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# Syntheses and Structures of Photochromic Silver(I) Coordination Polymers with *cis*-1,2-Dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene

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Five novel silver(I) coordination polymers with *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3- thienyl)ethene (*cis*-dbe) were synthesized and are characterized in this paper. Treatment of $AgCF_3SO_3$ or $AgCF_3CO_2$ with *cis*-dbe afforded $[Ag_2(cis\text{-dbe})(CF_3SO_3)_2]$ (**1**) and $[Ag_2(cis\text{-dbe})(CF_3CO_2)_2]$ (**2**), and both complexes exhibit a 1-D infinite chain structure with two cyano groups and two thienyl groups of the ligand bridging four metal ions. Reaction of $AgC_nF_{2n+1}CO_2$ with *cis*-dbe gave rise to an unprecedented cocrystallization of a 2-D sheet structure, $[Ag_2(cis\text{-dbe})(C_nF_{2n+1}CO_2)_2]$, where $n = 2$ (**3**), 3 (**4**), and 4 (**5**). Upon irradiation with 450 nm light, these five silver(I) complexes turned orange or red from yellow, and the color reverted to yellow on exposure to 560 nm light, indicative of the reversible cyclization/ring-opening reaction occurring in the crystalline phase. Furthermore, different anions gave not only the different structural dimensions but also the different photoresponsive patterns. The correlation between the crystal structures and the photochromic reactivity is discussed.

## Introduction

Photochromism is the reversible transformation by photoirradiation of a chemical species between two forms that have different absorption spectra.[1] It has attracted much attention because of its potential applications in photonic devices, such as optical memories and photooptical switches.[2] Among various photochromic compounds, diarylethenes with heterocyclic aryl groups have been found in solution as well as in the solid state to exhibit the reversible photoinduced electorocyclization/ring-opening process.[3−8] In fact, they are the most promising photochromic compounds in terms of practical applications due to their fatigue resistant and thermally irreversible properties.[9,10] Although various kinds

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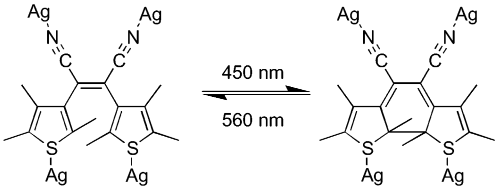
**Scheme 1**



of photochromic diarylethene derivatives have been developed, their metal complexes in the solid state have been rarely reported. The synthesis and photochromism of metal complexes of diarylethenes were first reported by our group in 1996 with a linear copper(I) coordination polymer bridged by the cyano groups of *cis*-1,2-dicyano-1,2-bis(2,4,5-trimehtyl-3-thienyl)ethene (*cis*-dbe).[11] Recently, a linear coordination polymer composed of diarylethene and Zn(II) ions has been synthesized, which undergoes a photochromic reaction in the single-crystalline phase monitored by polarized absorption spectroscopy.[12] The use of a diarylethene as a photoswitching bridging ligand is of interest. When metal ions are located at both ends of the aryl groups of the diarylethenes, the interactions between metal ions can be switched by photoirradiation, because the $\pi$-conjugated bond structures between the two aryl groups are different in the two isomers.[7,12] Crystalline photochromic compounds are of particular interest because of their potential usefulness for holographic and three-dimensional memories.[2] In crystals, molecules are regularly oriented and packed in fixed conformations. In many cases, free rotation is prohibited. Therefore, the photoreactivity in the crystalline phase is dependent on the space for free rotation of the aryl ring and the conformation formed in the crystal lattice.[8]

Silver(I) ion is regarded as an extremely soft acid favoring coordination to soft bases, such as ligands containing S and unsaturated N donors. Silver(I) complexes with these soft ligands give rise to an interesting array of stereochemistries and geometric configurations with 1-D chain, 2-D, and 3-D networks all occurring.[13] The final structures and frameworks of these complexes may well depend on a variety of factors such as the nature of the anions.[14] Here we describe the first crystallographycally characterized silver(I)−diarylethene coordination polymers with five different anions, which show different photochromic reactions in the crystalline phase (Scheme 1).

## Experimental Section

**General Methods.** Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Tokyo Kasei Chemicals, and Kanto Chemicals) and were used without further purification. $AgC_4F_9CO_2$ was prepared from the reaction of silver(I) oxide and nonafluorovaleric acid in ethanol. All reactions and manipulations were carried out under an argon atmosphere. Solvents were dried using standard procedures and distilled under an argon atmosphere prior to use.

