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Fluorescent Coordination Networks of 2,3,6,7,10,11-Hexakis(phenylthio)triphenylene and Silver(I) Triflate

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The polycyclic aromatic ligand 2,3,6,7,10,11-hexakis(phenylthio)triphenylene (HPhTT) coordinates with AgTf (Tf = trifluoromethylsulfonate) to form 1D networks with various solvent molecules included. In particular, the crystal structures and photoluminescent properties of compound **1** (formula = 2HPhTT·3AgTf·3toluene) and compound **2** (formula = 2HPhTT·3AgTf·2THF) are described. Both **1** and **2** feature similar network connectivity as well as similar local coordination environments around the silver(I) atoms. The organizations of the guest molecules in the two structures are, however, quite different: In **1**, the toluene molecules are enclathrated in isolated cavities by the host network; in **2**, the THF molecules are confined in continuous 1D channels. Because of the large aromatic system of the triphenylene moiety, strong fluorescent bands (room temperature) are observed for HPhTT, **1** and **2**, with $\lambda_{F,max} = 447$ nm for HPhTT and $\lambda_{F,max} = 440$ nm for both **1** and **2**.

Introduction

The study of coordination networks has in recent years generated a myriad of extended structures based on metal ions and organic molecules with multiple binding sites (e.g., carboxylates, carbonitriles, and pyridines).[1−5] One important goal now is to incorporate large, delocalized π-electron systems into the solid state framework.[6−13] Research efforts in this direction are largely driven by the generally more intense electronic and photophysical properties of the large π-systems.[10−12]

Along this line of research, we are interested in symmetric polycyclic aromatic chelating molecules such as 2,3,6,7,10,11-hexakis(phenylthio)triphenylene (HPhTT). Symmetrically substituted triphenylene molecules have been widely studied for their discotic liquid crystalline properties[14−17] and as potential organic semiconductors.[18,19] As building blocks for metal−organic frameworks, such molecules offer certain advantages. For example, the 1,2-bis(organylthio) unit tends to chelate metal ions[20−22] and can potentially strengthen electronic interactions between the organic π-system and the metal center. Also, the organic side groups (e.g., the phenyl groups in HPhTT) can be modified to integrate wider

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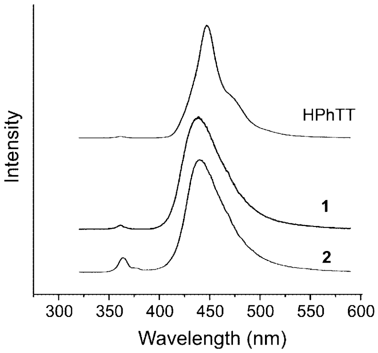

Figure 1. Room-temperature solid state emission spectra of HPhTT, **1**, and **2** (excitation wavelength $\lambda_{ex} = 300$ nm).

functionalities, while maintaining the essential chelating character of the molecule.

As initial results from the study of the network-forming properties of this new type of organic ligands, we here report two coordination networks based on HPhTT and silver(I) triflate (AgTf). The first one is obtained through diffusing *n*-hexane into a toluene solution of HPhTT and AgTf and has the formula 2HPhTT·3AgTf·3toluene (**1**); the second one is formed by vapor-transporting *n*-pentane into a THF (tetrahydrofuran) solution of HPhTT and AgTf and has the formula 2HPhTT·3AgTf·2THF (**2**, formula from the single crystal structure). Although both compounds feature similar 1D coordination networks, they contain rather different molecules as the guests (i.e., toluene in **1** and THF in **2**), suggesting that a wide range of guest−host complexes may be achieved in these systems. The emission spectrum for the solid state sample of the molecule HPhTT shows a strong fluorescence band with $\lambda_{F,max} = 447$ nm (with shouldering to the right) (Figure 1), while slightly blue-shifted fluorescence bands are exhibited by the extended solids of **1** and **2** ($\lambda_{F,max} = 440$ nm for both **1** and **2**). Although these networks are based on the relatively "inert" Ag^+ ions, they are intended as a basis for further studies on systems with more diverse properties of electroactivity, fluorescence, and guest−host interactions.

