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Construction of Pyridinethiolate-Bridged 2D and 3D Coordination Networks of d^{10} Metal Halides via Solvothermal *in Situ* Disulfide Cleavage Reactions

Jing Wang, Yue-Hua Zhang, Hao-Xiang Li, Zhuo-Jia Lin, and Ming-Liang Tong*

MOE Key Laboratory of Bioinorganic and Synthetic Chemistry, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

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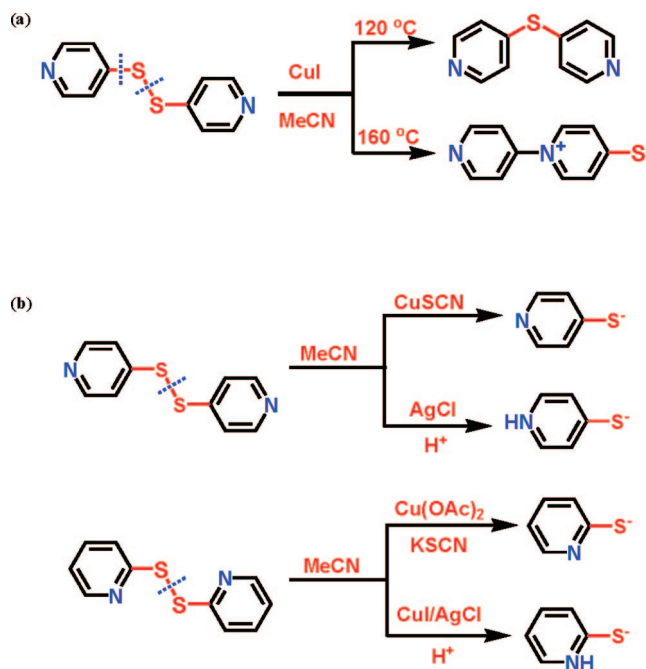
ABSTRACT: Five new pyridinethiolate-bridged 2D and 3D coordination networks of d^{10} metal halides formulated with $[\text{Cu}_2(\text{SCN})(4\text{-pyt})]$ (**1**), $[\text{Ag}_2\text{Cl}_2(4\text{-pytH})]$ (**2**), $[\text{Cu}_5(\text{SCN})_3(2\text{-pyt})_2]$ (**3**), $[\text{Cu}_4\text{I}_4(2\text{-pytH})]$ (**4**), and $[\text{Ag}_3\text{Cl}_3(2\text{-pytH})_2]$ (**5**) (4-pyt = 4-pyridinethiolate, 2-pyt = 2-pyridinethiolate) have been solvothermally synthesized, in which the pyt or pytH ligands were generated via *in situ* cleavage of S–S bonds of 4,4'-dithiodipyridine (4-dtdp) or 2,2'-dithiodipyridine (2-dtdp) in the presence of Cu(I) or Ag(I) ions. Complexes **1** and **3** are a 3D coordination network, constructed with the interesting inorganic Cu–S coordination layers in a (6,3) topology net bridged by the 4-pyt and SCN ligands for **1** and constructed with the $(\text{CuSCN})_n$ layers linked by the 2-pyt-supported (Cu_6S_6) units for **3**. Complexes **2**, **4**, and **5** are 2D coordination layer structures, which are constructed with 1D $(\text{AgCl})_n$ ladder chains linked by $[\text{Ag}_2(4\text{-pytH})_2]$ bridges for **2**, with double step-ladder and zigzag $(\text{Cu})_n$ chains linked by μ_3 -2-pytH bridges for **4**, and with the $(\text{Ag}_5\text{S}_2\text{Cl}_2)_n$ double step-ladder chains linked by the μ_2 -Cl atoms for **5**. The fluorescent properties of the three as-synthesized copper(I) complexes were studied in the solid state at room temperature.

Introduction

As a very important research field in both coordination chemistry and organic chemistry, *in situ* metal/ligand reactions have been extensively investigated for many decades for the discovery of new organic reactions and the elucidation of reaction mechanisms, as well as the generation of novel coordination compounds, especially for those that are inaccessible in direct preparation from the ligands.¹ The hydro (solvo)-thermal method has been widely adopted in the preparations of new metal–organic frameworks (MOFs).² High-temperature solvothermal *in situ* metal/ligand reactions in the presence of transition-metal ions may not only provide a good chance for the synthesis of functional coordination polymers in the context of crystal engineering but also allow access to new materials that are not easily obtainable via conventional methods. Many novel materials with different potential applications have been prepared from ligand reactions, including the hydrolysis of carboxylate esters, organic nitriles, and aldehydes into the corresponding carboxylates; the cleavage of acetonitrile/ethylene carbon–carbon bonds and 1,3,4-oxadiazole carbon–nitrogen/carbon–oxygen bonds;³ the cleavage and formation of disulfide bonds;⁴ the substitution of aromatic groups;⁵ and the decarboxylation of aromatic carboxylates.⁶ Here, we utilize these kinds of relatively straightforward ligand reactions to prepare new MOFs exhibiting different porosity, photoluminescence, and other physical properties.²

Pyridinethiones have attracted considerable interest in coordination chemistry as potentially ambidentate or multifunctional ligands via the exocyclic sulfur atoms and/or heterocyclic nitrogen atom donor due to their relevance in biological systems.⁷ Dithiodipyridine has recently drawn more and more attention due to not only its twisted conformation^{8a} with a C–S–S–C torsion angle of *ca.* 90° and axial chirality which potentially generates *M*- and *P*-enantiomers^{8b} but also the easy

Scheme 1. Schematic Representation of the *in Situ* Ligand Reactions



cleavage of the S–S bond.^{4a,8c–e} We recently reported three new copper(I) cluster-based coordination networks, $[\text{Cu}_4\text{I}_4(\text{tdp})_2]$, $[\text{Cu}_5\text{I}_5(\text{ptp})_2]$, and $[\text{Cu}_6\text{I}_6(\text{ptp})_2]$ (tdp = 4,4'-thiodipyridine and ptp = 1-(4-pyridyl)-4-thiopyridine), obtained from the solvothermal reactions at different temperatures.¹⁰ The tdp and ptp ligands in these compounds were generated from the *in situ* cleavage and rearrangement reactions of the 4,4'-dithiodipyridine (4-dtdp) ligand in the presence of Cu(I) ions (Scheme 1a). To further investigate hydro(solvo)thermal ligand reactivity⁹ and explore new coordination architectures of the d^{10} metal ion and dithiodipyridine, we report the solvothermal cleavage of S–S bonds for 4,4'-dithiodipyridine (4-dtdp) and 2,2'-dithio-

* Corresponding author. Phone: +86 20 8411-0966. Fax: +86 20 8411-2245. E-mail: tongml@mail.sysu.edu.cn.

