# Electronic Supporting Information

## Mechanoresponsive luminescence triggered by a supercooled transition of a copper(I) complex

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## Synthesis.

Copper(I) iodide, tetrabutylphosphonium iodide and the solvent were purchased from Aldrich and used as received.

**$(PBu_4)_2[Cu_2I_4]$ ($1_{AS}$).** CuI (132 mg, 0.7 mmol) and $PBu_4I$ (267 mg, 0.7 mmol) were dissolved in 20 mL of acetonitrile. After complete dissolution, the solvent is evaporated leading to a viscous product forming rapidly a white powder with yield of 95 % (M = 1154 $g.mol^{-1}$).
Anal. Calcd (% wt.) for $1_{AS}$ for $C_{32}H_{72}Cu_2I_4P_2$: C, 33.32; H, 6.29. Found: C: 33.14, H: 5.98.
Anal. Calcd (% wt.) for $1_{RE}$ for $C_{32}H_{72}Cu_2I_4P_2$: C, 33.32; H, 6.29. Found: C, 33.03; H, 6.01.

## Characterizations.

Elemental analyses (C, H, N) were performed by the Service de microanalyses de l'ICSN - CNRS Gif-sur-Yvette.

The TG (Thermogravimetric Analysis) analyses were performed with a NETZCH STA449 F3 equipment. The DSC (Differential Scanning Calorimetry) measurements were performed with a NETZSCH DSC 200 F3 equipment at 1 °C/min.

Luminescence spectra were recorded with a Fluorolog 3 spectrofluorimeter (Horiba Jobin Yvon). Low temperature measurements were realized in an OptistatDN-V Oxford cryostat. The absolute photoluminescence quantum yields (PLQY) were measured by using the Jobin Yvon integrating sphere. Emission lifetimes ($\tau$) were recorded with a time-resolved photoluminescence setup consisting of a frequency-tripled regenerative amplified femtosecond Ti:sapphire laser system from Spectra Physics to obtain $\lambda_{ex} = 267$ and 400 nm and a C7700 streak camera from Hamamatsu coupled to an SP2300 imaging Acton spectrograph for the luminescence detection. Data were analyzed by exponential curve fitting using *Origin* software.

Powder X-ray diffraction (PXRD) diagrams were recorded on a Bruker D8 Advance instrument in the Bragg-Brentano geometry, equipped with a front germanium monochromator, a copper anode (CuK-L3 radiation $\lambda = 1.540598$ Å) and a LynxEye PSD detector. The calculated patterns were obtained from the single crystal data (SCXRD) using the *Mercury* software.

Single crystal X-Ray diffraction (SCXRD) analyses were performed on a crystal of **1** (colorless prism, dimensions = 0.450 x 0.330 x 0.250 mm) mounted on the goniometer head of a D8 Venture (Bruker-AXS) diffractometer equipped with a CMOS-PHOTON70 detector, using Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å, multilayer monochromator) at $T = 297(2)$ K. Crystal structure was solved by dual-space algorithm using *SHELXT* program,[1] and then refined with full-matrix least-squares methods based on $F^2$ (*SHELXL*).[2] All non-Hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The $(PBu_4)^+$ cations present structural disorder with two positions for each, having 75/25 and 50/50 occupancy ratio. Details of the crystal data and structure refinements are summarized in Table S1.

Raman spectra from 73 to 1500 cm$^{-1}$ and from 2500 to 3500 cm$^{-1}$ were measured with a Raman T64000 Jobin Yvon triple spectrometer. All spectra were recorded using an excitation wavelength of 633 nm emitted by a Helium Neon laser. The Rayleigh line was eliminated with a premonochromator.