Experimental section

Starting materials, reagents, and solvents were purchased from commercial sources (Aldrich and Fisher Scientific) and used without further purification. 2,3,6,7,10,11-Hexabromotriphenylene was prepared from a reported procedure.[23] Solution ^{1}H and ^{13}C NMR spectra were taken on a 200 MHz Varian Mercury spectrometer at room temperature. X-ray diffraction patterns for the bulk samples were collected at room temperature on a Scintag XDS 2000 diffractometer (Cu Kα, $\lambda = 1.5418$ Å). The powder samples were pressed onto a glass slide for data collection. A 2θ range 3−50° was collected. Photoluminescence measurements on the solid samples (ground with KBr and pressed into pellets) were performed on a Shimadzu RF-5301PC spectrofluorimeter at ambient temperature. Thermogravimetric analysis (TGA) was performed on a Pyris TGA-1 instrument under flowing N_2 gas (20 mL/min), and the heating rate was 5 °C/min.

Table 1. Selected Crystallographic Data for **1** and **2**

	1	**2**
chem formula	$C_{132}H_{96}Ag_3F_9O_9S_{15}$	$C_{119}H_{88}Ag_3F_9O_{11}S_{15}$
fw	2801.60	2669.40
space group	$P\bar{1}$	$P\bar{1}$
a, Å	12.0810(5)	12.0730(5)
b, Å	16.5071(7)	16.3911(7)
c, Å	31.897(1)	16.4728(7)
α, deg	78.850(1)	107.544(1)
β, deg	82.068(1)	92.037(1)
γ, deg	76.844(1)	104.555(1)
V, Å^3	6047.6(4)	2986.5(2)
Z	2	1
ρ_{calcd}, g/cm^3	1.539	1.484
wavelength, Å	0.71073 (Mo Kα)	0.71073 (Mo Kα)
abs coeff (μ), cm^{-1}	8.13	8.21
$R_1{}^a$	5.65% [$I > 2s(I)$]	7.02% [$I > 2s(I)$]
$wR_2{}^b$	15.53% [$I > 2s(I)$]	22.88% [$I > 2s(I)$]

^{a} $R_1 = \sum||F_o| - |F_c||/\sum(|F_o|)$. ^{b} $wR2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$.

Organic Synthesis of 2,3,6,7,10,11-Hexakis(phenylthio)triphenylene (HPhTT). Inside an argon-filled glovebox, sodium hydride (0.45 g, anhydrous, 60% in mineral oil, 11 mmol) and a stirring bar were loaded into a three-neck round-bottom flask. The flask was then connected to a vacuum manifold under argon protection, and 15 mL of anhydrous pentane was added via cannula. The suspension was stirred for 5 min and the pentane was taken out via cannula. This process was repeated for another two times, and then, 30 mL of freshly distilled diethyl ether (from CaH_2) was added. The reaction vessel was then chilled in an ice−water bath, and stirring was started. Thiophenol (0.9 mL, 97+%, 8.5 mmol) was then injected under argon protection. When the bubbling almost stopped, the suspension was heated in an oil bath to reflux for 15 min, and the diethyl ether was evaporated afterward to yield a white solid. 1,3-Dimethyl-2-imidazolidinone (DMEU, 30 mL, 99%, anhydrous) was added via cannula into the solution, and hexabromotriphenylene (HBT, 0.48 g, 0.7 mmol) was then added under argon protection. The reaction mixture was heated in oil bath at 70 °C for 2 h, during which time the reaction mixture turned into a burgundy solution. Into the solution was injected bromobenzene (0.9 mL, 99%, 8.5 mmol, purged by argon for 15 min). The mixture was heated at 70 °C for another 2 h and then poured into 100 mL of water. The mixture was extracted with dichloromethane (150 mL × 3), and the organic phase was washed with water (300 mL × 4) and brine (saturated, 300 mL) and then dried on anhydrous sodium sulfate. The solvent was evaporated in vacuo to yield a light yellow solid (0.46 g, 77% based on HBT). The solid was washed well with hexane and then purified by flash chromatography (CH_2Cl_2/hexane = 2:8, 0.37 g pure product obtained, 62% based on HBT, mp 183−184 °C). ^{1}H NMR (200 MHz, chloroform-*d*): 7.31 (m, 30 H), 7.99 (s, 6 H). ^{13}C NMR (50 MHz, chloroform-*d*): 126.7, 127.6, 128.3, 129.4, 131.3, 134.6, 137.6.

