Multiple Topological Isomerism of (n,3) Networks In Silver-Based Metal-Organoboron Frameworks

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1. Materials and General Procedures.

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, H and N were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 $^{o}C\ min^{-1}$ 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. Solid-state UV-vis absorption spectra were recorded on a Lambda 20 UV/vis Spectrometer (Perkin Elmer, Inc., USA). The fluorescence spectra were carried out on a LS 50B Luminescence Spectrometer (Perkin Elmer, Inc., USA). The morphologies of samples were characterized by S-2150 field-emission scanning electron microscopy (FESEM, Hitachi High-Technologies Corp., Japan).

X-ray Crystallography. Single-crystal XRD data for the compounds was collected on a Bruker SMART Apex II CCD-based X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å) for **1** and **3** or with Cu-Kα radiation (λ = 1.54178 Å) for **2** at 123 K. 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 *F*2 (G. M. Sheldrick, SHELXTL97, program for crystal structure refinement, University of Göttingen, Germany, 1997). All aromatic groups *were* input as idealized planar *rings* with *C-C bond* lengths of 1.39 Å angstrom. Some *C-C bonds* from the aromatic *rings* to the methyl groups are somewhat short and so were constrained to be ca. 1.50 Å. These bonds of the guest molecules were constrained to be reasonably in all three complexes. In complex 2, one perchlorate anion was disordered around a 3-fold. All non-H atoms except for the disordered ones were refined anisotropically. Crystal data and details of the data collection are given in Table S1. The selected bond distances and angles are presented in Tables S2-S4. CCDC-747394, 747395 and 747396 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. The single-crystal diffraction showed that the products have the formula $[(Ag\mathbf{L})NO_3]\cdot 2H_2O$ (**1**), $[Ag(\mathbf{L})CF_3SO_3]\cdot 3CH_3CN\cdot 13/6H_2O$ (**2**) and $[Ag(\mathbf{L})ClO_4]\cdot 3/2CH_3CN$ (**3**). Microanalysis and TGA indicated that **1-3** partially lost guest molecules upon exposure to air.

2. Antibacterial Testing:

The *paper disc diffusion method* was used to *test antibacterial* activity. 0.005 mol/L aqueous solution of compounds **1-3** and the Ligand **L** were prepared respectively, and the antibacterial activity of all the compounds against *S.* aureus and

E.coli were studied. The bacterium suspension concentration was controlled as 5×10^5~5×10^6 cfu/mL; the diameters of filter paper were 5 mm, and for the experiments, flat plates were incubated at 37 ^oC (bacterium) for different *periods of time*. Their inhibition diameter (including filter paper) was measured with a vernier caliper. (cfu: colony forming units)

Minimum inhibition concentration (MIC):

Nutrition broth was employed for bacterial growth. The tested compounds **1-3** and **L** were prepared in nutrition broth medium and diluted in concentrations of the range 50-800 μg/mL. Inocula containing 1×10^6 cfu/mL were obtained from broth cultures. The lowest concentration (μg/mL) of compounds, which inhibited the growth of bacteria after 24 h incubation at 37 ^oC was taken as the MIC. All experiments were carried out in duplicate and the results were confirmed in three independent experiments. The results in the forms of the diameter of growth inhibition area in mm and the MIC (μg/ml) are listed in Table 1.

3. Silver ion release tests.

To investigate the silver ion release from the samples, crystalline samples **1-3** of ~100 μm grain sizes were immersed in 10 ml of distilled water. At defined times the immersion liquid was exchanged completely. The concentration of silver ions in the immersion liquid was measured by ICP-AES on an Iris Advangtage 1000 Inductively Coupled Plasma Emission Spectrometer.

0.4 mmol of the products (**1**: 33.9 mg, **2**: 37.4 mg, and **3**: 34.7 mg, containing **1.15** mg of Ag; all of them contain 4.32 mg Ag) were immersed in 50 mL of distilled water at 37 °C; the liquids recovered at various times (up to 4 days) were concentrated to 5 mL in a rotary evaporator and analyzed by ICP/AES. A commercial ICP multistandard solution containing 50 ± 0.1 ppm of Ag^+ was used for calibration).

4**. Synthesis of compounds 1-3**

***Synthesis of* 1:** The mixture of ligand **L** (0.005 mmol) dissolved in CH_2Cl_2 (0.5 mL) and the metal salt $AgNO_3$ (0.5 mL) dissolved in MeCN (0.5 mL) was put into a 5 mL glass tube in turn, with 0.5ml DMF in the middle. After layering for 2 days, colorless crystals of **1** suitable for X-ray diffraction were collected, washed with diethyl ether, and dried in air. Yield: **66%**, 3.5 mg. The product can be best formulated as $[(Ag\mathbf{L})NO_3]\cdot2H_2O$ on the basis of microanalysis, IR and TGA.

Elemental Analysis data: Anal (%). Calcd for C45H52AgBN4O5: C, 63.77; H, 6.18; N, 6.61. Found: C, 63.38; H, 5.87; N, 6.41. IR (KBr, cm^{-1}): 3436(w), 2956(w), 2424(w), 1602(m), 1536(w), 1384(s), 1256(w), 1166(m), 1066(m), 798(m)

***Synthesis of* 2:** The similar method used in synthesis of crystal **1**. The mixture of ligand **L** (0.005 mmol) dissolved in CH_2Cl_2 (0.5 mL) and the metal salt AgOTf (0.005 mmol) dissolved in MeCN (0.5 mL) was put into a 5 mL glass tube in turn, with another 0.5ml DMSO in the middle. After layering for 5 days, colorless crystals of **2** suitable for X-ray diffraction were collected, washed with diethyl ether, and dried in air. Yield: **53%**, 2.4 mg. The product can be best formulated as $[Ag(\mathbf{L})CF_3SO_3]\cdot 2H_2O$ on the basis of microanalysis, IR and TGA.
Elemental Analysis data: Anal (%). Calcd for C46H52AgBF3N3O5S: C, 59.11; H, 5.61; N, 4.50; S, 3.43. Found: C, 59.50; H, 5.42; N, 4.42; S, 3.34. IR (KBr, cm^{-1}): 3436(w), 2956(w), 2424(w), 1602(m), 1536(w), 1384(s), 1256(w), 1166(m), 1066(m), 798(m)

***Synthesis of* 3:** A mixture of $AgClO_4$ (0.005 mmol), **L** (0.005 mmol), DMA (0.5 mL), CH_2Cl_2 (1.0 mL) and MeCN (0.5 mL) was sealed in a 10 mL vial with a screw cap and heated at 60 ºC for two days. The mixture was then cooled to room temperature and colorless crystals of **3** suitable for X-ray diffraction were collected, washed with ether and dried in air. Yield: **80%**, 3.4 mg. The product can be best formulated as $[Ag(\mathbf{L})ClO_4]\cdot H_2O$ on the basis of microanalysis, IR and TGA.
Elemental Analysis data: Anal (%). Calcd for C45H50AgBClN3O5: C, 62.34; H, 5.81; N, 4.85;. Found: C, 62.70; H, 5.71; N, 4.64. IR (KBr, cm^{-1}): 3398 (w), 2914 (w), 1662 (s), 1454 (m), 1392(s), 1260(m), 1068(s), 952(m), 820 (m), 800(m), 798(m), 620 (m)

