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Article

Construction of the Multidecker Anthracene–Silver(I) System by Intramolecular π–π Interactions

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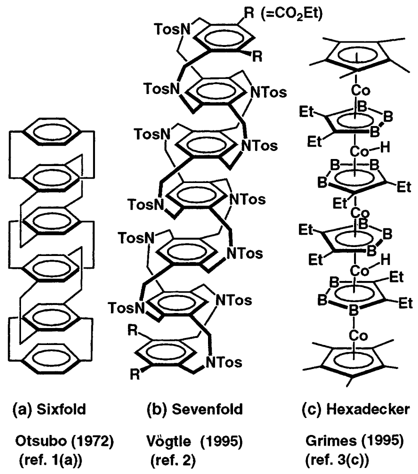
As a continuation of the study on the construction of the multidecker aromatic compounds with π–π interactions, the anthracene derivatives 9,10-dimethylanthracene (dman), 9,10-diphenylanthracene (dpan), and 7,12-dimethylbenz-[*a*]anthracene (dmban) have been studied toward complexation with the silver(I) ion. The crystal structures of [Ag(dman)$_{0.5}$(*p*-xylene)(ClO$_4$)], [Ag$_2$(dpan)$_{0.5}$(C$_6$H$_6$)$_{0.5}$(CF$_3$SO$_3$)$_2$], and [Ag$_2$(dmban)$_2$(ClO$_4$)$_2$](*p*-xylene), together with the metal-free ligand dpan, have been determined by single-crystal X-ray diffraction. These π-electron-rich aromatic compounds are found to have great promise as an approach to the effective self-assembly of high nuclearity in a multilayer fashion.

Introduction

Multilayer compounds continue to attract considerable attention as a result of their structural diversity, interesting and unusual properties, and application as special materials.[1−8] A series of multilayered cyclophanes up to sixfold were reported as early as 1972 with [2,2]paracyclophane,[1] Chart 1. Unique nanometer-scale molecular ribbons with up to sevenfold [3,3]metacyclophane units were synthesized using a new interactive synthetic strategy.[2] Carboranes[3] and thiaborolenes[4] account for another type of multilayer system in organometallic chemistry, among which a hexadecker sandwich complex based on the carborane unit was reported by Grimes et al.[5] In addition, metal complexes with polycyclic aromatics have generated a number of columnar aromatic stacks through $\pi-\pi$ interactions, Chart 2. Silver(I) coordination polymers of [2,2]paracyclophane with zigzag chain structures have been reported to involve weak intramolecular $\pi-\pi$ interactions.[6] Recently, we have reported a multidecker silver(I) complex with decacyclene, in which the highly symmetric aromatic ligand exhibits a μ-tetra-η^2 coordination bound to four metal centers with two on each side of the ring.[7,8] In this paper, we continue our study on the construc-

Chart 1. Multilayered Organic Cyclophanes and η^5-Coordination Compounds



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(1) (a) Otsubo, T.; Tozuka, Z.; Mizogami, S.; Sakata, Y.; Misumi, S. *Tetrahedron Lett.* **1972**, *29*, 2927. (b) Otsubo, T.; Mizogami, S.; Otsubo, I.; Tozuka, Z.; Sakagami, A.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1973**, *46*, 3519.

(2) Breidenbach, S.; Ohren, S.; Nieger, M.; Vögtle, F. *J. Chem. Soc., Chem. Commun.* **1995**, 1237.

(3) (a) Grimes, R. N. *Chem. Rev.* **1992**, *92*, 251. (b) Greiwe, P.; Sabat, M.; Grimes, R. N. *Organometallics* **1995**, *14*, 3683. (c) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1995**, *117*, 12227.

(4) Siebert, W.; Edwin, J.; Wadepohl, H.; Pritzkow, H. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 149.

(5) Wang, X.; Sabat, M.; Grimes, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 2687.

(6) Schmidbaur, H.; Bublak, W.; Huber, B.; Reber, G.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1089.

(7) Munakata, M.; Wu, L. P.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Maeno, N. *J. Am. Chem. Soc.* **1999**, *121*, 4968.

(8) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171.