Melting points were determined on a Yanagimoto MP-S3 instrument and are not corrected. Infrared spectra were recorded as KBr disk on JASCO FT-IR 8000 and FT/IR-430 spectrometers. Absorption spectra in crystalline state were measured by diffuse reflection using the Kubelka−Munk method on a SHIMADZU UV-2450 spectrometer, and barium sulfate was used as a reference. Photoirradiation was carried out using a 150 W Xe lamp, and monochromatic light was obtained by passing the light through a monochromator. Elemental analyses were performed by the Department of Chemistry, Tokyo Metropolitan University.

**Syntheses. (a) [$Ag_2$(*cis*-dbe)($CF_3SO_3$)$_2$] (1).** To a mixed solution (3 mL) of tetrahydrofuran (THF) and hexane (2:3 by volume) containing $AgCF_3SO_3$ (46.2 mg, 0.18 mmol) was slowly added 6 mL of hexane containing *cis*-dbe (29.4 mg, 0.09 mmol). After 10 min of stirring, the resultant solution was filtered. The filtrate was introduced into a narrow-diameter glass tube, which, after standing in the dark at ambient temperature for 1 month, afforded complex **1** as yellow needle crystals (72.0 mg, 95%): mp 257 °C. Main IR bands ($cm^{-1}$): 2959−2869 (m), 2251 (m), 1604−1439 (m), 1292−1020 (vs), 635 (s). Anal. Calcd for $C_{20}H_{18}Ag_2F_6N_2O_6S_4$: C, 28.59; H, 2.16; N, 3.33. Found: C, 28.87; H, 2.12; N, 3.34.

**(b) [$Ag_2$(*cis*-dbe)($CF_3CO_2$)$_2$] (2).** To a benzene solution (3 mL) containing $AgCF_3CO_2$ (39.8 mg 0.18 mmol) was slowly added *cis*-dbe (29.4 mg, 0.09 mmol) in 6 mL of hexane. The mixed solution was allowed to stand in the dark at ambient temperature for 1 month and afforded complex **2** as yellow brick crystals (42.0 mg, 61%): mp 217 °C. Main IR bands ($cm^{-1}$): 2926−2869 (m), 2226 (m), 1641 (vs), 1605−1381 (m), 1202−1144 (vs), 839−725 (s), 521(m). Anal. Calcd for $C_{22}H_{18}Ag_2F_6N_2O_4S_2$: C, 34.40; H, 2.36; N, 3.68. Found: C, 34.27; H, 2.29; N, 3.72.

**(c) [$Ag_2$(*cis*-dbe)($C_2F_5CO_2$)$_2$] (3).** The yellow brick crystals of **3** were grown similarly to those of **2** using $AgC_2F_5CO_2$ (48.8 mg, 0.18 mmol) instead of $AgCF_3CO_2$ (61.4 mg, 78%): mp 242 °C. Main IR bands ($cm^{-1}$): 2922−2870 (w), 2226 (w), 1665 (s), 1605−1331 (m), 1215−1161 (s), 1030 (s), 814 (m), 733(m). Anal. Calcd for $C_{24}H_{18}Ag_2F_{10}N_2O_4S_2$: C, 33.20; H, 2.09; N, 3.23. Found: C, 33.01; H, 2.02; N, 3.25.

**(d) [$Ag_2$(*cis*-dbe)($C_3F_7CO_2$)$_2$] (4).** The yellow needle crystals of **4** were grown similarly to those of **2** using $AgC_3F_7CO_2$ (57.8 mg, 0.18 mmol) instead of $AgCF_3CO_2$ (68.2 mg, 78%): mp 228 °C. Main IR bands ($cm^{-1}$): 2928−2869 (w), 2223 (m), 1671 (vs), 1607−1341 (m), 1213−1117 (s), 966 (s), 812 (s), 743(s). Anal. Calcd for $C_{26}H_{18}Ag_2F_{14}N_2O_4S_2$: C, 32.25; H, 1.87; N, 2.89. Found: C, 32.01; H, 1.80; N, 2.92.

**(e) [$Ag_2$(*cis*-dbe)($C_4F_9CO_2$)$_2$] (5).** To a benzene solution (3 mL) containing $AgC_4F_9CO_2$ (133.5 mg, 0.36 mmol) was slowly added *cis*-dbe (58.8 mg, 0.18 mmol) in 12 mL of hexane. After standing in the dark at ambient temperature for 1 month, the mixed solution afforded complex **5** as yellow brick crystals (42.0 mg, 61%): mp 217 °C. Main IR bands ($cm^{-1}$): 2928−2870 (w), 2228 (w). 1671−1644 (vs), 1551−1350 (m), 1238−1130 (vs), 1157(s), 808 (m), 743(s). Anal. Calcd for $C_{28}H_{18}Ag_2F_{18}N_2O_4S_2$: C, 31.45; H, 1.68; N, 2.62. Found: C, 31.50; H, 1.78; N, 2.48.

