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Article

Silver(I) Coordination Polymers of Fluorescent Oligo(phenylenevinylene) with π–π Stackings: Luminescence and Conductivity

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Three luminescent silver(I)–oligo(phenylenevinylene) complexes, $[Ag_2(bmsb)(ClO_4)_2]$ (**1**), $[Ag_2(bmsb)(H_2O)_4](BF_4)_2$ (**2**), and $[Ag_2(bdb)(CF_3SO_3)_2]$ (**3**) (bmsb = 1, 4-bis(methylstyryl)benzene, bdb = 4,4′-bis(2, 5-dimethylstyryl)biphenyl), have been synthesized and structurally characterized. Complexes **1** and **2** are 2D networks with unique metallocyclophane motifs. Complex **3** affords a 2D zigzag sheet, in which silver triflates form tubelike double chains and bdb molecules act as linkages. Complex **2** exhibits high electric conductivity because of columnar aromatic stackings formed through intra- and intermolecular π–π interactions. Complexes **1**–**3** in the solid state exhibit luminescence, of which excitation and emission maxima are shifted to longer wavelength as compared to those of the corresponding metal-free ligands.

Introduction

Conjugated organic π-systems in rings and chains have captured considerable interest from many research groups and have been used to construct intriguing organometallic complexes with potential application in nonlinear optics, electronics, and molecular electronics.[1−9] The delocalized π-bridges provide an effective pathway for electronic transfer between the two metal centers across these bridging ligands. In the past decade, polyenes and polycyclic aromatic hydrocarbons have been extensively employed to develop metal−organic frameworks with novel structures and conductive properties.[1,10−20] Oligo(phenylenevinylene) is another kind of π-conjugated compound.[21,22] However, nothing is known about the reaction behavior toward transition metal ions, although the polymeric oligo(phenylene)-ynes contain-

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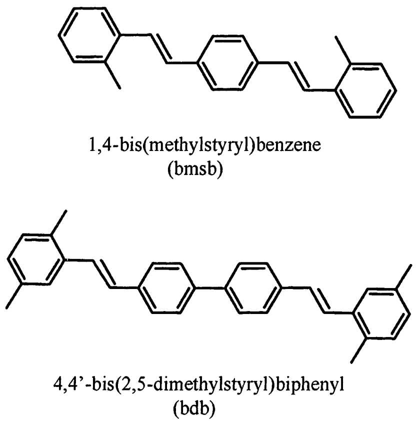
Chart 1



1,4-bis(methylstyryl)benzene
(bmsb)

4,4'-bis(2,5-dimethylstyryl)biphenyl
(bdb)

ing transition metals in the main chain were synthesized.[5−7,23,24] In recent years, we have been interested in the construction of silver(I) complexes with π-conjugated polycyclic aromatic hydrocarbons and polyenes.[1,2,10,11,19,20] As an extension of these studies, two fluorescent oligo(phenylenevinylene)s, 1,4-bis(methylstyryl)benzene (bmsb), and 4,4′-bis(2,5-dimethylstryryl)biphenyl (bdb) were selected as ligands in this study (Chart 1) to construct the luminescent silver(I) coordination polymers with aromatic stackings. The reaction of bmsb and bdb with different silver(I) salts afforded three novel luminescent silver(I) coordination polymers: $[Ag_2(bmsb)(ClO_4)_2]$ (**1**), $[Ag_2(bmsb)(H_2O)_4](BF_4)_2$ (**2**), and $[Ag_2(bdb)(CF_3SO_3)_2]$ (**3**). The single-crystal structures, conductivity, and luminescent properties were investigated in this paper.

