Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting information

Rational direct synthesis of $[Fe(Htrz)_2(trz)](BF_4)$ polymorphs: temperature and concentration effects.

Marlène Palluel, Liza El Khoury, Nathalie Daro, Sonia Buffière, Michaël Josse, Mathieu Marchivie, Guillaume Chastanet

Content :

Synthesis procedure of $[Fe(Htrz)_2(trz)](PF_6)$

The synthesis of $[Fe(Htrz)_2(trz)](PF_6)$ consists first in an anion exchange between the SO_4^{2-} of the $FeSO_4$ salt and the PF_6^- of the KPF_6 to give the $Fe(PF_6)_2$ (in solution) followed by its reaction with the triazole ligand.

$FeSO_4$ (16 mmol) and the KPF_6 (32 mmol) are dissolved in 14 mL of water in a 50 mL round flask closed by a glass stopper with some ascorbic acid to prevent oxidation of the Fe(II). The overall is stirred at 80 °C for 2 h 30 leading to a light green solution. After cooling to room temperature, 16 mL of ethanol are added to precipitate the K_2SO_4 and the solution is stirred one hour more. The precipitate of K_2SO_4 is removed from the $Fe(PF_6)$ solution by filtration and washed once with about 50 mL of ethanol. The filtrated solution is put into a fridge during 1 h to favor the precipitation of the remained solubilized K_2SO_4 and further filtrated and washed with 16 mL of ethanol. This operation is repeated one more time. Then, a solution of 16 mmol of Htrz in 14 mL of ethanol is prepared and added dropwise to the $Fe(PF_6)_2$ solution with magnetic stirring and reflux at 80 °C under N_2 atmosphere. After 15 min, the white suspension is obtained and let to cool down at 5°C (into a fridge) during 1 h to promote precipitation. After centrifugation (12 000 rcf, 5 minutes) of the suspension, the precipitate is washed twice with ethanol and once with diethyl ether (with 50 mL each time). For these washing steps, the precipitate is separated from the solvent by the same procedure of centrifugation. The precipitate is then let to dry at RT under ambient atmosphere overnight and a white powder is obtained.

Figure SI1: Thermal dependence of the $\chi_M T$ product recorded at 15 kOe at the temperature scan rate of 5 K/min of $[Fe(Htrz)_2(trz)](PF_6)$. This measurement has been obtained using a Vibrating Sample Magnetometer.

