

Supporting Information

Mononuclear iron(II) complex: cooperativity, kinetics and activation energy of solvent-dependent spin transition

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1. CHEMISTRY

General

The synthesis was carried out in deoxygenated EtOH under an inert atmosphere of argon using standard glovebox techniques. The ligand L was prepared according to the procedure previously reported.^{S1} All other reagents and solvents were commercially available and were used without additional purification. Elemental analysis (C, H, N) was performed with a EuroEA3000 analyzer using standard technique.

S1 M. B. Bushuev, Y. V. Gatilov, E. B. Nikolaenkova, V. G. Vasiliev and V. P. Krivopalov, *Inorg. Chim. Acta*, 2013, **395**, 95.

Synthesis of $[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, ($1^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$) and $[\text{FeL}_2](\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ ($\beta\text{-}1^{\text{LS}} \cdot x\text{H}_2\text{O}$)

A solution of L (0.040 mmol, 10.6 mg) in EtOH (0.7 mL) was added to a solution of $\text{Fe}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.020 mmol, 6.8 mg) in EtOH (0.7 mL). The solution turned dark red. Dark red needle crystals began to form in ca. 1 min. The formation of a new crystalline phase (prismatic well shaped dark red crystals) was detected in 2 – 3 days. Transformation of needle crystals into prismatic ones took ca. 2 weeks. After that, the prismatic crystals were filtered off, washed with EtOH, and dried in the ambient air. Yield: 14.0 mg (86%). Elemental analysis for a freshly prepared sample (%), calcd for $\text{C}_{32}\text{H}_{38}\text{N}_{10}\text{B}_2\text{F}_8\text{FeO}_2$ ($[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, 824.18): C 46.6, H 4.4, N 17.0; found C 46.9, H 4.4, N 16.8.

In the ambient air the crystals of $1^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ lose the solvent molecules transforming into the phase $[\text{FeL}_2](\text{BF}_4)_2 \cdot x\text{H}_2\text{O}$ ($\beta\text{-}1^{\text{LS}} \cdot x\text{H}_2\text{O}$). Elemental analysis for a sample after staying at room temperature in the ambient air for four days (%), calcd for $\text{C}_{32}\text{H}_{37}\text{N}_{10}\text{B}_2\text{F}_8\text{FeO}$ ($[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$, 778.11): C 46.3, H 4.1, N 18.0; found C 46.7, H 4.3, N 17.8. Elemental analysis for a sample after staying at room temperature in the ambient air for a month (%), calcd for $\text{C}_{32}\text{H}_{37}\text{N}_{10}\text{B}_2\text{F}_8\text{FeO}$ ($[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{H}_2\text{O}$, 778.11): C 46.3, H 4.1, N 18.0; found C 46.4, H 4.0, N 18.1. This tendency shows that EtOH molecules easily evaporate even at room temperature.

2. CRYSTAL STRUCTURES

Experimental details

The data were collected with crystals of $[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, $[\text{FeL}_2](\text{BF}_4)_2$ and $[\text{FeL}_2](\text{BF}_4)_2 \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ ($y = 0.41$, $z = 0.40$) with a Bruker APEX II CCD diffractometer using graphite monochromated Mo- $K\alpha$ radiation ($[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ $T = 200$ K, $[\text{FeL}_2](\text{BF}_4)_2$ $T = 296$ K, $[\text{FeL}_2](\text{BF}_4)_2 \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ ($y = 0.41$, $z = 0.40$) $T = 296$ K; $\lambda = 0.71073$ Å). The structures were solved by direct methods and the refinement on F^2 and all further calculations were carried out with the SHELX suite.^{S2} All non-hydrogen and major parts of disordered atoms were refined anisotropically. All disordered parts were refined with restraints. Hydrogen atoms were placed geometrically on their carrier atoms and were refined with a riding model.

S2 G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3 – 8.

Crystallographic data for $[\text{FeL}_2](\text{BF}_4)_2 \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ ($\mathbf{1}^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$)

Formula $\text{C}_{32}\text{H}_{38}\text{B}_2\text{F}_8\text{FeN}_{10}\text{O}_2$, $M = 824.19$, monoclinic, space group $P2/c$, $a = 16.9811(4)$, $b = 11.3326(3)$, $c = 20.1037(6)$ Å, $\beta = 105.433(1)^\circ$, $V = 3729.26(17)$ Å³, $Z = 4$, $D_{\text{calc}} = 1.468$ g·cm⁻³, $\mu = 0.490$ mm⁻¹, min/max transmission = 0.916/0.954, $\theta_{\text{max}} = 27.9^\circ$, measured 70474, unique 8911 ($R_{\text{int}} = 0.0351$), observed [$I_o > 2 \sigma(I)$] 7290 reflections, $R_1 = 0.0513$ (I_o), $wR_2 = 0.1744$ (all), Gof = 0.959, $\Delta\rho_{\text{max}} = 1.17$, $\Delta\rho_{\text{min}} = -0.58$ e·Å⁻³, CCDC 1409266.

One tetrafluoroborate ion is disordered over two positions with occupancies 0.745(7):0.255(7). The ethanol molecules and water molecules (O2 and O3) are also disordered with occupancies 0.5:0.5. Hydrogen atoms of water molecules could not be found and were omitted in the structural model.

Crystallographic data for $[\text{FeL}_2](\text{BF}_4)_2$ ($\mathbf{1}^{\text{ALS}}$)

After the thermal cycling of the samples **1**, **14** and **15** (high m/V ratio, parent phase $\mathbf{1}^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, see below) had been done we found that the samples looked like bunches of single crystals and managed to find one suitable for X-ray single crystal analysis. The single crystal which appeared to be that one of the phase $\mathbf{1}^{\text{ALS}}$ was taken from the sample **14**.

Formula $\text{C}_{30}\text{H}_{30}\text{B}_2\text{F}_8\text{FeN}_{10}$, $M = 760.11$, orthorhombic, space group $Pbca$, $a = 12.8079(14)$, $b = 19.1932(19)$, $c = 27.373(3)$ Å, $V = 6729.1(12)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.501$ g·cm⁻³, $\mu = 0.532$ mm⁻¹, min/max transmission = 0.605/0.970, $\theta_{\text{max}} = 25.4^\circ$, measured 61787, unique 6143 ($R_{\text{int}} = 0.1356$), observed [$I_o > 2 \sigma(I)$] 3840 reflections, $R_1 = 0.0653$ (I_o), $wR_2 = 0.2179$ (all), Gof = 0.901, $\Delta\rho_{\text{max}} = 0.74$, $\Delta\rho_{\text{min}} = -0.51$ e·Å⁻³, CCDC 1409267.

Both tetrafluoroborate ion are disordered over two positions with occupancies 0.61(1):0.39(1) and 0.613(9):0.387(9).

Crystallographic data for $[\text{FeL}_2](\text{BF}_4)_2 \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ ($1^{\text{E/LS}} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$)

A single crystal of the phase $1^{\text{E/LS}} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ ($y = 0.41$, $z = 0.40$) suitable for X-ray analysis was taken from the sample **21** after thermal cycling.

Formula $\text{C}_{30.82}\text{H}_{33.26}\text{B}_2\text{F}_8\text{FeN}_{10}\text{O}_{0.81}$, $M = 786.20$, monoclinic, space group $C2/c$, $a = 46.241(3)$, $b = 8.2140(5)$, $c = 18.5849(10)$ Å, $\beta = 93.444(4)^\circ$, $V = 7046.3(7)$ Å³, $Z = 8$, $D_{\text{calc}} = 1.482$ g·cm⁻³, $\mu = 0.512$ mm⁻¹, min/max transmission = 0.831/0.912, $\theta_{\text{max}} = 25.4^\circ$, measured 50445, unique 6402 ($R_{\text{int}} = 0.0475$), observed [$I_o > 2 \sigma(I)$] 5086 reflections, $R_1 = 0.0715$ (I_o), $wR_2 = 0.1968$ (all), Gof = 1.133, $\Delta\rho_{\text{max}} = 0.78$, $\Delta\rho_{\text{min}} = -0.46$ e·Å⁻³, CCDC 1409268.

One tetrafluoroborate ion, ethanol and water molecules are disordered over two positions with occupancies 0.37(2):0.63(2), 0.41(1):0.41(1), 0.40(1):0.40(1) accordingly.

