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Silver coordination polymers based on newly designed bis-(cyanobenzyl)bipiperidine ligand: synthesis, anion exchange, guest inclusion, electrochemical and photoluminescence properties

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Abstract

A new flexible ligand, bis-(cyanobenzyl)bipiperidine (L), has been synthesized and structurally characterized. Nine novel silver(I) coordination polymers (CPs), the dimensionality of which depends on the counter-anion; $[Ag_2(L)(NO_3)_2]_n$ (1), $[Ag_2(L)(NO_3)_2]_n$ (2), $\{[Ag_2(L)(NO_3)_2)](C_{16}H_{10})\}_n$ (3), $\{[Ag_2(L)(NO_3)_2)](C_{20}H_{12})\}_n$ (4), $[Ag_2(L)(ClO_4)_2]_n$ (5), $[Ag_2(L)(CF_3SO_3)_2(C_4H_8O)_2]_n$ (6), $[Ag_2(L)(CF_3SO_3)_2(C_3H_6O)_2]_n$ (7), $\{[Ag_2(L)_2] \cdot (BF_4) \cdot 2(C_3H_6O)\}_n$ (8) and $[Ag_2(L)_3(PF_6)_2] \cdot x(C_3H_6O)$ (9) have been prepared by self-assembly of L with AgX (X = NO₃⁻, ClO₄⁻, CF₃SO₃⁻, BF₄⁻ and PF₆⁻), and aromatic guest molecules. Reactions of L with AgNO₃ in acetone in either 1:2 or 1:1 stoichiometric ratio occurred rapidly at room temperature, yielding topologically different structural isomers of the three-dimensional (3D) CPs 1 and 2. Additional reactions of linker L with AgNO₃ in the presence of aromatic guest molecules (pyrene, perylene) formed CPs of 3 and 4 with the inclusion of the corresponding guest in the crystal lattice associated with the reduction of dimensionality of the self-assembled product from 3D to 2D. Reaction of L with AgTf (Tf = (CF_3SO_3) in acetone and THF gave two structurally related two-dimensional (2D) CPs (6 and 7). Compound 8 represents a 1D coordination polymer where the BF_4 anions are not linked to the silver nodes, while 9 is a discrete coordination complex. Anion exchange accompanying an irreversible structural conversion from 7 to 1 and 7 to 8 was monitored in the crystalline state by IR and PXRD techniques. On the other hand, a reversible anion exchange process was observed between 1 and 8. The electrochemical and solid-state photoluminescence properties of these Ag(I)-CPs were also characterized.

INTRODUCTION

Research towards the exploration of coordination polymers (CPs) has rapidly progressed over the past decades because of the versatile utility of such materials in a wide range of potential applications, e.g. as solid-state luminescence sensors, light emitting diodes, proton conductors, heterogeneous catalysts, gas sorbants and supercapacitors.¹⁻¹⁸ Manv different factors play an important role in the synthesis of such materials, including nature (coordination preferences of the metal ions, functionality and flexibility of the organic linkers) and stochiometric ratio of the reacting partners, reaction conditions/environment, and the solvents used. Possible inclusion of guest components within the coordination lattice provides an additional important parameter that may further influence the properties of the resulting product.¹⁹⁻²⁵ In this context, several rigid multitopic organic ligands and transitional metal ions have been used to explore CPs with predictable and well defined porous frameworks that can undergo reversible guest or anion exchange, with or without losing their structural integrity.²⁶⁻³⁵ The structural features of coordination polymers with flexible multitopic organic ligands appear to be less predictable. Yet the use of flexible linkers could be advantageous in other respects, as such coordination networks are more adaptive to guestinclusion, more responsive to external stimuli and may reveal higher propensity to singlecrystal-to-single-crystal transformation.³⁶⁻³⁸

The coordination chemistry of multi-topic organic ligands bearing pyridine, carboxylate and/or imidazole functionalities have been widely investigated in relation to the construction of coordination polymeric networks.³⁹⁻⁴⁴ Several rigid organic ligands substituted with nitrile groups have been successfully utilized as well in the formation of both porous or non-porous CPs with silver(I) ions as nodes. This has been facilitated by the ready availability of nitriles, low cost of silver (with its soft Lewis acid character), and the simplicity of the Ag(I)–N≡C interaction.^{30,45-54} On the other hand, very few flexible ligands containing nitrile groups have been explored for construction of CPs with silver(I) ions.^{25,55} Among those nitrile-based silver(I) CPs, some showed supramolecular structural transformations in the crystalline state, concomitant with anion exchange, while other CP compounds exhibited solid-state photoluminescence.^{22,25,56-61} Issues of guest inclusion and electrochemical behaviour of nitrile-based silver(I) CPs deserved lesser attention.^{25,62}

In this work we report on the synthesis of a new divergent heterotopic flexible ligand, namely bis-(cyanobenzyl)bipiperidine, L, which contains both amine and nitrile nitrogen

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donors (Scheme 1). The two nitrile groups along with the two sp³ N-atoms of the molecule provide attractive sites for metal coordination. Due to the presence of inter-connecting aliphatic methylene spacers, **L** has conformational degrees of freedom primarily about the N- $C-C_{aromatic}$ bonds (Scheme 1).







Scheme 2. Schematic representation of the synthesis of the Ag(I) coordination polymers of ligand (L) in question with the variation of anions, reaction stoichiometry, and the aromatic guest molecules.

We then reacted this ligand with a series of silver salts and explored the resulting coordination polymers (Scheme 2) in order to study the influence of anions on the dimensionality of the coordination networking. Indeed, the structures of the polymeric products were found to be affected by the nature of the counter anions (NO_3^- , ClO_4^- , CF₃SO₃, BF₄ and PF₆), reaction stoichiometry and possible insertion of large aromatic guests into the crystallizing materials. The available compounds (which are not porous) have been examined, therefore, with respect to post-synthetic anion-induced structural transformations (Scheme 3) and guest inclusion. While compounds 1 and 2 represent 3D coordination frameworks, upon inclusion of a large aromatic guest (as pyrene in 3 or perylene in 4) the dimensionality of the polymeric ensemble is reduced to 2D, exhibiting the same metal-ligand connectivity features in 3 and 4. The inclusion of large aromatic guests is expected to affect the interlayer π - π stacking in the corresponding structures and thus their emission properties. Correspondingly, solid-state photoluminescence study was conducted for both of the guest-included CPs, in relation to the guest free CPs, and the free ligand. The organic linker L used in this study contains nitrile functions and exhibits redox-active behaviour. This led us to explore also the electrochemical properties of the coordinationpolymeric compounds presented here; there is only a rare literature example reporting on the electrochemical performance of such nitrile-based Ag(I)-CPs.^{62,63}



Scheme 3. Schematic representation for the structural transformation of the products via post-synthetic anion exchange procedures.

