Porous microstructure in gel grown crystals.

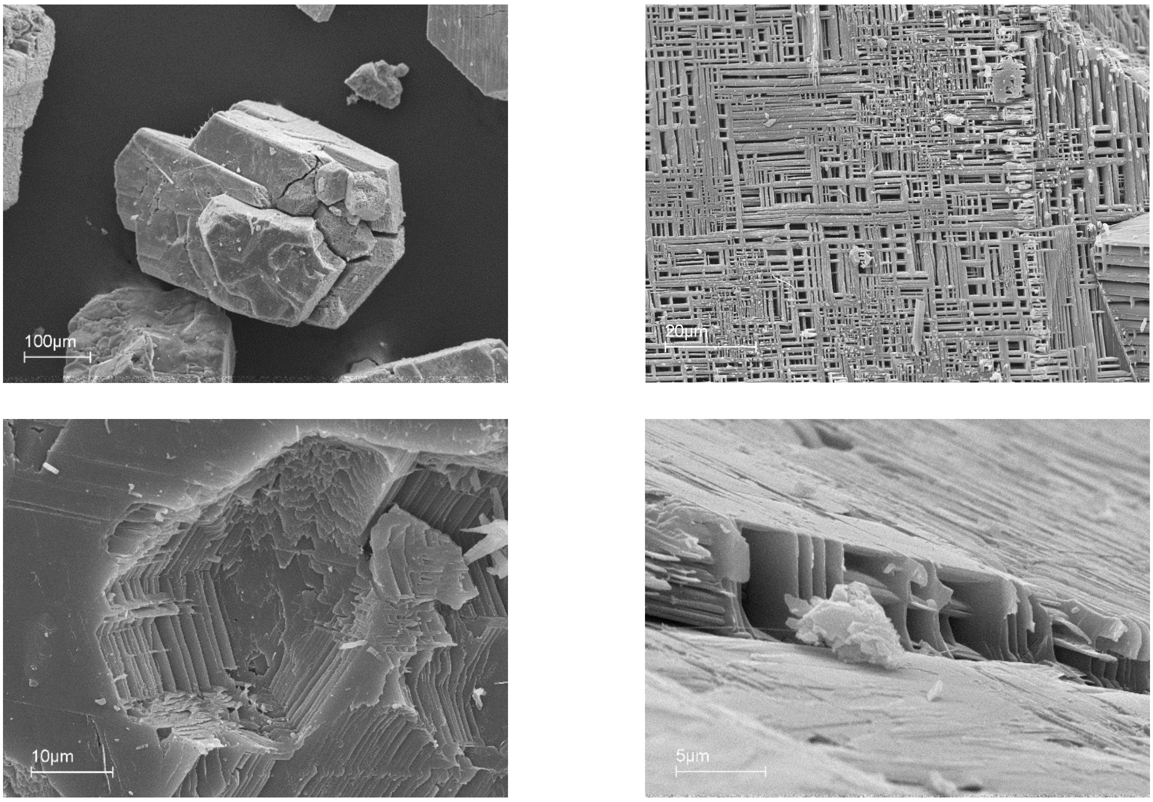


Figure S1. Scanning electron microscope views, at different magnifications, of a silica-gel grown crystal of the porous coordination polymer (**1**). The images show clearly the singular microstructure of the crystalline solid composed of stacking layers of void channels. Note the traces of the gel present outside, on the crystal surface.

High-pressure data

a = b	c	V	p	V_{norm}	Δ%
28.407(1)	18.801(3)	15172(6)	0,04	1,000	0,00
28.431(3)	18.687(8)	15105(12)	0,20	0,996	0,44
28.339(2)	18.593(7)	14932(8)	0,35	0,984	1,58
28.267(3)	18.695(9)	14938(10)	0,45	0,985	1,54
28.129(3)	18.809(8)	14883(7)	0,65	0,981	1,90
28.129(6)	18.686(18)	14785(13)	0,70	0,974	2,55
28.441(4)	17.59(3)	14232(8)	0,76	0,938	6,20
28.508(12)	16.57(9)	13468(13)	1,76	0,888	11,23
27.81(2)	16.45(5)	12730(30)	3,27	0,839	16,10

Table S1. Structural data (unit cell axis and volume) at different pressures (p) for the coordination network $[Cu(bpy)_2(SO_3CF_3)_2]$·*solv.* (**1**), which crystallized in the tetragonal space group I 4_1/acd. The parameters refinement was performing imposing a tetragonal symmetry constrain to unit cell. The values of normalized unit cell volume (V_{norm}= V/V_0, where V_0 is the initial volume of the unit cell at ambient pressure) and the corresponding percentage change in volume (Δ%) of the sample are also reported to highlight the effect of pressure on the system.