Table S1

Selected bond lengths (Å) and angles (°) in the crystal structures of [FeL₂](BF₄)₂·EtOH·H₂O, [FeL₂](BF₄)₂ and [FeL₂](BF₄)₂·0.41EtOH·0.4H₂O.

Bond length	1^{LS}·EtOH·H₂O	1^{A/LS}	1^{E/LS}·0.41EtOH·0.4H₂O
Fe(1)–N(2)	1.8882(18)	1.884(4)	1.889(3)
Fe(1)–N(3)	1.9869(19)	1.981(3)	1.983(4)
Fe(1)–N(5)	1.998(2)	1.982(4)	2.005(4)
Fe(1)–N(7)	1.8860(18)	1.882(4)	1.888(3)
Fe(1)–N(8)	1.983(2)	1.984(4)	1.982(4)
Fe(1)–N(10)	1.998(2)	1.992(4)	1.998(4)
Angle			
N(2)–Fe(1)–N(3)	80.80(8)	80.75(15)	80.68(15)
N(2)–Fe(1)–N(5)	79.28(8)	79.69(15)	79.06(14)
N(2)–Fe(1)–N(7)	178.46(8)	178.53(16)	179.21(15)
N(2)–Fe(1)–N(8)	100.53(8)	100.78(15)	99.47(15)
N(2)–Fe(1)–N(10)	99.13(8)	98.84(15)	100.51(15)
N(3)–Fe(1)–N(5)	160.00(8)	160.43(16)	159.64(14)
N(3)–Fe(1)–N(7)	98.44(8)	99.96(15)	98.63(15)
N(3)–Fe(1)–N(8)	90.70(8)	92.29(15)	93.29(15)
N(3)–Fe(1)–N(10)	92.34(8)	88.74(15)	89.38(15)
N(5)–Fe(1)–N(7)	101.52(8)	99.59(15)	101.65(15)
N(5)–Fe(1)–N(8)	91.24(8)	91.85(16)	88.20(15)
N(5)–Fe(1)–N(10)	92.50(8)	93.74(14)	96.13(15)
N(7)–Fe(1)–N(8)	80.80(8)	80.50(16)	80.91(15)
N(7)–Fe(1)–N(10)	79.54(8)	79.91(15)	79.10(15)
N(8)–Fe(1)–N(10)	160.34(8)	160.26(16)	160.01(15)

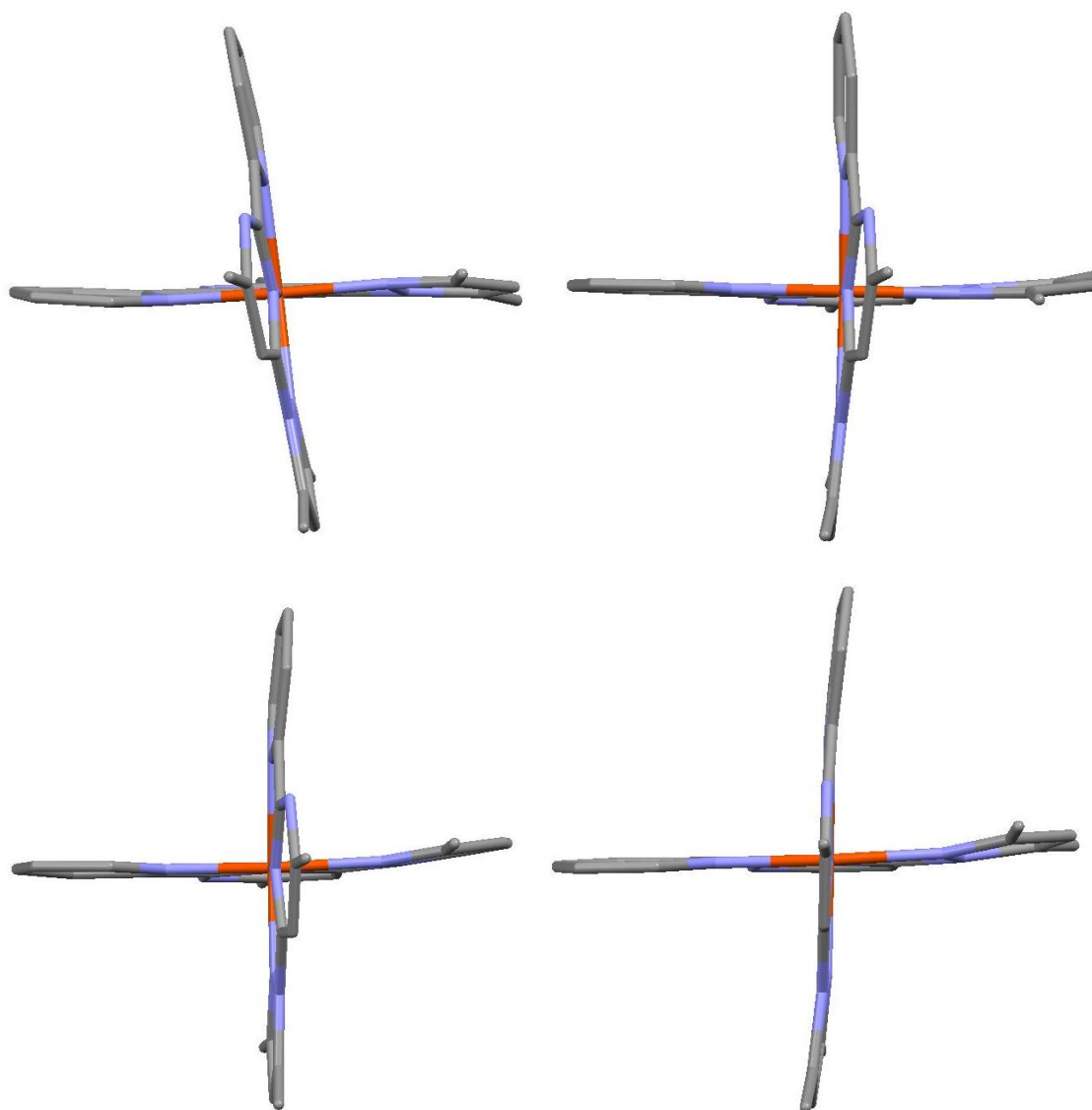


Figure S1. Structural distortions exhibited by $[\text{FeL}_2]^{2+}$ in the phases $\alpha\text{-1}^{\text{LS}}\cdot x\text{H}_2\text{O}$ (top, left, $\varphi = 177.4^\circ$, $\theta = 82.1^\circ$), $1^{\text{LS}}\cdot \text{EtOH}\cdot \text{H}_2\text{O}$ (top, right, $\varphi = 178.5^\circ$, $\theta = 88.0^\circ$), 1^{ALS} (bottom, left, $\varphi = 178.6^\circ$, $\theta = 86.0^\circ$) and $1^{\text{ELS}}\cdot y\text{EtOH}\cdot z\text{H}_2\text{O}$ (bottom, right, $\varphi = 179.2^\circ$, $\theta = 83.3^\circ$). Hydrogen atoms are omitted for clarity.

