Luminescent Coordination Polymers Constructed from Flexible, Tetradentate Diisopyrazole Ligand and Copper(I) Halides

Tomoki Yoneda,[a] Chika Kasai,[a] Yumehiro Manabe,[a] Makoto Tsurui,[a] Yuichi Kitagawa,[a,b] Yasuchika Hasegawa,[a,b] Parantap Sarkar [b] and Yasuhide Inokuma*[a,b]

Abstract: One- and Two-dimensional Coordination polymers composed of structurally flexible, tetradentate diisopyrazole ligand and copper(I) halides were synthesized as crystalline solids. Complexation with copper(I) chloride or bromide resulted in the formation of infinite coordination chains through connecting each diisopyrazole ligand with two copper(I) ions in a trigonal planar coordination geometry. Contrarily, the combination of diisopyrazole ligand and copper(I) iodide gave a two-dimensional coordination network comprising Cu_4I_4 units with stair-step type geometry and diisopyrazoles that acted as both tetradentate and bidentate bridging ligands. All the coordination polymers exhibited visible photo-emission upon UV-irradiation, and the Cu_4I_4 complex showed thermochromic behavior.

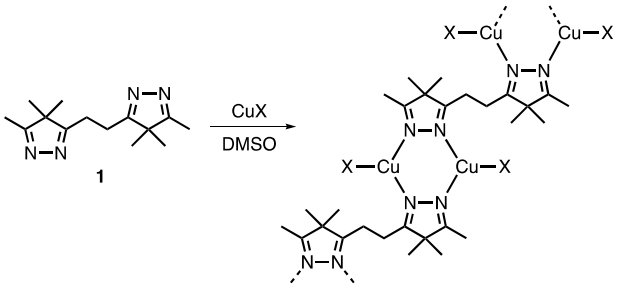
Introduction

Structural diversity of coordination complexes derives from coordination geometry of metal centers and organic ligands. In particular, flexible, multidentate organic ligands have attracted much attention as the key components in varying structures of a favored complex in response to the chemical environment.[1] Recently we have reported ethylene-bridged oligoisopyrazole ligands with flexible carbon skeleton that allowed them to adopt various conformations and coordination geometries.[2] Diisopyrazole **1** provides both divergent and convergent binding sites for metal ions, thus leading to infinite coordination polymers and discrete molecular complexes, respectively. For example, complexation of **1** with zinc(II) or cadmium(II) ions gave two-dimensional grid-like coordination network where only terminal iminic nitrogen atoms of ligand **1** were utilized as metal binding sites.[1,3] Ligand **1** changed its coordination number from two to four in discrete palladium(II) complexes.[4] Such unique structural features of **1** prompted us to further explore its coordination behavior with other transition metals.

In this work, we investigated the complexation behavior of ligand **1** with copper(I) halides. Complexes of copper halides have shown various coordination structures derived from copper(I) centers in trigonal planar or tetrahedral coordination geometries.[5] When halide anions act as μ-halo bridging ligands, a simple set of a metal salt and a ligand can also afford various multinuclear copper(I) clusters.[6] Furthermore, interesting photophysical properties of such copper(I) complexes originated from the d^{10} electronic configuration of copper(I) centers are of abiding significance.[7] Here we report the synthesis, crystal structures, and photoluminescence properties of CuX (X = Cl, Br, I) complexes with flexible diisopyrazole ligand **1**. While infinite coordination polymers were obtained in each case, those for copper(I) bromide and chloride exhibited isostructural one-dimensional chains in which each ligand **1** was connected by copper(I) ions in the trigonal planar coordination geometry. Only copper(I) iodide formed stair-step-like Cu_4I_4 cluster units incorporated in two-dimensional coordination net. Thermochromic behavior of Cu_4I_4 complex was also observed by variable temperature photo-emission measurement.

Results and Discussion

In the first attempt, the typical synthesis of copper(I) chloride complex **2** was achieved when a 400 mM dimethyl sulfoxide (DMSO) solution of ligand **1** (5 mL) was mixed with a suspension of one equivalent of CuCl in DMSO (20 mL). Although almost all the solids were immediately dissolved upon mixing while turning the solution to dark brown, complex **2** was precipitated after one day as a pale yellow solid in 63% yield (Scheme 1).