Experimental Section

General Procedures. All reactions were carried out under an argon atmosphere by using the usual Schlenk techniques. Toluene and tetrahydrofuran (THF) were distilled by standard method prior to use and stored under argon. Reagent grade silver(I) perchlorate, silver(I) tetrafluoroborate, and silver(I) trifluoromethanesulfonate were purchased from Aldrich. Bmsb and mesitylene were obtained from Wako Chemicals Co., Ltd., while bdb was purchased from Lancaster Co., Ltd. All chemicals were used as received without further purification. IR spectra were recorded with KBr disks on a JASCO FT/IR 8000 spectrometer. UV−visible absorption spectra were recorded in reflectance mode (in solid state) and in CH_2Cl_2 at a concentration of 2×10^{-5} M on a UV-2400PC/2450 UV−visible spectrophotometer and presented uncorrected. Excitation and emission spectra were recorded on JASCO FP-6500/6600 fluorescence spectrophotometer, using band pathways of 1 nm of excitation and 1 nm of emission for both the solid state and the liquid state (in 2×10^{-5} M of CH_2Cl_2). The electrical conductivity of compacted pellets was measured by the conventional two-probe technique at room temperature.

Caution: Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

Synthesis. $[Ag_2(bmsb)(ClO_4)_2]$ (1). A solution of $AgClO_4 \cdot H_2O$ (23 mg, 0.1 mmol) in 7.5 mL of toluene was added to bmsb (30 mg, 0.1 mmol). After being stirred for 10 min, the resultant solution was introduced into a 7 mm diameter glass tube and layered with *n*-pentane as a diffusion solvent. The glass tube was sealed under argon and wrapped with tin foil. After the glass tube was allowed to stand at room temperature in a dark room for 3 days, yellow block crystals of **1** were obtained. Yield: 11 mg (1.6×10^{-2} mmol, 31%). Anal. Calcd for $C_{24}H_{22}Ag_2Cl_2O_8$: C, 39.76; H, 3.06. Found: C, 39.46; H, 2.91.

$[Ag_2(bmsb)(H_2O)_4](BF_4)_2$ (2). Similar to the synthesis of **1**, to a solution of $AgBF_4$ (12 mg. 0.06 mmol) in 4 mL of mesitylene was added bmsb (19 mg, 0.06 mmol). After being stirred for 5 min, the resultant solution was filtered. The filtrate was introduced to a 7 mm diameter glass tube and layered with *n*-pentane. The glass tube was kept at room temperature for 3 days. Yellow block crystals suitable for single-crystal X-ray analysis, corresponding to **2**, were obtained. Yield: 7 mg (8.5×10^{-3} mmol, 28%). Anal. Calcd for $C_{24}H_{30}Ag_2B_2F_8O_4$: C, 37.35; H, 3.92. Found: C, 37.69; H, 3.79.

$[Ag_2(bdb)(CF_3SO_3)_2]$ (3). Mixing of $AgCF_3SO_3$ (51.4 mg, 0.2 mmol) and bdb (41.5 mg, 0.1 mmol) in 5 mL of THF produced a solution that was stirred for 20 min. The resultant solution was introduced to a glass tube and layered with *n*-hexane. After the mixture was left standing at 50 °C in a dark room for 1 month, yellow block crystals of **3** were obtained. Yield: 34 mg (3.6×10^{-2} mmol, 36%). Anal. Calcd for $C_{34}H_{30}Ag_2S_2F_6O_6$: C, 43.98; H, 3.26. Found: C, 43.70; H, 3.49.

X-ray Data Collection and Structure Solutions and Refinements. A suitable single crystal was fixed on a glass fiber, and diffraction data were collected at −123 °C for complexes **1** and **2**, and 22 °C for complex **3** on a Rigaku/MSC Mercury CCD area detector diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) by the ω scan mode. A symmetry-related absorption correction was applied which resulted in transmission factors ranging from 0.55 to 0.68 for **1**, from 0.74 to 0.85 for **2**, and from 0.72 to 0.88 for **3**, respectively. All intensity data were corrected for Lorentz and polarization effects. Additionally, a correction for secondary extinction was applied for **2**.

