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Synthesis, Structure, and Emissive Properties of Copper(I) Complexes $[Cu^I_2(\mu\text{-}X)_2(\mu\text{-}1,8\text{-naphthyridine})(PPh_3)_2]$ ($X = I, Br$) with a Butterfly-Shaped Dinuclear Core Having a Short Cu–Cu Distance

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New dinuclear copper(I) complexes $[Cu_2(\mu\text{-}X)_2(\mu\text{-}1,8\text{-naphthyridine})(PPh_3)_2]$ ($X = I, Br$) having the butterfly-shaped $\{Cu_2(\mu\text{-}X)_2\}$ unit show red phosphorescence at room temperature in the solid state. Molecular orbital calculations show that the emissions of the new complexes are not directly related to their short Cu···Cu separations [2.6123(5) and 2.6271(4) Å] and are assignable to the triplet charge-transfer excited states from the $\{Cu_2(\mu\text{-}X)_2\}$ core to 1,8-naphthyridine.

Monovalent group 11 metal ions, Au^I, Ag^I, and Cu^I, are known to afford emissive complexes.[1] Several excited states such as metal-centered transitions, intraligand transitions, and charge-transfer (CT) transitions between metal and ligand exist as emissive states, depending on the ligands and steric factors.[1a] In addition, emissions originating from the metal–metal interactions have also been known for multinuclear complexes.[1a,d,g] Among them, recent developments of the copper(I) halide complexes are particularly noteworthy because of their intense emissions,[2] tunable emission energies,[3] and dual emissions due to juxtaposed excited states.[1a] We have reported the solid-state emissions of a series of copper(I) complexes having planar diamond $\{Cu_2(\mu\text{-}X)_2\}$ units ($X = Br, I$) with various mono- and bidentate N-heteroaromatic ligands using PPh_3 as the ancillary ligand.[3] All of the complexes show emissions at room temperature, which were unequivocally assigned to the triplet CT excited states from the $\{Cu_2(\mu\text{-}X)_2\}$ core to N-heteroaromatic ligands by a comparison of the emission energies and reduction potentials of the N-heteroaromatic ligands. The Cu–Cu distances are in the range of 2.82–3.43 Å, which are long enough to neglect Cu–Cu interaction in both the ground and excited states. We are interested in the influence of short Cu–Cu distances upon the emission behaviors of the $\{Cu_2(\mu\text{-}X)_2\}$ complexes. In order to prepare the complexes with short Cu–Cu distances, bridging ligands bearing short bite distances would be useful. Here, we utilize 1,8-naphthyridine (1,8-nap) as the intramolecular bridging N-heteroaromatic ligand, which should bring two Cu^I ions into closer contact with concomitant distortion of the $\{Cu_2X_2\}$ core. Hitherto, over 200 complexes with a $\{Cu^I_2X_2\}$ unit have been prepared with various ligands and most of them possess a planar diamond core.[4] The examples of a folded $\{Cu_2X_2\}$ unit by the small chelating ligand are limited to those with N-heterocyclic carbene,[5a] bis(diphenylphosphino)ethane,[5b,c] allylamine,[5d] dithiocarboxylato,[5e] and (phenylamino)bis(phosphonite).[5f]

The naphthyridine complexes $[Cu_2(\mu\text{-}X)_2(\mu\text{-}1,8\text{-nap})(PPh_3)_2]$ [$X = I$ (**1**), Br (**2**)] are prepared by the reaction of CuX, PPh_3, and 1,8-nap in organic solvents.[6]

The structures of the complexes **1** and **2** are determined by the single-crystal X-ray analysis.[7] Figure 1 shows the structure of iodide complex **1**. Two Cu^I ions are bridged by two I ions and one 1,8-nap. Coordinated by PPh_3 additionally, each Cu atom is in a distorted tetrahedral geometry. The bromide complex **2** adopts an almost identical structure;

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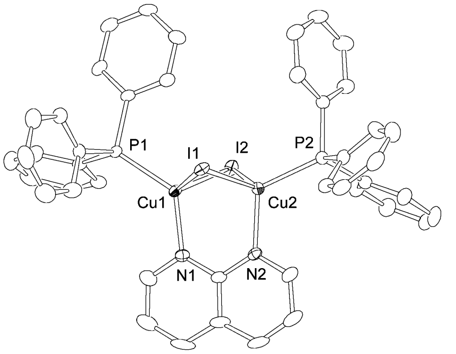

Figure 1. ORTEP drawing of iodide complex **1** with a probability level of 50%. H atoms are omitted for clarity.