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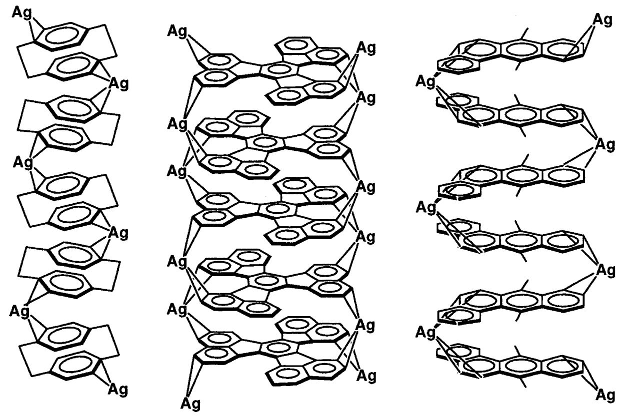
Chart 2. Multidecker η^2-Coordination Compounds



(b) Schmidbaur (1986, ref. 6)
(a) Munakata (1999, ref. 7)
(c) This work

tion of the multilayer metal complexes with anthracene derivatives assembled by silver η^2 coordination.

Experimental Section

General Methods. All reactions and manipulations were carried out under an argon atmosphere by using the usual Schlenk techniques. Solvents were dried and distilled by using standard methods prior to use. High-purity argon was used to deoxygenate the solvents. Reagent-grade 9,10-dimethylanthracene (dman), 9,10-diphenylanthracene (dpan), and 7,12-dimethylbenz[*a*]anthracene (dmban) were purchased from Tokyo Chemical Industry Co., Ltd., while silver(I) perchlorate and silver(I) trifluoromethanesulfonate were from Aldrich. All other chemicals were from Wako Pure Chemical, Inc., and were used as received. The IR spectra were recorded as KBr disks on a JASCO FT-IR-8000 spectrometer.

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

Synthesis of [Ag(dman)$_{0.5}$(*p*-xylene)(ClO$_4$)] (1). To a *p*-xylene solution (5 mL) containing silver perchlorate (20.7 mg, 0.1 mmol) was added dman (10.3 mg, 0.05 mmol). The mixture was stirred for 10 min and filtered. A portion of the filtrate (3 mL) was transferred to a 7-mm-diameter glass tube and gently layered with 3 mL of *n*-hexane as the diffusion solvent. The glass tube, sealed under Ar and wrapped with aluminum foil, was left standing at room temperature for 2 weeks; yellow brick crystals of **1** were obtained (25 mg, 60%). Anal. Calcd for $C_{16}H_{17}AgClO_4$: C, 46.12; H, 4.08. Found: C, 46.54; H, 4.10. Main IR bands (cm^{-1}): 3065(m), 1620(w), 1460(m), 1365(m), 1107(vs), 680(s), 626(s).

[Ag$_2$(dpan)$_{0.5}$(C$_6$H$_6$)$_{0.5}$(CF$_3$SO$_3$)$_2$] (2). To a benzene solution (10 mL) containing silver trifluoromethanesulfonate (51.4 mg, 0.2 mmol) was added dpan (33.1 mg, 0.1 mmol). The pale-yellow mixture was treated in the same manner as that for **1**, and after the mixture stood at room temperature for 7 days, pale-yellow brick crystals of **2** were obtained (42 mg, 58%). Anal. Calcd for $C_{18}H_{12}Ag_2S_2F_6O_6$: C, 30.10; H, 1.67. Found: C, 30.15; H, 1.76. Main IR bands (cm^{-1}): 3065(m), 1599(w), 1440(m), 1391(m), 1265(vs), 1100(s), 1036(s), 642(s).

[Ag$_2$(dmban)$_2$(ClO$_4$)$_2$](*p*-xylene) (3). This compound was synthesized in a manner similar to that for **1** with equimolar (0.15 mmol) silver perchlorate and dmban in *p*-xylene. The yield was 49% (38 mg). Anal. Calcd for $C_{48}H_{40}Ag_2Cl_2O_8$: C, 55.89; H, 3.88. Found: C, 55.36; H, 3.59. Main IR bands (cm^{-1}): 3054(s), 1458(m), 1379(m), 1082(s), 625(s).

X-ray Data Collection and Structure Solutions and Refinements. A suitable single crystal was mounted on a glass fiber, and diffraction data were collected at room temperature in all cases on a Quantum charge-coupled device area detector coupled with a Rigaku AFC7 diffractometer with graphite monochromated Mo Kα radiation. The $\omega/2\theta$ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time versus background counting time being 2:1. Weak reflections [$I < 10.0\sigma(I)$] were rescanned up to three times and counts accumulated to improve the counting statistics. The intensities of three reflections were monitored regularly after the measurement of 150 reflections and indicated crystal stability in all cases. Azimuthal scans of several reflections for each compound indicated no need for an absorption correction. All intensity data were corrected for Lorentz polarization effects.

