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Reversible photochromism of novel silver(I) coordination complexes with 1,2-bis(2'-methyl-5'-(2"-pyridyl)-3'-thienyl)perfluorocyclopentene in crystalline phase

Megumu Munakata ^{a,*}, Jing Han ^a, Atsuhiro Nabei ^a, Takayoshi Kuroda-Sowa ^a, Masahiko Maekawa ^b, Yusaku Suenaga ^a, Nozomu Gunjima ^a

^a Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka 577-8502, Japan ^b Research Institute for Science and Technology, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

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Abstract

Three novel silver(I) complexes with 1,2-bis(2-methyl-5'-(2"-pyridyl)-3'-thienyl)perfluorocyclopentene (BM-2-PTP) were synthesized by the reaction of $Ag(CF_3SO_3)$ or $Ag(CF_3COO)$ with BM-2-PTP in benzene at different temperatures. The structures of these metal complexes were revealed by X-ray crystallographic analyses and the correlation between crystal structures and photochromic performance was discussed. In complexes 1 and 2, silver(I) is three-coordinated to two nitrogens from distinct ligand molecules as well as one oxygen from anions to form a 1-D polymeric structure. On the other hand, complex 3 contains two crystallographic independent Ag(I) with different coordination environments, and the adjacent BM-2-PTP molecules are connected by $Ag-CF_3CO_2-Ag$ chains to afford a 1-D double chain structure. The difference in structures of three complexes shows the interesting anionic effect on coordination and the subtleness of crystal engineering. It is noted that complex 3 underwent reversible photochromic reaction in crystalline state despite the unfavorable framework to the rotation of thiophene groups.

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Keywords: Diarylethene; Photochromism; Crystalline phase; Ag(I) complexes

1. Introduction

Recently, photochromic compounds have attracted remarkable interests because of their potential application as photonic switch device, erasable-memory media, optical data storage and photo-drive actuators, due to their outstanding thermally irreversible and fatigue-resistant photochromic abilities [1–4]. Spirobenzopyrans, azobenzenes, fulgids and diarylethene moieties have been employed so far. Among these known photochromic systems, diarylethene bearing two thienyl-derived groups is the best candidate because it is especially well suited as switching units [5–9]. Furthermore, when metal ions are located at both ends of the thienyl groups of the diarylethenes, the interaction between metal ions can be switched by photoirradiation because the π -conjugated bond structures between the two thienyl groups are different in the open and closed isomers [10]. It has also been found that some dithienylethene complexes undergo photochromic reaction even in crystalline phase, showing its promising application value [11–17].

Previously, we reported a series of silver(I) coordination polymers with photochromic *cis*-1,2-dicyano-1,2-bis(2,4,5trimethyl-3-thienyl)ethene (*cis*-dbe), which shows an interesting anion effect on coordination modes and photoresponsive patterns [13]. In this work, we prepared a derivative of dithienylethene family, BM-2-PTP, namely, 1,2-bis(2'-methyl-5'-(2"-pyridyl)-3'-thienyl)perfluorocycl-

^{*} Corresponding author. Tel.: +81 6 6723 2332x4119; fax: +81 6 6723 2721.

E-mail address: munakata@chem.kindai.ac.jp (M. Munakata).

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opentene, which has sulfur and nitrogen protons and is favorable to coordinate with silver(I) in the assembly of various kinds of coordination polymers [13,18–23]. A similar photochromic ligand, BM-4-BTP (1,2-bis(2'-methyl-5'-(4"-pyridyl)-3'-thienyl)perfluorocyclopentene), was first prepared by Lehn's group in 1995 [7,17]. Recently, some metal complexes with BM-4-PTP were synthesized and their photoreactivities were studied both in solution and solid state [3,10,24–26]. Herein, we present three novel silver(I) complexes with BM-2-PTP characterized by X-ray crystallographic analysis. The phototogenerated behaviors of free ligand (BM-2-PTP) and three metal complexes were also investigated in crystalline state. All compounds displayed normal reversible photochromism in crystalline state when irradiated with appropriate light. The photochromism of complex 3 is especially striking, ascribed to the rigid double chain structure.

