Supplementary information

Exploring a novel preparation method of 1D metal organic frameworks based on supercritical CO_2

A. Structure determination of [Cu(hfacac)$_2$bpy] from powder diffraction data

Diffraction data for [Cu(hfacac)$_2$bpy] were measured on the high resolution powder diffraction endstation of the MSPD beamline (BL04) of ALBA synchrotron using the microstrip MYTHEN-II detector (6 modules, 1280 channels/module, 50 μm/channel, sample-to-detector distance 550 mm). The specimen was introduced into a Ø0.7 mm capillary and measured at room temperature with a wavelength of 0.61978Å.

The powder pattern was indexed using DICVOL04 (Boultif & Louer, 2004) introducing 40 peaks [M(40)=47.3; F(40)=237.7 (0.0010, 170)]. Further refinement of the unit cell parameters, the identification of the space group from the reflection conditions and the extraction of intensities was performed with DAJUST software (Vallcorba et al., 2012a). Extracted intensities were used by the direct-space program TALP (Vallcorba et al., 2012b) to solve the crystal structure taking the geometry from a previously reported structure (Yu et al., 1991) as starting model for the geometrical restraints. The obtained solution was refined with the restrained Rietveld refinement program RIBOLS with the H atoms placed in calculated positions and constrained to the respective carbon atoms. Four atomic displacement factors have been refined (Cu atom, bpy, F atoms, acac) and also, a slight preferred orientation of the crystals was modeled with the March–Dollase correction (Dollase, 1986) by applying a coefficient of 0.88 to the [110] direction. Crystallographic data and refinement details are summarized in Table 1, and the Rietveld plot with observed, calculated and difference profile is shown in Figure 1.

In the crystal structure, the F atoms in the CF_3 groups may exhibit disorder (rotation of the group) as the atomic displacement factor for these atoms is higher than the rest (0.11 A^2). Most of the intermolecular contacts are equal or longer than the sum of the van der Waals radius, as can be seen in the Hirschfeld surface (Spackman & Jayatilaka, 2009) (Figure S1). The volume

enclosed by this surface is 583.61Å^3, which for Z=4 results in 2334.4A^3 for the whole unit cell content, slightly smaller than the cell volume (2369.1A^3).

Table I. Crystallographic data, structure solution and refinement details for Cu(hfacac)$_2$bpy

	[Cu(hfacac)$_2$bpy]
Molecular formula	$C_{20}H_{10}CuF_{12}N_2O_4$
Formula weight	633.85
Crystal System	Tetragonal
Space group	P 4_1 2_1 2
a (Å)	7.8882(2)
b (Å)	7.8882(2)
c (Å)	38.0767(7)
Volume (Å^3)	2369.27(13)
Z	4
Powder diffraction data used	
No. of reflections	1083
2θ range (º)	3.000 to 39.996
Data points	6167
Structure refinement details	
Profile function	Pseudo-Voigt
Parameters	67
Restraints	64
R_{wp}	0.056
Goodness of fit (χ)	5.309

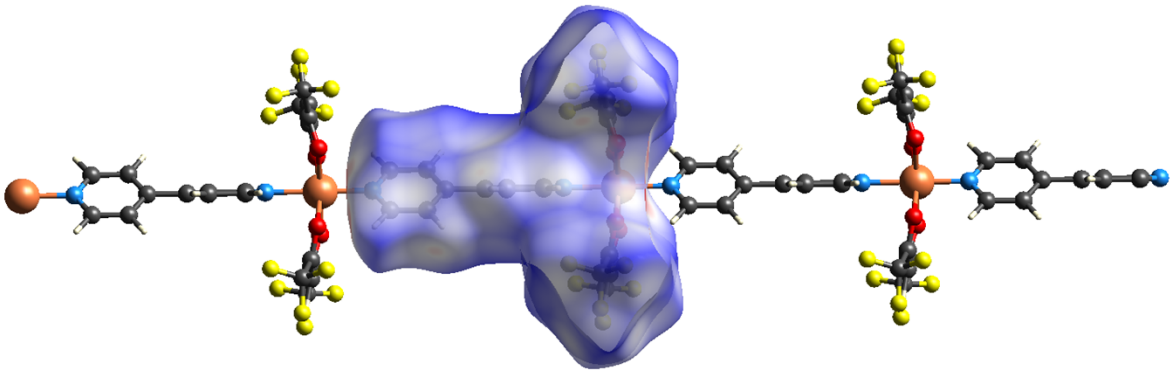

Fig. S1. Hirshfeld surface with d_{norm} as mapped property.