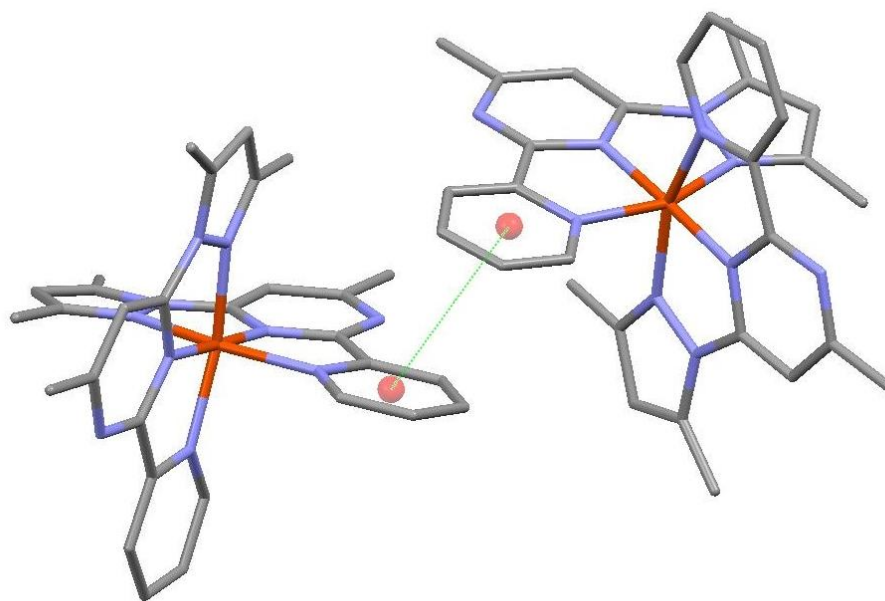


Figure S2. π - π stacking interactions between N3C6–C10 pyridine rings of neighboring FeL_2 units in the structure of $\mathbf{1}^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$. Hydrogen atoms are omitted for clarity. $\text{Cg} \cdots \text{Cg} = 3.8829(16) \text{ \AA}$, $\alpha = 15^\circ$, $\beta = \gamma = 23.91^\circ$, where α is the dihedral angle between the planes I and J, β is the angle between the $\text{Cg}(\text{I}) \rightarrow \text{Cg}(\text{J})$ vector and the normal to the plane I, γ is the angle between the $\text{Cg}(\text{I}) \rightarrow \text{Cg}(\text{J})$ vector and the normal to the plane J.

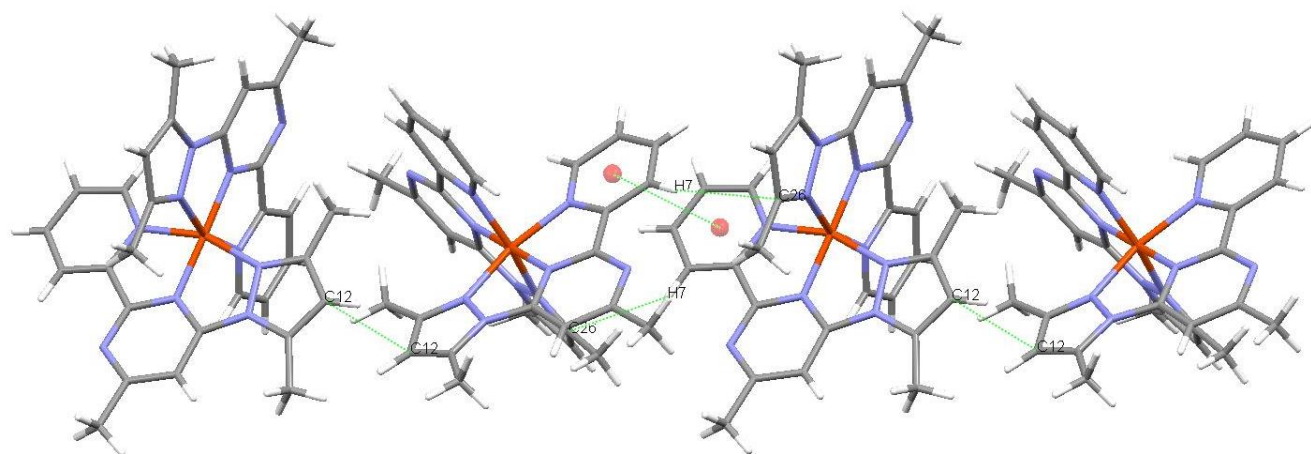


Figure S3. 1D-chain in the structure of $\mathbf{1}^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ ($\text{C12} \cdots \text{C12} \ 3.34 \text{ \AA}$, $\text{H7} \cdots \text{C26} \ 2.85 \text{ \AA}$).

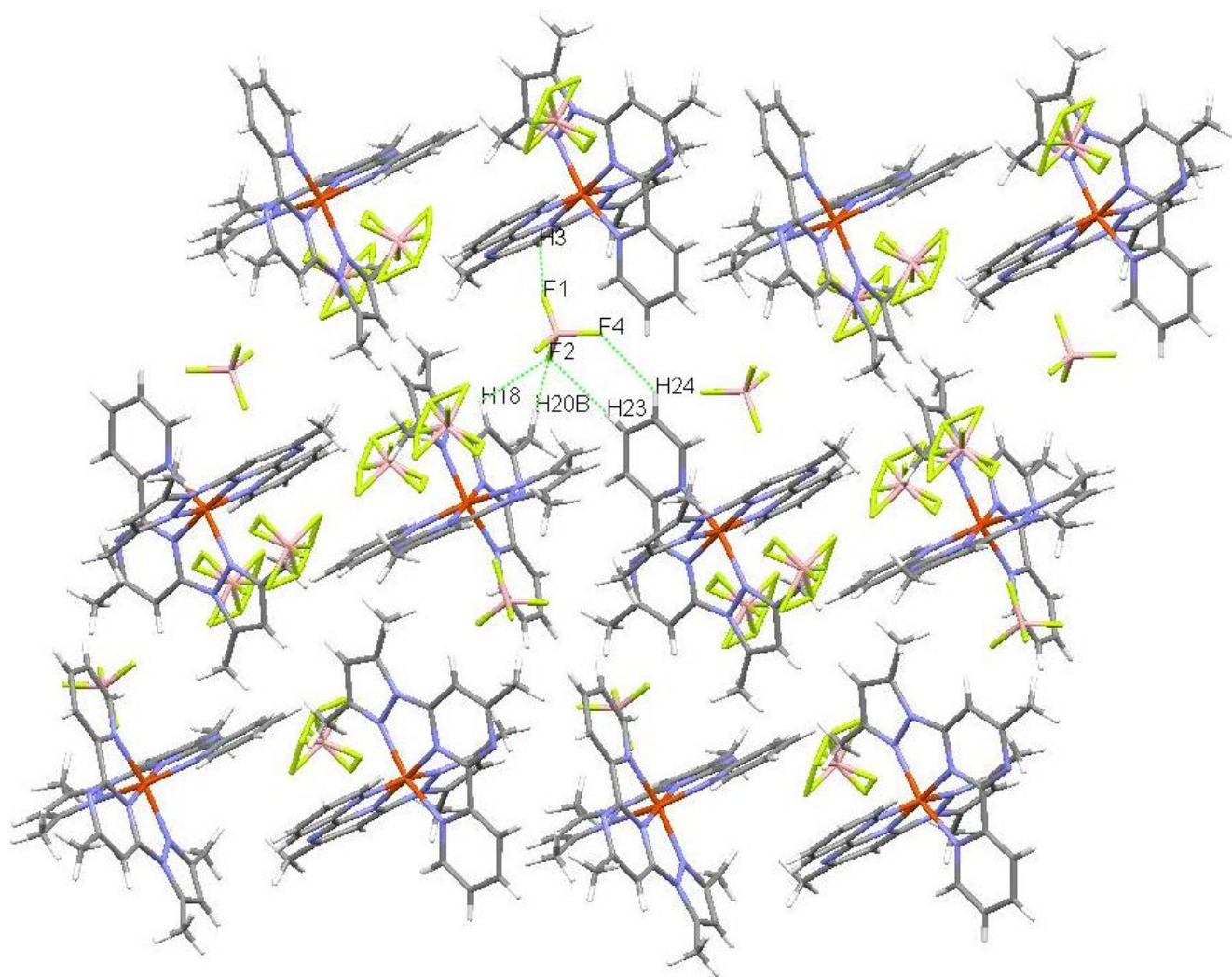


Figure S4. Packing of 1D chains in the structure of $1^{LS}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$. Short F \cdots H contacts between the $[\text{FeL}_2]^{2+}$ cation and the non-disordered anion are shown (H3 \cdots F1 2.54 Å, H20B \cdots F2 2.63 Å, H18 \cdots F2 2.62 Å, H23 \cdots F2 2.63 Å, H24 \cdots F4 2.66 Å).

