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# Anion-Directed Self-Assembly of Coordination Polymer into Tunable Secondary Structure

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***Abstract:*** A bent-shaped bipyridine ligand containing a dendritic aliphatic side chain has been synthesized as a ligand and complexed with silver ion through a self-assembling process. The resulting complexes were observed to self-assemble into supramolecular structures that differ significantly as a function of the counteranion size in the solid state, as confirmed by 1-D and 2-D X-ray diffraction experiments. The secondary structure of a cationic coordination chain appears to be dependent on the size of the counteranion. As the size of anion increases, the secondary structure of the coordination chain changes, from a helical chain, via a dimeric cycle, to a zigzag chain in the solid state. Interestingly, dilute solutions of the complexes exhibiting a columnar structure in polar solvents undergo spontaneous gelation and the resulting gels display a significant Cotton effect in the chromophore of the aromatic unit. These results represent a significant example that small variation in the anion size can provide a useful strategy to manipulate the secondary structure of linear chain and thereby solid-state supramolecular structure.

## Introduction

Self-assembly of designed molecules is a challenging topic of research in the fields of chemical biology and materials science because it provides the spontaneous generation of a well-defined, discrete supramolecular architecture from molecular components under thermodynamic equilibrium.[1] In particular, there is growing interest in the design of synthetic molecules that are able to self-assemble into a polymeric chain with compact helical conformations, analogous to the folded state of natural proteins.[2,3] Helical organization in synthetic self-assembling systems has been achieved by a variety of strategies including intramolecular hydrogen bonding,[3−5] solvophobic effects,[6] and metal−ligand interactions.[7] For example, discrete oligomer chains based on the connection of aromatic moieties in a *meta* geometry can fold through specific intramolecular interactions into a helical object which, in turn, undergoes self-assembly into a columnar entity.[6−9] Relatively strong, directional interactions, such as complexation between conformationally restricted bent shaped ligands and transition metals that adopt a linear coordination geometry, can also give rise to extended polymeric chains with a helical secondary structure.[10−12] The crystal structure of the complex based on a bipyridyl ligand derived from a 1,1′-binaphthyl unit and a Ni(II) ion, for example, demonstrated the formation of an infinite helical chain in which there are four ligands for each turn of the helix.[11] Similar to this, silver ion-mediated self-assembly of a ditopic pyridine ligand has been reported to result in extended helical springs with a tunable helix.[12] In contrast, for a conformationally flexible, bent shaped ligand, one can envisage the formation of linear coordination chains that can adopt folded or unfolded secondary structures, triggered by counteranion binding of cationic polymeric backbones through electrostatic interactions.[13] Depending on the size of the counteranion, one of these possibilities may be favored because the internal binding site of a cationic scaffold would be complementary in size to anionic guests. As a consequence, the secondary structure of the coordination chain would be tuned by variation in the size of the binding counteranion.

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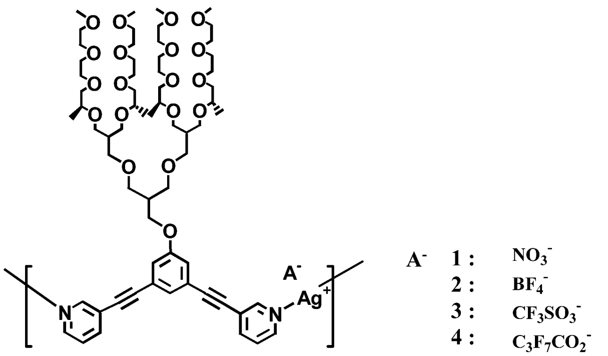
*Chart 1*



In this report, a conformationally flexible, bent-shaped bipyridine ligand containing a dendritic aliphatic side chain has been synthesized as a ligand and complexed with silver ion through a self-assembling process (Chart 1). Remarkably, the secondary structure of the resulting coordination chain appears to be dependent on the size of the anionic guest. As the size of the anion increases, the secondary structure changes, from a folded helical chain, via a dimeric cycle, to an unfolded zigzag conformation in the solid state. The sensitivity to anion size is highlighted by dramatic differences in the aggregation behavior of the coordination chains.