Scheme 1. Synthesis of one-dimensional coordination chains **2** and **3**.

[a] Dr. T. Yoneda, C. Kasai, Y. Manabe, Prof. Dr. Y. Inokuma
Division of Applied Chemistry, Faculty of Engineering
Hokkaido University
Kita 13, Nishi 8 Kita-ku, Sapporo, Hokkaido 060-8628 (Japan)
E-mail: inokuma@eng.hokudai.ac.jp
[b] Dr. Y. Kitagawa, Prof. Dr. Y. Hasegawa, Dr. S. Parantap, Prof. Dr. Y. Inokuma
Institute for Chemical Reaction Design and Discovery (WPI-ICReDD)
Hokkaido University
Kita 21, Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021 (Japan)

Supporting information and the ORCID identification number(s) for the authors of this article can be found under:

Elemental analysis indicated the complexation of complex **2** with a ligand/metal ratio of 1:2, representing the chemical formula as $[(CuCl)_2(\mathbf{1})]_n$. Infrared (IR) spectrum of **2** showed remarkable changes for the imine stretching bands; while a rather broad signal was observed at 1572 cm^{-1} for pure ligand **1**, complex **2** exhibited split signals at 1576 and 1591 cm^{-1} as a result of metal coordination. Similarly, the combination of ligand **1** with one equivalent of CuBr in DMSO resulted in the formation of coordination polymer $[(CuBr)_2(\mathbf{1})]_n$ (**3**) as a pale yellow solid in 62% yield.

Single crystals of **2** for X-ray diffraction analysis were grown from a 40 mM DMSO solution of **1** and a suspension of CuCl in DMSO. Thorough comparison between single crystal diffraction and powder X-ray diffraction data left no ambiguity in the formation of identical structures of complex **2** under the crystallization conditions to that of the bulk synthesis (see Supporting Information(SI)). Crystal structure of complex **2** exhibited an infinite coordination chain structure in which ligands **1** were doubly bridged by two trigonal planar copper(I) ions (Figure 1a). All the iminic nitrogen atoms of ligand **1** were coordinated by four different copper(I) ions. Diisopyrazole ligand **1** adopted a planar conformation with a mean plane deviation (calculated with 10 carbon and 4 nitrogen atoms) of 0.020 Å. The dihedral angle between two mean planes of neighboring ligands **1** was calculated to be 82.09º. Sum of the bond angles around copper(I) center (∠Cl–Cu–N, ∠N–Cu–N', and ∠N'–Cu–Cl) was 359.9º, indicating trigonal planar geometry. Bond lengths around the copper(I) center were 2.013(3), 1.992(3) Å and 2.1760(10) Å for Cu–N and Cu–Cl, respectively.

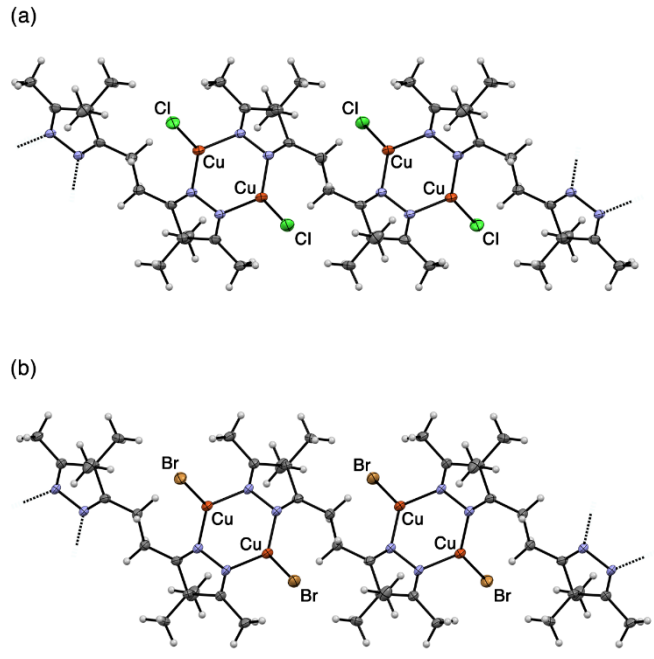
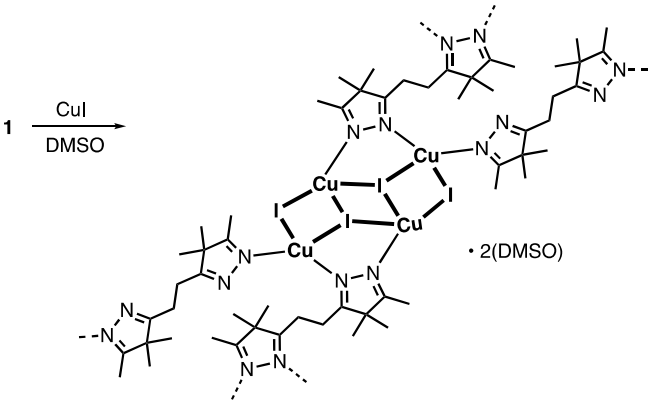


