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Organometallic Silver(I) Coordination Polymers and Supramolecular Complexes Based on Novel Multidentate Thiophene- and Benzenenitrile-Containing Symmetric and Unsymmetric Fulvene Ligands

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Seven new conjugated symmetric and unsymmetric fulvene ligands **L1**−**L7** were synthesized. Thirteen new organometallic coordination polymers and supramolecular complexes were obtained through self-assembly based on these new fulvene ligands in the benzene/toluene mixed solvent system. Compounds **1**−**13** have been fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The results indicate that the coordination chemistry of new fulvene ligands is versatile. They can adopt either a cis or a trans conformation to bind Ag(I) ion through not only the terminal −CN and thiophene functional groups but also the fulvene carbon atoms into organometallic coordination polymers or discrete complexes. In addition, the luminescent properties of **L1**, **L3**, **L5**, and **L7** and some of their Ag(I) complexes were investigated preliminarily in EtOH and the solid state.

Introduction

The self-assembly of coordination polymers or supramolecular complexes with novel structures and properties have attracted considerable interest by chemists.[1,2] It is well-known that the most efficient approach to prepared polymeric frameworks is via direct chemical combination of inorganic and organic components, a method which has proven quite fruitful.[3,4] Fulvene,[5] as one type of important organic ligand, has been widely used in the construction of organometallic complexes: for example, metallocene and related complexes.[6] Up to date, the chemistry of polymeric organic−inorganic architectures based on fulvene molecules has received considerably less attention. It is expected that the abundant coordination chemistry of fulvene could afford us an excellent opportunity to construct organic−inorganic hybrid materials that might be different from those based on common organic spacers in topologies and physical and chemical properties. A continuing project in our laboratory has been the development of organometallic coordination architectures generated from conjugated symmetric fulvene ligands (II).[7] Our previous study demonstrated that fulvene (II) with two symmetric substituted benzonitrile arms could act as a bidentate or multidentate organic spacer to bind soft metal centers through both carbon−metal and heteroatom−metal coordination interactions into novel luminescent organometallic coordination polymers and supramolecular complexes.[7]

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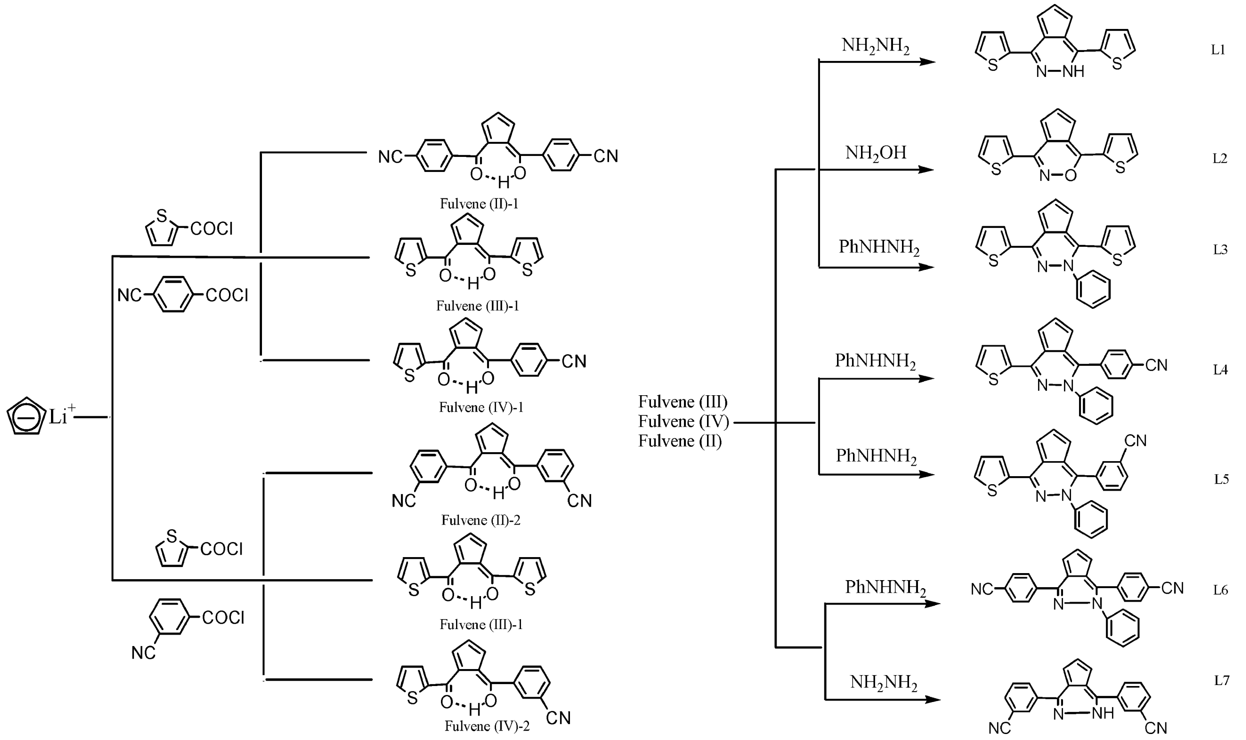
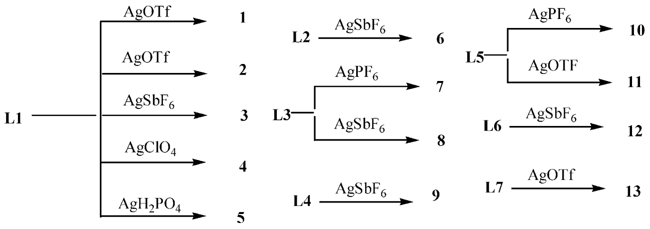
Scheme 1. Synthesis of Fulvene (II)−(IV) and the New Symmetric and Unsymmetric Pyridazine-Containing Fulvene Ligands L1−L7



As we know, in addition to the benzonitrile moiety, five-membered heterocyclic rings are also good candidates for constructing coordination polymers or supramolecular complexes as either terminal[8] or bridging moieties,[8] due to their specific donor orientation and bridging style. For example, the thiophene unit is widely used to prepare organic and organic−inorganic functional materials for conductor, sensor, and catalyst applications.[9] The aroylation of cyclopentadienyl or substituted cyclopentadienyl anions with five-membered 2-thiophenecarbonyl chloride and cyanobenzoyl chloride in one pot would introduce benzonitrile and thiophenecarbonyl moieties into one molecule in a single step, which is our synthetic approach to access unsymmetric fulvene ligands of this type (Scheme 1). In comparison to the well-developed coordination chemistry based on symmetric organic ligands,[1,2] coordination chemistry based on unsymmetric organic bridging spacers has received relatively less attention.[10] Unsymmetric organic ligands might generate coordination polymers or supramolecular architectures not achievable by symmetric ligands, which results from their more diverse coordination styles around the metal centers.

Scheme 2. Synthesis of Ag(I)−Fulvene Complexes



In this contribution, we present 7 new pyridazine-containing symmetric and unsymmetric fulvene ligands **L1**−**L7** by reaction of fulvene (II), (III), and (IV) with $PhNHNH_2$, $NH_2NH_2\cdot H_2O$, and NH_2OH, respectively (Scheme 1) and 13 new organometallic Ag(I) polymeric and discrete complexes, namely $[Ag(\mathbf{L1})(SO_3CF_3)]\cdot 0.5C_6H_6$ (**1**), $[Ag_2(\mathbf{L1})_2(SO_3CF_3)]\cdot 2C_6H_6$ (**2**), $[Ag(\mathbf{L1})(SbF_6)(\mu\text{-bis-}C_6H_6)_{0.5}]\cdot H_2O$ (**3**), $[Ag(\mathbf{L1})(ClO_4)]\cdot 0.5C_6H_6$ (**4**), $[Ag(\mathbf{L1})(H_2PO_4)]\cdot 0.5C_6H_6$ (**5**), $[Ag(\mathbf{L2})_2]SbF_6$ (**6**), $[Ag(\mathbf{L3})]PF_6\cdot C_7H_8$ (**7**), $[Ag(\mathbf{L3})(SbF_6)]\cdot C_7H_8$ (**8**), $\{[Ag(\mathbf{L4})]SbF_6\}\cdot C_7H_8\cdot 0.5C_6H_6$ (**9**), $[Ag(\mathbf{L5})(C_6H_6)]PF_6$ (**10**), $[Ag(\mathbf{L5})SO_3CF_3]$ (**11**), $\{[Ag_2(\mathbf{L6})(C_6H_6)(SbF_6)]SbF_6\}\cdot 2.5C_6H_6$ (**12**), and $[Ag(\mathbf{L7})(SO_3CF_3)]\cdot 0.5C_6H_6$ (**13**), based on them (Scheme 2). In addition, luminescent properties of **L1**, **L3**, **L5**, and **L7** and some of their Ag(I) complexes were investigated primarily in the solid state and in solution.

Results and Discussion

1. Synthesis and Structural Analysis of ligands L1−L7. The interesting coordination chemistry exhibited by fulvene (II)

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Table 1. Crystallographic Data for 1−4

	1	**2**	**3**	**4**
formula	$C_{19}H_{13}AgF_3N_2O_3S_3$	$C_{44}H_{30}Ag_2F_6N_4O_6S_6$	$C_{18}H_{15}AgF_6N_2OS_2Sb$	$C_{18}H_{13}AgClN_2O_4S_2$
formula wt	578.36	1232.82	683.06	528.74
cryst syst	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.2883(12)	10.376(4)	7.262(2)	7.228(3)
b (Å)	12.429(2)	14.152(5)	12.546(3)	10.800(4)
c (Å)	12.539(2)	18.151(7)	13.309(4)	13.795(5)
α (deg)	112.386(2)	75.767(6)	114.817(4)	112.361(5)
β (deg)	102.811(2)	74.094(6)	99.764(4)	101.523(5)
γ (deg)	90.246(3)	69.456(6)	92.531(4)	93.377(5)
V (Å^3)	1019.2(3)	2366.7(16)	1075.6(5)	965.0(6)
Z	2	2	2	2
ρ_{calcd} (g/cm^3)	1.885	1.730	2.109	1.820
μ (mm^{-1})	1.349	1.168	2.425	1.427
temp (K)	293(2)	293(2)	293(2)	293(2)
no. of rflns	3490	12 250	3863	4984
R1; wR2 ($I > 2\sigma(I)$)	0.0714; 0.1290	0.0706; 0.1616	0.0771; 0.1531	0.0500; 0.1380

Table 2. Crystallographic Data for 5−8

	5	**6**	**7**	**8**
formula	$C_{18}H_{15}AgN_2O_4PS_2$	$C_{30}H_{18}AgF_6N_2O_2S_4Sb$	$C_{28}H_{22}AgF_6N_2PS_2$	$C_{56}H_{44}Ag_2F_{12}N_4S_4Sb_2$
formula wt	578.36	1232.82	683.06	528.74
cryst syst	triclinic	monoclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$C2/c$	$Pbca$	$P2_1/c$
a (Å)	7.228(3)	15.722(11)	18.884(3)	22.412(3)
b (Å)	10.800(4)	26.788(11)	12.9143(18)	19.241(3)
c (Å)	13.795(5)	7.388(4)	22.152(3)	13.0265(18)
α (deg)	112.361(5)	90	90	90
β (deg)	101.523(5)	100.455(10)	90	90
γ (deg)	93.377(5)	90	90	90
V (Å^3)	965.0(6)	3060(3)	5402.4(13)	5617.5(14)
Z	2	4	8	4
ρ_{calcd} (g/cm^3)	1.811	1.831	1.730	1.878
μ (mm^{-1})	1.372	1.866	1.024	1.870
temp (K)	293(2)	293(2)	293(2)	293(2)
no. of rflns	4984	8098	26 700	28 972
R1; wR2 ($I > 2\sigma(I)$)	0.0455; 0.1219	0.0403; 0.1103	0.0914; 0.2247	0.0753; 0.2235

Table 3. Crystallographic Data for 9−13

	9	**10**	**11**	**12**	**13**
formula	$C_{34}H_{26}AgF_6N_3SSb$	$C_{30}H_{21}AgF_6N_3PS$	$C_{25}H_{15}AgF_3N_3O_3S_2$	$C_{48}H_{37}Ag_2F_{12}N_4Sb_2$	$C_{50}H_{30}Ag_2F_6N_8O_6S_2$
formula wt	852.26	708.40	634.39	1357.06	1232.68
cryst syst	monoclinic	triclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	7.8712(19)	7.6547(12)	23.755(2)	12.5677(10)	10.410(3)
b (Å)	14.214(4)	11.7027(19)	13.5252(12)	13.8217(12)	13.126(4)
c (Å)	29.383(7)	17.768(3)	18.0666(17)	15.4528(13)	19.282(6)
α (deg)	90	72.093(3)	90	80.297(2)	86.692(6)
β (deg)	96.393(4)	77.580(2)	108.540(2)	66.647(2)	78.256(6)
γ (deg)	90	78.561(2)	90	83.489(2)	76.867(5)
V (Å^3)	3266.9(14)	1464.1(4)	5503.4(9)	2425.9(4)	2511.8(14)
Z	4	2	8	2	2
ρ_{calcd} (g/cm^3)	1.733	1.607	1.531	1.858	1.630
μ (mm^{-1})	1.553	0.878	0.935	1.981	0.943
temp (K)	293(2)	293(2)	293(2)	293(2)	293(2)
no. of rflns	16 510	7562	16 250	12 700	13 701
R1; wR2 ($I > 2\sigma(I)$)	0.0794; 0.1843	0.0769; 0.2034	0.0681; 0.1557	0.0881; 0.1545	0.0585; 0.1164

has encouraged us to undertake further studies on the design and synthesis of new types of fulvene ligands. Following this approach, we have expanded the symmetric benzonitrile-containing fulvene (II) to the symmetric thiophene-containing fulvene (III) and unsymmetric thiophene- and benzonitrile-containing fulvene (IV) by the one-pot reaction of 2-thiophenecarbonyl chloride and 4-cyanobenzoyl chloride or 3-cyanobenzoyl chloride with cyclopentadiene anion (Scheme 1), respectively. Symmetric fulvene (II), fulvene (III), and unsymmetric fulvene (IV) further reacted with hydrazine, benzohydrazine, or hydroxylamine to generate the novel target cyclopenta[*d*]pyridazine ligands **L1−L7**. Ligands **L1−L7** were isolated as deep yellow crystalline solids. In comparison to fulvene (II) and (III), ligands **L1−L7** are more soluble in organic solvents, such as CH_2Cl_2, $CHCl_3$, THF, benzene, toluene, CH_3OH, C_2H_5OH, and so on. In the ^1H NMR spectra of **L1−L7**, a single peak related to the imine group was observed around 14 ppm, which is about 4 ppm shifted to higher field compared to the proton resonance (∼17−19 ppm) of the hydroxy hydrogen on their precursors of fulvene (II)−(IV). The IR spectra of ligands **L1−L7** showed a −NH absorption band around 3200 cm^{-1}. The strong absorption bands around 1600 and 1350 cm^{-1} are consistent with the >C=N and fulvene absorptions, respectively, which are comparable to those corresponding bands in known compounds.[7,11] There are two NS-chelating moieties in **L1−L7**. These two NS-chelating coordination moieties and electron-rich cyclopentadienide group cause them to possess two totally different potential coordination sites: i.e., organometallic vs inorganic sites. Thus, **L1**−**L7** reported herein could be considered as the multidentate ligands that could afford not only carbon but also heteroatom donors. This affords us a good opportunity to synthesize polymeric organometallic complexes. **L4** and **L5** are unsymmetric ligands. As shown in Scheme 1, thiophenecarbonyl and cyanobenzoyl (4-cyanobenzoyl for **L4** and 3-cyanobenzoyl for **L5**) moieties are attached to the center five-membered rings, respectively. Different orientations together with different coordinative abilities of C , S, and N donors in **L4** and **L5** would result in abundant coordination chemistry for this type of ligand. In addition, the >N−H functional group on pyridazine in these ligands could be potentially linked by other types of organic spacers into larger multidentate fulvene ligands,[12] which might lead to more new and novel supramolecular systems.

