Spiral, Herringbone, and Triple-Decker Silver(I) Complexes of Benzopyrene Derivatives Assembled through η^2-Coordination

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Three novel silver(I) complexes with benzopyrene derivatives were synthesized and characterized in this paper. Treatment of $AgClO_4{\bullet}H_2O$ with 7-methylbenzo[*a*]pyrene (L^1) afforded $[Ag_2(L^1)(toluene)_{0.5}(ClO_4)_2]_n$ (**1**) which exhibits a 2-D sheet structure with double-stranded helical motifs. Reaction of $AgCF_3SO_3$ with dibenzo[*b*,*def*]chrysene (L^2) gave rise to an unprecedented cocrystallization structure, $\{[Ag_2(L^2)(CF_3SO_3)_2][Ag_2(toluene)_2(CF_3SO_3)_2]\}_n$ (**2**), formed by a 2-D neutral lamellar polymer and a 1-D neutral rodlike one. The ligand benzo[*e*]pyrene (L^3) coordinated to silver(I) ions generating a closed triple-decker tetranuclear complex $[Ag_4(L^3)_4(p\text{-xylene})(ClO_4)_4]$ (**3**) which can be regarded as a stacking polymer owing to existing intermolecular $\pi-\pi$ stack interactions. The structural diversity of the silver(I) coordination polymers with polycyclic aromatic hydrocarbons is not only related to the stacking patterns of free polycyclic aromatic hydrocarbons in the crystalline state, but also the geometric shapes of the molecules for these free ligands. In addition, the coordination of solvents to metal ions plays a crucial role in the formation of the unprecedented coordination polymeric architectures. The ESR spectroscopic results, conductivity, and synthesis properties are also discussed.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent an important family of organic molecules, and rich polycyclic aromatic chemistry has stimulated a renaissance of interest in the study of synthesis, coordination, property, and theory for aromatic systems.[1,2] Many polycyclic aromatic hydrocarbons have been employed as exceptional donor molecules or as acceptor molecules for affording donor−acceptor complexes or charge-transfer molecular complexes owing to their extended delocalized π system and low ionization energy.[3,4,5] On the other hand, cation-π interactions between metal ions and polycyclic aromatic hydrocarbons have received considerable attention in the synthesis of coordination compounds mainly due to the potential of introducing a variety of useful electric and electrochemical properties and giving rise to novel molecular architectures.[2a,2d−e,6−12] Generally, metal ions are coordinated to polycyclic aromatic hydrocarbons or other planar cyclic ligands such as cyclopentadiene and its derivatives to afford a variety of sandwich complexes.[12a,13]

The synthesis and design of supramolecular coordination polymeric architectures attracts considerable attention currently

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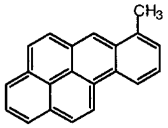
and is dominated by selection of molecular building blocks, i.e., ligand structures and metal ion coordination spheres.[14] Polycyclic aromatic hydrocarbons, by virtue of the fact that they possess multiple ring sites and coordination versatility such as η^1, η^2, η^3, η^4 and η^6 modes,[6e−f,10] can often form a number of intriguing transition metal complexes. Silver(I) also exhibits a coordinative diversity when coordinated to organic ligands,[15] and its complexes with smaller aromatic hydrocarbons have been well-documented, such as benzene,[6a−c] toluene,[6d] *o*-xylene,[6e] *m*-xylene,[6f] mesitylene,[6g] 1,4-benzodioxan,[16] indene,[7a] cyclohexylbenzene,[7b] ancenaphthene,[7c] ancenaphthylene,[7c] naphthalene,[8a] anthracene,[8b] paracyclophane,[9a] $[2_3](1,4)$ cyclophane,[9b−c] deltphane,[9b] and stilbene.[17] Despite these achievements, few examples of silver(I) coordination polymers with large polycyclic aromatic hydrocarbons were reported. Consequently, in recent years we directed our research interest toward the synthesis and characterization of silver(I) coordination polymers with large polycyclic aromatic hydrocarbons. In this respect, we have reported a variety of silver(I) coordination polymeric structures with PAHs, such as W-type,[12a,18] helical,[19] double-decker,[12] triple-decker,[19a] multidecker,[12a] and herringbone structures.[20] In addition, many polycyclic aromatic hydrocarbons can be visualized as pyrene derivatives and we envisaged that the change of the molecular structures of them relative to pyrene molecules might bring a dramatic influence on the structures and properties of these silver(I) complexes. As a result, we present herein three novel silver(I) coordination polymers with benzopyrene derivatives, formed from silver(I) salts and 7-methylbenzo[*a*]pyrene (L^1), dibenzo[*b*, *def*]chrysene(L^2), and benzo[*e*]pyrene(L^3) and exhibiting spiral, herringbone, and triple-decker frameworks, respectively.



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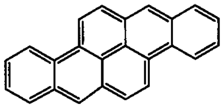

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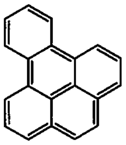

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Experimental Section

General Methods. All preparations and manipulations were carried out under an argon atmosphere using the conventional Schlenk techniques. All chemicals were reagent grade and used as received without further purification. Solvents were dried and distilled by standard methods before use. 7-Methylbenzo[*a*]pyrene, benzo[*e*]pyrene, and silver trifluoromethanesulfonate were purchased from Aldrich. Dibenzo[*b,def*]chrysene was obtained from Tokyo Kasei Kogyou Co. Ltd., while silver perchlorate monohydrate was obtained from Mitsuwa Chem. Co. Microanalyses were performed by the Department of Chemistry, Tokyo Metropolitan University. IR spectra were measured as KBr disks on a JASCO 8000 FT-IR spectrometer. ESR spectra were recorded on a JEOL JES-TE200 ESR spectrometer. The measurements of electric conductivity were made by the conventional two-probe technique at room temperature with compacted pellets.

SAFETY NOTE. *Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared, and these should handed with great caution.*

Synthesis of $[Ag_2(L^1)(toluene)_{0.5}(ClO_4)_2]_n$ (1). $AgClO_4{\cdot}H_2O$ (20.3 mg, 0.09 mmol) was dissolved in 3 mL of toluene at room temperature, and the resultant colorless solution was then transferred to the reactor where L^1 (24.0 mg, 0.09 mmol) was added in advance. After stirring for a while, the solution was introduced into a 7 mm glass tube and covered by *n*-pentane slowly. The glass tube was sealed under argon and kept at room temperature in the dark. After standing 3 days, yellow prismatic crystals suitable for X-ray analysis were isolated. Anal. Calcd for $C_{24.5}H_{18}Ag_2Cl_2O_8$: C, 40.47; H, 2.50. Found: C, 40.76; H, 2.47. Main IR bands (cm^{-1}): 3045−2860 (m), 1599 (m), 1087 (s), and 627 (m).