B. Additional fits figures.

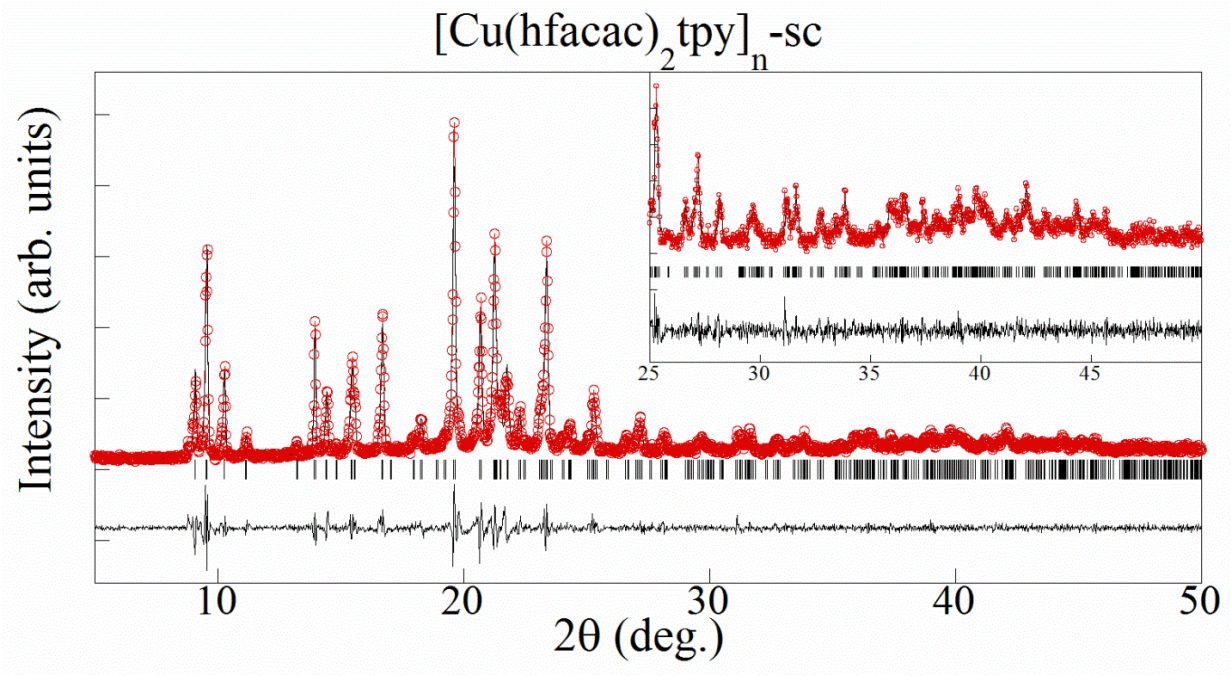

Fig. S2. Final Le Bail whole pattern matching plot for the $[Cu(hfacac)_2tpy]_n$-sc sample. The inset is a zoom of the main diagram.