The structures were solved by direct methods,[25] expanded using Fourier techniques,[26] and refined by full matrix least-squares analysis on F using the TEXSAN package.[27] All of the full-occupancy non-hydrogen atoms were refined anisotropically. Hydrogen atoms of all of the structures were introduced in their calculated positions. They were included but not refined in the refinement. Details of X-ray experiment and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results and Discussion

Characterization and IR Spectra of the Products. The reaction of bmsb and bdb with silver(I) salts readily afforded the complexes **1**−**3**, which are stable at room temperature

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Table 1. Crystallographic Data for Complexes **1**−**3**

	1	**2**	**3**
formula	$C_{12}H_{11}AgClO_4$	$C_{24}H_{30}Ag_2B_2F_8O_4$	$C_{34}H_{30}Ag_2S_2F_6O_6$
fw	362.54	771.84	928.45
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$P2/n$
a, Å	8.017(3)	8.954(2)	12.588(2)
b, Å	10.106(6)	8.220(1)	5.0727(5)
c, Å	7.949(3)	20.057(3)	28.600(4)
α, deg	89.586(7)		
β, deg	78.930(4)	105.106(7)	101.229(7)
γ, deg	68.85(2)		
V, Å^3	588.2(5)	1425.3(4)	1791.4(4)
Z	2	2	2
ρ, g/cm^3	2.047	1.798	1.721
μ, cm^{-1}	19.38	14.51	12.80
measd reflns (unique)	2614	3171	4104
obsd reflns [$I > 2\sigma(I)$]	2520	2850	3175
parameters	196	182	226
R_1[a]	0.042	0.066	0.051
R_w[b]	0.092	0.184	0.102

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **1**−**3**

Complex **1**			
Ag(1)−O(1)	2.430(3)	Ag(1)−O(3)*	2.575(4)
Ag(1)−C(3)	2.479(4)	Ag(1)−C(4)	2.482(4)
Ag(1)−C(8)*	2.412(3)	Ag(1)−C(9)*	2.350(4)
O(1)−Ag(1)−O(3)*	90.0(1)	O(1)−Ag(1)−C(3)	91.3(1)
O(1)−Ag(1)−C(4)	87.8(1)	O(1)−Ag(1)−C(8)*	136.8(1)
O(1)−Ag(1)−C(9)*	112.2(1)	O(3)*−Ag(1)−C(3)	81.9(1)
O(3)*−Ag(1)−C(4)	114.4(1)	O(3)*−Ag(1)−C(8)*	113.1(1)
O(3)*−Ag(1)−C(9)*	96.6(1)	C(3)−Ag(1)−C(4)	32.7(1)
C(3)−Ag(1)−C(8)*	126.4(1)	C(3)−Ag(1)−C(9)*	156.4(1)
C(4)−Ag(1)−C(8)*	112.1(1)	C(4)−Ag(1)−C(9)*	143.4(1)
C(8)*−Ag(1)−C(9)*	33.2(1)		
Complex **2**			
Ag(1)−O(1)	2.374(5)	Ag(1)−O(2)	2.34(1)
Ag(1)−C(4)	2.629(6)	Ag(1)−C(5)	2.469(6)
Ag(1)−C(10)*	2.533(4)	Ag(1)−C(12)″	2.472(4)
O(1)−Ag(1)−O(2)	107.3(3)	O(1)−Ag(1)−C(4)	125.3(2)
O(1)−Ag(1)−C(5)	94.6(2)	O(1)−Ag(1)−C(10)*	110.8(2)
O(1)−Ag(1)−C(12)″	89.5(2)	O(2)−Ag(1)−C(4)	92.2(3)
O(2)−Ag(1)−C(5)	95.6(3)	O(2)−Ag(1)−C(10)*	93.6(2)
O(2)−Ag(1)−C(12)″	124.3(2)	C(4)−Ag(1)−C(5)	31.7(2)
C(4)−Ag(1)−C(10)*	118.5(1)	C(4)−Ag(1)−C(12)″	120.7(2)
C(5)−Ag(1)−C(10)*	149.0(2)	C(5)−Ag(1)−C(12)″	136.5(2)
C(10)*−Ag(1)−C(12)″	32.4(2)		
Complex **3**			
Ag(1)−O(1)	2.376(3)	Ag(1)−O(2)′	2.449(3)
Ag(1)−O(3)″	2.603(3)	Ag(1)−O(3)*	2.569(3)
Ag(1)−C(12)	2.389(4)		
O(1)−Ag(1)−O(2)′	85.4(1)	O(1)−Ag(1)−O(3)″	82.35(9)
O(1)−Ag(1)−O(3)*	132.00(9)	O(1)−Ag(1)−C(12)	128.8(1)
O(2)′−Ag(1)−O(3)″	130.21(9)	O(2)′−Ag(1)−O(3)*	78.01(9)
O(2)′−Ag(1)−C(12)	115.0(1)	O(3)″−Ag(1)−O(3)*	75.3(1)
O(3)″−Ag(1)−C(12)	110.1(1)	O(3)*−Ag(1)−C(12)	98.8(1)