Synthesis of $\{[Ag_2(L^2)(CF_3SO_3)_2]\ [Ag_2(toluene)_2(CF_3SO_3)_2]\}_n$ (2). To a toluene solution (5 mL) containing silver triflate (50.0 mg, 0.2 mmol) was added dibenzo[*b*, *def*]chrysene (3.0 mg, 0.01 mmol). The mixture was stirred for a 1 h and filtered. A portion of the filtrate (2 mL) was transferred to a 7 mm glass tube and gently layered with 2 mL of *n*-hexane as a diffusion solvent. Then, the glass tube was sealed and stored in the dark at room temperature. After standing about 2−3 weeks, yellow needle crystals suitable for single-crystal X-ray diffraction determination can be collected. Anal. Calcd for $C_{42}H_{30}Ag_4S_4F_{12}O_{12}$: C, 33.28; H, 1.98. Found: C, 32.23; H, 1.93. Main IR bands (cm^{-1}): 3053−2856 (m), 1620−1460 (m), 1257−1178 (vs), 1035 (s), and 650 (s).

Synthesis of $[Ag_4(L^3)_4(ClO_4)_4(p\text{-xylene})]$ (3). AgClO4·H_2O (6.7 mg, 0.03 mmol) and benzo[*e*]pyrene (15.1 mg, 0.06 mmol) were dissolved in 1 mL of *p*-xylene. The resultant yellow solution was introduced into a 7 mm glass tube and covered with *n*-pentane slowly. The glass tube was sealed under argon and kept in the dark. After standing for 1 day, colorless block-shaped crystals were obtained. Anal. Calcd for $C_{88}H_{58}Ag_4Cl_4O_{16}$: C, 54.35; H, 3.00. Found: C, 54.04; H, 3.01. Main IR bands (cm^{-1}): 3047−2926 (s), 1601−1410 (m), 1101 (vs), and 626 (m).

X-ray Crystallography. A single crystal suitable for X-ray determination was mounted on a glass fiber with adhesives. All measurements for **1** were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation and a rotating anode generator at room temperature, while all diffraction data of **2** and **3** were collected at −73 °C and room temperature, on a Quantum CCD area detector coupled with a Rigaku AFC8 and Rigaku AFC7 diffractometer with graphite monochromated Mo Kα radiation, respectively. Intensity data were measured by continuous $\omega-2\theta$ scans. The intensities of three representative reflections were measured after every 150 reflections for all complexes and remained constant, indicative of crystal and electronic stability. Thus, no decay correction was applied. For complex **1**, an empirical absorption correction based on azimuthal scans of

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Table 1. Crystallographic Data for Complexes 1−3

	1	**2**	**3**
formula	$C_{24.5}H_{18}Ag_2Cl_2O_8$	$C_{42}H_{30}Ag_4S_4F_{12}O_{12}$	$C_{88}H_{58}Ag_4Cl_4O_{16}$
fw	727.05	1514.38	1944.70
space group	*C*2/*c* (No.15)	*P*2/*c*(No.13)	$P\bar{1}$(No.2)
a, Å	22.809(4)	22.285(3)	11.8376(7)
b, Å	13.199(3)	5.032(2)	12.547(1)
c,Å	15.552(4)	21.405(8)	13.151(2)
α, deg			91.438(2)
β, deg	98.73(2)	93.703(5)	12.547(1)
γ, deg			109.7054(9)
V, $Å^3$	4627(1)	2395(1)	1772.6(2)
Z	8	2	1
temp, °C	23	−73	23
λ(Mo Kα), Å	0.71069	0.71069	0.71069
ρ,g/cm^3	2.087	2.099	1.822
μ, cm^{-1}	19.70	18.9	13.1
R^a	0.053^b	0.061	0.043
$R_w{}^c$	0.156	0.120	0.112