X-ray Quality Single Crystals of 2HPhTT·3AgTf·3toluene (1). A toluene solution of HPhTT (6.4 mM, 0.3 mL) was mixed with a toluene solution of AgTf (9.7 mM, 0.3 mL) in a glass tube (10 mm o.d./6 mm i.d.). On top of the mixed solution was then layered sequentially toluene (0.5 mL) and hexane (0.8 mL). The tube is then sealed and kept in the dark. Blocklike, colorless crystals suitable for X-ray studies formed after one week (1.9 mg, 71% based on HPhTT). X-ray powder diffraction indicated a single phase consistent with the single crystal structure (see Supporting Information).

X-ray Quality Single Crystals of 2HPhTT·3AgTf·2THF (2). HPhTT (4.6 mg, 0.0050 mmol) was dissolved with AgTf (4.0 mg, 0.016 mmol) in 0.6 mL of THF in a small vial (2 mL). The small

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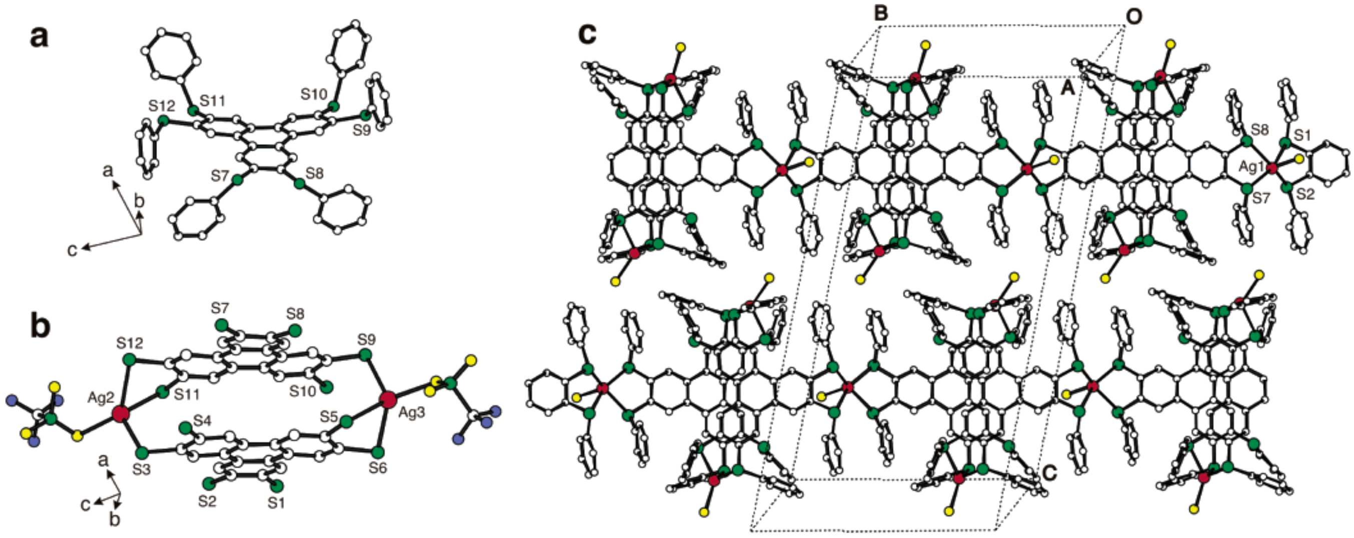

