

# Self-Assembly and Characterization of Three-Dimensional Silver(I) Coordination Polymers Containing *N,N,N',N'*-Tetrakis(pyridin-4-yl)methanedi-amine

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Silver(I) coordination polymers, [Ag(tpmd)](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**1**), [Ag(tpmd)](CF<sub>3</sub>SO<sub>3</sub>) (**2**), and [Ag(tpmd)](CF<sub>3</sub>CO<sub>2</sub>)·0.5CH<sub>3</sub>OH (**3**), have been obtained by the self-assembly of AgX (X = NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>) and *N,N,N',N'*-tetrakis(pyridin-4-yl)methanedi-amine (tpmd) in MeOH/MeCN. The coordination geometries of silver(I) ions in **1** and **2** are distorted tetrahedral structures, while that of **3** is a distorted trigonal bipyramid. **1** and **2** feature three-dimensional coordination polymers formed by coordination of the silver(I) ions to the tpmd ligands. **3** shows two-dimensional network basically. However, the network of **3** can be considered three-dimensional structure by the weak axial bonding of the fourth pyridine group from another tpmd ligand. **1–3** display strong emissions at 331, 342, and 326 nm, respectively.

**Keywords:** Coordination polymer, Silver(I) compound, Ligand, Crystal structure, Photoluminescence

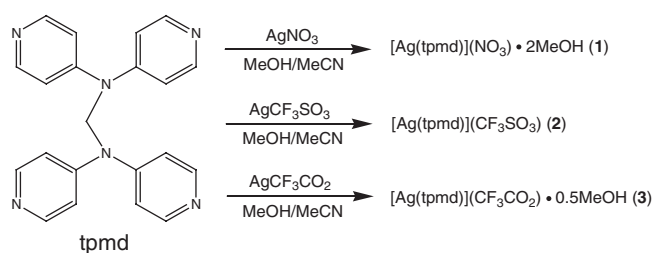
## Introduction

Silver(I) ion with a d<sup>10</sup> electronic configuration has various coordination geometries and is able to construct unusual coordination polymers with multidentate ligands. From the structural diversities of silver(I) ions, a large number of silver(I)-based coordination polymers with 1D chain, 2D layer, and 3D network structures have been extensively studied.<sup>1</sup> The network structures are mostly dependent upon ligands, counter anions, and solvents. These coordination polymer networks have attracted much attention because of their potential applications for anion exchange and light-emitting diodes.<sup>2</sup> For example, supramolecular solids of silver(I) ions with flexible ethylenediaminetetrapropionitrile ligand are formed 1D and 2D polymeric structures depending on anions (*i.e.*, NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup>).<sup>3</sup> The most interesting behavior in the solids is the transformation of supramolecular structure by anion exchange in the solid state. Recently, Ho *et al.* reported four pyrazine-based silver(I) coordination polymers. The compounds displayed significant correlation between structures and luminescence properties.<sup>4</sup> In addition, we have reported two one-dimensional silver(I)-based coordination polymers, *i.e.*, [Ag(bpba)(CF<sub>3</sub>SO<sub>3</sub>)]·0.5MeCN and [Ag<sub>2</sub>(bpba)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>]·MeCN·H<sub>2</sub>O (bpba = bis(4-pyridyl)benzylamine), in which the polymers have shown anion-dependent structures and luminescence properties.<sup>5</sup> Very recently, we have reported a tetradentate ligand *N,N,N',N'*-tetrakis(pyridin-4-yl)methanedi-amine (tpmd) by modification of bpba ligand, which can be exploited as a good building block for multidimensional network structures.<sup>6</sup> Herein, we report on the self-assembly of silver(I) salts (AgX, X = NO<sub>3</sub><sup>-</sup>,

CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>) by using *N,N,N',N'*-tetrakis(pyridin-4-yl)methanedi-amine (tpmd) as well as the structures and luminescence properties of new tpmd-based silver(I) coordination polymers, [Ag(tpmd)](NO<sub>3</sub>)·2CH<sub>3</sub>OH (**1**), [Ag(tpmd)](CF<sub>3</sub>SO<sub>3</sub>) (**2**), and [Ag(tpmd)](CF<sub>3</sub>CO<sub>2</sub>)·0.5CH<sub>3</sub>OH (**3**) (Scheme 1). The coordination polymers have shown different solid structures and luminescence properties depending on counteranions.

## Experimental

**General.** All chemicals used in the synthesis were of reagent grade and used without further purification. *N,N,N',N'*-tetrakis(pyridin-4-yl)methanedi-amine (tpmd) was prepared according to literature procedure.<sup>6</sup> Infrared spectra were recorded with a Thermo Fisher Scientific IR200 spectrophotometer (±1 cm<sup>-1</sup>) (Thermo Fisher Scientific Inc., Madison, WI, USA) using KBr disk. Elemental analyses were carried out using a Fisons/Carlo Erba EA1108 instrument (Fisons Instruments Inc., Dearborn, MI, USA). Thermogravimetric



**Scheme 1.** Synthesis of silver(I) coordination polymers **1–3**.

analyses (TGA) were performed at a scan rate of 5 °C/min using a Seiko TG/DTA 320 & SSC 5200H Disk Station system (Seiko Instruments Inc., Tokyo, Japan). Luminescence spectra were obtained with a SCINCO FS-2 fluorescence spectrometer (SCINCO Co. Ltd., Seoul, Korea).