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RESULTS AND DISCUSSION

Synthesis and crystal structure of bis-(cyanobenzyl)bipiperidine (L). L was synthesized by reaction of 4,4'-bipiperidine with 4-(bromomethyl) benzonitrile under reflux condition. The structure of L was determined by ¹H NMR, IR, and single-crystal X-ray diffraction (crystallization from acetone). Compound L crystallises in the monoclinic space group $P_{1/n}$ and the asymmetric unit consists of one and a half molecules of L (the latter being located on inversion) The two crystallographically independent units (depicted in green and red in Figure 1b, respectively) have an extended conformation, the anti-periplanar C_{aromatic}-C_{methylene}-C_{aromatic} torsion angles being near 180°. They overlay almost perfectly, both displaying similar hydrogen bonding $\mathbf{R}_2^2(10)$ patterns (Figure 1a). The N•••H-C intermolecular contact distances are 2.61 and 2.71 Å for the green molecules and 2.56 Å for the red moieties. The two entities exhibit zig-zag type 1D 'hydrogen-bonding polymers', the H-bonded chains of the red molecules being interspaced by two parallel chains of the green species (Figure 1b). There is no apparent hydrogen bonding between the 'polymeric' chains. It has been anticipated that the preferred anti-periplanar conformation of L will be preserved in the reaction of this ligand with silver salts.



Figure 1. (a) The intermolecular hydrogen bonding synthon along the zig-zag 'polymeric chains'. (b) Crystal packing viewed down the *a*-axis, showing the two crystallographically independent molecules of L in green (located on general positions and red (on centers of inversion) colours.

Self-assembly of bis-(cyanobenzyl)bipiperidine (L) with silver(I) ions. Ligand L was reacted with a series of silver(I) salts at room temperature in acetone/THF solution. Five different reagents (AgNO₃, AgClO₄, AgCF₃SO₃, AgBF₄, AgPF₆) were employed, also in order to assess the effect of the different anions on the topology of the resulting networks. The preparative procedures were carried out with varying ligand-to-metal stoichiometric ratios, but only crystallizations of L with $AgNO_3$ (but not with the other reagents) led to two different products. In some syntheses large aromatic guest molecules were also added to the reaction mixture to induce their co-crystallization with the coordination polymeric ensembles. Crystallization of L with AgNO₃ in 1:1 and 1:2 ratios in acetone at room temperature afforded within 30-60 minutes single crystals of [Ag₂(L)(NO₃)₂]_n, 1 (Figure 2) and 2 (Figure 3) respectively. The two structures reveal 3D coordination frameworks, but are characterized by different topologies. When L was reacted with silver nitrate (1:2) in the presence of different polycyclic aromatic hydrocarbons as possible guest entities, single crystals suitable for X-ray diffraction were obtained with pyrene { $[Ag_2(L)(NO_3)_2](C_{16}H_{10})\}_n$ (3), and pervlene $\{[Ag_2(L)(NO_3)_2)](C_{20}H_{12})\}_n$ (4). Inclusion of the guest components reduced the dimensionality of the silver-ligand coordination-polymeric ensemble from 3D to 2D in 3 (Figure 4) and 4 (Figure 5). Self-assembly of L with the other Ag(I) salts in acetone or tetrahydrofuran at room temperature afforded within 24 hours single crystals of $[Ag_2(L)(ClO_4)_2]_n$ (5), $[Ag_2(L)(CF_3SO_3)_2(C_4H_{8O})_2]_n$ (6), $[Ag_2(L)(CF_3SO_3)_2(C_3H_6O)_2]_n$ (7), $\{[Ag_2(L)_2] \cdot (BF_4) \cdot 2(C_3H_6O)\}_n$, (8) and $[Ag_2(L)_3(PF_6)_2] \cdot x(C_3H_6O)$ (9). Compound 5 was found to exhibit 3D networking pattern, while 6 and 7 show 2D coordination networks. 1D coordination polymerization was found in 8, and discrete complexes compose crystals of compound 9 (Scheme 2). All the crystalline samples (1-9) were stored in the dark; yet no strong light sensitivity has been observed.

Structural description of the 3D coordination polymers in (1) and (2). Colourless block-like crystals of **1**, were readily formed within 30 minutes. This type of rapid formation of CPs is quite rare in the literature.⁶⁴ The asymmetric unit of **1** contains half molecule of **L**, one Ag(I) ion and one nitrate (NO₃⁻) anion. Each silver ion exhibits a distorted tetrahedral geometry, being coordinated by two nitrate O-atoms, one bipiperidine N-atom and one nitrogen atom from a nitrile group (Figures 2a and 2b). The coordination distances of the Ag(I)-O contacts are 2.48 and 2.57 Å, while the Ag(I)-N bond lengths are 2.32 and 2.25 Å. Every ligand (in its characteristic anti-periplanar conformation) is bound through its four N-sites to four Ag-centers, and every nitrate anion connects along the *a*-axis between two silver

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nodes. The shortest distance between the silvers ions is 5.75 Å. The inter-connected ligands are arranged in the crystals in a herringbone fashion (Figure 2c).



Figure 2. 3D coordination polymer 1, $[Ag_2(L)(NO_3)_2]_n$. (a) View of the ligand coordination environment. (b) View of the metal coordination environment. (c) Perspective view of the 3D framework and its coordination connectivity (Ar represents the aromatic part of the ligand. Hatoms and parts of the ligands were omitted for clarity). (d) The simplified topological illustration of the network (*mot* topology) where blue nodes represent the Ag-ions and the green linkers represent the ligands.

The two nodal net can be simplified by a node-and-linker-type representation, using the TOPOS 4.0 software.⁶⁵ It exhibits a known *mot*-type topology; a 4,4-connected network with a point symbol of $\{6^4.8^2\}_2\{6^6\}$ (Figure 2d). In the TOPOS Topological Database (TTD) there are fifteen crystal structures (their CCDC ref. codes are: AGAYOW, AGONIU, ASAYOJ, AWIDIU, CEBJAV, DAKNAG, KIYMIP, LUJPUC, MIJNAU, PUNSOH, RESSAK, SEHZUB, SEJBAL, UPERAJ, XANMIJ)^{66,67} identified as *mot* networks. Among these frameworks only one of them (CEBJAV)⁶⁸ exhibits a silver node coordinated to nitrate and nitrile groups, and its connectivity pattern is similar to that observed in **1**.



Figure 3. a) Comparison between the nitrate's bridging mode in 1 (right) and 2 (left). The silver spheres represent the Ag(I)-atoms. b) Illustration of 3D framework (viewed along *a*-axis) of 2 and its simplified net (green depicts the organic linkers and blue are the silver nodes).

