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Mobility of Silver(I) Ions around the Propeller Ligand, Hexaphenylbenzene (HPB), in Silver(I) π-Complexes

Gui Ling Ning, Megumu Munakata,* Liang Ping Wu, Masahiko Maekawa, Yusaku Suenaga, Takayoshi Kuroda-Sowa, and Kunihisa Sugimoto

Department of Chemistry, Kinki University, Kowakae, Higashi-Osaka, Osaka 577-8502, Japan

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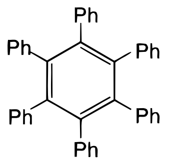
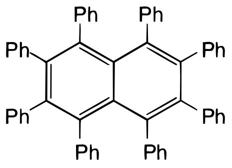
This paper describes three novel and distinctive organosilver(I) complexes with propeller ligand, hexaphenylbenzene (HPB), whose structures are controlled by selected solvents and anions. Treatment of HPB with $AgClO_4$ and $AgCF_3SO_3$ in toluene gave, complexes $[Ag_4(HPB)(ClO_4)_4]$ **1** and $[Ag_2(HPB)(CF_3SO_3)_2(toluene)]$ **2**, respectively. The single-crystal X-ray analysis revealed that **1** contains 2-D sheet framework whereas **2** consists of 1-D chain structure. In both complexes the anions play the role of linkers instead of spacers in the construction of polymeric structures. In contrast, complex $[Ag_2(HPB)(ClO_4)_2(THF)_2]$ **3**, obtained by using tetrahydrofuran (THF) in place of toluene in the synthetic process of **1**, exhibits a discrete dimer. The fundamentals of the synthesis of these complexes, influences of anions and solvents on their coordination networks, and physicochemical properties are discussed. The present findings may serve as a basis for understanding the construction of solid-state materials with designed architecture in crystal engineering. Crystallographic data are as follows. **1**: $C_{21}H_{15}Ag_2Cl_2O_8$, monoclinic, $P2_1/c$, $a = 10.543(2)$ Å, $b = 11.934(4)$ Å, $c = 16.884(3)$ Å, $\beta = 94.08(2)°$, $Z = 4$. **2**: $C_{51}H_{38}Ag_2S_2F_6O_6$, monoclinic, $C2/c$, $a = 18.200(4)$ Å, $b = 16.831(7)$ Å, $c = 16.244(3)$ Å, $\beta = 110.96(2)°$, $Z = 8$. **3**: $C_{25}H_{23}AgClO_5$, monoclinic, $P2_1/c$, $a = 11.321(3)$ Å, $b = 12.511(4)$ Å, $c = 16.357(3)$ Å, $\beta = 99.98(2)°$, $Z = 4$.

Introduction

The recent studies in organometallic chemistry have revealed that the incorporation of metal ions into the polycyclic aromatic hydrocarbon (PAH) system through cation-π interactions can dramatically influence the physical properties of the fused polyaromatic solid surfaces[1−3] and may result in potential applications in electrical conductors and photosensitive devices.[4,5] As members of the PAH family, polyphenyl polycyclic aromatic hydrocarbons have attracted remarkable current interest owing to their unusual molecular conformations, exceptional stability, and potential to serve as building blocks for very large organic structures.[6] Some of these compounds such as hexaphenylbenzene,[7] octaphenylnaphthalene,[8] decaphenylbiphenyl,[6,9] decaphenylanthracene,[8] and others[6−10] have been synthesized and structurally characterized. However, the investigations of these compounds for functional organometallic solid materials are quite rare, and in particular, the use of their coordination complexes as potential building blocks for supramolecular architectures by virtue of their unique geometry and overall dimensions, has been neglected.[11]



hexaphenylbenzene (HPB)



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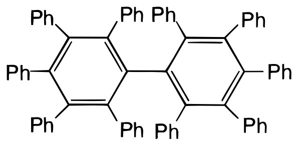
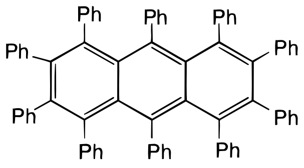


decaphenylbiphenyl



decaphenylanthracene

Our continuing interest in construction of supramolecular architectures of metal ions with polycyclic aromatic hydrocarbons[4,12,13] lets us consider the incorporation of metal ions into

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* To whom correspondence should be addressed. E-mail: munakata@chem.kindai.ac.jp.