Figure 2. Crystal structure of **1**: green spheres, S; white, C; red, Ag; yellow, O; purple, F. (a) An HPhTT ligand. (b) Two HPhTT molecules linked by two Ag^+ atoms (also bonded to the triflate anion). For clarity, the pendant phenyl groups on the HPhTT ligands and the disordering of the anion are omitted. Bond lengths: Ag2−S3, 2.5295(9) Å; Ag2−S11, 2.6286(9) Å; Ag2−S12, 2.6409(9) Å; Ag2−O, 2.339(4) Å; Ag3−S5, 2.6832(8) Å; Ag3−S6, 2.5788(9) Å; Ag3−S9, 2.5442(9) Å; Ag3−O, 2.310(3) Å. Nonbonding distances: Ag2−S4, 4.9136(9) Å; Ag3−S10, 4.4165(9) Å. (c) Two 1D coordination networks. For clarity, the triflate anion is truncated (only the O atom bonded to the Ag^+ is shown). Bond lengths: Ag1−S1, 3.077(1) Å; Ag1−S2, 2.5621(9) Å; Ag1−S7, 2.6520(9) Å; Ag1−S8, 2.5679(8) Å; Ag1−O, 2.325(3) Å.

vial was placed in a big vial (10 mL) containing about 5 mL of pentane. The big vial was capped and put in the dark. Blocklike colorless crystals suitable for X-ray studies formed after about 4 days (3.6 mg, 55% based on HPhTT). X-ray powder diffraction indicated a single phase consistent with the single crystal structure (see Supporting Information).

X-ray Single Crystal Diffraction Studies of 1. A colorless block with dimensions $0.49 \times 0.16 \times 0.14\ mm^3$ was placed and optically centered on a Bruker SMART CCD system at 173 K. A total of 54849 reflections were collected and corrected for Lorentz and polarization effects and absorption using Blessing's method as incorporated into the program SADABS[24,25] with 27670 unique reflections. The SHELXTL[26] program package was implemented to determine the probable space group and set up the initial files. System symmetry, lack of systematic absences, and intensity statistics indicated the centrosymmetric triclinic space group $P\bar{1}$ (No. 2). The structure was first determined by direct methods (with the successful location of nearly a complete molecule) and subsequently refined with SHELXL 97. One of the three triflate anions was refined over two sets of disordered positions. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions without further refinement. An empirical correction for extinction was also attempted but found to be negative and therefore not applied. Selected crystallographic results are summarized in Table 1.

X-ray Single Crystal Diffraction Studies of 2. Similar procedures were applied to a single crystal of **2** ($0.35 \times 0.23 \times 0.10\ mm^3$). The final structure solution contains a number of disordered fragments. First, one of the Ag atoms (Ag2) and the associated triflate anion were disordered over two sets of centrosymmetrically related positions (the site occupancy factor for each set of positions are therefore fixed at 0.5). Second, the other triflate anion in the asymmetric unit (bonded to Ag1) was refined over two sets of disordered positions. The entire fragment of CF_3SO_3 on one set of the positions was located, whereas only the SO_3 fragment can be located from the Fourier map on the other set of positions. The triflate anions were restrained in the regular conformation (e.g., equal distances between the F atoms and equal distances between the O atoms) during the structure refinement. The SOF for each set was refined as free variables. Third, one of the pendant phenyl groups on the organic molecule was disordered over two sets of positions, with the SOF for each set refined as free variables. Finally, the solvent molecule shows large thermal parameters, indicating significant uncertainty in the atomic positions. All non-hydrogen atoms except those on the solvent molecule were refined anisotropically. Hydrogen atoms were placed in calculated positions of all atoms except those of the disordered phenyl group (which was refined without any H atoms added). Selected crystallographic results are summarized in Table 1.