**Computational details.**
Density Functional Theory (DFT) calculations were conducted using the Gaussian16 package[3] based on previous computations on $(PPh_4)_2[Cu_2I_4]$.[4] The PBE0 functional, in conjunction with the triple $\zeta$ basis set DEF2TZVP for Cu and I atoms,[5,6] was employed to examine the $[Cu_2I_4]^{2-}$ moiety within the ideal $D_{2h}$ symmetry point group. Inner electrons (relativistic effects) were not explicitly treated, as they are accounted for in the pseudo-potentials. Spin-orbit coupling was not considered in this study. The vibrational analysis utilized the anharmonic GVPT2 model, as described in previous publications.[7] Within this model, it becomes feasible to simulate the Raman signature, including energies and intensities, while considering various anharmonic effects such as overtones, combination bands, Fermi, and Darling-Dennisson resonances. Given the small size of the structure under investigation, our analysis extended to computing second overtones (MaxQuanta=3). In this context, we identified a strong band at 105 cm$^{-1}$ corresponding to Cu-I stretching which must correspond to the experimental 120 cm$^{-1}$ band. Two vibrational overtones were also calculated at 138 and 147 cm$^{-1}$ (corresponding fundamentals peaking at 69 ($b_{2g}$, Cu-I twisting) and 73 ($b_{3u}$, Cu-I wagging) cm$^{-1}$, respectively). These vibrational overtones can correspond to the experimental 146 cm$^{-1}$ band.
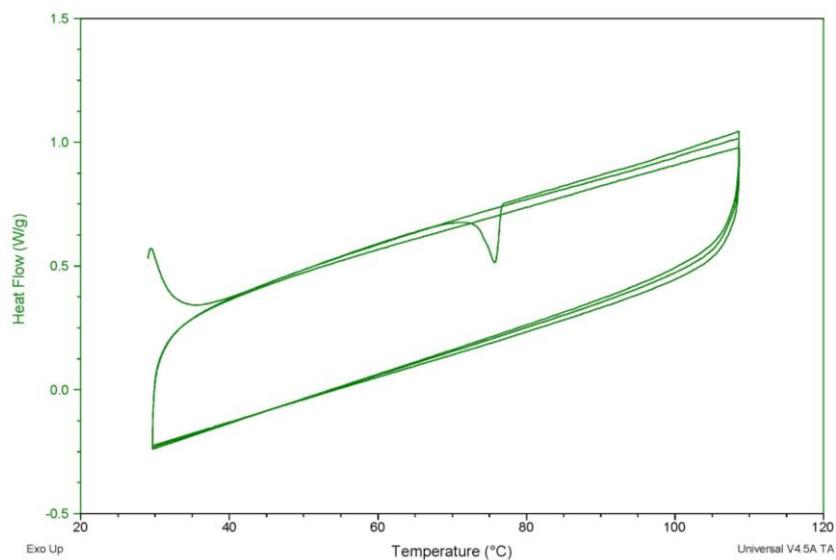
**Additional Data.**



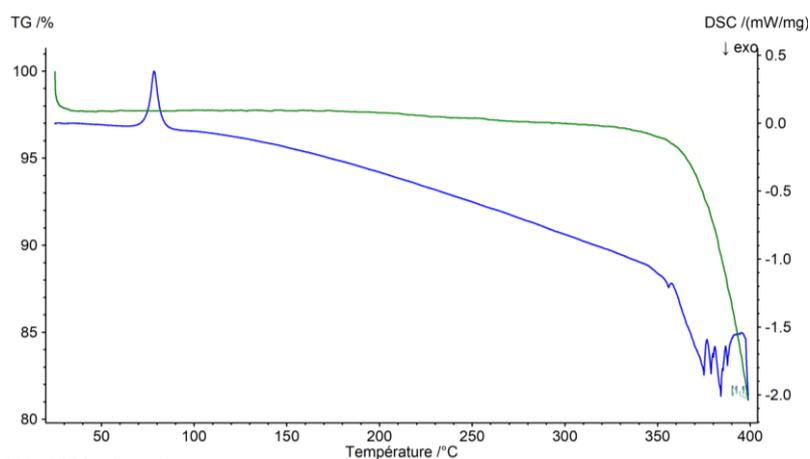**Figure S1.** DSC (differential scanning calorimetry) curves of **1** at 1 °C/min.



