Electronic Supplementary Material (ESI) for CrystEngComm.

Polymorphism to master the spin crossover mechanism in $[Fe(PM\text{-}PeA)_2(NCSe)_2]$

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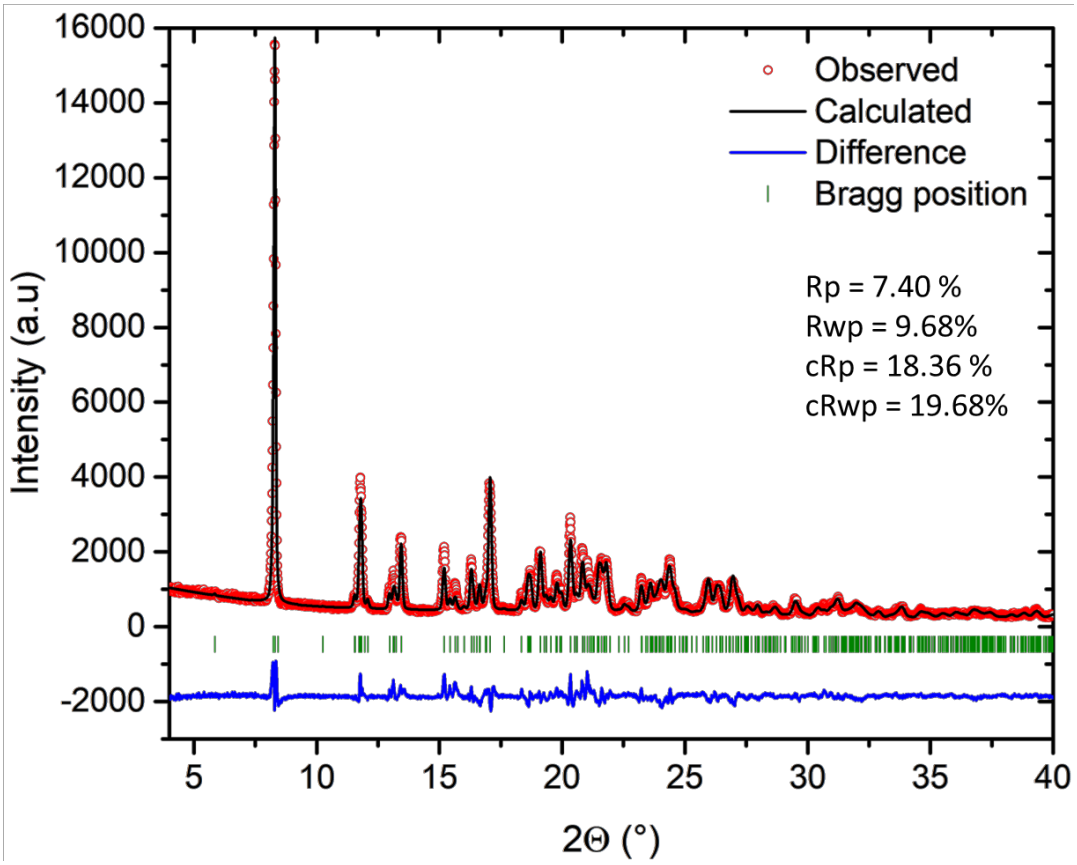


Figure 1: X-ray pattern recorded at room temperature (red circle), calculated diffractogram (black line) and the difference curve (blue line) of the polymorph-II of the molecular complex [Fe(PM-PeA)$_2$(NCSe)$_2$] in the HS state, with the Bragg positions in green.

Table 1: Elementary analysis on the crystalline powder of both polymorphs of [Fe(PM-PeA)$_2$(NCSe)$_2$] complex.

