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Mechanochromic and Thermochromic Luminescence of a Copper Iodide Cluster

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Abstract: The mechanochromic and thermochromic luminescence properties of a molecular copper(I) iodide cluster formulated $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ are reported. Upon mechanical grinding in a mortar, its solid-state emission properties are drastically modified as well as its thermochromic behavior. This reversible phenomenon has been attributed to distortions in the crystal packing leading to modifications of the intermolecular interactions and thus of the $[Cu_4I_4]$ cluster core geometry. Notably, modification of the Cu−Cu interactions seems to be involved in this phenomenon directly affecting the emissive properties of the cluster.

Luminescent materials based on transition-metal complexes have been receiving increasing attention due to their wide field of applications in, for instance, detection, sensing, biological labeling,[1] and display visualization devices.[2] Controlling or tuning the photoluminescence properties of these compounds by external stimuli is particularly attractive in order to obtain photofunctional materials. In this context, modification of the luminescence color in response to mechanical or thermal stimuli is one strategy to achieve this goal. Such materials exhibiting luminescence mechanochromism[3] (piezochromism) or thermochromism[4] have potential applications in optical recording, memory, sensing pressure, or motion systems.[5]

In the literature, examples of luminescent mechanochromic materials based on transition-metal complexes or organic compounds are relatively limited.[6] These materials are characterized by emission wavelength change upon mechanical grinding or pressing of the solid sample. The subsequent reversion to their original solid-state emission is usually achieved upon thermal treatment or recrystallization. Concerning transition-metal complexes, examples reported so far are mainly based on multinuclear gold(I) complexes.[7−12] Examples of a zinc complex,[13] one silver derivative,[14] and two platinum complexes[15] can be also found in the literature.

During the course of studies on luminescent hybrid materials based on copper(I) iodide clusters namely $[Cu_4I_4L_4]$ (L = phosphine ligands),[16] we have discovered the mechanochromic luminescence properties of one of them. Copper iodide clusters are well-known for their thermochromic luminescence properties.[17] This phenomenon is characterized by two emission bands of different energy whose relative intensities vary in temperature.[18] At room temperature, the luminescence is usually dominated by a low energy band (LE, around 550 nm) attributed to a combination of a halide-to-metal charge transfer (XMCT) and copper-centered d → s, p transitions. This emission is called “cluster centered” (CC) as it involves a $[Cu_4I_4]$ cluster centered triplet excited state. At low temperature, this band is extremely weak and the emission is dominated by a higher energy one (HE, around 420 nm) attributed to a triplet halide-to-ligand charge-transfer (XLCT) excited state. Here, we report on the mechanochromic luminescence properties of the $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ cluster whose photoemission properties are modified upon mechanical grinding. This molecular cluster undergoes a great change of its solid state emission properties and in particular shows modification of its thermochromic luminescence properties. This phenomenon is reversible since, upon exposure to solvent or heating, this compound recovers its original crystalline phase and emission properties. Study of the optical properties and structure by X-ray diffraction and NMR analysis of the cluster before and after the grinding process suggests that the mechanochromic behavior originates from local distortions in the crystal packing where the intermolecular arrangement is modified, thus affecting the Cu−Cu distances of the $[Cu_4I_4]$ cluster core. This copper-based coordination cluster enlarges the small family of photoluminescent mechanochromic compounds and represents the first example of a mechano-switchable emissive compound combining both mechanochromic and thermochromic luminescence properties.

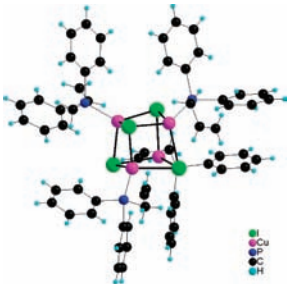

Figure 1. Molecular structure of $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$.

