Phosphorescence quantum yield enhanced by intermolecular hydrogen bonds in Cu_4I_4 clusters in the solid state

P. P. Mazzeo,[a] L. Maini,[*a] A. Petrolati, [a] V. Fattori,[*b] K. Shankland,[c] and D. Braga[a]

a Dipartimento di Chimica "G.Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy.

b Istituto per la Sintesi Organica e la Fotoreattività (ISOF) – CNR,Via Gobetti 101, 40129 Bologna, Italy.

c School of Pharmacy, University of Reading, Whiteknights, Reading, RG6 6AD, UK.

Supporting information

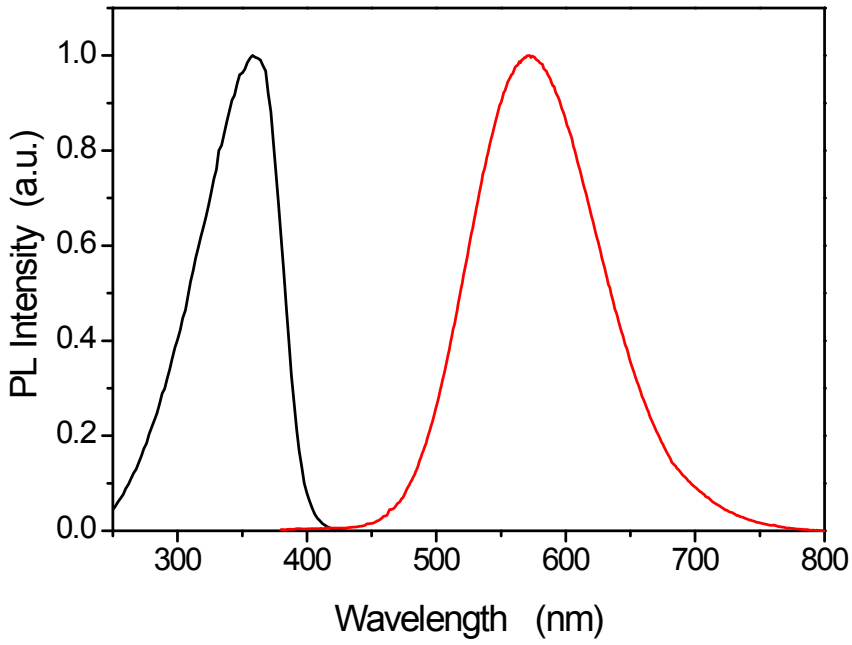

Figura ESI1. Normalized excitation (black) and emission (red) spectra recorded on microcrystalline powder of **1**.

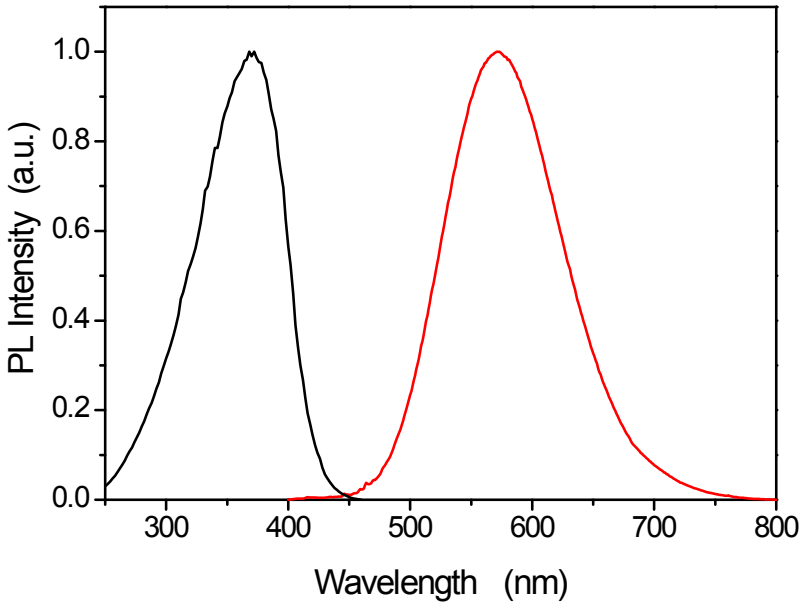

Figura ESI2. Normalized excitation (black) and emission (red) spectra recorded on microcrystalline powder of **2**.