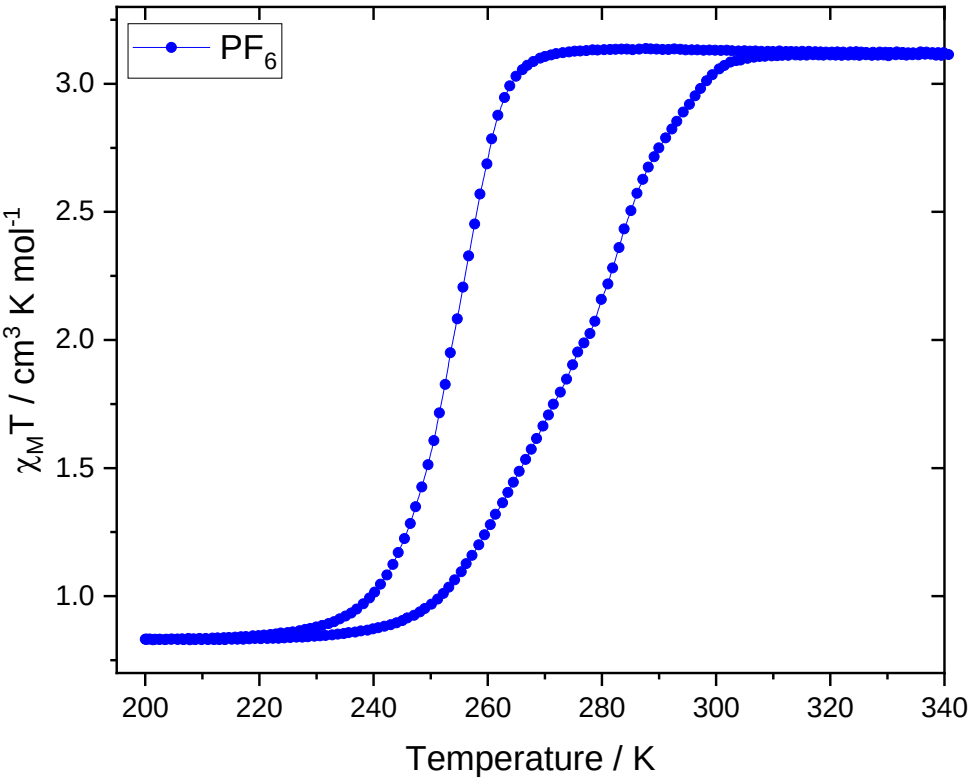

Figure SI2: X-Ray powder pattern of the $[Fe(Htrz)_2(trz)](PF_6)$, black crosses are experimental data, red continuous line is the calculated pattern from Rietveld refinement, continuous green line is the difference curve and blue lines represent the Bragg peak positions (Rp = 0.059; Rwp = 0.079, $\chi^2 = 4.5$).

