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New In Situ Cleavage of Both S–S and S–C(sp^2) Bonds and Rearrangement Reactions toward the Construction of Copper(I) Cluster-Based Coordination Networks

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Solvothermal reaction of 4,4′-dithiodipyridine (dtdp) with CuI at 120 or 160 °C results in the formation of three new coordination networks formulated with $[Cu_4I_4(tdp)_2]$ (**1**; tdp = 4,4′-thiodipyridine), $[Cu_5I_5(ptp)_2]$ (**2**), and $[Cu_6I_6(ptp)_2]$ [**3**; ptp = 1-(4-pyridyl)-4-thiopyridine]. The starting dtdp reagent was unprecedentedly converted into two tdp and ptp ligands via new in situ cleavage of both S–S and S–C(sp^2) bonds and temperature-dependent in situ ligand rearrangement of dtdp. **1** is a two-dimensional (2D) Cu_4I_4 cubane-like coordination network of 2-fold interpenetration. While in **2**, the Cu_8I_8 and Cu_2I_2 cluster units are alternately connected by the μ_2-sulfur bridges into one-dimensional inorganic chains along the *a* axis, which are further joined by the ptp spacers into a three-dimensional (3D) coordination network of 2-fold interpenetration. **3** is a 3D non-interpenetrating coordination network constructed with 2D inorganic $(Cu_2I_2)_n$ layers and the ptp spacers. **1** displays an intense orange-red emission light with a maximum at ca. 563 nm. While luminescence quenching occurs in **2** and **3** by electron transfer of a photoelectron to the electronegative acceptor molecule of ptp.

Introduction

Significant interest has recently arisen in organic synthesis and coordination chemistry for the design and synthesis of novel coordination polymers via hydro(solvo)thermal in situ ligand reactions.[1] Upon coordination of a substrate (L) to a metal (M) center, a ligand's properties (such as electrophilic or nucleophilic character, acidity, and susceptibility to oxidation or reduction) are often significantly altered, and therefore its reactivity can be enhanced or inhibited; the coordination can even make possible a reaction that would otherwise not take place.[2] The hydro(solvo)thermal method has been proved to be a promising technique in the preparation of highly stable, infinite metal−ligand frameworks together with many interesting phenomena[3] such as a redox process of copper, ligand oxidative coupling, hydrolysis, and substitution. We and other groups have developed some in situ ligand syntheses including copper(II)-mediated ligand oxidative coupling, hydrolysis, substitution, and alkylation toward construction of novel metal−organic framework materials.[1i,4,5] Nevertheless, it is still a challenge to predict

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(1) (a) Constable, E. C. *Metals and Ligand Reactivity (New, revised, and expanded edition)*; VCH: Weinheim, Germany, 2005. (b) Michelin, R. A.; Mozzon, M.; Bertani, R. *Coord. Chem. Rev.* **1996**, *147*, 299−338. (c) Kukushkin, V. Y.; Pombeiro, A. J. L. *Chem. Rev.* **2002**, *102*, 1771−1802. (d) Evans, O. R.; Lin, W.-B. *Acc. Chem. Res.* **2002**, *35*, 511−522. (e) Burgess, J.; Hubbard, C. D. *Adv. Inorg. Chem.* **2003**, *54*, 71−155. (f) Ye, Q.; Wang, X.-S.; Zhao, H.; Xiong, R.-G. *Chem. Soc. Rev.* **2005**, *34*, 208−225. (g) Zhang, X.-M. *Coord. Chem. Rev.* **2005**, *249*, 1201−1219. (h) Zhang, J.-P.; Chen, X.-M. *Chem. Commun.* **2006**, 1689−1699. (i) Chen, X.-M.; Tong, M.-L. *Acc. Chem. Res.* **2006**, in press (ar068084p).

(2) Pombeiro, A. J. L.; Kukushkin, V. Y.; McCleverty, J. A.; Thomas, J. M. *Comprehensive Coordination Chemistry II*; Elsevier Pergamon: New York, 2004.

(3) (a) Lin, W.-B.; Wang, Z.-Y.; Ma, L. *J. Am. Chem. Soc.* **1999**, *121*, 11249−11250. (b) Evans, O. R.; Xiong, R.-G.; Wang, Z.-Y.; Wong, G.-K.; Lin, W.-B. *Angew. Chem., Int. Ed.* **1999**, *38*, 536−538. (c) Zhang, J.-P.; Zheng, S.-L.; Huang, X.-C.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2004**, *43*, 206−209.

(4) (a) Zhang, X.-M.; Tong, M.-L.; Chen, X.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 1029−1031. (b) Zheng, Y.-Z.; Tong, M.-L.; Chen, X.-M. *New J. Chem.* **2004**, *28*, 1412−1415. (c) Hu, S.; Chen, J.-C.; Tong, M.-L.; Wang, B.; Yan, Y.-X.; Batten, S. R. *Angew. Chem., Int. Ed.* **2005**, *44*, 5471−5475. (d) Tong, M.-L.; Li, L.-J.; Mochizuki, K.; Chang, H.-C.; Chen, X.-M.; Li, Y.; Kitagawa, S. *Chem. Commun.* **2003**, 428−429. (e) Hu, S.; Zhou, A.-J.; Zhang, Y.-H.; Ding, S.; Tong, M.-L. *Cryst. Growth Des.* **2006**, *6*, 2543−2550.

(5) (a) Cheng, J.-K.; Yao, Y.-G.; Zhang, J.; Li, Z.-J.; Cai, Z.-W.; Zhang, X.-Y.; Chen, Z.-N.; Chen, Y.-B.; Kang, Y.; Qin, Y.-Y.; Wen, Y.-H. *J. Am. Chem. Soc.* **2004**, *126*, 7796−7797. (b) Zhang, X.-M.; Fang, R.-Q.; Wu, H.-S. *J. Am. Chem. Soc.* **2005**, *127*, 7670−7671. (c) Li, D.; Wu, T.; Zhou, X.-P.; Zhou, R.; Huang, X.-C. *Angew. Chem., Int. Ed.* **2005**, *44*, 4175−4178.