The structures were solved by direct methods (MITHRIL),[9] followed by subsequent Fourier-difference calculations and refined by a full-matrix least-squares analysis on F^2 for complex **3** and on F for the rest, using the TEXSAN package.[10] All the full-occupancy non-hydrogen atoms were refined anisotropically, except in the case of **3**, where the carbon atoms for the *p*-xylene solvation were refined isotropically. Hydrogen atoms of all the structures were introduced in their calculated positions; they were included but not refined in the refinement. The counteranions ClO_4^- and $CF_3SO_3^-$ were found to have high thermal motions in **1** and **2**. Details of the X-ray experiments and crystal data are summarized in Table 1. Selected bond lengths and bond angles are given in Table 2.

Results and Discussion

Crystal Structure of dpan. The crystal and molecular structures of dman and dmban have been reported previously.[11,12] As a logical extension into the systematic study of the series, the crystal structure of the metal-free ligand dpan was determined by X-ray analysis. Single crystals for the compound were grown from *n*-pentane. The infrared bands of dpan appear at 3065 (ν_{C-H}) and 1490 ($\nu_{C=C}$) cm^{-1}. Structure determination revealed that the molecule possesses a planar conformation within experimental error. Structurally, there does not appear to be any significant difference between the parent part of dpan and anthracene. The two benzene rings are twisted against the plane defined by the anthracene moiety with dihedral angles of 31° and 33°, respectively. The detailed structural data are presented in the Supporting Information.

Crystal Structure of 1. Reaction of AgClO$_4$ with an equimolar ratio of dman in *p*-xylene afforded single crystals of **1**. The crystallographic study revealed that **1** exists in the solid state as an infinite chain arrangement of silver atoms linked alternately by the aromatic groups and perchlorate ions. The silver atom interacts with the counteranions in a manner that leads to bridging about a crystallographic inversion center, so that a dinuclear core, Ag$_2$O$_2$, is formed with two perchlorate anions symmetrically bridging between the two metal centers with an Ag−O of 2.465(9) Å. Each dman group exhibits a μ-di-η^2-coordination fashion interact-

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(9) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.
(10) *TEXSAN-TEXRAY: Structural Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985 and 1999.
(11) Iball, J.; Low, J. N. *Acta Crystallogr.* **1974**, *B30*, 2203.
(12) Klein, C. L.; Stevens, E. D.; Zacharias, D. E.; Glusker, J. P. *Carcinogenesis* **1987**, *8*, 5.

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

	dpan	**1**	**2**	**3**
formula	$C_{13}H_9$	$C_{16}H_{17}AgClO_4$	$C_{18}H_{12}Ag_2S_2F_6O_6$	$C_{48}H_{40}Ag_2Cl_2O_8$
fw	165.21	416.63	718.14	1031.48
space group	*C*2/*c*	*P*2$_1$/*n*	$P\bar{1}$	*C*2/*c*
a, Å	10.716(3)	7.885(2)	10.622(5)	7.504(2)
b, Å	13.563(4)	12.345(2)	11.474(4)	23.858(8)
c, Å	12.283(3)	17.059(3)	10.426(4)	23.062(1)
α, deg			94.67(3)	
β, deg	90.59(2)	97.32(2)	112.93(3)	89.238(1)
γ, deg			107.97(3)	
V, Å^3	1785.2(8)	1646.9(6)	1083.2(9)	4128(1)
Z	8	4	2	4
T, °C	23	23	23	22
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69	0.710 69
ρ, g/cm^3	1.229	1.680	2.202	1.660
μ, cm^{-1}	0.69	13.96	20.82	11.32
$R_1{}^a$	0.066	0.060	0.051	0.082
$R_w{}^b$	0.082	0.083	0.065	0.310^c