Changing the metal-ligand stoichiometry to 1:1 in the reaction mixture afforded colourless block-like crystals of **2** within 1-2 hours (Figure 3). The chemical and structural composition of **1** and **2** is identical in terms of the content of the asymmetric unit in the two structures and node-linker coordination connectivity. Yet, from the topological point of view the two polymeric structures belong to different topological types, and thus represent structural polymorphs. The silver nodes in **2** coordinate to two different Ls and two nitrate anions in a severely distorted tetrahedral geometry. As in the previous example, every ligand binds four different Ag ions, which in turn are also interconnected through the nitrate counter ions. The observed Ag-N and Ag-O bond distances are 2.31 and 2.30 Å, and 2.53 and 2.48 Å, respectively. The coordination framework in **2** belongs to the topological type *bbf*, alongside with 24 other crystalline materials (analyzed by TTD) (The CCDC ref. codes are: AHADUJ, AHAFAR, AVAQOD, DIPGAK, EXIDAR, EXIDEV, FAKJAE, FEZWAJ, IMIXEI,

ISIKOL, ISIKUR, ISILAY, ISILIG, ISIMAZ, ISIMED, ISIMIH, LISBEV, LISBOF, OWUGAP, QUPHIT, RAVKEG, SOCXEO, UHUNEQ, UJARIH)^{53,54} (Figure 3b). It represents a (4,4)-connected binodal network with point symbol of $\{6^4.8^2\}\{6^6\}_2$.



Figure 4. Illustrations of the polymeric chains (ID) and intermolecular interactions in (a) 3 and (b) 4. The dashed blue lines represent interactions of the silver cations (depicted as spheres) and nitrate anions.

Structural description of the guest-included coordination polymers in (3) and (4). Although several reactions were tried in the presence of different aromatic solid guest molecules, single crystals suitable for X-ray diffraction studies were obtained only in case of pyrene (3) and perylene (4). The structures of compounds 3 and 4 can be best described as composed of 1D coordination Ag-ligand chains (Figures 4a and 4b), which are further interlinked via the nitrate anions into quasi-2D sheets. In 3 the Ag(I)-cations bind to two L linkers through N_{sp3} and nitrile functions (at 2.24 and 2.34 Å), as well as to (in a mono-dentate fashion) the nitrate anion at 2.24-2.33 Å (Figure 4a). In 4 there are two crystallographically independent metal ions Ag(I) with different coordination environments (Figure 4b). The first metal center Ag₁ is linked to only one L *via* the N_{sp3} site and to the nitrate anion. The second cation Ag₂ is engaged in 1D coordination polymeric array by bridging between two adjacent

Ls through the nitrile function of one linker and the N_{sp3} site of another linker. In addition, the Ag₂ ion is coordinated to a nitrate group in a bidentate manner. The corresponding interaction distances Ag-N_{nitrile}, Ag-N_{sp3} and Ag-N_{nitrate} are respectively 2.30, 2.27 and 2.28, 2.36-2.57 Å. Noteworthy, only one (out of two) nitrile sites of L is involved in coordinative bonds with the silver ions.



Figure 5. Illustrations of the quasi-2D sheet with inclusion of (a) pyrene in 3 (structure viewed down the *b*-axis of the crystal), and (b) perylene in 4 (structure viewed down the *a*-axis).

Inclusion of the aromatic guest molecules between the coordination-polymeric layers in **3** and **4** is depicted in Figures 5a and 5b. In **3** the neighbouring pyrene moieties are laterally displaced one with respect to the other along the 2D sheets without any apparent $\pi^{--}\pi$ interactions between them (Figure 5a). The adjacent perylene molecules in **4**, show partial π -stacking with an interplanar distance of 3.38 Å (Figure 5b). The interaction of the pyrene and perylene guests with the surrounding coordination polymers is mainly by van der Waals forces between the contact surfaces of the parallel layers. These appear to compensate for breaking the cross-linking Ag-N_{nitrate} interactions (as observed in **1** and **2**) that result from the aromatic guest inclusion in **3** and **4**.

Structural description of silver(I) CPs incorporating different anions. Crystallization of L with AgClO₄ led to the formation of 3D network of $[Ag_2(L)(ClO_4)_2]_n$ (5), shown in Figure 6a. In structure of 5, the asymmetric unit consists of half a ligand moiety (located on crystallographic inversion), one ClO₄⁻ anion and a silver node. The framework shows a distorted tetrahedral Ag(I) metal centres, where the ligan-metal-ligand bond angles are within 84–142°. The observed bond distances of Ag-O_{ClO4} bonds are 2.53 and 2.71 Å, while the Ag-N_{ligand} bonds are considerably shorter 2.27 and 2.18 Å (Figure 6b). The 4-connected Ag(I) nodes are coordinated to two different L linkers and two bridging ClO₄⁻ anions. The Ag(I)...Ag(I) separation distance between the ClO₄⁻-bridged cations (approximately along the *c*-axis of the crystal) is 5.64 Å. Every ligand L is coordinated to four Ag(I) ion centres through both N_{sp3} and N_{nitrile} positions, forming a 3D *mot*-type framework of similar topology than that in structure 1. The specific torsion angle of L is about 180° and it is coordinated from two different directions creating the 3D network.



Figure 6. 3D silver(I) perchlorate coordination polymer 5. (a) Connectivity of the silver nodes (depicted as spheres). Red balls represent the perchlorate anions, and Ar stands for the aromatic fragment of the ligand. (b) Perspective view (down the *a*-axis) of the 3D network.

When silver(I) triflate was used in the reaction with L, in tetrahydrofuran or acetone at room temperature, it afforded 2-D networks of the $[Ag_2(L)(CF_3SO_3)_2(C_4H_8O)_2]_n$ (6),

 $[Ag_2(L)(CF_3SO_3)_2(C_3H_6O)_2]_n$ (7) composition. The two structures **6** and **7** are pseudoisostructural in their network geometry. The asymmetric unit of **6** contains one Ag(I) ion, a triflate anion, one tetrahydrofuran (THF) and half of the L molecule. Each Ag-center has a pseudo-tetrahedral coordination environment, being linked to N_{nitrile} and N_{sp3} of two different linkers, as well as to O_{triflate} and O_{THF} sites. Association of the ligands through the N_{sp3} and nitrile sites with the silver ions (at Ag-N = 2.21 and 2.24 Å) led to the formation of 2D coordination layers with parallelogram-like cavities (Figure 7), the latter being accommodated by the Tf⁻ anions and THF ligands (with Ag-O_{triflate} and Ag-O_{THF} contact distances of 2.55 and 2.59 Å, respectively). Coordination 2D networking of similar topology characterize structure **7**, where acetone molecules replace the THF entities in the coordination environment of the silver-ion nodes (the asymmetric unit of **7** contains two Ag(I) ions, two triflate anions, two acetone moieties and one L molecule). The corresponding coordination distances in **7** are: Ag-N = 2.16-2.27 Å, Ag-O_{triflate} = 2.47 Å, and Ag-O_{acetone} = 2.56 and 2.61 Å.