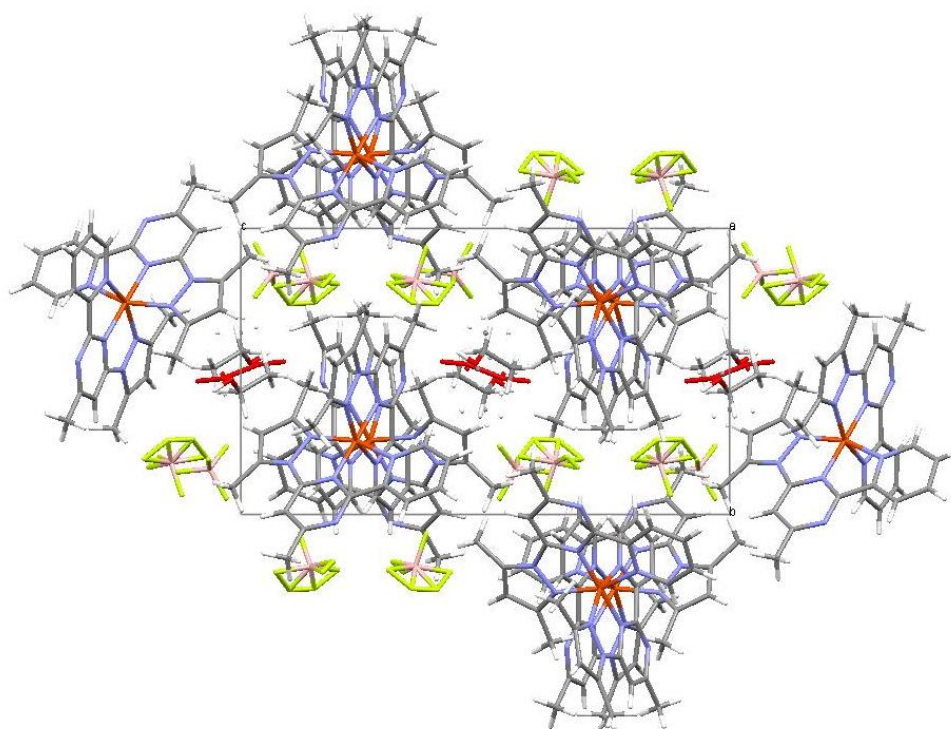


Figure S5. Packing diagram for $1^{\text{LS}}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$. View along the *a* axis.

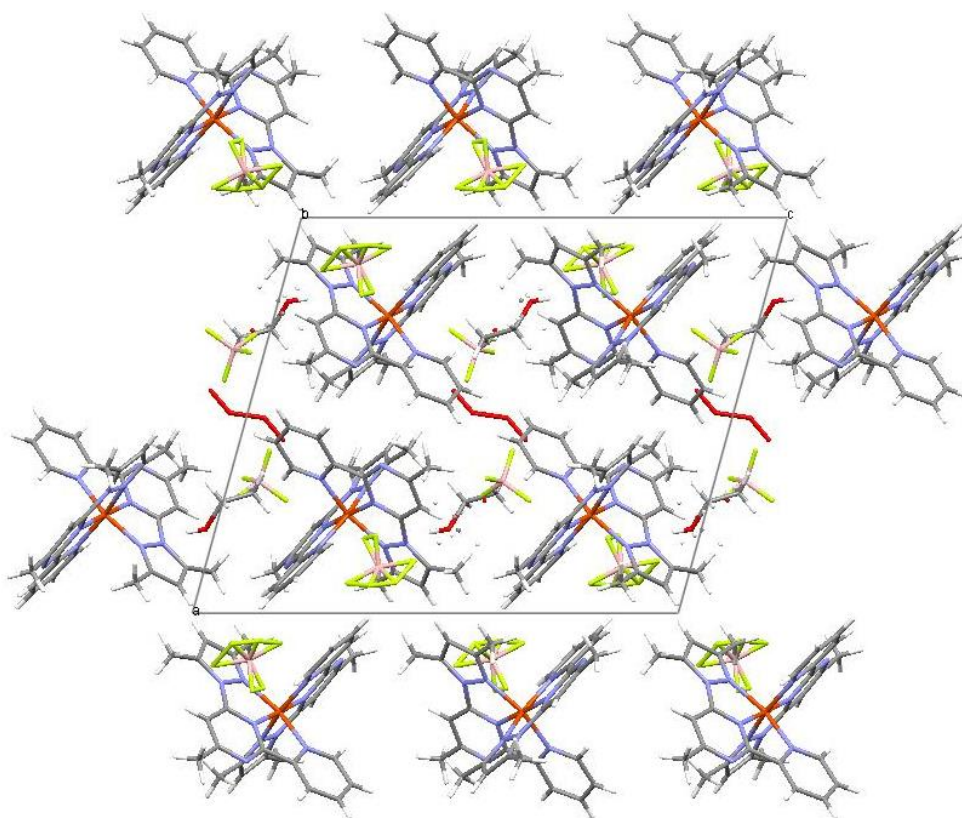


Figure S6. Packing diagram for $1^{\text{LS}}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$. View along the *b* axis.

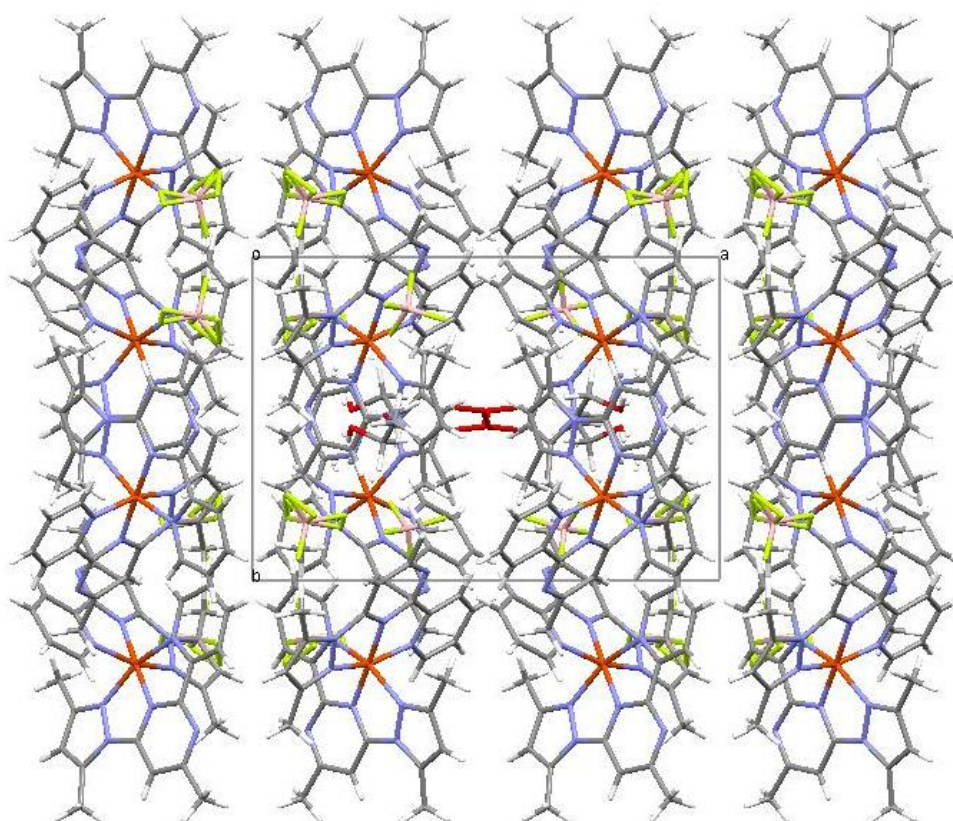


Figure S7. Packing diagram for $1^{\text{LS}}\cdot\text{EtOH}\cdot\text{H}_2\text{O}$. View along the *c* axis.