Figure 1. Crystal structures of coordination polymers (a) **2** and (b) **3** viewing along the *b*-axis. Thermal ellipsoids are set at the 50% probability (C: gray, N: sky blue, Cu: orange, Cl: yellow green, Br: brown).

Single crystals of complex **3** for X-ray analysis, obtained from diluted DMSO solution of **1** (8.0 mM) and a suspension of CuBr in DMSO, also revealed one-dimensional coordination chains that is isostructural to complex **2** (Figure 1b). Ligand **1** was similarly observed in its planar conformation (mean plane deviation of 0.019 Å). The sum of the bond angles around the trigonal planar copper(I) center was 360.0º, and the N–Cu and N–Br distances in complex **3** were 1.998(5), 1.997(5) Å and 2.3065(9) Å, respectively. These structural parameters of **3** were also similar to those in complex **2**.

Unlike chloride and bromide salts, when ligand **1** was mixed with CuI in DMSO, complex **4** comprising tetranuclear copper(I) cluster subunits was formed in 82% yield (Scheme 2). Although elemental analysis indicated the ligand/metal ratio of 1:2 in analogy to complexes **2** and **3**, solvent DMSO molecules were also incorporated in a 1:1 ratio to ligand **1**.



coordination network $[(Cu_4I_4)(\mathbf{1})_2 \cdot (DMSO)_2]_n$ (**4**)

Scheme 2. Synthesis of coordination network complex **4**.

Single crystal X-ray analysis of complex **4** revealed the presence of tetranuclear Cu_4I_4 subunits that were two-dimensionally networked by ligands **1**. In the unit cell, two different conformations were observed for ligands **1**. One was in a planar conformation (mean plane deviation of 0.008 Å) functioning as a bidentate bridging ligand where inner two imine groups remained uncoordinated (Figure 2b). The other adopted a stepped conformation and served as a tetradentate ligand that bridged two neighboring Cu_4I_4 subunits (Figure 2c). Owing to the dual role of ligand **1**, Cu_4I_4-embedded grid-like coordination sheets were formed in the crystal, and DMSO molecules were trapped in the interstitial voids by CH–I hydrogen bonds. Despite our attempts, removal or replacement of DMSO molecules from crystals of **4** was unsuccessful.

The centrosymmetric Cu_4I_4 subunits in complex **4** showed stair-step type structure (Figure 2d). Two copper(I) ions located at the corners of the Cu_4I_4 subunit were coordinated by two μ_2-iodo ligands (I1 and I1' in Figure 2d) and two imine groups of ligand **1**. Whereas, other two copper(I) ions at the middle of Cu_4I_4 subunits were coordinated by two μ_3-iodo (I2 and I2' in Figure 2d) and one

μ_2-iodo ligands along with one imine group. In consequence, all the copper(I) ions adopted tetrahedral coordination geometries. Two crystallographically unequivalent copper(I) ions (Cu1 and Cu2 in Figure 2d) were bridged by an isopyrazole ring of ligand **1**, forming a -N–Cu1–I2–Cu2–N- five membered ring system. The neighboring Cu–Cu distances were 3.3328(8), 2.7770(7), and 2.6798(8) Å for Cu1–Cu2, Cu1–Cu2', and Cu1–Cu1', respectively.

