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## A Novel, Highly Electrical Conducting, Single-Component Molecular Material: $[\text{Ag}_2(\text{ophen})_2]$ (Hophen = 1*H*-[1,10]phenanthrolin-2-one)

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Considerable research effort in chemistry has been focused on molecular conducting and superconducting materials.<sup>1–7</sup> Electron donor–acceptor complexes featuring condensed aromatic hydrocarbons were found around 1950,<sup>2</sup> but it was the discovery of metallic conduction<sup>3</sup> in molecular charge-transfer salts of the tetrathiafulvalene (TTF) in 1973 that set off a new flurry of intense activity.<sup>1</sup> These transition-metal complexes with dithiolene ligands, most frequently, act as anionic counterions in charge-transfer solids with a variety of donors. On the other hand, the organosilver(I) systems containing polycyclic aromatic hydrocarbon ligands with cation– $\pi$ -ligand interactions also displayed interesting electrical or magnetic properties associated with electron delocalization and electronic cooperative interactions;<sup>4,5</sup> however, they commonly act as the cationic components in charge-transfer solids and are not single-component molecular conducting materials. In other words, the coexistence of a donor molecule and an acceptor molecule seemed to be a prerequisite for design of electrical conducting molecular metals.<sup>1</sup> Thus, the spontaneous generation of free carriers in the molecular crystal composed of single-component molecules seemed almost impossible.<sup>6</sup> Until the mid-1990s, sporadic reports appeared in the literature<sup>7</sup> on neutral transition-metal complexes with dithiolene ligands which are all TTF-like compounds with strong interactions between the large and polarizable sulfur atoms, demonstrating that the hope of achieving metallic states in crystals consisting of single-component molecules is running high, although it is still challenging.<sup>6</sup> Very recently, we hydrothermally prepared a series of copper complexes with a novel 1*H*-[1,10]phenanthrolin-2-one (Hophen) ligand,<sup>8</sup> which features a large aromatic group. In this communication, we report the preparation and crystal structure of a novel, highly electrical conducting, single-component molecule  $[\text{Ag}_2(\text{ophen})_2]$  (**1**) with a non-TTF-dithiolate type ligand. The compacted intermolecular aromatic  $\pi$ – $\pi$  stacking interactions and significant interactions between the Ag(I) ion and aromatic group contribute to its electrical conducting behavior.

The pale-yellow crystalline neutral **1**<sup>9</sup> was synthesized by the reaction of  $\text{AgNO}_3$  (0.017 g, 0.10 mmol) in MeCN (5 mL) with Hophen·0.5*H*<sub>2</sub>O<sup>10</sup> (0.041 g, 0.10 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) via the liquid diffusion method [yield: ca. 62% based on silver], which is stable toward air and photodegradation, and is virtually insoluble in water and common organic solvents. Thermal analyses show that **1** is stable up to ca. 380 °C in N<sub>2</sub> atmosphere and starts to decompose at this temperature after an exothermic peak. The structure of **1** has been established by crystallography.<sup>11</sup>

As shown in Figure 1, each Ag(I) ion features a T-shaped geometry, being coordinated by two nitrogen atoms from an ophen ligand [Ag(1)–N 2.227(3) and 2.385(3) Å] and one oxygen atom from another ophen ligand [Ag(1)–O(1) 2.161(3) Å]. The intramolecular Ag(I)···Ag(I) distance is 2.801(1) Å, which is signifi-

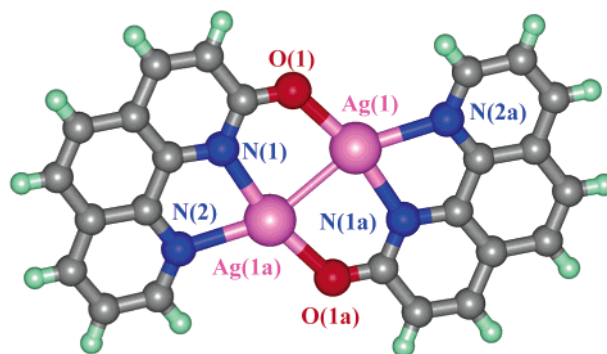


Figure 1. Perspective views showing the molecular structure of **1**.

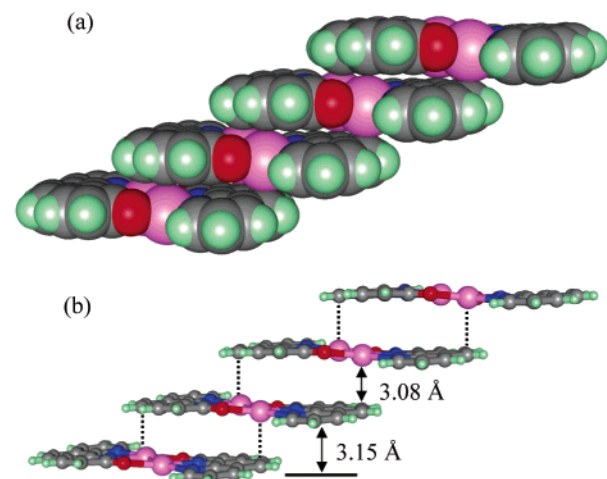


Figure 2. Perspective views showing the compacted aromatic  $\pi$ – $\pi$  stacking interactions and significant interactions between the Ag(I) ion and aromatic group in **1**. (a) Space-filling model; (b) ball-and-stick model.

