Electronic Supplementary Material (ESI) for Dalton Transactions.


# Supporting Information: *Ab Initio* Powder X-Ray Diffraction Structural Analysis of Bispidine Based 1D Coordination Polymer: Insight into their Guest Responsive Behavior.

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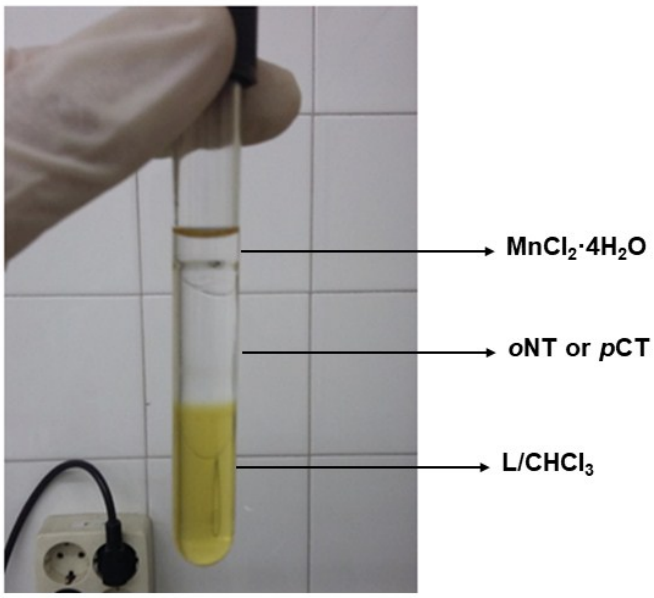
## Materials and Methods

## Isostructural bi-sovated 1D CPs 1·TCM·*o*NT and 1·TCM·*p*CT.

Single crystals **1·TCM·*o*NT** and **1·TCM·*p*CT** were prepared using a layering crystallization method using crystallization tubes and closed to avoid evaporation. In a typical experiment, a triple layered crystallization method is prepared by placing chloroform solution of ligand **L** (3ml; 0.035 mmol) at the bottom for the crystallization tube, a para-chlorotoluene (*p*CT) layer (3 ml), in the middle and a methanol solution of $MnCl_2 \cdot 4H_2O$ (1 ml; 0.035 mmol) as the top layer was added carefully dropwise (Scheme 1), to avoid rapid mixing, and therefore the formation of microcrystals. The crystallization tubes were left in the laboratory for one week and where not disturbed/moved. In this current case after 5 days colorless crystals were obtained in the walls of the tube.




**Scheme 1**. Image showing the three layering method used for the crystallization of **1·TCM·*p*CT**. Following the same method **1·TCM·*o*NT** was prepared.

## Single crystal X-ray Diffraction

Single crystal X-ray diffraction experiments where carried out using a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with a microfocusing mirror (Cu-$K_\alpha$

radiation, $\lambda$ = 1.54178 Å). All the single crystal data were carried out at room temperature conditions.

## Powder X-ray Diffraction Experiments

The powder X-ray diffraction experiments were carried outusing a Bruker D2-Phaser diffractometer equipped with Cu radiation ($\lambda$ = 1.54184 Å) using Bragg-Brentano geometry. The experiments were performed at room temperature.

## Synchrotron Powder X-ray Diffraction Experiments

The synchrotron powder XRD experiments were carried out at the Materials Science and Powder Diffraction Beamline (BL04-MSPD) at Alba synchrotron at Barcelona, Spain. The variable temperature experiments were carried out using a FMB Oxford hot air blower (RT-900 C) for samples in capillaries. The experiments were carried out in transmission mode using a radiation with a wavelength, $\lambda$ = 0.6197 Å.

## *Ab initio* powder X-ray structure of 1.

High quality X-ray synchrotron diffraction data was recorded in the BL04 MSPD Beamline of Alba Synchrotron at 306 K in transmission mode (using a 0.3 mm glass capillary; synchroton radiation, $\lambda$ = 0.6197 Å; 2$\theta$ range: 1.0259–42.7979; step width: 0.006°; data collection time 20 s) on a diffractometer equipped with the microstrip MYTHEN-II PSI detector.

## *In situ* thermal treatment of 1.

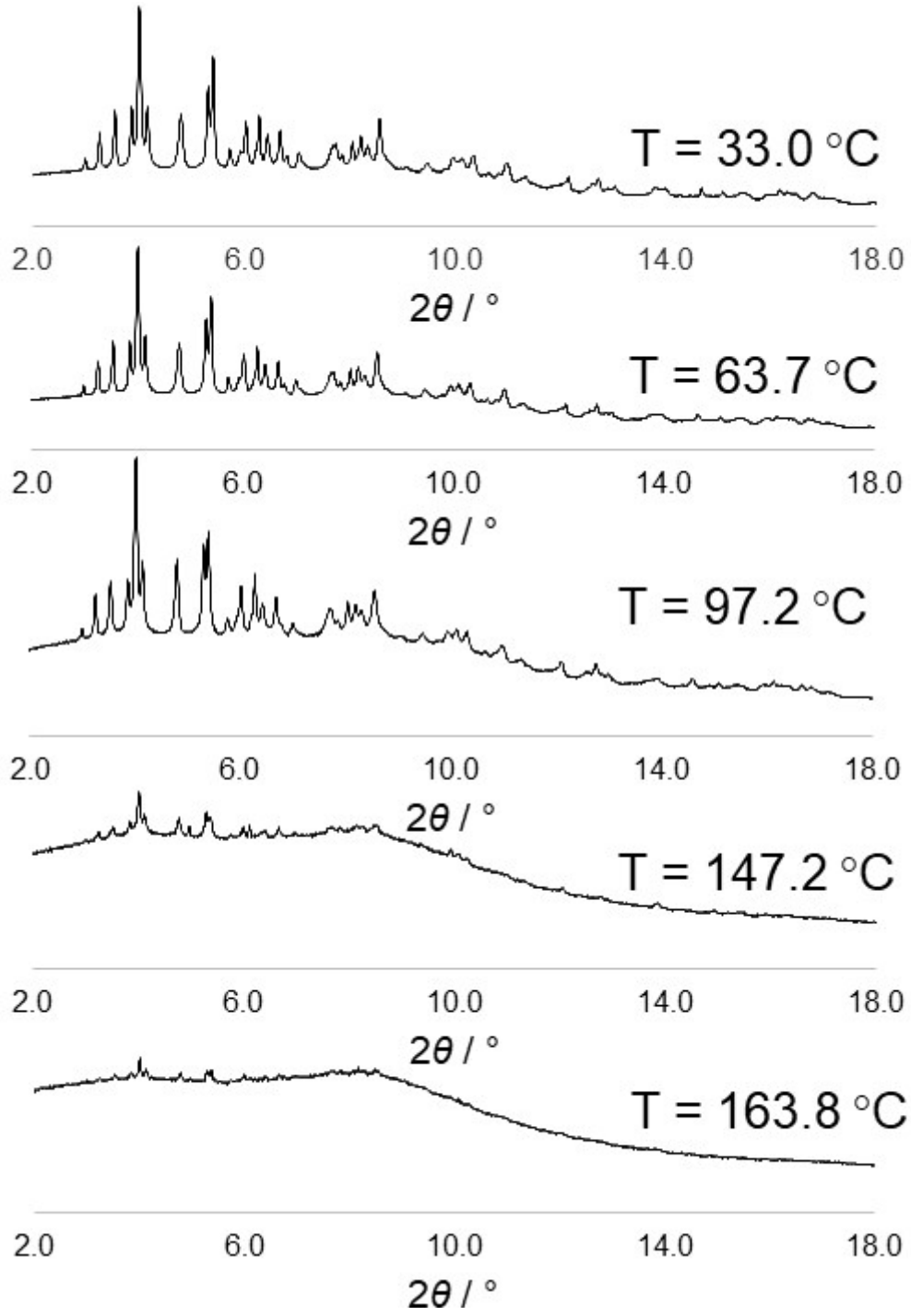



**Figure S1**. *In situ* synchrotron powder XRD thermal treatment of **1**. The two plots show the crystallinity of the 1D CP reaching 63.7 °C. The data was recorded using a $\lambda$ = 0.6197 Å.

## Guest exchange of 1·NB exposed to TCM for 14 days.

The guest exchange was carried out using **1·NB** exposed to TCM for two weeks.