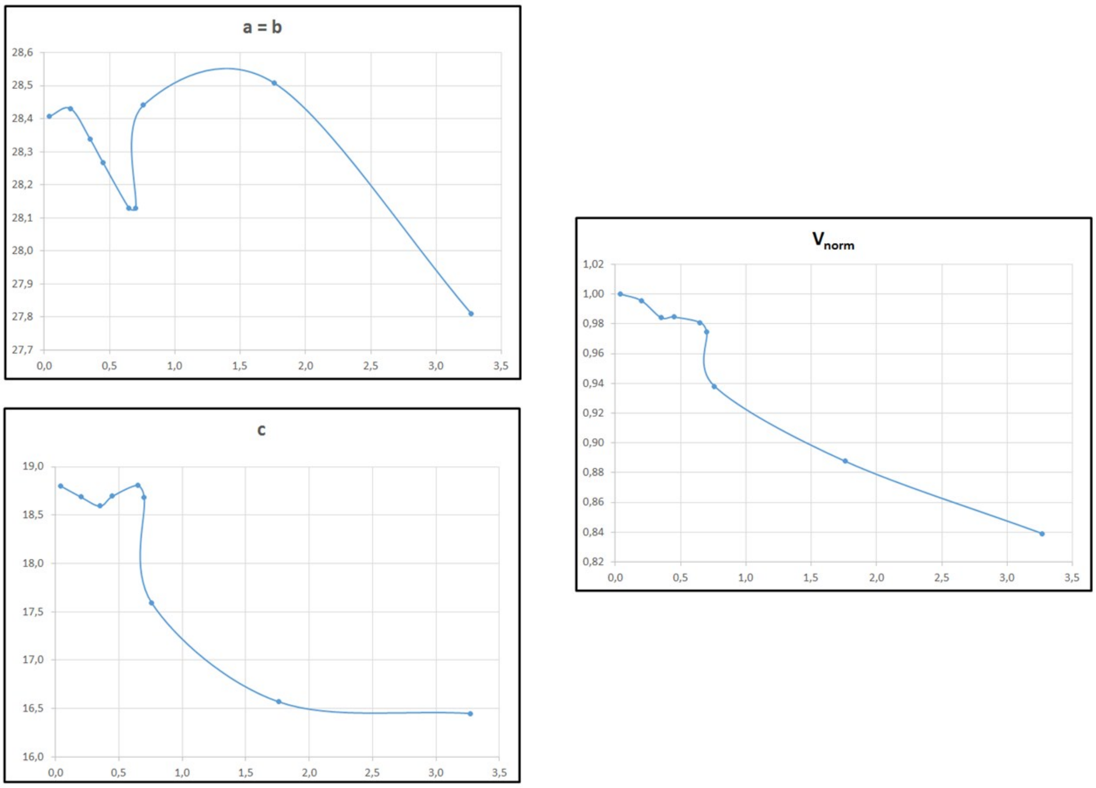


Figure S2. Plots showing the evolution of unit cell parameters (left) and normalized unit cell volume (right) of coordination polymer (**1**) with pressure. After an initial oscillation, a constant decrease of all parameters with the pressure was observed.

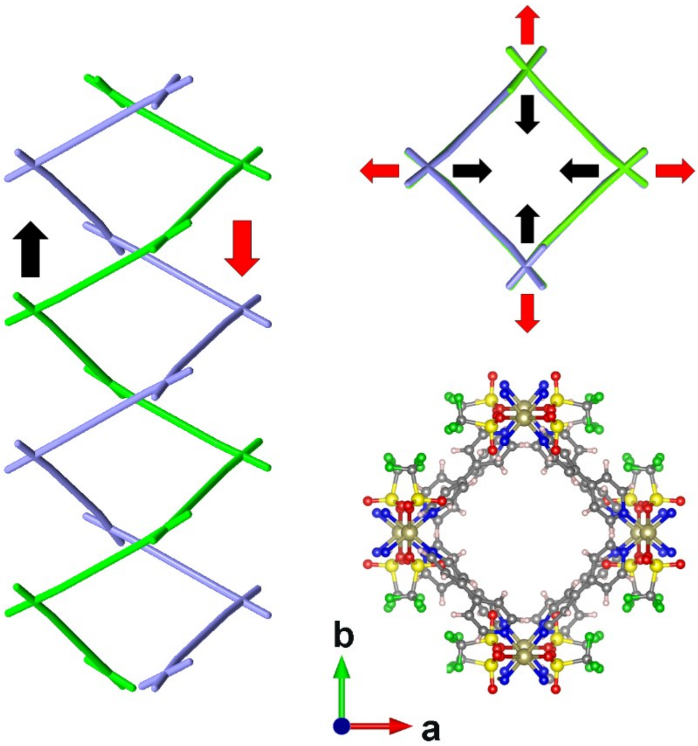
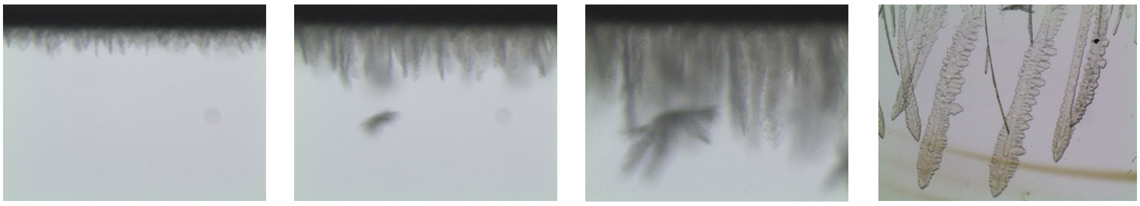