## Results

Scheme 1 outlines the synthesis of the bent-shaped bipyridine ligand containing a dendritic side chain and the silver complexes. The design of a dendritic side chain was focused on the construction of an aliphatic dendritic core based on a chiral tri(ethylene oxide) unit. The basic synthetic methodology to generate such a flexible dendrimer employed a facile convergent route reported previously,[14] in order to control the dendritic architecture precisely. The first step was performed by a Williamson etherification reaction of an alcoholic precursor with methallyl chloride, while the activation step of the resulting double bond was carried out through a repetitive hydroboration−oxidation reaction. Etherification of the dendritic ether containing tosyl group with 3,5-dibromophenol in the presence of potassium carbonate produced a precursor of ligand molecule. The final ligand was obtained by treating the molecule with 3-ethynylpyridine according to a Sonogashira reaction. The resulting ligand was purified by column chromatography (silica gel) using a mixture of methanol and ethyl acetate (1:8 v/v) as the eluent. The pyridine ligand was complexed with silver ions with different counteranions to prepare coordination complexes. All of the analytical data are in full agreement with the chemical structure presented.

In contrast to the ligand, all of the complexes show an ordered solid-state structure that is retained up to a melting temperature, determined by DSC heating and cooling scans (Table 1). As shown in Table 1, only a single peak is observed in both heating and cooling scans of **1**−**4**. It can be attributed to a melting transition of the aromatic coordination backbone because the dendritic side chain is not expected to crystallize due to its branched architecture. Between the cross polarizers, the complexes show strong birefringence corresponding to a crystalline phase which disappears over a narrow temperature range upon heating and reappeared upon cooling. Especially for the complex based on $NO_3^-$, the heat of fusion and the melting temperature are shown to be the lowest among the complexes.

The solid-state structure was confirmed by small- and wide-angle X-ray measurements. The small-angle X-ray diffraction patterns of **1** show three sharp reflections, which indicate the existence of an ordered nanoscopic structure (Figure 1). These reflections can be indexed as a 2-D hexagonal structure with a lattice parameter $a = 29.6$ Å. At the wide angle, only a diffuse halo remains as evidence of the lack of any positional long range order other than the 2-D hexagonal packing of supramolecular units. Similar to **1**, the small-angle X-ray diffraction patterns of **2** based on $BF_4^-$ show sharp reflections corresponding to a 2-D hexagonal structure with a lattice constant $a = 31.3$ Å. At the middle angles, however, two sharp reflections appear in the spacing ratio of 1:2. This is indicative of a modulation of the electronic density and suggests the existence of a periodicity in the direction of the stacks of repeating units. The periodicity of this modulation measured along the column axis is 9.6 Å. It is only possible to account for this modulation if we assume that the repeating units adopt a helical stacking in the column.[15,16] On the basis of these results and density considerations, the number ($n$) of repeating units per pitch can be estimated according to the following equation, where $M$ is the molecular weight, $\rho$ is density, $A$ is cross-sectional area of the column, and $N_A$ is Avogadro' number.

$$n = \frac{\rho \times \text{pitch} \times A \times N_A}{M} \qquad (1)$$

This calculation shows that the pitch of the single helix is composed of five repeating units, giving rise to a pentagonal helix in which the interior is occupied by $BF_4^-$ counteranions.[17] This encapsulation of the anions within the cavity is further supported by high density and aromatic $\pi-\pi$ stacking interaction which will be discussed later. The observed periodicity along the column axis suggests that an aromatic stacking distance within the column is 3.2 Å. Similar to those observed for other silver(I)−$\pi$ complexes of aromatic compounds, this small aromatic stacking distance could be attributed to the additional attractive force mediated by strong Ag−$\pi$ interaction.[18,19] In addition, similar small inter-aromatic distances (3.13−3.20 Å) have also been observed for discotic systems with a columnar order.[20]

The small-angle X-ray scattering of **3** based on triflate anion revealed several sharp reflections, corresponding to a 2-D hexagonal structure with a lattice constant of 34.8 Å, indicating that the complex self-assembles into a column (Figure 1). Similar to **2**, two sharp reflections with the spacing ratio of 1:2 appear in the middle-angle range, suggesting that the complex

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(17) As shown in Table 1, the calculated numbers appear to be 4.8 and 5.8 for **2** and **3**, respectively, which are less than expected integer values, 5 and 6. However, this is not unreasonable because the measured densities of the polydomain samples are expected to be less than the ideal values that would result from the single crystalline samples.

