

## **Supplementary Information**

### **Controlled Generation of Heterochiral or Homochiral Coordination Polymer: Helical Conformational Polymorphs and Argentophilicity-Induced Spontaneous Resolution\*\***

Xu-Dong Chen,<sup>a</sup> Miao Du<sup>b</sup> and Thomas C. W. Mak<sup>\*a</sup>

<sup>a</sup> Department of Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong SAR, P. R. China.

Fax: 852 26035057; Tel: 852 26096279; E-mail: tcwmak@cuhk.edu.hk

<sup>b</sup> College of Chemistry and Life Science, Tianjin Normal University, Tianjin, P. R. China.

Fax: 86 23540315; Tel: 86 23540315; E-mail: dumiao@public.tpt.tj.cn

## Experimental

### General

Diethyl ether were purchased from LAB-SCAN and further refluxed over sodium and benzophenone. All other chemicals were obtained commercially from Aldrich and used without further purification.

Elemental analyses of C, H and N were performed by the MEDAC LTD Brunel Science Centre, United Kingdom. IR spectra were recorded with a Nicolet Impact 420 FT-IR spectrometer using KBr pellets.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were taken at 300MHz with a Bruker-300 spectrometer using  $\text{DMSO-d}_6$  as solvent. Mass spectrometry was conducted on a ThermoFinnigan MAT 95 XL spectrometer. Luminescent spectra were measured on a CARY Eclipse luminescence spectrometer (VARIAN Company). TGA analyses were performed on a Hi-Res TGA 2950 Thermogravimetric Analyzer. Optical rotations were recorded on a PERKIN ELMER Polarimeter (PE 341). Powder X-ray diffraction patterns were performed on a Bruker D8 Advance Powder X-ray diffractometer ( $\text{Cu K}\alpha$ ,  $\lambda = 0.15418 \text{ nm}$ ) operating at 40 kV and 40 mA, with a graphite reflected beam monochromator and variable divergence slits (scanning rate  $0.067^\circ \text{ s}^{-1}$ ). X-ray photoelectron spectroscopy was taken on a PHI Quantum 2000 X-ray Photoelectron Spectrometer. Melting point was measured on a WRS-1B digital apparatus.

### Syntheses

#### 2-pyridinyl-3-pyridinylmethanone (L)

Under the protection of  $\text{N}_2$ , 6.32g 2-bromopyridine in 20ml anhydrous diethyl ether were added slowly into 25.2ml *n*-butyllithium (15% solution in hexane) in 50ml anhydrous diethyl ether at  $-50^\circ\text{C}$ . After addition was complete, the mixture was stirred at  $-50^\circ\text{C}$  for 0.5 hours. After cooling to  $-90^\circ\text{C}$ , to the mixture was added 5.4g methyl nicotinate in 50ml anhydrous diethyl ether with vigorous stirring within 30 minutes. After further stirring at  $-90^\circ\text{C}$  for another 30 minutes, the solution was allowed to slowly warm to room temperature and stand overnight. The reaction solution was quenched by 40ml HCl solution in water and methanol (water/methanol/conc. HCl = 5:5:1) at  $0^\circ\text{C}$  and extracted with dichloromethane. The combined organic extract was then dried over anhydrous sodium sulfate, concentrated in vacuo, and purified by chromatography on silica-gel using ethyl acetate/hexane as the eluent. Colorless needle-like L (4.7g) was obtained in 64% yield; m.p.  $69.1 - 69.6^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 M Hz,

DMSO- $d_6$ ):  $\delta$  9.13(d,  $J = 2.1$  Hz, 1H), 8.80(dd,  $J_1 = 1.5$ ,  $J_2 = 4.8$  Hz, 1H), 8.75(d,  $J = 4.8$  Hz, 1H), 8.34(td,  $J_1 = 2.1$ ,  $J_2 = 7.8$  Hz, 1H), 8.11(s, 1H), 8.10(s, 1H), 7.72(dd,  $J_1 = 4.8$ ,  $J_2 = 7.5$  Hz, 1H), 7.58(dd,  $J_1 = 4.8$ ,  $J_2 = 7.8$  Hz, 1H); IR (KBr): 1668s, 1578s, 1471w, 741m, 704s  $\text{cm}^{-1}$ ; MS  $m/z$ : 185.07 ( $[MH]^+$ ); Anal. for  $\text{C}_{11}\text{H}_8\text{N}_2\text{O}$ : Calcd. C 71.73, H 4.38, N 15.20; Found C 71.65, H 4.37, N 15.19 %.

#### **[AgL(SO<sub>3</sub>CF<sub>3</sub>)]<sub>∞</sub> (1)**

L (37mg, 0.2 mmol) in 2ml Y (Y = methanol, ethanol, acetone or THF) and  $\text{AgSO}_3\text{CF}_3$  (52mg, 0.2 mmol) in 2ml Y were mixed together with stirring at room temperature (20°C). The pale-white precipitate was collected by filtration and dried to give **1** in 67% yield. The nature of **1** as a crystalline powder was confirmed by powder X-ray diffraction. Single crystals of **1** were obtained from the following procedure: L (37mg, 0.2 mmol) in 2ml  $\text{CH}_3\text{OH}$  was added dropwise into  $\text{AgSO}_3\text{CF}_3$  (52mg, 0.2 mmol) in 3ml  $\text{CH}_3\text{OH}$  with stirring and the resulting solution was filtered and then diffused by diethyl ether to give flake-like colorless crystals of **1** after three days in 39% yield. Anal. for  $\text{C}_{12}\text{H}_8\text{F}_3\text{N}_2\text{O}_4\text{SAg}$ : Calcd. C 32.67, H 1.83, N 6.35; Found C 32.58, H 1.52, N 6.01 %. IR (KBr): 1666s, 1637w, 1583m, 1471w, 1419w, 1309s, 1281vs, 1254vs, 1171s, 1090w, 1036s, 995w, 941w, 831w, 800w, 744w, 704m, 644m, 579w, 519w  $\text{cm}^{-1}$

