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Reversible Crystal Transformations and Luminescence Vapochromism by Fast Guest Exchange in Cu(I) Coordination Polymers

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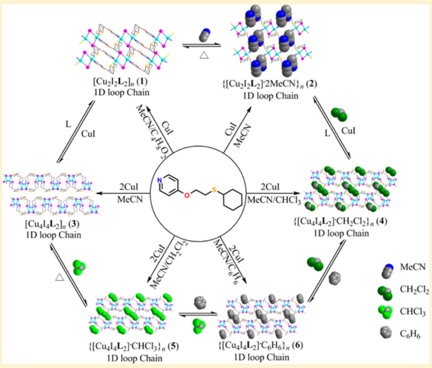
Supporting Information

ABSTRACT: Six Cu(I) coordination polymers (CPs)—$[Cu_2I_2\mathbf{L}_2]_n$ (**1**), $\{[Cu_2I_2\mathbf{L}_2]\cdot 2MeCN\}_n$ (**2**), $[Cu_4I_4\mathbf{L}_2]_n$ (**3**), $\{[Cu_4I_4\mathbf{L}_2]\cdot CH_2Cl_2\}_n$ (**4**), $\{[Cu_4I_4\mathbf{L}_2]\cdot CHCl_3\}_n$ (**5**), and $\{[Cu_4I_4\mathbf{L}_2]\cdot C_6H_6\}_n$ (**6**)—were synthesized by self-assembly reactions of CuI and the flexible mixed N/S donor ligand 4-(2-(cyclohexylthio)-ethoxy)pyridine (**L**). Single-crystal X-ray diffraction analyses reveal that these 1D CPs form sets of supramolecular isomers; **1** and **2** are based on Cu_2I_2 rhomboids, while **3**−**6** are based on cubane Cu_4I_4 clusters. Crystal-to-crystal transformations of CPs **1**−**6** were reversible under heat or in an appropriate solvent (acetonitrile, dichloromethane, chloroform, or benzene). In addition, crystal transformations between CPs **1** and **3** occurred through addition of **L** or CuI. Moreover, CPs **3**−**6** exhibited reversible guest exchange and crystal transformations on exposure to the vapor of volatile organic compounds and heat. Remarkably, a guest molecule was exchanged by other guest molecules in the vapor phase within very short times and without the use of acetonitrile as a solvent, which normally plays a key role in trapped solvent exchange experiments.



INTRODUCTION

Luminescent Cu(I) complexes often draw the interest of researchers due to their colorful appearance, variety of structures, and strong emission properties.[1−4] These copper complexes are becoming increasingly popular as ingredients for organic light-emitting diodes (OLEDs), thanks to the affordability and abundance of copper. Furthermore, continual research on copper has been conducted across a wide range of areas, not only because of its photochemical and physical properties but also because it forms complexes including coordination polymers (CPs)[5] with organic ligands containing nitrogen, phosphorus, and/or sulfur, with which chemical compounds with a variety of structures can be made. $(CuI)_n$-cluster-based complexes have relatively small energy differences with respect to n and the molecular structure, implying that they can bind different types of ligands to form other $(CuI)_n$-containing complexes of the same CuI stoichiometry but with different geometries,[4] depending on the reaction conditions. As such, the structure of any new complex produced is determined by the metal to ligand ratio, the temperature, and the reaction medium. In addition, ligand rigidity and the presence of guest molecules also affect the geometric and luminescent properties of the resulting complexes. Such complexes are being intensely researched due to their luminescences,[6−12] electrical conductivities,[13,14] and catalytic properties,[15,16] as well as their applicabilities in sensors,[17,18] semiconductors,[19,20] molecular switches,[21,22] OLEDs,[23−25] and gas adsorption and storage.[26,27]

Prior studies placed emphasis on structural changes and solvent exchange, including thermochromatic,[28−31] piezochromatic,[32−34] solvatochromatic,[35−37] and vapochromatic[38−40] properties of luminescent complexes. Previously, we examined the structures and vapochromatic characteristics of luminescent complexes of nitrogen−sulfur-donor ligands and sulfur-donor ligands, notably 2-pyrazinyl-4-thiomorpholinylmethanone, 2-(*tert*-butylthio)-*N*-(pyridin-3-yl)acetamide, and *N*,*N*′-bis[2-(cyclohexylthio)ethyl]pyromellitic diimide. Complexes with 2-pyrazinyl-4-thiomorpholinylmethanone were examined in mixed solvents containing acetonitrile,[41] while those of the other ligands were examined in the vapor state using acetonitrile as the solvent,[42,43] which played a pivotal role in opening up the frameworks of these complexes, thereby facilitating solvent exchange. In the current study, however, we sought to investigate the rapid transformation of vapochromatic compounds by guest molecules in the absence of acetonitrile. To facilitate the exchange of trapped guest molecules, a flexible organic ligand, 4-(2-(cyclohexylthio)-ethoxy)pyridine (**L**), containing pyridine and sulfur/nitrogen donor atoms was designed and synthesized.

