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How subtle molecular changes can strongly impact luminescence properties of copper iodide complexes

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Abstract.

Copper halides present a wide range of luminescence properties which are relevant for developing sustainable light-emitting materials. A copper iodide complex displaying an unexpected phase transition characterized by a great change of its photoluminescence properties is reported here. Results from different optical and structural characterizations indicate that this contrasted effect involves local defects in the crystalline structure at which the molecular structure is modified. Even minor, these intramolecular changes impact the energetic layout of the complex leading to modifications of the photophysical properties. This study highlights the structural flexibility of the copper halide compounds and the rich panel of stimuli-responsive properties that can result.

Keywords. copper iodide complexes, photoluminescence, phase transition, structural flexibility.

Introduction.

Rare-earth and lead free phosphors are highly demanded for developing ecofriendly, sustainable and non-toxic solid-state light-emitting materials.¹⁻⁴ Because of the readily accessibility of copper element and the remarkable photophysical properties of copper(I) complexes,⁵ Cu-based materials are ideal candidates for developing economic and efficient emissive materials with low toxicity.⁶⁻⁸ Among the Cu(I) complexes, copper halides present a wide range of luminescence properties.⁹⁻¹⁴ By displaying highly intense and air stable photoluminescence properties, copper iodide compounds are indeed very attractive and are even envisioned as alternative to the hybrid perovskites.¹⁵⁻¹⁷ In addition, they can display stimuli-responsive properties such as luminescence thermochromism,^{8,18-22} mechanochromism,²³⁻³⁰ rigidochromism,³¹⁻³³ and solvatochromism.³⁴⁻³⁸ The possibility of combining stimuli-responsive properties is of high interest to access original multifunctional emitting materials offering many applicative perspectives.

Due to the adaptability of the d^{10} electronic configuration of Cu(I) and the various coordination modes of halides, a large structural diversity characterizes the family of copper(I) halides.^{18,39,40} Because the physical properties depend on the structure, this structural diversity leads to a very large range of photophysical properties for these compounds. The experimental synthetic conditions represent important factors impacting their structure and for a considered composition, materials exhibiting different structural features can be synthesized.⁴¹ This variability propensity is clearly illustrated by crystalline polymorphism commonly encountered in this family of compounds.⁴²⁻⁴⁴ The small energetic difference between different structures arising from labile coordination numbers and geometries, makes these compounds particularly sensitive to external factors. Indeed, the luminescence mechanochromism is a neat example of structural changes resulting from soft mechanical forces.⁴⁵ The flexibility of copper(I) halides is also demonstrated by their vapochromic properties for which structural changes are induced upon exposure to solvents.⁴⁶⁻⁴⁸ This structural variability constitutes relevant characteristics for designing original stimuli-responsive materials.

Here, we report on a copper iodide complex displaying an unexpected phase transition characterized by a great change of the photoluminescence properties. The non-luminescent pristine compound is transformed into a highly intense emissive phase, under UV irradiation. Different optical and structural characterizations were used to investigate the origin of this intriguing phenomenon. Results indicate that this contrasted effect is based on a phase transformation involving formation of local defects in the crystalline structure where intramolecular structural changes occur. Although small, these changes impact the energetic layout of the compound leading to important emission properties changes. This study shows that minor structural changes can induce strong modifications of the luminescence properties in copper halides and thus highlights the structural flexibility of this family of compounds.

Results and Discussion.

The studied copper iodide complex is formulated $[\text{Cu}_4\text{I}_4(\text{Ph}_2\text{PCH}(\text{CH}_3)_2)_4]$ (**1**) with a diphenylphosphine ligand bearing an isopropyl group (Figure 1). This molecular cluster is synthesized by reacting CuI and the corresponding ligand in acetonitrile. The luminescence mechanochromic properties of this complex were previously reported by our group.⁴⁹ Upon grinding, the white crystalline powder of this compound displays contrasted changes of its luminescence properties from an almost non-luminescent state to a yellow emitting one (Figure 1). These stimuli-responsive properties were further exploited for the preparation of mechanochromic films.⁴⁹ In the present article, another phase transformation of **1** is reported that is different from the grinding induced one. Indeed, an unexpected change in the color of the crystalline powder of **1** from white to green was observed several weeks after the synthesis without any manipulation (Figure 1). This new phase, labelled **2**, exhibits also different and contrasting luminescence properties. While **1** presents a very weak emission at room temperature, **2** displays a much more intense green light, under UV. The luminescence thermochromic properties are also modified, the blue emission displayed by **1** at 77 K is not observed for **2** which instead presents a brighter green emission.

