Supramolecular Silver(I) Complexes with Highly Strained Polycyclic Aromatic Compounds

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Abstract: Four organosilver(I) complexes of polycyclic aromatic hydrocarbons (PAHs) have been investigated crystallographically. The aim was to establish whether a favorable combination of cation-π interactions and aromatic stackings might produce functional organometallic solid materials with novel networks. Complete structures of the silver(I) perchlorate with 9,10-diphenylanthracene (L^1), rubrene (L^2), benzo[*a*]pyrene (L^3), and coronene (L^4) were determined by X-ray diffraction. All compounds are organometallic species based on cation-π interactions. While complex **1** with L^1 revealed a discrete mononuclear structure, complex **2** with rubrene displayed a π-bonded 3-D polymer. Complexes **3** and **4** can be regarded as both coordination polymer and stacking polymer, and the detailed differences in the geometries and the stacking patterns of L^3 and L^4 gave helical and triple-decker networks, respectively. The ESR spectroscopic results and conductivity of the compounds are also discussed. The present findings may serve as a basis for understanding specific interactions responsible for self-assembly of multinuclear aggregates involving PAHs.

Introduction

Polycyclic aromatic hydrocarbons or PAHs form an important class of organic molecules. The latest developments in materials science initiated a renaissance in the exploration of aromatic systems.[1,2] Due to the overall planarity of the molecules and the extended delocalized π system, many polycyclic hydrocarbons have been selected as potential donor molecules for preparing donor−acceptor materials both in the solid state and in solution.[3−7] Incorporation of metal ions into the PAHs systems through cation-π interactions has meanwhile brought further dramatic influence on the reactive properties of the fused polyaromatic solid surfaces.[8−10] Despite these achievements, the potential of PAHs for building macromolecules and forming supramolecular assemblies with helical, cylindrical, and host−guest topologies has only recently been explored.[11−14] The study includes linkage of the macrocycles through the multiple hydrogen bonding sites and a variety of van der Waals contacts,

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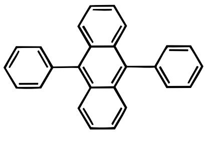
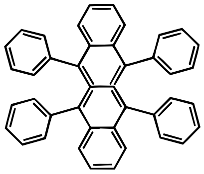
including $\pi-\pi$ and related dipole−dipole-induced interactions associated with arene−arene interactions.

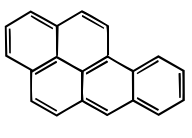
The development of methods for the efficient synthesis of polynuclear PAHs offers exciting prospects in the field of supramolecular chemistry. Modern supramolecular chemistry is currently dominated by the biomimetic motive of weak interactions such as hydrogen bonding and $\pi-\pi$ stackings. Interactions between aromatic molecules represent an important class of intermolecular forces in chemistry, which have been well-characterized both experimentally and theoretically.[15] They control a range of molecular recognition and self-assembly phenomena such as the packing of aromatic molecules in the crystalline state and, hence, the material properties. While being involved in a research program aimed at designing new assemblies of copper(I) and silver(I) complexes with macrocyclic polyhapto organic ligands for the development of functional supramolecular materials,[16] we became interested in the molecular and crystal structures of complexes between Ag(I) and very large PAH compounds. With their unique shape, size, and a large number of closely spaced molecular orbitals, large polycyclic aromatics are promising to act favorably as prototype compounds for a wide range of functional solid materials.[17] Relevant silver(I) complexes with smaller aromatics such as benzene,[18] cyclophane,[19] indene,[20] acenaphthene,[21] naphthalene,[22] and anthracene[23] are known. The study of these compounds is mainly concerned with the nature of π bonding, packing, and steric effects. Recently, we have reported polymeric silver(I) complexes of pyrene and perylene in which both aromatic compounds display an unusual symmetric tetra-η^2-coordination, linking four metal atoms forming W-type sandwich polymeric chain and sheets.[24] Here, we continue our exploration on the construction of supramolecular architectures of metal ions linked by π macrocycles including 9,10-diphenylanthracene (L^1), rubrene (L^2), benzo[*a*]pyrene (L^3), and coronene (L^4). These aromatics have been so far used in donor−acceptor compounds with alkali metal ions[4−6] or as model studies.[25] Extensive Chemical Abstracts Service (CAS) and Cambridge Structural Database searches gave no hint of known structures of π-hydrocarbon coordinative compounds. Our results have shown that employment of π macrocycles as precursors incorporating metal−ligand interactions and $\pi-\pi$ stackings as recognition motifs has been proved to be a new approach for the generation of novel molecular and supramolecular architectures with potential electrical properties.



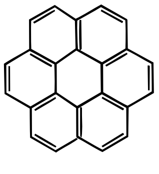
9,10-diphenylanthracene (L^1)



rubrene (L^2)



benzo[a]pyrene (L^3)



coronene (L^4)

Experimental Section

General Procedures. All reactions and manipulations were carried out under an argon atmosphere by using the standard Schlenk vacuum line techniques. Solvents were dried using standard procedures and distilled under an argon atmosphere prior to use. Reagent grade 9,10-diphenylanthracene and coronene were purchased from Tokyo, Kasei Kogyou Co. Ltd. while rubrene, benzo[*a*]pyrene, and silver(I) perchlorate were purchased from Aldrich. $AgClO_4 \cdot H_2O$ was dried at 40 °C under reduced pressure for 5 h before use. All other chemicals were purchased from Wako Pure Chemical, Inc. and used without further purification. Microanalyses were performed by the Department of Chemistry, Tokyo Metropolitan University. IR spectra were recorded as KBr disks on a JASCO 8000 FT-IR spectrometer. ESR spectra were obtained on JEOL JES-TE200 ESR spectrometer. Electrical resistivities of compacted pellets were measured by the conventional two-probe technique. **CAUTION:** The following preparations use $AgClO_4 \cdot H_2O$, which is potentially explosive.

Syntheses. $[Ag(L^1)(ClO_4)(C_6H_6)_2]$ (1). A solution of $AgClO_4 \cdot H_2O$ (22.5 mg, 0.1 mmol) in 10 mL of benzene was added to 9,10-diphenylanthracene (33.0 mg, 0.1 mmol). After being stirred for 10 min, the resultant light-yellow solution was filtered. The filtrate was introduced into a 7-mm diameter glass tube and layered with 2 mL of *n*-pentane as a diffusion solvent. The glass tube was sealed under Ar and wrapped with tin foil. After the filtrate was allowed to stand at room temperature in a dark room for 3 d, light-yellow brick crystals of **1** were obtained. Anal. Calcd for $C_{38}H_{30}AgClO_4$: C, 65.71; H, 4.32. Found: C, 65.52; H, 4.29.