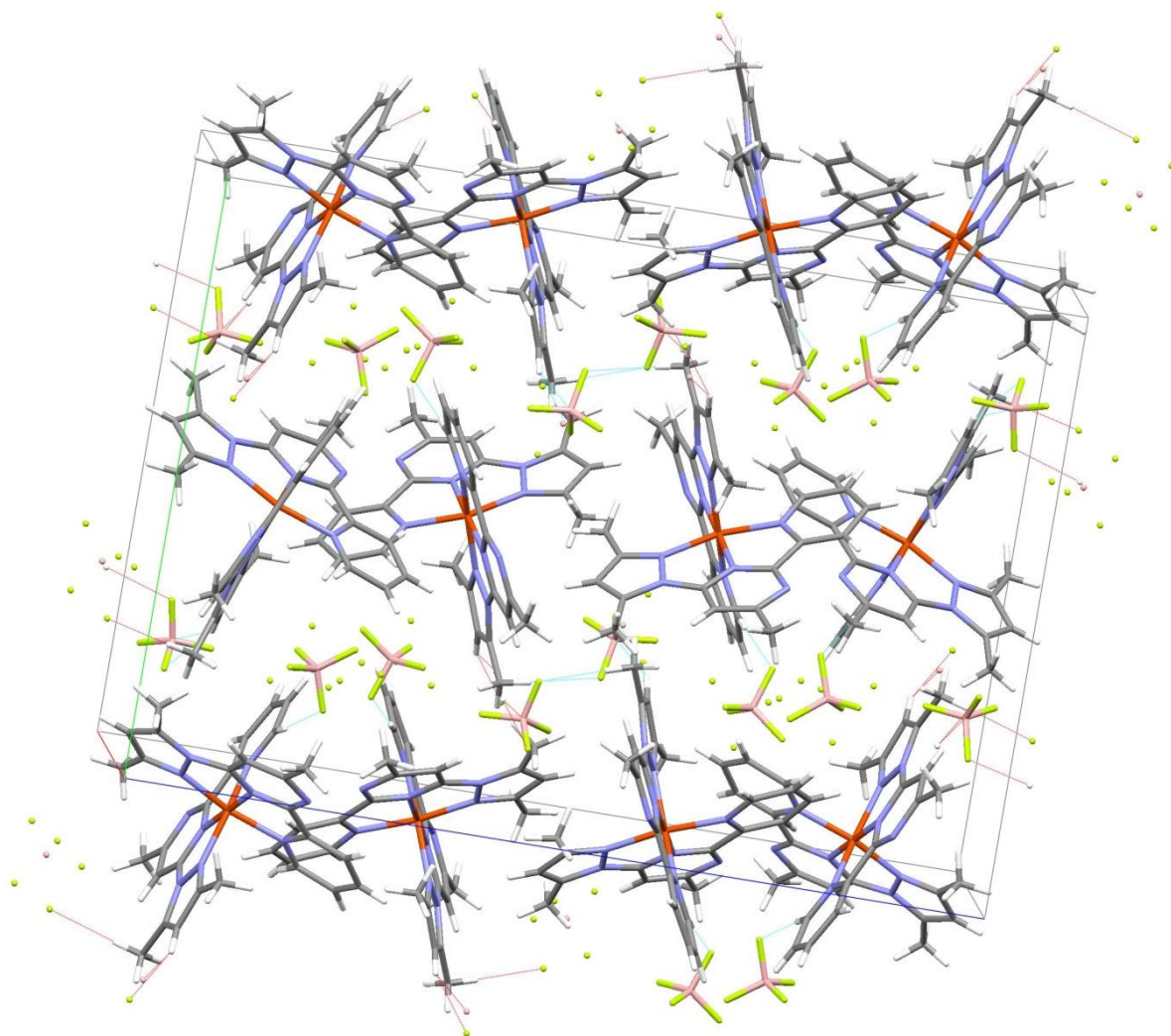


Figure S8. Packing diagram for 1^{ALS} . View along the *a* axis. Short contacts (less than sum of VDW radii by 0.2 Å) are also displayed.

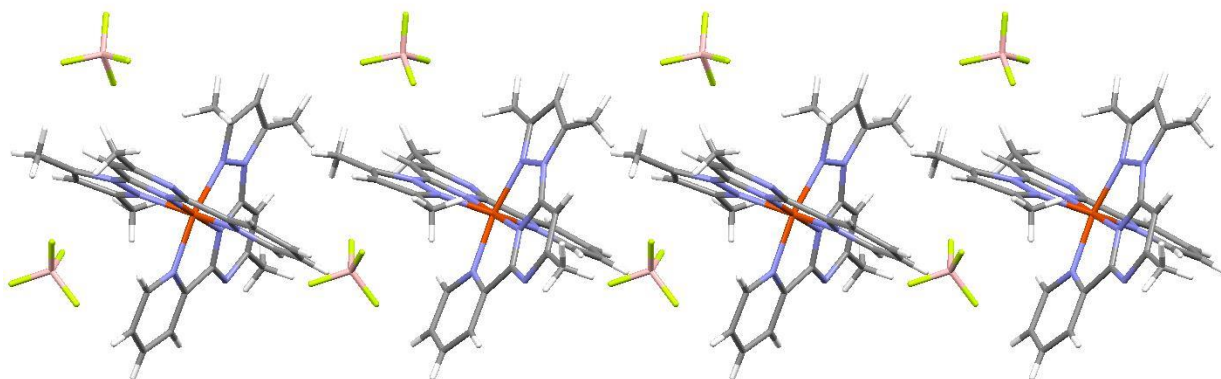


Figure S9. 1D chain in the structure of $1^{A/LS}$ (only one orientation for each disordered anion is shown).

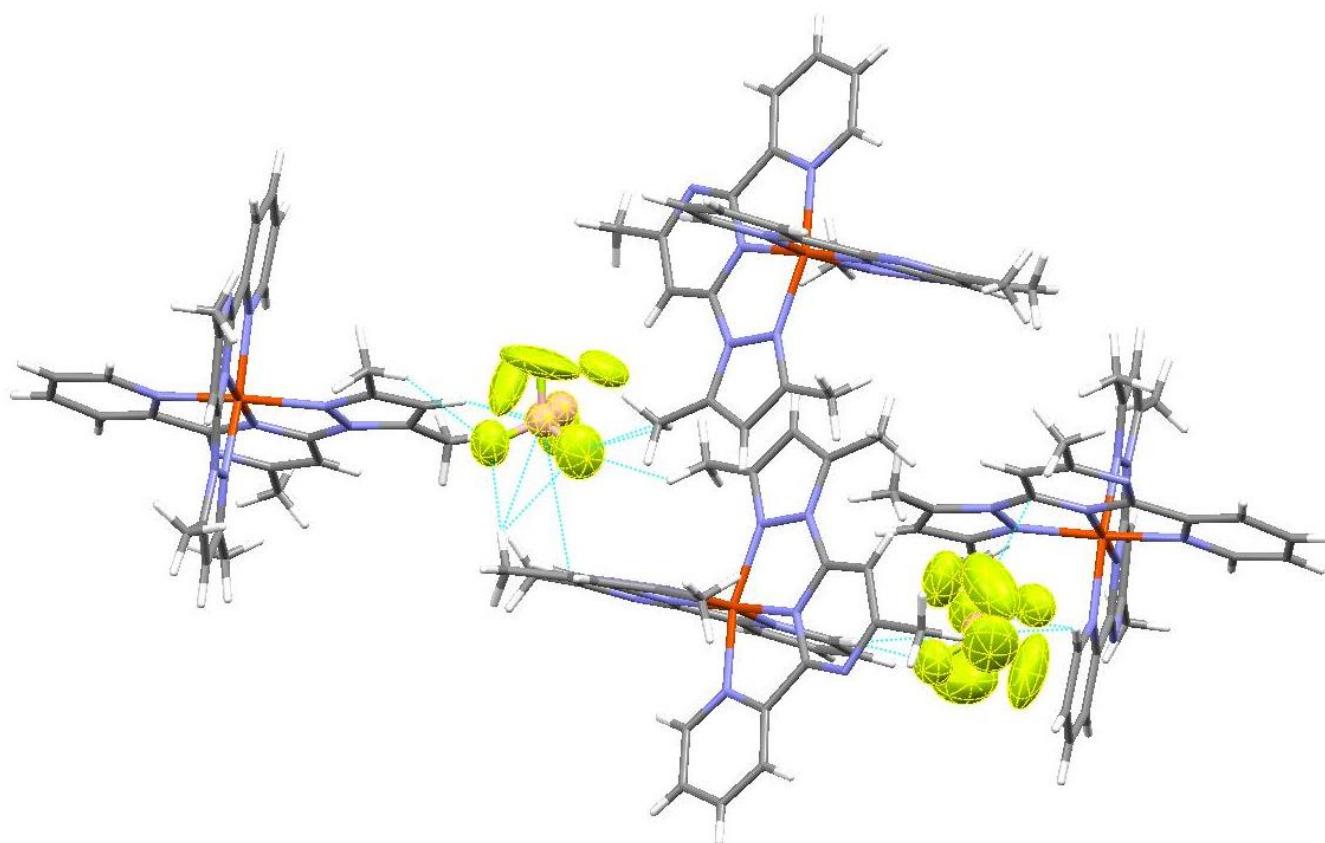


Figure S10. Disordered BF_4^- anions in the structure of $1^{A/LS}$.

