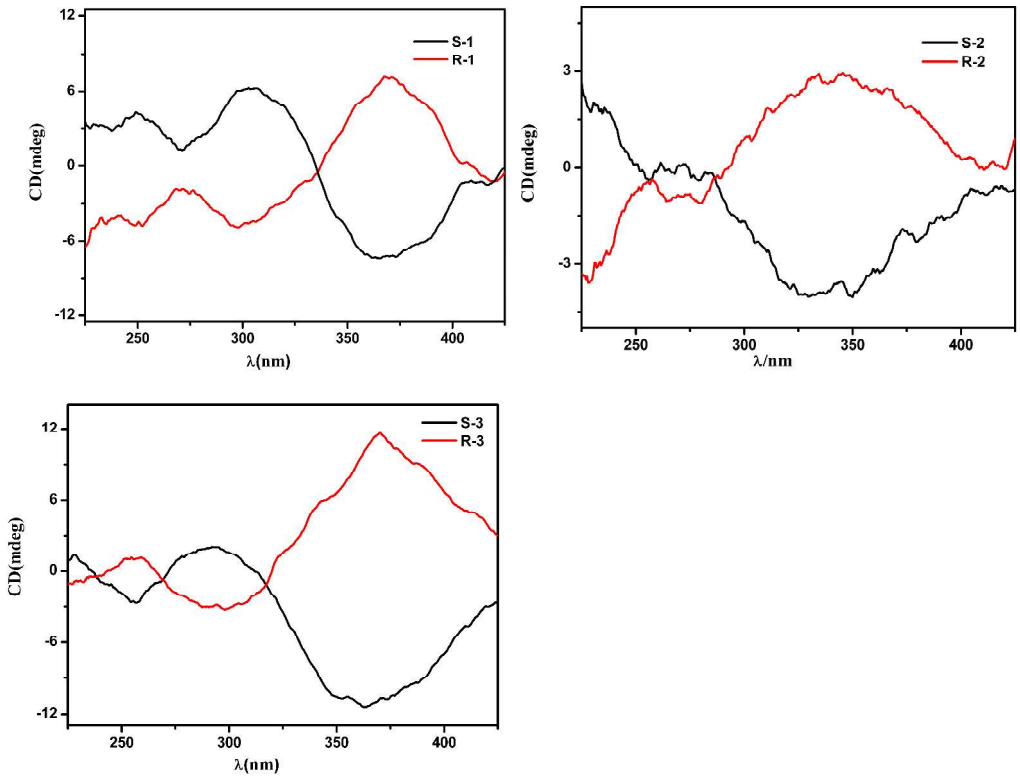
12. Figure S9. The PL changes of **1-3** and **L** in the heating-cooling recycling process.



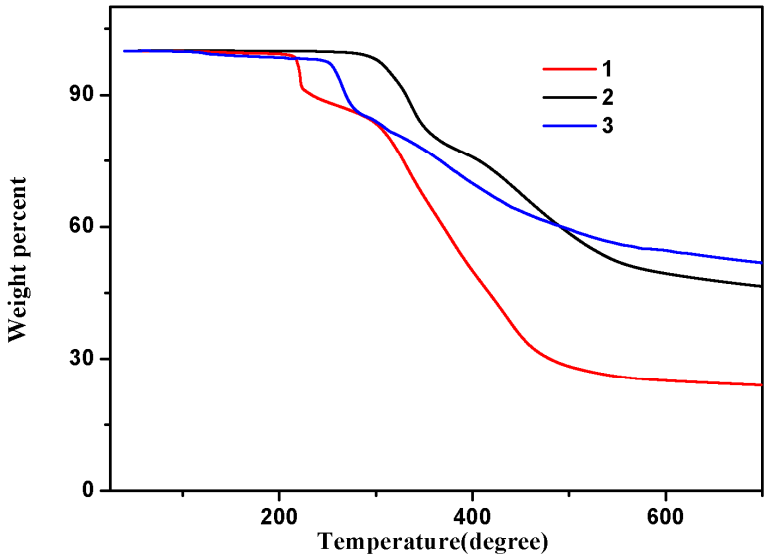
13. Figure S10. PL lifetimes of **1-3** and **L**