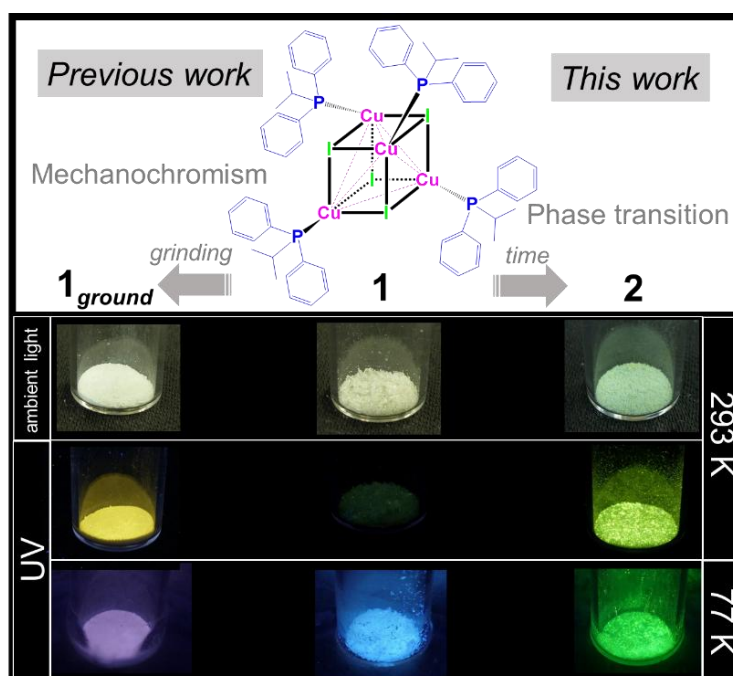


Figure 1. Molecular structure of the $[\text{Cu}_4\text{I}_4(\text{Ph}_2\text{PCH}(\text{CH}_3)_2)_4]$ studied cluster and photos of the powders of **1** and **2** under ambient light and UV (365 nm lamp) at 293 K and 77 K and of **1** after grinding (**1_{ground}**) from previous work.

The results of the elemental analyses of **2** gave similar composition to **1** corresponding to the $[\text{Cu}_4\text{I}_4(\text{Ph}_2\text{PCH}(\text{CH}_3)_2)_4]$ formula (experimental details in SI). These results indicate that the phase transition does not imply chemical reaction with atmospheric molecules and that the chemical composition of the cluster is preserved within this new phase **2**. This is also consistent with the fact that **1** \rightarrow **2** transition occurs regardless of the atmosphere (oxygen, nitrogen and humidity), in which the sample is stored. The change in reactants has no effect too. The impact of different external factors were also studied by exposing **1** to UV, visible light, dark, X-rays, heat (100 °C) but no particular effect on the transition was observed. Ultrasounds treatment of **1** lead to similar effects as the mechanical grinding does but not to the formation of **2**. These results are in agreement with a thermodynamic evolution of **1** to a more stable molecular structure of the cluster in **2**. The metastable

state of the pristine **1** phase is indeed ascertained by the occurrence of its luminescence mechanochromic properties. No reversibility was neither observed when submitting **2** to these different conditions. The oxidation of Cu(I) to Cu(II) is refuted on the basis of elemental analysis, which indicates no change in composition, and by the absence of paramagnetic species that would affect NMR measurements (see below).

