[Ag₂(C₃₃H₂₆N₂O₂)(H₂O)₂(SO₃CF₃)₂]·0.5C₆H₆: A Luminescent Supramolecular Silver(I) Complex Based on Metal–Carbon and Metal–Heteroatom Interactions

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A novel fulvene-type bidentate ligand **1** has been synthesized by an aroylation reaction of cyclohexyl-substituted cyclopentadienyl anions. Compound **1** crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.0419(5)$ Å, $b = 11.9360(8)$ Å, $c = 15.6470(11)$ Å, $\alpha = 85.1440(10)°$, $\beta = 78.1140(10)°$, $\gamma = 74.5360(10)°$, $V = 1239.76(15)$ Å³, and $Z = 2$. The coordination chemistry of **1** was investigated, and a novel Ag-containing coordination polymer (**2**), linked by both Ag–heteroatom and Ag–carbon interactions, has been synthesized. The coordination polymer has been fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. Compound **2** crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.1654(5)$ Å, $b = 15.7277(11)$ Å, $c = 18.8157(13)$ Å, $\alpha = 73.5150(10)°$, $\beta = 89.0410(10)°$, $\gamma = 89.0970(10)°$, $V = 1355.19(14)$ Å³, and $Z = 2$. The solid-state structure of **2** features a one-dimensional double-chain motif. These double chains are in turn cross-linked to each other via strong interchain O–H···O hydrogen bonds, forming a novel two-dimensional network with remarkably large cavities (effective cross section of ca. 21 × 15 Å) that are occupied by benzene guest molecules. Both compounds **1** and **2** are luminescent in the solid state, and a large blue-shift in the emission between the free ligand **1** and the ligand incorporated into complex **2** is observed.

Introduction

Self-assembly of organic ligands and inorganic metal ions is one of the most efficient and widely used approaches for the construction of supramolecular architectures. Owing to their potential as new functional solid materials, interest in self-assembled coordination polymers with interesting physical properties has grown rapidly. Up to now, metal–heteroatom and metal–carbon interactions are two of the most important interactions in the construction of polymeric networks in the solid state. Two main lines of study have been followed, based on metal–heteroatom and metal–carbon interactions: (1) Extended frameworks are comprised of organic spacers containing heteroatom donors via metal–heteroatom coordination bonds. So far, many organic–inorganic coordination polymers of this type have been successfully synthesized by us as well as by many other research groups.[1,2] (2) Networks are assembled from aromatic ligands via metal–carbon bonds. For example, Ag-containing organometallic coordination polymers generated from smaller aromatics and also polycyclic aromatic hydrocarbons based on cation–π interactions were reported by the Amma and Munakata research groups.[3]

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Scheme 1. Synthesis of Compound **1**[a]
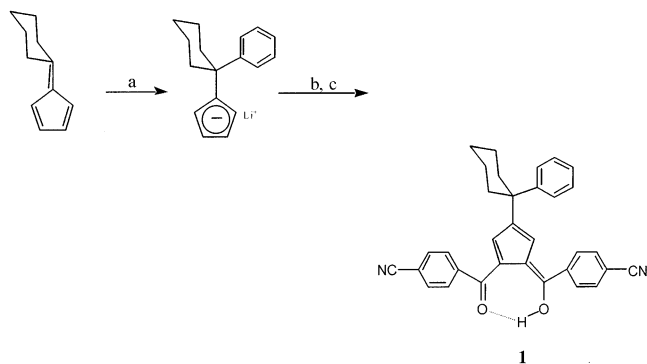
[a]Key: (a) PhLi, ether, 0 °C; (b) 4-cyanobenzoyl chloride, ether, 0 °C; (c) HCl (5%), room temperature.

