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# Pressure Control of Cuprophilic Interactions in a Luminescent Mechanochromic Copper Cluster

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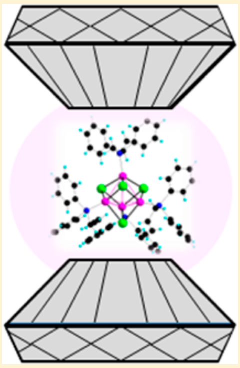
*Supporting Information*

**ABSTRACT:** For the development of applications based on mechanochromic luminescent materials, a comprehensive study of the mechanism responsible for the emission changes is required. We report the study of a mechanochromic copper iodide cluster under hydrostatic pressure, which allows control of crystal packing via modification of the intermolecular interactions. In situ single-crystal powder X-ray diffraction analysis and emission measurements under pressure permit one to establish a direct correlation between the molecular structure and luminescence properties and, in particular, to demonstrate that cuprophilic interactions are responsible for the stimuli-responsive luminescence properties of such multinuclear coordination compounds.



## INTRODUCTION

Stimuli-responsive materials based on luminescent compounds raise tremendous interest because of their potential technological applications as smart photoactive systems.[1−3] Mechanochromic luminescent materials that exhibit reversible modification of the emission wavelength in response to external mechanical forces (grinding, shearing, etc.) are promising candidates for the development of memory devices and motion or damage sensors.[4−11] Despite the increasing number of reported pressure-sensitive luminescent compounds based on organic dyes[12] and, to a much lesser extent, on transition-metal complexes,[13] the understanding of the underlying mechanism remains limited. This can be attributed to the difficulty in characterizing the ground phase, which is usually amorphous and/or in small amount. However, in order to rationally design and develop new stimuli-responsive materials with intriguing properties, an in-depth understanding of mechanochromism mechanisms is still in high demand.

The solid-state luminescence properties of molecular materials depend on the molecular structure and packing mode of the molecules. Therefore, it is usually accepted that mechanical grinding, by modification of intermolecular interactions, alters the structural arrangements and thus changes the emitting energy states.[14] To elucidate the origin of the mechanochromism, it is thus essential to achieve a molecular-level understanding of the structural modifications correlated with the corresponding emissive properties. For such a study, the experiment of choice is combined single-crystal X-ray diffraction (SCXRD) measurements and luminescence characterizations under the application of mechanical stress. The use of a diamond anvil cell (DAC) allows such characterizations along with perfect control of the pressure applied.[15] A few recent studies report the emission evolution of mechanochromic compounds under hydrostatic pressure,[16−22] but only two combine SCXRD and luminescence characterizations.[23,24] In those cases, the effect of hydrostatic pressure on the luminescence properties appeared to be different from that of manual grinding; thus, only indirect information into the mechanochromism mechanism could have been obtained.[23,24] In this context, the study of mechanochromic compounds that exhibit similar behavior under both hydrostatic pressure and grinding is particularly attractive.

The molecular copper iodide cubane clusters [$Cu_4I_4L_4$] (L = phosphine ligand) constitute an original family of luminescent mechanochromic compounds exhibiting a great change of the luminescence properties upon grinding.[25−28] The metallic interactions are highly suspected to be involved in the mechanochromism mechanism. Interestingly, these compounds are rare examples combining both luminescence mechanochromism and thermochromism, a particularly appealing property for the development of multifunctional sensing systems. Here, we report on the study of a luminescent mechanochromic copper iodide cluster under hydrostatic pressure, whose effect is similar to that of the grinding process, thus providing further understanding into the luminescence