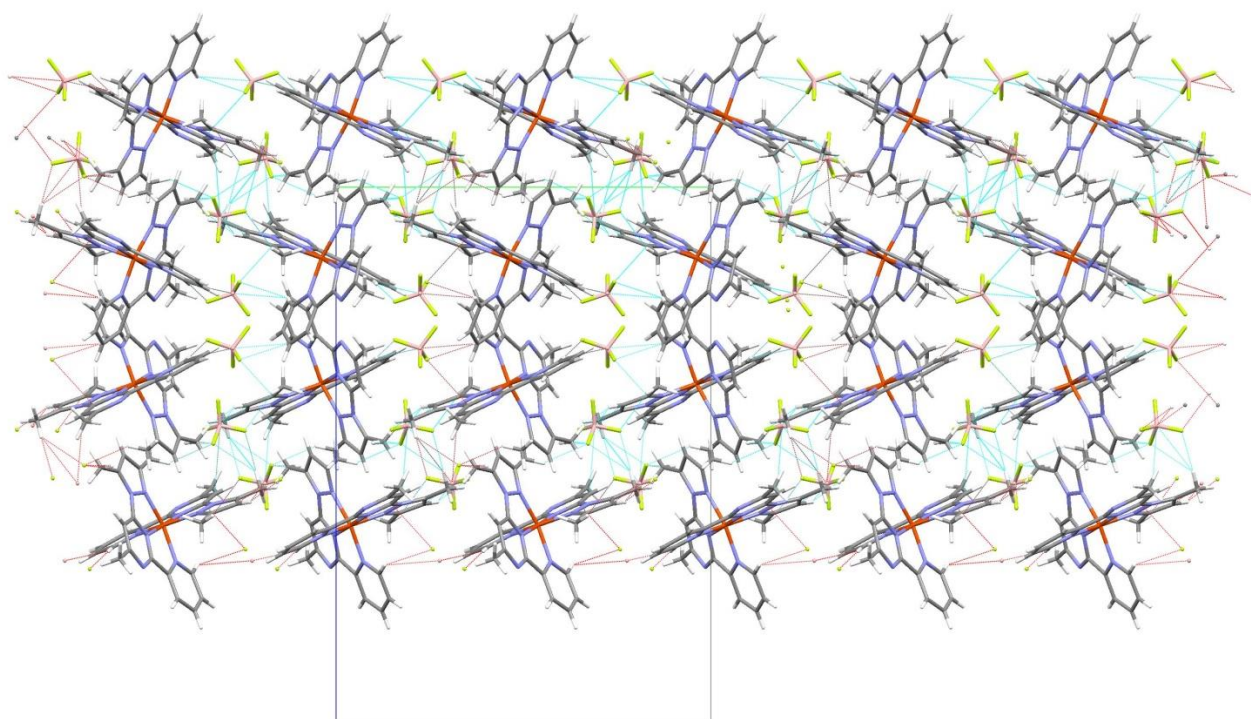


Figure S11. Projection of the crystal structure of 1^{ALS} on the bc -plane. Side view of two 2D corrugated layers running into the opposite direction. Short contacts ($<$ sum of VDW radii) within layers are shown.

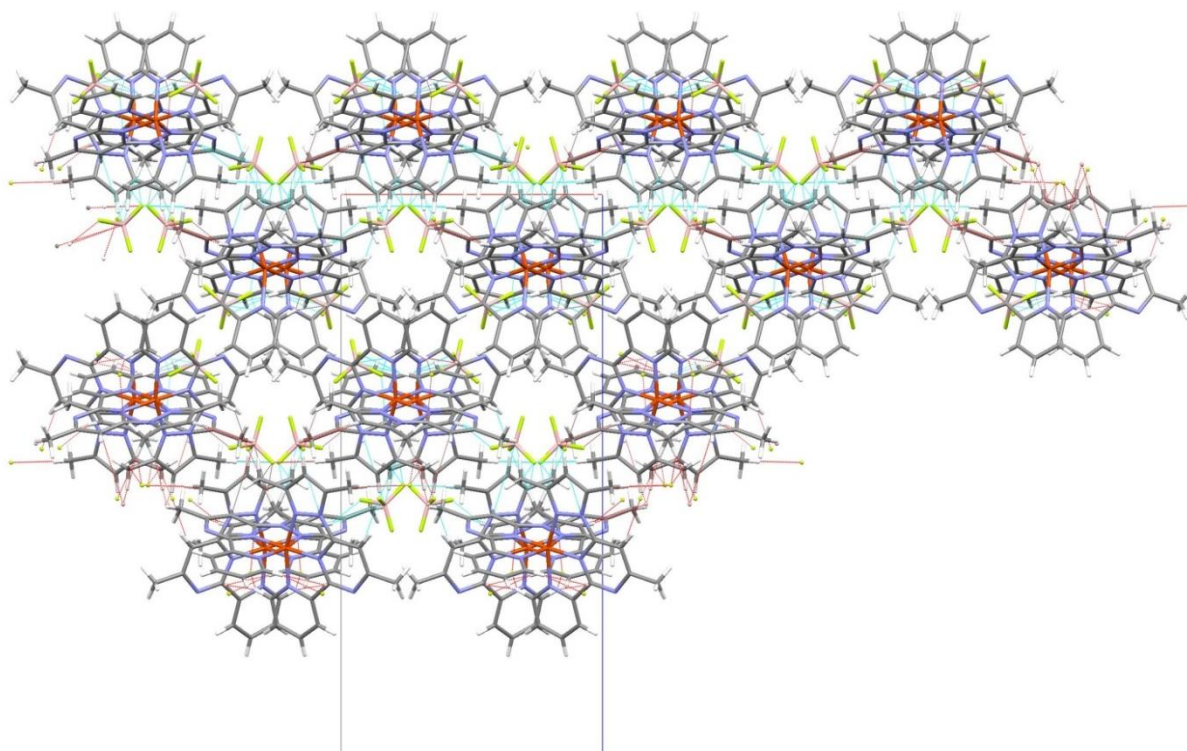


Figure S12. Projection of the crystal structure of 1^{ALS} on the ac -plane (front view along 1D chains forming corrugated layers).