The powder X-ray diffraction diagram of **2** matches that of **1** which corresponds to the calculated one from the SCXRD data (Figure S2). This indicates that no long-range structural modification occurs from **1** to **2**. One single crystal of **2** could be isolated in a crystalline sample and was analyzed by Single Crystal X-ray Diffraction (details in SI). **2** was found isostructural to **1** (I-4 space group)⁴⁹ having a crystalline packing built on layers of clusters in the *a-c* plane stacked along the *b* axis, with no solvent included (Figure 2). No significant intermolecular interaction is observed in the structure such as π - π stacking between the phenyl groups. The molecular structure of the cluster is very close to that of **1** with intramolecular mean values of Cu-Cu (3.387(1) Å), Cu-I (2.7006(5) Å), Cu-P (2.235(1) Å), distances and I-Cu-I (100.09(2) °) angles (Table S2). These values are in the range of those reported for cubane copper iodide clusters, excepted the Cu-Cu distances which are amongst the longest ones reported in the literature⁵⁰ and much longer than twice the van der Waals radius of copper (I) (2.8 Å).⁵¹ Analysis of the various structural parameters of **2** (Tables S1-2) finally indicates that the differences from **1** are within experimental error. This means that the **1** \rightarrow **2** transition implies local changes in the crystalline structure in low amount.

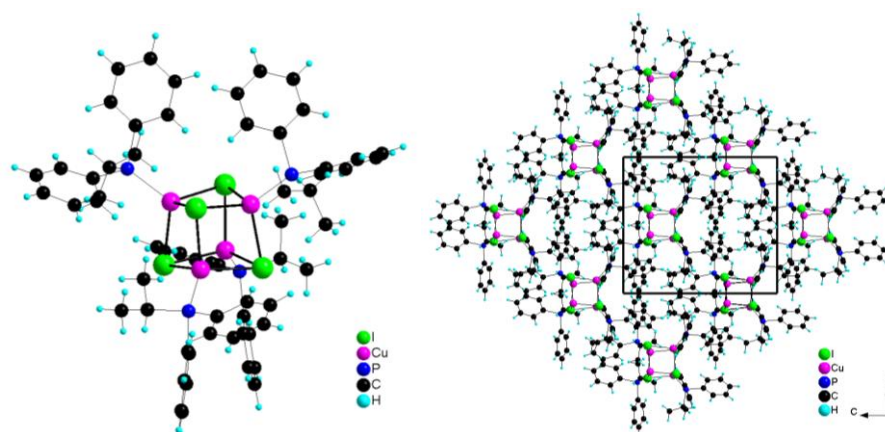


Figure 2. Molecular structure of $[\text{Cu}_4\text{I}_4(\text{Ph}_2\text{PCH}(\text{CH}_3)_2)_4]$ in **2** at 150 K.

The solid-state ^{63}Cu NMR (Nuclear Magnetic Resonance) spectrum of **2** presents a very broad pattern as expected from the large quadrupolar moment of ^{63}Cu nucleus (Figure 3).⁵² This spectrum is similar to that of **1** which presents characteristic signature of the $[\text{Cu}_4\text{I}_4]$ cluster in cubane geometry.⁵³ The ^{31}P CPMAS (Cross Polarization Magic Angle Spinning) spectrum of **2** is composed of quartets which result from the one bond *J*-coupling between the ^{31}P nucleus and the two copper isotopes (spin 3/2 for both)⁵⁴. A main quartet is thus observed for the ^{31}P - ^{63}Cu coupling and the shoulders of smaller intensity are due to the second quartet from the ^{31}P - ^{65}Cu coupling (Figure 4). Chemical shift values $\delta_{\text{iso}} = -20.5$ ppm for **1** and for **2** are both in the range of classical values of cubane copper iodide cluster.^{42,55} Compared with **1**, a broadening of the peaks can be detected in the spectra of **2**. This is also observed in the ^{31}P - ^{63}Cu *J*-HMQC (Heteronuclear Multiple Quantum Coherence) MAS NMR experiment allowing simplification of the ^{31}P spectra (Figure S3).⁵⁶ The peak broadening indicates modification of the molecular structure of the cluster at local scale, consistent with the absence of

detection in the XRD analysis. The lack of difference in the ^{63}Cu spectra can be explained by the lower sensitivity of this nucleus.