2. Supramolecular Complexes Based on Symmetric Thiophene-Containing Ligands L1−L3 and Ag(I) Ion. As we know, coordination chemistry based on symmetric organic ligands has been the dominating subject in the self-assembly field. So far, numerous attractive supramolecular complexes based on symmetric organic spacers, such as symmetric bridged bipyridine and biphenylcyanide and also related types of ligands, have been widely used to construct supramolecular complexes.[1−4] However, the coordination chemistry based on a fulvene unit bridging five-membered heterocyclic-ring-containing symmetric ligands, such as **L1** reported herein, is still unprecedented. The multiple functionalities of **L1** and its versatile conformations have attracted us to test its coordinative ability toward metal acceptors, especially soft acid Ag(I) ion.[9d−f,13]

(a) Synthesis and Structural Analysis of 1 and 2. Reaction of **L1** with $AgSO_3CF_3$ (1:2 ratio) in the mixed solvent systems benzene/methylene chloride and benzene/toluene at room temperature afforded compounds **1** (yield, 59%) and **2** (yield, 64%) as yellow blocklike and platelike crystals, respectively. Crystalllographic data for **1** and **2** are given in Table 1, and selected interatomic distances and bond angles are given in Table 4. Single-crystal analysis revealed that compound **1** crystallizes in the triclinic system with the space group $P\bar{1}$. As shown in Figure 1, the Ag(I) center in **1** lies in a distorted-tetrahedral organometallic coordination sphere {AgπNSO} consisting of one pyridazine N atom ($d_{Ag(1)-N(2)} = 2.593(7)$ Å), one thiophene S atom ($d_{Ag(1)-S(2)} = 2.767(3)$ Å), one triflate oxygen atom ($d_{Ag(1)-O(2)} = 2.347(3)$ Å), and one π-donor from the cyclopentadienide moiety on the other **L1** ligand (C(3) and C(4)). All $Ag^{I}-C$ bond distances lie in the range of normal silver−carbon bond lengths (2.47−2.80 Å).[7,14−16] Two Ag(I) centers are linked together by two *trans*-**L1** species into a {Ag_2(*trans*-**L1**)$_2$} cationic dinuclear boxlike unit (Figure 2). The Ag(I)···Ag(I) separation in the {Ag_2(*trans*-**L1**)$_2$} moiety is 7.087(3) Å. These boxlike units are connected to each other by three sets of weak F···H−C[17] (F(1)···H(14) = 2.6 Å, F(2)···H(13) = 2.5 Å, F(2)···H(2) = 2.7 Å) hydrogen-bonding systems into one-dimensional chains extended along the crystallographic *b* axis. Benzene solvent molecules are located between these chains. As shown in Figure 3, the benzene molecules are close to Ag(I) centers, and the closest Ag···C distance is 3.0 Å, which is beyond of the normal range of Ag−C bond lengths.

Table 4. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for 1−4

Compound **1**			
Ag(1)−O(3)	2.347(7)	Ag(1)−C(4)#1	2.396(8)
Ag(1)−C(3)#1	2.488(9)	Ag(1)−N(2)	2.593(7)
Ag(1)−S(2)	2.767(3)		
O(3)−Ag(1)−C(4)#1	146.0(3)	O(3)−Ag(1)−C(3)#1	115.5(3)
C(4)#1−Ag(1)−C(3)#1	31.6(3)	O(3)−Ag(1)−N(2)	93.1(2)
C(4)#1−Ag(1)−N(2)	104.3(2)	C(3)#1−Ag(1)−N(2)	106.5(3)
O(3)−Ag(1)−S(2)	99.78(17)	C(4)#1−Ag(1)−S(2)	114.0(2)
C(3)#1−Ag(1)−S(2)	144.4(2)	N(2)−Ag(1)−S(2)	65.06(16)
Compound **2**			
Ag(1)−O(4)	2.337(6)	Ag(1)−N(2)	2.369(5)
Ag(1)−C(24)#1	2.410(8)	Ag(1)−C(23)#1	2.590(8)
Ag(1)−S(2)	2.827(3)	Ag(2)−O(1)	2.378(6)
Ag(2)−N(3)	2.397(6)	Ag(2)−C(9)	2.420(8)
Ag(2)−C(8)	2.592(9)	Ag(2)−S(4)	2.795(2)
O(4)−Ag(1)−N(2)	111.5(3)	O(4)−Ag(1)−C(24)#1	147.4(3)
N(2)−Ag(1)−C(24)#1	101.1(2)	O(4)−Ag(1)−C(23)#1	115.7(3)
N(2)−Ag(1)−C(23)#1	132.0(2)	C(24)#1−Ag(1)−C(23)#1	32.8(2)
O(4)−Ag(1)−S(2)	84.62(17)	N(2)−Ag(1)−S(2)	70.78(14)
C(24)#1−Ag(1)−S(2)	108.53(18)	C(23)#1−Ag(1)−S(2)	104.96(19)
O(1)−Ag(2)−N(3)	113.0(3)	O(1)−Ag(2)-C(9)	147.7(3)
N(3)−Ag(2)−C(9)	99.2(3)	O(1)−Ag(2)−C(8)	116.1(3)
N(3)−Ag(2)−C(8)	129.2(2)	C(9)−Ag(2)−C(8)	32.1(3)
O(1)−Ag(2)−S(4)	81.33(17)	N(3)−Ag(2)−S(4)	70.52(15)
C(9)−Ag(2)−S(4)	108.09(18)	C(8)−Ag(2)−S(4)	104.8(2)
Compound **3**			
Ag(1)−N(2)	2.337(9)	Ag(1)−C(12)	2.469(14)
Ag(1)−C(9)	2.53(2)	Ag(1)−C(1)#1	2.636(13)
Ag(1)−S(2)	2.927(4)		
N(2)−Ag(1)−C(12)	104.7(4)	N(2)−Ag(1)−C(9)	156.1(5)
C(12)−Ag(1)−C(9)	98.2(6)	N(2)−Ag(1)−C(1)#1	109.4(4)
C(12)−Ag(1)−C(1)#1	30.6(4)	C(9)−Ag(1)−C(1)#1	93.9(6)
N(2)−Ag(1)−S(2)	66.3(2)	C(12)−Ag(1)−S(2)	113.2(3)
C(9)−Ag(1)−S(2)	98.3(5)	C(1)#1−Ag(1)−S(2)	143.5(3)
Compound **4**			
Ag(1)−O(4)	2.379(5)	Ag(1)−C(24)#1	2.449(5)
Ag(1)−O(4)#2	2.463(4)	Ag(1)−N(2)	2.477(4)
Ag(1)−C(23)#1	2.613(6)	Ag(1)−S(1)	2.8546(18)
O(4)−Ag(1)−C(24)#1	131.9(2)	O(4)−Ag(1)−O(4)#2	75.67(17)
C(24)#1−Ag(1)−O(4)#2	96.56(17)	O(4)−Ag(1)−N(2)	104.49(15)
C(24)#1−Ag(1)−N(2)	103.63(14)	O(4)#2−Ag(1)−N(2)	151.04(18)
O(4)−Ag(1)−C(23)#1	102.5(2)	C(24)#1−Ag(1)−C(23)#1	31.84(19)
O(4)#2−Ag(1)−C(23)#1	102.43(19)	N(2)−Ag(1)−C(23)#1	105.69(15)
O(4)−Ag(1)−S(1)	111.61(15)	C(24)#1−Ag(1)−S(1)	115.37(14)
O(4)#2−Ag(1)−S(1)	87.25(14)	N(2)−Ag(1)−S(1)	65.46(10)
C(23)#1−Ag(1)−S(1)	145.91(13)		

Compound **2** crystallizes in the triclinic system with the space group $P\bar{1}$. As shown in Figure 4, the asymmetric unit contains two different Ag(I) centers, two **L1** ligands, two triflate

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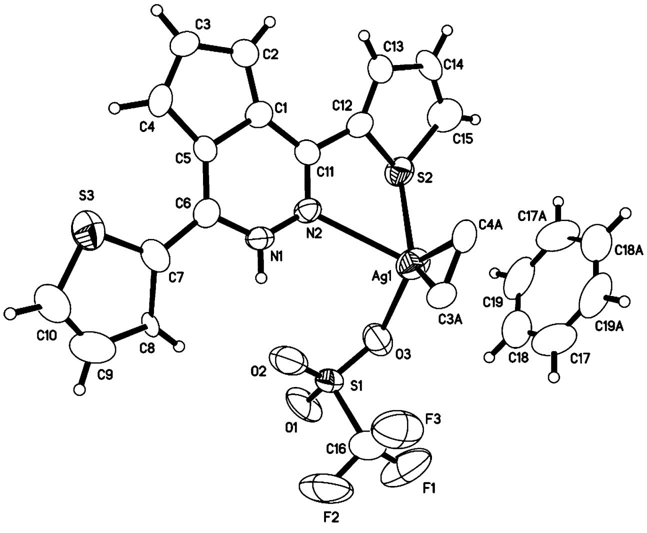

Figure 1. ORTEP drawing of **1**.

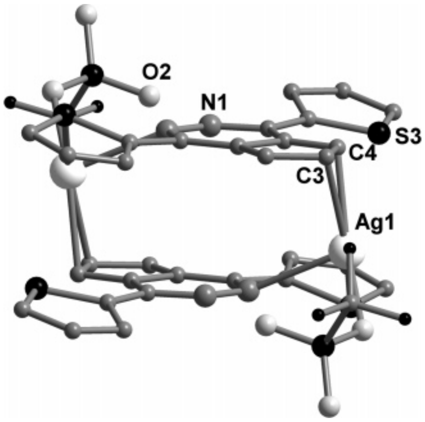

Figure 2. Organometallic dinuclear boxlike unit in **1**.

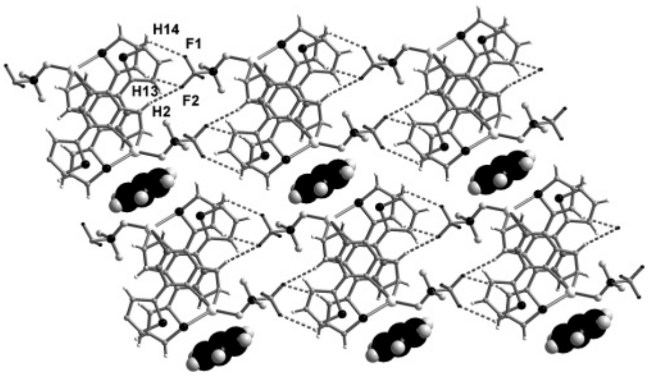

Figure 3. Crystal packing of **1**. Benzene guest molecules are located between chains.

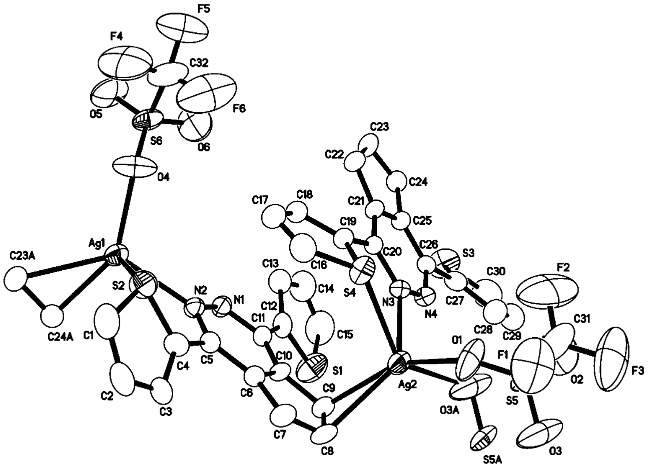

Figure 4. ORTEP drawing of **2**.

