Dual mechanoluminescence system comprising a solid-state di-copper(I) complex containing N-heterocyclic carbene ligands†

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A simple N-heterocyclic carbene (NHC) ligand linked to a flexible propylene linker allows the formation of "Cu–Cu"- and "2 Cu"-type geometries inside a molecular framework. The incorporation of two Cu(I) ions in close proximity was observed in the Cu–Cu-type geometry but not in the 2 Cu-type geometry. In this study, the ground-state geometries of solid-state di-copper(I) complexes containing NHC ligands with ethyl substituents were modulated by external stimuli. A crystal with the 2 Cu-type geometry was obtained by the mechanical grinding and heating of a crystal with the Cu–Cu-type geometry, as confirmed by the disappearance of the absorption peak attributed to cuprophilic interaction in the diffuse reflection spectrum. The mechanical grinding of both crystals afforded composite states comprising small crystallites of the corresponding crystalline phases and an amorphous domain. This structural transition was accompanied by tribochromism and chronochromism. The results suggest that these di-copper(I) complexes show promise for the development of stimuli-responsive photoluminescent Cu(I) complexes.

1. Introduction

There is a growing interest in photoluminescent materials with properties that change in response to external stimuli for application in versatile, advanced photosystems. Exploring novel design concepts for Cu complexes is important in terms of sustainability because Cu is an abundant resource. A number of Cu(i) complexes have recently been found to possess sophisticated photoluminescent properties, and interest in cuprophilic interactions is growing rapidly.

For the past four decades, d10–d10 Cu(i)–Cu(i) contact has been assumed to occur based on the single-crystal X-ray structural analyses of Cu(i) complexes. Spectroscopic studies have confirmed that cuprophilic interactions do indeed occur. It has been reported that intermolecular Cu(i)–Cu(i) distances from 2.4–2.8 Å may indicate cuprophilic interactions. Cuprophilic interactions often occur between Cu(i) complexes that contain two or more Cu atoms bridged by multidentate ligands. Che et al. found that cuprophilic interactions resulted in absorptions at wavelengths above 300 nm, which were attributed to a distinct ndσ* → σ∗(n+1) transition.

Interest in Cu(i) complexes containing N-heterocyclic carbene (NHC) ligands is rapidly increasing due to their synthetic versatility and potential for use in innovative photonic applications. Simple NHC ligands joined by flexible propylene linkers allow two Cu(i) ions to be in close proximity, which is referred to as the Cu–Cu geometry (Fig. 1, left). However, when NHC ligands have bulky substituents,
The ions are not in close proximity due to unfavorable molecular self-packing. These binuclear Cu(i) complexes have a 2 Cu geometry, which prohibits cuprophilic interaction (Fig. 1, right). Recently, Steffen et al. reported the tribochromism of binuclear Cu(i) complexes with tert-butyl substituents and 2 Cu geometries. They proposed that the change in emission was caused by the mechanically induced formation of an exciplex between the Cu center and the F atom of PF₆⁻. They also reported that the Cu(i)-F⁻ interactions in the two-coordinated [Cu(NHC)(pyridine)] complexes make the complex strongly luminescent. These results show that cuprophilic interactions and other Cu-X interactions can drastically alter the photophysical properties of compounds.

We have demonstrated that the formation of the eight-shaped geometry, which has considerable Cu-Cu interactions, as opposed to the O-shaped geometry, which has no Cu-Cu interactions, depends on the substituents. Time-dependent density functional theory calculations suggested a distinct difference in electronic state between the Cu-Cu and 2 Cu geometries; electronic absorption was observed at a longer wavelength (ca. 330 nm) in the Cu-Cu geometry compared to in the 2 Cu geometry. Since both geometries have been found in the crystals of complexes with analogue ligands, the cuprophilic interactions can be altered by applying external stimuli. However, to date, no detailed structural analysis has been conducted on analogue di-Cu(I) complexes after exposure to external stimuli.

In this study, we investigated the effects of external stimuli on the solid-state di-Cu(i) NHC complex 1 (Fig. 1, R = ethyl) using differential scanning calorimetry (DSC), powder X-ray diffraction (PXRD), diffuse reflectance spectroscopy, and photoluminescence spectroscopy. The results indicate that mechanical grinding and heating unexpectedly induced a ground-state structural modulation (Fig. 2). We confirmed the transition and distinct changes in the photophysical properties of complex 1.

2. Materials and methods

2.1. Materials

Complex 1 [Cu₂(LEt)₂][PF₆]₂ and the corresponding di-silver(i) complex [Ag₂(LEt)₂][PF₆]₂ were prepared as described previously (Scheme 1). Solid A (without solvent acetone) was obtained by grinding the as-synthesized sample and heating it at 130 °C for 30 min under vacuum. Sample A was mechanically ground by hand for 5 min under ambient atmosphere at 20 °C, resulting in solid AG. Solid B was obtained by mechanically grinding and heating solid A to 180 °C under vacuum. Solid BG was obtained by mechanically grinding B.