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

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

Complex **1**			
Ag−O(2)	2.465(9)	Ag−C(1)	2.47(1)
Ag−C(2)	2.42(1)	Ag−C(9)	2.41(1)
Ag−C(10)	2.53(1)		
C(1)−Ag−C(2)	32.1(4)	C(1)−Ag−C(9)	131.45(5)
C(1)−Ag−C(10)	129.0(6)	C(2)−Ag−C(9)	139.9(6)
C(2)−Ag−C(10)	157.8(5)	C(9)−Ag−C(10)	31.2(5)
O(2)−Ag−O(2)	70.5(4)		
Complex **2**			
Ag(1)−O(2)	2.297(4)	Ag(1)−O(4)	2.28(1)
Ag(1)−C(1)	2.434(6)	Ag(1)−C(2)	2.600(5)
Ag(1)−C(17)	2.67(1)	Ag(1)−C(18)	2.66(1)
Ag(2)−O(1)	2.439(5)	Ag(2)−O(3)	2.557(5)
Ag(2)−O(5)	2.401(9)	Ag(2)−O(6)	2.32(1)
Ag(2)−C(11)	2.540(7)	Ag(2)−C(12)	2.679(8)
O(4)−Ag(1)−O(2)	107(1)	C(1)−Ag(1)−C(2)	31.9(2)
C(1)−Ag(1)−C(18)	114.3(3)	C(1)−Ag(1)−C(17)	135.9(6)
C(2)−Ag(1)−C(18)	96.7(2)	C(2)−Ag(1)−C(17)	108.9(5)
C(18)−Ag(1)−C(17)	28.1(7)	O(6)−Ag(2)−O(5)	86.0(6)
O(6)−Ag(2)−O(1)	142.2(4)	O(6)−Ag(2)−O(3)	93.6(5)
O(5)−Ag(2)−O(1)	79.0(3)	O(5)−Ag(2)−O(3)	143.7(4)
O(1)−Ag(2)−O(3)	79.5(2)	C(11)−Ag(2)−C(12)	30.6(3)
Complex **3**			
Ag(1)−O(1)	2.477(8)	Ag(1)−C(6)	2.45(1)
Ag(1)−C(7)	2.443(9)	Ag(2)−O(1*)	2.509(8)
Ag(2)−C(13)	2.337(9)	Ag(2)−C(14)	2.445(8)
O(1)−Ag(1)−O(1′)	74.2(4)	C(6)−Ag(1)−C(6′)	164.2(5)
C(6)−Ag(1)−C(7)	32.5(4)	C(6)−Ag(1)−C(7′)	135.3(4)
C(7)−Ag(1)−C(7′)	122.5(5)	O(1*)−Ag(2)−O(1**)	73.1(4)
C(13)−Ag(2)−C(13*)	162.7(5)	C(13)−Ag(2)−C(14)	33.2(3)
C(13)−Ag(2)−C(14*)	133.9(4)	C(14)−Ag(2)−C(14*)	123.2(4)

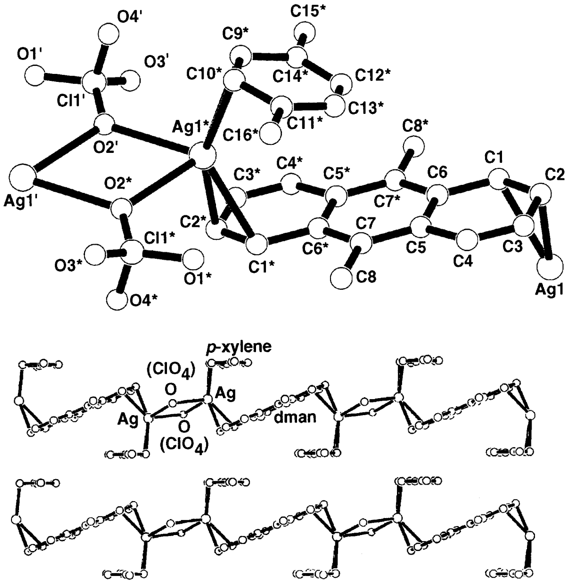

Figure 1. Molecular structure (top) and perspective view (bottom) of the intermolecular and intramolecular aromatic stackings in **1**.

ing with two symmetry-related metal ions to bridge two Ag_2O_2 dinuclear units. The pseudotetrahedral coordination sphere around the silver atom is completed by the further coordination of one crystallized solvent molecule. This results in a one-dimensional array of silver atoms sandwiched by dman and *p*-xylene molecules propagating parallel to the *b* axis, Figure 1. The packing diagram shows that the complex involves both intramolecular and intermolecular *π*−*π* interactions between the dman and *p*-xylene planes, with the closest contacts of 3.50 and 3.70 Å, respectively. Compared with the modeled porphyrin−porphyrin interactions (3.4 Å) in solution,[13] these contacts can be categorized as moderate *π*−*π* interactions. Nevertheless, they constitute columnar aromatic stacks and give rise to a pseudo triple-decker structure.

Crystal Structure of 2. The previous crystallographic study of the dpan complex of silver(I) perchlorate, [Ag(dpan)(ClO_4)(C_6H_6)$_2$], shows a discrete monomeric structure.[14] In the present work, silver(I) triflate was chosen to further study the coordination behavior of dpan. The X-ray structural determination of **2** reveals an elaborate three-dimensional network structure as shown in Figure 2. There are two crystallographically independent silver(I) ions in the complex. While Ag(1) involves a common distorted tetrahedral geometry comprised of one oxygen atom of two different triflate anions and two C═C moieties (one from dpan and the other from benzene), Ag(2) adopts an unusual square-pyramidal coordination environment with one oxygen

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(13) Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(14) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8610.