Figure 7. Perspective view of 2D-network of the silver(I) triflate coordination polymers in 6. Hydrogen atoms are omitted for clarity. The silver cation and atoms of the triflate anion are depicted as spheres.

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Figure 8. Perspective view of 1D helical chains of silver(I) tetrafluroborate coordination polymers in 8. Hydrogen atoms are omitted for clarity. The silver•••BF₄⁻ interactions are indicated by green lines. The Ag cations and atoms the tetrfluoroborate anions are depicted as spheres.

A similar reaction of L with silver(I) tetrafluoroborate afforded 1D wavy coordination chains of $\{[Ag_2(L)_2] \cdot (BF_4) \cdot 2(C_3H_6O)\}_n$ composition (8) (Figure 8). The asymmetric unit of 8 contains one Ag(I) ion, a tetrafluoroborate anion, two acetone moieties and one molecule of L. The two organic linkers are bonded to one silver cation *via* the N_{sp3} functions in a nearly linear geometry (N-Ag-N = 177°), where the corresponding Ag-N contact distances are 2.18 and 2.19 Å. The BF₄⁻ anion is positioned near, and weakly associated with, Ag at Ag•••F-BF₃⁻ distance of 2.84 Å. Acetone and anion molecules are surrounding the helical coordination chains, hindering possible engagement of the nitrile groups in coordination to the cation centres.

Finally, reaction of silver(I) hexafluorophosphate with L afforded the oligomeric complex $[Ag_2(L)_3(PF_6)_2]_n$ (9) (Figure 9). The asymmetric unit of 9 contains one Ag(I) ion, a hexaflurophosphate anion, and one and half of L molecule. In this oligomer, each of the two Ag(I) centers coordinates to two organic linkers through one of their N_{sp3} functions (at 2.20 and 2.21 Å), as well as to the bulky PF₆⁻ anion group *via* one of the F-atom (at F-Ag = 2.47 Å, as opposed to 2.84 Å in the previous example). The terminal nitrile groups are involved in weak intermolecular hydrogen bonds. The Cambridge Crystallographic database (CCDC, ConQuest Version 1.17, 2014) contains 944 entries of complexes involving the Ag(I) and PF₆⁻ ion pair.⁵⁴ Out of them only four exhibit directional Ag-F coordination between the two

ions at (2.54 - 2.55 Å).⁶⁹⁻⁷² as compared to the Ag(I)-F coordination bond distance of 2.47 Å in **9**. The coordination geometry around the Ag ions is of the T-shape type with two N-Ag-F bond angles of 97 and 99°, and the N-Ag-N angle of 164°. A similar T-shape coordination to two trans-related N-sites and an F- ion has been observed by Bu et al. in a silver tetrafluorobrate complex with an N-ligand (CCDC refcode ETOPIM: Ag-F bond distance 2.53 Å).⁷³



Figure 9. Illustration of the oligomeric structure of silver(I) hexafluorophosphate coordination complex **9** (Ag centres are depicted as spheres). P-atoms are shown in orange, F-atoms in green, N-atoms in blue and C-atoms in black. Hydrogen atoms are omitted for clarity.

The influence of the various silver salts on the polymeric assembly. The above observations provide interesting insights regarding the kinetics, anionic coordination ability and steric effects in the available structures. As expected, the poly-dentate O-anions (NO₃⁻, ClO₄⁻) have the capacity of coordinating simultaneously to at least two silver ions, and are readily incorporated into the polymeric assembly. This feature along with the multi-dentate nature of the organic linker led to the formation of 3D frameworks. The NO₃⁻ anions have a dramatic effect on the crystallization process. Reactions to obtain crystals of **1** and **2** (with 1:2 and 1:1 ligand-to-Ag salt ratios, respectively) are very fast (30-60 minutes). When the silver salt concentration is increased with respect to that of the ligand, e.g. to 4:1, rapid precipitation of either polycrystalline or amorphous solids occurs. It appears that the small nitrate anions engage readily in the construction of 3D polymeric assemblies. When the ClO₄⁻ anions of large size were used (in **5**), the reaction times increased to 24 hours or more, although still the 3D supramolecular connectivity was preserved in the resulting product. Raising further the

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anionic size by reacting the organic ligand with silver triflate salt (in 6 and 7) yielded only 2D coordination patterns, the bulkier Tf ions showing only a mono-dentate (rather than bridging) coordination mode to the silver ions. In the above context, a survey of the Cambridge Crystallographic Database was made to learn about the relative abundance of polymeric structures based on component species with similar functionalities. The search model used involved molecules with phenyl-nitrile coordination ligands and nitrate, perchlorate or triflate silver salts. Examples with Ph-CN-Ag coordination modes, where the given anion bridges between two or more silver ions, were searched for. Of the correspondingly retrieved crystal structures: one out of fifteen structures of perchlorate salts contain a bridging ClO₄⁻ anion between silver centers,⁴⁴ three out of eight structures of nitrate salts contain a bridging NO_3^- anion,⁷⁴ and 15 out of 50 structure with triflate salt contain bridging Tf⁻ ions. Structures 8 and 9 involved fluorinated anions, which show much lower propensity to act as a bridging component between the silver nodes. Correspondingly, the intermolecular coordination in 8 and 9 yielded only 1D chain and 0D oligometric entities, respectively, wherein the nitrile functions are not linked to metal ions. The use of the fluorinated anions of weaker coordination affinity in this work was intended to invoke the formation of polymeric structures with direct metallic Ag(I)-Ag(I) bridging between the silver nodes, but this effort turned out to be unsuccessful.