In contrast, the chemistry of supramolecular architectures generated from organic spacers that can afford both heteroatoms and carbon atoms as coordinating sites has received considerably less attention. In principle, such materials might exhibit enhanced physical properties, such as electrical conductivity or fluorescence resulting from the synergy between the two distinctly different types of interactions. Very recently, we designed and synthesized a series of luminescent conjugated organic ligands with both aromatic rings and −CN functional groups, such as **1**, by the aroylation of substituted cyclopentadienyl anions, which were obtained from 6,6′-dialkylfulvene and phenyllithium (Scheme 1).[4] This new class of organic ligands gives us the opportunity to synthesize such new types of polymeric compounds containing both metal−carbon and metal−heteroatom coordination interactions. In this paper we wish to report on the use of this ligand in the synthesis of a new luminescent Ag-containing polymeric compound $[Ag_2(C_{33}H_{26}N_2O_2)(H_2O)_2(SO_3CF_3)_2]\cdot 0.5C_6H_6$ (**2**) based on both metal−carbon and metal−nitrogen coordination interactions. The results reported herein demonstrate that the use of organic spacers containing both aromatic groups and coordinating heteroatom groups as precursors to bind transition metal ions is in fact a new approach for the formation of novel organometallic molecular and supramolecular networks with interesting physical properties.

Experimental Section

Materials and Methods. 4-Cyanobenzoyl chloride and 6,6′-pentamethylenefulvene were prepared according to literature methods. AgOTf was purchased from Acros and used without

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(4) (a) Dormond, A. *J. Organomet. Chem.* **1975**, *101*, 71. (b) Howie, R. A. *J. Organomet. Chem.* **1986**, *303*, 213.

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. ^{1}H NMR data were collected using a JEOL FX 90Q NMR spectrometer. Chemical shifts are reported in δ relative to TMS. Element analyses were performed on a Perkin-Elmer model 240C analyzer. Thermogravimeric analysis was performed on **2** (6.45 mg) by heating the compound from 25 to 500 °C under flowing N_2 using heating rate of 10 °C/min on a TA Instrument SDT 2960 with simultaneous DTA−TGA.

Synthesis of 1. A solution of 4-cyanobenzoyl chloride (1.80 g, 10.8 mmol) in anhydrous ether (20 mL) was added dropwise to a solution of (1-phenylcyclohexyl)cyclopentadienyl anions[4] (16.2 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 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, 6:5) to afford an orange crystalline solid (1.70 g, 65%). IR (KBr pellet) [ν (cm^{-1})]: 2995 (m), 2885 (w), 2225 (s), 1624 (s), 1600 (s), 1570 (m), 1540 (m), 1515 (s), 1490 (s), 1430 (s), 1410 (s), 1350 (s), 840 (s). ^{1}H NMR (90 MHz, CDCl$_3$, 25 °C, TMS): δ 17.79 (s, 1H, OH), 7.79 (s, 8H, C_6H_4), 7.25 (m, 5H, C_6H_5), 6.97 (s, 2H, C_5H_2), 1.50−2.62 (m, 10H, C_6H_{10}). Anal. Calcd for $C_{33}H_{26}O_2N_2$: C, 82.16; H, 5.39; N, 5.81. Found: C, 82.20; H, 5.36; N, 5.79.

Synthesis of 2. AgOTf (13 mg, 0.050 mmol) was added to a solution of **1** (16 mg, 0.033 mmol) in 10 mL of benzene. After about 30 min of stirring at room temperature, the resultant yellow solution was introduced into a 7 mm diameter tube and layered with hexane as a diffusion solvent. After standing at room temperature for 1 month, orange crystals of **2** were obtained (85%). IR (KBr pellet) [ν (cm^{-1})]: 3500 (s), 2993 (s), 2850 (m), 2275 (s), 2250 (s), 1620 (w), 1595 (m), 1575 (w), 1540 (w), 1510 (m), 1415 (m), 1350 (s), 1255 (vs), 1150 (s), 1030 (s), 845 (s). Anal. Calcd for $Ag_2C_{38}H_{33}O_{10}N_2F_6S_2$: C, 42.56; H, 3.08; N, 2.61. Found: C, 42.55; H, 3.08; N, 2.59.

Single-Crystal Structure Determination. Suitable single crystals of **1** and **2** were selected and mounted in air onto thin glass fibers. X-ray intensity data covering the full sphere of reciprocal space were measured at 293 K on a Bruker SMART APEX CCD-based diffractometer system (Mo Kα radiation, $\lambda = 0.710\,73$ Å).[5] The raw frame data for **1** and **2** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[5] Corrections for incident and diffracted beam absorption effects were applied to **2** using SADABS;[5] no absorption correction was applied to **1**. No significant crystal decay was observed in either case. Both structures were solved by direct methods and refined by full-matrix least squares against F^2 using all data, with the SHELXTL software package.[5] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms (except H1 for **1** and H2A for **2**) were calculated and refined as riding atoms. H1 (**1**) and H2A (**2**) were located in the Fourier difference maps and refined freely with an isotropic displacement parameter. Crystal data, data collection parameters, and refinement statistics for **1** and **2** are listed in Table 1. Relevant interatomic bond distances and bond angles for **1** and **2** are given in Tables 2 and 3.

