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Organometallic Silver(I) Supramolecular Complexes Generated from Multidentate Furan-Containing Symmetric and Unsymmetric Fulvene Ligands and Silver(I) Salts

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One new conjugated symmetric fulvene ligand **L1** and two new unsymmetric fulvene ligands **L2** and **L3** were synthesized. Five new supramolecular complexes, namely $Ag_2(\mathbf{L1})_3(SO_3CF_3)_3$ (**1**) (**1**, monoclinic, $P2_1/c$; $a = 12.702(3)$ Å, $b = 26.118(7)$ Å, $c = 13.998(4)$ Å, $\beta = 96.063(4)°$, $Z = 4$), $[Ag(\mathbf{L1})]ClO_4$ (**2**) (monoclinic, $C2/c$; $a = 17.363(2)$ Å, $b = 13.2794(18)$ Å, $c = 13.4884(18)$ Å, $\beta = 100.292(2)°$, $Z = 8$), $[Ag(\mathbf{L1})(C_6H_6)SbF_6]\cdot 0.5C_6H_6\cdot H_2O$ (**3**) (monoclinic, $P2_1/c$; $a = 6.8839(11)$ Å, $b = 20.242(3)$ Å, $c = 18.934(3)$ Å, $\beta = 91.994(3)°$, $Z = 4$), $Ag(\mathbf{L2})(SO_3CF_3)$ (**4**) (triclinic, $P\bar{1}$; $a = 8.629(3)$ Å, $b = 10.915(3)$ Å, $c = 11.178(3)$ Å, $\alpha = 100.978(4)°$, $\beta = 91.994(3)°$, $\gamma = 105.652(4)°$, $Z = 2$), and $Ag(\mathbf{L3})(H_2O)(SO_3CF_3)$ (**5**) (triclinic, $P\bar{1}$; $a = 8.914(5)$ Å, $b = 10.809(6)$ Å, $c = 11.283(6)$ Å, $\alpha = 69.255(8)°$, $\beta = 87.163(9)°$, $\gamma = 84.993(8)°$, $Z = 2$) were obtained through self-assembly based on these three new fulvene ligands in a benzene/toluene mixed-solvent system. Compounds **1**–**5** 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 cis- or trans-conformation to bind soft acid Ag(I) ion through not only the terminal –CN and furan functional groups but also the fulvene carbon atoms into organometallic coordination polymers or discrete complexes. In addition, the luminescent properties of **L1**–**L3** and their Ag(I) complexes were investigated preliminarily in EtOH and solid state.

Introduction

The design and synthesis of supramolecular complexes exhibiting novel structures and properties has provided exciting new prospects for the chemists.[1,2] It is no doubt that the most efficient approach to prepared supramolecular frameworks is via direct chemical combination of functional inorganic and organic components, a method which has proven quite fruitful.[3,4] Fulvene,[5] as one type of important organic ligand, was widely used in construction of organometallic complexes, for example metallocene and related complexes.[6] To date, the chemistry of supramolecular architectures based on fulvene molecules has received considerably less attention. In principle, 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 frameworks generated from conjugated symmetric fulvene ligands (II), by the aroylation of cyclopentadienyl or substituted cyclopentadi-

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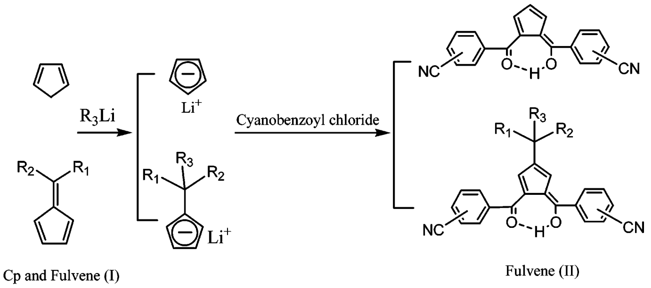
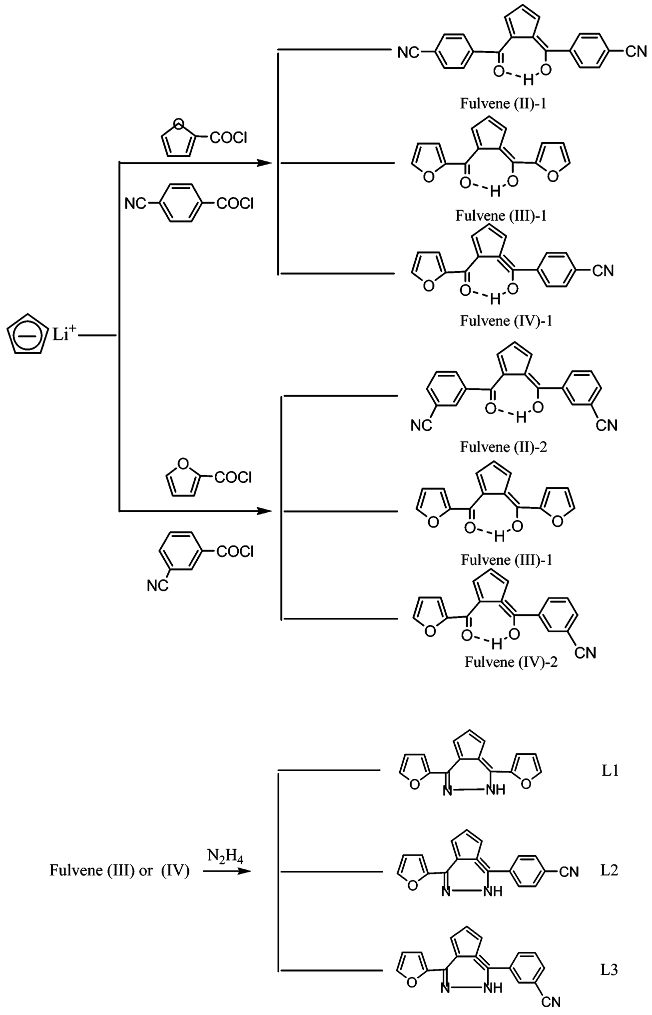
Scheme 1. Synthesis of Fulvene II



enyl anions that generated from fulvene I and R$_3$Li (R$_3$ = phenyl or substituted phenyl and methyl groups), with substituted cyanobenzoyl chloride (Scheme 1).[7] Our previous study demonstrated that this type of molecule (fulvene II) with two symmetric substituted benzonitrile arms could act as a bidentate or multidentate organic spacer to bind metal centers through both carbon−metal and heteroatom−metal coordination interactions into novel luminescent organometallic coordination polymers and supramolecular complexes.[7]

As we know, besides benzonitrile and its various derivatives, five-membered heterocyclic rings are also good candidates for constructing coordination polymers or supramolecular complexes either as terminal[8] or bridging moieties[9] due to their specific donor orientation and bridging style. The aroylation of cyclopentadienyl or substituted cyclopentadienyl anions with five-membered furoic chloride and cyanobenzoyl chloride in one pot would introduce benzonitrile and five-membered heterocyclic moieties into one molecule in a single step, which is our synthetic approach to access to unsymmetric fulvene ligands of this type. In principle, such one-pot reaction could generate three kinds of organic spacers, i.e., common symmetric ligand fulvenes II and III and an unusual unsymmetric ligand fulvene IV (Scheme 2). It is well-known that coordination chemistry based on symmetric organic ligands has been the main theme in the self-assembly field.[1,2] In contrast, the chemistry of supramolecular architectures based on unsymmetric organic

Scheme 2. Synthesis of Fulvenes II−IV and **L1**−**L3**



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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 coordinated styles around the metal centers. In this contribution, we present one new symmetric five-membered furan ring-containing fulvene ligand **L1**, two new unsymmetric furan- and benzonitrile-containing fulvene ligands **L2** and **L3**, and five new organometallic Ag(I)-containing supramolecular complexes, namely $Ag_2(\mathbf{L1})_3(SO_3CF_3)_3$ (**1**), $[Ag(\mathbf{L1})]ClO_4$ (**2**), $[Ag(\mathbf{L1})(C_6H_6)SbF_6]\cdot 0.5C_6H_6\cdot H_2O$ (**3**), $Ag(\mathbf{L2})(SO_3CF_3)$ (**4**), and $Ag(\mathbf{L3})(H_2O)(SO_3CF_3)$ (**5**), based on our ligands, respectively. In addition, luminescent properties of **L1**−**L3** and their Ag(I) complexes were investigated primarily in the solid state and EtOH solution.