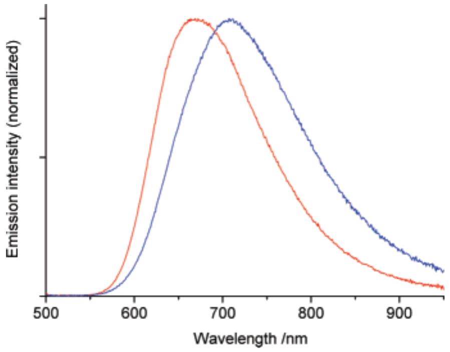

Figure 2. Emission spectra of complexes **1** (red) and **2** (blue) in the solid state at room temperature excited at 337 nm.

indeed, **1** and **2** form the isomorphous crystals.[7] The Cu−Cu distances are 2.6123(5) and 2.6271(4) Å for **1** and **2**, respectively, which are comparable with those found in other copper(I) dimeric complexes bridged by 1,8-nap (2.51−2.61 Å).[8] The dihedral angles between two XCuX triangles are 125.29(2)° and 127.87(2)° respectively for **1** and **2**. Except for the carbene-bridged $\{Cu_2X_2\}$ unit,[5a] the $\{Cu_2X_2\}$ units in the present complexes are among the most distorted cores because of the short Cu−Cu distances and parallel direction of naphthyridine lone pairs.

Figure 2 shows the emission spectra of the bromide and iodide complexes at 290 K in the solid state. The two complexes show broad structureless bands with emission maxima at 670 nm (1.49×10^4 cm^{-1}) and 720 nm (1.39×10^4 cm^{-1}) for iodide and bromide complexes, respectively. The emission lifetimes are 0.83 μs (X = I) and 0.22 μs (X = Br), indicating that the emissions are phosphorescence.[9] The emission spectra at lower temperatures are almost identical with those at room temperature for both **1** and **2** (Figure S1 in the Supporting Information). The decay curves are well fitted as single exponential, and lifetimes become longer at lower temperatures (Figure S2 and Table S1 in the Supporting Information).

The apparent colors of the bromide and iodide complexes are quite similar red-orange. In fact, both complexes show the lowest energy band around 530 nm in absorption spectra in the solid state. The excitation spectra of the complexes are also similar between two complexes and correspond to each absorption spectrum (Figure S1 in the Supporting Information). Therefore, the red shift of the bromide complex is difficult to explain from ground-state properties. Similar observations have been reported for the related copper(I) halide systems, and plausible electron correlations in the excited states have been suggested.[10] Because the involved molecular orbital (MO) corresponds to a weak Cu−X antibonding orbital (vide infra), the bond strength in the excited state may affect the differences of the emission energies.

In order to obtain information about the ground-state electronic structure and the nature of the transitions, we carried out MO calculations of the iodide and bromide complexes using the density functional theory (DFT) method[11] based on the crystal structures. The energy levels near frontier orbitals of **2** are shown in Figure 3, and the components of the MOs are listed in Table S2 in the Supporting Information. The lowest unoccupied MO (LUMO), L + 1, and L + 2 were almost pure 1,8-nap π* orbitals. The highest occupied MO (HOMO) and occupied orbitals near the HOMO are mainly composed of copper and bromide orbitals, where the