Table 1. Crystal Data and Structure Refinements for 1–5

	1	2	3	4	5
empirical formula	C ₆ H ₄ Cu ₂ N ₂ S ₂	C ₅ H ₅ Ag ₂ Cl ₂ NS	C ₃₉ H ₂₄ Cu ₁₅ N ₁₅ S ₁₅	C ₅ H ₅ Cu ₄ I ₄ NS	C ₁₀ H ₁₀ Ag ₃ Cl ₃ N ₂ S ₂
<i>M</i>	295.31	397.80	2136.73	872.97	652.30
crystal system	orthorhombic	monoclinic	monoclinic	monoclinic	orthorhombic
space group	<i>Ama</i> 2	<i>P</i> 2 ₁ / <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>m</i>	<i>Pcca</i>
<i>a</i> /Å	7.3433(13)	4.2314(8)	14.2925(11)	22.106(2)	16.022(3)
<i>b</i> /Å	8.5921(15)	10.732(2)	21.7939(17)	4.1222(4)	4.0404(7)
<i>c</i> /Å	12.889(2)	18.842(4)	19.6890(16)	15.5059(15)	25.154(4)
α /°	90	90	90	90	90
β /°	90	91.697(4)	100.709(2)	97.947(2)	90
γ /°	90	90	90	90	90
vol/Å ³	813.2(2)	855.3(3)	6026.1(8)	1399.4(2)	1628.4(5)
<i>Z</i>	4	4	4	4	4
ρ_{calcd} /g cm ^{−3}	2.412	3.089	2.355	4.143	2.661
μ /cm ^{−1}	5.674	5.373	5.738	14.936	4.308
reflins collected	2172	3237	15036	2998	5158
unique reflins	792	1591	6344	1501	1582
<i>R</i> _{int}	0.0204	0.0144	0.0419	0.0243	0.0257
<i>S</i>	1.096	1.026	1.037	1.051	1.116
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (<i>I</i> > 2σ(<i>I</i>))	0.0204, 0.0483	0.0573, 0.1298	0.0549, 0.1067	0.0708, 0.1937	0.0598, 0.1396
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.0206, 0.0484	0.0618, 0.1330	0.0826, 0.1184	0.0732, 0.1969	0.0705, 0.1457

$$^a R_1 = \sum |F_o| - |F_c| / \sum F_o, \quad ^b wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

dipyridine (2-dtdp) and the formation of five new copper(I) and silver(I) inorganic/organic hybrid networks, [Cu₂(SCN)(4-pyt)] (1), [Ag₂Cl₂(4-pytH)] (2), [Cu₅(SCN)₃(2-pyt)₂] (3), [Cu₄I₄(2-pytH)] (4), and [Ag₃Cl₃(2-pytH)₂] (5) (4-pyt = 4-thiopyridine, 2-pyt = 2-thiopyridine).

Experimental Section

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The C, H, N, and S microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The FT-IR spectra were recorded from KBr tablets in the range 400–4000 cm^{−1} on a Bio-Rad FTS-7 spectrometer. X-ray powder diffraction (XRPD) intensities for 1–5 (Figure S1, Supporting Information) were measured at 293 K on a Bruker D8 Advance Diffractometer (Cu Kα, λ = 1.54056 Å). The polycrystalline powder samples were prepared by crushing the crystals and were scanned from 5 to 60° with a step of 0.1°/s. Calculated patterns of 1–5 were generated with PowderCell. The low-temperature (77 K) electron spin resonance spectrum of complex 3 was recorded on a Bruker ESP 300E spectrometer operating at the X-band (9.1–9.9 GHz) and equipped with a Bruker NMR gaussmeter ER 035 M and a Hewlett-Packard microwave frequency counter. Photoluminescence measurements of complexes 1, 3, and 4 were performed on an Edinburgh FLS-920 spectrophotometer equipped with a continuous Xe-900 Xenon lamp and a μF900 microsecond flash lamp at room temperature.

Solvothermal Synthesis. [Cu₂(SCN)(4-pyt)] (1). CuSCN (0.063 g, 0.5 mmol) and 4-dtdp (0.052 g, 0.25 mmol) were stirred in a MeCN solution for 15 min in air. The mixture was transferred to a 25 mL Teflon reactor, sealed, and heated in an oven to 150 °C for 72 h. After 15 h of gradual cooling to room temperature, orange needle crystals were obtained and then filtered, washed, and dried in the air (yield ca. 45%). Elem anal. calcd (%) C₃H₂CuNS: C 24.40, H 1.37, N 9.49; found: 24.29, H 1.46, N 9.38. IR (KBr, cm^{−1}): 3414(w), 3095(w), 3014(w), 2879(w), 2454(w), 2122(vs), 1585(s), 1478(m), 1415(m), 1311(w), 1214(m), 1107(m), 1057(w), 1020(w), 809(s), 771(w), 718(s), 501(s), 440(w).

[Ag₂Cl₂(4-pytH)] (2). A mixture of AgCl (0.148 g, 1.0 mmol) and 4-dtdp (0.052 g, 0.25 mmol) in a MeCN solution was stirred for 15 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated in an oven to 160 °C for 48 h. After 15 h of gradual cooling to room temperature, gray needle crystals were obtained and then filtered, washed, and dried in the air (yield ca. 52%). Elem anal. calcd (%) C₅H₅Ag₂Cl₂NS: C 15.10, H 1.27, N 3.52; found: C 14.82, H 1.22, N 3.36. IR (KBr, cm^{−1}): 3447(w), 3165(w), 3071(w), 3041(w), 2858(w), 2522(w), 1959(w), 1876(w), 1715(w), 1607(vs), 1575(s), 1460(vs), 1362(w), 1287(w), 1232(w), 1189(s), 1141(m), 1101(s), 1057(w), 1003(w), 894(w), 789(s), 711(s), 641(m), 485(m), 425(m).

[Cu₅(SCN)₃(2-pyt)₂] (3). A mixture of Cu(OAc)₂·H₂O (0.100 g, 0.5 mmol), KSCN (0.049 g, 0.5 mmol), and 2-dtdp (0.052 g, 0.25 mmol) in a MeCN solution was stirred for 15 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated in an oven to 160 °C for 72 h. After 15 h of gradual cooling to room temperature, brown block crystals were obtained and then filtered, washed, and dried in the air (yield ca. 71% based on Cu(OAc)₂·H₂O). Elem anal. calcd (%) C₃₉H₂₄Cu₁₅N₁₅S₁₅: C 21.92, H 1.13, N 9.83; found: 21.69, H 1.28, N 9.75. IR (KBr, cm^{−1}): 3414(w), 3043(w), 2892(w), 2140(vs), 1579(vs), 1549(s), 1449(vs), 1414(vs), 1270(m), 1232(w), 1149(w), 1125(vs), 1084(m), 1047(m), 1009(w), 875(w), 755(vs), 720(s), 619(w), 488(m), 442(m), 415(m). EPR signal (X-band): silent.

[Cu₄I₄(2-pytH)] (4). A mixture of CuI (0.095 g, 0.5 mmol) and 2-dtdp (0.052 g, 0.25 mmol) in a MeCN solution was stirred for 15 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated in an oven to 160 °C for 96 h. After 15 h of gradual cooling to room temperature, orange block crystals were obtained and then filtered, washed, and dried in the air (yield ca. 85% based on CuI). Elem anal. calcd (%) C₆H₅Cu₄I₄NS: C 8.14, H 0.57, N 1.58; found: 7.82, H 0.56, N 1.75. IR (KBr, cm^{−1}): 3182(w), 3121(w), 3075(m), 2929(w), 1585(vs), 1515(s), 1440(s), 1367(s), 1258(s), 1152(m), 1122(s), 1080(w), 1038(w), 1002(w), 877(m), 798(w), 730(vs), 705(s), 474(s), 433(m).

[Ag₃Cl₃(2-pytH)₂] (5). A mixture of AgCl (0.074 g, 0.5 mmol) and 2-dtdp (0.052 g, 0.25 mmol) in a MeCN solution was stirred for 15 min in air, then transferred and sealed in a 25 mL Teflon reactor, which was heated in an oven to 160 °C for 96 h. After 15 h of gradual cooling to room temperature, gray needle crystals were obtained and then filtered, washed, and dried in the air (yield ca. 46% based on AgCl). Elem anal. calcd (%) C₁₀H₂Ag₃Cl₃N₂S₂: C 18.41, H 1.55, N 4.29; found: C 18.27, H 1.40, N 4.22. IR (KBr, cm^{−1}): 3426(w), 3173(w), 3110(w), 3032(m), 2982(m), 2911(m), 2871(m), 1951(w), 1874(w), 1605(m), 1585(vs), 1510(s), 1444(s), 1369(s), 1254(s), 1148(m), 1128(vs), 1040(w), 1000(w), 979(w), 899(m), 863(m), 753(vs), 720(s), 622(m), 480(s), 436(m).

