## Anion Effects on the Formation of Silver(I) Complexes with the Flexible Ligand 4,4'-Bis(1,2,4-triazol-1-ylmethyl)biphenyl

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Abstract. The reaction of 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (btmb) with silver(I) salts of  $BF_4^-$ ,  $NO_3^-$  and  $N_3^-$  led to the formation of four new silver(I) coordination polymers { $[Ag(btmb)]BF_4\}_n$  (1), { $[Ag_2(btmb)_3](NO_3)_2(H_2O)_5\}_n$  (2),  $[Ag_2(btmb)(N_3)_2]_n$  (3), and [ $Ag(btmb)(N_3)_3$ ]\_n (4). Their coordination number varies from 2 (in 1) to 3 (in 2), 4 (in 3), and 5 (in 4). Different from the single chain structure of 1, complex 2 displays a 1D ladder-like double chain framework, whereas complex 3 exhibits a 2D layered architecture. Complex 4 has the same anion as complex 3 but shows a different metal-to-ligand ratio and a 1D double-zigzag chain structure. Both 3 and 4 have Ag···Ag argentophilic interactions. The ligand btmb adopts both *cis* or

# *trans* configuration in the studied complexes. A *trans*- or *cis*-btmb ligand link silver ions with Ag···Ag distances of $\approx 18$ and 13 Å, respectively. BF<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup> are non-coordinating anions in **1** and **2**. N<sub>3</sub><sup>-</sup> is the bridging anion in **3** (1,3-bridging fashion) and **4** (1,1-bridging fashion). These findings suggest that the coordination numbers around the Ag<sup>I</sup> ion correlate to the coordination abilities of anions and the btmb to silver ratio. In addition, the influence of anions on thermal stability were also investigated. This work is a good example that nicely supports the less explored field of anion-dependent structures of complexes with non-pyridyl ligands.

### 1. Introduction

In recent years, the rational design, synthesis, and characterization of novel well-defined metal-organic frameworks (MOFs) have found great research interest. Much of their appeal comes from their intriguing variety of architectures and topologies as well as their tremendous potential applications such as electronic, magnetic, optical, absorbent, and catalytic materials.<sup>[1-4]</sup> Currently, one of the greatest challenges in this area is the assembly of novel supramolecular entities with desired structures and properties and there are still lots of research to be done.<sup>[5]</sup> It was proved that some factors such as anion control, metal-to-ligand ratio, and the coordination arrangement of metal atoms have a profound effect upon the resulting network topology.<sup>[6,7]</sup> Among them, the study of the silver(I) coordination architectures is particularly interesting because of the flexibility of its coordination sphere and the

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ease to vary the coordination number.<sup>[8–13]</sup> Several studies of the structural dependence on anions were reported by *Klausmeyer* et al.,<sup>[6,14]</sup> which concentrated on silver(I) complexes with ligands containing a coordinating pyridyl function. A related area of this research that proved lacking, however, was the one that concerned ligands, which involved other coordination groups. As it is known, ligands containing triazole groups are another class of N-heterocyclic building blocks, which are used extensively in crystal engineering. The triazole group has different coordination modes that could result in different solid-state architectures when reacting with metal ions compared to the pyridyl function.

For a better understanding of the silver(I) network topology constructed from ligands different from those with a pyridyl function under anion control, the ligand 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (btmb, Scheme 1) was synthesized, in which the two triazole groups are linked by a biphenylmethyl group. Another reason of adopting btmb was because that the rigid biphenyl group could provide thermal stability for the framework, whereas the flexible methylene group could induce







Scheme 2. Effect of counterions and reaction ratio on the structure of silver(I) coordination polymers.

subtle environmental changes that may modify the resulting structures.<sup>[15–21]</sup> Additionally, to the best of our knowledge, the coordination chemistry of the ligand btmb is less studied and there exist only one Cu<sup>II</sup> polymer reported by *Su Zhong-Min*<sup>[22]</sup> and two polymers involving Zn<sup>II</sup> and Co<sup>II</sup> ions investigated by our group hitherto.<sup>[23]</sup>