% atomic	C	H	N	Fe	Se
Calculated	60.74	3.40	10.12	6.73	19.02
Polymorph-I	59.60	3.69	9.82	6.58	16.59
Polymorph-II	57.85	3.24	9.86	6.37	15.38

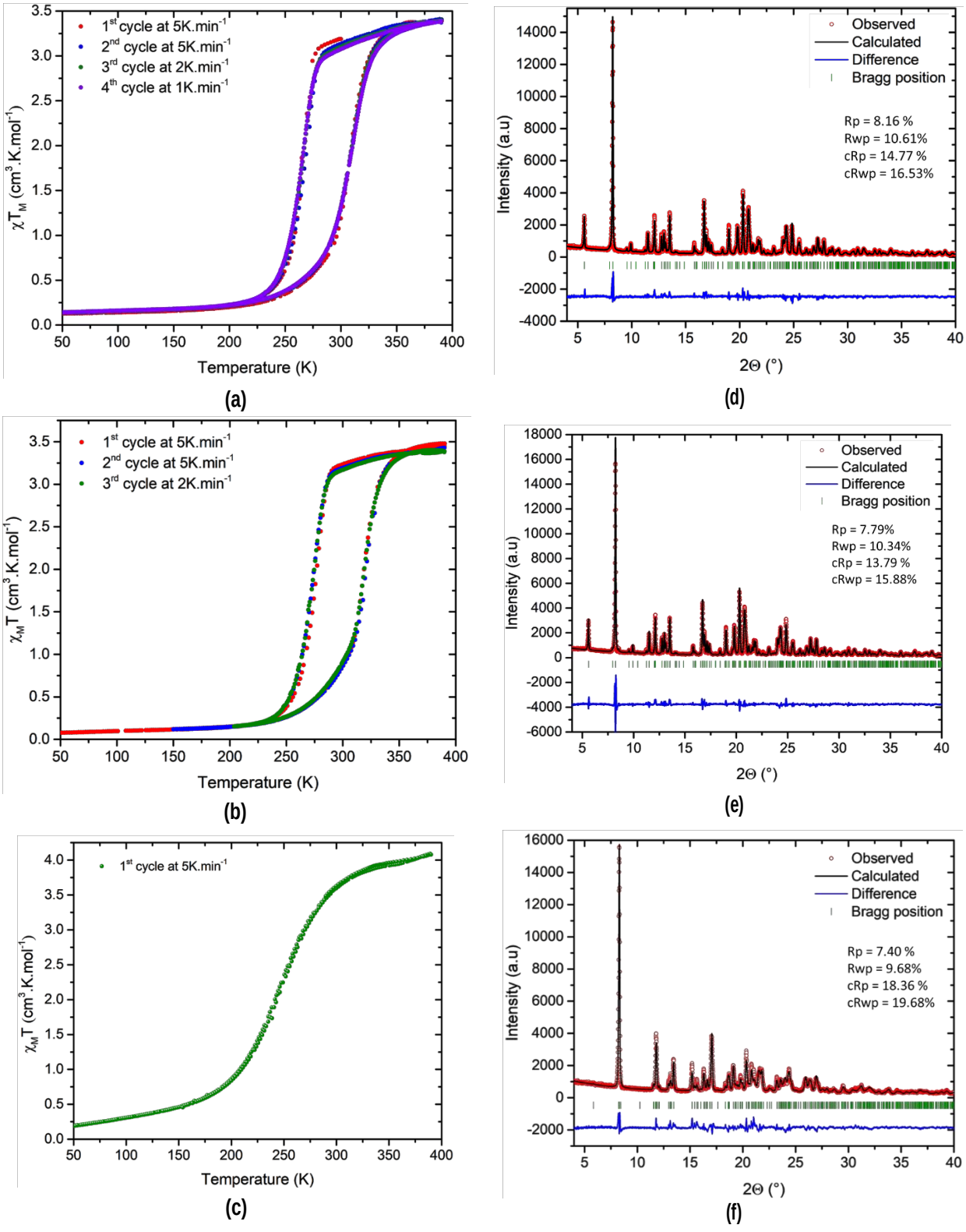


Figure 2: $\chi_M T$ as function of temperature determined on polymorph-I (a) batch 1 (b) and batch 2 and (c) on polymorph-II. Rietveld refinement on PXRD pattern recorded at room temperature in the HS state for polymorph-I (d) batch 1 (e) and batch 2 and (f) on polymorph-II.