$[Ag_4(L^2)(ClO_4)_4(H_2O)_4]$ (2). The red brick crystals of **2** were prepared in the same way as **1**, using rubrene (13.3 mg, 0.025 mmol) instead of 9,10-diphenylanthracene, and *n*-hexane was used as the diffusion solvent. Anal. Calcd for $C_{42}H_{36}Ag_4Cl_4O_{20}$: C, 35.18; H, 2.53. Found: C, 35.91; H, 2.36.

$[Ag_4(L^3)_2(ClO_4)_4(C_6H_5CH_3)_2]$ (3). Mixing of $AgClO_4 \cdot H_2O$ (67.5 mg, 0.3 mmol) and benzo[*a*]pyrene (37.9 mg, 0.15 mmol) in 10 mL of toluene produced a light-yellow solution which was stirred and filtered. The filtrate was introduced into a glass tube and layered with *n*-hexane. After the filtrate was allowed to stand at room temperature in a dark room for 7 d, light-yellow plate crystals of **3** were obtained. Anal. Calcd for $C_{40}H_{24}Ag_4Cl_4O_{16}$: C, 35.98; H, 1.81. Found: C, 35.92; H, 1.94.

$[Ag_4(L^4)_3(ClO_4)_4]$ (4). This compound was prepared by vapor diffusion. To a saturated solution (10 mL) of coronene in benzene (less than 1.5 mmol/L) was added $AgClO_4 \cdot H_2O$ (22.5 mg, 0.1 mmol). The resultant light-yellow solution was introduced into one compartment of an h-shaped glass tube. The second compartment was filled with *n*-hexane. The glass tube was sealed, and after standing for 7 d yellow prism single crystals of **4** were isolated. Anal. Calcd for $C_{36}H_{18}Ag_2Cl_2O_8$: C, 49.93; H, 2.10. Found: C, 49.64; H, 2.06.

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Table 1. Crystallographic Data

	1	**2**	**3**	**4**
formula	$C_{38}H_{30}AgClO_4$	$C_{42}H_{36}Ag_4Cl_4O_{20}$	$C_{54}H_{40}Ag_4Cl_4O_{16}$	$C_{36}H_{18}Ag_2Cl_2O_8$
fw	693.97	1434.00	1518.18	865.18
crystal color, habit	yellow, brick	red, brick	yellow, plate	yellow, prisms
crystal size, mm	0.20 × 0.20 × 0.25	0.20 × 0.28 × 0.16	0.30 × 0.30 × 0.30	0.20 × 0.20 × 0.20
crystal system	triclinic	orthorhombic	orthorhombic	triclinic
space group	$P\bar{1}$	*Fddd*	$Pca2_1$	$P\bar{1}$
a, Å	9.516(1)	16.638(5)	15.662(4)	12.771(4)
b, Å	10.671(1)	34.949(3)	13.037(8)	11.224(2)
c, Å	7.8315(7)	14.634(3)	25.434(3)	10.894(3)
α, deg	92.131(8)			89.43(2)
β, deg	103.812(7)			65.25(2)
γ, deg	91.283(9)			79.57(2)
V, Å^3	771.4(3)	8509(2)	5193(4)	1391(8)
Z	1	8	4	2
D_{calcd}, g cm^{-3}	1.494	2.239	1.942	2.066
F(000)	354	5632	2992	852
diffractometer	Rigaku AFC5R	Rigaku AFC5R	Rigaku AFC7R	Rigaku AFC7R
radiation	Mo Kα(λ = 0.71069 Å)	Cu Kα(λ = 1.54178 Å)	Mo Kα	Mo Kα
μ, cm^{-1}	7.79	179.92	17.60	16.58
scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
scan rate, deg min^{-1}	16.0 (in ω)	32.0	16.0	16.0
2θ range, deg	6−55	6−120	6−55	6−55
no. of reflns measd	3748	1762	6593	6714
no. of obsd data ($I > 3.00\sigma(I)$)	2355	1127	4306	4974
no. of params	374	181	697	433
R^a	0.055	0.075	0.043	0.036
$R_w{}^b$	0.062	0.091	0.050	0.045
goodness of fit	2.12	2.90	2.01	1.56

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

X-ray Data Collection, Structure Solution, and Refinement. The single-crystal X-ray diffraction experiments for complexes **1**, **3**, and **4** were performed at room temperature on a Rigaku AFC-7R or Rigaku AFC-5R four-circle diffractometer equipped with a 12-kW rotating anode Mo X-ray source (λ (Kα) = 0.71069 Å), while that for **2** was carried out with graphite monochromated Cu Kα radiation (λ = 1.54178 Å). In each case, a suitable single crystal was mounted on a glass fiber or enclosed in a glass capillary. Unit cell parameters were obtained from a least-squares analysis of the setting angles of 25 high-angle reflections in which the appropriate cell angles were constrained to their ideal values. Intensity data were collected by using standard scan techniques ($\omega - 2\theta$). Space groups were selected on the basis of systematic absences and intensity statistics which, in all cases, led to satisfactory refinements. In each case, the intensities of three standard reflections, monitored at 150-reflection intervals throughout data collection, remained constant within experimental error, indicating crystal and electronic stability. Thus, no decay correction was applied.

For complex **2**, an empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.63 to 1.00. For the rest, azimuthal scans of several reflections indicated no need for an absorption correction. The diffracted intensities were corrected for Lorentz and polarization effects. The structures were solved by a direct method[26] and expanded using Fourier techniques.[27] All non-hydrogen atoms were refined with anisotropic thermal parameters, except for some disordered O atoms in **1**−**3**. The positions of all the hydrogen atoms were determined from difference electron density maps and were included but not refined. For **1**−**3**, the hydrogen atoms for benzene, H_2O and toluene molecules are excluded. Final refinements for all the structures were performed on these data having $I > 3\sigma(I)$ and included anisotropic thermal parameters for non-hydrogen atoms. Reliability factors are defined as $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$ and $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[28] Hydrogen atoms were assumed to be isotropic. All crystallographic computations were performed on a VAX computer by using the program system TEXSAN.[29] Details of the X-ray experiments and crystal data are summarized in Table 1. Final atomic coordinates for all of the structures are given in the Supporting Information. Important bond lengths and bond angles for four complexes are given in Table 2.