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and control the ligand reactions toward our target products, and more knowledge of this field is needed.

Besides the reversible cleavage involving in the protein folding and unfolding process in biological systems, both the oxidative formation of the disulfide bond and the reductive cleavage of the disulfide bond have been explored as an attractive route to functional ligands and new matrials.[6] 4,4′-Dithiodipyridine (dtdp) has recently stricken coordination chemists' attention because of its twisted conformation[7a] with a C−S−S−C torsion angle of ca. 90° and axial chirality that potentially generate *M* and *P* enantiomers in chiral crystal engineering[7b] as well as easy cleavage of the S−S bond.[7c−g] As an extension of our continuing interest in hydro(solvo)thermal ligand reactivity and new coordination architectures,[4] we carried out the solvothermal reactions of CuI with dtdp in MeCN in different ratios at different temperatures, from which a two-dimensional (2D) coordination network of $[Cu_4I_4(tdp)_2]$ (**1**; tdp = 4,4′-thiodipyridine) was obtained at 120 °C and two three-dimensional (3D) coordination networks of $[Cu_5I_5(ptp)_2]$ (**2**) and $[Cu_6I_6(ptp)_2]$ (**3**) [ptp = 1-(4-pyridyl)-4-thiopyridine] were obtained at 160 °C. The three products are stable in air and are insoluble in water and common organic solvents.

Experimental Section

Materials and Physical Measurements. The reagents and solvents employed were commercially available and used as received without further purification. The carbon, hydrogen, and nitrogen microanalyses were carried out with an Elementar Vario-EL CHNS elemental analyzer. The Fourier transform IR spectra were recorded from KBr pellets in the range 4000−400 cm^{-1} on a Bio-Rad FTS-7 spectrometer. Powder X-ray diffraction intensities for **1** (Figure S1 in the Supporting Information) were measured at 293 K on a Rigaku D/max-IIIA diffratometer (Cu Kα, $\lambda = 1.540\,56$ Å). The crushed single-crystalline powder samples were prepared by crushing the crystals and scanned from 5 to 60° with a step of 0.1°/s. The calculated pattern of **1** was generated with PowderCell. UV−vis absorption experiments were performed on a Perkin-Elmer Lambda 35 UV−vis spectrometer equipped with an integrating sphere for diffuse-reflectance spectroscopy. The spectra were collected in the 210−800-nm range at room temperature. Powdered crystals homogeneously diluted with a nonabsorbing matrix (MgO) and gently tapped into a sample holder were used as samples. Photoluminescence measurements of compound **1** were measured on an Edinburgh FLS-920 spectrophotometer equipped with a continuous Xe-900 xenon lamp and a μF900 microsecond flash lamp at room temperature. Photoluminescence measurements of compounds **2** and **3** were carried out on a home-assembled emission detection system. A single-crystal sample was mounted on a copper pin attached to a Displex cryorefrigerator. A metallic vacuum chamber with quartz windows was attached to the cryostat, and the chamber was evacuated to approximately 7−10 bar with a turbomolecular pump, which allows cooling down to ca. 17 K. The crystals were irradiated with 450-nm light from a pulsed dinitrogen dye laser. The emitted light was collected by an Oriel 77348 PMT device, positioned at 17° to the incident laser beam, and processed by a LeCroy digital oscilloscope with a 1−4-GHz sampling rate.

Synthesis of $[Cu_4I_4(tdp)_2]$ (1). A mixture of CuI (0.095 g, 0.5 mmol) and dtdp (0.052 g, 0.25 mmol) in a MeCN solution was stirred for 15 min in air and then transferred to and sealed in a 25-mL Teflon reactor, which was heated in an oven to 120 °C for 75 h. After 15 h of gradual cooling to room temperature, orange block crystals were obtained and then filtered, washed, and dried in air (yield ca. 85%). Elem anal. Calcd for $C_{20}H_{16}Cu_4I_4N_4S_2$: C, 21.10; H, 1.42; N, 4.92; S, 5.63. Found: C, 21.14; H, 1.48; N, 4.97; S, 5.91. IR (KBr, cm^{-1}): 3426(w), 3040(w), 1583(vs), 1535(w), 1476(s), 1413(s), 1217(m), 1102(m), 1062(m), 1013(m), 807(s), 721(s), 532(m), 487(m).

Synthesis of $[Cu_5I_5(ptp)_2]$ (2). A mixture of CuI (0.095 g, 0.5 mmol) and dtdp (0.052 g, 0.25 mmol) in a MeCN solution was stirred for 15 min in air and then transferred to and sealed in a 25-mL Teflon reactor, which was heated in an oven to 160 °C for 80 h. After 15 h of gradual cooling to room temperature, black block crystals were obtained and then filtered, washed, and dried in air (yield ca. 35%). Elem anal. Calcd for $C_{20}H_{16}Cu_5I_5N_4S_2$: C, 18.08; H, 1.21; N, 4.22; S, 4.83. Found: C, 17.97; H, 1.20; N, 4.22; S, 4.88. IR (KBr, cm^{-1}): 3432(w), 3045(w), 1616(vs), 1585(vs), 1492(w), 1465(s), 1411(w), 1280(m), 1212(m), 1106(vs), 1062(w), 814(m), 780(w), 556(w), 496(m).

Synthesis of $[Cu_6I_6(ptp)_2]$ (3). The process is similar to that above but where the molar ratio of CuI/dtdp was increased from 0.5:0.25 to 1.0:0.25. Red block crystals were obtained (yield ca. 15%). Elem anal. Calcd for $C_{10}H_8Cu_3I_3N_2S$: C, 15.81; H, 1.06; N, 3.69; S, 4.22. Found: C, 15.85; H, 1.03; N, 3.66; S, 4.35. IR (KBr, cm^{-1}): 3403(w), 3050(w), 1614(s), 1589(vs), 1492(w), 1464(s), 1407(m), 1281(m), 1226(w), 1100(vs), 1059(m), 1023(w), 814(m), 780(w), 696(w), 559(m), 488(m).