Six different coordination polymers (CPs)—$[Cu_2I_2\mathbf{L}_2]_n$ (**1**), $\{[Cu_2I_2\mathbf{L}_2]\cdot 2MeCN\}_n$ (**2**), $[Cu_4I_4\mathbf{L}_2]_n$ (**3**), $\{[Cu_4I_4\mathbf{L}_2]\cdot CH_2Cl_2\}_n$ (**4**), $\{[Cu_4I_4\mathbf{L}_2]\cdot CHCl_3\}_n$ (**5**), and $\{[Cu_4I_4\mathbf{L}_2]\cdot C_6H_6\}_n$ (**6**)—were prepared using Cu(I) ions and the

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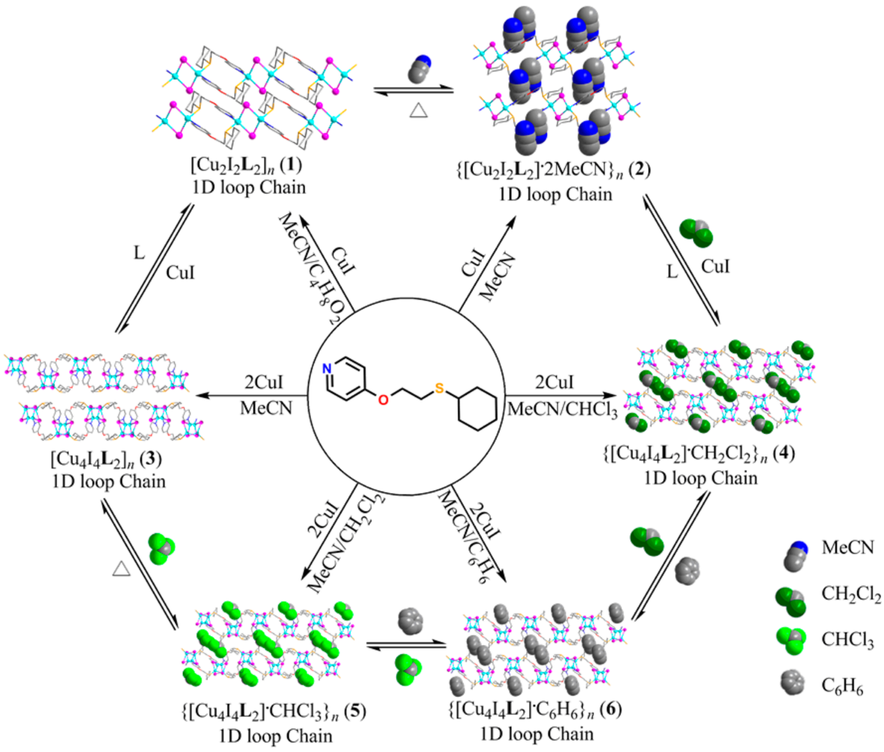
Scheme 1. Preparation and Reversible Crystal Transformations of Cu(I) Coordination Polymers (CPs) 1−6



synthesized ligands (see Scheme 1). Crystal structures of the six CPs were determined via single-crystal X-ray diffraction, while emission characteristics, namely solvatochromatic and vapochromatic properties, were examined by photoluminescence (PL). Thermal properties were also determined using thermogravimetric analysis/differential thermal analysis (TGA/DTA). This paper addresses the effect of heat and guest molecules on the structures of the synthesized coordination polymers, as well as the reversibilities of any changes.

EXPERIMENTAL SECTION

Methods and Materials. All reagents and solvents were commercially available and were used without further purification. The ^1H and ^{13}C NMR spectra of **L** were recorded on a Bruker Avance-300 (300 MHz) NMR spectrometer. The Fourier transform infrared (FT-IR) spectra of **L** and **1**−**6** were recorded on a Varian 640-IR spectrometer, using KBr disks. Elemental analysis (EA) was performed on a PerkinElmer Model 2400 analyzer. TGA and DTA for **1**−**6** were carried out under nitrogen at a scan rate of 10 °C min^{-1} using a TA SDT Q600 thermogravimetric analyzer. The EI-mass spectrum of **L** was collected on a JMS-700 instrument (JEOL). The solid-state luminescence spectra of **1**−**6** were recorded on a Hitachi F-7000 spectrophotometer. For field emission scanning electron microscopy (FE-SEM), a small amount of the compound was placed on a glass plate; after Pt coating, the specimen was examined with a JEOL JSM-6701F SEM instrument.

Synthesis of 4-(2-(Cyclohexylthio)ethoxy)pyridine (L).[44] Thionyl chloride (2.38 g, 20.0 mmol) was added dropwise to 2-(cyclohexylthio)ethanol (3.21 g, 20.0 mmol) in chloroform. The mixture was stirred at boiling temperature for 1 h and cooled to 20 °C. Chloroform was removed, yielding crude 2-chloroethylcyclohexyl sulfide. 4-Hydroxypyridine (1.90 g, 20.0 mmol) and potassium hydroxide (1.12 g, 20.0 mmol) were dissolved in 10 mL of tetrahydrofuran and 5 mL of water, and then the solution was added dropwise to the crude chloride. The solution was refluxed for 24 h and cooled. The crude product was extracted by dichloromethane. The dichloromethane layer was dried with anhydrous Na_2SO_4 and evaporated to give a crude oil (see Scheme S1 in the Supporting Information). Column chromatography (silica gel, MeCOOEt/n-C_6H_{14} = 30/70 (v/v), R_f = 0.28) produced **L** (3.4 g, 72%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.35 (d, 2H, Py), 6.73 (d, 2H, Py), 4.07 (t, 2H, OCH_2), 2.84 (t, 2H, CH_2S), 2.68 (m, H, SCH), 1.95−1.17 (m, 10H, $(CH_2)_5$). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 164.4, 151.0, 110.2, 67.8, 44.0, 33.7, 28.5, 26.0, and 25.7. IR (KBr, ν, cm^{-1}): 3028 (m); 2928 (s); 2852 (s); 1592 (s); 1570 (s); 1499 (s); 1448 (m); 1418 (m); 1281 (s); 1210 (s); 1063 (m); 1012 (s); 885 (m); 846 (m); 818 (m); 536 (m). MS (EI): m/z 237 $[M^+]$.