**Preparation of [Ag(tpmd)](NO<sub>3</sub>)-2CH<sub>3</sub>OH (1).** To an acetonitrile solution (3 mL) of AgNO<sub>3</sub> (12 mg, 0.071 mmol) was added a mixture solution (MeOH/MeCN, 1:2, v/v, 3 mL) of tpmd (25 mg, 0.071 mmol). After stirring for 10 min at room temperature, MeOH (3 mL) was added to the mixture. Then the mixture solution became transparent, and stirred for 10 min at room temperature. Colorless crystals of **1** were obtained by diffusion of diethyl ether into the colorless solution for several days in a dark place, washed with MeOH, and dried in air. Yield: 27 mg (65%). IR (KBr, cm<sup>-1</sup>): 3432, 3047, 1585, 1499, 1365, 1219, 1046, 814, 594. Anal Calcd for C<sub>21</sub>H<sub>23</sub>AgN<sub>7</sub>O<sub>5.5</sub>: C, 44.30; H, 4.07; N, 17.22. Found: C, 44.34; H, 3.78; N, 17.44.

**Preparation of [Ag(tpmd)](CF<sub>3</sub>SO<sub>3</sub>) (2).** To an acetonitrile solution (3 mL) of AgCF<sub>3</sub>SO<sub>3</sub> (18 mg, 0.071 mmol) was added a mixture solution (MeOH/MeCN, 1:2, v/v, 3 mL) of tpmd (25 mg, 0.071 mmol). The resulting solution was stirred for 10 min at room temperature, and then 3 mL of MeOH was added to the mixture. The solution became colorless and was stirred for 10 min at room temperature. Colorless crystals of **2** were obtained by diffusion of diethyl ether into the colorless solution for several days in a dark place, washed with MeOH, and dried in air. Yield: 20 mg (46%). IR (KBr, cm<sup>-1</sup>): 3446, 3100, 3048, 1855, 1503, 1367, 1262, 1030, 852, 635. Anal Calcd for C<sub>22</sub>H<sub>19</sub>AgF<sub>3</sub>N<sub>6</sub>O<sub>3.5</sub>S: C, 42.59; H, 3.09; N, 13.55; S, 5.17. Found: C, 42.40; H, 2.97; N, 13.64; S, 5.02.

**Preparation of [Ag(tpmd)](CF<sub>3</sub>CO<sub>2</sub>)-0.5CH<sub>3</sub>OH (3).** To a methanol solution (3 mL) of AgCF<sub>3</sub>CO<sub>2</sub> (16 mg, 0.071 mmol) was added a methanol solution (2 mL) of tpmd (25 mg, 0.071 mmol). The resulting solution was stirred at room temperature for 10 min, and then 1 mL of MeCN was added to the mixture. The solution became colorless and was stirred for 10 min at room temperature. Colorless crystals of **3** were obtained by diffusion of diethyl ether into the colorless solution for several days in a dark place, washed with MeOH, and dried in air. Yield: 23 mg (53%). IR (KBr, cm<sup>-1</sup>): 3434, 3051, 16896, 1586, 1501, 1366, 1202, 1048, 815, 593. Anal Calcd for C<sub>23</sub>H<sub>23</sub>AgF<sub>3</sub>N<sub>6</sub>O<sub>4.5</sub>: C, 44.53; H, 3.74; N, 13.55. Found: C, 44.65; H, 3.39; N, 13.73.

**X-ray Crystallographic Data Collection and Refinement.** Crystals of **1–3** were mounted on a CryoLoop<sup>®</sup> (Hampton Research, Aliso Viejo, CA, USA) with Paratone<sup>®</sup> oil (Chevron Oronite Pte Ltd Korea Branch, Seoul, Korea). Intensity data for all structures were collected with a Bruker APEX CCD-based diffractometer (Korea Basic Science Institute, Chonju Branch) and using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å, graphite monochromator) at 200(2) K. The raw data were processed to give structure factors using the Bruker SAINT program and corrected for Lorentz and polarization effects.<sup>7</sup> The intensity data of **3** were corrected for absorption using the SADABS program with multi-scan data

( $T_{\min}/T_{\max} = 0.8945$ ).<sup>8</sup> The crystal structures of **1–3** were solved by direct methods,<sup>9</sup> and refined by full-matrix least-squares refinement using the SHELXL-2013 computer program.<sup>10</sup> The positions of all non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms were placed using a riding model, and their positions were constrained relative to their parent atoms using the appropriate HFIX command in SHELXL-2013. The crystallographic data and the result of refinements of **1–3** are summarized in Table 1.

Crystallographic data for the structures reported here have been deposited with CCDC (Deposition No. CCDC-994985 (**1**), CCDC-994986 (**2**), and CCDC-994987 (**3**)). These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## Results and Discussion