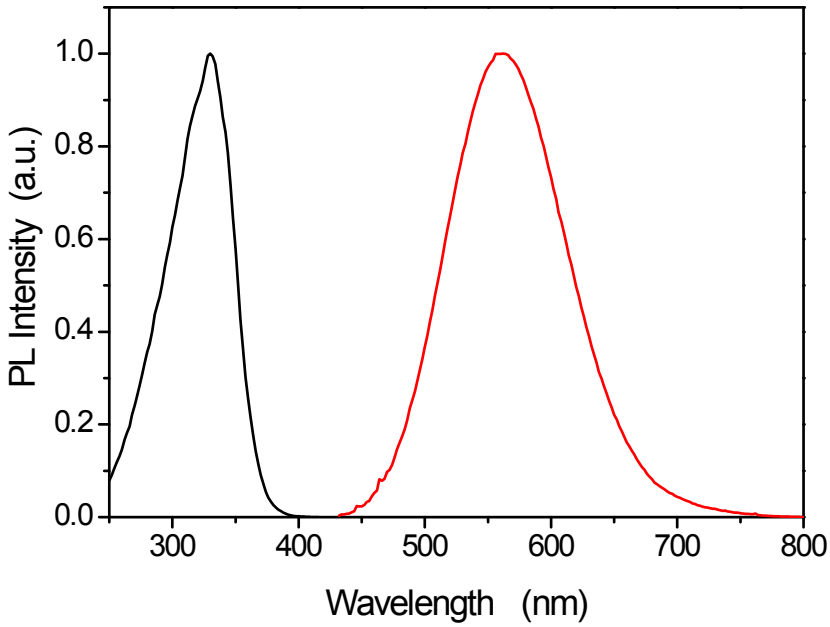

Figura ESI3. Normalized excitation (black) and emission (red) spectra recorded on microcrystalline powder of **3**.

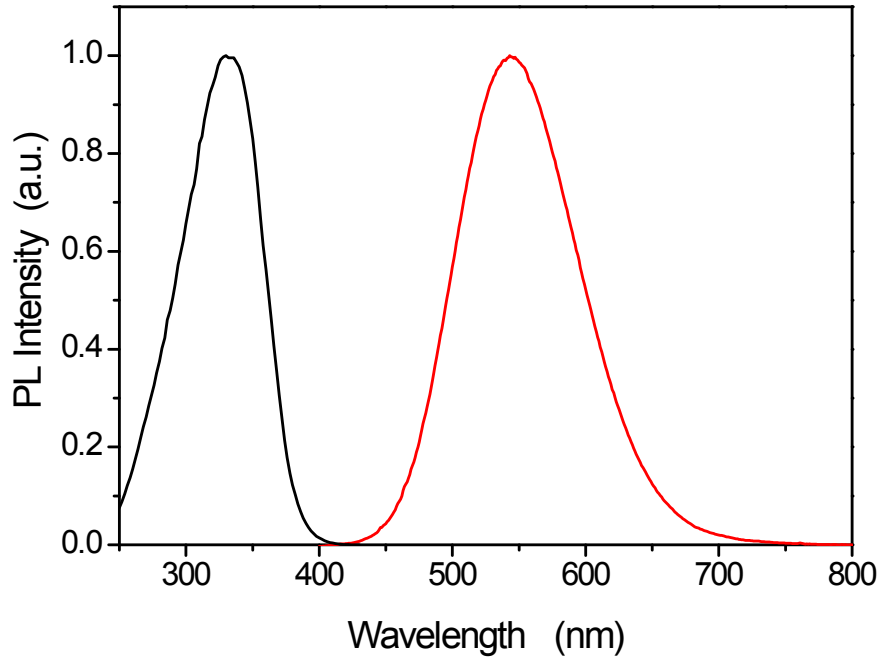

Figura ESI4. Normalized excitation (black) and emission (red) spectra recorded on microcrystalline powder of **4**.