$[Cu_2I_2L_2]_n$ (1). An ethyl acetate (1 mL) solution of **L** (0.012 g, 0.050 mmol) was mixed with an acetonitrile (1 mL) solution of CuI (0.010 g, 0.050 mmol). Colorless precipitates were filtered and washed with diethyl ether/acetonitrile (2/1) solution. Single crystals suitable for X-ray analysis were obtained by slow evaporation. Yield: 77% (0.017 g). IR (KBr, ν, cm^{-1}): 3049 (w); 2923 (m); 2852 (m); 1602 (s); 1568 (m); 1501 (s); 1455 (m); 1427 (m); 1381 (m); 1280 (s); 1206 (s); 1064 (m); 1017 (s); 898 (m); 828 (m); 790 (m); 741 (w); 535 (m). Anal. Calcd for $[Cu_2I_2L_2]_n$, $C_{26}H_{38}Cu_2I_2N_2O_2S_2$: C, 36.50; H, 4.48; N, 3.27; O, 3.74; S, 7.50. Found: C, 36.58; H, 4.41; N, 3.49; S, 7.59.

$\{[Cu_2I_2L_2]{\cdot}2MeCN\}_n$ (2). **2** was synthesized under the same conditions as for **1** except that acetonitrile for **L** dissolution was replaced by ethyl acetate as solvent. Yield: 70% (0.016 g). IR (KBr, ν, cm^{-1}): 3051 (w); 2924 (m); 2853 (m); 2248 (w); 1603 (s); 1568 (m); 1502 (s); 1456 (m); 1281 (s); 1207 (m); 1064 (m); 1018 (m); 828 (m); 790 (w); 535 (m). Anal. Calcd for $[Cu_2I_2L_2{\cdot}2MeCN]_n$, $C_{30}H_{44}Cu_2I_2N_4O_2S_2$: C, 38.42; H, 4.73; N, 5.97; O, 3.41; S, 6.84. Found: C, 38.14; H, 4.59; N, 6.03; S, 6.99.

$[Cu_4I_4L_2]_n$ (3). An acetonitrile (1 mL) solution of **L** (0.012 g, 0.050 mmol) was mixed with an acetonitrile (1 mL) solution of CuI (0.020 g, 0.10 mmol). Colorless precipitates were filtered and washed with diethyl ether/acetonitrile (2/1) solution. Single crystals suitable for X-ray analysis were obtained by slow evaporation. Yield: 68% (0.042 g). IR (KBr, ν, cm^{-1}): 3052 (w); 2925 (m); 2849 (m); 1606 (s); 1565 (m); 1504 (s); 1288 (s); 1209 (s); 1054 (w); 1020 (s); 997 (m); 851 (w); 823 (m); 724 (w); 532 (m). Anal. Calcd for $[Cu_4I_4L_2]_n$,

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Table 1. Crystallographic and Structure Refinement Data for CPs 1−6

	1	2	3	4	5	6
formula	$C_{13}H_{19}CuINOS$	$C_{15}H_{22}CuIN_2OS$	$C_{26}H_{38}Cu_4I_4N_2O_2S_2$	$C_{27}H_{40}Cl_2Cu_4I_4N_2O_2S_2$	$C_{27}H_{39}Cl_3Cu_4I_4N_2O_2S_2$	$C_{32}H_{44}Cu_4I_4N_2O_2S_2$
formula wt	427.79	468.84	1236.46	1321.39	1355.83	1314.57
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	8.2253(14)	8.247(2)	11.0237(7)	11.1112(2)	11.0794(7)	10.959(2)
b (Å)	9.7915(16)	10.828(3)	12.5785(8)	12.1975(2)	12.3620(8)	12.571(3)
c (Å)	10.6017(18)	11.082(3)	15.3163(10)	16.3991(3)	16.6793(10)	16.387(3)
α (deg)	66.374(10)	115.098(11)	70.414(3)	103.2820(10)	106.755(2)	111.975(5)
β (deg)	87.827(10)	93.741(11)	80.213(4)	98.1660(10)	97.839(2)	98.893(5)
γ (deg)	76.420(9)	95.292(12)	67.046(3)	109.7030(10)	104.827(3)	94.429(5)
V (Å^3)	758.9(2)	886.5(4)	1840.6(2)	1977.16(6)	2059.4(2)	2045.8(7)
Z	2	2	2	2	2	2
ρ_{calcd} (g cm^{-3})	1.872	1.756	2.231	2.220	2.186	2.134
μ (mm^{-1})	3.599	3.091	5.773	5.513	5.359	5.201
F(000)	420	464	1168	1252	1284	1252
no. of data/restraints/ params	3687/0/163	3026/0/191	6446/0/361	9069/0/388	10100/0/397	9400/0/415
GOF (F^2)	1.086	1.026	1.042	1.047	1.035	1.044
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0301, 0.0566	0.0228, 0.0468	0.0388, 0.0808	0.0297, 0.0641	0.0267, 0.0621	0.0242, 0.0537
R1, wR2 (all data)[a]	0.0431, 0.0616	0.0353, 0.0509	0.0525, 0.0884	0.0390, 0.0676	0.0349, 0.0655	0.0284, 0.0554

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = \sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_o^2)^2]^{1/2}$.