Results and Discussion

Single crystal X-ray diffraction studies of **1** revealed a seemingly intricate metal−organic polymeric structure, but with relatively simple framework connectivity. The asymmetric portion of the unit cell contains two molecules of HPhTT, three molecules of AgTf, and three molecules of toluene (C_7H_8), which are incorporated during the crystallization process: the asymmetric unit thus has the formula $2HPhTT{\cdot}3AgOTf{\cdot}3C_7H_8$ and consists of a total of 165 non-hydrogen atoms. The two crystallographically inequivalent molecules of HPhTT adopt fairly similar conformations (one of which is shown in Figure 2a), and they are linked into a dimeric unit by two silver(I) atoms (Ag2 and Ag3, see Figure 2b), with their triphenylene moieties stacked in an offset face-to-face manner (interplanar distance, 3.4 Å; center-to-center distance between the two triphenylene fragments, 4.8 Å). Within the dimeric structure, each of the two silver atoms (Ag2 and Ag3) is coordinated by two adjacent sulfur atoms from one ligand, and one sulfur atom from the other. Each

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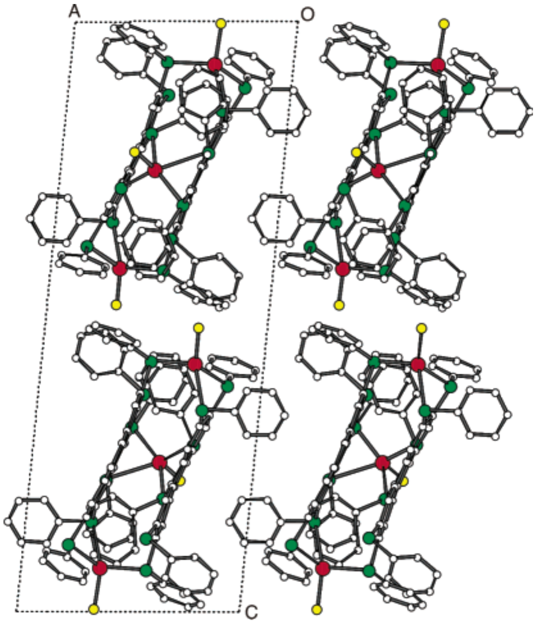

Figure 3. Crystal structure of **1** along the *b*-axis: red spheres, Ag$^+$; green spheres, S; white, C; yellow, O (from the triflate anion, for clarity the rest of the anion is omitted). The toluene molecules are omitted.

of the Ag2 and Ag3 atoms is also bonded to one of the oxygen atoms from the triflate anions, resulting in a distorted tetrahedral geometry around the Ag$^+$ center (see captions of Figure 2b for bond lengths).

The dimeric units are then connected into a one-dimensional network through further bonding between the third silver(I) atom (Ag1) and the remaining sulfur atoms of S1, S2, S7, and S8 (see Figure 2b,c). The Ag1 atom is also coordinated to an oxygen atom from a triflate anion, furnishing a distorted square-pyramidal coordination geometry (see captions of Figure 2c for bond lengths). Each individual chain thus formed in **1** is noncentrosymmetric, and the crystal structure contains equal numbers of the two enantiomorphs related by the center of symmetry (space group $P\bar{1}$).

The overall packing of the chains is shown in Figure 3. Substantial voids exist between the chains, which are occupied by the toluene molecules (see Figure S1 in Supporting Information). The toluene molecules interact with the surrounding HPhTT molecules, forming aromatic−aromatic contacts in the face-to-face as well as edge-to-face manners (with typical C···C contacts of 3.6 Å and above). The toluene molecules are thus enclathrated in isolated (zero-dimensional) cavities. Overall, the toluene molecules are rather uniformly distributed along the [100] plane (see Figure S1), suggesting a relatively easy cleavage along the [100] plane (which is also consistent with the orientation preference observed in the powder diffraction studies, see Figure S2).

