Submitted to ADVANCED MATERIALS

Supporting Information

Freezing the non-classic crystal growth of a coordination polymer by employing controlled dynamic gradients

Marta Rubio-Martínez,[a] Inhar Imaz,[a] Neus Domingo,[a] Afshin Abrishamkar,[b,c] Tiago Sotto Mayor,[b] René Rossi,[b] Carlos Carbonell,[a] Andrew J. deMello,[c] David B. Amabilino,[d] Daniel Maspoch,[*,a,e] and Josep Puigmartí-Luis[*,b]

[a] Institut Catala de Nanociencia i Nanotecnologia, ICN2, Esfera UAB, Campus UAB, 08193 Bellaterra, Spain.

[b] Empa, Swiss Federal Laboratories for Materials Science and Technology, Lerchenfeldstrasse 5, CH-9014 St. Gallen, Switzerland. E-mail: josep.puigmarti@empa.ch

[c] Institute of Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Zurich, Switzerland

[d] School of Chemistry, The University of Nottingham, University Park, NG7 2RD, UK.

[e] Institució Catalana de Recerca i Estudis Avançats (ICREA), 08100 Barcelona, Spain. E-mail: daniel.maspoch@icn.cat

Table SI.1 | Crystal and structure refinement data.

Submitted to ADVANCED MATERIALS

Compound	**1**
Empirical formula	$C_{20}H_{18}Cu_2N_6O_8$,NO_3, H_2O
Formula weight	677.3
Crystal system	triclinic
Space group	P-1
CCDC ref	1059883
Unit cell dimensions	
a (Å)	10.385(4)
b (Å)	11.555(4)
c (Å)	11.790(4)
α(deg)	73.91(3)
β(deg)	84.08(3)
γ(deg)	70.54(3)
V ($Å^3$)	1,281.6(7)
Z	2
F (000)	686
Ind refln (R_{int})	4,905 (0.0199)
θ_{max}(deg.)	27.12
Final R indices	R1 = 0.0528
[I > 2σ(I)]	wR2 = 0.1553