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

Identification code	**1**	**2**	**3**
Empirical formula	C45H52AgBN4O5	C52H61.33AgBF3N6O5.17S	C48H52.5AgBClN4.5O4
Formula weight	847.59	1060.81	910.58
Temperature (K)	123(2)	123(2)	123(2)
Wavelength (Å)	0.71073	1.54178	0.71073
Crystal system	Tetragonal	Orthorhombic	Trigonal
Space group	$P4_12_12$	$P2_12_12_1$	R32
Unit cell dimensions	a = 22.3511(4) Å alpha=90º b = 22.3511(4) Å beta=90º c = 25.3776(5) Å gamma=90º	a =13.6581(2) Å alpha=90º b =32.4156(5) Å beta=90º c =40.5791(6) Å gamma=90º	a =18.2533(14)Å alpha=90º b =18.2533(14)Å beta=90º c =47.517(7) Å gamma=120º
Volume ($Å^3$), Z	12677.9(4), 8	17965.8(5), 12	13711(3), 12
Density (calculated) (mg/m^3)	0.888	1.177	1.323
Absorption coefficient (mm^{-1})	0.351	3.475	0.547
F(000)	3536	6620	5676
Theta range for data collection (º)	2.99 to 25.00	2.73 to 50.32	2.23 to 27.54
Limiting indices	-26<=h<=26, -26<=k<=26, -27<=l<=30	-12<=h<=13, -31<=k<=29, -38<=l<=37	-23<=h<=17, -16<=k<=23, -61<=l<=61
Reflections collected	99180	35420	28389
Independent reflections	11116 (Rint = 0.0453)	15204 (Rint=0.0425)	7002 (Rint=0.0526)
Completeness to theta	25.00º, 99.2 %	50.32º, 87.7 %	27.54º, 99.0 %
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	11116/ 84 / 483	15204 / 79 / 1464	7002 / 36 / 312
Goodness-of-fit on F^2	1.055	1.164	1.028
Final R indices [I>2sigma(I)]	R1=0.0572, wR2=0.1565	R1=0.0968, wR2=0.2381	R1=0.0716, wR2=0.1845
R indices (all data)	R1=0.0625, wR2=0.1630	R1=0.1155, wR2=0.2562	R1=0.1232, wR2=0.2194
Absolute structure parameter	-0.01(3)	0.057(12)	-0.02(4)

Largest diff. peak and hole ($e.Å^{-3}$)	0.590 and -0.391	0.901 and -0.475	0.566 and -0.741

6**. Table S2**. Selected bond lengths [Å] and angles [º] for **1**

Ag(1)-N(3)#1	2.265(3)
Ag(1)-N(1)	2.270(3)
Ag(1)-N(2)#2	2.336(4)
B(1)-C(24)	1.587(5)
B(1)-C(39)	1.591(5)
B(1)-C(9)	1.606(6)
N(3)#1-Ag(1)-N(1)	129.51(15)
N(3)#1-Ag(1)-N(2)#2	110.58(16)
N(1)-Ag(1)-N(2)#2	106.11(15)
C(24)-B(1)-C(39)	124.6(3)
C(24)-B(1)-C(9)	117.7(3)
C(39)-B(1)-C(9)	117.6(3)
C(1)-N(1)-Ag(1)	121.9(3)
C(5)-N(1)-Ag(1)	121.3(3)
C(8)-C(9)-B(1)	121.2(3)
C(10)-C(9)-B(1)	119.3(3)
C(23)-C(24)-B(1)	121.4(3)
C(25)-C(24)-B(1)	119.8(3)
C(40)-C(39)-B(1)	121.0(4)
C(38)-C(39)-B(1)	119.6(3)

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

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

Ag(1)-N(4)	2.201(7)
Ag(1)-N(6)#1	2.250(7)
Ag(1)-N(1)	2.272(9)
Ag(2)-N(3)#2	2.246(7)
Ag(2)-N(5)	2.271(8)
Ag(2)-N(7)	2.280(7)
Ag(3)-N(8)	2.269(6)
Ag(3)-N(2)#4	2.303(7)
Ag(3)-O(3)	2.598(15)
B(1)-C(24)	1.53(2)
B(1)-C(39)	1.58(2)
B(1)-C(9)	1.60(2)
B(2)-C(84)	1.57(2)
B(2)-C(54)	1.62(2)
B(3)-C(129)	1.59(2)
N(4)-Ag(1)-N(6)#1	121.5(4)
N(4)-Ag(1)-N(1)	122.6(4)
N(6)#1-Ag(1)-N(1)	106.7(4)
N(3)#2-Ag(2)-N(5)	119.6(4)
N(3)#2-Ag(2)-N(7)	126.3(3)
N(5)-Ag(2)-N(7)	113.6(4)

N(9)#3-Ag(3)-N(8)	126.0(4)
N(9)#3-Ag(3)-N(2)#4	111.9(4)
N(8)-Ag(3)-N(2)#4	101.7(4)
N(9)#3-Ag(3)-O(3)	94.9(4)
N(8)-Ag(3)-O(3)	130.1(4)
N(2)#4-Ag(3)-O(3)	84.9(4)
C(24)-B(1)-C(39)	123.5(13)
C(24)-B(1)-C(9)	117.3(13)
C(39)-B(1)-C(9)	119.0(12)
C(84)-B(2)-C(69)	124.9(12)
C(84)-B(2)-C(54)	119.6(14)
C(69)-B(2)-C(54)	115.4(14)
C(114)-B(3)-C(129)	121.0(11)
C(114)-B(3)-C(99)	119.1(11)
C(129)-B(3)-C(99)	119.9(11)

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

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

Ag(1)-N(3)	2.252(7)
Ag(1)-N(1)	2.272(2)
Ag(2)-N(2)	2.219(7)
B(1)-C(9)	1.605(5)
B(1)-C(22)	1.624(12)
B(2)-C(31)	1.611(6)
N(3)-Ag(1)-N(1)	118.09(9)
N(1)-Ag(1)-N(1)#1	123.82(18)
N(2)#2-Ag(2)-N(2)#3	120.000(1)
C(9)#4-B(1)-C(9)	121.4(7)
C(9)-B(1)-C(22)	119.3(3)
C(31)#5-B(2)-C(31)#6	120.000(1)