X-ray Crystallography. Data collection of **1**−**3** was performed with Mo Kα radiation ($\lambda = 0.710\,73$ Å) on a Bruker Apex CCD diffractometer at 293(2) K. The raw data frames were integrated with *SAINT*$^+$, which also applied corrections for Lorentz and polarization effects. Absorption corrections were applied by using the multiscan program *SADABS*.[8] The structures were solved by direct methods, and all non-hydrogen atoms were refined anisotropically by least squares on F^2 using the *SHELXTL* program.[9] Hydrogen atoms on organic ligands were generated by the riding mode (C−H = 0.93 Å). Crystal data as well as details of data collection and refinements for complexes **1**−**3** are summarized in Table 1. Selected bond distances and bond angles are listed in Table 2.

Results and Discussion

Synthesis. As reported, the dtdp ligand in most of the compounds tends to adopt the pyridine form that coordinates with metal atoms through the nitrogen donor without S−S bond cleavage under room temperature.[7a,b] However, in our case, when we conduct the reactions of the dtdp ligand with

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(6) (a) Humphrey, S. M.; Mole, R. A.; Rawson, J. M.; Wood, P. T. *Dalton Trans.* **2004**, 1670−1678. (b) Caradoc-Davies, P. L.; Hanton, L. R. *Dalton Trans.* **2003**, 1754−1758. (c) Horikoshi, R.; Mochida, T.; Moriyama, H. *Inorg. Chem.* **2002**, *41*, 3017−3024.

(7) (a) Tabellion, F. M.; Seidel, S. R.; Arif, A. M.; Stang, P. J. *J. Am. Chem. Soc.* **2001**, *123*, 7740−7741. (b) Horikoshi, R.; Mochida, T. *Coord. Chem. Rev.* **2006**, *250*, 2595−2609. (c) Diaz, C.; Arancibia, A. *Polyhedron* **2000**, *19*, 2679−2687. (d) Han, L.; Bu, X.; Zhang, Q.; Feng, P. *Inorg. Chem.* **2006**, *45*, 5736−5738. (e) Sukcharoenphon, K.; Moran, D.; Schleyer, P. v. R.; McDonough, J. E.; Abboud, K. A.; Hoff, C. D. *Inorg. Chem.* **2003**, *42*, 8494−8503. (f) Horikoshi, R.; Mochida, T.; Moriyama, H. *Inorg. Chem.* **2002**, *41*, 3017−3024. (g) Diaz, C.; Arancibia, A. *Polyhedron* **2000**, *19*, 2679−2687.

(8) Sheldrick, G. M. *SADABS 2.05*; University of Göttingen: Göttingen, Germany.

(9) *SHELXTL 6.10*; Bruker Analytical Instrumentation: Madison, WI, 2000.

Table 1. Crystal Data and Structure Refinements for **1**−**3**

	1	**2**	**3**
formula	$C_{20}H_{16}Cu_4I_4N_4S_2$	$C_{20}H_{16}Cu_5I_5N_4S_2$	$C_{10}H_8Cu_3I_3N_2S$
fw	1138.25	1328.69	759.56
cryst size	0.13 × 0.12 × 0.08	0.20 × 0.11 × 0.07	0.20 × 0.09 × 0.07
cryst syst	monoclinic	monoclinic	triclinic
space group	$P2/n$	$C2/c$	$P\bar{1}$
a (Å)	8.004(1)	36.073(3)	9.745(1)
b (Å)	10.385(1)	11.6925(9)	10.221(1)
c (Å)	18.407(3)	14.624(1)	10.287(1)
α (deg)	90	90	60.877(2)
β (deg)	93.330(2)	96.524(2)	61.959(1)
γ (deg)	90	90	81.087(2)
V (Å^3)	1527.4(4)	6128.4(8)	786.4(1)
Z	2	8	2
D_c (g cm^{-3})	2.475	2.880	3.208
μ (mm^{-1})	6.943	8.607	10.025
reflns collcd	5599	12298	4661
unique reflns (R_{int})	2876 (0.0202)	5873 (0.0272)	2879 (0.0166)
no. of param	154	325	172
S on F^2	1.044	1.020	1.078
R1,[a] wR2[b] [$I > 2\sigma(I)$]	0.0388, 0.0949	0.0440, 0.0932	0.0330, 0.0783
R1,[a] wR2[b] (all data)	0.0472, 0.0998	0.0577, 0.0992	0.0362, 0.0801

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

CuI under solvothermal conditions, the starting dtdp reagent was unprecedentedly converted into two isomeric tdp and ptp ligands at 120 and 160 °C, respectively (Scheme 1), rather than into a common pyridine-4-thiolate ligand.[7c−g] Compound **1** was prepared by CuI and dtdp in a 2:1 molar ratio at 120 °C. When the same reaction as that of **1** was carried out at 160 °C, compound **2** was obtained, and concomitantly, the starting dtdp reagent was in situ converted into a new ptp ligand, which is an unprecedented zwitterionic functional ligand characteristic of mixed nitrogen and sulfur donors. Moreover, the successful isolation of **2** with a μ_2-sulfur bridging mode prompted us to increase the molar ratio of CuI/dtdp. As expected, compound **3** was successfully obtained from the solvothermal reaction of CuI and dtdp in a 4:1 molar ratio at 160 °C. Considering the character of the dtdp ligand as well as the colorless block crystals of S_8[10] observed as byproducts of all three reactions and the fact that **1** can also be obtained as the unique product from the solvothermal reaction of CuI with tdp at 160 °C, we speculated that the formation of isomeric tdp and ptp ligands was involved in both the S−S bond cleavage[7c,d] and the S−C(sp^2) bond cleavage. The tdp ligand presumably resulted from the recomplexation of both cleavaged subunits at 120 °C, whereas ptp was formed at a higher temperature of 160 °C, which suggests that the energy barrier in the formation of ptp is larger and the temperature plays a critical role in the formation of the final products.