under ambient light for several days. Infrared spectroscopy is a good indicator of incorporation of metal ions into the oligo(phenylenevinylene) systems. The infrared spectra were recorded in the region 4000−400 cm^{-1} on KBr disks. Bmsb and bdb have several very distinctive signals, including the region from 2855 to 3030 cm^{-1}, which contains the C−H stretching absorptions. A second region, from 1414 to 1510 cm^{-1}, consists of three to four intense signals, corresponding to the in-plane vibrations of C═C bonds. All of these are present in the infrared spectra of **1**−**3**. In addition, strong absorptions of ν(OCl) at 1088−1144 cm^{-1} for **1**, ν(BF) at 1036−1083 cm^{-1} for **2**, and ν(CF) at 1170−1270 cm^{-1} for **3** were exhibited, respectively. The corresponding strong absorption of ν(OH) for complex **2** appeared at 3540 cm^{-1}, confirming the presence of a water molecule in the compound.

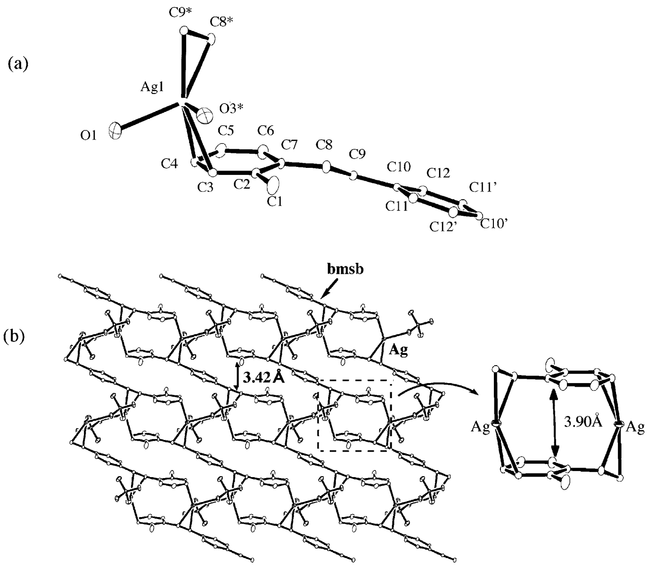

Figure 1. (a) Part of the molecular structure and atom labeling of **1**, showing the environment of the silver center. All H atoms, noncoordinated O, and Cl atoms are omitted for clarity. (b) 2D sheet network of **1** along the *ab* plane, showing intermolecular $\pi-\pi$ interactions and metallocyclophane motifs.

Description of Structure. [Ag_2(bmsb)(ClO_4)$_2$] (1). The crystallographic studies revealed that complex **1** exists in the solid state as a 2D polymer. Figure 1a depicts a view with atom numbering of the molecule. Each silver(I) ion is η^2-bonded to the terminal phenyl moiety of one bmsb molecule and the C═C bond of the vinylene fragment from another bmsb, respectively, to form an interesting 12-membered metallocyclophane as shown in Figure 1b (right). Two oxygen atoms from different perchlorate groups complete the remaining sites around the silver(I) ion with Ag−O distances of 2.430(3) and 2.575(4) Å. The Ag−(η^2-C═C) bonds with 2.479(4) [Ag(1)−C(3)], 2.482(4) Å [Ag(1)−C(4)] and 2.412(3) [Ag(1)−C(8)*], 2.350(4) Å [Ag(1)−C(9)*] are typical for this type of bonding,[1,2,10,11,20] while they are much longer than those of the silver(I) complex which feature η^2-bound acetylide units (Ag−C 2.324 Å).[23] Each bmsb is symmetrically π-bonded to four crystallographically equivalent silver atoms with two above and two below it, respectively. Thus, a 1D chain with metallocyclophane motifs is formed by silver atoms linking bmsb molecules. Moreover, such chains are bridged by perchlorate groups through dinuclear octatomic ring $Ag_2O_4Cl_2$, with an Ag···Ag distance of 5.67 Å, to create a 2D sheet network (Figure 1b (left)). The intramolecular distance of 3.9 Å indicates no intramolecular $\pi-\pi$ interactions in metallocyclophane motifs, but interchain $\pi-\pi$ interactions exist between the phenyl and C═C moiety (the shortest spacing: 3.42 Å).