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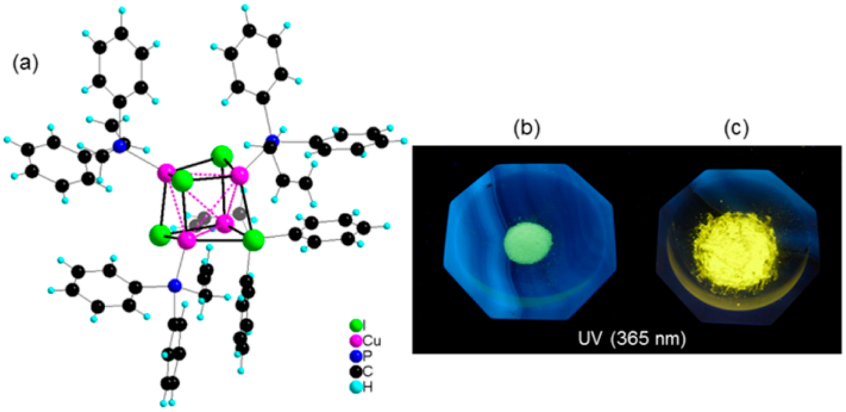

**Figure 1.** (a) Molecular structure of **1** and its crystalline powder (b) before and (c) after manual grinding in an agate mortar under UV.

properties of this family of compounds and especially into the luminescence mechanochromism mechanism. In situ pressure SCXRD and powder X-ray diffraction (PXRD) analyses were correlated with luminescence emission characterizations. By control of the intermolecular interactions via the pressure, this study gives direct proof of the key role of the cuprophilic interactions on the stimuli-responsive luminescence properties of such multinuclear coordination compounds.

## ■ RESULTS

The studied cluster-formulated $[Cu_4I_4(PPh_2CH_2CH{=}CH_2)_4]$ (**1**) is synthesized by reacting copper iodide with allyldiphenylphosphine in dichloromethane according to our previous report.[25] Recrystallization from a dichloromethane/cyclohexane mixture leads to colorless crystals exhibiting a weak green emission under UV excitation. From SCXRD analysis (ambient pressure, 293 K), the cluster crystallizes in the tetragonal space group $P\bar{4}2_1c$. The molecular structure of the cluster presents a cubane geometry formed by four Cu and four I atoms, which alternatively occupy the corners of a distorted cube, with the phosphine ligands coordinated to the Cu atoms (Figure 1a). The cluster sits on a −4 axis and presents relatively long Cu−Cu distances of 3.425(1) and 3.220(1) Å compared to those commonly observed in this family of compounds.[29] Even if the only intercluster interactions are CH···H contacts between the allyl groups, these interligand interactions must be responsible for the unusual stretched $[Cu_4I_4]$ cluster core geometry. The mechanochromic properties of the cluster are characterized by a drastic red shift of the emission color upon grinding of the crystalline powder, from green to yellow, accompanied by enhancement of the luminescence quantum yield from 2 to 14% (Figure 1b,c).[25] The reversibility of the phenomenon is achieved by annealing (100 °C) or fuming ($CH_2Cl_2$) treatments, restoring the initial crystalline and emissive states. Grinding induces only a broadening of the PXRD peaks, suggesting a small portion of phase transformation. The mechanochromism phenomenon is therefore attributed to local defects in the crystal packing induced by grinding when the interligand interactions are modified, allowing formation of a yellow emissive "unstretched" or "relaxed" cluster. From these results, it appears that applying hydrostatic pressure on the crystal will permit one to probe the exact nature of these defects by modifying in a controlled way the intercluster interactions and directly correlating the effect with the luminescence properties.

Measurements under hydrostatic pressure were performed by placing the sample (a single crystal for luminescence and SCXRD experiments and a polycrystalline powder for PXRD experiments) in a DAC equipped with a steel gasket (experimental details in the Supporting Information). A small ruby chip was inserted into the sample compartment for in situ pressure calibration according to the R1 ruby fluorescence method.[30] In order to avoid any interaction with the surrounding medium, neon gas was used as the hydrostatic pressure transmitting medium. All experiments were conducted at room temperature. In situ photoluminescence measurements were performed on an optical microscope equipped with a 377 nm laser as the excitation source. The X-ray diffraction experiments (PXRD and SCXRD) were both performed using a microfocus rotating-anode diffractometer ($\lambda_{Mo\ K\alpha_1}$ = 0.709319 Å; $\lambda_{Mo\ K\alpha_2}$ = 0.713609 Å) equipped with an image-plate detector. The measurements at 0 GPa (1 atm) were realized with the sample inside the DAC.