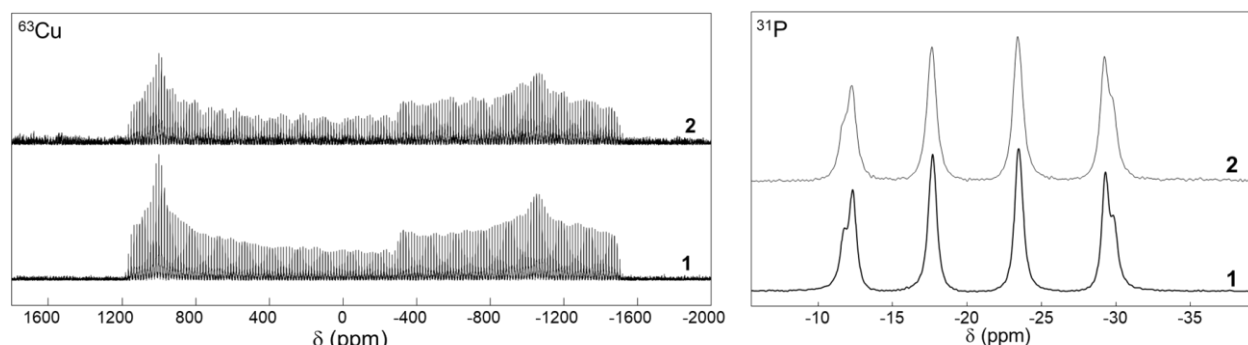


Figure 3. Solid-state static ^{63}Cu and ^{31}P CPMAS NMR spectra of **1** and **2**.

Infrared and Raman spectra are reported in Figure 4. Previous DFT calculations permit spectra simulation and possible assignment of the vibrational bands.⁴⁹ The IR spectra of **2** presents a very close vibrational signature to **1** from 45 to 4000 cm^{-1} (Figures 4 and S4). However, three additional bands are clearly observed for **2** at 540, 709 and 1120 cm^{-1} . In this mid-IR region, bands are attributed to Cu-P and phenyl vibrations (C=C stretching and C-H wagging among others), so these additional bands indicate modifications of the ligand in **2**. Band shifting are also detected in the far-IR region with bands at 90, 101 and 119 cm^{-1} . These shifted bands correspond to vibrations (breathing, rocking and wagging motions) implying Cu-Cu, Cu-I and I---I displacements,^{57,58} indicative of a modified $[\text{Cu}_4\text{I}_4]$ cluster core in **2**.

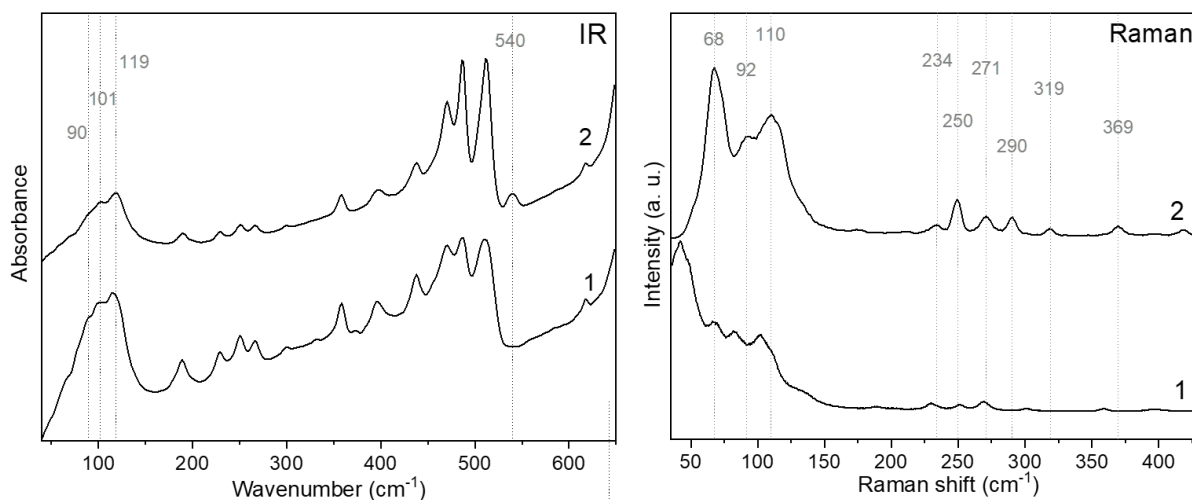


Figure 4. Infrared and Raman spectra of **2** and **1**.