2. Experimental

2.1. General methods

Unless otherwise indicated, all starting materials were obtained from commercial suppliers (Aldrich, Tokyo Kasei Chemicals, and Kanto Chemicals) and used without further purification. 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.

2.2. Syntheses

2.2.1. 1,2-Bis(2'-methyl-5'-(2"-pyridyl)-3'-thienyl)perfluorocyclopentene (BM-2-PTP)

BM-2-PTP was synthesized using a modified literature method by employing 2-bromopyridine in the place of 4-bromopyridine hydrochloride [7], see Scheme 1. *Anal.* Calc. for $C_{25}H_{16}F_6N_2S_2$: C, 57.46; H, 3.09; N, 5.36. Found: C,

57.57; H, 3.10; N, 5.34%. IR (KBr pellet): 3067 (w), 2854 (w), 1590 (m), 1564 (m), 1555 (m), 1494 (m), 1455 (m), 1433 (m), 1275 (s). EI-MS: m/z (%): 522 ([M]⁺), 507 ([M–CH₃]⁺). ¹H NMR (CD₂Cl₂,270.5 MHz): $\delta = 1.98$ (s, 6H), 7.151–7.202 (m, 2H), 7.564 (m, 2H), 7.626–7.664 (m, 2H), 7.683–7.746 (m, 2H), 8.495–8.524 (m, 2H). UV–Vis (solid state) λ_{max} 340 nm: after irradiation with 340 nm light (solid state) λ_{max} 580 nm.

2.2.2. $[Ag(BM-2-PTP)(CF_3SO_3)](benzene)_{1.5}$ (1)

To a solution of AgCF₃SO₃ (10.6 mg, 40 µmol) in benzene (2 mL) was added a solution of BM-2-PTP (16.1 mg, 30 µmol) in benzene (2 mL). After mixing thoroughly, a white precipitate was recrystallized from THF to afford the colorless block single crystals suitable for X-ray analysis. *Anal.* Calc. for C₃₀H₂₀AgF₉N₂O₃S₃: C, 43.33; H, 2.42; N, 3.37. Found: C, 43.46; H, 2.65; N, 3.27%. IR (KBr pellet): 3071 (w), 2855 (w), 1595 (m), 1562 (m), 1494 (m), 1459 (m), 1434 (m), 1275 (s), 1060 (m), 1028 (m), 637 (m). UV– Vis (solid state) λ_{max} 340 nm: after irradiation with 340 nm light (solid state) λ_{max} 590 nm.

2.2.3. $[Ag(BM-2-PTP)(CF_3COO)](benzene)(H_2O)$ (2)

To a solution of AgCF₃COO (8.2 mg, 37 µmol) in benzene (5 mL) was added BM-2-PTP (18.7 mg, 35 µmol), and was then layered with a hexane solution. After standing at -30° C for 1 week, colorless block crystals were obtained at the interface between two solutions. IR (KBr pellet): 3051 (w), 2949 (w), 1590 (m), 1555 (m), 1494 (w), 1455 (w), 1433 (s), 1273 (s), 1191 (s), 1108 (s), 1059 (m), 985 (m), 777 (s). UV–Vis (solid state) λ_{max} 340 nm: after irradiation with 340 nm light (solid state) λ_{max} 575 nm.

2.2.4. $[Ag_2(BM-2-PTP)(CF_3COO)_2](benzene)$ (3)

The colorless needles of complex **3** were obtained similar to those of complex **2** at room temperature. *Anal.* Calc. for $C_{35}H_{22}Ag_2F_{12}N_2O_4S_2$: C, 40.33; H, 2.13; N, 2.69. Found: C, 39.80; H, 2.15; N, 2.71%. IR (KBr pellet): 3051 (w), 2949 (w), 1682 (s), 1591 (m), 1554 (m), 1494 (m), 1433 (m), 1273 (s), 1191 (s), 1109(s), 1060 (m), 985 (m), 777 (m). UV–Vis (solid state) λ_{max} 340 nm: after irradiation with 340 nm light (solid state) λ_{max} 570 nm.