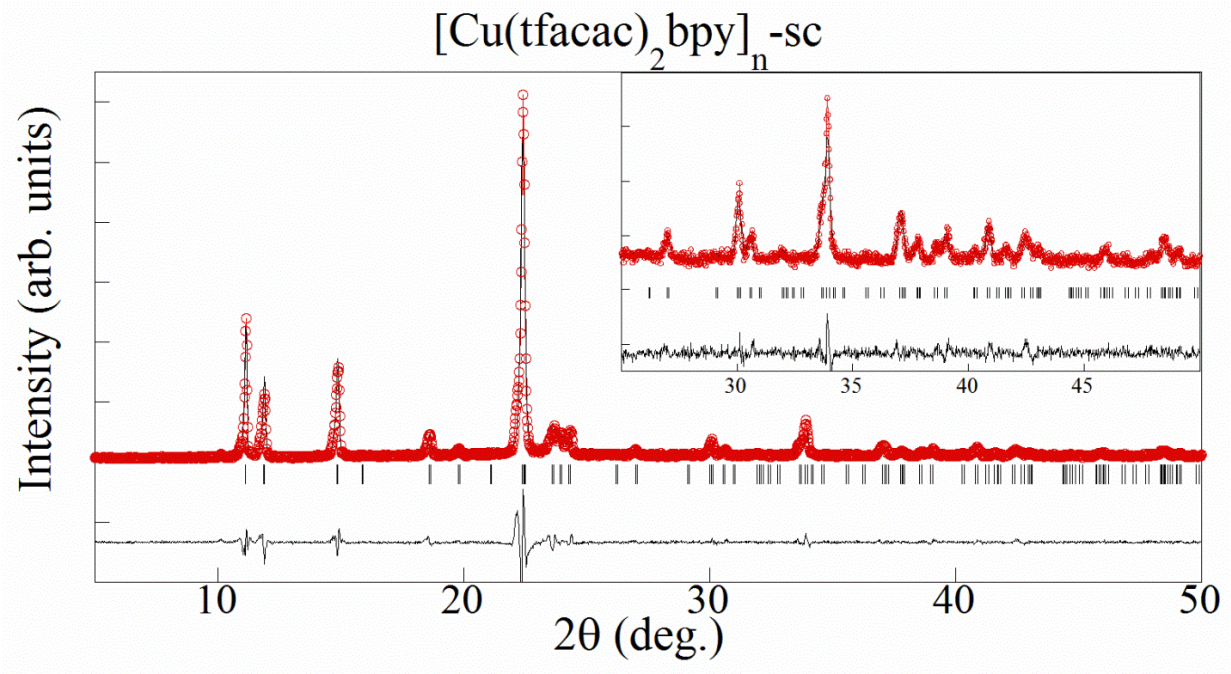

Fig. S3. Final Le Bail whole pattern matching plot for the $[Cu(tfacac)_2bpy]_n$-sc sample. The inset is a zoom of the main diagram.