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

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

Complex **1**			
Ag(1)−O(1)	2.360(6)	Ag(1)−O(6)	2.636(9)
Ag(1)−C(8)	2.499(7)	Ag(1)−C(9)	2.536(8)
Ag(1)−C(23)	2.586(8)	Ag(1)−C(24)	2.470(9)
Ag(2)−O(3)	2.492(6)	Ag(2)−O(6)	2.69(1)
Ag(2)−C(1)	2.431(7)	Ag(2)−C(2)	2.571(6)
Ag(2)−C(12)	2.517(7)	Ag(2)−C((13)	2.499(8)
O(1)−Ag(1)−O(6)	76.0(3)	O(1)−Ag(1)−C(8)	112.2(2)
O(1)−Ag(1)−C(9)	94.9(2)	O(1)−Ag(1)−C(23)	113.8(2)
O(1)−Ag(1)−C(24)	117.4(3)	O(6)−Ag(1)−C(8)	121.4(3)
O(6)−Ag(1)−C(9)	92.2(3)	O(6)−Ag(1)−C(23)	129.7(3)
O(6)−Ag(1)−C(24)	99.1(4)	C(8)−Ag(1)−C(23)	100.9(3)
C(9)−Ag(1)−C(24)	147.4(3)	O(3)−Ag(2)−O(6)	103.4(2)
O(3)−Ag(2)−C(1)	99.0(2)	O(3)−Ag(2)−C(2)	113.3(2)
O(3)−Ag(2)−C(12)	117.5(2)	O(3)−Ag(2)−C(13)	93.5(2)
O(6)−Ag(2)−C(1)	78.5(3)	O(6)−Ag(2)−C(2)	101.4(3)
O(6)−Ag(2)−C(12)	89.4(3)	O(6)−Ag(2)−C(13)	117.2(3)
C(1)−Ag(2)−C(12)	143.4(2)	C(2)−Ag(2)−C(13)	126.2(2)
Complex **2**			
Ag(1)−O(1)	2.416(5)	Ag(1)−O(2)	2.414(5)
Ag(1)−O(3)	2.627(5)	Ag(1)−O(3)	2.458(5)
Ag(1)−C(1)	2.432(6)	Ag(1)−C(2)	2.402(6)
Ag(2)−O(4)	2.417(6)	Ag(2)−O(5)	2.407(6)
Ag(2)−O(6)	2.698(6)	Ag(2)−O(6)	2.446(6)
Ag(2)−C(14)	2.42(2)	Ag(2)−C(15)	2.53(3)
O(1)−Ag(1)−O(2)	84.8(2)	O(1)−Ag(1)−O(3)	80.5(1)
O(1)−Ag(1)−O(3)	130.5(1)	O(3)−Ag(1)−O(3)	74.6(2)
O(2)−Ag(1)−O(3)	129.0(1)	O(2)−Ag(1)−O(3)	79.1(1)
O(1)−Ag(1)−C(1)	94.8(2)	O(1)−Ag(1)−C(2)	126.8(2)
O(2)−Ag(1)−C(1)	134.0(2)	O(2)−Ag(1)−C(2)	123.2(2)
O(3)−Ag(1)−C(1)	95.9(2)	O(3)−Ag(1)−C(2)	104.3(2)
O(3)−Ag(1)−C(1)	129.3(2)	O(3)−Ag(1)−C(2)	100.7(2)
O(4)−Ag(2)−O(5)	84.7(2)	O(4)−Ag(2)−O(6)	76.0(2)
O(4)−Ag(2)−O(6)	126.4(2)	O(5)−Ag(2)−O(6)	131.0(2)
O(5)−Ag(2)−O(6)	82.8(2)	O(6)−Ag(2)−O(6)	74.1(2)
O(4)−Ag(2)−C(14)	103.9(4)	O(4)−Ag(2)−C(15)	131.2(5)
O(5)−Ag(2)−C(14)	132.4(4)	O(5)−Ag(2)−C(15)	113.1(6)
O(6)−Ag(2)−C(14)	96.2(4)	O(6)−Ag(2)−C(15)	113.6(5)
O(6)−Ag(2)−C(14)	122.6(4)	O(6)−Ag(2)−C(15)	101.5(5)
Complex **3**			
Ag(1)−O(1)	2.378(5)	Ag(1)−O(5)	2.493(4)
Ag(1)−C(13)	2.438(4)	Ag(1)−C(14)	2.687(4)
Ag(1)−C(21)	2.546(4)	Ag(1)−C(22)	2.628(4)
Ag(2)−O(2)	2.556(5)	Ag(2)−O(5)	2.493(3)
Ag(2)−C(2)	2.452(4)	Ag(2)−C(3)	2.535(4)
Ag(2)−C(42)	2.461(4)		
O(1)−Ag(1)−O(5)	80.9(2)	O(1)−Ag(1)−C(13)	99.1(2)
O(1)−Ag(1)−C(14)	117.9(1)	O(1)−Ag(1)−C(21)	136.3(2)
O(1)−Ag(1)−C(22)	113.8(1)	O(5)−Ag(1)−C(13)	144.4(1)
O(5)−Ag(1)−C(14)	118.8(1)	O(5)−Ag(1)−C(21)	89.3(1)
O(5)−Ag(1)−C(22)	108.0(1)	C(13)−Ag(1)−C(21)	112.6(1)
C(13)−Ag(1)−C(22)	104.6(1)	C(14)−Ag(1)−C(21)	104.2(1)
C(14)−Ag(1)−C(22)	113.4(1)	O(2)−Ag(2)−O(5)	89.4(1)
O(2)−Ag(2)−C(2)	83.5(1)	O(2)−Ag(2)−C(3)	114.6(1)
O(2)−Ag(2)−C(42)	103.5(1)	O(5)−Ag(2)−C(2)	125.6(1)
O(5)−Ag(2)−C(3)	114.2(1)	O(5)−Ag(2)−C(42)	92.7(1)
C(2)−Ag(2)−C(42)	141.38(10)	C(3)−Ag(2)−C(42)	132.49(9)

several reflections was applied, whereas a symmetry-related absorption correction for complexes **2** and **3** was applied. In addition, a correction of secondary extinction for **3** was applied. The data for all complexes were corrected for Lorentz and polarization effects.

The structures were solved by direct methods, expanded using Fourier techniques, and refined by full-matrix least-squares analysis on F^2. All calculations were performed using the TEXAN package. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. Details of the X-ray experiments and crystal data are summarized in Table 1. The selected bond distances and angles for three complexes are given in Table 2.

Results and Discussion

Syntheses and Properties. The construction of silver(I) coordination polymers with polycyclic aromatic hydrocarbons not only depends on the properties of these ligands but also on counteranions such as ClO_4^- and $CF_3SO_3^-$ which play a crucial role in stabilizing the silver(I)-π complexes and in the formation of the extended polynuclear systems. Despite the reaction of silver(I) perchlorate with L^1 and L^3 forming complexes, our attempt to synthesize a silver(I) complex of L^2 with silver(I) perchlorate failed due to the formation of an oxidized carbon black precipitate. We have tried reaction of L^2 and silver(I) triflate in benzene or *p*-xylene and only obtained $Ag(CF_3SO_3)$ crystals. To our surprise, reaction of L^2 with silver(I) triflate in toluene led to the formation of an unprecedented cocrystallization coordination polymer in which triflate acts as tetradentate spacers. The coordinative properties of $CF_3SO_3^-$ anions have been well-documented, and generally the triflate anions act as a good leaving group.[21] In most cases, the triflate ions are noncoordinated[22] and sometimes exhibit unidentate,[23] bidentate,[23b,24] and tridentate[20,23b,25] behaviors; however, the occurrence of its tetradentate bonding in coordination chemistry is very rare, only one example of a tetradentate coordination was observed in our recent work.[26]

At room temperature, all three polymers exhibit a well resolved intense resonance with $g = 2.007$, 2.006, and 2.002, which can be ascribed to aromatic hydrocarbon radicals.[27] However, no ESR signal for silver(0) and silver(II) species formed by electron transfer was observed probably due to the low sensitivity. The electric conductivities of polymers **1**, **2**, and **3** were measured at room temperature; **2** and **3** show

