

Supporting Information for

**Multifunctional coordination polymers based on Copper(I) and mercaptonicotinic ligands: synthesis, structural, optical and electrical characterization**

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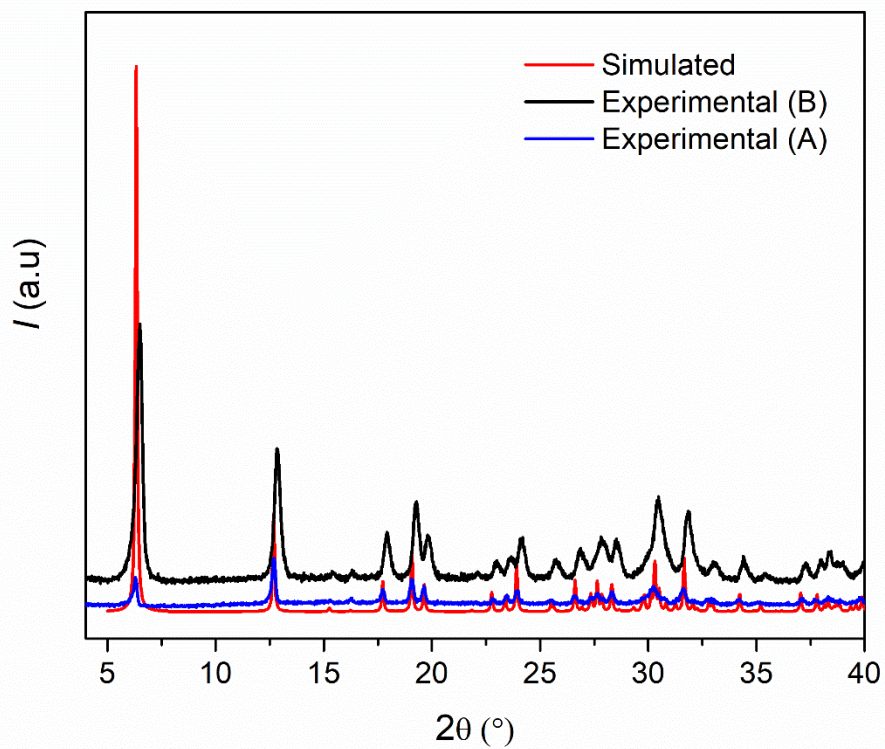


Figure S1. Experimental (obtained by methods A and B) and calculated powder diffractograms of **CP1**.

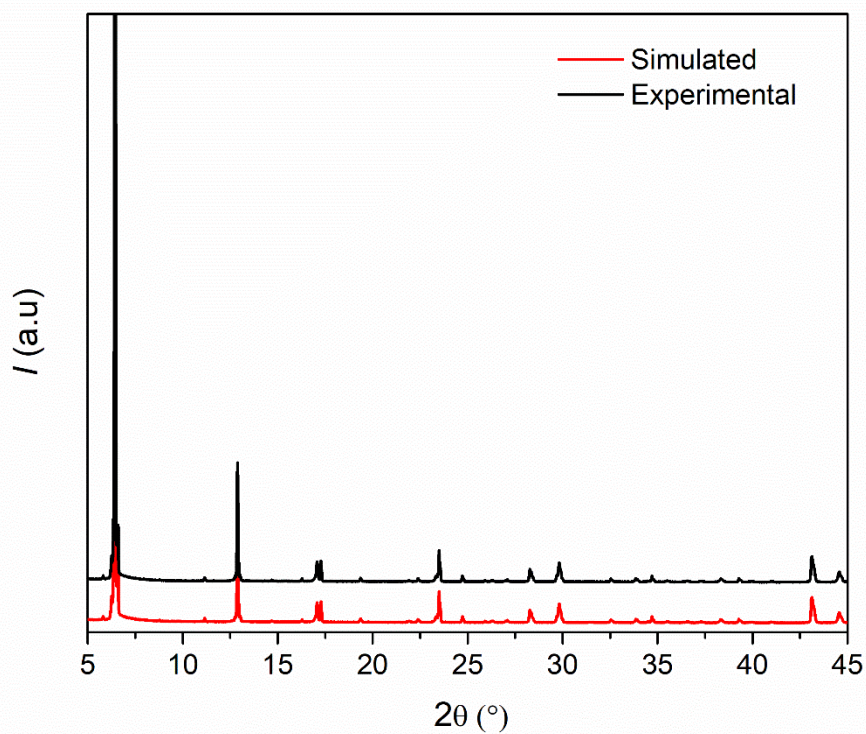


Figure S2. Experimental and calculated powder diffractograms of **CP2**.

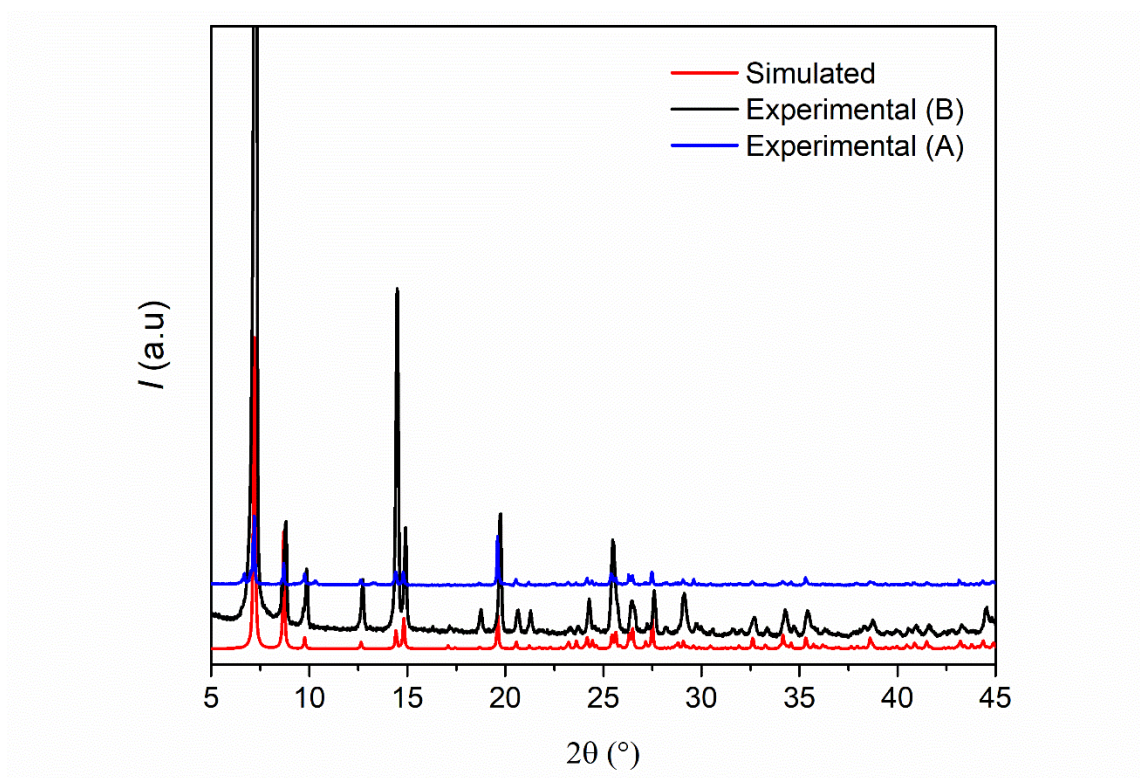


Figure S3. Experimental (obtained by methods A and B) and calculated powder diffractograms of CP3.