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the polyphenyl aromatic hydrocarbon systems for the generation of novel molecular or supramolecular networks with potential physicochemical properties. We have targeted our study on the propeller ligand hexaphenylbenzene (HPB), the simplest member of the polyphenyl family. Silver(I) ion is chosen as the metal center because of its diverse and flexible stereochemistry. The initial results with the characterization of the structure and electrical property of $[Ag_4(HPB)(ClO_4)_4]$, **1**, reported in our preliminary communication,[14] have shown that the mobile silver(I) ions can exhibit varied coordination topologies around the peripheral rings of the propeller depending on the synthetic conditions selected. This has prompted us to consider the possibility that the crystal engineering of such a system with designed structures may be realized by using simple controlling factors such as anions or solvents.[15] With this idea in mind, we successfully synthesized two other complexes, $[Ag_2(HPB)(CF_3SO_3)_2(toluene)]$, **2** and $[Ag_2(HPB)(ClO_4)_2(THF)_2]$, **3**. Here we describe the syntheses and characterizations of this system to show how the mobile silver(I) ions are assembled around the highly symmetrical propeller ligand to build up distinctive molecular/supramolecular architectures and result in different physicochemical properties.

Experimental Section

General Procedures. All reactions and manipulations were carried out under an argon atmosphere using the usual Schlenk techniques. Solvents were dried and distilled by using standard methods before use. Hexaphenylbenzene, silver(I) perchlorate, and silver(I) trifluoromethanesulfonate were purchased from Aldrich Chemical Co., Inc. and used without further purification. $AgClO_4 \cdot H_2O$ was dried at 40 °C under reduced pressure for 5 h before use. Microanalyses were performed by the Department of Chemistry, Tokyo Metropolitan University. IR spectra were recorded as KBr disks on a JASCO8000 FT-IR spectrometer. ESR spectra were obtained on JEOL JES-TE200 ESR spectrometer. The electrical conductivity of compacted pellets was measured by the conventional two-probe technique at room temperature. **Caution:** Perchlorate salts of metal complexes with organic ligands are potentially explosive! Only small amounts of materials should be prepared and handled with great care.

Syntheses. $[Ag_4(HPB)(ClO_4)_4]$ (1). HPB (5.4 mg, 0.01 mmol), was added to a vessel containing 6 mL of toluene. The suspension was heated gently to make the solute dissolve completely and then $AgClO_4$ (12.5 mg, 0.06 mmol) was added. After being stirred for about 20 min, the resultant colorless solution was introduced into a 7-mm-diameter glass tube and layered with *n*-hexane as a diffusion solvent. The glass tube was sealed under Ar and wrapped with aluminum foil. After keeping the glass tube at room temperature for 3 weeks, colorless prismatic crystals suitable for single-crystal X-ray analysis, corresponding to **1**, were obtained. Anal. Calcd for $C_{21}H_{15}Ag_2Cl_2O_8$: C, 36.98; H, 2.22. Found: C, 36.40; H, 2.31.

$[Ag_2(HPB)(CF_3SO_3)_2(toluene)]$ (2). Similar to the synthesis of **1**, to a solution of HPB (5.4 mg, 0.01 mmol) in 6 mL of toluene. $AgCF_3SO_3$ (25 mg, 0.1 mmol) was added. After being stirred for about 20 min, the resultant colorless solution was introduced into a glass tube and layered with *n*-hexane. The glass tube, sealed under Ar and wrapped with aluminum foil, was left standing at room temperature for 5 weeks; colorless prismatic crystals suitable for single-crystal X-ray analysis, corresponding to **2**, were obtained. Anal. Calcd for $C_{51}H_{38}Ag_2S_2F_6O_6$: C, 53.70; H, 3.35. Found: C, 53.23; H, 3.42.

$[Ag_2(HPB)(ClO_4)_2(THF)_2]$ (3). The colorless prismatic crystals of **3** were prepared in the same way as **1**, using tetrahydrofuran (THF) instead of toluene. Anal. Calcd for $C_{25}H_{23}AgClO_5$: C, 54.92; H, 4.24. Found: C, 54.57; H, 4.42.

Table 1. Crystallographic Data

	1	**2**	**3**
formula	$C_{21}H_{15}Ag_2Cl_2O_8$	$C_{51}H_{38}Ag_2S_2F_6O_6$	$C_{25}H_{23}AgClO$
fw	681.99	1140.70	546.77
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$C2/c$	$P2_1/c$
T, °C	23.0	23.0	23.0
a, Å	10.543(2)	18.200(4)	11.321(3)
b, Å	11.934(4)	16.831(7)	12.511(4)
c, Å	16.884(3)	16.244(3)	16.357(3)
β, deg	94.08(2)	110.96(2)	99.98(2)
V, Å^3	2118.9(8)	4646(2)	2281.7(9)
Z	4	8	4
d(calcd), g cm^{-3}	2.138	1.630	1.592
radiation	Mo Kα ($\lambda = 0.710\ 69$ Å)	Mo Kα ($\lambda = 0.710\ 69$ Å)	Mo Kα ($\lambda = 0.710\ 69$ Å)
μ, (Mo Kα) cm^{-1}	21.44	10.05	10.32
R,[a] R_w[b]	0.056, 0.052	0.057, 0.067	0.050, 0.056

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

X-ray Crystallography. The single-crystal suitable for X-ray measurement was fixed on a glass fiber with adhesives. All diffraction data were collected at room temperature on Rigaku AFC7R four-circle diffractometer equipped with graphite-monochromated Mo Kα radiation and a rotating anode generator (λ (Kα) = 0.71069 Å). 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. For **1** and **2**, the intensities of three representative reflections, measured at 150 reflection intervals throughout data collection, remained constant, indicating crystal and electronic stability. Thus, no decay correction was applied. For complex **3**, the standards decreased by 5.6% during the data collection. A linear correction factor was applied to the data to account for this phenomenon.