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

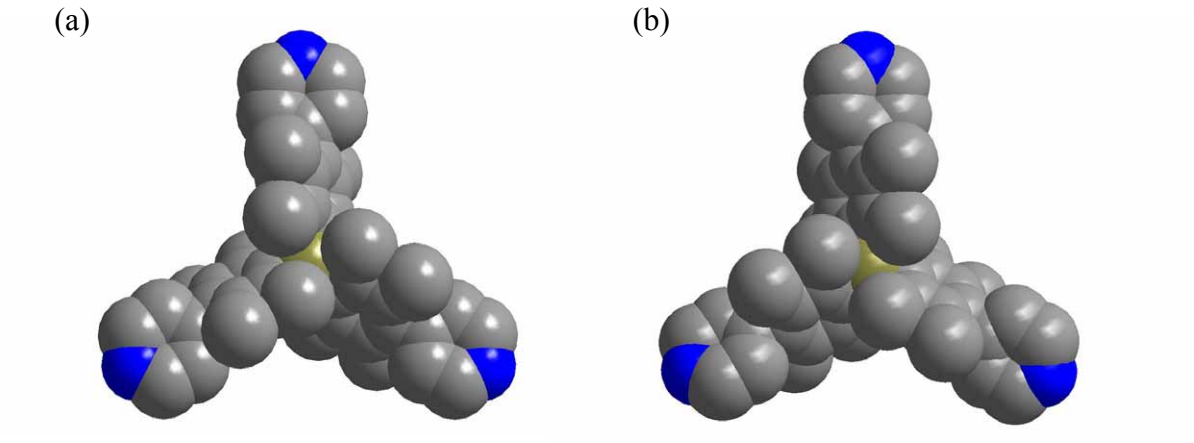
9. **Table S5.** Mean diameter of inhibition area against *E.* Coli (1) and *S.* aureus for compounds **1** and **3** after immersing in distilled water. Tested samples: 2.0 mg (Ag content ~0.24 mg); Incubation condition: 37 ^{o}C, 24 h. **(**See Figure S17**)**

Time (day)	Compounds	Inhibition area (mm)	
		E. coli	*S.* aureus
0	**1**	12	15
	3	14	16
1	**1**	10	14
	3	12	14
2	**1**	12	15
	3	12	12
4	**1**	13	14
	3	13	15
8	**1**	12	16
	3	10	13

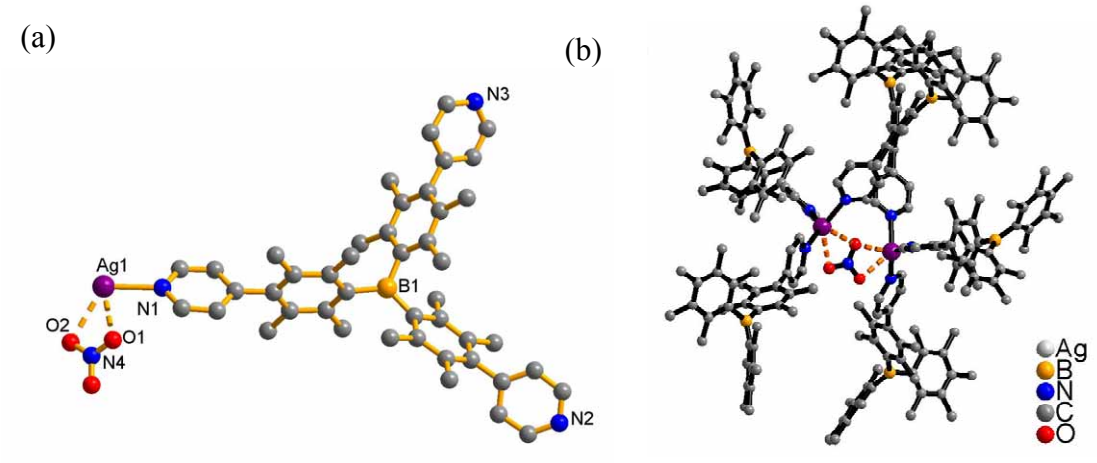
10. **Table S6.** Cumulative Ag^{+} ion concentrations of compounds **1-3** in distilled water with the passage of time

Time (h)	Concentrations (ppm)		
	1	**2**	**3**
0	0	0	0
2	0.1021	0.1002	0.1047
12	0.1434	0.1393	0.1651
24	0.1902	0.172	0.2108
48	0.2817	0.2586	0.3091
72	0.3721	0.3331	0.4262
96	0.4636	0.4272	0.5107

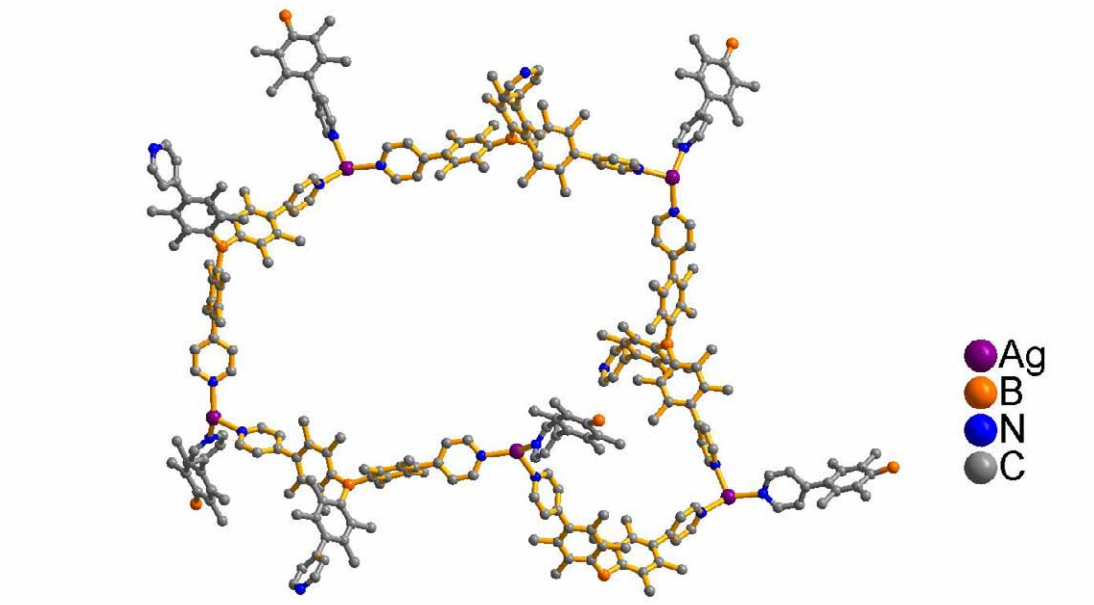
11. **Figure S1.** (a) Δ- and (b) Λ-**L** in **1-3**.



12.1. **Figure S2.** (a) The asymmetric unit and (b) the binding mode of NO_3^- in **1**.

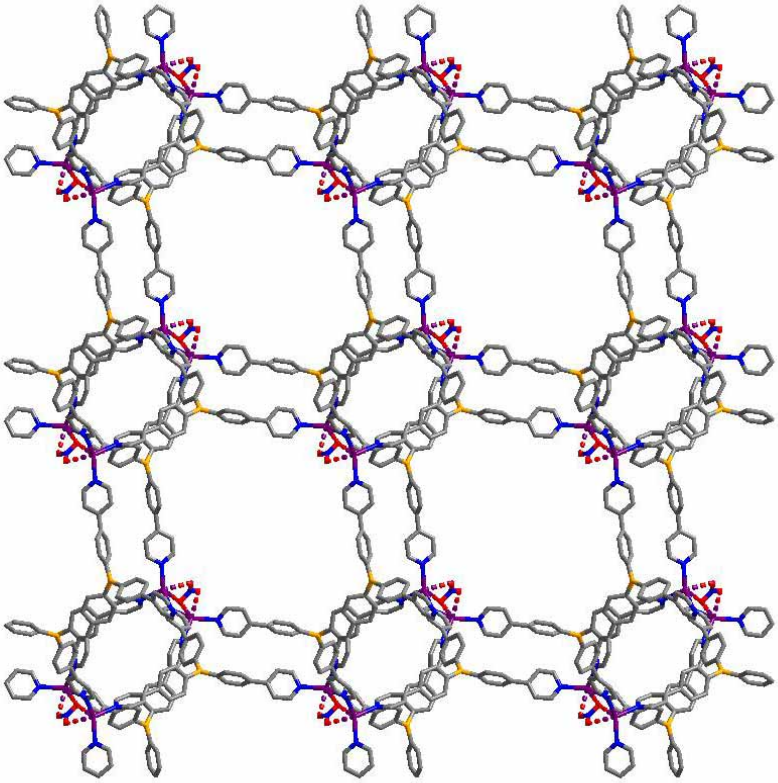


12.2. **Figure S3.** A view of one 10-membered ring containing five silver and five boron atoms in **1**

