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# Novel CpAg(I)-Containing Organometallic Coordination Polymers Generated from Fulvene Ligands

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Two new fulvene ligands, **L1** and **L2**, have been synthesized by an aroylation reaction of the cyclopentadienyl anion. The coordination chemistry of **L1** and **L2** was investigated. Two novel CpAg(I)-containing polymeric compounds, **1** ($[Ag_4(\mathbf{L1})_2(\mu\text{-}H_2O)_2(SO_3CF_3)_4]\cdot(\mu\text{-bis-}\eta^1\text{-}C_6H_6))\cdot H_2O$) and **2** ($[Ag_2(\mathbf{L2})(H_2O)(SO_3CF_3)_2]\cdot 0.5(C_6H_6)$)), have been synthesized. Compounds **1** and **2** have been fully characterized by infrared spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The solid state structure of **1** features a macro-ring-containing one-dimensional chain motif. The solid state structure of **2** features a one-dimensional double-chain motif. These double chains are further cross-linked to each other via $CpAg(SO_3CF_3)_2$-AgCp (Ag···Ag contact of 4.215(15) Å) linkage into a novel 2-D network with large cavities (effective cross-section of ca. 21 × 9 Å), in which the benzene guest molecules are located.

## Introduction

The construction of new polymeric materials through the rational combination of organic ligands and metal ions is an area of intense current interest.[1−4] These materials not only exhibit encouraging potential applications[5−8] but also generate new insights into structural diversity. In this context, metal−heteroatom (such as N) and metal−carbon interactions could be considered as the two most important interactions in the construction of supramolecular architectures. Rigid organic bidentate ligands containing pyridine rings separated by various spacers such as 4,4′-bipyridine, 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethyne, 1,4-bis(3-pyridyl)-2,3-diaza-1,3-butadiene, and 2,5-bis(3-pyridyl)-3,4-diaza-2,4-hexadiene have been used by us[9] and by many other research groups[10] in recent years and have resulted in a number of inorganic coordination polymers exhibiting a rich variety of structural motifs. At the same time, smaller aromatic and polycyclic aromatic

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(1) (a) Iwamoto, T. In *Inclusion Compounds: Inorganic and Physical Aspects of Inclusion*; Iwamoto, T., Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford University Press: Oxford, 1991; Vol. 5, Chapter 6, p 177. (b) Robson, R.; Abrahms, B. F.; Batten, S. R.; Gable, R. W.; Hoskin, B. F.; Liu, F. In *Supramolecular Architecture*; Bein, T., Ed.; American Chemical Society: Washington, DC, 1992; p 256. (c) Constable, E. C. *Prog. Inorg. Chem.* **1994**, *42*, 67. (d) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997**, *36*, 2960. (e) Dunbar, K. R.; Heintz, K. R. *Prog Inorg. Chem.* **1996**, 283. (f) Whiteford, J. A.; Rachlin, E. M.; Stang, P. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2524. (g) Gardner, G. B.; Venkataraman, D.; Moore, J. S.; Lee, S. *Nature* **1995**, *374*, 792. (h) Barton, T. J.; Bull, L. M.; Klemperer, W. G.; Loy, D. A.; McEnaney, B.; Misono, M.; Monson, P. A.; Pez, G.; Scherer, G. W.; Vartuli, J. C.; Yaghi, O. M. *Chem. Mater.* **1999**, *11*, 2633.

(2) (a) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703. (b) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401. (c) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096. (d) Fujita, M.; Oka, H.; Yamaguchi, K.; Ogura, K. *Nature* **1995**, *378*, 469. (e) Fujita, M.; Kwon, Y, J.; Sasaki, O.; Yamaguchi, K.; Ogura, K. *J. Am. Chem. Soc.* **1995**, *117*, 7287. (f) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779. (g) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *Chem. Commun.* **1998**, 595.

(3) (a) Heintz, R. A.; Zhao, H.; Ouyang, X.; Grandinetti, G.; Cowen, J.; Dumbar, K. R. *Inorg. Chem.* **1999**, *38*, 144. (b) Choi, H. J.; Suh, M. P. *J. Am. Chem. Soc.* **1998**, *120*, 10622. (c) Sharma, C. V. K.; Broker, G. A.; Huddleston, J. G.; Baldwin, J. W.; Metzger, R. M.; Rogers, R. D. *J. Am. Chem. Soc.* **1999**, *121*, 1137.

(4) (a) Kobel, W.; Hanack, M. *Inorg. Chem.* **1986**, *25*, 103. (b) Kato, R.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **1989**, *111*, 5224. (c) Sinzger, K.; Hünig, S.; Jopp, M.; Bauer, D.; Bietsch, W.; von Schütz, J. U.; Wolf, H. C.; Kremer, R. K.; Metzenthin, T.; Bau, R.; Khan, S. I.; Lindaum, A.; Lengauer, C. L.; Tillmanns, E. *J. Am. Chem. Soc.* **1993**, *115*, 7696. (d) Erk, P.; Gross, H.-J.; Hünig, U. L.; Meixner, H.; Werner, H.-P.; von Schütz, J. U.; Wolf, H. C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1245. (e) Jung, O.; Pierpont, C. G. *J. Am. Chem. Soc.* **1994**, *116*, 2229. (f) Patoux, C.; Loudret, C.; Launay, L. P.; Joachim, C.; Gourdon, A. *Inorg. Chem.* **1997**, *36*, 5037.