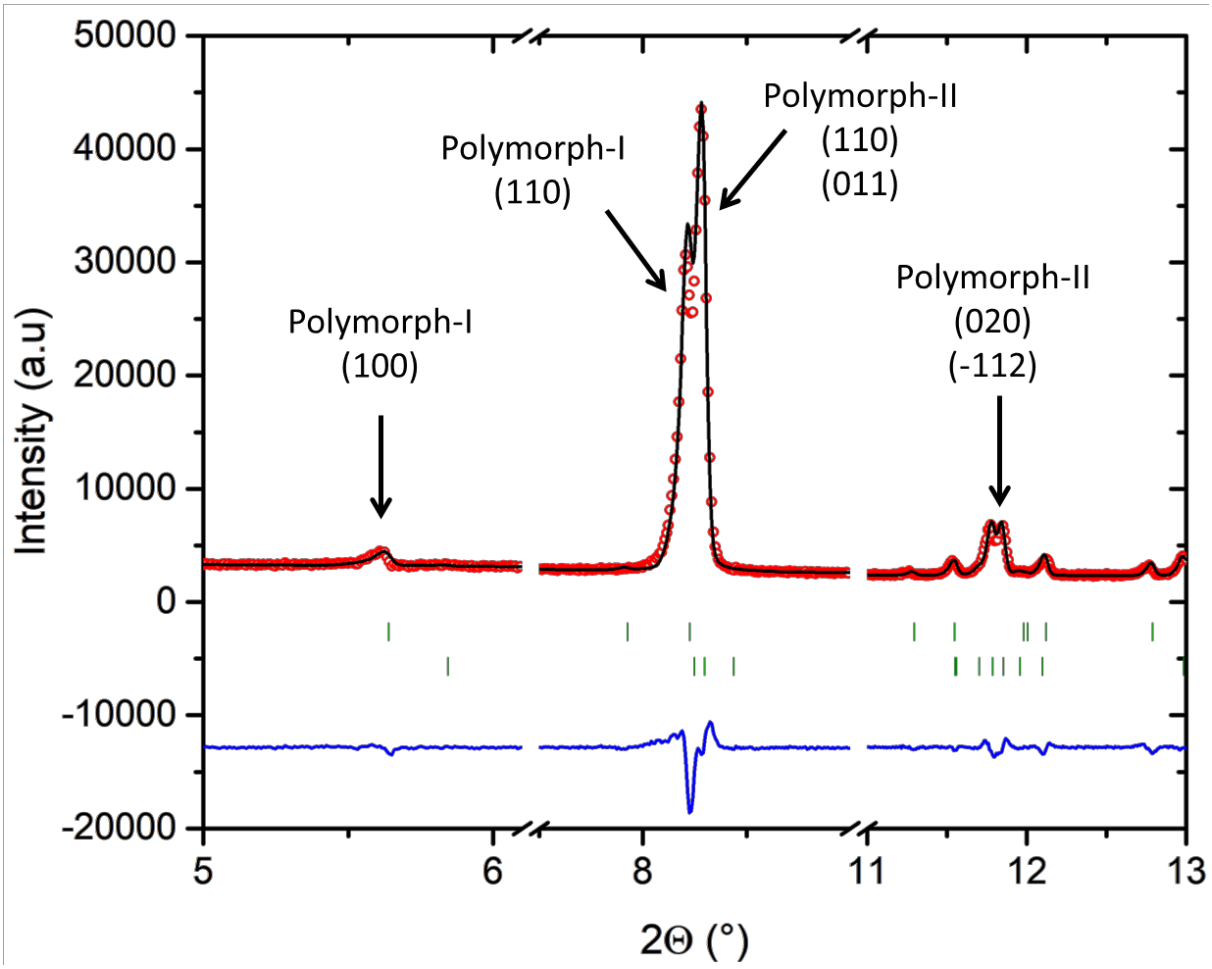
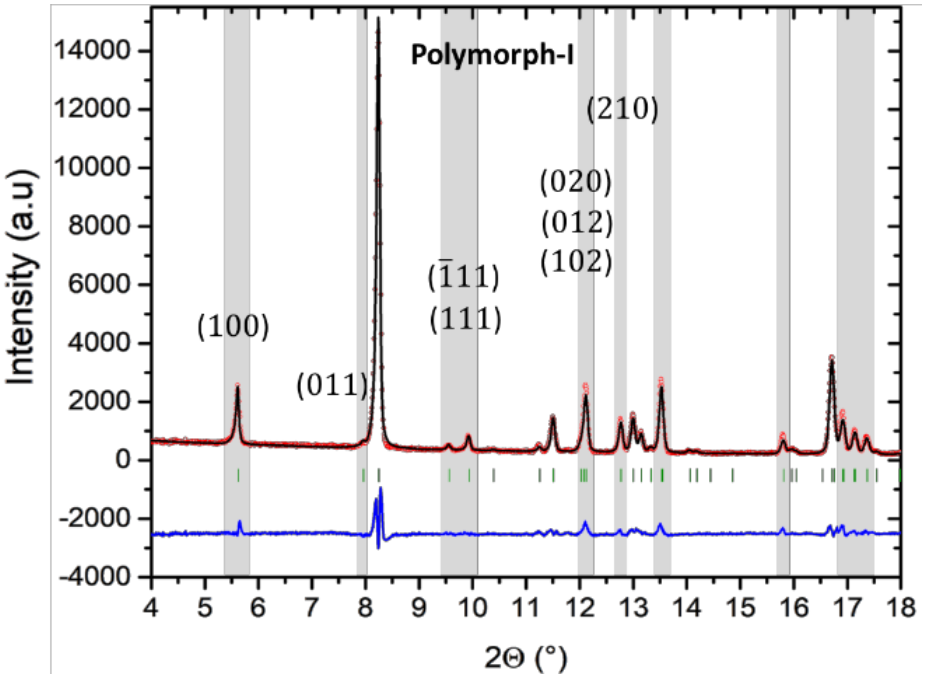