Table 2. Bond Lengths (Å) and Angles (deg) for **1**−**3**[a]

Compound **1**			
Cu1−I1	2.658(1)	Cu1−N2B	2.019(5)
Cu1−I2	2.697(1)	Cu1−I2A	2.797(1)
Cu2−I1	2.846(1)	Cu2−N1	2.017(5)
Cu2−I2	2.652(1)	Cu2−I1A	2.668(1)
Cu1−I1−Cu2A	57.54(2)	N2B−Cu1−I2A	97.8(1)
Cu1−I1−Cu2	56.93(2)	I1−Cu1−I2A	113.96(3)
Cu2A−I1−Cu2	58.66(3)	I2−Cu1−I2A	111.07(3)
Cu2−I2−Cu1	58.86(3)	N1−Cu2−I2	108.4(2)
Cu2−I2−Cu1A	56.05(2)	N1−Cu2−I1A	108.2(2)
Cu1−I2−Cu1A	59.65(3)	I2−Cu2−I1A	118.58(3)
N2B−Cu1−I1	109.7(2)	N1−Cu2−I1	95.6(2)
N2B−Cu1−I2	106.0(2)	I2−Cu2−I1	111.66(3)
I1−Cu1−I2	116.37(3)	I1A−Cu2−I1	111.83(3)
Compound **2**			
Cu1−I1	2.693(1)	Cu3−I4A	2.629(1)
Cu1−I2	2.883(1)	Cu3−N1C	2.033(6)
Cu1−S2	2.239(2)	Cu4−I4	2.617(1)
Cu1−S1	2.277(2)	Cu4−I4A	2.641(1)
Cu2−I1	2.519(1)	Cu4−S1	2.262(2)
Cu2−I2	2.647(1)	Cu5−I5	2.691(1)
Cu2−I3	2.540(1)	Cu5−I5B	2.662(1)
Cu3−I2	2.677(1)	Cu5−S2	2.313(2)
Cu3−I3	2.689(1)	Cu5−N3D	2.040(6)
Cu2−I1−Cu3	58.00(4)	I1−Cu2−I2	124.49(5)
Cu2−I1−Cu1	59.56(3)	I1−Cu2−I2	116.24(4)
Cu2−I2−Cu3	56.96(3)	I3−Cu2−I2	124.48(4)
Cu2−I2−Cu1	55.74(3)	N1C−Cu3−I4A	107.3(2)
Cu3−I2−Cu1	104.28(3)	N1C−Cu3−I2	107.1(2)
Cu2−I3−Cu3	58.01(3)	I4A−Cu3−I2	112.77(4)
Cu4−I4−Cu3A	106.06(5)	N1C−Cu3−I3	102.0(2)
Cu4−I4−Cu4A	60.19(4)	I4A−Cu3−I3	108.96(4)
Cu3A−I4−Cu4A	65.70(4)	I2−Cu3−I3	117.66(4)
Cu5B−I5−Cu5	65.44(4)	S1−Cu4−I4	111.42(7)
S2−Cu1−S1	128.50(9)	S1−Cu4−I4A	118.15(8)
S2−Cu1−I1	100.73(6)	I4−Cu4−I4A	119.81(4)
S1−Cu1−I1	116.04(7)	N3D−Cu5−S2	113.4(2)
Cu2−Cu1−I1	56.89(3)	N3D−Cu5−I5B	103.7(2)
S2−Cu1−I2	116.63(7)	S2−Cu5−I5B	113.10(6)
S1−Cu1−I2	89.26(6)	N3D−Cu5−I5	106.8(2)
I1−Cu1−I2	103.75(4)	S2−Cu5−I5	109.99(6)
I1−Cu2−I3	116.66(5)	I5B−Cu5−I5	109.38(4)
Compound **3**			
Cu1−I1	2.705(1)	Cu2−S1	2.296(2)
Cu1−I2	2.579(1)	Cu2−N2D	2.052(5)
Cu1−I1A	2.620(1)	Cu3−I1	2.767(1)
Cu1−S1	2.555(2)	Cu3−I3	2.628(1)
Cu2−I2	2.801(1)	Cu3−I3C	2.621(1)
Cu2−I2B	2.668(1)	Cu3−S1A	2.323(2)
Cu1A−I1−Cu1	75.81(4)	N2D−Cu2−I2B	104.3(2)
Cu1A−I1−Cu3	76.05(4)	S1−Cu2−I2B	113.31(6)
Cu1−I1−Cu3	121.14(4)	N2D−Cu2−I2	100.4(2)
Cu1−I2−Cu2B	105.21(4)	S1−Cu2−I2	108.97(6)
Cu1−I2−Cu2	66.78(4)	I2B−Cu2−I2	117.58(4)
Cu2B−I2−Cu2	62.42(4)	S1A−Cu3−I3C	112.48(5)
Cu3C−I3−Cu3	67.70(4)	S1A−Cu3−I3	117.51(6)
S1−Cu1−I2	108.18(6)	I3C−Cu3−I3	112.30(4)
S1−Cu1−I1A	97.32(5)	S1A−Cu3−I1	99.14(6)
I2−Cu1−I1A	123.58(5)	I3C−Cu3−I1	103.05(4)
S1−Cu1−I1	115.14(5)	I3−Cu3−I1	110.52(4)
I2−Cu1−I1	108.51(5)	Cu2−S1−Cu3A	123.04(7)
I1A−Cu1−I1	104.19(4)	Cu2−S1−Cu1	75.18(6)
N2D−Cu2−S1	111.3(2)	Cu3A−S1−Cu1	85.65(6)

[a] Symmetry codes for **1**: (A) $-x - {}^5/_2, y, -z - {}^1/_2$; (B) $x + 1, y - 1, z$. Symmetry codes for **2**: (A) $-x + {}^1/_2, -y + {}^3/_2, -z + 1$; (B) $-x + 1, y, -z + {}^1/_2$; (C) $x, y, z + 1$; (D) $x, y + 1, z$. Symmetry codes for **3**: (A) $-x, -y + 3, -z + 2$; (B) $-x + 1, -y + 3, -z + 2$; (C) $-x, -y + 2, -z + 2$; (D) $x + 1, y + 1, z - 1$.