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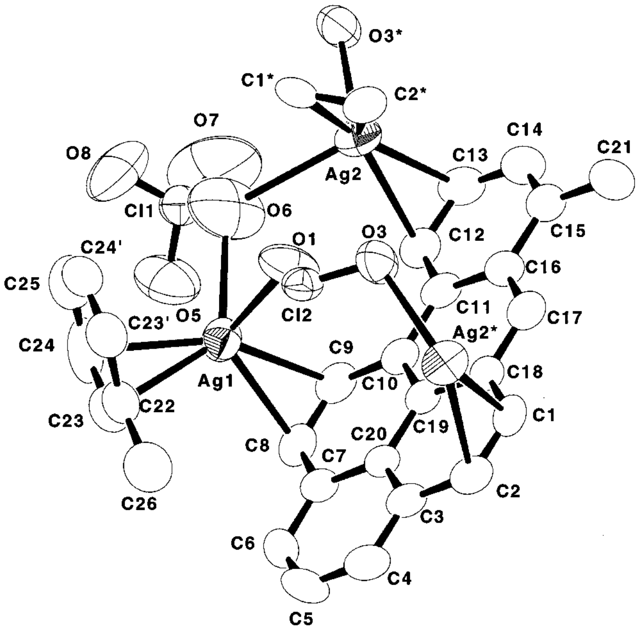

Figure 1. ORTEP view of the structure of **1**, showing 50% thermal ellipsoids.

semiconducting behavior with $\sigma = 5.77 \times 10^{-2}$ and 6.3×10^{-3} S cm^{-1}, respectively. Polymer **1** is however an insulator probably because of $\pi-\pi$ interactions in **1** not being column stacks.

[Ag$_2$(L^1)(toluene)$_{0.5}$(ClO$_4$)$_2$]$_n$ (1). The single-crystal X-ray determination indicates that polymer **1** possesses two crystallographically independent Ag(I) ions and exhibits a 2-D sheet structure. An ORTEP drawing is shown in Figure 1 together with the atom-numbering scheme. Two silver(I) ions of **1** have a similar distorted tetrahedral environment; Ag(1) is surrounded by two perchlorate oxygen atoms and one carbon−carbon π bond from a ligand L^1 molecule, while the fourth coordination site is completed by η^2 coordination to one toluene molecule; the coordination environment around Ag(2) comprises two oxygen atoms from different perchlorate anions and two carbon−carbon π bonds of distinct L^1 molecules. The ligand L^1 molecules bridge Ag(2) ions, and the perchlorate anions link Ag(1) and Ag(2) ions, respectively, leading to formation of double helical arrangement of polycyclic aromatic molecules and perchlorate ions, and then these double helical chains are further connected by the Ag(1) ions through toluene molecules to give rise to a 2-D sheet structure (Figures 2). In this structure, the perchlorate ions display two bridging modes, one linking Ag(1) and Ag(2) by using one oxygen atom and the other making use of two oxygen ones. In addition, the polyaromatic moieties of two adjacent strands between the layers stack on top of each other with an interplanar separation of 3.53 Å (Figure 3), indicative of existing $\pi-\pi$ interactions and affording a 3-D network.

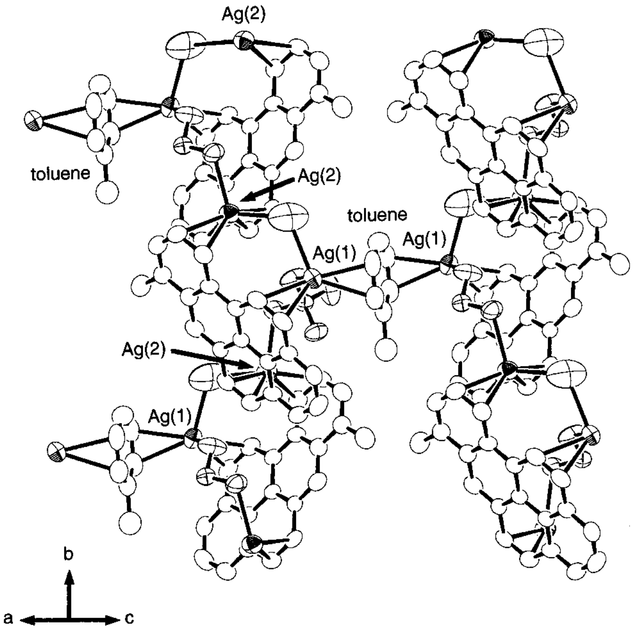

Figure 2. Perspective drawing of the 2-D structure with double-stranded helical motifs for **1**.

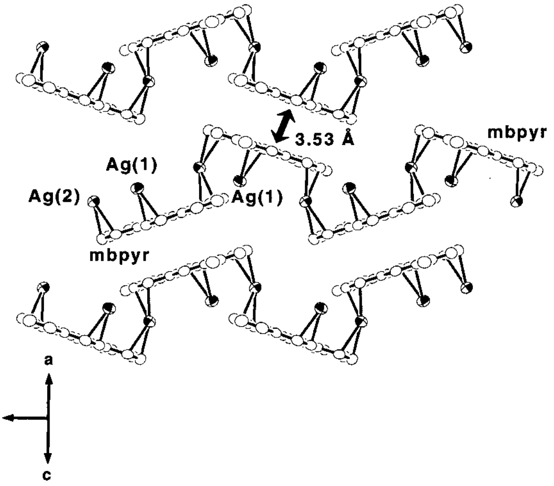

Figure 3. Intermolecular $\pi-\pi$ interactions in **1**.

[Ag$_2$(L^2)(CF$_3$SO$_3$)$_2$][Ag$_2$(toluene)$_2$(CF$_3$SO$_3$)]$_n$ (2). The reaction of Ag(CF$_3$SO$_3$) with dibenzo[*b,def*]chrysene(L^2) in toluene generated yellow needle crystals suitable for X-ray analysis. X-ray crystallography reveals that the structure of polymer **2** consists of alternate 2-D layers and 1-D chains which are formed from cation-π interactions of Ag(I) and L^2, Ag(I) and solvent toluene, respectively. Hence, there exist two crystallographically independent Ag(I) cations, both of them have a similar square pyramidal coordination geometry in which one site is completed by one C=C π-bond from a L^2 or a toluene molecule and the other four ones are occupied by four oxygen atoms from four different CF$_3$SO$_3^-$ anions (Figure 4). In the 2-D lamellar frameworks, each L^2 ligand adopts a μ-di-η^2 coordination to bridge two Ag atoms which sit above and beneath the aromatic ring plane, resulting in a moiety similar to a chair conformation; furthermore, the tetradentate triflate groups link these moieties to give rise to a 2-D layer in which the L^2 moieties exhibit a herringbone stack motif, and while the triflate anions give a