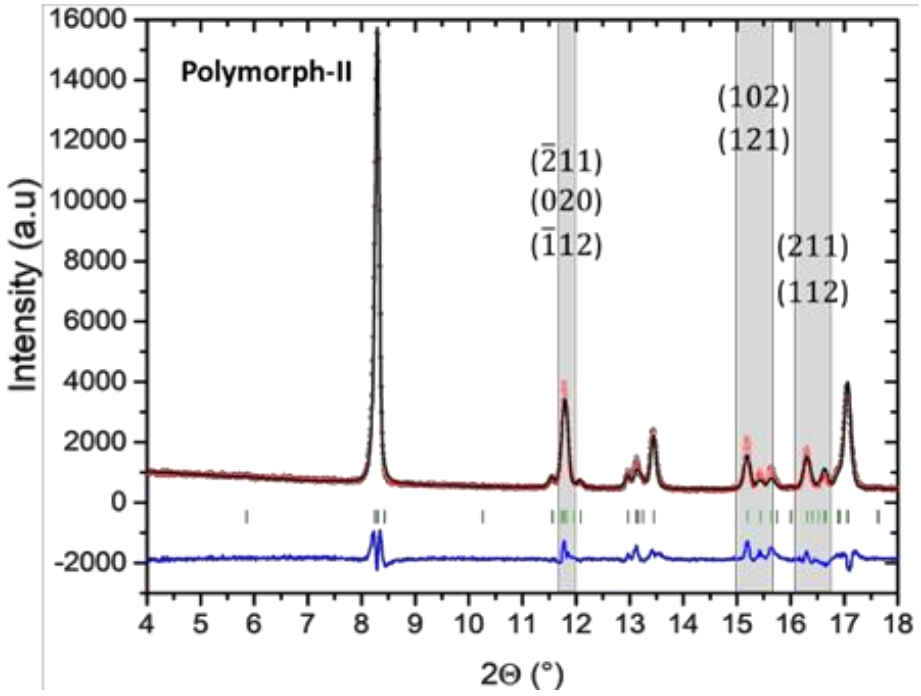