Results and Discussion

1. Synthesis and Structural Analysis of Ligands L1−L3. The interesting coordination chemistry exhibited by fulvene II encourages us to undertake further studies on the design and synthesis of new types of fulvene ligand. Following this approach, we expand symmetric benzonitrile-containing fulvene II to symmetric furan-containing fulvene III and unsymmetric furan- and benzonitrile-containing fulvene IV by one-pot reaction of 2-furoic chloride and 4-cyanobenzoyl chloride or 3-cyanobenzoyl chloride with cyclopentadiene anion (Scheme 2), respectively. Symmetric fulvene III and unsymmetric fulvene IV further reacted with hydrazine to generate novel target cyclopenta[*d*]pyridazine ligands **L1**−**L3**. Ligands **L1**−**L3** were isolated as deep-yellow crystalline solids. They are very soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, THF, benzene, toluene, and so on. In the ^1H NMR spectra of **L1**−**L3**, a proton resonance was observed around 14 ppm as a single peak, which was attributed to the proton on the imine group. The IR spectra of these ligands showed an −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 absorption, respectively, which is comparable to those corresponding bands in known compounds.[7] The structure of **L1** was further confirmed by single-crystal X-ray diffraction. The crystal structure of **L1** reveals that the unsymmetric unit contains two crystallographically and conformationally inequivalent molecules *trans*-**a** and *cis*-**b**. For example of molecule **b**, as shown in Figure 1, two 2-furoyl groups on the cyclopetadienyl ring are adjacent. The C−C bond lengths on the center five-membered ring and also C(5)−C(6) and C(10)−C(11) range from 1.377 (7) to 1.378(7) Å, which is significantly shorter than a normal C−C single bond distance. Evidently, **L1** exists in the fulvene form.[7,11] There are two NO-chelating moieties in **L1** (O(4) vs N(1) and O(3) vs N(2)). These two NO-chelating coordination moieties and an electron-rich cyclopentadienide group make **L1** a ligand that possesses two totally different potential coordination sites, i.e. organometallic vs inorganic sites. Thus, **L1** reported herein could be considered as a multidentate ligand that could afford not only carbon but also heteroatom donors. This affords us a good opportunity to synthesize organometallic supramolecular complexes. **L2** and **L3** are unsymmetric ligands. As shown in Scheme 2, furoyl and cyanobenzoyl (4-cyanobenzoyl for **L2** and 3-cyanobenzoyl for **L3**) moieties are attached to a center five-membered ring, respectively. Different orientations together with different coordinative abilities of C-, O-, and N-donors in **L2** and **L3** would result in an abundant coordination chemistry of 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.

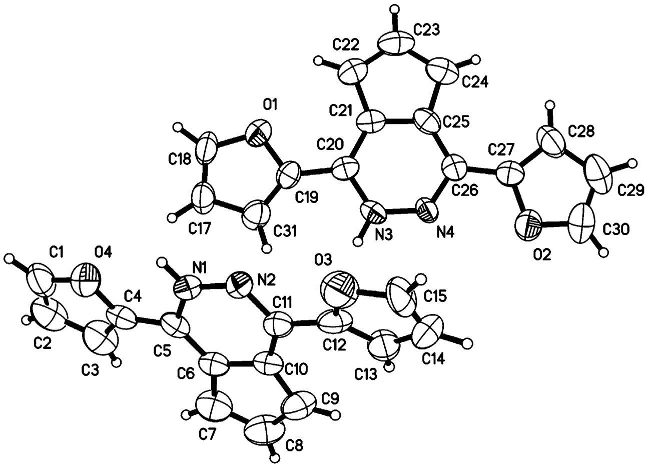

Figure 1. Molecular structure of **L1** (30% probability displacement ellipsoids).

2. Supramolecular Complexes Based on Symmetric Ligand L1 and Ag(I) Ion. As we know, coordination chemistry based on symmetric organic ligand 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, biphenylcyanide, and also related types of ligand have been widely used to construct supramolecular complexes.[1−4] However, the coordination chemistry based on fulvene unit bridging five-membered heterocyclic ring-containing symmetric ligands, such as **L1** reported herein, is still unprecedented. Multifunctionalities of **L1** and its versatile conformations attract us to test its coordinative ability toward metal acceptors, especially soft acid Ag(I) ion.[9d−f,13]

Synthesis and Structural Analysis of 1. Reaction of **L1** with $AgSO_3CF_3$ (1:2 ratio) in benzene at room temperature afforded compound **1** as red rodlike crystals in 74% yield. Compound **1** is air stable. Single-crystal analysis revealed that compound **1** crystallizes in the monoclinic system $P2_1/$

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[10] For example, see: (a) Khlobystov, A. N.; Brett, M. T.; Blake, A. J.; Champness, N. R.; Gill, P. M. W.; O'Neill, D. P.; Teat, S. J.; Wilson, C.; Schröder, M. *J. Am. Chem. Soc.* **2003**, *125*, 6753. (b) Uemura, K.; Kitagawa, S.; Kondo, M.; Fukui, K.; Kitaura, R.; Chang, H.-C.; Mizutani, T. *Chem.−Eur. J.* **2002**, *8*, 3586. (c) Lee, I.; Shin, D. M.; Chung, Y. K. *Chem.−Eur. J.* **2004**, *10*, 3158.

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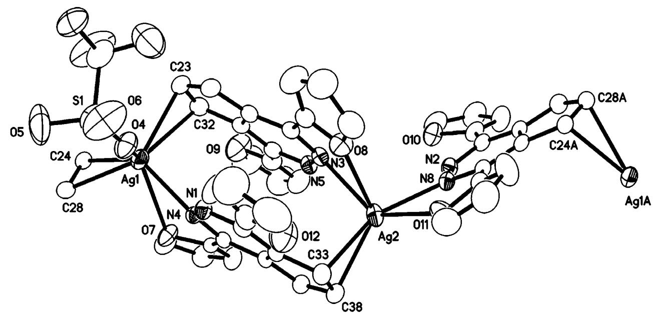

Figure 2. ORTEP figure of **1** (30% probability displacement ellipsoids).

c. As shown in Figure 2, there are two different Ag(I) centers in **1**. The first silver atom lies in a $\{AgNO_2\pi_2\}$ coordination sphere, being made of one N-donor (N(4), $d_{Ag(1)-N(4)} = 2.365(4)$ Å) and two O-donors (O(4) and O(7); $d_{Ag(2)-O(4)} = 2.631(5)$ and $d_{Ag(2)-O(7)} = 2.879(5)$ Å) from one **L1** ligand and one coordinated $SO_3CF_3^-$ counterion and two π-donors (Ag(1)−C bond distances range from 2.482(5) to 2.769(4) Å) from the cyclopentadienide groups on the two other **L1** ligands, respectively**.** The remaining Ag−C contacts are greater than 2.80 Å, which is beyond the limits (2.47−2.80 Å) commonly observed in Ag(I)−π complexes.[14] Thus, the cyclopentadienide in **1** coordinates to the Ag(I) ion with an η^2 bonding mode, which is normally observed in cyclopentadienide−Ag(I) complexes.[7] The second Ag(I) center adopts a $\{AgN_2O_2\pi\}$ coordination environment. Two sets of NO-chelating moieties (Ag(2)−N and Ag(2)−O bond lengths range from 2.3−2.494 and 2.709−2.804 Å, respectively) and one π-donor from three **L1** ligands (Ag(2)−C bond lengths range from 2.478 to 2.481 Å) surround the Ag(2) atom into a five-coordinated sphere. As shown in Figure 2, Ag(1) and Ag(2) atoms are linked together by two *trans*-**L1** ligands into a dinuclear organometallic molecular boxlike moiety, in which the Ag(1)···Ag(2) distance is 6.97(3) Å. These Ag_2(*trans*-**L1**)$_2$ dinuclear species are further linked together by *cis*-**L1** ligands through one set of an NO-chelating coordination site and two cyclopentadienide carbon atoms into a novel zigzag chain along the crystallographic *b* axis (Figure 3). The coordinated $SO_3CF_3^-$ counterions are hydrogen bonded to the Ag_2(*trans*-**L1**)$_2$ molecular unit through N−H···O hydrogen bonding ($d_{N(1)-O(4)} = 2.767(3)$ and $d_{O(4)}$···H(1) = 2.000(3) Å) interaction.

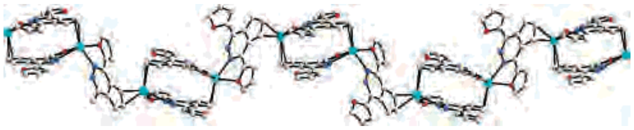

Figure 3. One-dimensional organometallic zigzag chain in **1** (along the crystallographic *b* axis).