Differences are also detected in the Raman spectra (Figures 4 and S4), with either additional bands or band shifting. The bands in the 230 to 2930 cm^{-1} range all correspond to the phosphine ligand with Cu-P and C-P vibrations (phenyl groups and isopropyl groups). The new band at 290 cm^{-1} and the shifts of those at 234 and 369 cm^{-1} for instance, indicates modification of the ligand in **2**, in agreement with IR analysis. The three bands at 68, 92 and 110 cm^{-1} are also modified compared to those of **1** and the main difference is the disappearance of the band at 42 cm^{-1} in **2**. These low frequencies bands correspond to multiple and entangled Cu-Cu and Cu-I vibrations comprising Cu-I twisting, Cu-Cu wagging and torsions. Raman analyses confirm modifications of the $[\text{Cu}_4\text{I}_4]$ cluster core in **2** and of the phosphine ligands in agreement with ^{31}P solid-state NMR data. To summarize, distortions of the

cubane geometry of the $[\text{Cu}_4\text{I}_4]$ core involving changes of the Cu-I and Cu-Cu distances must occur in **2**, along with modifications of the respective orientation of the ligand in the solid-state. These identified punctual structural defects are likely to be at the origin of the different optical properties observed between **1** and **2**.

Photoluminescence spectra of **2** and **1** are reported in Figure 5. At 293 K, **2** presents a broad emission band centered at 540 nm (LE band for low energy) which corresponds to the observed green emission (Figure 1). Upon cooling down to 77 K, this emission band is blue shifted to 525 nm with a narrower profile. This contrasts with **1** which shows a very weak emission at 293 K centered at 550 nm and an additional intense blue one at 420 nm (HE band for high energy) upon cooling at 77 K (Figure 5), responsible for the observed blue emission. The excitation spectra are also different with a broad band centered at 400 nm for **2** instead of the narrow one at 340 nm of **1**. Measurement of the emission lifetime at room temperature of **2** showed a mono-exponential decay with $\tau = 1.82 \mu\text{s}$ (Figure S1), a value in the usual range for such copper iodide compound.⁵⁶ This result indicates that the **1** \rightarrow **2** transition corresponds to the formation of a single emissive specie in **2**. The photoluminescence quantum yield (PLQY) of **2** is 14.5 %. Lifetime and PLQY measurements for **1** were not possible due to its very weak emission. Note that the insolubility of the compounds in common organic solvents prevents characterizations in solution.

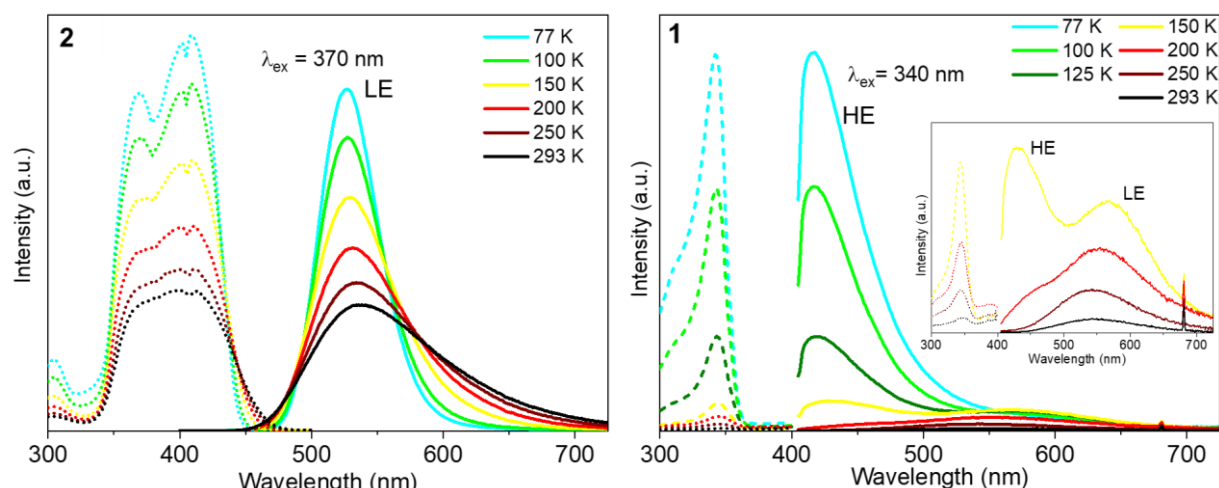


Figure 5. Temperature-dependent luminescence spectra of **2** and **1** from 77 to 293 K. In plain line are the emission spectra, in dashed lines are the excitation spectra recorded at HE band ($\lambda_{\text{em}} = 415 \text{ nm}$ for **1**) and in dotted lines are the excitation spectra recorded at the LE band ($\lambda_{\text{em}} = 525$ or 540 nm , for **2** and **1**, respectively). The sharp peaks at 680 are artefacts due to the second harmonic of the excitation wavelength.

