Molecular Strands and Related Properties of Silver(I) Triflate with 3,3'-Oxybispyridine *vs* 3,3'-Thiobispyridine

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Studies on subtle spacer ligand effects of $AgCF_3SO_3$ with 3,3'-Py_2X (X = O *vs* S) have been carried out. The reaction of $AgCF_3SO_3$ with 3,3'-Py_2O and 3,3'-Py_2S produces [Ag(CF_3SO_3)(3,3'-Py_2O)] and [Ag(3,3'-Py_2S)] (CF_3SO_3), respectively. Crystallographic characterization of [Ag(CF_3SO_3)(3,3'-Py_2O)] (monoclinic $P\bar{1}$, $a = 8.405(2)$ Å, $b = 10.714(2)$ Å, $c = 18.031(2)$ Å, $\alpha = 77.36(2)$, $\beta = 107.83(2)°$, $\gamma = 66.92(2)$, $V = 1438.0(5)$ Å^3, $Z = 2$, $R = 0.0486$) reveals that the skeletal structure is an anion-bridged double-strand. The double-strands are packed like a plywood. The framework of [Ag(3,3'-Py_2S)](CF_3SO_3) (orthorhombic *Pcab*, $a = 17.330(2)$ Å, $b = 8.640(1)$ Å, $c = 19.933(6)$ Å^3, $Z = 8$, $R = 0.0437$) is a sinusoidal single-strand. The formation of each coordination polymer appears to be primarily associated with the donating ability and the conformational energy barrier of the spacer ligands. Thermal analyses indicate that [Ag(CF_3SO_3)(3,3'-Py_2O)] and [Ag(3,3'-Py_2S)](CF_3SO_3) are stable up to 250 °C and 210 °C, respectively. For the anion exchangeability, the nature of the spacer ligand is more significant factor than the distance of silver(I)···triflate.

Key words : Strands, Coordination polymers, Silver(I) complexes, Bipyridines, Anion exchange

Introduction

Rational design strategies for functional coordination motifs are now of great interest due to applicable properties such as electrical conductors,[1,2] molecular magnets,[3-7] host-guest molecules,[8-11] crystal bending materials,[12] and nonlinear optical materials.[13] Such desirable coordination polymers have been constructed by selecting the coordination geometry of central metals, the structure of spacer ligands, the nature of counterions, and the reaction condition.[14-22] In particular, delicate differences between spacer ligands may significantly affect the formation of the coordination polymers. We previously reported that the reaction of Ag(I) with 3,3'-chalcogenobispyridine (3,3'-Py_2X; X = O, S) results in the formation of cylindrical helices and that the helices reversibly stretch via counteranion exchange.[23-25] 3,3'-Oxybispyridine (3,3'-Py_2O) and 3,3'-thiobispyridine (3,3'-Py_2S) as spacer ligands have similar angular and flexible components that possess non-rigid interannular dihedral angles between two pyridyl groups.[26-28] However, both anions exhibit delicate differences in the size, lone-pair delocalization, conformational energy barrier, and donating ability.

In order to scrutinize differences in bonding effects between the 3,3'-Py_2S and 3,3'-Py_2O, we describe the studies on the structures and related properties of Ag(I)CF_3SO_3 with 3,3'-Py_2O *vs* 3,3'-Py_2S. Trifluoromethanesulfonate ($CF_3SO_3^-$: triflate) is a common, readily available (counter)anion, which coordinates relatively weakly to metal centers. The triflate anion has been known as a weak base and hence as a good leaving group.[29]
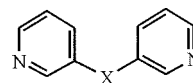
X =O, 3,3'-Py_2O; X = S, 3,3'-Py_2S

Experimental Section

Materials and Measurements. Silver(I) triflate ($AgCF_3SO_3$) was purchased from Aldrich Chemical Co, and used without further purification. 3,3'-Py_2O and 3,3'-Py_2S were prepared according to the literature procedures.[27] Elemental analyses (C, H, N) were performed on crystalline samples by the Advanced Analytical Center at KIST with a Perkin-Elmer 2400 CHNS Analyzer. Thermal analyses were carried out under dinitrogen atmosphere at a scan rate of 10 °C/min with a Stanton Red Croft TG 100. X-ray powder diffraction data were recorded on a Rigaku RINT/DMAX-2500 diffractometer at 40 kV, 126 mA for Cu Kα. Infrared spectra were obtained on a Perkin Elmer 16F PC FTIR spectrophotometer with samples prepared as KBr pellet.