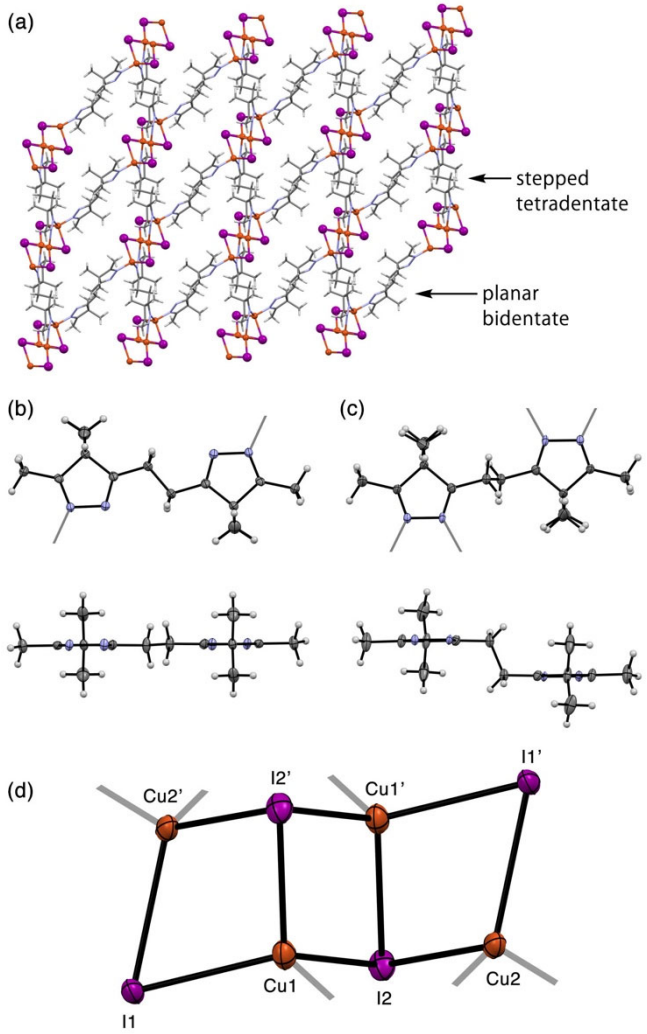


Figure 2. Crystal structures of coordination network **4**. (a) Network structure. ORTEP drawings of ligands **1** in (b) planar conformation and (c) stepped conformation (top: top views, bottom: side views), and (d) Cu_4I_4 subunit. (C: gray, N: sky blue, Cu: orange, I: purple) Solvent molecules were omitted for clarity.

The unique structural features of copper(I) complexes **2**–**4** prompted us to further investigate photophysical properties of them. Although complexes **2**–**4** were not soluble in common organic solvents or water, as anticipated from their pale-yellow color in the solid state, complexes **2**–**4** showed no intense absorption band in the visible region in the diffuse reflectance spectra (See SI). However, copper(I) chloride complex **2** displayed bright green-yellow luminescence (λ_{em} = 530 nm) upon UV irradiation (Figure 3a). The emission quantum yield was determined to be 2.8% for complex **2**. The emission decay was fitted by a double exponential model with emission lifetimes of **2** were recorded as τ_1 = 5.9 and τ_2 = 11.8 μs, as observed for other copper(I) complexes.[5f–g] Despite their structural similarity, emission from copper(I) bromide complex **3** was slightly blue-shifted (λ_{em} = 513 nm) and the emission quantum yield and lifetimes was low (1.3%) as compared with complex **2**. The emission lifetimes of **3** were recorded as τ_1 = 6.8 and τ_2 = 14.2 μs. Since pure ligand **1** is non-emissive, such visible emissions of complexes **2** and **3** were likely to be accounted for the metal-to-ligand charge transfer (MLCT) and/or halogen-to-ligand charge transfer (XLCT) as observed for various copper(I) halide complexes.[8]