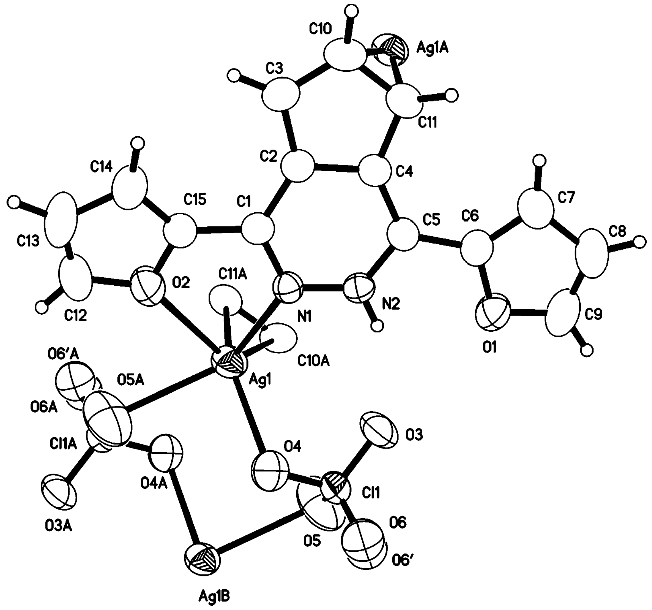

Figure 4. ORTEP figure of **2** (30% probability displacement ellipsoids).

Figure 5. One-dimensional linear chain in **2**.

Synthesis and Structural Analysis of 2. Compound **2** was obtained by combination of **L1** and $AgClO_4$ in the same mixed-solvent system as red crystals in 82% yield. Compound **2** crystallizes in the monoclinic system *C*2/*c*. As shown in Figure 4, there is only one Ag(I) center in **2**, which lies in a $\{AgO_3N\pi\}$ coordination environment which consist of one pyridazine N-donor ($d_{Ag(I)-N(1)} = 2.383(3)$ Å), three O-donors from the furan group ($d_{Ag(I)-O(2)} = 2.588(3)$ Å) and two ClO_4^- counterions ($d_{Ag(I)-O(4)} = 2.428(4)$ and $d_{Ag(I)-O(5)} = 2.664(4)$ Å), and one π-donor (C(10) and C(11), Ag−C bond lengths rang from 2.420(4) to 2.652(4) Å). Compared to **1**, a similar molecular boxlike Ag_2(**L1**)$_2$ moiety was found. It is noteworthy that the **L1** ligand in **2** adopts a cis-conformation in forming the Ag_2(*cis*-**L1**)$_2$ moiety, which is distinctly different from that in **1**. The Ag(I)···Ag(I) distance in the Ag_2(*cis*-**L1**)$_2$ unit is 6.92(4) Å, which is almost identical with that in **1**. In the solid state, as shown in Figure 5, two ClO_4^- anions are located between Ag_2(*cis*-**L1**)$_2$ units and link them together through four long Ag−O bonds (2.43(4) and 2.66(4) Å) into a one-dimensional linear chain. It is interesting that there are two sets of chains in **2**; they extend along the crystallographic [1$\bar{1}$0] and [110] directions, respectively (Figure 6). These two sets of perpendicular one-dimensional chains are stacked together along the crystallographic *c* axis to generate elliptical channels (Figure 7) with effective cross section ca. 11 × 8 Å. It is interesting

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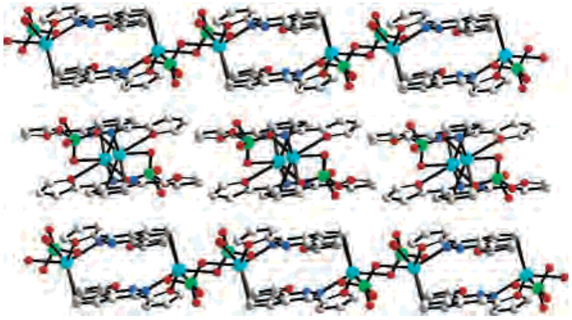

Figure 6. Two sets of perpendicular one-dimensional chains in **2**.

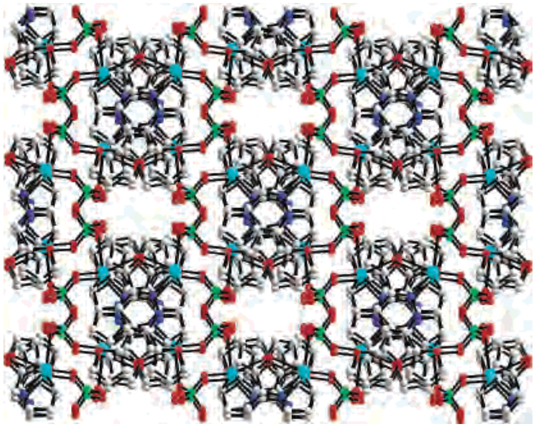

Figure 7. Crystal packing of **2**.

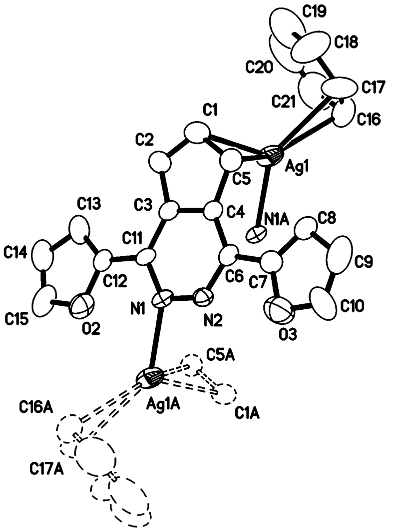

Figure 8. ORTEP figure of compound **3** with 30% probability ellipsoids.

that there are no guest molecules located in the channels. It is different from **1** as a ClO_4^- counterion herein instead of **L1** ligand serves as a connector to bind Ag_2(*cis*-**L1**)$_2$ units into a polymeric chain.

Synthesis and Structural Analysis of 3. To explore the templating role of counterions in the self-assembly process, $AgSbF_6$ was used instead of $AgClO_4$ to carry out the reaction under the same reactive conditions. Compound **3** was isolated as a discrete organometallic complex instead of polymeric compound in a benzene/toluene mixed-solvent system in 87% yield. As shown in Figure 8, the Ag(I) center in **3** lies in a distorted tetrahedral organometallic coordination sphere {Agπ_2NO} consisting of one pyridazine N atom ($d_{\mathrm{Ag(1)-N(1)}} = 2.368(7)$ Å) and one furan oxygen atom ($d_{\mathrm{Ag(1)-O(2)}} = 2.751(7)$ Å) and two π-donors from the cyclopentadienide moiety on one **L1** ligand (C(16) and C(17)) and one coordinated benzene solvent molecule (C(1) and C(5)), respectively. All Ag(I)−C bond distances lie in the range of normal silver−carbon bond lengths (2.47−2.80 Å).[15] Two Ag(I) centers are linked together by two *cis*-**L1** into a {Ag_2(*cis*-**L1**)$_2$} cationic dinuclear boxlike unit again (Figure 9). The Ag(I)···Ag(I) separation in {Ag_2(*cis*-**L1**)$_2$} moiety is 6.910(3) Å, which is similar to the corresponding Ag(I)···Ag(I) distances found in compounds **1** and **2**. Two benzene solvent molecules herein as a terminal coligand attach an Ag(I) atom in η^2 fashion and block the compound **3** into polymeric species. It is well-known that small and big arene molecules could act as bidentate or multidentate ligands to coordinate soft metal ions, especially Ag(I) ion, into polymeric complexes.[15,16] We earlier reported a supramolecular Ag(I)−fulvene II complex, wherein the benzene solvent molecule serves as a bridging coligand to connect a cationic molecular loop {Ag_4(fulvene II)$_2$} through two *meso*-carbon atoms into a one-dimensional chain in the solid state.[7d] It is not clear why the benzene solvent molecule herein did not act as a bridging ligand while it did in most of the other cases. We tried several times to change the metal-to-ligand ratios; however, compound **3** was the only compound that could be isolated from the reactions probably due to the templating effects of different counterions.

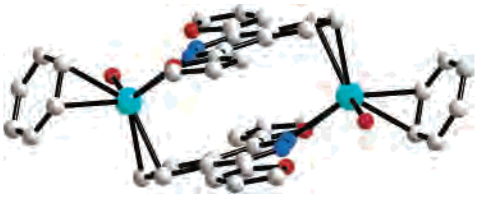

Figure 9. Organometallic dinuclear boxlike unit in **3**.