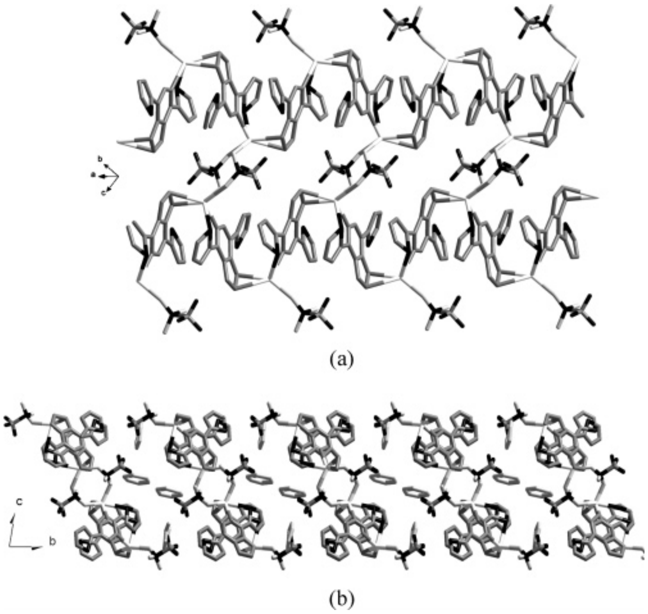

Figure 5. (a) View of twin chain formed by linking a single chain through the Ag−(SO_3CF_3)$_2$−Ag linkage. (b) Twin chains arranged one by one along the *b* axis, with benzene molecules filling in the clearance.

counterions, and two benzene solvent molecules. The first silver atom lies in a {AgNOSπ} coordination sphere, being made of one N donor (N(2), $d_{\mathrm{Ag(1)-N(2)}} = 2.369(5)$ Å), one O donor (O(4), $d_{\mathrm{Ag(1)-O(4)}} = 2.337(6)$ Å), one S donor ($d_{\mathrm{Ag(1)-S(2)}} = 2.827(3)$ Å), one π donor from one **L1** ligand and one coordinated $SO_3CF_3^-$ counterion, and two π donors (Ag(1)−C bond distances range from 2.410(8) to 2.592(9) Å) from the cyclopentadienide groups on the other **L1** ligand, respectively. The second Ag(I) center adopts a {AgNO$_2$Sπ} coordination environment. One set of NS-chelating moiety (Ag(2)−N(3) and Ag(2)−S(4) bond lengths are 2.397(6) and 2.795(6) Å, respectively) and one π donor from the other **L1** ligand (Ag(2)−C bond lengths range from 2.478 to 2.481 Å) and two triflate O donors (O(1), $d_{\mathrm{Ag(1)-O(1)}} = 2.378(6)$ Å; O(3), $d_{\mathrm{Ag(1)-O(3)}} = 2.828(6)$ Å) surround the Ag(2) atom into a five-coordinated sphere. In the solid state, *trans*-**L1** binds the Ag(1) and Ag(2) centers through the η^2-cyclopentadienide group and NS-chelating interactions into one-dimensional chains along the crystallographic [100] direction. Every two of these chains are further linked together by interchain Ag−(SO_3CF_3)$_2$−Ag linkages into a twin-chain motif (Figure 5a). The shortest intrachain and interchain Ag···Ag distances are 7.6 and 5.6 Å. These twin chains arrange in the crystallographic *bc* plane in parallel, and the uncoordinated benzene molecules are located between them (Figure 5b).

(b) Synthesis and Structural Analysis of 3. Compound **3** was obtained by combination of **L1** with AgSbF$_6$ in a benzene/toulene mixed solvent system as yellow platelike crystals in 41% yield. Compound **3** crystallizes in the triclinic system with the space group $P\bar{1}$. Crystalllographic data for **3** are given in Table 1, and selected interatomic distances and bond angles are given in Table 4. As shown in Figure 6, there is one kind of crystallographically independent Ag(I) atom in the asymmetric

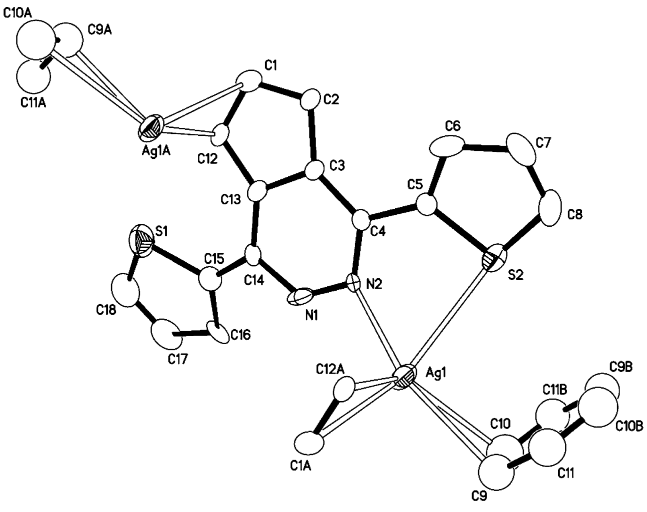

Figure 6. Molecular structure of **3**.

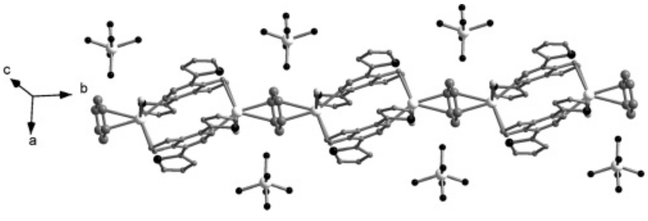

Figure 7. μ_2-η^2-benzene molecules bridging $\{Ag_2(trans\text{-}\mathbf{L1})_2\}$ units into a one-dimensional chain.

unit. It adopts a $\{AgNS\pi_2\}$ distorted coordination sphere which consists of an NS chelating moiety ($d_{Ag(1)-N(2)} = 2.337(9)$Å) and $d_{Ag(1)-S(2)} = 2.927(4)$ Å), two π donors (Ag^I-C bond distances range from 2.469(14) to 2.636(13) Å) from the cyclopentadienide group on the other **L1** ligand, and one solvent benzene molecule, respectively.

As shown in Figure 7, two silver atoms are bound together by two *trans*-**L1** ligands into boxlike $\{Ag_2(trans\text{-}\mathbf{L1})_2\}$ units, which are further bridged together by μ_2-η^2 solvent benzene molecules through Ag$-\pi$ interactions into a one-dimensional chain along the crystallographic *b* axis.

(c) Synthesis and Structural Analysis of 4 and 5. Ligand **L1** together with $AgClO_4$ in a benzene/toluene mixed solvent system generates compound **4** as orange crystals in 60% yield. Crystallographic data for **4** are given in Table 1, and selected interatomic distances and bond angles are given in Table 4. Each Ag(I) atom is coordinated by one NS chelating moiety (Ag(1)$-$N(2) = 2.477(4) and Ag(1)$-$S(1) = 2.8546(18) Å) from one **L1**, two O donors from two ClO_4^- anions (Ag(1)$-$O(4)#2 = 2.463(4) Å), and one π donor (Ag(1)$-$C(24)#1 = 2.449(5) Å and Ag(1)$-$C(23)#1 = 2.613(6) Å) to generate the five-coordinated sphere $\{AgNSO_2\pi\}$ (Figure 8). Two *trans*-**L1** ligands and two Ag(I) atoms again constitute a boxlike moiety (Figure 9) which is the same as that in **1** and **3**. The difference is that the “glue” between these moieties is a metal$-$heteroatom coordination bond instead of the H-bonding interaction in **1** and **2** or metal$-\pi$ interaction in **3**. As shown in Figure 10, boxlike units are connected to each other by coordinated ClO_4^- counterions into a linear chain running along the crystallographic *b* axis.

It is worth pointing out that all these one-dimensional chains are parallel (Figure 11), which is different from the case in $[Ag(C_{15}H_{10}N_2O_2)]ClO_4$, composed of a homologous furan$-$fulvene ligand and $AgClO_4$ from the same solvent system, wherein two sets of one-dimensional chains are perpendicular.[7e] In **4**, uncoordinated benzene molecules are located between chains and are vertical to the chain-extending direction (Figure 11).

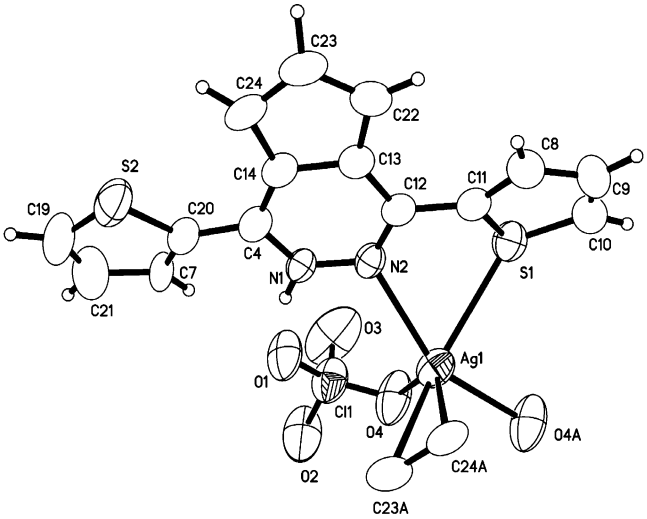

Figure 8. Coordination environment of Ag(I) in **4**.

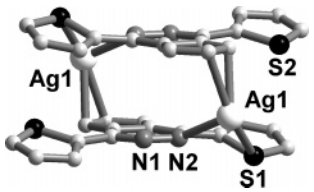

Figure 9. Boxlike moiety in compound **4**.

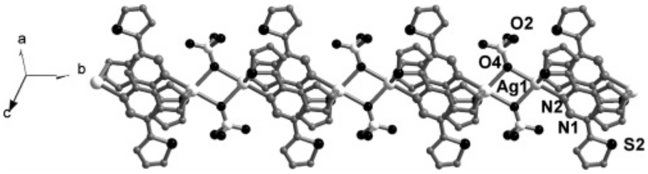

Figure 10. Bidentate ClO_4^- anions linking boxlike moieties into a one-dimensional chain.

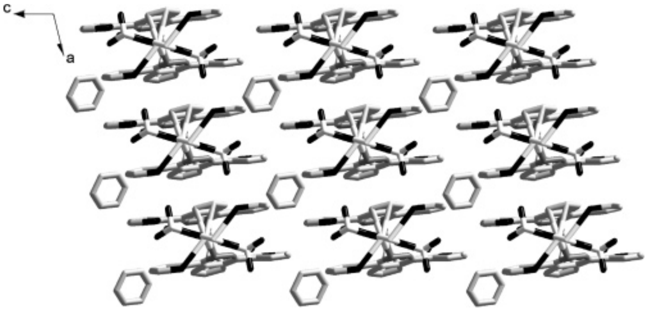

Figure 11. Crystal packing of **4** (view down the chain direction).

Compound **5** was synthesized by the same method as for **4**. Single-crystal X-ray diffraction analysis revealed that **5** and **4** are isostructural. Crystallographic data for **5** are given in Table 2, and selected interatomic distances and bond angles are given in Table 5. As indicated in Figure 12, the coordination environment of the Ag(I) atom in **5** is the same as that in **4**. All the bond lengths around Ag(I) centers are comparable with those in **4**.

The common feature of compounds **1**$-$**5** lies in the fact that they all possess a $\{Ag_2(\mathbf{L1})_2\}$ molecular boxlike building block. In compounds **1**$-$**5**, **L1** exhibits similar coordination behavior: i.e., it uses both organometallic (cyclopentadienide) and inor-

Table 5. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for 5−8

Compound **5**			
Ag(1)−O(4)	2.383(4)	Ag(1)−C(9)#1	2.451(5)
Ag(1)−O(4)#2	2.465(4)	Ag(1)−N(2)	2.479(4)
Ag(1)−C(8)#1	2.616(5)	Ag(1)−S(1)	2.8534(17)
O(4)−Ag(1)−C(9)#1	131.95(18)	O(4)−Ag(1)−O(4)#2	75.87(16)
C(9)#1−Ag(1)−O(4)#2	96.51(16)	O(4)−Ag(1)−N(2)	104.51(14)
C(9)#1−Ag(1)−N(2)	103.56(13)	O(4)#2−Ag(1)−N(2)	150.97(16)
O(4)−Ag(1)−C(8)#1	102.26(18)	C(9)#1−Ag(1)−C(8)#1	32.08(17)
O(4)#2−Ag(1)−C(8)#1	102.50(17)	N(2)−Ag(1)−C(8)#1	105.66(14)
O(4)−Ag(1)−S(1)	111.70(14)	C(9)#1−Ag(1)−S(1)	115.24(13)
O(4)#2−Ag(1)−S(1)	87.13(13)	N(2)−Ag(1)−S(1)	65.47(9)
C(8)#1−Ag(1)−S(1)	146.02(12)		
Compound **6**			
Ag(1)−N(1)#1	2.155(3)	Ag(1)−N(1)	2.155(3)
Ag(1)−S(1)	3.0805(14)		
N(1)#1−Ag(1)−N(1)	174.51(16)	N(1)#1−Ag(1)−S(1)	116.25(8)
N(1)−Ag(1)−S(1)	68.53(8)	C(11)−N(1)−O(1)	118.4(3)
Compound **7**			
Ag(1)−N(1)	2.253(5)	Ag(1)−C(9)#1	2.335(7)
Ag(1)−C(8)#1	2.551(8)	Ag(1)−S(1)	2.888(3)
N(1)−Ag(1)−C(9)#1	153.5(2)	N(1)−Ag(1)−C(8)#1	144.2(2)
C(9)#1−Ag(1)−C(8)#1	33.7(3)	N(1)−Ag(1)−S(1)	73.10(15)
C(9)#1−Ag(1)−S(1)	96.0(2)	C(8)#1−Ag(1)−S(1)	128.98(19)
Compound **8**			
Ag(1)−N(3)	2.283(7)	Ag(1)−C(18)	2.349(9)
Ag(1)−C(17)	2.550(10)	Ag(1)−S(3)	2.889(4)
Ag(2)−N(2)	2.273(7)	Ag(2)−C(4)	2.340(9)
Ag(2)−C(3)	2.556(10)	Ag(2)−S(1)	2.881(4)
N(3)−Ag(1)−C(18)	154.9(3)	N(3)−Ag(1)−C(17)	144.0(3)
C(18)−Ag(1)−C(17)	33.3(3)	N(3)−Ag(1)−S(3)	73.10(19)
C(18)−Ag(1)−S(3)	97.7(3)	C(17)−Ag(1)−S(3)	130.3(3)
N(2)−Ag(2)−C(4)	154.9(3)	N(2)−Ag(2)−C(3)	143.7(3)
C(4)−Ag(2)−C(3)	34.3(3)	N(2)−Ag(2)−S(1)	73.05(19)
C(4)−Ag(2)−S(1)	97.0(3)	C(3)−Ag(2)−S(1)	130.4(2)

ganic faces (SN chelating site) to bind the Ag(I) atom. It is worth pointing out that, in **1**−**5**, **L1** always adopts a trans conformation to form an {Ag_2(**L1**)$_2$} boxlike unit. The coordination behavior of **L1** herein is different from that of its furan−fulvene analogue.[7g] As noted above, only one of two NS chelating moieties in **L1** involves the metal coordination sphere and the other is free, which might indicate that two NS chelating metal rings formed by **L1** are strained. Different metal-to-ligand ratios (1:2, 1:3, and even 1:4) were tried, but compounds **1**−**5** were always isolated as the only products. It is interesting that the connectors between the {Ag_2(**L1**)$_2$} unit change from an F···H−C H-bond (**1**) to **L1** (**2**) to a benzene solvent molecule (**3**) and then to a counterion (**4** and **5**). The only possible explanation for this change might be the different coordinating strengths resulting from the different counterions, due to all five reactions being carried out under exactly the same conditions, including solvent system, metal-to-ligand ratio, and temperature. The templating effect of the counterion in determining the type and topology of the product was well demonstrated by many earlier studies.[18] Compounds **1**−**5** reported herein represent additional examples for this kind of phenomenon.