2.2. Methods

¹H nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECA500 spectrometer (Tokyo, Japan) to determine the solvation state using the residual solvent signal as a reference (δ = 2.50 ppm for DMSO-d₆). NMR measurements were conducted in degassed solvent due to the high probability of oxidation in solution. The spectra were analyzed using Delta version 5. The solvation states were determined by differential thermal analysis and thermogravimetric analysis using a TG 8120 instrument (Rigaku Corp., Tokyo, Japan). DSC was carried out using a DSC-60 instrument (Shimadzu Co., Kyoto, Japan) to investigate the thermal behavior. The measurements...
were performed under N$_2$ gas flow (100 mL min$^{-1}$) at a heating rate of 5 °C min$^{-1}$. The measurements were carried out using a non-sealed sample to evaluate the desolvation behaviors as well as the phase transition behaviors (e.g., recrystallization and crystal-to-crystal phase transitions). The ultraviolet (UV)–visible spectra of the powder states were obtained in diffuse reflection mode using a UV-2600i instrument (Shimadzu Co., Kyoto, Japan). PXRD measurements were performed using an Ultima-IV diffractometer (Rigaku Corp., Tokyo, Japan) to evaluate the solid state. All measurements were performed over an angular range of 5°–20° using CuKα radiation (1.542 Å, 40 kV, and 40 mA). The emission spectra and emission quantum yields (Φ) of the solid states were determined using a spectrometer with an integrating sphere (Labsphere, Model 4P-GPS-030-SF NH, USA), a monochromated xenon light source, and a cooled charge-coupled device as detectors. For lifetime measurements, a nitrogen laser (Model NL 100, Stanford Research Systems, Inc., CA, USA) was used as the excitation source, and the emission was detected using a monochromator equipped with a photomultiplier tube. Signal analysis was carried out using a digital oscilloscope.

3. Results and discussion

3.1. Preparation of solid A

We prepared di-copper(i) complex 1 [Cu$_2$(LEt)$_2$](PF$_6$)$_2$ bearing 1,3-propanediylbis[3-ethyl-1H-imidazol-1-yl-2(3H)-ylidene] (LEt) NHC ligands (Fig. 1, R = ethyl) as described previously (Scheme 1). Since the substituents were not bulky, the complex adopted a Cu–Cu geometry both in methanol solution and as a crystalline solid. One acetone molecule was solvated in each crystal of complex 1 after synthesis. The acetone was removed by heating the di-copper(i) complex to 130 °C (Fig. S1†). Since the solvated molecules could affect the cuprophilicity in unpredictable ways, the desolvated sample was denoted as solid A. A showed emission at 510 nm, which can be attributed to phosphorescence based on reported structures with Cu–Cu interactions.

3.2. Structural modulation by external stimuli from solids A to B

The mechanical grinding of A yielded the powder AG, which showed a slight bathochromic shift of 10 nm in the emission maxima ($\lambda_{em,max}$) compared to A. Tribochromism is a property wherein the color of a material is altered by mechanical grinding. The peak shift observed for AG can be attributed to tribochromism. As shown in Fig. S3 and Table S1 (ESI†), the emissions of the solids all show two-components decays. The major constituent for all solids was the long-lifetime component. No obvious differences were observed in the lifetimes of the major components (21–25 μs). No differences in the PXRD peak positions were observed between samples A and AG, indicating that grinding did not significantly alter the crystalline structure of the material (Fig. 3b). The broad peaks observed in the PXRD pattern of AG in Fig. 3b suggest that the crystals in AG were smaller than those in A (Fig. S4a, ESI†). That is, mechanical grinding disrupted the crystalline arrangement. The quantum yield (Φ) was significantly lower after mechanical grinding (Fig. 3c). An exothermic peak near 82 °C is observed in the DSC heating thermogram of AG (Fig. 3d), indicating the presence of an amorphous domain that coexisted with the crystallites of A after mechanical grinding, in agreement with the PXRD analysis (Fig. 3b). The exothermic peak observed at $T_{rec}$ in the thermogram of the ground sample can be attributed to recrystallization from the amorphous state. After recrystallization, the Φ value of the sample obtained by heating AG to 130 °C was higher than that of AG. However, it was not as high as the Φ value of the complex in its initial state (A), suggesting the presence of a low-intensity or non-emitting species. The endothermic peak at 150 °C in the DSC curve of AG (Fig. 3d) suggests that a new phase formed after grinding AG and recrystallization by heating at 130 °C. In contrast, heating A without grinding did not generate a new phase, as indicated by the lack of a DSC peak at approximately 150 °C (Fig. 3d). These results indicate an unexpected phase transition caused by the mechanical grinding of the solid state.

Heating AG to 180 °C resulted in a loss of photoluminescence (Fig. 2, B). The PXRD patterns of samples A and B show different diffraction peaks (Fig. 4a). The electronic spectrum of B shows lower absorption intensity at 330 nm compared to the spectrum of A (Fig. 4b). As mentioned, electronic absorption at long wavelength (ca. 330 nm) was observed for the dinuclear copper-NHC complexes with less bulky substituents, indicating the Cu-Cu-type geometry. Thus, the endothermic peak at 150 °C in the DSC thermogram
of AG (Fig. 3d) can be reasonably attributed to the structural transition of crystals with Cu–Cu-type geometry to those with 2 Cu-type geometry.