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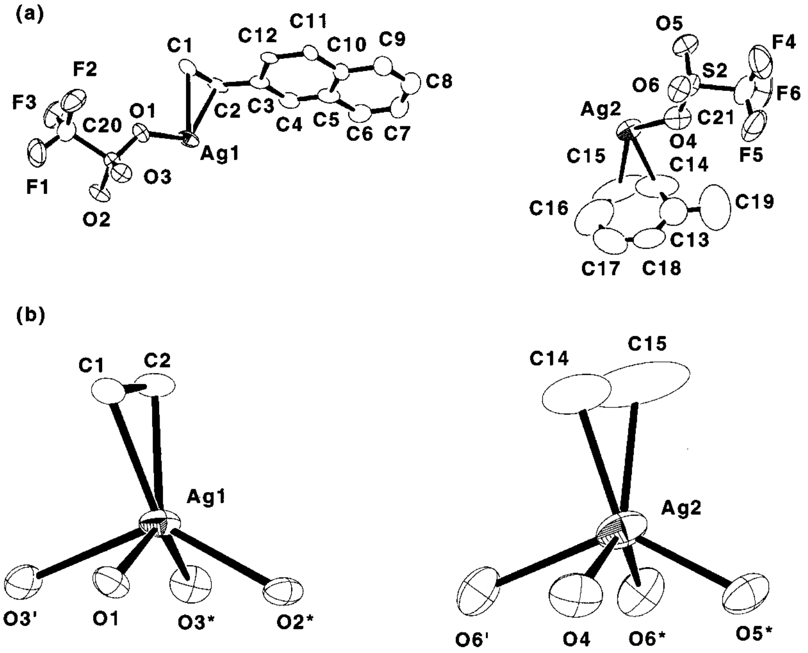

Figure 4. Structure and labeling of **2**: (a) local molecular structure; (b) coordination geometry of Ag1 and Ag2 (ORTEP, 50% probability).

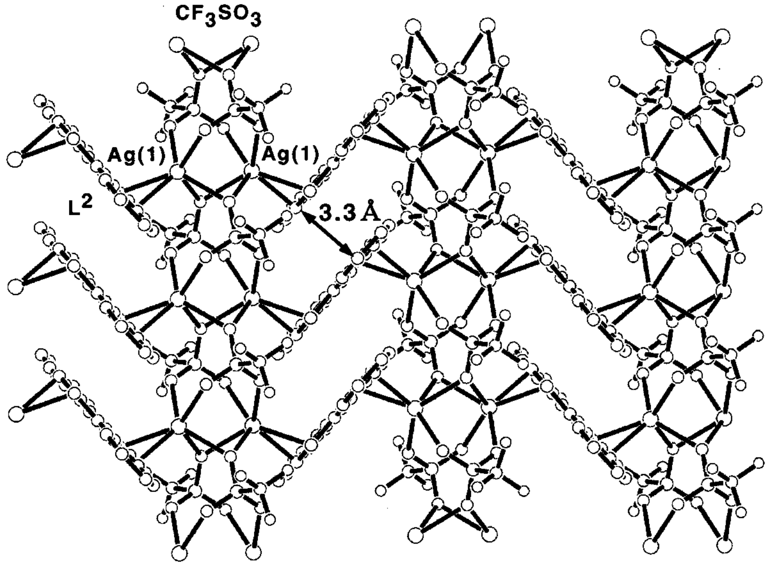

Figure 5. 2-D sheet structure with herringbone stack motifs for **2a**.

double tubular appearance with a tetragon inside tube and a octagon outside one. There exist very strong $\pi-\pi$ interactions within the layers owing to much shorter distances of 3.3 Å between the aromatic ring planes of the L^2 molecules in the herringbone stack mode (Figure 5). On the other hand, solvent toluene coordinates to Ag(I) in an η^2 fashion and the silver(I) ions are then linked by the triflate groups similar to that in the 2-D layers, forming 1-D rods with pendent toluene molecules. Interestingly, the separation of 3.32 Å between two adjacent Ag(2) ions in the 1-D chains is slightly longer than that of 3.25 Å between two Ag(1) ions in the 2-D layers. The stacking structure of the 2-D layers and 1-D chains is depicted in Figure 6.

$[Ag_4(L^3)_4(p\text{-xylene})(ClO_4)_4]$ (3). Polymer **3** can be regarded as a stacking polymer. As illustrated in Figure 7, this complex contains a discrete tetranuclear structure in which there are two crystallographically independent Ag(I) ions. The coordination sites of Ag(1) are occupied by two perchlorate oxygen atoms and two carbon−carbon π bonds with different L^3 molecules, while Ag(2) is complexed with two oxygen atoms from distinct perchlorate ions and coordinated by an η^2 coordination mode to a L^3 molecule and by an η^1 fashion to a *p*-xylene one, respectively. The two silver(I) ions adopt a distorted tetrahedral coordination geometry. In this structure, two L^3 moieties coordinate to Ag(1) and A(2), forming an upper layer and a lower one, respectively, while a *p*-xylene molecule is inserted between the two layers and bridges two Ag(2) atoms in μ−di−η^1 coordination to generate the third layer. Hence, complex **3** can be assigned to a closed triple-decker structure with two pendent η^2 coordination L^3 molecules. Similar to polymer **1**, the perchlorate ions here exhibit two kinds of different linkage modes where the Ag(1) and Ag(2) ions are coordinated to the same oxygen atom of a perchlorate ion or linked by two different oxygen atoms of a perchlorate ion. The molecular packing diagram displays that there exist intramolecular and intermolecular $\pi-\pi$ interactions with an separation of 3.27 Å between *p*-xylene and L^3 and an intermolecular one of 3.41 Å and 3.43 Å, respectively, leading to a 2-D stacking structure (Figure 8).