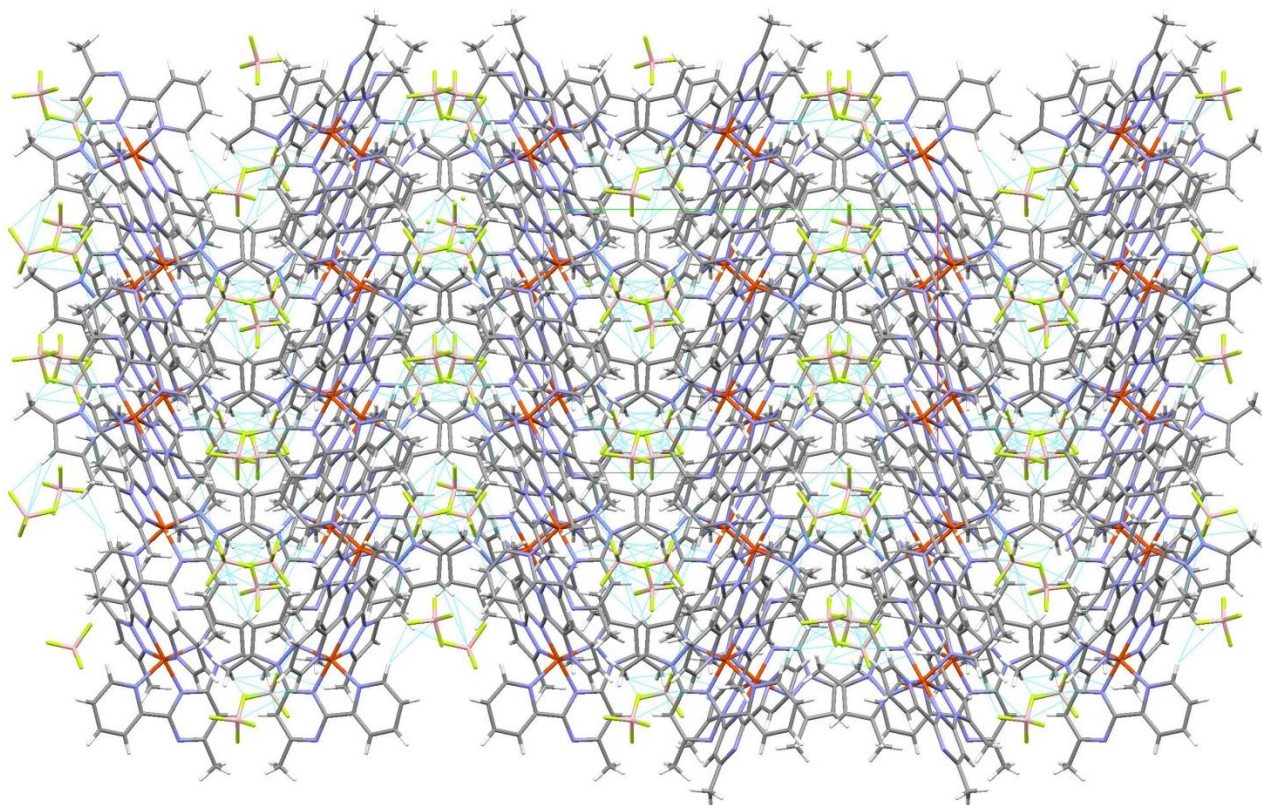


Figure S13. Projection of the crystal structure of 1^{ALS} on the *ab*-plane.

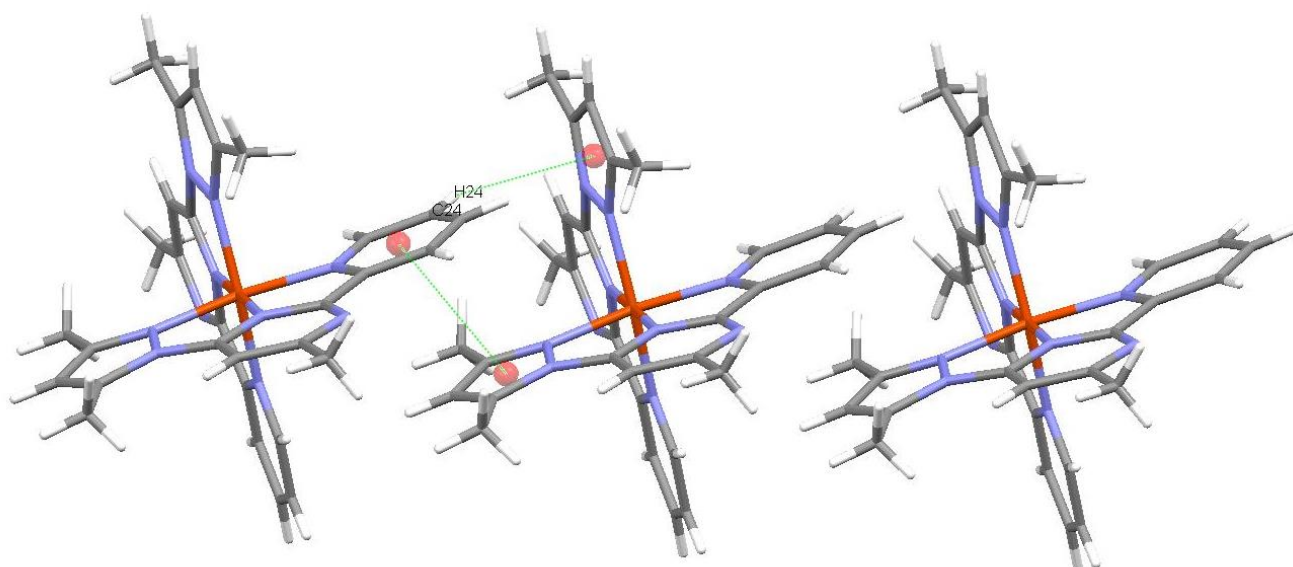


Figure S14. CH $\cdots\pi$ interactions and π - π stacking in the structure of $1^{E/LS}\cdot y\text{EtOH}\cdot z\text{H}_2\text{O}$. C-H $\cdots\pi$, C24-H24 \cdots Cg 2.98 Å, $\gamma = 5.38^\circ$, C-H \cdots Cg 139° ; π - π , Cg \cdots Cg = 3.544(3) Å, $\alpha = 2.8(3)^\circ$, $\beta = 16.35$, $\gamma = 16.46^\circ$.

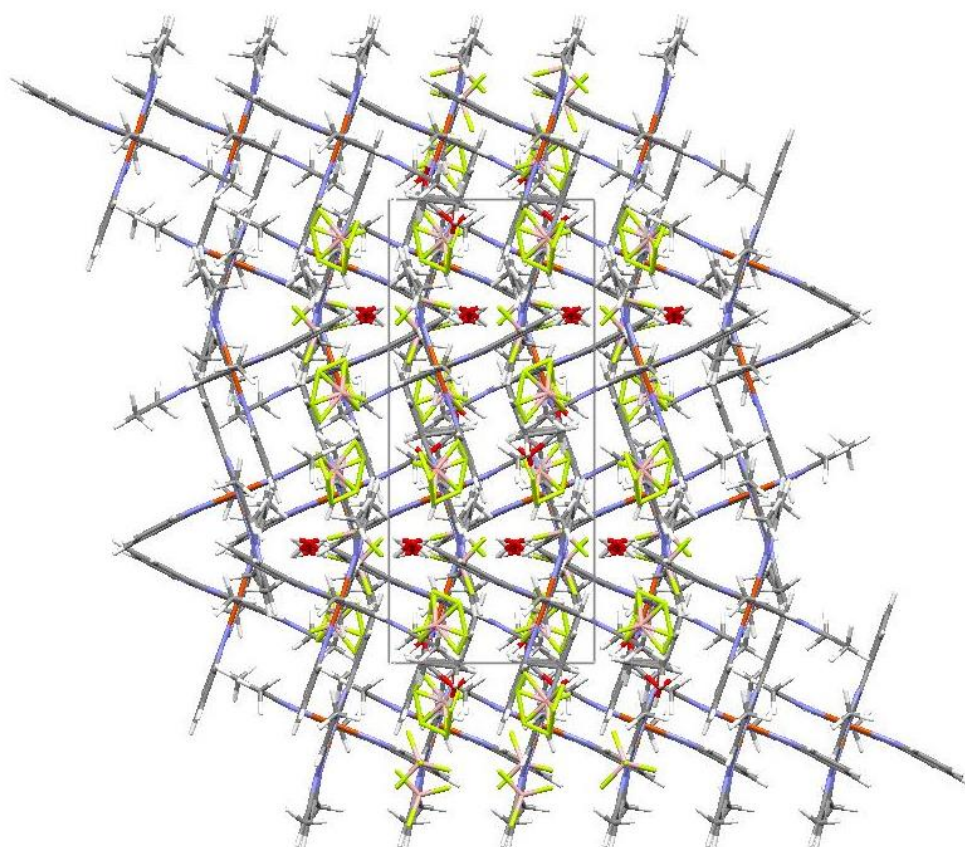


Figure S15. Packing diagram for $1^{E/LS}\cdot y\text{EtOH}\cdot z\text{H}_2\text{O}$. View along the a axis.

