Supporting Information

Siloxanol Functionalized Copper Iodide Cluster as Thermochromic Luminescent Building Block

Sandrine Perruchas,[a] Nicolas Desboeufs,[a] Sébastien Maron,[a] Xavier F. Le Goff,[b] Alexandre Fargues,[c] Alain Garcia,[c] Thierry Gacoin[a] and Jean-Pierre Boilot[a]**

[a] *Laboratoire de Physique de la Matière Condensée (PMC), CNRS - Ecole Polytechnique, 91128 Palaiseau Cedex, France. Phone: (+33) (0)1 69 33 46 85 - Fax: (+33) (0)1 69 33 47 99*
E-mail: sandrine.perruchas@polytechnique.edu
[b] *Laboratoire Hétéroéléments et Coordination (DCPH), CNRS - Ecole Polytechnique, 91128 Palaiseau Cedex, France.*
[c] *Institut de Chimie de la Matière Condensée de Bordeaux (ICMCB) - CNRS, 87 Avenue du Docteur A. Schweitzer, 33608 Pessac Cedex, France.*

I. Experimental section

Characterizations.

Liquid state NMR spectra were recorded on a Bruker AvanceII 300 spectrometer (radiofrequency 300.06 MHz) for ^{1}H and on a Tecmag Apollo360 spectrometer for ^{31}P and ^{29}Si (Larmor frequency 145.77 MHz and 71.54 MHz respectively) at room temperature. ^{1}H spectra were internally referenced from peaks of residual protons in deuterated solvents or from tetramethylsilane ($Si(CH_3)_4$). Solutions of H_3PO_4 85 % wt and of tetraethoxysilane (TEOS -82 ppm *vs* $Si(CH_3)_4$) were used as external standards for ^{31}P and ^{29}Si spectra, respectively.

MAS (Magic Angle Spinning) ^{31}P and ^{29}Si solid-state NMR experiments were recorded at room temperature on a Tecmag Apollo360 spectrometer using a CP/MAS Bruker probe. ^{31}P spectra (Larmor frequency: 145.77 MHz, spinning rotation: 15 kHz) and ^{29}Si (Larmor frequency: 71.54 MHz, spinning rotation: 10 kHz) spectra were externally referenced to a solution of H_3PO_4 or TEOS respectively.

Elemental analyses (C, H) were performed by the Service Central d'Analyses - CNRS of Vernaison.

Luminescence spectra were recorded on a SPEX Fluorolog FL 212 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 (Peltier cooled Hamamatsu R928P photomultiplier). Low temperature measurements have been done with a liquid helium circulation

cryostat SMC TBT Air Liquid model C102084. For the measurements in solution, the cluster was dissolved in dimethylformamide $c = 2.10^{-2}$ mol.L^{-1}.
The internal quantum luminescence yields (Q_{int}) have been determined according to the following equation $Q_{int} = Q_{ext} / (Abs)$. The external quantum yields (Q_{ext}) were obtained by comparison with the calibrated reference powder sample ($Zn_2SiO_4:Mn^{2+}$ National Bureau of Standard NBS 1028: $Q_{ext.\lambda ex260nm} = 0.70$). The absorption distribution (Abs) was obtained from a diffuse reflectance experiment using the synchronous scan technique: excitation and emission monochromators were moved simultaneously at the same wavelength with a defocalized sample position and with the collected light in a fixed Ω solid angle. Three measurements were thus recorded ($Diff._{sample}$, $Diff._{white-reference}$ and $Diff._{black-reference}$).

FT-IR spectra were measured in ATR mode using a Nicolet 6700 spectrometer.

EDX (Energy Dispersive X-ray spectrometry) analyses were performed with a FEG-SEM Hitachi 4800 scanning electron microscope operating between 1 and 10 kV equipped with a Thermo Electron Corporation NORAN System SIX analyzer.

X-Ray structure determination was realized on single crystal obtained as described in the synthesis section. Crystal was mounted on fiberglass using paraton oil and immediately cooled to 150 K in a cold stream of nitrogen. All data were collected on a Nonius Kappa CCD diffractometer at 150(1) K using Mo K_α ($\lambda = 0.71073$ Å) X-ray source and a graphite monochromator. The cell parameters were initially determined using more than 50 reflections. The crystal structures were solved in SIR 97[1] and refined in SHELXL-97[2] by full-matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. All the hydrogen atoms were placed in geometrically calculated positions excepted those of the silanol groups which have been found and refined. Details of crystal data and structure refinements are summarized in Table S1.

Table S1. Crystal Data and Structure Refinement for **2** at T = 150 K.