In light of the above mentioned, in this work, we select three anions, which have different size, arrangement, and coordination abilities [i.e. the tetrahedral  $BF_4^-$ , the planar  $NO_3^-$  and the linear  $N_3^-$  (size:  $BF_4^- > NO_3^- > N_3^-$ ; coordination abilities:  $BF_4^- < NO_3^- < N_3^-$ ] to synthesize four new silver(I) com-4,4'-bis(1,2,4-triazol-1kN<sup>4</sup>,1'kN<sup>4</sup>'-1-ylplexes, namely, methyl)biphenyl-silver(I) tetrafluoroborate  $\{[Ag(btmb)]BF_4\}_n$ (1), tris(4,4'-bis(1,2,4-triazol- $1\kappa N^4$ , $2\kappa N^{4'}$ -1-ylmethyl)biphenyldisilver(I) nitrate pentahydrate  $\{[Ag_2(btmb)_3](NO_3)_2(H_2O)_5\}_n$ (2),  $bis(\mu_2 - azide - 1\kappa N^1, 2\kappa N^3) 4, 4' - bis(1, 2, 4 - triazol - 1\kappa N^4, 2\kappa N^4' - bis(1, 2, 4 - triazol - 1\kappa N^4, 2\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2, 4 - triazol - 1\kappa N^4) - bis(1, 2,$ 1-ylmethyl)biphenyl-disilver(I)  $[Ag_2(btmb) (N_3)_2]_n$  (3), and  $\mu_2$ azide-1:1' $\kappa^2$ N<sup>1</sup>-4,4'-bis(1,2,4-triazol-1 $\kappa$ N<sup>4</sup>,1' $\kappa$ N<sup>4</sup>'-1-ylmethyl)biphenyl-silver(I)  $[Ag(btmb)(N_3)]_n$  (4). The influence of the counterion on the composition, dimensionality, conformational, coordination number around the silver ion and the thermal stabilities of complexes were investigated. The relationship between the counterions and metal-to-ligand ratio and the resulting crystal structures are summarized in Scheme 2.

### 2. Experimental Section

### 2.1. Materials and Measurements

The flexible ligand 4,4'-bis(1,2,4-triazol-1-ylmethyl)biphenyl (btmb) was synthesized according to the literature method.<sup>[24]</sup>  $[Ag(NH_3)_2]N_3$ ,  $[Ag(NH_3)_2]BF_4$ , and  $[Ag(NH_3)_2]NO_3$  were prepared as described elsewhere.<sup>[25]</sup> Other chemicals of reagent grade were used as received without further purification. Elemental analyses were performed with a Vario EL III elemental analyzer. Infrared spectra were recorded with

a Nicolet A370 FT–IR spectrometer as KBr pellets in the range 400– 4000 cm<sup>-1</sup>. Thermogravimetric analyses were completed with a Netzsch STA–409PC thermal analyzer at a heating rate of 10 °C·min<sup>-1</sup> in air. Fluorescent spectra were recorded with a Shimadzu RF-5301 spectrophotometer. All of the silver complexes reported herein were stable in air and at room temperature with little sign of decomposition within several hours upon exposure to light. In solution, the complexes tend to undergo decomposition to form an oily black product.

**CAUTION:** Although not encountered in our experiments, azido compounds of metal ions are potentially explosive. Only a small amount of the materials should be prepared, and it should be handled with care.

### 2.2. Synthesis of the Complexes

### 2.2.1 $\{[Ag(btmb)]BF_4\}_n$ (1)

A solution of btmb (31.6 mg, 0.1 mmol) in acetone (10 mL) was added to an aqueous solution of freshly prepared  $[Ag(NH_3)_2]BF_4$  (0.05 mol·L<sup>-1</sup>, 2 mL) and was stirred for 15 minutes. After filtration, the mixture was allowed to stand at room temperature for a week. Colorless crystals of **1** were obtained with yield 68 % based on btmb. Anal. for C<sub>18</sub>H<sub>16</sub>AgN<sub>6</sub>BF<sub>4</sub>: calcd. C 42.31, H 3.16, N 16.45 %; found: C 42.27, H 3.21, N 16.55 %. FT-IR (KBr):  $\tilde{v} = 3446$  m, 3141 m, 1634 m, 1516 s, 1440 m, 1405 w, 1370 w, 1345 m, 1276 s, 1214 s, 1139 s, 1082 s, 880 m, 842 m, 808 m, 750 s, 732 s, 675 s, 649 s, 520 w, 483 w cm<sup>-1</sup>.

### 2.2.2 { $[Ag_2(btmb)_3](NO_3)_2(H_2O)_5$ } (2)

A solution of btmb (31.6 mg, 0.1 mmol) in acetone (10 mL) was added to an aqueous solution of freshly prepared  $[Ag(NH_3)_2]NO_3$  (0.05 mol·L<sup>-1</sup>, 4 mL) and was stirred for 15 minutes. Colorless crystals of **2** were obtained with a yield of 37 % based on btmb after the filtrate was allowed to stand for three weeks. Anal. for  $C_{54}H_{58}Ag_2N_{20}O_{11}$ : calcd. C 47.04, H 4.24, N 20.32 %; found: C 47.21, H 4.18, N