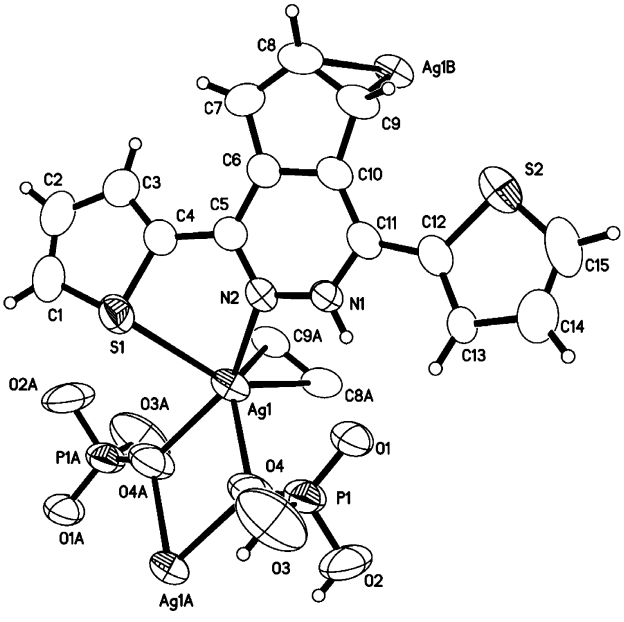

Figure 12. ORTEP drawing of **5**.

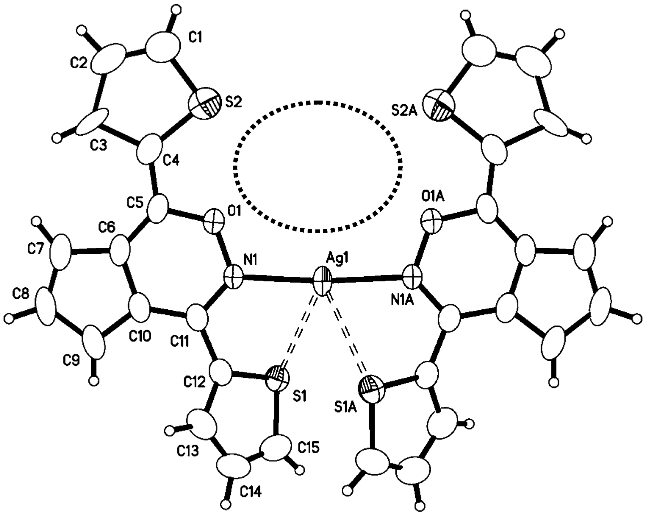

Figure 13. Molecular structure of **6**., with two **L2** ligands binding the Ag(I) ion in a face-to-face fashion to form a {S_2O_2} crown ether like moiety.

(d) Synthesis and Structural Analysis of 6. Compound **6** was obtained by combination of **L2** with $AgSbF_6$ in a benzene/toluene mixed solvent system as yellow block crystals in 51% yield. Crystallographic data for **6** are given in Table 2, and selected interatomic distances and bond angles are given in Table 5. In **6**, the Ag(I) center is linearly coordinated by two N donors (N(1)#1−Ag(1)−N(1) = 174.51(16)°) with a short Ag−N bond distance of 2.155(3) Å. The two S donors from two NS chelating sites are only weakly interacting with Ag(I) (Ag(1)−S(1) = 3.0805(14) Å). As shown in Figure 13, two *cis*-**L2** ligands are present, with two coordinating SN and two uncoordinating SO chelating moieties being located on both sides of the N−Ag−N axis. Two uncoordinated SO chelating sites form an {S_2O_2} crown ether like cavity (S···S and O···O distances are ca. 5.6 and 5.2 Å, respectively) that provides a potential metal ion recognition site. In the solid state, {Ag(**L2**)$_2$} building blocks are parallel and are driven by intermolecular $\pi-\pi$ interactions (the related aromatic ring centroid to ring centroid distance is 3.5 Å) into a one-dimensional chain along the crystallographic

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(18) (a) Kuroda-Sowa, T.; Horrino, T.; Yamamoto, M.; Ohno, Y.; Maekawa, M.; Munakata, M. *Inorg. Chem.* **1997**, *36*, 6382. (b) Hennigar, T. L.; MacQuarrie, D. C.; Losier, P.; Rogers, R. D.; Zaworotko. M. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 972. (c) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (d) Munakata, M.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Harino, T. *Inorg. Chem.* **1998**, *37*, 5651. (e) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *New J. Chem.* **1998**, *22*, 177. (f) Jung, O. S.; Park, S. H.; Kim, K. M.; Jang, H. G. *Inorg. Chem.* **1998**, *37*, 5781. (g) Withersby, M. A.; Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2327.

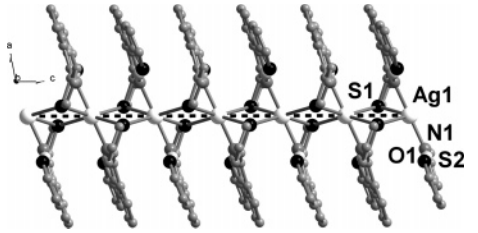

Figure 14. One-dimensional chain in **6** driven by Ag⋯S and $\pi-\pi$ interactions.

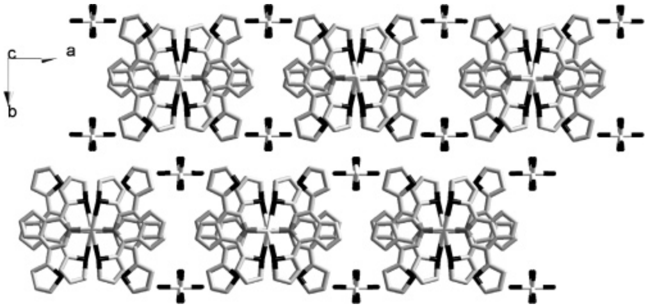

Figure 15. Crystal packing of **6** (view down the chain direction).

c axis (Figure 14). The shortest intrachain Ag⋯Ag distance is 3.70 Å, which is slightly longer than the sum of the van der Waals radii of two silver atoms, 3.44 Å.[19] At the same time, additional weak Ag⋯S interactions (3.355(4) Å) further strengthen the one-dimensional chains. Thus, the S atom herein behaves as a μ_2-bridging atom. As shown in Figure 15, all of these one-dimensional chains align parallel; the uncoordinated SbF_6^- anions are located between chains. It is interesting that the coordination behavior of **L2** is different from that of **L1** in this specific reaction. As shown above, the cyclopentadienide moiety in **L2** was not involved in the Ag(I) coordination sphere, but it was in **L1**. The coordination difference between **L2** and **L1** results in the different polymeric motifs of **6** and **1**−**5**.

(e) Synthesis and Structural Analysis of 7 and 8. Compound **7** was obtained as brown platelike crystals by combination of **L3** with $AgPF_6$ in a benzene/toluene mixed solvent system (yield 54%). Single-crystal analysis revealed that compound **7** crystallizes in the orthorhombic system with the space group *Pbca*. Crystallographic data for **7** are given in Table 2, and selected interatomic distances and bond angles are given in Table 5. As shown in Figure 16, the Ag(I) center lies in a five-coordinated $\{AgSN\pi_2\}$ coordination environment consisting of one SN chelating site ($d_{Ag(1)-N(1)} = 2.253(5)$ Å and $d_{Ag(1)-S(1)} = 2.888(3)$ Å), two π-donors from a coordinated cyclopentadienide ring ($d_{Ag(1)-C(9)\#1} = 2.335(7)$ Å, and $d_{Ag(1)-C(8)\#1} = 2.551(8)$ Å), and one coordinated toluene solvent molecule ($d_{Ag(1)-C(23)} = 2.8507(5)$ Å). All other $Ag^I-C_{toluene}$ bond distances are beyond the range of normal silver−carbon bond lengths (2.47−2.80 Å).[7] As shown above, the coordination behavior of **L3** is similar to that of **L1**. One of the two SN chelating sites and cyclopentadienide ring on **L3** are involved in the Ag(I) coordination sphere.

In the solid state, Ag(I) centers are bound together through SN chelating and cyclopentadienide π donors into a sinusoidal chain running along the crystallographic *b* axis (Figure 17). The coordinated toluene molecules are located on both sides of the chain but apparently make no contribution to the topology of the network. Uncoordinated PF_6^- counterions lie in the concave part of the sinusoidal chain.

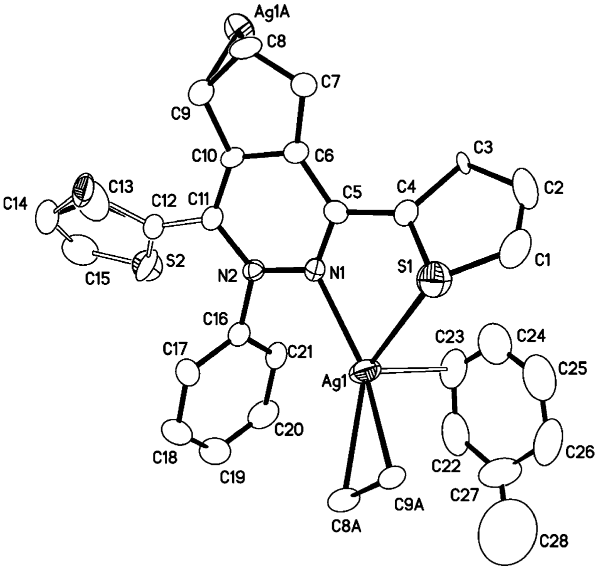

Figure 16. Coordination sphere around Ag(I) in **7**.

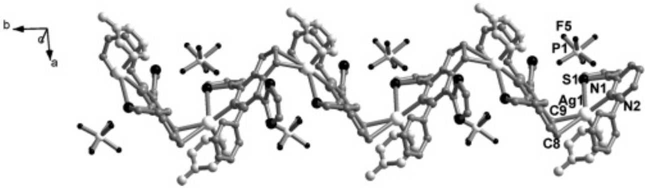

Figure 17. One-dimensional sinusoidal chain in **7**.

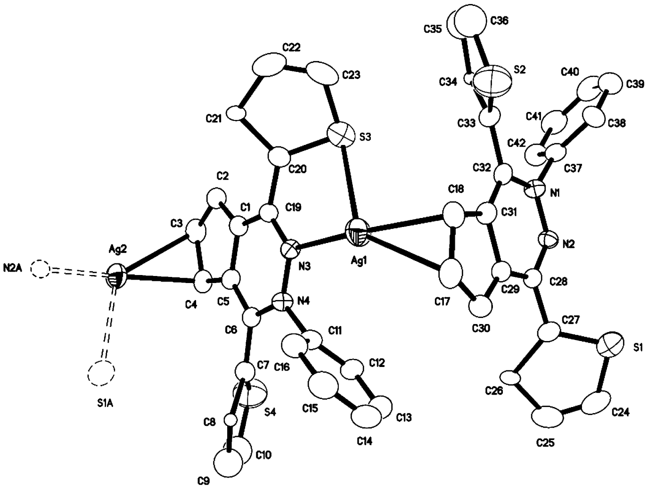

Figure 18. ORTEP drawing of **8**.

To explore the templating role of counterions in the self-assembly process, $AgSbF_6$ was used instead of $AgPF_6$ to carry out the reaction under the same reaction conditions. As shown in Figure 18, there are two different crystallographic silver atoms in **8**; they are all trigonally coordinated by one SN chelating donor (Ag−N bond lengths 2.273(7)−2.283(7) Å) and one cyclopentadienide π donor (Ag(1)−C(18) = 2.349(9) Å and Ag(1)−C(17) = 2.550(10) Å). No coordinated solvent molecules were found in **8**, which is different from the case in **7**. Crystallographic data for **8** are given in Table 2, and selected interatomic distances and bond angles are given in Table 5. It is noteworthy that two coordinated and uncoordinated thiophene planes of **L3** in **7** and **8** are perpendicular to each other, which is a result of the steric influence of the phenyl ring adjacent to the uncoordinated thiophene ring. As indicated in Figure 19, the coordination pattern of **8** is the same as that of **7**, which is

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(19) Bertelli, M.; Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Mater. Chem.* **1997**, *7*, 1271.

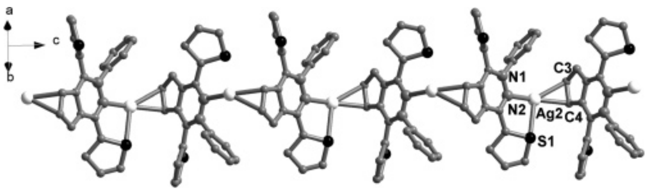

Figure 19. One-dimensional chain in **8**.

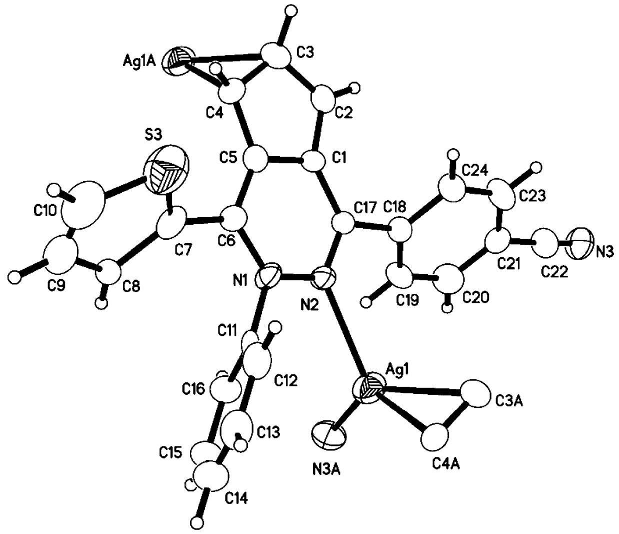

Figure 20. Molecular structure of **9**.

a result of the similar coordination preference of the Ag(I) ion toward the ligand **L3**.