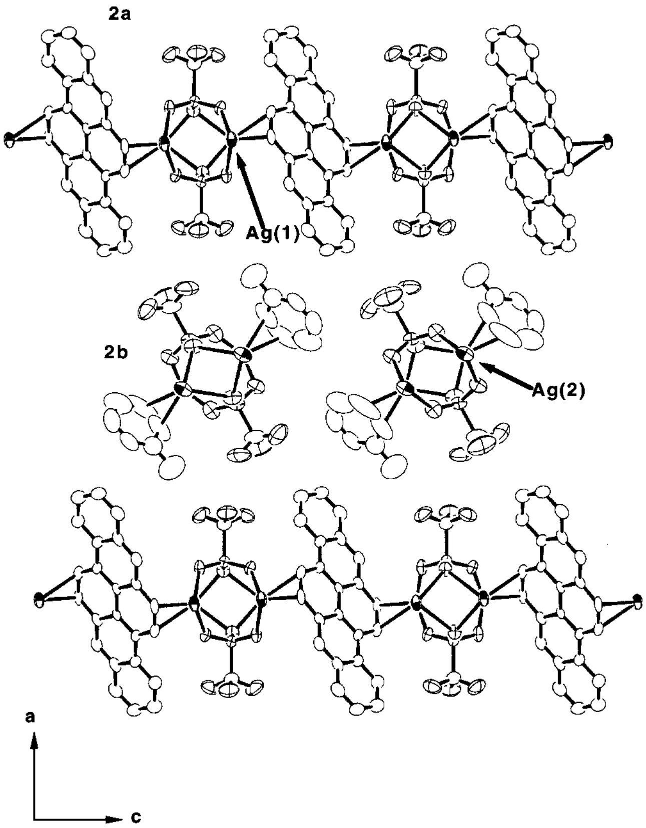

Figure 6. Cocrystallization structure with two distinct neutral polymers for **2**. **2a**: $[Ag_2(L^2)(CF_3SO_3)_2]_n$, **2b**: $[Ag_2(toluene)_2(CF_3SO_3)_2]_n$.

Effect of Solvent Coordination on Structure of Silver(I) Polymers with Benzopyrene Derivatives. Though the properties and molecular structures of ligands and the coordination sphere of metal ions are predominantly responsible for the structural construction of complexes, the incorporation and coordination of solvents can often bring a dramatic influence on the structures of complexes.[28] Interestingly, three polymers reported here demonstrate several different solvent coordination modes which play an important role in the construction of the silver(I) complexes.

The structure of ligand L^1 presented here is similar to that of benzo[*a*]pyrene except for a substituted methyl group. However, two ligands coordinate to silver(I) perchlorate to give rise to different polymeric structures, one exhibiting a 1-D double helical structure with benzo[*a*]pyrene[19a] and the other having a 2-D sheet framework with double-stranded helical motifs owing to solvent toluene bridging two Ag(1) ions in polymer **1**. It is obvious that the difference of the structures and coordination modes between the two polymers mainly arises from the coordination versatility of the toluene molecules and the substitution of the methyl groups on benzo[*a*]pyrene molecules probably because the induction effect of the methyl groups brings on the change of electronic density distribution on the polycyclic aromatic hydrocarbon molecules. Interestingly, compared with the 2-D silver(I) polymer of benzo[*e*]acephenanthrylene (bpa) with double-stranded helical motifs,[19b] polymer **1** exhibits a similar 2-D framework; however, unlike the former in which the helical moieties are linked via the ligand bpa molecules, the double-helical chains of **1** are connected by the solvent toluene molecules instead of the L^1 ones. To the best of our knowledge, this is the first example of a μ-di-η^2 bridging toluene molecule and only one example of a bridging toluene, in which a toluene molecule linked two iron atoms in μ-di-η^3 coordination to give rise to a dinuclear complex, was reported.[29]

Polymer **2** can be regarded as an unprecedented cocrystallization structure formed by a 2-D neutral lamellar coordination polymer $[Ag_2(L^2)(CF_3SO_3)_2]_n$ **2a** and a 1-D neutral rodlike coordination polymer $[Ag_2(toluene)_2(CF_3SO_3)_2]_n$ **2b** owing to the coordination of toluene molecules. Although a few cocrystallization examples of different small neutral molecules were reported,[30-32] to the best of our knowledge, no cocrystallization example of two different neutral coordination polymeric molecules was observed. Solvent molecules generally act as auxiliary or complementary ligands to take part in the formation

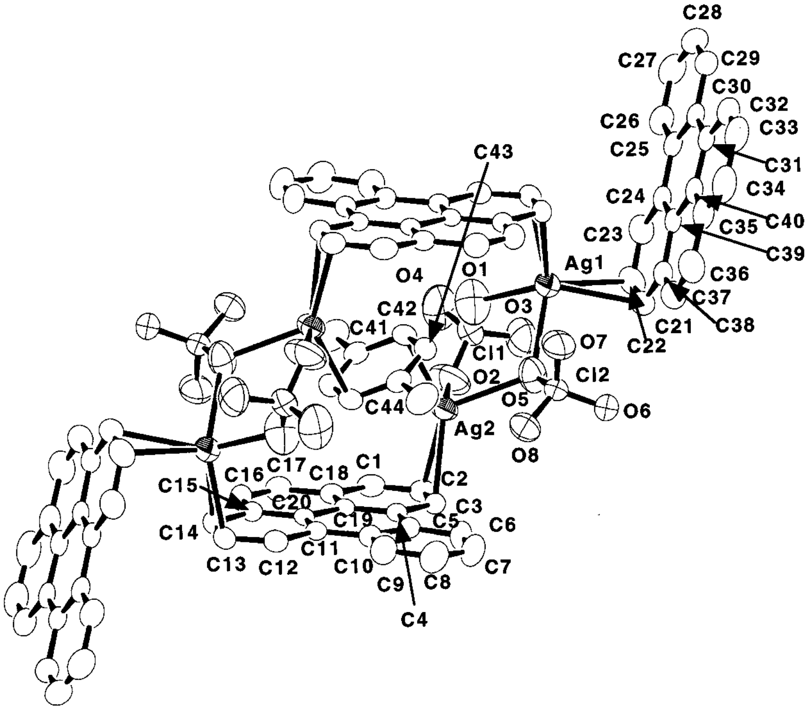

Figure 7. Molecular structure and partial labeling of **3** (ORTEP, 50% probability).