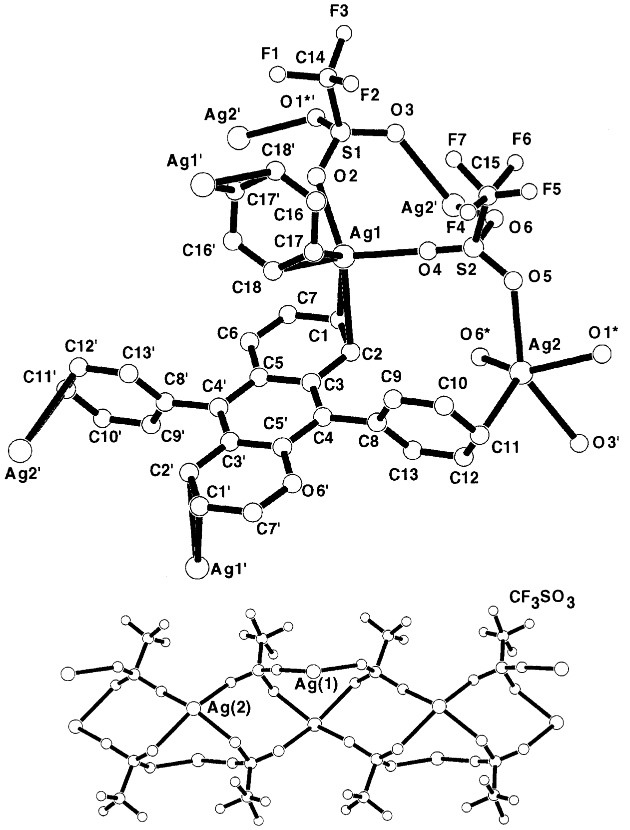

Figure 2. Molecular structure (top) and ionic chain (bottom) in **2**.

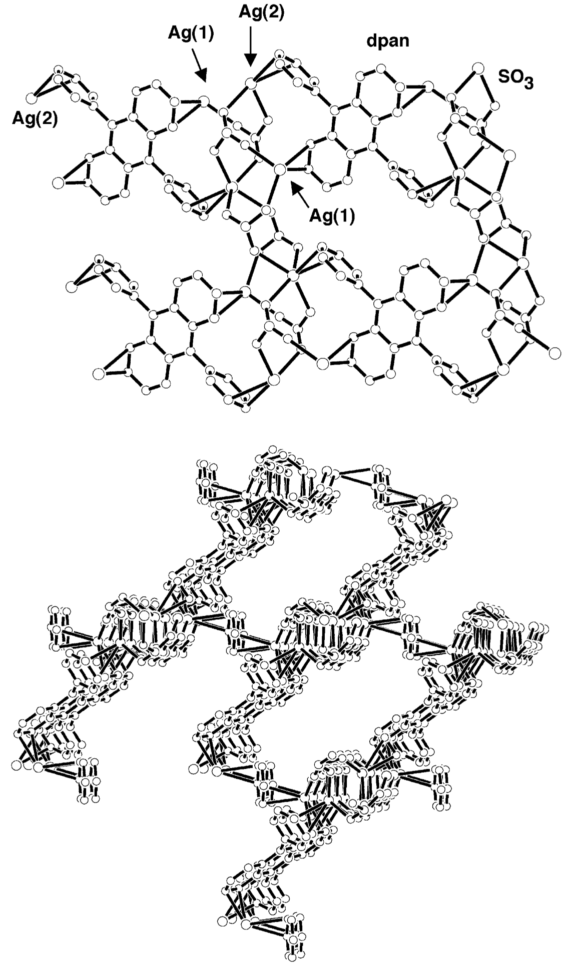

Figure 3. Perspective views of the two-dimensional (top) and three-dimensional (bottom) networks in **2**.

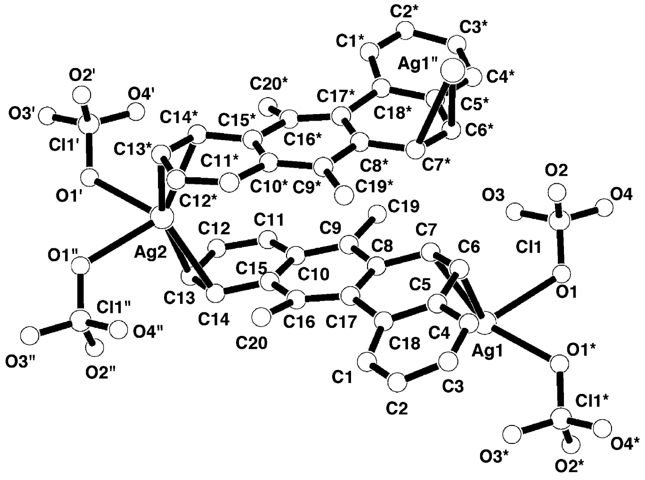

Figure 4. Molecular structure and atom numbering system in **3**.