An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.88 to 1.00 and from 0.82 to 1.00 for **1** and **3**, respectively. For complex **2**, azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods,[16] expanded using Fourier techniques,[17] and refined by full matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$ with anisotropic thermal parameters for all of the non-hydrogen atoms. The positions of all the hydrogen atoms were determined from difference electron density maps and included, but not refined. Reliability factors are defined as $R = \sum(|F_o| - |F_c)|/\sum|F_o|$ and $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$. Atomic scattering factors and anomalous dispersion terms were taken from the usual sources.[18] All of the calculations were performed using the teXsan package.[19] 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. The selected bond distances and angles for three complexes are listed in Table 2.

Results and Discussion

Syntheses and Properties. A ligand generally is coordinated to metal ions via a stoichiometric reaction,[4,12] but the complexes presented here are prepared via reactions of excess metal ions

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with the ligand HPB. In the experiments, when the molar ratio of metal ions to ligand is less than 6 for complexes **1** and **3**, 10 for **2**, the crystallized solid at room temperature contained only the free ligand. The reason for this phenomenon is 2-fold: (i) solvent toluene may react with silver(I) ions to form a complex,[20] which consumes partial silver(I) ions; and (ii) when a complex formed in solution is “incongruently saturating”,[21] its crystal cannot be obtained via a stoichiometric reaction. This can be simply interpreted with the help of an equilibrium diagram at room temperature for the solid−liquid system[22a] in Scheme 1 based on the following equation.

$$\begin{tikzcd}
m\mathbf{M}\text{(metal ion)} \arrow[d, shift left] & +\, n\mathbf{L}\text{(ligand)} \arrow[d, shift left] \arrow[r, shift left] & \mathbf{C}\text{(complex)} \arrow[l, shift left] \arrow[d, shift left] & \text{(in solution)} \\
\mathbf{M} \arrow[u, shift left] & \mathbf{L} \arrow[u, shift left] & \mathbf{C} \arrow[u, shift left] & \text{(crystallized solid)}
\end{tikzcd}$$

The diagram is composed of four areas, I−IV, representing, respectively, the unsaturated solution of **C**, crystallization of the pure **L**, crystallization of **C** and crystallization of the metal salt **M**. The equimolar-ratio line **SC** indicates that any point on this line has the same mole ratio of metal ion/ligand (i.e., m/n).[22b] If the reactants are added to the reaction system stoichiometrically, their total composition will be on the line **SC** at a given position, such as **f**, which is decided by the amount of solvent. The gradual diffusion of *n*-hexane, just like removing solvent (toluene or THF) from solution, makes the unsaturated solution saturated (that is, **f** moves to **g** or goes into II). In this case, only free ligand **L** is crystallized. To obtain complex **C**, it is necessary to add an excess of metal salt to make the total composition on line **SD**, or on any position which can fall into the area III. Depending on different ligand, metal salt and solvent, the positions of $\mathbf{b_1}$, $\mathbf{b_2}$, $\mathbf{e_1}$, $\mathbf{e_2}$, and **C** are changeable. If the complex **C** is “congruently saturating”, it can be obtained via a stoichiometric reaction. That is why we are sometimes lucky enough to isolate the complex through a stoichiometric reaction, and sometimes we are unable to obtain the solid product without adding an excess of metal salts or ligands. In some cases, two or more complexes exist which correspond to different positions in the scheme owing to different components. If it is so, changing the molar ratio of metal ion/ligand can lead to different complexes. In the present work, only one complex exists in each synthetic condition, thus no new complex was obtained by changing the molar ratio.

These three compounds are sparingly soluble in common organic solvents. They are reasonably stable at ambient daylight within one week, but exhibit moisture sensitivity at atmospheric conditions. Complex **1** showed a increased conductivity with time during the measurement by two probe method, $\sigma_{50\mathrm{min}} = 0.015$ (S cm^{-1}), whereas complex **2** is an insulator and **3** displays semiconductive behavior with $\sigma = 3.0 \times 10^{-5}$ (S cm^{-1}).