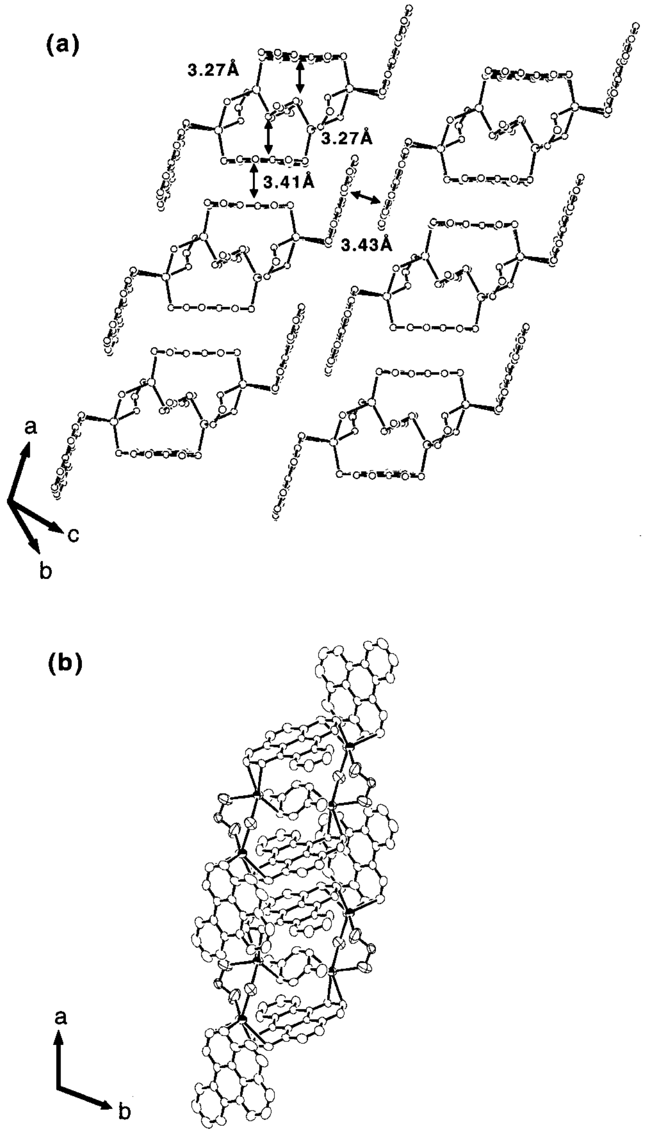

Figure 8. Packing structure of **3**: (a) side view; (b) perspective view *via c*-axis.

of coordination polymers.[12a,19a,b,33a] However, the solvent toluene in polymer **2** cannot be only viewed as an auxiliary ligand because the silver(I) ions in **2b** are coordinated to one η^2 toluene molecule and four oxygen atoms from different $CF_3SO_3^-$ anions to generate a 1-D neutral chain structure which cocrystallizes with **2a**. The coordination of a toluene molecule to silver(I) has been reported; however, only a dinuclear complex $[Ag(OTeF_5)(toluene)]_2$ was formed.[6d] Interestingly, compared with the coordination of naphtho(2,3-*a*)pyrene to silver(I) trifluoromethanesulfonate where toluene is also employed as a solvent, **2b** in polymer **2** exhibits a similar herringbone stacking motif to that of the silver(I) coordination polymer with naphtho(2,3-*a*)pyrene;[20] however, the coordination of the solvent toluene leads to a novel and unique cocrystallization structure of **2**.

It is noteworthy that the formation of the triple-decker structure for polymer **3** can be ascribed to the insertion of the solvent molecules between two μ−di−η^2 benzo[*e*]pyrene molecules, while the triple-decker or multidecker structures reported previously are generally made up of different ligand molecules.[12a,19a] In addition, the insertion of *p*-xylene gives rise to intramoleclar $\pi-\pi$ interactions, which are responsible for the stabilization of the tetranuclear unit, and results in 1-D $\pi-\pi$ columnar stacks. With respect to the coordination of *p*-xylene to metal ions in a μ−di−η^1 mode, to our knowledge, this is the first example of a bridging *p*-xylene molecule in silver(I) coordination polymers. Prior to this work, we have observed that silver(I) can be coordinated to an η^2 *p*-xylene molecule as a terminal ligand.[26]

As mentioned above, despite the coordination of several solvents to the silver(I) ions adopting different fashions, a common feature is that the incorporation of the solvents is not only responsible for the structural construction of the silver(I) coordination polymers but also stabilizes the silver(I) extended arrays. Such a strong solvent-dependent phenomenon has not been observed previously in other silver(I) coordination polymers with PAHs regardless of silver(I) having a remarkable high affinity for aromatic π-donor systems and coordinative versatility and flexibility.

Packing Patterns of PAHs and Their Silver(I) Complexes. Several structures of the silver(I) complexes with pyrene derivatives are summarized in Scheme 1, involving W-type, helical, herringbone, and triple-decker motifs. As is well-known, free polycyclic aromatic hydrocarbons crystallize in four basic structure types, i.e., herringbone, sandwich herringbone, γ herringbone, and β structure.[1c,34] Generally, linear molecules favor a herringbone stack, while ellipsoid and disk molecules often adopt a sandwich herringbone or a γ packing pattern.[34] Pyrene (L^4) adopts a sandwich herringbone stacking mode in the crystalline state[1c] and the coordination of silver(I) to pyrene generated a 1-D W-type polymer;[18] however, the molecular packing pattern of pyrene in the 1-D W-type silver(I) polymer has obviously been changed from a sandwich herringbone to a herringbone structure. Benzo[*a*]pyrene (L^5) in the crystalline state exhibits a γ structure[34] and its silver(I) complex possesses a 1-D double-strand helical structure.[19a] From the stacking diagram in Scheme 1, the partial structural features of the silver(I) complex with L^5 are still similar to those of a γ structure despite there existing a transformation tendency from a γ structure to a sandwich herringbone. According to the theory and prediction of Desiraju and Gavezzotti, benzo[*e*]pyrene (L^3) should have the same packing structure as pyrene, namely, sandwich herringbone.[1c] Although polymer **3** can be visualized as a triple-decker structure owing to the insertion of solvent *p*-xylene into two L^3 molecules, two pendent η^2 L^3 molecules of the unit imply that the local stacking mode of the L^3 molecules of **3** in the crystalline state still keeps a sandwich