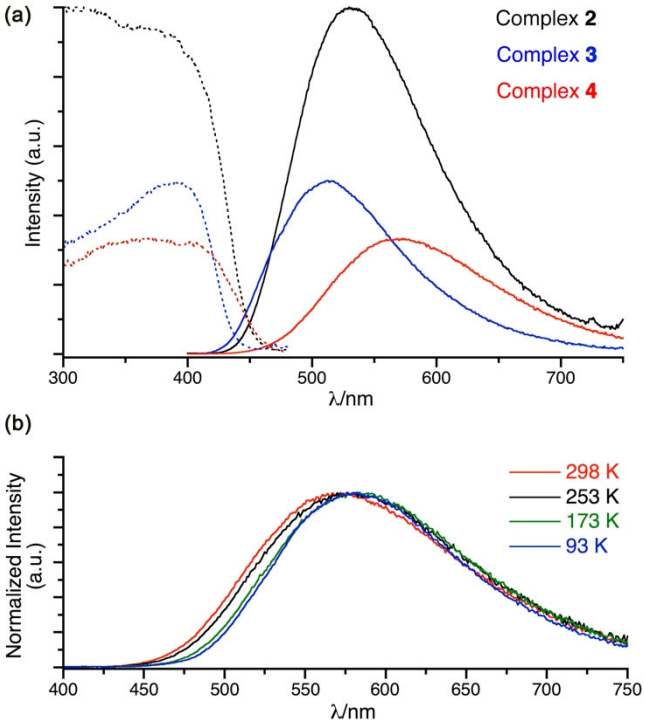


Figure 3. (a) Solid-state excitation (dotted lines; at λ_{em} = 530, 515, and 573 nm for **2**, **3**, and **4**, respectively) and emission (solid lines; λ_{ex} = 380 nm) spectra of complexes **2**–**4** at room temperature. (b) Thermochromic changes of emission spectra of complex **4** (λ_{ex} = 380 nm).

While emission quantum yield was low (<1%), thermochromic behavior was observed for copper(I) iodide complex **4**[9]. At room temperature (298 K), complex **4** showed emission at λ_{em} = 572 nm upon irradiation at 380 nm. The emission lifetimes of **4** were recorded as τ_1 = 2.6 and τ_2 = 6.9 μs. As the temperature decreases from 298 K to 93 K, the emission spectra became slightly sharp and the emission wavelength was red-shifted from 572 nm to 580 nm. Although the spectral changes

seemed to be trivial, the emission color change from yellow-ocher to vivid yellow was even detectable with the naked eyes (see SI).

Conclusions

In summary, we have demonstrated that one- and two-dimensional coordination polymers with different coordination geometries of metal centers could efficiently be synthesized from simple combinations of diisopyrazole ligand **1** and copper(I) halides. Owing to the inherent structural flexibility, ligand **1** adopted both planar and stepped conformations in the solid state. Furthermore, ligand **1** altered the number of coordination bonds in response to the copper(I) halide units. It should be noted that coordination polymers with copper(I) centers in trigonal planar geometries are still rare, because such complexes are usually synthesized from concentrated ligand solutions in which tetra-coordinated complexes are rather preferred. Nonetheless, ligand **1** allowed to isolate trigonal planar copper(I) complexes **2** and **3** as stable crystalline solids presumably due to the tight packing enabled by conformational flexibility. Depending on the structures and halides, various photoluminescence including thermochromic behavior was observed for the obtained complexes. Our results imply that there still exist a lot of unknown coordination structures with interesting photophysical properties that can only be achieved by structurally flexible, multidentate organic ligands.

Experimental Section

General: Solvents and reagents were purchased from WAKO Pure Chemical Industries Ltd., TCI Co., Ltd., and Sigma-Aldrich Co., and used without further purification. Infrared spectra were measured using a JASCO Co. FT/IR-4600 spectrometer. Elemental analysis was performed using a CE440 elemental analyzer (Exeter Analytical, Inc.). Diffuse reflectance spectrum was measured using a JASCO V-670 spectrometer with an integrating sphere unit (JASCO ISN-723). Emission spectra and emission lifetimes were recorded on a HORIBA/Jobin-Yvon Fluorolog-3 spectrofluorometer and corrected for the response of the detector system. Quantum yields were measured using an FP-6300 spectrofluorometer with an integration sphere. Ligand **1** was synthesized according to a reported procedure[2].