IR Spectra. The interest in the IR spectra of these compounds lies mainly in the coordinative interactions associated with the ligand and the counteranions. In Table 3 are recorded the IR spectra of complexes **1**−**3** together with the free ligand HPB. A broad strong absorption occurs in the region 1090−1254 cm^{-1} in these three complexes, and their peaks are shifted to slightly higher (**1**, **3**) or lower (**2**) frequencies compared with the normal absorption of $AgClO_4$ at 1140, 1109, 1087 cm^{-1} and $AgCF_3SO_3$ at 1256, 1179 cm^{-1}. This suggests that the perchlorate and trifluoromethanesulfonate groups in these complexes are present not as ionic species, but as coordinated ones.[23] In addition, whereas **1** contains three very strong, well-resolved, peaks between 1090 and 1144 cm^{-1}, complex **3** shows only one very strong peak at 1096 cm^{-1}, because of the different coordination modes of the perchlorate ions.[23,24] The coordination of silver(I)

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

1			
Ag(1)−O(3)	2.478(8)	Ag(1)−O(5)	2.50(1)
Ag(1)−C(3)	2.420(9)	Ag(1)−C(4)	2.72(1)
Ag(1)−C(19)	2.75(1)	Ag(2)−O(3)	2.412(7)
Ag(2)−O(6)	2.44(1)	Ag(2)−C(10)	2.669(8)
Ag(2)−C(11)	2.572(9)	Ag(2)−C(17)	2.593(10)
Ag(2)−C(18)	2.68(1)		
O(3)′-Ag(1)-O(5)′	71.2(3)	O(3)′-Ag(1)-C(3)	141.3(3)
O(3)′-Ag(1)-C(4)	119.7(3)	O(3)′-Ag(1)-C(19)′	80.7(3)
O(5)′-Ag(1)-C(3)	94.6(3)	O(5)′-Ag(1)-C(4)	108.9(3)
O(5)′-Ag(1)-C(19)′	110.0(3)	C(3)−Ag(1)-C(19)′	137.4(3)
C(4)−Ag(1)-C(19)′	140.3(3)	O(3)−Ag(2)-O(6)	98.7(3)
O(3)−Ag(2)-C(10)	129.0(3)	O(3)−Ag(2)-C(11)	112.7(3)
O(3)−Ag(2)-C(17)	108.1(3)	O(3)−Ag(2)-C(18)	86.2(3)
O(6)−Ag(2)-C(10)	118.6(3)	O(6)−Ag(2)-C(11)	102.3(4)
O(6)−Ag(2)-C(17)	118.8(4)	O(6)−Ag(2)-C(18)	102.9(4)
C(10)−Ag(2)-C(17)	84.2(3)	C(10)−Ag(2)-C(18)	114.9(3)
C(11)−Ag(2)-C(17)	115.2(3)	C(11)−Ag(2)-C(18)	145.6(3)
C(17-Ag(2)−C(18)	30.7(3)	C(10)−Ag(2)-C(11)	31.0(3)
C(3)−Ag(1)-C(4)	30.2(3)		
2			
Ag−O(2)	2.388(9)	Ag−O(3)	2.315(8)
Ag−C(3)	2.609(10)	Ag−C(8)	2.58(1)
Ag−C(9)	2.70(1)		
O(2)−Ag-O(3)	97.0(3)	O(2)−Ag-C(3)	94.0(4)
O(2)−Ag-C(8)	97.4(3)	O(2)−Ag-C(9)	119.0(4)
O(3)−Ag-C(3)	101.0(4)	O(3)−Ag-C(8)	117.4(5)
O(3)−Ag-C(9)	94.1(5)	C(8)−Ag-C(9)	28.8(3)
3			
Ag−O(1)	2.61(2)	Ag−O(2)	2.66(2)
Ag−O(5)	2.44(1)	Ag−C(2)	2.66(2)
Ag−C(3)	2.73(2)	Ag−C(8)	2.53(2)
Ag−C(9)	2.75(2)		
O(1)−Ag-O(2)	47.9(4)	O(1)−Ag-O(5)	131.3(5)
O(1)−Ag-C(2)	114.2(6)	O(1)−Ag-C(3)	85.7(6)
O(1)−Ag-C(8)	113.5(6)	O(1)−Ag-C(9)	84.2(5)
O(2)−Ag-O(5)	86.4(4)	O(2)−Ag-C(2)	99.4(5)
O(2)−Ag-C(3)	84.4(5)	O(2)−Ag-C(8)	136.5(6)
O(2)−Ag-C(9)	118.5(5)	O(5)−Ag-C(2)	84.8(5)
O(5)−Ag-C(3)	108.8(7)	O(5)−Ag-C(8)	86.7(5)
O(5)−Ag-C(9)	110.8(6)	C(8)−Ag-C(9)	29.8(5)
C(2)−Ag-C(3)	29.2(5)	C(2)−Ag-C(8)	122.7(7)
C(3)−Ag-C(8)	138.1(6)	C(2)−Ag-C(9)	139.1(5)
C(3)−Ag-C(9)	134.9(7)		