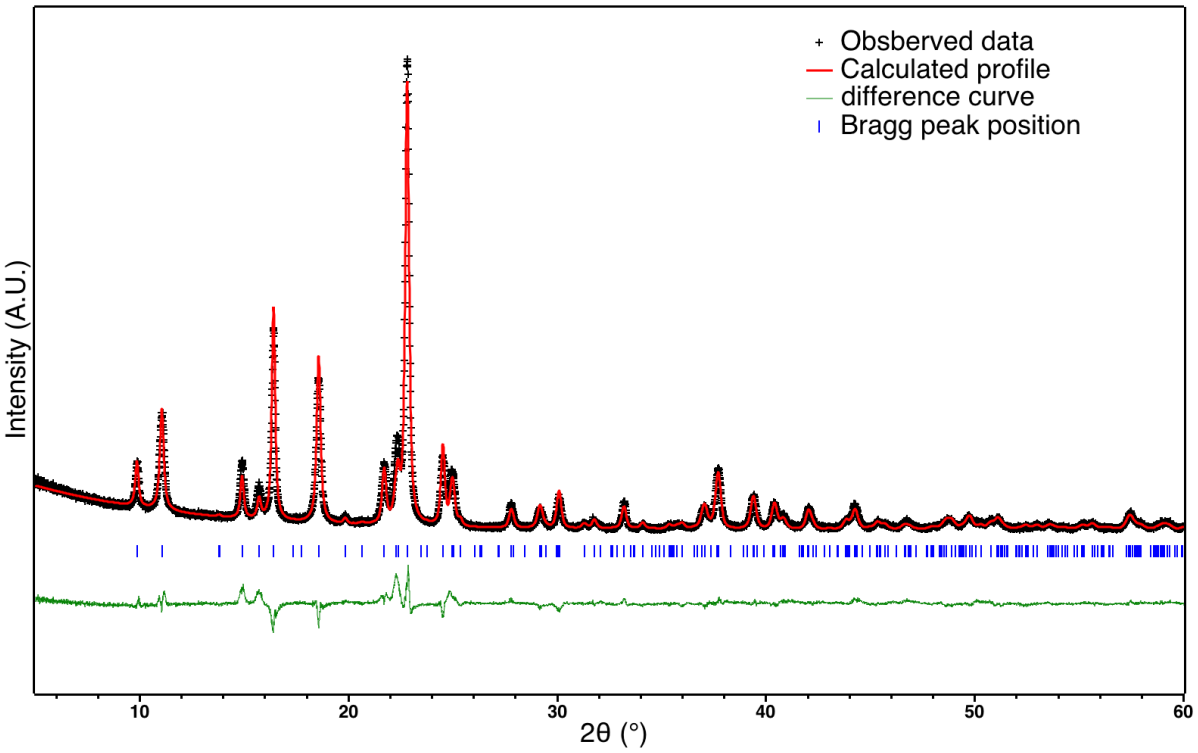

Figure SI3: Crystal packing of the polymeric chains of a. $[Fe(Htrz)_2(trz)](PF_6)$ compared to b. $[Fe(Htrz)_2(trz)](BF_4)$-**I**. View along the a axis of the polymeric chains of c. $[Fe(Htrz)_2(trz)](PF_6)$ compared to d. $[Fe(Htrz)_2(trz)](BF_4)$-**I**. Red circles and arrow highlight the rotation of triazole ligand regarding the a axis.

