Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2016

Electronic Supplementary Information

Impact of crystalline packing on the mechanochromic luminescence properties of copper based compounds: towards functional coatings

Quentin Benito,[a] Isabelle Maurin,[a] Mélanie Poggi,[a] Charlotte Martineau-Corcos,[b,c] Thierry Gacoin,[a] Jean-Pierre Boilot[a] and Sandrine Perruchas*[a]

a. Laboratoire de Physique de la Matière Condensée (PMC), CNRS - Ecole Polytechnique, 91128 Palaiseau Cedex, France. *E-Mail : sandrine.perruchas@polytechnique.edu; Fax : +33 (0)1 69 33 47 99 ; Tel : +33(0)1 69 33 46 85.
b. Tectospin, Institut Lavoisier de Versailles (ILV), UMR CNRS 8180, Université de Versailles St-Quentin en Yvelines (UVSQ), 45, avenue des Etats-Unis, 78035 Versailles Cedex, France.
c. CEMHTI-CNRS, UPR 3079, 1D avenue de la recherche scientifique, 45071 Orléans cedex 2, France.

Synthesis.

The mechanochromic coatings were synthesized by spin-coating a solution of cluster **1** (c = 2.10^{-2} mol.L^{-1} in CH_2Cl_2) on a glass substrate (2.5 * 2.5 cm^2). The spin coating speed was set at 2000 rpm for a duration of 60 s.

Characterizations.

NMR (Nuclear Magnetic Resonance). The static ^{63}Cu NMR spectra were recorded on a Bruker a Avance III 900 MHz spectrometer (B_0 = 21.1 T) using the wideband uniform rate and smooth truncation[1] Carr–Purcell Meiboom–Gill[2] (WURST-Q-CPMG)[3] pulse sequence in static conditions, with an inter-pulse delay of 202 μs. The WURST pulse had a length of 25 μs and a sweep of 1 MHz. ^{1}H spinal64[4] decoupling (8 μs pulse with 60 kHz rf-field) was applied during acquisition. The recycle delay was 1 s. Number of transients was to 4096, number of echoes was 85. The chemical shifts were referenced to CuI at 0 ppm. The samples were packed in 2.5 mm outer diameter rotors.
The magic-angle spinning (MAS) ^{1}H NMR spectra were recorded on an Avance III Bruker 900 spectrometer (B_0 = 21.1 T) at MAS of 60 kHz (1.3 mm rotors) using a DEPTH[5] pulse sequence to suppress the probe background. 1.2 μs π/2 pulse durations were used. The recycle delay was 5 s, and 64 transients were accumulated for each sample. The chemical shifts are referenced to TMS. The ^{13}C cross-polarization (CPMAS) NMR spectra were recorded on an Avance Bruker 500 spectrometer (B_0 = 11.7 T), while the ^{31}P CPMAS spectra were recorded on an Avance III Bruker 750 spectrometer (B_0 = 11.7 T). The samples were packed in 3.2 or 4 mm outer diameter rotors and spun at 10 kHz. The ^{13}C chemical shifts were referenced to TMS at 0 ppm. The ^{31}P chemical shifts were reference to a solution of H_3PO_4 at 0 ppm. ^{1}H SPINAL-64 decoupling was applied during the signal acquisition. The recycle delay was set to 5-20 s, depending on the sample, with 64 to 128 accumulated transients. All NMR spectra were analyzes using the Dmfit software.[6]

Optics. The luminescence spectra were recorded on a Fluoromax-4 spectrofluorimeter (Horiba Jobin Yvon). The excitation source is a 450 Watt xenon lamp, excitation spectra were corrected for the variation of the incident lamp flux, as well as emission spectra for the transmission of the monochromator and the response of the photomultiplier. The absolute internal quantum yields (Φ) were measured by using a Fluoromax-4 integrating sphere (Horiba Jobin Yvon). The error evaluation of the measured values is about 10 %.

UV-visible absorption spectra were recorded with a Varian Cary 50 spectrophotometer with dichloromethane solutions of the clusters and ligands.

SEM (Scanning Electron Microscopy). The imaging was realized using an FEG-SEM Hitachi 4800 microscope operating at 5 kV.

X-ray Diffraction. Powder patterns were recorded using a PANalytical X'Pert diffractometer equipped with CuK_{α} radiation (λ = 1.5418 Å) at room temperature. Note that an internal silicon calibrant was used to obtain the lattice parameters values with accuracy. Structural coherence length and strain parameter values derived from through Pseudo-Voigt peak profile refinement using the Langford method[7] combined with Williamson-Hall analysis,[8] as implemented in the Fullprof[9] suite of programs. The calculated diagram obtained from the single crystal data (at 150 K) was obtained with the Mercury software.