**Synthesis and Characterization.** Coordination polymers **1–3** were prepared from AgX (X = NO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>, CF<sub>3</sub>CO<sub>2</sub><sup>-</sup>) and tpmd ligand in mixed solvent (CH<sub>3</sub>OH/CH<sub>3</sub>CN) at room temperature, respectively (Scheme 1). The coordination networks are obtained in good yields and characterized by EA, IR, and X-ray crystallography. **1–3** are slightly soluble in water, but insoluble in acetone, CH<sub>3</sub>OH, and Me<sub>2</sub>SO, and also sensitive to light. The IR spectrum of **1** in KBr pellet shows a strong band of the nitrate ion at 1365 cm<sup>-1</sup> and displays CH peak corresponding to the pyridine groups at 3047 cm<sup>-1</sup>.<sup>11</sup> The IR spectrum of **2** exhibits strong absorption at 1262 and 635 cm<sup>-1</sup> that is assigned to the triflate ions as counterion and displays CH peaks corresponding to the pyridine groups at 3048 cm<sup>-1</sup>.<sup>11</sup> The IR spectrum of **3** in KBr pellet shows a strong band of the trifluoroacetate ion at 1686 cm<sup>-1</sup> and exhibits CH peak corresponding to the pyridine groups at 3051 cm<sup>-1</sup>.<sup>11</sup> TGA of **1** showed a weight loss of 10.3% at 100 °C, which corresponds to the loss of all solvent molecules per unit formula (Figure S1, Supporting Information); no chemical decomposition was observed up to 200 °C. It was shown that the major weight loss (64.5%, 200–326 °C) is due to degradation of the tpmd ligand. Further chemical decomposition was not observed between 326 and 500 °C, in which the final product is expected to be AgNO<sub>3</sub>. TGA of **2** showed that no solvents were included and decomposition starts at 260 °C (Figure S2). Between 260 and 451 °C, the main weight loss (56.2%) is shown due to degradation of the tpmd. The resulting weight was almost constant over the temperature range of 451–500 °C, in which the remaining product is regarded as AgCF<sub>3</sub>SO<sub>3</sub>. TGA of **3** showed a weight loss of 6.5% at 100 °C, which corresponds to the loss of all solvent molecules per unit formula (Figure S3); no chemical decomposition was observed up to 170 °C. The major weight loss (59.3%, 170–316 °C) was observed and was attributed to decomposition of the tpmd. However, no chemical decomposition was observed between 316 and 500 °C, in which the resulting

**Table 1.** Summary of the crystallographic data for **1–3**.

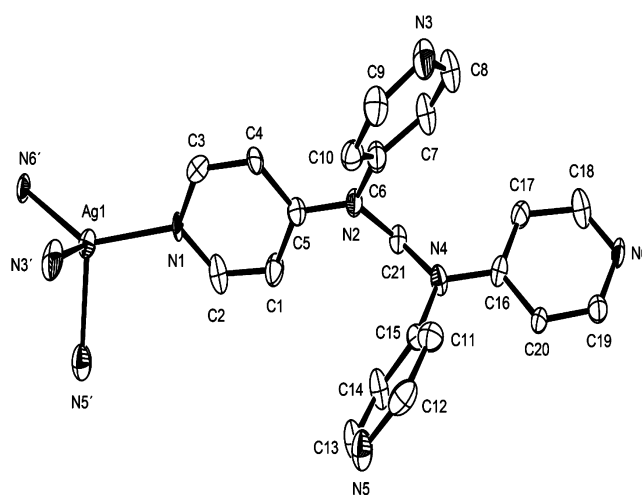
	1	2	3
Formula	C <sub>23</sub> H <sub>26</sub> AgN <sub>7</sub> O <sub>5</sub>	C <sub>22</sub> H <sub>18</sub> AgF <sub>3</sub> N <sub>6</sub> O <sub>3</sub> S	C <sub>47</sub> H <sub>40</sub> Ag <sub>2</sub> F <sub>6</sub> N <sub>12</sub> O <sub>5</sub>
<i>M<sub>r</sub></i>	588.38	611.35	1182.65
Crystal system	Trigonal	Trigonal	Monoclinic
Space group	<i>P</i> 3 <sub>1</sub>	<i>P</i> 3 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
Color	Colorless	Colorless	Colorless
Crystal shape	Block	Block	Block
<i>a</i> , Å	10.387 (1)	10.748 (1)	10.962 (1)
<i>b</i> , Å	10.387 (1)	10.748 (1)	11.346 (1)
<i>c</i> , Å	20.958 (2)	19.663 (3)	22.046 (1)
β, deg	90	90	99.997 (1)
<i>V</i> , Å <sup>3</sup>	1958.2 (2)	1966.9 (4)	2700.3 (3)
<i>Z</i>	3	3	2
<i>d</i> <sub>calc</sub> (g cm <sup>-3</sup> )	1.497	1.548	1.455
λ, Å	0.71073	0.71073	0.71073
<i>T</i> , K	200(2)	200(2)	200(2)
μ, mm <sup>-1</sup>	0.818	0.904	0.799
<i>F</i> (000)	900	918	1188
θ <sub>min–max</sub>	2.26–27.68	2.19–28.32	1.88–28.31
Collected	14 496	14 694	19 550
Unique	6427	6473	6681
Observed	4502	2236	3184
GOF	1.110	0.858	1.017
<i>R</i> <sub>1</sub> <sup>a</sup> (4σ data)	0.0778	0.0971	0.0830
<i>wR</i> <sub>2</sub> <sup>b</sup> (4σ data)	0.1641	0.2340	0.2306

<sup>a</sup>  $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$ .

<sup>b</sup>  $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$ .

product is considered to be AgCF<sub>3</sub>CO<sub>2</sub>. In **1–3**, the decompositions of the tpmd ligands occurred in two steps with shoulders. It was displayed that the cleavages of the tpmd ligands are very dependent on the anions of silver salts. From the TGA data, we were able to deduce that **2** is the most stable species thermally in the coordination networks.

**Description of Crystal Structure of 1.** Compound **1** crystallizes in the trigonal space group *P*3<sub>1</sub>, and the ORTEP view of **1** is shown in Figure 1. Selected bond lengths and angles are listed in Table 2. The asymmetric unit of **1** consists of one silver(I) cation, one nitrate anion, one tpmd ligand, and two methanol molecules. The tpmd ligand exploits all its pyridyl nitrogens to coordinate four different silver(I) ions. Each silver(I) ion has a slightly distorted tetrahedral coordination geometry with four pyridyl nitrogens from four different tpmd ligands. The average Ag–N<sub>py</sub> bond length and N<sub>py</sub>–Ag–N<sub>py</sub> angle are 2.283(6) Å and 109.1(2)°, respectively. The two bis(4-pyridyl)amine (bpa) groups in the tpmd ligand are connected by a methylene carbon at an angle of 111.4(12)°. The shortest Ag⋯Ag separation is 8.3729(9) Å. Through the linkage of four tetra-connected tpmd ligands and four tetra-connected silver(I) ions, **1** is formed a 3D network structure (Figure 2). As shown in Figure 2(c), the 3D network of **1** displays different types of loops interlinked by coordination of silver(I) ion and tpmd. The loops are composed of two silver(I) ions and two different tpmds. The remaining pyridine