Scheme 1. Synthesis of BM-2-PTP.

Table 2

2.3. X-ray data collection and structure solutions and refinements

Diffraction data for free ligand and complexes 1-3 were collected on a Ouantum CCD area detector coupled with a Rigaku MSC Mercury CCD diffractometer with graphitemonochromated Mo K α radiation ($\lambda = 0.71070$ Å). The intensity data were collected at 150 K using the multi-scan technique and a total of 5183, 8230, 7544 and 8808 reflections were collected for ligand and complexes 1-3, respectively. The linear absorption coefficient μ for Mo K α radiation is 2.99, 8.19, 8.22, and 12.17 cm^{-1}

The structures were solved by direct n by subsequent Fourier calculations [27]. T atoms were refined anisotropically for al final cycle of the full-matrix least-square based on 4538, 6914, 5064, 6998 observe 364, 478, 488, and 533 variable parameter complexes 1-3, respectively, converged wit and weighted agreement factors of R $\sum |F_{\rm o}|$ and $R_{\rm w} = \left[\sum w(F_{\rm o}^2 - F_{\rm c}^2)^2 / \sum w(F_{\rm o}^2)^2 \right]$ scattering factors and anomalous disper taken from the International Tables for X-ray Crystallography, vol. IV [28]. All calculations were performed using the teXsan crystallographic software package [29]. 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.

3. Results and discussion

3.1. Structural characterizations

3.1.1. BM-2-PTP

The crystal structure of metal free ligand was determined by X-ray crystallographic analysis, as depicted in

Table 1				
Crystallographic	data	for	complexes	1–3

n ⁻¹ , respectively.	$\operatorname{Hg}(1)$ $\operatorname{H}(2)$	2.237(4)
nethods followed	O(1)-Ag(1)-N(1)	105.0(2)
he non-hydrogen	$O(1^*)-Ag(1^*)-N(2)$	103.6(1)
l complexes. The	Ag(1)-N(1)-C(15)	116.0(3)
s refinement was	$Ag(1^*)-N(2)-C(25)$	117.0(4)
d reflections and	Complex 3	
ers for ligand and	Ag(1)-N(2)	2.247(4)
h the unweighted	Ag(1) - O(1)	2.432(3)
$P = \sum \ F\ = \ F\ /$	Ag(1)–O(3)	2.232(3)
$x = \sum_{ T_0 } - T_{c }$	$Ag(1) - O(1^*)$	2.494(4)
$\left[\right]^{1/2}$. The atomic	N(2)-Ag(1)-O(1)	99.6(1)
sion terms were	$O(3) = A \sigma(1) = O(1^*)$	96.0(1)

Symmetry codes: complex 1 (*) 1/2 + x, -1/2 + y, z; (#) -1/2 + x, 1/2 + xy, z; complex 2 (*) x, 1 + y, z; (#) x, -1 + y, z; complex 3 (*) x, 1 + y, z.

Fig. 1. The two thienyl rings of BM-2-PTP adopt antiparallel conformations with the dihedral angles of $59.6(2)^{\circ}$. The distance of 3.49 Å between two reactive carbons C(6)and C(16) is short enough for the occurrence of cyclization/cycloreversion in crystalline phase [30]. The mean dihedral angle between thiophene and pyridyl rings is 14.16°, indicating that the two groups slightly deviate from coplanar conformations.