3. Supramolecular Complexes Based on Unsymmetric Ligands L4 and L5. The idea behind the use of ligands **L4** and **L5** is to explore the coordination chemistry and self-assembly principles of this unsymmetric type of ligand. There is no doubt that unsymmetrically bridging ligands with two or more coordination sites with differing donor abilities are expected to result in more unprecedented coordination polymers or supramolecular complexes with novel topologies than can be achieved with symmetric ligands.[10]

(a) Synthesis and Structural Analysis of 9. Compound **9** was obtained as yellow crystals by combination of **L4** with $AgSbF_6$ in a benzene/toluene mixed solvent system at 57% yield. As shown in Figure 20, compound **9** crystallizes in the monoclinic system with the space group $P2_1/c$. Crystallographic data for **9** are given in Table 3, and selected interatomic distances and bond angles are given in Table 6. There is only one type of crystallographic Ag(I) center in **9**, and it lies in the distorted inorganic tetrahedral coordination environment $\{AgN_2\pi\}$ defined by two N donors from one −CN group ($d_{Ag(1)-N(3)\#1} = 2.219(8)$ Å) and one pyridazine ring ($d_{Ag(1)-N(2)} = 2.422(6)$ Å) on the other **L4** ligand, respectively. The π donor comes from cyclopentadienide with Ag(1)−C bond lengths of 2.402(8) and 2.527(8) Å, respectively. All of these bond distances are similar to the corresponding bond lengths found in compounds **1**−**8** and previous polymeric Ag(I) complexes based on fulvene (II) ligands.[7]

Table 6. Interatomic Distances (Å) and Bond Angles (deg) with Esds in Parentheses for 9−13

Compound **9**			
Ag(1)−N(3)#1	2.219(8)	Ag(1)−C(3)#2	2.402(8)
Ag(1)−N(2)	2.422(6)	Ag(1)−C(4)#2	2.527(8)
N(3)#1−Ag(1)−C(3)#2	135.6(3)	N(3)#1−Ag(1)−N(2)	113.2(2)
C(3)#2−Ag(1)−N(2)	107.0(2)	N(3)#1−Ag(1)−C(4)#2	130.6(3)
C(3)#2−Ag(1)−C(4)#2	33.2(3)	N(2)−Ag(1)−C(4)#2	113.9(2)
Compound **10**			
Ag(1)−N(3)#1	2.196(7)	Ag(1)−N(2)	2.305(5)
Ag(1)−C(25)	2.440(15)	Ag(1)−C(30)	2.620(17)
N(3)#1−Ag(1)−N(2)	128.5(2)	N(3)#1−Ag(1)−C(25)	105.3(4)
N(2)−Ag(1)−C(25)	122.5(3)	N(3)#1−Ag(1)−C(30)	130.3(4)
N(2)−Ag(1)−C(30)	101.3(4)	C(25)−Ag(1)−C(30)	30.0(3)
Compound **11**			
Ag(1)−N(2)	2.262(5)	Ag(1)−O(3)	2.333(5)
Ag(1)−C(2)#1	2.448(7)	Ag(1)−C(3)#1	2.493(7)
N(2)−Ag(1)−O(3)	119.38(18)	N(2)−Ag(1)−C(2)#1	134.20(19)
O(3)−Ag(1)−C(2)#1	105.92(19)	N(2)−Ag(1)−C(3)#1	127.69(18)
O(3)−Ag(1)−C(3)#1	106.09(19)	C(2)#1−Ag(1)−C(3)#1	32.5(2)
Compound **12**			
Ag(1)−N(4)#1	2.235(10)	Ag(1)−N(2)	2.274(8)
Ag(2)−N(3)#2	2.350(11)	Ag(2)−C(2)	2.368(12)
Ag(2)−C(28)	2.4698(13)	Ag(2)−C(33)	2.7238(13)
Ag(2)−C(3)	2.752(12)		
N(4)#1−Ag(1)−N(2)	122.1(4)	N(3)#2−Ag(2)−C(2)	103.0(4)
N(3)#2−Ag(2)−C(28)	95.7(3)	C(2)−Ag(2)−C(28)	143.7(3)
N(3)#2−Ag(2)−C(33)	110.6(3)	C(2)−Ag(2)−C(33)	113.9(3)
N(3)#2−Ag(2)−C(3)	129.9(4)	C(2)−Ag(2)−C(3)	30.0(3)
C(28)−Ag(2)−C(3)	117.4(3)	C(33)−Ag(2)−C(3)	88.9(3)
Compound **13**			
Ag(1)−N(7)#1	2.275(7)	Ag(1)−N(2)	2.350(6)
Ag(1)−N(3)#2	2.370(7)	Ag(1)−N(6)	2.403(6)
Ag(2)−N(4)#3	2.272(8)	Ag(2)−N(8)	2.279(8)
Ag(2)−O(3)	2.374(9)	Ag(2)−C(4)#4	2.388(8)
Ag(2)−C(3)#4	2.542(9)		
N(7)#1−Ag(1)−N(2)	132.4(2)	N(7)#1−Ag(1)−N(3)#2	97.9(2)
N(2)−Ag(1)−N(3)#2	100.5(2)	N(7)#1−Ag(1)−N(6)	103.2(2)
N(2)−Ag(1)−N(6)	109.4(2)	N(3)#2−Ag(1)−N(6)	112.5(2)
N(4)#3−Ag(2)−N(8)	100.4(3)	N(4)#3−Ag(2)−O(3)	109.3(3)
N(8)−Ag(2)−O(3)	98.7(3)	N(4)#3−Ag(2)−C(4)#4	111.0(3)
N(8)−Ag(2)−C(4)#4	130.8(3)	O(3)−Ag(2)−C(4)#4	105.1(3)
N(4)#3−Ag(2)−C(3)#4	138.0(3)	N(8)−Ag(2)−C(3)#4	99.9(3)
O(3)−Ag(2)−C(3)#4	103.5(3)	C(4)#4−Ag(2)−C(3)#4	33.1(2)

As shown in Figure 21, tridentate **L4** ligands link silver atoms through cyclopentadienide π−Ag and pyridazine N−Ag interactions into zigzag chains running conversely. These two sets of chains are further bound together alternately through the side benzonitrile arm of **L4** into a two-dimensional net extending in the crystallographic *ab* plane (Figure 21). This net contains the trinuclear squarelike ring $\{Ag_3(\mathbf{L4})_3\}$, in which the Ag···Ag distances are ca. 11, 9, and 8 Å. Uncoordinated benzene and toluene solvent molecules and SbF_6^- counterions are located on both sides of the ring plane (Figure 22). In the solid state, these two-dimensional nets stack parallel along the crystallographic *c* axis. When the structure is viewed down the crystallographic *a* axis, rectangular channels containing benzene and toluene molecules and SbF_6^- anions have been found (Figure 23).

(b) Synthesis and Structural Analysis of 10. The idea behind the use of ligand **L5** is to control supramolecular motifs through different donors' orientations. It is well-known that the relative different orientations of the terminal coordination donors and also the different bridging spacing might result in unusual building blocks, which can lead to the construction of supramolecular motifs that have not been achieved using normal rigid linear bidentate organic ligands.[20] We earlier reported on a series

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[20] (a) Barnett, S. A.; Champness, N. R. *Coord. Chem. Rev.* **2003**, *246*, 145. (b) Kaes, C.; Katz, A.; Hosseini, M. W. *Chem. Rev.* **2000**, *100*, 3553. (c) Withersby, M. A.; Blake, A. J.; Champuess, N. R.; Cooke, P. A.; Hubberstey, P.; Li, W.-S.; Schröder, M. *Inorg. Chem.* **1999**, *38*, 2259. (d) Campos-Fernández, C. S.; Clérac, R.; Dunbar, K. R. *Angew, Chem., Int. Ed.* **1999**, *38*, 3477. (e) Albrecht, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 3463.

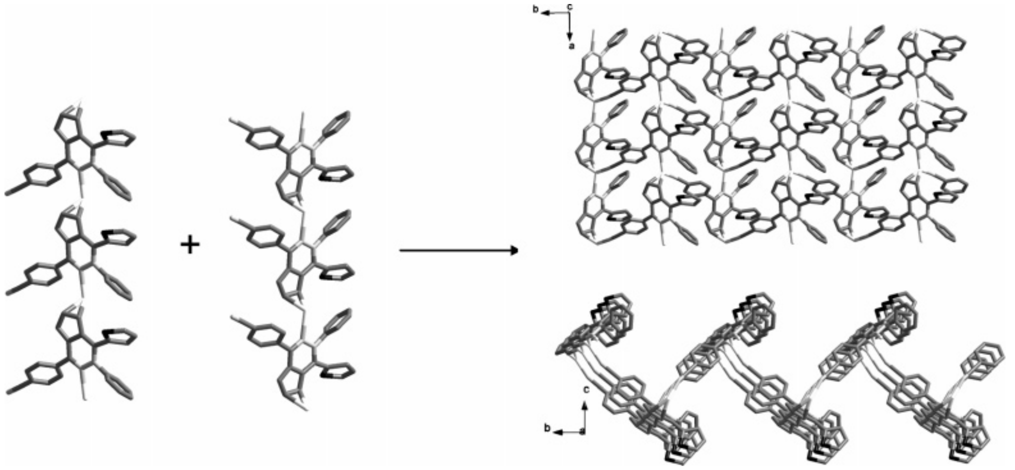

Figure 21. From one-dimensional zigzag chains to a two-dimensional net.

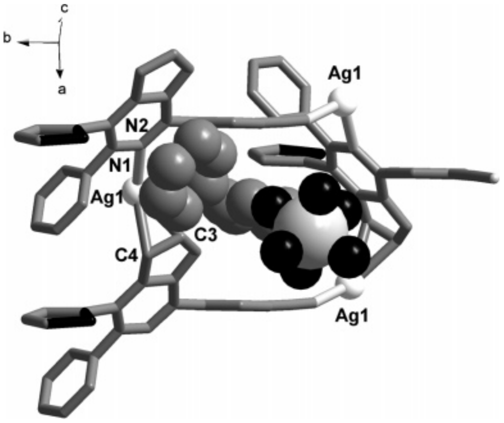

Figure 22. Trinuclear squarelike ring $\{Ag_3(\mathbf{L4})_3\}$ containing benzene, toluene guest molecules, and SbF_6^- counterions.

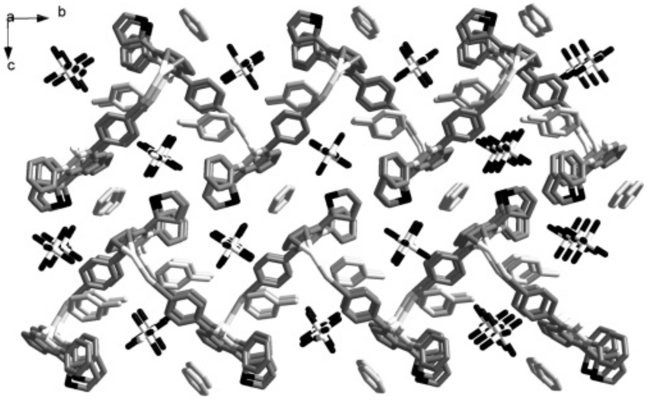

Figure 23. Rectangular channels containing benzene, toluene molecules, and SbF_6^- anions (view down the crystallographic *a* axis).

of novel coordination polymers generated from rigid bidentate 4,4′-bipyridine- and 3,3′-bipyridine-type double Schiff-base ligands. Indeed, our previous studies demonstrated that the relative orientation of the coordinating sites is one of the most important factors in controlling the polymeric motifs.[7,21]

Reaction of **L5** with $AgPF_6$ (1:2 ratio) in benzene/toluene at room temperature afforded compound **10** as green-yellow platelike crystals in 71% yield. Single-crystal analysis revealed that compound **10** crystallizes in the triclinic system with the space group $P\bar{1}$. Crystallographic data for **10** are given in Table 3, and selected interatomic distances and bond angles are given in Table 6. As shown in Figure 24, the Ag(I) center lies in a distorted triangular $\{AgN_2\pi\}$ coordination environment consisting of one −CN donor ($d_{Ag(1)-N(3)\#1} = 2.196(7)$ Å), one pyridazine ($d_{Ag(1)-N(2)} = 2.305(5)$ Å), and one π donor from a coordinated benzene ($d_{Ag(1)-C(25)} = 2.440(15)$ Å and $d_{Ag(1)-C(30)} = 2.620(17)$ Å). The corresponding bond distances are very close to those found in compounds **1**−**9**. As indicated in Figure 24, two Ag(I) centers are connected to each other by two *cis*-**L5** ligands in a face-to-face fashion through −CN and $N_{pyridazine}$ donors into a bimetallic 16-membered molecular $\{Ag_2(\mathbf{L5})_2\}$ ring. Two uncoordinated PF_6^- anions are situated on the both sides of the ring plane. The intra-ring Ag···Ag distance is 6.8 Å. Herein, **L5** acts as an angular ligand (the bite angle between one terminal −CN donor and its adjacent $N_{pyridazine}$ donor being around 60°) which has a strong tendency to form a metallacyclic moiety with inorganic metal ions. Such a type of geometric configuration together with different electron donors would be expected to form new metallacycle-containing coordination polymers or supramolecular complexes. It is obvious that the coordination motif of **10** is distinctly different from that of **9**, which does result from the different relative orientations of the −CN donors on them. In addition, the cyclopentadienide moiety remains uncoordinated, which is probably due to the solvent benzene molecule taking its coordinating position.

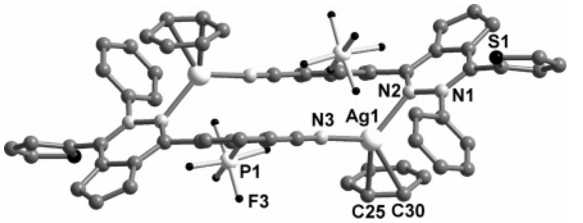

Figure 24. Ag(I) coordination environment and dinuclear metallacycle in **10**.

(c) Synthesis and Structural Analysis of 11. For exploring the templating role of counterions in the self-assembly process, $AgSO_3CF_3$ was used instead of $AgPF_6$ to carry out the reaction under the same reaction conditions. Combination of **L5** with $AgSO_3CF_3$ (1:2 ratio) in benzene/toluene at room temperature afforded compound **11** as yellow crystals in 59% yield. Single-crystal analysis revealed that compound **11** crystallizes in the monoclinic system with the space group *C*/2*c*. Crystallographic data for **11** are given in Table 3, and selected interatomic

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[21] (a) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Chem. Mater.* **2000**, *12*, 1156. (b) Dong, Y.-B. Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2000**, *39*, 4927. (c) Ciurtin, D. M.; Dong, Y.-B.; Smith, M. D.; Barclay, T.; zur Loye, H.-C. *Inorg. Chem.* **2001**, *40*, 2825.