**Figure 1.** ORTEP view of **1**. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms, NO<sub>3</sub><sup>-</sup>, and MeOH are omitted for clarity.

groups of both tpmds are contributed to form different two loops. Thus, these loops are interconnected and extended to each other, which gives rise to the 3D network structure. Furthermore, in the 3D network the pyridine ring involving N1 undergoes offset π–π interaction with pyridine group involving N6 (1 + *y* – *x*, 2 – *x*, –1/3 + *z*) (Figure 3).<sup>12</sup> The

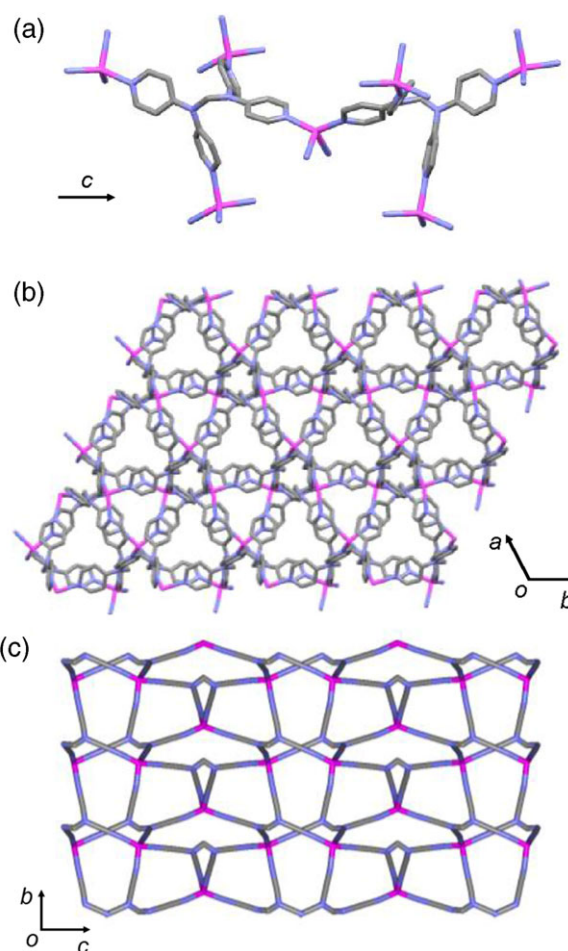
**Table 2.** Selected bond distances (Å) and angles (°) for **1**.

Ag1–N1	2.22(1)	Ag1–N3 <sup>ii</sup>	2.38(1)
Ag1–N5 <sup>iii</sup>	2.39(2)	Ag1–N6 <sup>i</sup>	2.25(1)
N1–C2	1.35(2)	N4–C16	1.42(2)
N1–C3	1.36(2)	N4–C21	1.43(2)
N2–C5	1.38(2)	N4–C15	1.44(2)
N2–C6	1.41(2)	N5–C13	1.32(3)
N2–C21	1.50(2)	N5–C12	1.36(3)
N3–C8	1.30(3)	N6–C18	1.29(2)
N3–C9	1.31(2)	N6–C19	1.31(2)
N1–Ag1–N6 <sup>i</sup>	136.8(5)	N1–Ag1–N5 <sup>iii</sup>	106.0(5)
N1–Ag1–N3 <sup>ii</sup>	94.7(5)	N6 <sup>i</sup> –Ag1–N5 <sup>iii</sup>	102.2(5)
N6 <sup>i</sup> –Ag1–N3 <sup>ii</sup>	111.2(5)	N3 <sup>ii</sup> –Ag1–N5 <sup>iii</sup>	101.1(6)
C2–N1–Ag1	122(1)	C3–N1–Ag1	124(1)
C8–N3–Ag1 <sup>iv</sup>	118(1)	C9–N3–Ag1 <sup>iv</sup>	128(1)
C13–N5–Ag1 <sup>v</sup>	126(1)	C12–N5–Ag1 <sup>v</sup>	120(1)
C18–N6–Ag1 <sup>vi</sup>	118(1)	C19–N6–Ag1 <sup>vi</sup>	125(1)
N4–C21–N2	111(1)	C16–N4–C21	123(1)
C2–N1–C3	114(1)	C16–N4–C15	120(1)
C5–N2–C6	124(1)	C21–N4–C15	117(1)
C5–N2–C21	121(1)	C13–N5–C12	113(2)
C6–N2–C21	115(1)	C18–N6–C19	117(1)
C8–N3–C9	113(2)		

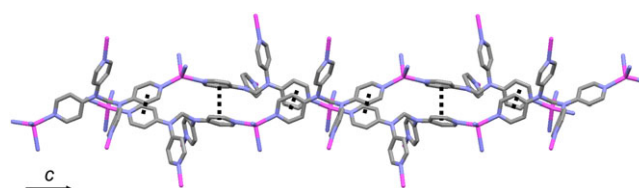
Symmetry transformations used to generate equivalent atoms: (i)  $-y + 2, x - y + 1, z - 2/3$ ; (ii)  $-x + y, -x + 2, z - 1/3$ ; (iii)  $-x + y, -x + 1, z - 1/3$ ; (iv)  $-y + 2, x - y + 2, z + 1/3$ ; (v)  $-y + 1, x - y + 1, z + 1/3$ ; (vi)  $-x + y + 1, -x + 2, z + 2/3$ .

inter-planar separation of the pyridine rings is 3.238(1)–3.493(1) Å (centroid⋯centroid, 3.538 Å) and the dihedral angle between the pyridine ring planes are 5.9897(3)°. Due to the interactions, **1** forms a strong network structure.