The copper iodide cluster was synthesized in solution from CuI and allyldiphenylphosphine and was obtained as a white crystalline powder (95% yield see Experimental section in the Supporting Information (SI)). Colorless crystals suitable for single crystal X-ray diffraction analysis were also obtained, and the resulting molecular structure is depicted in Figure 1 (view of the unit cell in Figure S1). The cluster presents the classical cubane structure formed by four copper atoms and four iodine atoms which alternatively occupy the corners of a distorted cube. The phosphine ligands are coordinated to each copper atom by the phosphorus atom. Intramo-

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lecular bond lengths and angle values are close to those previously reported for other copper iodide clusters coordinated with phosphine derivatives,[19] but relatively longer Cu−Cu distances (3.3904(7) and 3.1792(6) Å) are observed.

The $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ cluster is a white powder under ambient light (Figure 2). At room temperature and under UV lamp irradiation (peak wavelength at 365 nm), a weak green emission is observed as shown in Figure 2a. The mechanochromic luminescence properties are revealed by grinding the solid sample using a pestle. The weak green emission is then converted into a much more intense yellow one (Figures 2b and 2c show partially and completely crushed samples, respectively), while the color of the sample remains white (Figure 2e). Upon dissolution of the crushed powder in dichloromethane and subsequent evaporation of the solvent, the compound is reverted to the initial pale green emissive phase. The yellow emission is recovered when the solid is ground one more time which indicates a completely reversible phenomenon. After grinding, the weak green emission is also restored by heating the crushed powder at 100 °C for 30 min. The grinding process also affects the thermochromic luminescence properties of the compounds. As shown in Figure 2d, at 77 K in liquid nitrogen, the green emission of the pristine crystalline cluster turns into a bright blue one under UV excitation. This is different for the crushed compound, for which the room temperature yellow emission is replaced by a purple one at 77 K (Figure 2f). When both samples are progressively warmed up, the room temperature emission is recovered, showing a completely reversible thermochromic luminescence mechanism.

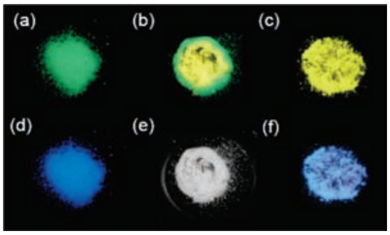

Figure 2. Photos showing luminescence changes of $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ upon grinding and at different temperatures. (a) Cluster before grinding and (b−c) cluster upon grinding under 365 nm (UV lamp) at room temperature. Cluster (d) before and (f) after grinding under 365 nm (UV lamp) at 77 K. (e) Corresponding photo of (b) under ambient light at room temperature.

Powder X-ray diffraction (PXRD) diagrams were recorded for the compound before and after grinding (Figure 3). The diffraction peaks correspond to those calculated from the diffraction data of the single crystal X-ray structure analysis confirming the purity of the powdered sample. No new diffraction peak appears so no new crystalline phase is formed during the grinding process. However, the intensities of the diffraction peaks decrease and their widths increase. The Rieltveld analysis indicates that the grinding process induces a reduction of the crystalline domains down to 150 nm whereas the microstrain contribution is negligible (details in SI). After dissolution and crystallization of the crushed powder or after heating at 100 °C for 30 min (Figure S2), the compound presents an identical diagram of the initial phase confirming the reversibility of the phenomenon. Differential scanning calorimetry (DSC) measurement shows an exothermic peak occurring between 100 and 200 °C only for the compound after grinding which can be assigned to this recrystallization phenomenon. As the heating treatment anneals the grinding ‘effect’, one can suggest that the yellow emissive species result from local distortions in the whole crystalline structure. Note that their photoluminescence efficiency is probably high because small constraints imposed on crystallites by the manual grinding lead to a drastic change of the optical properties of the whole sample.