(5) (a) *SMART Version 5.624, SAINT Version 6.02a, and SADABS*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998. (b) Sheldrick, G. M. *SHELXTL Version* 5.*1*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1997.

[Ag₂(C₃₃H₂₆N₂O₂)(H₂O)₂(SO₃CF₃)₂]·0.5C₆H₆

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

	C₃₃H₂₆N₂O₂ (**1**)	Ag₂C₃₈H₃₃N₂O₁₀S₂F₆ (**2**)
fw	482.56	1071.52
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.0419(5)	7.1654(5)
b (Å)	11.9360(8)	15.7277(11)
c (Å)	15.6470(11)	18.8157(13)
α (deg)	85.1440(10)	73.5150(10)
β (deg)	78.1140(10)	89.0410(10)
γ (deg)	74.5340(10)	89.0970(10)
V (Å³)	1239.76(15)	1355.19(14)
Z	2	2
ρ_{calc} (g/cm³)	1.293	1.751
μ(Mo Kα) (mm⁻¹)	0.079	1.153
temp (°C)	20	20
no. of reflcns	5082	7170
residuals:[a] R1; wR2 (all data)	0.0575; 0.1093	0.0560; 0.1097

[a] $R1 = \sum ||F_o| - |F_c||/\sum |F_o|$. $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Table 2. Interatomic Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for **1**

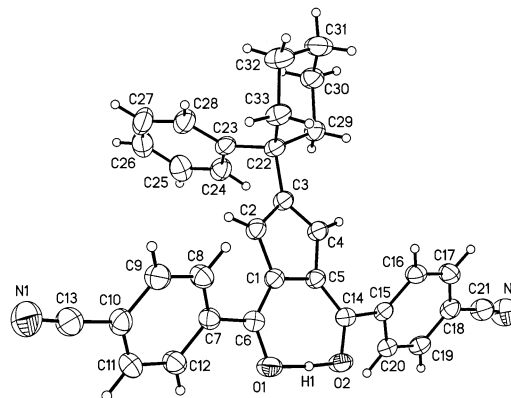| C(1)−C(2)	1.4002(17)	C(1)−C(5)	1.4778(16)
C(3)−C(22)	1.5233(16)	C(2)−C(3)	1.4048(16)
C(3)−C(4)	1.3846(16)	C(5)−C(4)	1.4125(16)
C(6)−O(1)	1.2746(14)	C(6)−C(7)	1.4938(16)
C(7)−C(8)	1.3909(18)	C(13)−N(1)	1.1416(18)
C(2)−C(1)−C(5)	105.73(10)	C(2)−C(3)−C(22)	125.86(10)
C(1)−C(2)−C(3)	110.71(11)	C(6)−C(1)−C(5)	127.46(11)
O(1)−C(6)−C(7)	113.46(11)	C(9)−C(10)−C(13)	119.22(14)
C(11)−C(10)−C(9)	120.12(13)	N(1)−C(13)−C(10)	176.87(17)

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for **2**[a]

