

# Assembly of luminescent Ag(I) coordination architectures adjusted by modification of pyrimidine-based thioether ligands

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## Abstract

Two new structurally related pyrimidine-based thioether ligands, angular ditopic ligand 1,3-bis(2-pyrimidinylthiomethyl)benzene ( $L^2$ ) and linear ditopic ligand 1,4-bis(2-pyrimidinylthiomethyl)benzene ( $L^3$ ), have been designed and prepared. Reaction of two shaped-specific ligands with different silver(I) salts affords three novel luminescent coordination architectures: discrete metallomacrocyclic  $[Ag_4(L^2)_2(NO_3)_4] \cdot 2MeOH$  (**3**), 1D chain  $\{[Ag_2L^3(NO_3)_2] \cdot 2CCl_3\}_n$  (**4**) and 2D wire netlike structure  $\{[AgL^3(DMF)] \cdot ClO_4 \cdot 0.25H_2O\}_n$  (**5**). The results show that the nature of organic ligands, geometric requirement of metal atoms and counter anions have great influence on the structures of metal-organic frameworks.

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## 1. Introduction

The designed construction of metal-organic frameworks (MOFs), obtained by metal-directed self-assembly from labile metal centers and multidentate bridging ligands, is a rapidly developing area of supramolecular chemistry. Besides the aesthetic structural and fascinating functional motifs, they are of interest both for understanding the mechanisms of the assembly process and for the host-guest chemistry associated with their large central cavities [1,2]. The structural topology of polymeric networks can be regarded as a programmed system in which the stereo and interactive information stored in the ligands is read by the labile metal ions through the algorithm defined by their coordination geometry.

Hence, the selection or design of suitable ligands containing certain features, such as flexibility and versatile binding modes, is crucial for the construction of specific supramolecular architectures. This concept has been demonstrated by a great variety of structural topologies of discrete supramolecular complexes or infinite supramolecular arrays [3–9], such as molecular ring and grids as well as helices. In this respect, we believe that the introduction of chemical interaction sites in flexible bridging ligands is a challenging subject in developing new discrete and polymeric systems. Accordingly, the aesthetic structural and fascinating functional motifs may be obtained.

Currently, we mainly investigate sulfur-containing ligands due to their useful photoelectrical properties [10]. For the design of new coordination architectures with sulfide interaction sites, we have developed a convenient method for syntheses of flexible thioether-heterocyclic ligands possessing rich structural information, and a

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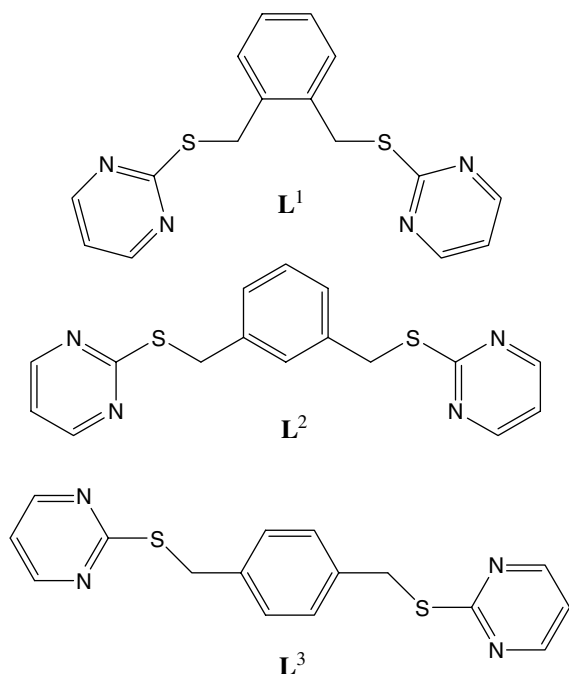
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series of interesting structures have been obtained, such as nanometer-sized cube, tube, single-stranded helical chain, and two-dimensional lamellar network [11]. In our continuing efforts to systematically investigate the effects of the linker units of flexible ligands on the structures of silver(I) complexes with thioether, herein, we wish to report the design of two new structurally related pyrimidine-based thioether ligands, 1,3-bis(2-pyrimidinylthiomethyl)benzene ( $L^2$ ) and 1,4-bis(2-pyrimidinylthiomethyl)benzene ( $L^3$ ) (Scheme 1), and the syntheses, crystal structures and luminescent properties of their novel silver(I) coordination architectures with discrete metallomacrocyclic, 1D chain and 2D wire net-like structures adjusted by ligand modifications.

## 2. Experimental

### 2.1. Materials and physical techniques

All chemicals were of reagent grade and used as commercially obtained without further purification. Elemental analyses (C, H, N) were performed on a Perkin–Elmer model 240C automatic instrument. IR spectra were recorded on a Magna 750 FT-IR spectrophotometer with KBr pellet.  $^1\text{H}$  NMR was measured on a Bruker AM500 spectrometer with  $\text{SiMe}_4$  as the internal reference. Fluorescence spectroscopy was performed on an Edinburgh Analytical instrument FLS920.