Elemental analysis of the cluster both before and after grinding gave the expected composition (based on the formula $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ see SI) indicating that no chemical reaction related to adsorption or removal of atmospheric molecules was induced by the grinding. ^{31}P and ^{1}H liquid NMR spectra, UV−vis. absorption spectra (λ_{max} = 300 nm in Figure S4), and luminescence spectra at room temperature under UV excitation (λ_{max} = 615 nm in Figure S5) are similar whether the cluster is crystalline or crushed before the dissolution, showing that the molecular structure of the cluster is preserved in the crushed compound. Solid-state ^{31}P MAS NMR analysis shows identical spectra for the compounds before and after grinding with a single quartet originating from the $^{63,65}Cu-^{31}P$ coupling of the four equivalent phosphorus atoms of the cluster (Figure S3). This suggests that the yellow emissive compound is in low concentration and not detectable.

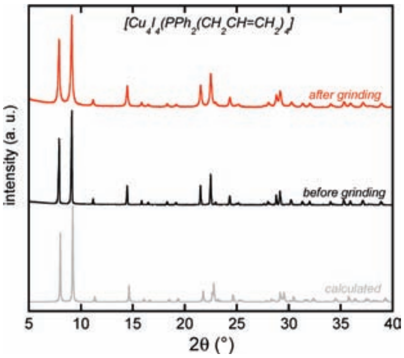

Figure 3. PXRD (Cu Kα) of $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ before and after grinding measured at room temperature and calculated from the single crystal data recorded at 150 K.

Solid state emission and excitation spectra were recorded for the cluster before and after grinding from room temperature down to 8 K (Figure 4a and 4b respectively and Table 1). At 275 K, for the cluster before grinding, a broad emission band is observed at λ_{max} = 530 nm under excitation at λ_{ex} = 360 nm (absolute quantum yield $\Phi_{365\ nm}$ = 2%). This is in agreement with the pale green emission observed in Figure 2a. After grinding, a broad emission band is observed at λ_{max} = 580 nm (λ_{ex} = 360 nm at 275 K, Figure 4b) in agreement with the yellow emission observed in Figure 2c. This yellow band is much more intense as compared to the one of the pristine crystalline powder (absolute quantum yield $\Phi_{365\ nm}$ = 14%). For both uncrushed and crushed clusters, these green and yellow emission bands can be attributed to the CC low energy band (LE) common for $[Cu_4I_4L_4]$ type clusters (see introductary discussion).

At 8 K, for the cluster before grinding, an intense emission band (30 times higher compared to the one at 275 K) is observed at λ_{max} = 440 nm. This emission band can be attributed to the XLCT high energy band (HE) of these clusters. As shown in Figure 4a, by increasing the temperature, the intensity of this blue band (HE) progressively decreases with a concomitant red shift to progressively reach λ_{max} = 530 nm at 275 K (LE). For the crushed cluster, two emission bands with comparable intensities are observed at 8 K (λ_{ex} = 360 nm): a structured one with a maximum at 470 nm (HE) and a second less intense band at λ_{max} = 580 nm (LE) corresponding to the one observed at 275 K. By increasing the temperature from 8 to 275 K, the intensity of the HE band progressively decreases with a concomitant increase of the LE one without significant wavelength shifts. Note that the blue emission band at 440 nm of

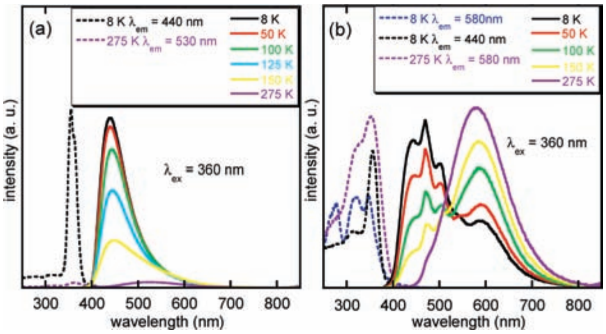

Figure 4. Solid-state luminescence spectra of (a) uncrushed and (b) crushed $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ recorded between 275 and 8 K.

the crystalline phase is also present in the spectrum of the crushed compound at low temperature, in accordance with the remaining crystalline cluster shown by the PXRD analysis.