Anion exchange and structural transformations. Anion exchange reactions were attempted with coordination complexes 1, 7 and 8 of different connectivity patterns (3D, 2D and 1D). The experiments were carried out by immersing the crystalline samples of the corresponding CPs in a 3 M aqueous sodium salt solution of the replacement anion and left undisturbed at ambient temperature to allow anion-exchange. The possible anion-exchange-induced structural transformations were investigated by IR spectra and PXRD patterns, as the exchanged product were found unsuitable for single crystal X-ray diffractions due to their poor/deteriorated crystallinity. Evidently, in particular cases the anion-exchange procedure led to significant modification of the coordination pattern in the crystal. For example, when a crystal of 7 was immersed in an aqueous solution of 3 M NaNO₃ (in which it is insoluble) and left undisturbed at ambient temperature, the IR spectra for the solid sample collected after 0.5 and 1 h manifested fast generation of a new intense band at 1338 cm⁻¹ for NO₃⁻ (green asterisk in Figure 10a) and consequently the disappearance of an intense CF₃SO₃⁻ peak at 1173 cm⁻¹ (purple asterisk in Figure 10a). Eventually, the CF₃SO₃⁻ peak disappeared completely after 2 h, and the consequent IR spectrum is almost similar with that of compound

1. This implies that the $CF_3SO_3^-$ ion is quantitatively displaced by the NO_3^- ion (Figure 10a). In addition, the PXRD pattern obtained after 2h was coincident with that of 1, indicating that the 2D coordination polymer in 7 was converted to the 3D polymeric structure of 1 by the exchange of $CF_3SO_3^-$ with NO_3^- (Figure S1 in the Supporting Information). In another example, crystals of 1 and 7 were immersed in an aqueous solution of 3 M NaBF₄ and left undisturbed at ambient temperature to allow for the anticipated anion exchange. IR spectra collected for these samples after 1 h and 2 h were found to be almost coincident with the IR spectrum of **8**, evidencing a complete exchange of the $CF_3SO_3^-$ and NO_3^- ions by BF_4^- (Figure 10b and Figure S2 in the Supporting Information). The reverse anion exchange between **8** and **1** was also performed successfully (Figure S2 in the Supporting Information).



Figure 10. (a) IR spectra of 7 after anion-exchange employing 3M NaNO₃ aqueous solution for 0.5, 1, and 2 h. The top and bottom curves represent the IR spectra for 7 and 1 as prepared by direct synthesis. (b) IR spectra of 7 after anion-exchange employing 3M NaBF₄ aqueous solution for 0.5, 1, and 2 h. The top and bottom curves represent the IR spectra for 7 and 8 as prepared by direct synthesis.

Electrochemical behaviour. The electrochemical behaviour of complexes **1**, **3**, **4** and **7-9**, as well of ligand **L**, were investigated by cyclic voltammetry (CV) using 0.2 M 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM TFSI) ionic liquid/CH₃CN non-aqueous electrolyte (Figure 11). The experiments were carried out using three electrode system with Platinum (Pt) foil as working electrode, Pt wire as counter electrode and

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saturated calomel electrode (SCE) as a reference electrode. The analysed complexes were dispersed in dimethylacetamide (1 mg/mL) and then deposited on the working electrode in a suspension state. Subsequently, 0.02 mL nafion solution (as a binder) was deposited over the dried samples on the working electrode. Figure 11 shows the cyclic voltammograms of complexes **1**, **3**, **4** and **7**-9, along with that of L at 100 mV/s. Ligand L was found to exhibit good redox-active behaviour with the appearance of first reversible oxidation wave at -0.55 V vs. SCE, followed by irreversible one at 0.49 V vs. SCE. After complexation of L with Ag(I), in complexes of **1**, **3**, **4** and **7**-9, the reduction peak of silver (I) is not present, indicating that reduction of silver (I) when coordinated to the N-sites of the ligand is difficult.^{63,75} Along the opposite course, the characteristic first reversible oxidation wave in the complexes was found to occur in the range of -0.46 V~ 0.50 V vs. SCE, followed by irreversible oxidation wave in the range of 0.63 V~ 0.66V vs. SCE which can involve the ligand as well. With respect to the oxidation of L, all the oxidation peaks in the complexes shifted towards positive potentials by about 0.05 ~ 0.10 V for the reversible oxidation wave and by 0.14 ~ 0.1V vs. SCE for the irreversible oxidation wave.



Figure 11. Cyclic voltammograms of ligand L and complexes **1**, **3**, **4** and **7-9** (in CH₃CN), using 0.2 M EMIM TFSI as the supporting electrolyte.

We have further studied the cyclic voltammograms of L as well as of their Ag(I) complexes at different scan rates, varying from 10 mV/s to 200 mV/s (Figures S3 to S8 in the Supporting Information). The CV curves of all the samples appear well maintained with the cathodic and anodic peaks almost unchanged even at high scan rate, indicating that stability of L and its silver (I) complexes is retained. The electrochemical properties of the redox active materials (CPs) were calculated in terms of specific capacitance (SC) from the area under the CV curve. Specific capacitance of the samples at different scan rates is shown in Figures S3 to S8. Interestingly, the Ag(I) complexes exhibit higher specific capacitance as compared to that of L. This may be due to the existence of favourable diffusion channels in the solid complexes that allow cations and anions to transport.⁷⁶

In order to assess the stability of the complex during CV tests, we have monitored the electrochemical performance of complex **1** during 50 cycles (Figure S9 in the Supporting Information). It has been observed that the CV curves after 5th, 10th, 20th, 30th, 40th and 50th cycles are well maintained (in relation to the 1st cycle) and that the cathodic and anodic peaks are almost unchanged after the 50th cycle, attesting to the remarkable stability of the compound. Estimation of the specific capacitance from the area under the CV curves showed retention of 96.7% of the initial specific capacitance even after 50 cycles.



Figure 12. Solid-state photoluminescence spectra (PL) of L (black line), 1 (red line), 3 (blue line) and 4 (dark cyan line) at room temperature (excitation at 275 nm).

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Luminescent properties. The development of new luminescent materials is of particular interest for potential application as light-emitting diodes.⁷⁷ Recently, a study of solid-state luminescent properties of organic nitrile ligands and their Ag(I) coordination polymers revealed that the emission wavelengths of organic nitrile ligands strongly depend on their crystal packing.^{25,78} In this study, the luminescent properties of the crystalline solids of **L**, **1**, **3** and **4** were investigated at room temperature by exciting at wavelength of 275 nm (Figure 12). Ligand **L** was found to exhibit a strong emission at 451 nm. Its complexation with Ag(I) significantly affected the emission, which for **1** was found to be red-shifted to 470 nm. For **3** and **4** emission bands were observed at 465-470 nm. Compound **4** showed also a green emission with a maximum at 530 nm. The generation of this new emission band in **4** is most probably due to of the interlayer π - π stacking interactions between aromatic units of guest molecules in the solid-state (Figure 5b).⁷⁹⁻⁸³