Preparation of [Ag(CF_3SO_3)(3,3'-Py_2O)]. A methanol solution (5 mL) of 3,3'-Py_2O (65 mg, 0.3 mmol) was slowly diffused into an aqueous solution (5 mL) of $AgCF_3SO_3$ (77 mg, 0.3 mmol). Colorless crystals of [Ag(CF_3SO_3)(3,3'-Py_2O)] suitable for crystallographic characterization formed at the interface, and were obtained in 7 days in 83% yield. Mp: 250-251 °C (dec). Found: C, 30.60; H, 1.83; N, 6.38. Anal. Calcd for $C_{11}H_8N_2AgF_3O_4S$: C, 30.79; H, 1.88; N, 6.58. IR (KBr, cm^{-1}): ν(SO_3), 1264(s).

Preparation of [Ag(3,3'-Py_2S)](CF_3SO_3). The diffusion of a methanol solution (6 mL) of 3,3'-Py_2S (60 mg, 0.3

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mmol) into an aqueous solution (6 mL) of $AgCF_3SO_3$ (77 mg, 0.3 mmol) afforded the colorless crystals of $[Ag(Py_2S)]$ (CF_3SO_3) in 85% yield. Mp: 213-220 $^{\circ}$C (dec). Found: C, 29.50; H, 1.78; N, 6.30. Anal Calcd for $C_{11}H_8N_2AgF_3O_3S_2$: C, 29.68; H, 1.81; N, 6.29. IR (KBr, cm^{-1}): $\nu(SO_3)$, 1250 (s).

Anion Exchange. The procedure of a typical anion exchange is outlined: an aqueous solution (5 mL) of $NaBF_4$ (35 mg, 0.32 mmol) was added to a suspension of micro-crystalline $[Ag(CF_3SO_3)(3,3'-Py_2O)]$ (43 mg, 0.10 mmol) in water (5 mL). The reaction mixture was stirred at room temperature, and the precipitates after 1, 3, 6, 12, and 24 h were monitored by IR spectra. After 24 h, the reaction mixture was filtered, and washed with several aliquots of water and methanol. Found: C, 32.60; H, 2.16; N, 7.65. Anal. Calcd for $C_{10}H_8N_2OBF_4Ag$ prepared by the anion exchange: C, 32.74; H, 2.20; N, 7.64. The anion exchange of $[Ag(CF_3SO_3)(3,3'-Py_2O)]$ with other anions, ClO_4^- and PF_6^-, were similarly achieved. The exchanged species still give a sharp X-ray powder diffraction pattern. The anion exchange of $[Ag(3,3'-Py_2S)](CF_3SO_3)$ with above anions were attempted.

X-ray Crystallography. All X-ray data were collected on an Enraf-Nonius CAD4 automatic diffractometer with gra-phite-monochromated Mo Kα ($\lambda = 0.71073$ Å) at ambient temperature. Unit cell dimensions were based on 25 well-centered reflections by using a least-square procedure. During the data collection, three standard reflections moni-tored after every hour did not reveal any systematic variation in intensity. The data were corrected for Lorentz and polarization effects. Absorption effects were corrected by the empirical ψ−scan method. The structures were solved by the Patterson method (SHELXS 97) and refined by full-matrix least square techniques (SHELXL 97).[30] The non-

hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined only for the isotropic thermal factors. Crystal parameters and procedural information corresponding to data collection and structure refinement are given in Table 1.

Crystallographic data for the structures reported here have been deposited with the Cambridge Crystallographic Data Cetre (Deposition No. CCDC-187885 and CCDC-187886). The data can be obtained free of charge *via http://www. ccdc.cam.ac.uk/perl/catreq/catreq.cgi* (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1233 336033; e-mail: deposit@ccdc.cam.ac.uk).

Results and Discussion

Synthesis. The reaction of $AgCF_3SO_3$ with $3,3'-Py_2O$ and $3,3'-Py_2S$ in appropriate solvents affords $[Ag(CF_3SO_3)(3,3'-Py_2O)]$ and $[Ag(3,3'-Py_2S)](CF_3SO_3)$, respectively (Scheme 1). Elemental analyses confirm that both products are 1 : 1 (Ag : Py_2X (X = O, S)) adducts. The molecular formulae of the two compounds are very similar, but their infinite structures are basically different, which will be explained in detail. The reactions are independent of the variation of the mole ratio, reaction time, and concentration, indicating that the products are favorable species. Moreover, when acetone or ethanol was used as a solvent instead of methanol, the same products were obtained. The compounds are insoluble in water and common organic solvents, but are stable for several days at pH = 3.5 9.0 aqueous suspensions.