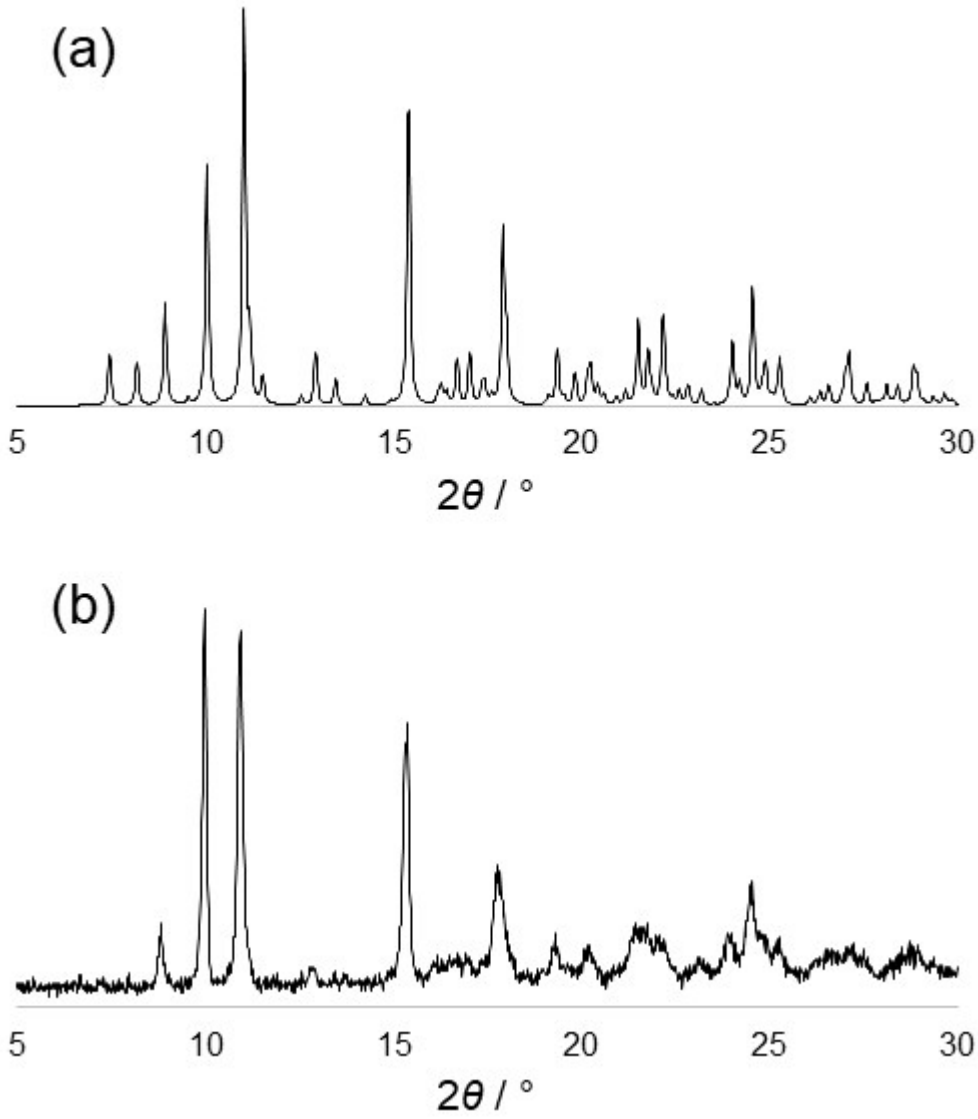



**Figure S2**. (a) Simulated PXRD pattern of **1TCM·oNT** at room temperature and (b) experimental PXRD obtained after 14 of exposition of **1NB** to TCM. Wavelength $\lambda$ = 1.54184 Å.

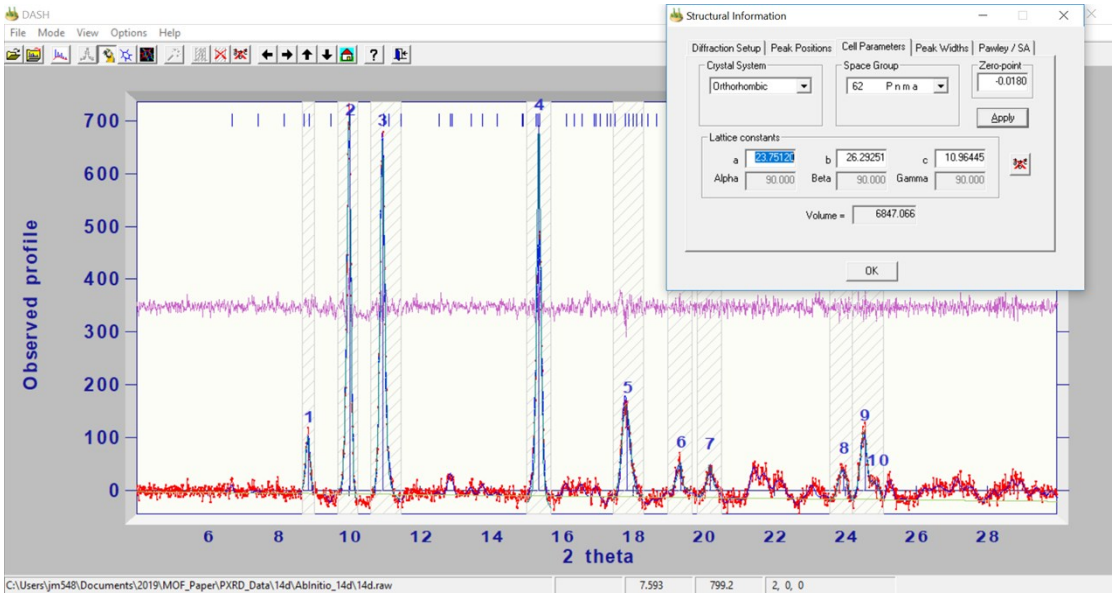



**Figure S3**. LeBail refinement corresponding to the structure of **1NB** exposed to TCM for 14 days. ($R_{wp}$ = 11.32 % (with DASH)).

## Single crystal X-ray structure of 1·TCM·*o*NT

The single crystal X-ray structure determination of **1·TCM·*o*NT** was carried out at room temperature in order to compare its simulated PXRD pattern with the ones obtained experimentally at room temperature using fast crystallization methods. In the asymmetric unit there is one ligand, half $MnCl_2$, half chloroform and half o-nitrobenzene guest molecules with a structural formula $[(L)_2(MnCl_2)]$•TCM•*o*NT.

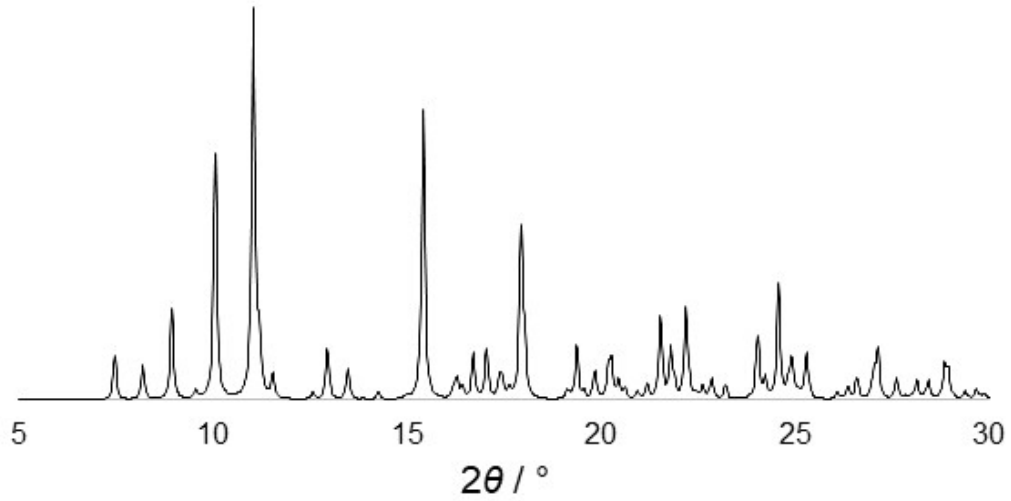



**Figure S4**. Simulated PXRD pattern of **1·TCM·*o*NT** at room temperature. Wavelength $\lambda$ = 1.54184 Å.

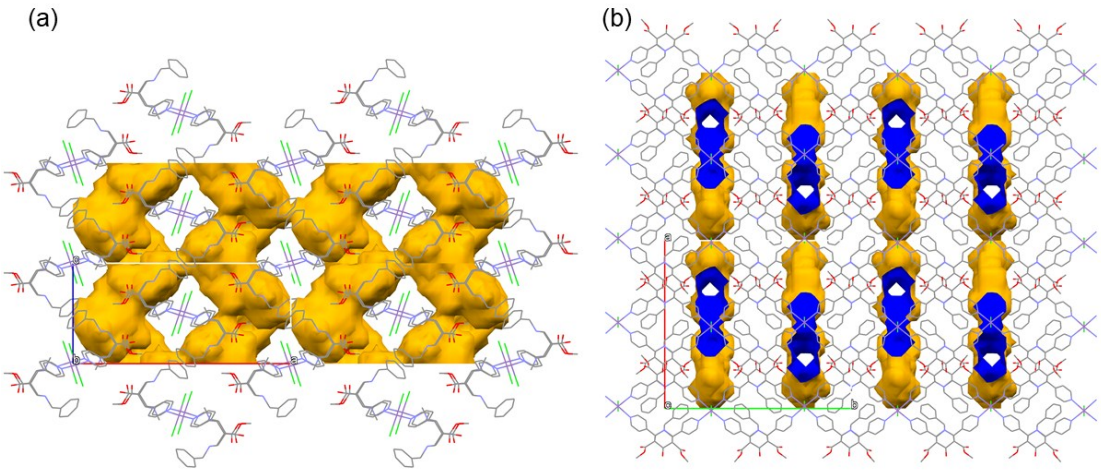



**Figure S5**. Crystal structure of **1·TCM·*o*NT** showing the voids after manually removing the solvent molecules. The voids space corresponds to *ca*. 17 % of the total unit cell volume. Color code: Mn: pale violet; N: blue; C: grey; O: red; H: white.