**Description of Crystal Structure of 2.** Compound **2** crystallizes in the trigonal space group  $P3_1$ , and the ORTEP view of **2** is shown in Figure 4. Selected bond lengths and angles are listed in Table 3. The asymmetric unit of **2** consists of one silver(I) cation, one trifluoromethanesulfonate anion, and one tpmd ligand. As the structure of **1**, four pyridyl groups in the tpmd ligand are coordinated to four different silver(I) ions. In addition, each silver(I) ion is bound by four pyridyl nitrogen atoms derived from four different tpmd ligands. The silver(I) ion of **2** has a slightly distorted tetrahedral structure. The average Ag–N<sub>py</sub> bond length and N<sub>py</sub>–Ag–N<sub>py</sub> angle are 2.313(9) Å and 109.0(3)°, respectively. The two bpa groups in the ligand are connected by a methylene carbon at an angle of 108.7(16)°. The shortest Ag⋯Ag separation is 7.7973(13) Å. Due to the coordination bonds between silver(I) ions and tpmd ligands, **2** forms a 3-D network and is similar to the packing structure of **1** (Figure 5). Contrary to **1**, the 3D structure of **2** is well-ordered. This can be attributed to the anion shape of CF<sub>3</sub>SO<sub>3</sub><sup>−</sup>. In the structure, the pyridine ring involving N3 is  $\pi$ – $\pi$  stacked with the offset  $\pi$ – $\pi$  interaction with pyridine group involving N4 ( $2 + y - x, 3 - x, -1/3 + z$ ) (Figure 6).<sup>12</sup> The inter-planar separation of the pyridine rings is 3.64(3)–3.75(3) Å (centroid⋯centroid,



**Figure 2.** (a) The linkage of four tetra-connected tpmd ligands and four tetra-connected silver(I) ions in **1**. (b) Perspective view of **1**, showing an extended 3D structure via the coordination of silver(I) ions and tpmds. (c) Schematic representation of **1**, showing the 3D network (purple: silver(I) ion, blue: nitrogen, gray: carbon).

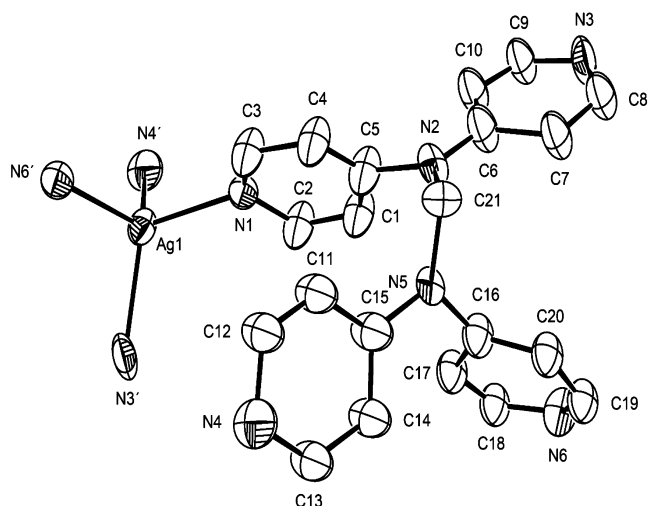


**Figure 3.** The offset  $\pi$ – $\pi$  stacking interaction via pyridine groups leading to a supramolecular structure is indicated as ■■■ (purple: silver(I) ion, blue: nitrogen, gray: carbon).

4.0812 Å) and the dihedral angle between the pyridine ring planes are 1.7(7)°. Due to the interactions, **2** forms a robust network.

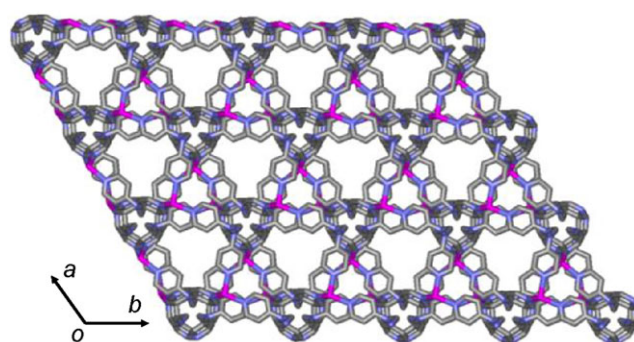
**Description of Crystal Structure of 3.** Compound **3** crystallizes in the monoclinic space group  $P2_1/c$ , and the ORTEP view of **3** is shown in Figure 7. Selected bond lengths and angles are listed in Table 4. The asymmetric unit is composed of one silver(I) cation, one trifluoroacetate anion, one tpmd ligand, and a half methanol molecules. The structure of **3** is

quite different to those of **1** and **2**, due to the  $\text{CF}_3\text{CO}_2^-$  anion (*i. e.*, weak bonding). In the structure, silver(I) ion is coordinated with three nitrogens of three different tpmd ligands, leading to a distorted T-shape geometry. Each tpmd ligand links three silver(I) ions because three pyridine groups of the ligand are coordinated to different silver(I) ions. Therefore, **3** becomes a 2D layered structure, which extends parallel to the *ac* plane as shown in Figure 8. That is, the structure forms 3-connected



**Figure 4.** ORTEP view of **2**. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms and  $\text{CF}_3\text{SO}_3^-$  are omitted for clarity.