Submitted to
ADVANCED MATERIALS

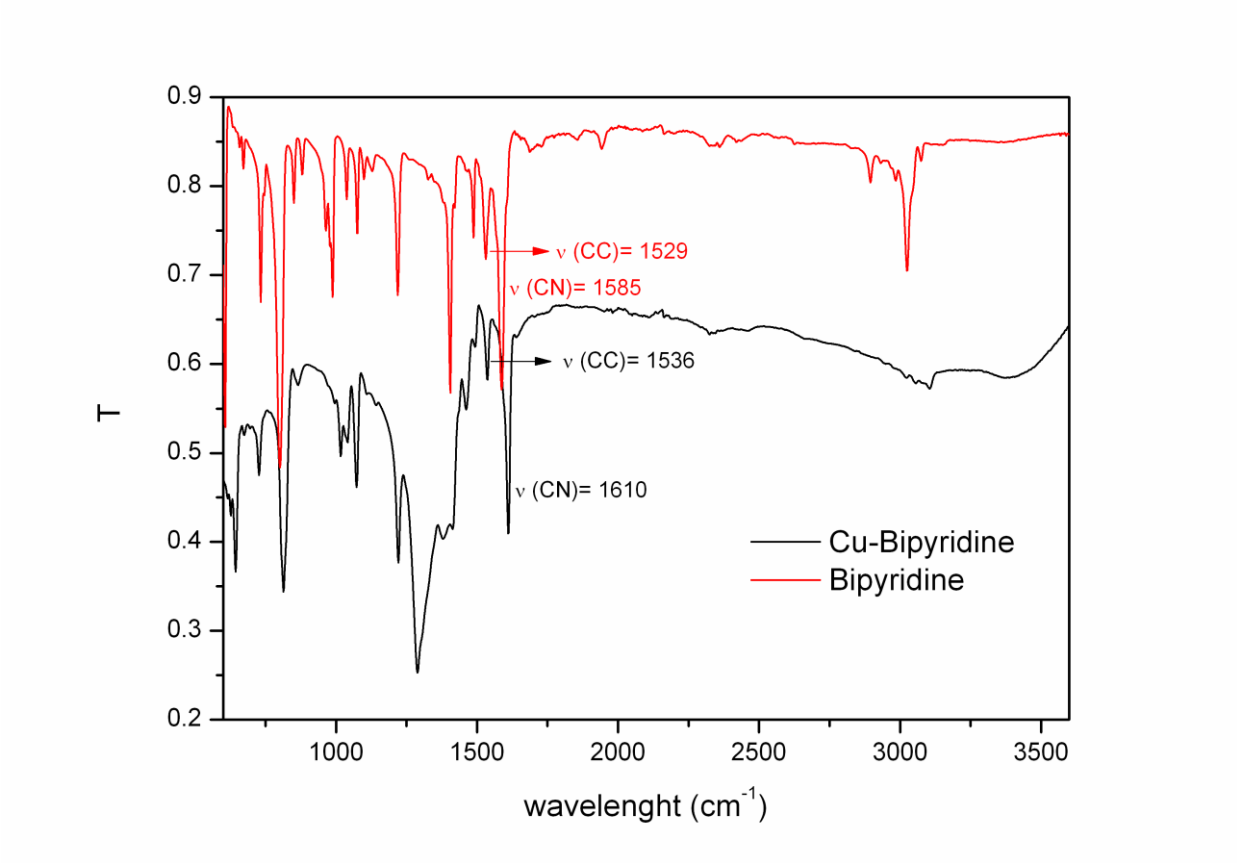

Figure SI.1 | Infrared spectrum of crystals of **1**.

Submitted to
ADVANCED MATERIALS

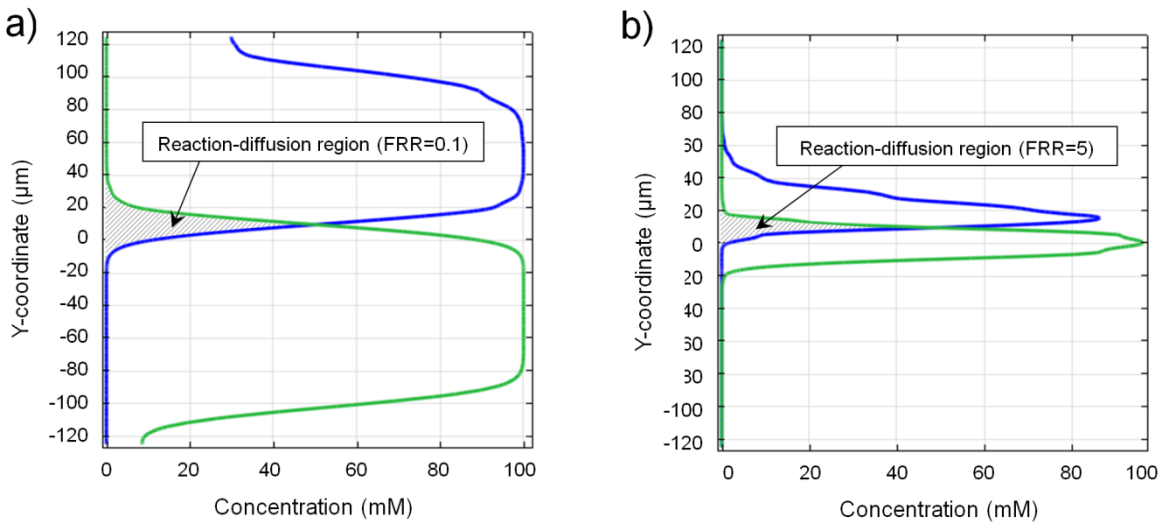

Figure SI.2 | Concentration profiles of $Cu(NO_3)_2 \cdot 6H_2O$ (blue) and 4,4'-bpy (green) at the microfluidic reactor exit at FRR=0.1 (TFR=220 µL/min) (**a**) and FRR=5 (TFR=1,200 µL/min) (**b**) calculated using constant values of the reagents flow rates (Q_2 and Q_3=100 µL/min). In the reaction-diffusion region both reagents are present.