atom of the four $CF_3SO_3^-$ anions forming the base and one C=C unit from dpan occupying the axial position. The three oxygen atoms of each triflate anion in turn bind three different Ag ions with Ag−O distances ranging from 2.28(1) to 2.557(5) Å to form an infinite one-dimensional Ag−CF_3SO_3 ionic chain, Figure 2 (bottom). Each dpan group displays a μ-tetra-η^2 coordination to interact sequentially with four metal centers, resulting in an association of the two adjacent ionic chains, Figure 3 (top). The resulting segregated two-dimensional frameworks are further bridged by μ-di-η^2-benzene molecules to give the final three-dimensional network, Figure 3 (bottom). The Ag−C bond distances for Ag(1) and Ag(2), ranging from 2.434(6) to 2.67(1) Å and from 2.540(7) to 2.679(8) Å, respectively, are comparable. In contrast with complex **1**, no aromatic stackings are observed in **2**.

Crystal Structure of 3. The unit-cell contents, as determined by the structural study, showed that the stoichiometry of the complex was a 1:1:1 metal-to-ligand-to-anion tertiary system; however, molecules of solvent also exist independently of the complex in lattice interstices. The molecular structure of **3** together with the atomic numbering scheme is given in Figure 4. The complex can be regarded as both a coordination polymer and a stacking polymer. The basic unit of the well-defined portion of the structure contains an aromatic-linked zigzag chain structure propagating along the *a* axis. The chain is formed by the cationic $[Ag_2(dmban)_2]$ building blocks having an alternate −Ag−aromatic−Ag−aromatic− sequential arrangement. The two adjacent chains are connected by two perchlorate anions bridging between the two metal centers with Ag−O distances of 2.477(8) and 2.509(8) Å for Ag(1) and Ag(2), respectively. The double-bridged dinuclear core of Ag_2O_2 is thus formed with an Ag(1)···Ag(2) separation of 4.40 Å.

The L-shaped dmban molecules are arranged alternately in two orientations and adopt a staggered conformation within a pair such that the intramolecular $\pi-\pi$ interactions between the benz[*a*]anthracene moieties form a columnar

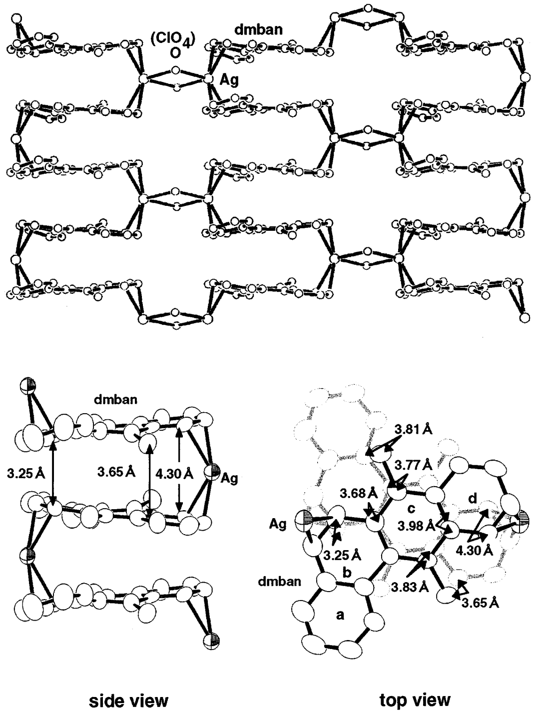

Figure 5. Multidecker structure (top) and intermolecular aromatic stackings (bottom) in **3**.

aromatic stacking on the *a*−*b* plane, as shown in Figure 5. Perpendicular to the columns lie the uncoordinated *p*-xylene molecules on the *b*−*c* plane to avoid the steric hindrance of the methyl groups. The interplanar distances between the stacked aromatic planes are unequal, ranging from 3.25 to 4.30 Å. The closest contact of 3.25 Å between the benz[*a*]-anthracene planes is significantly shorter than that between the dman and *p*-xylene planes in complex **1** (3.50 Å) but comparable with that between the intermolecular coronene planes in $[Ag_4(coronene)_3(ClO_4)_4]$ (3.23 Å).[14] Consequently, the strong intramolecular $\pi-\pi$ interactions between the benz-[*a*]anthracene in **3** leads to an appreciable deviation of the carbon atoms (the maximum deviation being 0.15 Å) from the mean plane and loss of the geometric characteristic planarity of the aromatic compound.