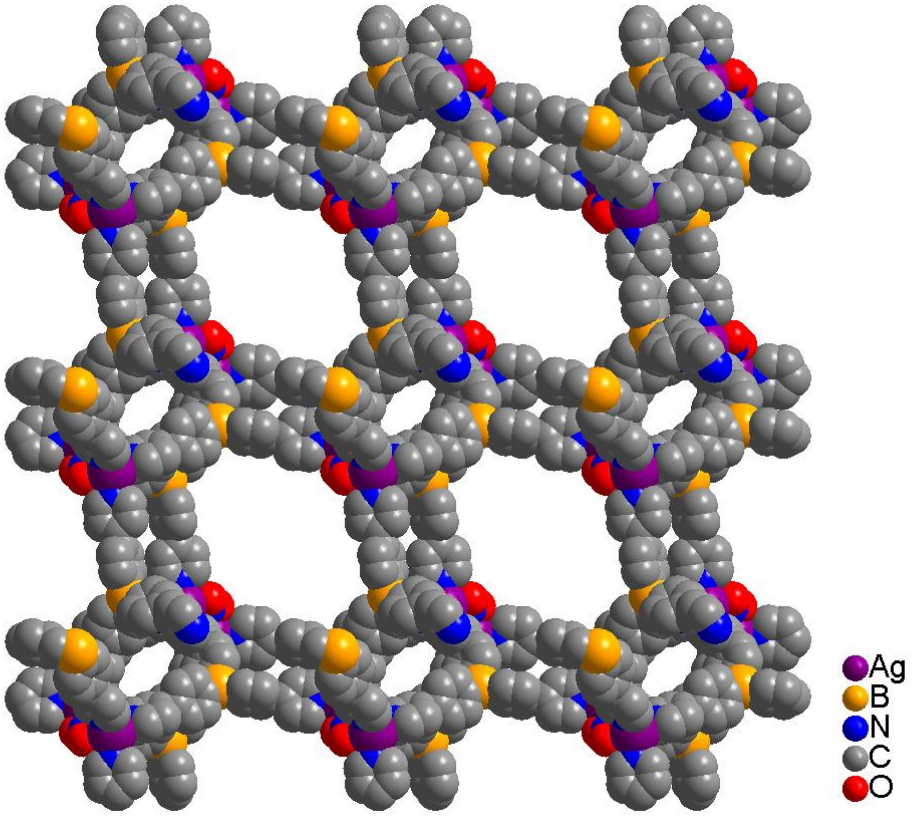


12.3. **Figure S4**. (a) A view of one (10,3) network of **1** down the *c* axis and (b) its space-filling mode

(a)

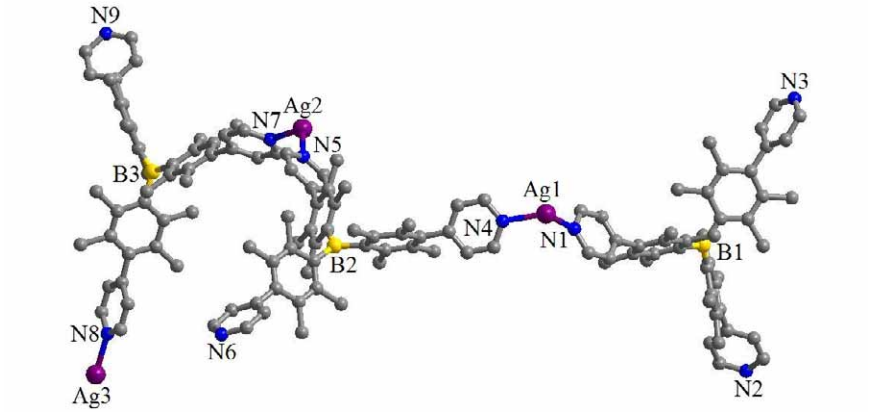


(b)

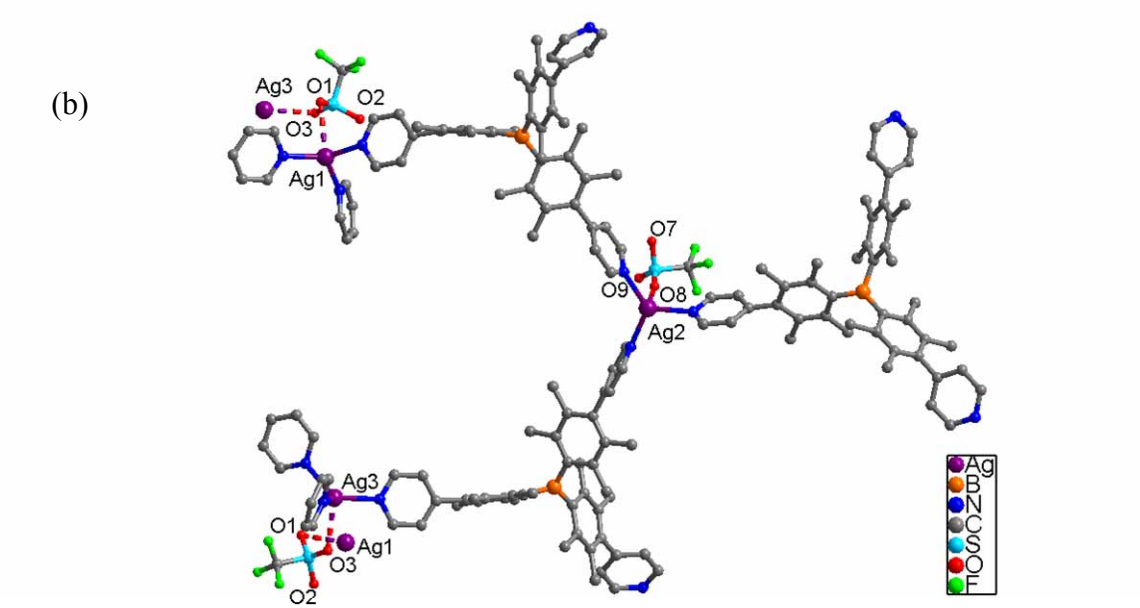


13.1. **Figure S5**. (a) The asymmetric unit and (b) the binding mode of OTf in **2.**