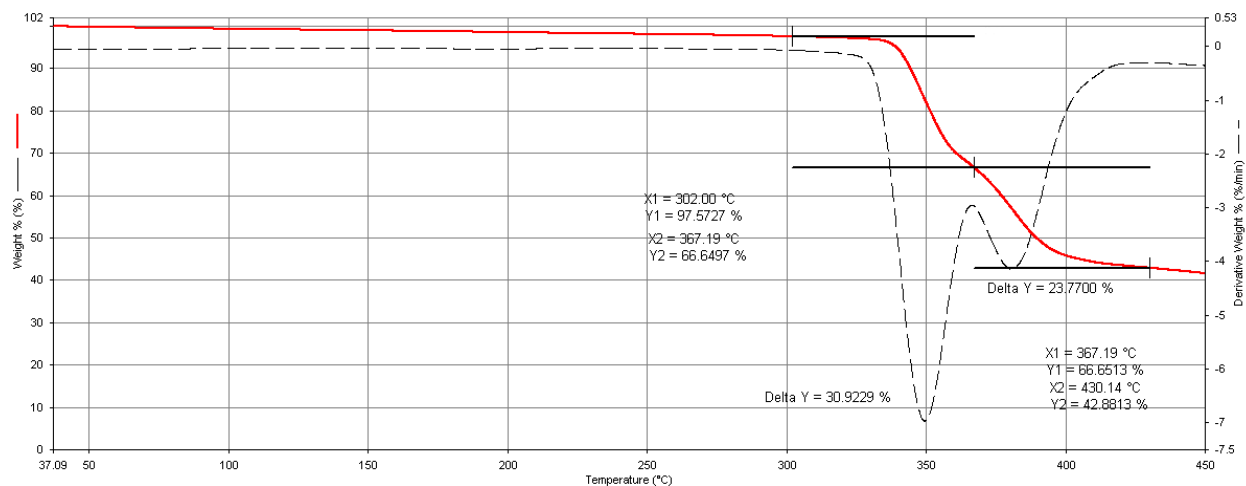


Figure S4. TGA of CP1.

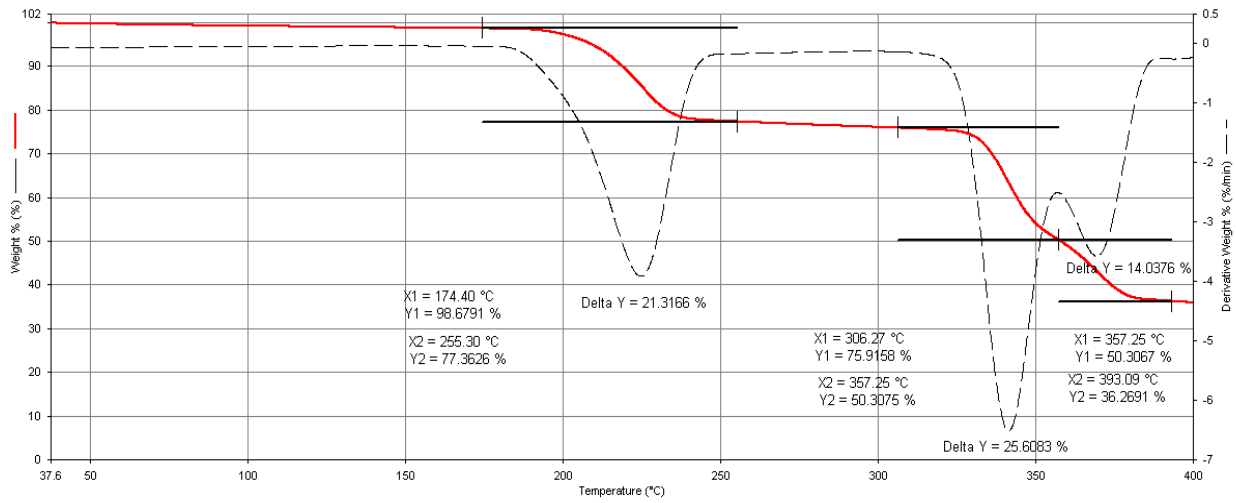


Figure S5. TGA of CP2.

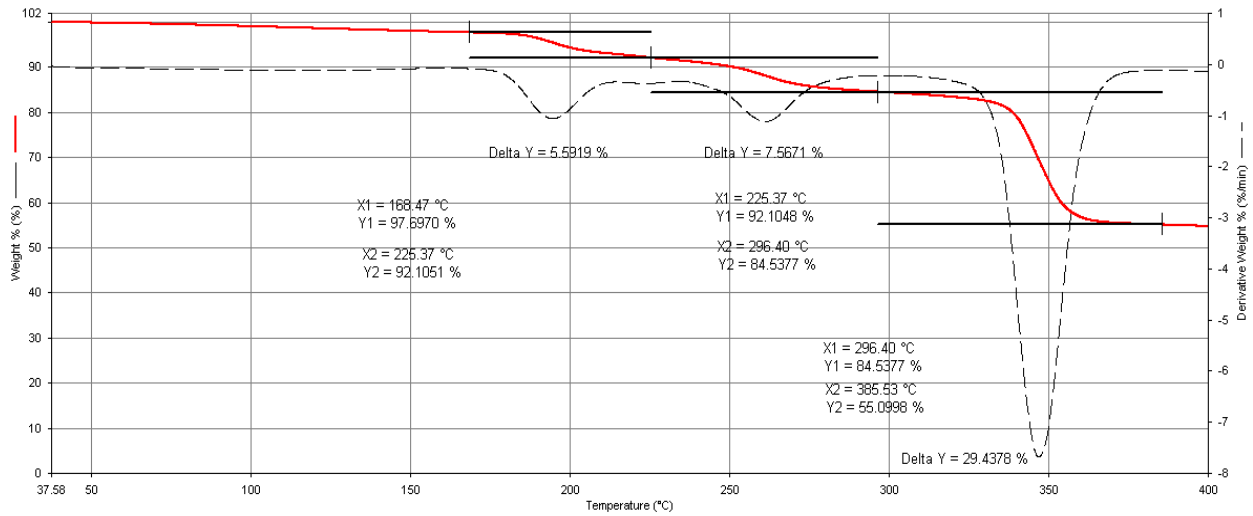


Figure S6. TGA of CP3.

Table S1. Crystallographic data of **CP1** and **CP3**.

	<b>CP1</b>	<b>CP3</b>
Empirical formula	C6 H4 Cu N O2 S	C14 H11 Cu2 I2 N3 O4 S2
Formula weight	217.71	730.28
Temperature	296(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	P 2 <sub>1</sub> /c	P 2 <sub>1</sub> /c
Unit cell dimensions	a = 3.90740(10) Å b = 5.9276(2) Å c = 27.9248(10) Å α = 90° β = 92.441(2)° γ = 90°	a = 18.4346(7) Å b = 4.2211(2) Å c = 28.6476(14) Å α = 90° β = 101.236(4)° γ = 90°
Volume	646.19(4) Å <sup>3</sup>	2186.47(17) Å <sup>3</sup>
Z	4	4
Density (calculated)	2.228 Mg/m <sup>3</sup>	2.218 Mg/m <sup>3</sup>
Absorption coefficient	3.633 mm <sup>-1</sup>	4.984 mm <sup>-1</sup>
Theta range for data collection	1.46 to 25.35°	3.3078 to 25.993°
Reflections collected	10890	9060
Independent reflections	1180 [R(int) = 0.0464]	4287 [R(int) = 0.0415]
Completeness to theta = 25°	99.9 %	99.9 %
Data / restraints / parameters	1180 / 0 / 100	4287 / 0 / 244
Goodness-of-fit on F <sup>2</sup>	1.043	1.118
Final R indices [I > 2σ(I)]	R1 = 0.0304, wR2 = 0.1172	R1 = 0.0561, wR2 = 0.952
R indices (all data)	R1 = 0.0867, wR2 = 0.1773	R1 = 0.0808, wR2 = 0.1025

Table S2. Crystallographic data of **CP2** collected at 293 and 100K.

