Electronic Supplementary Information (ESI)

(11 pages)

Too much water? Not enough? *In situ* monitoring of the mechanochemical reaction of copper salts with dicyandiamide

Lucia Casali,[a] Torvid Feiler,[b] Maria Heilmann,[b] Dario Braga,[a] Franziska Emmerling,*[b] Fabrizia Grepioni*[a]

a. Department of Chemistry "G. Ciamician", University of Bologna, 40126 Bologna, Italy; Email: fabrizia.grepioni@unibo.it

b. BAM Federal Institute for Materials Research and Testing, 12489 Berlin, Germany; Email: franziska.emmerling@bam.de

Powder X-ray diffraction

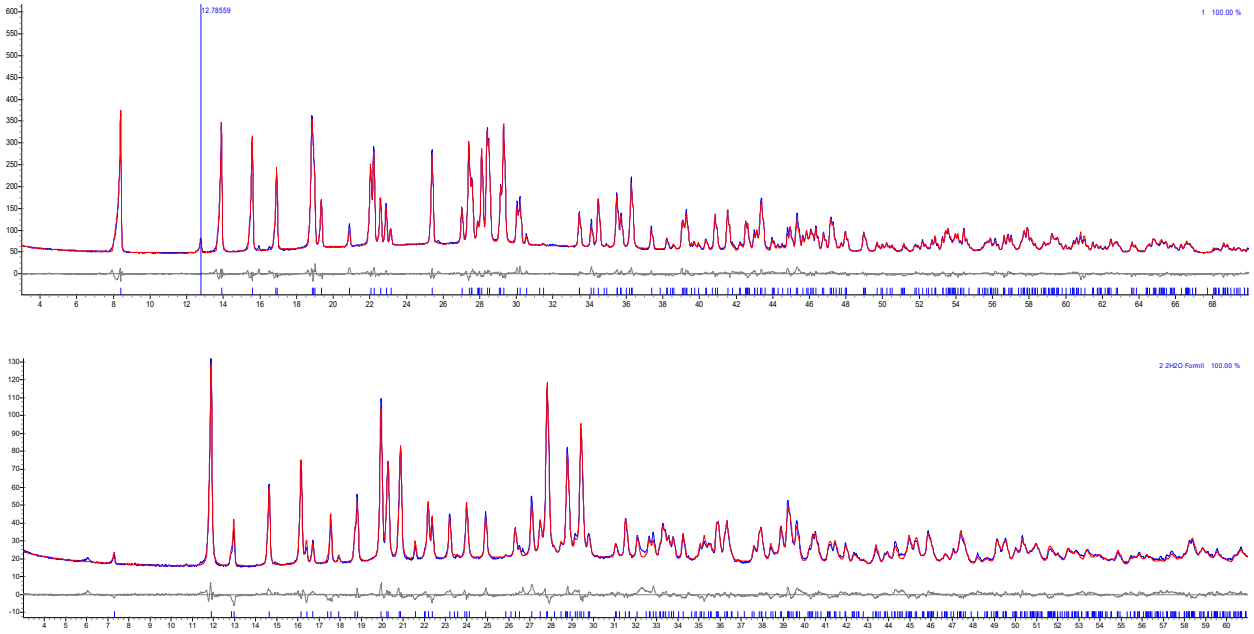

Fig. ESI-1. Rietveld refinements. Experimental (blue curve), calculated (red curve) and difference (grey curve) powder patterns for $[Cu(DCD)_2(OH_2)_2(NO_3)_2]$ **2** (top) and $[Cu(DCD)_2(OH_2)Cl_2]\cdot H_2O$ (**4**) (bottom). The peak marked in blue is due to an excess of DCD.

Table ESI-1. Cell parameters and Rwp values for $[Cu(DCD)_2(OH_2)_2(NO_3)_2]$ (**2**) and $[Cu(DCD)_2(OH_2)Cl_2]\cdot H_2O$ (**4**) (powder data).

	$[Cu(DCD)_2(OH_2)_2(NO_3)_2]$, 2	**$[Cu(DCD)_2(OH_2)Cl_2]\cdot H_2O$, 4**
crystal system	triclinic	monoclinic
space group	P-1	$P2_1/c$
a (Å)	10.822(1)	13.138(3)
b (Å)	6.931(7)	9.424(8)
c (Å)	5.156(1)	10.967(7)
α (°)	67.235(1)	90
β (°)	102.797(1)	113.063(1)
γ (°)	99.693(1)	90
V (Å^3)	346.32	1249.54
Rwp	7.14%	6.4%
CCDC number	CCDC 2128518	CCDC 2128519