In the solid state, the {Ag_2(*cis*-**L1**)$_2$} cationic dinuclear building blocks are connected to each other by two sets of weak C−H···F hydrogen bonds,[17] which involve the F(1) and F(3) atoms of the SbF_6^- anion and the C(2) and C(5) atoms and the H(2) and H(7) atoms on the cyclopentadienide ring of **L1** ($d_{\mathrm{F(1)\cdots H(2)}} = 2.570(3)$ Å, $d_{\mathrm{F(1)\cdots C(2)}} = 3.455(4)$ Å and $<$C(2)−H(2)···F(1) = 159.24(3)°; $d_{\mathrm{F(3)\cdots H(7)}} = 2.644(3)$ Å, $d_{\mathrm{F(3)\cdots C(5)}} = 3.50(4)$ Å and $<$C(5)−H(7)···F(3) = 163.28(3)°), forming a two-dimensional H-bonded network extending in the crystallographic *bc* plane (Figure 10). These two-dimensional nets stack together along the crystallographic *a* axis to generate rhombic channels (crystallographic dimensions, ca. 11.4 × 18.0 Å), in which uncoordinated benzene molecules are located (Figure 11). It is apparent that these C−H···F hydrogen bonds, although weak,

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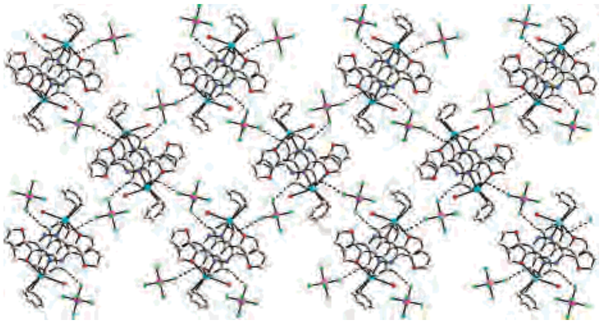

Figure 10. View perpendicular to one two-dimensional H-bonded network in **3**. Hydrogen bonds are shown as dotted lines.

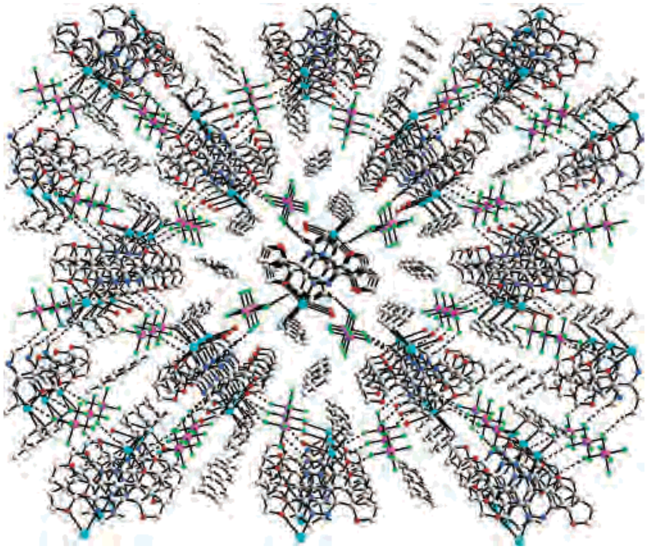

Figure 11. Crystal packing of **3**. Benzene guest molecules are located in rhombic channels.

contribute significantly to the alignment of the molecules of **3** in the crystalline state.

The common feature of compounds **1**−**3** lies in the fact that they all possess a $\{Ag_2(\mathbf{L1})_2\}$ molecular boxlike building block. The coordination preference and potential symmetry relationship of the silver atom might be the key factor to determine the structures. In compounds **1**−**3**, **L1** exhibits a similar coordination behavior, i.e., using both organometallic (cyclopentadienide) and inorganic (NO-chelating site) faces to bind the Ag(I) atom. It is worthwhile to point out that, in **1**, **L1** adopts a trans-conformation in forming a $\{Ag_2(\mathbf{L1})_2\}$ boxlike unit, whereas in **2** and **3** it is cisoid. In principle, a trans-conformation orients the two terminal coordination donors in two different directions and would allow them to bind metal centers into higher dimensional framework; meanwhile, a cis-conformation orients the two terminal groups in the same direction and would allow them to bind at the neighboring metal center as discrete molecules or lower dimensional architectures. For example, *cis*- and *trans*-fulvene II (Scheme 1) reacted with $AgSbF_6$ in different solvent systems to result in a two-dimensional net and three-dimensional diamondoid framework, respectively, which was reported earlier by us.[7e] We anticipate that **L1** with inorganic Ag(I) salts could give rise to more versatile coordination supramolecular complexes or polymeric compounds in the future. As noted above, only one of two NO-chelating moieties in **L1** involves the metal coordination sphere and the other is free, which might indicate that two NO-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**−**3** were always isolated as the only products. It is interesting that the connectors between the $\{Ag_2(\mathbf{L1})_2\}$ unit change from **L1** in **1** to counterion ClO_4^- in **2**, whereas only semibridged benzene molecule is found in **3**. The only possible explanation for this change might be the templating effect resulting from the different counterions due to all three reactions carried out under exactly the same conditions including solvent system, metal-to-ligand ratio, and temperature. That the templating effect of the counterion could be the influence in determining the type and topology of the product was well demonstrated by many earlier studies.[18] Compounds **1**−**3** reported herein represent additional examples for this kind of phenomenon.

3. Supramolecular Complexes Based on Unsymmetric Ligands L2 and L3. The idea behind the use of ligands L2 and L3 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 ability are expected to result in more unprecedented coordination polymers or supramolecular complexes with novel topologies than can be achieved with symmetric ligands.[10] In addition, **L2** and **L3** could be considered as angular ligands with a bite angle between one terminal −CN donor and one $N_{pyridazine}$ donor around 60°, which has a strong tendency to form cyclic moieties with inorganic metal ions. Such kind of geometric configuration together with different electron donors would be expected to form new metallacycle-containing coordination polymers or supramolecular complexes.

Synthesis and Structural Analysis of 4. Compound **4** was obtained as red crystals by combination of **L2** with $AgSO_3CF_3$ in a benzene/toluene mixed-solvent system at 84% yield. As shown in Figure 12, compound **4** crystallizes in the triclinic system with the space group $P\bar{1}$. There is only one type of crystallographic Ag(I) center in **4**, and it lies in a distorted inorganic tetrahedral coordination environment $\{AgN_2O_2\}$ defined by two N-donors from one −CN group ($d_{Ag(1)-N(2)} = 2.369(4)$ Å) and one pyridazine ring ($d_{Ag(1)-N(1)} = 2.215(4)$ Å) on the other **L2** ligand, respectively. The two O-donors come from two coordinate $SO_3CF_3^-$ counterions with Ag(1)−O bond lengths of 2.497(3) and 2.725(4) Å, respectively. All these bond distances are similar to the corresponding bond lengths found in compounds **1**−**3** and

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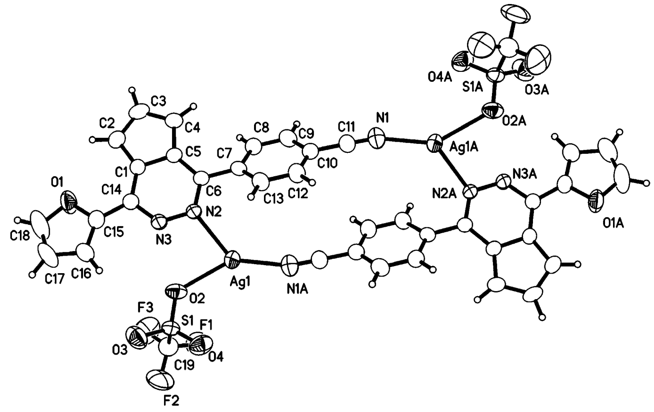

Figure 12. ORTEP figure of compound **4** with 30% probability ellipsoids.

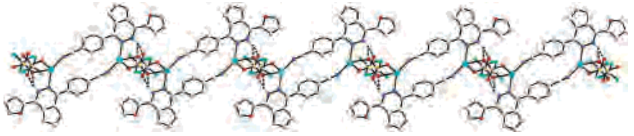

Figure 13. One-dimensional chain in **4**. Hydrogen bonds are shown as dotted lines.

previous polymeric Ag(I) complexes based on fulvene II ligands.[7] It is worthwhile to point out that the cyclopentadienide and furan ring in **L2** did not involve the Ag(I) coordination sphere, which shows coordination behavior different from that of symmetric **L1** ligand for $AgSO_3CF_3$ in the same solvent template.