The luminescence properties of **1** and in particular its very weak emission at room temperature contrasting with the intense emission commonly displayed by the $[\text{Cu}_4\text{I}_4\text{L}_4]$ cubane clusters, were previously rationalized by DFT calculations⁴⁹ using Gaussian 16.⁵⁹ These DFT calculations were conducted using a global hybrid functional associated to the LANL2DZ basis set augmented by polarization functions on all atoms. The geometry of the ground state (S_0) was optimized enforcing the S_4 symmetry point group from the SCXRD structure. All the geometries (ground and excited states) were relaxed and checked to be minima on their potential energy surfaces. Vibrational contributions to electronic transition responsible for the observed luminescence were taken into account using the Vertical Hessian⁶⁰ approach which takes into account mode-mixing between initial and final states. From the computed electronic structure, the HOMOs (highest occupied molecular orbitals) of **1** are localized on the Cu and I atoms mainly with the HOMO having on equal contribution of Cu-d and I-p orbitals (41%). Its first 16 LUMOs (lowest unoccupied molecular orbitals) are combinations of the 16

π^* phenyl orbitals of the ligands (simplified energetic diagram in Figure S5). Above this block of 16 orbitals lie orbitals with important Cu contribution. While the LUMO+16, 17, 18 are of Cu-p character, the LUMO+19 is different entirely localized on the cluster core with Cu-s orbitals having bonding Cu-Cu character (Figure S6). Based on its geometry and spin density localized on the ligands, the first calculated triplet excited state corresponds to a $^3(X+M)LCT$ ($X = I$, $M = Cu$ and $L = ligand$) transition. The corresponding simulated spectra presents a maxima at 454 nm which agrees with the experimental HE emission band centered at 415 nm. This result is in accordance with the classical case of $[Cu_4I_4L_4]$ clusters. However, no other triplet state could have been calculated for **1** and in particular that corresponding to the LE band characteristic of the $[Cu_4I_4L_4]$ cubane clusters. This band is usually assigned to a cluster-centered transition ($^3CC = XMCT$ and MM) with a triplet state based on the $[Cu_4I_4]$ cluster core endorsing a strong shortening of the Cu-Cu bond distances compared with the ground state. This second triplet state is generally associated with an unoccupied orbital with a strong Cu-Cu-s bonding character close in energy to the block of π^* orbitals. Such vacant orbital is actually very similar to the LUMO+19 calculated for **1**. However in this case, the LUMO+19 is separated from the block of π^* orbitals by a much larger energy gap (1 eV vs. 0.2 eV typical for such compounds^{56,57}) limiting its accessibility that can explained the very weak emission observed for **1** at room temperature. From this theoretical study, the quenched LE emission of **1** can be related to the high energy of Cu-Cu bonding orbital which can be directly linked to the uncommonly long Cu-Cu distances ($> 3.3 \text{ \AA}$). Based on these results, an interpretation of the intense green emission observed for **2** can be suggested. The molecular structural modifications detected by NMR, IR and Raman analyses of **2** can induce changes of the energy of the orbitals and in particular those implying the $[Cu_4I_4]$ cluster core. Because of their atypical presence, the three vacant orbitals (LUMO+16, 17, 18) are the most likely to be involved with possible stabilization in **2**. The corresponding additional triplet state of $^3XMCT/MM$ nature different from the 3CC one leads consequently to the observed green emission (Figures 6 and S5-6). Note that this is different from the mechanochromism mechanism established for **1** for which the mechanical solicitations induced a shortening of the Cu-Cu bond distances leading to the stabilization of the vacant Cu-Cu bonding orbital (LUMO+19) and to a lower energy emission.⁴⁹