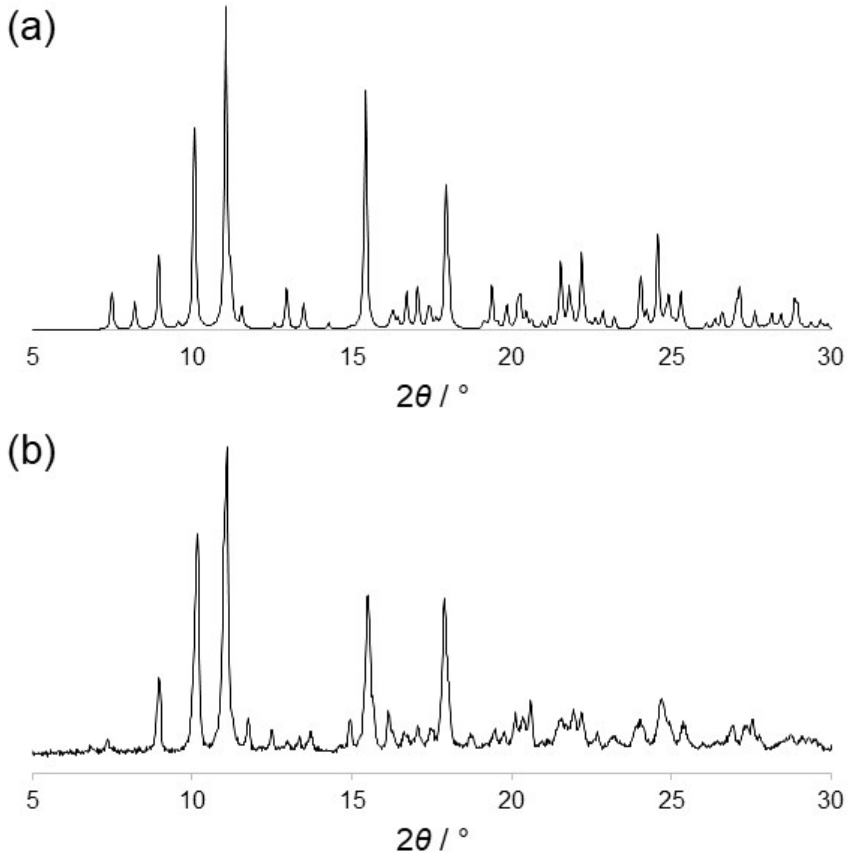



**Figure S6**. Comparison among the PXRD patterns of the simulated form single crystal **1·TCM·*o*NT** (a) and experimental obtained after fast crystallization methods (b). Wavelength $\lambda$ = 1.54184 Å.

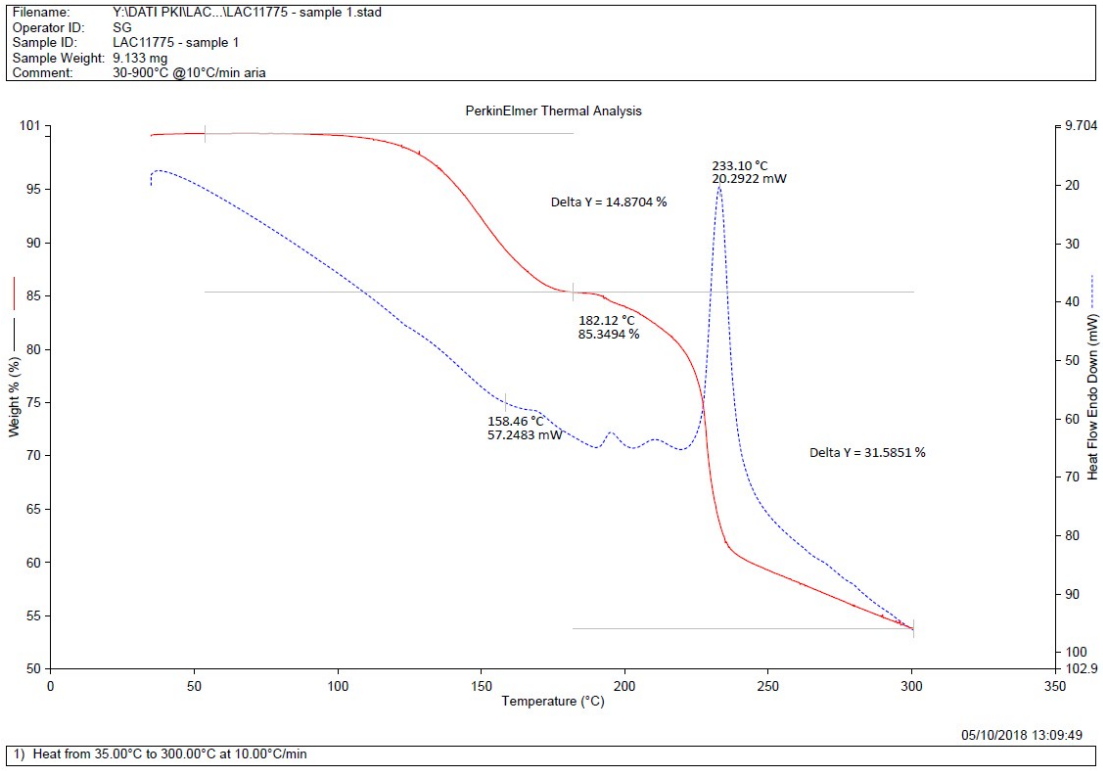



**Figure S7**. TGA corresponding to the structure of **1·TCM·*o*NT** showing weight loss of the two solvent molecules (expd *ca.* 15 %, calcd *ca.* 18 %). Note: The starting temperature is 35 °C and not 25 °C due to experimental set up conditions. Clearly, this can have an effect in the measure of the weight loss, that eventually can be lower that the one calculated based on single crystal data.

## In situ thermal powder XRD monitoring of 1·TCM·*o*NT

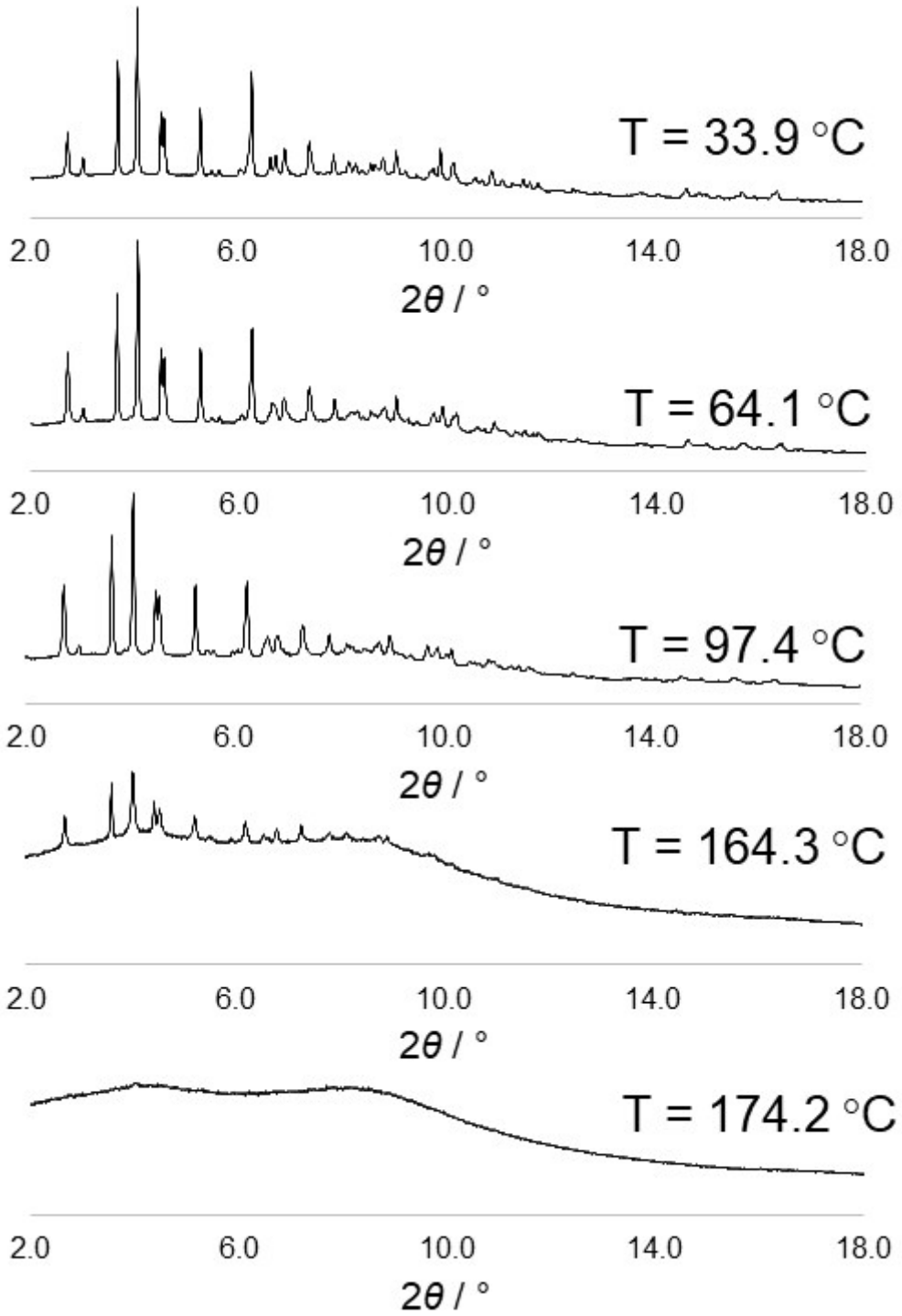



**Figure S8**. *In situ* synchrotron powder XRD thermal treatment of **1·TCM·*o*NT**. The two plots show the crystallinity of the 1D CP reaching 65.8 °C. The data was recorded using a $\lambda$ = 0.6197 Å. Two-theta range: 1.0259-42.7979; step size: 0.006° and acquisition time 20 seconds.