X-Ray Crystallography. Data collection of 1–5 was performed with Mo Kα radiation (λ = 0.71073 Å) on a Bruker Apex CCD diffractometer at 293(2) K. The intensities were integrated with SAINT⁺, which also applied corrections for Lorentz and polarization effects. Absorption corrections were applied by using the multiscan program SADABS.¹¹ The structures were solved by direct methods, and all nonhydrogen atoms were refined anisotropically by the least-squares method on *F*² using the SHELXTL program.¹² Hydrogen atoms on organic ligands were calculated in ideal positions and were refined using a riding model with C–H = 0.93 Å. For 1, Flack parameter *x* = 0.05(2). Crystal data as well as details of data collection and refinements for complexes 1–5 are summarized in Table 1. Selected bond distances are listed in Table

Table 2. Selected Bond Lengths (Å) for 1–5^a

complex 1			
Cu(1)–N(1a)	2.018(4)	Cu(2)–N(2)	1.925(6)
Cu(1)–S(1)	2.283(1)	Cu(2)–S(1)	2.2529(8)
Cu(1)–S(2b)	2.3598(8)		
complex 2			
Ag(1)–S(1)	2.529(2)	Ag(2)–Cl(2)	2.463(2)
Ag(1)–Cl(1a)	2.598(2)	Ag(2)–S(1)	2.470(2)
Ag(1)–Cl(1b)	2.629(2)	Ag(2)–S(1c)	2.865(2)
Ag(1)–Cl(1)	2.865(2)		
complex 3			
Cu(1)–N(1)	1.998(5)	Cu(5)–S(8b)	2.397(2)
Cu(1)–S(2)	2.233(2)	Cu(6)–N(7)	1.918(6)
Cu(1)–S(3a)	2.257(2)	Cu(6)–S(2c)	2.267(2)
Cu(2)–N(2)	2.022(5)	Cu(6)–S(5d)	2.352(2)
Cu(2)–S(1)	2.241(2)	Cu(6)–S(5)	2.550(2)
Cu(2)–S(3)	2.280(2)	Cu(7)–N(8)	1.967(6)
Cu(3)–N(3a)	2.021(5)	Cu(7)–S(7)	2.277(2)
Cu(3)–S(1)	2.233(2)	Cu(7)–S(6)	2.325(2)
Cu(3)–S(2a)	2.262(2)	Cu(7)–S(7d)	2.690(2)
Cu(4)–N(4)	1.943(6)	Cu(8)–N(5e)	1.919(8)
Cu(4)–S(6b)	2.318(2)	Cu(8)–S(8)	2.239(2)
Cu(4)–S(4)	2.343(1)	Cu(1)···Cu(2)	2.861(1)
Cu(4)–S(1)	2.446(2)	Cu(1)···Cu(3)	2.943(1)
Cu(5)–N(6)	1.944(5)	Cu(2)···Cu(3)	3.050(1)
Cu(5)–S(3)	2.310(2)	Cu(7)···Cu(7d)	2.806(2)
Cu(5)–S(5)	2.355(2)		
complex 4			
Cu(1)–I(1)	2.662(3)	Cu(1)–I(1a)	2.681(2)
Cu(1)–I(2)	2.560(3)	Cu(2)–S(1)	2.376(3)
Cu(2)–I(1)	2.617(3)	Cu(3)–S(1)	2.288(5)
Cu(2)–I(2)	2.672(4)	Cu(4)–I(4d)	2.684(4)
Cu(3)–I(3)	2.666(3)	Cu(1)···Cu(1a)	2.886(4)
Cu(3)–I(4)	2.688(3)	Cu(1)···Cu(2)	2.980(4)
Cu(4)–I(3)	2.591(4)	Cu(3)···Cu(4)	3.052(4)
Cu(4)–I(4)	2.687(2)	Cu(4)···Cu(4d)	2.923(5)
complex 5			
Ag(1)–Cl(1)	2.480(2)	Ag(2)–Cl(2)	2.540(2)
Ag(1)–S(1)	2.551(3)	Ag(2)–S(1)	2.592(2)
Ag(1)–S(1a)	2.634(3)	Ag(1)···Ag(1b)	3.176(2)
Ag(1)–Cl(3)	2.6755(9)		

^a Symmetry codes for 1: (a) $x, y + 1/2, z + 1/2$; (b) $x, y + 1/2, z - 1/2$. For 2: (a) $-x + 3, -y, -z + 1$; (b) $-x + 2, -y, -z + 1$; (c) $-x + 2, -y + 1, -z + 1$. For 3: (a) $-x + 5/2, -y - 1/2, -z$; (b) $-x + 5/2, y - 1/2, -z + 1/2$; (c) $x + 1/2, -y - 1/2, z + 1/2$; (d) $-x + 3, y, -z + 1/2$; (e) $x, y + 1, z$. For 4: (a) $-x + 1/2, -y + 1/2, -z + 1$; (d) $-x + 1/2, -y - 3/2, -z$. For 5: (a) $x, y - 1, z$; (b) $-x + 1/2, -y, z$.

2. Selected bond angles are listed in Tables S1–S5 of the Supporting Information.

Results and Discussion

Synthesis. In most of the reported compounds, dithiodipyridine (dtdp) tends to coordinate with metal atoms through the pyridine N donor without S–S bond cleavage when reacted at room temperature.^{8a,b} However, in our previous report, when the reactions of the 4,4'-dithiodipyridine ligand with CuI were conducted under solvothermal conditions, the dtdp reagent was unprecedentedly converted into two isomeric ligands, 4,4'-thiodipyridine (tdp) and 1-(4-pyridyl)-4-thiopyridine (ptp) at 120 and 160 °C, respectively. It is notable that tdp is an unprecedented zwitterionic functional ligand characteristic of mixed N,S donors (Scheme 1a). We speculated that the formation of isomeric tdp and ptp ligands were involved in both the S–S bond cleavage and the S–C(sp²) bond cleavage and rearrangement reactions.¹⁰ In this report, changing the metal salt from CuI to CuSCN resulted in a new three-dimensional (3D) network [Cu₂(SCN)(4-pyt)] (**1**), in which the 4-thiopyridine (4-pyt) ligand

was formed *in situ* through the cleavage of the S–S bond of 4-dtdp (Scheme 1b).^{8c–f} Interestingly, when the reaction medium was acidified with a trace of hydrochloric acid, the *in situ* synthesized 4-pyt ligand was protonated to the 4-pyH ligand and formed with AgCl a new 2D inorganic layer-based coordination framework [Ag₂Cl₂(4-pyH)] (**2**).