(5) (a) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981. (b) Kobayashi, H.; Tomita, H.; Naito, T.; Kobayashi, A.; Sakai, F.; Watanabe, T.; Cassoux, P. *J. Am. Chem. Soc.* **1996**, *118*, 368.

(6) (a) Sato, O.; Iyoda, T.; Fujishima, A.; Hashimoto, K. *Science* **1996**, *271*, 49. (b) Day, P. *Science* **1993**, *261*, 431. (c) Whiteside, G. M.; Mathias, J. P.; Seto, C. T. *Science* **1991**, *254*, 1312.

(7) (a) Bruce, D. W. *J. Chem. Soc., Dalton Trans.* **1993**, 2983. (b) Simon, J.; Engel, M. K.; Soulie, C. *New J. Chem.* **1992**, *16*, 287.

(8) Dagani, R. *Chem. Eng. News* **1991**, May 27, 24.

(9) (a) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Angew. Chem., Int. Ed.* **2000**, *39*, 4271. (b) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2000**, *39*, 4927. (c) Dong, Y.-B.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2000**, *39*, 1943. (d) Dong, Y.-B.; Smith, M. D.; Layland, R. C.; zur Loye, H.-C. *Chem. Mater.* **2000**, *12*, 1156. (e) Dong, Y.-B.; Cheng, J.-Y.; Huang, R.-Q.; Tang, B.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 5699. (f) Dong, Y.-B.; Cheng, J.-Y.; Wang, H.-Y.; Huang, R.-Q.; Tang, B.; Smith, M. D.; zur Loye, H.-C. *Chem. Mater.* **2003**, *15*, 2593.

(10) (a) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem.* **1999**, *111*, 2798; *Angew. Chem., Int. Ed.* **1999**, *38*, 2638. (b) Blake, A. J.; Champness, N. R.; Hubberstey, P.; Li, W.-S.; Withersby, M. A.; Schröder, M. *Coord. Chem. Rev.* **1999**, *183*, 117, and references therein.

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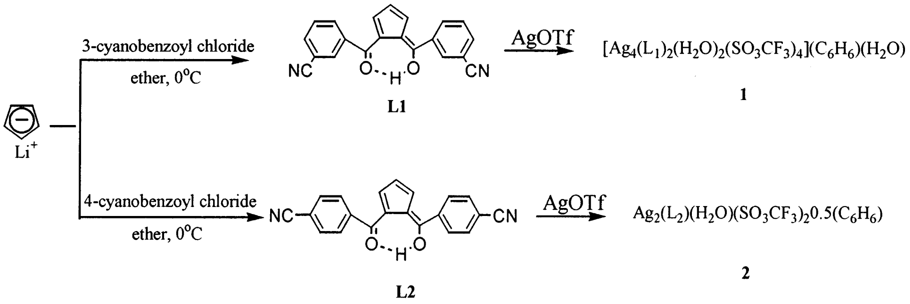
**Scheme 1. Synthesis of Ligands L1/L2 and Organometallic Coordination Polymers 1/2**



hydrocarbons (PAHs), acting as electron-donor species, were shown to be capable of incorporating metal ions into organometallic polymeric systems through cation−$\pi$ interactions, as was previously demonstrated by Amma and Munakata.[11] In contrast, the chemistry of polymeric compounds generated from multidenate organic ligands that can afford both heteroatoms and carbon atoms as coordination sites has received considerably less attention.[12,13] Fulvene is one of the most important ligands in organometallic chemistry and is capable of coordinating metal ions into organometallic complexes through carbon−metal interaction. Likewise, a −CN functional group on the aromatic ring is a good candidate for coordination bonding, as has been exploited in the self-assembly of Ag-supramolecular architectures. Specifically, a series of very attractive Ag-coordination polymers based on 1,3,5-tris(4-cyanophenylethynyl)benzene,[1g] 4,4′-biphenyldicarbonitrile,[14] 3,3′-dicyanodiphenylacetylene,[15] and phenylacetylene nitriles with pendant oligo-(ethylene oxide) side chains[16] has been reported by Moore and Lee. Very recently, we designed and synthesized a series of luminescent conjugated organic ligands with both a fulvene unit and −CN functional groups,[17] such as **L1** and **L2**, by the aroylation of cyclopentadienyl anions, which were obtained from cyclopentadiene and phenyllithium (Scheme 1). This new class of organic ligands gives us the ability to synthesize 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 these ligands in the synthesis of a new Ag-containing polymeric compounds $[Ag_4(\mathbf{L1})_2(\mu\text{-}H_2O)_2(SO_3CF_3)_4]$ $(\mu\text{-bis-}\eta^1\text{-}C_6H_6)]\cdot H_2O$ (**1**) and $[Ag_2(\mathbf{L2})(H_2O)(SO_3CF_3)_2]\cdot 0.5(C_6H_6)]$ (**2**) based on both metal−carbon and metal−nitrogen coordination interactions. The results reported herein demonstrate that the use of organic spacers containing both fulvene 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.** 3-Cyanobenzoyl chloride, 4-cyanobenzoyl chloride, and PhLi were prepared according to literature methods. AgOTf and Li 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. $^1$H NMR data were collected using a JEOL FX 90Q NMR spectrometer. Chemical shifts are reported in $\delta$ relative to TMS. Element analyses were performed on a Perkin-Elmer model 240C analyzer. Thermogravimetric analysis was performed on **1** by heating the compound from 25 to 500 °C under flowing $N_2$ using a heating rate of 10 °C/min on a TA Instrument SDT 2960 simultaneous DTA-TGA.