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(6) $[Cu_2(\mu\text{-}I)_2(\mu\text{-}1,8\text{-nap})(PPh_3)_2]$ (**1**). To the solution obtained by dissolving CuI (39.8 mg, 0.21 mmol) and PPh_3 (131.8 mg, 0.50 mmol) in CH_3CN (16 mL) was added 1,8-nap (13.9 mg, 0.11 mmol) to obtain a clear orange solution. After 1 week, red crystals were deposited in 40% yield (45.6 mg). Anal. Calcd for $C_{44}H_{36}N_2Cu_2I_2P_2$: C, 51.03; H, 3.50; N, 2.70. Found: C, 50.77; H, 3.59; N, 2.7. $[Cu_2(\mu\text{-}Br)_2(\mu\text{-nap})(PPh_3)_2]$ (**2**). To the solution obtained by dissolving CuBr (24.8 mg, 0.17 mmol) and PPh_3 (45.7 mg, 0.17 mmol) in CH_3CN (16 mL) was added 1,8-nap (11.1 mg, 0.085 mmol) to obtain a clear orange solution. After 1 week, red crystals were deposited in 55% yield (43.4 mg). Anal. Calcd for $C_{44}H_{36}N_2Cu_2I_2P_2$: C, 56.12; H, 3.85; N, 2.98. Found: C, 56.24; H, 4.03; N, 3.05. **1** and **2** were substantially insoluble in common organic solvents such as acetonitrile, chloroform, dichloromethane, *N*,*N*-dimethylformamide, dimethyl sulfoxide, tetrahydrofuran, and alcohols, which prevented measurement of their properties in solution.

(7) Crystal data for **1**: $C_{44}H_{36}Cu_2I_2N_2P_2$, $M = 1035.63$, monoclinic, space group $P2_1/a$, $a = 18.068(2)$ Å, $b = 9.9984(7)$ Å, $c = 23.394(2)$ Å, $\beta = 107.103(4)°$, $V = 4039.3(6)$ Å^3, $Z = 4$, $T = -120$ °C, 17 545 measured reflections and 7815 independent reflections, and R1 = 0.0285 and wR2 = 0.0879 for 7350 observed reflections [$I > 2\sigma(I)$] and 469 parameters. Crystal data for **2**: $C_{44}H_{36}Cu_2Br_2N_2P_2$, $M = 941.63$, monoclinic, space group $P2_1/a$, $a = 17.766(3)$ Å, $b = 9.701(2)$ Å, $c = 23.392(4)$ Å, $\beta = 107.009(3)°$, $V = 3855(1)$ Å^3, $Z = 4$, $T = -170$ °C, 23 521 measured reflections and 8470 independent reflections, and R1 = 0.0277 and wR2 = 0.0697 for 6921 observed reflections [$I > 2\sigma(I)$] and 469 parameters.

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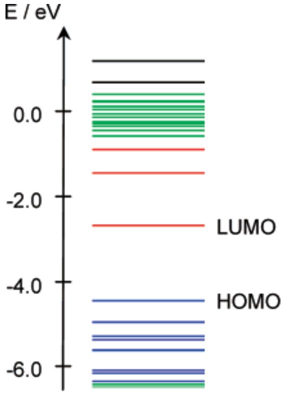

Figure 3. Energy levels of complex **2** near frontier orbitals. Each level was colored according to the main components: blue, Cu 3d and Br 3p; red, 1,8-nap; green, PPh_3; black, Cu 4s and 4p.

Cu d orbitals mix well with the Br p orbitals, showing that the Cu and Br ions afford mixed orbitals in the $\{Cu_2Br_2\}$ core. It is noted that, in spite of the short Cu−Cu distance, the Cu−Cu interaction does not affect these occupied orbitals significantly because the interaction between the Cu and halide orbitals is dominant in the $\{Cu_2X_2\}$ core. The unoccupied orbital composed of the Cu 4s and 4p orbitals that is somewhat perturbed by the Cu−Cu interaction was observed above the vacant π^* orbitals of 1,8-nap and PPh_3. The results for the iodide complex are very similar to those of the bromide complex (Table S3 in the Supporting Information).

The time-dependent (TD)-DFT calculation shows that the HOMO−LUMO transitions are substantially forbidden for **1** and **2** and that the substantially allowed lowest singlet excited states are the (H − 5)−LUMO transitions (Tables S4 and S5 in the Supporting Information).[12] As mentioned above, the H − 5 is the Cu−X mixed orbitals in both complexes (Figure S4 in the Supporting Information). Therefore, the absorption and corresponding phosphorescence can be ascribed to the singlet and triplet CT excited states from the $\{Cu_2(\mu\text{-}X)_2\}$ core to 1,8-nap, respectively.