**Figure S2.** ATG-DTA curves of **1**.

**Table S1.** SCXRD and structure refinement data of $(Bu_4P)_2[Cu_2I_4]$ (**1**) at 293 K.

|  | $(Bu_4P)_2[Cu_2I_4]$ |
|---|---|
| CCDC n° | 2314646 |
| Chemical formula | C32 H72 P2 Cu2 I4 |
| fw | 1153.51 |
| Crystal system | Triclinic |
| Space group | $P$ -1 |
| a, Å | 12.4248(14) |
| b, Å | 12.9746(16) |
| c, Å | 16.828(2) |

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| | |
|---|---|
| α, deg | 86.253(5) |
| β, deg | 75.221(4) |
| γ, deg | 64.491(4) |
| V, Å$^3$ | 2364.3(5) |
| Z | 2 |
| $\rho_{calc}$, g/cm$^3$ | 1.620 |
| μ, mm$^{-1}$ | 3.596 |
| Reflections collected | 31523 |
| Independent reflections | 8951 |
| $R_{int}$ | 0.0457 |
| Reflections I > 2σ(I) | 6254 |
| Parameters | 489 |
| GOF on F$^2$ | 1.035 |
| $R_1$[a]/$wR_2$[b] (I > 2σ(I)) | 0.0561/0.1429 |
| $R_1$[a]/$wR_2$[b](all) | 0.0807/0.1673 |

[a] $R_1 = [\Sigma \text{ abs}(\text{abs}(F_O) - \text{abs}(Fc))]/ [\Sigma \text{ abs}(F_O)]$. [b] $wR_2 = [\Sigma(w(F_O^2-F_c^2)^2)/ \Sigma[w(F_O^2)^2]^{0.5}$.

**Table S2.** Selected intramolecular bonds lengths and angles of $(Bu_4P)_2[Cu_2I_4]$ (**1**) from SCXRD at 293 K.

| | **1$_{CRYST}$** |
|---|---|
| **Cu···Cu** | 2.6576(14) |
| **Cu-Iμ$_2$** | 2.5450(12) <br> 2.5805(12) <br> 2.5855(12) <br> 2.5924(13) |
| **Cu-Iμ$_1$** | 2.4936(11) <br> 2.4907(12) |
| **Iμ$_1$-Cu-Iμ$_2$** | 125.02(4) <br> 118.34(4) <br> 122.03(5) <br> 122.85(5) |
| **Iμ$_2$-Cu-Iμ$_2$** | 116.62(4) <br> 115.12(4) |
| **I-Cu-I-Cu** | 165.52(7) <br> 164.75(7) <br> 165.68(7) <br> 164.59(7) |

**Table S3.** Photophysical data of **1**.

|  | $\lambda_{max}$ (nm) | PLQY | $\tau$ ($\mu s$) | $k_r$ ($\mu s^{-1}$) | $k_{nr}$ ($\mu s^{-1}$) |
|---|---|---|---|---|---|
| **1_AS** | 520 | 0.90 | 4.6 | 0.20 | 0.02 |
| **1_SC** | 650 | 0.04 | 0.47 | 0.09 | 2.04 |
| **1_RE** | 520 | 0.87 | 3.0 | 0.29 | 0.04 |
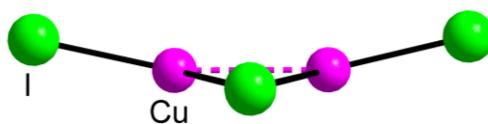


**Figure S3.** Molecular structure of $[Cu_2I_4]^{2-}$ anion showing its folded geometry with $I\mu_1$-Cu-$I\mu_2$-Cu mean torsional angles of 165.14(7)° at 293 K.
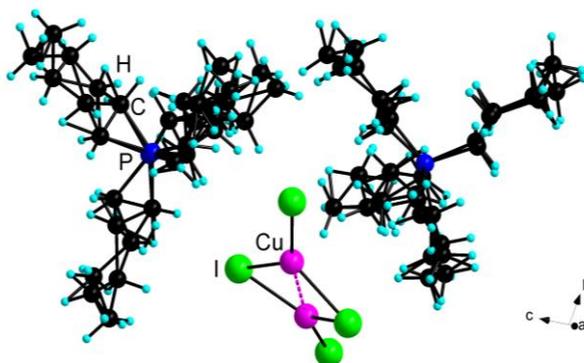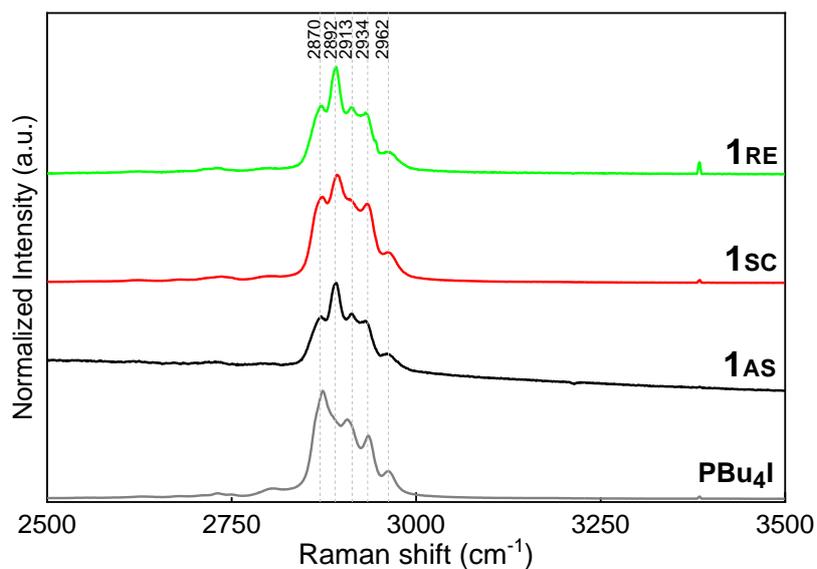