**Synthesis of ligands.** A solution of 3- or 4-cyanobenzoyl chloride (1.77 g, 10.7 mmol) in anhydrous ether (20 mL) was added dropwise to a solution of cyclopentadiene anion (1.32 mL, 16.0 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, 3:1) to afford a yellow crystalline solid, **L1**: yield, 64%. IR (KBr pellet): $\nu$ (cm$^{-1}$) 3110(w), 2255(s), 1630(s), 1590(s), 1550(s), 1485(s), 1430(vs), 1410(s), 1365(s), 765(m), 720(m). $^1$H NMR (90 MHz, $CDCl_3$, 25 °C, TMS): $\delta$ 18.20 (s, 1H, −OH), 8.07−7.48 (m, 8H, $-C_6H_4$), 7.28−7.21, 6.58 (d, 2H; t, 1H, $C_5H_3$). Anal. Calcd for $C_{21}H_{13}O_2N_2$: C 77.78, H 4.01, N 8.64. Found: C 77.74, H 4.06, N 8.60. **L2**: yield, 50%. IR (KBr pellet cm$^{-1}$): 3110(vw), 2250(s), 1635(s), 1600(s), 1575(m), 1540(vs), 1500(m), 1475(s), 1413(vs), 1410(s), 1365(s), 845(ms). $^1$H NMR (90 MHz, $CDCl_3$, 25 °C, TMS, ppm): 18.20 (s, 1H, −OH), 7.85 (s, 8H, $-C_6H_4$), 7.25−7.20, 6.57 (d, 2H; t, 1H, $-C_5H_3$). Anal. Calcd for $C_{21}H_{13}O_2N_2$: C 77.78, H 4.01, N 8.64. Found: C 77.80, H 4.00, N 8.66.

**Synthesis of Coordination Polymers.** A solution of $AgSO_3CF_3$ (9 mg, 0.035 mmol) in benzene (2 mL) was added to a solution of ligand **L1** or **L2** (11 mg, 0.034 mmol) in 10 mL

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(11) (a) Munakata, M.; Wu, L. P.; Ning, G. L. *Coord. Chem. Rev.* **2000**, *198*, 171. (b) Rodesiler, P. F.; Amma, E. L. *Inorg. Chem.* **1972**, *11*, 388. (c) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 743. (d) Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1974**, *96*, 5407. (e) Turner, R. W.; Amma, E. L. *J. Am. Chem. Soc.* **1966**, *88*, 3243. (f) Barnes, J. C.; Blyth, C. S. *Inorg. Chim. Acta* **1985**, *98*, 181. (g) Rundle, R. E.; Goring, J. H. *J. Am. Chem. Soc.* **1950**, *72*, 5337. (h) Smith, H. G.; Rundle, R. E. *J. Am. Chem. Soc.* **1958**, *80*, 5075. (i) Schmidbaur, H.; Bublak, W.; Huber, B.; Reber, G.; Muller, G. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1089. (j) Rodesiler, P. F.; Griffith, E. A. H.; Amma, E. L. *J. Am. Chem. Soc.* **1972**, *94*, 761. (k) Ning, G. L.; Wu, L. P.; Sugimoto, K.; Munakata, M.; Kuroda-Sowa, T.; Mackawa, M. J. *Chem. Soc., Dalton Trans.* **1999**, 2529. (l) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Ning, G. L.; Kojima, T. *J. Am. Chem. Soc.* **1998**, *120*, 8610.

(12) An attractive group of bimetallic coordination polymers based on Pd−C≡N and Cu−N≡C interactions and also Ag-containing coordination polymers including Ag−C≡N and Ag−N≡C interactions were reported by Prof. A. Mayr: (a) Mayr, A.; Guo, J. *Inorg. Chem.* **1999**, *38*, 921. (b) Mayr, A.; Mao, Li, F. *Inorg. Chem.* **1998**, *37*, 5776. (c) Mao, L. F.; Mayr, A. *Inorg. Chem.* **1996**, *35*, 3183.

(13) Reger, D. L.; Semeniuc, R. F.; Smith, M. D. *Inorg. Chem. Commun.* **2002**, *5*, 278.