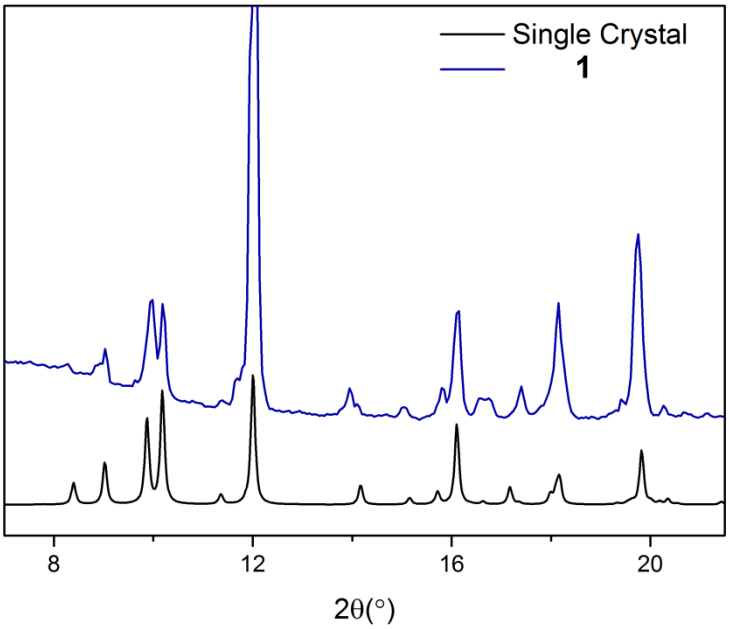

Figure SI.3 | Comparison of the experimental XRPD pattern (blue) of the microcrystals of **1** obtained by simple mixture of $Cu(NO_3)_2 \cdot 6H_2O$ and 4,4'-bpy with the XRPD pattern simulated from its single-crystal structure (black).