Crystal Structures. The crystallographic asymmetric unit and extended structures of $[Ag(CF_3SO_3)(Py_2O)]$ are shown in Figure 1, and selected bond lengths and angles are listed in Table 2. There are two independent silver units in the asymmetric region of the triclinic unit cell and the features of the two molecules are within error of being identical. The Py_2O spacer connects two silver ions to give a single strand (Ag-N = 2.173(5)-2.196(5) Å). The two single strands are double-bridged via one oxygen atom of the triflate anion in "up and down" to give double strand (Ag-O = 2.555(6)-2.577(5) Å), resulting in the approximately four-coordinate Ag(I) ion. The Ag-O distances are comparable to the corre-sponding bond in $[Ag_3(NO_3)_3(Py_2S)_2 \cdot 2H_2O]$.[16] The dihedral angles between two pyridine rings around O and Ag are 80.5(2)$^{\circ}$-80.6(2)$^{\circ}$. A salient feature is that the double strands are packed like a plywood.

The asymmetric unit and infinite structures of $[Ag(Py_2S)]$

Table 1. X-ray Crystal Data and Details of Data Collections and Structure Refinements

	$[Ag(CF_3SO_3)$ $(3,3'-Py_2O)]$	$[Ag(3,3'-Py_2S)]$ (CF_3SO_3)
Formula	$C_{11}H_8N_2AgO_4S$	$C_{11}H_8N_2Ag F_3O_3S_2$
Formula weight	429.13	445.19
Space group	$P\bar{1}$	$Pcab$
a (Å)	8.405(2)	17.330(2)
b (Å)	10.714(2)	8.640(1)
c (Å)	18.031(2)	19.933(6)
α ($^{\circ}$)	77.36(2)	
β ($^{\circ}$)	76.56(2)	
γ ($^{\circ}$)	66.92(2)	
V (Å^3)	1438.0(5)	2984.6(1)
Z	2	8
D_{cal} (gcm^{-3})	1.982	1.981
μ, mm^{-1}	1.599	1.674
Goodness-of-fit on F^2	1.102	1.105
R [I>2σ(I)]	R1 = 0.0486	0.0437
	wR2 = 0.1264	0.1234

$R1 = \sum ||F_o|-|F_c||/\sum |F_o|$. $wR2 = \sum w(F_o^2-F_c^2)^2/\sum wF_o^4)^{1/2}$, where $w = 1/\{\sigma^2F_o^2+(aP)^2+bP\}$, where $P = \{Max(F_o^2, o)+ 2F_c^2\}/3$
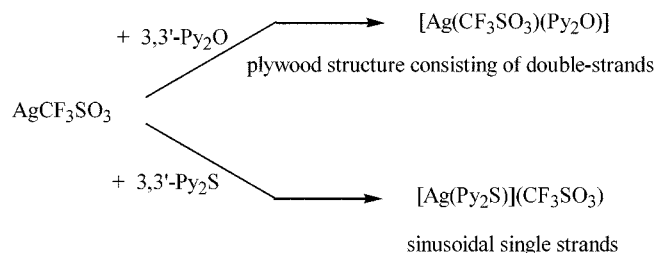
Scheme 1
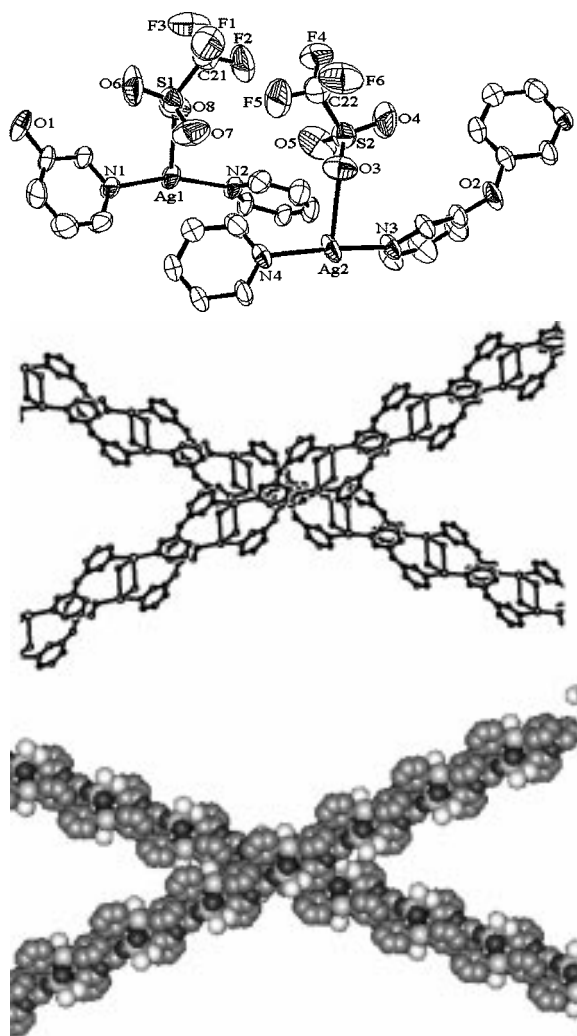
Figure 1. ORTEP view (top) and infinite structure (middle), and space-filling (bottom) of [Ag(3,3'-Py$_2$O)(CF$_3$SO$_3$)]. Hydrogen atoms and solvate molecules are omitted for clarity. For the infinite structure, triflate moiety is presented as a circle.