Construction of the Multidecker Anthracene−Silver-(I) System by Intramolecular $\pi-\pi$ Interactions. It has been found that the Ag(I) ion is prone to form adducts with a variety of aromatic compounds.[7,8,14−17] Among them, the anthracene−silver(I) complexes, because of the perfect planarity of the aromatics, present a unique approach for the construction of the multilayer system by intermolecular or intramolecular $\pi-\pi$ interactions, Chart 3. The preparation and molecular structure of $[Ag_2(anthracene)_{0.5}(ClO_4)_2]\cdot H_2O$ was reported in this series by Amma and Griffith in 1974, and the structure is made up of a three-dimensional cross-hatched network of $AgClO_4$ and water with anthracene molecules stacked 5.3 Å apart around the ionic network.[15] Recently, we have reported silver(I) complexes of benz[*a*]-anthracene and dibenz[*a*,*h*]anthracene.[17] The silver(I) complex of the monobenz-substituted anthracene possesses a herringbone packing similar to that of the anthracene, while the structure of the dibenz-substituted anthracene consists of a polymeric W-type chain of alternating aromatic and $AgClO_4$ groups running along the *b* axis.

In this work, we have added three more examples of Ag−anthracene derivatives to the series. To rationalize the synthesis and structures of these complexes, several points can be made. We have studied systematically the reactivity of the silver(I) salts with anthracene derivatives in different solvents and found that benzene and its methyl-substituted solvents such as toluene and xylene are the ideal media for the preparation of the silver(I)−π complexes. Sometimes for a given reaction, changing a solvent can produce an isomorphous precipitate rather than single crystals as expected. For example, efforts have been made to synthesize single crystals of Ag−dman in *o*-xylene or mesitylene, but the reactions isolated precipitate or microcrystalline material instead. This indicates that Ag−π interaction is rather weak, and the related reactivity in solution is solvent-dependent. Nevertheless, the coordination of *p*-xylene to the silver(I) ion in complex **1** is the first case for the coordination of the solvent despite steric hindrance of the methyl groups, and it suggests that the construction of multilayered complexes becomes possible by using coordination of aromatic solvents.

The anions often affect the formation and structure of the silver(I) complexes with aromatic compounds because of the varieties of coordinative modes exhibited by the anions. Thus, it is also very important before starting the synthesis to understand empirically the anion effect on each complex formation. Among the silver salts in hand, nitrate, acetate, and sulfate are scarcely soluble in most organic solvents and, thus, are excluded from consideration as the metal source. Comparatively, $AgCF_3SO_3$ is the most accessible, safe, and stable. In this work, we attempted to synthesize the Ag−dpan complex using $AgCF_3SO_3$ salt in place of $AgClO_4$ in the same kind of solvent (benzene) to argue the importance of a counterion in building silver−π frameworks. Indeed, the two complexes isolated, **2** and $[Ag(dpan)(ClO_4)(C_6H_6)_2]$,[14] involve different space groups and different topologies. The tridentate structure of $CF_3SO_3^-$ in the present work involves each oxygen atom bound to one metal center and results in a three-dimensional polymeric structure, whereas the terminal bonding of the ClO_4^- ion in a previous report leads to a mononuclear structure. It should be noted that, because of the large size of the polycyclic aromatics, the unique functions of the counteranions as spacers and linkages between Ag−π frameworks should not be underestimated in the construction and stabilization of the extended multilayered structures.

One of our purposes in this study is to examine the coordination sites of silver(I) on the aromatic compounds and rationalization of the aromatic stackings in the system. As previously observed in silver(I) complexes with aromatic compounds,[7,8,14−17] silver(I) ions are virtually inclined to bond

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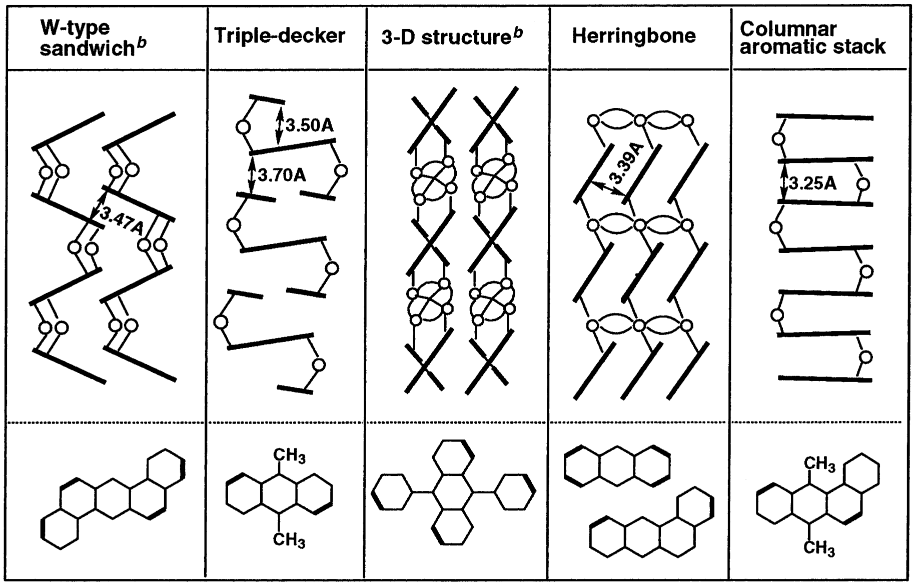
[15] Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 5407 and references therein.