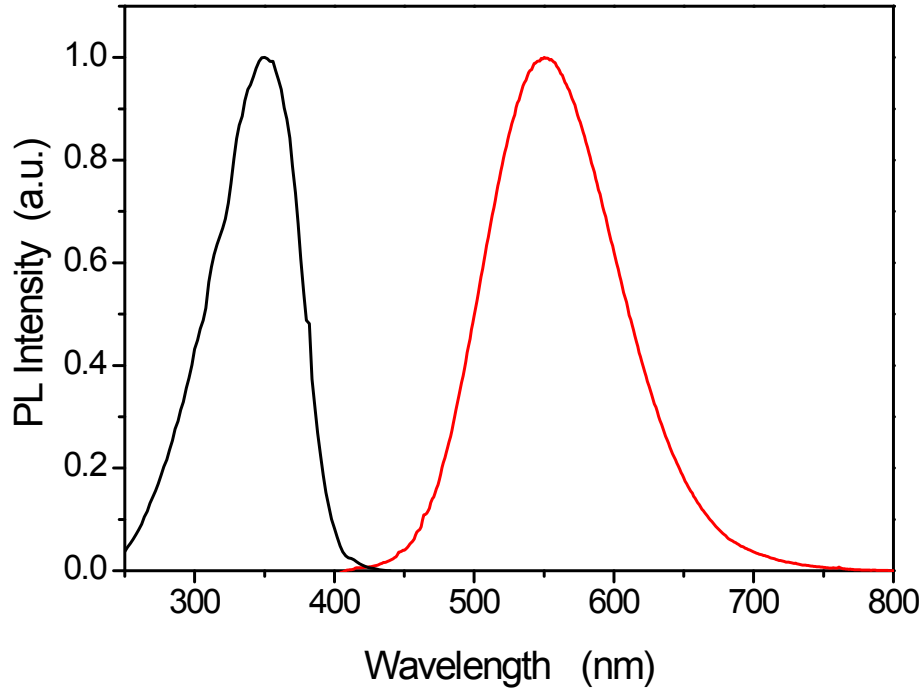

Figura ESI5. Normalized excitation (black) and emission (red) spectra recorded on

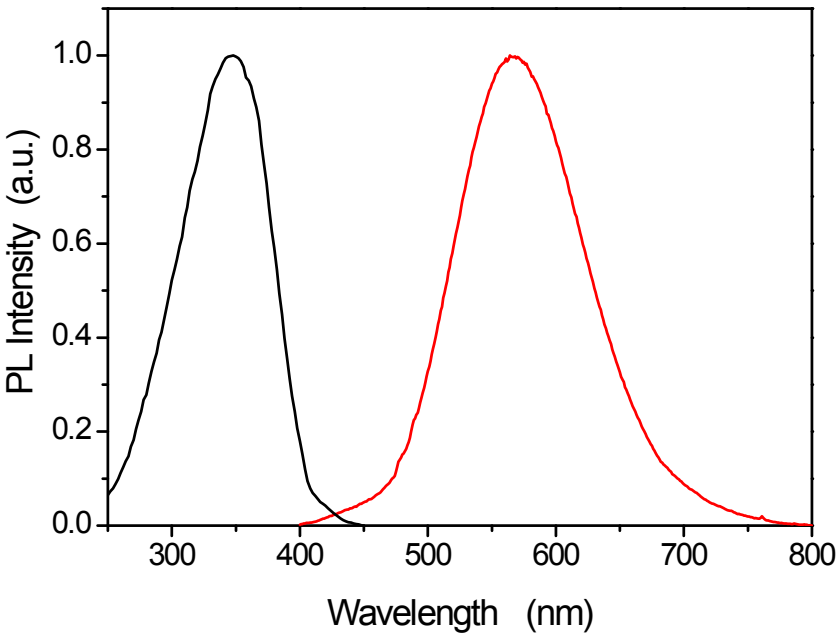

Figura ESI6. Normalized excitation (black) and emission (red) spectra recorded on microcrystalline powder of **5b**.

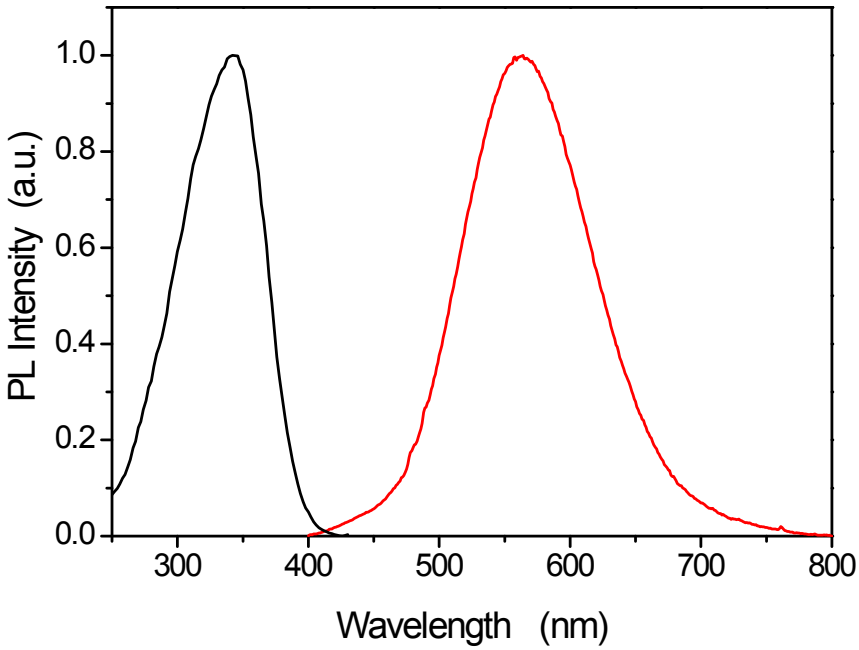

Figura ESI7. Normalized excitation (black) and emission (red) spectra recorded on microcrystalline powder of **5b** (desolvated).