$C_{26}H_{38}Cu_4I_4N_2O_2S_2$: C, 25.25; H, 3.10; N, 2.27; S, 5.19. Found: C, 25.20; H, 2.98; N, 2.58; S, 5.29.

{[$Cu_4I_4L_2$]·CH_2Cl_2}$_n$ (4). **4** was synthesized under the same conditions as for **3** except that acetonitrile for **L** dissolution was replaced by dichloromethane as solvent. Yield: 56% (0.037 g). IR (KBr, ν, cm^{-1}): 3052 (w); 2925 (s); 2849 (m); 1606 (s); 1565 (m); 1503 (s); 1458 (m); 1444 (m); 1431 (m); 1386 (w); 1288 (s); 1208 (s); 1054 (m); 1020 (s); 996 (m); 888 (w); 852 (m); 823 (m); 734 (m); 532 (m). Anal. Calcd for [Cu_4I_4**L**$_2$·CH_2Cl_2]$_n$, $C_{27}H_{40}Cl_2Cu_4I_4N_2O_2S_2$: C, 24.54; H, 3.05; N, 2.12; S, 4.85. Found: C, 23.73; H, 2.82; N, 2.53; S, 5.11.

{[$Cu_4I_4L_2$]·$CHCl_3$}$_n$ (5). **5** was synthesized under the same conditions as for **3** except that acetonitrile for **L** dissolution was replaced by chloroform as solvent. Yield: 60% (0.041 g). IR (KBr, ν, cm^{-1}): 3053 (w); 2924 (m); 2849 (m); 1608 (s); 1565 (m); 1504 (s); 1288 (s); 1209 (s); 1054 w, 1021 (s); 851 w, 824 (m); 757 (m); 532 (m). Anal. Calcd for [Cu_4I_4**L**$_2$·$CHCl_3$]$_n$, $C_{27}H_{39}Cl_3Cu_4I_4N_2O_2S_2$: C, 23.92; H, 2.90; N, 2.07; S, 4.73. Found: C, 23.50; H, 2.74; N, 2.50; S, 4.90.

{[$Cu_4I_4L_2$]·C_6H_6}$_n$ (6). **6** was synthesized under the same conditions as for **3** except that acetonitrile for **L** dissolution was replaced by benzene as solvent. Yield: 61% (0.040 g). IR (KBr, ν, cm^{-1}): 3030 (w); 2929 (m); 2849 (m); 1607 (s); 1564 (m); 1504 (s); 1293 (s); 1208 (s); 1053 (w); 1020 (s); 996 (m); 851 (w); 825 (m); 680 (m); 532 (m). Anal. Calcd for [Cu_4I_4**L**$_2$·C_6H_6]$_n$, $C_{32}H_{44}Cu_4I_4N_2O_2S_2$: C, 29.24; H, 3.37; N, 2.13; S, 4.88. Found: C, 29.41; H, 3.27; N, 2.06; S, 5.05.

X-ray Single Crystal Structural Analysis. The crystal structures of **1**−**6** were determined by single-crystal X-ray diffraction (SCXRD) methods. Preliminary examination and data collection were performed with using monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART APEX II ULTRA diffractometer. The powder X-ray diffraction (PXRD) data were collected at a 25° interval in the 2θ range of 0−30° for 30 s at a detector distance of 5 cm. The one frame was integrated from 3 to 30°. SCXRD data for CPs **1**−**6** were collected with a Bruker SMART APEX II ULTRA diffractometer. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 for all data using SHELXTL software.[45] The cell parameters for the compounds were obtained from a least-squares refinement of the spots (from 36 collected frames). All calculations were performed using the APEX2 package.[46] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in calculated positions and refined with a riding model. Crystallographic data and structural refinement data for CPs **1**−**6** are summarized in Table 1.

■ RESULTS AND DISCUSSION

4-(2-(Cyclohexylthio)ethoxy)pyridine (**L**), a flexible organic ligand containing sulfur and nitrogen donor atoms, was synthesized from 2-(cyclohexylthio)ethanol and 4-hydroxypyridine. Subsequently, the six luminescent CPs **1**−**6** were prepared using 1:1 and 2:1 molar ratios of CuI and the ligand, under suitable solvent conditions. **L** was characterized using NMR, MASS, and FT-IR (see Figures S1−S3 in the Supporting Information). CPs **1**−**6** were characterized using EA, TGA, DTA, PL, SCXRD, and FT-IR (see Figure S4 in the Supporting Information), PXRD (see Figures S5−S10 in the Supporting Information), and SEM (see Figure S11 in the Supporting Information). Crystallographic data and selected bond lengths/angles for CPs **1**−**6** are summarized in Table 1 and Table S1 in the Supporting Information.