The successful isolation of these complexes from 4-dtdp raised our interest in investigating the similar ligand 2,2'-dithiodipyridine (2-dtdp). However, no *in situ* ligand formation, such as the formation of tdp or ptp mentioned above through both the S–S bond cleavage and the S–C(sp²) bond cleavage and rearrangement reactions, was observed. It may be because of the different dispositions of the nitrogen and sulfur donors. A new copper coordination network, [Cu₅(SCN)₃(2-pyt)₂] (**3**), was obtained in which the 2-thiopyridine (2-pyt) ligand came from the S–S bond cleavage of 2-dtdp (Scheme 1b) in the reaction of Cu(OAc)₂·H₂O, KSCN, and 2-dtdp in a molar ratio of 2:2:1. The Cu(II) reduction to Cu(I) under solvothermal conditions was observed, which has been revealed in recent reports,¹¹ in which some organonitrogen species had intriguing reactivity as reducing agents that could reduce Cu(II) to Cu(I). The SCN[−] anions were vital in the formation of a multidimensional framework. Without SCN[−], only the reported [Cu₆(2-pyt)₆] cluster can be obtained,¹³ which is also indicative of ligand cleavage during the synthesis. Similarly, in an acidic environment, the reaction of CuI and the 2-dtdp ligand in a molar ratio of 2:1 resulted in a 3D inorganic layer-based supramolecular framework, [Cu₄I₄(2-pyH)] (**4**), through hydrogen bonds between layers, similar to the reported structures.¹⁴ When the CuI salt was replaced by AgCl, another new 3D inorganic layer-based supramolecular framework, [Ag₃Cl₃(2-pyH)₂] (**5**), was obtained, which was different from other silver 2-thiopyridine coordination structures,¹⁵ which can also be obtained from the original 2-pyt ligand in our *in situ* reactions with the AgCl salt replaced by AgNO₃, indicating another way to acquire pyt-containing coordination complexes.¹⁶ In summary, the metal ions and the acidity of the solution have played a more important role in the ligand cleavage from dithiodipyridine to the thiopyridine ligand, while in our previous work, the temperature was more important.¹⁰ The *in situ* ligand reactions are summarized in Scheme 1b. The purity of the five complexes was confirmed by the measurement of the XRPD patterns (Figure S1, Supporting Information).

Crystal Structures. Structure of [Cu₂SCN(4-pyt)] (1**).** A single-crystal X-ray diffraction study of **1** reveals an infinite 3D coordination polymer that crystallizes in space group *Ama*2. There are two unique Cu(I) atoms, a μ_4 -4-pyt ligand and a μ_3 -SCN ligand in the asymmetric unit of **1** (Figure 1a). Cu1 adopts a slightly distorted tetrahedral coordination geometry, which is surrounded by a N atom from a 4-pyt ligand, one S atom from a 4-pyt ligand, and two S atoms from two SCN ligands [Cu–N = 2.018(4) Å, Cu–S = 2.283(1) and 2.3598(8) Å, S–Cu–S = 117.94(3)°, N/S–Cu–S/N = 101.58(8)–116.30(3)°]. Cu2 is coordinated by a N atom from a SCN ligand and two S atoms from two 4-pyt ligands in a trigonal coordination geometry [Cu–N = 1.925(6) Å, Cu–S = 2.2529(8) Å, S–Cu–S = 127.39(7)°, N/S–Cu–S/N = 116.30(3)°]. The 4-pyt ligand generated from the cleavage of the S–S bond of the 4-dtdp ligand adopts the $\mu_4:\eta^3:\eta^1$ coordination mode in which the S atom connects one Cu1 and two Cu2 atoms, while the linear SCN ligand acts as a $\mu_3:\eta^2:\eta^1$ bridge in which the S atom connects two Cu1 atoms. An interesting inorganic Cu–S coordination layer in a (6,3) topology net is observed in the crystallographic *ab* plane, which is composed of three tetrahedral Cu1 atoms,

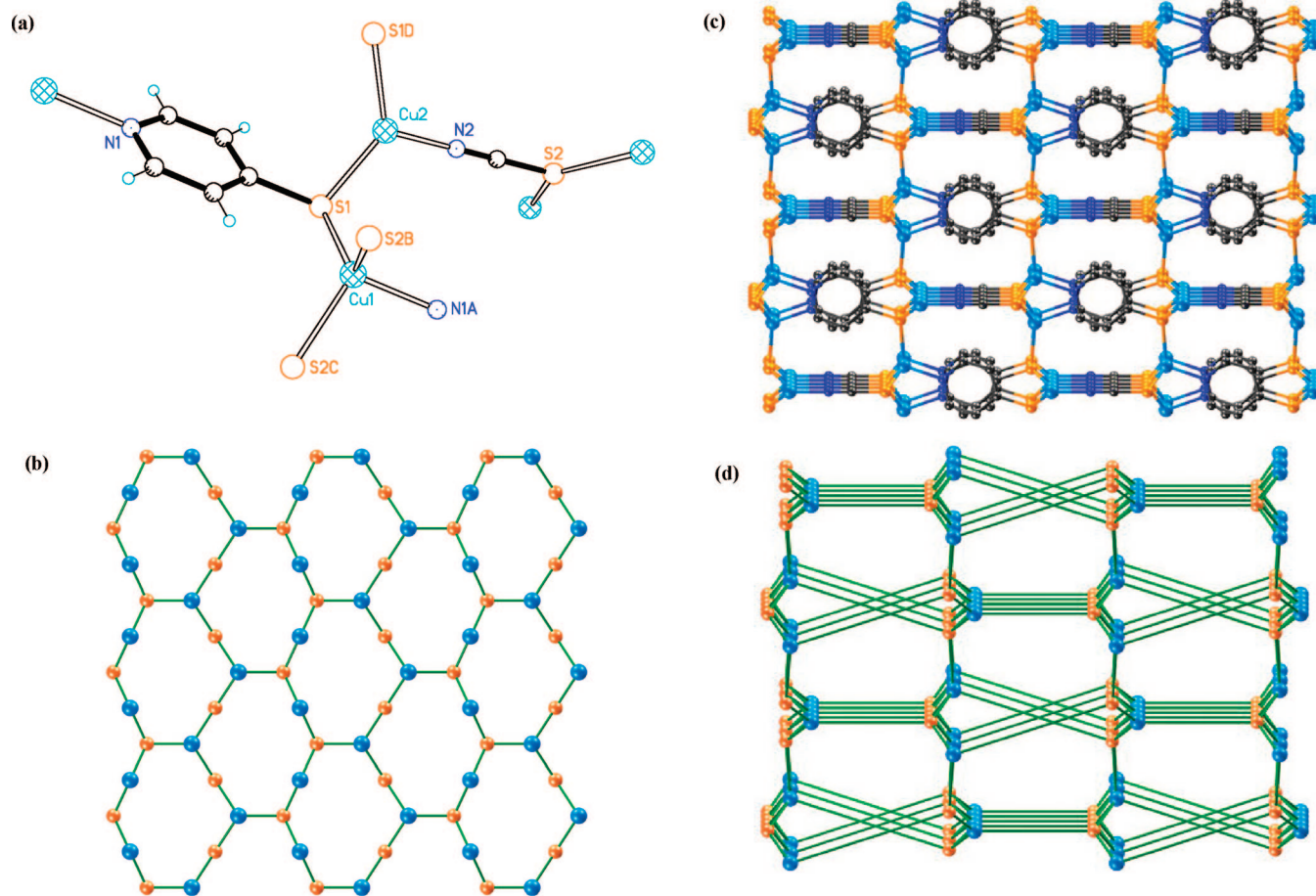


Figure 1. Coordination environment (a), the (6,3)-Cu-S net viewed along the *c* axis (b), the 3D coordination network (c), and the (4,3)-connected topology net viewed along the *a* axis (d) in **1**. Atom color code: Cu, light blue; S, orange; N, blue; C, gray.

two trigonal Cu2 atoms, three μ_3 -S (4-pyt) atoms, and two μ -S (SCN[−]) atoms per ring through coordination interactions (Figure 1b). Adjacent layers are further linked by the 4-pyt and SCN ligands to generate a 3D coordination network (Figure 1c).

The network topology of **1** can be simplified by considering the Cu1 and S1 atoms as the tetrahedral four-coordinated nodes and the Cu2 and S2 as the trigonal three-coordinated nodes. The resulting net is shown in Figure 1d, which is an unusual 3D (4,3)-connected net with two types of four- and three-coordinated nodes in a ratio of 1:1:1:1. A topological analysis of this net was performed using OLEX.¹⁷ The long topological (O'Keeffe) vertex symbol is 6.8₃.6.8₂.6.8₃ for the Cu1 and S1 nodes and 6.6.6 for the Cu2 and S2 nodes, giving the short vertex symbol (6³.8³)_{Cu1}(6³.8³)_{S1}(6³)_{Cu2}(6³)_{S2}.