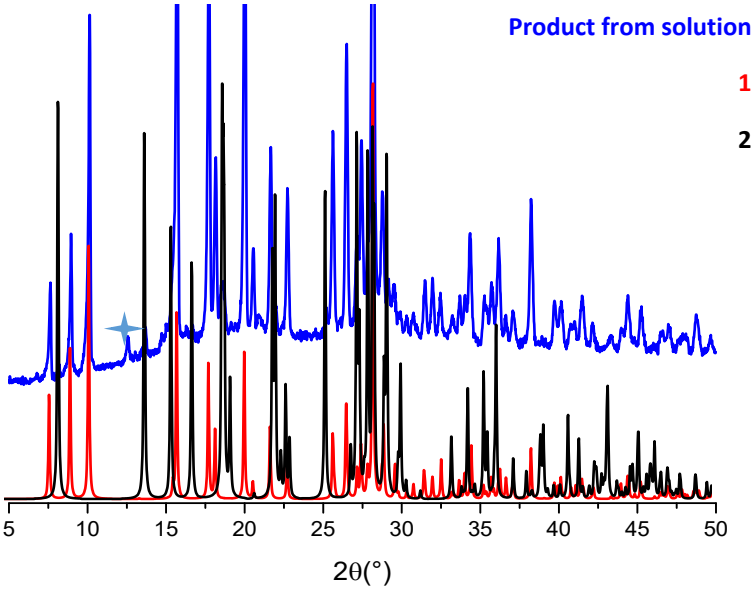

***Fig. ESI-2*.** Comparison between the product from solution (blue line) and the calculated pattern of **1** (red line) and **2** (black line). Extra-peaks are due to the reagent DCD.

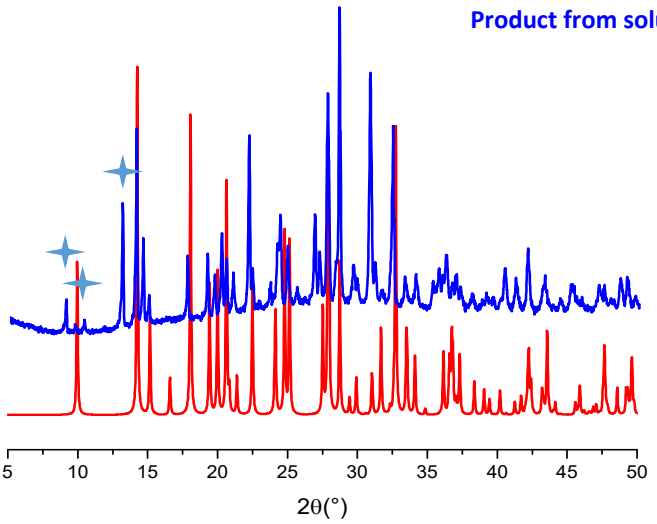

***Fig. ESI-3*.** Comparison between the product from solution (blue line) and the calculated pattern of **3** (red line). The extra-peaks are due to the undefined phase **X.**

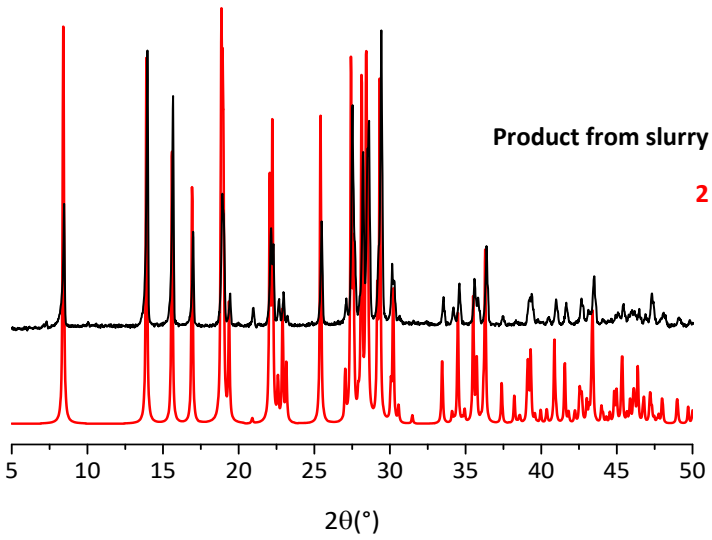

Fig. ESI-4. Comparison between the slurry product (black line) and the calculated pattern of **2** (red line).

