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Silver(I) Complexes with Dithioether Ligands: Syntheses, Crystal Structures, and Fluorescence Properties

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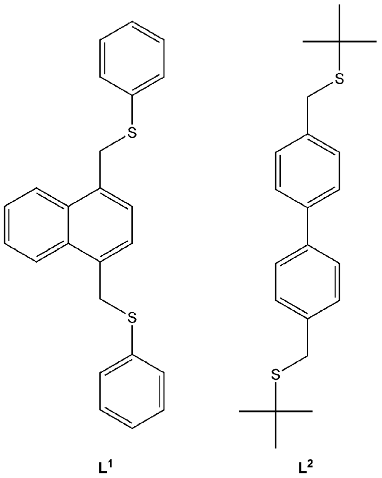
Abstract. Two new dithioether ligands, 1,4-bis[(phenylsulfanyl)methyl]naphthalene (**L**^{1}), and 4,4'-bis[(*tert*-butylsulfanyl)methyl]biphenyl (**L**^{2}) were synthesized and their silver(I) complexes were studied. Both Ag^I complexes, [Ag**L**^{1}(NO$_3$)]$_n$ (**1**) and [Ag**L**^{2}(NO$_3$)]$_2$ (**2**), were synthesized at ambient temperature and characterized by elemental analysis, IR spectroscopy, and single-crystal X-ray diffraction analysis. Single-crystal X-ray analysis shows that complex **1** has a one-dimensional helical chain structure with the neutral repeating unit [Ag(μ_2-**L**^{1})(NO$_3$)], whereas complex **2** has a centrosymmetrical neutral dinuclear structure. Moreover, complexes **1** and **2** are further extended into three-dimensional supramolecular frameworks by hydrogen bonding and π–π stacking interactions, respectively. In addition, complexes **1** and **2** display strong blue emission in the solid state at room temperature.

1. Introduction

The rational design of supramolecular polymeric architectures has attracted considerable interest by chemists, not only because of their intrinsic aesthetic appeal, but also because of their potentially exploitable properties.[1] The combination of organic ligand "spacers" and metal ion "nodes" is regarded as the most common synthetic approach to produce such coordination architectures.[2] The supramolecular chemistry of silver(I) coordination assemblies is a dynamic, thriving field that has drawn ever increasing research interests during the last decade. The silver(I) ion is a favorable and fashionable connecting node for the construction of coordination polymers due to its coordination diversity and flexibility, and it shows positive coordination tendency with sulfur donors.[3]

Dithioether ligands with flexible or rigid spacers are successfully used to construct various structures of complexes including discrete molecules and one-dimensional (1D), two-dimensional (2D) and three-dimensional (3D) coordination polymers.[4] In order to enrich the coordination chemistry of silver(I) ion, two new semi-rigid dithioether ligands, 1,4-bis[(phenylsulfanyl)methyl]naphthalene (**L**^{1}), and 4,4'-bis[(*tert*-butylsulfanyl)methyl]biphenyl (**L**^{2}) (Scheme 1), and two new silver(I) complexes of these ligands, [Ag**L**^{1}(NO$_3$)]$_n$ (**1**) and [Ag**L**^{2}(NO$_3$)]$_2$ (**2**), are synthesized and characterized. We report herein the syntheses and crystal structures of these Ag^I complexes. In addition, the photoluminescent properties of these complexes were also studied in the solid state at room temperature.



Scheme 1. Two new semirigid dithioether ligands **L**^{1} and **L**^{2}.

2. Experimental Section

2.1. Materials and Ggeneral Methods

All commercially available reagents for synthesis and analyses were of analytical grade and used as received without further purification. Elemental analyses (C, H, and N) were performed with a Perkin–Elmer 240C analyzer. IR spectra were measured with a TENSOR 27 (Bruker) FT-IR spectrometer with KBr pellets in the range 4000–400 cm^{-1}. ^{1}H NMR spectra were recorded with a Bruker AC-P500 spectrometer (300 MHz) in CDCl$_3$ medium at 25 °C with tetramethylsilane as the internal reference. Solid-state fluorescence spectra were recorded with a Cary Eclipse spectrofluorometer (Varian) equipped with a xenon lamp and quartz carrier at room temperature.