Figure 3: X-ray pattern recorded at room temperature showing the coexistence of the two polymorphs of the molecular complex [Fe(PM-PeA)$_2$(NCSe)$_2$], in the HS state, with characteristic Bragg peaks from each polymorph highlighted by arrows.



(a)



(b)

Figure 4: Characteristic Bragg peaks of (a) polymorph-I and (b) polymorph-II in the HS state, at room temperature. Differences between both polymorphs are highlighted by gray areas.

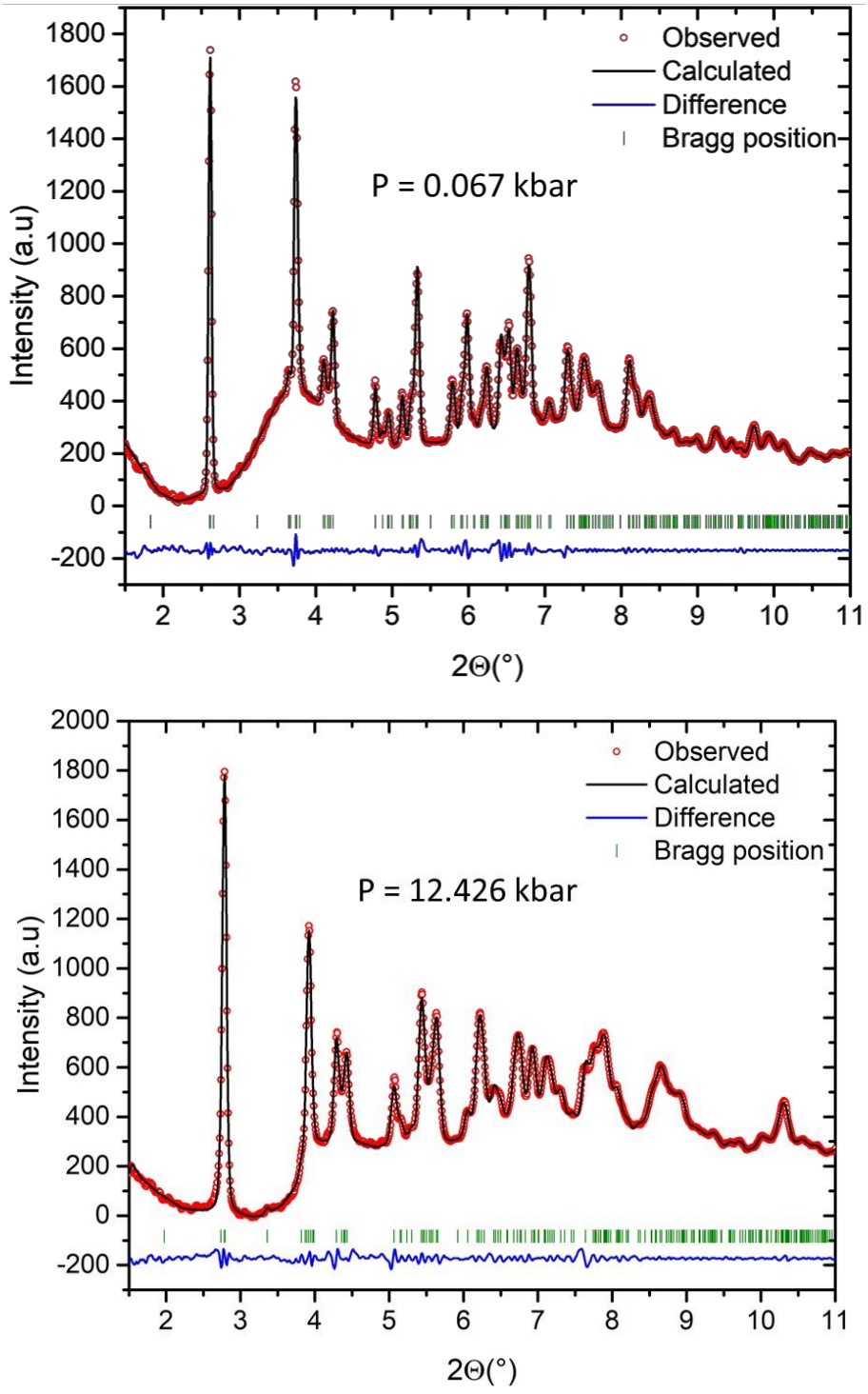


Figure 5: X-ray pattern recorded at room temperature in a pressure cell environment (red circle), without pressure (top) with a pressure of 12.426 kbar (down), the calculated diffractograms (black line), the difference curve (blue line) and the Bragg positions (green) for the polymorph-II of the molecular complex [Fe(PM-PeA)$_2$(NCSe)$_2$]. PXRD patterns recorded with λ=0.4859 Å.

Two complete collections of the diffracted intensities (293 K and 100 K) were carried out [1] on the same single-crystal, having a size of approximatively 10x10x50 µm3. The single-crystal was mounted on a polymer pen and positioned in the diffractometer, a Rigaku FRX microfocus with a copper rotating anode (Cu-Kα, λ = 1.54184 Å) associated with a hybrid Dectris Pilatus 200 K detector. The strategies for data collection were calculated for a monoclinic P2/m system and are given in the table 2 and table 3, respectively.

CrysalisPro software [2] was used to perform the data reduction. The crystal structures were solved by the direct methods and the atomic parameters were refined by the least squares method using the SHELX [3] suite in the Olex2 environment [4].