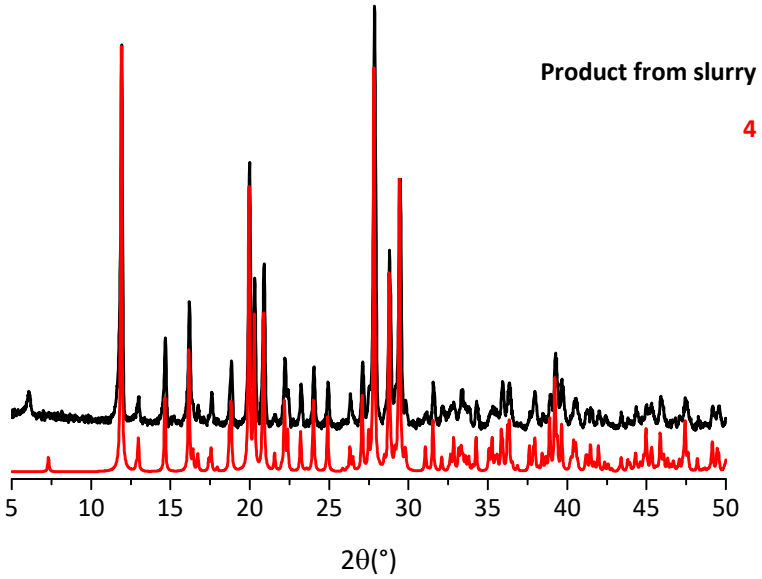

Fig. ESI-5. Comparison between the product from slurry (black line) and the calculated pattern for **4** (red line)**.**

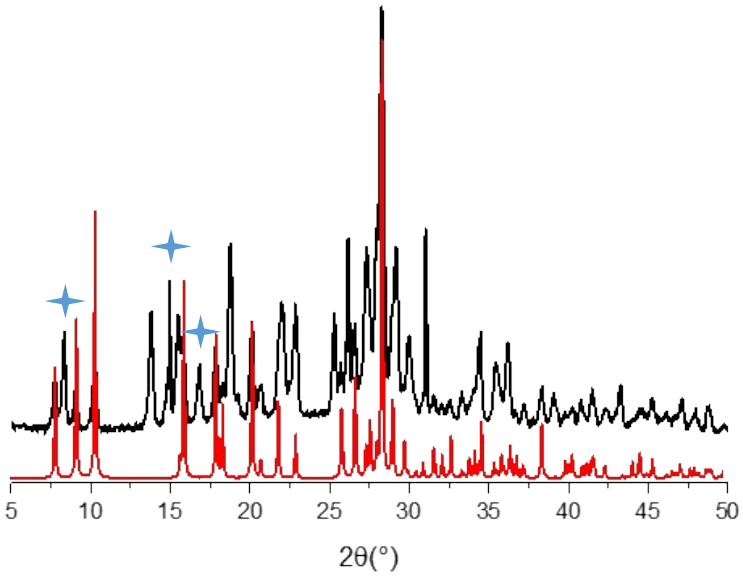

Fig. ESI-6. Comparison between the experimental diffractogram resulting from the milling reaction in MM200 (black line) and the one calculated on the basis of single crystal data for **1** (red line). The extra-peaks (blue stars) are due to form **2**.

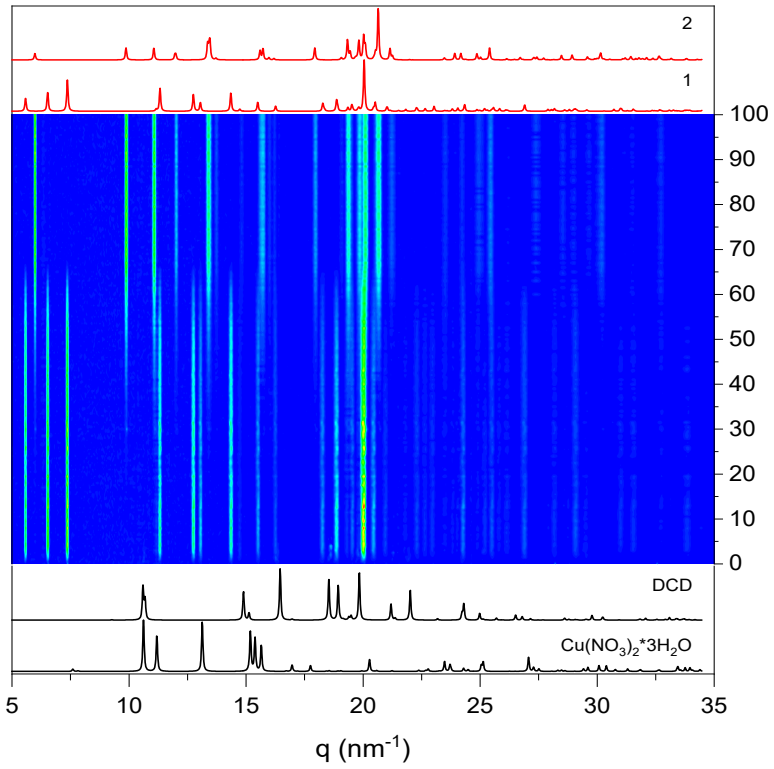

Fig. ESI-7. Time-evolution of the milling reaction between DCD and $Cu(NO_3)_2 \cdot 2H_2O$ with 50 µL of water at 20 Hz (vector number *vs* milling time).