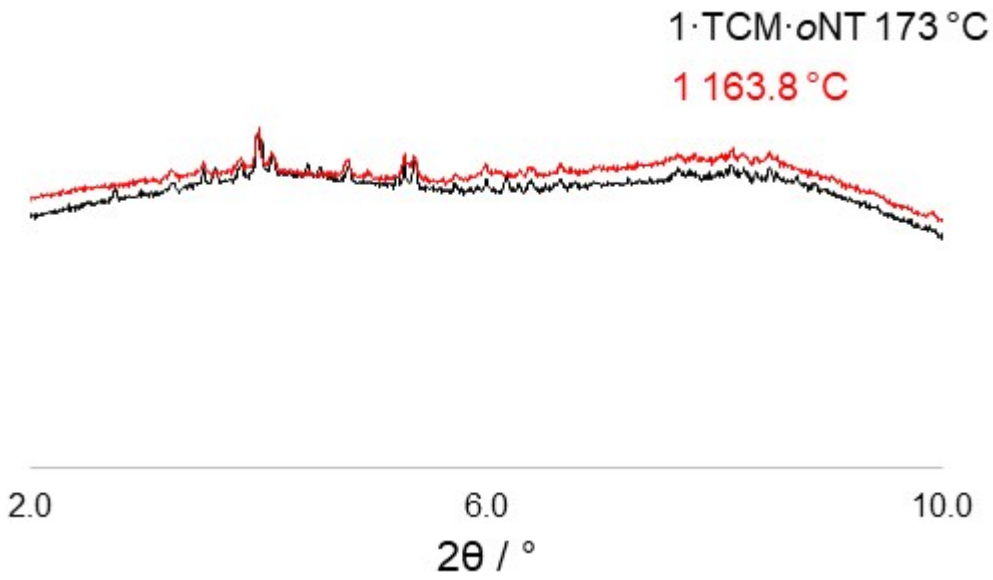



**Figure S9**. Overlapping of the *in situ* synchrotron powder XRD thermal treatment of **1** and **1·TCM·*o*NT**. The peaks corresponding to phase **1** in the thermal treatment of the *bi-solvated* microcrystalline material **1·TCM·*o*NT** show good agreement. $\lambda$ = 0.6197 Å.

## Single crystal X-ray structure of 1·TCM·*p*CT (TCM/*p*-Cl-toluene)

A colorless single crystal of **1·TCM·*p*CT** was selected and mounted for the single crystal X-ray diffraction experiments. The single crystal X-ray structure determination of **1·TCM· *p*CT** was carried out at room temperature in order to compare its simulated PXRD pattern with the ones obtained experimentally at room temperature using fast crystallization methods.

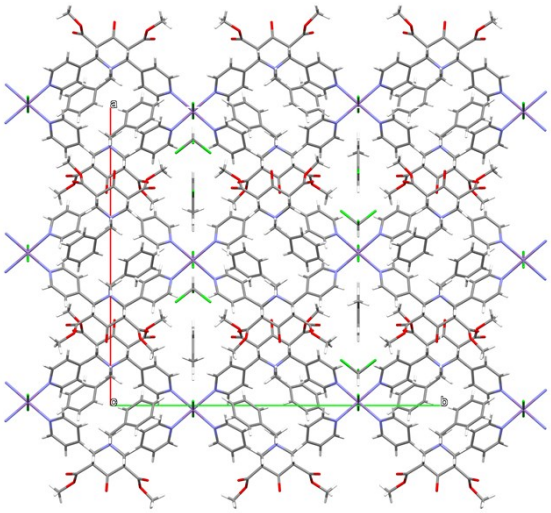


**Figure S10**. Crystal structure of **1·TCM·*p*CT** showing the two guest molecules viewed along the *c*-axis. Color code: Mn: pale violet; N: blue; C: grey; O: red; H: white

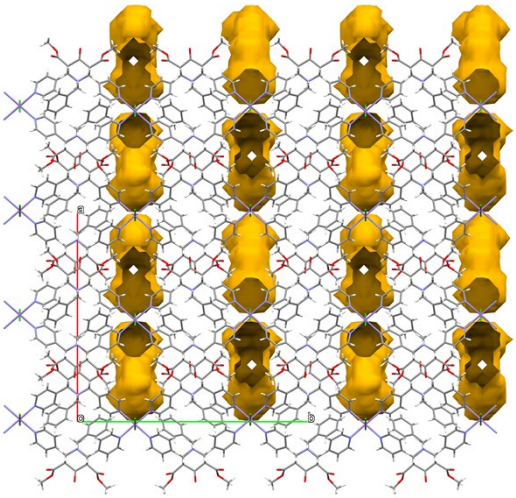


**Figure S11**. Crystal structure of **1·TCM·*p*CT** showing the voids after manually removing the solvent molecules. The voids space corresponds to *ca*. 15 % of the total unit cell volume. The voids do not form connected 1D channels. Color code: Mn: pale violet; N: blue; C: grey; O: red; H: white.

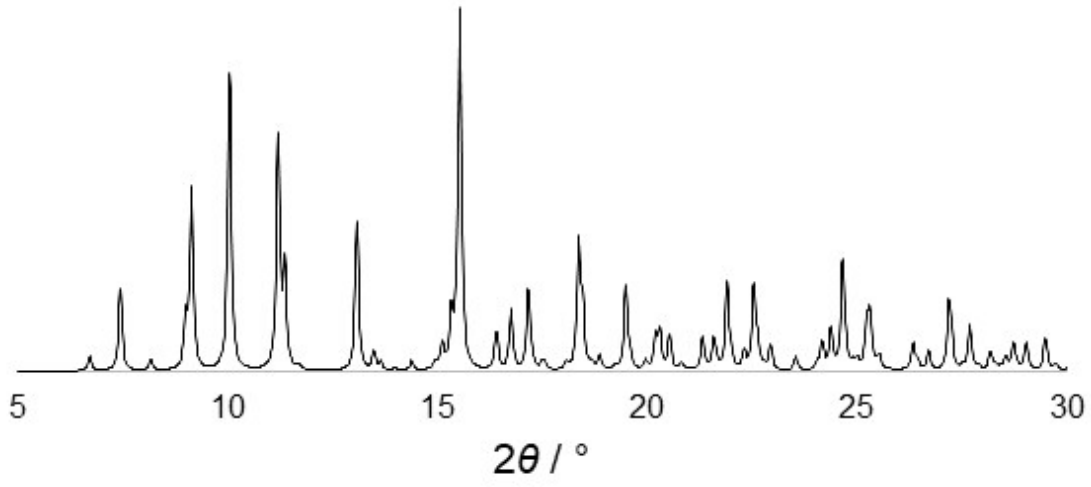



**Figure S12**. PXRD pattern of the simulated form single crystal **1·TCM·*p*CT**. Wavelength: $\lambda$ = 1.54184 Å.

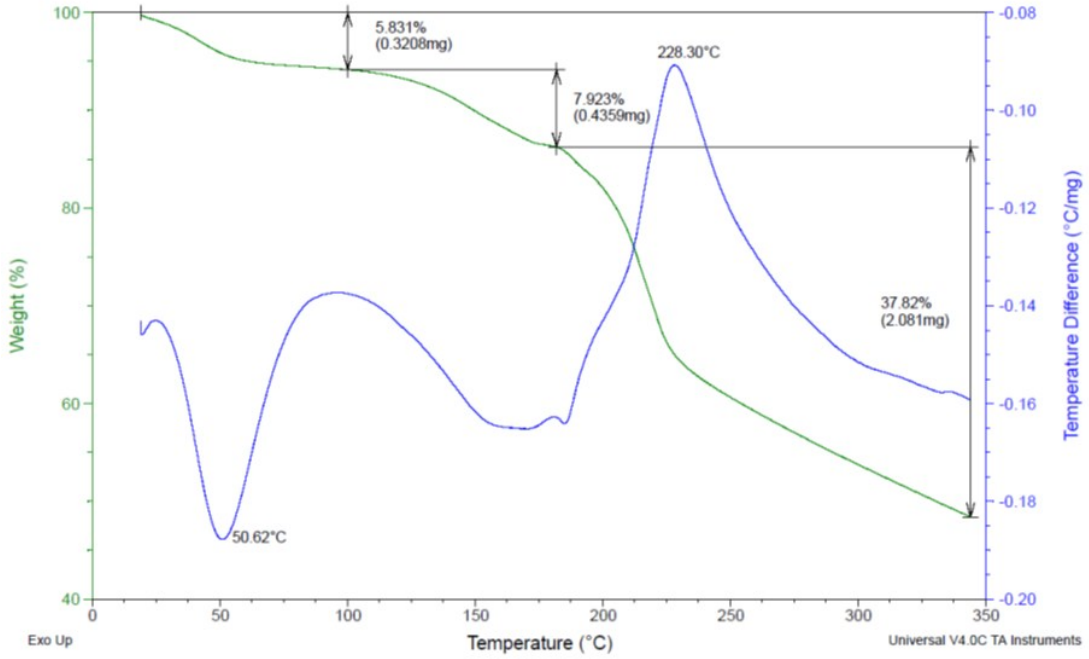



**Figure S13**. TGA corresponding to the structure of **1·TCM·*p*CT** showing weight loss of the two solvent molecules *ca*. 8.5 % while the theoretical value is *ca.* 18 %. We believe that this lack of solvent is due to the guest loss after keeping the sample several days in the laboratory at *r.t*. conditions.