	BM-2-PTP	Complex 1	Complex 2	Complex 3
Formula	$C_{25}H_{16}F_6N_2S_2$	C35H25AgF9N2O3S3	$C_{33}H_{24}AgF_9N_2O_3S_2$	$C_{35}H_{22}Ag_2F_{12}N_2O_4S_2$
Formula weight	522.53	896.63	839.54	1042.41
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (#14)	<i>C</i> 2/ <i>c</i> (#15)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	13.104(5)	15.831(5)	16.534(9)	13.886(5)
$b(\mathbf{A})$	9.330(4)	17.299(5)	11.223(5)	9.193(3)
c (Å)	18.906(8)	26.573(8)	18.761(10)	30.06(1)
β (°)	98.614(5)	98.956(3)	108.067(6)	102.930(4)
$V(Å^3)$	2285(1)	7188(3)	3309(2)	3864(2)
Ζ	4	8	4	4
$D_{\text{calc}} (\text{g/cm}^3)$	1.519	1.657	1.685	1.792
$\mu (\mathrm{mm}^{-1})$	2.99	8.19	8.22	12.17
Observed reflections with $[I > 2\sigma(I)]$	4538	6914	5064	6998
R ^a	0.041	0.049	0.072	0.059
R_w^{b}	0.089	0.101	0.146	0.111
Goodness-of-fit	1.08	1.11	1.09	1.10

^a $R = \sum ||F_{o}| - |F_{c}|| / \sum_{i=1}^{n} |F_{o}|.$

^b
$$R_w = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2\right]^{1/2}$$

$\frac{Complex 1}{Ag(1)-O(1)}$	2.1640(2)	Ag(1)–N(1)	2.184(3)
$\begin{array}{l} Ag(1) - N(2^{n}) \\ O(1) - Ag(1) - N(1) \\ O(1) - Ag(1) - N(2^{\#}) \\ Ag(1) - N(1) - C(15) \\ Ag(1^{*}) - N(2) - C(25) \end{array}$	2.171(3) 88.63(9) 105.86(9) 119.0(2) 115.6(2)	N(1)-Ag(1)-N(2 [#]) Ag(1)-N(1)-C(11) Ag(1 [*])-N(2)-C(21)	164.46(10) 122.6(2) 126.1(2)
Complex 2 Ag(1)–O(1) Ag(1*)–N(2)	2.396(5) 2.237(4)	Ag(1*)-N(1*)	2.244(4)
O(1)-Ag(1)-N(1) O(1*)-Ag(1*)-N(2) Ag(1)-N(1)-C(15) Ag(1*)-N(2)-C(25)	105.0(2) 103.6(1) 116.0(3) 117.0(4)	$\begin{array}{l} N(1) - Ag(1) - N(2^{\#}) \\ Ag(1) - N(1) - C(11) \\ Ag(1^{*}) - N(2) - C(21) \end{array}$	150.0(2) 126.0(3) 126.1(2)
Complex 3 Ag(1)-N(2) Ag(1)-O(1) Ag(1)-O(3) Ag(1)-O(1*)	2.247(4) 2.432(3) 2.232(3) 2.494(4)	Ag(2)–N(1*) Ag(2)–O(2) Ag(2)–O(4)	2.298(4) 2.243(4) 2.344(4)
N(2)-Ag(1)-O(1) O(3)-Ag(1)-O(1*) O(2)-Ag(2)-O(4) O(4)-Ag(2)-N(1*)	99.6(1) 96.0(1) 127.4(1) 93.4(1)	N(2)-Ag(1)-O(3) O(1)-Ag(1)-O(1*) O(2)-Ag(2)-N(1*)	164.9(1) 77.1(1) 126.3(1)

Selected bond lengths (Å) and angles (°) for complexes 1-3



Fig. 1. ORTEP view with an atomic labeling scheme of BM-2-PTP, showing 50% thermal ellipsoids.