Complex [(1)(CuCl)$_2$]$_n$ (2): To a 400 mM DMSO solution of ligand **1** (5 mL) in a 100 mL round-bottom flask, was added a suspension of copper chloride (198 mg, 2.00 mmol) in DMSO (20 mL) with stirring at room temperature. After stirring the solution for 90 min, the reaction solution was then allowed to stand at room temperature for 24 h. A pale yellow precipitate formed from the solution was collected by suction filtration, washed successively with DMSO (10 mL) and chloroform (10 mL), and air-dried on a funnel to give complex **2** (281 mg) in 63% yield. IR (ATR, neat): $\tilde{\nu}$ = 2969 (m), 2950 (w), 2932 (w), 2916 (w), 2909 (w), 2892 (w), 2873(w), 1591 (s), 1576 (s) 1459 (m), 1432 (m), 1398 (s), 1368 (m), 1119 (m), 1037 (m), 965 (m), 869 (m), 768 (s), 612 (s) cm^{-1}; Elemental analysis (%): observed C, 37.73; H, 4.89; N, 12.41. (calcd. for [(CuCl)$_2$(C$_{14}$H$_{22}$N$_4$)]$_n$ (%): C, 37.84; H, 4.99; N, 12.61).

Complex [(1)(CuBr)$_2$]$_n$ (3): To a 200 mM DMSO solution of ligand **1** (10 mL) in a 300 mL round-bottom flask, was added a suspension of copper(I) bromide (287 mg, 2.00 mmol) in DMSO (170 mL) with stirring at room temperature. After stirring the solution for 90 min, the reaction solution was then allowed to stand at room temperature for 24 h. A pale yellow precipitate formed from the solution was collected by suction filtration, washed successively with DMSO (10 mL) and chloroform (10 mL), and air-dried on a funnel to give complex **3** (328 mg) was obtained in 62% yield as a pale yellow solid. IR (ATR, neat): $\tilde{\nu}$ = 2967 (m), 2952 (w), 2928 (w), 2912 (w), 2909 (w), 2892 (w), 2870 (w) 1592 (s), 1575 (s) 1458 (m), 1427 (m), 1395 (s), 1366 (m), 1320(m) 1119 (m), 1037 (m), 963 (m), 867 (m), 763 (s), 609 (s) cm^{-1}; Elemental analysis (%): observed C, 31.49; H, 4.07; N, 10.26. (calcd. for [(CuBr)$_2$(C$_{14}$H$_{22}$N$_4$)]$_n$ (%): C, 31.53; H, 4.16; N, 10.51).

Complex [(1)$_2$(CuI)$_4$•(DMSO)$_2$]$_n$ (4): To a 200 mM DMSO solution of ligand **1** (10 mL) in a 300 mL round-bottom flask, was added a 23.5 mM DMSO solution of copper(I) iodide (170 mL). After 90 min stirring at room temperature, a pale-yellow precipitate was formed. The reaction mixture was kept at room temperature for 24 h without stirring. The precipitate was collected by suction filtration, washed successively with DMSO (10 mL) and chloroform (10 mL) to give complex **4** (1.16 g) in 82% yield. IR (ATR, neat): $\tilde{\nu}$ = 2967(m), 2927(w), 2906(w), 2871(w), 1595(m), 1573(s), 1462(m), 1427(m), 1393(s), 1054(s), 760(m), 609(m) cm^{-1}; Elemental analysis (%): observed C, 26.85; H, 3.66; N, 8.09. (calcd. for [(Cu$_4$I$_4$)(C$_{14}$H$_{22}$N$_4$)$_2$•(DMSO)$_2$]$_n$ (%): C, 27.24; H, 4.00; N, 7.94).

Single crystal X-ray analysis of complexes 2–4: Single crystal X-ray diffraction data were collected by a Rigaku XtaLAB P200 diffractometer equipped with a PILATUS200K detector using a multi-layer mirror (MoK_α radiation λ = 0.71073 Å). All the structures were solved using a dual-space algorithm (SHELXT[10a]) and refined using full-matrix least-squares method (SHELXL[10b]). All non-hydrogen atoms were refined anisotropically.