	CP2 (room temperature)	CP2 (100 K)
Empirical formula	C6 H5 Cl Cu N O2 S	C6 H5 Cl Cu N O2 S
Formula weight	254.16	254.16
Temperature	293(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Hexagonal	Hexagonal
Space group	P 6 <sub>3</sub>	P 6 <sub>3</sub>
Unit cell dimensions	a = 15.8853(9) Å b = 15.8853(9) Å c = 6.6096(4) Å α = 90° β = 90° γ = 120°	a = 15.8563(5) Å b = 15.8563(5) Å c = 6.5650(2) Å α = 90° β = 90° γ = 120°
Volume	1444.43(10) Å <sup>3</sup>	1429.45(10) Å <sup>3</sup>
Z	6	6
Density (calculated)	1.753 Mg/m <sup>3</sup>	1.771 Mg/m <sup>3</sup>
Absorption coefficient	2.719 mm <sup>-1</sup>	2.748 mm <sup>-1</sup>
Theta range for data collection	3.4196 to 29.2541°	3.4397 to 29.4297°
Reflections collected	3517	3367
Independent reflections	1906 [R(int) = 0.0260]	1613 [R(int) = 0.0286]
Completeness to theta = 26.3154°	99.7 %	99.53 %
Data / restraints / parameters	1906 / 2 / 96	1613 / 2 / 99
Goodness-of-fit on F <sup>2</sup>	1.064	1.085
Final R indices [I > 2σ(I)]	R1 = 0.0532, wR2 = 0.1135	R1 = 0.0453, wR2 = 0.1215
R indices (all data)	R1 = 0.0767, wR2 = 0.1241	R1 = 0.0607, wR2 = 0.1276

Table S3. List of the bond lengths in the three coordination polymers.

	<b>CP1</b>
S1 – Cu1	2.197(1) Å / 2.295(1) Å
N1 – Cu1	2.00(4) Å

	<b>CP2_HT</b>
S01A – Cu01	2.480(7) Å / 2.326(7) Å / 2.254(8) Å
S01B – Cu01	2.498(8) Å / 2.285(5) Å / 2.233(8) Å

	<b>CP2_LT</b>
S01A – Cu01	2.258(8) Å / 2.316(6) Å / 2.439(8) Å
S01B – Cu01	2.217(6) Å / 2.301(8) Å / 2.464(9) Å

	<b>CP3</b>
I1 – Cu1	2.724 (1) Å / 2.690(1) Å / 2.601(1) Å
I2 – Cu2	2.721(1) Å / 2.709(1) Å / 2.631(1) Å
Cu1 – Cu1	3.218(2) Å
Cu2 – Cu2	2.822(1) Å / 3.420(1) Å

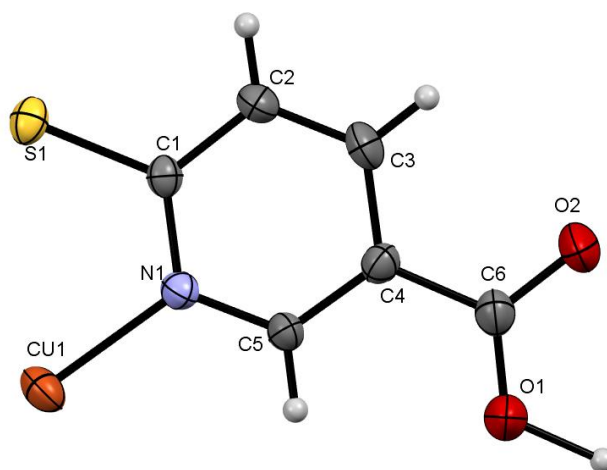


Figure S7. Detail of the **CP1** asymmetric unit, with the representation of the thermal ellipsoids.

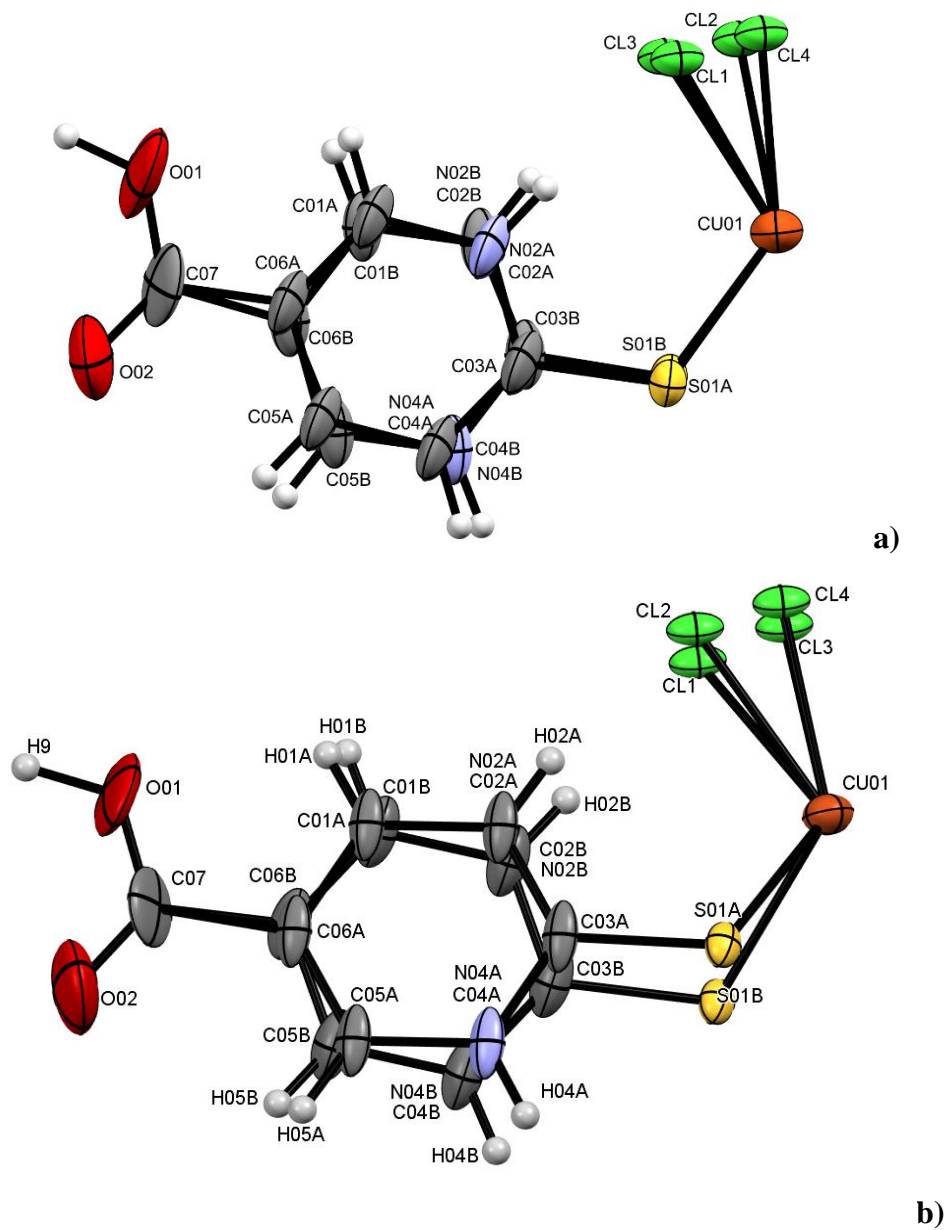


Figure S8 . Detail of the **CP2** asymmetric unit, with the representation of the thermal ellipsoids; a) structure collected at room temperature, b) structure collected at 100K.