#### **[AgL(SO<sub>3</sub>CF<sub>3</sub>)]<sub>∞</sub> (2)**

L (37mg, 0.2 mmol) and  $\text{AgSO}_3\text{CF}_3$  (52mg, 0.2 mmol) were mixed in 15ml  $\text{H}_2\text{O}$  with stirring to yield **2** as a white precipitate in 69% yield, which can be re-crystallized from hot water (30mg / 5ml  $\text{H}_2\text{O}$ , 60°C) to give colorless single crystals of **2a** and **2b** as a conglomerate. Anal. for  $\text{C}_{12}\text{H}_8\text{F}_3\text{N}_2\text{O}_4\text{SAg}$ : Calcd. C 32.67, H 1.83, N 6.35; Found C 32.51, H 1.81, N 6.35 %. IR (KBr): 1666s, 1637w, 1583m, 1471w, 1419w, 1281brs, 1171s, 1090w, 1038s, 995w, 941w, 831w, 800w, 744w, 704m, 646s, 579w, 520w  $\text{cm}^{-1}$

#### **Reactions under different conditions**

Reaction of L with  $\text{AgSO}_3\text{CF}_3$  in  $\text{CH}_3\text{OH}$  under heating (60°C) leads to the formation of single crystals of **1** after two weeks in 17% yield.

Re-crystallization of the powder of **1** in hot methanol (60°C) afforded crystals of **1** in 34% yield.

Reaction of L with  $\text{AgSO}_3\text{CF}_3$  in  $\text{CH}_3\text{CN}$  or  $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$  gave a mixture of crystals of **1** and **2**, as confirmed by X-ray determination of the unit cell.

### Unsuccessful attempts toward complete inter-conversion between **1** and **2**

Identification of the crystalline products in each case is conducted by X-ray measurements of the unit cell.

- i) Re-crystallization of **1** in hot water followed by cooling and standing at room temperature gave mixed crystals of **1** and **2**.
- ii) **2** did not dissolve in methanol at room temperature. Re-crystallization of **2** using a mixed solvent of CH<sub>3</sub>OH and CH<sub>3</sub>CN gave mixed crystals of **1** and **2**.
- iii) Diffusion of diethyl ether into the CH<sub>3</sub>OH/CH<sub>3</sub>CN solution of **2** gave mixed crystals of **1** and **2**.
- iv) Re-crystallization of **2** in hot CH<sub>3</sub>OH followed by cooling and standing at room temperature gave mixed crystals of **1** and **2**.
- v) Re-crystallization of **1** or **2** from acetone/CH<sub>3</sub>CN gave mixed crystals of **1** and **2**.
- vi) Re-crystallization of **1** or **2** from H<sub>2</sub>O/CH<sub>3</sub>CN gave mixed crystals of **1** and **2**.

### X-ray diffraction studies

Crystal of **1** mounted inside Lindemann glass capillaries were used for data collection at 293 K on a Bruker SMART 1000 CCD diffractometer operating at 50 KV and 30 mA using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Data of **2a** and **2b** were collected on an APEX 2 CCD diffractometer operating at 50 KV and 30 mA using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 293 K with crystals mounted inside Lindemann glass capillaries. Data collection and reduction were performed using the SMART and SAINT software.<sup>1</sup> An empirical absorption correction was applied using the SADABS program.<sup>2</sup> All the structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  using the SHELXTL program package.<sup>3</sup> The crystal data and details of refinement for **1**, **2a** and **2b** are summarized in Table S1. The absolute structure of **2a** and **2b** were established from the value of the Flack parameter.<sup>4</sup>

### References:

- 1 Bruker, SMART 5.0 and SAINT 4.0 for Windows NT, Area Detector Control and Integration Software. Bruker Analytical X-Ray Systems Inc. Madison, WI, 1998.
- 2 G. M. Sheldrick, *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Göttingen, Germany, 1996.
- 3 G. M. Sheldrick, *SHELXTL 5.1 for Windows NT: Structure Determination Software Programs*; Bruker Analytical X-ray Systems, Inc.; Madison, WI, 1997.
- 4 H. D. Flack and G. Bernardinelli, *Acta Crystallogr.* 1999, **A55**, 908-915.

Table S1 Crystallographic data of compounds **1**, **2a** and **2b**.

Complex	<b>1</b>	<b>2a</b>	<b>2b</b>
Empirical formula	C <sub>12</sub> H <sub>8</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> SAg	C <sub>12</sub> H <sub>8</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> SAg	C <sub>12</sub> H <sub>8</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub> SAg
Formula weight	441.13	441.13	441.13
Crystal size	0.45×0.23×0.15	0.34×0.30×0.17	0.38×0.33×0.20
Crystal system	Monoclinic	Tetragonal	Tetragonal
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 4 <sub>1</sub> 2 <sub>1</sub> 2	<i>P</i> 4 <sub>3</sub> 2 <sub>1</sub> 2
<i>a</i> (Å)	9.5431(6)	10.2355(4)	10.2364(4)
<i>b</i> (Å)	12.4438(8)	10.2355(4)	10.2364(4)
<i>c</i> (Å)	13.3198(9)	28.105(2)	28.109(2)
$\alpha$ (°)	90	90	90
$\beta$ (°)	105.165(1)	90	90
$\gamma$ (°)	90	90	90
<i>V</i> (Å <sup>3</sup> )	1526.7(2)	2944.4(3)	2945.4(3)
<i>Z</i>	4	8	8
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.919	1.990	1.990
$\mu$ (Mo-K $\alpha$ ) (mm <sup>-1</sup> )	1.509	1.565	1.564
<i>F</i> (000)	864	1728	1728
Reflections collected	10599	15946	15972
Independent reflections ( <i>R</i> <sub>int</sub> )	3927 (0.0338)	2596 (0.0193)	2596 (0.0194)
Observed reflections [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	2687	2490	2486
Parameters	208	208	208
Goodness-of-fit	1.049	1.080	1.082
<i>R</i> <sub>1</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0536	0.0229	0.0227
<i>wR</i> <sub>2</sub> (all data) <sup>b</sup>	0.1669	0.0582	0.0576
Flack parameter	-----	0.00(3)	0.00(3)