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2.2. Synthesis of Ligands L^1 and L^2

1,4-Bis[(phenylsulfanyl)methyl]naphthalene (L^1): 1,4-Bis(bromomethyl)naphthalene (3.14 g, 0.01 mol) was added to a hot solution (about 50 °C) of thiophenol sodium salt (2.64 g, 0.02 mol) in ethanol (30 mL), and the mixture was further stirred at 50 °C for 6 h. After cooling, water (30 mL) was added and the resulting mixture was left to stand for 5 h. The yellow precipitate was filtered off, washed with ethanol and water, and recrystallized from a mixture of chloroform and diethyl ether to obtain a light yellow powder.[5] Yield 80 %. M.p.: 132–134 °C. $C_{24}H_{20}S_2$: calcd. C 77.37; H 5.41 %; found: C 77.52; H 5.49 %. **^{1}H NMR:** δ = 4.54 (s, 4 H, –S–CH_2–), 7.19–7.35 (m, 12 H, Ar), 7.57–7.61 (d, 2 H, Ar), 8.18–8.21 (d, 2 H, Ar). **IR** (KBr): $\tilde{\nu}$ = 1585 m, 1480 vs, 1439 s, 1221 m, 1090 v, 1024 m, 854 m, 774 vs, 763 m, 734 vs, 700 m, 688 vs, 472 m cm^{-1}.

4,4'-Bis[(*tert*-butylsulfanyl)methyl]biphenyl (L^2): L^2 was synthesized by the similar procedure as described above. To the hot ethanol solution (30 mL, 50 °C) of *tert*-butylthiol sodium salt (2.24 g, 0.02 mol), 4,4'-bis(chloromethyl)biphenyl (2.51 g, 0.01 mol) was added. The mixture was further stirred at 50 °C for 4 h. After cooling, water (30 mL) was added and left to stand for 2 h. The colorless precipitate was filtered off, washed with water and ethanol, and recrystallized from a mixture of chloroform and diethyl ether to obtain a white powder.[5] Yield 75 %. M.p.: 120–122 °C. $C_{22}H_{30}S_2$: calcd. C 73.68; H 8.43 %; found: C 73.42; H 8.51 %. **^{1}H NMR:** δ = 1.38 (s, 18 H, –S–$C(CH_3)_3$), 3.80 (s, 4 H, S–CH_2–Ar), 7.39 (d, 4 H, Ar), 7.49–7.52 (m, 4 H, Ar). **IR** (KBr): $\tilde{\nu}$ = 2361m, 1559w, 1541w, 1457s, 1364m, 1163s, 881m, 830 w, 745 w, 563 w cm^{-1}.

2.3. Synthesis of Complexes 1 and 2

$[AgL^1(NO_3)]_n$ (1): A buffer layer of a solution (5 mL) of chloroform and methanol (v/v = 1:1) was carefully layered over a chloroform (5 mL) solution of L^1 ligand (0.1 mmol) in a test tube. Afterwards, a solution of $AgNO_3$ (0.1 mmol) in methanol (5 mL) was layered over the buffer layer and left undisturbed in room temperature in the dark. Finally, light yellow single crystals were harvested after about four weeks. Yield 60 % (based on ligand). $C_{24}H_{20}AgNO_3S_2$: calcd. C 53.14; H 3.72; N 2.58 %; found: C 53.35; H 3.81; N 2.37 %. **IR** (KBr): $\tilde{\nu}$ = 1473 m, 1442 s, 1385 vs, 1301 vs, 1255 m, 1154 m, 1070 w, 1023 w, 1001 m, 877 w, 837 m, 776 s, 751 vs, 691 s, 501 m cm^{-1}.

$[AgL^2(NO_3)]_2$ (2): Complex **2** was synthesized by the similar method to that of **1**. Yield 65 % (based on ligand). $C_{44}H_{60}Ag_2N_2O_6S_4$: calcd. C 50.00; H 5.72; N 2.65 %; found: C 50.17; H 5.63; N 2.46 %. **IR** (KBr): $\tilde{\nu}$ = 2961 m, 1496 w, 1458 m, 1437 m, 1385 vs, 1369 s, 1317 s, 1167 m, 1004 w, 822 m, 739 w cm^{-1}.