Structure of [Ag₂Cl₂(4-pytH)] (2). An X-ray structural analysis reveals that **2** contains two unique Ag(I) atoms, a 4-pytH ligand, and two Cl[−] anions, all of which lie in general positions (Figure 2a). Ag1 adopts tetrahedral coordination geometry, coordinated by a S atom from the 4-pytH ligand and three Cl atoms [Ag–S = 2.529(2) Å, Ag–Cl = 2.598(2)–2.865(2) Å, S–Ag–Cl = 103.11(7)–129.05(8)°, Cl–Ag–Cl = 87.78(7)–108.09(8)°]. Ag2 is surrounded by two S atoms from 4-pytH ligands and one Cl anion in a distorted trigonal coordination environment [Ag–S = 2.470(2) and 2.865(2) Å, Ag–Cl = 2.463(2) Å, S–Ag–S = 100.68(7)°, S–Ag–Cl = 101.03(7) and 157.79(9)°]. The 4-pytH ligand, generated from the S–S cleavage of the 4-dtdp ligand and then protonated in an acidic environment, acts as a μ_3 bridge through the S atom with Ag–S–Ag angles of 79.32(7), 85.21(7), and 143.97(8)°. Cl1 also

acts as a μ_3 bridge connecting three Ag atoms to form a 1D (AgCl)_n ladder chain along the *a* axis, while Cl2 is a terminal ligand coordinated to the Ag2 atom. Two μ_3 -S atoms from two distinct 4-pytH ligands bridge two trigonal silver atoms to form a square four-member ring, which is further connected to the (AgCl)_n chains to form a (4,4) layer in the *ab* plane (Figure 2b). The 4-pytH ligands are arranged up and down the layers (Figure 2c) and link the adjacent layers to a 3D supermolecular framework by hydrogen bonds (C2...Cl2 = 3.462 Å, C2–H...Cl2 = 128.9° and N1...Cl2 = 3.153 Å, N1–H...Cl2 = 149.6°; Figure 2d).¹⁸

Structure of [Cu₅(SCN)₃(2-pyt)₂] (3). An X-ray structural analysis of **3** reveals a complicated 3D coordination network. The asymmetric unit contains eight Cu(I) atoms, three 2-pyt ligands, and five SCN[−] ligands. One of the copper atoms (Cu8) and one of the SCN[−] anions lie on the special positions (Figure 3a). Similar to 4-pyt, the 2-pyt ligand was *in situ* generated from the S–S bond cleavage of 2-dtdp. All of the 2-pyt ligands act as a μ_4 bridge through the S atom to connect three Cu(I) atoms. Cu1, Cu2, and Cu3 have the same trigonal coordination environment, connected by two S atoms and one N atom from the 2-pyt ligands [Cu–S = 2.2326(17)–2.2803(17) Å, Cu–N = 1.998(5)–2.022(5) Å, S/N–Cu–N/S = 106.84(14)–128.33(14)°]. Because of the close disposition of two coordination sites on 2-pyt, there exists relatively weak Cu...Cu interaction between the three Cu(I) atoms [Cu1–Cu2 = 2.8614(11) Å, Cu1–Cu3 = 2.9430(11) Å, Cu2–Cu3 = 3.0500(11) Å], which is slightly longer than the sum of the van der Waals radii of copper(I) (2.8 Å), compared to other copper coordination

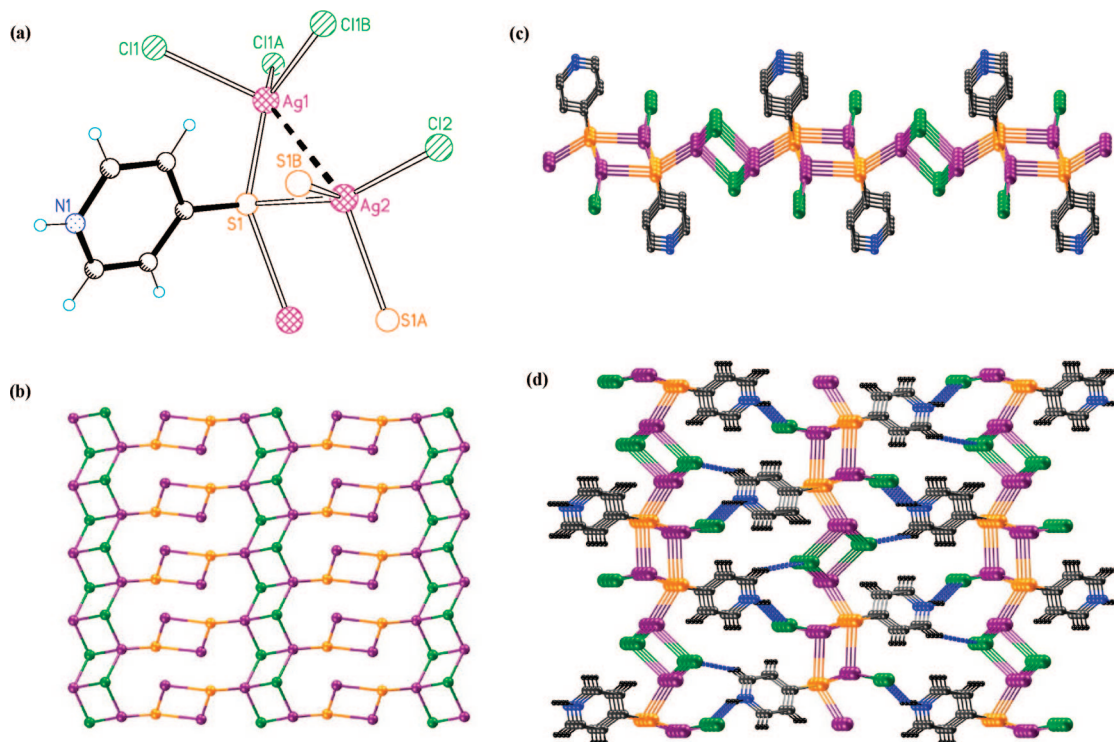


Figure 2. Coordination environment (a), perspective views of the 2D inorganic layer composed of $(\text{AgCl})_n$ chains and the (Ag_2S_2) subunits along the c axis (b), the 2D layer with the pyridine rings up and down viewed along the a axis (c), and the hydrogen-bonds (blue dashed line) interaction between the adjacent layers along the a axis (d) in **2**. Atom color code: Ag, purple; Cl, green; S, orange; N, blue; C, gray.