In situ pressure emission spectra of cluster **1** recorded from ambient pressure up to 4.2 GPa are shown in Figure 2 (the evolution of the emission wavelength versus pressure is reported in Figure 3a). With increasing pressure, a 60 nm red shift of the emission band is observed, with values ranging from 513 to 573 nm. As was already mentioned, manual grinding also induces a red shift of the emission band to 590 nm, as reported in Figure 2. Both hydrostatic pressure and grinding have thus a similar effect on the emission properties. When the pressure is released, the sample keeps its yellow emission at 573

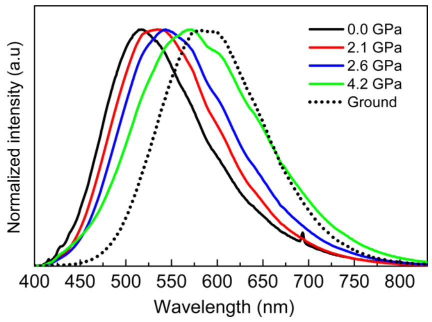

**Figure 2.** Pressure dependence of normalized emission spectra of **1**. The emission spectrum of a manually ground cluster powder under ambient pressure is indicated by dotted lines ($\lambda_{ex}$ = 377 nm).

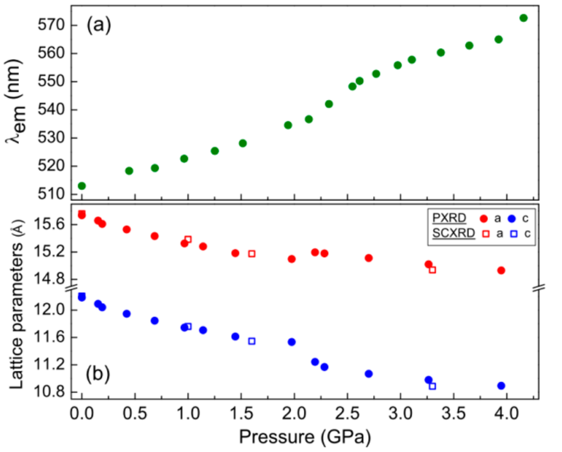

**Figure 3.** Pressure dependence of (a) emission wavelengths and (b) *a* and *c* lattice parameters determined by PXRD (circles) and SCXRD (squares) analyses of **1**.

nm. This is again similar to grinding; when it is interrupted, no change of the emission is recorded.

In situ pressure PXRD measurements were performed over the pressure range of 0−4 GPa. The crystallographic lattice parameters determined from refinement of the recorded powder patterns correspond to those of the crystalline phase of the cluster (details are given in the Supporting Information). The tetragonal space group $P\bar{4}2_1c$ is maintained over the entire pressure range; therefore, no phase transition occurred (as confirmed by SCXRD). As expected, a lattice compression is observed with increasing pressure. The unit cell volume decreases by 20%, with values varying from 3017(2) $Å^3$ at ambient pressure to 2429(2) $Å^3$ at 4 GPa. This value is typical for molecular solids considered as soft materials.[31] The evolution of the lattice parameters over the entire pressure range is reported in Figure 3 along with the corresponding emission wavelengths. The *a* and *c* parameters compress differently by 5 and 11%, respectively. A change in the evolution is observed around 2 GPa, which also appears in the emission wavelengths. After the pressure is released, the initial powder pattern is recovered, indicating reversibility of the pressure effect.