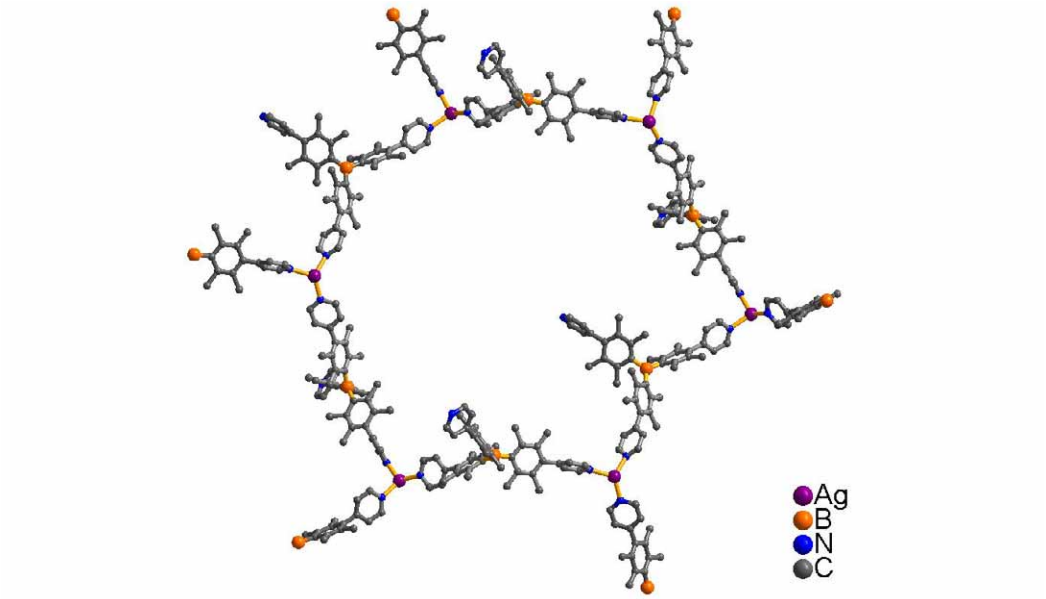
(a)



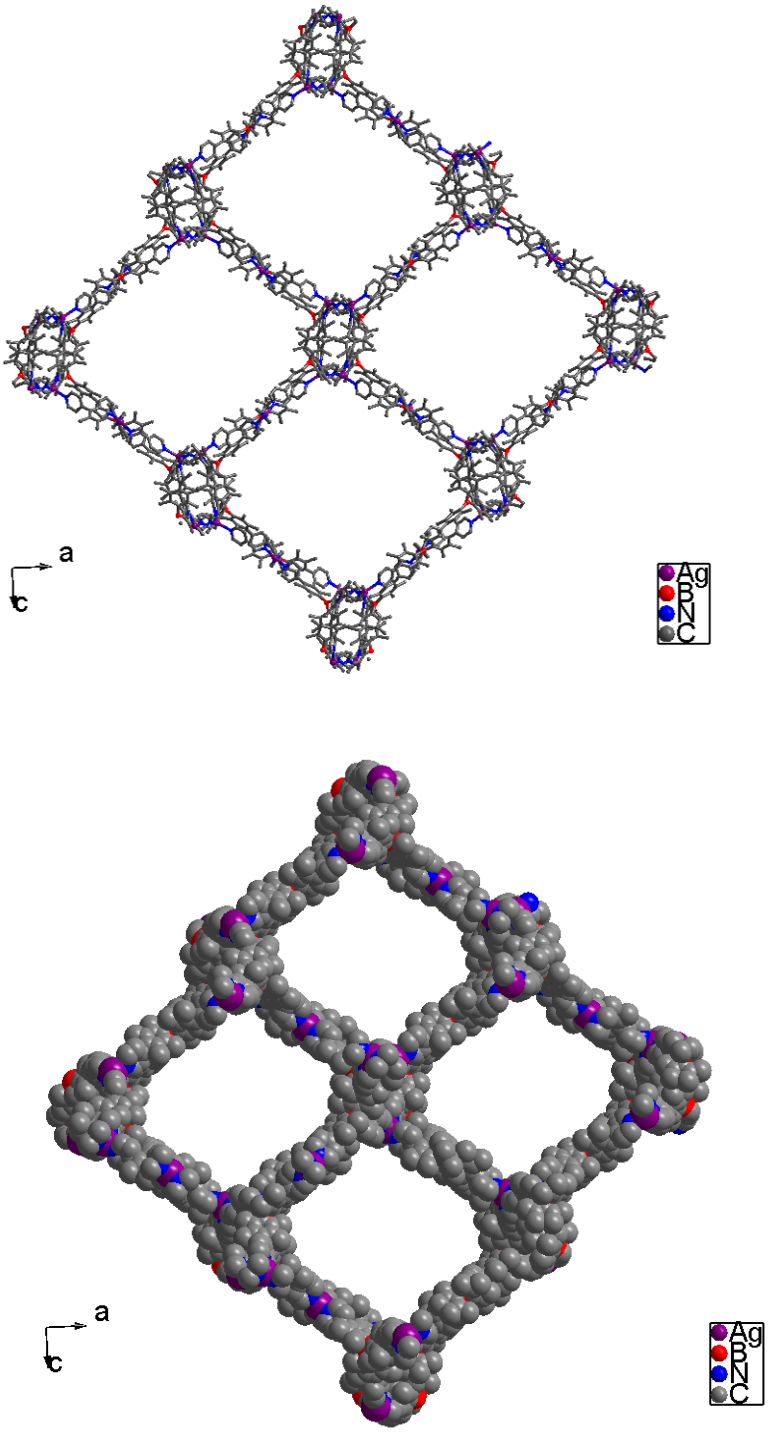
(b)



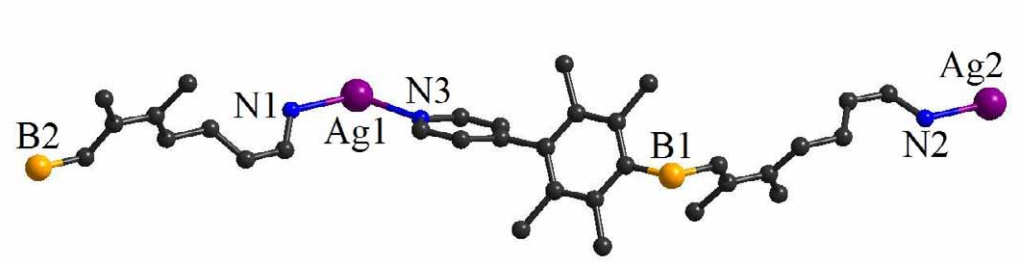
13.2. **Figure S6.** A view of one 12-membered ring containing six silver and six boron atoms in **1**