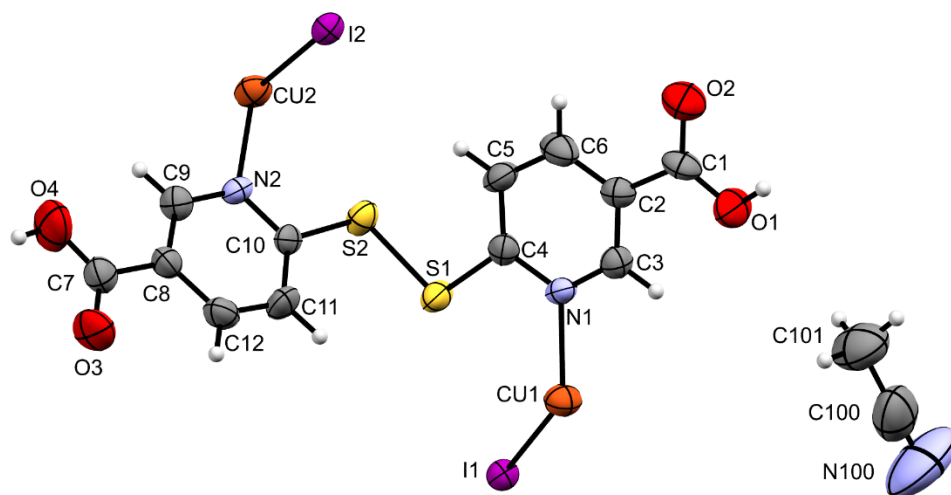


Figure S9. Detail of the **CP3** asymmetric unit, with the representation of the thermal ellipsoids.

## Structure refinement details for CP2

SHELXT[1] was used for structure solution and SHELXL[2] for the refinement based on  $F^2$ . The non-hydrogen atoms were refined anisotropically. Hydrogen atoms bound to carbon atoms were added in calculated positions.

**CP2** presents some internal disorder. Part of the ligand (the pyridinic ring and the sulphur) is disordered over two positions, their occupancy was refined to 50% at RT and 53% and 47% at LT. The pyridinic ring was constrained as hexagon and it was not possible to determine the N position, so it was modeled over the two sites (C02/N02 and C04/N04) with occupancy 50%.

The chlorine atom is split in four positions, the occupancy of the different positions is 33% / 31% / 20% / 16% for the structure at room temperature, and 34% / 31% / 18% / 17% for the structure at 100K. The disorder of the chlorine is probably connected to the splitting of the ligand in two positions. **The four Cl sites can be divided in two couple with an occupancy near to 50% each, a value compatible with the occupancy of the two ligand configurations. By the distances between the Cl and the nearest H atom (H02A/H02B), it seem that the sites Cl1 and Cl4 are relative to the configuration A of the ligand, while the sites Cl2 and Cl3 are relative to the configuration B.**

A channel with disordered solvent is run along the 3-fold axes. The solvent was impossible to model and the SQUEEZE[3] procedure has been applied to complete the refinement. The TGA analysis suggests the presence of 1/3 of water molecule in the asymmetric unit.

All the internal disorder is supposed to be static, in fact, the same disorder is present also in the structure solved at 100K with almost the same distribution.

The program Mercury[4] was used for all graphical representations and for the calculated powder pattern.

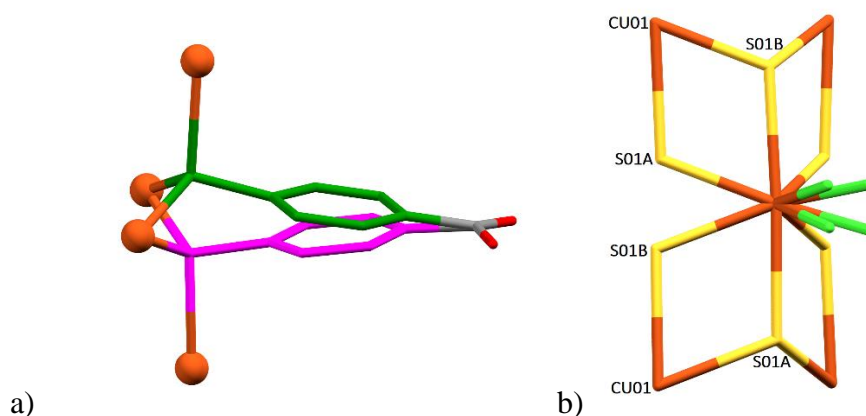


Figure S10. a) Detail of the disordered ligand with conformation A (pink) and conformation B (green) visible, H atoms are omitted for clarity; b) detail of the chlorine (light green) disorder in the four positions.

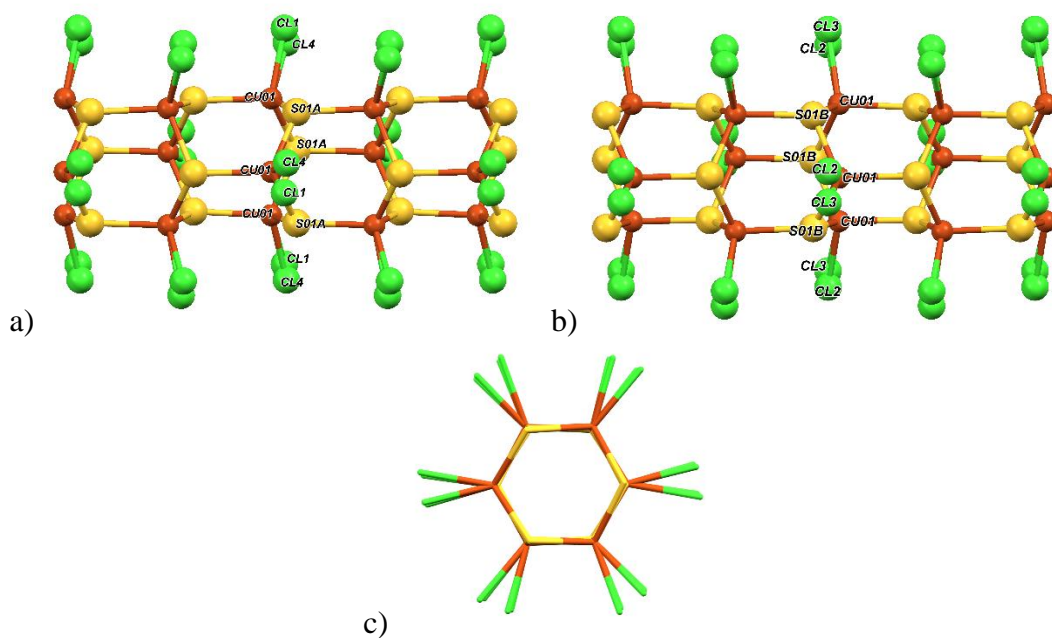


Figure S11. Appearance of the disordered chain (ligand omitted), a) configuration A seen along b-axis; b) configuration B seen along b-axis; c) view along c-axis.