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***Scheme 1.*** Syntheis of Complexes **1**−**4**

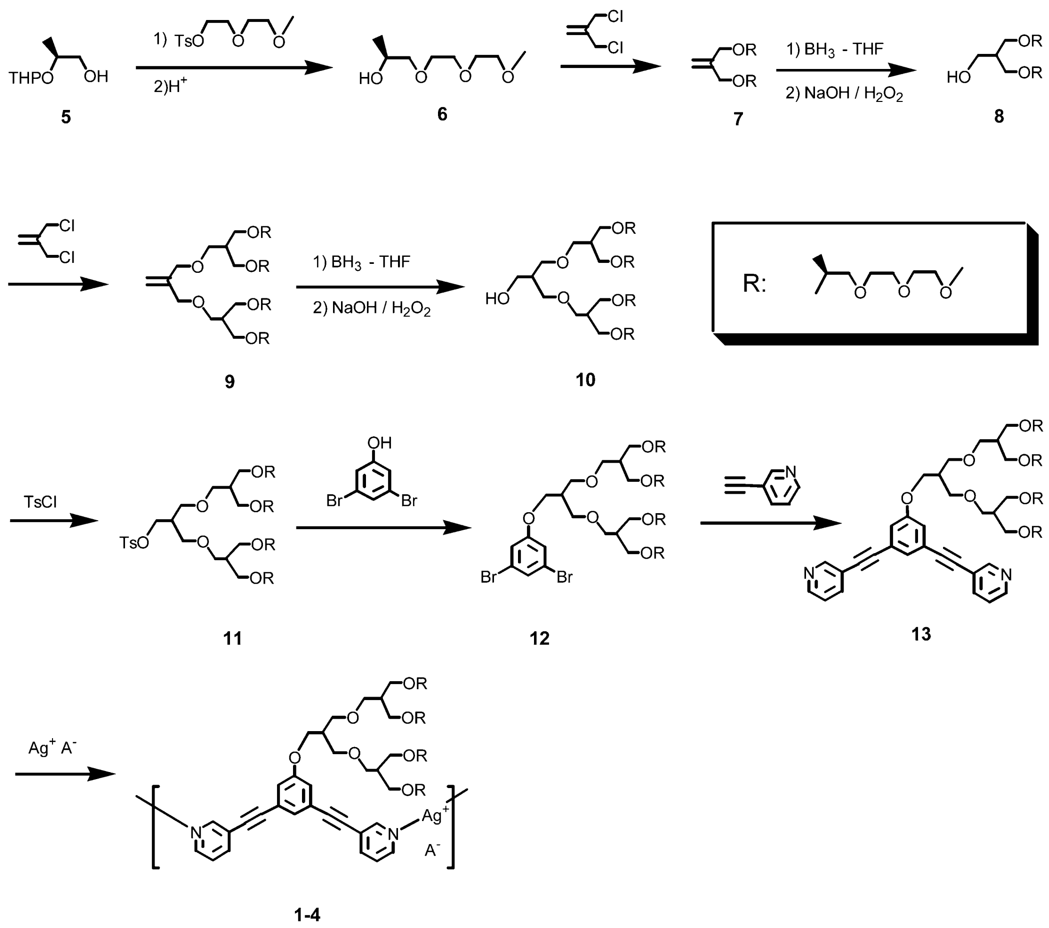

***Table 1.*** Characterization of Complexes of **1**−**4** by X-ray Scattering Experiments and Thermal Transition

| complex | anion vol (cm$^3$/mol) | density (g/cm$^3$) | phase transition (°C) and corresponding enthalpy changes (kJ/mol) heating | cooling | lattice constant *a* (Å) | pitch (Å) | $n^b$ |
|---|---|---|---|---|---|---|---|
| **1** | 34 | 1.40 | col$_h$ 56.9 (6.0) i | i 43.5 (5.1) col$_h$ | 29.6 | | |
| **2** | 49 | 1.38 | col$_h$ 165.3 (4.1) i | i 142.2 (3.9) col$_h$ | 31.3 | 9.6 | 4.8 |
| **3** | 66 | 1.44 | col$_h$ 163.1 (10.3) i | i 147.9 (10.1) col$_h$ | 34.8 | 9.3 | 5.8 |
| **4** | 94 | 1.43 | lam 89.3 (11.4) i | i 65.0 (11.5) lam | 29.9$^a$ | | |

$^a$ Inter-lamellar spacing. $^b n$ = number of repeating units per pitch. col$_h$ = hexagonal columnar, lam = lamellar, i = isotropic.

adopts a helical stacking in the column with the periodicity of the helix of 9.3 Å. Additional information on the structural dimensionality of **3** was obtained by 2-D X-ray diffraction with an annealed sample exhibiting macroscopic orientation. As shown in Figure 2, the X-ray beam was directed perpendicular to the principal axes of the hexagonally arranged columns within the domain.

At small angle, a pair of strong (100) reflections were diffracted along the meridian. These reflections are related to a 2D hexagonal array of columns, as confirmed by the powder X-ray diffraction pattern. At wide angle, a pair of (001) reflections were diffracted along the equator. This 2-D X-ray diffraction pattern demonstrates that *d* spacing (001) reflection at 9.3 Å accounts for the existence of a periodicity in the direction of the column axis.