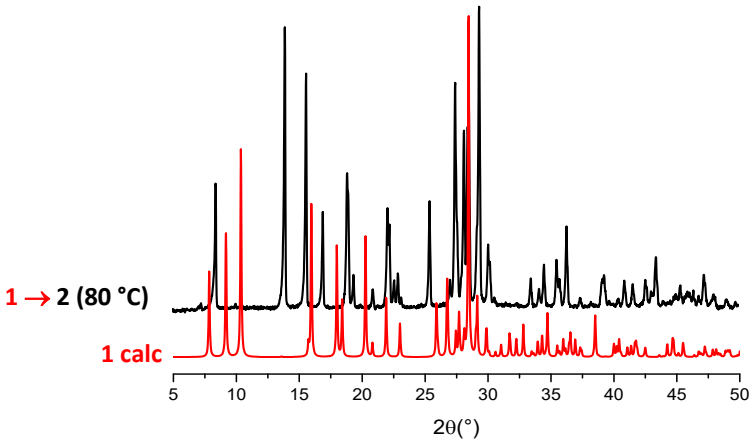

Fig. ESI-8. Conversion of compound **1** (red line, calculated pattern) into **2** is observed by variable temperature powder X-ray diffraction at ca. 80 °C (black line). Upon cooling back to room temperature the solid is stable, and does not reabsorb water from the atmosphere.

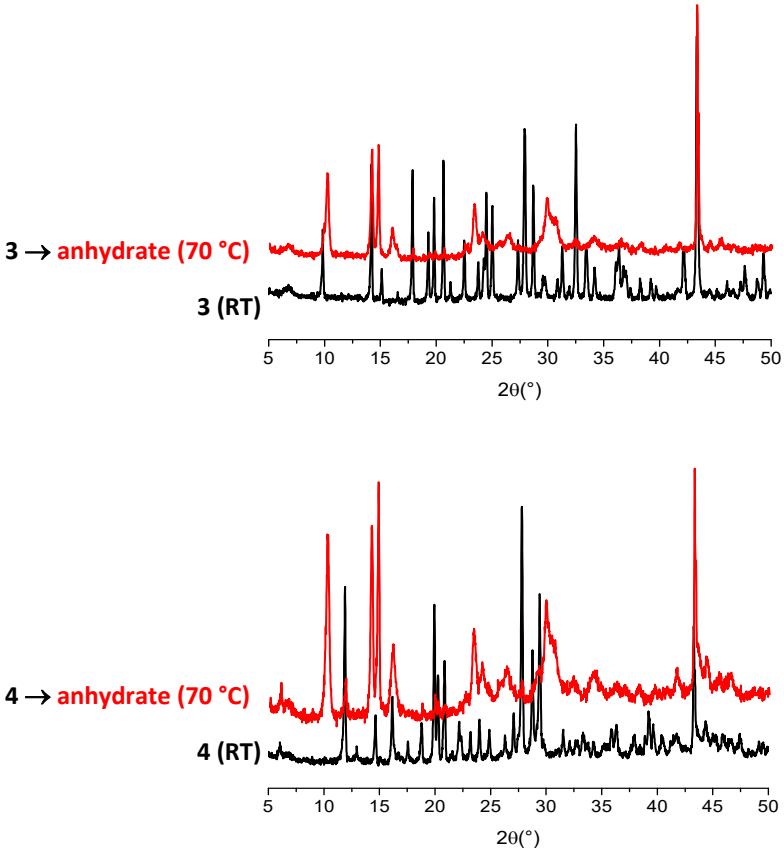

Fig. ESI-9. Crystalline **3** and **4** do not show interconversion: upon heating they both transform into the same anhydrous form, which is stable at ambient condition. [The existance of an anhydrous form as the result of dehydration of compound 3 was mentioned in ref. 16 (main text), but the phase was not structurally characterized.]