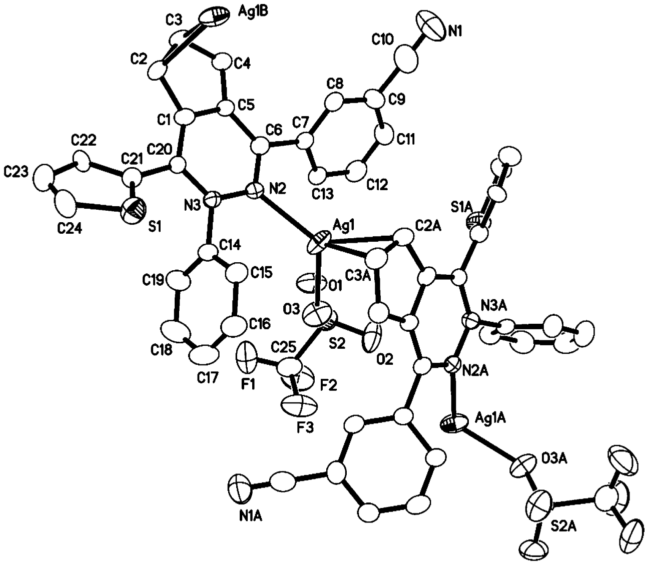

Figure 25. Coordination sphere of Ag(I) in **11**.

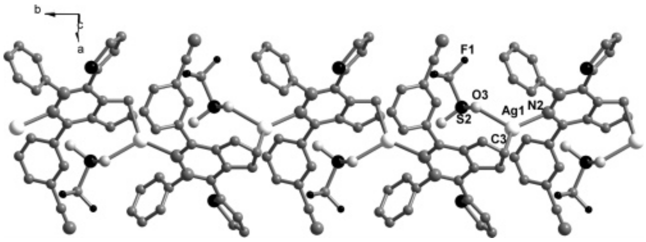

Figure 26. One-dimensional zigzag chain in **11**.

distances and bond angles are given in Table 6. The unsymmetric unit contains only one type of Ag(I) ion, which lies in a $\{AgNO\pi\}$ coordination sphere. One pyridazine N donor ($d_{Ag(1)-N(2)} = 2.262(5)$ Å), one O_{OTf} donor ($d_{Ag(1)-O(3)} = 2.333(5)$ Å), and the cyclopentadienide π donor ($d_{Ag(1)-C(2)\#1} = 2.448(7)$ Å and $d_{Ag(1)-C(3)\#1} = 2.493(7)$ Å) constitute the Ag(I) coordination environment (Figure 25). It is noteworthy that the −CN group was not involved in the silver coordination sphere. We tried several times to change the metal-to-ligand ratios; however, compound **11** was the only compound that could be isolated from the reactions, probably due to the templating effects of different counterions (from uncoordinated PF_6^- to weakly coordinated $SO_3CF_3^-$). As shown in Figure 26, **L5** acts as a bidentate linker to bunch silver atoms into zigzag chains extended along the crystallographic *b* axis. In **11**, weak hydrogen-bonding interactions are present. As shown in Figure 27, the one-dimensional polymer chains of **11** have close neighboring chains resulting from two sets of interpolymer hydrogen-bonding interactions. The first *set of* hydrogen-bonding system involves F(1) of the $SO_3CF_3^-$ group and H(24) on the **L5** ligand of the neighboring chain. The F(1)···H(24) contact is 2.7 Å, and the F(1)···C(24) distance and F(1)···H(24)−C(24) angle are 3.3 Å and 123°, respectively. The second hydrogen-bonding system consists of N(1) of the uncoordinated −CN group and H(22) on the thiophene ring of the neighboring chain. The N(1)···H(22) contact is 2.7 Å, and the N(1)···C(22) distance and N(1)···H(22)−C(22) angle are 3.3 Å and 119°, respectively. These interpolymer hydrogen-bonding interactions give rise to a 2-D layered arrangement of 1-D polymers parallel to the crystallographic *ab* plane.

4. Supramolecular Complexes Based on Symmetric Benzonitrile-Containing Ligands L6 and L7 and Ag(I) Ion. (a) Synthesis and Structural Analysis of 12. Compound **12** was obtained from a benzene/toluene system. The yellow plate crystals of **12** were obtained in 2 weeks in 63% yield when a toluene solution of **L6** was allowed to diffuse into a benzene solution of $AgSbF_6$. The single-crystal structure reveals that compound **12** crystallizes in the triclinic system with the space group $P\bar{1}$. Crystallographic data for **12** are given in Table 3, and selected interatomic distances and bond angles are given in Table 6. As indicated in Figure 28, the unsymmetric unit of **12** contains two different crystallographic Ag(I) centers. The first Ag(I) atom is four-coordinated ($\{AgN_2\pi_2\}$) by one benzonitrile N donor ($d_{Ag(1)-N(4)\#1} = 2.235(10)$ Å), one pyridazine N donor ($d_{Ag(1)-N(2)} = 2.274(8)$ Å), and two π-donors from two coordinated benzene molecules ($d_{Ag(1)-C(37)} = 2.879(8)$ Å, $d_{Ag(1)-C(41)} = 2.777(8)$ Å, and $d_{Ag(1)-C(40)} = 2.878(8)$ Å). It is worthwhile to point out that the two coordinated benzene molecules behave as η^2 and η^1 spacers, respectively, which is indicated by the Ag−C bond distances. The second Ag(I) ion lies in a $\{AgNF\pi_2\}$ coordination sphere which is composed of one N_{CN} donor ($d_{Ag(2)-N(3)\#2} = 2.350(11)$ Å), one F_{SbF_6} donor ($d_{Ag(2)-F(1)} = 2.693(11)$ Å), and two π donors from one η^2-coordinated benzene molecule (Ag(2)−C(2) = 2.368(12) Å and Ag(2)−C(3) = 2.752(12) Å) and one η^2-cyclopentadienide moiety (Ag(2)−C(28) = 2.4698(13) Å and Ag(2)−C(33) = 2.7238(13) Å), respectively. It is worth pointing out that there are four types of benzene molecules in **12**. The first and second types of benzene molecules act as the coligands attached to the Ag^I−**L6** chain, which contains a 19-membered metallacyclic

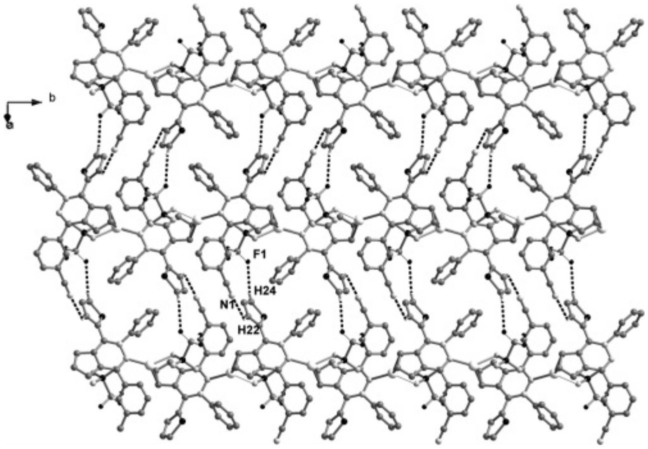

Figure 27. Two-dimensional H-bonded net in **11**.

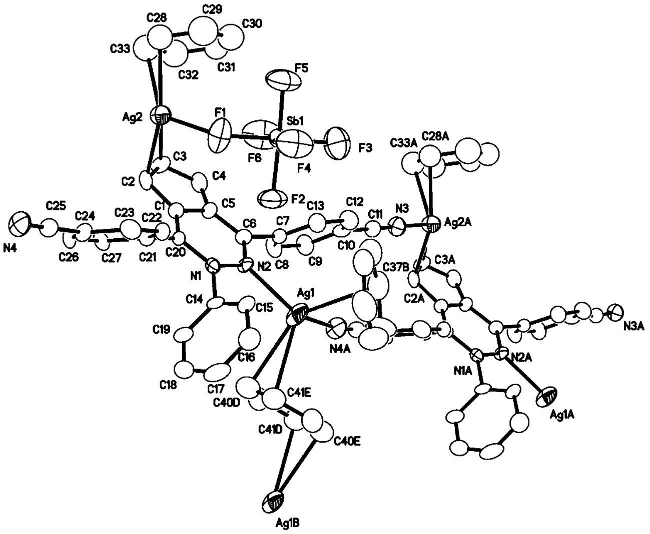

Figure 28. ORTEP drawing of **12**.

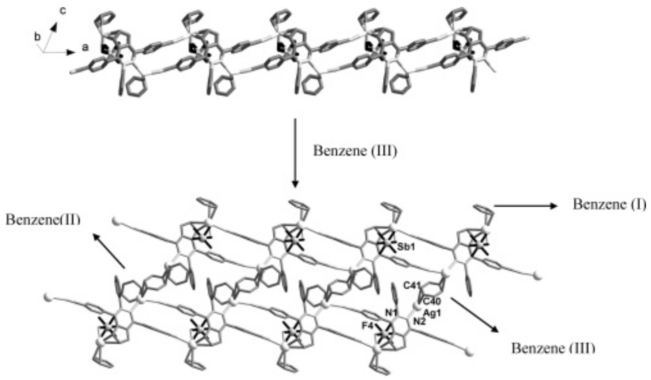

Figure 29. From a one-dimensional metallacyclic ring-containing chain to a two-dimensional net.

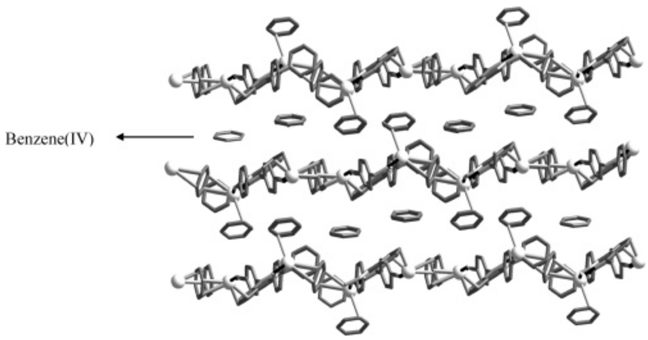

Figure 30. Crystal packing of **12**. Benzene guest molecules are located between two-dimensional nets.

ring. Meanwhile, the third type of benzene molecule acts as a bidentate spacer to bridge these one-dimensional chains into a two-dimensional net which is composed of large (ca. 10 × 8 Å) and small (ca. 10 × 4 Å) rectangle-like cavities (Figure 29). The fourth type of benzene molecule is located between these layers as guest molecules (Figure 30).

(b) Synthesis and Structural Analysis of 13. The combination of **L7** with $AgSO_3CF_3$ in a benzene/toluene mixed solvent system generated compound **13** as yellow crystals in 68% yield. Crystallographic data for **13** are given in Table 3, and selected interatomic distances and bond angles are given in Table 6. As in **12**, the unsymmetric unit of **13** contains two crystallographically different Ag(I) atoms. The first Ag(I) center is defined by four N donors ($d_{\mathrm{Ag(1)-N(7)\#1}} = 2.275(7)$ Å, $d_{\mathrm{Ag(1)-N(2)}} = 2.350(6)$ Å, $d_{\mathrm{Ag(1)-N(3)\#2}} = 2.370(7)$ Å, and $d_{\mathrm{Ag(1)-N(6)}} = 2.403(6)$ Å) of two benzonitrile and two pyridazine moieties. The second Ag(I) center lies in a $\{AgN_2O\pi\}$ coordination sphere which consists of two benzonitrile N donors ($d_{\mathrm{Ag(2)-N(4)\#3}} = 2.272(8)$ Å and $d_{\mathrm{Ag(2)-N(8)}} = 2.279(8)$ Å), one O donor from the $SO_3CF_3^-$ anion ($d_{\mathrm{Ag(2)-O(3)}} = 2.374(9)$ Å), and a π donor from a η^2-cyclopentadienide group (Ag−C bond lengths from 2.388(8) to 2.542(9) Å) (Figure 31). In compound **13**, *cis*- and *trans*-**L7** ligands are concomitant (Figure 32). As indicated in Figure 33, *cis*- and *trans*-**L7** ligands arrange alternately and link Ag(1) and Ag(2) atoms through the pyridazine group and one of the two sets of benzonitrile groups into a novel double-helical chain extending along the crystallographic [1−10] direction. The intrachain Ag(1)···Ag(1) and Ag(2)···Ag(2) distances are ca. 10 Å. The other set of benzonitrile groups surrounds the column and extends outward in four different directions. Each column connects four other equivalent columns through $N_{\mathrm{benzonitrile}}$−Ag interactions into a novel noninterpenetrating porous framework. The network contains large channels with different shapes extending in the different directions. When the structure is viewed down the crystallographic [1−10] direction, large rectangular channels (crystallographic dimensions ca. 18 × 9 Å) are evident in **13**. The benzene guest molecules are located in the center of the channels; when the structure is viewed down the crystallographic *b* axis, distorted rectangular channels (crystallographic dimensions ca. 15 × 5 Å) have been found, and encapsulated benzene guest molecules are close to the wall of the channels (Figure 34). When the structure is viewed down the [−111] direction, distorted honeycomb-like channels could be found. As indicated in Figure 35, the aromatic rings are arrayed toward the channels, which potentially makes possible the recognition of aromatic molecules.

5. Photoluminescence Properties. Inorganic−organic hybrid coordination polymers have been investigated for fluorescence properties and for potential applications as light-emitting diodes (LEDs). Owing to the ability of inorganic−organic coordination polymers to affect the emission wavelength of organic materials, syntheses of these compounds by the judicious choice of organic spacers and transition-metal centers can be an efficient method for obtaining new types of luminescent materials,[23] especially for d^{10} or $d^{10}-d^{10}$ systems[24] and conjugated ligand containing complexes.[25] We have been exploring the luminescent properties of fulvene ligands and organic/inorganic coordination polymers and supramolecular complexes based on them in the solid state. The results indicate that emission colors of organic spacers were affected by their incorporation into metal-containing coordination compounds. The luminescence properties of **L1**, **L3**, **L5**, and **L7** and polymeric compounds **1**−**3** and **5** were investigated in CH_3OH and the solid state. In the solid-state case, single-crystalline samples were used for the measurements. The ground microcrystalline samples were housed in the solid sample quartz carrier. The excitation and emission slit widths are 5 nm. The fluorescence spectra of the ligands and their complexes are summarized in Table 7. As indicated in Figure 36, in CH_3OH, **L1** and **L5** present two maxima at 400 and 387 nm for **L1** and 349 and 367 nm for **L5**, respectively. **L3** and **L7** present one maximum at 371 nm for **L3** and 345 nm for **L7**. In the solid state, **L1**, **L3**, **L5**, and **L7** exhibit only one emission maximum at 363, 390, 385, and 378 nm, respectively. As shown in Table 7, the emission colors of the Ag(I) complexes, in comparison to those of their corresponding free ligands, for all the emission bands in the solid state are red-shifted. Meanwhile, the emission

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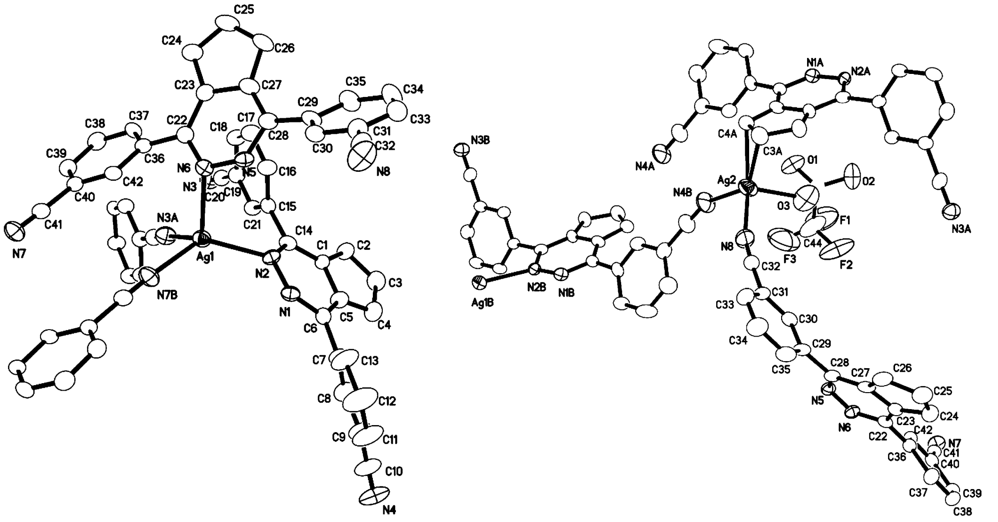

Figure 31. Coordination environments of Ag(1) and Ag(2) in **13**.