On the basis of the calculation according to eq 1, the number of repeating units in each pitch is estimated to be 6.[17] Assuming that the coordination chain adopts a helical chain conformation, 6 repeating units per pitch indicate that bulky dendritic chains are located approximately on top of each other. This packing structure based on a helical chain is energetically unfavorable because they are arranged in a row along the helical chain axis. This packing consideration, the presence of the sharp X-ray reflections corresponding to a 2-D hexagonal columnar symmetry, and the absence of a wide-angle reflection corresponding to a Ag−Ag interaction rule out the formation of the helical chains. Inspection of CPK models in combination with X-ray results revealed that a triflate counteranion can be closely wrapped by two ligands and two silver ions, leading to a dimeric cyclic species. The resulting dimeric cycles self-assemble into a tubular structure which organizes into a 2-D hexagonal lattice. When we compare the periodicity of the helix, measured from the middle-angle scattering and the calculated number of ligands, we find that one helix period contains three stacked dimeric cycles. To avoid steric hindrance between the dendritic chains, two neighboring cycles are mutually rotated, giving rise to a

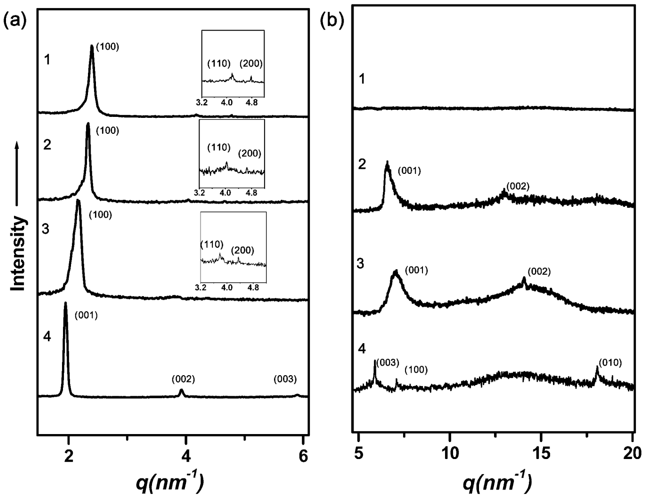

*Figure 1.* Small-angle X-ray diffraction patterns (a) and wide-angle X-ray diffraction patterns (b) of **1**−**4**.