3.1.2. Complexes 1 and 2

According to X-ray crystallographic analysis, complex 1 is a one-dimensional polymer as shown in Fig. 2. Selected bond distances and bond angles were listed in Table 2. The basic coordination structure of complex 2 is similar to complex 1, except the different anions. In one unit, silver(I) is three-coordinated by two pyridine nitrogens from two distinct BM-2-PTP and one oxygen atom from triflate or trifluoroacetate, respectively, showing a distorted T-shaped coordination geometry with the N-Ag(1)-N



Fig. 2. Crystal structure of complex 1. (a) ORTEP view with an atomic labeling scheme, showing 50% thermal ellipsoids (b) Schematic view of 1-D chain structures.

bond angle of $164.46(1)^{\circ}$ for complex 1 and $150.0(2)^{\circ}$ for complex 2, respectively (Fig. 3). The Ag–N bond lengths in both complexes fall within the expected values [31-39]and are shorter than those of silver(I) complexes with cisdbe [13]. For comparison, the Ag–N distances of complex 1 [Ag(1)-N = 2.171(3)-2.184(3) Å] are shorter than those of complex 2 [Ag(1)-N = 2.237(4)-2.244(4) Å]. On the other hand, the Ag–O distance of complex 1 [2.640(2) Å] is longer than that of complex 2 [2.396(5) Å]. The difference of bond length between complexes 1 and 2 is well explained by the fact that the three-coordination complexes deviated from regular trigonal planar, and are compensated for by regulating their bond distances [40]. In addition, the length between Ag(1) and S(1) is 2.96–3.06, and 2.88 Å in complexes 1 and 2, respectively, which is longer than the common values of Ag-S bond [18,23,41-45] indicating the weak Ag. . . S interaction. Further the two thienyl rings in both complexes 1 and 2 adopt an antiparallel fashion with the dihedral angles of $64.1(2)^{\circ}$ and $62.0(1)^{\circ}$, and the distance between the two reactive carbons C(6) and C(16) is 3.63 and 3.57 Å in complexes 1 and 2, respectively, which is slightly longer than that of metal free ligand [3.49 Å] and Ag(I) complexes with *cis*-dbe [3.45–3.58 Å], but still short enough to undergo photocyclization [30]. The mean torsion angles between thiophene and perfluorocyclopentene rings [C(2)-C(1)-C(7)-C(6)] and C(1)-C(2)-C(17)-C(1C(16)] are 53.35° and 51.36° for complexes 1 and 2, respectively, which are responsible for the differences in the distance between reactive carbons. The mean rotation angles between thiophene and pyridyl ring [C(8)-C(9)-C(11)-C(12) and C(18)-C(19)-C(21)-C(22)] are 33.01° and 28.26° for complexes 1 and 2, respectively.

3.1.3. Complex 3

Complex 3 was obtained using the same procedure as complex 2 at 25 °C. Interestingly, the structure of complex 3 is significantly different from complex 2 as determined by X-ray crystallographic analysis (Fig. 4). The asymmetric unit contains two crystallographically unique Ag(I) centers: the first one is coordinated by one nitrogen from one ligand [Ag(1)-N(2) = 2.247(4) Å] and three oxygen atoms from three different triflate anions [Ag(1)-O = 2.232(3)-2.464(4) Å], showing a distorted tetrahedral structure of $[O_3N_1]$ donor set. The second one has a three-coordinate



Fig. 3. Coordination environment of complex 1 (a) and complex 2 (b).



Fig. 4. Crystal structure of 3. (a) ORTEP view with an atomic labeling scheme, showing 50% thermal ellipsoids (b) Schematic view of 1-D double chain structures. Symmetry codes: (') 1 - x, 2 - y, -z; (#) x, -1 + y, z; (A) 1 - x, 1 - y, -z; (B) 1 - x, 3 - y, -z.

structure of $[O_2N_1]$ donor set and is defined by one nitrogen from another ligand $[Ag(2)-N(1^*) = 2.298(4) \text{ Å}]$ and two oxygen atoms from triflate anions [Ag(2)-O(2) = 2.243(4) Å, Ag(2)-O(4) = 2.344(4) Å]. The two crystallographically independent Ag(I) ions are coupled in pairs through Ag-O-C-O-Ag bonds to form a $[Ag_2O_4C_2]$ unit, which are bridged by Ag-O bonds to give two unit chains. In turn, each BM-2-PTP molecule links two Ag-CF₃CO₂-Ag chains through N atoms to afford a 1-D double chain structure. The bond lengths of Ag-N and Ag-O in complex **3** are well within the ranges of those of photochromic Ag(I) complexes with *cis*-dbe [13]. The Ag-S distance of 2.860(1) and 3.006(1) Å is a little longer than the common distances observed for an Ag-S bond, indicating weaker interaction.