Results and Discussion

Characterization and IR Spectra of the Products. The reactions of four aromatics with silver(I) perchlorate under mild conditions readily afforded the complexes **1**−**4**. Compounds **1**, **2**, and **4** are reasonably stable at room temperature under ambient light for several days. However, great care is needed to get satisfactory elemental analyses for **3**. The product cannot be dried in vacuo, and even trying to remove excess toluene with a slow stream of dry argon resulted in the loss of coordinated toluene and the loss of transparency of the crystals at room temperature. Therefore, the theoretical value for the elemental analysis of **3** is based on the formula without toluene molecules. The crystal used for X-ray structure determination was enclosed in a glass capillary. Infrared spectroscopy is a good indicator of incorporation of metal ions into the PAH system. The infrared spectra were recorded in the region 4000−400 cm^{-1} on KBr disks. PAHs have several very distinctive signals, including the region from 3030 to 3065 cm^{-1}, which contains the C−H stretching absorptions. A second region, from 1314 to 1620 cm^{-1}, consists of three or four quite intense signals, corresponding to the in-plane vibrations of the C═C bonds. All of these are present in the infrared spectrum of **1**−**4**. In addition, each complex exhibits strong absorptions of υ(OCl) at 1086−1100 cm^{-1}. The corresponding strong absorption of

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Table 2. Selected Bond Lengths (Å) and Bond Angles (deg)

	1		
Ag−O(2)	2.67(3)	Ag−C(6)	2.68(1)
Ag−C(7)	2.57(1)	Ag−C(29)	2.62(1)
Ag−C(30)	2.49(1)	Ag−C(34)	2.57(1)
O(2)−Ag−C(6)	102.7(7)	O(2)−Ag−C(7)	74.1(7)
O(2)−Ag−C(29)	103.1(7)	O(2)−Ag−C(30)	118.5(8)
O(2)−Ag−C(34)	84.4(8)	C(6)−Ag−C(7)	29.6(4)
C(6)−Ag−C(29)	113.9(4)	C(6)−Ag−C(30)	129.2(4)
C(6)−Ag−C(34)	96.3(4)	C(7)−Ag−C(29)	113.0(4)
C(7)−Ag−C(30)	142.0(4)	C(7)−Ag−C(34)	101.2(4)
C(29)−Ag−C(30)	32.3(5)	C(29)−Ag−C(34)	145.7(5)
C(30)−Ag−C(34)	115.1(5)		
	2		
Ag−O(1)	2.46(2)	Ag−O(5)	2.27(3)
Ag−C(1)	2.40(1)	Ag−C(2)	2.68(1)
Ag−C(9)	2.54(2)		
O(1)−Ag−O(5)	95.6(8)	O(1)−Ag−C(1)	97.4(5)
O(1)−Ag−C(2)	91.2(5)	O(1)−Ag−C(9)	114.7(6)
O(5)−Ag−C(1)	142.3(9)	O(5)−Ag−C(2)	114.5(8)
O(5)−Ag−C(9)	98.9(8)	C(1)−Ag−C(2)	30.3(4)
C(1)−Ag−C(9)	107.3(5)	C(2)−Ag−C(9)	135.6(6)
	3		
Ag(1)−O(1)	2.51(1)	Ag(1)−O(14)	2.53(1)
Ag(1)−C(1)	2.36(1)	Ag(1)−C(2)	2.56(1)
Ag(1)−C(33)	2.39(1)	Ag(2)−O(2)	2.40(1)
Ag(2)−O(5)	2.52(2)	Ag(2)−C(8)	2.51(1)
Ag(2)−C(9)	2.44(1)	Ag(2)−C(42)	2.56(2)
Ag(2)−C(43)	2.44(2)	Ag(3)−O(6)	2.59(1)
Ag(3)−O(9)	2.49(1)	Ag(3)−C(13)	2.41(1)
Ag(3)−C(14)	2.73(1)	Ag(3)−C(21)	2.40(1)
Ag(3)−C(22)	2.54(1)	Ag(4)−O(10)	2.42(1)
Ag(4)−O(13)	2.71(2)	Ag(4)−C(28)	2.55(1)
Ag(4)−C(29)	2.50(1)	Ag(4)−C(49)	2.53(2)
O(1)−Ag(1)−O(14)	78.9(3)	O(6)−Ag(3)−C(13)	105.9(5)
O(1)−Ag(1)−C(1)	115.3(4)	O(6)−Ag(3)−C(14)	135.8(4)
O(1)−Ag(1)−C(2)	124.4(4)	O(6)−Ag(3)−C(21)	87.7(4)
O(1)−Ag(1)−C(33)	86.5(4)	O(6)−Ag(3)−C(22)	117.0(4)
O(14)−Ag(1)−C(1)	93.3(5)	O(9)−Ag(3)−C(13)	85.9(5)
O(14)−Ag(1)−C(2)	24.0(4)	O(9)−Ag(3)−C(14)	86.7(4)
O(14)−Ag(1)−C(33)	98.7(5)	O(9)−Ag(3)−C(21)	113.8(4)
C(1)−Ag(1)−C(2)	31.8(4)	O(9)−Ag(3)−C(22)	121.3(4)
C(1)−Ag(1)−C(33)	156.9(4)	C(13)−Ag(3)−C(14)	30.4(5)
C(2)−Ag(1)−C(33)	129.2(4)	C(13)−Ag(3)−C(21)	157.9(4)
O(2)−Ag(2)−O(5)	90.8(6)	C(13)−Ag(3)−C(22)	131.1(5)
O(2)−Ag(2)−C(8)	119.6(5)	C(14)−Ag(3)-C(21)	135.5(4)
O(2)−Ag(2)-C(9)	102.2(5)	C(14)−Ag(3)-C(22)	105.6(5)
O(2)−Ag(2)−C(42)	128(1)	C(21)−Ag(3)−C(22)	29.9(4)
O(2)−Ag(2)−C(43)	106(1)	O(10)−Ag(4)−O(13)	69.8(4)
O(5)−Ag(2)−C(8)	111.6(5)	O(10)−Ag(4)−C(28)	111.6(4)
O(5)−Ag(2)−C(9)	87.5(4)	O(10)−Ag(4)−C(29)	96.6(4)
O(5)−Ag(2)−C(42)	85.9(7)	O(10)−Ag(4)−C(49)	97.4(6)
O(5)−Ag(2)−C(43)	102(1)	O(13)−Ag(4)−C(28)	144.0(5)
C(8)−Ag(2)−C(9)	31.2(4)	O(13)−Ag(4)−C(29)	112.7(5)
C(8)−Ag(2)−C(42)	109.4(8)	O(13)−Ag(4)−C(49)	94(1)
C(8)−Ag(2)−C(43)	121.4(7)	C(28)−Ag(4)−C(29)	32.3(4)
C(9)−Ag(2)−C(42)	129.1(9)	C(28)−Ag(4)−C(49)	120.3(9)
C(9)−Ag(2)−C(43)	150.1(7)	C(29)−Ag(4)−C(49)	152.6(9)
C(42)−Ag(2)−C(43)	27.3(8)	O(1)−Cl(1)−O(2)	106.9(8)
	4		
Ag(1)−O(1)	2.456(3)	Ag(1)−O(5)	2.425(4)
Ag(1)−C(1)	2.517(4)	Ag(1)−C(2)	2.499(4)
Ag(1)−C(25)	2.455(4)	Ag(1)−C(26)	2.448(4)
Ag(2)−O(2)	2.483(3)	Ag(2)−O(6)	2.452(4)
Ag(2)−C(4)	2.402(4)	Ag(2)−C(5)	2.516(4)
Ag(2)−C(28)	2.478(4)	Ag(2)−C(29)	2.456(4)
O(1)−Ag(1)−O(5)	81.5(1)	O(1)−Ag(1)−C(1)	93.2(1)
O(1)−Ag(1)−C(2)	106.5(1)	O(1)−Ag(1)−C(25)	00.6(1)
O(1)−Ag(1)−C(26)	121.7(1)	O(5)−Ag(1)−C(1)	117.8(2)
O(5)−Ag(1)−C(2)	91.0(2)	O(5)−Ag(1)−C(25)	118.1(2)
O(5)−Ag(1)−C(26)	94.4(2)	C(1)−Ag(1)−C(2)	31.6(1)
C(1)−Ag(1)−C(25)	123.7(1)	C(1)−Ag(1)−C(26)	136.3(1)
C(2)−Ag(1)−C(25)	142.8(1)	C(2)−Ag(1)−C(26)	131.7(1)
C(25)−Ag(1)−C(26)	32.7(1)	O(2)−Ag(2)−O(6)	89.4(1)
C(4)−Ag(2)−C(29)	136.3(1)	O(2)−Ag(2)−C(4)	118.1(1)
O(2)−Ag(2)−C(5)	96.0(1)	O(2)−Ag(2)−C(28)	106.6(1)
O(2)−Ag(2)−C(29)	91.7(1)	O(6)−Ag(2)−C(4)	97.5(1)
O(6)−Ag(2)−C(5)	123.3(1)	O(6)−Ag(2)−C(28)	86.1(1)
O(6)−Ag(2)−C(29)	115.1(1)	C(4)−Ag(2)−C(5)	32.6(1)
C(4)−Ag(2)−C(28)	135.1(1)	C(5)−Ag(2)−C(28)	143.3(1)
C(5)−Ag(2)−C(29)	121.0(1)	C(28)−Ag(2)−C(29)	32.5(1)