SUMMARY

We have designed and synthesized a new flexible ditopic ligand namely bis-(cyanobenzyl)bipiperidine (L), which was then utilized in the synthesis of its coordination polymers with different silver salts AgX (X = NO₃⁻, ClO₄⁻, CF₃SO₃⁻, BF₄⁻ and PF₆⁻). In the given reaction conditions the resulting coordination patterns and their dimensionality were found to depend on the anion type: 3D with X = NO₃⁻ and ClO₄⁻, (1, 2 and 5) 2D with X = CF₃SO₃⁻ (6 and 7), 1D with X = BF₄⁻ (8) and 0D with X= PF₆⁻ (9). Large aromatic guests could be co-crystallized with L and AgNO₃ in a layered fashion (3 with pyrene and 4 with perylene), reducing the metal-ligand coordination networking from 3D to 2D). Anion exchange reactions in the crystalline state have been demonstrated for coordination polymers 1, 7 and 8, including reversible transformation between 1 and 8. All the compounds exhibited good redox-active behaviour with higher specific capacitance of the CPs in relation to L. Among the polymeric species, 4 showed a red-shifted peak (530 nm) with green emission, reflecting the presence of the interlayer π - π stacking interactions between the aromatic units in the solid-state. **General.** All the chemicals were received as reagent grade and used without any further purification. Fourier-transform (FT)-IR spectra were recorded on a Bruker Tensor 27 system spectrophotometer in ATR mode. Powder X-ray diffraction data were recorded on Bruker D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.54056$ Å) over a 2 θ range of 5–40° at a scan rate of 1° min⁻¹. 1H NMR (400 MHz) spectra were recorded on Bruker-AC 400MHz spectrometer. Photoluminescence measurements were carried out by using a Fluorolog-3, HORIBA Scientific commercial set-up.

Synthesis of 4,4'-(4,4'-bipiperidine-1,1'-diylbis(methylene)dibenzonitrile (L). A round-bottomed flask with a reflux condenser was charged with 4,4'-bipiperidine (0.2 g, 1.18 mmol), 4-(bromomethyl) benzonitrile (0.52 g, 2.65 mmol), potassium carbonate (0.7g, 5.06 mmol) and potassium iodide (0.0015 g, 0.009 mmol). Then, acetonitrile (50 mL) was added to the flask under nitrogen and the reaction mixture was stirred with reflux at 70° C for overnight. After cooling, the mixture was filtered, and the residue which comprised a mixture of the product and inorganic salts, was added to 50 mL water and stirred for 30 minutes. The resulting precipitate was collected by filtration, washed with water, and dried under vacuum. The final product was purified by recrystallization from acetone to afford colourless needlelike single crystals of compound L suitable for X-ray diffraction, ~65–70% yield within one day. 1H NMR (CDCl₃, ppm): 7.58 (d, 4H, 8Hz), 7.42 (d, 4H, 8Hz), 3.49 (s, 4H), 2.82 (d, 4H, 12Hz), 1.19 (t, 4H, 12Hz), 1.64 (d, 4H, 6Hz), 1.25 (q, 4H, 8Hz), 1.05 (m, 2H). IR (KBr, pellet): 2933, 2904, 2804, 2358, 2226, 1504, 1362, 1342, 1260, 1121, 1035, 972, 820, 705, 652, 563, 526 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₂₆H₃₀N₄: C, 78.36 (78.07); H, 7.59 (7.69); N, 14.06 (14.11).

In all the following procedures the solution mixtures containing the given amounts of the corresponding reactants were allowed to stand in a sealed vial covered entirely by aluminium foil, and were left at room temperature to crystallise until the appearance of sizeable crystals suitable for X-ray diffractions analysis.

Synthesis of 1, $[Ag_2(L)(NO_3)_2]_n$. A solution of $AgNO_3$ (8.52 mg, 0.050 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Colourless block-like crystals were obtained in about 65–70% yield within 30 minutes. IR (KBr, pellet): 3188, 2922, 2241, 2127, 1585, 1338, 1294, 1117, 1083, 1018, 971, 862, 850,

820, 785, 643, 566, 527 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₁₃H₁₅AgN₃O₃: C, 42.30 (42.43); H, 4.10 (4.04); N, 11.38 (11.41).

Synthesis of 2, $[Ag_2(L)(NO_3)_2]_n$. A solution of AgNO₃ (4.26 mg, 0.025 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Colourless needle-like crystals were obtained in about 65–70% yield within one hour. IR (KBr, pellet): 2946, 2907, 2850, 2357, 2241, 1604, 1501, 1297, 1202, 1117, 1063, 1018, 962, 862, 850, 782, 744, 643, 566, 531 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₁₃H₁₅AgN₃O₃: C, 42.30 (42.46); H, 4.10 (4.02); N, 11.38 (11.43).

Synthesis of 3, {[Ag₂(L)(NO₃)₂)](C₁₆H₁₀)}**n.** A solution of AgNO₃ (8.52 mg, 0.050 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Then, three equivalent of pyrene (15.18 mg, 0.075 mmol) was dissolved in 2-3 mL of acetone and added to that previous solution of AgNO₃ and L. Yellow colour needle-like poor-quality crystals were obtained in about 70% yield within 12 hours. IR (KBr, pellet): 2946, 2907, 2849, 2358, 2241, 2049, 1607, 1297, 1109, 1036, 1018, 969, 862, 850, 782, 744, 643, 566, 550, 531 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₂₆H₃₀Ag₂N₆O₆·C₁₆H₉: C, 53.63 (54.03); H, 4.18 (4.22); N, 8.94 (9.02).

Synthesis of 4, {[Ag₂(L)(NO₃)₂)](C₂₀H₁₂)}n. A solution of AgNO₃ (8.52 mg, 0.050 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Then three equivalent of perylene (18.98 mg, 0.075 mmol) was dissolved in 2-3 mL of acetone and added to that previous solution of AgNO₃ and L. Yellow colour needle-like crystals were obtained in about 75% yield within 12 hours. IR (KBr, pellet): 2963, 2843, 2358, 2234, 1762, 1590, 1297, 1228, 1109, 1082, 1034, 965, 853, 817, 776, 650, 571, 487, 460 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₂₆H₃₀Ag₂N₆O₆·C₂₀H₁₂: C, 55.77 (56.15); H, 4.27 (4.33); N, 8.48 (8.60).

Synthesis of 5, $[Ag_2(L)(CIO_4)_2]_n$. A solution of AgClO₄ (10.41 mg, 0.050 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Colourless block-like crystals were obtained in about 65– 70% yield within 1-2 days. IR (KBr, pellet): 2940, 2872, 2358, 2255, 1607, 1439, 1372, 1261, 1230, 1091, 1047, 967, 852, 785, 654, 617, 533, 453 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₁₃H₁₅AgClN₂O₄: C, 38.40 (38.56); H, 3.72 (3.69); N, 6.89 (6.84).