In the solid state, two Ag(I) centers are connected to each other by −CN and $N_{pyridazine}$ donors into a bimetallic 18-membered $\{Ag_2(\mathbf{L2})_2\}$ ring (Figure 12). The intra- and inter-ring Ag···Ag distances are 8.85(3) and 6.064(3) Å, respectively. These binuclear rings interact with each other via bidentate bridging $SO_3CF_3^-$ anions (Ag(I)−O bond lengths of 2.497(3) and 2.752(3) Å) to form an infinite one-dimensional coordination polymer (Figure 13). It is worth pointing out that two chiral Ag(I) centers in $\{Ag_2(\mathbf{L2})_2\}$ possess opposing absolute configurations Δ and Λ, which results in the binuclear rings arranging in a *meso* fashion instead of a helical array.[10a,19] In addition, $\{Ag_2(\mathbf{L2})_2\}$ rings are further fixed by two sets of complementary binary N−H···O hydrogen bonds[20] consisting of the two O(2) and two O(4) atoms on the two $SO_3CF_3^-$ counterions and the two H(3A) atoms on the two neighbor pyridazine moieties. The O(2)···H(3A) and O(4)···H(3A) distances are 2.32(5) and 2.26(5) Å, respectively. The corresponding O(2)···N(3) and O(4)···N(3A) distances are 2.893(5) and 2.900(5) Å, respectively, and the corresponding N(3)−H(3A)···O(2) and N(3)−H(3A)···O(4)$^{\#2}$ angles are 124.1(5) and 130.8(5)°, respectively.

Synthesis and Structural Analysis of 5. The idea behind the use of ligand **L3** is to control supramolecular motifs through different donor 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.[21] We earlier reported on a series 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 to control the polymeric motifs.[22] Reaction of **L3** with $AgSO_3CF_3$ (1:2 ratio) in benzene/toluene at room temperature afforded compound **5** as yellow crystals in 72% yield. Compound **5** is air stable. Single-crystal analysis revealed that compound **5** crystallizes in the triclinic system, $P\bar{1}$. As shown in Figure 14, Ag(I) center lies in a distorted tetrahedral $\{AgN_2O\pi\}$ coordination environment consisting of one −CN donor ($d_{Ag(1)-N(3)^{\#1}} = 2.197(5)$ Å), one coordinated water molecule ($d_{Ag(1)-O(5)} = 2.533(5)$ Å), and one π-donor from a coordinated cyclopentadienide ring ($d_{Ag(1)-C(2)^{\#2}} = 2.350(6)$ and $d_{Ag(1)-C(2)^{\#2}} = 2.731(6)$ Å). The corresponding bond distances are very close to those found in compounds **1**−**4**. The coordination behavior of **L3** is different from that of **L2** for $AgSO_3CF_3$ in this specific reaction. As shown above, the cyclopentadienide moiety in **L2** did not involve in the Ag(I) coordination sphere, but it did in **L3**. In addition, the $SO_3CF_3^-$ counterion in **5** acts as a coordinated species but not in **4**. The coordination differences between **L2** and **L3** might be a consequence of the different relative orientations of the −CN donors on them.

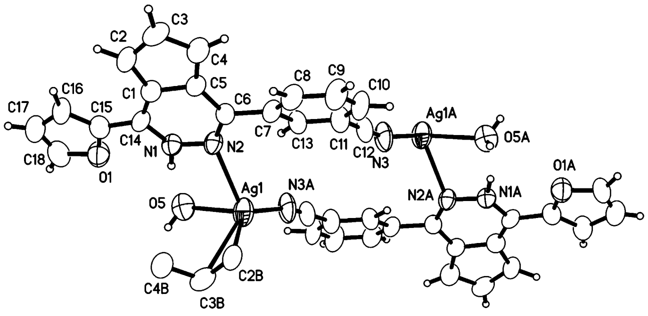

Figure 14. ORTEP figure of compound **5** with 30% probability ellipsoids.

In the solid state, two **L3** ligands link two Ag(I) atoms through π−Ag(I) interaction into an organometallic boxlike moiety (Figure 15), in which two 3-cyanobenzoyl arms stretch out in opposite directions and bind two Ag(I) atoms on neighbor boxlike building blocks into a novel molecular necklace extending along the crystallographic $[0\bar{1}1]$ direction (Figure 16). The Ag···Ag distances of intra- and inter-boxlike

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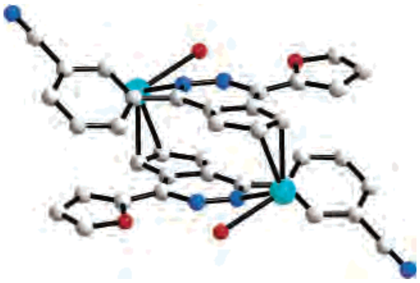

Figure 15. Organometallic boxlike unit in **5**.

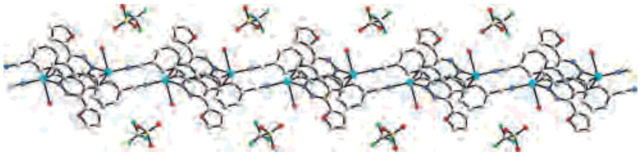

Figure 16. One-dimensional molecular necklacelike chain in **5**.

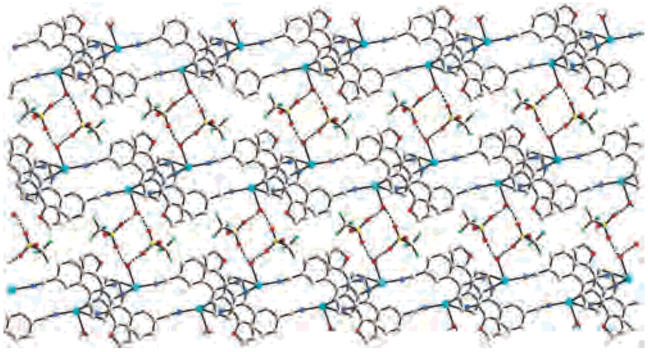

Figure 17. Two-dimensional H-bonded network in **5**.

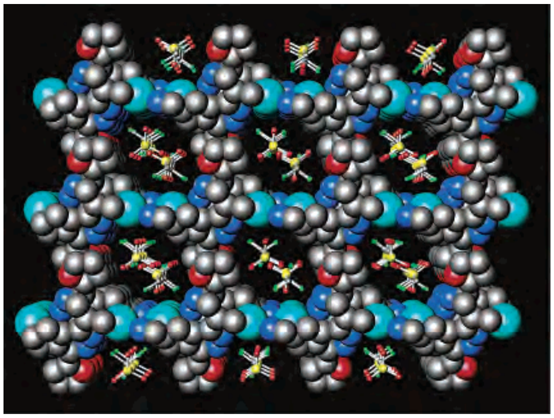

Figure 18. Crystal packing of **5**. Uncoordinated $SO_3CF_3^-$ counterions are located in the channels.

building blocks are 10.81(3) and 11.28(3) Å, respectively. These one-dimensional organometallic necklaces are further linked together through two sets of complementary binary O−H···O hydrogen bonds into a novel H-bonded two-dimensional network extending along the crystallographic [011] plane. The hydrogen-bonding systems consist of the two O(2) and two O(4) atoms on the two uncoordinated $SO_3CF_3^-$ anions and the two H(5A) atoms on the coordinated water molecule. The O(2)···H(5A) and O(4)···H(5B) distances are 1.961(5) and 1.962(5) Å, respectively. The corresponding O(2)···O(5) and O(4)···O(5) distances are 2.778(5) and 2.782(5) Å, respectively, and the corresponding O(5)−H(5A)···O(2) and O(5)−H(5B)···O(4) angles are 162.1(5) and 164.8(5)°, respectively (Figure 17). These two-dimensional nets are stacked together along the crystallographic *c* axis to generated squarelike channels with dimensions of 8.9 × 8.8 Å, in which uncoordinated $SO_3CF_3^-$ anions are located (Figure 18). It is well-known that the most important driving forces in crystal engineering are coordination-bonding and hydrogen-bonding interactions. Extended networks assembled by both coordination and hydrogen bonds are one of the important strategies to construct supramolecular networks.[23] In principle, higher dimensionality networks can be obtained by the assembly of lower dimensionality polymers (or molecules) via hydrogen-bonding interactions. A series of such compounds, namely $[Zn(H_2O)(bipy)](NO_3)_2 \cdot bipy$, $[Zn(H_2O)_4(bipy)](NO_3)_2 \cdot 2bipy$, $[Zn(H_2O)_4(bipy)][SO_3CF_3]_2 \cdot 2bipy$, $Fe(H_2O)_3(ClO_4)(bipy)](ClO_4) \cdot 1.5bipy \cdot H_2O$, $Cd_2(H_2O)_4(bipy)_5(NO_3)_2(PF_6)_2$, and $[Co(H_2O)_4(bipy)][PF_6]_2 \cdot 3bipy$, was reported before.[24] The extended frameworks of these compounds are based on the one-dimensional $[M(bipy)]_n$ (M = Zn(II), Fe(II), and Co(II)) linear chains or molecular $[M_2(bipy)_5]$ [M = Cd(II)] units, which are cross-linked to each other by $M(H_2O)$···bipy···H_2O−M hydrogen-bond bridges to produce two- and three-dimensional networks. In compound **5**, the uncoordinated $SO_3CF_3^-$ anions and coordinated water molecules do play a critical role in the formation of a H-bonding system and, moreover, serve as the agents which allow hydrogen-bonding interactions to expand the dimensionality of **5** from one to two.