FTIR (Fourier Transform Infra-Red). The spectra were measured on KBr disks in a transmission mode using a Bruker Equinox 55 spectrometer.

Table S1. Crystal Data and Structure Refinement for clusters **1** and **2** at 150 K.

Compound	$[Cu_4I_4(PPh_2CH_2CH{=}CH_2)_4]$	$[Cu_4I_4(PPh_2CH_2CH_2CH_3)_4]$
Label	**1**	**2**
Chemical formula	(C60 H60 Cu4 I4 P4)*2	(C60 H68 P4 Cu4 I4)*2
fw	3333.66	3341.72
Crystal system	Tetragonal	Tetragonal
Space group	P -421c	$I\,\bar{4}2m$
a, Å	15.596(1)	15.951(1)
b, Å	15.596(1)	15.951(1)
c, Å	12.165(1)	12.006(1)
α, deg	90.00	90.00
β, deg	90.00	90.00
γ, deg	90.00	90.00
V, Å^3	2959.0(4)	3054.7(4)
Z	2	2
ρ_{calc}, g/cm^3	1.871	1.816
μ, mm^{-1}	3.650	3.536
Reflections collected	12958	16954
Independent reflections	4310	2332
R_{int}	0.0231	0.0303
Reflections $I > 2\sigma(I)$	3942	2208
Parameters	163	35
GOF on F^2	1.020	1.118
$R_1{}^a/wR_2{}^b(I > 2\sigma(I))$	0.0234/0.0468	0.0731/0.1953
$R_1{}^a/wR_2{}^b(all)$	0.0281/0.0482	0.0861/0.2144
Reference	(10)	(11)

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

Note that in the structure of **2**, the propyl chains on the phosphine ligands are disordered therefore carbon and hydrogen atom positions were refined using isotropic thermal displacement parameters.

Figures.

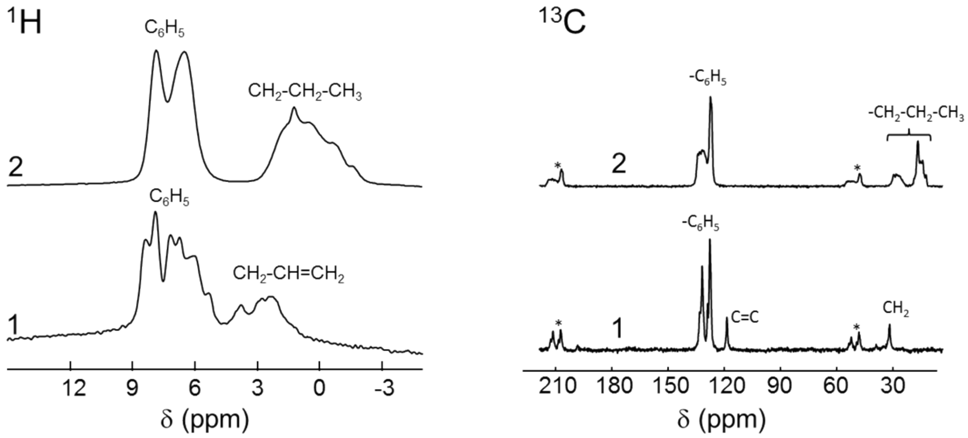

Figure S1. Solid state MAS ^{1}H and ^{13}C CPMAS NMR spectra of [$Cu_4I_4(PPh_2CH_2CH=CH_2)_4$] (**1**) and [$Cu_4I_4(PPH_2CH_2CH_2CH_3)_4$] (**2**). The peaks marked with * are spinning sidebands.