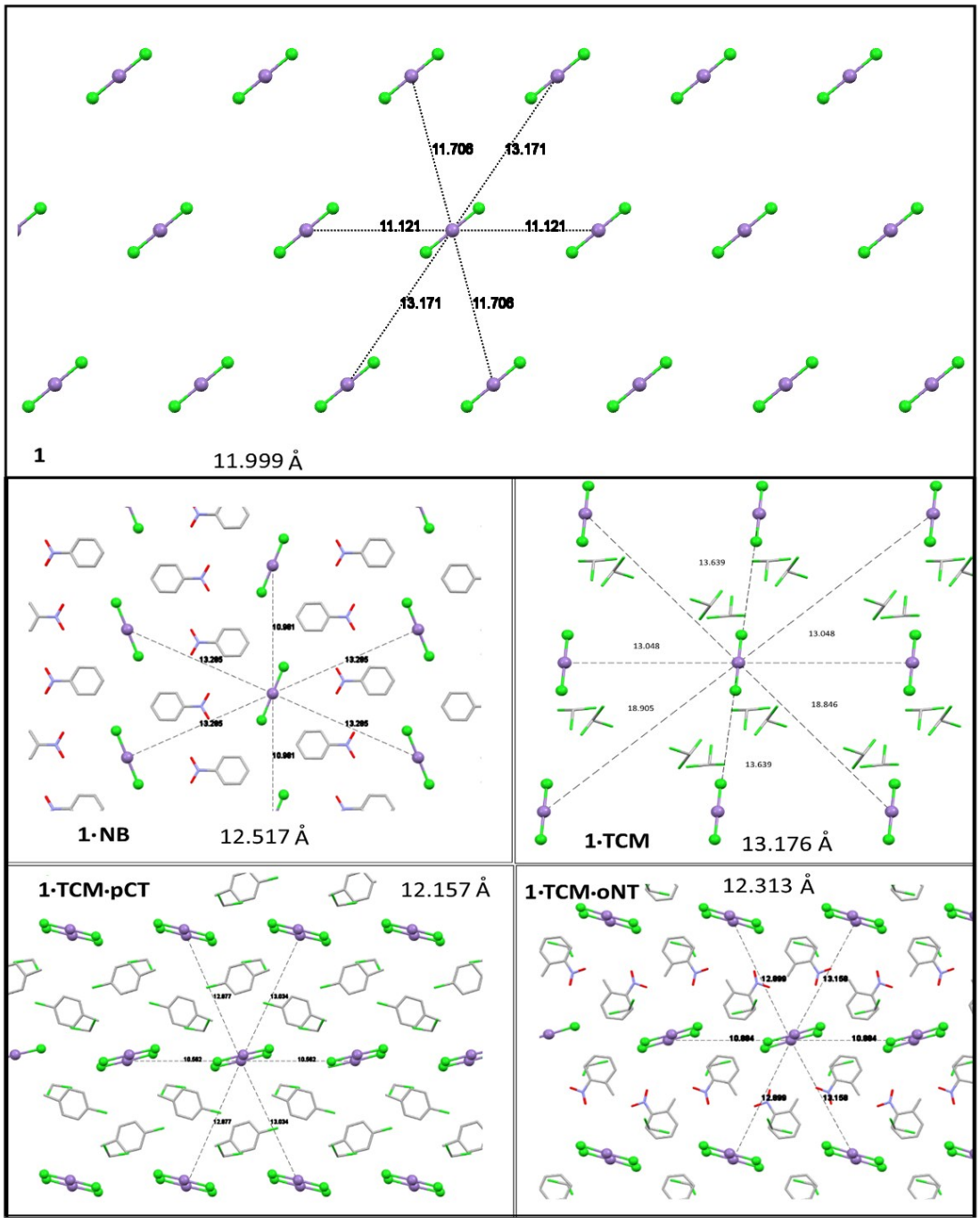



**Figure S14**. Cartoon showing the distances of adjacent 1D ribbons for the 1D CPs **1**, **1·NB, 1·TCM, 1·TCM·*o*NT** and **1·TCM·*p*CT**.

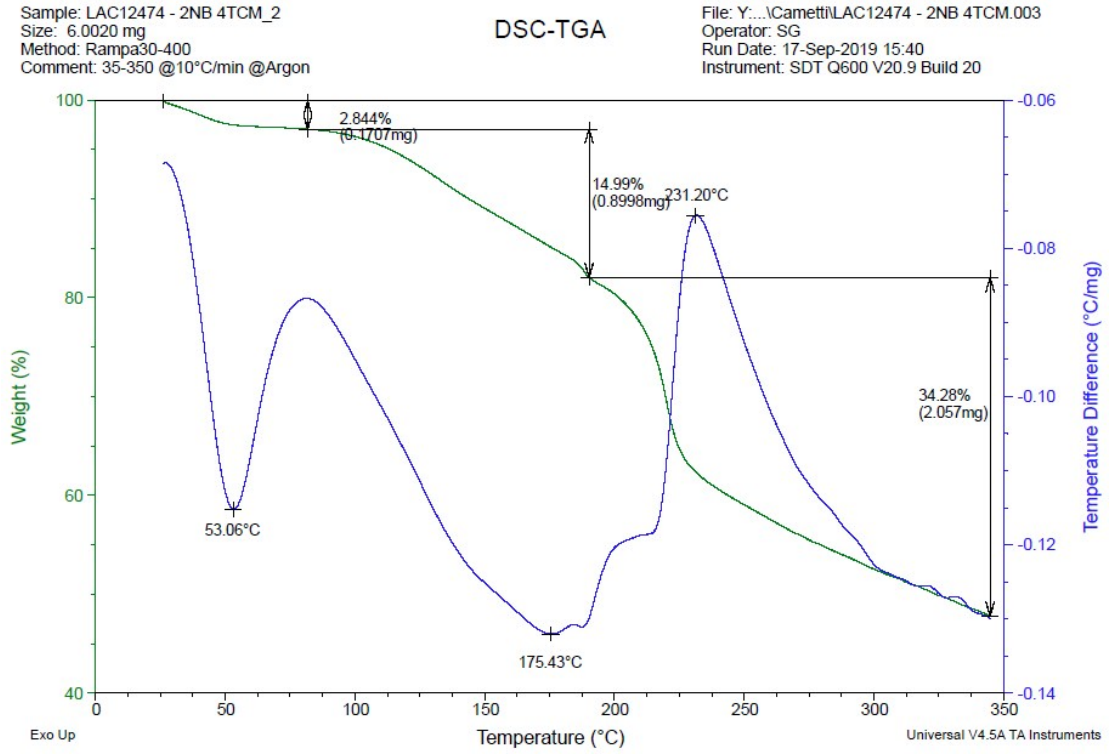



**Figure S15**. TGA corresponding to the structure of **1'** showing weight loss of the two solvent molecules The endothermic process corresponding to a weight loss of 14.99 % compares well with the expected value of 17.3 % calculated from the molecular formula of the material **1·TCM-NB** assuming that it has the same structre of **1·TCM-*o*NT** known by the SC study.

## In situ thermal powder XRD monitoring of 1·TCM·*p*CT

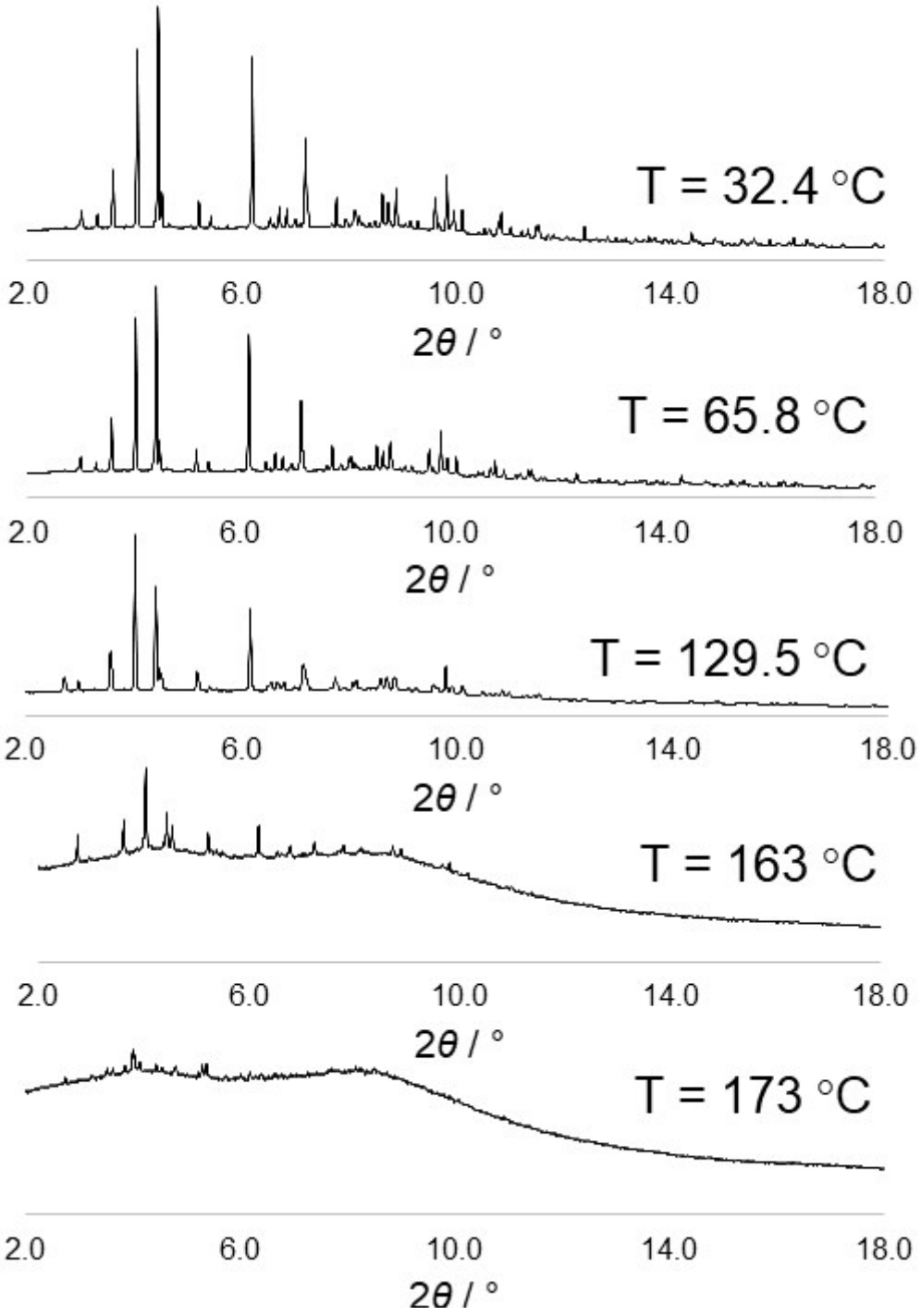



**Figure S16**. *In situ* synchrotron powder XRD thermal treatment of **1·TCM·*p*CT**. The two plots show the crystallinity of the 1D CP reaching 64.1 °C. The data was recorded using a $\lambda$ = 0.6197 Å.