Raman Spectroscopy

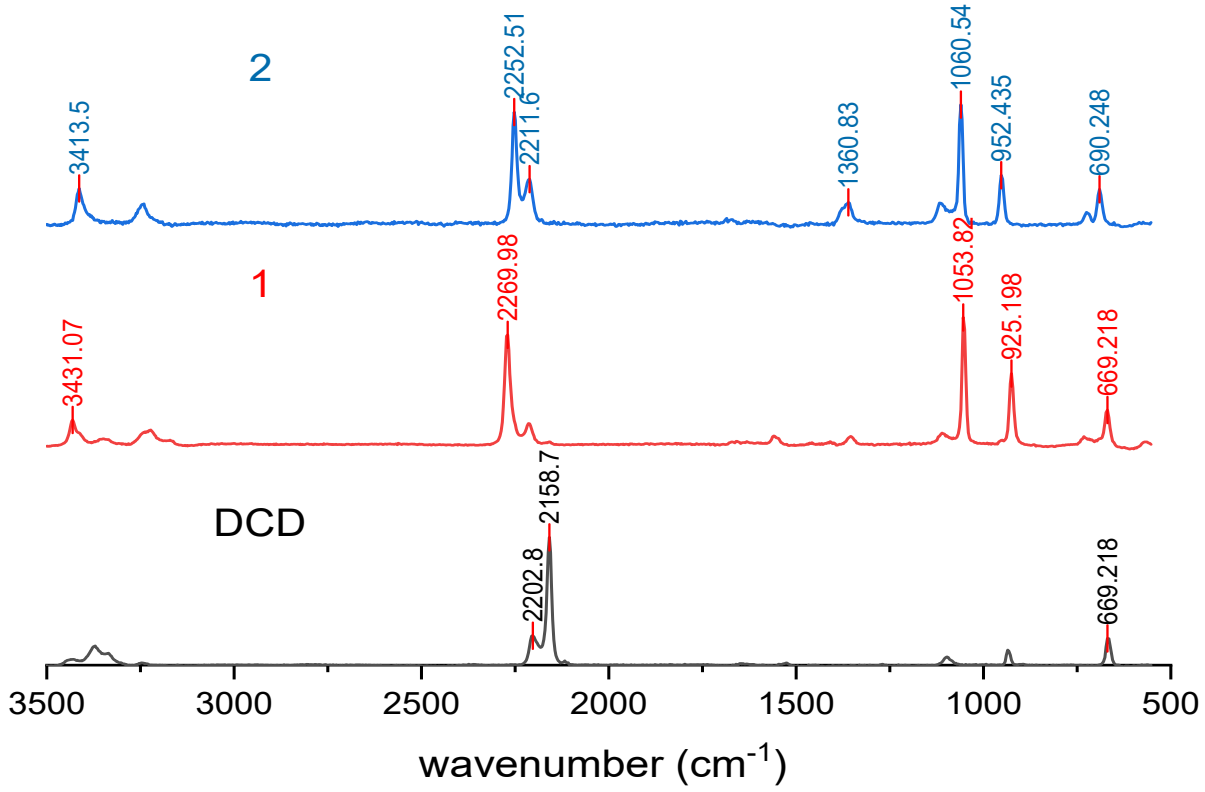

Fig. ESI-10: Raman spectra of DCD (black line), **1** (red line) and **2** (blue line).

Thermal Gravimetric Analysis (TGA)