Crystal Structures. (a) Structure of 1. The structure of **1** is a 2D coordination network of 2-fold interpenetration (Figure 1a,b). Each copper(I) atom is tetrahedrally coordinated by three iodide anions and a nitrogen atom from the tdp ligand with Cu−I and Cu−N distances of 2.652(1)−2.846(1) and 2.017(5)−2.019(5) Å, respectively. In each Cu_4I_4 core, the four copper(I) atoms are linked by four μ_3-iodide anions to complete a distorted cubane unit, similar to

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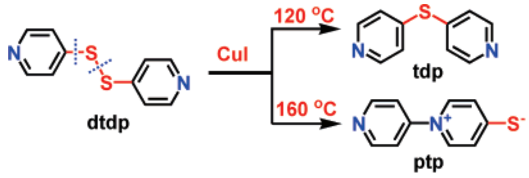
(10) Crystal data for S_8: orthorhombic, space group $Fddd$, $a = 10.464(4)$ Å, $b = 12.851(5)$ Å, $c = 24.51(1)$ Å, $V = 3296(2)$ Å^3.

Scheme 1. Schematic Representation of the In Situ Ligand Reactions



those of other reported Cu_4I_4 tetramer units.[11] The intracubane Cu−Cu distances are 2.563(1)−2.734(2) Å, which are comparable to those found in other 0D structurally characterized $Cu_4I_4L_4$ complexes (L = nitrogen-containing ligand),[11b] a 1D necklace structure of $[Cu_4I_4(dtdp)_2]$·EtCN, a 1D tubular structure of $[Cu_4I_4(dtdp)_2]$·MeCN,[12a] and a 3D triple-interpenetrated network of $[Cu_4I_4(bpp)_2]$ [bpp = 1,3-bis(4-pyridyl)propane],[12b] but are slightly shorter than those [2.778(2) and 2.802(1) Å] found in a 2D square-grid network of $[Cu_4I_4L_2]$ (L = 1,12-diphenyl-5,8-dioxa-2,11-dithiadodecane).[12c] Each cubane-like Cu_4I_4 cluster acts as the four-connected node and the angular tdp ligand as the spacer to construct a 2D undulating net of (4,4) topology. The 2D net has enough empty space to provide for a 2-fold interpenetration.

To our knowledge, the in situ generated tdp ligand is, for the first time, derived from dtdp under solvothermal conditions, though it has been employed to synthesize some metal−tdp compounds.[13]

(b) Structure of 2. There are five unique copper(I) atoms, five iodide anions in two types (μ_2- and μ_3-iodide), and two ptp ligands in the asymmetric unit of **2** (Figure 2a). Three of the five copper(I) atoms (Cu1, Cu3, and Cu5) adopt slightly distorted tetrahedral coordination geometries, while the other two (Cu2 and Cu4) adopt trigonal coordination geometries. The Cu1 atom is surrounded by two iodide anions and two sulfur atoms of two ptp ligands [Cu−I = 2.693(1) and 2.883(1) Å; Cu−S = 2.239(2)−2.277(2) Å; I/S−Cu−S/I = 89.26(6)−128.50(9)°] as well as by a Cu···Cu contact [Cu1···Cu2 = 2.593(1) Å]. Cu2 is coordinated by three iodide anions [Cu−I = 2.519(1)−2.647(1) Å; I−Cu−I = 116.65(5) and 124.49(5)°] as well as by three Cu···Cu contacts [2.539(1)−2.927(2) Å]. Cu3 is coordinated by three iodide anions and one nitrgoen atom of the ptp ligand [Cu−I = 2.677(1)−2.689(1) Å; Cu−N = 2.033(6) Å; I/N−Cu−N/I = 102.0(2)−117.66(4)] as well as two Cu···Cu contacts [2.539(1) and 2.859(2) Å]. Cu4 is surrounded by two iodide anions and one sulfur atom from a ptp ligand [Cu−I = 2.617(1) and 2.641(1) Å; Cu−S = 2.262(2) Å; S/I−Cu−I = 111.42(7)−119.81(4)°] as well as by three Cu···Cu contacts [2.637(2)−2.927(2) Å]. Cu5 is coordinated by two iodide anions, one sulfur atom, and one nitrogen atom from two ptp ligands [Cu−I = 2.662(1) and 2.691(1) Å; Cu−S = 2.313(2) Å; Cu−N = 2.040(6) Å; I/S−Cu−N/S/I = 103.9(2)−113.10(6)°] as well as by a Cu···Cu contact [2.893(2) Å]. Each ptp ligand acts as a μ_3 bridge in which the sulfur donor coordinates to two copper(I) atoms. There are two types of inorganic units: the Cu_8I_8 cluster unit (the Cu···Cu contacts of 2.538−2.928 Å) and the Cu_2I_2 dimer unit (the Cu4···Cu4A contact of 2.894 Å). Interestingly, both types of inorganic cluster units are alternately connected by the μ_2-sulfur bridges into 1D inorganic chains along the *a* axis (Figure 2b), which are further joined by the ptp spacers into a 3D network with 2D channels (Figure 2c). The 3D net adopts a 2-fold interpenetration to achieve a close-packed structure.