Ag(1)−N(1)	2.149(3)	Ag(1)−N(2)#1	2.162(4)
Ag(1)−O(3)	2.549(3)	Ag(1)−O(3)#2	2.665(4)
Ag(2)−O(4)	2.262(4)	Ag(2)−O(8)	2.390(3)
Ag(2)−O(5)	2.427(3)	Ag(2)−C(25)	2.458(5)
C(1)−C(2)	1.403(4)	C(1)−C(5)	1.467(4)
C(3)−C(22)	1.523(5)	C(2)−C(3)	1.395(4)
C(3)−C(4)	1.395(4)	C(5)−C(4)	1.415(5)
C(6)−O(1)	1.265(4)	C(6)−C(7)	1.499(4)
C(7)−C(8)	1.388(5)	C(13)−N(1)	1.137(5)
N(1)−Ag(1)−N(2)#1	167.41(16)	N(1)−Ag(1)−O(3)	89.36(13)
N(2)#1−Ag(1)−O(3)	93.14(15)	N(1)−Ag(1)−O(3)#2	83.85(15)
O(3)−Ag(1)−O(3)#2	83.38(12)	O(4)−Ag(2)−O(8)	114.91(13)
O(4)−Ag(2)−O(5)	89.68(14)	O(8)−Ag(2)−O(5)	115.40(12)
O(4)−Ag(2)−C(25)	128.76(18)	O(8)−Ag(2)−C(25)	105.34(17)
O(5)−Ag(2)−C(25)	100.78(14)	O(7)−S(1)−O(6)	115.8(2)
C(2)−C(1)−C(5)	106.1(3)	C(2)−C(3)−C(22)	125.5(3)
C(1)−C(2)−C(3)	110.9(3)	C(6)−C(1)−C(5)	128.3(3)
O(1)−C(6)−C(7)	114.5(3)	C(9)−C(10)−C(13)	119.7(3)
C(11)−C(10)−C(9)	120.6(3)	N(1)−C(13)−C(10)	178.6(3)

[a] Superscripted number sign indicates symmetry-equivalent atoms.

Figure 1. Compound **1** (30% probability displacement ellipsoids).
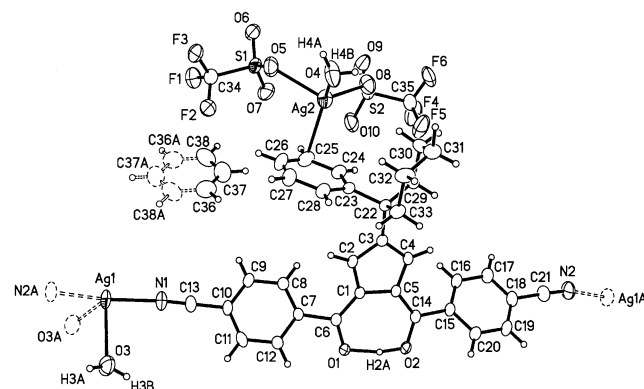
Figure 2. Asymmetric unit of compound **2** (30% probability displacement ellipsoids). Symmetry-equivalent atoms are shown as dotted ellipsoids.

Results and Discussion

Synthesis and Structural Analysis of 1. Ligand **1** was prepared in 65% yield as a deep-yellow crystalline solid by the reaction of 4-cyanobenzoyl chloride with cyclohexyl-substituted cyclopentadienyl anions, which in turn were prepared from 6,6′-pentamethylenefulvene and phenyllithium in ether at 0 °C (Scheme 1). The structure of **1** was determined by ¹H NMR, IR, elemental analysis, and single-crystal X-ray diffraction. In the ¹H NMR spectrum of **1**, a proton resonance was observed at 17.79 ppm as a singlet, which was attributed to the chelated proton, which is hydrogen bonded to the carbonyl next to the 1-aroyl group. The IR spectrum of **1** showed a −CN absorption band at