In complex 3, the two thiophene rings of ligand run antiparallel to each other with the dihedral angles of $61.0(1)^{\circ}$. The length between the reactive carbons is as short as 3.55 Å, which is the shortest of the three complexes corresponding to the smallest torsion angles of 48.43° between thiophene and perfluorocyclopentene rings, implying the effective photochromism in crystals.

Silver(I) salts with counterions such as perchlorate $(ClO_4^{-}),$ triflate $(CF_{3}SO_{3}^{-}),$ and trifluoroacetate (CF_3COO^-) exhibit labile coordination modes [19,20]. In this work, the counteranions were chosen as triflate and trifluoroacetate and they are coordinated to Ag(I) metal centers in three complexes to generate different structures. For photochromic Ag(I) complexes with *cis*-dbe, the structures of Ag(I) complexes with triflate and trifluoroacetate are isomorphous with near-isostructural unit. Complexes 1 and 3, which were prepared using different counteranions at room temperature, have quite distinct structure showing that the anions virtually have direct influence on the molecular structures. Complexes 2 and 3 were synthesized at different temperatures to give different structures, respectively, indicative of the subtleness of crystal engineering. All complexes have indispensable antiparallel conformations and short reactive distances, which govern the photochromic reaction in crystals suggesting the possible photoreactivities in crystalline phase.

3.2. Photochromism in crystalline phase

The photoirradiation process of BM-2-PTP and three silver(I) complexes were 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 Fig 5. All complexes are insoluble in common solvent due to polymer structures.

3.2.1. Photochromism of BM-2-PTP

The photochromic reaction of free ligand (BM-2-PTP) was examined in solid state. Colorless powders of BM-2-PTP have a strong absorption at 340 nm before irradiation. Upon irradiation with 340 nm light, the sample changed color to blue and a new strong peak at 580 nm was observed, indicating that the open form was transferred to closed form, and the blue color originated from the closed form (Fig. 5(a)). After photostationary state is reached, the blue color of closed isomer converted to the initial color with irradiation of 580 nm light. The absorption of 580 nm gradually flattened, suggesting that reversible photochromism occured in crystalline phase (Scheme 2). The λ_{max} of 580 nm of the closed isomer in solid state is much longer than that of cis-dbe, which was observed at 513 nm in CCl₄ and 520 nm in solid state, respectively [13,46].

3.2.2. Photochromism of complexes 1–3

As described above, both thienyl groups of ligand in complexes 1–3 are packed into antiparallel conformations. The distances between the two carbon atoms, C(6) and C(16), where a σ bond is formed during cyclization, are 3.63, 3.57, and 3.55 Å for complexes 1-3 respectively, and



Fig. 5. Absorption spectral changes of BM-2-PTP (a), complex 1 (b), complex 2 (c), and complex 3 (d). Open form (solid line), closed form (broken line).



Scheme 2. Photochromic reaction of BM-2-PTP in solid state.