The crystal structure of **2** consists of 1D networks similar to those of **1** (Figure S3 in Supporting Information), and it contains the THF molecules as the guest. In contrast to the enclathrated toluene molecules in **1**, the THF molecules in **2** are aggregated into continuous channel-like domains along the crystallographic *c*-axis (see Figure S4A for the empty channels, Figure S4B for the structure with the THF molecules). We suspect that the THF molecules aggregate into the continuous domain for an energetic reason, since the ether-like THF molecules are chemically distinct from the predominantly aromatic networks, and such a microscopic phase separation helps to minimize the interface between the two different components.[27,28] Also, the inclusion phenomena here seem related to the irregular and branchy (or starlike) shape of the organic ligands,[29−31] which may likely obstruct the close packing of the networks and lead to substantial voids that readily take up the solvent molecules as the guests. Following this observation, we are trying to incorporate guest molecules of diverse functionalities (e.g., nitrobenzenes, benzoquinones) in order to provide stronger guest−host interactions.

Thermogravimetric analysis of **1** and **2** (see Figure 4) indicates the guest molecules can be evacuated at relatively low temperatures (220 °C for **1** and 150 °C for **2**). X-ray powder diffraction studies indicate that the evacuation of guest molecules resulted in near complete loss of the crystalline order of the original frameworks. The fragility of the crystalline host−guest complexes may be partly due to the low dimensionality of the chainlike host networks. Further studies are ongoing for obtaining higher-dimensional (e.g., 3D) and more robust frameworks.

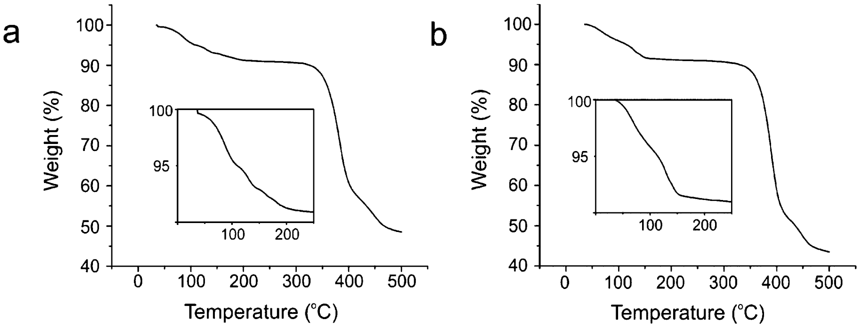

Figure 4. Thermograms for solid samples of **1** (a) and **2** (b) in an argon atmosphere. The heating rate is 5 °C/min. The insets amplify the regions of solvent loss (toluene for **1** and THF for **2**). In part a, the solvent loss (up to 250 °C) corresponds to the value (9.87%) calculated from the crystallographically determined formula 2HPhTT·3AgTf·3toluene. In part b, the solvent loss (up to 200 °C) corresponds to a formula of 2HPhTT·3AgTf·3THF (calculated value 7.89%), indicating there may be another THF molecule in the unit cell (current unit cell content 2HPhTT·3AgTf·2THF) that has not been located by the X-ray diffraction study.

Conclusion

In summary, compounds **1** and **2** feature fluorescent coordination networks based on the newly synthesized polycyclic aromatic ligand HPhTT.[32] The crystal structures point to a rather flexible ability to incorporate different guest molecules such as toluene and THF. We are now experimenting with wider functionalities on the side chains of the organic ligand as well as other more redox-active metal ions, in the hope of achieving porous networks with higher dimensionality and stability, as well as more intense photophysical and electronic properties.

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Supporting Information Available: Full crystallographic data in CIF format for **1** and **2**. Figures of the crystal structure of **2**. X-ray powder diffraction patterns for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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