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**Table 1.** Crystallographic Data for Complexes **1**−**5**

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| formula | $C_{20}H_{18}Ag_2F_6N_2O_6S_4$ | $C_{22}H_{18}Ag_2F_6N_2O_4S_2$ | $C_{24}H_{18}Ag_2F_{10}N_2O_4S_2$ | $C_{26}H_{18}Ag_2F_{14}N_2O_4S_2$ | $C_{28}H_{18}Ag_2F_{18}N_2O_4S_2$ |
| fw | 840.34 | 768.24 | 868.26 | 968.27 | 1068.29 |
| cryst syst | monoclinic | monoclinic | monoclinic | monoclinic | monoclinic |
| space group | $C2/c$ | $C2/c$ | $C2/c$ | $C2/c$ | $C2/c$ |
| $a$/Å | 21.303(9) | 21.233(2) | 23.583(2) | 25.038(5) | 27.695(3) |
| $b$/Å | 10.199(1) | 10.647(4) | 10.675(2) | 10.574(2) | 10.684(2) |
| $c$/Å | 13.2531(8) | 12.212(2) | 12.370(2) | 12.3950(4) | 12.1666(4) |
| $\beta$/deg | 103.578(1) | 102.240(9) | 105.150(9) | 99.7825(9) | 104.5283(9) |
| $V$/Å$^3$ | 2799.0(8) | 2697(1) | 3006.1(8) | 3233.9(9) | 3484.9(6) |
| $Z$ | 4 | 4 | 4 | 4 | 4 |
| $D_{calcd}/(g\cdot cm^{-3})$ | 1.994 | 1.891 | 1.918 | 1.989 | 2.036 |
| $\lambda$(Mo K$\alpha$)/Å | 0.710 69 | 0.710 69 | 0.710 69 | 0.710 69 | 0.710 69 |
| $\mu$/cm$^{-1}$ | 17.73 | 16.75 | 15.34 | 14.54 | 13.76 |
| $T$/K | 296 | 296 | 296 | 296 | 200 |
| measd reflns | 3077 | 3089 | 3449 | 3703 | 3938 |
| obsd reflns ($I > 2\sigma(I)$) | 1841 | 2210 | 2073 | 2892 | 3518 |
| $R^a$ | 0.089 | 0.042 | 0.040 | 0.053 | 0.036 |
| $R_w{}^b$ | 0.310 | 0.128 | 0.133 | 0.161 | 0.089 |
| GOF | 1.07 | 1.04 | 1.02 | 1.08 | 1.07 |

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

**X-ray Data Collection and Structure Solution and Refinement.** Diffraction data for **1**, **4**, and **5** were collected on a Quantum CCD area detector coupled with a Rigaku AFC7 (for **1**) or a Rigaku AFC8 (for **4** and **5**) diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). The intensity data were collected at 296 K (for **1** and **4**) and 200 K (for **5**) using the $\omega$ scan technique, and a total of 3077, 3703, and 3938 reflections were collected, respectively. No decay correction was applied. The linear absorption coefficient $\mu$ for Mo K$\alpha$ radiation is 17.73, 14.54, and 13.76 cm$^{-1}$, respectively. A symmetry-related absorption correction was applied. In addition, a correction of secondary extinction was applied. The data were corrected for Lorentz and polarization effects. For **2** and **3**, a suitable crystal of each was attached to the end of a glass fiber and mounted on a Rigaku AFC-7R automated diffractometer with graphite monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 69 Å). Intensity data were collected at 296 K using the $\omega-2\theta$ scan technique, and a total of 3089 and 3449 reflections were collected, respectively. The intensities of three representative reflections were measured after every 150 reflections and remained constant, indicative of crystal and electronic stability. Thus, no decay correction was applied. The linear absorption coefficient $\mu$ for Mo K$\alpha$ radiation is 16.75 and 15.34 cm$^{-1}$, respectively. An empirical absorption correction based on azimuthal scans of several reflections was applied, whereas a symmetry-related absorption correction was applied. In addition, a correction of secondary extinction was applied. The data were corrected for Lorentz and polarization effects.