Scheme 1

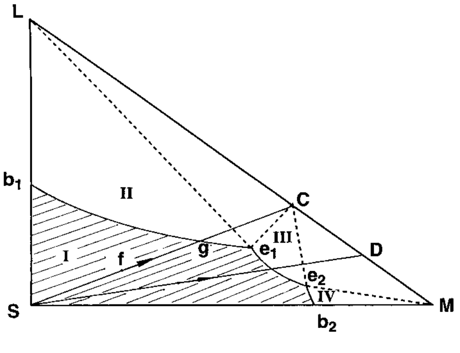

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Table 3. IR Data for HPB and Complexes **1**−**3** (in cm^{-1})[a]

HPB	**1**	**2**	**3**	assignment
3057 (w)	3057 (vw)	3057 (w)	3053 (w)	ν(CH)
3024 (m)		3024 (w)	3024 (w)	ν(CH)
1599 (m)	1618 (w),1599 (w), 1587 (w)	1599 (m)	1599 (m)	ν(CC)
1497 (m)	1493 (m)	1495 (m)	1495 (m)	ν(CC)
1441 (m)	1437 (w)	1441 (m)	1441 (m)	ν(CC)
1400 (m)	1402 (w)	1402 (m)	1400 (m)	ν(CC)
1072 (m)	$\underline{1144}$ (vs), $\underline{1111}$ (vs), $\underline{1090}$ (vs)	$\underline{1254}$ (vs), $\underline{1175}$ (vs)	$\underline{1096}$ (vs)	β(CH)
1028 (m)	$\underline{1016}$ (s)	$\underline{1034}$ (vs)	$\underline{1028}$ (m)	β(CH)
783 (m)	792 (s)	$\underline{783}$ (m)	783 (m)	γ(CH)
729 (s)	740 (s)	731 (m)	731 (s)	γ(CH)
696 (vs)	706 (s), $\underline{629}$ (s)	696 (s), $\underline{648}$(s)	696 (s), $\underline{627}$ (s)	γ(CH)

[a] The underlined data are the frequencies for ClO_4^- or $CF_3SO_3^-$. s, strong; m, medium; w, weak; v, very.; ν, stretching mode; β, in-plane deformation mode; γ, out-of-plane deformation mode.

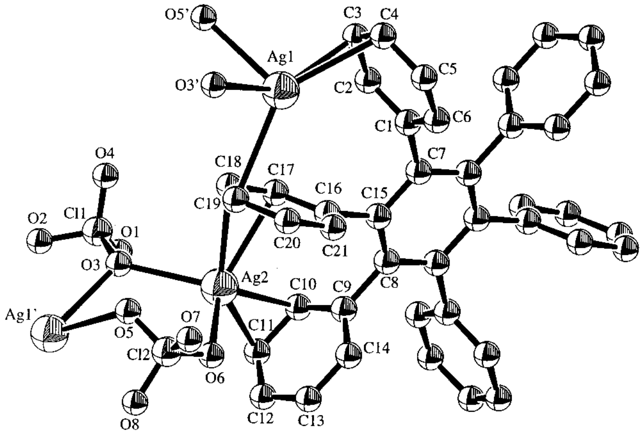

Figure 1. Structure and labeling of **1** (ORTEP, 50% probability).

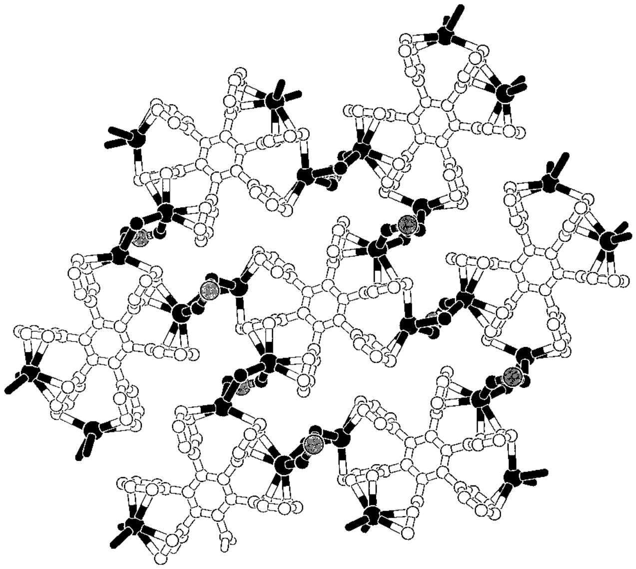

Figure 2. Two-dimensional sheet framework of **1** (uncoordinated O and Cl omitted for clarity).