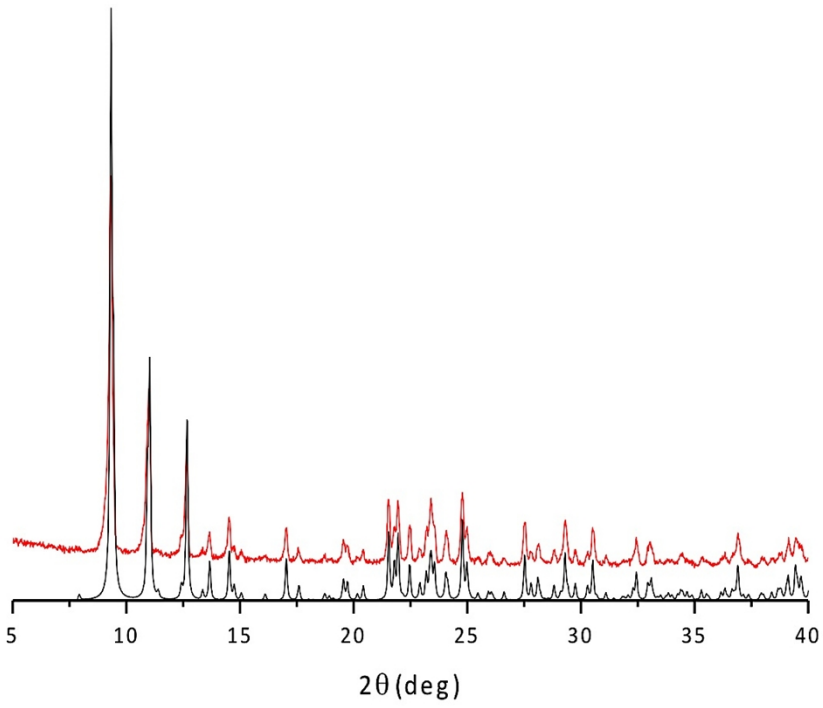

Figure ESI8: Experimental (red line) and calculated (black line) powder pattern comparison of **1**

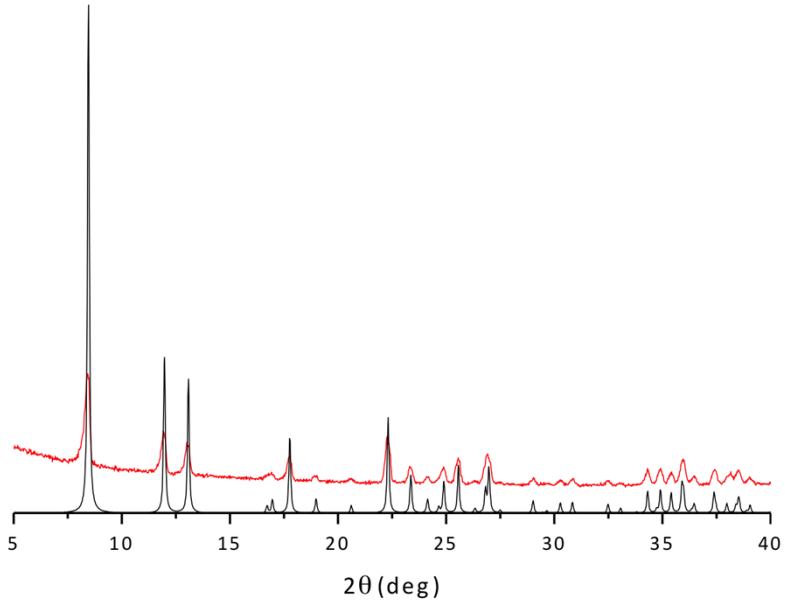

Figure ESI9: Experimental (red line) and calculated (black line) powder pattern comparison of **2**