layer, graphite (6,3) topology. Considering weak bonds around the silver(I) ion relatively in **3**, the silver(I) ion has four pyridines of different tpmd ligands and one oxygen atom of  $\text{CF}_3\text{CO}_2^-$  anion.<sup>13</sup> Thus, the geometry of the silver(I) ion shows a distorted trigonal bipyramid and the structure gives rise to a 3D supramolecular network (Figure 9). The  $\text{Ag1-N1}$ ,  $\text{Ag1-N6}(x-1, -y+1/2, z-1/2)$ , and  $\text{Ag1-N5}(x-1, y, z)$  bond lengths are 2.214(6), 2.237(6), and 2.400(6) Å, respectively, and the average  $\text{Ag-N}_{\text{py}}$  bond length is 2.284(3) Å. The  $\text{Ag1-N3}(x+1, y, z)$  and  $\text{Ag1-O1}$  bond lengths relating weak bonds are 2.7631(1) and 2.8858(1), respectively (Figure 9 and Table 4). The two bpa groups in the ligand are connected by a methylene carbon at an angle of



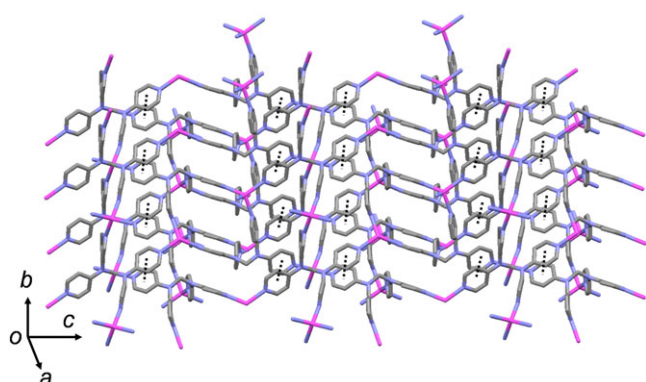
**Figure 5.** Perspective view of **2**, showing an extended 3D supramolecular structure via the coordination of silver(I) ions and tpmds (purple: silver(I) ion, blue: nitrogen, gray: carbon).

**Table 3.** Selected bond distances (Å) and angles (°) for **2**.

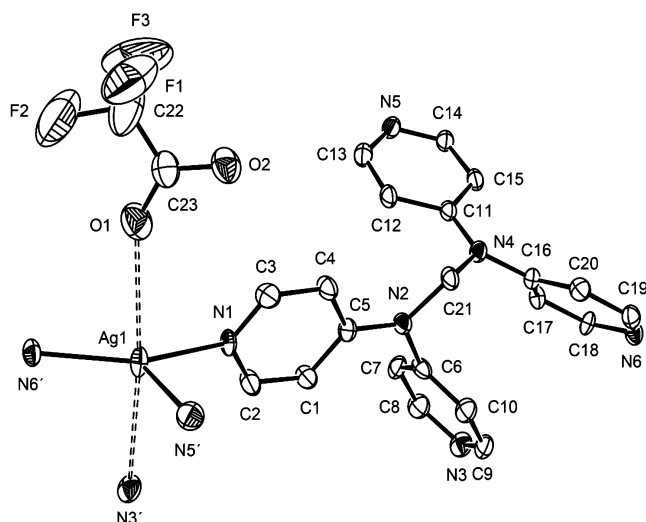
$\text{Ag1-N1}$	2.34 (2)	$\text{Ag1-N3}^{\text{ii}}$	2.30 (2)
$\text{Ag1-N4}^{\text{i}}$	2.30 (2)	$\text{Ag1-N6}^{\text{iii}}$	2.31 (2)
$\text{N1-C2}$	1.34 (3)	$\text{N4-C12}$	1.38 (3)
$\text{N1-C3}$	1.32 (3)	$\text{N4-C13}$	1.30 (3)
$\text{N2-C5}$	1.52 (3)	$\text{N5-C15}$	1.46 (3)
$\text{N2-C6}$	1.38 (3)	$\text{N5-C16}$	1.46 (3)
$\text{N2-C21}$	1.38 (3)	$\text{N5-C21}$	1.41 (3)
$\text{N3-C8}$	1.40 (3)	$\text{N6-C18}$	1.33 (3)
$\text{N3-C9}$	1.30 (3)	$\text{N6-C19}$	1.32 (3)
$\text{N4}^{\text{i}}-\text{Ag1}-\text{N3}^{\text{ii}}$	116 (1)	$\text{N4}^{\text{i}}-\text{Ag1}-\text{N1}$	104 (1)
$\text{N4}^{\text{i}}-\text{Ag1}-\text{N6}^{\text{iii}}$	114 (1)	$\text{N3}^{\text{ii}}-\text{Ag1}-\text{N1}$	113 (1)
$\text{N3}^{\text{ii}}-\text{Ag1}-\text{N6}^{\text{iii}}$	103 (1)	$\text{N6}^{\text{iii}}-\text{Ag1}-\text{N1}$	106 (1)
$\text{C3-N1-Ag1}$	122 (2)	$\text{C9-N3-Ag1}^{\text{iv}}$	124 (2)
$\text{C2-N1-Ag1}$	121 (1)	$\text{C8-N3-Ag1}^{\text{iv}}$	122 (2)
$\text{C13-N4-Ag1}^{\text{v}}$	123 (2)	$\text{C19-N6-Ag1}^{\text{vi}}$	124 (2)
$\text{C12-N4-Ag1}^{\text{v}}$	123 (2)	$\text{C18-N6-Ag1}^{\text{vi}}$	121 (1)
$\text{N2-C21-N5}$	109 (2)	$\text{C13-N4-C12}$	114 (2)
$\text{C3-N1-C2}$	116 (2)	$\text{C21-N5-C15}$	123 (2)
$\text{C6-N2-C21}$	126 (2)	$\text{C21-N5-C16}$	120 (2)
$\text{C6-N2-C5}$	114 (2)	$\text{C15-N5-C16}$	116 (2)
$\text{C21-N2-C5}$	121 (2)	$\text{C19-N6-C18}$	114 (2)
$\text{C9-N3-C8}$	114 (2)		