Figure 1 depicts the structures and key interactions in CPs **1** and **2**; these CPs are triclinic systems belonging to the $P\bar{1}$ space group. Both of these CPs contain a 1:1 CuI:**L** ratio, but CP **1** does not contain a solvent, while CP **2** contains acetonitrile solvent molecules. CPs **1** and **2** were prepared in ethyl acetate/acetonitrile and acetonitrile solvents, respectively, and this difference is responsible for their different structures. While the CP **1** crystal grows rapidly since ethyl acetate lowers dielectric constant of the solution on mixing an acetonitrile solution of CuI and an ethyl acetate solution of **L**. However, the CP **2** crystal grows relatively more slowly, as the degree of solvation of CuI and **L** is higher in acetonitrile in comparison with ethyl acetate/acetonitrile. Thus, both CPs **1** and **2** are solvent-induced pseudopolymorphic supramolecular isomers in which rhomboid Cu_2I_2 dimer clusters are interconnected by ligands to form a linear 1D loop-chain structure. The asymmetric unit of CPs **1** and **2** consists of one copper(I) ion, one μ_2-iodide ion,

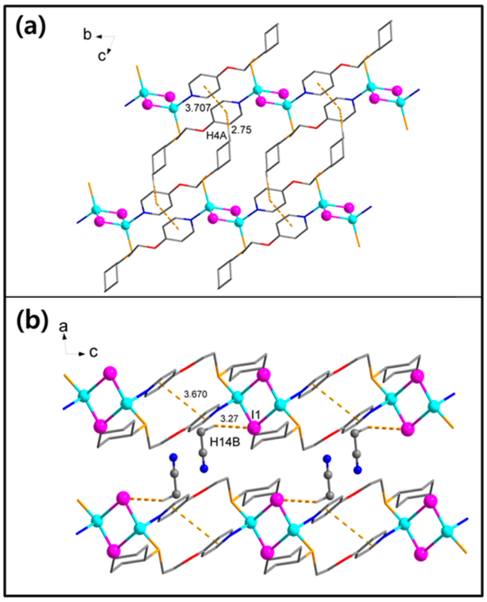

Figure 1. Structures and key intermolecular interactions in CPs **1** and **2**: (a) CP **1**; (b) CP **2**. Intermolecular π···π, C−H···I⁻, and C−H···π interactions are represented by dashed yellow lines. Hydrogen atoms that do not participate in intermolecular interactions have been omitted for clarity. Color scheme: sky blue, Cu; pink, I; orange, S; red, O; blue, N; gray, C; light gray, H.

and one **L**, excluding acetonitrile molecules (see Figures S12 and S13 in the Supporting Information). In addition, the coordination environment indicates that each copper ion is coordinated by the N and S of a single ligand and two distinct iodide ions to form a distorted-tetrahedral structure (see Figure S14 in the Supporting Information). Figure 1a depicts the π−π interactions (Cg1···Cg1 = 3.707 (2) Å, where Cg1 is the centroid of the ring formed by N1 and C9−C13 atoms) within the chain and the C−H···π interactions (C4−H4A···Cg1 = 2.75 Å) between adjacent chains along the [010] direction in CP **1**. As a result of these interactions, CP **1** forms a 2D network structure parallel to the (011) plane. On the other hand, as can be seen in Figure 1b, CP **2** leads to a 1D loop-chain structure along the [001] direction because of the absence of interactions between the chains and shows the π−π interactions (Cg1···Cg1 = 3.670 (2) Å) within the chain as for CP **1**. Unlike CP **1**, the presence of C−H···I⁻ hydrogen bonds (C14···I1, 4.036(4) Å; H14B···I1, 3.27 Å) to acetonitrile molecules stabilizes CP **2**.

Figure 2 depicts the packing structures and key interactions in CPs **3**−**6**; these CPs are triclinic systems belonging to the $P\bar{1}$ space group and consist of cubane tetramers with CuI and **L** in a 2:1 molar ratio. CP **3** does not contain any solvent molecules, although acetonitrile solvent was used, while CPs **4**−**6** contain dichloromethane, chloroform, and benzene, respectively, since mixed solvents were used. CPs **3**−**6** are solvent-induced pseudopolymorphic supramolecular isomers since they have identical chemical formulas when the solvent molecules are excluded. All four of these CPs have 1D loop-chain structures that form in the [001] direction. One copper(I) ion, one μ_2-iodide ion, and one **L** can be identified in their asymmetric units (see Figures S15−S18 in the Supporting Information). Furthermore, two different types of Cu are evident in the structures of CPs **3**−**6**, the first being coordinated by one sulfur atom from the ligand and three iodide ions and the second by the nitrogen atom of the pyridine ring and three iodide ions; all copper(I) ions form distorted-tetrahedral structures (see Figure S19 in the Supporting Information). Figure 2a shows that there are no intermolecular interactions in CP **3**, which lacks solvent molecules. All four polymers exhibit packing structures composed of 1D loop chains. In contrast, as can be seen in Figure 2b−d, CPs **4**−**6** are stabilized by intermolecular interactions. CP **4** exhibits C−H···S (C20···S2, 3.719(5) Å; H20B···S2, 2.87 Å) and C−Cl···π (C27−Cl1···Cg1 = 3.575 (3) Å) interactions, while CP **5** contains C−H···S (C27···S2, 3.656(6) Å; H27···S2, 2.81 Å) and C−H···Cl (C4···Cl3, H4A···Cl3) and C−Cl···π (C27−Cl1···Cg1) interactions with associated separations of 3.535(4), 2.80, and 3.590(2) Å, respectively. CP **6** displays C−H···π interactions (C28−H28···Cg1 = 3.048 Å). CPs **4** and **5** also form 2D networks parallel to the (011) plane due to C−H···S intermolecular interactions