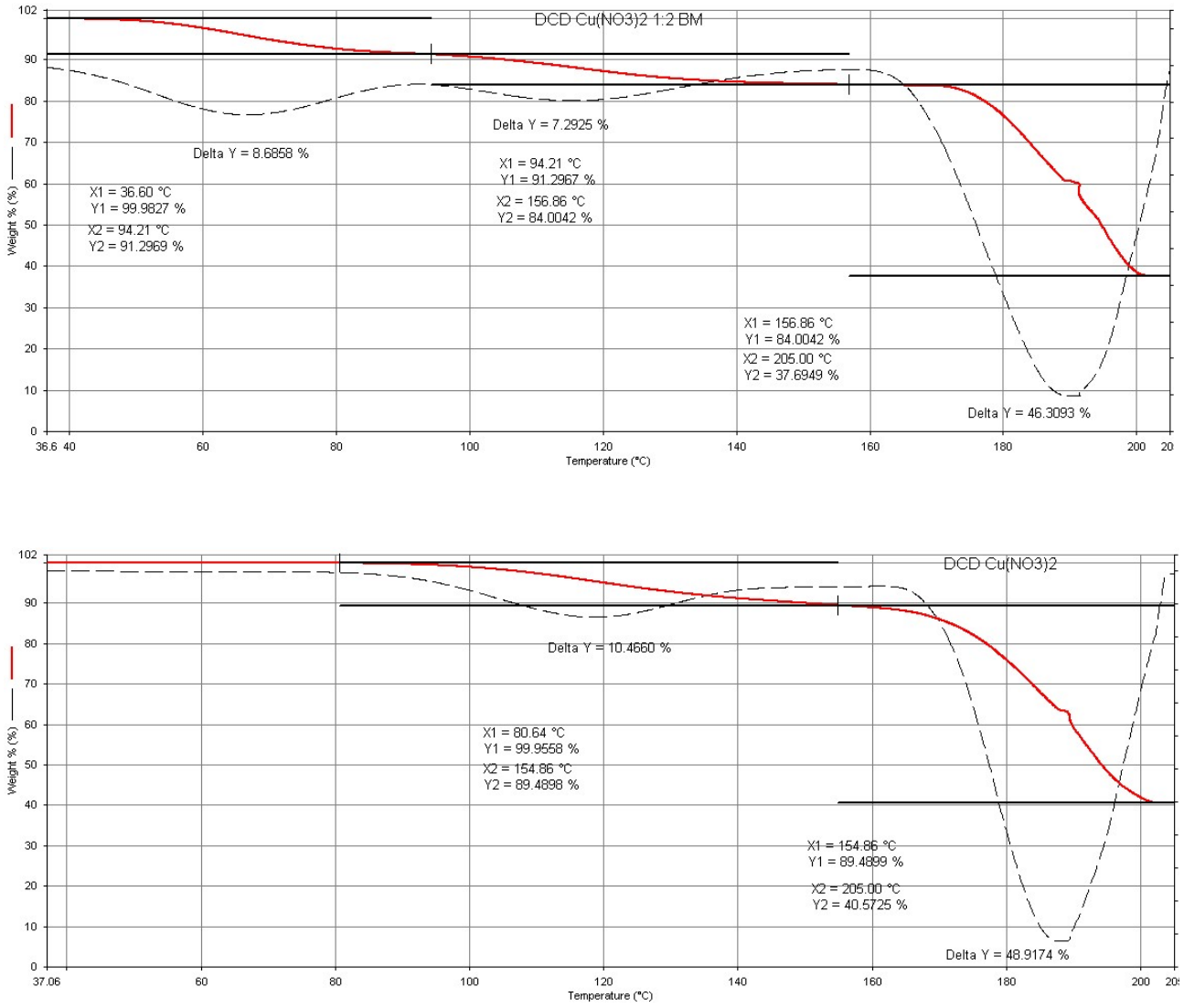

Fig. ESI-11: TGA for (top) **1** and (bottom) **2.**

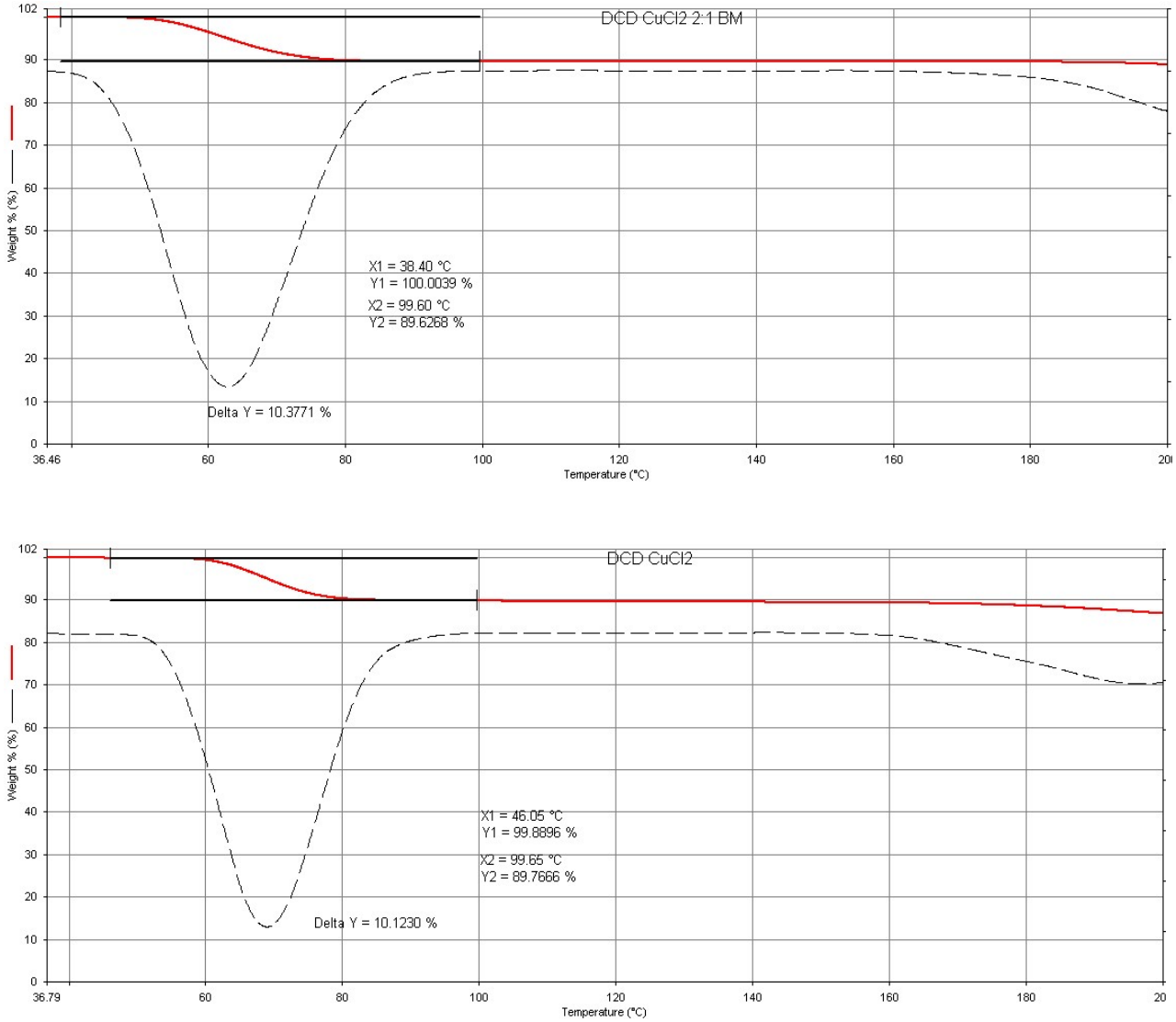

Fig. ESI-12: TGA for (top) **3** and (bottom) **4.**

Differential Scanning Calorimetry (DSC)