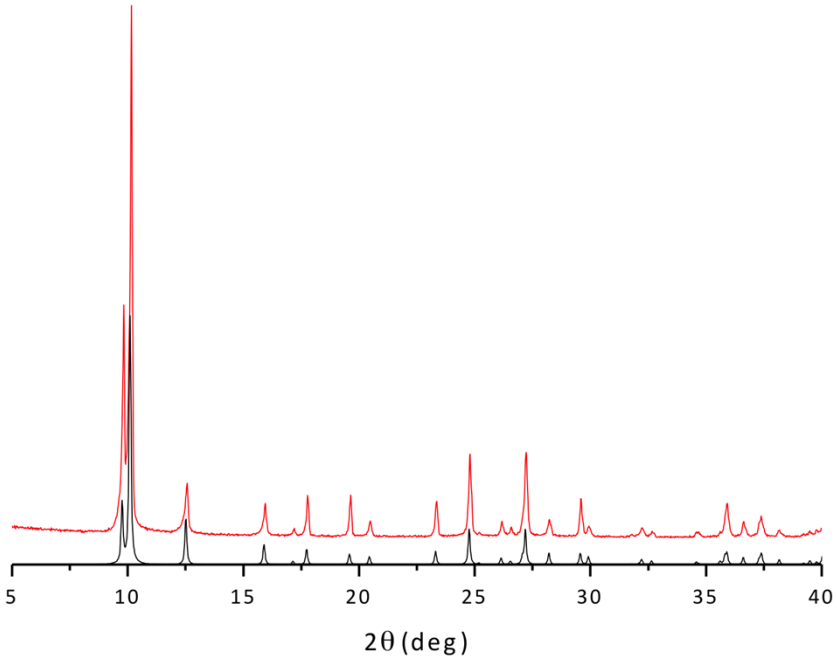

Figure ESI10: Experimental (red line) and calculated (black line) powder pattern comparison of **3**

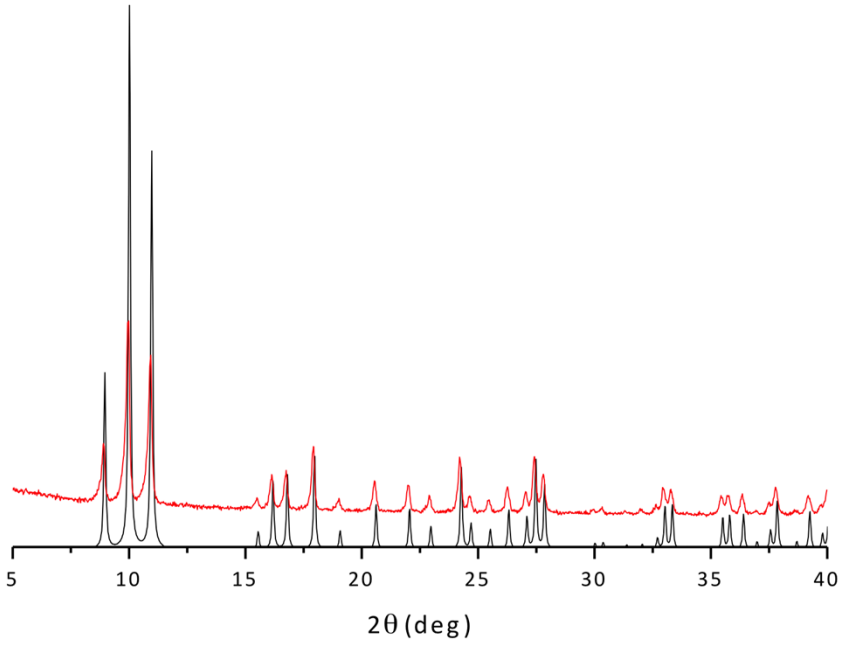

Figure ESI11: Experimental (red line) and calculated (black line) powder pattern comparison of **4**

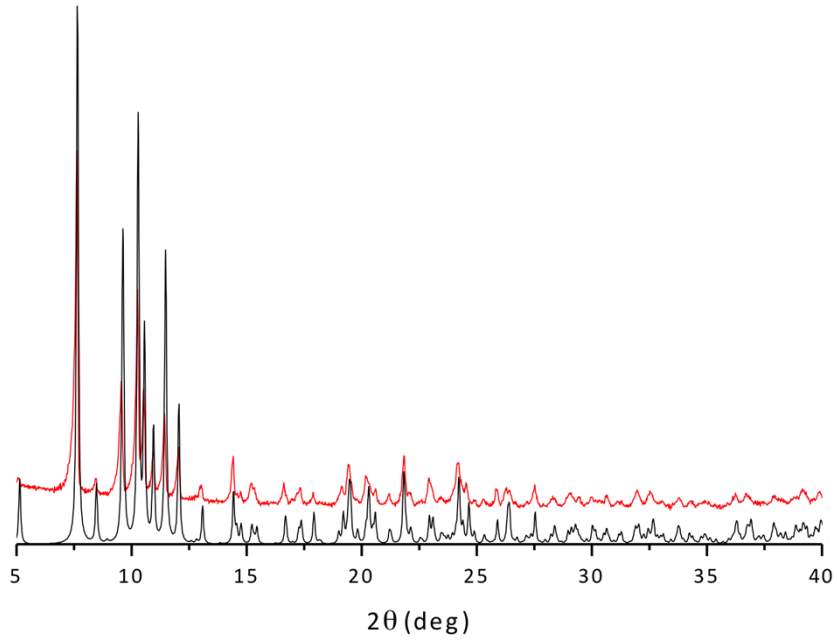

Figure ESI12: Experimental (red line) and calculated (black line) powder pattern comparison of **5b**