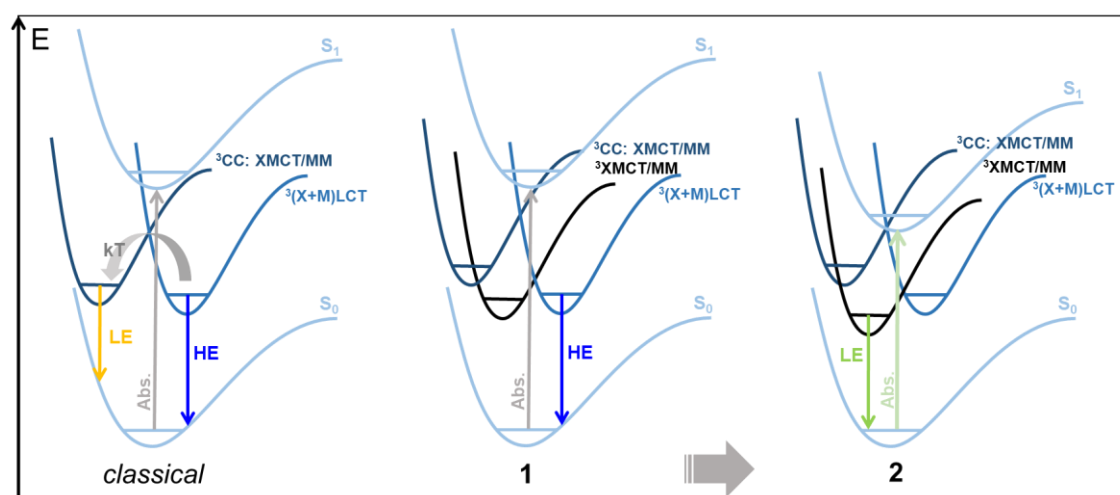


Figure 6. Simplified schema of the energetic diagram illustrating possible changes occurring from **1** to **2**. The three different triplet states are 3CC ($XMCT/MM$), $^3XMCT/MM$ and $^3(X+M)LCT$ with $X = I$, $M = Cu$ and $L = ligand$.

The luminescence thermochromism usually displayed by the $[Cu_4I_4L_4]$ clusters^{22,57} is characterized by a variation in temperature of the relative intensity of the two HE and LE emission bands resulting from

thermal equilibrium between the two corresponding excited triplet states (^3CC and $^3(\text{X}+\text{M})\text{LCT}$ in Figure 6). The absence of thermochromism for **1** with the lack of the LE band is correlated to the non-accessibility of the ^3CC state, as already mentioned. In opposite, no HE band is recorded for **2**. The important changes of the excitation spectra of **2** compared with that of **1** indicate modification of the absorption processes too. The absorption (excitation) band of **1** centered at 330 nm is assigned to $^1(\text{M}+\text{X})\text{LCT}$ transitions.⁴⁹ In opposite, the excitation band centered at 400 nm for **2** corresponding to its green body color, indicates a different transition which can be related to the new emissive state ($^3\text{XMCT/MM}$). Competition with the $^3(\text{X}+\text{M})\text{LCT}$ state can be also at the origin of the absence of the HE band for **2**.

Conclusion.

An unexpected transition from a non-luminescent phase into an intensely emissive one of a copper iodide complex, has been characterized using different techniques. Raman, IR and solid-state NMR analyses indicate structural modifications of the molecular structure and reveal in particular that this phase transformation involves the $[\text{Cu}_4\text{I}_4]$ cluster core. These structural intramolecular distortions must be localized at punctual defects sites in the crystalline packing. Even minor, these changes impact the energetic layout of the cluster and thus its photophysical properties. This phenomenon is made possible by the metastability of the pristine phase and the existence of several excited states which can compete with each other, a specific characteristic of the copper halide complexes. Close examination of other copper iodide clusters is underway to evaluate whether the phenomenon can be generalized. Finally, by highlighting the structural sensitivity of the copper halides, the present study aims at giving insights into the understanding of their photophysical properties and the stimuli-responsive properties that can result.

Acknowledgments.

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Supporting Information.

Supporting Information (SI) available: Details of synthetic procedures, characterizations data and additional figures.

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