Table 1.	Crystallographic	data for	complexes	1 - 4



Complexes	1	2	3	4
Empirical formula	C <sub>18</sub> H <sub>16</sub> AgBF <sub>4</sub> N <sub>6</sub>	C <sub>54</sub> H <sub>58</sub> Ag <sub>2</sub> N <sub>20</sub> O <sub>11</sub>	C <sub>9</sub> H <sub>8</sub> AgN <sub>6</sub>	C <sub>18</sub> H <sub>16</sub> AgN <sub>9</sub>
Formula weight	511.05	1378.94	308.08	466.27
Т /К	298(2)	298(2)	298(2)	298(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Triclinic
Space group	C2/c	Pccn	$P2_1/c$	$P\overline{1}$
a /Å	29.358(4)	16.6439(16)	14.752(3)	7.6537(8)
b /Å	4.2576(5)	17.6983(16)	5.5035(10)	8.3467(9)
c /Å	17.341(2)	19.7571(18)	12.324(2)	15.1008(16)
$\alpha$ /°	90	90	90	96.4400(10)
β /°	113.605	90	91.713(2)	103.9040(10)
γ /°	90	90	90	102.3680(10)
$V/Å^3$	1986.2(4)	5819.8(9)	1000.1(3)	900.96(17)
Ζ	4	4	4	2
$D_c / \text{Mg} \cdot \text{m}^{-3}$	1.709	1.574	2.046	1.719
$\mu / \text{mm}^{-1}$	1.069	0.751	1.994	1.144
F (000)	1016	2816	604	468
R(int)	0.0155	0.0742	0.0254	0.0158
Data / restraints / pa-	1745 / 0 / 151	5154 / 3 / 389	1772 / 0 / 145	3120 / 0 / 253
rameters				
GOF on $F^2$	1.073	1.039	1.084	1.080
$R_1, wR_2 [I > 2\sigma(I)]$	0.0409, 0.1244	0.1027,0.2540	0.0260, 0.0611	0.0243, 0.0607
$R_1$ , $wR_2$ (all data)	0.0454, 0.1290	0.1856,0.3012	0.0286, 0.0627	0.0260, 0.0619
largest diff peak and hole $/e \cdot A^{-3}$	0.943, -0.422	1.372, -0.775	0.321, -0.442	0.217, -0.546

20.39 %. FT-IR (KBr):  $\tilde{v} = 3445$  br, 3109 m, 1517 s, 1381 vs, 1277 s, 1212 m, 1184 m, 1135 s, 1075 w, 1017 w, 1006 w, 982 w, 844 w, 826 w, 805 w, 754 s, 675 m, 648 m, 634 m, 581 w, 507 w cm<sup>-1</sup>.

### 2.2.3 $[Ag_2(btmb) (N_3)_2]_n$ (3)

A solution of btmb (31.6 mg, 0.1 mmol) in acetone (10 mL) was added to an aqueous solution of freshly prepared  $[Ag(NH_3)_2]N_3$  (0.05 mol·L<sup>-1</sup>, 4 mL). Afterwards, the mixture was stirred for 15 minutes and filtered. Colorless crystals of **3** were obtained with a yield of 63 % based on btmb after the filtrate was allowed to stand for a week. Anal. for C<sub>18</sub>H<sub>16</sub>Ag<sub>2</sub>N<sub>12</sub>: calcd. C 35.09, H 2.62, N 27.28 %; found: C 35.16, H 2.53, N 27.37 %. FT-**IR** (KBr):  $\tilde{\nu} = 3448$  m, 3116 m, 2035 s, 1997 s, 1512 s, 1429 w, 1321 w, 1270 s, 1214 w, 1131 s, 1011 s, 978 m, 875 m, 834 m, 801 s, 756 s, 674 m, 648 m, 469 m cm<sup>-1</sup>.

### $2.2.4 [Ag(btmb)(N_3)]_n$ (4)

Complex **4** was obtained by a procedure similar to the one reported for complex **3** with the exception that a greater amount of  $[Ag(NH_3)_2]N_3$  was added (2 mL, 0.05 mol·L<sup>-1</sup>). The Ag/btmb ratio was 1:1, not 2:1 as in complex **3**. Colorless crystals were obtained with a yield of 41 % based on btmb after the filtrate was allowed to stand for three weeks. Anal. for  $C_{18}H_{16}AgN_9$ : calcd. C 46.37, H 3.46, N 27.04 %; found: C 46.25, H 3.32, N 27.16 %. FT-IR (KBr):  $\tilde{v} =$  3297 w, 3111 w, 3078 m, 2015 s, 1607 w, 1514 s, 1433 m, 1369 m, 1341 m, 1278 s, 1210 m, 1168 w, 1132 s, 1013 s, 983 m, 920 m, 842 m, 802 m, 752 s, 700 s, 673 m, 651 m, 633 m, 583 w, 497 m cm<sup>-1</sup>.