Luminescent 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 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 luminescent materials,[25] especially for d^{10} or $d^{10}-d^{10}$ systems[26] and conjugated ligand-containing complexes.[27] The luminescent properties of free ligands **L1**−**L3** and their metal complexes **1**−**5** were investigated in EtOH and the solid state at room temperature. The spectra of **L1**−**L3** in EtOH are shown in Figure 19. **L1**−**L3** exhibit two emission maxima at 384 and

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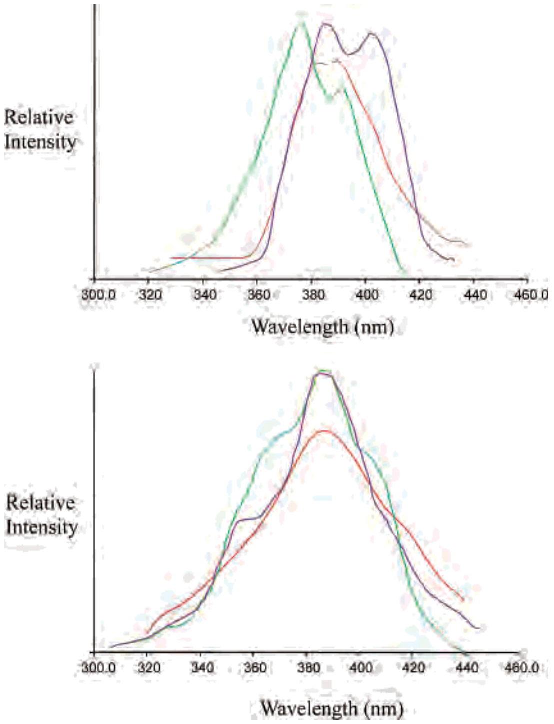

Figure 19. Photoinduced emission spectra of **L1** (red line), **L2** (green line), and **L3** (purple line) in EtOH at room temperature (top) and in the solid state (bottom).

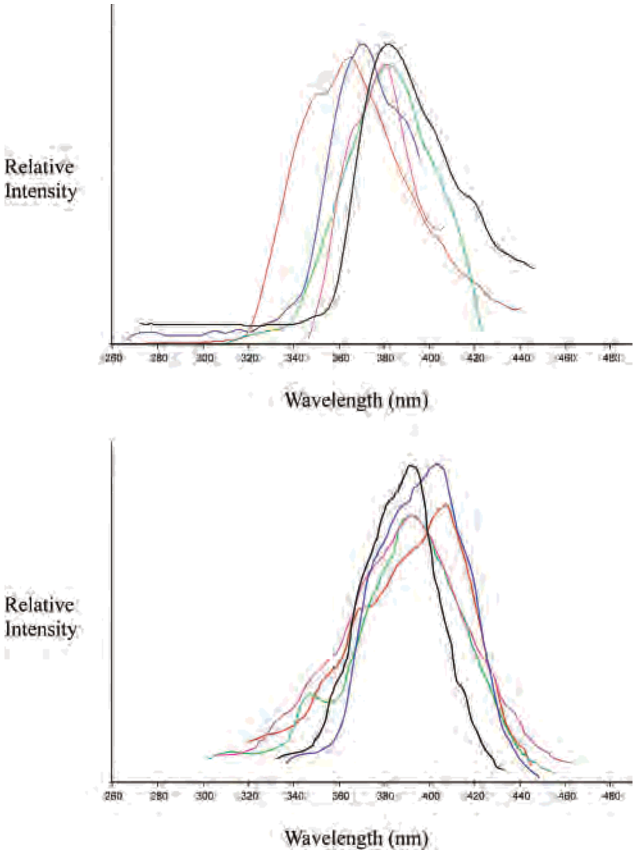

Figure 20. Photoinduced emission spectra of **1** (red line), **2** (green line), **3** (purple line), **4** (blue line), and **5** (black line) in EtOH at room temperature (top) and in the solid state (bottom).

396 nm for **L1** (under 257 nm excitation), 392 and 377 nm for **L2** (under 216 nm excitation), and 385 and 403 nm for **L3** (under 218 nm excitation), respectively. In the solid state, they exhibit only one emission maximum at 387 nm for **L1** (upon photoexcitation at 250 nm), 386 nm for **L2** (upon photoexcitation at 213 nm), and 386 nm for **L3** (upon photoexcitation at 223 nm), respectively. In EtOH, the emission colors of Ag(I)-containing complexes **1**−**5** are shown in Figure 20. As indicated in Figure 20, complexes **1**−**5** exhibit one emission band at 365 nm (**1**, $\lambda_{\text{excitation}} = 242$ nm), 384 nm (**2**, $\lambda_{\text{excitation}} = 217$ nm), 382 nm (**3**, $\lambda_{\text{excitation}} = 216$ nm), 379 nm (**4**, $\lambda_{\text{excitation}} = 215$ nm), and 384 nm (**5**, $\lambda_{\text{excitation}} = 213$ nm), respectively. In EtOH, the emission colors of **1**−**5**, compared to their corresponding free ligands **L1**−**L3**, are blue-shifted. Solid samples of **1**−**5** show no detectable luminescence at ambient temperature. As shown in Figure 20, complexes **1**−**5** show their emission bands at 404 nm (**1**, $\lambda_{\text{excitation}} = 224$ nm), 394 nm (**2**, $\lambda_{\text{excitation}} = 204$ nm), 396 nm (**3**, $\lambda_{\text{excitation}} = 214$ nm), 405 nm (**4**, $\lambda_{\text{excitation}} =$ 225 nm), and 394 nm (**5**, $\lambda_{\text{excitation}} = 213$ nm), respectively. Compared to their corresponding emission colors in solution, all the emission bands for **1**−**5** in the solid state are red-shifted, probably due to the polymeric frameworks in polar solvents breaking down and resulting in the formation of oligomers or even discrete molecular complexes. Overall, the emission colors of free ligands **L1**−**L3** were significantly affected by their incorporation into the Ag(I)-containing complexes, as evidenced by the large shift in the emission.

Conclusions. One new symmetric ligand **L1** and two unsymmetric **L2** and **L3** were synthesized. The results indicate that the coordination chemistry of new fulvene ligands with soft acid Ag(I) ion is versatile. They can adopt either the cis- or trans-conformation to bind Ag(I) not only through the terminal N- and O-donors but also through a cyclopentadienide group into organometallic coordination polymers or discrete complexes. In the solid state and solution, ligands **L1**−**L3** and their Ag(I) complexes are luminescent. 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, 6,6′-dimethylenefulvene, and PhLi were prepared according to literature methods. Inorganic metal salts were pur-

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chased 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 or AM-300 spectrometer. Chemical shifts are reported in δ relative to TMS. Elemental analyses were performed on a Perkin-Elmer model 240C analyzer. All fluorescence measurements were carried out on a Cary Eclipse spectrofluorometer (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 Fulvenes II-1, III-1, and IV-1. A solution of 4-cyanobenzoyl chloride (1.76 g, 10.6 mmol) and 2-furoyl chloride (1.06 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 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 fulvenes II-1, III-1, and IV-1. Fulvene II-1 (0.11 g, yield 4%): corresponding spectral data for fulvene II-1 are identical with those of reported data.[7d] Fulvene III-1 (0.43 g, yield 14%): mp 102−106 °C; IR (KBr pellet) ν (cm^{-1}) = 3441 (s), 2924 (w), 1644 (s), 1572 (s), 1537 (s), 1456 (s), 1403 (vs), 1083 (m), 1019 (s), 839 (w), 754 (m), 729 (m); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 18.51 (s, 1H, −OH), 8.17 (d, 2H, $-C_4H_3O$), 7.74 (t, 2H, $-C_4H_3O$), 7.42 (m, 2H, $-C_4H_3O$), 6.64 (m, 3H, $-C_5H_3$). Anal. Calcd for $C_{15}H_{10}O_4$: C, 70.87; H, 3.94. Found: C, 70.79; H, 3.78. In addition, fulvene III-1 could be obtained by following method, too: A solution of 2-furoyl chloride (1.9 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 crystalline solid. Fulvene IV-1 (0.61 g, yield, 20%): mp 126−128 °C; IR (KBr pellet) ν (cm^{-1}) = 3446 (s), 3100 (w), 3000 (w), 2229 (m), 1620 (s), 1539 (m), 1460 (s), 1404 (vs), 1142 (w), 1084 (s), 1020 (m), 952 (m), 851 (s), 743 (s); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 18.36 (s, 1H, −OH), 8.26 (d, 1H, $-C_4H_3O$), 7.78−7.87 (m, 5H, $-C_6H_4$, $-C_4H_3O$), 7.49 (m, 1H, $-C_4H_3O$), 7.14, 6.68, 6.60 (d, q, s, 3H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}NO_3$: C, 74.74; H, 3.81; N, 4.84. Found: C, 74.56; H, 3.82; N, 4.78.