2.4. X-ray Crystallography

Single crystal X-ray diffraction was carried out with a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator at 293(2) K with Mo-K_α radiation (λ = 0.71073 Å) by ω scan mode. Unit cell dimensions were obtained with least-squares refinements and semi-empirical absorption corrections were applied using SADABS program.[6] The structure was solved by direct method.[7] The Ag^I ions were located from E-maps and the other non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinement was performed by full-matrix least-squares methods on F^2 by SHELXL-97 program package.[7] Hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on the parent atoms. Crystallographic data and experimental details for structural analysis are summarized in Table 1, and selected bond lengths and angles are presented in Table 2 and Table 3.

Table 1. Crystal data and structure refinement parameters for complexes **1** and **2**.

	1	**2**
Chemical formula	$C_{24}H_{20}AgNO_3S_2$	$C_{22}H_{30}AgNO_3S_2$
Formula weight	542.40	528.46
Space group	*C*2/*c*	$P\bar{1}$
a /Å	22.492(3)	9.7501(6)
b /Å	10.8855(2)	11.1392(7)
c /Å	18.331(3)	12.9793(8)
α /deg	90	92.349(3)
β /deg	101.308(2)	110.154(3)
γ /deg	90	114.948(3)
V /Å^3	4400.9(1)	1170.8(1)
Z	8	2
D /g·cm^{-3}	1.637	1.499
μ /mm^{-1}	1.132	1.061
R $^{a)}$ / wR $^{b)}$	0.0366 / 0.0854	0.0203 / 0.0553

a) $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. b) $Rw = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond lengths /Å and angles /° for complex **1**.

Ag(1)–S(1)	2.4963(9)
Ag(1)–O(1)	2.489(2)
Ag(1)–S(2)	2.4632(9)
S(2)–Ag(1)–S(1)	146.73(3)
S(2)–Ag(1)–O(1)	117.92(6)
O(1)–Ag(1)–S(1)	93.64(6)

Table 3. Selected bond lengths /Å and angles /° for complex **2**.

Ag(1)–S(1)	2.4838(5)
Ag(1)–O(1)	2.4294(2)
Ag(1)–S(2)	2.4687(5
S(2)–Ag(1)–S(1)	134.22(2)
S(2)–Ag(1)–O(1)	114.14(5)
O(1)–Ag(1)–S(1)	109.67(5)

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained on quoting the depository numbers CCDC-771944 (**1**) and CCDC-771945 (**2**). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk).

Supporting Information (see footnote on the first page of this article): ORTEP plots of **1** and **2.** Emission and excitation spectra of L^1 and L^2 in the solid state at room temperature.

3. Results and Discussion

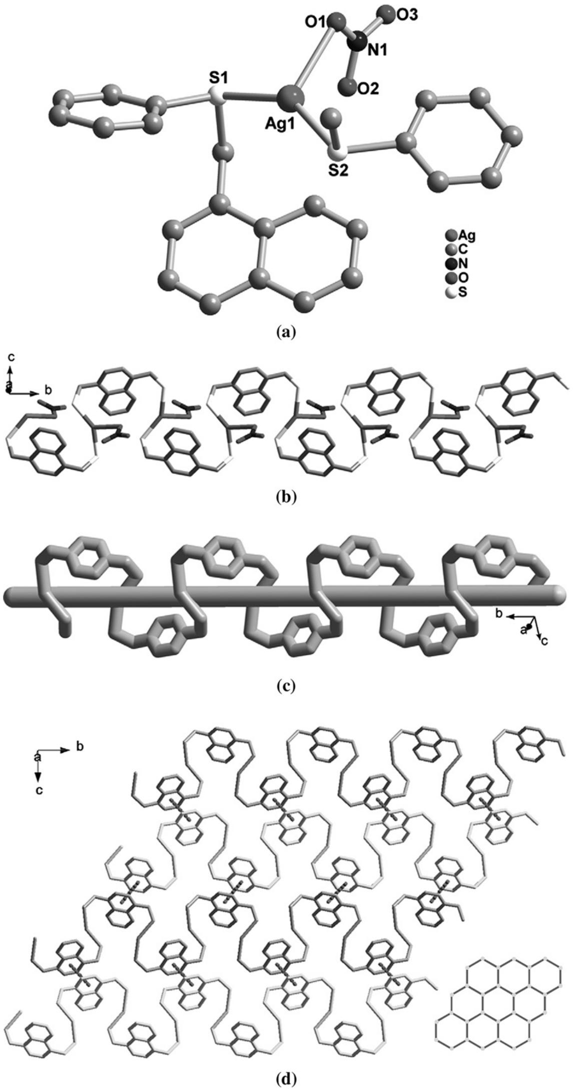
3.1. Synthesis and General Characterizations