The structures were solved by direct methods followed by subsequent Fourier calculations.[15] The non-hydrogen atoms were refined anisotropically. For complexes **2**, **3**, and **5,** the coordinates of the hydrogen atom were refined but their isotropic $B$'s were held fixed, while for **1** and **4,** the hydrogen atoms were included but not refined. The final cycle of the full-matrix least squares refinement was based on 1841, 2210, 2073, 2892, and 3518 observed reflections and 182, 209, 236, 227, and 317 variable parameters for **1**−**5**, respectively, converged with the unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. The atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography, Vol. IV.[16] All calculations were performed using the teXsan crystallographic software package.[17] Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

## Results

**Structural Characterizations.** Five silver(I) coordination polymers were prepared by the reaction of the appropriate starting material, $AgCF_3SO_3$ or $AgC_nF_{2n+1}CO_2$ ($n$ = 1−4), with *cis*-dbe in THF, hexane, or benzene. These air-stable yellow crystals were found to be light-sensitive in the solid state and in solution, thus the crystals and the solution of the complexes were stored in aluminum foil wrapped containers.

X-ray structure determination revealed that complexes of **1** and **2** are isomorphous with near-isostructural [Ag$_2$(*cis*-dbe)X$_2$] units. An ORTEP drawing of **1** with atom numbering scheme is shown in Figure 1a. The metal center in both complexes coordinates with one cyano group and one thienyl S atom of two different dithienylethene molecules, and each ligand group in turn employs its two CN and two thienyl groups to bridge four Ag(I) ions. This leads to a polymeric chain of the metal ions bridged sequentially by the ligand moieties running parallel to the $b$-axis of the monoclinic cell, as shown in Figure 1b,c. The distorted tetrahedral environment about the metal ion in both **1** and **2** is completed by further coordination with two counteranions bridging between the two Ag(I) ions. This gives rise to a dinuclear core with Ag···Ag separation of 4.11 and 3.51 Å in **1** and **2**, respectively. To achieve an effective chelating of the

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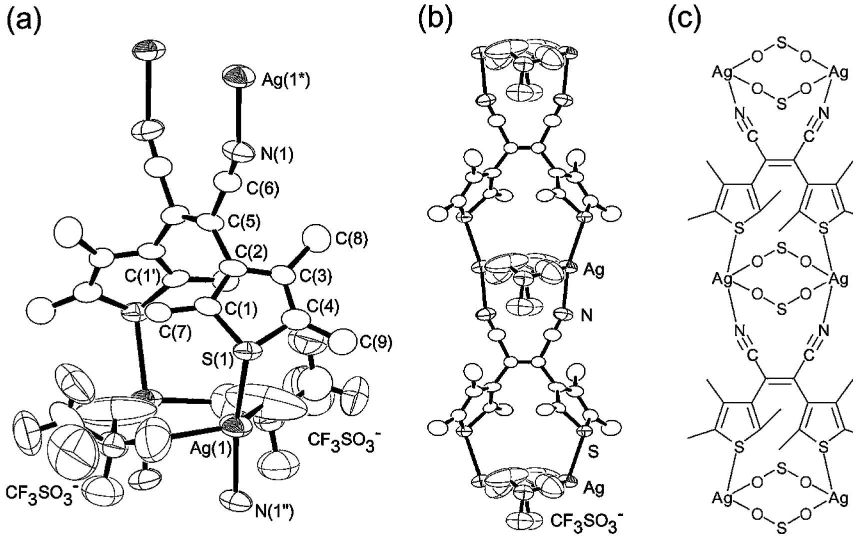

**Figure 1.** Crystal structure of **1**: (a) ORTEP view with an atomic labeling scheme, showing 50% thermal ellipsoids; (b) 1-D chain structure; (c) schematic view of 1-D chain structure.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**5**