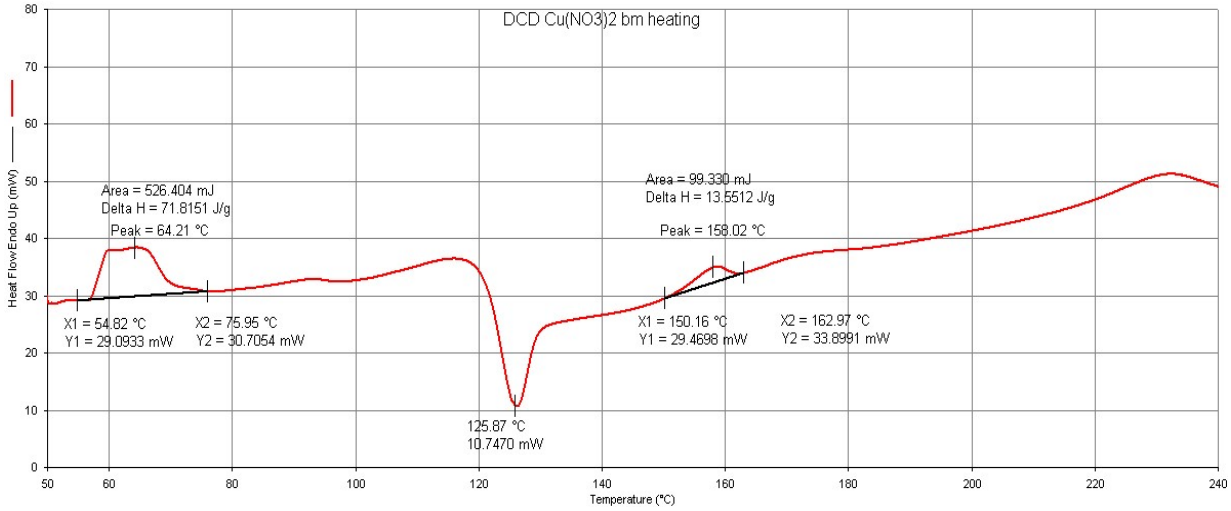

Fig. ESI-13: DSC trace for **1.**

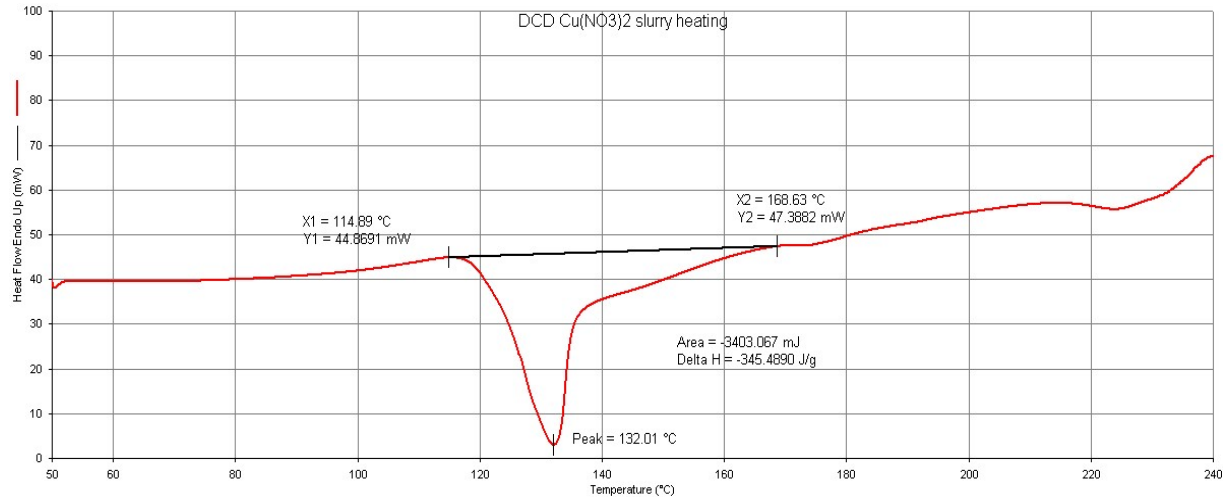

Fig. ESI-14: DSC trace for **2.**