### Variable Temperature X-ray diffraction

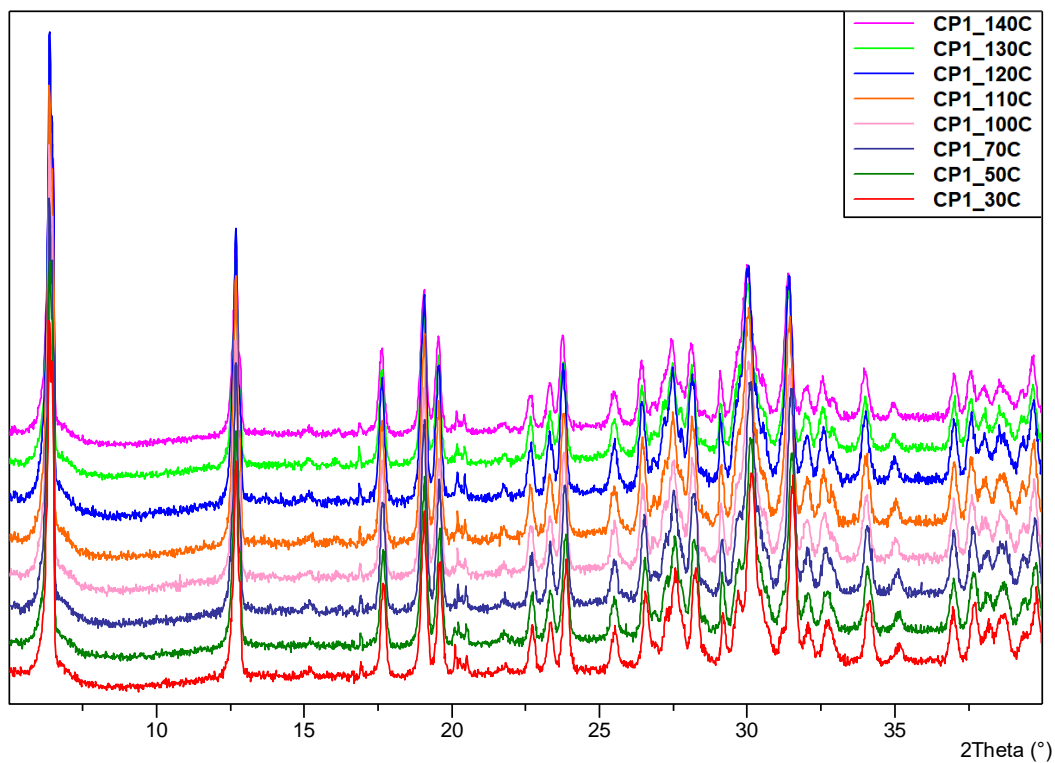


Figure S12. XRPD measurements at variable temperature for **CP1**.

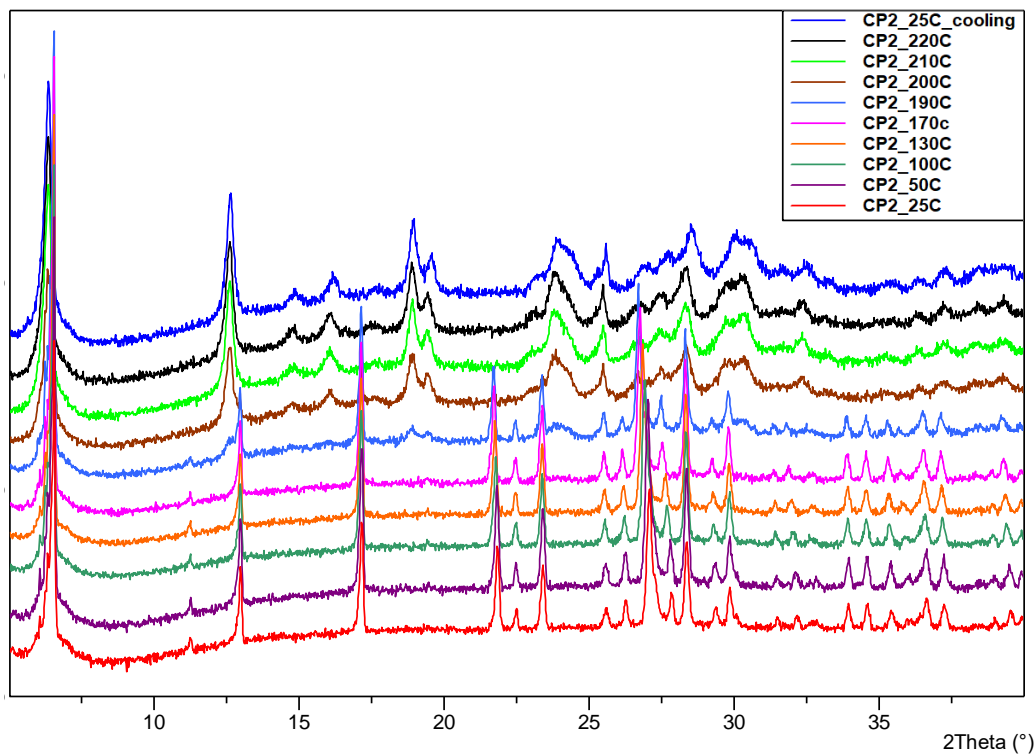


Figure S13. XRPD measurements at variable temperature for **CP2**.

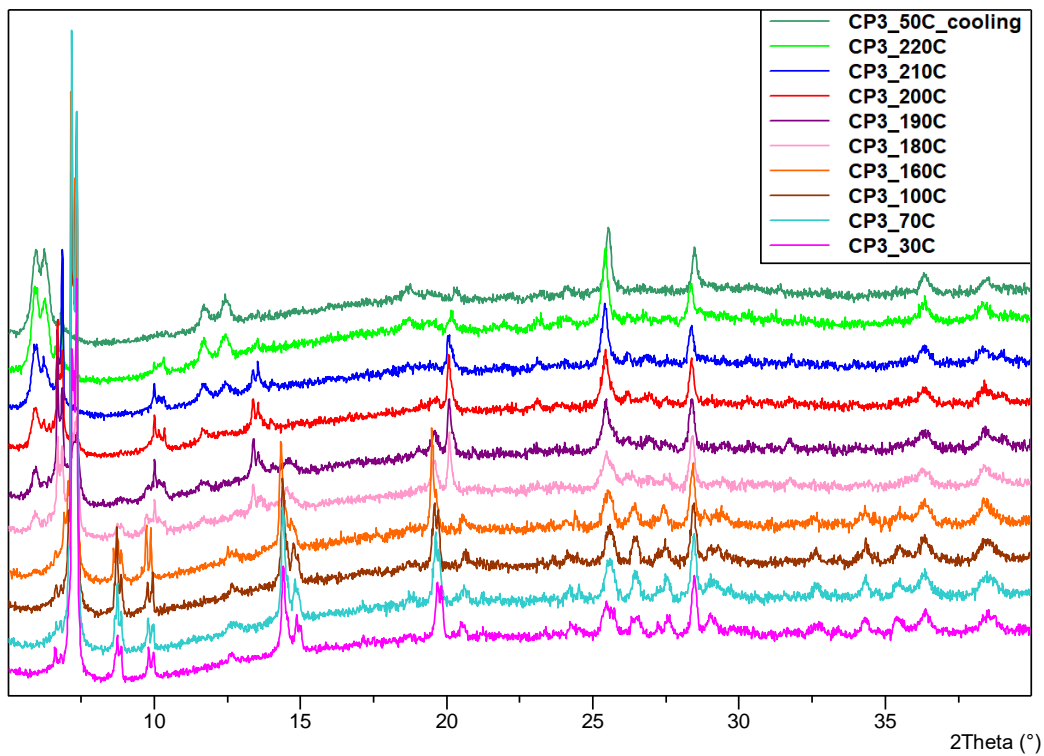


Figure S14. XRPD measurements at variable temperature for **CP3**.