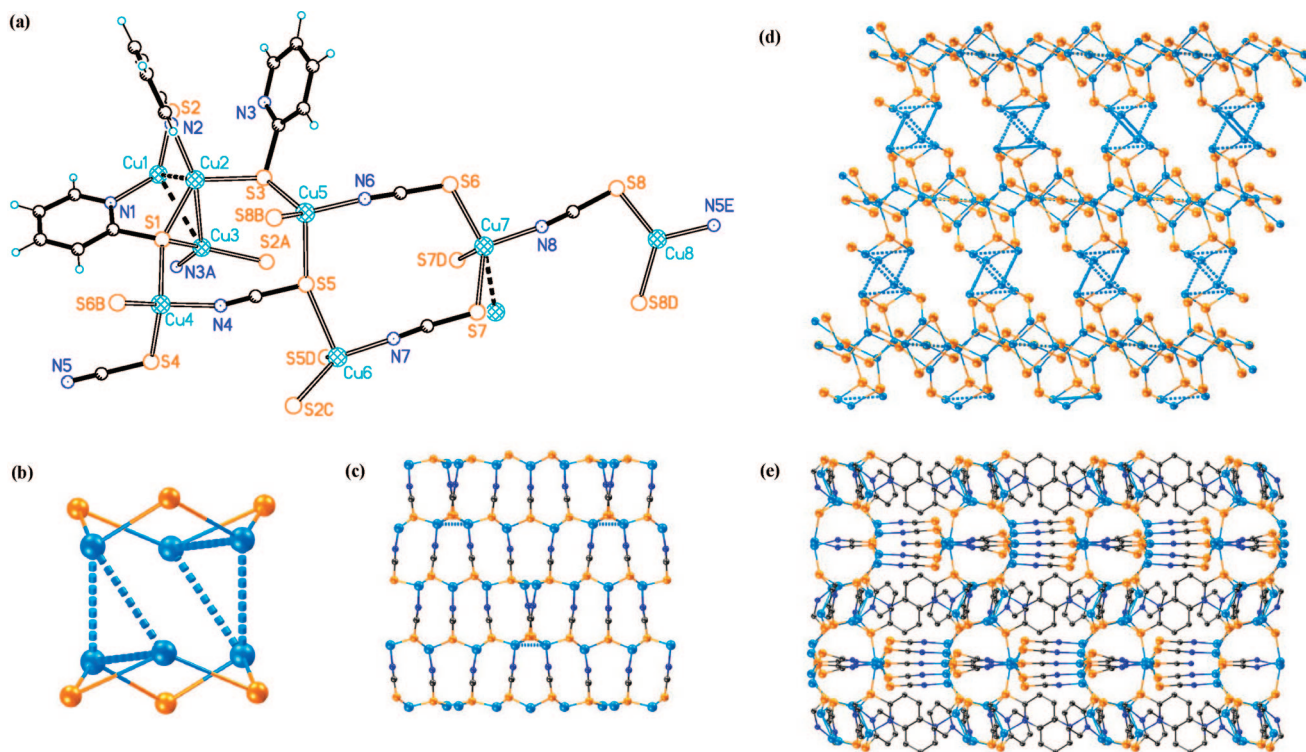


Figure 3. Coordination environment (a); the (Cu_6S_6) units composed of Cu1, Cu2, and Cu3 and S1, S2, and S3 (b); perspective views of the 1D $(\text{CuS})_n$ zigzag chain to 2D layer linked by SCN^- ligand along the c axis (c); the 2D layer to 3D framework linked by the (Cu_6S_6) units along the b axis (d); and the 3D coordination network by the 2-pyt ligands along the a axis (e) in **3**. Atom color code: Cu, light blue; S, orange; N, blue; C, gray.

complexes.^{9e} Two sets of the Cu1Cu2Cu3 and S1S2S3 create a pseudo (Cu_6S_6) cluster through the Cu–S coordination (Figure

3b), compared to the early reported compound $[\text{Cu}_6(\text{C}_5\text{H}_4\text{NS})_6]$ showing a distorted octahedral core of six copper atoms, with

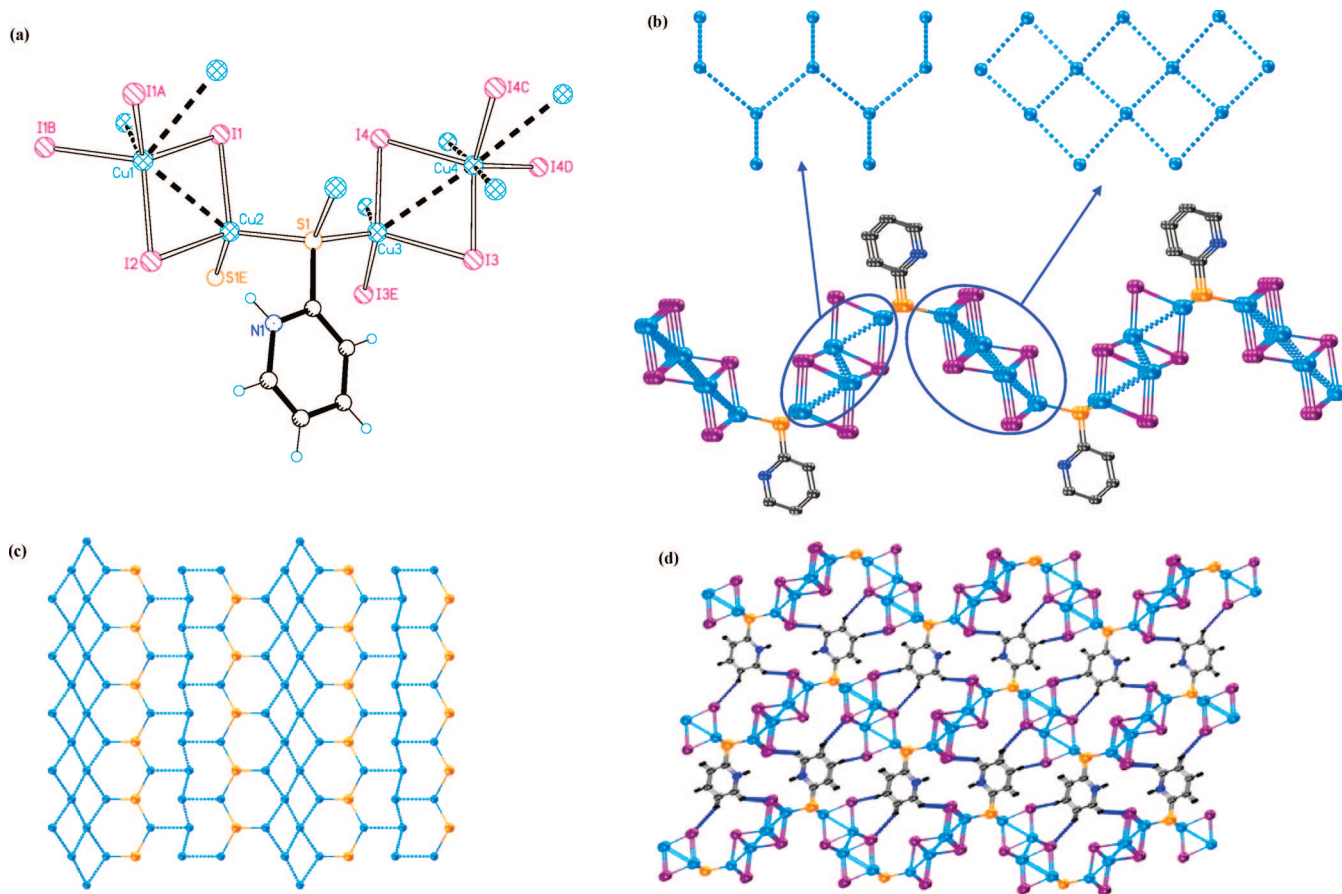


Figure 4. Coordination environment (a), perspective views of the waved 2D layer with the pyridyl rings up and down viewed along the *b* axis (b), the 1D (Cu...Cu) chains to 2D layer linked by μ_3 -S bridges along the *a* axis (c), and the hydrogen-bonds (blue dashed line) interaction between the adjacent layers along the *a* axis (d) in **4**. Atom color code: Cu, light blue; S, orange; N, blue; C, gray.

metal–metal distances ranging from 2.795(1) to 3.160(1) Å.¹³ Cu4, Cu5, and Cu6 have similar tetrahedral coordination environments surrounded by one S atom from the 2-pyt ligands, two S atoms from the SCN ligands, and one N atom from the third SCN ligand [Cu–S = 2.2670(17)–2.4461(17) Å, Cu–N = 1.918(6)–1.944(5) Å, S/N–Cu–N/S = 93.59(16)–132.99(17)°]. Cu7 is coordinated to three S atoms and one N atom from different SCN ligands [Cu–S = 2.277(2)–2.690(2) Å, Cu–N = 1.967(6) Å, S/N–Cu–N/S = 100.04(7)–129.70(8)°]. Two of the SCN ligands bridge two Cu7 atoms with a Cu...Cu distance of 2.806(2) Å, significantly smaller than those for the pseudo (Cu₆S₆) cluster. Cu8 on a special position also adopts a trigonal coordination geometry, linked by two S atoms and one N atom from the SCN ligand [Cu–S = 2.2392(18) Å, Cu–N = 1.919(8) Å, S/N–Cu–N/S = 116.32(5) and 127.36(10)°]. One of the SCN ligands adopts a μ_4 bridge through the S atom to connect three Cu(I) atoms while the others are μ_3 -bridged. Different from the (Cu₆S₆) cluster, Cu4, Cu5, Cu6, Cu7, and Cu8 form a 2D inorganic (CuSCN)_n layer by the linkage of SCN ligands (Figure 3c), compared to those (CuSCN)_n chain-based polymers.¹⁹ Interestingly, the (CuSCN)_n layers are further linked into a 3D inorganic network by the (Cu₆S₆) units (Figure 3d). The binding of the 2-pyt ligands helps to retain the (Cu₆S₆) cluster and results in a stable 3D coordination framework (Figure 3e).