ions to carbon or carbon−carbon π bonds of HPB can also be seen by comparing the spectra of **1**−**3** with that of the free ligand. The single peak at 1599 cm^{-1} in HPB appears split at 1618, 1599, and 1587 cm^{-1} in complex **1**. The absorption at 1599 cm^{-1} can be assigned to uncoordinated phenyl ring ν(CC), that at 1618 and 1587 cm^{-1} to the coordinated phenyl ring ν(CC). Similar splits have been observed for the coordinated phenylene ring in our recently reported silver(I) complex of thianthrene.[25] In **2** or **3** no split around 1599 cm^{-1} was observed, but slightly lower frequencies at 1495 cm^{-1} [ν(CC)] and 3053 cm^{-1} [ν(CH)] than those of the free HPB at 1497 and 3057 cm^{-1} were found. This suggests that different coordination modes and conformations of the ligand can result in varied shift of IR frequencies. It is impossible to assign the bands around 1072 cm^{-1}, owing to the overlap of the frequencies of ClO_4^- and HPB.

2-D Sheet Structure of [Ag4(HPB)(ClO$_4$)$_4$] (1). The single-crystal X-ray diffraction analysis of **1** reveals a 2-D framework constructed by Ag(I)−O linkage as well as carbon and/or carbon−carbon π coordination of HPB with Ag(I). As illustrated in Figure 1, the center of the propeller HPB molecule is coincided with the inversion center so that only half of its molecule is crystallographically unique. Two independent silver(I) ions exist around the propeller, bridged by interactions with the same phenyl ring, C(16)−C(21). Each metal center interacts asymmetrically with two phenyl rings. Although Ag(1) involves one η^1- and one η^2-carbon bonding at Ag−C distances ranging from 2.420(9) to 2.75(1) Å, Ag(2) involves two η^2-carbon interactions instead at Ag−C separations ranging from 2.572(9) to 2.68 Å. The next closest contact between the silver and the C atoms is 2.88 Å, well beyond the limits observed in the reported silver(I)-aromatic complexes.[4,12,26−29] Thus, each centrosymmetrical HPB molecule interacts with four pseudo-tetrahedral silver(I) ions in a hexa-η^2-di-η^1 fashion and is linked to the adjacent counterparts by two separate perchlorate ions each bridging between the two metal centers, Ag(1)−O(3)−Ag(2) and Ag(1)−O(5)−Cl(1)−O(6)−Ag(2) with the Ag···Ag separation of 4.13 Å. The dihedral angles between the planar phenyl ring and the central ring range from 76° to 89°. The overall structure thus formed is a neutral 2-D polymeric framework shown in Figure 2.

Chain Structure of [Ag$_2$(HPB)(CF$_3$SO$_3$)$_2$(toluene)] (2). When using $AgCF_3SO_3$ instead of $AgClO_4$ and changing molar ratio of metal ion/HPB to 10/1 in the synthetic process of **1**, the mobile silver(I) ions around the propeller form complex **2** with a one-dimensional chain structure. An ORTEP drawing of its local coordination is depicted in Figure 3 together with

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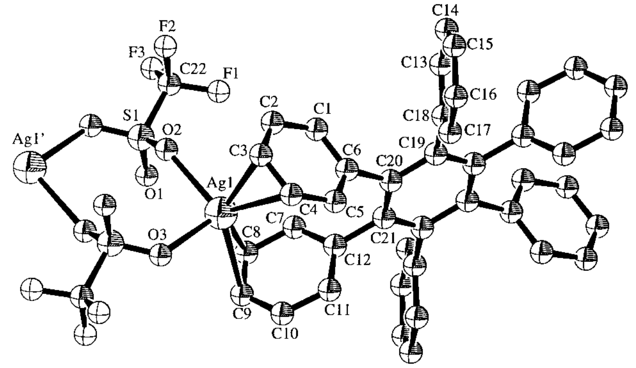

Figure 3. Structure and labeling of **2** (ORTEP, 50% probability).

the atom-numbering scheme. Similar to complex **1**, only half of the propeller molecule is unique owing to the coincidence of its center with the conversion center. The coordination geometry around the silver(I) ion is also pseudotetrahedral, comprising two oxygen atoms from two separate triflate ions and two η^2-carbon atoms from two neighboring phenyl rings of one propeller. The Ag−C bond distances range from 2.58(1) to 2.82(1) Å. The next closest contact between silver and carbon atoms is 2.88(1). Compared with **1**, although the silver(I) ions have quite similar local coordination environments and the HPB molecules adopt almost the same conformation with the dihedral angles between the peripheral phenyl ring and the central benzene ranging from 74 to 88°, it displayed its unique polymeric structure by special ordering of the mobile silver(I) ions around and between the propeller. Unlike **1** where all six substituted phenyl rings participate in π bonding, each centrosymmetrical HPB molecule in **2** interacts symmetrically with two Ag(I) ions in a tetra-η^2 fashion involving four phenyl rings, with other two at para-positions free of coordination. As the perchlorate ion in **1**, each $CF_3SO_3^-$ group bridges between two metal centers with the Ag···Ag separation of 5.21 Å. Such connections give an overall one-dimensional chain structure on the *ac* plane with the solvate toluene molecules occupying the void space between the two chains, Figure 4a. The four symmetry-related chains in the cell comprise a macromolecular cavity down *c* axis where the toluene molecules are incorporated in the center, Figure 4b. These solvent molecules are not involved in intermolecular contacts.