### 2.3. X-ray Crystallography

Single crystal diffraction data for complexes 1–4 were collected with a Bruker Smart Apex-II CCD diffractometer with graphite monochromatic Mo- $K_a$  radiation ( $\lambda = 0.71073$  Å) at room temperature. Empirical absorption corrections were applied using SADABS program. The structures were solved by direct method with SHELXS-97<sup>[26]</sup> and refined by full-matrix least-squares on  $F^2$  with SHELXL-97.<sup>[27]</sup> All non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed geometrically. Molecular graphics were drawn with using XP, and Diamond software.<sup>[28]</sup> The crystal data and refinement results are given in Table 1. Selected bond lengths and angles are presented in Table 2.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-767426 (1), -767427 (2), -767428 (3), and -767429 (4). (http://www.ccdc.cam.ac.uk/conts/retrieving.html, Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

**Supporting Information** (see footnote on the first page of this article): TG and DSC curves, IR and fluorescence spectra of the complexes under discussion.

### 3. Results and Discussion

### 3.1. Description of Crystal Structures

### 3.1.1. $\{[Ag(btmb)]BF_4\}_n$ (1)

The composition of **1** is identical to the synthesis reactants. The asymmetric unit is made up by half a btmb ligand, half a silver atom, and half a  $BF_4^-$  anion. The structure of **1** is shown in Figure 1. Each silver atom is coordinated by two nitrogen atoms of btmb ligands in a linear arrangement with the bond angle of N1–Ag1–N1B being 180° and a bond length of Ag1–N1 of 2.139(3) Å. It is noteworthy that the  $BF_4^-$  anion in **1** 

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Table 2. Selected bond lengths /Å and angles /° for complexes 1–4.

Complex 1			
Ag(1)–N(1)	2.139(3)		
Complex 2			
Ag(1)-N(6)#1 Ag(1)-N(1) N(6)#1-Ag(1)-N(1)	2.23(1) 2.25(1) 127.9(5)	Ag(1)–N(7) N(6)#1–Ag(1)–N(7) N(1)–Ag(1)–N(7)	2.32(1) 113.9(5) 118.0(5)
Complex 3			
Ag(1)-N(4) Ag(1)-N(1) N(6)#1-Ag(1)-Ag(1)#2 N(4)-Ag(1)-Ag(1)#2 N(1)-Ag(1)-Ag(1)#2	2.166(3) 2.211(2) 82.46(6) 122.21(7) 64.16(6)	Ag(1)-N(6)#1 Ag(1)-Ag(1)#2 N(4)-Ag(1)-N(1) N(4)-Ag(1)-N(6)#1 N(1)-Ag(1)-N(6)#1	2.604(3) 3.2745(6) 161.1(1) 105.7(1) 92.61(9)
Complex 4			
$\begin{array}{c} Ag(1)-N(6)\#1\\ Ag(1)-N(1)\\ Ag(1)-N(7)\\ N(7)-Ag(1)-N(7)\#2\\ N(6)\#1-Ag(1)-N(7)\end{array}$	2.221(2) 2.227(2) 2.508(2) 104.08(6) 105.99(8)	Ag(1)-Ag(1)#2 Ag(1)-N(7)#2 N(6)#1-Ag(1)-N(1) N(6)#1-Ag(1)-Ag(1)#2	3.1332(5) 2.584(2) 158.38(8) 111.06(5)
$\begin{array}{l} N(1) - Ag(1) - N(7) \\ N(6) \# 1 - Ag(1) - N(7) \# 2 \\ N(1) - Ag(1) - N(7) \# 2 \end{array}$	91.59(7) 99.69(7) 87.78(7)	$ \begin{array}{c} N(0) - Ag(1) - Ag(1) + 2g(1) - 2g(1) - Ag(1) - 4g(1) -$	89.44(5) 53.14(5) 50.94(5)

Symmetry codes: 1 #1–*x*, –*y*+2, –*z*. 2 #1 *x*, *y*–1, *z*; #3 *x*, *y*+1, *z*. 3 #1 *x*, *y*–1, *z*; #2 –*x*, –*y*+2, –*z*+1; #4 *x*, *y*+1, *z*. 4 #1 *x*+2, *y*+1, *z*+1; #2 – *x*+3, –*y*+1, –*z*+2; #3 *x*–2, *y*–1, *z*–1.

does not participate in the coordination with  $Ag^{I}$ . The  $BF_{4}^{-}$ anions are disordered and have two positions as shown in Figure 1a. Except the F3 atom, the occupancies of all other atoms in  $BF_4^-$  are 0.5. The centrosymmetric btmb unit in 1 adopts a trans conformation. The two benzene rings are exactly coplanar due to central symmetry. However, the dihedral angle between the phenyl ring and the adjacent triazole ring is 66.52°. There exists C-H···F H bonding as shown in Figure 1. Each btmb ligand connects two different silver ions through its two triazole nitrogen atoms to form a one-dimensional chain structure. The Ag. Ag separation across the bridging btmb is 17.80 Å (Figure 1b), which is similar to all other Ag. Ag distances that are linked by trans-btmb (17.657 Å in 3 and 18.383 Å in 4). The nearest Ag. Ag distance between adjacent chains is 4.258 Å. No Ag-Ag interaction exist in 1 due to the fact that the nearest Ag...Ag distance is longer than the sum of the van der Waals radii of 3.44 Å. From the b axis, the 1D chains are linked through C-H···F H bonds<sup>[29-32]</sup> (Figure 1b).