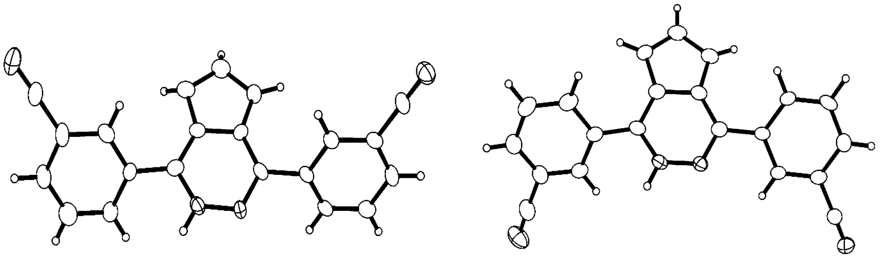

Figure 32. Cis and trans conformations of **L7** in compound **13**.

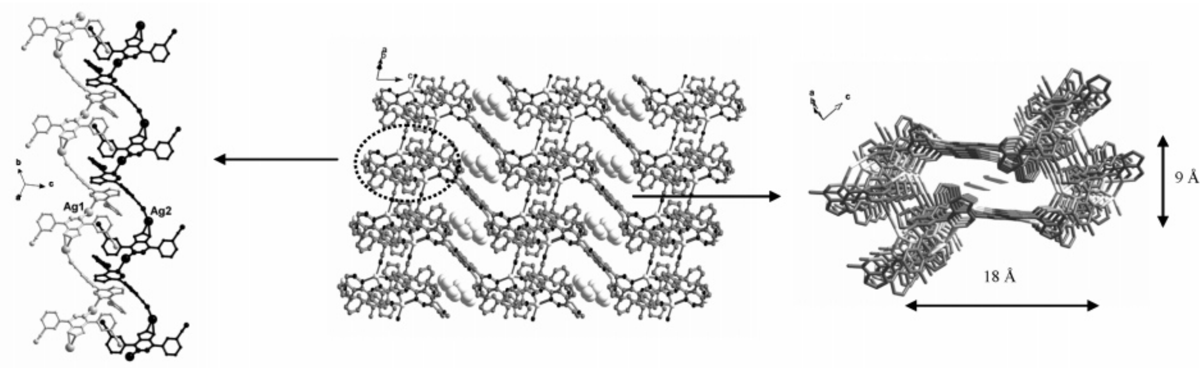

Figure 33. One-dimensional double-helical chain (left), three-dimensional framework (middle), and rectangular channel (right) in **13**.

colors of these complexes in solution are blue-shifted, probably due to the fact that the polymeric frameworks in polar solvent break down and result in the formation of oligomers and even discrete molecular complexes. As shown above, the middle fulvene and two terminal thiophene or benzonitrile groups are not coplanar but seriously twist, which is probably the reason that the excitation wavelengths for the ligands and complexes are relatively short.[25] Overall, the emission colors of the free ligands were significantly affected by their incorporation into the Ag(I)-containing complexes, as evidenced by the large shift in the emission.

Conclusions

The seven new symmetric and unsymmetric ligands **L1**−**L7** were synthesized. The results indicate that the coordination chemistry of new fulvene ligands with the soft acid Ag(I) ion is versatile. They can adopt either a cis or a trans conformation to bind Ag(I) not only through the terminal N and central N donors but also through the cyclopentadienide group into organometallic coordination polymers or discrete complexes.

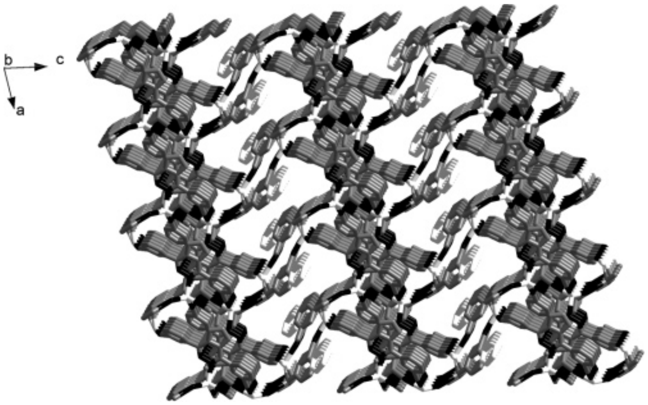

Figure 34. Three-dimensional framework in **13** (view down the [1−10] direction).

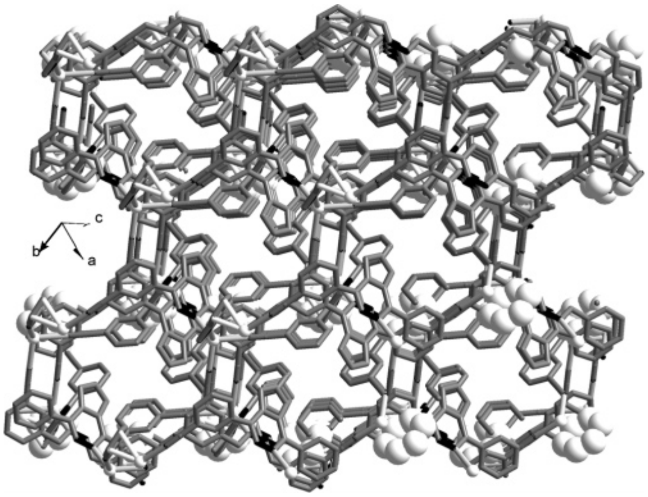

Figure 35. Three-dimensional framework in **13** (view down the [−111] direction).

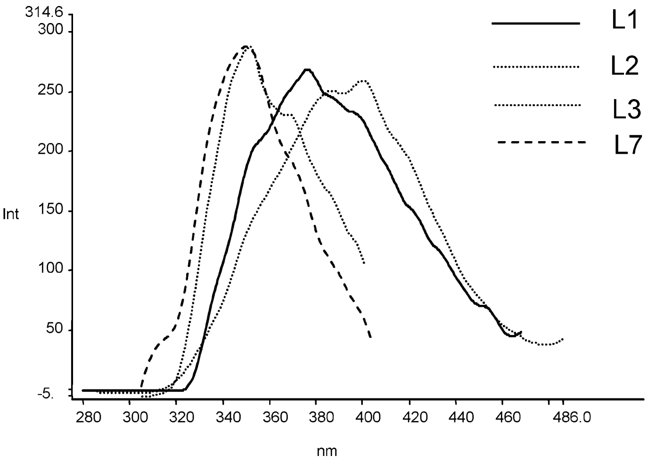

Figure 36. Photoinduced emission spectra of **L1**−**L3** and **L7** in EtOH at room temperature.

Table 7. Luminescence Properties of L1, L3, L5, L7, 1−3, and 5 in the Solid State and CH_3OH

	$\lambda_{ex}/\lambda_{em}$ (nm)			$\lambda_{ex}/\lambda_{em}$ (nm)	
compd	solid state	CH_3OH	compd	solid state	CH_3OH
L1	206/363	256/400, 387	**1**	215/382	242/368
L3	220/390	247/371	**2**	225/392, 404	241/348
L5	215/385	242/349, 367	**3**	214/394	222/384
L7	220/378	243/345	**5**	235/405, 416	224/381

We are currently extending this result by preparing new fulvene ligands of this type that have different substituted organic functional groups. We anticipate this approach to be useful for the construction of a variety of new transition-metal complexes and luminescent coordination polymers with novel structures that have the potential of leading to new fluorescent materials.

Experimental Section

Materials and Methods. 4-Cyanobenzoyl chloride, 3-cyanobenzoyl chloride, and 2-thiophenecarbonyl were prepared according to literature methods.[7] Inorganic metal salts were purchased from Acros and used without further purification. Infrared (IR) samples were prepared as KBr pellets, and spectra were obtained in the 400−4000 cm^{-1} range using a Perkin-Elmer 1600 FTIR spectrometer. ^1H NMR data were collected using a JEOL FX 90Q NMR or AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. Element analyses were performed on a Perkin-Elmer Model 240C analyzer. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorimeter (Varian, Australia) equipped with a xenon lamp and quartz carrier at room temperature.

Safety note**:** *Perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care*.

Preparation of Fulvene (II)-1, Fulvene (III)-1, and Fulvene (IV)-1. A solution of 4-cyanobenzoyl chloride (1.76 g, 10.6 mmol) and 2-thiophenecarbonyl (1.46 mL, 10.6 mmol) in anhydrous ether (20 mL) was added dropwise to a solution of cyclopentadienyl anions (31.8 mmol) in anhydrous ether at 0 °C, which was derived from Cp (31.8 mmol) and PhLi (31.8 mmol) in anhydrous ether. The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Hexane was added, and an orange solid precipitated. The solid was washed with hexane several times and stirred in HCl (5% in water) overnight. The final product was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 2:1) to afford fulvene (II)-1, fulvene (III)-1, and fulvene (IV)-1. Fulvene(II)-1: 0.63 g, yield 18.4%; corresponding spectral data of fulvene(II)-1 are identical with those of reported data.[7d] Fulvene (III)-1 (0.31 g, yield 10.2%): mp 106−108 °C; IR (KBr pellet) ν (cm^{-1}) 3480 (s), 3100 (s), 1615 (s), 1540 (s), 1510 (s), 1460 (s), 1400 (s), 1215 (vs), 1130 (vs), 1100 (vs), 1050 (vs), 830 (w), 710 (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 18.30 (s, 1H, −OH), 8.13 (d, 2H, $-C_4H_3S$), 8.02 (d, 2H, $-C_4H_3S$), 7.59 (d, 2H, $-C_4H_3S$), 7.33 (q, 2H, $-C_5H_3$), 6.64 (t, 1H, $-C_5H_3$). Anal. Calcd for $C_{15}H_{10}S_2O_2$: C, 62.94; H, 3.50. Found: C, 62.77; H, 3.43. In addition, fulvene (III)-1 could be obtained by following method as well: a solution of 2-thiophenecarbonyl (2.6 mL, 19 mmol) in anhydrous ether (20 mL) was added dropwise to a solution of cyclopentadiene anion (2.4 mL, 28.5 mmol) in anhydrous ether at 0 °C. The mixture was stirred overnight at room temperature. The solvent was then reduced to about 10 mL under vacuum. Hexane was added, and a yellow solid precipitated. The solid was washed with hexane several times and stirred in HCl (5% in water) overnight. The final product was purified by column chromatography on silica gel (CH_2Cl_2/hexane, 1:1) to afford fulvene (III)-1 as a red-orange crystalline solid: yield 40.0%. Fulvene (IV)-1 (0.91 g, yield 28.1%): mp 114−117 °C; IR (KBr pellet) ν (cm^{-1}) 3446 (s), 2229 (m), 1630 (s), 1539 (m), 1471 (s), 1420 (s), 1281 (vs), 1229 (vs), 1129 (vs), 904 (vs), 849 (s), 707 (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 18.33 (s, 1H, −OH), 8.26, 8.02, 7.93, 7.88 (m, 7H, $-C_4H_3S$, $-C_6H_4$), 7.34, 7.14, 6.63 (t, t, d, 3H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}NO_2S$: C, 70.82; H, 3.61. Found: C, 70.73; H, 3.52.

Preparation of Fulvene (II)-2, Fulvene (III)-1, and Fulvene (IV)-4. Fulvene (II)-2, fulvene (III)-1, and fulvene (IV)-2 were prepared by following the procedure descried for fulvene (II)-1, fulvene (III)-1, and fulvene (IV)-1, except with 3-cyanobenzoyl chloride (1.76 g, 10.6 mmol) instead of 4-cyanobenzoyl chloride (1.76 g, 10.6 mmol), to afford fulvene (II)-2, fulvene (III)-1, and fulvene (IV)-2 as orange crystalline solids. Fulvene(II)-2: 0.21 g, yield 7.0%; corresponding spectral data of fulvene(II)-2 are identical with those of reported data.[7d] Fulvene (III)-1: 0.73 g, yield 21.3%. Fulvene (IV)-2: 1.21 g, yield 37.4%; mp 102−104 °C; IR (KBr pellet) ν (cm^{-1}) 3447 (s), 2231 (s), 1621 (s), 1545 (s), 1518 (s), 1478 (s), 1399 (s), 1131 (m), 1084 (m), 1052 (m), 803 (s), 759 (s), 716 (s); ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ 18.30 (s, 1H, −OH), 8.18, 8.06, 7.77, 7.33 (m, 7H, $-C_4H_6$, $-C_4H_3S$), 7.15, 6.65 (m, 3H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}NO_2S$: C, 70.82; H, 3.61. Found: C, 70.74; H, 3.51.