(14) (a) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Chem. Eur. J.* **1997**, *3*, 765. (b) Venkataraman, D.; Lee, S.; Moore, J. S.; Zhang, P.; Hirsch, K. A.; Gender, G. B.; Covey, A. C.; Prentice, C. L. *Chem. Mater.* **1996**, *8*, 2030.

(15) Hirsch, K. A.; Wilson, S. R.; Moore, J. S. *Inorg. Chem.* **1997**, *36*, 2960.

(16) Xu, Z. T.; Kiang, Y.-H.; Lee, S.; Lobkovsky, E. B.; Emmott, N. *J. Am. Chem. Soc.* **2000**, *122*, 8376.

(17) Dong, Y.-B.; Jin, G.-X.; Smith, M. D.; Huang, R.-Q.; Tong, B.; zur Loye, H.-C. *Inorg. Chem.* **2002**, *41*, 4909.

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

| | **1** | **2** |
|---|---|---|
| formula | $C_{52}H_{36}Ag_4F_{12}N_4O_{19}S_4$ | $C_{26}H_{17}Ag_2F_6N_2O_9S_2$ |
| fw | 1808.57 | 895.28 |
| cryst syst | monoclinic | monoclinic |
| space group | *C*2/*c* | *C*2/*c* |
| *a* (Å) | 18.6999(10) | 20.287(16) |
| *b* (Å) | 15.4499(8) | 21.059(16) |
| *c* (Å) | 21.6929(11) | 14.585(12) |
| α (deg) | 90 | 90 |
| β (deg) | 93.8040(10) | 100.719(14) |
| γ (deg) | 90 | 90 |
| *V* (Å$^3$) | 6253.5(6) | 6122(8) |
| *Z* | 4 | 8 |
| $\rho_{calc}$ (g/cm$^3$) | 1.921 | 1.943 |
| $\mu$(Mo Kα) (mm$^{-1}$) | 1.478 | 1.478 |
| temperature (K) | 190(2) | 298(2) |
| no. of reflns | 5556 | 6256 |
| R1; wR2 indices ($I > 2\sigma(I)$)[a] | 0.0486, 0.1298 | 0.0475, 0.0849 |

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

of methylene chloride. After about 0.5 h of stirring at room temperature, the resultant bright yellow solution was introduced into a 7 mm diameter tube and layered with hexane (5 mL) as a diffusion solvent. After standing at room temperature for one month, light orange crystals appeared. **1**: yield 69%. IR (KBr pellet): $\nu$ (cm$^{-1}$) 3500(s, br), 3100(w), 2300(m), 2275(m), 2250(s), 1620(s), 1595(s), 1555(s), 1489(w), 1430(s), 1415(s), 1280(vs), 1250(vs), 1235(vs), 1170(s), 1045(s), 765(m), 723(s). Anal. Calcd for $Ag_4C_{52}H_{36}O_{19}N_4F_{12}S_4$: C 34.50, H 1.99, N 3.10. Found: C 34.50, H 2.00, N 3.12. **2**: yield 58%. IR (KBr pellet): $\nu$ (cm$^{-1}$) 3500(s, br), 3115(w), 2280(m), 2250(m), 1620(s), 1578(s), 1540(s), 1480(w), 1418(s), 1280(vs), 1255(vs), 1175(s), 1038(s), 850(s) 770(m), 742(s). Anal. Calcd for $C_{26}H_{17}Ag_2F_6N_2O_9S_2$: C 34.85, H 1.98, N 3.26. Found: C 34.87, H 1.97, N 3.22.

**Single-Crystal Structure Determination.** A suitable single crystal of **1** or **2** was selected and mounted onto the end of a thin glass fiber using an inert oil. X-ray intensity data covering the full sphere of reciprocal space were measured on a Bruker SMART APEX CCD-based diffractometer system (Mo Kα radiation, $\lambda = 0.71073$ Å) for **1** and measured on a Bruker Smart-1000 CCD and Bruker SMART APEX CCD-based diffractometer system (Mo Kα radiation, $\lambda = 0.71073$ Å) for **2**, respectively.[18] The raw frame data for **1** and **2** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[18] Corrections for incident and diffracted beam absorption effects were applied to **1** and **2** using SADABS.[18] No significant crystal decay was observed during data collection. The structure was solved by direct methods and refined by full-matrix least squares against $F^2$ using all data, with the SHELXTL software package.[18] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were calculated and refined as riding atoms. 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.