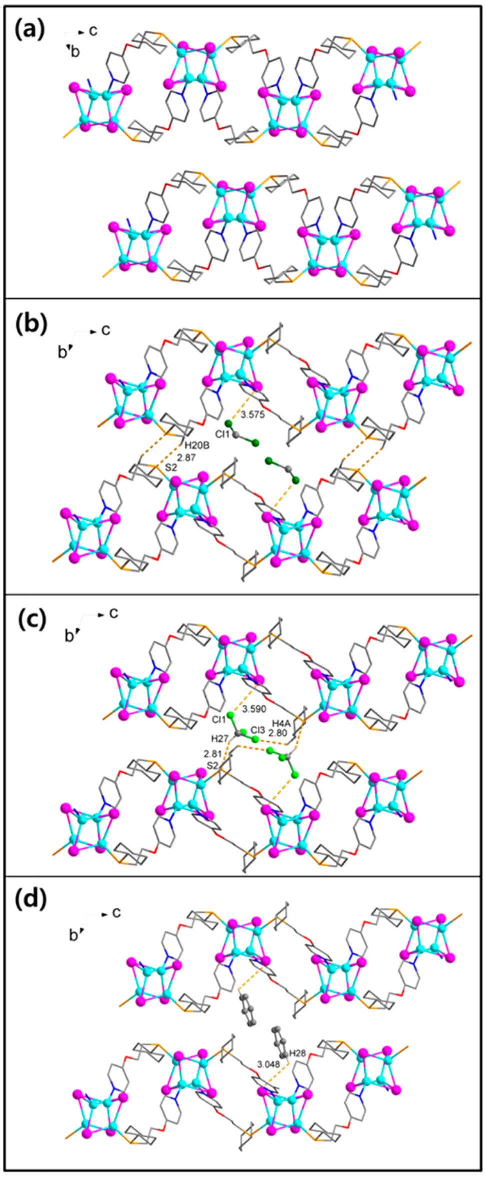

Figure 2. Structures and key intermolecular interactions in CPs **3**−**6**: (a) CP **3**; (b) CP **4**; (c) CP **5**; (d) CP **6**. Intermolecular C−H···S, C−H···π, and C−Cl···π interactions are represented by dashed yellow lines. Hydrogen atoms that do not participate in intermolecular interactions have been omitted for clarity.

and C−Cl⋯π interactions with the solvent molecules, respectively.

Luminescence Properties. Figure 3 depicts the emission spectra of CPs **1**−**6** in the solid state. CPs **1** and **2** were measured at an excitation wavelength of 325 nm, while CPs **3**−**6** were excited at 350 nm. Emission spectra of CPs **1** and **2** are assigned to metal to ligand charge-transfer (MLCT) excited states with some mixing of the halide to ligand (XL) CT character.[47−49] The emission wavelength maximum for CP **1** was observed at 419 nm, resulting in a violet color, while CP **2** emitted 432 nm blue light. On comparison of CPs **1** and **2**, with 1:1 CuI:**L** ratios, the emission of CP **2** is red-shifted in comparison to that of CP **1**, which was taken to be the standard since it is devoid of solvent molecules. Prior research focused on the effects of the trapped solvent molecules on PL.[41,50] In CP **2**, the reason for the red shift is probably due to the fact that C−H⋯I^- hydrogen-bonding interactions between acetonitrile molecules and Cu_2I_2 clusters may reduce the electron density of I^-.[50]

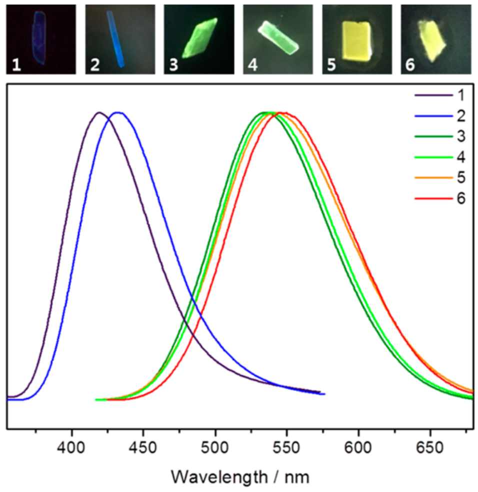

Figure 3. Solid-state luminescence spectra and photographic images of CPs **1** and **2** (excitation at 325 nm) and **3**−**6** (excitation at 350 nm) at room temperature.