Preparation of L1. A solution of fulvene (III)-1 (0.40 g) in anhydrous EtOH (20 mL) and a large excess of $N_2H_4 \cdot H_2O$ was heated to reflux for about 7 h. After the mixture was cooled to room temperature, the solvent was removed under reduced pressure to give a red-orange solid. The product was recrystallized from EtOH to give orange crystals of **L1**: yield 87.1%; mp 178−180

°C; IR (KBr pellet) ν (cm^{-1}) 3320 (s), 3150 (s), 1600 (s), 1540 (s), 1510 (s), 1450 (s), 1405 (m), 1385 (s), 1300 (vs), 1245 (vs), 1200 (vs), 1100 (vs), 910 (vs), 850 (s), 700 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 14.09 (s, 1H, $-$NH), 8.03, 7.75, 7.38 (s, s, m, 6H, $-C_4H_3S$), 7.28, 7.17 (s, d, 3H, $-C_5H_3$). Anal. Calcd for $C_{15}H_{10}N_2S_2$: C, 63.83; H, 3.55; N, 9.93. Found: C, 63.95; H, 3.67; N, 9.81.

Preparation of L2. L2 was prepared by following the procedure described for **L1**, except with NH_2OH instead of $N_2H_4{\cdot}H_2O$, to afford **L2** as an orange crystalline solid: 0.28 g, yield 70.3%; mp 84−86 °C; IR (KBr pellet) ν (cm^{-1}) 1613 (s), 1540 (s), 1510 (s), 1450 (s), 1398 (m), 1385 (s), 1300 (vs), 1245 (vs), 1200 (vs), 1100 (vs), 905 (vs), 846 (s), 708 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 14.09 (s, 1H, $-$NH), 8.03, 7.75, 7.38 (s, s, m, 6H, $-C_4H_3S$), 7.28, 7.17 (s, d, 3H, $-C_5H_3$). Anal. Calcd for $C_{15}H_9NOS_2$: C, 63.60; H, 3.18; N, 4.95. Found: C, 63.54; H, 3.12; N, 4.90.

Preparation of L3. L3 was prepared by following the procedure described for **L1**, except with PhNHNH$_2$ instead of $N_2H_4{\cdot}H_2O$, to afford **L3** as a yellow-orange crystalline solid: 0.42 g, yield 82.7%; mp 212−216 °C; IR (KBr pellet) ν (cm^{-1}) 3200 (vs), 1595 (s), 1560 (s), 1540 (s), 1500 (s), 1410 (s), 1320 (s), 1310 (s), 1230 (s), 1170 (s), 1090 (s), 850 (s), 700 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 8.02, 7.54, 7.47, 7.38, 7.24 (m, t, m, s, m, 11H, $-C_6H_5$, $-C_4H_3S$), 7.18, 7,03 (m, t, 3H, $-C_5H_3$). Anal. Calcd for $C_{21}H_{14}N_2S_2$: C, 70.39; H, 3.91; N, 7.82. Found: C, 70.23; H, 3.67; N, 7.74.

Preparation of L4. L4 was prepared by following the procedure described for **L3**, except with fulvene (IV)-1 instead of fulvene (III)-1, to afford **L4** as a yellow-orange crystalline solid: 0.31 g, yield 78.0%; mp 113−116 °C; IR (KBr pellet) ν (cm^{-1}) 3446 (s), 3316 (s), 2221 (s), 1610 (vs), 1591 (s), 1395 (s), 1365 (s), 1240 (vs), 1095 (vs), 1061 (vs), 894 (vs), 853 (s), 755 (s), 717 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 14.20 (s, 1H, $-$NH), 8.05−8.28 (q, 4H, $-C_6H_4$), 7.88−7.43 (m, 3H, $-C_4H_3S$), 7.12−6.94 (m, 3H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}N_3S$: C, 71.76; H, 3.65; N, 13.95. Found: C, 71.47; H, 3.48; N, 13.67.

Preparation of L5. L5 was prepared by following the procedure described for **L4**, except with PhNHNH$_2$ and fulvene (IV)-2 instead of $N_2H_4{\cdot}H_2O$ and fulvene (IV)-1, to afford **L5** as a yellow-orange crystalline solid: 0.40 g, yield 80.0%; mp 186−189 °C; IR (KBr pellet) ν (cm^{-1}) 3223 (s), 2226 (s), 1650 (s), 1576 (s), 1520 (s), 1488 (s), 1434 (s), 1309 (s), 1182 (s), 1093 (vs), 900 (vs), 849 (s), 806 (s), 754 (s), 699 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 7.79−8.38 (m, 4H, $-C_6H_4$), 7.47−7.31 (m, 8H, $-C_4H_3S$, $-C_6H_5$), 7.10−6.90 (m, 3H, $-C_5H_3$). Anal. Calcd for $C_{24}H_{15}N_3S$: C, 76.39; H, 3.98; N, 11.14. Found: C, 76.26; H, 3.89; N, 11.22.

Preparation of L6. L6 was prepared by following the procedure described for **L5**, except with fulvene (II)-1 instead of fulvene (IV)-2, to afford **L6** as a yellow-orange crystalline solid: 0.30 g, yield 75.4%; mp 194−197 °C; IR (KBr pellet) ν (cm^{-1}) 3433 (s), 2233 (s), 1681 (s), 1620 (m), 1546 (s), 1450 (s), 1400 (s), 1112 (vs), 951 (vs), 902 (vs), 835 (vs), 800 (vs), 691 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 14.12 (s, 1H, $-$NH), 8.38−7.40 (m, 8H, $-C_6H_4$), 7.29, 7.20, 6.89 (s, s, s, 3H, $-C_5H_3$). Anal. Calcd for $C_{21}H_{12}N_4$: C, 78.75; H, 3.75; N, 17.50. Found: C, 78.64; H, 3.63; N, 17.14.

Preparation of L7. L7 was prepared by following the procedure described for **L6**, except with fulvene (II)-2 and $N_2H_4{\cdot}H_2O$ instead of fulvene (II)-1 and PhNHNH$_2$, to afford **L7** as a yellow-orange crystalline solid: 0.60 g, yield 77.8%; mp 175−177 °C; IR (KBr pellet) ν (cm^{-1}) 2229 (m), 1610 (m), 1580 (s), 1490 (m), 1410 (vs), 1326 (s), 1185 (m), 1120 (m), 850 (s), 760 (s), 730 (m), 633 (m); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ 8.38−7.37 (m, 13H, $-C_6H_4$, $-C_6H_5$), 7.05, 6.63 (d, p, 3H, $-C_5H_3$). Anal. Calcd for $C_{27}H_{16}N_4$: C, 81.80; H, 4.07; N, 14.13. Found: C, 81.91; H, 4.31; N, 14.03.

Preparation of 1. Compound **1** was synthesized in 59% yield by layering a benzene solution (10 mL) of $AgSO_3CF_3$ (14.4 mg, 0.06 mmol) over a CH_2Cl_2 solution (10 mL) of **L1** (8.5 mg, 0.03 mmol). IR (KBr pellet): γ (cm^{-1}) 3448 (s), 1643 (s), 1540 (s), 1399 (s), 1267 (vs), 1179 (s), 1034 (s), 847 (m), 704 (m), 646 (d). Anal. Calcd for $C_{19}H_{13}N_2AgF_3O_3S_3$: C, 39.45; H, 2.25; N, 4.84. Found: C, 39.28; H, 2.21; N, 4.67.

Preparation of 2. Compound **2** was synthesized in 64% yield by layering a toluene solution (10 mL) of $AgSO_3CF_3$ (14.4 mg, 0.06 mmol) over a benzene solution (10 mL) of **L1** (8.5 mg, 0.03 mmol). IR (KBr pellet): γ (cm^{-1}) 3448 (s), 1643 (s), 1540 (s), 1399 (s), 1267 (vs), 1179 (s), 1034 (s), 847 (m), 704 (m), 646 (d). Anal. Calcd for $C_{44}H_{30}Ag_2F_6N_4O_6S_6$: C, 42.83; H, 2.43; N, 4.54. Found: C, 42.68; H, 2.31; N, 4.29.

Preparation of 3. Compound **3** was synthesized in 41% yield by layering a toluene solution (7 mL) of **L1** (8.5 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (20.6 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 3450 (s), 1616 (s), 1361 (s), 1021 (s), 890 (s), 752 (s), 661 (s). Anal. Calcd for $C_{18}H_{15}AgF_6N_2OS_2Sb$: C, 31.63; H, 2.20; N, 4.10. Found: C, 31.41; H, 2.13; N, 4.05.

Preparation of 4. Compound **4** was synthesized in 60% yield by layering a toluene solution (7 mL) of **L1** (8.5 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgClO_4$ (12.75 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 3449 (s), 1625 s), 1520 (m), 1388 (s), 1358 (s), 1144 (s), 1117 (s), 1083 (s), 891 (s), 747 (s), 630 (s). Anal. Calcd for $C_{18}H_{13}AgClN_2O_4S_2$: C, 40.85; H, 2.46; N, 5.30. Found: C, 40.97; H, 2.31; N, 5.19.

Preparation of 5. Compound **5** was synthesized in 64% yield by layering a toluene solution (7 mL) of **L1** (8.5 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgPF_6$ (14.4 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 3421 (s), 3120 (w), 1600 (s), 1538 (m), 1510 (m), 1438 (s), 1398 (vs), 1278 (s), 1234 (vs), 1170 (s), 918 (m), 850 (m), 759 (m), 706 (s), 630 (s). Anal. Calcd for $C_{44}H_{32}N_4Ag_2F_6O_6S_6$: C, 42.79; H, 2.59; N, 4.54. Found: C, 42.15; H, 2.41; N, 4.61.

Preparation of 6. Compound **6** was synthesized in 51% yield by layering a toluene solution (7 mL) of **L2** (8.4 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (20.6 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 3420 (s), 3122 (w), 1603 (s), 1536 (m), 1616 (s), 1361 (s), 1024 (s), 891 (s), 752 (s), 662 (s). Anal. Calcd for $C_{30}H_{18}AgF_6N_2O_2S_4Sb$: C, 39.55; H, 1.98; N, 3.08; Found: C, 39.25; H, 1.77; N, 2.99.

Preparation of 7. Compound **7** was synthesized in 54% yield by laying a toluene solution (7 mL) of **L3** (11.4 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgPF_6$ (14.4 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 1637 (s), 1618 (s), 1453 (s), 1400 (s), 1306 (s), 1398 (s), 1158 (s), 849 (s), 778 (m), 750 (m), 701 (m), 620 (s). Anal. Calcd for $C_{28}H_{22}AgF_6N_2PS_2$: C, 47.80; H, 3.13; N, 3.98. Found: C, 47.71; H, 3.10; N, 3.91.

Preparation of 8. Compound **8** was synthesized in 57% yield by layering a toluene solution (7 mL) of **L3** (11.4 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (20.6 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}): 1632 (s), 1557 (s), 1536 (s), 1492 (s), 1445 (s), 1398 (s), 1346 (s), 1321 (s), 1222 (s), 1171 (s), 1031 (s), 931 (m), 878 (s), 776 (m), 749 (m), 700 (s), 670 (vs). Anal. Calcd for $C_{56}H_{44}Ag_2F_{12}N_4S_4Sb_2$: C, 42.31; H, 2.77; N, 3.53. Found: C, 42.22; H, 2.71; N, 3.47.

Preparation of 9. Compound **9** was synthesized in 57% yield by layering a toluene solution (7 mL) of **L4** (11.3 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (20.6 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 3442 (s), 2248 (s), 1634 (s), 1400 (s), 1021 (s), 848 (s), 779 (s), 657 (vs). Anal. Calcd for $C_{34}H_{26}N_3AgF_6$ SSb: C, 47.89; H, 3.05; N, 4.93. Found: C, 47.76; H, 3.00; N, 4.87.

Preparation of 10. Compound **10** was synthesized in 71% yield by layering a toluene solution (7 mL) of **L5** (11.3 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgPF_6$ (14.5 mg, 0.06 mmol).

IR (KBr pellet): γ (cm^{-1}) 3419 (s), 3128 (s), 2264 (s), 1631 (s), 1400 (s), 1337 (m), 1127 (s), 924 (s), 839 (s), 750 (s), 637 (s), 557 (s). Anal. Calcd for $C_{30}H_{21}AgF_6N_3PS$: C, 51.82; H, 2.96; N, 5.93. Found: C, 51.71; H, 3.10; N, 5.76.

Preparation of 11. Compound **11** was synthesized in 59% yield by layering a toluene solution (7 mL) of **L5** (11.3 mg, 0.03 mmol) over a benzene solution (10 mL) of AgOTf (14.4 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 3226 (s), 2231 (s), 1621 (s), 1580 (s), 1510 (s), 1488 (s), 1434 (s), 1263 (vs), 1100 (s), 911 (s), 846 (s), 806 (s). Anal. Calcd for $C_{25}H_{15}AgF_3N_3O_3S_2$: C, 47.29; H, 2.36; N, 6.62. Found: C, 47.16; H, 2.31; N, 6.54.

Preparation of 12. Compound **12** was synthesized in 63% yield by layering a toluene solution (7 mL) of **L6** (11.9 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (20.6 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 2230 (s), 1612 (s), 1580 (s), 1504 (s), 1402 (s), 1325 (s), 1124 (s), 842 (s), 776 (m), 700 (s), 670 (vs). Anal. Calcd for $C_{48}H_{37}Ag_2F_{12}N_4Sb_2$: C, 42.45; H, 2.73; N, 4.13. Found: C, 45.33; H, 2.65; N, 4.02.

Preparation of 13. Compound **13** was synthesized in 68% yield by layering a toluene solution (7 mL) of **L7** (9.6 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (14.4 mg, 0.06 mmol). IR (KBr pellet): γ (cm^{-1}) 2233 (s), 1605 (s), 1501 (s), 1398 (s), 1136 (s), 878 (s), 776 (m), 749 (m), 674 (vs). Anal. Calcd for $C_{50}H_{30}Ag_2F_6N_8O_6S_2$: C, 48.66; H, 2.43; N, 9.08; Found: C, 48.53; H, 2.36; N, 9.01.

Crystallography. Suitable single crystals of **1**−**13** were selected and mounted onto thin glass fibers. X-ray intensity data were measured on a Bruker SMART APEX CCD-based diffractometer (Mo Kα radiation, $\lambda = 0.710\,73$ Å). The raw frame data for **1**−**13** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[27] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[27] There was no evidence of crystal decay during data collection for any compound. Space groups were determined by a combination of systematic absences in the intensity data, intensity statistics, and the successful solution and refinement of the structures. All structures were solved by direct methods followed by difference Fourier synthesis and refined against F^2 by the full-matrix least-squares technique, using SHELX.[26] Crystal data, data collection parameters, and refinement statistics for **1**−**13** are listed in Tables 1−3. Relevant interatomic bond distances and bond angles for them are given in Tables 4−6.

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Supporting Information Available: CIF files giving crystallographic data for **1**−**13**. This material is available free of charge via the Internet at http://pubs.acs.org.

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