[17] ICL-1 crystallizes from a mixture of composition Ga_2O_3:4H_3-PO_4:4.25$NH_3(CH_2)_4NH_3$:4HF:70H_2O after standing at 50 °C in a covered Teflon tube for 20 days. The Ga_2O_3 was prepared by thermal decomposition of hydrated gallium(III) nitrate (99.9%, Aldrich) at 220 °C for 18 h; powder X-ray diffraction showed this material to be amorphous. H_3PO_4 (85% in water), and 1.4-diaminobutane were supplied by Aldrich and HF (40% in water) by BDH.

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A One-Dimensional Metallocyclophane with Columnar Aromatic Stacking: The Silver(I) η^2-Coordination Complex of 1,2-Benztriphenylene[**]

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Cation–π interactions between metal ions and polycyclic aromatic hydrocarbons (PAHs) provide a powerful tool for building novel molecular architectures and allow the introduction of a wide variety of useful electrical and electrochemical properties.[1–5] With the aim of designing new solids with structural diversity and desirable physical and chemical properties, we synthesized a number of organosilver(I) complexes of PAHs with remarkable features, such as W-type sandwiches,[2, 6] helical structures,[7] and double-decker,[5] triple-decker,[7] and multidecker frameworks.[5] In spite of these achievements, complexes with high conductivity are very rare. The dependence of the electrical conductivity of the complexes on the manner in which their aromatic rings are stacked has not been investigated. Here we present the unprecedented supramolecular architecture of the *para*-metallocyclophane polymer $[Ag_{0.5}(btp)_{0.5}(ClO_4)_{0.5}]$ (**1**; btp = 1,2-benztriphenylene), which shows an interesting cyclophane structure,[8] unusual aromatic interactions, and high electrical conductivity.

Cyclophanes form an important class of organic molecules. Since the first report on the synthesis of [2.2]paracyclophane (**2**), in which two benzene rings are held face to face by methylene bridges,[8a,b] the attractively simple naming of **2** led to the development of the cyclophane nomenclature for bridged aromatic compounds.[9] Complex **1** shows interesting structural similarities to cyclophanes such as **2**, [2.2](2.7)pyrenophane (**3**),[10] and the like,[8, 10–15], and hence can be regarded as a metallocyclophane, in which metal ions form the bridges. The silver(I) ions and the T-shaped planar btp ligand are assembled into a stacked structure with high electrical conductivity.

The reaction of btp with $AgClO_4$ in *p*-xylene leads to formation of **1**. The X-ray structural determination[16] revealed a one-dimensional framework held together by cation–π interactions between Ag^I and btp and perchlorate

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anions. The coordination sphere around the silver(I) ion is tetrahedral (taking the C=C group as one ligand) and is made up of two C=C π bonds and two oxygen atoms from two symmetry-related btp ligands and perchlorate anions, respectively (Figure 1). The Ag–O and Ag–C distances are almost equal, being 2.487(2) Å for O(3/3′), 2.423(3) Å for C(8), and 2.436(3) Å for C(7). Each btp moiety exhibits μ-di-η^2 coordination, and two such moieties are held face to face by two bridging silver(I) ions to generate a metallocyclophane motif, which is further linked to its adjacent counterpart by bridging O atoms of the perchlorate ions (Ag-O(3/3′)-Ag) to form a polymeric chain structure. Between chains, aromatic $\pi-\pi$ stacking occurs with an interplanar separation of 3.48–3.64 Å. The overall structure thus formed is a two-dimensional polymeric metallocyclophane framework involving columnar aromatic stacks (Figure 2a).

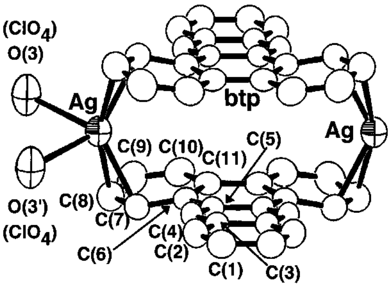

Figure 1. Structure of **1**.

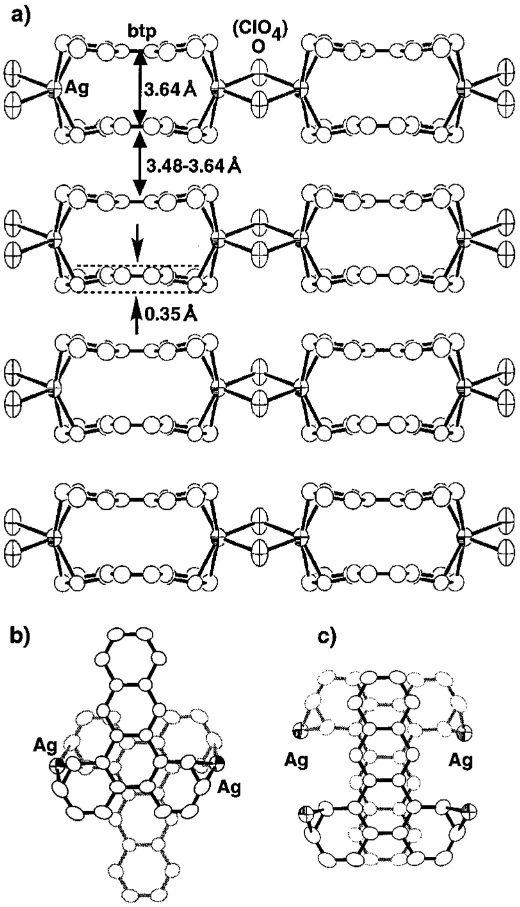

Figure 2. Columnar aromatic stacking in **1** with $\pi-\pi$ interactions within and between polymeric chains (a) and intra- (b) and intermolecular overlap (c) of btp ligands (black and gray lines represent the upper and lower btp molecules, respectively).