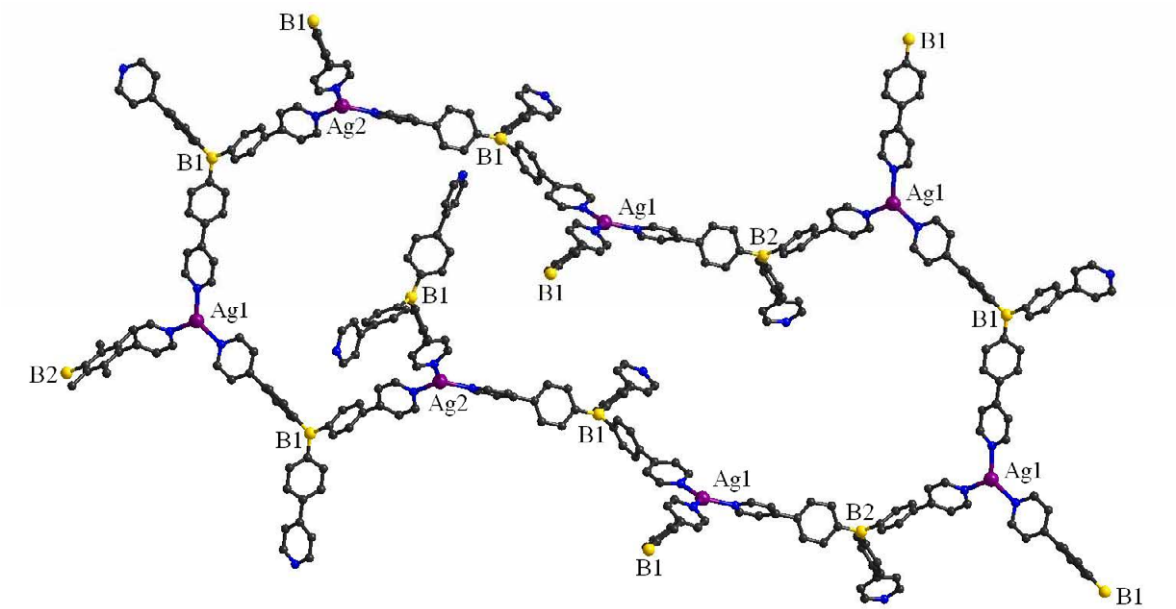
13.3. **Figure S7**. (a) A view of one (14,3) network of **2** down the *b* axis and (b) its space-filling mode



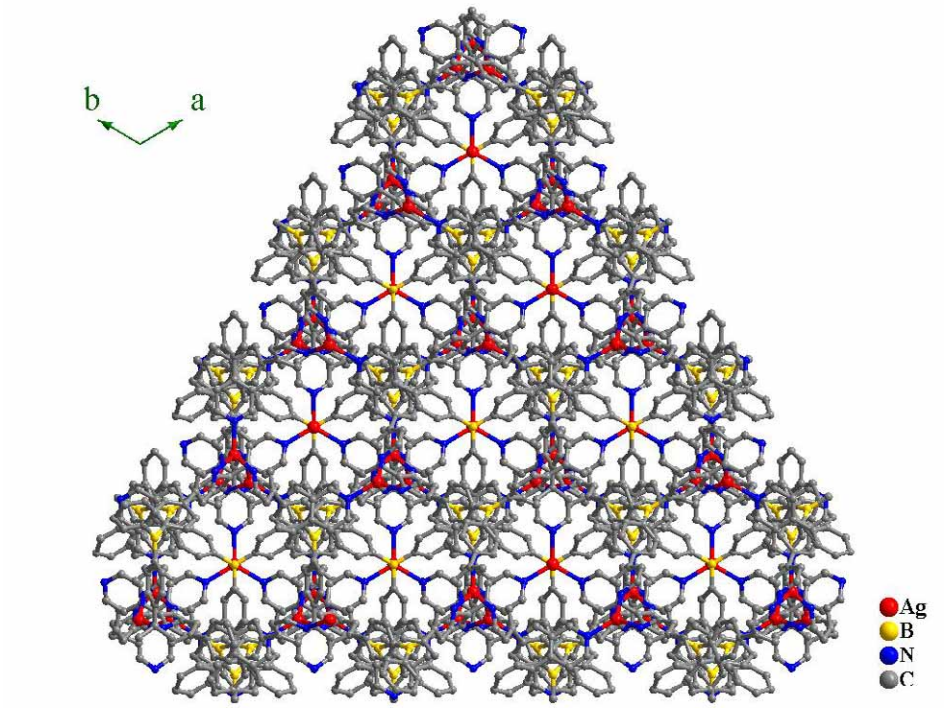
14.1. **Figure S8**. The asymmetric unit of **3**



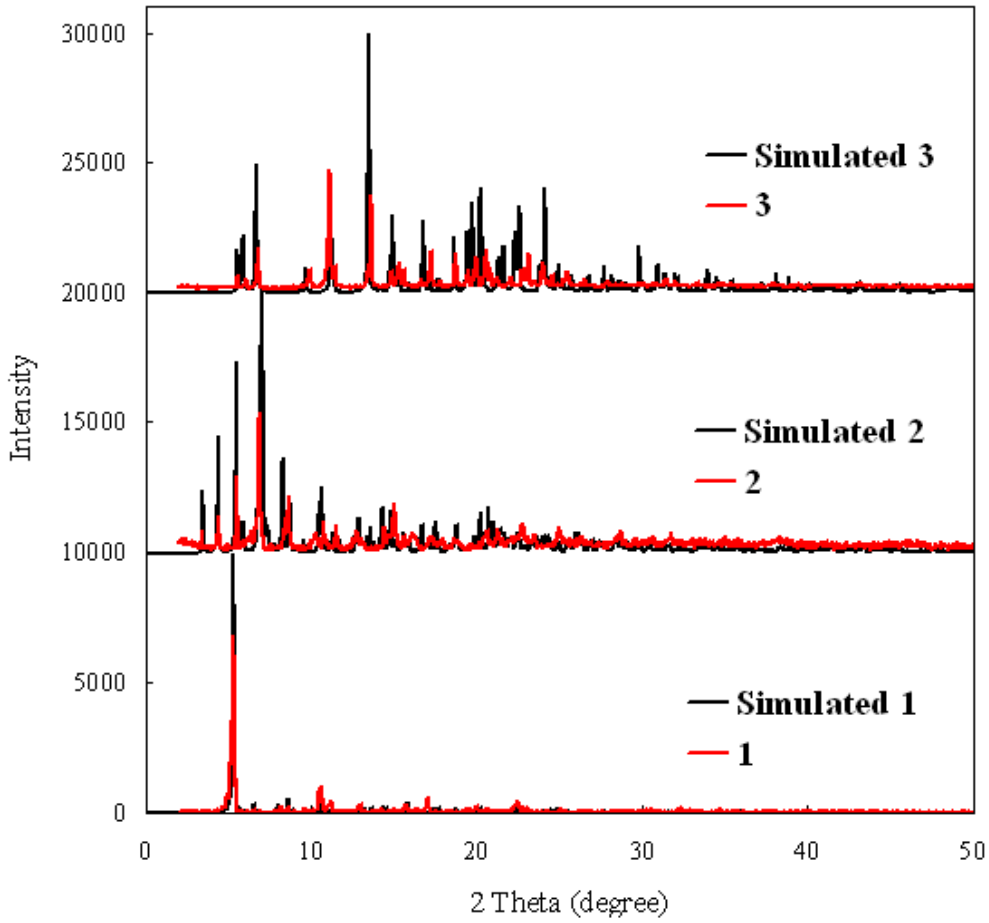
14.2. **Figure S9.** A view of one 14-membered ring containing seven silver and seven boron atoms in **3**