Dimeric Structure of [$Ag_2(HPB)(ClO_4)_2(THF)_2$] (3). This complex contains a discrete dinuclear structure as shown in Figure 5. Unlike complex **1** or **2**, where the metal ions involve a distorted tetrahedral geometry, the coordination sphere around the silver(I) ion in **3** can be regarded as five-coordinate if bond length of 2.66(2) Å for Ag−O(2) is taken as an effective interaction[12]. Thus, each metal center in the dimeric unit interacts with two η^2-carbon atoms from two neighboring phenyl rings of one propeller and two oxygen atoms from one perchlorate group. The coordination geometry of the metal ion is completed to five by interaction with one solvent THF molecule. The bond distances of Ag−C distances range from 2.53(2) to 2.75(2) Å, and those of Ag−O range from 2.44(1) to 2.66(2) Å. As observed in **2**, the centrosymmetric HPB molecule also exhibits a tetra-η^2-coordination, symmetrically bridging two metal centers.

Complex **3** was obtained only by using solvent THF instead of toluene in the synthetic process of **1**. The pronounced solvent effect on complex structures is manifest. Compared with the structure of **1**, the solvated THF molecule in **3** interacts somewhat with the Ag(I) ion in place of one bridging perchlorate group. This results in changing the bonding mode of the second perchlorate group from bridging two metal centers to chelating one metal center, leading to a final dimeric, rather than polymeric, structure. In addition, the participation of THF molecules in bonding with metal ions causes considerable concomitant effect on conformation of the π donor hexaphenylbenzene. The three independent peripheral phenyl rings of each HPB are found almost perpendicular to the central benzene plane with dihedral angles ranging from 81° to 85°.

Mobility of Silver(I) Ions Around Propeller. The propeller ligand is coordinated to silver(I) ions in a η^1/η^2 fashion in all three complexes, which, to the best our knowledge, is the first example of metal complexation of a polyphenyl aromatic hydrocarbon ligand. There is only one report in the literature describing HPB-coordinated compound, $(\eta^6\text{-}C_6Ph_6)Co(\eta^2\text{-}C_2Ph_2)$, where the central benzene ring of C_6Ph_6 interacts with the cobalt ion in an η^6 fashion to construct a monomer structure.[11] The other reported complexes with propeller-type ligands, C_nPh_n ($n = 3-5$), also take central-ring coordination in a η^n-C_nPh_n ($n = 3-5$) fashion to form monomer, dimer, or metal cluster.[30] The polymeric structures of **1** and **2** in this study, owing to the bulky hexasubstituted benzene preventing the approaching of the two adjacent HPB molecules, are accomplished by bridging ClO_4^- or $CF_3SO_3^-$ anions between two silver(I) ions. The ClO_4^- and $CF_3SO_3^-$ anions play a role of linker in such polyphenyl polymeric structures, instead of spacers as those found in most silver(I) complexes of polycyclic aromatic hydrocarbons.[4,12] Complexes **1**−**3** retain the propeller configuration of HPB moiety[31] with the individual phenyl rings being still planar within the limits of experimental error after the coordination to silver(I) ions. However, the dihedral angles between the phenyl rings and the central benzene ring, ranging from 74 to 89°, are significantly larger than those observed in the noncoordinated HPB molecule (62−70.7°),[6b] indicating that the conjugation between the phenyl rings and the central benzene ring diminishes.[32] In complex **3**, for example, the π conjugation is almost disrupted (the dihedral angles are near 90°). These twists undoubtedly are attributed to the steric interference, involving the silver(I)−π interaction of the peripheral rings, and solvent effect.

The most remarkable feature of this study is the variable arrangements and high degree of silver(I) ions ordering around the peripheral rings of each HPB molecule controlled by solvents and anions. We have demonstrated that with the same bridging ligand and metal ions, these complexes may display quite different topologies: complex **1** exhibits a 2-D sheet structure, **2** gives a 1-D chain structure, whereas **3** is a discrete dimer. All these observations may be attributable to the steric requirements[33] of the ClO_4^- and $CF_3SO_3^-$ groups and solvent effect.[34] With the proper size of the ClO_4^- ion and suitable organic solvent, toluene, in **1**, the mobile silver(I) ions occupy four coordinating sites for each HPB molecule forming a polymeric