Generally, properly lowering the reaction speed may facilitate the slow growth of well-shaped larger single crystals suitable for X-ray diffraction. Considering this point, the synthesis and isolation of **1** and **2** in this work were carried out through self-assembly reaction of **L** with $AgNO_3$ by using the slow diffusion method in a test tube under mild conditions of ambient temperature and pressure. The IR spectra of **1** and **2** shows absorption bands resulting from the skeletal vibrations of the aromatic rings in the 1400–1600 cm^{-1} range, and the spectra of **1** and **2** exhibit strong absorption bands at 1385 cm^{-1} because of the stretch of the NO_3^- anions, which is in agreement with the X-ray analysis.[8]

3.2. Description of the Crystal Structures

*3.2.1. [Ag**L**^{1}(NO$_3$)]$_n$ (**1**)*

Single-crystal X-ray analysis shows that complex **1** has a one-dimensional polymeric structure with the neutral [Ag(μ_2-**L**^{1})(NO_3)] as repeating unit (Figure 1). In the neutral chain, there is one crystallographic independent silver(I) atom, which adopts slightly distorted trigonal planar coordination arrangement coordinated by two sulfur donors from distinct **L**^{1} ligands and one oxygen donor from NO_3^- anion. The Ag^I atom deviates from the coordination plane by ca. 0.173 Å. All Ag–donor bond lengths (Table 2) are within the normal range for such coordination bonds,[9] and the bond angles around Ag^I atoms range from 93.64(6) to 146.73(3)°.



(a)

(b)

(c)

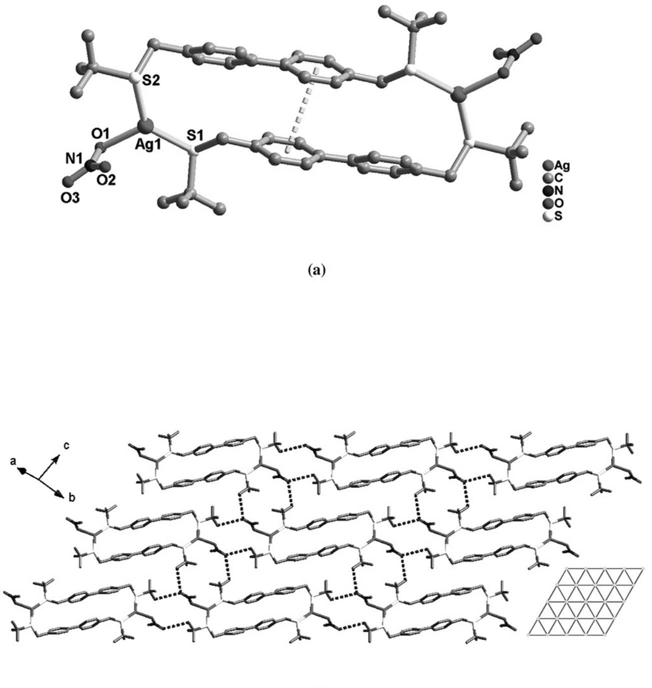
(d)

Figure 1. (a) Coordination environment of Ag^I in **1** with all hydrogen atoms omitted for clarity; (b) and (c) 1D helical chain along *b* direction in **1**; (d) 2D plane formed through the face-to-face π–π stacking interactions in **1** (some of the **L**^{1} ligands and nitrate anions were omitted for clarity); schematic view of the 2D (3^6) network.