## Guest exchange behavior 1·TCM·*o*NT (TCM/*o*-nitro-toluene) in nitrobenzene (solid-liquid experiments).

White powders of **1·TCM·*o*NT** (*ca*. 30 mg) were introduced immersed in NB (5 mL) and left overnight at r.t. The sample after filtration using low vacuum pump was analyzed by powder XRD analysis. The sample was crystalline after filtration.

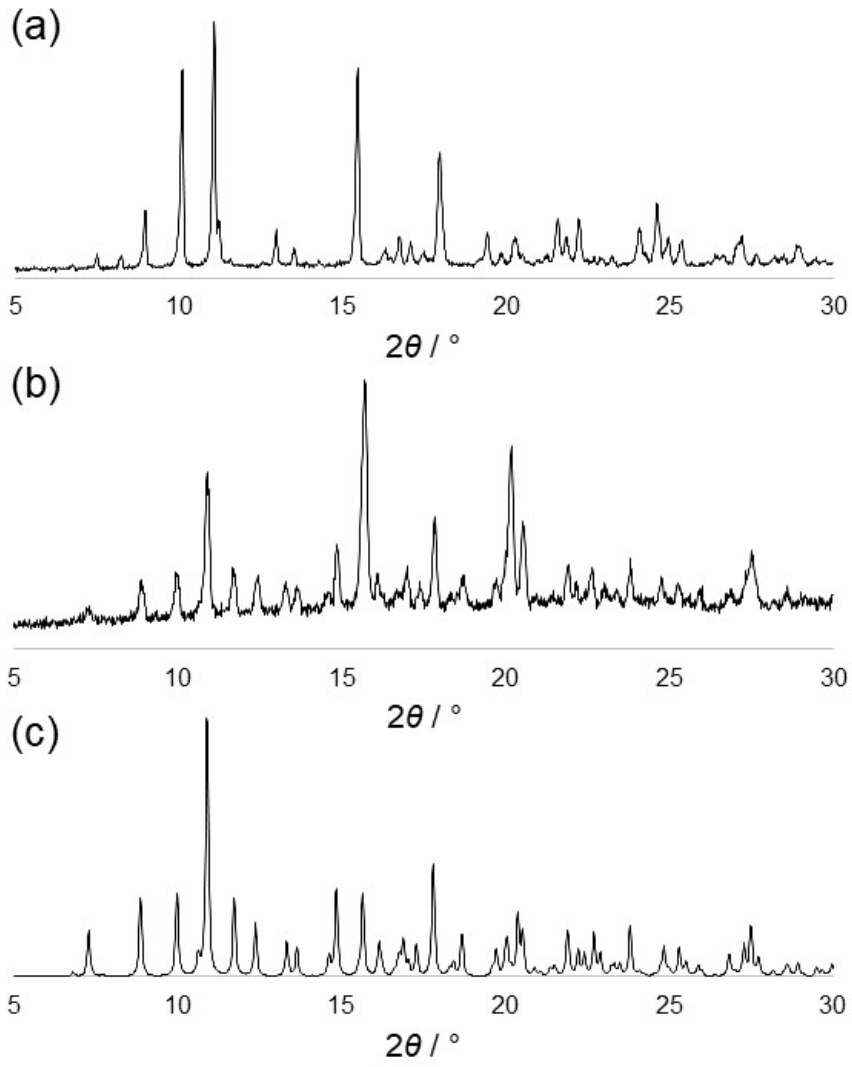



**Figure S17**. (a) Experimental powder XRD pattern of **1·TCM·*o*NT** obtained by fast crystallization. (b) Experimental powder XRD pattern obtained by dipping **1·TCM·*o*NT** in nitrobenzene overnight. (c) Simulated powder XRD pattern from the single crystal structure of **1·NB**. All the plots correspond to data at *r.t.* conditions. Wavelength: $\lambda$ = 1.54184 Å.

## Guest exchange behavior 1·TCM·*p*CT (TCM/*p*-Cl-toluene) in nitrobenzene (solid-liquid experiments).

White powders of **1·TCM·*p*CT** (*ca*. 30 mg) were introduced immersed in NB (5 mL) and left overnight at r.t. The sample after filtration using low vacuum pump was analyzed by powder XRD analysis. The sample was crystalline after filtration.

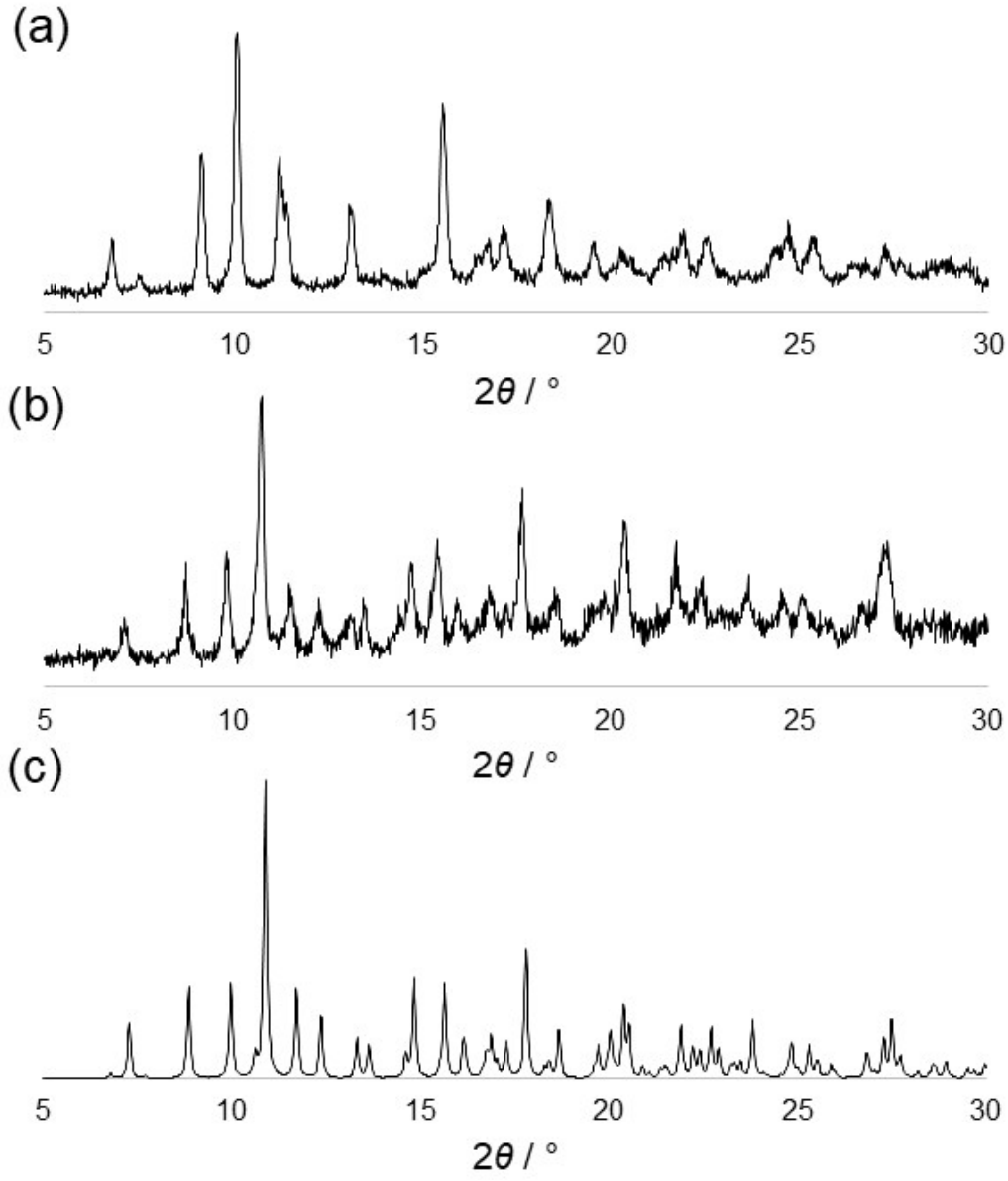



**Figure S18**. (a) Experimental powder XRD pattern of **1·TCM·*p*CT** obtained by fast crystallization. (b) Experimental powder XRD pattern obtained by dipping **1·TCM·*p*CT** in nitrobenzene overnight. (c) Simulated powder XRD pattern from the single crystal structure of **1·NB**. All the plots correspond to data at *r.t*. conditions. Wavelength: $\lambda$ = 1.54184 Å.

## LeBail refinements using 1·TCM/*p*-CT inmersed in nitrobenzene (solid-liquid experiments).

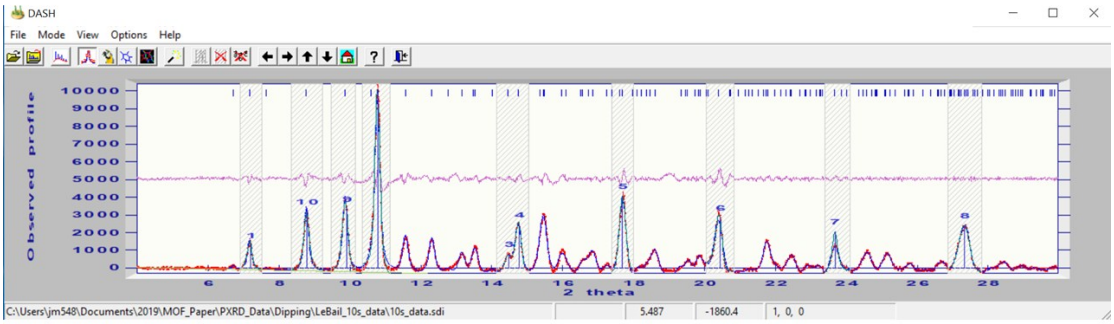



**Figure S19**. Pawley fit carried out corresponding to the sample obtained after the immersion of **1·TCM·*p*CT** into nitrobenzene overnight. The starting unit cell was that of **1·NB** from which the Pawley refinement was carried out.