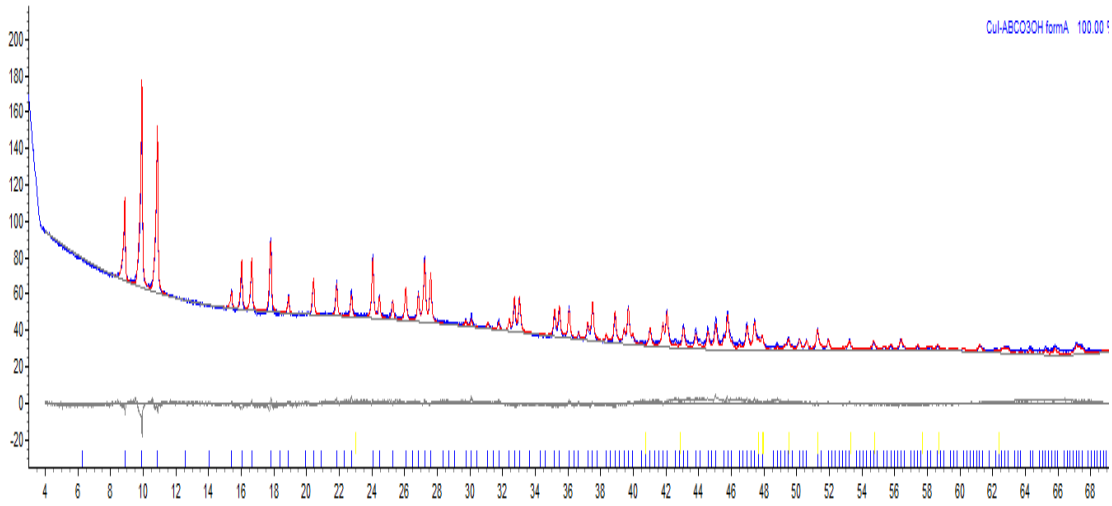

Figure ESI13: Rietveld analysis output graph of **5a**.

The data set was background subtracted and truncated to 50° 2θ for Pawley fitting (χ^2 = 1.9). A shifted Chebyshev function with 12 parameters and Pseudo-Voigt (type II) were used to fit respectively background and peak shape. A scale-only Rietveld refinement, perfomed with TOPAS 4.2 software package,[1] against the original data set in the range 4°–65° 2θ to give a good final fit, R_{wp} = 2.89. No preferred orientation model have been used while rigid-body was built to model the chemical entities. An overall thermal parameter for each atom species was adopted.