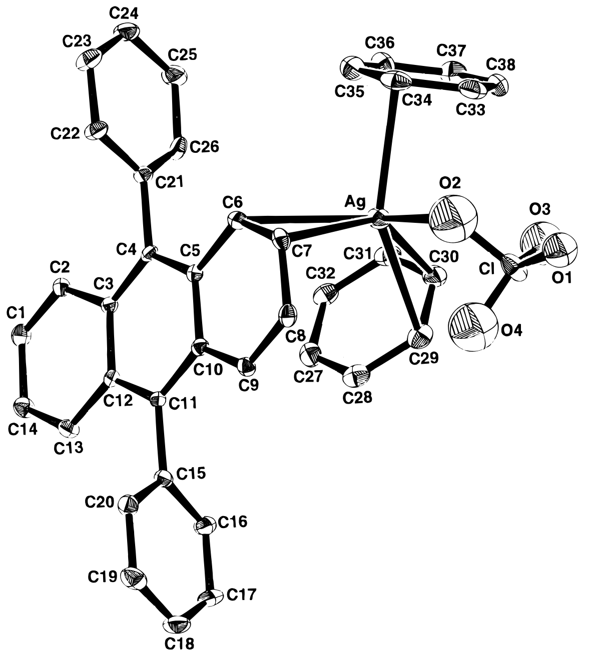

Figure 1. Structure and labeling of **1**.

υ(OH) for complex **2** appeared at 3540 cm^{-1}, confirming the presence of water molecule in the compound.

Monomeric Structure of $[Ag(L^1)(ClO_4)(C_6H_6)_2]$ (1). The crystallographic studies of **1** revealed a discrete mononuclear structure shown in Figure 1. The coordination sphere around the silver atom is pseudotetrahedral, being made up of two crystallized solvate benzene molecules, one oxygen atom from the perchlorate ion, and one carbon−carbon π interaction from η^2-diphenylanthracene. The Ag−C distances for L^1 are unequal, being 2.68(1) and 2.57(1) Å for C(6) and C(7), respectively. The silver−benzene π interaction is asymmetrical, having Ag−C distances of 2.49(1) and 2.62(1) Å for one benzene and of 2.57(1) Å for the other. The remaining silver−carbon interactions are greater than 2.93 Å, well beyond the limits from 2.47 to 2.76 Å observed in the reported silver(I)−aromatic complexes.[18−24] Thus, using the shortest Ag−C distances, the two benzene moieties are best considered to involve different coordination modes, one with η^2 and the other with η^1 bonding. Complex **1** is a rare example of monomeric silver compound with benzene and its derivatives. Normally, the arenes are found to be η^2-coordinated to the metal ions, and each benzene molecule is associated with two metal ions lying above and below the ring.[18,30] With perchlorate ions acting as spacers, such a connection sometimes can generate an infinite chain structure as observed in the silver perchlorate complex of benzene.[18] Least-squares plane calculation indicates that the polycycle in **1** has no molecular constraint and the maximum deviation from the anthracene plane is 0.02 Å. The two phenyl groups are also essentially planar and lie almost perpendicular to the anthracene with dihedral angles of 77° and 81°, respectively, between the anthracene and Ph planes. The structure with the metal atoms interacting with only one localized C═C bond of the benzene molecule explains the distortion of the ring. Compared with the average C═C distance of 1.399 Å for the uncoordinated benzene molecule, the donation of electrons from the benzene π system to Ag results in the lengthening of C(29)−C(30) bond to 1.42(2) Å, while the remaining five distances of the ring average 1.38(2) Å.

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(30) (a) Schier, A.; Wallis, J. M.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 757. (b) Frank, W.; Schneider, J.; Müller-Becker, S. *J. Chem. Soc., Chem. Commun.* **1993**, 799.