### $3.1.2 \{ [Ag_2(btmb)_3](NO_3)_2(H_2O)_5 \}_n$ (2)

The replacement of  $BF_4^-$  with  $NO_3^-$  and an increase in the Ag:btmb ratio afforded complex **2**. The structure of **2** is shown in Figure 2. The asymmetric unit is made up of one silver ion, one nitrate anion, 1.5 btmb ligands, and 2.5 crystalline water molecules. Different from complex **1**, there are two different btmb ligands in **2**, only one of them is centrosymmetric. Each Ag<sup>I</sup> atom is tricoordinated to three nitrogen atoms (N1, N6 from the asymmetric btmb, and N7 from the symmetric btmb) from three different btmb ligands to form a triangular coordination environment since the three N–Ag–N angles are all



**Figure 1.** Crystal structure of  $[Ag(btmb)]BF_4\}_n$  (1). (a) Coordination environments and (b) packing from *b* axis. Dotted lines are hydrogen bonds. Symmetry codes: #1 -*x*, -*y*+2, -*z*; #2 -*x*+1/2, -*y*+3/2, -*z*+1.

close to 120° (Table 2). The Ag–N distances are in the range 2.229 to 2.316 Å (Table 2), which are similar to those observed for complex 1 and agree well with the reported values.<sup>[33–35]</sup> NO<sub>3</sub><sup>-</sup> is a very weak ligand and does not participate in the coordination with Ag<sup>I</sup> in 2, similar to the uncoordinated BF<sub>4</sub><sup>-</sup> ion in 1.





**Figure 2.** Crystal structure of { $[Ag_2(btmb)_3](NO_3)_2(H_2O)_5\}_n$  (2). (a) Coordination environments;  $H_2O$  and  $NO_3^-$  are omitted for clarity. (b) Double-strand 1D ladder viewed from *a* axis. (c) The 1D ladder viewed from *b* axis (left) and crystal packing from *b* axis (right). Red thin lines represent  $NO_3^-$  anions. Symmetry codes: #1: *x*, *y*–1, *z*; #2: –*x*–1/2, –*y*+1/2, *z*.

In contrast to the trans configuration of the ligand btmb in 1, in complex 2 the ligand exhibits *trans* and *cis* configuration for the asymmetrical and symmetrical btmb, respectively. In complex 2, the dihedral angle between the two benzene rings of the biphenyl group in the asymmetric trans-configured btmb ligand is 8.84°, whereas in the cis-configured symmetric btmb ligand, the dihedral angle between two benzene rings is 22.752° (Figure S1, Supporting Information). The trans-btmb ligand links adjacent Ag<sup>I</sup> ions to form an infinite non-interpenetrated molecular chain (Figure 2b). Two chains are linked through a symmetric btmb ligand to form a double chain ladder. The Ag···Ag distance within trans-btmb links is 17.70 Å along the side chain, whereas the Ag…Ag distance of cis-btmb links is 13.05 Å. Furthermore, the centroid-centroid distances and the dihedral angles between two triazole rings A and B in neighboring btmb ligands are 3.884 Å and 13.100°, respectively. For B and C planes, the distances and angles are 4.235 Å and 7.488°, respectively (Figure 2b). This indicates the presence of T-type edge-to-face  $\pi$ - $\pi$  interactions (Figure 2b).<sup>[36–41]</sup> The complex is packed alternatingly up and down into a 3D framework as shown in Figure 2c.

Complexes 1 and 2 have different coordination environments due to the different anions and different ligand to metal ratios. To highlight the anion effects at the same reaction ratio, we tried the same reaction ratio in syntheses of 1 and 2, but all reactions other than those reported for the syntheses of 1 and 2 have very low yield with considerable light reaction to form dark films and ligand precipitates. The crystals we could obtain in a series of reactions with different ratio were either 1 or 2.