Scheme 1.

### 2.2. Synthesis of the ligand $L^2$

2-Mercaptopyrimidine (1.12 g, 10 mmol) was added to a stirred solution of KOH (0.56 g, 10 mmol) in ethanol (20 ml). After 30 min, 1,3-bis(bromomethyl)benzene (1.32 g, 5 mmol) was added and the mixture was heated to 70 °C for 6 h with vigorous stirring. After adding additional water (30 ml), the mixture was left to stand overnight. The precipitate was filtered off and washed with ethanol and water, giving a fine white powder in 85% yield. *Anal.* Calc. for  $\text{C}_{16}\text{H}_{14}\text{N}_4\text{S}_2$ : C, 58.87; H, 4.32; N, 17.16. Found: C, 58.68; H, 4.45; N, 17.09%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  4.397 (s, 4H,  $-\text{SCH}_2-$ ), 6.961–6.980 (t,  $J_1 = 4.5$  Hz,  $J_2 = 5$  Hz, 1H, ph), 7.227–7.263 (m,  $J_1 = 8.5$  Hz,  $J_2 = 7$  Hz,  $J_3 = 2.5$  Hz, 2H, pym), 7.315–7.329 (d,  $J = 7$  Hz, 2H, ph), 7.519 (s, 1H, ph), 8.517–8.526 (d,  $J = 4.5$  Hz, 4H, pym). IR (KBr)  $\nu$ : 3043 (w), 2985 (w), 2926 (w), 1574 (vs), 1549 (vs), 1375 (vs), 1203 (s), 1169 (s), 793 (m), 769 (s), 715 (s), 631 (m)  $\text{cm}^{-1}$ .

### 2.3. Synthesis of the ligand $L^3$

Reaction of 1,4-bis(bromomethyl)benzene (1.32 g, 5 mmol) and 2-mercaptopyrimidine (1.12 g, 10 mmol) as described above for  $L^2$ , giving compound  $L^3$  as a white powder in 90% yield. *Anal.* Calc. for  $\text{C}_{16}\text{H}_{14}\text{N}_4\text{S}_2$ : C, 58.87; H, 4.32; N, 17.16. Found: C, 58.73; H, 4.40; N, 17.04%.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz): 4.395 (s, 4H,  $-\text{SCH}_2-$ ), 6.980–6.999 (t,  $J_1 = 4.5$  Hz,  $J_2 = 5$  Hz, 2H, pym), 7.376 (s, 4H, ph), 8.531–8.540 (d,  $J = 4.5$  Hz, 4H, pym). IR (KBr)  $\nu$ : 3033 (w), 2981 (w), 1564 (vs), 1548 (vs), 1375 (vs), 1195 (s), 1170 (s), 804 (m), 771 (s), 746 (m), 690 (m), 630 (m)  $\text{cm}^{-1}$ .

### 2.4. Synthesis of $[\text{Ag}_4(\text{L}^2)_2(\text{NO}_3)_4] \cdot 2\text{MeOH}$ (3)

A solution of  $\text{AgNO}_3$  (34 mg, 0.2 mmol) in 10 ml of MeOH was carefully layered on top of a solution of  $L^2$  (33 mg, 0.1 mmol) in 5 ml of  $\text{CHCl}_3$  in a test tube. After 3 days at room temperature, colorless prism single crystals appeared at the boundary between  $\text{CH}_3\text{OH}$  and  $\text{CHCl}_3$ . Yield: 70%. *Anal.* Calc. for  $\text{C}_{34}\text{H}_{36}\text{Ag}_4\text{N}_{12}\text{O}_{14}\text{S}_4$ : C, 29.24; H, 2.60; N, 12.04. Found: C, 29.43; H, 2.71; N, 12.12%. IR (KBr)  $\nu$ : 3467 (m), 3035 (w), 2925 (w), 2374 (w), 1632 (m), 1566 (s), 1548 (s), 1382 (vs), 1200 (m), 1170 (m), 1020 (w), 748 (w), 630 (w)  $\text{cm}^{-1}$ .

### 2.5. Synthesis of $\{\text{Ag}_2\text{L}^3(\text{NO}_3)_2\} \cdot 2\text{CCl}_3$ (4)

A solution of  $\text{AgNO}_3$  (34 mg, 0.2 mmol) in 10 ml of MeOH was carefully layered on top of a solution of  $L^3$  (33 mg, 0.1 mmol) in 5 ml of  $\text{CHCl}_3$  in a test tube. After 7 days at room temperature, colorless prism single crystals

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