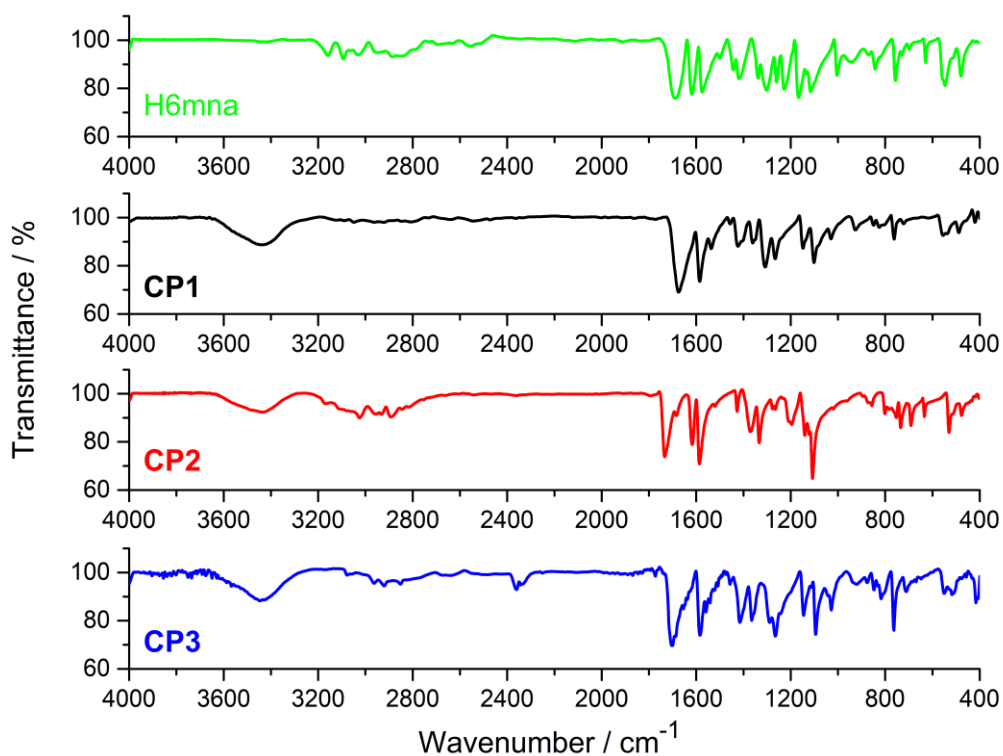


Figure S15. IR spectra of the H6mna ligand and the three CPs.

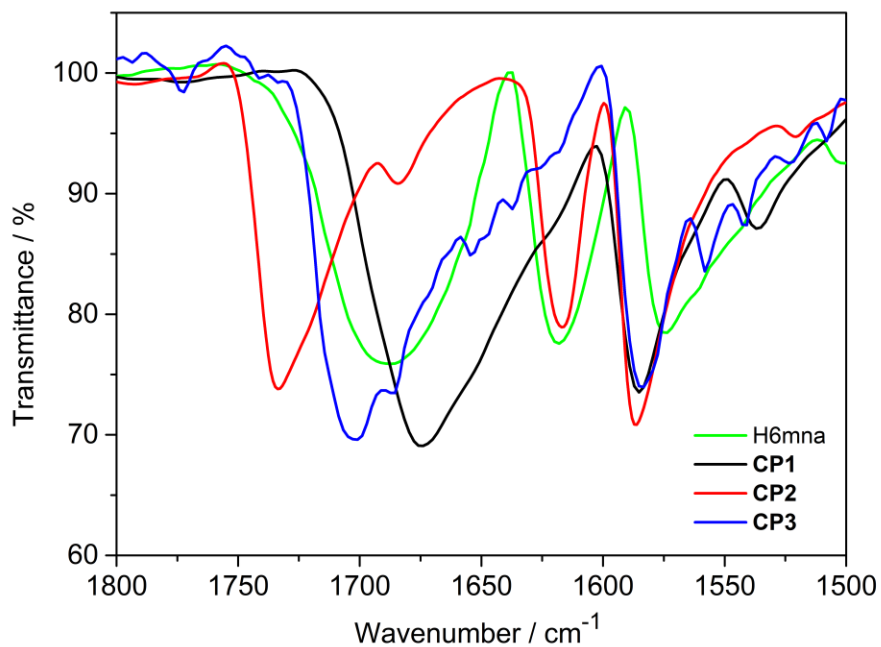


Figure S16. Comparison of the IR spectra of H6mna and the three CPs in the region 1800-1500 cm<sup>-1</sup>.

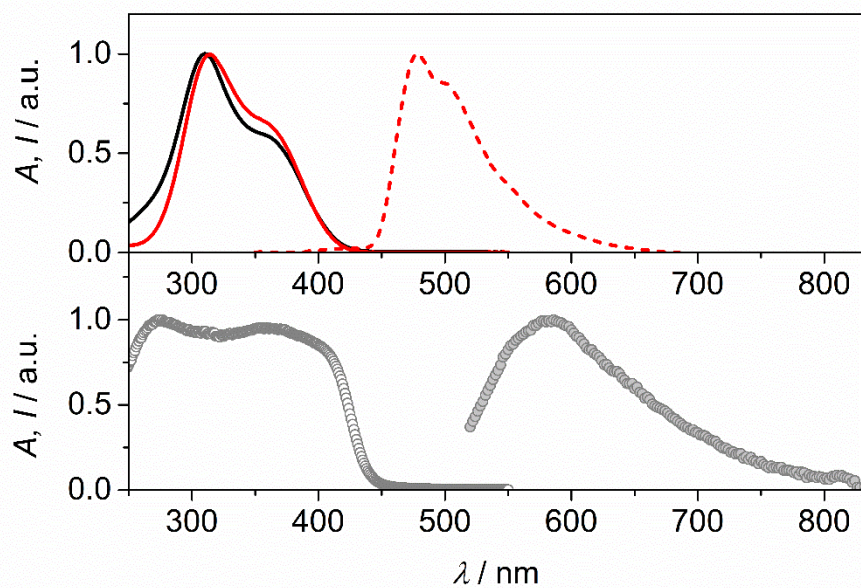


Figure S17. (top) Absorption (full line) and emission (dashed line) of H6mna in EtOH (black) and in DCM:MeOH 1:1 (red, the emission spectrum is recorded at 77K); (bottom) absorption (empty circles) and emission (full circles) spectra of 6mna in the solid-state at room temperature.

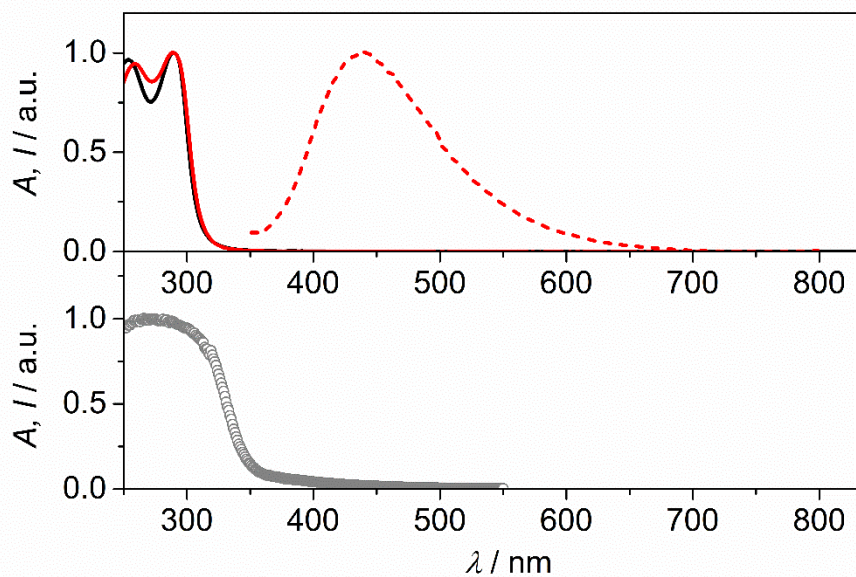


Figure S18. (top) Absorption (full line) and emission (dashed line) of H<sub>2</sub>tdn in EtOH (black) and in DCM:MeOH 1:1 (red, the emission spectrum is recorded at 77K); (bottom) absorption spectrum of H<sub>2</sub>tdn in the solid-state at room temperature.