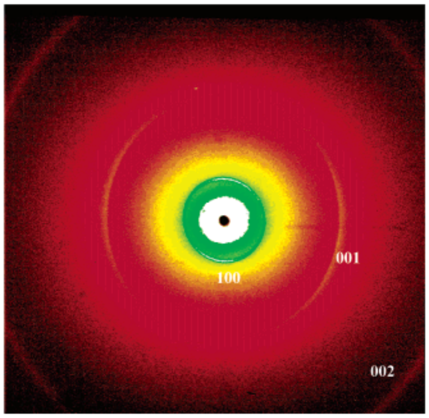

*Figure 2.* 2-D X-ray diffraction pattern of **3**.

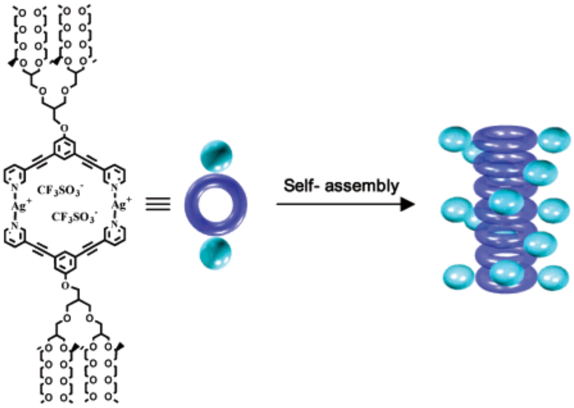

*Figure 3.* Schematic representation of the self-assembly of **3** into a helical column.

helical column (Figure 3). All these data are consistent with a columnar structure in which cyclic dimers are stacked along the column axis; however, the cycles do rotate around the normal to their plane. Rotation of one cycle with respect to the adjacent one within the column is the method by which these cycles fill empty space, thus improving molecular packing within the supramolecular packing. This process allows a better arrangement of the dendritic chains around the aromatic core of the column and thus prevents the steric hindrance that could otherwise occur between bulky chains of neighboring cycles. Consequently, this rotation gives rise to a helical structure within the column with the helical periodicity of 9.3 Å, as evidenced by the middle-angle X-ray reflections (Figure 2). Similar to **2**, the observed periodicity within the column suggests that an aromatic stacking distance within the column is 3.1 Å which could be attributed to the additional attractive force mediated by strong Ag−$\pi$ interaction. Similar aromatic stacking distances have also been observed for silver(I)−$\pi$ complexes of phenanthroline compounds, as described above.[18]

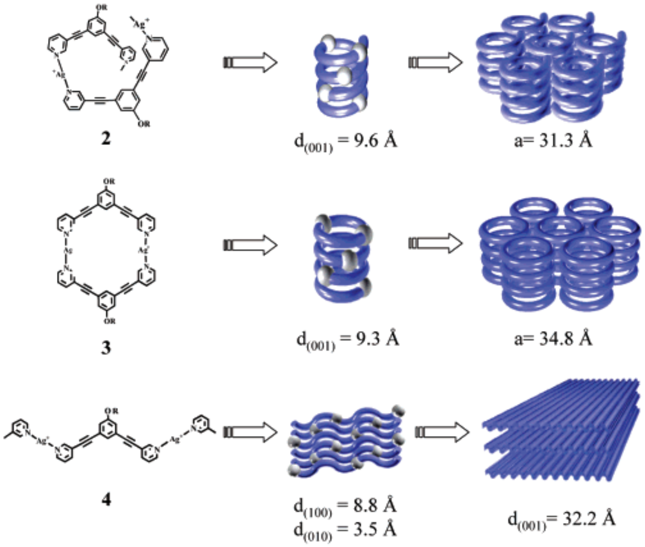

*Figure 4.* Schematic representation of the self-assembly of **2**−**4** and their subsequent self-organization.

In contrast to the cationic scaffolds based on small counteranions described above, the complex **4** based on the largest counteranion, heptafluorobutyrate, self-assembles into a lamellar structure with in-plane 2-D order with the layer thickness of 32.2 Å, as evidenced by X-ray diffraction (Figure 1).