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

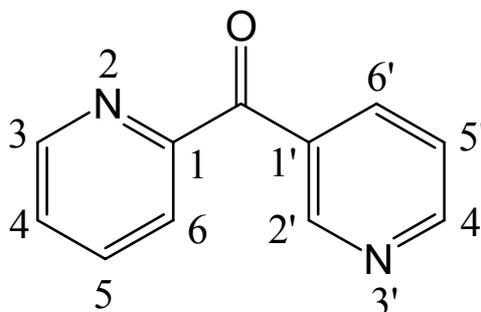
$$^b wR_2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

## Structural description of **1** and **2**

In **1** and **2** ligand L takes the *anti* configuration with similar conformation, as illustrated in Table S2 by comparison of the pair of torsion angles with respect to the carbonyl group. Each L molecule acts as a bridging ligand with its two N atoms coordinated to Ag atoms in opposite directions. In both cases the carbonyl O atom weak interacts with the Ag atom (Figure S1). Both kinds of single helical chains in **1** and **2** are stabilized by weak interaction with the triflate anions (Figure S1). In **1**, by C-H...O (triflate) hydrogen bonding, Ag... $\pi$  stacking and Ag...O (triflate) weak interaction, the *P*- and *M*- helices assemble alternately into a heterochiral layer, and stacking of such layers generates a racemic crystal. In **2**, spontaneous resolution induced by argentophilic interaction occurs to assemble homochiral helical chains into a chiral crystal, which was further stabilized by C-H...O=C hydrogen bonding, Ag...O (triflate), C-H...O (triflate) and  $\pi$ - $\pi$  stacking interactions. Comparison of the conformations of L and the Ag...O (triflate / carbonyl) weak interactions in **1** and **2** are listed in Table S2 and S3, respectively.

Concerning the difference of the two kinds of helical chains, the angle of the carbonyl bond of ligand L with respect to the helical  $2_1/4_1$  axis is  $3.4^\circ$  for **1** and  $113.4^\circ$  for **2a**, indicating that in **1** ligand L is wound around the  $2_1$  axis latitudinally while it runs longitudinally with respect to the  $4_1$  axis in **2**.

Table S2 Torsion angles of the two pyridyl rings with respect to the carbonyl group in **1**, **2a** and **2b**.



Torsion Angle(°)	Compound <b>1</b>	Compound <b>2a</b>	Compound <b>2b</b>
N2-C1-C=O	-24.1(7)	23.2(5)	-23.2(5)
C2'-C1'-C=O	136.0(5)	-133.1(3)	133.1(3)

Table S3 Comparison of Ag $\cdots$ O (triflate / carbonyl) weak interactions between **1** and **2**.

Type of interaction	Compound <b>1</b>	Compound <b>2a</b>	Range of observed values in the literature
Ag $\cdots$ O (carbonyl)	2.757(4)	2.744(3)	2.16-2.60
Ag $\cdots$ O (triflate)	2.855(5),2.906(9)	2.700(3)	2.21-2.61

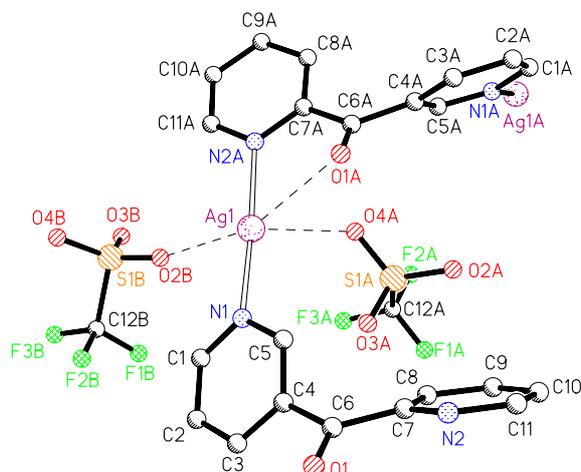


Figure S1 (a) Coordination environment of Ag atom in **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths: Ag1-N1 2.163(4), Ag1-N2A 2.176(4), Ag1-O1A 2.757(4), Ag1-O2B 2.855(5), Ag1-O4A 2.906(9) Å.

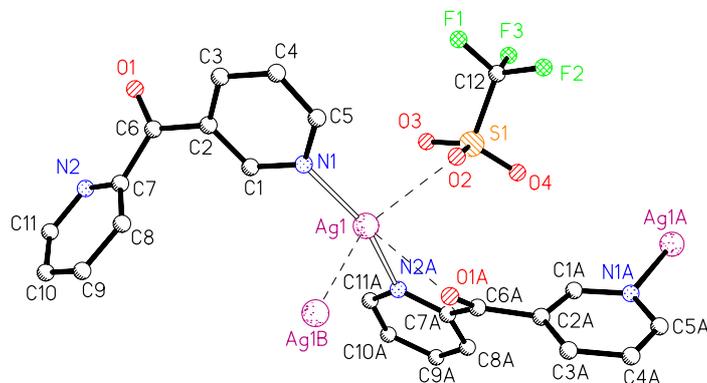


Figure S1 (b) Coordination environment of Ag atom in **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths in **2a**: Ag1-N1 2.170(3), Ag1-N2A 2.194(3), Ag1-O2 2.700(3), Ag1-O1A 2.744(3), Ag1-Ag1B 2.9980(6) Å.