[16] Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K. *Inorg. Chem.* **1997**, *36*, 4903.

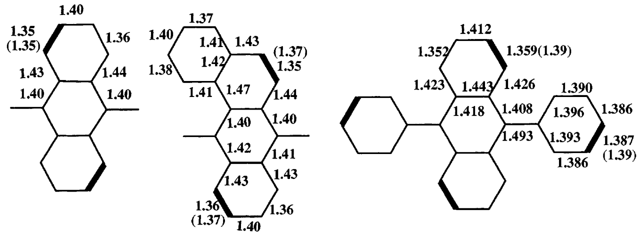
[17] Ning, G. L.; Wu, L. P.; Sugimoto, K.; Munakata, M.; Kuroda-Sowa, T.; Maekawa, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2529.

Chart 3. Schematic Figures of the Ag(I) Coordination Polymers of Anthracene Derivatives[a]



[a] The bold lines of the organic compounds represent the coordination sites to the silver(I) ions. [b]The three-dimensional structure is represented by its two-dimensional moiety for clarity.

Chart 4 π-Coordination Sites (Bold Lines) in dman, dpan, and dmban[a]



[a] The bond lengths are in Å, and those in parentheses are for the complexes.

at the shortest C=C bond portions of the metal-free hydrocarbons in complexes **1**−**3**, Chart 4, indicative of a large electron density accumulated on the π-bonded carbon atoms. However, by comparing the coordination sites of the benz[*a*]anthracene in ref 17 with those of the dimethyl derivative of benz[*a*]anthracene in this work, we have found that the coordinations occur at different sites of the parent molecule, even though both aromatic compounds exhibit a μ-di-η^2-coordination fashion bridging two Ag ions, Chart 3. It is not clear why the silver(I) ions do not interact at the shortest C=C bond portion in the Ag(I)−benz[*a*]anthracene complex. This discrepancy may be due to the stabilization energy of the resulting complex and the molecular packing energy.

The π back-donation from metal to ethylene in the metal complexes of ethylene decreases in the order of Ni(0) > Pt(0) > Rh(I) > Cu(I) > Ag(I),[18] indicating that the π back-bonding ability of silver(I) is very weak and σ donation in Ag−ethylene bonding is dominant. Silver(I) ions, nevertheless, form stable η^2/η^1 coordination complexes with aromatic compounds. The ^{1}H NMR chemical shifts of Ag(I) complexes with aromatic compounds and the theoretical calculation with the density functional method (B3LYP) are designed to study whether the σ donation of an aromatic compound in the η^2/η^1 coordination of Ag(I) is stronger than that of an olefin such as ethylene.

Among the three anthracene derivatives reported in this work, dman is found to involve both intramolecular and intermolecular π−π interactions with *p*-xylene to give a triple-decker structure in **1**, whereas in **3** dmban molecules form columnar stacks by solely intermolecular π−π interactions with *p*-xylene molecules as spacers. Comparatively, dpan is far less favorable to form aromatic stacks in **2**, presumably due to the steric hindrance of the two large benzene groups on both sides of anthracene. This assumption is further supported by the monomeric dpan complex of silver(I) perchlorate, in which equally no aromatic stackings are observed.[14]

In conclusion, this work was part of our research effort aimed at extending the range of silver(I)−π complexes by designing new hydrocarbons and changing the nature of the counterion in the organic−inorganic hybrid networks. The work demonstrates that anthracene derivatives could be used as possible components for the self-assembly of multidecker systems based on cation−π bonding and noncovalent aromatic stackings. To obtain further information on the nature of the bonds involved therein and the physiochemical properties exhibited, a theoretical-model study, together with spectroscopic measurements, is underway as described above.

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

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(18) (a) Munakata, M.; Kitagawa, S.; Kosome, S.; Asahara, A. *Inorg. Chem.* **1986**, *25*, 2622. (b) Suenaga, Y.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Munakata, M. *Polyhedron* **1996**, *16*, 67.