Table S4. Absorption data for ligands 6mna and H<sub>2</sub>dtdn in EtOH at room temperature.

	$\lambda_{\text{max abs}} / \text{nm} (\epsilon / 10^4 \text{ M}^{-1} \text{ cm}^{-1})$
H6mna	310 (2.27), 360 sh (1.33)
H <sub>2</sub> dtdn	253 (3.33), 290 (3.45)

Table S5. Luminescence data for CPs **1-3** in the solid state at 77 K (in square brackets values at room temperature).

	$\lambda_{\text{max em}} / \text{nm}^{\text{a}}$	$\tau / \mu\text{s}^{\text{b}}$
<b>CP1</b>	692	4.1
<b>CP2</b>	622 [620]	3.6 [2.7]
<b>CP3</b>	624	2.6 (50%), 11.4 (50%)

<sup>a</sup> From corrected spectra. <sup>b</sup> Excitation at 373 or 465 nm.

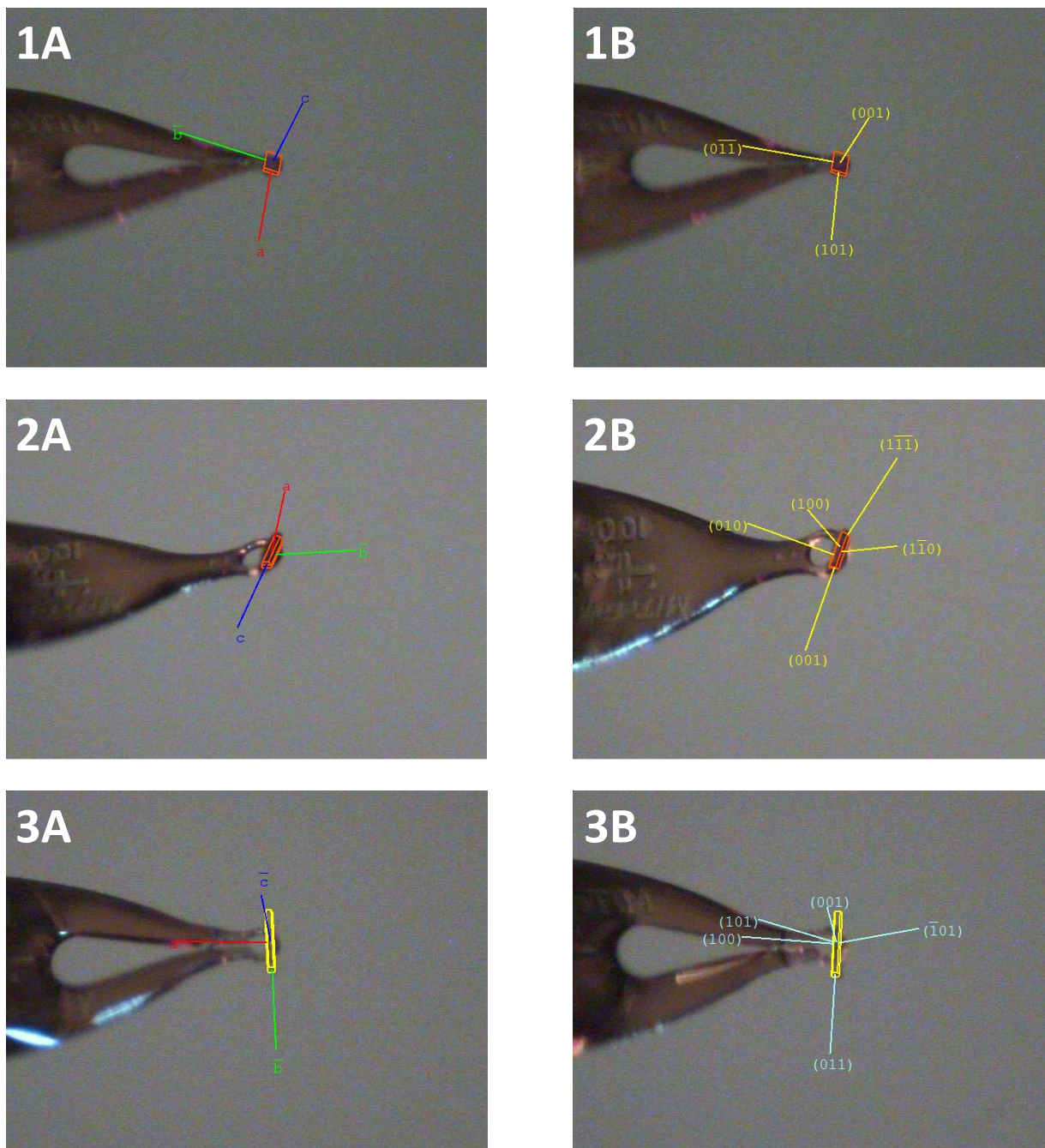


Figure S20. Crystallographic orientations data of single crystals. First column: abc parameters of **CP1** (1A), **CP2** (2A) and **CP3** (3A). Second column: hkl planes of **CP1** (2A), **CP2** (2B) and **CP3** (3B).



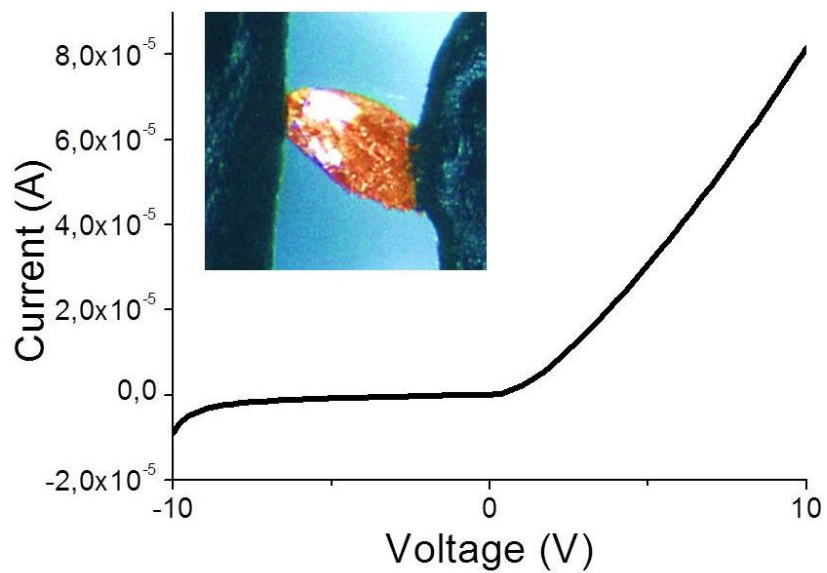


Figure S21. Graph intensity versus voltage of **CP1** measured at 300 K.