Submitted to ADVANCED MATERIALS

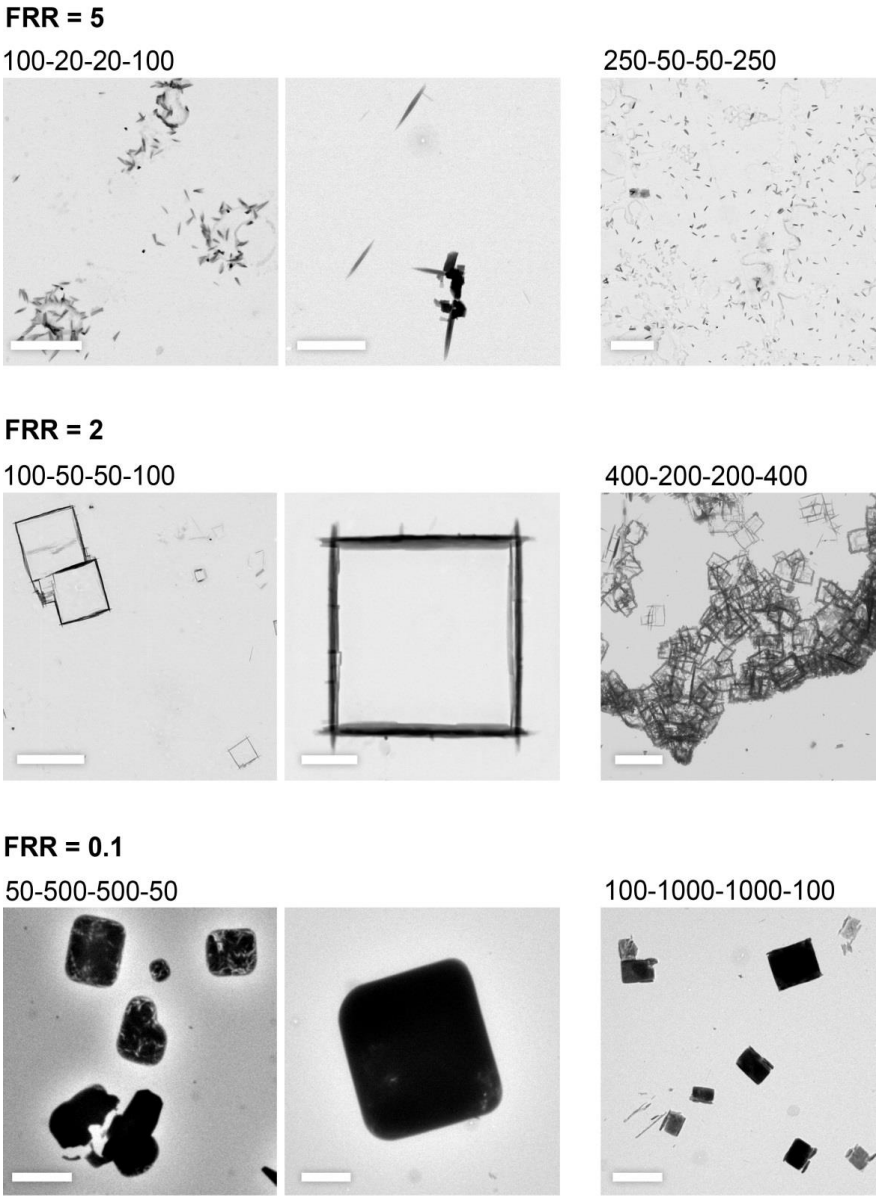

Figure SI.4 | TEM images of crystals of **1** fabricated in the microfluidic device at FRR = 5, 2 and 0.1, respectively, from top to down. Note that different TFR combinations have been used to work under the same FRR. Also note that identical crystalline phases -from needles to hollow frames to plate-like crystals (top to down)- have been synthesized for the same FRR values, independently of the flow rates used. The scale bars are 2 μm (top row), 5 μm (left and right middle row), 2 μm (centred middle row), 10 μm (left and right bottom row) and 4 μm (centred bottom row).

Submitted to ADVANCED MATERIALS

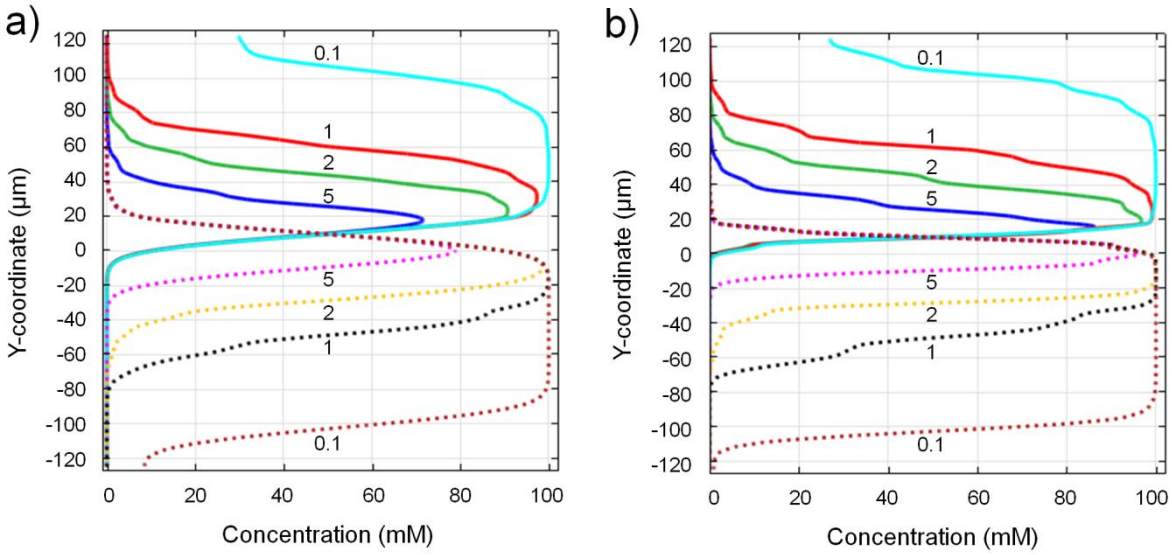

Figure SI.5 | Concentration profiles of reagents at the microfluidic reactor exit, for increasing values of flow rate ratio (FRR = 0.1, 1, 2 and 5) and two values of total flow rate *i.e.* TFR=220 µL/min (**a**) and 1,200 µL/min) (**b**). Solid and dashed lines correspond to concentration profiles of $Cu(NO_3)_2 \cdot 6H_2O$ and 4,4'-bpy, respectively.