[Cu$_4$I$_4$(PPh$_2$(CH$_2$)$_2$Si(OH)$_2$-O-Si(OH)$_2$(CH$_2$)$_2$PPh$_2$)$_2$]•(THF)$_4$			
Chemical formula	C56 H64 Cu4 I4 O10 P4 Si4, 4(C4H8O)	Z	4
fw	2183.49	ρ_{calc}, g/cm^3	1.675
Crystal system	Tetragonal	μ, mm^{-1}	2.580
Space group	I41/a	Reflections collected	10900
a, Å	22.616(1)	Independent reflections	4618
b, Å	22.616(1)	R_{int}	0.0295
c, Å	16.932(1)	Reflections $I > 2\sigma(I)$	3665
α, deg	90	Parameters	237
β, deg	90	GOF on F^2	1.074
γ, deg	90	R_1[a]/wR_2[b] $(I > 2\sigma(I))$	0.0351/0.0990
V, Å^3	8660.4(7)	R_1[a]/wR_2[b] *(all)*	0.0484/0.1050

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

II. Figures

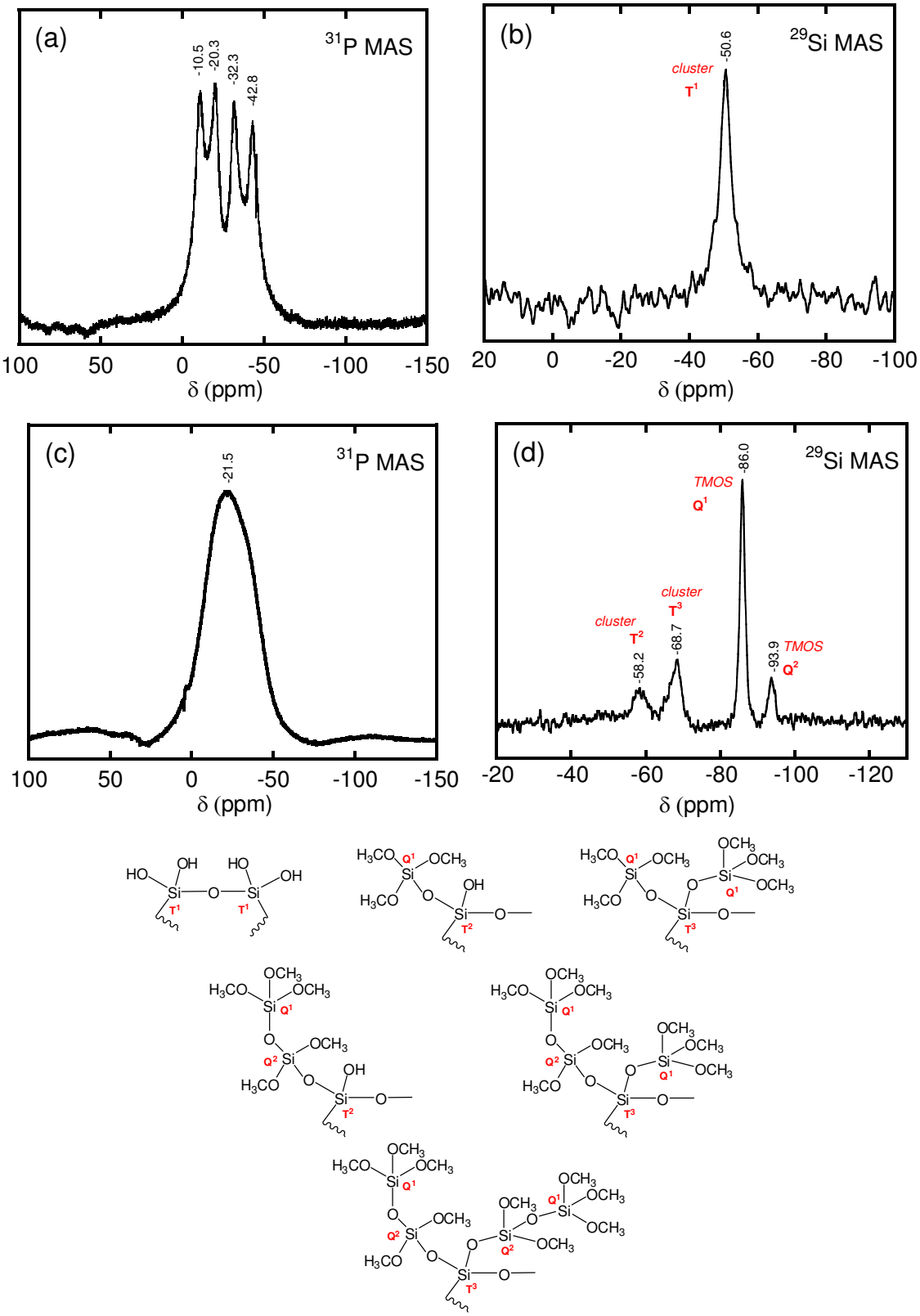

Figure S1. Solid-state NMR spectra (a-b) of cluster **2** and (c-d) of compound **3** and possible ^{29}Si peak attribution.