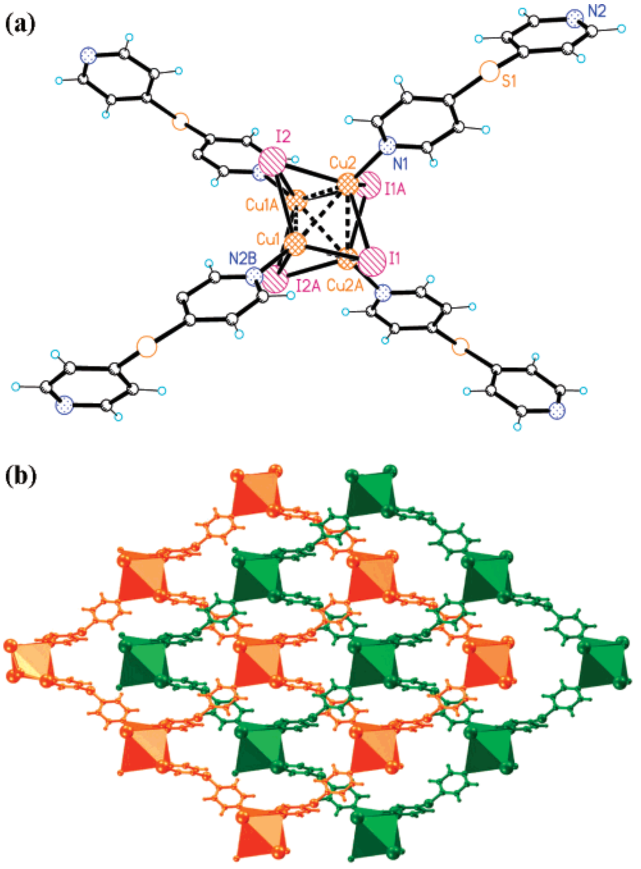


Figure 1. Coordination environment (a) and the 2-fold interpenetrating sheets (b) in **1**. Atom color code: Cu, orange; I, purple; S, yellow; N, blue; C, green.

(c) Structure of 3. The asymmetric unit of **3** contains three unique copper(I) atoms, three iodide anions in two types (μ_2- and μ_3-iodide), and one ptp ligand (Figure 3a). All of the copper atoms adopt tetrahedral coordination environments. The Cu1 and atoms are surrounded by three iodide anions and one sulfur atom of a ptp ligand. Cu2 is coordinated by two iodide anions, one sulfur atom, and one nitrogen atom from two ptp ligands. The Cu−I, Cu−S, and Cu−N distances are 2.579(1)−2.801(1), 2.296(2)−2.555(2), and 2.052(5) Å, respectively. The ptp ligand acts as a μ_4 bridge in which the sulfur donor coordinates to three copper(I) atoms [Cu−S−

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(11) (a) Kyle, K. R.; Ryu, C. K.; DiBenedetto, J. A.; Ford, P. C. *J. Am. Chem. Soc.* **1991**, *113*, 2954−2965. (b) Vega, A.; Saillard, J. Y. *Inorg. Chem.* **2004**, *43*, 4012−4018.

(12) (a) Blake, A. J.; Brook, N. R.; Champness, N. R.; Crew, M.; Deveson, A.; Fenske, D.; Gregory, D. H.; Hanton, L. R.; Hubberstey, P.; Schröder, M. *Chem. Commun.* **2001**, 1432−1433. (b) Hu, S.; Tong, M. L. *Dalton Trans.* **2005**, 1165−1167. (c) Kim, T. H.; Lee, K. Y.; Shin, Y. W.; Moon, S.-T.; Park, K.-M.; Kim, J. S.; Kang, Y.; Lee, S. S.; Kim, J. *Inorg. Chem. Commun.* **2005**, *8*, 27−30.

(13) (a) Ni, Z.; Vittal, J. J. *Cryst. Growth Des.* **2001**, *1*, 195−197. (b) Jung, O. S.; Park, S. H.; Kim, D. C.; Kim, K. M. *Inorg. Chem.* **1998**, *37*, 610−611.

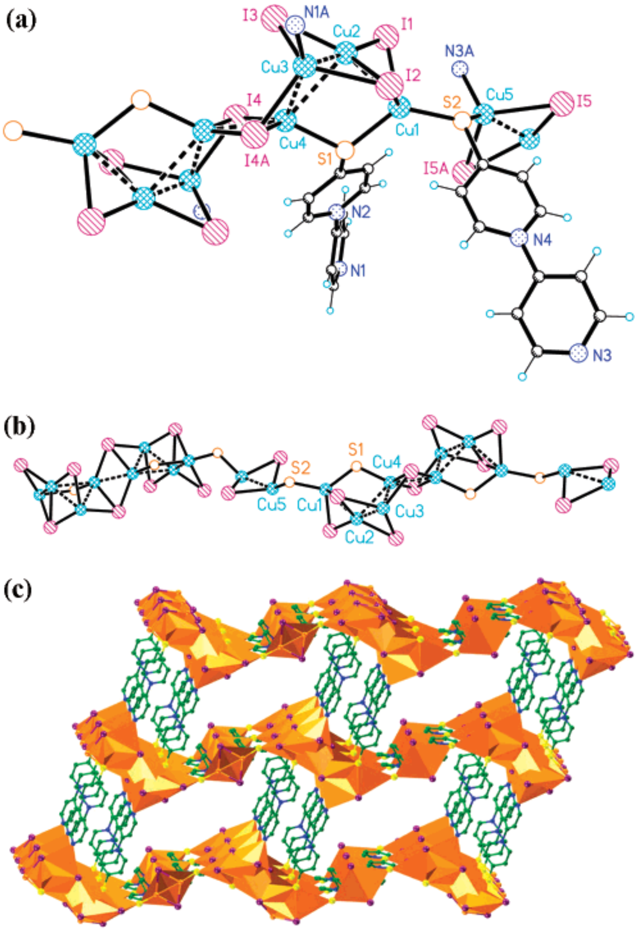

Figure 2. Perspective views of the 1D inorganic chain composed of Cu_8I_8, μ_2-sulfur, and Cu_2I_2 subunits along the *a* axis direction (a) and a single 3D coordination network (b) of the 2-fold interpenetrating nets in **2**. Atom color code: Cu, orange; I, purple; S, yellow; N, blue; C, green.

Cu = 75.18(6)−123.04(7)°]. The adjacent Cu···Cu distances among the Cu1, Cu2, and Cu3 atoms fall in range of 2.836−2.966 Å.