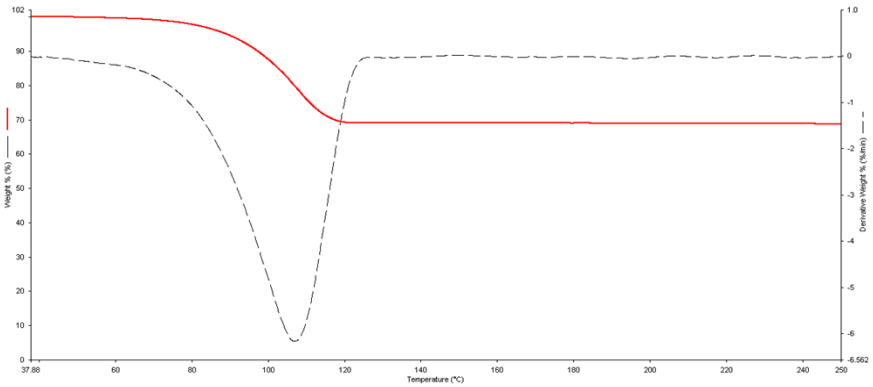

Figure ESI14: TGA analysis of **3**

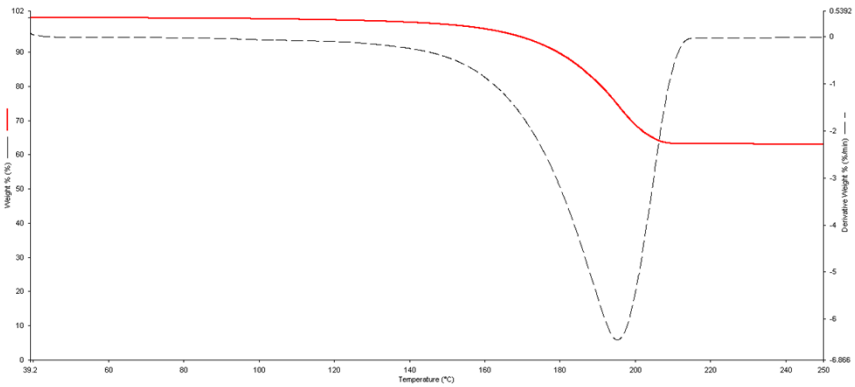

Figure ESI15: TGA analysis of **4**

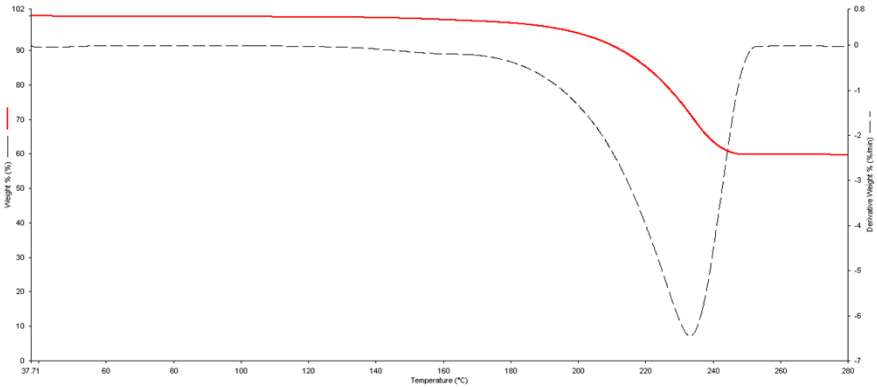

Figure ESI6: TGA analysis of **5a**

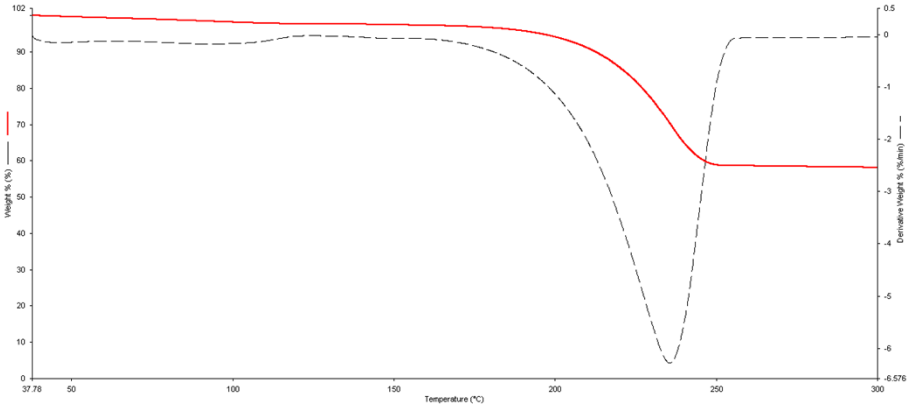

Figure ESI17: TGA analysis of **5b**

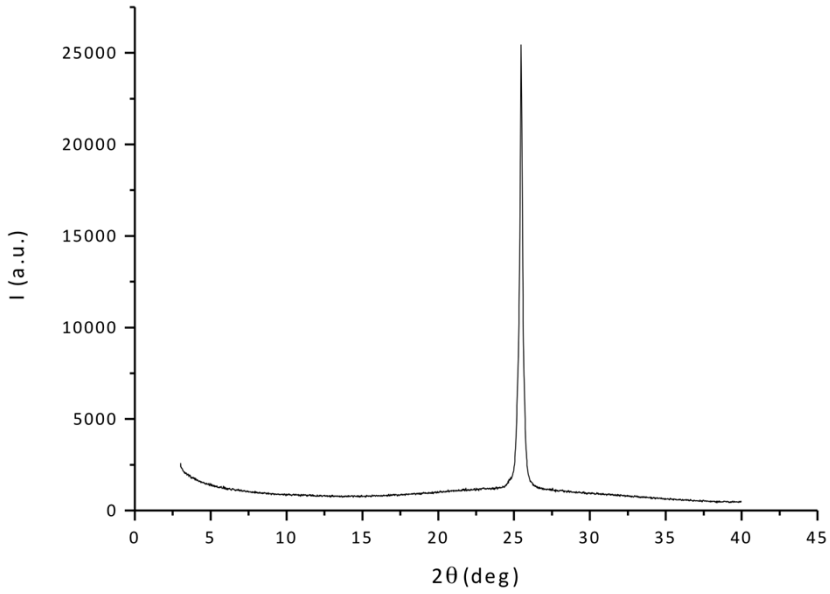

Figure ESI18: XRPD analysis performed in Bragg-Brentano geometry on a silica glass slide vacuum-deposited CuI thin film. The peak at 25.45 2θ° corresponds to the preferentially oriented (111) plane of the γ-CuI phase.