### 3.3. Multichromism of solid B

Although the photoluminescence of solid B was weak, the solid BG obtained after mechanical grinding emitted distinct yellow luminescence under UV light (Fig. 2 and 5a), similar to the di-copper(i) complex with tert-butyl substituents reported by Steffen et al. A comparison of the PXRD profiles obtained before and after mechanical grinding showed that the spectra of B and BG had similar peaks (Fig. 5b); however, mechanical grinding resulted in decreased peak intensity and peak broadening (Fig. S4b, ESI†), indicating the formation of an amorphous solid. Similar to the DSC thermogram of AG, the DSC thermogram of BG contained an exothermic peak (Fig. 5c) attributed to the recrystallization of the amorphous domain. From both the PXRD and DSC analyses, we can reasonably conclude that an amorphous domain coexisted with the small crystallites of B in BG. We also confirmed that the transition from B to BG was reversible by heating the solid to a temperature above $T_{\text{rec}}$ after mechanical grinding (Fig. 5d).

The PXRD profile obtained after heating BG at 130 °C was similar to that of B, strongly supporting the reversibility of the transition from B to BG (Fig. S4b, ESI†). Photofunctional amorphous solids occasionally exhibit chronochromic behavior after grinding due to an isothermal transition from a disordered (amorphous) state to an ordered (crystalline) state. Chronochromism is the variation in emission over time at room temperature and without additional external stimuli. In this study, complex 1 exhibited chronochromic behavior (Fig. 5e). BG transitioned back to B when it was stored at 20 °C for 4 h after mechanical grinding. While luminescence was scarcely observed, the sample became highly emissive after additional mechanical grinding. These phenomena clearly indicate the presence of a thermodynamically unstable amorphous domain in the composite system after mechanical grinding but before recrystallization. Notably, weak luminescence was observed after 245 min (Fig. 5e), whereas no luminescence was recognized for fresh B (Fig. 5a). This suggests that complex 1 can nucleate solid A from the amorphous state via recrystallization at room temperature. A possible explanation for this phenomenon is given in section 3.4.

Notably, a distinct absorption band can be found near 330 nm in the spectrum of sample BG (Fig. 5f), whereas this band is not seen in the spectrum of sample B. These results indicate that mechanical grinding induced the structural transition; the cuprophilic interaction, which was absent in B, was recovered in BG (Fig. 5g). However, even though both A and
BG had cuprophilic interactions, the emission colors of the two complexes were extremely different. One possible explanation for this phenomenon is that BG has a Cu–F interaction in addition to the Cu–Cu interaction, which could modify the emission properties. The difference in the short-lifetime component of each emission (0.1–5 μs) might result from this modification (Table S1, ESI†).

3.4. Proposed mechanism of chromic behaviors

We observed a structural transition leading to dual mechano-chromic and chronochromic behaviors in di-copper(i) complexes with NHC ligands joined by propylene bridges; this behavior was directed by the cuprophilicity modulations and interaction with anions.8 As observed for both A and B, mechanical grinding induced the formation of an amorphous domain (Fig. 6). A solvent-free di-Ag(i) complex 2, which is a precursor of complex 1 (Scheme 1), exhibited similar behavior (Fig. S5, ESI†). Therefore, the ability to form composites may be a general property of d10 metal complex analogues. Since the nuclei of B were assumed to form via the mechanical grinding of A and vice versa, the Cu–Cu and 2 Cu geometries were both present in the amorphous domain of complex 1, indicating that some crystals with Cu–Cu geometry transformed into a phase with 2 Cu geometry and vice versa (Fig. 6). Because A exhibited a higher Φ value than B and BG, the mixing of BG and B after the mechanical grinding of A reduced the value of Φ (Fig. 3c).

As previously reported, di-copper(i) complexes with NHC ligands joined by propylene bridges can form both geometries.18 Since solid B tends to form at higher temperatures, we believe that the 2 Cu geometry is promoted at higher temperatures due to the disconnection of the Cu–Cu interaction, which is accelerated by the enhancement of molecular thermal energy. In addition, the reversibility between the B and BG phases at room temperature strongly suggests that the crystalline phase recrystallized via the growth of the remaining small crystallites after mechanical grinding. Therefore, we think that the remaining small crystallites are key to selectively inducing the recrystallization of B from BG. However, a weak luminescence peak assigned to solid A after isothermal annealing is observed in Fig. 5e, suggesting that the nuclei of A can be formed in the amorphous domain at room temperature. Thus, the recrystallization from the remaining crystals and nucleation from the amorphous domain may occur cooperatively.

4. Conclusions

The findings of this study provide a novel concept for molecular design by controlling cuprophilic interactions. They also demonstrate the importance of understanding the amorphous state after mechanical grinding. We observed multi-chromic luminescence in di-copper(i) complexes containing NHC ligands. The complexes exhibit dual tribochromism and chronochromism in the powdered state in the absence of solvent adduct. Based on these properties, the complexes show great potential for use in photoluminescence switches, data storage, and safety applications.

Conflicts of interest

There are no conflicts to declare.

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Notes and references