In **1**, the **L**^{1} ligands adopt bidentate bridging mode to coordinate to Ag^I atoms using two sulfur donors to form a 1D helical chain along *b* direction (the helical pitch, given by one full rotation around the 2_1 screw axis, is 10.886 Å) (Figure 1b, c). Along the spiral chain, the intramolecular separation of Ag···Ag is 5.636 Å. And all **L**^{1} ligands adopt a *syn* configuration with the two coordinated sulfur atoms distances of 7.462 Å. In the chain, the adjacent two naphthalene rings on opposite sides of silver(I) atoms are not parallel to each other with the dihedral angle of 25.6°. The interplanar distance between two neighboring parallel naphthalene rings of the adjacent chains is ca. 3.45 Å, which indicates the presence of face-to-face π–π stacking interactions that pack the 1D chains into a two-dimensional supramolecular architecture (Figure 1d). From the topological point of view, this 2D network can be regarded as a three-connected net with (3^6) topology, in which the **L**^{1} ligands all act as three-connecting nodes (Figure 1d). In addition, there are C–H···O interactions between the carbon atoms in the benzene ring of **L**^{1} and the uncoordinated oxygen atoms of NO_3^- ($d_{C\cdots O}$ = 3.385–3.509 Å), which enhance the stability of **1**, and these interactions further assemble adjacent two-dimensional architecture mentioned above to form a three-dimensional supramolecular framework.

*3.2.2. [Ag**L**^{2}(NO$_3$)]$_2$ (**2**)*

The molecular structure of the centrosymmetrical neutral dinuclear complex **2** is shown in Figure 2a. The silver(I) ion is three-coordinate to two sulfur atoms of two distinct **L**^{2} and one oxygen atom from the coordinated nitrate to form a slightly distorted trigonal planar arrangement. The Ag^I atom deviates from the coordination plane defined by two coordinated sulfur atoms and one oxygen atom from nitrate anion by ca. 0.197 Å. The selected bond lengths and angles are listed in Table 3. In **2**, two **L**^{2} ligands bridge two Ag^I atoms to form a dinuclear structure containing 26-membered ring, in which the Ag···Ag distance is 13.621 Å. And both **L**^{2} ligands adopt a *trans* configuration with the two coordinated sulfur atoms distances of 12.004 Å. In the crystal structure of **2**, the two benzene rings of one **L**^{2} ligand are not parallel to each other with the dihedral angle of 32.9°. However, the corresponding benzene rings between the two **L**^{2} ligands in one molecule are parallel to each other and the interplanar distance between two neighboring parallel benzene rings in **2** is ca. 3.33 Å, which indicates the presence of face-to-face π–π stacking interactions that enhance the stability of the molecule.



(a)

(b)

Figure 2. (a) Molecular structure of the dinuclear complex **2**; (b) 2D plane formed by intermolecular hydrogen bonds interactions in **2**; schematic view of the 2D (6^3) network.

In the crystal net, as shown in Figure 2b, the neutral molecules of **2** are bound together by intermolecular hydrogen bonds to create a two-dimensional plane. The hydrogen bonding system in **2** consists of the uncoordinated oxygen atom on nitrate with the hydrogen atoms on the tertiary butyls of two neighboring molecules. The O$\cdots$H distances are 2.583 and 2.593 Å, the corresponding C$\cdots$O distances are 3.474 and 3.541 Å and the C–H$\cdots$O angles are 154.43 and 169.18°, respectively. From the topological point of view, the 2D network mentioned above can be regarded as a six-connected net with (6^3) topology, in which the dinuclear units all act as six-connecting nodes (Figure 2b). In addition, there are other C–H$\cdots$O interactions between the carbon atoms in $\mathbf{L^2}$ and the oxygen atoms of NO_3^- ($d_{C\cdots O}$ = 3.521–3.542 Å), which enhance the stability of **2**, and these interactions further assemble adjacent two-dimensional architecture mentioned above to form a three-dimensional supramolecular framework. It is no doubt that these hydrogen bonding interactions contribute significantly to the alignment of the molecules of **2** in the crystalline state.