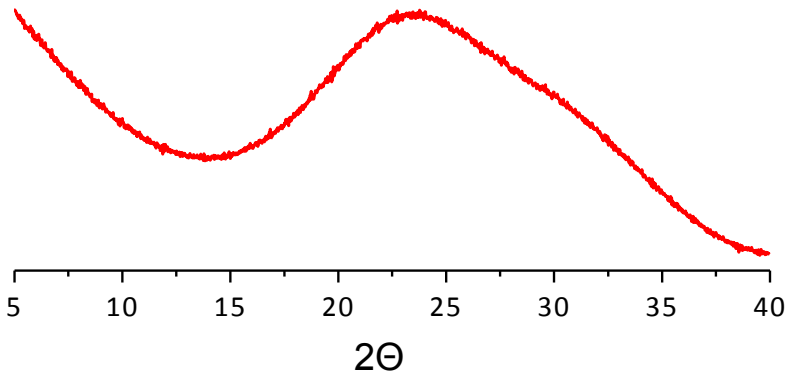

Figure ESI19: XRPD analysis performed in Bragg-Brentano geometry directly on silica glass slice after gas-solid reaction between 35nm deposited CuI and quinuclidine vapours.

Table 1. Crystal data and structure refinement for **3, 4, 5a, 5b**

	3	**4**	**5a**	**5b**
Empirical formula	C24 H52 Cu4 I4 N4	C28 H52 Cu4 I4 N4	C28 H52 Cu4 I4 N4 O4	C28 H48 Cu4 I4 N4 O4
Formula weight	1158.46	1206.50	1270.50	1270.50
Temperature	293(2) K	293(2) K	293(2) K	293(2) K
Wavelength	0.71073	0.71073	1.54056	0.71073
Crystal system	Tetragonal	Cubic	Cubic	Monoclinic
Space group	I -4 2 m	P-43n	P-43n	C 1 2/c 1
Unit cell dimensions	a = 9.9963(7)	a = 19.7281(6)	a = 19.9029(2)	a = 37.444(4)
	b = 9.9963(7)	b = 19.7281(6)	b = 19.9029(2)	b = 12.2662(8)
	c = 18.114(2)	c = 19.7281(6)	c = 19.9029(2)	c = 20.000(2)
	β = 90	β= 90	β= 90	β= 113.38(1)
Volume	1810.1(3)	7678.1(4)	7884.0 (3)	8431(1)
Z	2	8	8	8
Density (calculated)	2.133 Mg/m^3	2.087 Mg/m^3	2.096 Mg/m^3	2.002 Mg/m^3
Absorption coefficient	5.749 mm^{-1}	5.426 mm^{-1}	-	4.953 mm^{-1}
F(000)	1112	4608	-	4864
Crystal size	0.06 x 0.04 x 0.03 mm^3	0.5 x 0.1 x 0.08 mm^3	-	0.06 x 0.05 x 0.05 mm^3
Reflections collected	2132	7799	-	21503
Independent reflections	1090 [R(int) = 0.0408]	2484 [R(int) = 0.0486]	-	9738 [R(int) = 0.0720]
Max. and min. transmission	1.00000 and 0.96619	1.00000 and 0.85425	-	1.00000 and 0.63350
Data / restraints / parameters	1090 / 0 / 30	2484 / 0 / 122	-	9738 / 245 / 382
Goodness-of-fit on F^2	0.917	1.043	-	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0735,	R1 = 0.0489,	-	R1 = 0.0972,
	wR2 = 0.1348	wR2 = 0.0669	-	wR2 = 0.1945
Rwp	-	-	0.027	-
Rp	-	-	0.021	-
$R(F^2)$	-	-	0.015	

Crystal structures of **4** and **5b** present disorder on organic ligand; all the thermal parameters have been refined anisotropically but static or dynamic disorder is still present and neither SIMU or DELU command instructions during the refinement are able to model it.

1. *Bruker AXS, Karlsruhe, Germany, 2008, TOPAS v.4.2: General Profile and Structure Analysis Software for Powder Diffraction Data.*
2. Spek, A. L., *Acta Cryst.* **1990,** *A46*, C34.