are close enough for the ring-closure. These essential conditions are favorable for the occurrence of photochromic reaction in solid state. Fig. 5(b)–(d) shows the absorption spectral changes of complexes 1–3, respectively. Before irradiation, complexes 1–3 have the same shoulder at ca. 340 nm, which is agreeable with the shoulder of free ligand. Upon irradiation with 340 nm light, the colorless crystals of three complexes turned blue and a new intense absorption at 590, 575, and 570 nm was observed for complexes 1–3, respectively, indicative of the formation of the closed-form conformers. The blue species reverted to their initial color by further irradiation with 590, 575, and 570 nm light, respectively, indicative of the reversible photochromic properties in crystalline phase. Compared with the free ligand, bathochromic shift of 10 nm was observed on the λ_{max} value of closed form of complex **1**. While the λ_{max} values of closed form of complexes **2** and **3** moved to shorter wavelength due to an increase in the strain upon complexation [10,11]. The λ_{max} values of all Ag(I) complexes with BM-2-PTP are longer than those of complexes with *cis*-dbe (513–560 nm), which correspond to the longer λ_{max} of BM-2-PTP (580 nm) than *cis*-dbe (520 nm).

The thiophene rings are required to approach each other by rotating along the C–C bond between thiophene and ethylene moieties during the cyclization process upon irradiation [12–15]. In crystals, the molecules are packed in fixed antiparallel conformation, which increases the photochromic reactivity greatly, but meanwhile, a marked rotation is prohibited. Among the metal complexes with photochromic cis-dbe, some Cu(I), Mo(II) and Rh(II) complexes fail to undergo the photochromic reactions due to various reasons, such as parallel conformation, steric hindrance of the counteranions and/or thienvl rings being coordinated to the metal center [12–15]. In the present study, all complexes underwent the effective reversible photochromism in crystalline state. In complex 3, BM-2-PTP is incorporated into double chain framework and thus the rotation of thiophene group from the twisted ring-opening form to coplanar ring-closed form will be hindered by the rigidity of the framework and packing. Moreover, the neighboring chains in complex 3 were connected by sharing two Ag(I) atoms of the [Ag-CF₃CO₂-Ag]₂ chain, which further suppressed the free rotation of thiophene rings. In spite of these adverse features of complex 3, the reversible photochromic reaction proceeded in a crystalline state and the circles of coloration/decoloration can be repeated many times, which demonstrate the excellent fatigue resistance and the reasonable stabilities of complex 3. Although we also found that some 1-D chain and 2-D sheet Ag(I) complexes of *cis*-dbe underwent photochromism even with S atoms bonded to metal atoms in the previous studies, no double chain structure as complex 3 had been witnessed [13]. This finding is of special interest as it indicates the possibility of combining the photochromic properties with versatile functions arising from the construction of MOFs. This strategy may give rise to new multi-functional materials and will be applied in the rational design of novel photochromic compounds in a later program.

4. Conclusions

Three novel silver(I) complexes with photochromic BM-2-PTP were prepared and their photochromic properties in crystalline phase were studied. Complexes [Ag(BM-2-[Ag(BM-2-PTP) PTP)(CF₃SO₃)](benzene)_{1.5} (1) and (CF_3COO) (benzene) (H_2O) (2) were determined as onedimensional polymers and the metal ions are coordinated to N atoms from ligand and O atom from anion, whereas in [Ag₂(BM-2-PTP)(CF₃COO)₂](benzene) (3), two unique silver(I) have different coordination geometries to form a one-dimensional double chain structure. The difference in structures of complexes 1 and 3 showed an interesting anion effect as observed in silver(I) complexes with cisdbe. Moreover, complexes 2 and 3 were obtained in the same solvent but at different temperatures, indicating the minor difference of syntheses condition due to different structures. All complexes contain essential antiparallel thiophene rings and short distances between bridging carbons during ring-closure process, and subsequently display reversible photogenerated behavior in crystalline state upon appropriate excitation although the structures differ from each other. The results obtained here provide a proof that a photochromic complex based on dithienylethene could undergo an effective ring-closure/ring-opening reaction induced by light with rigid coordination geometry. This finding has inspired us to combine the construction of MOFs with photochromic ligand and the strategy will be addressed in further studies.

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Appendix A. Supplementary material

Crystallographic data for the X-ray crystal structural analysis have been deposited with the Cambridge Crystallographic Data Center, Nos. (0155) 602805–602808 for BM-2-PTP and complexes 1–3, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1233 336 033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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