Submitted to ADVANCED MATERIALS

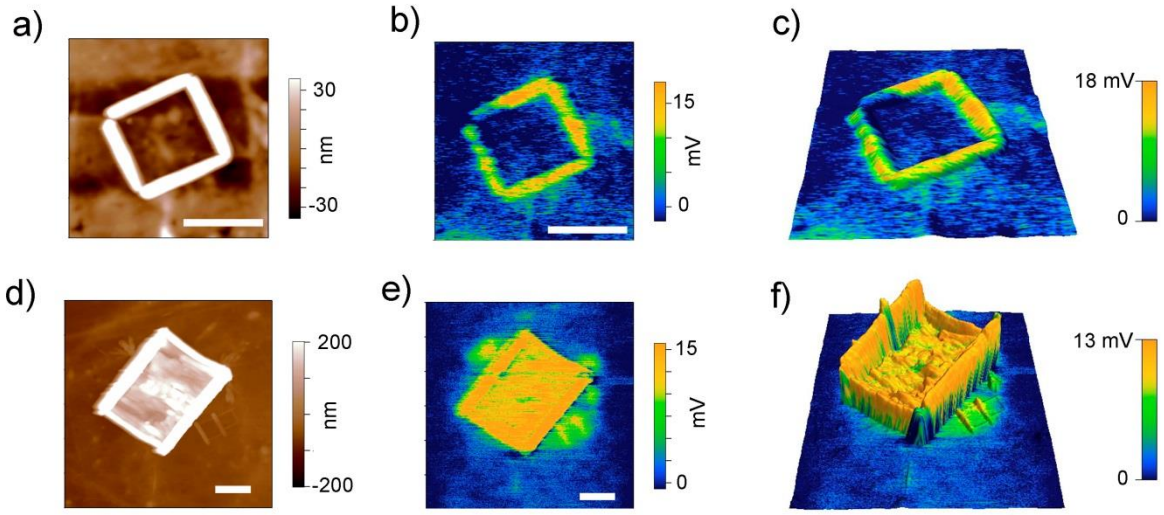

Figure SI.6 | AFM topography images of a hollow frame (**a**) and a partially filled frame (**d**). Kelvin Probe Microscopy images (KPFM); **b**,**e**, 2D and **c**,**f**, 3D AFM topography images with KPFM signal as the colour scale. The surface potential function difference measured by KPFM confirms the absence of CP material inside of the frame.