2225 cm⁻¹. It did not, however, show absorptions above 1630 cm⁻¹ in the region normally assigned to organic carbonyl groups. The strong absorption band at 1620 cm⁻¹ is, however, consistent with the hydrogen-bonded enol structure, since it has been shown that conjugation and chelation lead to a large shift in the carbonyl infrared band.[6] The structure of **1** was further confirmed by single-crystal X-ray diffraction. As shown in Figure 1, the crystal structure of **1** reveals that the two aroyl groups on the tetracarbon substituted cyclopeta-dienyl ring are adjacent. The C−C bond lengths on the substituted Cp ring and also C(1)−C(5) and C(5)−C(14) range from 1.3846(16) to 1.4778(16) Å, which are significantly shorter than a normal C−C single bond distance. Evidently, compound **1** exists in the fulvene form,[6] which is one of the most important moieties in organometallic chemistry. The enol hydrogen atom (H(1)) is hydrogen bonded to the carbonyl oxygen atom (O(2), $d_{O(2)\cdots H(1)} =$ 1.312 (17) Å, ∠O(1)−H(1)⋯O(2) = 175.9(15)°, and $d_{O(1)\cdots O(2)} = 2.4245(12)$ Å) to provide a hydrogen-bonded seven-membered ring. It is worth pointing out that the two −C₆H₄CN-*p* rings and hydrogen-bonded seven-membered ring are not in the same plane. The dihedral angles between −C₆H₄CN-*p* rings and hydrogen-bonded seven-membered ring are 36.9 and 43.6°, respectively. The terminal (−CN) N⋯N separation in **1** is 16.66(5) Å, significantly longer than the terminal N⋯N separations of 7.122(4), 9.385(5), and
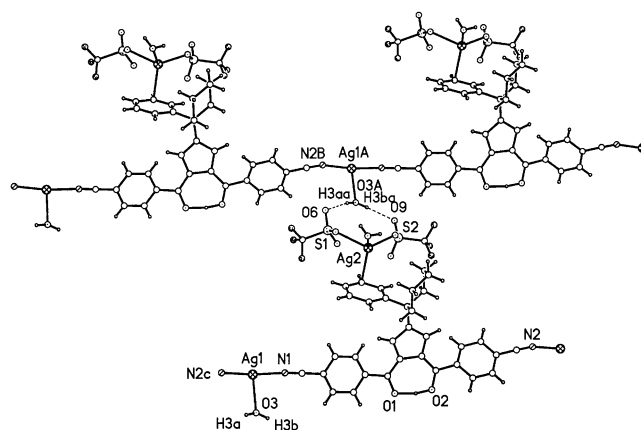
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(6) William, J. L.; William, H. S. *J. Am. Chem. Soc.* **1957**, *79*, 4970.
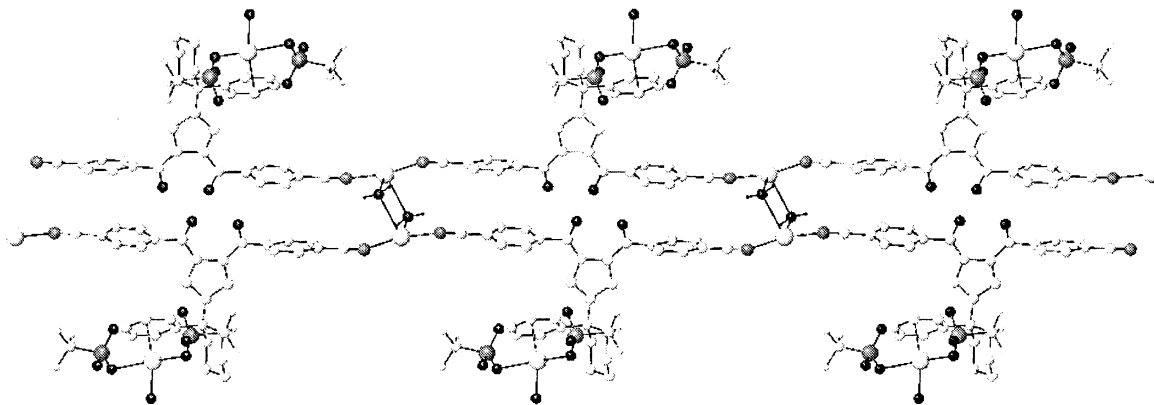
Figure 3. 1-D double chain in **2**, viewed down the crystallographic *a* axis. Ag, C, and F atoms are shown as large, medium, and small open circles, respectively. S and N atoms are shown as large and small gray circles, respectively. O and H atoms are shown as large and small black circles, respectively. Hydrogen atoms on carbon and oxygen atoms are omitted for clarity.

9.685(4) Å found in 4,4′-bipyridine,[7,2e] *trans*-1,2-bis(4-pyridyl)ethene,[2f] and 1,2-bis(4-pyridyl)ethyne,[8] respectively. Rigid bidentate or tridentate ligands containing CN donors such as 4,4′-dicyanobiphenyl, 1,3,5-tris(4-cyanophenylethynyl)benzene, and also others are excellent bridging ligands to construct porous frameworks.[1d−g] However, to our knowledge, no fulvene-bridged CN donors containing ligand have been reported and used to construct coordination polymers. In addition to the two −CN groups, the carbonyl and enol groups in **1** could act as potential chelating coordinating sites to bind transition metal ions; they could also be potentially transferred to other types of organic functional groups, such as heterocyclic rings, by reaction with hydroxylamine, hydrazine, or the like.[6] Compound **1** can be classified as a new type of ligand that can be used for the construction of polymeric compounds containing both inorganic and organometallic moieties.