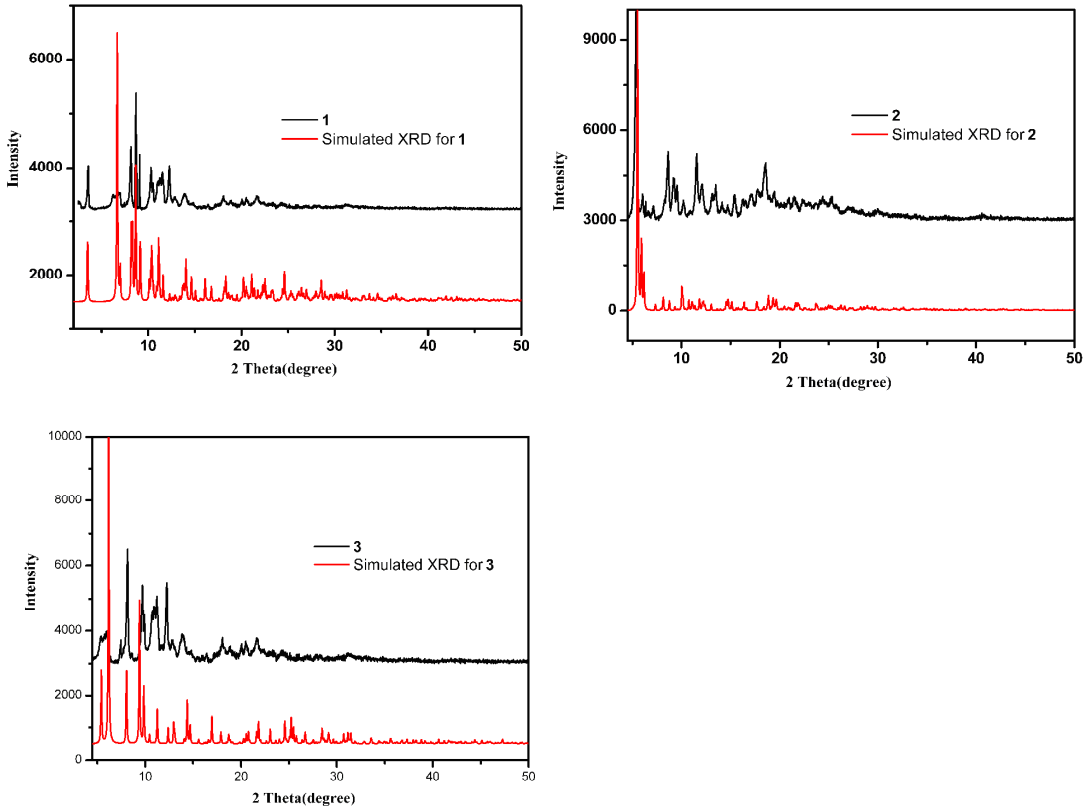
14. Figure S11. CD spectra of (*R*)/(*S*)-**1**, (*R*)/(*S*)-**2** and (*R*)/(*S*)-**3**