**Figure S4.** Molecular structure of $(Bu_4P)_2[Cu_2I_4]$ (**1**) showing the structural disorder of the two $(Bu_4P)^+$ cations at 293 K.
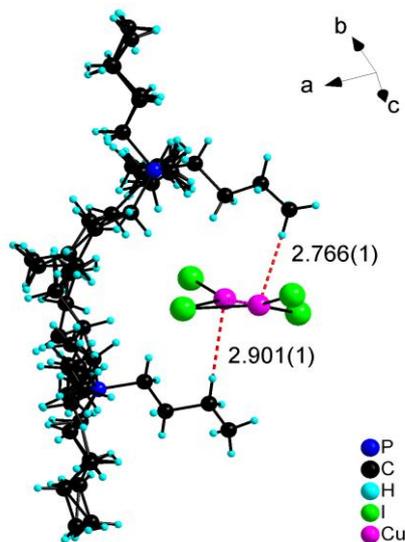
**Figure S5.** Intermolecular Cu···H contacts in **1** structure at 293 K.
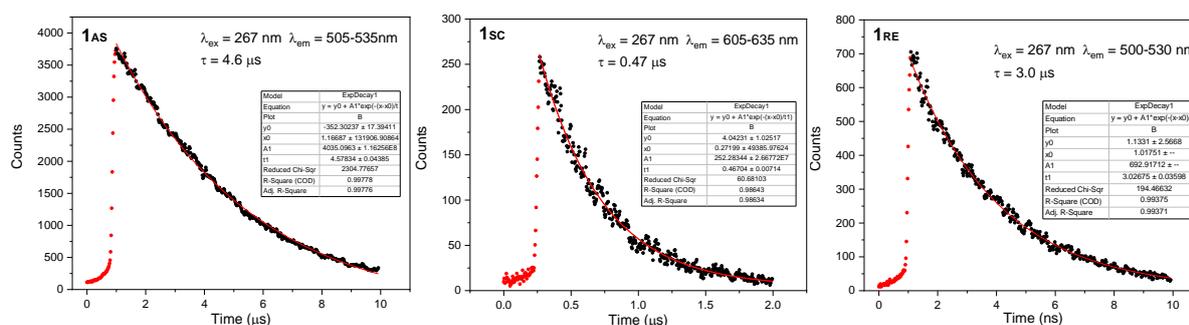


**Figure S6.** Fitted emission decay curves at 293 K. The red dots are not considered for the fits.



**Figure S7.** Raman spectra of **1**, as synthesized (**1AS**), in the supercooled state (**1SC**) and in the mechanically recrystallized state (**1RE**), from 2500 to 3500 cm$^{-1}$ at 293 K. The vibrations are from the butyl chains of the (Bu$_4$P)$^+$ cation.

# References SI

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(**4**) Thefioux, Y.; Cordier, M.; Massuyeau, F.; Latouche, C.; Martineau-Corcos, C.; Perruchas, S. *Inorg. Chem.* 2020, **59** (8), 5768–5780.

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