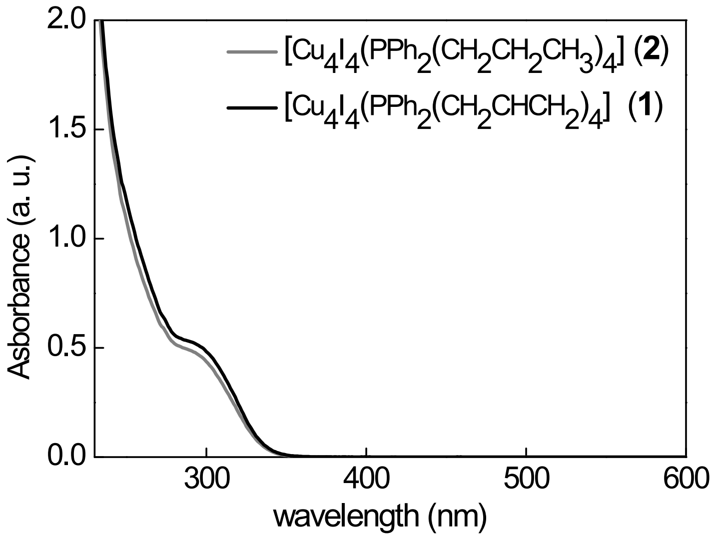

Figure S2. UV-visible absorption spectra of **1** and **2** in dichloromethane (c = 1.2 10^{-2} mol. L^{-1}).

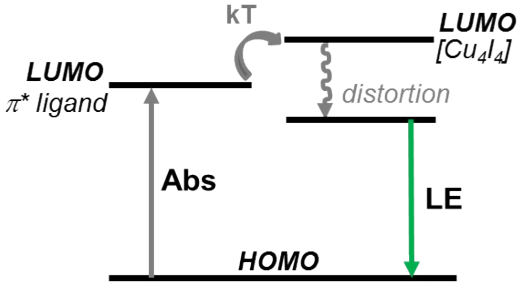

Figure S3. Schema of the emision mechanism of the studied clusters.

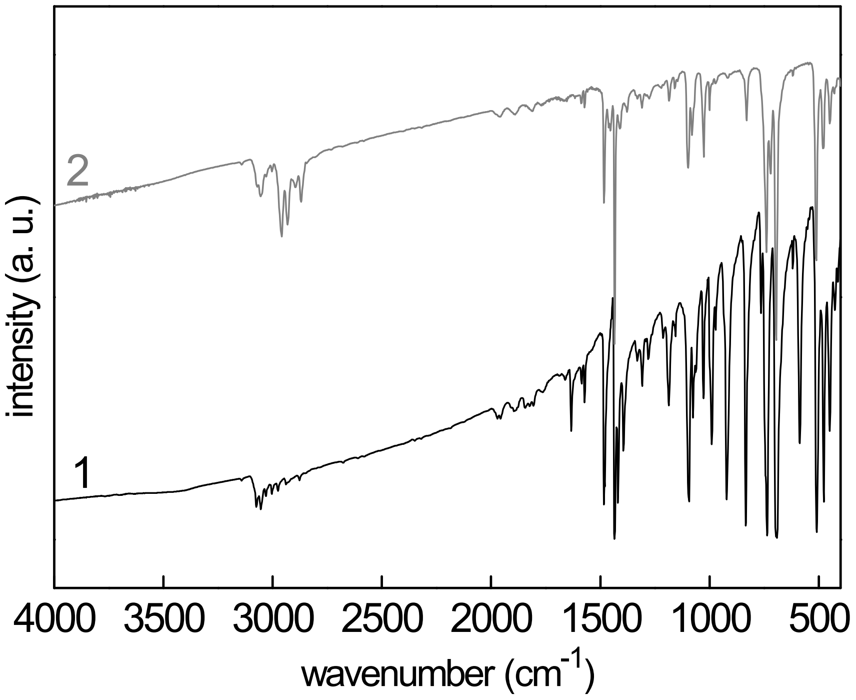

Figure S4. FTIR spectra of **1** and **2** clusters.