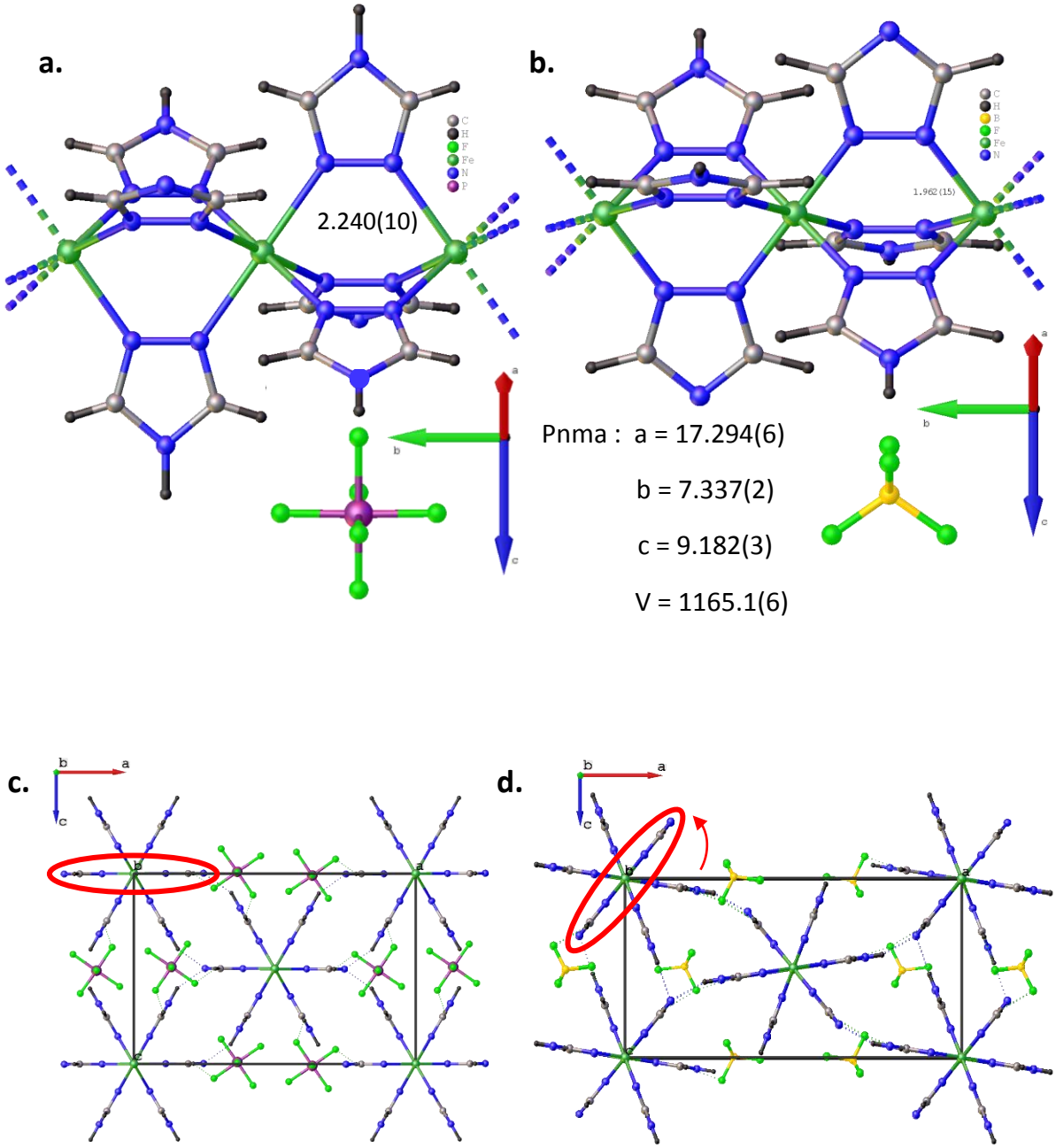

Figure SI4: -Ray powder pattern of the $[Fe(Htrz)_2(trz)](BF_4)$ polymorph **II**, black crosses are experimental data, red continuous line is the calculated pattern from Rietveld refinement, continuous green line is the difference curve and green blue lines represent the Bragg peak positions (Rp = 0.067; Rwp = 0.087)

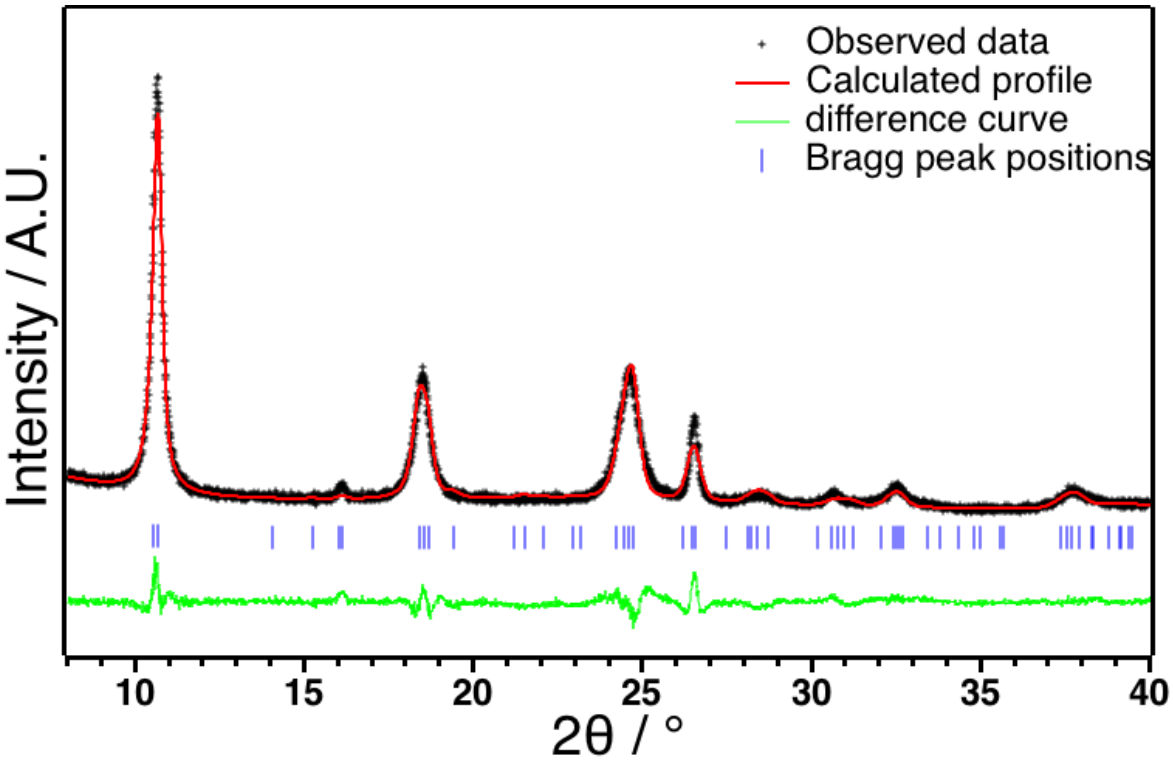

Table SI1: Magnetic data recorded for all 16 compounds at 5 kOe at the temperature scan rate of 0.7 K/min.