Table 2: Strategy for the data collection to determine the crystal structure of polymorph-II of [Fe(PM-PeA)$_2$(NCSe)$_2$] complex, at room temperature.

	Dx (mm)	2θ (°)	ω (°)	ϕ (°)	χ (°)	t_{exp} (s)	°/image (°)	Lenght of ω scan (°)
1st ω scan	45	-105	-195	144	24	25	1	180
2nd ω scan	45	5	-38	144	24	5	1	48
3rd ω scan	45	-105	-164	-180	60	25	1	149
4th ω scan	45	-41	-131	-144	60	5	1	180
5thω scan	45	-105	-178	108	60	25	1	126
6th ω scan	45	-105	-195	-36	48	25	1	149
7th ω scan	45	-41	-131	0	36	5	1	180
8th ω scan	45	-105	-164	-144	60	25	1	131
9thω scan	45	-105	-182	144	60	25	1	94
10th ω scan	45	-105	-194	-108	60	25	1	132
11th ω scan	45	-41	-124	0	60	5	1	54
12th ω scan	45	-105	-195	-36	60	25	1	80

Table 3:Strategy for the data collection to determine the crystal structure of polymorph-II of [Fe(PM-PeA)$_2$(NCSe)$_2$] complex, at 100K.

	Dx (mm)	2θ (°)	ω (°)	ϕ (°)	χ (°)	t_{exp} (s)	°/image (°)	Lenght of ω scan (°)
1st ω scan	45	-105	-195	-36	60	20	1	180
2nd ω scan	45	5	-85	-108	48	5	1	48
3rd ω scan	45	-105	-195	144	36	20	1	180
4th ω scan	45	-41	-131	-108	60	10	1	180
5th ω scan	45	-105	-195	-108	60	20	1	180
6th ω scan	45	-105	-194	72	48	20	1	179
7th ω scan	45	-41	-105	-72	48	10	1	153
8th ω scan	45	-105	-184	-72	12	20	1	57
9th ω scan	45	-41	-128	72	36	10	1	61
10th ω scan	45	-105	-179	-144	60	20	1	45
11th ω scan	45	-105	-60	-108	12	20	1	45
12th ω scan	45	-105	-190	0	60	20	1	45
13th ω scan	45	-105	-158	-72	60	20	1	84
14th ω scan	45	-105	-195	72	60	20	1	80

References :

[1] CrystalClear-SM Expert 2.1 (Rigaku, Jun 7th 2013) Software, Version 5.6.2.0, Tokyo, Japan.