It is noteworthy that there exist rare 2D inorganic $(CuI)_n$ layers with 20-membered $(CuI)_{10}$ circular units in **3** (Figure 3b). Each layer of (4,4) topology consists of three types of Cu_2I_2 dimeric units: the four-connected Cu_2I_2 unit, the two-connected Cu_2I_2 unit via the two iodide atoms as connectors, and the two-connected Cu_2I_2 unit via the two copper atoms as connectors. Each four-connected Cu_2I_2 unit connects four two-connected Cu_2I_2 units via sharing two copper corners and two iodide corners, and each two-connected Cu_2I_2 unit connects two four-connected Cu_2I_2 units via sharing two copper corners or two iodide corners into the resulting 2D $(CuI)_n$ layers. These 2D layers are further pillared by ptp spacers into a non-interpenetrating 3D coordination network (Figure 3c). It should be noted that the majority of reported copper(I) halide polymeric species are based on 0D cluster units, such as rhomboid Cu_2X_2 dimers, cubane or step-cubane Cu_4X_4 tetramers, and 1D zigzag $[CuX]_n$ chain, double-stranded $[Cu_2X_2]_n$ ladders, and ribbon and hexagonal $[Cu_6X_6]_n$ column motifs,[14] and a limited number of examples containing 2D inorganic copper(I) halide sheets have been observed.[15]

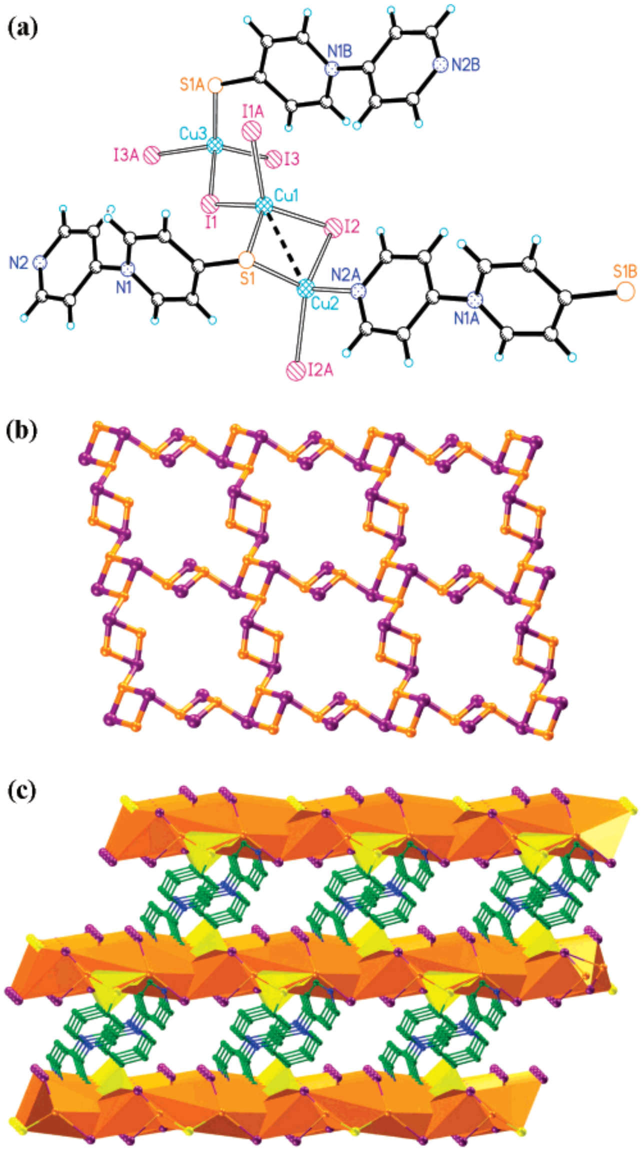

Figure 3. 2D inorganic sheet with $(CuI)_{10}$ square subunits viewed along the *c* axis (a) and the 3D coordination network (b) in **3**. Atom color code: Cu, orange; I, purple; S, yellow; N, blue; C, green.

UV−Vis Reflectance and Photoluminescence Spectroscopy. The UV−vis absorption spectra for complexes **1**−**3** were recorded in reflectance mode in the solid state at room temperature (Figure 4). According to the spectra, the wavelength absorption bands of **1** occur at 242, 340, and

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(14) (a) Graham, P. M.; Pike, R. D. *Inorg. Chem.* **2000**, *39*, 5121−5132. (b) Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S. Lorimer, K. R. *J. Chem. Soc., Chem. Commun.* **2000**, 935−936. (c) Dai, J.; Munakata, M.; Wu, L.-P.; Kuroda-Sowa, T.; Suenaga, Y. *Inorg. Chim. Acta* **1997**, *258*, 65−69. (d) Wilkinson, G.; Gillard, R. D.; McCleverty, J. *Comprehensive Coordination Chemistry*; Pergamon: Oxford, U.K., 1987; Vol. 5, p 533. (e) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T. *Adv. Inorg. Chem.* **1999**, *46*, 173−303. (f) Li, G.; Shi, Z.; Liu, X.; Dai, Z.; Feng, S. *Inorg. Chem.* **2004**, *43*, 6884−6886 and references cited therein.

(15) (a) Massaux, M.; Le Bihan, M.-T.; Chevalier, R. *Acta Crystallogr., Sect. B* **1977**, *33*, 2084−2091. (b) Blake, A. J.; Brooks, N. R.; Champness, N. R.; Cooke, P. A.; Deveson, A. M.; Fenske, D.; Hubberstey, P.; Li, W.-S.; Schröder, M. *J. Chem. Soc., Dalton Trans.* **1999**, 2103−2110. (c) Arnby, C. H.; Jagner, S.; Dance, I. *CrystEngComm* **2004**, *6*, 257−275.