Symmetry transformations used to generate equivalent atoms: (i)  $-x + y + 1, -x + 2, z - 1/3$ ; (ii)  $-y + 2, x - y, z + 1/3$ ; (iii)  $x - 1, y, z$ ; (iv)  $-x + y + 2, -x + 2, z - 1/3$ ; (v)  $y + 2, x - y + 1, z + 1/3$ ; (vi)  $x + 1, y, z$ .





**Figure 6.** Perspective view of **2**, showing the offset  $\pi$ - $\pi$  stacking interaction via pyridine groups. The interactions are indicated as dashed lines (purple: silver(I) ion, blue: nitrogen, gray: carbon).



**Figure 7.** ORTEP view of **3**. The atoms are represented by 30% probable thermal ellipsoid. Hydrogen atoms and MeOH are omitted for clarity.

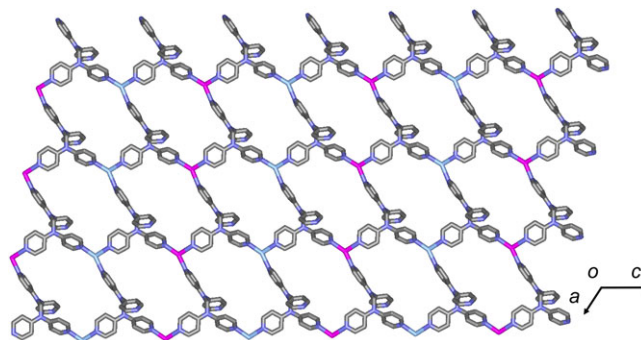
111.5(6)°. The shortest Ag...Ag separation is 9.6579(4) Å. Between the 2D sheet coordination polymers, the pyridine ring involving N5 is  $\pi$ - $\pi$  stacked with the offset  $\pi$ - $\pi$  interaction with pyridine group involving N5, which is positioned at the neighboring 2D sheet network (Figure 10).<sup>12</sup> The inter-planar separation of the pyridine rings is 3.5133(2)–3.5264(2) Å (centroid...centroid, 4.2194 Å) and the dihedral angle and the offset angle between the pyridine ring planes are 0 and 22.61(11)°, respectively.

**Photoluminescence Properties.** The solid-state luminescent properties of **1–3** were investigated at room temperature. The fluorescence spectra of **1–3** are shown in Figure 11. Upon excitation at  $\lambda_{\text{ex}} = 290$  nm, compounds **1–3** display strong fluorescent emission bands with maxima at 331, 342, and 326 nm, respectively. The  $\lambda_{\text{max}}$  values of **1–3** are shorter than those of zinc(II) and Cd(II) complexes with tpmd ligands reported elsewhere,<sup>6a</sup> which can be attributed to the heavy atom and coordination effects due to the different types and

**Table 4.** Selected bond distances (Å) and angles (°) for **3**.

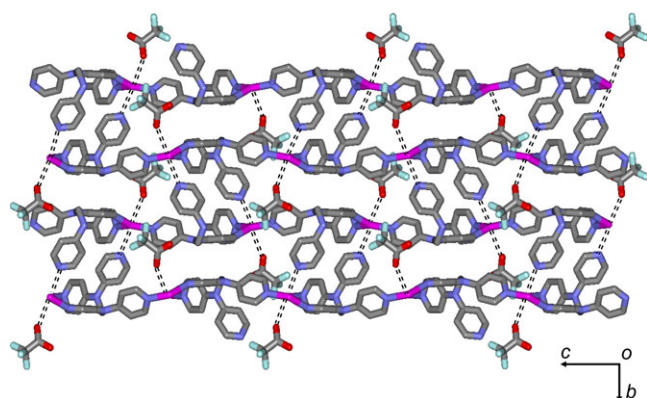
Ag1–N1	2.237 (6)	Ag1–O1	2.886 (1)
Ag1–N6 <sup>i</sup>	2.214 (6)	Ag1–N3 <sup>iii</sup>	2.763 (1)
Ag1–N5 <sup>ii</sup>	2.400 (6)	N4–C11	1.38 (1)
N1–C3	1.33 (1)	N4–C16	1.43 (1)
N1–C2	1.35 (1)	N4–C21	1.45 (1)
N2–C5	1.38 (1)	N5–C14	1.32 (1)
N2–C6	1.44 (1)	N5–C13	1.32 (1)
N2–C21	1.47 (1)	N6–C18	1.33 (1)
N3–C8	1.33 (1)	N6–C19	1.36 (1)
N3–C9	1.33 (1)		
N6 <sup>i</sup> –Ag1–N1	147.7 (3)	N3 <sup>iii</sup> –Ag1–O1	174.1 (1)
N6 <sup>i</sup> –Ag1–N5 <sup>ii</sup>	115.9 (2)	O2–Ag1–N1	90.51 (3)
N1–Ag1–N5 <sup>ii</sup>	96.4 (2)	O1–Ag1–N5 <sup>i</sup>	99.68 (4)
O1–Ag1–N6 <sup>iv</sup>	83.81 (3)	C14–N5–Ag1 <sup>iii</sup>	119.5 (5)
C3–N1–Ag1	118.9 (5)	C13–N5–Ag1 <sup>iii</sup>	119.5 (5)
C2–N1–Ag1	124.4 (5)	C18–N6–Ag1 <sup>iv</sup>	120.0 (5)
C19–N6–Ag1 <sup>iv</sup>	121.5 (5)	C8–N3–C9	116.3 (7)
N4–C21–N2	111.5 (6)	C11–N4–C16	120.7 (6)
C2–N1–C3	115.5 (6)	C11–N4–C21	120.2 (6)
C5–N2–C6	121.1 (6)	C16–N4–C21	118.1 (6)
C5–N2–C21	123.4 (6)	C14–N5–C13	116.7 (7)
C6–N2–C21	114.5 (6)	C18–N6–C19	117.9 (6)