Figure S2

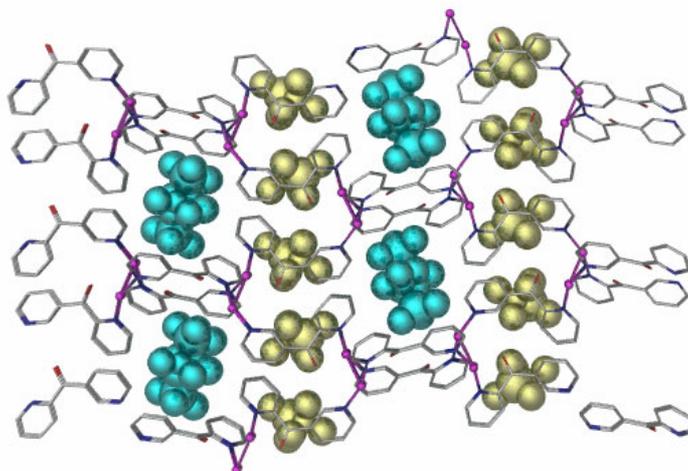


Figure S2 Channels in different directions that accommodate the trifluoromethanesulfonate anions in **2**. The balls in turquoise represent anions located in channels along [100], the balls in yellow represent anions located in channels along [010], and the small balls in purple represent silver atoms. Color code: C: light gray, N: blue, O: red.

## Powder-XRD spectra of compounds **1** and **2**

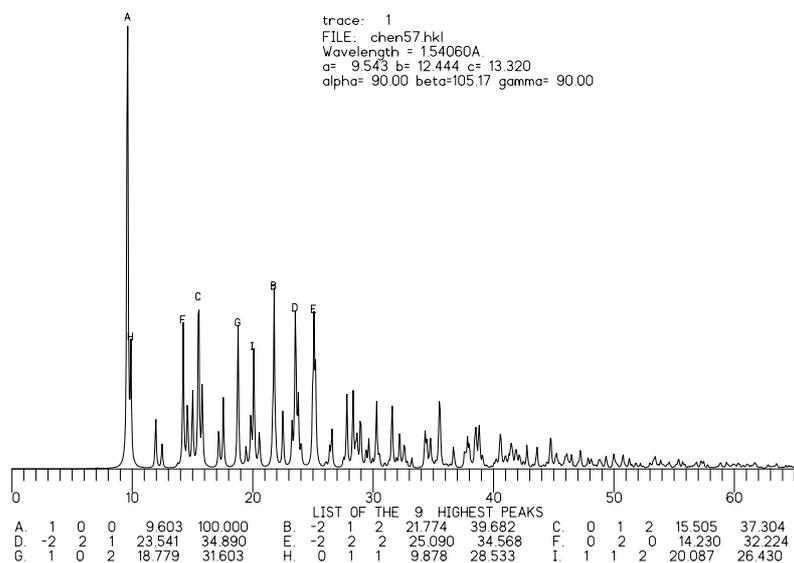


Figure S3 (a) Simulated powder X-ray diffraction spectra of compound **1**.

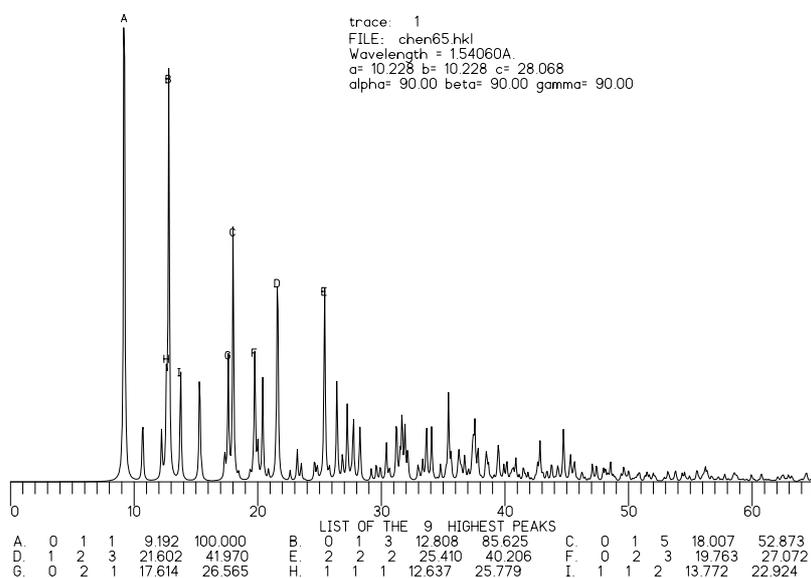


Figure S3 (b) Simulated powder X-ray diffraction spectra of compound **2**.