CPs **3** and **4**, with peaks at 535 and 539 nm, emit green light, while CPs **5** and **6** are yellow, with emission maxima at 542 and 546 nm, respectively. Similar to the case for CPs **1** and **2**, taking CP **3** as a standard, CPs **4**−**6** are also red-shifted. The strong low-energy (LE) emission observed for the Cu_4I_4 cubane clusters at room temperature was assigned to cluster-centered (CC) transitions mixed with halogen to metal charge transfer (XMCT) transitions.[51−56] Emission wavelengths of LE bands depend upon the variation of electron density on S donor atoms and pyridyl groups owing to C−Cl⋯π, C−H⋯S, and C−H⋯π intermolecular interactions between the trapped solvent and **L**. However, without computations for CPs **4**−**6**, the explanation for red shifts by electron density variation is difficult to correlate with intermolecular interactions, since the extent of contribution of each intermolecular interaction is not known.

Thermoanalytical Properties. To examine the thermal stabilities of CPs **1**−**6**, TGA and DTA were carried out at a rate of 10 °C min^{-1} under N_2 gas, the results of which are presented in Figure 4. The data in Figure 4 show that the acetonitrile molecule in CP **2** is lost from the complex at around 80 °C. In CPs **4**−**6**, elimination of solvents begins in the early stages of the experiments due to the volatile properties of dichloromethane, chloroform, and benzene. Aside from weight loss due to the loss of solvent, the TGA curves for CPs **1** and **2** and CPs **3**−**6** exhibit similar weight loss trends, notably in the 300−400 °C region in which the ligands decompose. Furthermore, the DTA curves indicate that CPs **1** and **2** exhibit a heat-absorption peak at 150 °C, while the analogous absorptions for CPs **3**−**6** occur at around 200 °C. These peaks are presumably due to the breaking of Cu−S bonds, which are weaker than aromatic Cu−N bonds.

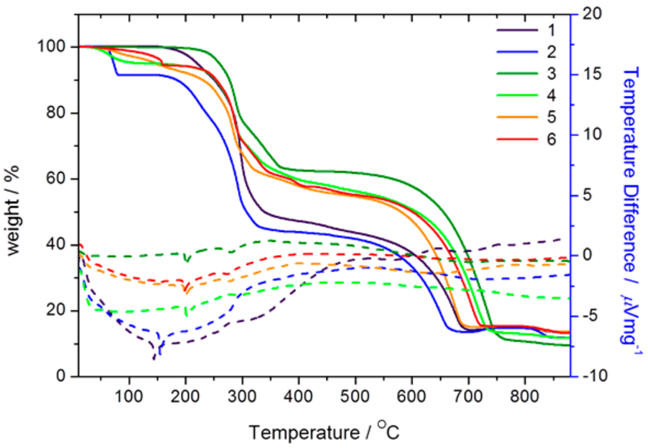

Figure 4. Thermogravimetric analysis (TGA, solid lines) and differential thermal analysis (DTA, dashed lines) traces for CPs **1**−**6**.

Crystal Transformations and Vapochromism. Figure 5 depicts the solvatochromatic and vapochromatic characteristics, and the PXRD patterns, of each sample following crystal transformation. Figure 5a shows that the transformations between crystals of CPs **1**−**6** are reversible. CP **2** is converted to CP **1** when it is heated at 80 °C for 30 min, and CPs **4**−**6** can be converted to CP **3** under similar conditions. Conversely, CP **1** can be converted to CP **2** by dispersing it in acetonitrile. This conversion was not proceeded by acetonitrile vapor. Likewise, addition of dichloromethane, chloroform, or benzene to solid CP **3** immersed in its mother liquor converts CP **3** into CPs **4**−**6**, respectively. Furthermore, transformations among CPs **4**−**6** are observed when any of these CPs is exposed to the target solvent vapor; these transformations can be followed by PXRD, as shown in Figure 5a.

In addition, CPs **1** and **3** can be interconverted by varying the CuI:**L** ratio under 1 min ultrasonication conditions at room temperature, as shown in Figures S20 and S21 in the Supporting Information. For instance, adding more CuI to CP **1**, or additional ligand to CP **3**, results in the transformation to the other structure, indicating that transformations between CPs **1** and **3** are indeed reversible. In more detail, CuI and **L** were gradually added to CP **1** and CP **3** from 0.5 to 1.0 equiv, respectively. When more CuI was added to CP **1**, the PXRD pattern of CP **3** increased, while the PXRD pattern of CP **1** decreased. Conversely, when more **L** was added to CP **3**, the PXRD pattern of CP **1** increased, while the PXRD pattern of CP **3** decreased. These phenomena are observed in the vapor state, where it is referred to as "vapochromism". Vapochromatic experiments were conducted by exposing a sample to the target solvent vapor while the sample was laid on a slide glass, as shown in Figure 5b.