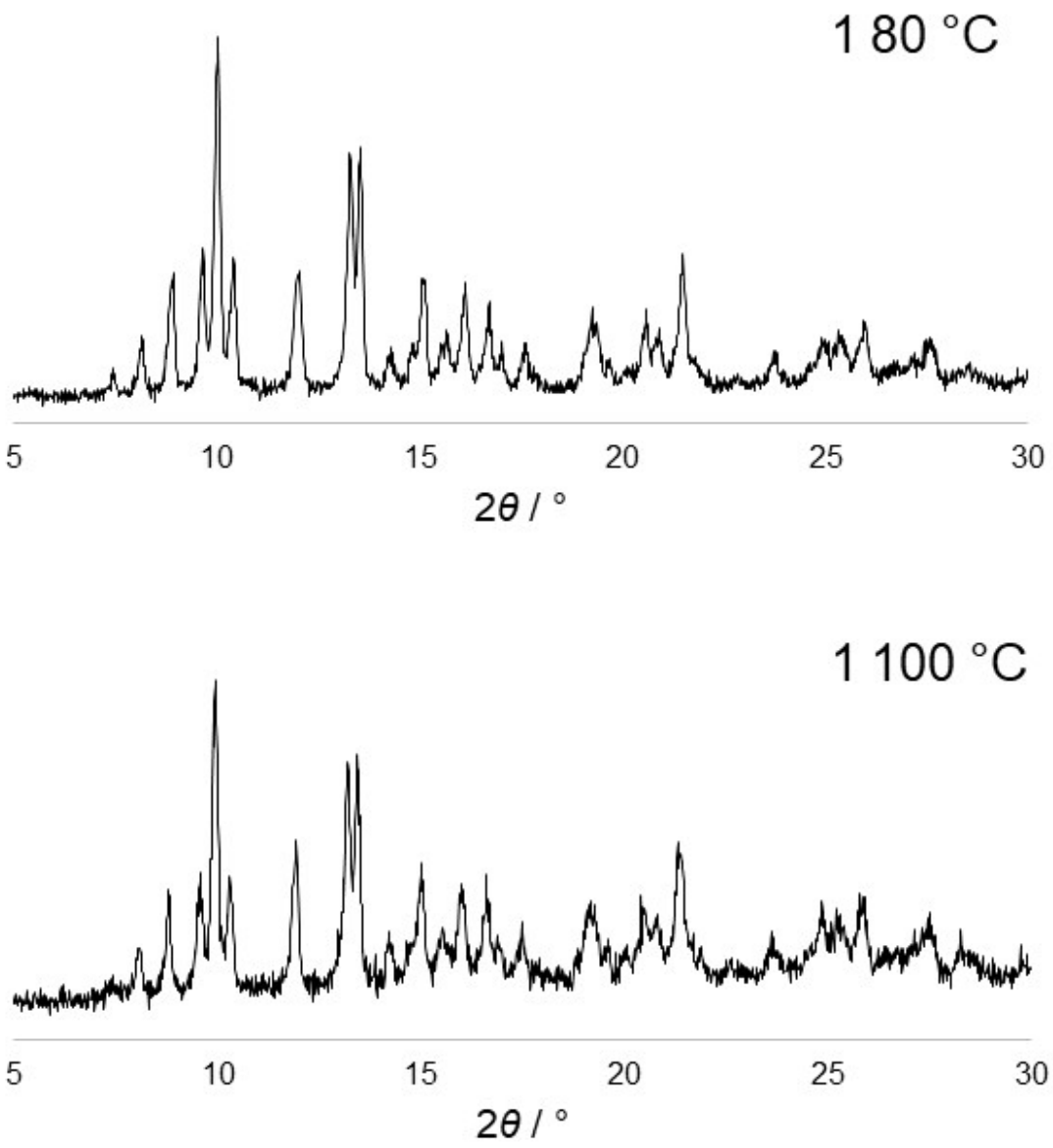



**Figure S20**. Stepwise heating of **1** at 80 °C and 100 °C. Wavelength: $\lambda$ = 1.54184 Å.

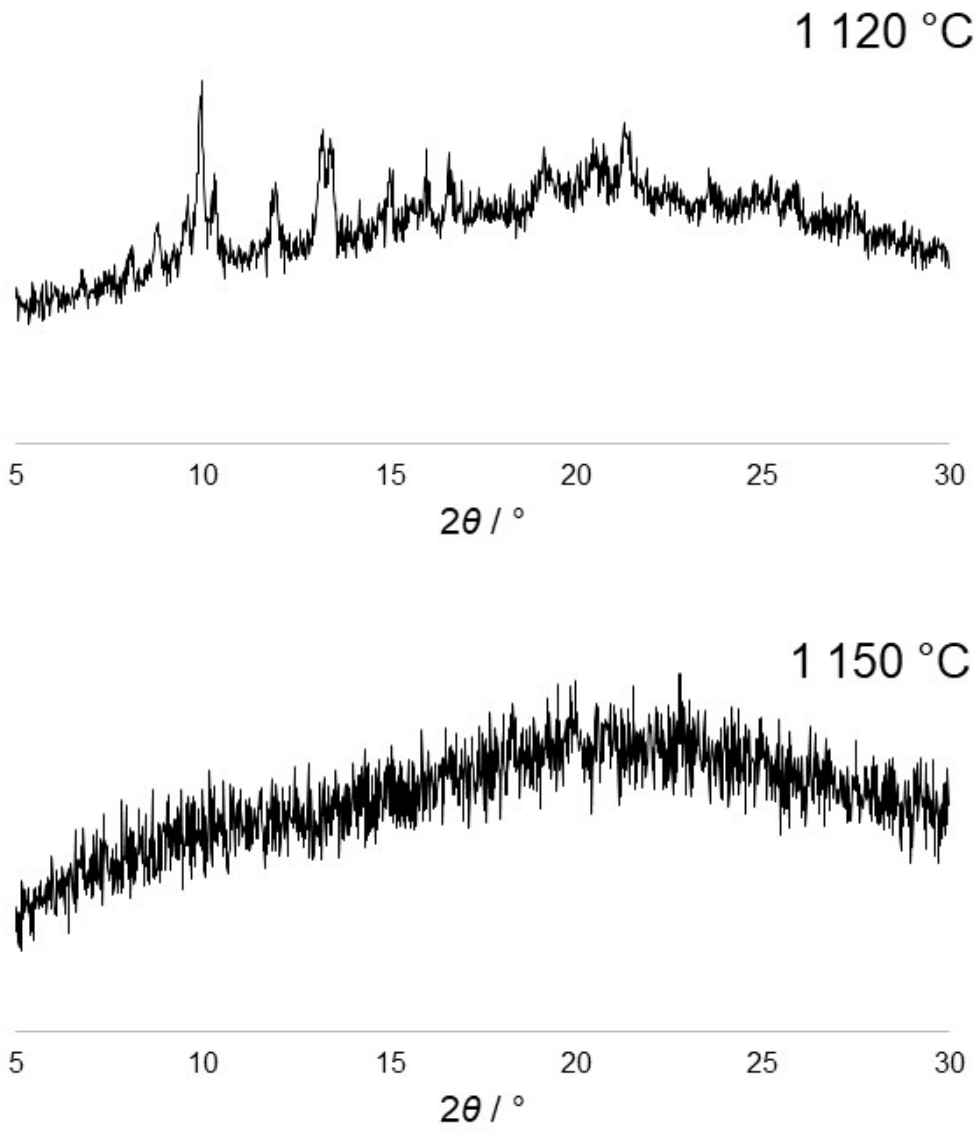



**Figure S21**. Stepwise heating of **1** at 120 °C and 150 °C. Wavelength: $\lambda$ = 1.54184 Å.

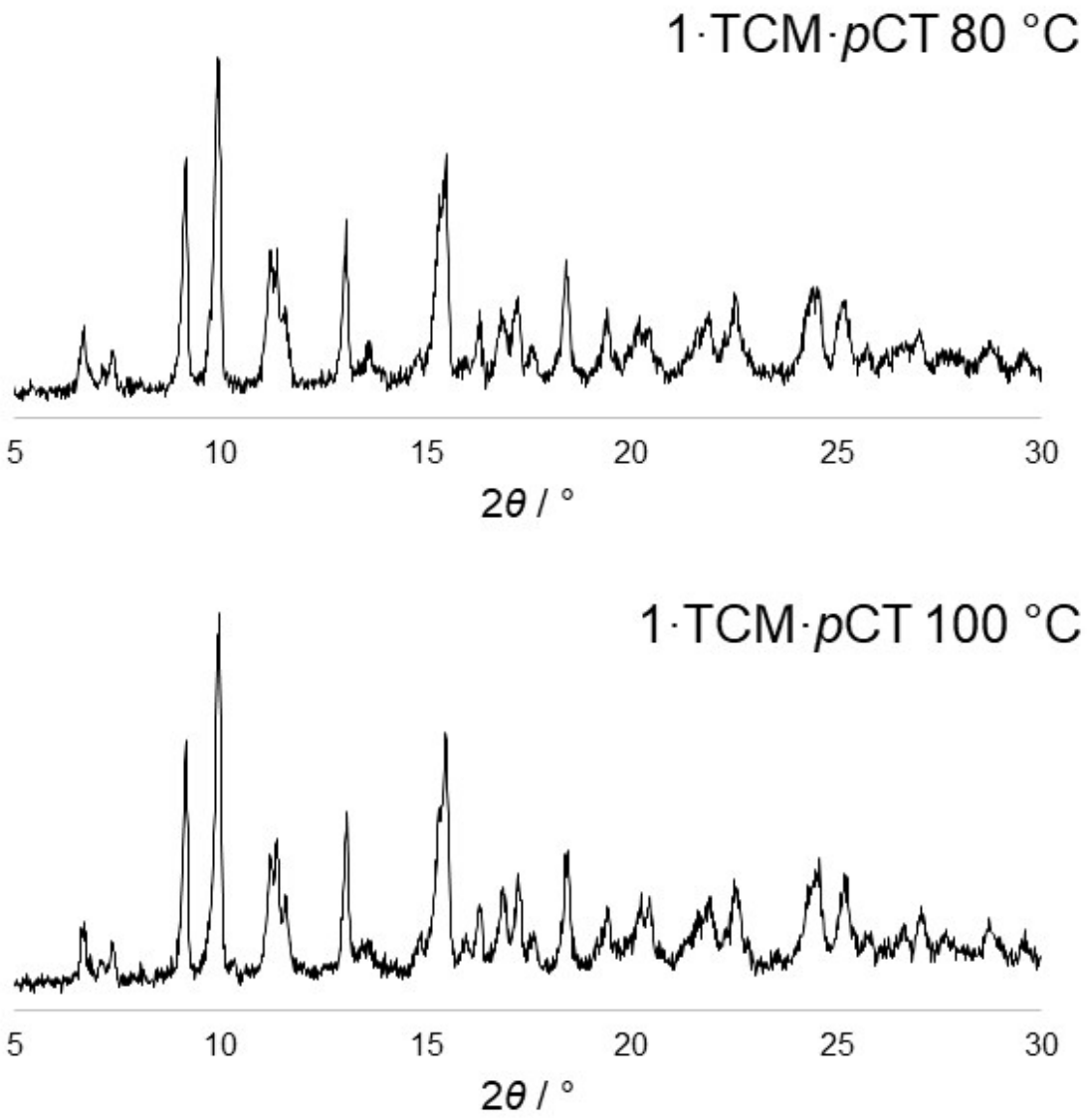