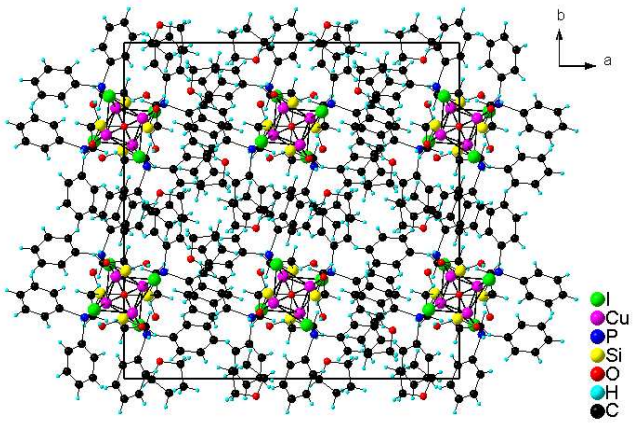

Figure S2. Unit cell structure of $[Cu_4I_4(PPh_2(CH_2)_2Si(OH)_2\text{-}O\text{-}Si(CH_2)_2(OH)_2PPh_2)_2]\bullet(THF)_4$ (**2**•$(THF)_4$).

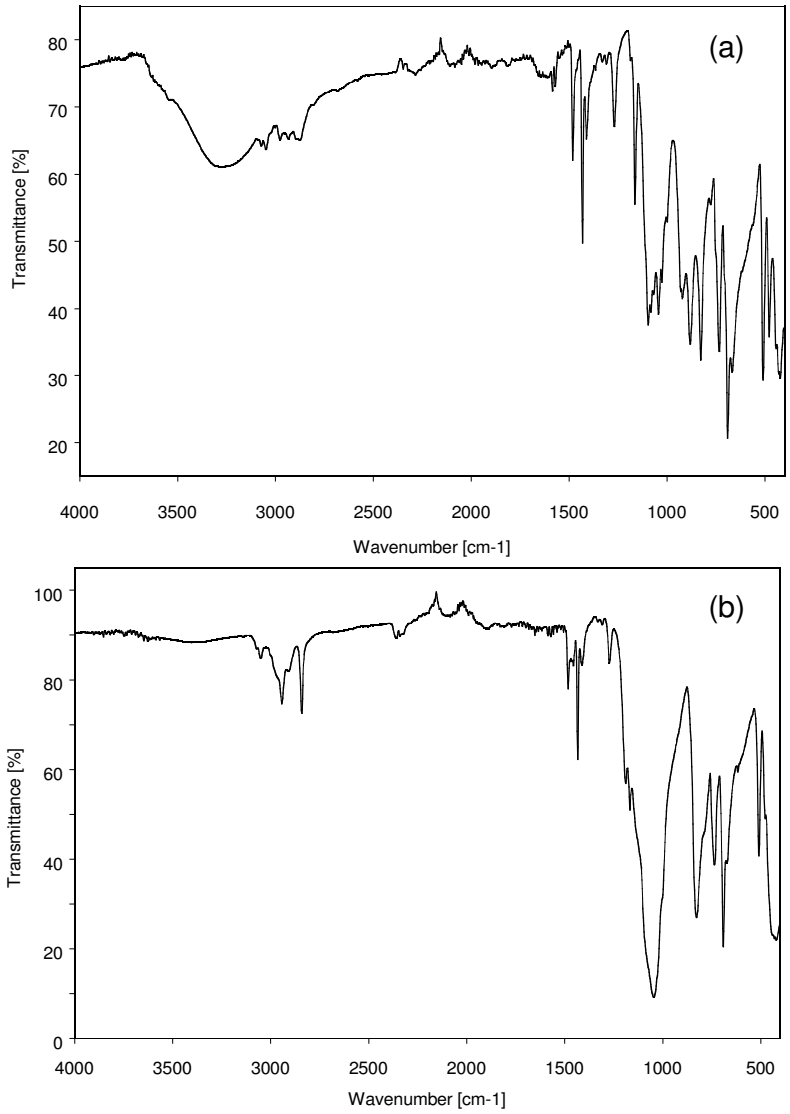

Figure S3. FTIR spectra of (a) cluster **2** and (b) compound **3**.

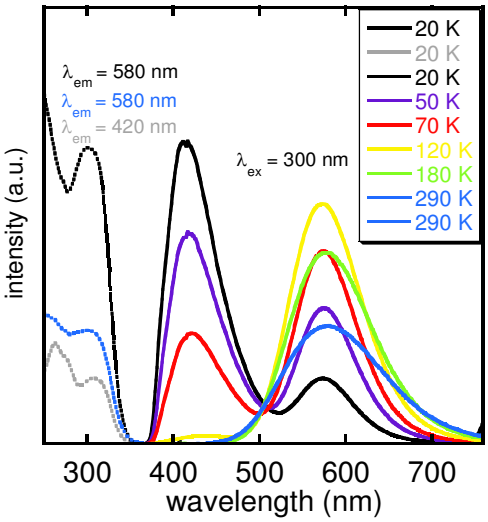

Figure S4. Temperature dependant luminescence spectra from 20 to 290 K of **3** in thin film deposited on glass substrate. Emission (λ_{ex} = 300 nm) and excitation spectra are solid and dotted lines respectively.

References

(1) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *SIR97, an integrated package of computer programs for the solution and refinement of crystal structures using single crystal data.*

(2) Sheldrick, G. M. *SHELXL-97*, Universität Göttingen, Göttingen, Germany, **1997**.