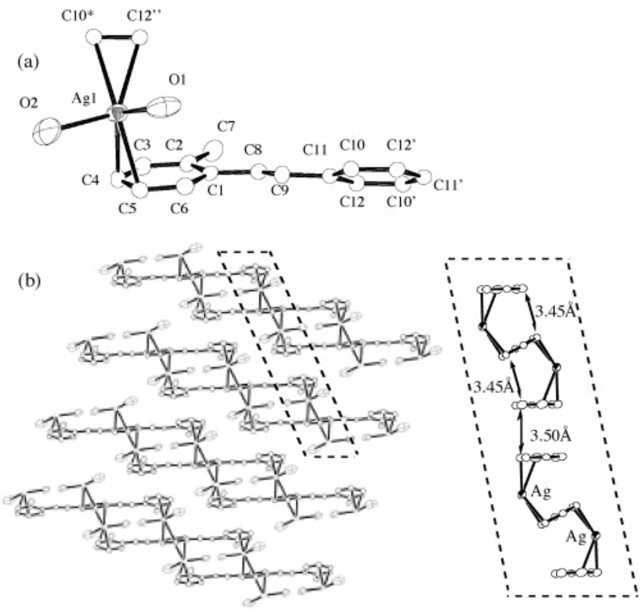

Figure 2. (a) Part of the molecular structure and atom numbering of **2**. (b) 2D network of **2** along the *ab* plane (left), showing strong $\pi-\pi$ interactions between intra- and interchains to form columnar aromatic stackings (right). All H atoms and BF_4 groups are omitted for clarity.

$[Ag_2(bmsb)(H_2O)_4](BF_4)_2$ (2). Figure 2a indicates a portion of the molecular structure of **2**, in which each silver(I) ion is coordinated to a middle phenyl moiety of one bmsb molecule, and a terminal one of another bmsb to give a 1D chain structure. In contrast to **1**, two waters are coordinated to silver(I) ion in place of ClO_4^- anions because BF_4^- anion did not take part in coordination in **2**. The water probably comes from silver(I) tetrafluoroborate due to its easily adsorption of water at ambient atmosphere. The Ag−O distances in **2** are 2.34(1) and 2.374(5) Å, which are shorter than those of **1**, indicative of strong interactions between oxygen and silver. On the other hand, the Ag−C bond lengths from 2.469(6) to 2.629(6) Å are longer than those of **1**. Unlike polymer **1**, the silver(I) ions in polymer **2** failed to be coordinated to the vinylene fragment of bmsb, which is presumably due to the strong Ag−O interactions resulting in the weak Ag−C interactions so that phenyl motifs have a preference of coordinating to the silver(I) center over the vinylene fragments. Each bmsb exhibits μ-tetra-η^2 coordination, and two such ligands are held face to face in an offset fashion by two bridging silver(I) ions to generate a 16-membered metallocyclophane motif. There are strong $\pi-\pi$ interactions between both intrachains (the shortest spacing: 3.45 Å) and interchains (the shortest spacing: 3.50 Å) to form columnar aromatic stackings as shown in Figure 2b. The intramolecular $\pi-\pi$ interactions between neighboring phenyl groups are formed at the end part, opposite to the metal coordination site because the coordination of phenyl groups to silver(I) ions makes them come close to each other (Figure 2b (right)). The overall structure thus formed is a 2D polymeric framework via columnar aromatic stackings involving metallocyclophane motifs (Figure 2b (left)), which is the most remarkable feature of complex **2**.