Table 2. Selected Bond Lengths (Å) and Bond Angles (°)

	[Ag(CF$_3$SO$_3$) (3,3'-Py$_2$O)]	[Ag(3,3'-Py$_2$S)] (CF$_3$SO$_3$)
Ag(1)-N(2)	2.174(5)	2.167(5)
Ag(1)-N(1)	2.196(5)	2.172(5)
Ag(1)-O(8)#1	2.560(6)	
Ag(1)-O(8)	2.577(5)	
Ag(2)-N(4)	2.173(5)	
Ag(2)-N(3)	2.195(5)	
Ag(2)-O(3)#2	2.555(6)	
Ag(2)-O(3)	2.575(5)	
O(3)-Ag(2)#2	2.555(6)	
O(8)-Ag(1)#1	2.560(6)	
N(2)-Ag(1)-N(1)	156.9(2)	157.5(2)
N(2)-Ag(1)-O(8)#1	110.2(2)	
N(1)-Ag(1)-O(8)#1	92.0(2)	
N(2)-Ag(1)-O(8)	99.5(2)	
N(1)-Ag(1)-O(8)	91.9(2)	
O(8)#1-Ag(1)-O(8)	75.1(2)	
N(4)-Ag(2)-N(3)	156.9(2)	
N(4)-Ag(2)-O(3)#2	110.1(2)	
N(3)-Ag(2)-O(3)#2	92.1(2)	
N(4)-Ag(2)-O(3)	99.7(2)	
N(3)-Ag(2)-O(3)	92.0(2)	
O(3)#2-Ag(2)-O(3)	74.8(2)	

For [Ag(3,3'-Py$_2$S)](CF$_3$SO$_3$), symmetry transformations used to generate equivalent atoms: #1 x, -y-1/2, z-1/2; #2 x, -y-1/2, z+1/2.

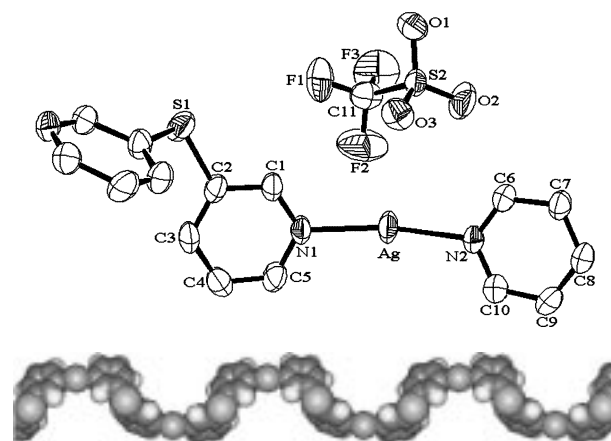**Figure 2**. ORTEP view (top) and infinite space-filling (bottom) of [Ag(3,3'-Py$_2$S)](CF$_3$SO$_3$). Hydrogen atoms and solvate molecules are omitted for clarity.