The lamellar structure of the complex indicates that the coordination chain adopts an unfolded zigzag conformation rather than folded helical or cyclic conformations. Considering the size of the counteranion, this observation is not entirely unexpected. Molecular models indicate that the heptafluorobutyrate counteranion is too large to be completely encapsulated by two ligands. Consequently, for optimum interaction of the cationic chain with the anionic guest, the coordination chain is likely to adopt an unfolded zigzag conformation, leading to a layered organization. On the basis of the results described above, the possible models responsible for the generation of the 2-D hexagonal columnar and lamellar solid-state structures depending on the size of counteranion can be presented as shown in Figure 4.

Remarkably, dilute solutions of **1**−**3** in polar solvents undergo spontaneous gelation and the resulting gels display a significant Cotton effect in the chromophore of the aromatic unit (Figure 5), indicating the presence of elongated helical columnar aggregates in solution.[3,21] This is in sharp contrast to the solution behavior of **4** which does not form a gel and displays the lack of a Cotton effect. Macroscopic gelation and a Cotton effect is considered to be the result of the presence of elongated cylin-

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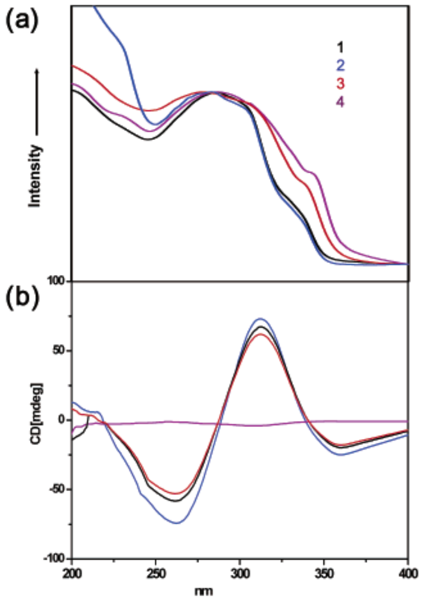


***Figure 5.*** (a) UV spectra of **1**−**4** in solide state. The spectra have been normalized with respect to their maximum intensity. (b) CD spectra of **1**−**4** at 25 °C (10 wt % in MeOH).

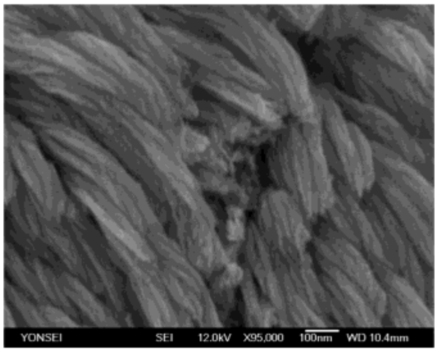
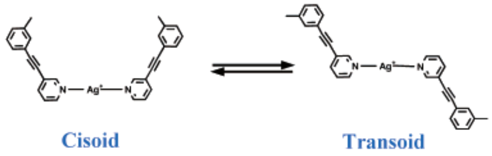


***Figure 6.*** SEM image of a dried gel of **2**.

drical aggregates with a chiral superstructure in polar solutions of complexes **1**, **2,** and **3**, as deduced from the X-ray experiments discussed above. A scanning electron microscopy image of the dried methanol gel of **2** shows a fibrous nanostructure with a diameter of approximately 10 nm, suggesting that the fiber consists of a bundle of helical columns (Figure 6).[22,23]

## Discussion

The results described here demonstrate that, as the size of counteranion increases, the secondary structure of the coordination chain changes significantly from a folded helix, a dimeric cycle, to an unfolded zigzag chain in the solid state. This variation in the secondary structure of the coordination chain can be rationalized by considering the size of the binding counteranion. This binding of the counteranions by the coordination chains is reflected in the systematic increment in the lattice constant of a columnar structure with increasing the size of counteranion (Table 1). This result implies that the counteranions are located in the cavities of the columns rather than between the columns. The encapsulation of the counteranion in the cavities of the columns is further supported by density measurements that show high-density values for these complexes (Table 1).