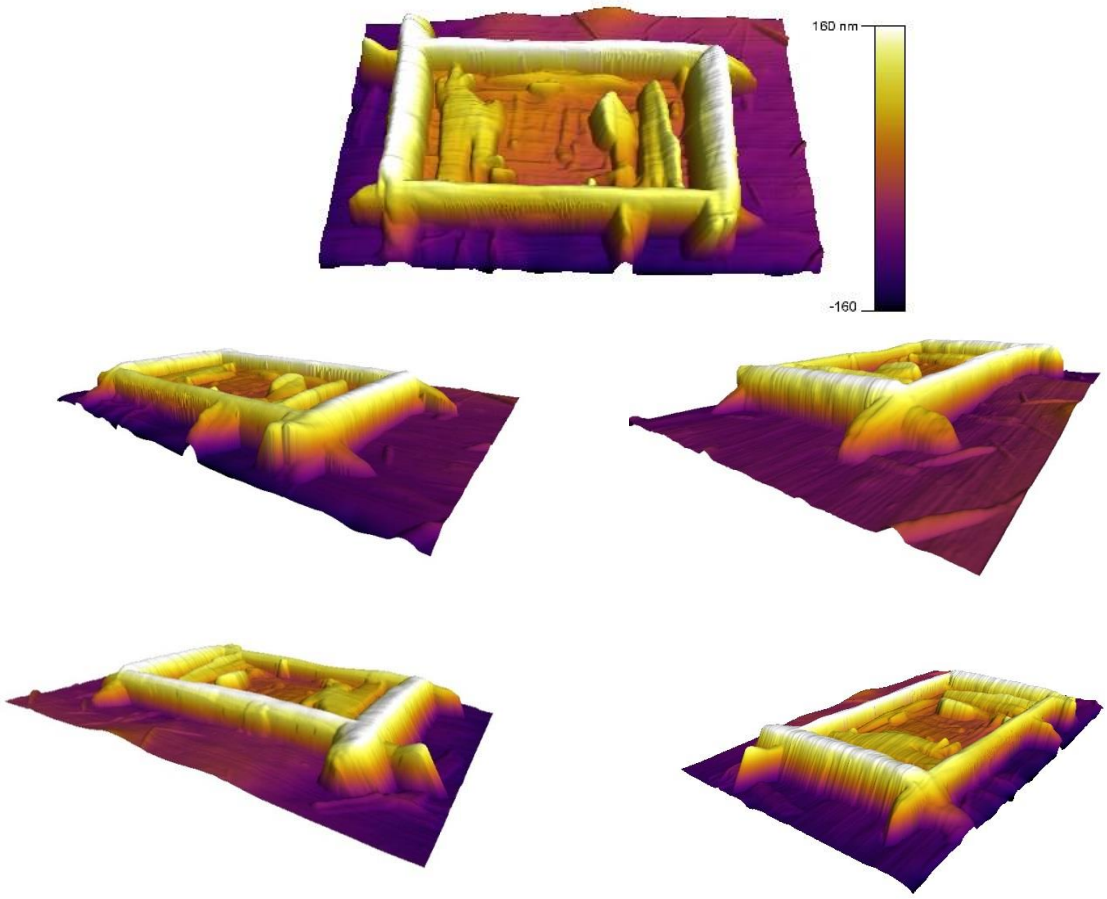

Figure SI.7 | 3D AFM topography images of a single frame, showing different perspectives for the vertices. Note that the vertices are interpenetrated.

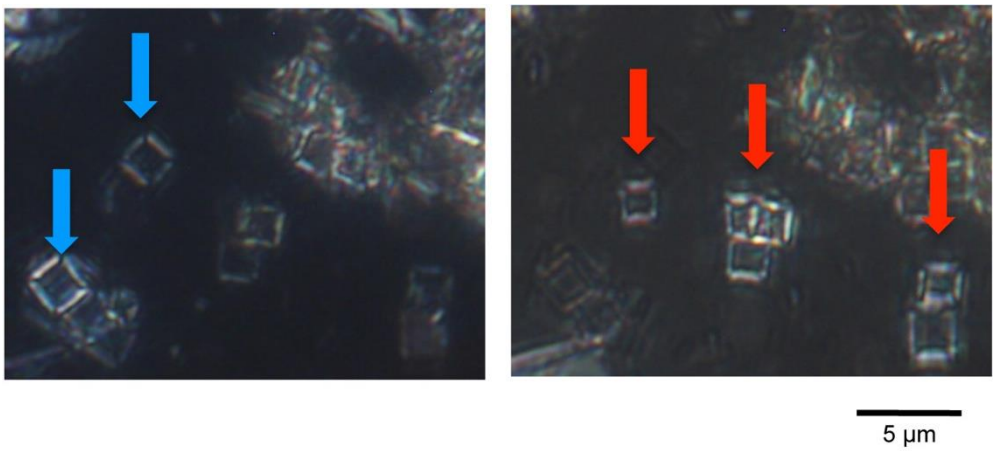

Figure SI.8 | POM images showing the optical axes of two frames that indicate that the four sides have perfect orientational order.

References

[1] Z. Otwinowski, W. Minor, in *Method Enzym.*, Elsevier, **1997**, pp. 307–326.
[2] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112.
[3] K. C. Pratt, W. A. Wakeham, *Proc. R. Soc. Lond. Math. Phys. Eng. Sci.* **1974**, *336*, 393.