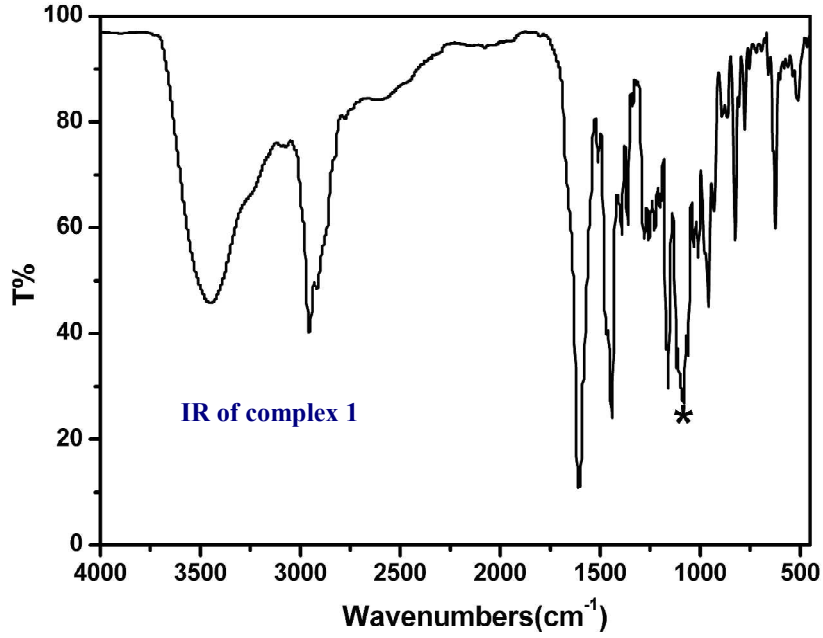
15. Figure S12. TGA curves of **1-3**

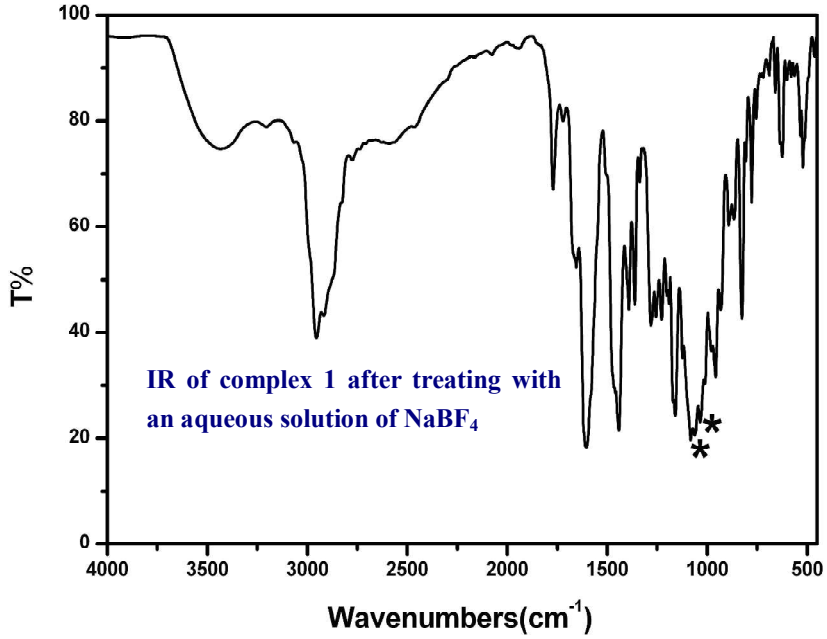


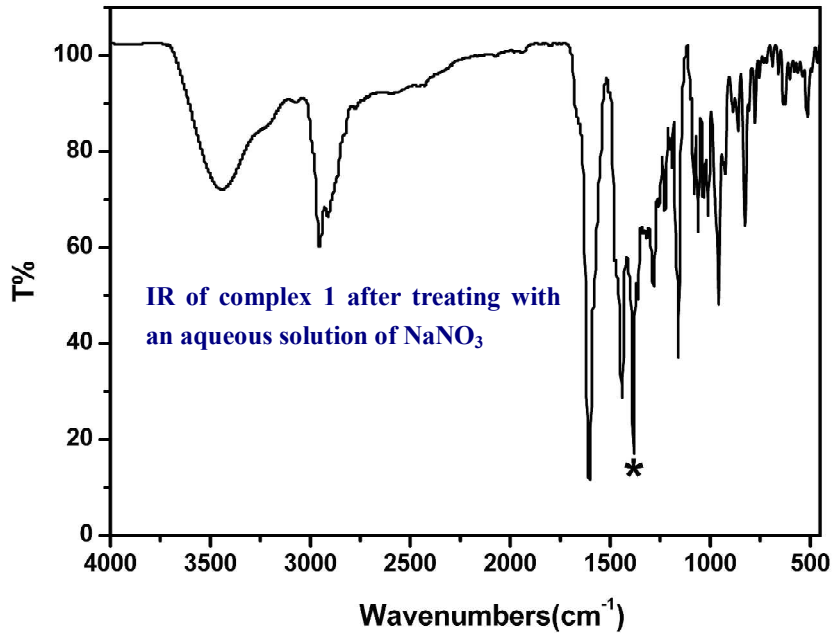
16. Figure S13. PXRD patterns of **1-3**