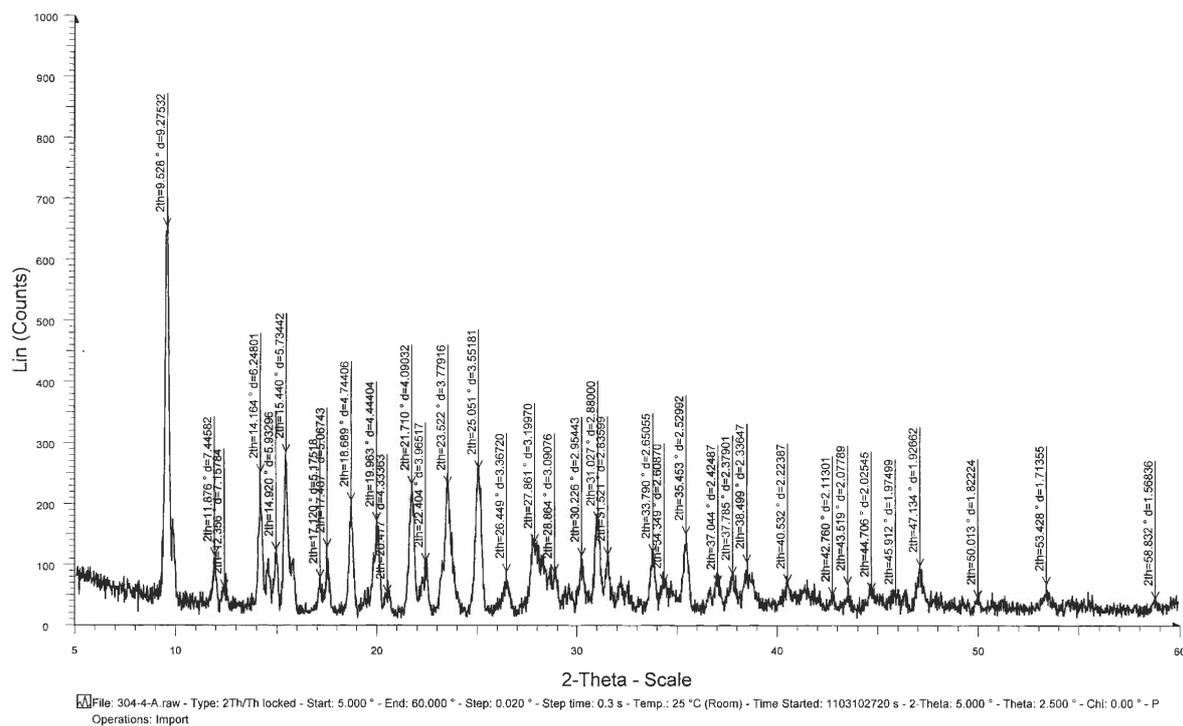


Figure S4 (a) Powder X-ray diffraction spectra of compound 1.

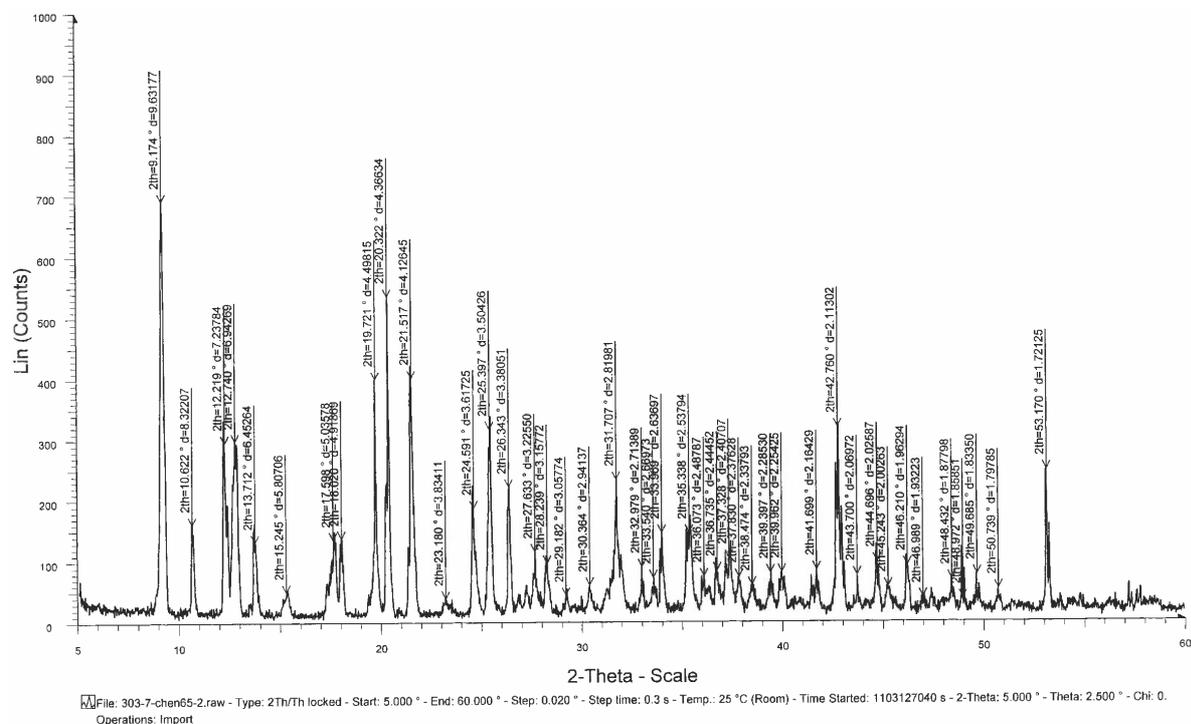


Figure S4 (b) Powder X-ray diffraction spectra of compound 2.