### 3.1.3. $[Ag_2(btmb) (N_3)_2]_n$ (3)

X-ray crystallographic analysis shows that the asymmetric unit in 3 contains the basic building block of one Ag<sup>I</sup> ion, half a btmb ligand, and one azide anion. The ligand btmb is located at an inversion center. Each Ag<sup>I</sup> ion is bound to one nitrogen atom from a btmb triazole group, two nitrogen atoms from two azide molecules, and one silver ion to form tetracoordinated environments as illustrated in Figure 3. Four atoms in the AgN<sub>3</sub> unit are essentially located in the same plane (Figure S2). The distances Ag1-N4 (2.166(3) Å) and Ag1-N1 (2.211(2) Å) are similar to those of other Ag<sup>I</sup> triazole complexes.<sup>[33-35]</sup> The distance between the Ag1 and N6 atom of the azide anion is longer (2.603(3) Å), which indicates that only weak bonding is present.<sup>[42]</sup> The Ag<sup>I</sup>N<sub>3</sub> unit shows a distorted Y-shaped coordination arrangement with N1-Ag1-N6A = 92.6°, N1-Ag1-N4 = 161.1°, and N6A-Ag1-N4 = 105.7°. The Ag1-Ag1 distance of 3.275 Å is shorter than the sum of the van der Waals radii of two silver atoms (3.44 Å).<sup>[43–45]</sup>



**Figure 3.** Crystal structure of  $[Ag_2(btmb) (N_3)_2]_n$  (3). (a) Coordination environments of 3. Hydrogen atoms were omitted for clarity. (b) Structure of coordination sheet by Ag–Ag bonds. The red and green sticks are Ag<sup>+</sup>–N<sub>3</sub><sup>-</sup> coordination chains in left and right–hand helix. (c) Crystal packing from *b* axis. Symmetry codes: #1 *x*, *y*–1, *z*; #2 –*x*, –*y*+2, – *z*+1.

As a comparison, the distances of Ag…Ag argentophilic interactions in many coordination complexes are in the range

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of 3.0–3.4 Å.<sup>[46–49]</sup> We hypothesize that Ag–Ag argentophilic interactions exist in complex **3**. The unusual feature of this structure is due to the fact that the 1D ladder chains are connected to each other by interchain Ag–Ag interactions, which result in a 2D grid sheet structure shown in Figure 3b.  $[Ag_2(btmb)(N_3)_2]_n$  (**3**) is one of a few silver coordination networks with a 2D grid structure built by weak Ag···Ag argentophilic interactions between the 1D ladder chains (Scheme 2). Taken Ag–Ag argentophilic interactions into consideration, the Ag<sup>I</sup> ion is tetracoordinated to form an AgN<sub>3</sub>Ag chromophore.

It was noted that btmb in complex 3 adopts trans conformation, in which the two triazole rings are on the opposite direction of the central phenyl ring. The dihedral angle between the phenyl ring and the adjacent triazole rings amounts 78.6° and the two triazole rings are parallel to each other. Each btmb ligand bridges two silver atoms by two exodentate nitrogen atoms at the 4-position of the triazole rings, which are identical to those in 1 and 2. The Ag. Ag separations across the bridging btmb ligand and the 1,3-bridging azide molecule are 17.656(1) and 5.5034(5) Å, respectively (Figure 3b). The 1,3bridging azide molecule and the silver atom connect alternatingly to form 10-membered rings. The bidentate btmb ligand and the silver atom are bound alternatingly to form a 42-membered macrocycle (Figure 3b). In each macrocycle, the phenyl or triazole rings between the two adjacent ligands are found to be strictly coplanar and the intermetallic distance between the atoms the ladder two silver(I) in square is 5.503 Å  $\times$  17.656 Å. The metallamacrocyclic unit and the 10membered Ag-azide rings link the complex into a 2D grid polymer as shown in Figure 3b. It is noteworthy that the Ag-N<sub>3</sub> chains are in both left and right-hand helix (Figure 3b). The length of a repeating Ag–N<sub>3</sub> chain is 5.50 Å. From b axis, the 2D sheets overlap to pack into a 3D structure (Figure 3c).

### 3.1.4. $[Ag(btmb)(N_3)]_n$ (4)

Complex 4 is synthesized by the same procedure as reported for 3 with the exception that less silver ions are employed. The reaction of [Ag(NH<sub>3</sub>)<sub>2</sub>]N<sub>3</sub> with btmb is carried out in 1:1 ratio and complex 4 can be isolated. X-ray structural analysis reveals that the fundamental unit of 4 contains one Ag<sup>I</sup> atom, one btmb ligand, and one azide anion, which is in agreement with the reaction ratio of the starting materials. In comparison to 3, complex 4 contains more btmb ligand molecules and only one btmb ligand is located in the asymmetric unit of 4. The composition of 4 is identical to that of complex 1 with the exception that BF<sub>4</sub><sup>-</sup> is replaced by N<sub>3</sub><sup>-</sup>. Different from the symmetric trans configuration in 1, the btmb ligand in 4 is in the asymmetric trans configuration. Each AgI ion is coordinated to two nitrogen atoms (N1 and N6) from two different btmb ligands and two nitrogen atoms (N7) from two azide anions (Figure 4). The adjacent silver ions are also weakly coordinated at 3.1332(4) Å, which is slightly stronger than the Ag-Ag bond in 3. Thus, silver is pentacoordinated with  $\tau = 0.79$ . It can be described that silver is in a trigonal bipyramidal environment, in which triazole-Ag-triazole has the largest angle of 159.4°. Silver complexes with a coordination number of four or higher are scarce.<sup>[50-54]</sup> A CCDC search was conducted and revealed about pentacoordinated 40 silver complexes with Ag–Ag bonds.<sup>[55-59]</sup>



**Figure 4.** Crystal structure of  $[Ag(btmb)(N_3)]_n$  (4). (a) Coordination environment. (b) Double strand 1D coordination chain with Ag–Ag bond. (c) Packing from *a* axis. Symmetry codes: #1 *x*+2, *y*+1, *z*+1; #2 -*x*+3, -*y*+1, -*z*+2.