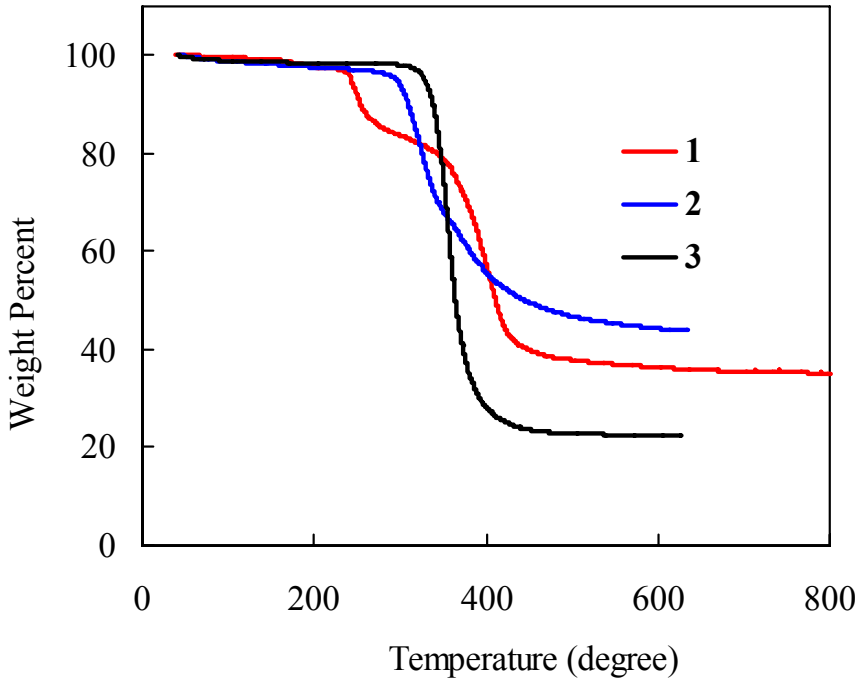
14.3. **Figure S10.** A view of 3D structure of **3** along the c-axis.



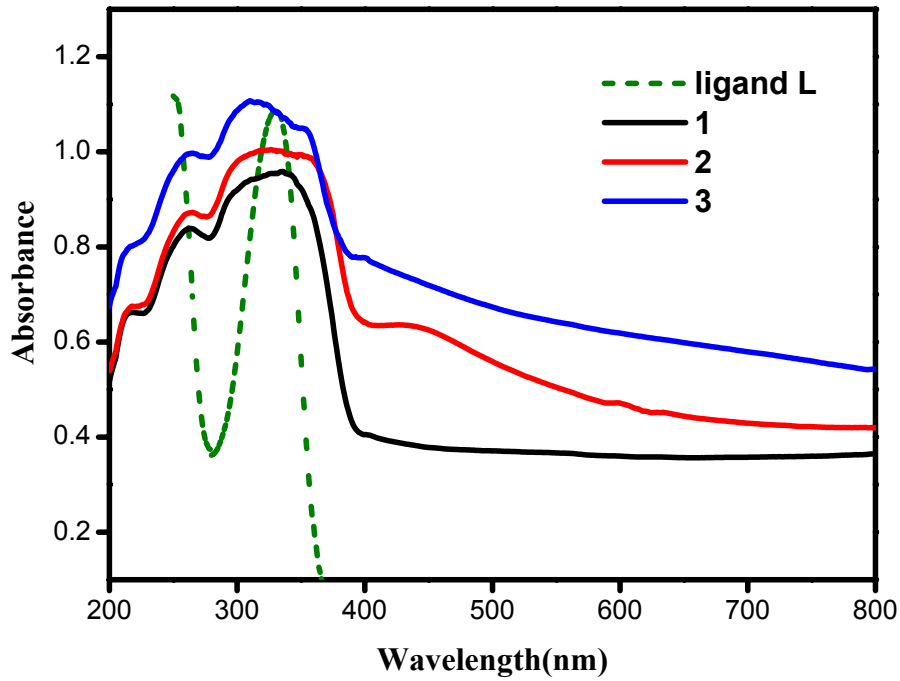
15. **Figure S11**. The PXRD patterns of **1-3**



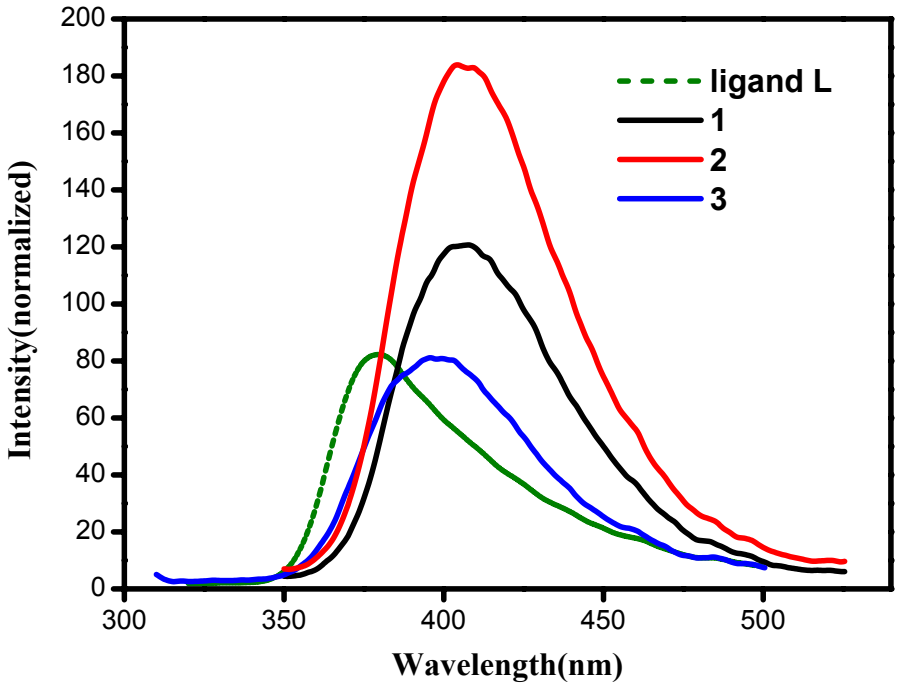
16. **Figure S12**. TGA curves of **1-3**



17. **Figure S13**. The Soild-state UV-vis spectra of **1-3** and the free ligand **L**.

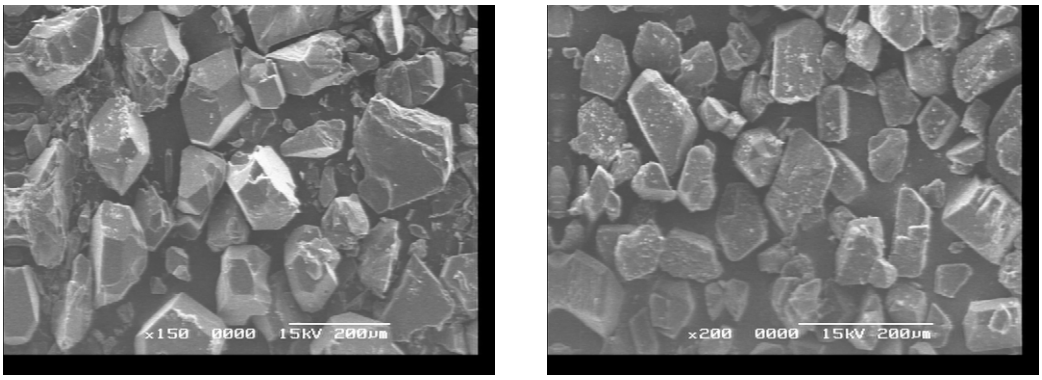


18. **Figure S14**. The fluorescence spectrum of **1-3** and the free ligand **L**.