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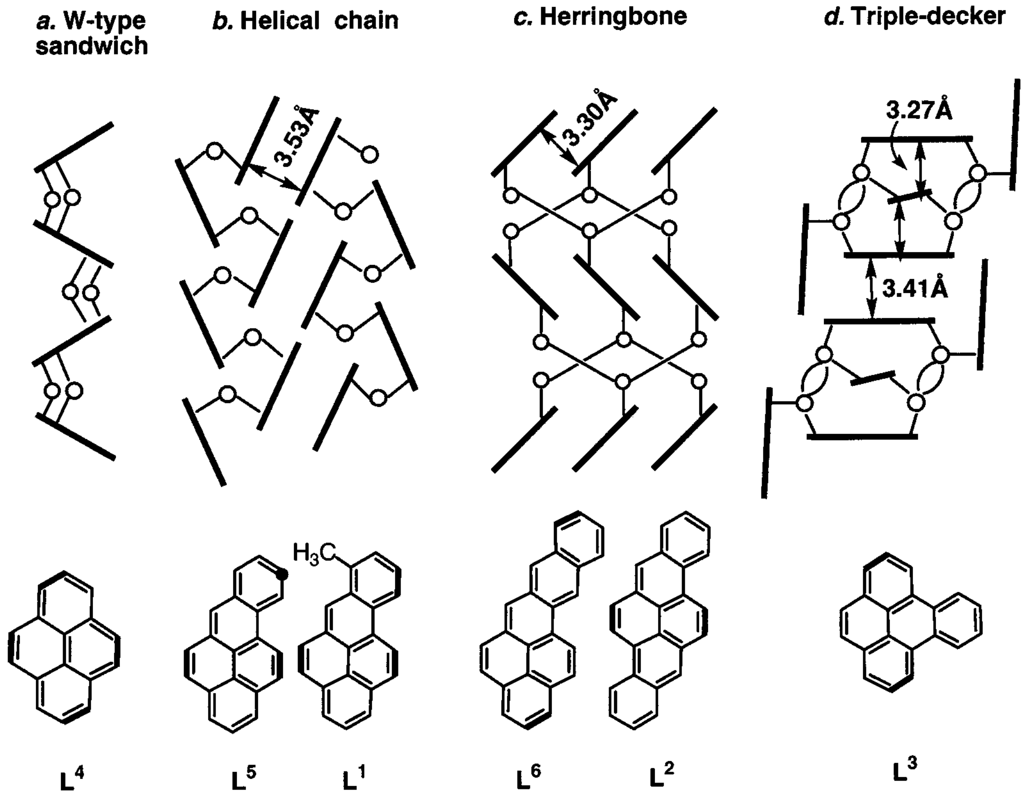
Scheme 1. Schematic representation of several structural types of silver(I) complexes with pyrene derivatives[a]



[a] L^4, pyrene; L^5, benzo[*a*]pyrene; L^6, naphtho(2,3-*a*)pyrene. Bold lines and a black circle of organic compounds represent the coordination sites to silver(I) ions.

herringbone (Figure 8a). Similarly, on the basis of the method in the literature[34] we can predict that free ligands L^2 and L^6 should possess a γ herringbone packing mode. It is noted that the ligands L^2 and L^6 molecules in their silver(I) coordination polymers present a similar herringbone stacking pattern.[20] The coordination of silver(I) to benzo[*ghi*]perylene and coronene, whose molecules exhibit a disk or close disk shape, gave rise to a double-decker structure[12a] and a triple-decker one,[19a] respectively; the crystal packcring patterns of metal-free benzo[*ghi*]perylene and coronene however demonstrate a sandwich herringbone and a γ structure,[34] respectively. The phenomena indicate that the more the molecular shape approximates to a disk, an ellipsoid, or a sphere, the more easily the reorientational motion for the ligand molecule takes place, mainly because the molecules with shapes such as these cannot be efficiently blocked in the crystal structures.[35] Generally, a slight glide of the PAH molecules takes place in the herringbone structures of silver(I) complexes with PAHs, while the stronger reorientational motion of the PAH molecules occurs in the decker-like structures of silver(I) complexes with PAHs. The motion of the PAH molecules in other types of structures for silver(I) complexes with PAHs can be regarded as lying between the two aforementioned cases.

On the other hand, the aromatic rings of metal-free PAHs pack through two distinct driving forces.[36] One is the so-called C···H interactions which have been suggested as an electrostatic interaction (positive CH versus negative π-cloud),[37] such as those in herringbone and sandwich herringbone structures; while the other is the C···C interactions by which adjacent aromatic molecules are parallel and highly overlapped, such as those in γ and β structures. It is however worth mentioning that the edge to face C···H hydrogen bonding of the native packing in PAHs has disappeared in these silver(I) complexes owing to the coordination of silver(I) to the PAHs to lead to the glides and the reorientational motions of the PAH molecules. Interestingly, it is this change that often results in the formation of close $\pi-\pi$ column stacks in these silver(I) complexes of PAHs, while some potential properties of the polymers arise from the $\pi-\pi$ column stacks; for example, polymers **2** and **3** exhibit semiconducting behavior mainly because they involve columnar aromatic $\pi-\pi$ stacks. As described above, the C···H interactions play an important role in the crystal stabilization of metal-free PAHs in herringbone and sandwich herringbone modes.[34,38] In contrast, $\pi-\pi$ interactions and coordination and linkage of counteranions stabilize the silver(I)-π complexes and construct the extended polynuclear silver(I) coordination polymers. Thus, the packing driving force of the polycyclic aromatic hydrocarbons in the silver(I) complex crystals is different from that in the metal-free PAH crystals despite their sometimes existing similar packing patterns of the PAH molecules in the silver(I) complexes and the free PAHs.

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Conclusion

We have demonstrated that three silver(I) complexes with benzopyrene derivatives exhibit the coordination versatility of polycyclic aromatic hydrocarbons and the structural novelty of these polymers which are not only related to the packing patterns of the free ligands in the crystalline state and the geometric shapes of their molecules but also to other factors such as solvent coordination and counteranion bridging. Polymer **1** possesses a 2-D sheet structure with double-stranded helical motifs. Due to the novel coordination of solvent toluene to silver(I) ions and the rare bridging mode of triflate, complex **2** displays an unprecedented cocrystallization structure constructed from two different neutral polymers. While polymer **3** consists of closed tetranuclear triple-decker moieties with $\pi-\pi$ stacks which result in formation of a 2-D stacking polymer. The silver(I) complexes with linear PAHs generally exhibit a herringbone structure, while the silver(I) complexes with disk PAHs are inclined to adopt a decker-like structure. The future rational design of silver(I) coordination complexes of PAHs with potential physicochemical properties might draw great inspiration from the understanding of the relationship between the molecular structures of the free ligands and those of their complexes in this work, especially the design of solid materials with properties which depend on the arrangement of molecules in the crystalline state.

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Supporting Information Available: X-ray crystallographic files in CIF format for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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