3.3. Photoluminescence Properties

Luminescent compounds are currently of great interest because of their potential applications in chemical sensors, photochemistry, and electroluminescent (EL) displays.[10] It is universally acknowledged that many d^{10} complexes exhibit excellent luminescence properties.[11] To examine the luminescent properties of the d^{10} metal complexes, the excitation and emission spectra of **1** and **2** in the solid state at room temperature were studied, and are shown in Figure 3 and Figure 4, respectively. It can be observed that complex **1** exhibits blue photoluminescence with emission bands at 362(max), 423, 439, and 486 nm upon excitation at 264 nm, and complex **2** exhibits blue photoluminescence with emission bands at 421 nm with a small shoulder at 407 nm upon excitation at 357 nm. To further analyze the nature of these emission bands mentioned above, the photoluminescent properties of the ligands $\mathbf{L^1}$ and $\mathbf{L^2}$ were also explored at the same testing conditions. The free $\mathbf{L^1}$ molecule exhibits an intense emission peak at 431 nm, with shoulder bands at 455, 512, and 563 nm upon excitation at 365 nm, whereas the $\mathbf{L^2}$ molecule displayed emission peaks at 508 nm with a shoulder at 488 nm upon excitation at 300 nm. By comparing the locations and profiles of their excitation/emission peaks with the corresponding complexes **1** and **2**, we can presume that emission peaks in the range of ca. 360–490 nm for both complexes should originate

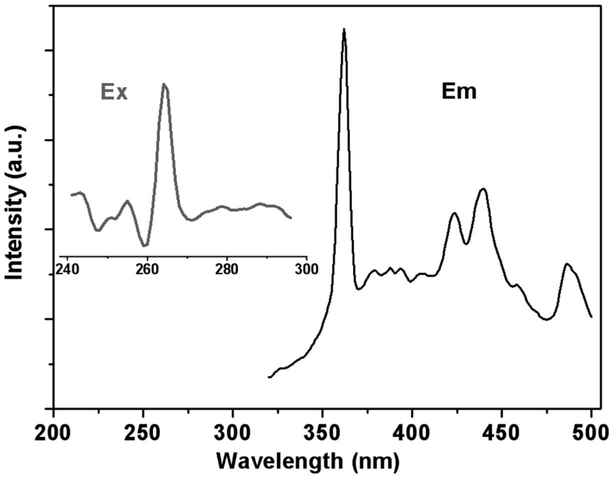


Figure 3. Emission and excitation spectra of **1** in the solid state at room temperature (the excitation and emission wavelengths are 264 and 362 nm, respectively).

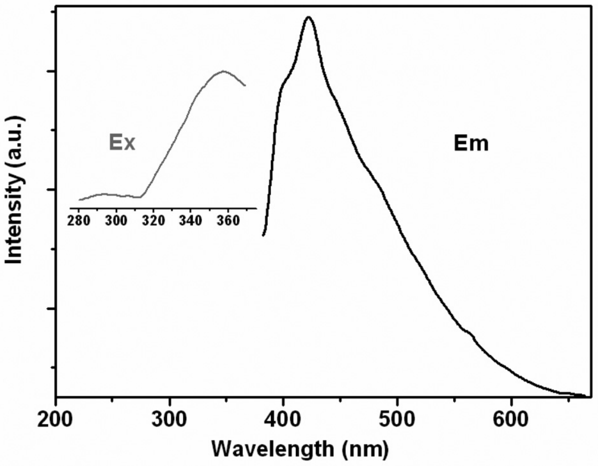


Figure 4. Emission and excitation spectra of **2** in the solid state at room temperature (the excitation and emission wavelengths are 357 and 421 nm, respectively).

from intraligand π→π* transitions mainly through the naphthalene, benzene and biphenyl rings of ligands, namely ligand-to-ligand charge transfer (LLCT).[12] In comparison with the free ligands, the blue-shifts of the luminescence emission in **1** and **2** are presumably a result of coordination of the relevant ligands to a metal atom, which effectively increase the rigidity and asymmetry of the ligands and thereby reduce the non-radiative decay of the intraligand (π→π*) excited state.[12]

4. Conclusions

Two new semirigid dithioether ligands, $\mathbf{L^1}$ and $\mathbf{L^2}$, and two new Ag^I complexes of these ligands were synthesized and characterized. The structure analysis shows that complex **1** has a one-dimensional helical chain structure, whereas complex **2** has a centrosymmetrical neutral dinuclear structure. π–π Stacking interactions and hydrogen bonding exist in the crystal nets of **1** and **2**, and both complexes are further extended into three-dimensional supramolecular frameworks by these interactions, respectively. The blue emission of the compounds suggests that they may be potential candidates for blue-light emitting materials.

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