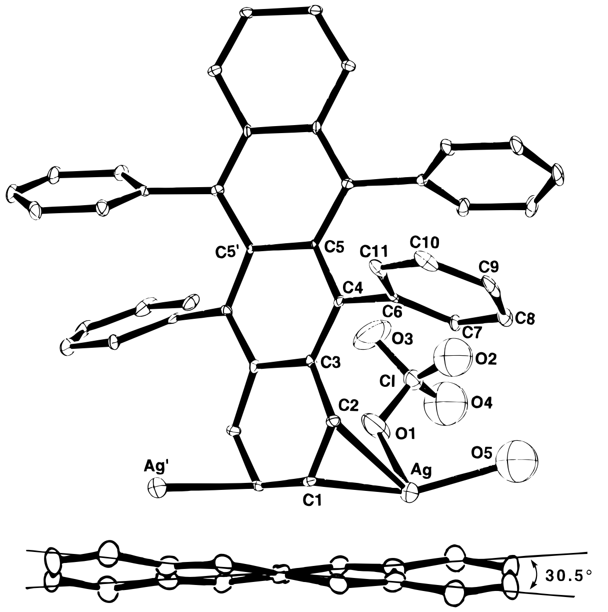

Figure 2. Structure and labeling of **2** with twisted conformation of the naphthacene skeleton shown at the bottom.

3-D Polymeric Structure of [$Ag_4(L^2)(ClO_4)_4(H_2O)_4$] (2). The X-ray analysis of **2** showed that the unit cell contains eight rubrenes, whose structure is depicted in Figure 2 together with atom numbering scheme. The complex consists of a 3-D framework of the metal ions bridged by the polycyclic aromatics. The molecular center of the rubrene coincides with the crystallographic inversion center; thus, each aromatic molecule is symmetrically π bonded to eight crystallographically equivalent Ag atoms. Each metal center interacts asymmetrically with two rubrenes, one with η^2 bonding at C(1) and C(2) positions with Ag−C distances of 2.40(1) and 2.68(1) Å, respectively, and the other with η^1 coordination at C(9) with Ag−C separation of 2.54(2) Å. The tetrahedral coordination sphere around the silver cation is completed by one water molecule and one perchlorate ion with Ag−O separations of 2.27(3) and 2.46(2) Å, respectively. Repeating the connection generates an infinite 3-D framework of metal ions linked by rubrene groups as shown in Figure 3. To achieve π interactions with eight metal atoms, the naphthacene skeleton of the bulky rubrene is no longer planar; instead, it is severely twisted against the central C(5)−C(5′) bond resulting in a dihedral angle of 30.5° between the two halves of the ring.

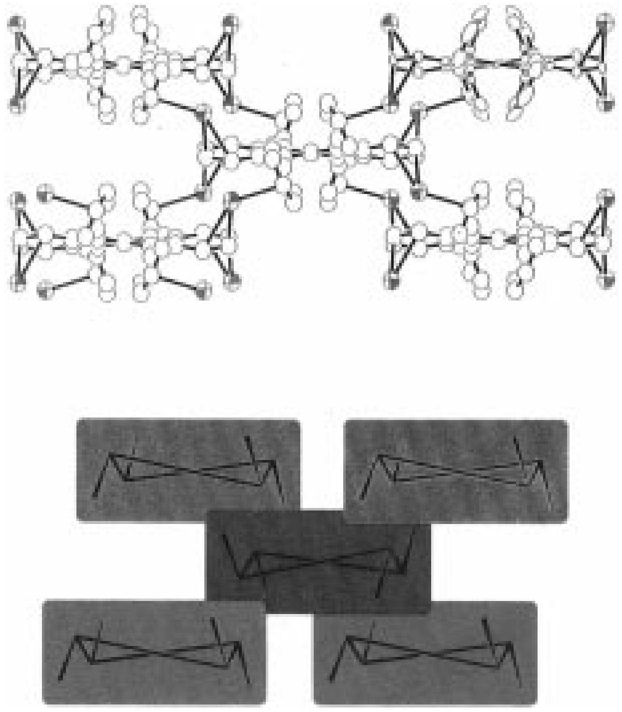

Figure 3. Packing diagram of 3-D polymer **2**. Top: showing eight Ag atoms (red) bound to one rubrene; ClO_4^- and H_2O are not shown. Bottom: schematic presentation of the twisted rubrene molecules in the cell.

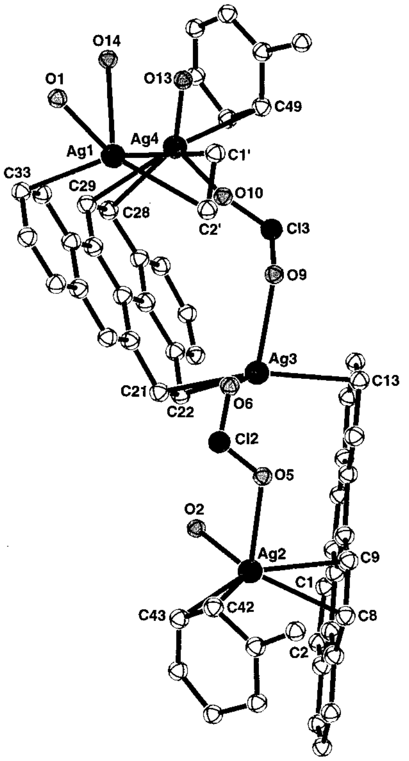

Figure 4. Structure and partial labeling of **3**.

Helical Structure of [$Ag_4(L^3)_2(ClO_4)_4(C_6H_5CH_3)_2$] (3). The structure of **3** displays formation of double helical arrangement of polycyclic molecules and perchlorate ions. The compound can be regarded as both a coordination polymer and a stacking polymer. The structure of the compound contains an extraordinary tetranuclear silver building block as shown in Figure 4. While there are four crystallographically distinct Ag(I) cations, these have a similar pseudotetrahedral environment comprising two perchlorate oxygen atoms and one carbon−carbon π bond with the polyaromatic. The fourth coordination site for both Ag(1) and Ag(3) is completed by η^1 coordination to the second polycycle, while Ag(2) and Ag(4) are further π bonded to one toluene molecule with η^2 and η^1 bonding, respectively. The Ag−C distances range from 2.36(1) to 2.56(1) Å, and Ag−O distances range from 2.40(1) to 2.71(2) Å. Within the building block, the four silver atoms are linked by two benzo[*a*]pyrene molecules and three bridging ClO_4^- ions. The two adjacent building blocks are bridged by the fourth perchlorate ion, resulting in an infinite chain structure of the metal cations. Due to the rigid conformation of L^3, the two independent polycyclic moieties are essentially planar and inclined with each other by 18.34°. The two toluene molecules act as complementary spacers to accommodate Ag atoms for a tetrahedral coordination. The total structure is arranged in a spiral fashion with the strand of polycycles and the strand of perchlorate ions interwound around the silver atoms, leading to the two strands of the double helical superstructure as illustrated in Figure 5.