## Results and Discussion

**Synthesis of Ligands.** Ligands **L1** and **L2** were prepared in moderate yield as bright yellow crystalline solids by the reaction of 3-cyanobenzoyl chloride and 4-cyanobenzoyl chloride with the cyclopentadienyl anion (Scheme 1), respectively. The structures of **L1** and **L2** were fully determined by $^1$H NMR, IR, and elemental analysis. The IR spectrum of **L1** and **L2** showed a −CN absorption band at 2225 cm$^{-1}$ and 2250 cm$^{-1}$, respectively, and did not show absorption above 1630 cm$^{-1}$ in the region normally assigned to organic carbonyl groups. However, the strong absorption bands at 1630 cm$^{-1}$ for **L1** and 1635 cm$^{-1}$ for **L2** are consistent with the hydrogen-bonded enol structure.[19] In the $^1$H NMR spectrum, for both **L1** and **L2** the proton resonances were observed at 18.20 ppm as a singlet, which was attributed to the chelated proton, which is hydrogen bonded to the carbonyl next to the 1-aroyl group. Consequently, we believe that compounds **L1** and **L2** exist in the form of a fulvene,[19] which is one of the most important constructing units in organometallic chemistry. To date, rigid bidentate or tridentate ligands containing benzonitrile groups, such as 4,4′-dicyanobiphenyl, 1,3,5-tris(4-cyanophenylethynyl)benzene, as well as others, are excellent bridging ligands to construct porous frameworks.[1d,14−16] However, to our knowledge, no supramolecular architectures based on both fulvene−metal and heteroatom−metal interactions have been reported. Compounds **1** and **2** can be classified as a new type of ligand that could be used for the construction of polymeric compounds containing both inorganic and organometallic moieties.

**Synthesis and Structural Analysis of 1.** The coordination chemistry of **L1** was investigated. Reaction of **L1** with AgOTf (1:2 ratio) in a benzene/$CH_2Cl_2$ mixed solvent system at room temperature afforded **1** ($[Ag_4(\mathbf{L1})_2(\mu\text{-}H_2O)_2(SO_3CF_3)_4]\cdot(\mu\text{-bis-}\eta^1\text{-}C_6H_6))\cdot H_2O$) as orange crystals in 69% yield (Scheme 1). The IR spectrum of **1** showed a −CN absorption band split into three peaks at 2250, 2275, and 2300 cm$^{-1}$. The single-crystal structure analysis revealed, as shown in Figure 1, that there are two crystallographically distinct Ag(I) centers in **1**. The first kind of Ag(1) center is located in a $\{AgN_2OC\}$ (Ag(1)−N(2)#1 = 2.190(5), Ag(1)−N(1) = 2.200(4), Ag(1)−C(32) = 2.528(5), Ag(1)−O(21A) = 2.587(13) Å) organometallic peudotetrahedral coordination sphere, which consists of two N-donors from two −CN groups on two ligands **L1**, one O-donor from one triflate counterion and one carbon atom from a benzene solvent molecule. For the Ag(1) center, the shortest Ag−C distance (Ag(1)−C(32)) is 2.528(5) Å, while the remaining Ag−C contacts are greater than 2.85 Å, which is beyond the limits (2.47−2.76 Å) commonly observed in Ag(I)-aromatic complexes.[11] Thus, the benzene ring in **1** coordinates to the Ag(I) ion with an $\eta^1$ instead of an $\eta^2$ bonding mode, which is normally observed in arene-metal complexes.[11] The second Ag(2) center also lies in a pseudotetrahedral coordination environment comprised by two water (presumably coming from the air or solvent system) oxygen atoms, one triflate oxygen donor, and one carbon−carbon $\pi$ bond from a cyclopentadienyl unit (Ag(2A)−O(31A)#1 = 2.206(8), Ag(2A)−O(31A) = 2.538(7), Ag(2A)−O(11) = 2.490(5), Ag(2A)−C(1) = 2.423(5), and Ag(2A)−C(2) = 2.616(5) Å). It is worth pointing out that the Ag(2) center coordinates to the Cp ring with an $\eta^2$ bonding mode. The bond distances between two Cp-carbon atoms and the Ag(2) center are slightly different, but they all lie in the range 2.47−2.76 Å, commonly observed in Ag(I)−$\pi$ com-

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[18] (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.

[19] William, J. L.; William, H. S. *J. Am. Chem. Soc.* **1957**, *79*, 4970.