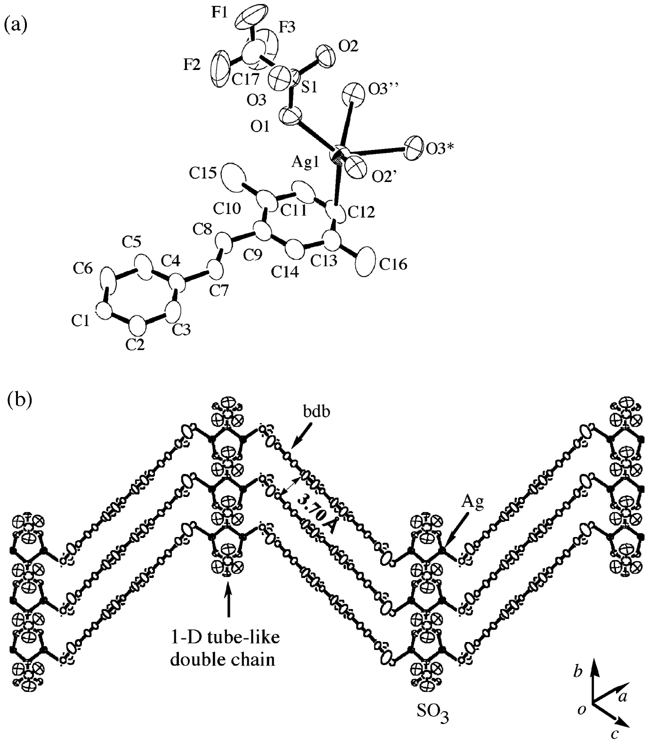

Figure 3. (a) Part of the molecular structure and atom numbering of **3**. (b) 2D zigzag sheet structure of **3**.

$[Ag_2(bdb)(CF_3SO_3)_2]$ (3). The structure of **3** features a 2D zigzag sheet made up of $AgCF_3SO_3$ tubelike chains separated by l bdb molecules as shown in Figure 3b. Each bdb molecule links two adjacent tubelike chains by one bridging silver(I) ion at the head and the tail of bdb, respectively, through the μ-di-η^1 coordination mode. Each silver ion acquires its coordination number of five by forming bonds with one terminal phenyl group of bdb and four oxygen atoms of different triflates (see Figure 3a). As observed in the complex of tphb (=1,1,4,4-tetraphenyl-1,3-butadiene) with $AgCF_3SO_3$,[28] each triflate anion is bonded to four metal centers with Ag−O bond lengths ranging from 2.376(3) to 2.603(3) Å. The average distance between bdb molecules is 3.70 Å, which is beyond the distance for significant $\pi-\pi$ interactions.

The polymeric silver(I)−oligo(phenylene)-yne complex containing platinum atoms in the main chain was obtained and exhibited 1D zigzag chain, which is formed by silver(I) triflates linking *trans*-$[Pt](C\equiv CPh)_2$ $\{[Pt] = (Ph_3P)_2Pt\}$, due to the bulky phenyl padents.[23] The present three silver(I)−oligo(phenylenevinylene) complexes, however, show 2D sheet frameworks in which the acyclic ligands are parallel to each other in an offset mode.

Discussion

We have obtained three silver(I) complexes with oligo(phenylenevinylene) bmsb and bdb. It is noteworthy that complexes **1** and **2** show structural similarities to cyclophanes, and hence can be regarded as metallocyclophane