(CF$_3$SO$_3$) are shown in Figure 2, and selected bond lengths and angles are listed in Table 2. Each Py$_2$S ligand connects two silver(I) ions in a bridged fashion to give a single strand. The Ag-N bonds (2.172(5) Å and 2.167(5) Å) are not exceptional. The shortest distance of Ag···O (CF$_3$SO$_3$) (2.80 Å) is much longer than the corresponding length of [Ag(CF$_3$SO$_3$) (Py$_2$O)]. However, the weak interaction is a partial responsibility for the ideal linear geometry (N(1)-Ag-N(2) = 157.5 (2)°). The packing diagram indicates that the single strand is a sinusoidal chain that is arrayed in alternate sin(α) and cos(α) fashion. The dihedral angle between two pyridine rings within the Py$_2$S ligand is 74.4(2)° while the dihedral angle around Ag(I) ion is 34.1(3)°. The Py-S-Py angle (101.4(3)°) is much smaller than the corresponding angle Py-O-Py (116.1(5)°; 116.0(5)°) of [Ag(CF$_3$SO$_3$)(Py$_2$O)].

Thermal Analyses. The thermal analyses have been used to establish a relationship between structure and properties.[14,15] The traces of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) indicate that

[Ag(CF$_3$SO$_3$)(Py$_2$O)] and [Ag(Py$_2$S)](CF$_3$SO$_3$) are thermally stable up to 250 and 213 °C, respectively, in the solid state (Figure 3). [Ag(CF$_3$SO$_3$)(Py$_2$O)] shows a two-step weight loss in the temperature range 250-403 °C and [Ag(Py$_2$S)] (CF$_3$SO$_3$) exhibits a similar thermal pattern in the range 213-410 °C. The two-step weight loss may be ascribed to the evaporation of the spacer and the anion. The thermal curves suggest that the anion-bridged double-strand, [Ag(CF$_3$SO$_3$) (Py$_2$O)], is more stable than the sinusoidal single-strand, [Ag(Py$_2$S)](CF$_3$SO$_3$).
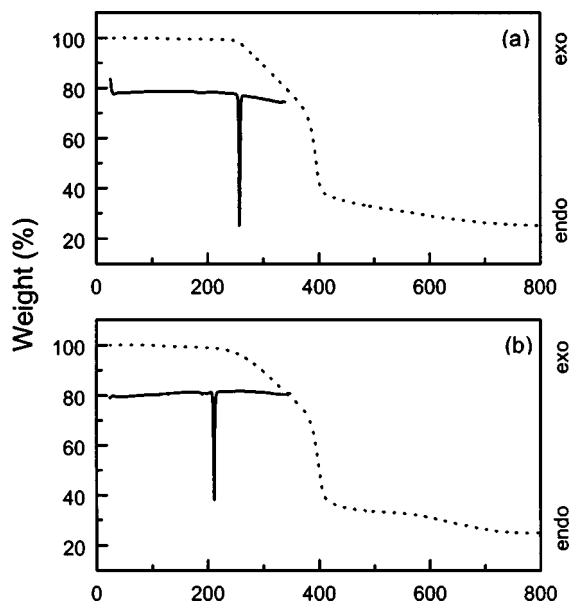
Figure 3. Overlay of TGA (····) and DSC (–) traces of [Ag(3,3'-Py₂O)(CF₃SO₃)] (a) and [Ag(3,3'-Py₂S)](CF₃SO₃) (b), each recorded at a heating rate of 10 °C min⁻¹.
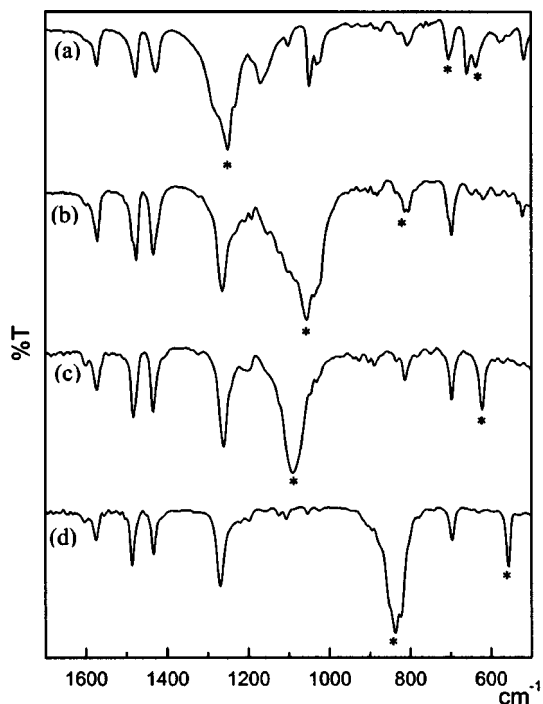
Figure 4. IR spectra of [Ag(3,3'-Py₂O)(CF₃SO₃)] (a), species exchanged by BF_4^- (b), ClO_4^- (c), and PF_6^- (d). *denotes the bands induced by each anion.