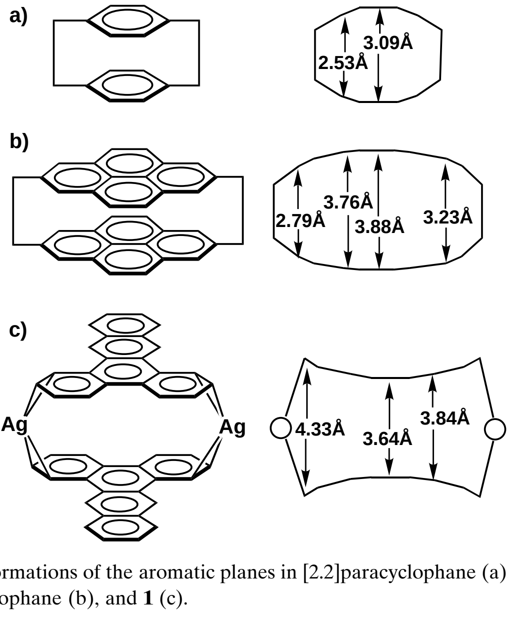

Figure 3. Deformations of the aromatic planes in [2.2]paracyclophane (a), [2.2](2.7)pyrenophane (b), and **1** (c).

Although the cyclophane theory is well established,[9, 17] most reported cyclophane species have C, O, S, or N atoms in the bridges. In the few reported metal-bridged aromatic compounds,[18, 19] no polymeric framework was found, and the metal ions interact with aromatic rings in an η^6 fashion[18] or form O-M-O linkages.[19] In **1**, the btp molecules participate in di-η^2 bonding to the silver(I) ions to form a polymeric metallocyclophane structure which, to the best of our knowledge, is unprecedented.[2, 5–7, 20] Interestingly, apart from structural similarities to organic cyclophanes, compound **1** also displays noticeable differences in its configuration. For organic cyclophanes **2** and **3**, the methylene-bridged aromatic moieties exhibit an out-of-plane deformation, and the intraplanar seperations vary from 2.53 and 2.79 Å at the sides to 3.09 and 3.80 Å at the center, respectively (Figure 3a, b). This indicates strong intraplanar repulsion between the overlapping aromatic rings caused by the conjugation of the bridging carbon atoms with aromatic rings.[6, 9] In contrast, the btp molecules in **1** are bent inward by 0.35 Å, and the intraplanar distances vary from side to center from 4.33 to 3.64 Å (Figures 2a and 3c). This indicates the existence of interplanar attraction. Such an attractive force may be attributable to the tetrahedral coordination environment of the silver(I) ions, which leads to Ag–btp bond angles and lengths suitable for the intraplanar aromatic $\pi-\pi$ interaction. In addition, complex **1** also exhibits interchain aromatic $\pi-\pi$ interactions with interchain distances of 3.48–3.64 Å in the columnar aromatic stacking along the *c* axis (Figure 2a). This is in sharp contrast to the crystal structures of **2** and **3**, in which no intermolecular contact shorter than the sum of the van der Waals radii was found.

The most remarkable feature is the recognition of silver(I) ions and the interesting assembly pattern of btp molecules to form a unique supramolecular argentophane architecture, which gives rise to a high conductivity. The silver(I) ions in **1** are symmetrically coordinated to C(7/7′) and C(8/8′) on both sides of the head of the T-shaped btp ligand to form a stable cyclophane structure (Figures 1 and 3c). Such coupling brings about a head-to-head connection of the pair of btp ligands in each argentophane moiety (Figure 3c) and results in an alternating tail-up and tail-down arrangement of the aromatic rings along the columnar aromatic stacks. The complex thus assembled exhibits alternating overlap of intra- and interaromatic moieties (Figure 2b, c), which contribute to the strong aromatic $\pi-\pi$ interactions.

As a result of this a columnar aromatic stacking of the metallocyclophane framework, **1** shows unusual conductivity. The electrical conductivity of a compacted pellet, measured by a two-probe technique with silver-paste-coated probes, showed the highest reported conductivity of all organosilver(I) complexes of PAH ligands with $\sigma = 1.32\,\mathrm{S\,cm^{-1}}$ at room temperature, although btp itself is nonconducting. We found that the conductity of silver(I) π complexes of PAH ligands is strongly dependent on inter- and/or intramolecular aromatic stacking. Complexes with weak or no aromatic stacking, such as those with discrete monomeric, W-type sandwich, or helical structures,[6, 7] have very low conductity ($\sigma = 0-1 \times 10^{-5}\,\mathrm{S\,cm^{-1}}$). In multilayer complexes with triple- or multidecker frameworks[5–7] and strong inter- and/or intramolecular aromatic $\pi-\pi$ interactions, higher σ values of 1.6×10^{-3} to $6.9 \times 10^{-2}\,\mathrm{S\,cm^{-1}}$ can be obtained, depending on the coordination or stacking mode. It is noteworthy that complex **1** exhibits ESR signals with a g value of about 2.002, attributable to the aromatic radicals[21].

Further studies directed toward the synthesis of other metallocyclophanes to establish the relationship between the structure and the electrical properties are underway.

Experimental Section

$AgClO_4 \cdot H_2O$(45 mg, 0.2 mmol) was added to a solution of btp (11.1 mg, 0.04 mmol) in *p*-xylene (4 mL). The solution was stirred for about 15 min and then transferred to a 7-mm glass tube and layered with *n*-hexane. The tube was sealed under Ar and wrapped in aluminum foil. After standing at room temperature for 1 d yellow prismatic crystals were obtained.

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