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structures, in which silver(I) ions act as bridges. Although the cyclophane theory is well established,[29] most reported cyclophane species have C, O, S, or N atoms in the bridges.[30] To the best of our knowledge, only two polymeric frameworks were found to show metallocyclophane motifs in the reported metal-bridged conjugated π-system compounds,[2,20] and the present polymers **1** and **2** are the third report on metallocyclophane structures. In general, flexible organic ligands can be used to construct metallocyclophane structures because the formation of metallocyclophane frameworks often makes ligands bend or twist. For example, in the previously reported metallocyclophane structure of [Ag$_{0.5}$(btp)$_{0.5}$(ClO$_4$)$_{0.5}$] (btp = 1,2-benztriphenylene)[2], or [Ag$_2$(dpot)(ClO$_4$)$_2$] (dpot = 1,8-diphenylocta-1,3,5,7-tetraene),[20] the btp and dpot molecules were bent inward. In the present complexes **1** and **2**, the C=C bond angles of bmsb (vinylene fragment) were twisted by 21.03° and 27.64°, respectively, indicative of the flexibility of bmsb. This finding indicates that oligo(phenylenevinylene) might be a rich field to develop supramolecular argentophane architecture. In addition, columnar $\pi-\pi$ stackings involving metallocyclophane units can exhibit very high conductivity as described later.

The present three complexes were obtained under the different experimental conditions such as counteranion, solvent, or temperature. The additional complexes of bmsb or bdb and silver salts, for example, that of bmsb and silver triflate, were not obtained, which indicates the formation of coordination networks is complicated by counteranions and solvents as well as ligand geometry and temperature.[31,32]

All UV−vis absorption spectra for both free ligands and complexes **1**−**3** were recorded in reflectance mode in solid state at room temperature as shown in Figure 4. The absorption bands profile for complexes **1** and **2** are very similar. The transitions at 444, 445, and 451 nm in the spectra of **1**−**3**, respectively, are assigned as $\pi^* \leftarrow \pi$ transitions of bmsb (for **1** and **2**) and bdb (for **3**). The absorption maxima of **1**−**3** are red-shifted as compared to those of the corresponding free ligands. Figure 5 shows the excitation and emission spectra for both the free ligands and complexes **1**−**3** in the solid state at room temperature. The excitation maxima for bmsb and bdb are at $\lambda_{\max} = 418$ and 419 nm, and the maxima for complexes **1**−**3** are at $\lambda_{\max} = 446$, 444, and 448 nm, respectively, which are consistent with those of absorption in UV−vis spectra. The emission maxima are at $\lambda_{\max} = 453$ and 472; 442 and 462; 485; 488; and 477 nm for bmsb, bdb, and complexes **1**−**3**, respectively. Complexes **1**−**3** exhibit a red-shift for both excitation and emission maxima in the solid state as compared to the corresponding free ligand values. Thus, the presence of the silver does cause a significant change in the UV−vis absorption spectra and emission spectra of the ligands[33] in the solid state.

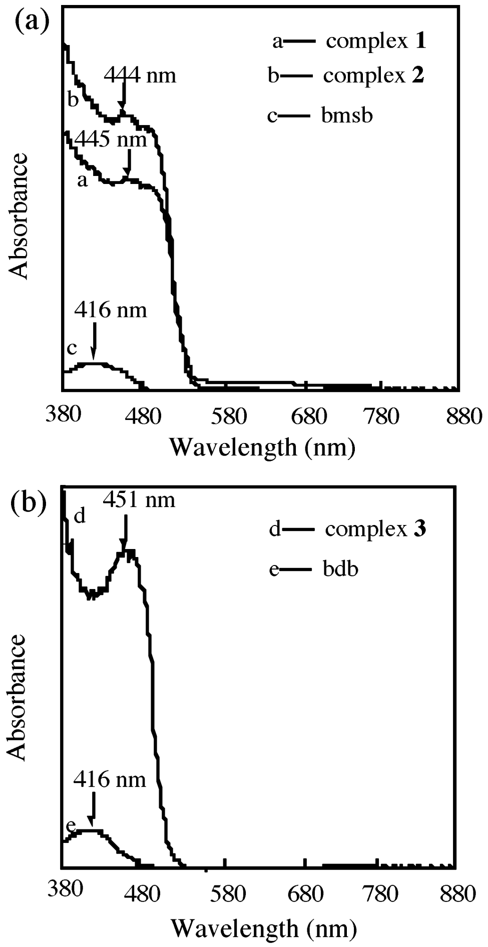

Figure 4. UV−vis absorption spectra of (a) ligand bmsb, **1** and **2**; and (b) ligand bdb and **3** in reflectance mode for the solid at room temperature.