[2] Oxford Diffraction/ Agilent Technologies UK Ltd, **n.d.**

[3] (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Crystallogr.* **2008**, *64*, 112–122 (b) G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

[4] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

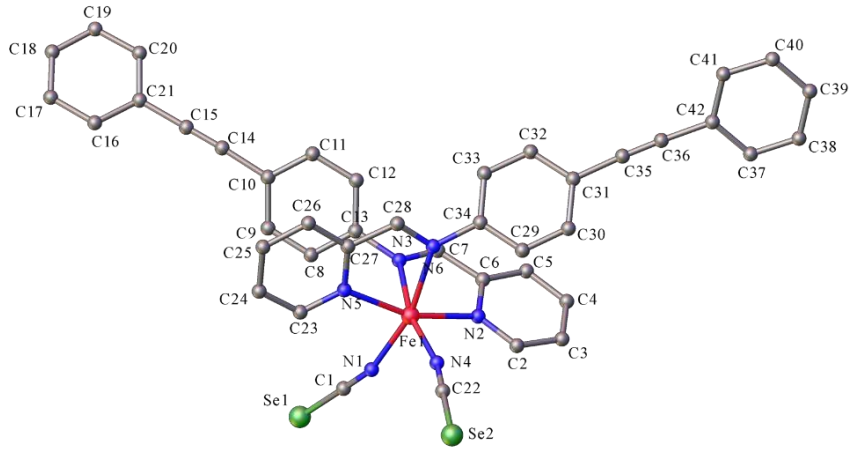


Figure 6: Labelling of the atoms of the asymmetric unit of mP2$_1$/c (HS) phase of polymorph-I of [Fe(PM-PeA)$_2$(NCSe)$_2$]. For more clarity, H atoms have been removed but their labelling are identical to the one of C atom they are bonded to.

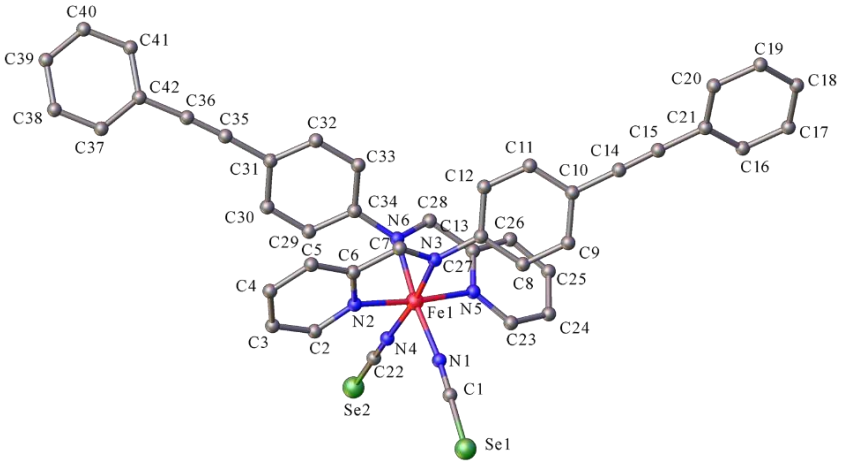


Figure 7: Labelling of the atoms of the asymmetric unit of mP2$_1$/c (HS) phase of polymorph-II of [Fe(PM-PeA)$_2$(NCSe)$_2$]. For more clarity, H atoms have been removed but their labelling are identical to the one of C atom they are bonded to.