Sample name	$T_{1/2\uparrow}$ (K)	$T_{1/2\downarrow}$ (K)	ΔT	Phase
C_2T_{20}	360	342	18	**II/Htrz$_3$**
C_1T_{20}	354	340	14	**II**
$C_{1/2}T_{20}$	364	346	18	**II**
$C_{1/3}T_{20}$	373	344	29	**II/I**
$C_{1/4}T_{20}$	376	345	31	**I/II**
$C_{1/6}T_{20}$	378	346	32	**I**
$C_{1/8}T_{20}$	376	345	31	**I**
C_2T_0	358	342	16	**I/Htrz$_3$/II**
C_1T_0	372	342	30	**II/Htrz$_3$**
$C_{1/8}T_0$	378	354	24	**Htrz$_3$/I/II**
C_2T_{50}	363	341	22	**I/Htrz$_3$/II**
C_1T_{50}	378	350	28	**I/II**
$C_{1/2}T_{50}$	383	348	35	**I**
$C_{1/3}T_{50}$	382	348	34	**I**
C_2T_{80}	380	352	28	**I/Htrz$_3$**
C_1T_{80}	385	351	34	**I**

Figure SI5: TEM images of the 16 compounds and their corresponding phases.

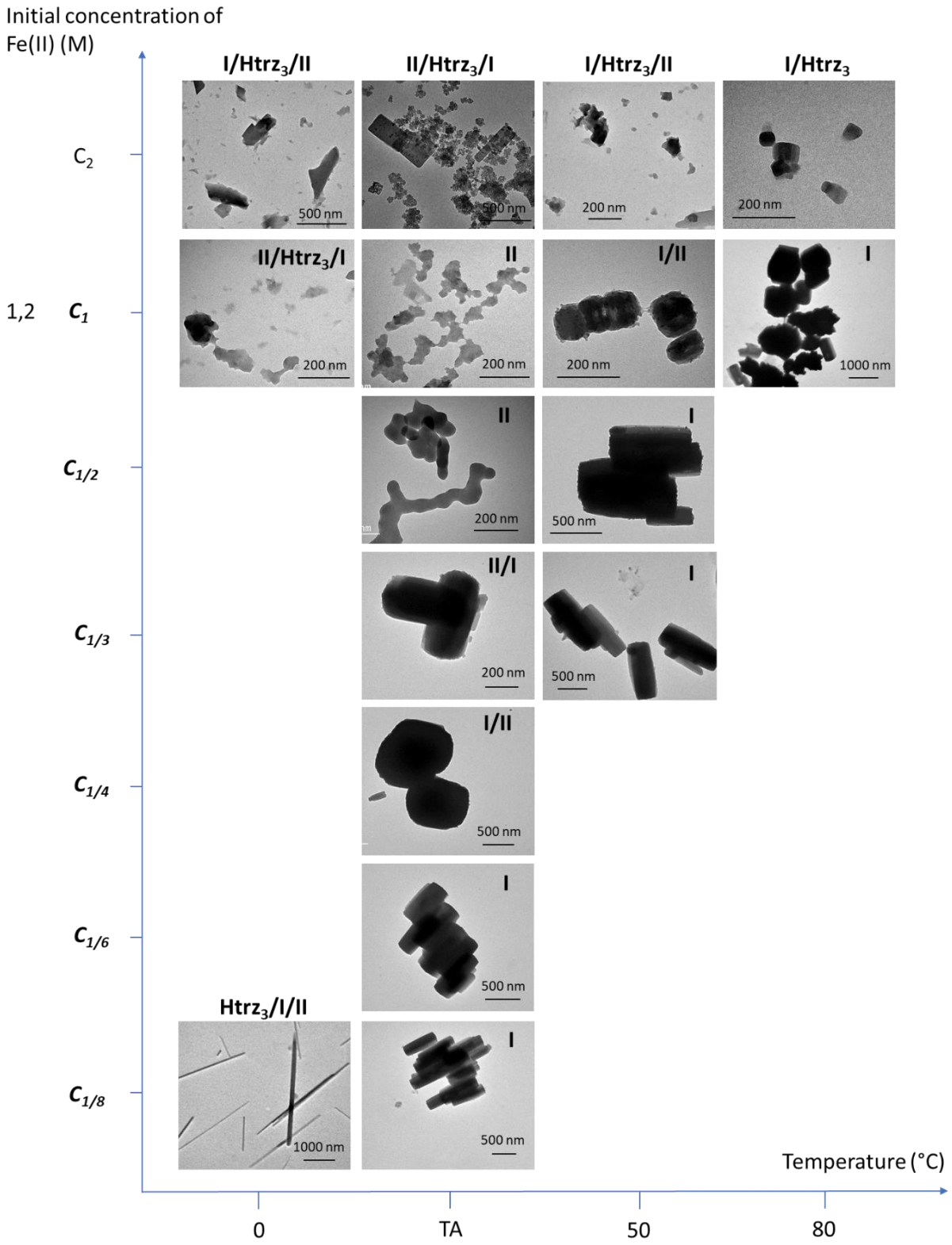

Figure SI6: Powder X-Ray diffractograms of the 16 compounds.

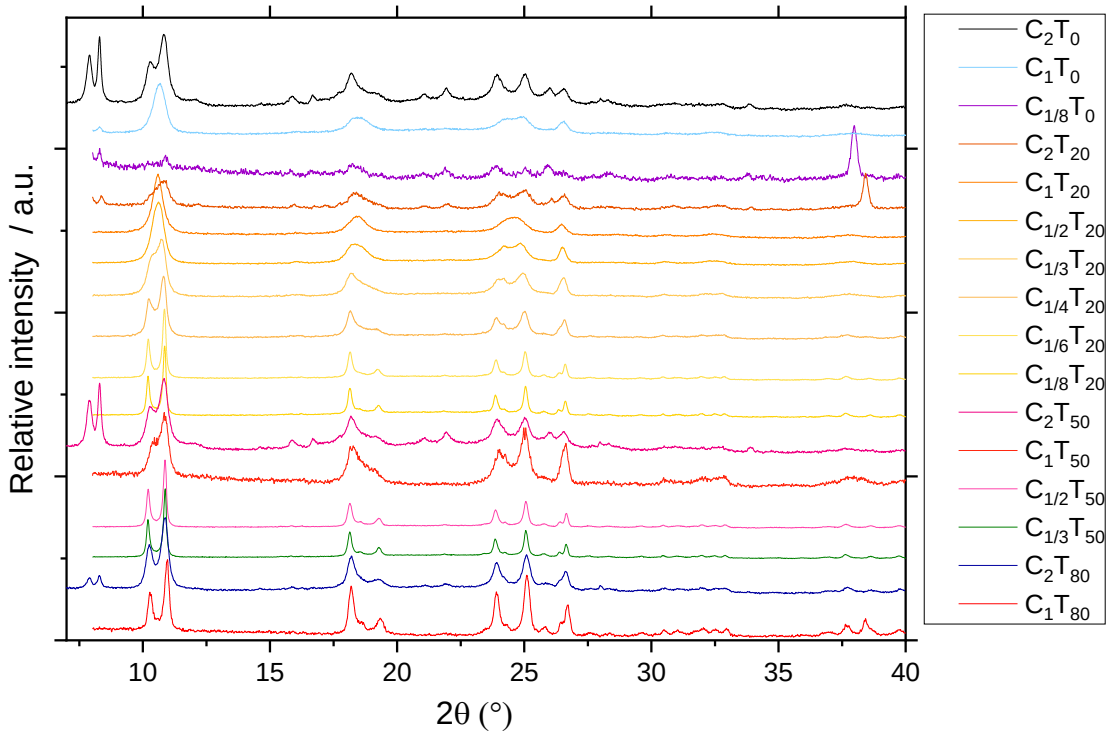

Figure SI7: Thermal dependence of the $\chi_M T$ product of the 16 compounds.