Thus, the $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ cluster presents two emission bands (LE and HE) with temperature dependent intensities, particularly evident for the crushed compound. For the crystalline cluster, it appears that the LE emission is somehow quenched as its intensity is very low and does not increase upon heating. In this case, the two different excited states (XLCT and CC) seem to be not coupled anymore with independent population of the two states. However, upon grinding, the LE emission is no longer quenched and a thermal activated mechanism seems to be recovered with possible energy transfer between the two excited states (this is even more evident when luminescence spectra are recorded at $\lambda_{ex} = 315$ nm as shown in Figure S6). By exhibiting the typical thermochromic luminescence of copper iodide clusters, this study constitutes another confirmation of the preservation of the $[Cu_4I_4L_4]$ cubane structure in the yellow emissive crushed compound.

Table 1. Luminescence Properties of $[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$ before and after Grinding[a]

$[Cu_4I_4(PPh_2(CH_2CH{=}CH_2))_4]$		λ^{em}_{max} (nm) HE	LE	λ^{ex}_{max} (nm)
uncrushed	8 K	440 (1)	−	360
	275 K	−	530 (0.04)	360−315
crushed	8 K	470 (1)	580 (0.4)	360−315−270
	275 K	−	580 (1.1)	360−315

[a] For each compound, the relative intensities for the HE and LE emission bands are reported in brackets.

Cu−Cu interactions have been reported as influencing the luminescence properties of the cooper iodide clusters and particularly the LE emission band.[18] Indeed, the position of the LE band has been directly related to the Cu−Cu distances in $[Cu_4I_4]$ derivatives.[20] From DFT calculations, the Cu−Cu interactions in the excited state (LUMO) are of bonding character. As the Cu−Cu distances become shorter, the bonding character increases, the energy level is lowered, and thus the LE emission band shifts to a longer wavelength. This effect is observed in our case, with $\lambda_{em} = 530$ nm for the crystalline cluster and 580 nm for the crushed one. This shift suggests that in the crushed state the cluster has shorter Cu−Cu distances. This hypothesis is supported by the surprising long Cu−Cu distances observed in the molecular structure of the cluster which can originate from packing constraints. Thus, after grinding, some clusters could present $[Cu_4I_4]$ cores with shorter Cu−Cu distances, allowing the recovery of the typical thermochromic luminescence properties observed for this cluster family.[21] The 'relaxation' of the Cu−Cu interactions in the crushed compound is also suggested by the cluster emission in solution ($\lambda_{max} = 615$ nm in Figure S5) which takes place at a wavelength closer to the one observed in the solid state for the cluster after grinding ($\lambda_{max} = 580$ nm) compared to the crystalline one ($\lambda_{max} = 530$ nm) and which shows a similar luminescence thermochromic behavior to that of the crushed solid. Thus, the mechanochromism luminescence observed in this study seems to be related to cuprophilic interactions. This is not surprising since most of the mechanochromic luminescent transition-metal complexes reported in the literature involve modulation of aurophilic interactions.[7−11]

In order to explain the origin of the modification of the $[Cu_4I_4]$ core and thus of the Cu−Cu interactions, the crystalline structure of the pristine powder has been analyzed in detail. However, no intermolecular interactions directly involving the $[Cu_4I_4]$ core are observed. Despite the presence of numerous phenyl groups in the crystal structure, no typical $\pi-\pi$ stacking interactions exist either. Only several short CH···H contacts involving the allyl groups of ligands are detected (2.85 Å in Figure S7). This suggests that the mechanical constraints induced by the grinding modify these interligand interactions leading to a different cluster packing in the crushed compound. These local distortions allow the relaxation of the $[Cu_4I_4]$ core, which is probably sterically constrained in the crystalline phase, and drastically modify the luminescence properties. This phenomenon clearly appears as a competition between the crystalline cohesion and the intracluster interactions. Note that this copper cluster is the first compound presenting both mechanochromic and thermochromic luminescence, and further photophysical studies combined with structural analysis are currently in progress to confirm our mechanism assumption.

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Supporting Information Available: Experimental procedures for the cluster synthesis, characterization data, and single crystal X-ray diffraction crystallographic file (CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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