**Figure S22**. Stepwise heating of **1·TCM·*p*CT** at 80 °C and 120 °C. Wavelength: $\lambda$ = 1.54184 Å.

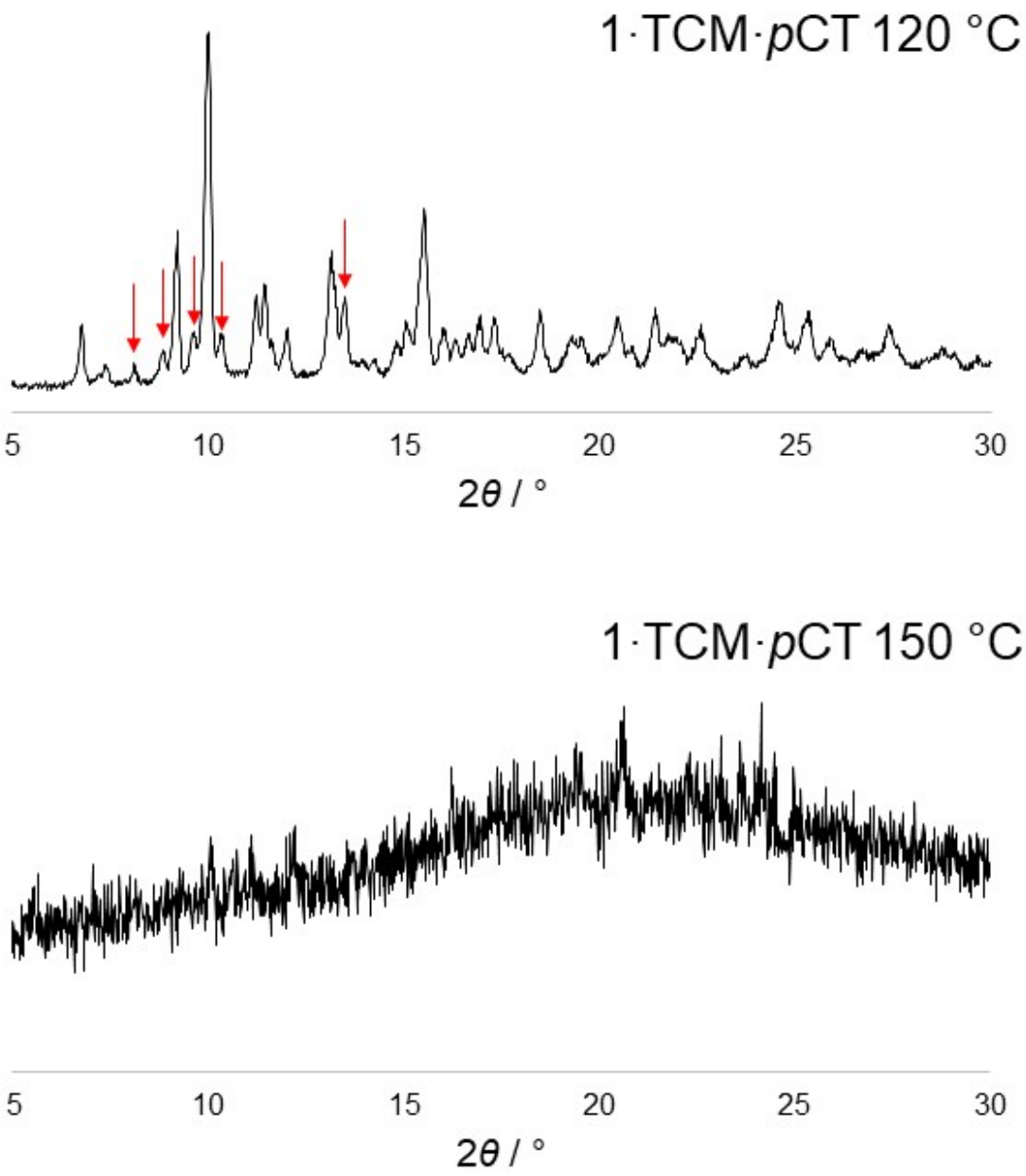



**Figure S23**. Stepwise heating of **1·TCM·*p*CT** at 120 °C and 150 °C. The red arrows indicate the presence of phase **1**. Wavelength: $\lambda$ = 1.54184 Å.

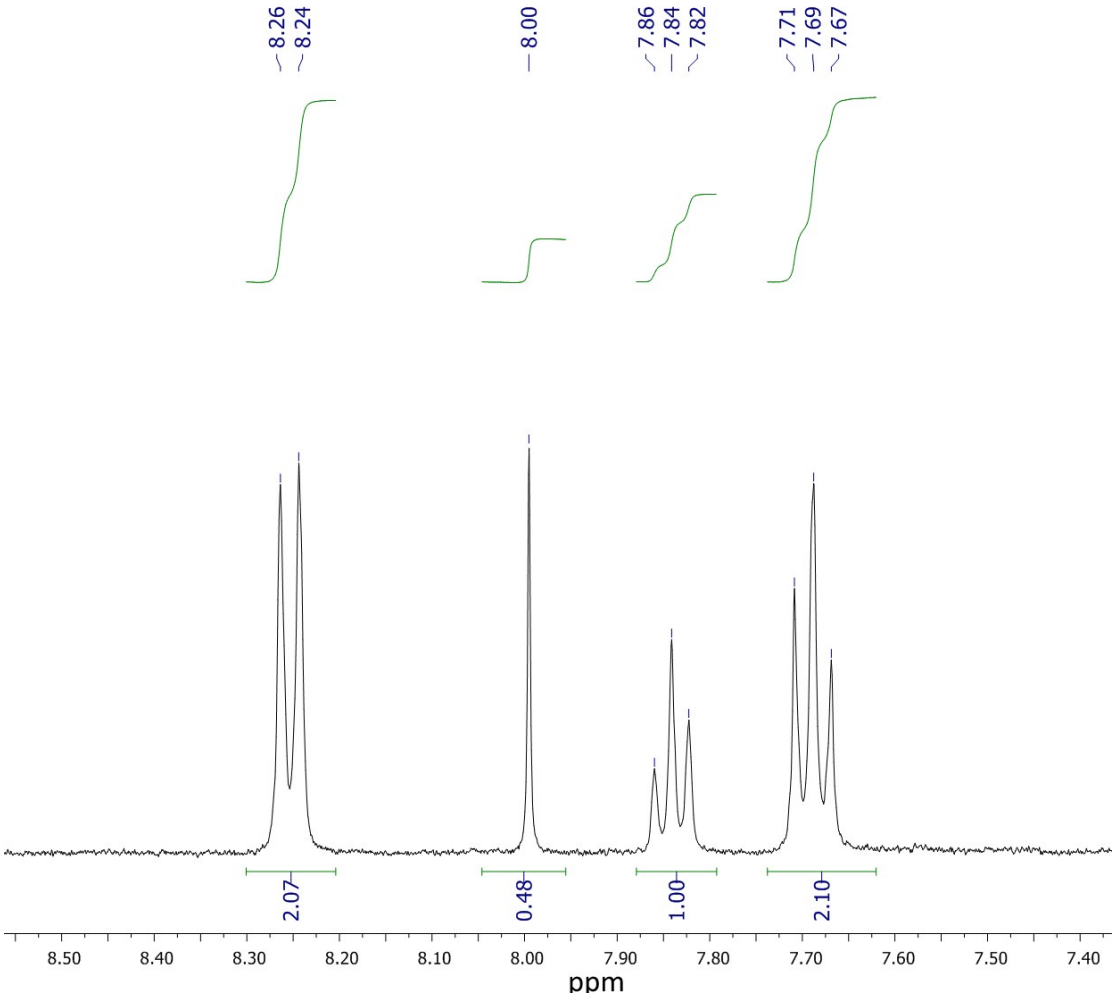



**Figure S24**. $^{1}$H NMR corresponding to **1′** including **NB** and **TCM**.