| | | | |
|---|---|---|---|
| Complex **1** | | | |
| Ag(1)−S(1) | 2.521(3) | Ag(1)−O(1) | 2.41(2) |
| Ag(1)−O(2) | 2.50(2) | Ag(1)−N(1) | 2.28(1) |
| S(1)−Ag(1)−O(1) | 100.3(4) | S(1)−Ag(1)−O(2) | 96.2(4) |
| S(1)−Ag(1)−N(1) | 166.7(3) | O(1)−Ag(1)−O(2) | 130(1) |
| O(1)−Ag(1)−N(1) | 87.1(5) | O(2)−Ag(1)−N(1) | 87.1(5) |
| Complex **2** | | | |
| Ag(1)−S(1) | 2.920(1) | Ag(1)−O(1) | 2.268(4) |
| Ag(1)−O(2) | 2.278(4) | Ag(1)−N(1) | 2.444(4) |
| S(1)−Ag(1)−O(1) | 85.7(1) | S(1)−Ag(1)−O(2) | 93.2(1) |
| S(1)−Ag(1)−N(1) | 151.6(1) | O(1)−Ag(1)−O(2) | 149.4(2) |
| O(1)−Ag(1)−N(1) | 91.4(2) | O(2)−Ag(1)−N(1) | 103.2(2) |
| Complex **3** | | | |
| Ag(1)−S(1) | 2.825(1) | Ag(1)−O(1) | 2.332(6) |
| Ag(1)−O(2) | 2.316(4) | Ag(1)−N(1) | 2.435(5) |
| S(1)−Ag(1)−O(1) | 73.9(1) | S(1)−Ag(1)−O(2) | 98.7(1) |
| S(1)−Ag(1)−N(1) | 158.8(1) | O(1)−Ag(1)−O(2) | 150.5(2) |
| O(1)−Ag(1)−N(1) | 90.5(2) | O(2)−Ag(1)−N(1) | 101.8(2) |
| Complex **4** | | | |
| Ag(1)−S(1) | 2.788(1) | Ag(1)−O(1) | 2.357(4) |
| Ag(1)−O(2) | 2.318(4) | Ag(1)−N(1) | 2.412(4) |
| S(1)−Ag(1)−O(1) | 73.3(1) | S(1)−Ag(1)−O(2) | 99.6(1) |
| S(1)−Ag(1)−N(1) | 158.7(1) | O(1)−Ag(1)−O(2) | 151.8(2) |
| O(1)−Ag(1)−N(1) | 90.5(1) | O(2)−Ag(1)−N(1) | 101.1(1) |
| Complex **5** | | | |
| Ag(1)−S(1) | 2.8573(8) | Ag(1)−O(1) | 2.298(2) |
| Ag(1)−O(2) | 2.330(2) | Ag(1)−N(1) | 2.456(3) |
| S(1)−Ag(1)−O(1) | 99.97(6) | S(1)−Ag(1)−O(2) | 72.14(6) |
| S(1)−Ag(1)−N(1) | 157.52(7) | O(1)−Ag(1)−O(2) | 154.28(9) |
| O(1)−Ag(1)−N(1) | 101.15(9) | O(2)−Ag(1)−N(1) | 91.62(9) |

Ag···Ag dinuclear core, the bond lengths of Ag−S [2.521(3) Å] and Ag−N [2.28(1) Å] in **1** are significantly shorter than those in **2** [2.920(1) and 2.444(4) Å, respectively], and as a result, the average twisted angle of the thiophene ring against the C(2)−C(5)−C(5′)−C(2′) least-squares plane in **1** (57.3°) is greater than that in **2** (53.8°). The two adjacent polymeric chains in the direction of the *c*-axis are associated together through weak, nondirectional Ag···O interaction [with a distance of 2.83 Å in **1** and 2.70 Å in **2**] and $\pi-\pi$ interaction between the thiophene rings [with a distance of 3.59 Å in **1** and 3.48 Å in **2**].

In the previously reported copper(I) and zinc(II) complexes of dithienylethene, the metal ions are found to have no direct interaction with the sulfur atoms of the thiophene ring, either in solution or in the solid state.[11,12] The polymeric chain structure is established on the basis of the two cyano or pyridyl nitrogen atoms of the ligand bridging two metal centers. The present work may be the first example of the metal ions coordinated to the thiophene ring of the dithienylethene molecules, indicating that the silver(I) ion has relatively high affinity for sulfur donors.

Complexes **3**−**5** crystallized in the same space group and with the same formula as **1** and **2**. As in **1** and **2**, the [$Ag_2$-(*cis*-dbe)$X_2$] unit in **3**−**5** also involves a polymeric chain of the metal ions bridged sequentially by the dithienylethene moieties, and the bond lengths and angles around the distorted tetrahedral metal center are normal. However, each counteranion in **3**−**5** bridges two silver(I) ions not within a linear chain but between the two adjacent chains. As a result, the juxtaposed infinite chains are connected with fluorocarboxylate anions to give a two-dimensional sheet structure spreading on the *bc*-plane of the monoclinic cell as shown in Figure 2. Thus, in contrast with **1** and **2**, where the adjacent two linear chains are associated together through weak, nondirectional Ag···O interaction and $\pi-\pi$ interaction between the thiophene rings, the polymeric chains in **3**−**5** are cross-linked by the fluorocarboxylate anions, which leads to a stronger $\pi-\pi$ interaction between the thiophene rings of the two adjacent chains with distances of 3.45, 3.43, and 3.36 Å, respectively.