**Table 2. Interatomic Distances (Å) and Bond Angles (deg) (with esds in parentheses) for 1**

| | | | |
|---|---|---|---|
| Ag(1)−N(2)#1 | 2.190(5) | Ag(1)−N(1) | 2.200(4) |
| Ag(1)−C(32) | 2.528(5) | Ag(1)−O(21A) | 2.587(13) |
| Ag(2A)−O(31A)#1 | 2.206(8) | Ag(2A)−C(1) | 2.423(5) |
| Ag(2A)−O(11) | 2.490(5) | Ag(2A)−O(31B) | 2.52(3) |
| Ag(2A)−O(31A) | 2.538(7) | Ag(2A)−C(2) | 2.616(5) |
| Ag(2A)−Ag(2A)#1 | 3.3574(15) | Ag(2B)−O(31A) | 1.988(7) |
| Ag(2B)−C(1) | 2.290(5) | Ag(2B)−C(5) | 2.460(5) |
| N(2)#1−Ag(l)−N(1) | 129.06(17) | N(2)#1−Ag(1)−C(32) | 113.18(19) |
| N(1)−Ag(1)−C(32) | 98.5(2) | N(2)#1−Ag(1)−O(21A) | 78.1(2) |
| N(1)−Ag(1)−O(21A) | 112.5(3) | C(32)−Ag(1)−O(21A) | 128.4(3) |
| O(31A)#1−Ag(2A)−C(1) | 116.0(2) | O(31A)#I−Ag(2A)−O(11) | 90.4(2) |
| C(1)−Ag(2A)−O(11) | 121.34(15) | 0(31A)#1−Ag(2A)−O(3 IB) | 61.6(4) |
| C(l1)−Ag(2A)−O(31B) | 161.0(6) | O(11)−Ag(2A)−O(31B) | 77.6(7) |
| O(31A)#1−Ag(2A)−O(31A) | 89.9(2) | C(1)−Ag(2A)−O(31A) | 104.5(2) |
| O(11)−Ag(2A)−O(31A) | 128.22(19) | O(31B)−Ag(2A)−O(31A) | 57.6(5) |
| O(31A)#1−Ag(2A)−C(2) | 104.3(2) | C(1)−Ag(2A)−C(2) | 31.61(14) |
| O(11)−Ag(2A)−C(2) | 93.97(15) | O(31B)−Ag(2A)−C(2) | 163.12(17) |
| O(31A)−Ag(2A)−C(2) | 135.7(2) | O(31A)#1−Ag(2A)−Ag(2A)#1 | 49.11(18) |
| C(1)−Ag(2A)−Ag(2A)#1 | 114.57(10) | O(11)−Ag(2A)−Ag(2A)#1 | 121.65(13) |
| O(31B)−Ag(2A)−Ag(2A)#1 | 48.3(7) | O(31A)−Ag(2A)−Ag(2A)#1 | 41.09(18) |
| C(2)−Ag(2A)−Ag(2A)#1 | 130.94(10) | O(31A)−Ag(2B)−C(1) | 133.0(3) |
| O(31A)−Ag(2B)−C(5) | 136.0(3) | C(1)−Ag(2B)−C(5) | 33.96(15) |
| C(2)−C(1)−C(5) | 108.9(4) | C(2)−C(1)−Ag(2B) | 104.0(3) |
| C(5)−C(1)−Ag(2B) | 79.7(3) | C(2)−C(1)−Ag(2A) | 81.9(3) |
| C(5)−C(1)−Ag(2A) | 95.8(3) | Ag(2B)−C(1)−Ag(2A) | 24.10(10) |
| C(1)−C(2)−Ag(2A) | 66.5(3) | C(3)−C(2)−Ag(2A) | 100.0(3) |

**Table 3. Interatomic Distances (Å) and Bond Angles (deg) (with esds in parentheses) for 2**

| | | | |
|---|---|---|---|
| Ag(1)−N(1) | 2.155(6) | Ag(l)−N(2)#1 | 2.168(7) |
| Ag(1)−O(3) | 2.536(7) | Ag(2)−O(4) | 2.290(7) |
| Ag(2)−O(4) | 2.290(7) | Ag(2)−O(7) | 2.361(8) |
| Ag(2)−C(4) | 2.414(8) | Ag(2)−O(6)#2 | 2.534(11) |
| Ag(2)−C(3) | 2.590(7) | | |
| N(1)−Ag(1)−N(2)#1 | 167.1(3) | N(1)−Ag(1)−O(3) | 98.7(2) |
| N(2)#I−Ag(1)−O(3) | 93.3(2) | O(4)−Ag(2)−O(7) | 109.4(4) |
| O(4)−Ag(2)−C(4) | 114.9(3) | O(7)−Ag(2)−C(4) | 113.2(3) |
| O(4)−Ag(2)−O(6)#2 | 110.6(4) | O(7)−Ag(2)−O(6)#2 | 86.3(3) |
| C(4)−Ag(2)−O(6)#2 | 118.9(4) | O(4)−Ag(2)−C(3) | 146.6(3) |
| O(7)−Ag(2)−C(3) | 93.9(3) | C(4)−Ag(2)−C(3) | 31.8(2) |
| O(6)#2−Ag(2)−C(3) | 94.1(4) | C(14)−N(1)−Ag(1) | 172.8(6) |

plexes.[11] It is noteworthy that the Ag(2) center is disordered over two crystallographically split positions with two Ag(2) sites separated by 0.99 Å and the relative occupancies of Ag2A/Ag2B refined (constrained to sum to unity) to 0.622/0.378, respectively. In addition, the Ag(2) site is bonded to a water molecule, which, probably due to the Ag(2) disorder, is itself disordered over two crystallographically unique sites (O(31A) and O31(B)), with site occupation factors 0.924 and 0.076, respectively. The two Ag(2) centers are bridged by the coordinated water molecule (O(31)) and generate a $Ag_2O_2$ cluster core with a Ag···Ag contact of 3.3574(15) Å. Taken all together, almost every type of bonding mode could be found in **1**, including coordination, covalent, and hydrogen bonding modes. The generality of this synthetic approach by combining noncovalent and covalent driving forces suggests that a range of structures with different sizes, morphologies, structural components, and functions could be produced with appropriate modifications.