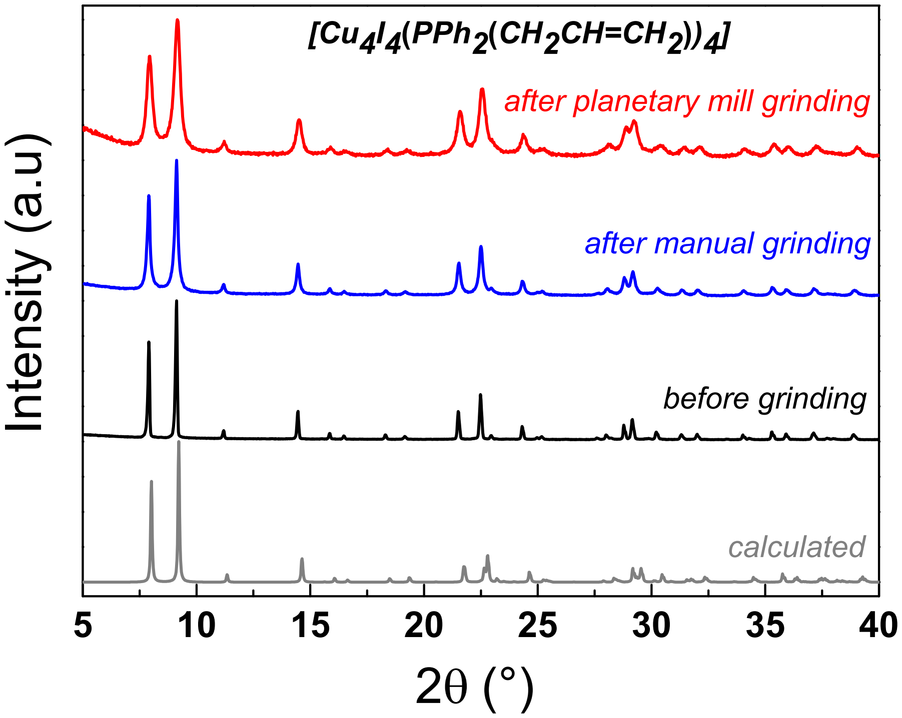

Figure S5. PXRD diagrams of **1** and before and after grinding recorded at RT.

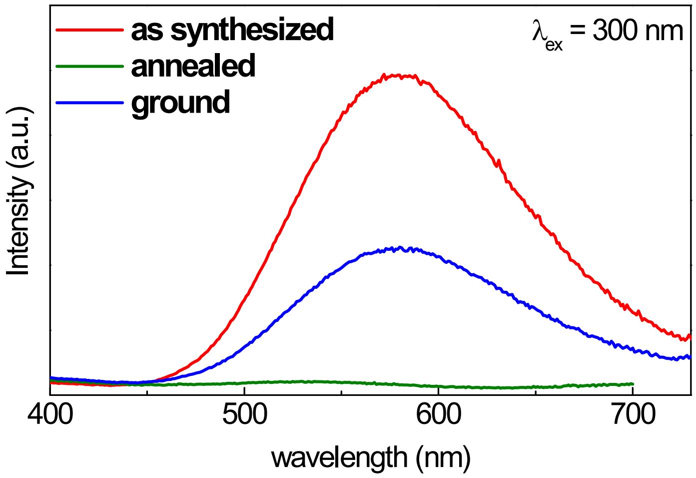

Figure S6. Emission spectra of mechanochromic films of **1**, as-synthesized, after annealing and ground. A further annealing lead to a similar emission spectra as recorded after the first thermal treatment.

REFERENCES

---

[1] E. Kupce and R. Freeman, *J. Magn. Reson. Ser. A*, **1995**, *115*, 273.
[2] (a) S. Meiboom and D. Gill, *Rev. Sci. Instrum.*, **1958**, *29*, 688. (b) H. Y. Carr and E. M. Purcell, *Phys. Rev.*, **1954**, *94*, 630.
[3] L. A. O'Dell and R. W. Schurko, *Chem. Phys. Lett.*, **2008**, *464*, 97.
[4] Fung, B. M., Khitrin, A. K. and Ermolaev, K., An Improved Broadband Decoupling Sequence for Liquid Crystals and Solids, *J. Magn. Reson.,* **2000***, 142*, 97.
[5] Cory, D. G. & Ritchey, W. M., Suppression of signals from the probe in bloch decay spectra, *J. Magn. Reson. (1969),* **1988***, 80*, 128.
[6] Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J. O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70.
[7] Langford, J. I., *National Institute of Standards and Technology*, Special Publication, **1992**, *846*, 110. NIST, Washington, DC.
[8] Williamson, G. K.; Hall, W. H. X-Ray Line Broadening from Filed Aluminium and Wolfram. *Acta Metall*. **1953**, *4*, 22.
[9] Rodriguez-Carvajal, J. Recent Advances in Magnetic Structure Determination by Neutron Powder Diffraction. *Physica B*, **1993**, *192*, 55.; http://www.ill.eu/sites/fullprof/index.html.
[10] S. Perruchas, X. F. Le Goff, S. Maron, I. Maurin, F. Guillen, A. Garcia, T. Gacoin, J.-P. Boilot, *J. Am. Chem. Soc.*, **2010**, *132*, 10967.
[11] C. Tard, S. Perruchas, S. Maron, X. F. Le Goff, F. Guillen, A. Garcia, J. Vigneron, A. Etcheberry, T. Gacoin J.-P. Boilot, *Chem. Mater*. **2008**, *20*, 7010.