Symmetry transformations used to generate equivalent atoms: (i)  $x - 1, -y + 1/2, z - 1/2$ ; (ii)  $x - 1, y, z$ ; (iii)  $x + 1, y, z$ ; (iv)  $x + 1, -y + 1/2, z + 1/2$ .

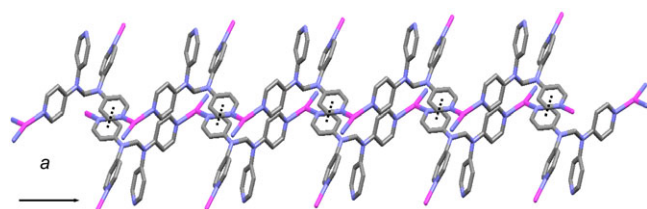


**Figure 8.** Perspective view of **3**, showing an extended 2D network structure via the coordination of silver(I) ions and tpmds (purple/sky blue: silver(I) ion, blue: nitrogen, gray: carbon).

coordination environments of the metal ions.<sup>14</sup> Indeed, silver(I) ions of **1** and **2** have tetrahedral geometries and show broaden emission bands at 305–420 and 310–420 nm, respectively. On the other hand, silver(I) ion of **3** has pseudo trigonal bipyramidal geometry and display emission band at 300–390 nm. The maximum peak of **3** was blue-shifted, compared with those of **1** and **2**. This can be attributed to the coordination geometry of silver(I) ion. The emissive behaviors in **1–3** can be mostly attributed to ligand-centered  $\pi \rightarrow \pi^*$  or  $n \rightarrow \pi^*$  transitions within the aromatic groups of the tpmd ligands.<sup>15</sup>



**Figure 9.** Perspective view of **3**, showing the 3D supramolecular structure due to the weak axial bonding between the 2D layers. The weak bondings between silver(I) ions and pyridine groups are indicated as dashed lines (purple: silver(I) ion, blue: nitrogen, gray: carbon, sky blue: fluorine).



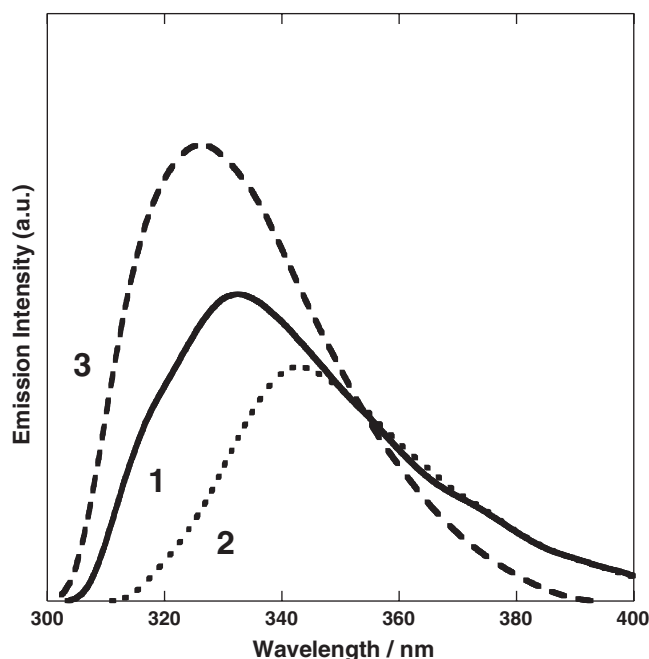
**Figure 10.** Perspective view of **3**, showing the offset  $\pi$ - $\pi$  stacking interaction via pyridine groups. The 3D supramolecular interactions are indicated as  $\cdots$  (purple: silver(I) ion, blue: nitrogen, gray: carbon).

## Conclusions

We have assembled three-dimensional coordination polymers **1–3** by using  $\text{AgX}$  ( $\text{X} = \text{NO}_3^-$  for **1**,  $\text{CF}_3\text{SO}_3^-$  for **2**, and  $\text{CF}_3\text{CO}_2^-$  for **3**) and  $N,N,N',N'$ -tetrakis(pyridin-4-yl)methanediamine (tpmd). In **1**, **2**, and **3**, the tpmd ligand undergoes to bind four silver(I) ions per tpmd. The coordination numbers of silver(I) ions in **1**, **2**, and **3** are four, four, and five, respectively. The topologies of **1** and **2** are 3D network structures with large loops which is composed of two silver(I) ions and two tpmds. **3** is a 3D coordination network based on three-connected layer. Furthermore, all coordination networks have strong  $\pi$ - $\pi$  interactions between the pyridine rings. **1–3** show strong emissions at 331, 342, and 326 nm, respectively, due to the topological structures and counteranions.

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**Supporting Information.** Additional supporting information is available in the online version of this article.



**Figure 11.** Solid state photo-induced emission spectra of **1** (solid line), **2** (dotted line), **3** (dashed line) at room temperature with  $\lambda_{\text{ex}} = 290$  nm.

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