Figure S5

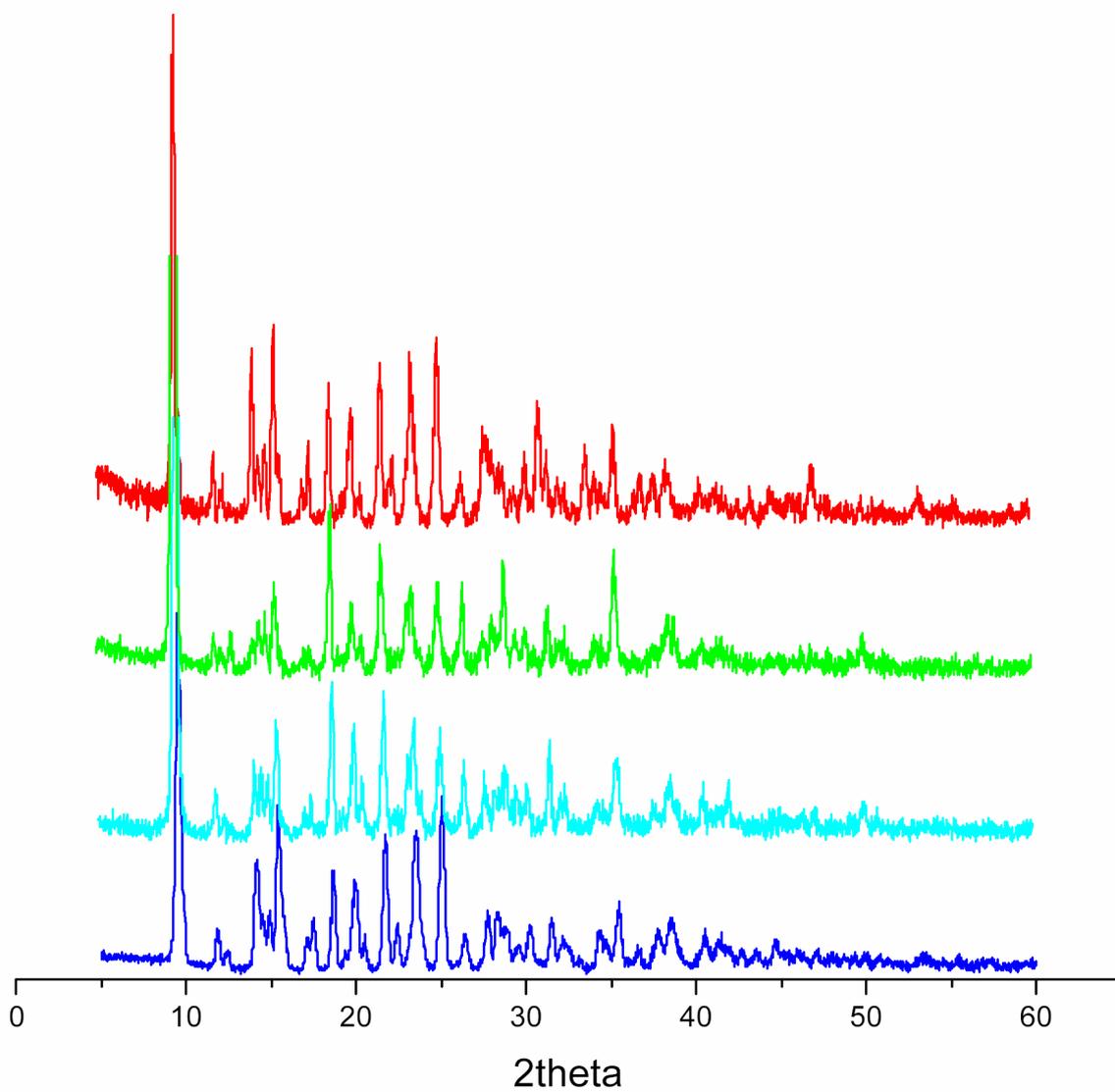


Figure S5 Powder X-ray diffraction spectra of compound **1** obtained from different solvents. Blue: from methanol; cyan: from ethanol; green: from acetone; red: from THF.

## TGA analyses of compounds 1 and 2

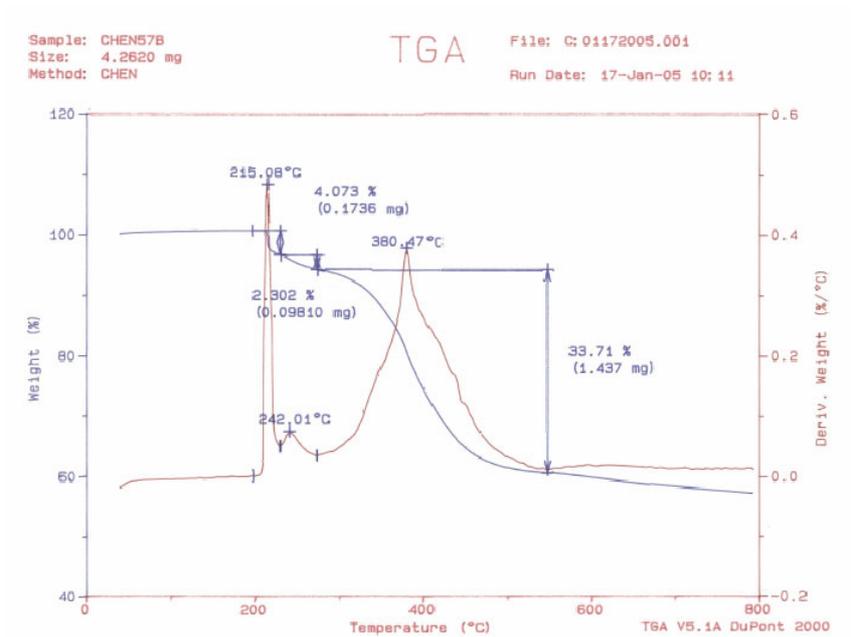


Figure S6 (a) TGA analyses of compounds 1.

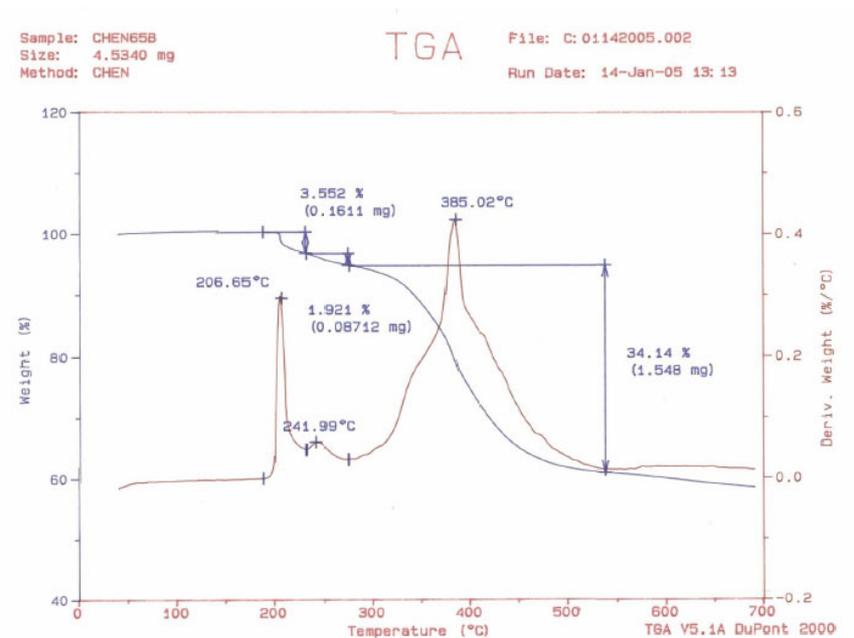


Figure S6 (b) TGA analyses of compounds 2.