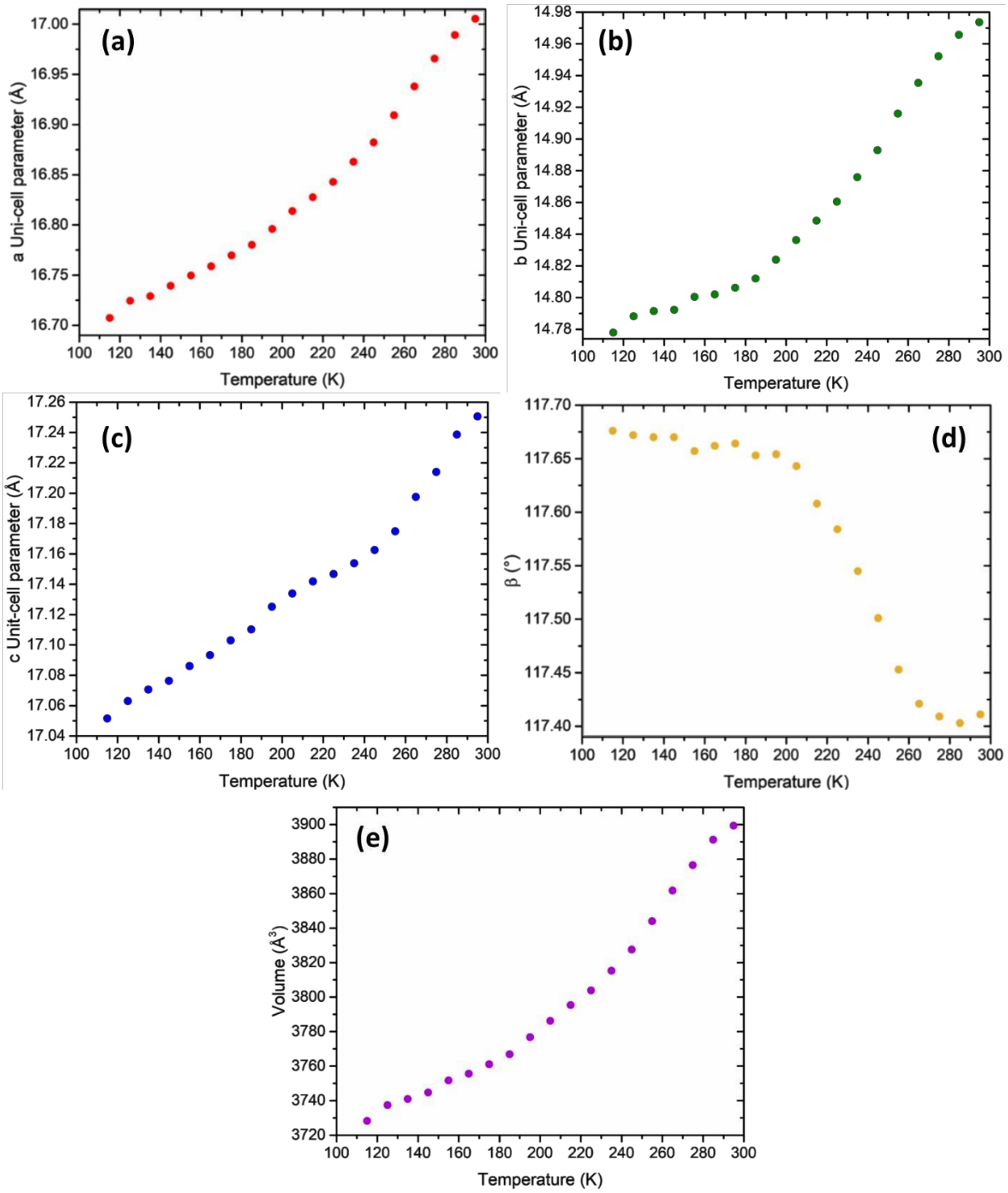


Figure 8: (a)-(d) Temperature dependences of lattice parameters and (e) evolution in temperature of the volume of the unit-cell of of [Fe(PM-PeA)$_2$(NCSe)$_2$], polymorph-II