Generally, the fluorescence intensity of a complex is decreased greatly when the energy received by ligand is partially lost. The intensity of emission of the present three complexes is of interest in the connection of $\pi-\pi$ interactions. We tried to measure the intensity in solution to make a quantitative comparison. The intensity was not, however, measured in solution because there is no good solvent in which the complexes **1**−**3** are dissolved without dissociation (see Supporting Information, Figure S1).

The electric conductivity of complexes **1**−**3** was measured via the silver-coated two-probe technique with compacted pellets at room temperature. Complex **2** gives a high electric conductivity of $\sigma = 1.2 \times 10^{-2}$ S cm^{-1} due to the columnar

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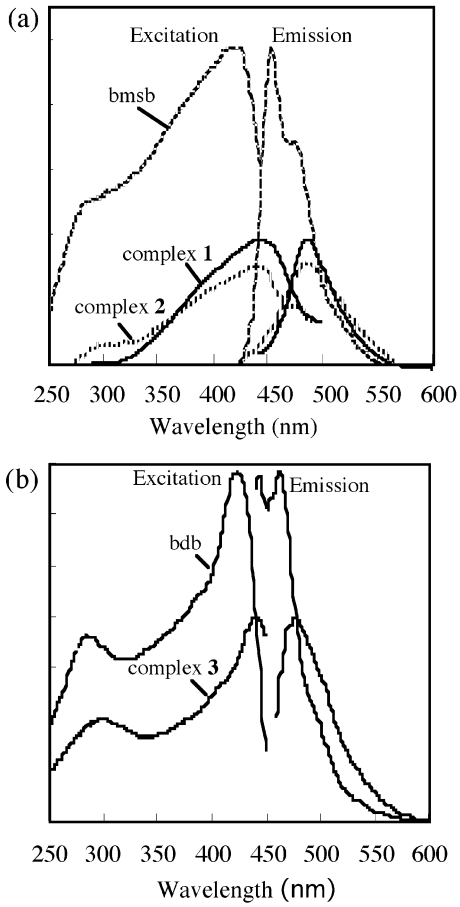

Figure 5. Excitation and emission spectra at room temperature in the solid state for (a) ligand bmsb, **1** and **2**, and (b) ligand bdb and **3**. Bmsb, bdb, and **1**−**3** were excited at 418, 419, 446, 444, and 448 nm, respectively.

stackings of phenyl groups with intra- and intermolecular $\pi-\pi$ interactions, which is unique despite the small size of the aromatic ring of the phenyl groups in comparison with pyrene[34] or coronene.[35] Complex **1** exhibits low conductivity ($\sigma = 1.0 \times 10^{-6}$ S cm^{-1}) because of only intermolecular $\pi-\pi$ interactions. Complex **3** is an insulator because of the absence of $\pi-\pi$ interactions. These results illustrate that columnar aromatic stackings with strong intra- and intermolecular $\pi-\pi$ interactions could give high conductivity (complex **2**).

Conclusions

We have demonstrated here three luminescent silver(I) complexes with fluorescent oligo(phenylenevinylene) bmsb and bdb. To the best of our knowledge, this is the first report on silver(I) complexes of oligo(phenylenevinylene). All complexes display luminescence in the solid state, which are red-shifted for both the excitation and the emission maxima as compared to those of the corresponding free ligands, due to the coordination of ligand to the silver(I) center. Complex **2** exhibits high conductivity, complex **1** is semiconductive, while complex **3** is insulator. Silver(I) complex with columnar aromatic stackings gives high conductivity. Further studies will be focused on the effect of various classes of oligo(phenylenevinylene) and their substituted groups on the reactivity of silver(I) with oligo(phenylenevinylene), and novel silver(I)−oligo(phenylenevinylene) complexes with much higher conductivity are anticipated.

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Supporting Information Available: Crystallographic data in CIF format and additional figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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