cantly shorter than the Ag···Ag separation of 2.88 Å in the metallic state, indicating a very strong Ag···Ag interaction.<sup>12</sup> It should be noted that adjacent molecules of **1** are stacked through the very strong, offset  $\pi$ – $\pi$  aromatic stacking interactions<sup>13</sup> with the face-to-face distance of ca. 3.15 Å to furnish staircase-like one-dimensional (1-D) arrays running along the *b*-axis direction. The 1-D arrays are further extended into 2-D layers along the (101) planes (see Figure S1 in the Supporting Information) via the intermolecular C–H···O hydrogen bonds between the ophen oxygen atoms and aromatic C–H groups (C9···O1 3.29 Å).<sup>14</sup>

A very significant structural feature of **1** is the offset face-to-face distance of only ca. 3.15 Å between adjacent molecules (Figure 2), which is extremely short between two adjacent aromatic rings.<sup>13</sup> Moreover, the closest Ag···C contact between adjacent molecules is only 3.082 Å. This contact is a slightly longer than those found for silver(I) complexes of other polycyclic aromatic compounds;<sup>4,5</sup>

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however, it is still shorter than the sum of van der Waals radii (3.11 Å) of Ag(I) ion and carbon atom,<sup>15</sup> implying significant Ag(I)– $\pi$  interaction. It should be pointed out that the coexisting phenomenon of strong  $\pi$ – $\pi$  stacking and Ag(I)– $\pi$  interactions in **1** has not been observed for the other organosilver(I) complexes.<sup>4,5</sup> Similar to the other Ag(I)– $\pi$  complexes,<sup>4,5</sup> neutral **1** exhibits a sharp ESR signal with  $g = 2.00$  at room temperature, attributable to the aromatic radicals, as well as a very broad ESR signal centered approximately at  $g \approx 2.05$  at 8.5 K indicating the formation Ag(0) or Ag(II) species (see Figure S2 in the Supporting Information). We may therefore suggest that the electron transfer takes place between adjacent molecules via two possible pathways: Ag(I)– $\pi$  and  $\pi$ – $\pi$  interactions,<sup>4,13</sup> resulting in the formation of organic radicals and Ag(0) or Ag(II) species,<sup>4a</sup> which may be proved by the spin density of 0.02% for the organic radicals, estimated from the comparison with 2,2-di(4-tert-octylphenyl)-1-picrylhydrazyl (DPPH) standard at room temperature.<sup>16</sup> The above-mentioned observations imply that both the electron donor and acceptor (required<sup>1</sup> to form a crossing band for the charge-transfer salts) have been achieved in a single molecule of **1**. Therefore, the solid of **1** is different from those of multicomponent organosilver(I) systems with Ag(I)– $\pi$  interactions.<sup>4</sup>

The room-temperature conductivities of **1** and the free ligand Hophen in compacted pellets were measured by the conventional two-probe technique, which showed a considerable conductivity ( $\Omega = 14 \text{ S cm}^{-1}$ ) for the brownish-yellow powder of **1** but negligible conductivity for Hophen. It is noteworthy that all documented conducting single-component molecular materials are transition-metal complexes of sulfur-containing  $\pi$ -delocalized dithiolene ligands, i.e., TTF-like metal complexes.<sup>6,7</sup> Therefore, the neutral **1** here is the first highly electrical conducting, single-component molecule material with non-TTF-dithiolate type ligand. It is quite obvious that in **1** the requirements<sup>6</sup> for designing single-component, neutral molecular metals have partially been fulfilled, such as a small HOMO–LUMO<sup>17</sup> energy gap, large 3-D transverse intermolecular interactions, and possibly the formation of parallel bands. Different from the intermolecular S...S contacts in other electrical conducting TTF-type single-component molecules,<sup>6,7</sup> the strong transverse interactions in **1** are the very strong  $\pi$ – $\pi$  stacking interactions and Ag(I)– $\pi$  interactions, which play an essential role to decrease the HOMO–LUMO gaps, providing the  $\pi$ -to- $\pi^*$  and  $\pi$ -to-metal/metal-to- $\pi^*$  electron-transfer pathways. To our knowledge, most of the room-temperature conductivity of Ag(I)– $\pi$  materials are usually much lower than the highest conductivity ( $1.32 \text{ S cm}^{-1}$ )<sup>4b</sup> in the Ag(I)– $\pi$  materials reported.<sup>4</sup> Thus, **1** is hitherto the highest-conducting molecular material based on the  $\pi$ – $\pi$  stacking interactions and Ag(I)– $\pi$  interactions.

In summary, we have prepared and characterized the first highly conducting, single-component molecular material based on very strong  $\pi$ – $\pi$  stacking interactions and Ag(I)– $\pi$  interactions, different from the TTF-type and multicomponent Ag(I)– $\pi$  materials. A single component, i.e., the molecule of **1**, can serve simultaneously as an electron donor and an electron acceptor. Thus, this work suggests a new strategy for the construction of electric conducting materials based on cation– $\pi$ -ligand and  $\pi$ – $\pi$  stacking interactions.

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**Supporting Information Available:** Additional figures and tables of crystallographic data (PDF) and an X-ray crystallographic file, in CIF format for the structure determinations of **1**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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