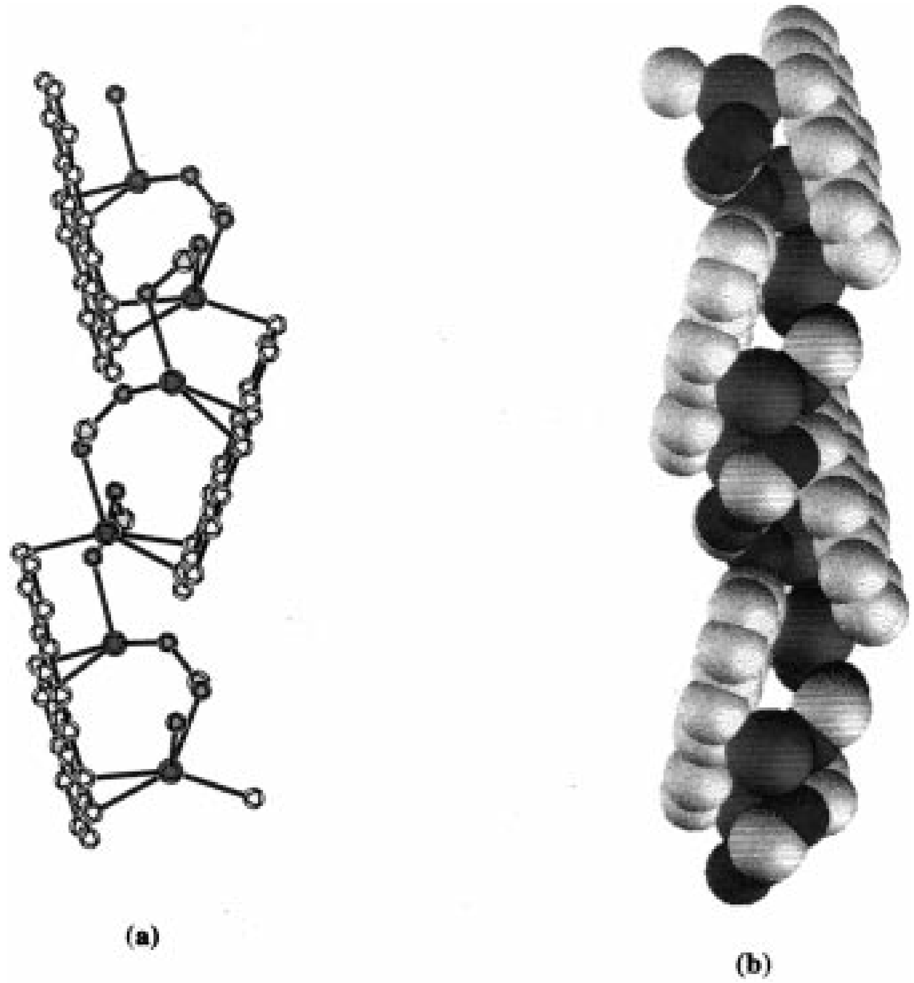

Figure 5. Double-helical structure of **3**, toluene and uncoordinated oxygen atoms of perchlorates are omitted for clarity. (a) Ball-and-stick model (red: Ag, blue: O, yellow: Cl, black: C). (b) Space-filling model.

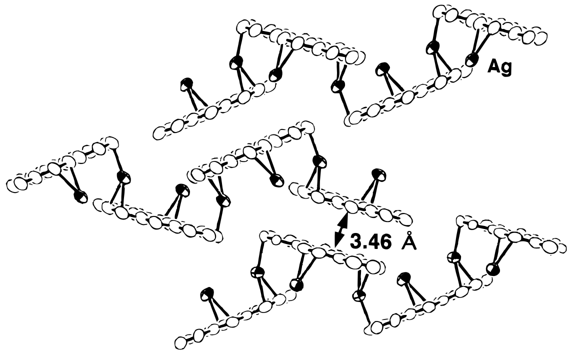

Figure 6. Intermolecular $\pi-\pi$ interactions in **3**.

Even the strands of polycycles are arranged in an unusual fashion. The packing diagram shows that the aromatic rings of two adjacent strands stack on top of each other, with an interplanar separation of 3.46 Å. This results in extended interweaved strands of polycycles associated by aromatic $\pi-\pi$ interactions, Figure 6.

Triple-Decker Polymeric Structure of $[Ag_4(L^4)_3(ClO_4)_4]$ (4). The compound **4** can also be regarded as both a coordination polymer and a stacking polymer. The structure exists in the solid state as an aromatic-linked polymer of dimers lying approximately on the *ab* plane as shown in Figure 7. Within the dimer, there are two independent Ag(I) ions coupled by one bridging perchlorate with Ag(1)···Ag(2) separation of 3.9798(5) Å. The tetrahedral metal center is coordinated to two carbon−carbon π bonds from two different coronene molecules with Ag−C bond distances ranging from 2.402(4) to 2.517(4) Å. The next closest contacts between silver and carbon atoms are 3.076(4) and 3.103(5) Å for Ag(1) and Ag(2), respectively. The two dimeric subunits are bridged by the second perchlorate ion with Ag−O bond distances of 2.456(3) Å for Ag(1) and 2.483(3) Å for Ag(2). Each coronene moiety exhibits a tetra-η^2-coordination, bridging sequentially four metal centers and resulting in a unique triple-decker polymeric structure shown in Figure 8.

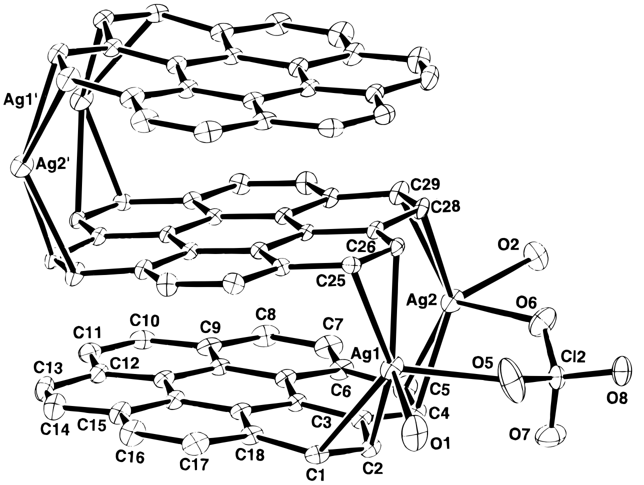

Figure 7. Structure and partial labeling of **4**.