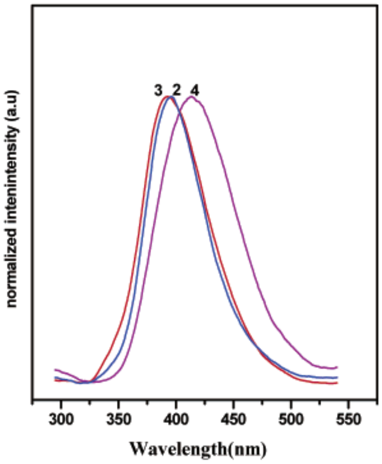


***Figure 7.*** Fluorescence spectra of **2**−**4** in the solid state.

In the case of the coordination chains based on small counteranions such as $NO_3^-$ and $BF_4^-$, a cationic scaffold can bind effectively an anionic guest through cisoid conformation, giving rise to a helical chain that organizes into a 2-D hexagonal columnar structure. In contrast to complex **2** which exhibits X-ray reflections corresponding to an intracolumnar order, complex **1** based on $NO_3^-$ shows only a broad halo at middle-angle X-ray range, indicative of the existence of only a liquidlike order within the column. Nitrate anion is likely to be too small against the cavity size formed by a pentagonal helix with an ordered helical pitch, and thus the cavity would be contracted for efficient binding of such a small counteranion, leading to a disorder of the helical pitch within the column. This is further supported by density measurements of the complexes, in which **2** shows a similar high density to those of the other complexes (Table 1). With increasing the size of counteranion as in the case of triflate ion of **3**, the cavity of helical chains would be enlarged to form a hexagonal helix for efficient binding of larger anions. However, the bulky dendritic side groups in the enlarged helical chains are located on top of each other, meaning that they are arranged in a row along the column axis. This results in strong repulsive interactions between the bulky side groups. To reduce the repulsive interactions, the helical chains would transform into dimeric cycles which stack atop of one another with mutual rotation to avoid steric hindrance between the dendritic side chains, giving rise to a helical column, as shown in Figure 3. These results indicate that the cationic coordination chains based on small counteranions can bind efficiently anionic guests through cisoid conformation.

However, heptafluorobutyrate anion as in the case of **4** is too large against the cavity size formed by cisoid conformation, and thus the chain conformation would adopt a transoid state

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for efficient binding of counteranion, leading to an unfolded zigzag conformation. This conformational change of the coordination chain to a transoid state is further supported by fluorescence measurements which show a 15 nm red shift of the emission maximum in **4** relative to those of **2**−**3** (Figure 6).

These results represent a significant example that a small change of the guest size in self-assembling system can provide a useful strategy to control the secondary structure and thereby solid-state supramolecular structure.

## Conclusions

A bent-shaped bipyridine ligand containing a dendritic aliphatic side chain has been synthesized as a ligand and complexed with silver ion through a self-assembling process. The resulting complexes were observed to self-assemble into ordered structures that differ as a function of the counteranion size in the solid state. The coordination chains based on small anions such as nitrate and tetrafluoroborate self-assemble into helical chains that organize into a 2-D hexagonal lattice. The complex based on triflate anion forms dimeric cycles stacking atop one another to make columns that laterally assemble in a hexagonal fashion. In contrast to the complexes based on small counteranions, the coordination chain based on a larger anion, heptafluorobutyrate, organizes into a lamellar structure. These results demonstrate that a systematic variation in the size of the counteranion can regulate the secondary structure of the coordination chain, from folded helical, cyclic, to unfolded linear chain conformations in the solid state. Interestingly, dilute solutions of the complexes exhibiting a columnar structure in polar solvents undergo spontaneous gelation and the resulting gels display a significant Cotton effect in the chromophore of the aromatic unit. This unique self-assembling behavior can be explained by considering the size of the counteranion and consequent chain conformation to maximize the electrostatic interactions.

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**Supporting Information Available:** Detailed synthetic procedures, characterization, and DSC traces. This material is available free of charge via the Internet at http//pubs.acs.org.

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