Anion Exchange. For the present compounds, a typical anion exchange can occur since the triflate is a good leaving group. The anion exchange of [Ag(CF₃SO₃)(Py₂O)] with X^- ($X^- = BF_4^-$, ClO_4^-, and PF_6^-) was accomplished in a typical aqueous media. To investigate the exchange procedure, the anion exchange was monitored by the characteristic IR bands of the anions.[23,24] The infrared spectra show the gradual disappearance of intense $CF_3SO_3^-$ bands (1264 cm⁻¹)

and the appearance and growth of new anion bands (1058 cm⁻¹ for BF_4^-; 1090 cm⁻¹ for ClO_4^-; 836 cm⁻¹ for PF_6^-). The anion exchanges were completed within 12 h (Figure 4). The elemental analysis and IR spectra of the exchanged species are coincident with those of the as-synthesized samples.[23,24] We expected that the anion of [Ag(Py₂S)](CF₃SO₃) could be more easily exchanged since the anion is more labile. However, the anion exchange of [Ag(Py₂S)](CF₃SO₃) is slower than that of [Ag(CF₃SO₃)(Py₂O)]. The anions of [Ag(Py₂S)](CF₃SO₃) were not completely exchanged after 24 h. The anion exchangeability of these compounds seems to be governed by the nature of the spacer ligand rather than the distance of Ag(I)···CF₃SO₃. The hydrophilicity-difference between the two spacer ligands may play an important role in the anion exchange. Such an interconversion via the anion exchange may be applied to the development of a tailored strategy that cannot be approached by direct synthetic methods.

Construction of Each Molecular Strand. Py₂O and Py₂S are similar noninnocent ligands that possess stable skewed conformers with nonrigid interannular dihedral angles between two pyridyl groups. The reaction of Ag(I)CF₃SO₃ with 3,3'-Py₂O affords a plywood structure consisting of double strands while the treatment of Ag(I)CF₃SO₃ with 3,3'-Py₂S produces a sinusoidal single strand. The formation of each structure may be ascribed to the intrinsic properties of the spacer ligands. There are delicate differences between the two spacers in the size, the bond angle, the lone-pair delocalization of chalcogens, the conformational energy barrier, and the donating ability of nitrogen atoms. First, the C-S-C angle of 3,3'-Py₂S was smaller than the C-O-C angle of 3,3'-Py₂O.[23] For the present works, the C-S-C angle (101.4(3)°) significantly contracts relative to the corresponding C-O-C angle in 3,3'-Py₂O (116.1(6)°). The contracted angle of the bridged-bidentate spacer may be an obstacle in the formation of higher coordination number. Therefore, the 3,3'-Py₂S spacer may afford the simple two-coordinate sinusoidal structure in contrast to the four-coordinate double strand. Second, the conformational energy barrier of 3,3'-Py₂S is slightly different from that of 3,3'-Py₂O.[31,32] The low energy barrier seems to be an unfavorable factor in the formation of crowded coordination. Third, the coordination numbers of each Ag(I) ion may be induced by the donating ability of the spacer ligands. The Ag-N bond lengths of [Ag(Py₂S)](CF₃SO₃) are slightly shorter than those of [Ag(CF₃SO₃)(Py₂O)]. Furthermore, [Ag(CF₃SO₃)(Py₂O)] is four-coordinate Ag(I) whereas [Ag(Py₂S)](CF₃SO₃) approximates to two-coordinate Ag(I). These facts indicate that the Lewis basicity of 3,3'-Py₂S is stronger than that of 3,3'-Py₂O.

In conclusion, the 3,3'-Py₂X spacers are a series of fascinating tectonic units without any serious strain in the formation of various coordination polymers. A direct comparison between 3,3'-Py₂S and 3,3'-Py₂O demonstrates that the delicate difference in intrinsic nature acts as a crucial factor in the construction of molecular materials. In particular, exchangable triflate is useful in generating new species that cannot be approached by direct synthetic

methods. For the present works, the anion exchangeability is strongly dependent upon the nature of a spacer ligand rather than the distance of silver(I)···triflate. The delicate differences may contribute to the development of useful molecular-based materials.

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