Synthesis and Structural Analysis of 2. Reaction of **1** with AgOTf (1:2 ratio) in benzene at room temperature afforded the title compound (**2**) as orange cubic crystals in 85% yield. Single-crystal analysis revealed, as shown in Figure 2, that there are two different Ag(I) centers in **2**. The first Ag(I) center adopts a {AgN_2O_2} (Ag(1)−N(1) = 2.149(3), Ag(1)−N(2) = 2.162(4), Ag(1)−O(3) = 2.549(3), and Ag(1)−O(3)* = 2.665(4) Å) coordination sphere, and the second lies in a {AgO_3C} (Ag(2)−O(4) = 2.262(4), Ag(2)−O(5) = 2.427(3), and Ag(2)−O(8) = 3.390(3) Å) organometallic pseudotetrahedral coordination environment. For the Ag(2) center the shortest Ag−C distance (Ag(2)−C(25)) is 2.458(5) Å while the remaining Ag−C contacts are greater than 2.831 Å, which is beyond the limits (2.47−2.76 Å) commonly observed in Ag(I)−aromatic complexes.[3a,9] Thus, the benzene ring in **1** coordinates to the Ag(I) ion with an η^1 instead of an η^2 bonding mode, which

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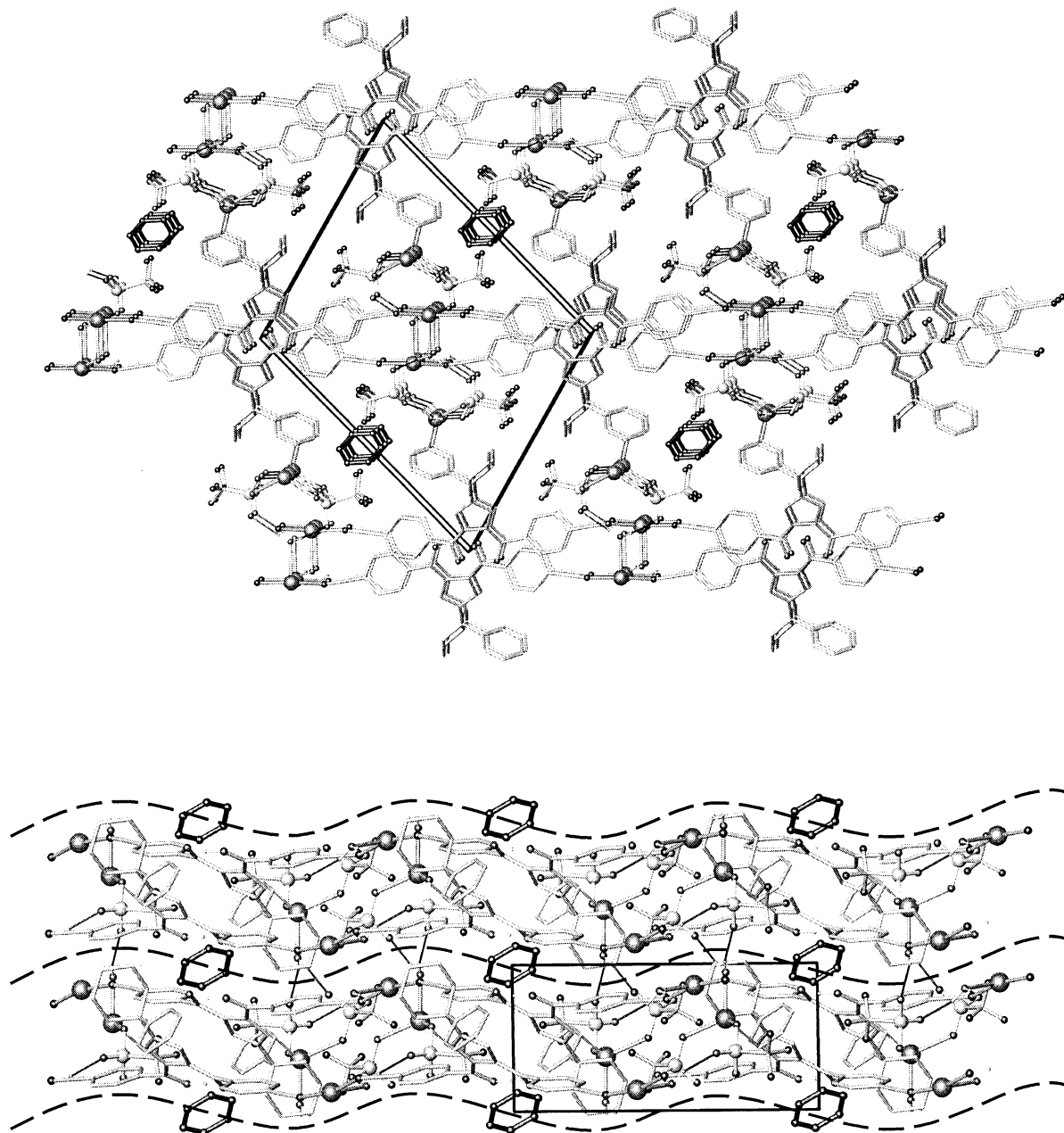(9) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 5407.