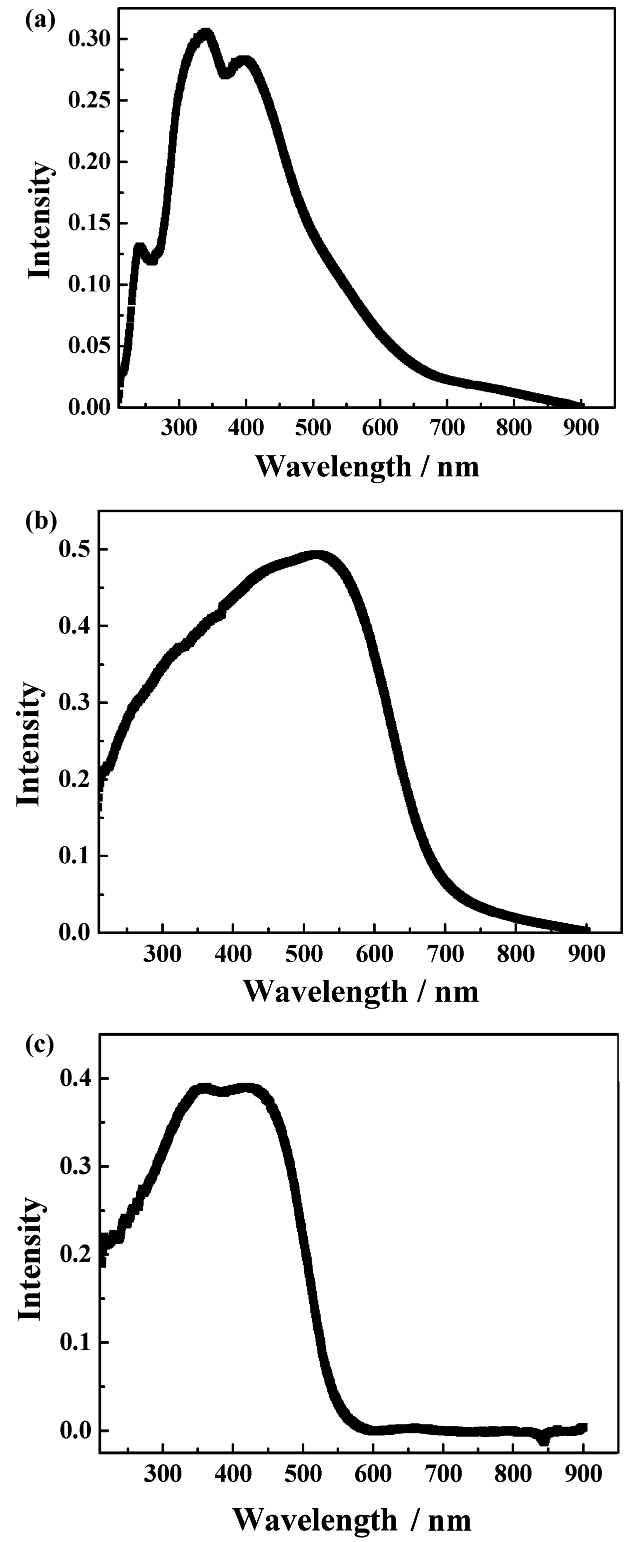

Figure 4. Solid-state UV−vis reflectance spectra of **1** (a), **2** (b), and **3** (c).

396 nm, corresponding to the ligand tdp and Cu_4I_4 clusters, respectively. The absorption bands of **2** (517 nm) and **3** (359 and 421 nm) are red-shifted compared with that of **1**. The absorption band of **2** is much wider and red-shifted than that of **3**, which may be related to the fact that it has the smaller dihedral angles between the pyridine rings of the ptp ligand (**2**, 47.0−49.0°; **3**, 61.8°).

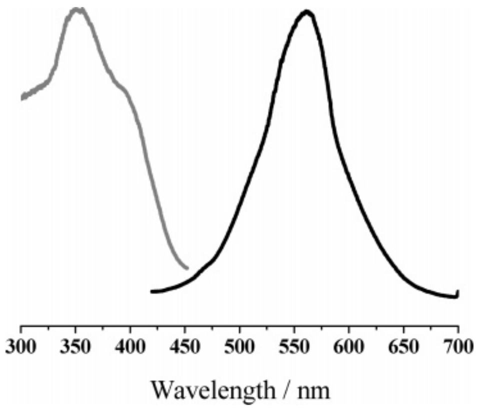

Figure 5. Emission spectra (gray) at 352 nm and excitation spectra (black) at 563 nm of **1**.

Under ambient conditions, solid **1** displays an intense orange-red emission light with a maximum at ca. 563 nm (Figure 5; $\tau = 2.61$ μs; Figure S2 in the Supporting Information), similar to other cuprous halide cluster complexes.[16] Luminescence quenching occurs in **2** and **3** by electron transfer of a photoelectron to the electronegative acceptor molecule of ptp. Such quenching is associated with pronounced color changes (**1**, orange; **2**, black, **3**, red) with the degree of the solid-UV spectra.[17] Even at 17 K, a crystal **2** exhibits very weak emission in the 650−775-nm range ($\tau < 100$ ns), while a crystal **3** exhibits a weak emission at ca. 586 nm with a lifetime of 0.42 μs. Compared with **2**, the quenching in **3** is reduced, which can be attributed to the larger dihedral angles between the pyridine rings, resulting in the decreasing trend of electron transfer.

Conclusions

In this study, we have investigated solvothermal reactions of dtdp with CuI under different reaction conditions, from which three new $(CuI)_x$-based coordination networks that incorporate a Cu_4I_4 cluster unit, Cu_8I_8 and Cu_2I_2 cluster units, and a $(CuI)_n$ layer, respectively, were successfully obtained and characterized. Moreover, two isomeric organosulfide ligands were generated in situ by the cleavage of both S−S and S−C(sp^2) bonds of dtpt and rearrangement reactions. Such an unprecedented in situ solvothermal ligand synthesis provides a useful route to the construction of metal−organosulfide compounds[18] and new materials.

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Supporting Information Available: X-ray crystallographic files of **1**−**3** (CIF) and the luminescence decay of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Ford, P. C.; Cariati, E.; Bourassa, J. *Chem. Rev.* **1999**, *99*, 3625−3648 and references cited therein. (b) Ford, P. C.; Vogler, A. *Acc. Chem. Res.* **1993**, *26*, 220−226.

(17) Andrews, D. L.; Demidov, A. A. *Resonance Energy Transfer*; John Wiley & Sons: Chichester, U.K., 1999.

(18) Xu, Z. *Coord. Chem. Rev.* **2006**, *250*, 2745−2757.