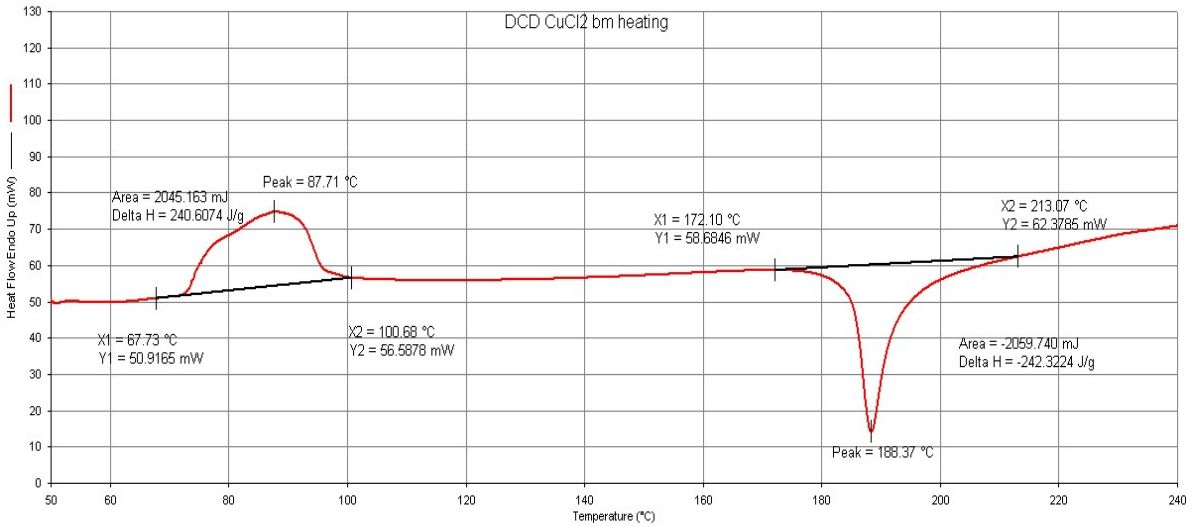

Fig. ESI-15: DSC trace for **3.**

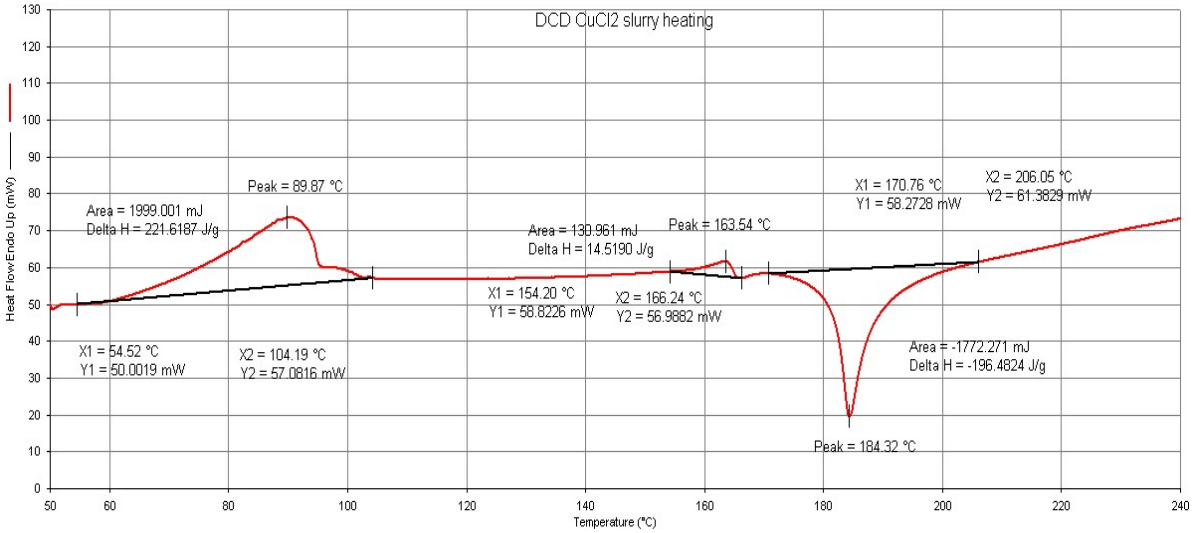

Fig. ESI-16: DSC trace for **4.**