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Synthesis of 6, $[Ag_2(L)(CF_3SO_3)_2(C_4H_8O)_2]_n$. A solution of AgCF₃SO₃ (13 mg, 0.050 mmol) in tetrahydrofuran (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in tetrahydrofuran (3 mL). Colourless needle-like single crystals were obtained in about 65% yield within 1-2 days. IR (KBr, pellet): 3446, 2938, 2840, 2360, 2340, 2246, 2078, 1608, 1447, 1238, 1163, 1061, 973, 864, 758, 634, 571, 515 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₃₆H₄₆Ag₂F₆N₄O₈S₂: C, 40.92 (40.34); H, 4.39 (4.50); N, 5.30 (4.36).

Synthesis of 7, $[Ag_2(L)(CF_3SO_3)_2(C_3H_6O)_2]_n$. A solution of AgCF₃SO₃ (13 mg, 0.050 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Colourless rectangular-like single crystals were obtained in about 65% yield within 1-2 days. IR (KBr, pellet): 2881, 2380, 2076, 1466, 1359, 1240, 1148, 1098, 1060, 960, 841, 634, 571, 529 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₁₇H₂₁AgF₃N₂O₄S: C, 39.70 (39.04); H, 4.12 (4.35); N, 5.45 (4.67).

Synthesis of 8, { $[Ag_2(L)_2](BF_4)(C_3H_6O)$ }n. A solution of AgBF₄ (9.7 mg, 0.049 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Colourless rectangular-like single crystals were obtained (as acetone solvate) in about 60% yield within 2-3 days. IR (KBr, pellet): 2851, 2360, 2230, 1706, 1605, 1443, 1345, 1223, 1051, 930, 841, 763, 571, 529 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₂₆H₃₀AgN₄·BF₄·2(C₃H₆O): C, 54.18 (52.60); H, 5.97 (5.15); N, 7.90 (9.38) (the marked discrepancies between the calculated and found values are most probably due to evaporation of the acetone crystallization solvent during the analysis).

Synthesis of 9, $[Ag_2(L)_3(PF_6)_2]_n$. A solution of AgPF₆ (12.68 mg, 0.050 mmol) in acetone (2 mL) was added to a solution of L (10 mg, 0.025 mmol) in acetone (3 mL). Colourless block-like single crystals were obtained (as acetone solvate) in about 60% yield within 2-3 days. IR (KBr, pellet): 2895, 2380, 2253, 1696, 1605, 1395, 1247, 1178, 1049, 838, 747, 689, 571, 537 cm⁻¹. Elem. Anal. (%) Calcd (found) for C₇₈H₉₀Ag₂F₁₂N₁₂P₂: C, 55.07 (54.99); H, 5.33 (5.27); N, 9.88 (9.83).

Anion-exchange experiments. The anion-exchange experiments were carried out with the freshly prepared crystals of 1, 7, 8 (5 mg) by immersing in 3 M aqueous solution (2 mL) of each corresponding sodium salt, and leaving undisturbed for 30 min to 3 h at ambient temperature. The resultant anion-exchanged solid was collected by filtration, washed several times with water, and then dried in air. The crystalline materials obtained from the anion-exchange experiments were not suitable for single-crystal X-ray diffraction because of their

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loss of transparency during the immersion. The products associated with the anion exchange were thus analysed by IR and PXRD.

Electrochemical measurements. CV Analysis for L and the CPs of 1, 3, 4 & 7-9. The electrochemical measurements were performed with a CH760D electrochemical workstation (CH Instruments, USA) using a standard three electrode cell setup. The experiments were carried out using three electrode system where Platinum (Pt) foil as working electrode, Pt wire as counter electrode and saturated calomel electrode (SCE) as reference electrode.

Single-crystal structure determinations. The X-ray measurements [Bruker-ApexDuo diffractometer, IµS microfocus MoKα radiation] were carried out at ca. 110(2) K on crystals coated with a thin layer of amorphous oil. These structures were solved by direct and Fourier methods and refined by full-matrix least-squares (using standard crystallographic software (SHELXT-2014, SHELXL-2014)).^{84,85} Compound 9 was found to contain severely disordered crystallization solvent (mostly acetone) within the intra-lattice voids, which couldn't be modeled by discrete atoms. Correspondingly, the contribution of the disordered solvent moieties was subtracted from the diffraction pattern by the Squeeze procedure and PLATON software.⁸⁶ The TOPOS software package was used to analyze the topological features of the available coordination networks.⁵⁷ The integrity of the crystalline products **1-9** was confirmed in each case by repeated measurements of the unit-cell dimensions from different single crystallites, inspection of their morphologies, as well as by routinely matching between the simulated and experimental powder X-ray diffraction patterns. The crystal data of the available structures are:

(L) $C_{26}H_{30}N_4$, Mr = 398.54, monoclinic, space group $P2_1/n$ (No. 14), a = 7.1553(5), b = 28.203(2), c = 16.4056(13) Å, β = 98.339(3)°, V = 3275.7(4) Å³, T = 110 K, Z = 6, μ (MoK α) = 0.07 mm⁻¹, ρ (calcd) = 1.21 g·cm⁻³, 23110 reflections measured to θ = 25.0°, of which 5771 were unique (Rint = 0.037) and 4476 with I > 2 σ (I). Final R1 = 0.041 (wR2 = 0.096) for the 4476 data above the intensity threshold, and R1 = 0.058 (wR2 = 0.106) for all unique data. CCDC 1449780.

(1) $C_{13}H_{15}AgN_{3}O_{3}$, Mr = 369.15, monoclinic, space group $P2_{1}/c$ (No. 14), a = 5.7530(6), b = 16.9877(14), c = 13.3029(12) Å, β = 90.020(6)°, V = 1300.1(2) Å³, T = 110 K, Z = 4, μ (MoK α) = 1.56 mm⁻¹, ρ (calcd) = 1.87 g·cm⁻³, 11063 reflections measured to θ = 28.39°, of which 3234 were unique (Rint = 0.044) and 2843 with I > 2 σ (I). Final R1 = 0.027 (wR2 =

0.067) for the 2843 data above the intensity threshold, and R1 = 0.032 (wR2 = 0.070) for all unique data. CCDC 1449781.

(2): $C_{13}H_{15}AgN_{3}O_{3}$, Mr = 369.15, monoclinic, space group $P2_{1}/c$ (No. 14), a = 8.6992(4), b = 9.4145(4), c = 17.7035(8) Å, β = 104.214(2)°, V = 1405.50(11) Å³, T = 110 K, Z = 4, μ (MoK α) = 1.44 mm⁻¹, ρ (calcd) = 1.74 g·cm⁻³, 21931 reflections measured to θ = 28.45°, of which 3543 were unique (Rint = 0.032) and 3236 with I > 2 σ (I). Final R1 = 0.018 (wR2 = 0.041) for the 3236 data above the intensity threshold, and R1 = 0.021 (wR2 = 0.042) for all unique data. CCDC 1449782.