Figure 4. Hydrogen-bonding interactions in **2**. Hydrogen bonds are shown as dotted lines.

is normally observed in arene−metal complexes.[9] It is noteworthy that two SO_3CF_3^− counterions in **2** coordinate the Ag(2) center simultaneously while being located far from the Ag(1) center. In the solid state, the Ag(1) centers are connected by ligand **1** through the two terminal −CN groups into a mild zigzag one-dimensional chain along the crystallographic [01̄1] direction (N(1)−Ag(1)−N(2) = 167.41(16)° and intrachain Ag(1)···Ag(1) = 20.82(6), Ag(1)···Ag(2) = 14.99(7), and Ag(1)···Ag(2) = 11.25(6) Å, respectively). As shown in Figure 3, two single chains are further double bridged by two coordinated water oxygen atoms O(3) into a one-dimensional double-chain motif. The individual "links" in the double chains consist of Ag_4O_4(**1**)_2 units, which can be viewed as 38-membered rings enclosed by four Ag(I) atoms, two coordinated oxygen atoms, and two **1** ligands. The crystallographic dimensions of the rings are 20 × 4 Å. In addition, these double chains are cross-linked into a two-dimensional sheet onto the crystallographic [011] plane (the shortest $d_{Ag(1)···Ag(1)}$ = 7.17(6) Å) by one set of complementary binary O−H···O (O(3)−H(3A)···O(6): O(3)···O(6) = 2.835(5) Å and O(3)−H(3A)···O(6) = 164.1°) and O(3)−H(3B)···O(9): O(3)···O(9) = 2.984(5) Å and O(3)−H(3B)···O(9) = 174.4°)) hydrogen bonds (Figure 4) involving one coordinated water molecule on the Ag(1) center and two SO_3CF_3^− counterions between chains. The

$[Ag_2(C_{33}H_{26}N_2O_2)(H_2O)_2(SO_3CF_3)_2]\cdot 0.5C_6H_6$

Figure 5. Extended 2-D framework of **2**. Top: View down the *a* axis perpendicular to two adjacent stacked layers, with the benzene molecules of crystallization highlighted. The unit cell is indicated. Bottom: View down the *c* axis parallel to two layers. The individual undulating layers are emphasized with the dashed curves. Hydrogen bonds between layers are shown as the thinner dark lines.

two-dimensional network has remarkably large cavities (Figure 5) (effective cross section of ca. 21 × 15 Å),[10] in which the benzene guest molecules are located.

To date, a number of Ag(I)-containing coordination polymers have been successfully generated from silver salts and various types of rigid and flexible organic spacers based on Ag−heteroatom[1] or Ag−π interactions,[3] respectively. To our knowledge, compound **2** reported herein represents the first example of a Ag-containing polymeric compound based on an organic ligand that can afford both aromatic carbon and heteroatoms as coordinating sites. A related example is the coordination of the rigid tridentate 1,3,5-tris(4-cyano-phenylethynyl)benzene ligand with AgOTf in benzene that led to the open-framework material [Ag(OTf)(1,3,5-tris(4-

cyanophenylethynyl)benzene)·2C$_6$H$_6$]. This framework contains 15 Å honeycomblike channels and can reversibly absorb and desorb benzene guest molecules.[1d] Similar channel dimensions are found in **2,** which, however, differ in their shape (parallelogram-like in **2**, Figure 5) due to the different geometry of the ligand. Furthermore, no Ag−C interactions serve as scaffolding in the framework of [Ag-(OTf)(1,3,5-tris(4-cyanophenylethynyl)benzene)·2C$_6$H$_6$] although four substituted phenyl groups and also three electron-rich −C≡C− groups are present in the 1,3,5-tris(4-cyanophenylethynyl)benzene ligand.