**Photochromic Behavior of the Silver(I) Complexes.** The photoirradiation process of *cis*-dbe and five silver(I) complexes was followed by electronic spectroscopy. The absorption spectra in the crystalline state were measured by diffuse reflection using barium sulfate as the reference and are illustrated in Figures 3 and 4. Upon mild irradiation (about 10 min) with 450 nm light, the yellow crystals of **1**−**5** turned orange or red while keeping the original crystalline shape, but after long time irradiation (about 1 h) they lost the surface

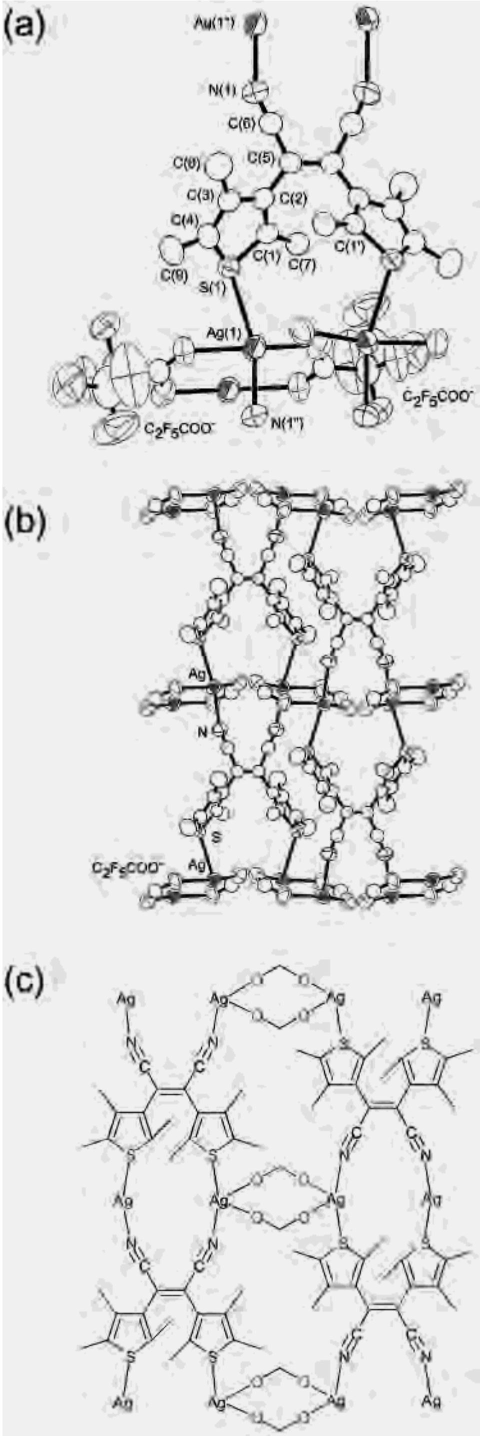

**Figure 2.** Crystal structure of **3**: (a) ORTEP view with an atomic labeling scheme, showing 50% thermal ellipsoids; (b) 2-D sheet structure ($C_2F_5$-groups are omitted for clarity); (c) schematic view of 2-D sheet structure in **3**−**5**.

luster and broke to pieces as concerns **2** and **3**. The orange or red species reverts to its initial yellow color by irradiation with visible light ($\lambda = 560$ nm), indicative of reversible photochromic behavior in the crystalline state.

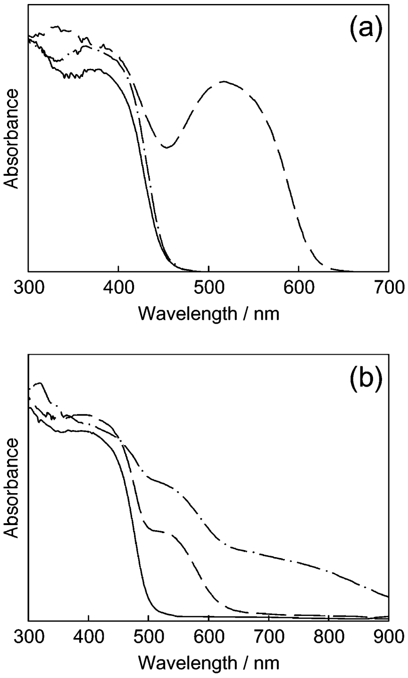

**Figure 3.** (a) Absorption spectra of *cis*-dbe before irradiation (solid line), after irradiation with 450 nm light (broken line), and further irradiation with 560 nm light (dot−dash line) in the crystalline phase. (b) Absorption spectra of **1** before irradiation (solid line), after irradiation with 450 nm light (broken line), and further irradiation with 450 nm light (dot−dash line) in the crystalline phase.