In the solid state, every two "U-shaped" ligands bind two Ag(1) centers through four terminal −CN functional groups into a large supramolecular Ag-containing ring, which is bridged by a $Cp_2Ag_2O_2$ linkage in the middle. The dihedral angle between two Cp-rings is around 120°, and therefore this linkage exists in a form of bent metallocene. The silver−oxygen cluster core is located between two substituted Cp ligands instead of a simple metal ion commonly observed in many other organometallic metallocene compounds. For each ligand in the ring, the dihedral angle between the Cp-ring and the plane in which two $-C_6H_4-$CN-m lie is around 40°. The shortest distance crossing the ring (C(1)···C(1)*) is 5.43(4) Å, and the Ag(1)···Ag(1) distance is 13.12(4) Å. It is really unexpected that these supramolecular rings are further connected to each other by benzene solvent molecules with $\eta^1$-coordination bonding through two carbon atoms on *meso*-positions into a novel macro-ring containing one-dimensional chains along the crystallographic *a* axis (Figure 2). As shown in Figure 2, the coordinated benzene plane is approximately perpendicular to the boatlike supramolecular units. Thus the benzene solvent molecules herein play a central role in the assembly of the supramolecule's structural components into a polymeric structure.

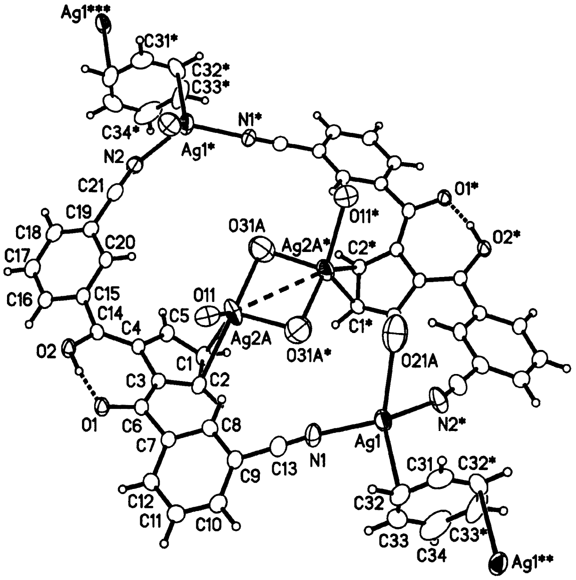

**Figure 1.** ORTEP view of **1** with 25% thermal ellipsoids (only coordinated oxygen atoms of triflate anions shown).

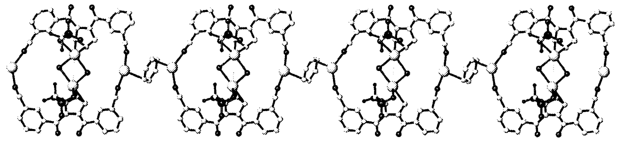

**Figure 2.** 1-D organometallic chain in **1**, viewed down the crystallographic *b* axis.

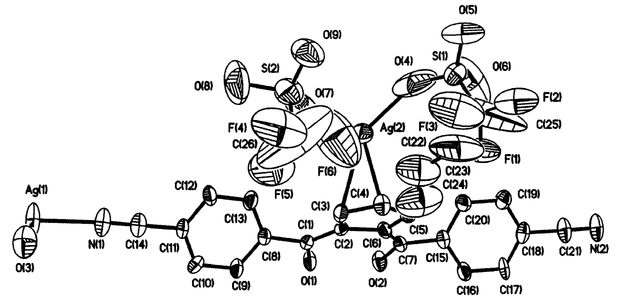

**Figure 3.** ORTEP view of **2** with 25% thermal ellipsoids.

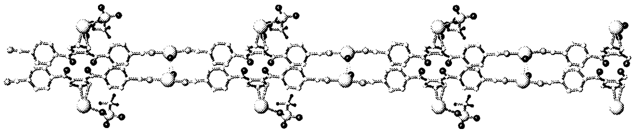

**Figure 4.** One-dimensional double-chain motif in **2**.

Compound **1** is air-stable and is insoluble in water or common organic solvents. Thermogravimetric analysis (TGA) shows that a first weight loss of 1.04% occurs from 55 to 100 °C, which corresponds to the loss of one of the three water molecules (calculated 1.00%). On further heating, another weight loss is observed between 110 and 230 °C, corresponding to the loss of the remaining two water molecules (observed 2.03%, calculated 2.00%). A drastic weight loss was observed between 260 and 475 °C, corresponding to the loss of two ligands **L1** (observed 35.50%, calculated 35.83%).