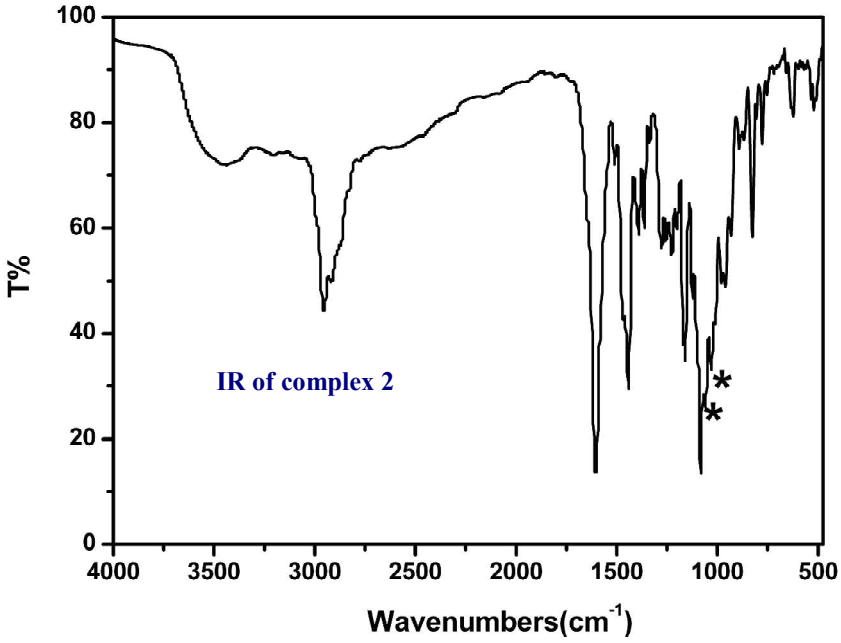


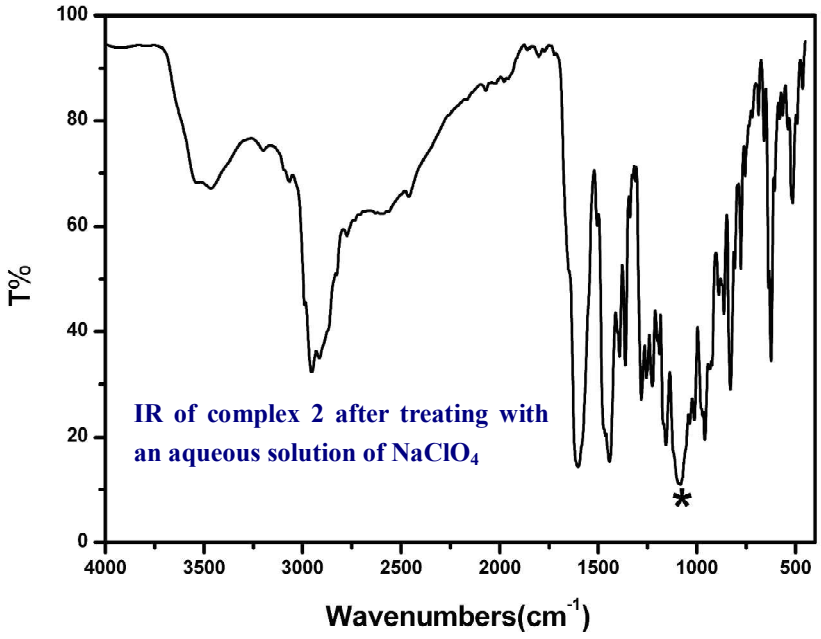
17. Figure S14. IR of anion exchange

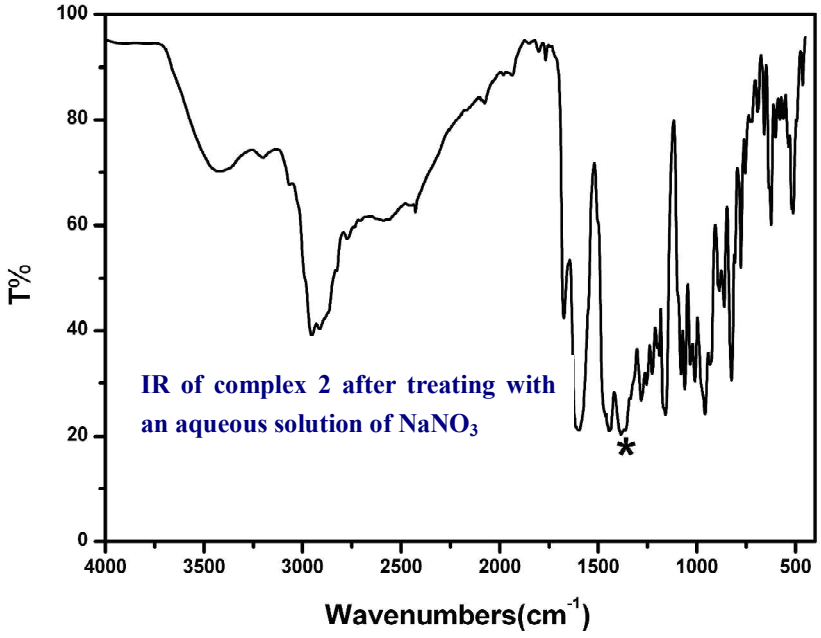





IR of complex 1 after treating with an aqueous solution of $NaNO_3$
T%
Wavenumbers(cm^{-1})
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
*


IR of complex 2
T%
Wavenumbers(cm^{-1})
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
*
*


100
80
60
40
20
0
T%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers(cm-1)
IR of complex 2 after treating with
an aqueous solution of NaClO4
*


100
80
60
40
20
0
T%
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers(cm-1)
IR of complex 2 after treating with
an aqueous solution of NaNO3
*

18. Figure S15. PXRD of **1** and **2** before and after anion exchange