Preparation of L1. A solution of fulvene III-1 (0.21 g, 0.83 mmol) in anhydrous EtOH (20 mL) and large excess $N_2H_4 \cdot H_2O$ was heated to reflux for about 7 h. After the sample 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 the orange crystals of **L1** (yield, 86%): mp 178−180 °C; IR (KBr pellet) ν (cm^{-1}) = 3200 (s), 1610 (s), 1590 (w), 1578 (s), 1550 (s), 1520 (s), 1500 (s), 1450 (s), 1420 (s), 1400 (m), 1360 (s), 1320 (s), 1250 (s), 1230 (w), 1190 (s), 1070 (s), 1020 (s), 890 (s), 750 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ = 14.19 (s, 1H, −NH), 8.19−8.06 (m, 2H, $-C_4H_3O$), 7.80−7.36 (m, 4H, $-C_4H_3O$), 7.25(d, 2H, $-C_5H_3$), 6.86 (t, 1H, $-C_5H_3$). Anal. Calcd for $C_{15}H_{10}N_2O_2$: C, 72.00; H, 4.00; N, 11.2. Found: C, 72.23; H, 4.13; N, 10.89.

Table 1. Crystallographic Data for **L1**, **1**, and **2**

param	L1	1	2
formula	$C_{15}H_{10}N_2O_2$	$C_{47}H_{30}Ag_2F_6N_6O_{12}S_2$	$C_{15}H_{10}AgClN_2O_6$
fw	250.25	1264.63	457.57
cryst system	monoclinic	monoclinic	monoclinic
space group	$P2_1$	$P2_1/c$	$C2/c$
a (Å)	12.982(5)	12.702(3)	17.363(2)
b (Å)	5.977(2)	26.118(7)	13.2794(18)
c (Å)	15.786(7)	13.998(4)	13.4884(18)
α (deg)	90	90	90
β (deg)	105.098(6)	96.063(4)	100.292(2)
γ (deg)	90	90	90
V (Å^3)	1182.7(8)	96.063(4)	3060.0(7)
Z	3	10	8
ρ_{calcd} (g/cm^3)	1.405	1.819	1.986
μ (mm^{-1})	0.096	1.036	1.530
temp (K)	293(2)	293(2)	293(2)
no. of reflcns	3571	10057	3343
R1; wR2 ($I > 2\sigma(I)$)	0.0789; 0.1290	0.0627; 0.1475	0.0402; 0.1107

Table 2. Crystallographic Data for **3−5**

param	3	4	5
formula	$C_{24}H_{21}AgF_6N_2O_3Sb$	$C_{19}H_{11}AgF_3N_3O_4S$	$C_{19}H_{13}AgF_3N_3O_5S_7$
fw	729.05	542.24	560.25
cryst system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a (Å)	6.8839(11)	8.629(3)	8.914(5)
b (Å)	20.242(3)	10.915(3)	10.809(6)
c (Å)	18.934(3)	11.178(3)	11.283(6)
α (deg)	90	100.978(4)	69.255(8)
β (deg)	91.994(3)	102.133(4)	87.163(9)
γ (deg)	90	105.652(4)	84.993(8)
V (Å^3)	2636.8(7)	956.4(5)	1012.6(9)
Z	6	2	2
ρ_{calcd} (g/cm^3)	1.831	1.883	1.838
μ (mm^{-1})	1.838	1.226	1.164
temp (K)	293(2)	293(2)	293(2)
no. of reflcns	5763	3670	3873
R1; wR2 ($I > 2\sigma(I)$)	0.0904; 0.1986	0.0481; 0.1055	0.0546; 0.0681

Preparation of L2. L2 was prepared by following the procedure described for **L1** except by using fulvene IV-1 instead of fulvene III-1 to afford **L2** as an orange crystalline solid (yield, 76%): mp 199−201 °C; IR (KBr pellet) ν (cm^{-1}) = 3279 (s), 2229 (s), 1606 (s), 1516 (s), 1409 (s), 1361 (s), 1020 (s), 847 (s), 753 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ = 14.22 (s, 1H, −NH), 8.11−7.23 (m, 9H, $-C_6H_4$, $-C_4H_3O$, $-C_5H_3$), 6.86 (t, 1H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}N_3O$: C, 75.79; H, 3.86; N, 14.74. Found: C, 75.43; H, 3.79; N, 14.59.

Preparation of Fulvene IV-2. Fulvene IV-2 was prepared by following the procedure descried for fulvene IV-1 except by using 3-cyanobenzoyl chloride (1.76 g, 10.6 mmol) and 2-furoyl chloride (1.06 mL, 10.6 mmol) instead of 4-cyanobenzoyl chloride (1.76 g, 10.6 mmol) and 2-furoyl chloride (1.06 mL, 10.6 mmol) to afford fulvene IV-2 as an orange crystalline solid (yield, 24%), fulvene II-1 (yield, 5%), and fulvene III-1 (yield, 11%). Fulvene IV-2: mp 152−154 °C; IR (KBr pellet) ν (cm^{-1}) = 3446 (s), 2232 (s), 1619 (s), 1543 (s), 1462 (s), 1404 (s), 1136 (m), 1086 (m), 1019 (m), 811 (s), 756 (s), 725 (s); ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS) δ = 18.34 (s 1H, −OH), 8.26 (d, 1H, $-C_4H_3O$), 7.78−7.33 (m, 6H, $-C_6H_4$, $-C_4H_3O$), 6.70−6.60 (m, 3H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}NO_3$: C, 74.74; H, 3.81; N, 4.84. Found: C, 74.66; H, 3.79; N, 4.65.

Preparation of L3. L3 was prepared by following the procedure descried for **L2** except by using fulvene IV-2 instead of fulvene IV-1 to afford **L3** as an orange crystalline solid (yield, 77%): mp

Table 3. Interatomic Distances (Å) and Bond Angles (deg) with Esd's in Parentheses for **L1** and **1**−**5**