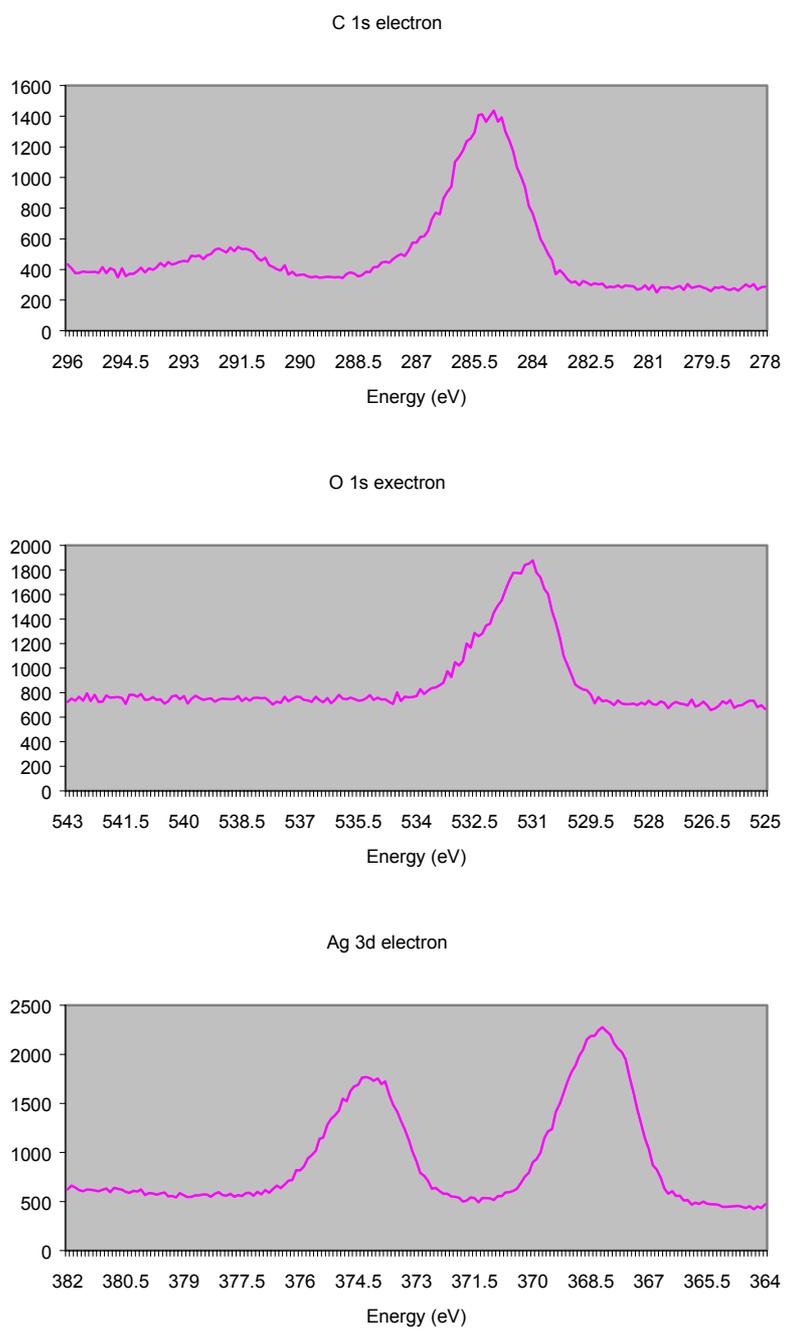


Figure S7 (a) XPS spectrum of compound **1**.

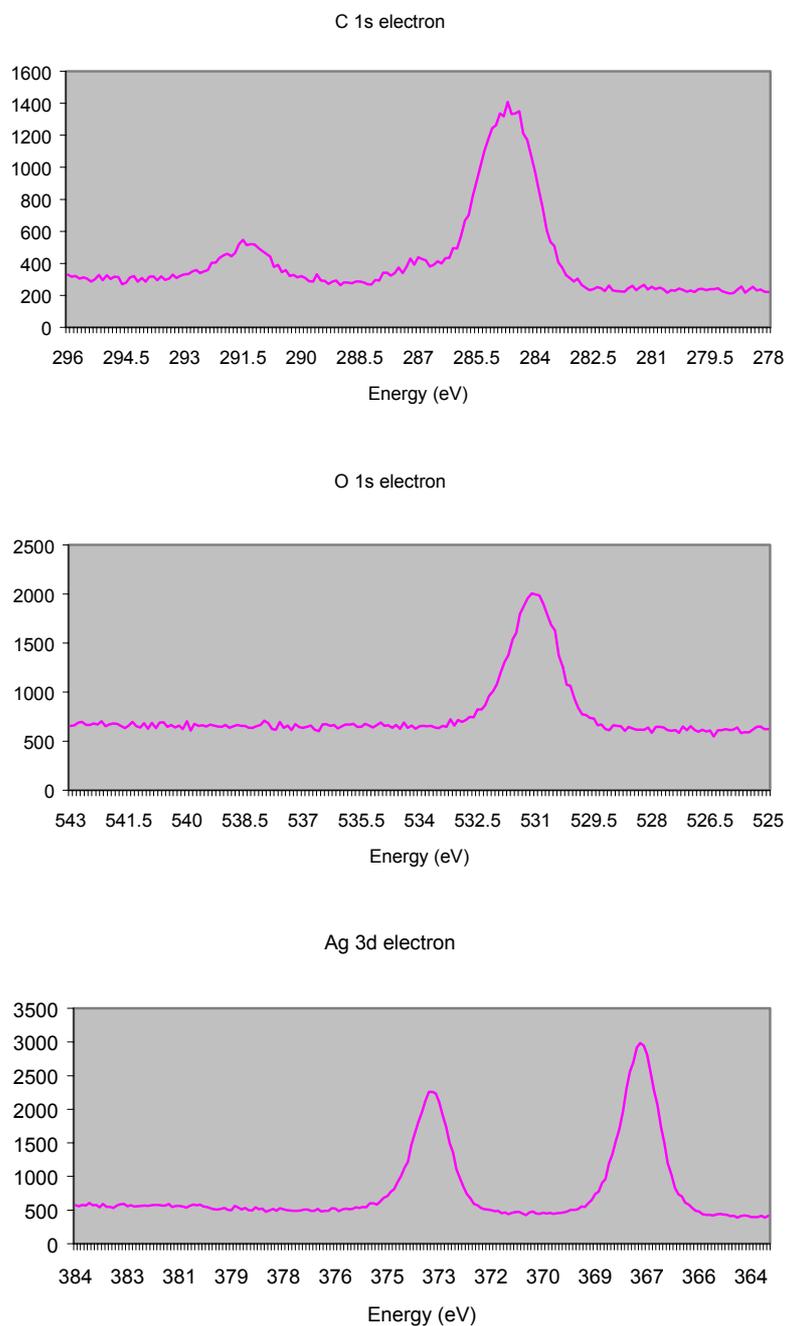
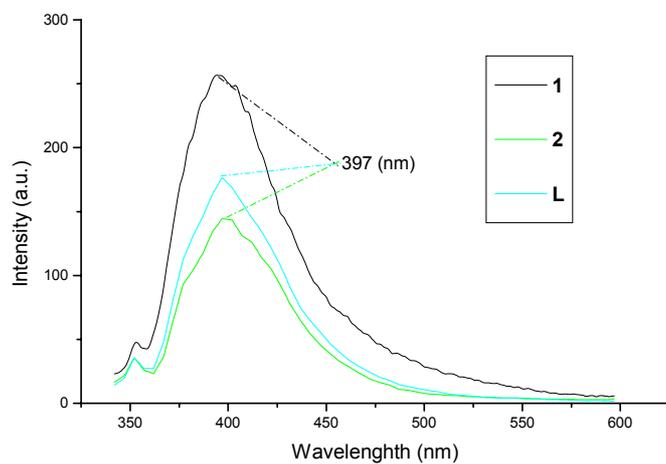