Structures of [Cu₄I₄(2-pytH)] (4). The asymmetric unit of **4** contains four unique Cu(I) atoms, four I anions (μ_2 -I, μ_3 -I, and μ_4 -I), and one 2-pytH ligand, all of which lie on special positions (Figure 4a). Cu1 adopts a tetrahedral coordination environment surrounded by four I atoms [Cu–I = 2.560(3)–

2.681(2) Å, I–Cu–I = 107.10(9)–114.61(8)°]. Cu2 adopts a distorted tetrahedral geometry surrounded by two S atoms from two 2-pytH ligands and two I atoms [Cu–I = 2.617(3) and 2.672(4) Å, Cu–S = 2.376(3) Å, I/S–Cu–S/I = 106.30(13)–120.3(2)°]. Cu3 adopts a slightly distorted tetrahedral geometry surrounded by one S atom of two 2-pytH ligands and three I atoms [Cu–I = 2.666(3) and 2.688(3) Å, Cu–S = 2.288(5) Å, I/S–Cu–S/I = 101.26(14)–111.16(15)°]. Cu4 adopts a slightly distorted tetrahedral geometry surrounded by four I atoms [Cu–I = 2.591(4)–2.687(2) Å, I–Cu–I = 100.20(11)–114.06(10)°]. The I atoms adopt three types of coordination modes, μ_2 -I, μ_3 -I, and μ_4 -I, bridging the copper atoms at a relatively short distance [Cu...Cu = 2.886(4)–3.052(4) Å], different from other copper-pyt halide coordination complexes.²⁰ As shown in Figure 4b, the four unique Cu atoms have two distinct packing patterns. Cu1 and Cu2 form zigzag chains, while Cu3 and Cu4 form double step-ladder chains along the *b* axis. The two different types of Cu...Cu chains are further linked by Cu–S coordination bonds into a novel 2D Cu...Cu–S–Cu...Cu layer (Figure 4c). The 2-pytH ligands are arranged outwards from the layers and link adjacent layers into a 3D supermolecular framework by hydrogen bonds (C3...I2 = 3.775 Å, C3–H...I2 = 137.0°, C4...I1 = 3.920 Å, C4–H...I1 = 149.6°, C5...I3 = 3.839 Å, C5–H...I3 = 127.1°)¹⁸ (Figure 4d).

Structures of [Ag₃Cl₃(2-pytH)₂] (5). Similar to compound **2**, **5** has a 2D inorganic sheet structure composed of silver, chloride, and sulfur atoms, which is further connected into a 3D framework via hydrogen bonds. The basic building block contains two Ag(I) atoms, one of which lies on a special

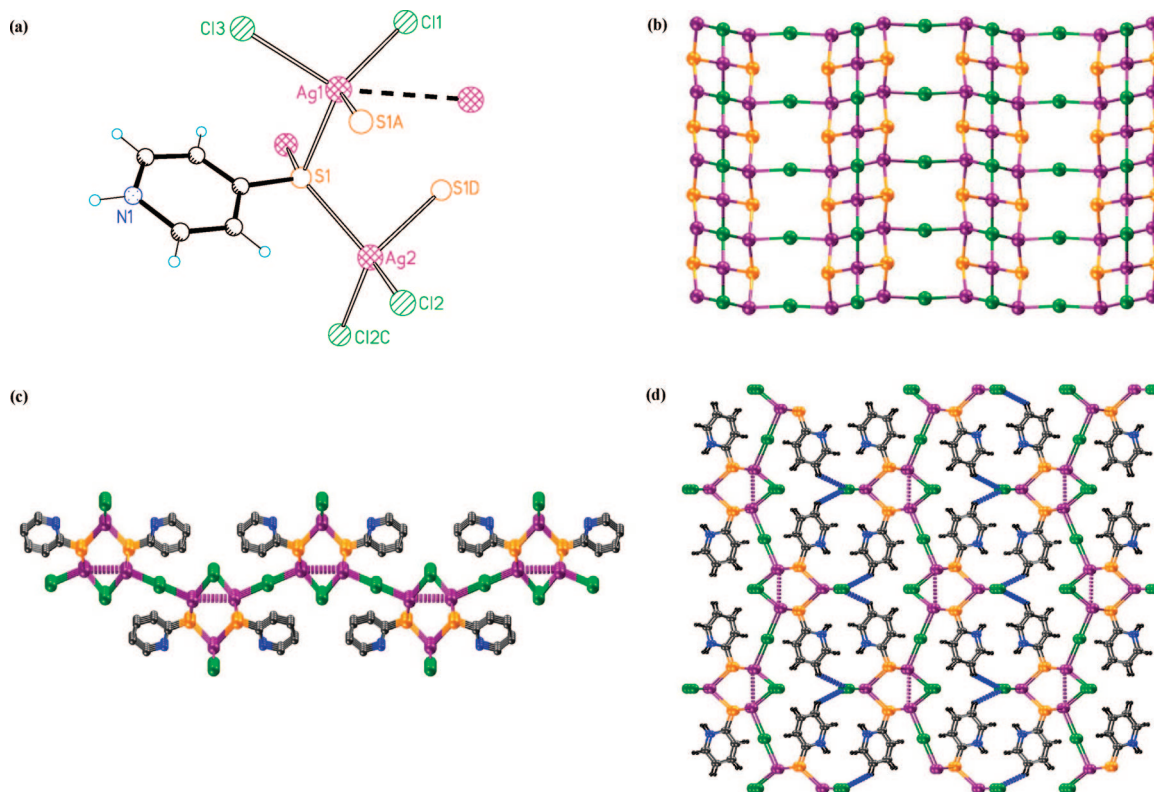


Figure 5. Coordination environment (a), perspective views of the 2D inorganic layer composed of $(\text{AgCl})_n$ chains and the $(\text{AgS})_n$ chains linked by the shared Ag atoms along the c axis (b), the 2D layer with the pyridyl rings up and down viewed along the a axis (c), and the hydrogen-bonds (blue dashed line) interaction between the adjacent layers along the a axis (d) in **5**. Atom color code: Ag, purple; Cl, green; S, orange; N, blue; C, gray.