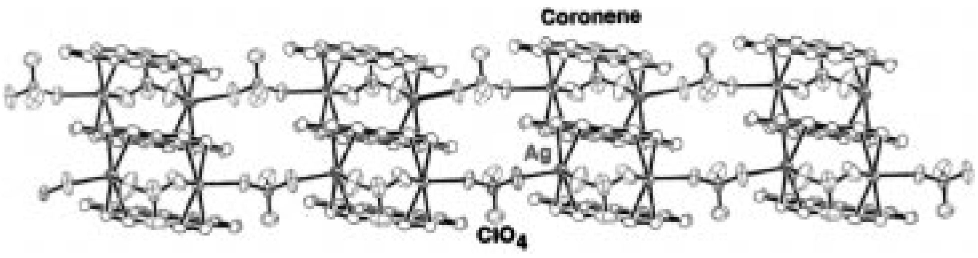

Figure 8. Triple-decker structure of **4**.

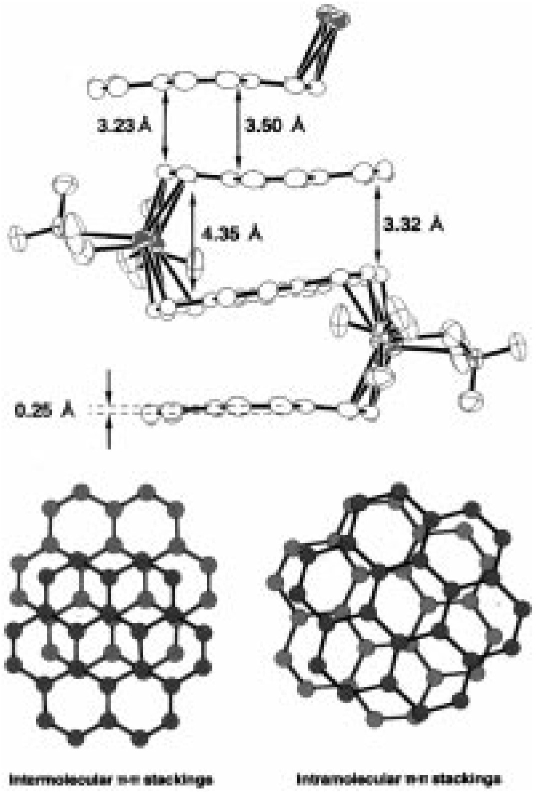

Figure 9. Intermolecular $\pi-\pi$ interactions in **4**.

The packing diagram shows that the compound involves both intramolecular and intermolecular $\pi-\pi$ interactions, which constitutes columnar aromatic stacks as shown in Figure 9. The interplanar distances are unequal, ranging from 3.23 to 3.5 Å. It is noted that the intermolecular $\pi-\pi$ interactions are significantly stronger as evidenced by the unusually close contacts of 3.23 Å between the two intermolecular coronene planes, much shorter than 3.4 Å for the modeled porphrin−porphrin interactions in solution.[15b] The unique stacking pattern in **4** can be a structure-determining factor. A closer insight into the intermolecular aromatic ring stacking may be obtained from studying the conformational changes accompanying the interaction. Each triple-decker unit consists of a centrosymmetric middle metallomacrocycle, an outer metallomacrocycle, and its centrosymmetric pair. The middle plane is essentially planar, having a maximum deviation of 0.018 Å from the best least-squares plane. The outer unit shows greater deviation from planarity with a maximum deviation of 0.087 Å. In this outer unit, the C(2) and C(4) atoms and the C(11) and C(13) atoms (see Figure 7), in particular, are displaced 0.1654 and 0.1311 Å and 0.1421 and 0.1974 Å, respectively, from the plane in a direction away from the middle plane. The total result is that the strong intermolecular interactions cause the two outer coronene planes in the triple-decker unit to severely bend outward by 0.25 Å. This phenomenon is certainly striking for a rigid polycyclic aromatic compound!

Molecular Planarity and Aromatic Stackings. An understanding of the relationship between molecular structure and physicochemical properties would provide insight into the design of solids with properties that depend on the arrangement of molecules in crystals. Planarity is often presumed to be the significant geometric characteristic of the molecular structures of PAHs. Upon PAHs coordinating with metal ions, however, this planarity may no longer exist. As discussed earlier, in complexes **1** and **3**, both 9,10-diphenylanthracene (L^1) and benzo[*a*]pyrene (L^3) are found to possess essentially planar molecular frameworks. The average deviation of carbon atoms from the mean plane is less than 0.027 Å, which is insignificant in both cases. In contrast to the planarity of L^1 and L^3, both rubrene (L^2) in **2** and coronene (L^4) in **4** exhibit nonplanarity. The average deviation of carbon atoms from the mean plane is 0.53 Å for L^2 and 0.087 Å for L.^{4} In fact, due to the octafold π coordination of L^2 and the strong intermolecular interactions of L,^{4} the two polycyclic aromatics exist with highly nonplanar, even twisted and bent, conformations, Table 3. It is immediately apparent that topological constrains resulted from cation-π bonding and that $\pi-\pi$ interactions are the structural features responsible for nonplanarity of aromatics in their coordination compounds.

The polycyclic aromatics L^1, L^2, and L^4 have been previously reported to form π-hydrocarbon anions with alkali metals.[4−6] Although crystal structural determination and elemental analysis as well as infrared spectroscopy in the present work are consistent with characteristic neutral aromatics, the formation of organic radicals was corroborated by an ESR measurement at room temperature. All complexes were found to exhibit a well-resolved intense resonance. The characteristic g values in Table 3 are attributable to the organic radicals,[17,31] indicative of partial electron transfer between Ag(I) and the aromatics. The spin densities for the organic radicals, estimated from the comparison with the DPPH (diphenylpicrylhydrazyl) standard, were measured. The significantly higher spin density of 0.18% for **2** is consistent with the highly strained molecular conformation of rubrene in the complex, indicating easy electron transfer between Ag(I) and the highly twisted polycyclic aromatics. Molecular constraint may assist the interaction by putting the interacting groups closer to each other in the coordination sphere and enhance the charge transfer between the donor and acceptor through the reduction of the electron density on the coordinated aromatics. Indeed, the formation of Ag(II) or Ag(0) accompanied by the electron transfer was observed by a broad ESR signal at $g = 2.1$ for **2** and **4**, whereas the corresponding signal was not observed for **1** or **3** because of the low sensitivity.