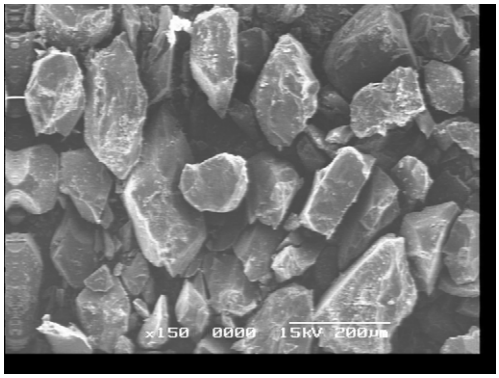


19. **Figure S15**. The SEM images of **1**(a)**, 2**(b) and **3**(c)

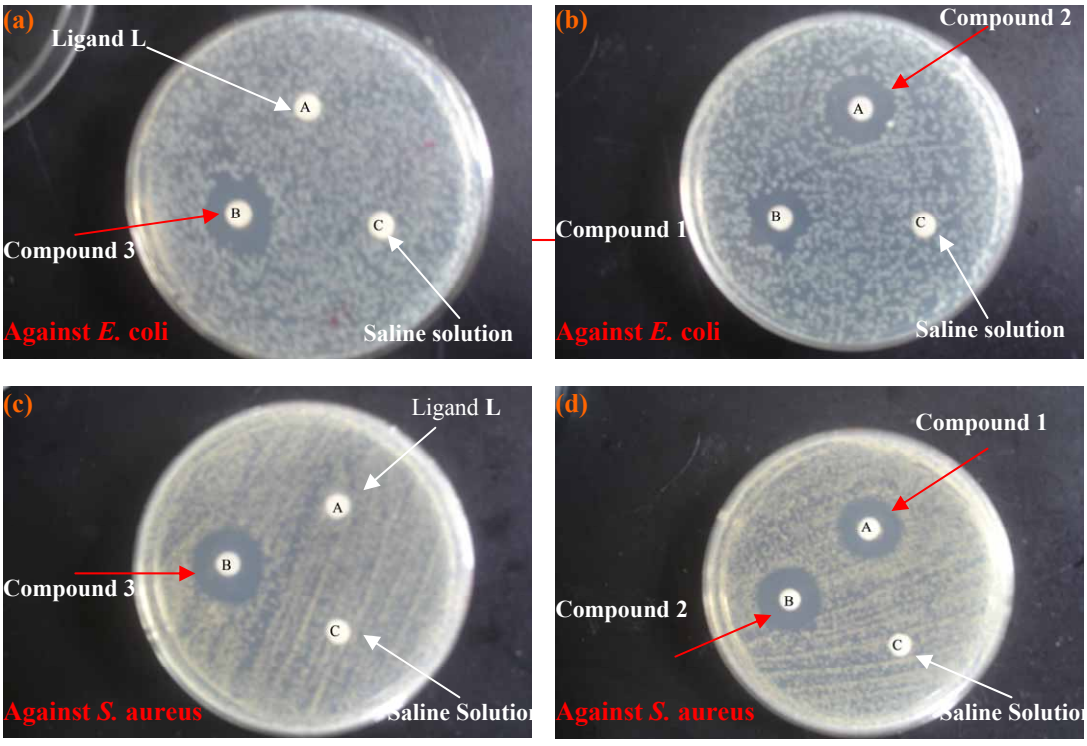
(a) (b)



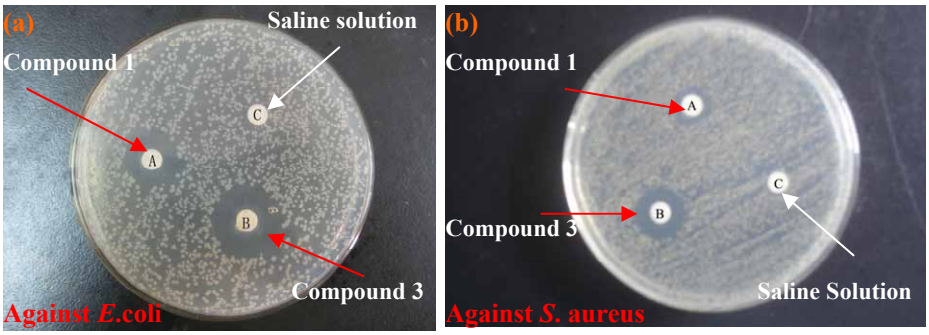
(c)



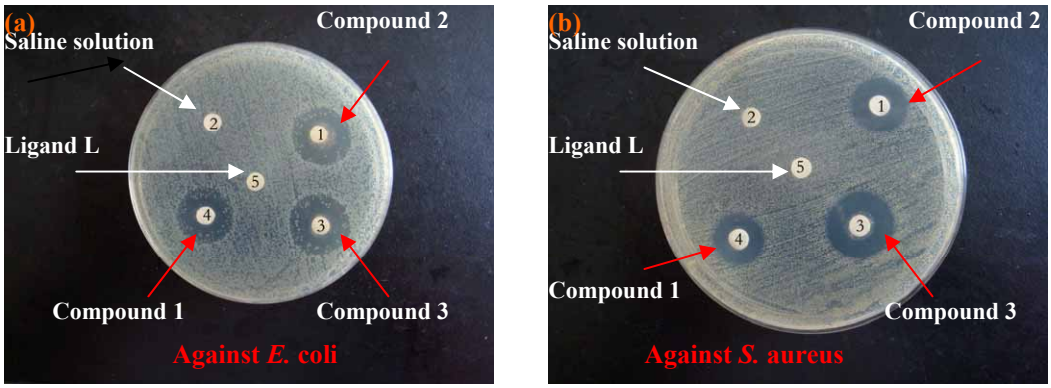
20**. Figure S16**. Optical images of the zone of inhibition against *E.* Coli (a and b) and *S.* auri (c and d) for compounds **1-3**. Each paper is 5 mm in diameter. Tested samples: ca. 3.0 mg (Ag content ~0.37 mg). Incubation condition: 37 ^{o}C, 24 h.



21. **Figure S17**. Optical images of the zone of inhibition against *E.* Coli (a) and *S.* aureus (b) for compounds **1** and **3** after immersing in distilled water for eight days. Each paper is 5 mm in diameter. Tested samples: 2.0 mg (Ag content ~0.24 mg); Incubation condition: 37 ^{o}C, 24 h. **(**See Table S5**)**



22. **Figure S18**. Optical images of the zone of inhibition against *E.* Coli (a) and *S.* aureus. (b) for compounds **1-3** after immersing in distilled water for 7 months. Each paper is 5 mm in diameter. Tested samples: ca. 4.0 mg (Ag content ~0.48 mg). Incubation condition: 37 ^{o}C, 24 h.



23. **Figure S19**. The Solid-state CD spectra of **1-3.**