In situ pressure SCXRD data were collected at four different pressures (0, 1, 1.6, and 3.3 GPa). The lattice parameters determined from the crystalline structure resolution at each pressure correspond to the PXRD data (Figure 3b). As expected, the compression induces a modification of the intercluster interactions, as presented in Figure 4 (top). The number of CH···H short contacts per cluster involving the allyl and phenyl groups of the ligands greatly increases from 8 at ambient pressure to 176 at 3.3 GPa. Even new I···H interactions appear at 1.6 GPa between the cluster core and ligands. Note that these intercluster interaction changes occur mainly along the *c* axis, in accordance with its observed larger contraction under pressure. Bringing the clusters closer also induces modifications of their molecular structure and, in particular, of the $[Cu_4I_4]$ cluster core (Figure 4, bottom). The values and relative variation of selected intramolecular bond distances and angles are reported in Table 1 and Figure 5. While the Cu−P and Cu−I bond lengths do not show a large decrease under pressure (around 1 and 2%, respectively), the Cu−Cu ones are greatly shortened (13%). Indeed, the mean Cu−Cu bond distances of 3.278(2) Å at ambient pressure undergo a striking shrinkage at 3.3 GPa with a value of 2.837(2) Å (−0.44 Å), which is then close to the sum of the van der Waals radii of $Cu^I$ (2.8 Å).[32] This change in the bond distances inevitably induces modification of the corresponding angles, leading to a decrease of the Cu−I−Cu and I−Cu−P angle values (13 and 6%, respectively) and an increase of the I−Cu−I ones (7%). All of these structural changes imply that the cluster core undergoes great geometrical modification with contraction of the Cu4 tetrahedron volume (−35%) while the I4 one shows only a small change (+7%). In summary, increasing pressure induces a volume contraction of the structure and brings the clusters closer, inducing stronger interligand interactions. With the ligands being coordinated to the Cu atoms, the steric hindrance between them induces a shortening of the Cu−Cu bond distances in the cluster core. This demonstrates the flexibility of the cluster core, which supports almost all of the stress because of its relatively weak Cu−I and Cu−Cu bonds. After the pressure is released, the single crystal is fractured, preventing further structure resolution.

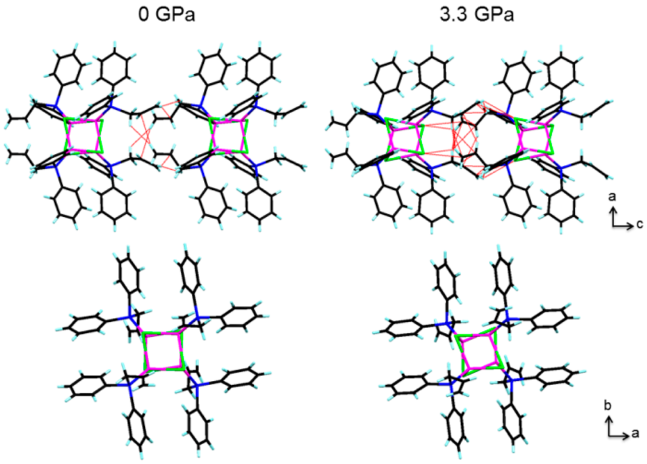

**Figure 4.** Selected short intercluster contacts (less than the van der Waals radii values) in red dotted lines and molecular structures at 0 and 3.3 GPa of **1**. Cu atoms are in magenta, I in green, P in blue, C in black, and H in cyan.

## ■ DISCUSSION

Compression of crystalline samples of **1** induces a red shift of the emission concomitantly with contraction of the cell volume. The evolutions of these parameters are similar, meaning that optical and structural changes are correlated. Modification of the molecular structure of the cluster mainly affects the $[Cu_4I_4]$ core with a great shortening of the Cu−Cu bonds. Previous density functional theory calculations established that the emission band (LE band for low energy) involves a $[Cu_4I_4]$ cluster-centered triplet excited state, commonly called $^3CC$, which originates from a combination of a halide-to-metal charge transfer and Cu-centered Cu 3d → 4s, 4p transitions.[33] Importantly, this emission band corresponds to a transition from a Cu−Cu nonbonding and Cu−I bonding highest occupied molecular orbital to a strongly Cu−Cu bonding and Cu−I antibonding lowest unoccupied molecular orbital. Therefore, the energy of the states depends on the Cu−Cu interactions in the ground state, with shorter distances leading to stabilization of the emissive state and a bathochromic shift of the emission. This theoretical result is totally confirmed by our observations under hydrostatic pressure. We have here direct