Crystallographic data of complexes 2–4

Complex 2: [C$_7$H$_{11}$CuClN$_2$], M = 222.17, crystal size: 0.07 × 0.07 × 0.05 mm^3, monoclinic, space group $C2/c$, a = 23.4558(13) Å, b = 5.9720(3) Å, c = 15.3655(8) Å, β = 125.855(5)º, V = 1744.50(18) Å^3 , Z = 8, T = 123(2) K, μ = 2.744 mm^{-1}, D_{calc} = 1.692 g/cm^3, F(000) = 904, 2.143º ≤ θ ≤ 26.000º, 1553 unique reflections out of 1709 with $I > 2\sigma(I)$, 103 parameters, $|\Delta\rho|_{max}$ = 0.750 eÅ^{-3}, $|\Delta\rho|_{min}$ = -0.497 eÅ^{-3}, GOF = 1.139, R_1 =0.0349 and wR_2 = 0.0926 for all data. (CCDC number: 1965217).

Complex 3: [C$_7$H$_{11}$CuBrN$_2$], M = 266.63, crystal size: 0.18 × 0.11 × 0.10 mm^3, monoclinic, space group $C2/c$, a = 23.8021(14) Å, b = 6.0366(3) Å, c = 15.6078(8) Å, β = 126.140(5)º, V = 1811.06(19) Å^3 , Z = 8, T = 123(2) K, μ = 6.761 mm^{-1}, D_{calc} = 1.956 g/cm^3, F(000) = 1048, 2.619º ≤ θ ≤ 24.981º, 1401 unique reflections out of 1590 with $I > 2\sigma(I)$, 103 parameters, $|\Delta\rho|_{max}$ = 2.419 eÅ^{-3}, $|\Delta\rho|_{min}$ = -0.661 eÅ^{-3}, GOF = 1.177, R_1 =0.0434 and wR_2 = 0.1278 for all data. (CCDC number: 1965218).

Complex 4: [C$_{14}$H$_{22}$Cu$_2$I$_2$N$_4$•(CH$_3$)$_2$SO], M = 705.36, crystal size: 0.19 × 0.13 × 0.04 mm^3, triclinic, space group P-1, a = 10.7966(3) Å, b = 10.7981(3) Å, c = 12.3333(3) Å, α = 69.652(3)º, β = 64.233(3)º, γ = 86.311(3)º, V = 1207.65(7) Å^3 , Z = 2, T = 123(2) K, μ = 4.416 mm^{-1}, D_{calc} = 1.940 g/cm^3, F(000) = 680, 2.605º ≤ θ ≤ 25.997º, 4063 unique reflections out of 4705 with $I > 2\sigma(I)$, 243 parameters, $|\Delta\rho|_{max}$ = 1.490 eÅ^{-3}, $|\Delta\rho|_{min}$ = -0.801 eÅ^{-3}, GOF = 1.031, R_1 =0.0251 and wR_2 = 0.0588 for all data. (CCDC number: 1965219).

Acknowledgements

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Keywords: • copper halide • coordination polymer • polyimine • luminescence

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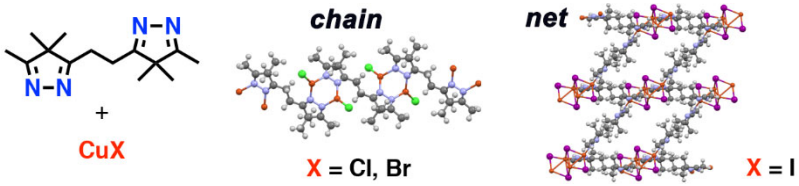

Luminescent one- and two-dimensional coordination polymers were synthesized by complexation of ethylene-bridged diisopyrazole ligand and copper(I) halide. While infinite coordination chains with trigonal planar copper(I) coordination geometry were formed from copper(I) chloride and bromide, coordination network composed of stair-step type Cu_4I_4 subunits was obtained from iodide. The Cu_4I_4-coordination network exhibited thermochromic emission behaviour in the solid state.

Coordination Polymers

*Tomoki Yoneda, Chika Kasai, Yumehiro Manabe, Makoto Tsurui, Yuichi Kitagawa, Yasuchika Hasegawa, Parantap Sarkar, Yasuhide Inokuma**

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Luminescent Coordination Polymers Constructed from Flexible, Tetradentate Diisopyrazole Ligand and Copper(I) Halides