	Ligand **L1**		
C(5)−C(6)	1.378(7)	C(6)−C(7)	1.397(8)
C(5)−N(1)	1.345(6)	N(1)−N(2)	1.380(6)
C(7)−C(8)	1.381(9)	C(4)−C(5)	1.450(8)
C(26)−N(4)−N(3)	125.4(5)	C(4)−O(4)−C(1)	105.4(6)
C(5)−N(1)−N(2)	125.7(5)	C(2)−C(1)−O(4)	111.5(7)
	Compound **1**		
Ag(1)−N(4)	2.365(4)	Ag(1)−C(28)	2.482(5)
Ag(1)−C(23)	2.495(6)	Ag(1)−C(24)	2.524(5)
Ag(2)−N(8)	2.300(4)	Ag(2)−C(38)	2.478(6)
Ag(2)−C(33)	2.481(5)	Ag(2)−N(3)	2.494(4)
N(4)−Ag(1)−C(28)	116.74(15)	N(4)−Ag(1)−C(23)	109.29(16)
C(28)−Ag(1)−C(23)	131.88(18)	N(4)−Ag(1)−C(24)	134.51(14)
C(28)−Ag(1)−C(24)	32.47(16)	C(23)−Ag(1)−C(24)	102.42(19)
N(8)−Ag(2)−C(38)	140.91(15)	N(8)−Ag(2)−C(33)	151.66(14)
C(38)−Ag(2)−C(33)	32.68(18)	N(8)−Ag(2)−N(3)	102.55(13)
C(38)−Ag(2)−N(3)	108.10(15)	C(33)−Ag(2)−N(3)	104.27(14)
	Compound **2**		
Ag(1)−N(1)	2.383(3)	Ag(1)−C(11)	2.420(4)
Ag(1)−O(4)	2.428(4)	Ag(1)−O(2)	2.588(3)
N(1)−Ag(1)−C(11)	104.60(11)	N(1)−Ag(1)−O(4)	96.59(12)
C(11)−Ag(1)−O(4)	142.62(14)	N(1)−Ag(1)−O(2)	64.81(9)
C(11)−Ag(1)−O(2)	99.52(13)	O(4)−Ag(1)−O(2)	117.41(12)
N(1)−Ag(1)−C(10)	107.19(11)	C(11)−Ag(1)−C(10)	31.82(13)
O(4)−Ag(1)−C(10)	112.40(13)	O(2)−Ag(1)−C(10)	130.08(12)
	Compound **3**		
Ag(1)−N(1)	2.368(7)	Ag(1)−C(5)	2.531(9)
Ag(1)−C(1)	2.583(10)	Ag(1)−C(16)	2.589(16)
Ag(1)−C(17)	2.70(2)		
N(1)−Ag(1)−C(5)	101.6(3)	N(1)−Ag(1)−C(1)	107.9(3)
C(5)−Ag(1)−C(1)	31.7(3)	C(5)−Ag(1)−C(1)	31.7(3)
N(1)−Ag(1)−C(16)	117.1(6)	C(5)−Ag(1)−C(16)	132.5(7)
C(1)−Ag(1)−C(16)	134.9(6)	N(1)−Ag(1)−C(17)	142.7(8)
C(5)−Ag(1)−C(17)	103.5(7)	C(16)−Ag(1)−C(17)	29.7(6)
	Compound **4**		
Ag(1)−N(1)$^{\#1}$	2.215(4)	Ag(1)−N(2)	2.369(4)
Ag(1)−O(2)	2.497(3)	N(1)−C(11)	1.143(6)
N(1)−Ag(1)$^{\#1}$	2.215(4)		
N(1)$^{\#1}$−Ag(1)−N(2)	129.14(14)	N(1)$^{\#1}$−Ag(1)−O(2)	145.07(14)
N(2)−Ag(1)−O(2)	83.94(11)	C(11)−N(1)−Ag(1)$^{\#1}$	160.6(4)
C(6)−N(2)−N(3)	117.3(3)	C(6)−N(2)−Ag(1)	123.9(3)
N(3)−N(2)−Ag(1)	111.8(2)		
	Compound **5**		
Ag(1)−N(3)$^{\#1}$	2.197(5)	Ag(1)−C(2)$^{\#2}$	2.350(6)
Ag(1)−N(2)	2.507(5)	Ag(1)−O(5)	2.533(5)
N(3)$^{\#1}$−Ag(1)−C(2)$^{\#2}$	135.8(2)	N(3)$^{\#1}$−Ag(1)−N(2)	112.6(2)
C(2)$^{\#2}$−Ag(1)−N(2)	106.66(19)	N(3)$^{\#1}$−Ag(1)−O(5)	94.63(19)
C(2)$^{\#2}$−Ag(1)−O(5)	113.4(2)	N(2)−Ag(1)−O(5)	77.27(18)
C(14)−N(1)−N(2)	126.1(6)	C(6)−N(2)−N(1)	116.6(5)
C(6)−N(2)−Ag(1)	130.5(4)	N(1)−N(2)−Ag(1)	107.3(4)
C(12)−N(3)−Ag(1)$^{\#1}$	166.0(7)		

190−192 °C; IR (KBr pellet) ν (cm^{-1}) = 3224 (s), 2230 (s), 1601 (s), 1514 (s), 1481 (s), 1431 (s), 1389 (s), 1357 (s), 1248 (s), 1065 (s), 1019 (s), 881 (s), 804 (s), 753 (s), 690 (s); ^{1}H NMR (300 MHz, DMSO, 25 °C, TMS) δ = 14.20 (s, 1H, −NH), 8.37−7.13 (m, 8H, $-C_6H_4$, $-C_4H_3O$, $-C_5H_3$), 6.87 (m, 2H, $-C_5H_3$). Anal. Calcd for $C_{18}H_{11}N_3O$: C, 75.79; H, 3.86; N, 14.74. Found: C, 75.65; H, 3.59; N, 14.67.

Preparation of 1. Compound **1** was synthesized in 82% yield by laying a toluene solution (7 mL) of **L1** (7.5 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSO_3CF_3$ (14.4 mg, 0.06 mmol): IR (KBr pellet) ν (cm^{-1}) = 3300 (s), 3200 (m), 1620 (s), 1590 (m), 1510 (s), 1400 (s), 1360 (m), 1300 (vs), 1250 (vs), 1230 (vs), 1170 (s), 1020 (s), 890 (m), 750 (s). Anal. Calcd for $C_{47}H_{30}Ag_2F_6N_6O_{12}S_2$: C, 44.60; H, 2.37; N, 6.64. Found: C, 44.51; H, 2.21; N, 6.55.

Preparation of 2. Compound **2** was synthesized in 68% yield by laying a toluene solution (7 mL) of **L1** (7.5 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgClO_4$ (12.75 mg, 0.06 mmol): IR (KBr pellet) ν (cm^{-1}) = 3449 (s), 3200 (w), 1625 (s), 1520 (m), 1388 (s), 1358 (s), 1144 (s), 1117 (s), 1083 (s), 891 (s), 747 (s), 630 (s). Anal. Calcd for $C_{15}H_{10}AgClN_2O_6$: C, 39.34; H, 2.18; N, 6.13. Found: C, 39.17; H, 2.11; N, 6.09.

Preparation of 3. Compound **3** was synthesized in 84% yield by laying a toluene solution (7 mL) of **L1** (7.5 mg, 0.03 mmol) over a benzene solution (10 mL) of $AgSbF_6$ (20.6 mg, 0.06 mmol). IR (KBr pellet) ν (cm^{-1}) = 3450 (s), 3200 (w), 1642 (s), 1557 (s), 1467 (s), 1430 (s), 1358 (s), 1225 (s), 1150 (s), 1071 (s), 1027 (s), 932 (s), 881 (s), 667 (s). Anal. Calcd for $C_{24}H_{21}AgF_6N_2O_3Sb$: C, 39.61; H, 2.61; N, 3.84. Found: C, 39.34; H, 2.39; N, 3.81.

Preparation of 4. Compound **4** was synthesized in 84% yield by laying a toluene solution (7 mL) of **L2** (8.0 mg, 0.028 mmol) over a benzene solution (10 mL) of $AgSO_3CF_3$ (13.0 mg, 0.056 mmol): IR (KBr pellet) ν (cm^{-1}) = 3449 (s), 3320 (s), 2247 (s), 1615 (s), 1482 (s), 1449 (s), 1409 (s), 1364 (s), 1253 (vs), 1163 (s), 1030 (s), 933 (w), 882 (m), 850 (s), 747 (s), 646 (s). Anal. Calcd for $C_{19}H_{11}AgF_3N_3O_4S$: C, 42.05; H, 2.03; N, 7.75. Found: C, 42.25; H, 2.43; N, 7.61.

Preparation of 5. Compound **5** was synthesized in 71% yield by laying a toluene solution (7 mL) of **L3** (8.0 mg, 0.028 mmol) over a benzene solution (10 mL) of $AgSO_3CF_3$ (13.0 mg, 0.056 mmol): IR (KBr pellet) ν (cm^{-1}) = 3446 (s), 3223 (s), 2231 (s), 1632 (s), 1540 (s), 1515 (s), 1481 (s), 1398 (s), 1359 (s), 1266 (vs), 1177 (s), 1034 (s), 882 (s), 804 (m), 755 (s), 646 (s). Anal. Calcd for $C_{19}H_{13}AgF_3N_3O_5S$: C, 40.70; H, 2.32; N, 7.50. Found: C, 40.45; H, 2.29; N, 7.48.

Crystallography. Suitable single crystals of **L1** and **1**−**5** 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, λ = 0.710 73 Å). The raw frame data for **L1** and **1**−**5** were integrated into SHELX-format reflection files and corrected for Lorentz and polarization effects using SAINT.[28] Corrections for incident and diffracted beam absorption effects were applied using SADABS.[28] There was no evidence of crystal decay during data collection for any compound. The final unit cell parameters were determined by the least-squares refinement of all reflections from each data set with $I > 5\sigma(I)$ (3571 for **L1**, 10 057 for **1**, 3343 for **2**, 5763 for **3**, 3670 for **4**, 3873 for **5**). 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.[28] Crystal data, data collection parameters, and refinement statistics for **L1** and **1**−**5** are listed in Tables 1 and 2. Relevant interatomic bond distances and bond angles for them are given in Table 3.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) *SMART Version 5.624, SAINT Version 6.02, SADABS, and SHELXTL Version 5.1*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.