Figure S7 (b) XPS spectrum of compound **2**.

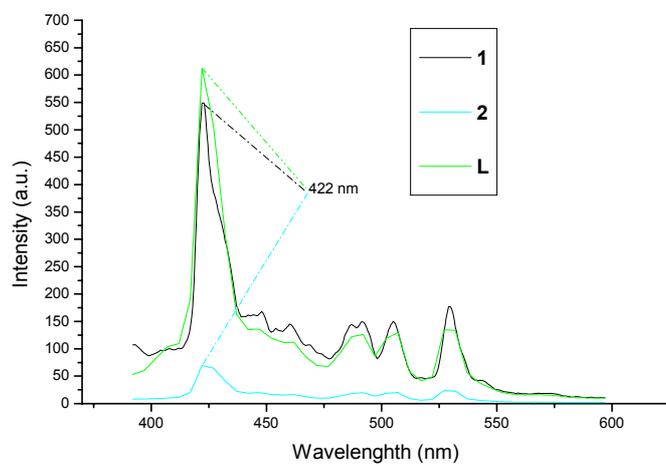
## Luminescent properties of compounds **1** and **2**

The luminescent properties of ligand L and compounds **1** and **2** were investigated in CH<sub>3</sub>CN solution and in the solid state at different temperatures. In all cases, the fluorescence spectra show no significant variation from room temperature to 77 K. As shown in Fig. S8(a) (CH<sub>3</sub>CN solution, excitation wavelength 320 nm), L exhibits an emission maximum at 397 nm (the emission peak at 351 nm may be attributed to the effect of the solvent), and compounds **1** and **2** have the same emission maximum but with lower intensity. In the solid state (Fig. S8(b), excitation wavelength 370 nm), all three compounds show the same emission maximum at 422 nm with different intensities. These results clearly indicate that the luminescence of compounds **1** and **2** should be assigned to intra-ligand transitions, being independent of metal-ligand interactions.

Figure S8



(a)



(b)

Figure S8 The luminescent properties of the ligand (L) and compounds **1** and **2**. (a) In CH<sub>3</sub>CN solution. (b) In solid state.

Unit cell parameters for other helical complexes generated from 2-pyridinyl-3-pyridinylmethanone:

$[(\text{AgL})(\text{ClO}_4)]_\infty$ , monoclinic,  $P2_1/c$ ,  $a = 8.1126(9)$ ,  $b = 12.513(1)$ ,  $c = 13.418(2)$  Å,  $\beta = 111.047(2)^\circ$ ,  $V = 1271.2(3)$  Å<sup>3</sup>.

$[(\text{AgL})(\text{NO}_3)]_\infty$ , monoclinic,  $P2_1/c$ ,  $a = 7.9514(6)$ ,  $b = 12.1163(9)$ ,  $c = 12.4823(9)$  Å,  $\beta = 107.077(1)^\circ$ ,  $V = 1149.5(2)$  Å<sup>3</sup>.

$\{[\text{CuL}(\text{CH}_3\text{CN})(\text{H}_2\text{O})(\text{ClO}_4)]\text{ClO}_4\}_\infty$ , orthorhombic,  $Pbca$ ,  $a = 18.9186(11)$ ,  $b = 8.1263(5)$ ,  $c = 24.8022(14)$  Å,  $V = 3813.0(4)$  Å<sup>3</sup>.

$\{[\text{CoL}(\text{H}_2\text{O})_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}\}_\infty$ , monoclinic,  $P2_1/n$ ,  $a = 13.0805(8)$ ,  $b = 11.1580(7)$ ,  $c = 13.8114(8)$  Å,  $\beta = 95.398(1)^\circ$ ,  $V = 2006.9(2)$  Å<sup>3</sup>.

$\{[\text{ZnL}(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_2 \cdot \text{H}_2\text{O}\}_\infty$ , monoclinic,  $P2_1/c$ ,  $a = 10.1623(5)$ ,  $b = 11.5785(5)$ ,  $c = 19.8500(9)$  Å,  $\beta = 97.017(1)^\circ$ ,  $V = 2318.1(2)$  Å<sup>3</sup>.