Table 1. Selected Intramolecular Bond Lengths and Angles of **1** at Different Pressures from SCXRD Experiments at 293 K

| | pressure (GPa) | | | |
|---|---|---|---|---|
| | 0 | 1.0 | 1.6 | 3.3 |
| Cu−Cu (Å) | 3.212(3) | 3.072(3) | 2.976(3) | 2.803(5) |
| | 3.410(3) | 3.290(2) | 3.194(3) | 2.906(4) |
| *mean* | *3.278(3)* | *3.145(3)* | *3.048(3)* | *2.837(5)* |
| Cu−I (Å) | 2.6908(16) | 2.6740(20) | 2.6571(17) | 2.598(2) |
| | 2.6938(18) | 2.6757(13) | 2.6575(15) | 2.640(4) |
| | 2.7487(17) | 2.7366(13) | 2.7203(15) | 2.706(2) |
| *mean* | *2.711(2)* | *2.695(2)* | *2.678(2)* | *2.648(4)* |
| I−Cu−I (deg) | 97.64(5) | 98.69(5) | 99.64(6) | 106.34(9) |
| | 105.43(6) | 108.05(6) | 109.58(6) | 110.28(10) |
| | 107.07(6) | 109.87(6) | 111.52(6) | 113.74(11) |
| *mean* | *103.38(6)* | *105.54(6)* | *106.91(6)* | *110.12(11)* |

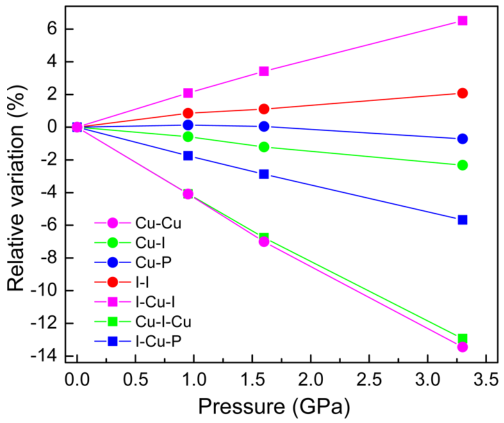

**Figure 5.** Relative variation of selected intramolecular bond lengths (circles) and angles (squares) of **1** at different pressures from SCXRD experiments.

proof that enhancing cuprophilic interactions induces a red shift of the emission. This result also agrees with the thermochromic luminescence properties commonly exhibited by copper iodide clusters, for which a red shift of the emission band upon cooling has been attributed to a shortening of the Cu−Cu bond distances.[34]

The effects of pressure on the emission properties of **1** are similar to those induced by mechanical grinding, thus providing further understanding into the mechanochromism mechanism. Therefore, the mechanochromic luminescence properties result from modification of the intercluster interactions upon grinding, inducing molecular structural changes and especially increasing cuprophilic interactions, which consequently lead to a red shift of the emission. The initial crystalline phase with clusters of distorted geometry and weak green emission is sort of a metastable state, and grinding, by modification of the intercluster interactions, allows relaxation of the clusters to a geometry with shorter Cu−Cu bond distances and a yellow emission. The structural changes appear as reversible, while the intense yellow emission is preserved upon pressure release. As previously mentioned, upon manual grinding, only a small amount of the crystalline phase is modified, with structural defects within highly emissive clusters being localized.[25] The formation of cracks in the crystals, as observed in SCXRD analysis, may account for the remaining yellow emissive clusters.

Opposite to previous studies,[23,24] here the effect of an isotropic constraint (hydrostatic pressure) is similar to that of an anisotropic one (grinding). The difference with other systems can be explained by the different mechanochromic mechanisms. In our case, it involves intramolecular interaction changes, whereas the others are based on intermolecular ones involving excimers[23] and intermolecular Au−Au interactions.[24]

## CONCLUSION

Hydrostatic compression of the cluster permits one to reduce, in a controlled way, the intramolecular Cu−Cu distances, inducing a red shift of the emission that is similar to the effect of manual grinding. The mechanochromism is therefore definitively explained by a reduction of Cu−Cu distances upon grinding. This study provides direct proof of the key role of the intramolecular copper interactions in the origin of the stimuli-responsive properties of these multinuclear coordination complexes. In addition, to give a fundamental understanding of their properties, this study also demonstrates their potential for applications in sensing and detection devices.

## ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01546.

Experimental details and SCXRD and PXRD data (PDF)
X-ray crystallographic data in CIF format (CIF)

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### Notes

The authors declare no competing financial interest.

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