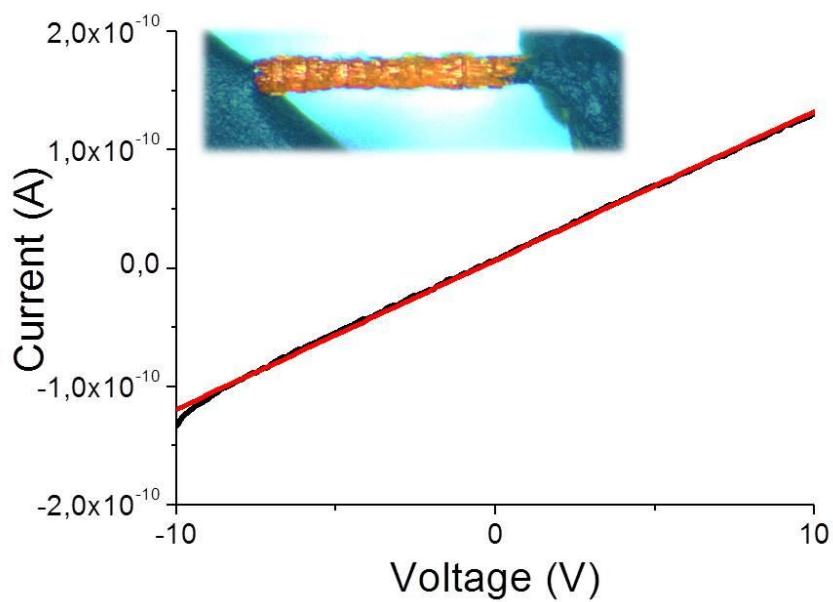


Figure S22. Graph intensity versus voltage of **CP2** measured at 300 K.

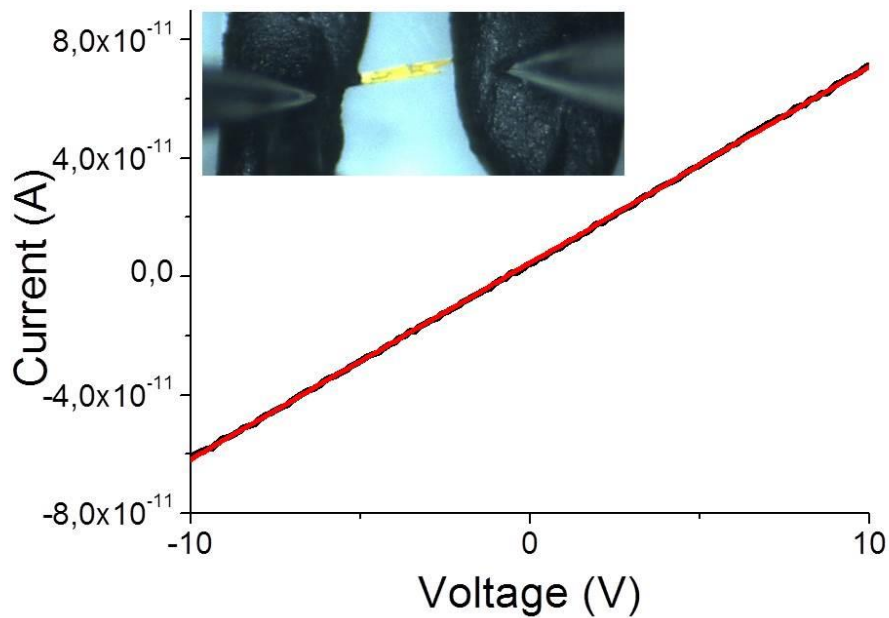


Figure S23. Graph intensity versus voltage of **CP3** measured at 300 K.

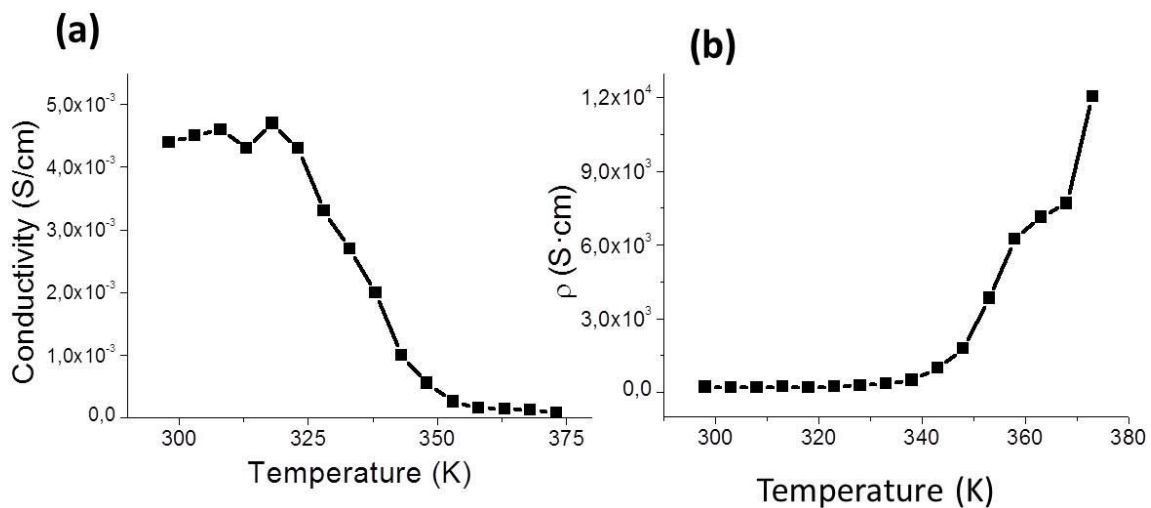


Figure S24. Variation of conductivity versus temperature (a) and resistivity versus temperature (b) of **CP1**.

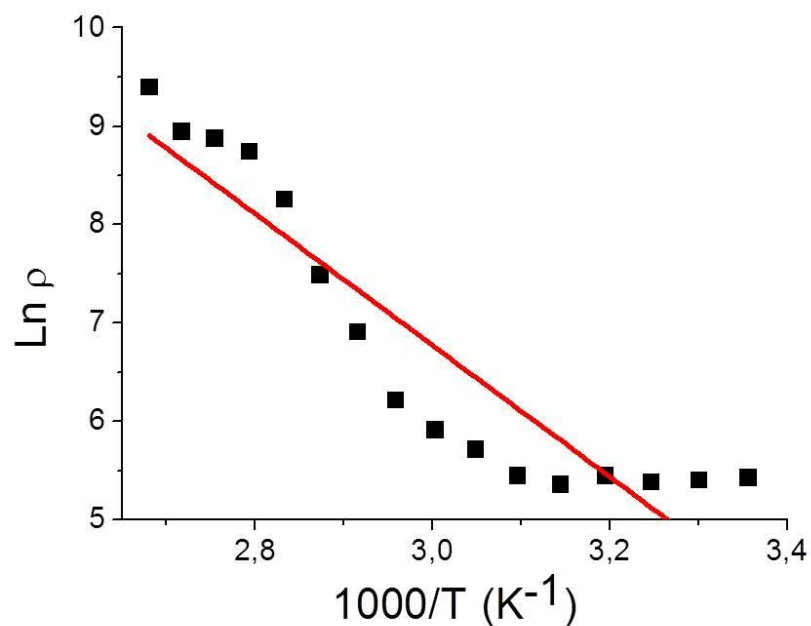


Figure S25. Variation of the neperian logarithm of the resistivity, versus the inverse of the temperature of the **CP1**.

## BIBLIOGRAPHY

- [1] G. M. Sheldrick, *Acta Crystallographica Section A: Foundations of Crystallography*, **2015**, *71*, 3-8.
- [2] G. M. Sheldrick, *Acta Crystallographica Section C: Structural Chemistry*, **2015**, *71*, 3-8.
- [3] A. L. Spek, *Acta Crystallographica Section C: Structural Chemistry*, **2015**, *71*, 9-18.
- [4] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *Journal of Applied Crystallography*, **2008**, *41*, 466–470.