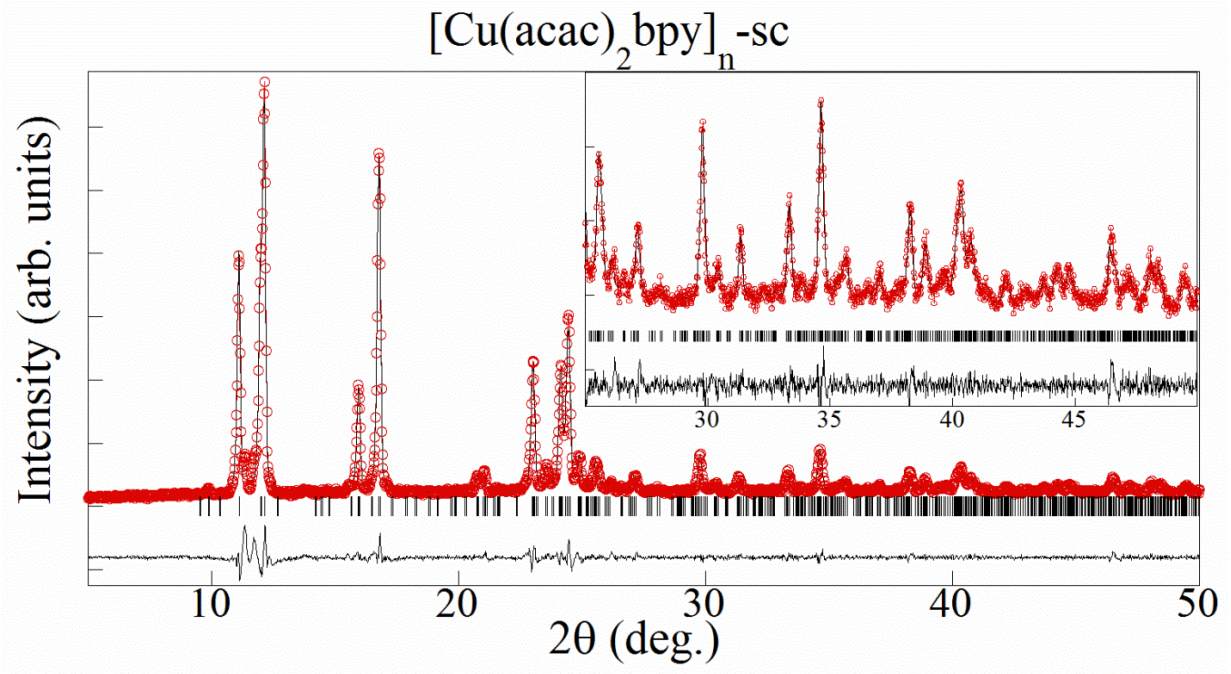

Fig. S4. Final Le Bail whole pattern matching plot for the $[Cu(acac)_2bpy]_n$-sc sample. The inset is a zoom of the main diagram.

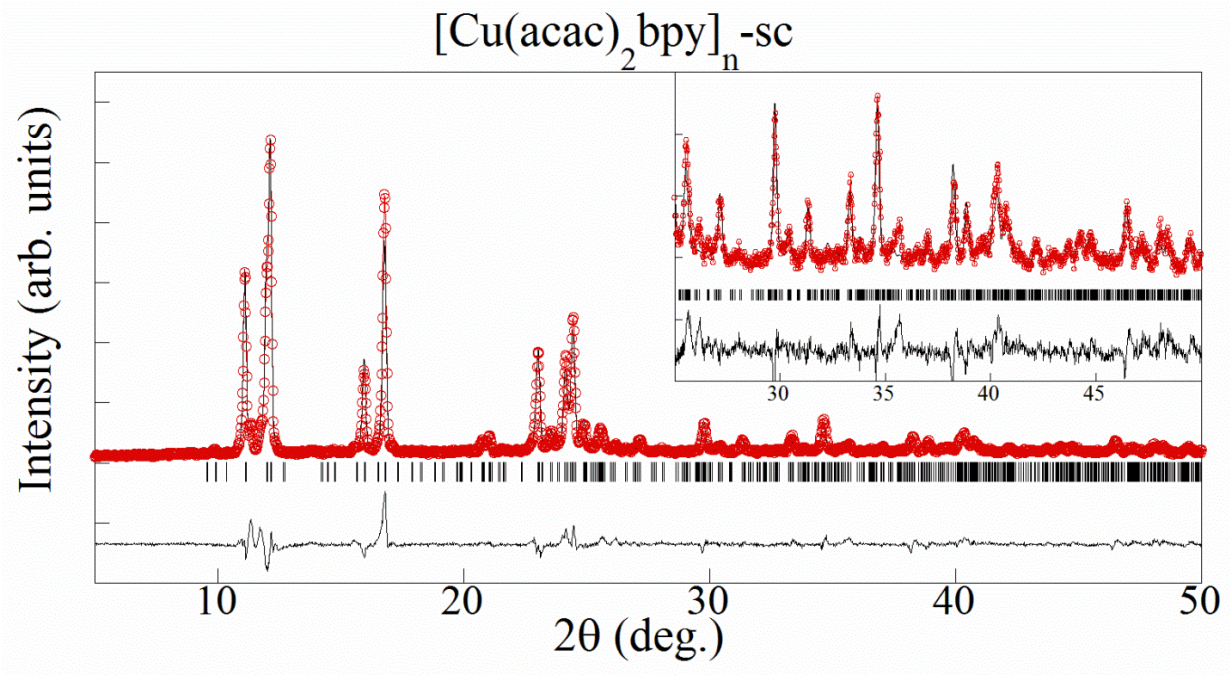

Fig. S5. Final Rietveld refinement plot for the $[Cu(acac)_2bpy]_n$-sc sample. The inset is a zoom of the main diagram.

References:

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