Figura S3. A simplified view of a channel with a rhombic mouth bordered by two intertwined single-stranded helices. The system of parallel opening channels extends along the c axes and is responsible for the nanoporous behaviour of the network polymer.

The overall flexibility of the network, that can be contracted or extended in a way that resemble a pantograph, supports the shrinking and expansion of the system during the emptying or filling process. The directions of movements are indicated by red and black arrows for the two process respectively. The orientation of the network with respect to the unit cell allows to describe the spongelike deformation of the system on the base of the crystallographic cell parameters.

Kinetic growth study



a – 2 min. b – 6 min. c – 16 min. d

Figure S4. Images of the glass optical cell used for monitoring the growth of crystals at the beginning (a, b, c) and at the end of the acquisition process (d).

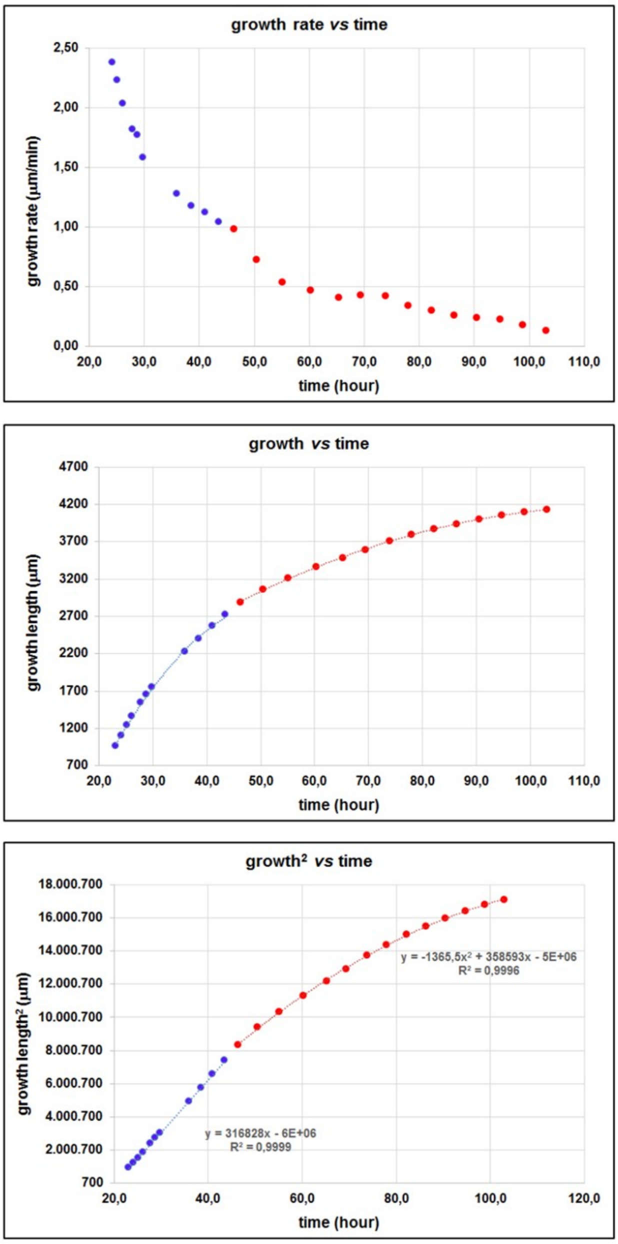


Figure S5. The late-stage growth kinetics. The variation of the growth rates with time and the increment of the crystals length and of its square as a function of time. Only some data have been reported for clarity. Dotted lines show the fitting of the data to a relation reported alongside the curve.