(10) The cavity dimensions described here are crystallographic scalar quantities and do not take into account the van der Waals radii of the atoms defining the cavity.
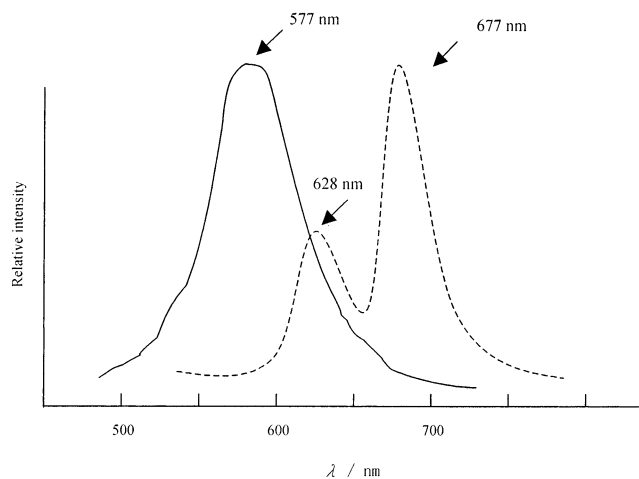
Figure 6. Photoinduced emission spectrum of **1** (dashed line) and **2** (solid line) in the solid state at room temperature.

Thermal Analysis. Compound **2** is air-stable and is insoluble in water or common organic solvents except CH$_3$CN. Thermogravimetric analysis (TGA) shows that a first weight loss of 6.98% occurs from 80 to 190 °C, which corresponds to the loss of the benzene guest molecule and two coordinated water molecules (calculated 6.98%). On further heating, another weight loss is observed between 200 and 478 °C, corresponding to the loss of ligand **1** (obsd, 43.98%; calcd, 45.04%).

Luminescent Properties of 1 and 2. Aromatic organic molecules, all-organic polymers, and mixed inorganic—organic hybrid coordination polymers have been investigated for fluorescence properties and for potential applications as light-emitting diodes (LEDs).[12] Owing to the higher thermal stability of inorganic—organic coordination polymers and the ability of affecting the emission wavelength of organic materials, syntheses of inorganic—organic coordination polymers by the judicious choice of organic spacers and transition metal centers can be an efficient method for obtaining new types of electroluminescent materials.[13] The luminescent properties of both compounds **1** and **2** were investigated in the solid state. The fluorescence spectrum of compound **1** is shown in Figure 6 and exhibits two emission maxima at 628 and 677 nm. The emission spectrum of **2**, also shown in Figure 6, is blue-shifted to 577 nm; however, no enhancement of the fluorescence intensity is realized. The

emission color of the free compound **1** was significantly affected by its incorporation into the Ag-containing polymeric compound **2**, as evidenced by the large shift in the emission. In general, Ag(I) complexes might emit weak photoluminescence at low temperature, and consequently, compound **2** reported herein represents an unusual example of a room-temperature luminescent Ag-containing polymeric compound.[14]

Conclusions. A new fulvene-type ligand **1** was synthesized by an aroylation reaction of cyclohexyl-substituted cyclopentadienyl anions. The coordination chemistry of **1** was investigated, and it was demonstrated that the new ligand can be used as a bidentate, chelating ligand for coordinating metal ions, such as Ag(I), into a coordination polymer. In the solid state, compounds **1** and **2** are luminescent. A large blue-shift in the emission was observed between the free ligand **1** and the one incorporated into complex **2**. We are currently extending this result by preparing additional fulvene-type ligands of this kind 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.

Note Added in Proof. While we were revising this manuscript, a paper by Reger et al. appeared (*Inorg. Chem. Commun.* **2002**, *5*, 278) that describes a coordination polymer containing both silver—carbon and silver—heteroatom interactions.

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