As can be seen in Figure 5b, the exchange of trapped guest molecules in CPs **4**−**6** causes structural changes that were

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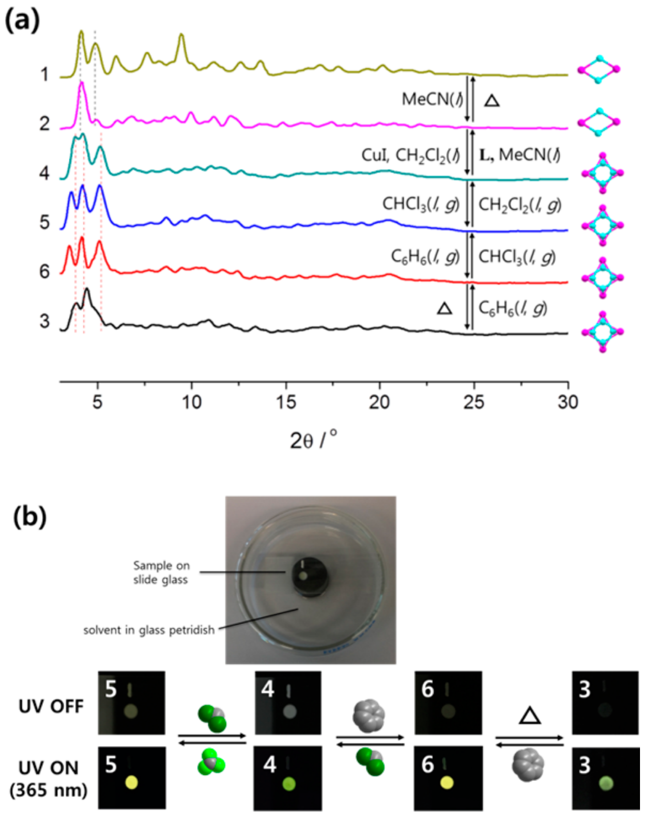

Figure 5. (a) PXRD patterns for CPs **1**−**6** showing reversible crystal transformations by exposure to volatile organic compounds (VOCs) and heat. (b) Photographic images under UV on/off conditions of CPs **3**−**6** after exposure to the vapors of different solvents.

identified by the emission color. Structural changes occurred rapidly. As evidenced by the videographic images, the time required for the complete transformations of CP **5** to **4**, **4** to **6**, **6** to **4**, and **4** to **5** are 15 s, 1 min, 1 min 20 s, and 1 min, respectively (videos S1−S4 in the Supporting Information). In addition, exposure of dichloromethane or chloroform vapor to CP **3** did not result in a transformation to either CP **4** or **5**; however, transformation to CP **6** was observed when benzene was added to CP **3**. It is most likely the relatively slim structure of benzene that allows it to penetrate efficiently into the CP **3** crystals. In order to investigate guest exchange by other solvent vapors, CP **6** was exposed to ethanol and diethyl ether. After 1 day of exposure, PXRD patterns for both solvents are the same as that of CP **3**. Therefore, trapped benzene molecules were removed instead of exchange by ethanol and diethyl ether vapors (see Figure S22 in the Supporting Information).

Prior crystal-transformation studies were conducted using acetonitrile or mixed solvents containing acetonitrile.[33−35] Although transformation did occur under these conditions, the ability to perform crystal transformations using only solvent vapor is scientifically intriguing. We believe that the flexibility of the ligand is responsible for transformations using vapor, since flexible ligands allow solvent molecules to slide between ligands, enabling the exchange of guest molecules.

■ CONCLUSION

In this paper, we report the synthesis of 4-(2-(cyclohexylthio)-ethoxy)pyridine (**L**), a ligand containing pyridine and sulfur. Subsequently, six coordination polymers—$[Cu_2I_2L_2]_n$ (**1**), $\{[Cu_2I_2L_2]\cdot 2MeCN\}_n$ (**2**), $[Cu_4I_4L_2]_n$ (**3**), $\{[Cu_4I_4L_2]\cdot CH_2Cl_2\}_n$ (**4**), $\{[Cu_4I_4L_2]\cdot CHCl_3\}_n$ (**5**), and $\{[Cu_4I_4L_2]\cdot C_6H_6\}_n$ (**6**)—were prepared by reacting the synthesized ligand (**L**) with CuI. Structural analyses and investigations into the luminescence and thermal properties of the six CPs were undertaken. Molecular exchange experiments of solvent molecules using two types of supramolecular isomers, CPs **1** and **2** and CPs **3**−**6**, were conducted under liquid- and vapor-state conditions; our experiments demonstrated that these transformations are reversible. We showed that exposure of the samples to vapors of solvents, namely dichloromethane, chloroform, and benzene, is sufficient for solvent exchange to occur, unlike the conventional technique that is heavily dependent on acetonitrile as the solvent. In addition, for both 1:1 and 2:1 CuI:**L** ratios, crystal transformations, in which all solvent molecules were removed, were achieved by heating the complexes at 80 °C for 30 min; these transformations were followed by PXRD as well as emission spectroscopy. Structural transformation experiments based on the copper to ligand ratio were also conducted. Notably, we observed that rapid solvent exchange occurs, even in nonporous structures, using the vapor conditions described in this work. In light of these findings, we conclude that these complexes may potentially be used as luminescent supramolecular materials (sensors) capable of separating and detecting volatile and potentially toxic organic compounds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.7b00951.

Details of experimental procedures for the preparation of CPs, optical and X-ray diffraction data, bond lengths and bond angles, and NMR, MASS, FT-IR, PXRD and SEM data (PDF)
Vapochromism (MPG)
Vapochromism (MPG)
Vapochromism (MPG)
Vapochromism (MPG)

Accession Codes

CCDC 1542505−1542510 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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