Associated with the distortion of molecular planarity of aromatics is the distance between the two carbon atoms and

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(31) (a) Davies, A. G.; McGuchan, D. C. *Organometallics* **1991**, *10*, 329. (b) Courtneidge, J. L.; Davies, A. G. *Acc. Chem. Res.* **1987**, *20*, 90. (c) Davies, A. G.; Shields, C. *J. Chem. Soc., Perkin Trans. II* **1989**, 1001.

Table 3. Physicochemical Properties

	1	**2**	**3**	**4**
coordinated aromatic C═C bond distance (Å)	1.35	1.37	1.35 (av)	1.38 (av)
noncoordinated aromatic C−C bond distance (av) (Å)	1.39	1.40	1.41	1.41
presence of molecular constraint	no	yes	no	yes
presence of $\pi-\pi$ stackings	no	no	yes (not column)	yes (column)
ESR *g* values	2.002	2.003 2.146	2.003	2.001 2.118
spin density		0.18%	0.00024%	0.01%
$\sigma_{25\ ^\circ\mathrm{C}}$ (S cm^{-1})	0	1.9×10^{-6}	1.0×10^{-5}	3.1×10^{-3}

interior angles on the ring. In all cases, the C═C bond lengths in the polycyclic ring coordinated to the silver atoms are significantly shortened by about 0.03−0.06 Å compared with the averaged distances of the noncoordinated C−C bonds, Table 3, indicative of large electron density accumulated on the π-bonded carbon atoms. A similar finding was reported for the coordinated benzene molecule in [Ag(C_6H_6)(ClO_4)] where the distances between the two carbon atoms in the ring nearest to the silver atoms is 1.35 Å, while the neighboring carbon−carbon distance is 1.43 Å.[18(d)] These observations are surprising since in either case, whether silver(I) acts as an electron acceptor or as a donor of electrons from a filled d orbital to an empty molecular orbital of the aromatic, it would change the coordinated carbon−carbon distances in the opposite direction to that observed. It is not clear whether the polarization of the mobile π electrons by the positive silver ions would increase the electron density in the bonds closest to the positive silver ion. The lack of detailed understanding of electron effects affecting these bond distances precludes any discussion of the significance of these variations.

Aromatic stacking is a common feature of PAH compounds regardless of considerable variations in the coordinative interactions. Complex **1** is a monomer, and there is no aromatic stackings observed in the structure. Likewise, intermolecular π interactions are not involved in the coordination of polymer **2**. Structure analysis confirmed the presence of strong aromatic interactions in **3** and **4**, which result in the assembly of coordination polymers into $\pi-\pi$ interacted supramolecular structures. Complex **4**, in particular, involves both intermolecular and intramolecular columnar aromatic stacks. The stacking interaction contributes not only to the stability of the complex but also to its electrical conducting behaviors. It is known that hydrocarbons form conducting radical salts.[32] The room-temperature conductivities for **1**−**4** were measured, and the results are listed in Table 3. Complex **1** is an insulator, whereas **2**−**4** exhibit semiconductivity. Although compound **2** has a relatively higher spin density, it exhibits low conductivity due to the lack of aromatic $\pi-\pi$ stackings. The value for **4** is 3 orders of magnitude greater than that of **2** and is comparable to the values for intrinsic atomic semiconductors, such as silicon. The semiconducting behavior can be rationalized when the nature of the conducting stacks is considered. The stacking interaction generally arises from the interaction between the π-orbitals of two aromatic rings, especially between the highest occupied molecular orbital (HOMO) of the donor ring and the lowest unoccupied orbital (LUMO) of the acceptor ring. Strong intermolecular as well as intramolecular aromatic stackings in **4** obviously offer the most effective electron-transfer pathway among four complexes.

Using PAHs for Multinuclear Aggregates. Although there is long-standing structural evidence for the efficacy of an aromatic compound as a ligand toward all types of metal ions, the structures of the present four organosilver compounds, together with those of pyrene and perylene,[24] provide an excellent illustration of the unique coordinative versatility of the large aromatic compounds. To accommodate the most favorable pseudotetrahedral stereochemistry of the silver(I) ion, each polycycle adjusts its conformation accordingly with all coordination modes occurring through molecular recognition. They can display a usual symmetric tetra-η^2-coordination, linking four metal atoms forming triple-decker molecular stacks as observed for coronene, and a W-type sandwich of polymeric chain and sheets as found in pyrene and perylene systems.[24] They can also exhibit symmetric tetra-η^1 and tetra-η^2-bonding, linking eight metals as described for rubrene. Furthermore, asymmetric coordination of η^2 and η^1, linking three metal ions for benzo[*a*]pyrene, or just η^2 bonding to one metal center as characterized for 9,10-diphenylanthracene is even unique. The conformation of these macrocycles is not necessarily coplanar in complexation with metal ions, and they can be significantly twisted or slightly bent as observed in rubrene and coronene, respectively. By the use of metal-containing molecular building blocks, the achievement of electron-transfer processes and unusual electroproperties looks promising. The power and versatility of these large aromatic hydrocarbons in complexing metal ions will undoubtedly offer considerable advantages over the planned synthesis of polynuclear aromatic molecules with defined form and function. We are presently working toward this direction.

Conclusions

Using perchlorate anions as complementary bridging ions and the crystallized solvent molecules such as benzene and toluene as spacers, the reactions of silver(I) perchlorate and four polycyclic aromatics afforded unique monomer and polymeric complexes based on cation-π interactions. Incorporation of transition metal ions into polycyclic aromatics has a dramatic influence on the physical properties of the resultant multidimensional π system of the aromatics. In each case, the silver ions are coordinated to the short C═C bond moiety by cation-π interactions, and large electron densities on the carbons close to the metal ions and molecular constraints are responsible for the observed high spin densities of the organic radicals. Formation of functional aromatic stack columns is essential for the characteristic conductivity of this type of compound. Although the X-ray structural data for four polycyclic compounds comprise the main results of this paper, the precise data confirmed our initial belief that, based on cation-π bonding and noncovalent aromatic stackings, the large aromatic compounds have the potential as possible components for the self-assembly of multinuclear functional organometallics with novel networks.

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Supporting Information Available: Tables of crystal data, intensity measurements, structure solution and refinement, atomic coordinates and thermal parameters, intramolecular bond lengths and angles, and least-squares planes for **1**−**4** (38 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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