Figure 3b shows the absorption spectral change for **1**. Before irradiation, **1** has no absorption band around 520 nm. Upon irradiation with 450 nm light, the yellow crystals turned orange and an absorption was observed at 520 nm as a shoulder rather than as a clear band found at 520 nm in the spectrum of the irradiated metal free *cis*-dbe as depicted in Figure 3a. This suggests that for the photochromic chromophore the conversion ratio from the ring-opened form to the ring-closed form in **1** is low. Upon further irradiation with 450 nm light for a half-hour, the orange solid changed to brownish green, which results in a flattened shoulder at 520 nm and appearance of a new absorption at 700 nm. The photoisomerization process of **1** indicates that the ring-closed isomer is not stable under the ambient conditions.

In contrast, both **2** and **3** show a normal photochromic behavior as *cis*-dbe. After irradiation with 450 nm light both **2** and **3** display a clear absorption band at 513 and 520 nm, respectively, as shown in Figure 4a,b. Both absorptions maintained their intensity and position upon further irradiation with the same light source. It suggests that the ring-closed isomers of **2** and **3** in photostationary state are reasonably stable. By comparison, the photochromic behavior of **4** is very close to that of **1** and the complex **5** shows unique twin shoulders at 450 and 540 nm, respectively, after irradiation with 450 nm light, Figure 4c,d.

## Discussion

The photochromic reaction of the dithienylethene derivatives needs rotation of the two thienyl groups in a conrotatory mode.[3] In **1**−**5**, both thienyl groups in *cis*-dbe are fixed to antiparallel conformation by the coordination with two silver(I) ions. Concerning whether these synthesized complexes are favorable to undergo a reversible electrocyclization/ring-opening process, several factors should be considered: (1) The first is the distance between the two reacting carbons. These two C atoms, C(1) and C(1′) as shown in

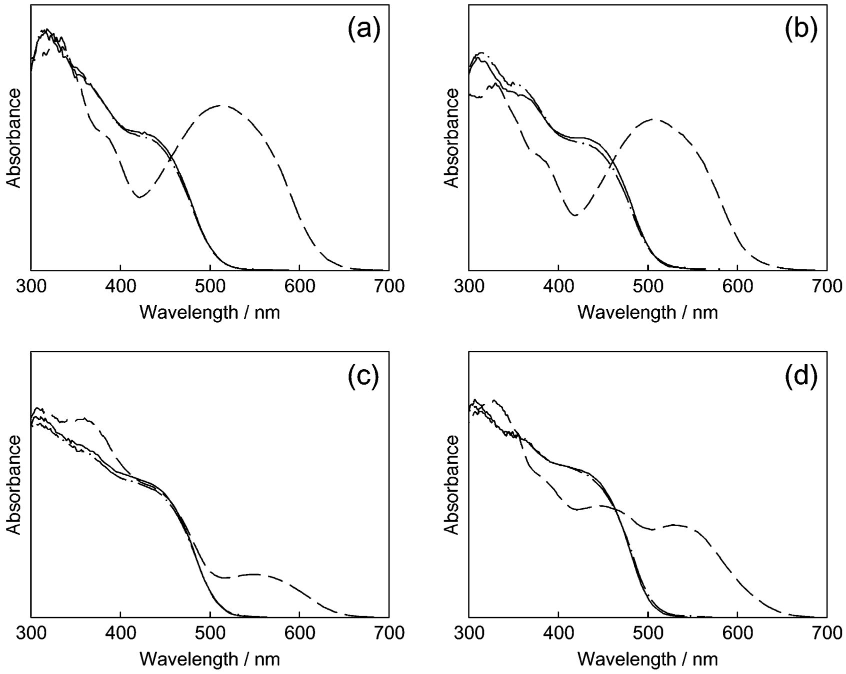

**Figure 4.** Absorption spectra of **2** (a), **3** (b), **4** (c), and **5** (d) before irradiation (solid line), after irradiation with 450 nm light (broken line), and further irradiation with 560 nm light (dot−dash line) in the crystalline phase.