This complex is a good example of high coordinated silver complexes. The Ag-N(triazole) distances fall in the range 2.221-2.227 Å, which are similar to those observed in complex 3, whereas the Ag-N(azide) distances (2.508-2.584 Å) are shorter than those in complex 3. The btmb ligand in 4 exhibits an asymmetric trans configuration, which is similar to the symmetric trans-btmb configuration in 3. Each btmb ligand connects to two silver atoms to form a 1D zigzag polymeric structure as shown in Figure 4b. The dihedral angles between the two triazole rings and the two phenyl rings in the btmb ligand are 18.26° and 31.83°, respectively. The dihedral angles between the phenyl ring and the adjacent triazole rings are slightly different in complexes 3 and 4. The Ag. Ag separation across the bridging btmb ligand is 18.383 Å, which is longer than the Ag. Ag separation of 17.656 Å in 3. The azide molecule in 4 rather acts as a 1,1-bridging ligand, than as a 1,3bridging ligand as reported for 3. In this configuration, two metal atoms and two nitrogen atoms from azide anions form four-membered  $[M_2(azide)_2]$  metallacyclic rings, which are further connected through btmb ligands to form a 1D chain.(Figure 4b). This is quite different from the 2D structure reported for complex 3. The Ag-Ag distance in 4 is with 3.1332(4) Å obviously shorter than the corresponding distance



in 3 (3.275 Å) and similar to those reported by *Chen* et al.<sup>[60]</sup> However, this is still considered a weak interaction in comparison to shorter Ag–Ag bonds (2.8–3.0 Å).<sup>[61–65]</sup> The composition of **4** is quite similar to that of **1**. However, the coordination number greatly differs from two in **1** to five in **4**. The coordinating ligand  $N_3^-$  greatly increases the coordination number around the silver ions.

### 3.2. Conformational Analysis

In order to understand the influence of the flexibility of the btmb ligand on the topologies of the motifs, the configuration of btmb, N···N distance between two donor atoms of btmb, Ag.Ag separation through btmb, and the torsion angles (degrees) in 1–4 are listed in Table 3. The btmb ligands in 1, 3, and 4 adopt trans conformation, whereas the btmb ligands in 2 adopt *trans* configuration for the asymmetric btmb molecule and cis configuration for the symmetric btmb molecule. Thus, btmb tends to adopt trans configuration in silver complexes. The trans- and cis-btmb ligands adopt a "Z" and "C" shape, respectively. Consequently, the distances between the metal atoms separated by trans-btmb are about 4.6-5.3 Å longer than those separated by cis-btmb. The intramolecular distances between the two donor nitrogen atoms N···N in trans-btmb in 1, 2, 3, and 4 are 14.627, 14.469, 14.859, and 14.752 Å respectively, which suggest similarity. It is interesting that the coordinating N···N distances in 4 are slightly shorter than those in 3, whereas the Ag. Ag separation in 4 is obviously longer than the corresponding distance in 3 (Table 3). This is due to the fact that the silver ion in 3 lies away from the triazole plane towards the symmetry center, whereas the silver ion in 4 is coplanar with the triazole molecule (Figure S3). The dihedral angles between two triazole rings in trans-configured btmb are 0° for btmb in 1 and 3, 13.43° in 2, and 18.26° in 4. Therefore, the two triazole planes in a trans-btmb ligand are essentially parallel to each other. The dihedral angle between the two benzene ring planes are 0° for btmb in 1 and 3, 8.34° in 2 and 31.79° in 4, which means a great difference. The dihedral angles between the phenyl and triazole rings, and the torsion angles (Table 3) indicate that the change of the spacer conformation and the relative orientation of the triazole rings are responsible for the N···N distance. From Table 3 it can be seen, that the ligand in trans configuration has dimensions of 14.5-14.8 Å, whereas the cis configured btmb is with at 12.87 Å much shorter. The two phenyl rings have dihedral angles of 0-32°, whereas the dihedral angles between the triazole units and

the adjacent phenyl rings are much larger at 60–85°. The Ag•••Ag distances of ions linked by *trans*- and *cis*-btmb are about 18 and 13 Å, respectively. These data demonstrate that btmb is a flexible ligand.