position, a 2-pyTH ligand, and three Cl anions (Figure 5a). Ag1 and Ag2 have similar coordination environments. Both of them are coordinated in a distorted tetrahedral geometry surrounded by two S atoms from two 2-pyTH ligands and two Cl anions [$\text{Ag1-S} = 2.551(3)$ and $2.634(3)$ Å, $\text{Ag1-Cl} = 2.480(2)$ and $2.6755(9)$ Å, $\text{S/Cl-Ag1-Cl/S} = 102.16(8) - 129.93(7)^\circ$, $\text{Ag2-S} = 2.592(2)$ Å, $\text{Ag2-Cl} = 2.540(2)$ Å, $\text{S/Cl-Ag2-Cl/S} = 86.77(11) - 121.93(6)^\circ$]. The $\text{Ag1} \cdots \text{Ag1}$ distance is $3.1758(17)$ Å, slightly shorter than the van der Waals contact distance of 3.40 Å,^{21a} but a little longer than those in silver benzenesulfonate (2.915 Å),^{21b} silver carboxylate (2.916 Å),^{21c} and the succinatodisilver complex (2.938 and 3.104 Å).^{21d} Similar to compound **2**, the 2-pyTH ligand, generated from the S-S cleavage of the 2-dtdp ligand and then protonated in an acidic environment, acts as a μ_3 bridge through the S atom with Ag-S-Ag angles of $102.37(8)$, $108.59(9)$, and $118.61(9)^\circ$. Nevertheless, all three Cl atoms in **5** adopt a μ_2 bridge to connect two Ag atoms. Interestingly, two 1D zigzag silver chloride chains, which run along the a and b axes, link across to form a 2D infinite layer. The μ_3 -S from 2-pyTH connects two $(\text{AgCl})_n$ chains to help retain the inorganic sheet in the crystallographic ab plane. Alternatively, the layer can be considered as the $(\text{Ag}_5\text{S}_2\text{Cl}_2)_n$ double step-ladder chains along the b axis linked by the μ_2 -Cl atoms (Figure 5b). The 2-pyTH ligands are arranged above and below the layers (Figure 5c) and link the adjacent layers to a 3D supermolecular framework by the hydrogen bonds ($\text{C4} \cdots \text{Cl2} = 3.548$ Å, $\text{C4-H} \cdots \text{Cl2} = 131.4^\circ$)¹⁸ (Figure 5d), compared to other silver-pyT coordination polymers.¹⁶

Photoluminescent Properties. The fluorescent properties of the as-synthesized copper complexes, **1**, **3**, and **4**, were studied in the solid state at room temperature (Figure 6 and Figure S2, Supporting Information). The results indicate that the three

copper(I) compounds of **1**, **3**, and **4** exhibit strong fluorescence at room temperature. As illustrated in Figure 6a, compound **1** shows strong green fluorescence, with an emission maximum at 540 nm upon excitation at 380 nm ($\tau = 1.65$ μs , Figure S2a, Supporting Information). According to Cu(I) clusters with chalcogen ligands²² and simple Cu(I) complexes of mixed-ligand systems,²³ the emission is tentatively assigned to be dominated by a ligand-to-metal charge transfer (LMCT) ($\text{S} \rightarrow \text{Cu}$) character. Compared to **1**, compound **4** has the same Stokes shift from the excitation at 362 nm to emission at 520 nm, with a slight shift of about 20 nm to the high-energy band. Obviously, the emission band is much broader and the decay lifetime is a bit shorter than those for compound **1**, which may be due to its less rigid 2D layer structure linked by relatively weak hydrogen-bond interaction. The most fascinating aspect is that compound **3** exhibits strong red fluorescence, with an emission maximum at 673 nm upon excitation at 480 nm, which follows a single-exponential decay ($\tau = 1.59$ μs , Figure S2b, Supporting Information). According to other Cu(I)-thiolate clusters²² and its characteristic structure (Figure 3), the emission is tentatively assigned as originating from the LMCT characters, mixed with metal-centered (ds/dp) states modified by $\text{Cu} \cdots \text{Cu}$ interactions with Cu_6S_6 clusters. To our knowledge, luminescent d^{10} transition-metal coordination polymers with so low-energy emissions are rare,²⁴ different from these large numbers of blue and green emission coordination polymers.²⁵ Furthermore, all three of the compounds may act as potential candidates for practical application as a green or red optical device.

Conclusion

In this study, we have investigated solvothermal reactions of 4,4'-dithiodipyridine (4-dtdp) and 2,2'-dithiodipyridine (2-dtdp)

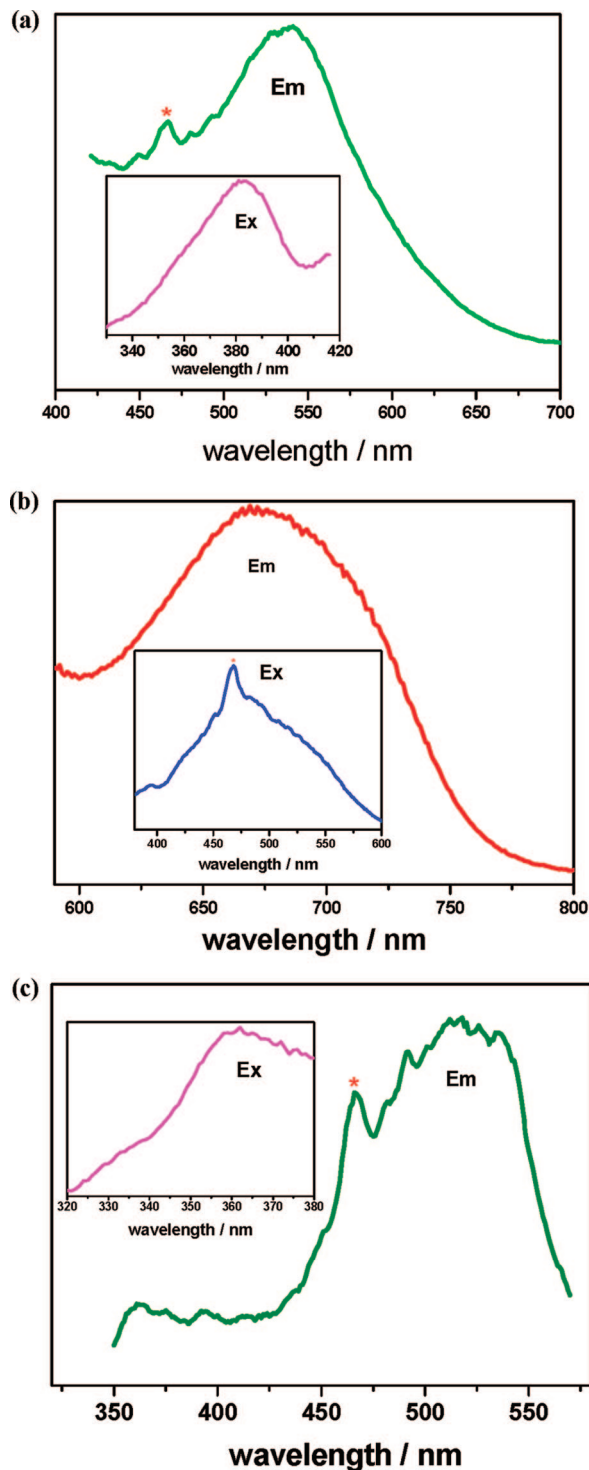


Figure 6. The emission spectra and excitation spectra insert of **1** (a), **3** (b), and **4** (c) (* = the emission of the sample carrier) in the solid state at room temperature.

with Cu(I) or Ag(I) salts under different reaction conditions. Five new $(M^I X)_n$ [$M = \text{Cu(I)}$ or Ag(I) , $X = \text{SCN}^-$, I^- , or Cl^-] layer-based coordination networks were successfully obtained and characterized. Our results demonstrate that solvothermal metal/ligand reactions not only provide good chances for the development of novel synthetic methods and the discovery of new ligand reactions but also pave a new way for the preparations of new materials with new structures and properties and their application in the crystal engineering of functional coordination polymers.

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Supporting Information Available: X-ray crystallographic files of **1–5** (CIF), simulated and experimental XRPD data of **1–5**, and the luminescence decay of **1**, **3**, and **4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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