Both the diamond and butterfly-shaped $\{Cu_2X_2\}$ complexes have common natures of HOMO (Cu−X mixed orbitals; Figure S5 in the Supporting Information) and LUMO (ligand π^* orbitals). The difference is that HOMO−LUMO transitions are symmetry-allowed for the former and symmetry-forbidden for the latter. This is due to the different orientations of the aromatic ligands and the core shape. As expected, in the case of the complexes with diamond $\{Cu_2X_2\}$ cores, the HOMO−LUMO transition has a large oscillator strength.[13] In the present complexes, the symmetry of LUMO and the π^* orbital of 1,8-nap do not match those of the HOMO because LUMO and HOMO are antisymmetric and symmetric to the virtual mirror plane on 1,8-nap, respectively. For the π^* orbital of 1,8-nap, the allowed transition is from H − 5 because it contains the symmetrically suitable d orbital by bending of the Cu_2X_2 core (Figure S4 in the Supporting Information). The present results show that, for the complexes having a $\{Cu(I)_2X_2\}$ core with an N-heteroaromatic ligand, the absorption and emission energies depend not only upon the energy of the π^* orbital but also upon its orientation and the shape of the $\{Cu_2X_2\}$ core.

For the d^{10} dinuclear and multinuclear complexes that have short metal−metal distances, the emissions related to metal−metal interactions have been reported.[1d,g] For several copper(I) complexes where the π^* orbitals are absent or have higher energies, the emissions involving the orbitals perturbed by the metal−metal interaction are suggested.[1a,14] As shown in Figure 3, in the present complexes, the vacant Cu orbitals that are responsible for the Cu−Cu interaction are found above the 1,8-nap π^* and PPh_3 orbitals. Therefore, although the Cu−Cu distances are short in the present complexes, the emissions originating from the Cu−Cu interaction were unobservable because of the lower-lying CT state from $\{Cu_2X_2\}$ to 1,8-nap.

In summary, we show the characteristic difference of the emissions between the butterfly-shaped and planar dinuclear copper(I) halide complexes by using 1,8-nap as a bridging ligand. Although the emissive excited states are related to the triplet CT excited states from the $\{Cu_2(\mu\text{-}X)_2\}$ core to 1,8-nap, as in the case of complexes with $\{Cu_2X_2\}$ diamond cores with N-heteroaromatic ligands, the MO associated with the emission is different because of the direction of the π^* orbital of the 1,8-nap ligand. It turns out that the short Cu−Cu distance does not directly affect the emission characteristics of the present butterfly-shaped complexes.

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Supporting Information Available: Crystallographic data of **1** and **2** in CIF format, absorption and excitation spectra at room temperature, temperature-dependent emission spectra and decay curves, tables of emission lifetimes, tables of Mulliken population near frontier orbitals, tables of calculated excited-state energies, and figures of selected MOs. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] TD-DFT calculations show that the energies and oscillator strengths of $S_0 \rightarrow S_1$ are 1.04 eV (1193 nm) and 0.0008 and 1.07 eV (1162 nm) and 0.0005 for iodide and bromide complexes, respectively (Tables S4 and S5 in the Supporting Information). However, the substantially lowest allowed transitions are $S_0 \rightarrow S_7$; their calculated energies and oscillator strengths are 2.22 eV (559 nm) and 0.0355 and 2.31 eV (536 nm) and 0.0404 for iodide and bromide complexes, respectively. Besides the acceptable oscillator strengths, considerable agreement of the calculated and observed energies also supports the assignments of the lowest absorptions of **1** and **2**. The $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_7$ transitions mainly correspond to HOMO−LUMO and (H − 5)−LUMO transitions for both iodide and bromide complexes (Tables S4 and S5 in the Supporting Information).

[13] Using the single-crystal structure data, we calculate the transition energies of the pyridine complexes, $[\{Cu_2X_2\}(PPh_3)_2(pyridine)_2]$, which have diamond $\{Cu_2X_2\}$ cores. The oscillator strengths of $S_0 \rightarrow S_1$, which correspond to the HOMO−LUMO transition, are 0.0183 and 0.0191 for X = I and Br, respectively.

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