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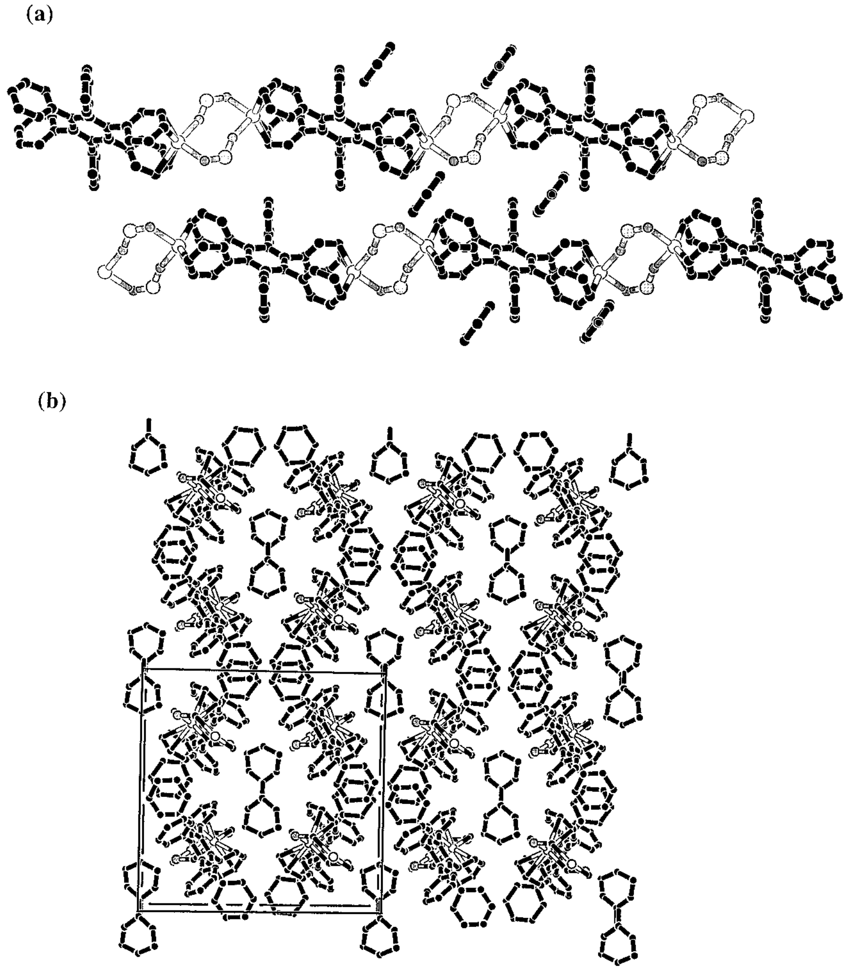

Figure 4. (a) Chain framework and (b) Molecular cell-packing of **2** (down the *c* axis).

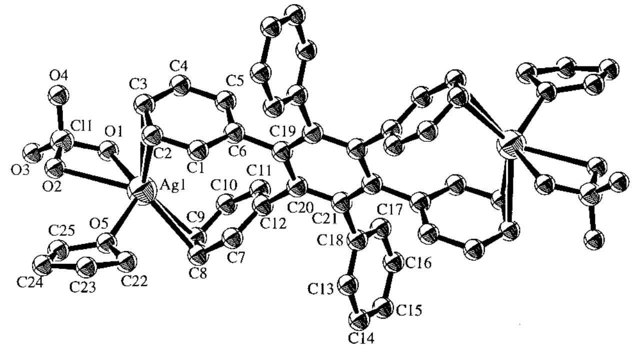

Figure 5. Molecular structure of **3** (ORTEP, 50% probability).

sheet framework. When the smaller anion ClO_4^- is changed to the drastically larger anion $CF_3SO_3^-$, the coordinated silver(I) ions around each propeller decreases to two forming one-dimensional chain framework of **2**. Further coordination of silver(I) ions to the uncoordinated phenyl rings may be prohibited by steric hindrance of the bulky anions, or by other unfavorable interactions associated with the bulky anions. A similar anion-size effect on the architecture of supramolecular network has been observed for the copper(I) complexes of pyridinone.[35] Interestingly, by using THF in place of toluene in the synthetic process of **1**, the coordination of THF as a spacer reduced the number of the interacting perchlorate groups about each metal center from two to one and changed the anion-bonding mode from bridging to chelating, leading to a final dimeric, rather than polymeric, structure in **3**. This indicates that the structure construction process in such systems is strongly solvent-dependent.

In conclusion, with the mobile silver(I) ions and propeller ligand HPB, three novel and distinct coordination compounds, **1**−**3**, have been synthesized at room temperature by changing anions and solvents. The polymeric networks for **1** and **2** are formed by the linkage of ClO_4^- or $CF_3SO_3^-$ anions between two silver(I)-HPB units. It is believed that self-assembly of aromatic compounds with transition metal ions can use the unique aromatic shape of ligand, the steric requirement of anions, and the solvent effect to construct a wide diversity of supramolecular architecture with novel networks and different physicochemical properties.

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Supporting Information Available: Three X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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