Figures 1 and 2, where bridging occurs during cyclization, are 3.58, 3.51, 3.45, 3.48, and 3.47 Å apart for **1**−**5**, respectively, close enough for the reaction.[8] During the cyclization reaction, the two thiophene rings are required to approach each other by rotating along the C(2)−C(5) bond between the thienyl and ethylene groups. (2) Then, there is the bond strength between Ag and S atoms. As described above, all five complexes showed normal photochromism in the single-crystalline state despite the coordination of the two thienyl groups of dithienylethene with two silver ions. This finding is rather unexpected since the previously reported dithienylethene−metal complexes, where the two thienyl S atoms are not involved in coordination with the metal ions,[11,12] would suggest that the photochromism of these complexes is based on free rotation of the two thienyl groups. The bond distances of Ag−S in **1**−**5** are 2.52, 2.92, 2.83, 2.79, and 2.86 Å, respectively, and the rotation of the thienyl groups is considered to be more difficult as such bond becomes shorter. Therefore, complex **1** is considered to be less favorable in photochromic reaction compared with the others. (3) Finally, there is the magnitude of the steric hindrance during the rotation of the thiophene rings. In five silver(I) complexes, when two thiophene rings approach each other by rotating along the C(2)−C(5) bond during cyclization, the three methyl groups on the thiophene ring are subjected to the steric hindrance of the anionic fluorine atoms. The nearest distances between the methyl carbon, C(8), and the fluorine atom during the rotational process are 2.56 (**1**), 2.58 (**2**), 3.07 (**3**), 2.28 (**4**), and 2.36 (**5**) Å, respectively, which suggests that the methyl groups in complexes **4** and **5** encounter greater steric hindrance from the fluorine atoms.

From the above structural considerations, the *cis*-dbe moieties in complexes **2** and **3** are more liable to undergo photochromic reaction and have higher conversion ratio from the ring-opened form to the ring-closed form in the photostationary state. This finding is consistent with the different photoresponsive patterns of five complexes toward irradiation of light, Figures 3 and 4.

Compared with the metal-free *cis*-dbe in the photostationary state, the conversion ratio of the metal complexes increased by 13% for **2** and 8% for **3**, but those for **1**, **4**, and **5** showed a decrease of 56, 73, and 44%, respectively. Nevertheless, the precise mechanism for interconversion of the twisted ring-opened form and coplanar ring-closed form is not clear yet.

Virtually, the distance between the reacting carbons for cyclization and the extent of the steric hindrance for rotation of the thiophene rings in the crystalline phase is determined by the crystal packing, but the bond length of Ag−S is determined by the silver(I) coordination environment. As characterized above, each silver(I) ion in **1**−**5** is coordinated with one sulfur atom of the thiophene ring, one nitrogen atom from the cyano group, and two oxygen atoms of the anion. Thus, the Ag−S bond distances depend cooperatively on the Ag−O bond distances as long as the tetrahedral stereochemistry of the metal ion is maintained. The averaged bond lengths of Ag−O(1) and Ag−O(2) are 2.46 (**1**), 2.27 (**2**), 2.32 (**3**), 2.34 (**4**), and 2.31 (**5**) Å, respectively, which are plotted against the bond lengths of Ag−S in Figure 5. Despite the limited data and proximity of the bond distances, the two sets of data are in good qualitative agreement. The correlation, where the longest Ag−O bond length corresponds to the shortest Ag−S distance, appears to be borne out. In other words, the Ag−S bond distance, which influences the photochromic reactivity of the system, is controllable by the counteranion selecting.

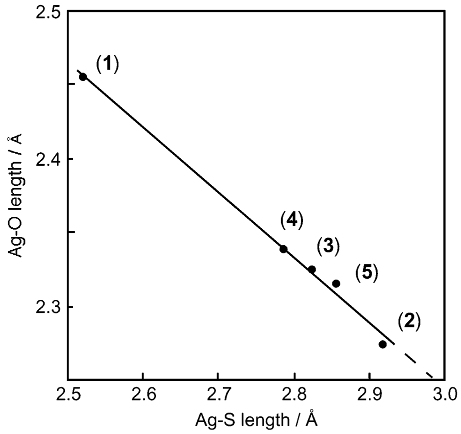

**Figure 5.** Correlation between the average bond lengths of Ag−S and Ag−O in **1**−**5**.

## Conclusions

It is hoped that this work will contribute to further understanding of the photochromic behavior of the coordination complexes. The study demonstrated that five silver(I)−diarylethene complexes consist of 1-D infinite chain or 2-D sheet networks and show different photochromic reactivity. The differences are attributable to the varied Ag−S bond distances involved and the steric hindrance encountered during the rotation of the thienyl ring. The structures resulting from this study, therefore, illustrate that the photoresponsive coordination compounds having high quantum yield and high conversion ratio in the photostationary state may be rationally synthesized by careful selection of the photochromic ligands, metal ions, and suitable counteranions. That should be investigated in a future program.

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**Supporting Information Available:** Stereoviews and X-ray crystallographic files, in CIF format, for the structure determinations of **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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