(3): $C_{26}H_{30}Ag_2N_6O_6 \cdot C_{16}H_9$, Mr = 939.53, orthorhombic, space group *Pca2*₁ (No. 29), a = 16.861(2), b = 15.8050(16), c = 13.9131(17) Å, V = 3707.7(7) Å³, T = 110 K, Z = 4, μ (MoK α) = 1.12 mm⁻¹, ρ (calcd) = 1.68 g·cm⁻³, 19865 reflections measured to θ = 25.0°, of which 6442 were unique (Rint = 0.045) and 5296 with I > 2 σ (I). Final R1 = 0.056 (wR2 = 0.131) for the 5296 data above the intensity threshold, and R1 = 0.073 (wR2 = 0.143) for all unique data. CCDC 1449783.

(4): $C_{26}H_{30}Ag_2N_6O_6C_{20}H_{12}$, Mr = 990.59, orthorhombic, space group *Pbca* (No. 61), a = 15.2465(6), b = 18.3060(9), c = 28.5486(15) Å, V = 7968.0(7) Å³, T = 110 K, Z = 8, $\mu(MoK\alpha) = 1.04 \text{ mm}^{-1}$, $\rho(calcd) = 1.65 \text{ g} \cdot \text{cm}^{-3}$, 30531 reflections measured to $\theta = 25.02^{\circ}$, of which 7033 were unique (Rint = 0.049) and 5223 with I > 2 σ (I). Final R1 = 0.042 (wR2 = 0.072) for the 5223 data above the intensity threshold, and R1 = 0.067 (wR2 = 0.081) for all unique data. CCDC 1449784.

(5): $C_{13}H_{15}AgClN_2O_4$, Mr = 406.59, monoclinic, space group $P2_1/c$ (No. 14), a = 5.6448(6), b = 16.1137(16), c = 15.8133(16) Å, β = 95.090(6)°, V = 1432.7(3) Å³, T = 110 K, Z = 4, μ (MoKa) = 1.61 mm⁻¹, ρ (calcd) = 1.88 g·cm⁻³, 11970 reflections measured to θ = 28.33°, of which 3562 were unique (Rint = 0.038) and 2850 with I > 2 σ (I). Final R1 = 0.036 (wR2 = 0.077) for the 2850 data above the intensity threshold, and R1 = 0.051 (wR2 = 0.082) for all unique data. CCDC 1449785.

(6): $C_{36}H_{46}Ag_2F_6N_4O_8S_2$, Mr = 1056.63, monoclinic, space group C2/c (No. 15), a = 32.192(3), b = 10.4571(13), c = 13.8435(15) Å, $\beta = 110.552(5)^\circ$, V = 4353.6(9) Å³, T = 110 K, Z = 4, μ (MoKa) = 1.07 mm⁻¹, ρ (calcd) = 1.61 g·cm⁻³, 14398 reflections measured to $\theta = 25.01^\circ$, of which 3839 were unique (Rint = 0.028) and 2921 with I > 2 σ (I). Preliminary R1 = 0.11 for the 2921 data above the intensity threshold. Due to the poor quality of the crystals and of the diffraction pattern (resulting from disorder of the triflate anions and THF ligands), as well as very low percentage of significant experimental data, this structure could not be

fully refined with acceptable precision, and further calculations were interrupted at this preliminary stage. Yet, the coordination pattern in this structure (with THF species coordinated to the Ag centers) is very similar to that in the isostructural compound 7 (with acetone molecules attached instead to the silver ions).

(7): $C_{17}H_{21}AgF_{3}N_{2}O_{4}S$, Mr = 514.29, monoclinic, space group *Cc* (No. 9), a = 33.327(3), b = 10.3153(10), c = 13.3212(11) Å, $\beta = 112.453(4)^{\circ}$, V = 4232.4(7) Å³, T = 110 K, Z = 8, μ (MoKa) = 1.10 mm⁻¹, ρ (calcd) = 1.61 g·cm⁻³, 18592 reflections measured to $\theta = 28.40^{\circ}$, of which 8609 were unique (Rint = 0.020) and 8203 with I > 2 σ (I). Final R1 = 0.050 (wR2 = 0.147) for the 8203 data above the intensity threshold, and R1 = 0.052 (wR2 = 0.151) for all unique data. Flack parameter = 0.05(5). CCDC 1449786.

(8): $C_{26}H_{30}AgN_4 \cdot BF_4 \cdot 2(C_3H_6O)$, Mr = 709.37, triclinic, space group *P*-1 (No. 2), a =9.3940(14), b = 14.0082(16), c = 15.0044(19) Å, $\alpha = 116.249(4)$, $\beta = 106.520(4)$, $\gamma = 91.906(4)^\circ$, V = 1668.5(4) Å³, T = 110 K, Z = 2, μ (MoKa) = 0.66 mm⁻¹, ρ (calcd) = 1.41 g·cm⁻³, 11907 reflections measured to $\theta = 25.09^\circ$, of which 5866 were unique (Rint = 0.025) and 5314 with I > 2 σ (I). Final R1 = 0.029 (wR2 = 0.065) for the 5314 data above the intensity threshold, and R1 = 0.034 (wR2 = 0.067) for all unique data. CCDC 1449787.

(9): $C_{78}H_{90}Ag_2F_{12}N_{12}P_2$, Mr = 1701.30, monoclinic, $P2_1/c$ (No. 14), a = 13.3243(14), b = 12.6404(13), c = 28.098(3) Å, β = 101.448(5)°, V = 4638.3(8) Å³, T = 110 K, Z = 2, μ (MoKa) = 0.52 mm⁻¹, ρ (calcd) = 1.22 g·cm⁻³, 53248 reflections measured to θ = 27.33°, of which 10373 were unique (Rint = 0.030) and 8744 with I > 2 σ (I). Final R1 = 0.035 (wR2 = 0.087) for the 8744 data above the intensity threshold, and R1 = 0.045 (wR2 = 0.093) for all unique data. CCDC 1449788.

ASSOCIATED CONTENT

Supporting information

IR-spectra, PXRD patterns, CV and X-ray crystallographic files (CIFs). CCDC 1449780-1449788 (compounds L, 1-5 and 7-9, respectively) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via <u>www.ccdc.cam.ac.uk/data_request/cif</u>. The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/acs.cgd.0000000.

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Silver coordination polymers based on newly designed bis-(cyanobenzyl)bipiperidine ligand: synthesis, anion exchange, guest inclusion, electrochemical and photoluminescence properties

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Synopsis: A new flexible ligand, bis-(cyanobenzyl)bipiperidine (**L**) and its nine coordination networks with silver salts, of anion dependent dimensionality, have been synthesized and structurally characterized. Anion-exchange, guest-inclusion, electrochemical and photoluminescence properties of selected materials have been investigated.