### 3.3. Thermal Analysis, IR and Fluorescent Spectra

The IR spectra of the free ligand btmb and complexes 1-4 are shown in Figure S4. Compared with the strong absorption band of the triazole ring at 1267 cm<sup>-1</sup> in free btmb this signal is shifted to 1278, 1277, 1271, and 1276  $cm^{-1}$  in complexes 1–4, respectively. The 1510  $\text{cm}^{-1}$  absorption band in btmb is shifted to slightly higher amplitudes (1516, 1516, 1514, 1514 cm<sup>-1</sup> in complexes 1–4, respectively, Figure S4). For complex 1, the absorption band at  $1082 \text{ cm}^{-1}$  corresponds to the free  $BF_4^-$  anion. The absorption band for the free  $NO_3^$ anion is observed at 1382  $\text{cm}^{-1}$  in 2. The IR data of the complexes agree well with their crystal structures. The strong absorption bands at 2034 and 1998 cm<sup>-1</sup> are assigned to the  $N_3^$ anion in 3, whereas the band of the 1,1-bridging azide in complex 4 is observed at 2015 cm<sup>-1</sup>, which is similar to the data reported for other azide complexes (bands in the range of 2000–2200 cm<sup>-1</sup>).<sup>[66]</sup> The thermal stabilities of coordination polymers 1-4 were investigated by thermogravimetric analysis (Figure S5-Figure S8, Supporting Information). The analyses showed that complex 1 is stable up to 300 °C. Compound 2 lost five lattice water molecules (found 6.28 %, calcd. 6.53 %) from 44 to 125 °C. At a temperature of 245 °C the compound began to decompose. A residue of Ag<sub>2</sub>O remained (found 17.2 %, calcd. 16.8 %) at 694 °C. Complex 3 is stable up to 219 °C, and subsequently displays a consecutive decomposition in the range of 220-350 °C with an exothermic peak at 216 °C. Compound 4 is stable up to 240 °C and also undergoes a consecutive decomposition in the temperature range 240-400 °C with an exothermic peak at 190 °C. Finally, complex 1 is the most stable of all four complexes. This can be explained by the fact that the BF<sub>4</sub><sup>-</sup> ion is more stable than the azide and nitrate anions.

The fluorescence properties of the Inorganic-organic hybrid coordination polymers and their potential applications as luminescent materials were investigated. The emission spectra of complexes 1-4 and of the free ligand in the solid state at room temperature were investigated. All the four complexes have similar emission peaks at  $\approx$ 428 nm when excited at 360 nm (Figure 5). An emission of free ligand btmb is observed at 428 nm when excited at 360 nm. These data are similar to free

Table 3. Structural data of complex 1-4.

complex 1	chromo AgN <sub>2</sub>	BF <sub>4</sub>	μ <sub>2</sub> -btmb configuration <i>trans</i> -symm	d(N····N) /Å	<i>d</i> ( <i>M</i> … <i>M</i> ) /Å 17.800	Dihedral angle /° of two triazole rings two phenyl rings		phenyl and triazole rings
						0	0	66.52
2	AgN <sub>3</sub>	$NO_3^-$	<i>trans</i> -asymm <i>cis</i> -symm	14.469 12.873	17.698 13.048	13.43 22.10	8.34 22.78	71.22, 74.90 84.45
3 4	AgN3Ag AgN4Ag	1,3-N <sub>3</sub> <sup>-</sup> 1,1-N <sub>3</sub> <sup>-</sup>	<i>trans</i> -symm <i>trans</i> -asymm	14.859 14.752	17.657 18.383	0 18.26	0 31.79	78.64 79.08, 59.40

btmb and btmb-Zn complexes,<sup>[11]</sup> therefore, we assigned this emission to be an intraligand  $n-\pi^*$  emission.



Figure 5. Fluorescence spectra of ligand (a), complex 1 (b), complex 2 (c), complex 3 (d), complex 4 (e) in solid state excited at 360 nm.

### 4. Conclusions

This study demonstrates that anion changes are able to greatly affect the structure and coordination environment of silver(I) complexes. Ligand btmb acts as a bidentate ligand and coordinates to two silver ions to form coordination polymers 1-4. The coordination environments around the silver(I) ion as well as the structures differ greatly amongst the four complexes. In particular, the coordination numbers around the silver ion in complex 1-3 depend on the size and coordination mode of the anions. The smallest and the strongest coordinating one amongst the three anions,  $N_3^-$ , mainly contributes to the great increase in the coordination number. Furthermore, different bridging fashions can also affect the coordination number. The 1,1-bridging fashion of the  $N_3^-$  ion in 4 effect an increase in the coordination number to 5. With an increase in the metal-to-ligand ratio, the  $N_3^-$  ion tends to adopt a 1,3bridging fashion in 3. Additionally, the result of thermal analysis implied that the introduction of the more stable anion BF<sub>4</sub> is able to improve the thermal stability of the framework.

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