**Synthesis and Structural Analysis of 2.** To confirm the universality of the above novel reaction, we investigated the effect of the different orientation of coordination donors for polymeric patterns. **L2** was used instead of **L1** to carry out the same reaction under the same reaction conditions. Reaction of **L2** with AgOTf (1:2 ratio) in a benzene/$CH_2Cl_2$ mixed solvent system at room temperature afforded **2** ($[Ag_2(\mathbf{L2})(H_2O)(SO_3CF_3)_2]\cdot 0.5(C_6H_6)$) as orange crystals in 58% yield (Scheme 1). As shown in Figure 3, there are two crystallographically distinct Ag(I) centers in **2**. The first kind of Ag(1) center lies in a $\{AgN_2O_2\}$ distorted tetrahedral coordination sphere, which is comprised of two N-donors from two −CN groups and two O-donors from two coordinated water molecules (presumbly coming from the air or solvent system). In the solid state, the Ag(1) centers are connected by **L2** through the two terminal −CN groups into a mild zigzag one-dimensional chain along the crystallographic [010] direction. The second kind of Ag(2) center adopts a $\{AgO_2C_2\}$ organometallic pseudotetrahedral coordination sphere, which consists of two O-donors from two triflate counterions, one carbon−carbon $\pi$ bond from the cyclopentadienyl unit (Ag(1)−C(4) = 2.414(8) and Ag(1)−C(3) = 2.590(7) Å). As shown in Figure 4, two single chains are 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 $Ag_4O_4(\mathbf{L2})_2$ units, which can be viewed as 38-membered rings enclosed by four Ag(I) atoms, two coordinated oxygen atoms, and two **L2** ligands. The crystallographic dimensions of the rings are 20 × 4 Å. It is interesting that these double chains are further linked by $CpAg(SO_3CF_3)_2AgCp$ (Ag···Ag contact of 4.215(15) Å) linkage into a novel 2-D network with large cavities (Figure 5) (effective cross-section of ca. 21 × 9 Å), in which the benzene guest molecules are located. Crystals of **2** lose solvent molecules and turn opaque within several minutes under ambient atmosphere.

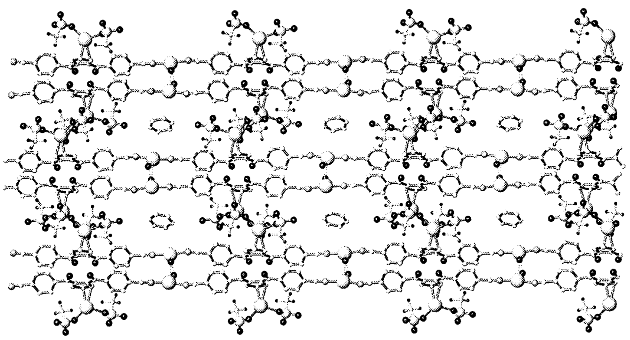

**Figure 5.** Two-dimensional network in **2**.

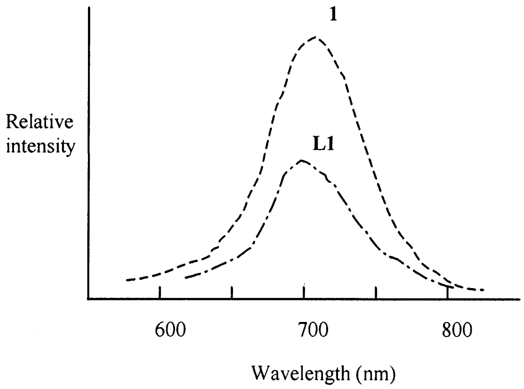

**Figure 6.** Photoinduced emission spectrum of **L1** and **1** in the solid state.

In both compounds **1** and **2**, almost every type of bonding mode could be found, including coordination and covalent bonding modes. 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−$\pi$ interactions,[8] respectively. To our knowledge, compounds **1** and **2** represent the first example of a CpAg(I)-containing polymeric compound based on the organic fulvene ligand that can afford both aromatic carbon and heteroatoms as coordinating sites. The results reported herein demonstrate that the use of organic spacers containing both aromatic and heteroatom functional groups as precursors incorporating metal−ligand interactions is a new approach for the generation of novel supramolecular frameworks. Studies toward the preparation of new ligands of this type and also the investigation of their organometallic coordination polymers are underway.

**Luminescent Properties of L1 and 1.** To investigate the influence of the structural environment on the fluorescent properties of ligand **L1**,[20] the emission properties of compounds **L1** and **1** were measured in the solid state at room temperature. The fluorescence of compound **L1** is shown in Figure 6 and exhibits an emission maximum at 710 nm. The emission of **1**, as shown in Figure 6, is red-shifted to 715 nm, with an obvious enhancement to the fluorescent intensity. The emission wavelength of the free ligand **L1** was only slightly affected by incorporation into the Ag-containing polymeric compound **1**.

## Conclusions

The results reported herein demonstrate that the use of organic spacers containing both aromatic and heteroatom functional groups as precursors incorporating metal−ligand interactions is a new approach for the generation of novel supramolecular frameworks with potentially novel physical properties. Studies toward the preparation of new organometallic ligands of this type and also the investigation of their coordination chemistry are underway.

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**Supporting Information Available:** This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) (a) Altmann, M.; Bunz, U. H. F. *Angew. Chem.* **1995**, *34*, 569. (b) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Ciurtin, D. M.; Pschirer, N. G.; Smith, M. D.; Bunz, U. H. F.; zur Loye, H.-C. *Chem. Mater.* **2001**, *13*, 2743. (c) Cariati, E.; Bu, X.; Ford, P. C. *Chem. Mater.* **2000**, *12*, 3385. (d) Würthner, F.; Sautter, A. *Chem. Commun.* **2000**, 445.