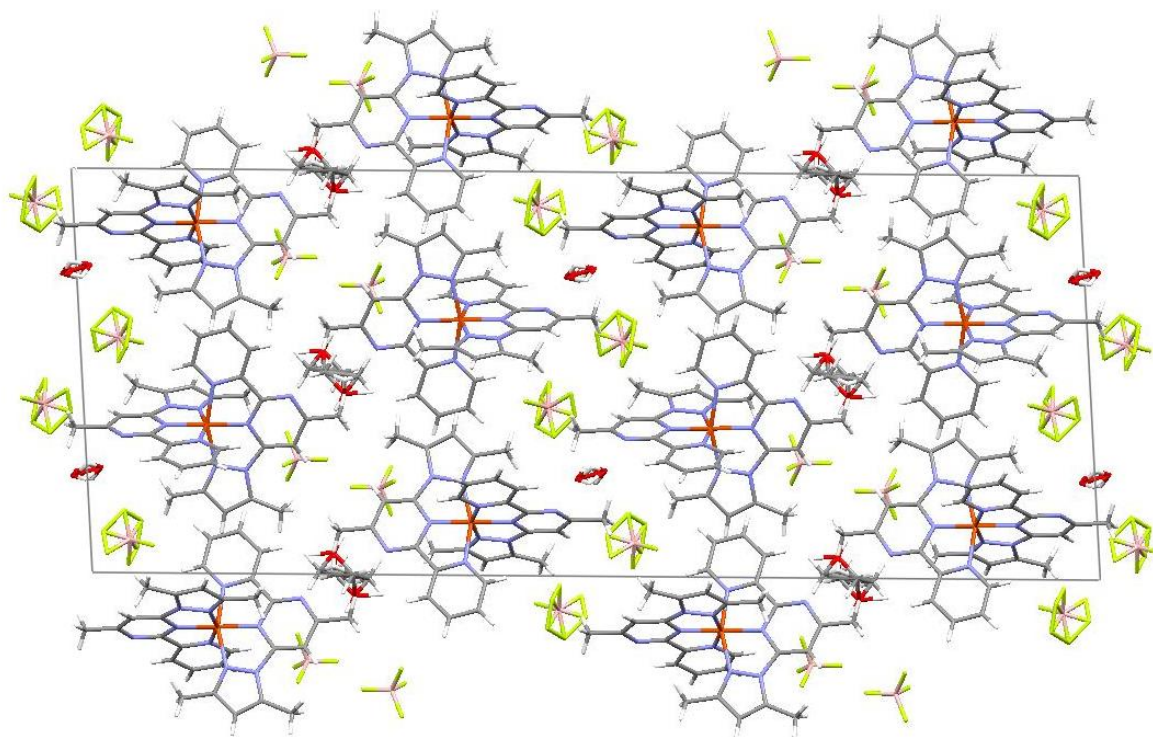


Figure S16. Packing diagram for $1^{E/LS} \cdot yEtOH \cdot zH_2O$. View along the b axis. Side view of two 2D double layers.

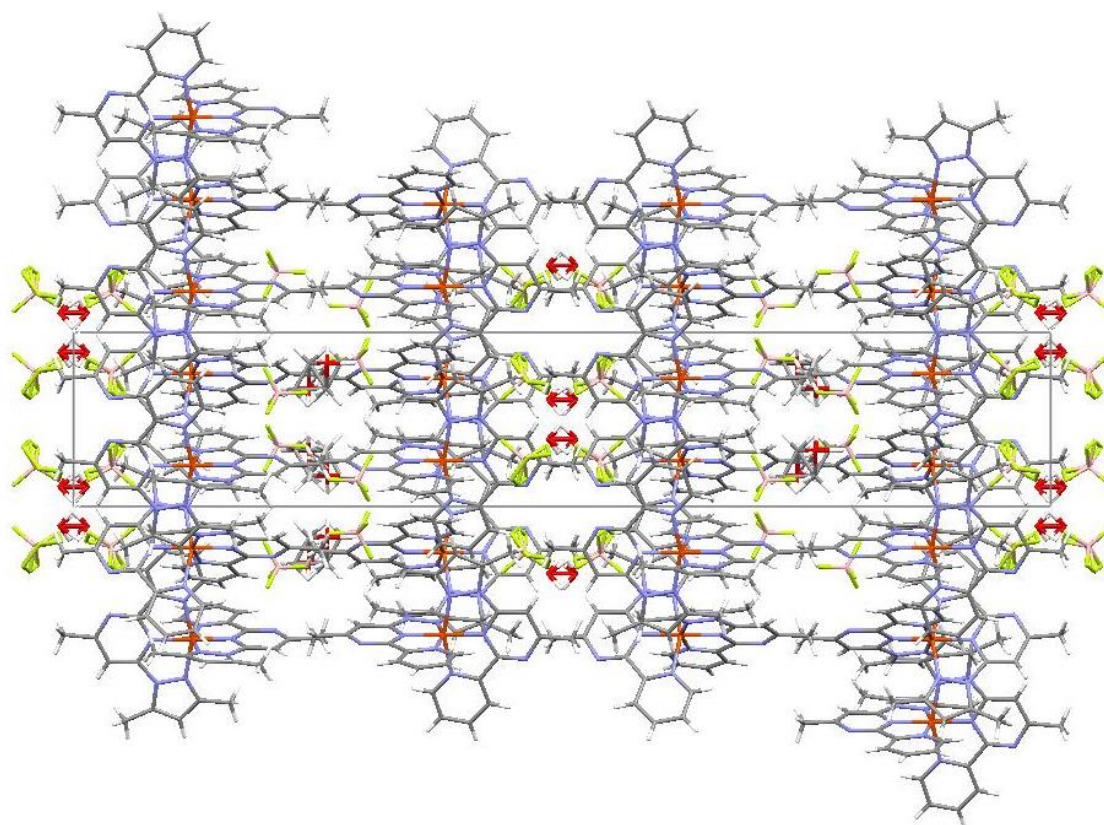


Figure S17. Packing diagram for $1^{E/LS} \cdot yEtOH \cdot zH_2O$. View along the c axis. Side view of two 2D double layers.

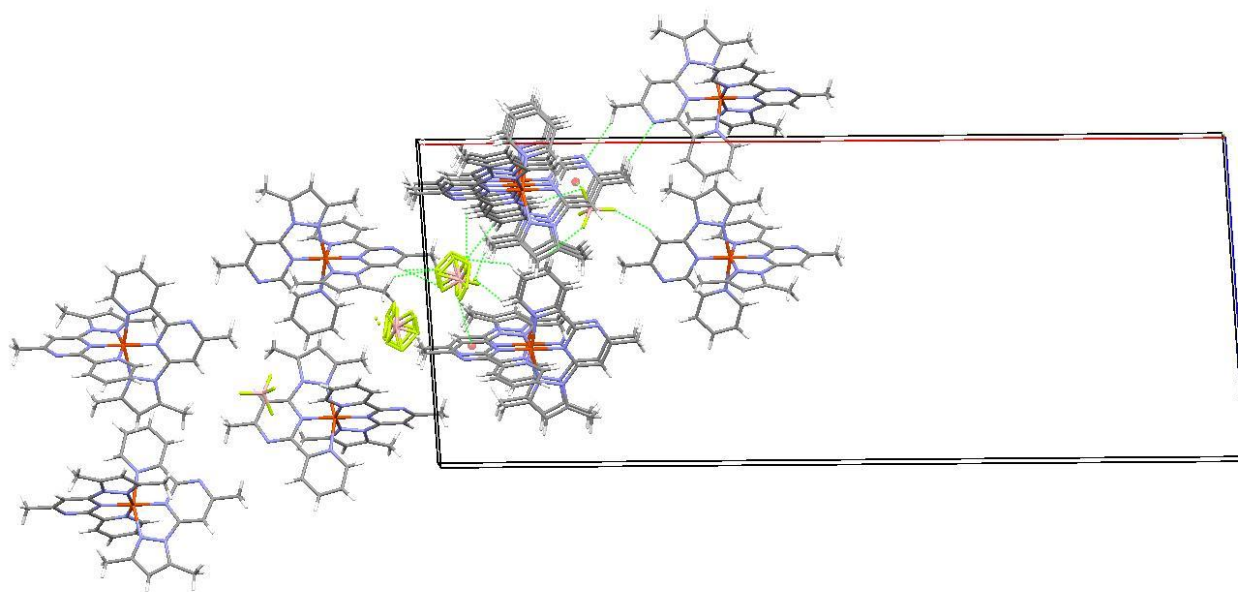


Figure S18. Supramolecular 3D structure of $1^{E/LS} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ formed due to $\text{BF} \cdots \text{HC}$ hydrogen bonds and lone pair – π interactions (two 2D double layers are shown, disordered solvent molecules are omitted for clarity). Short contacts between non-disordered BF_4^- and $[\text{FeL}_2]^{2+}$: $\text{B}-\text{F} \cdots \pi(\text{pyrimidine})$: $\text{F1} \cdots \text{Cg}$ 3.013(5) Å, $\gamma = 12.27^\circ$, $\text{B}-\text{F} \cdots \text{Cg}$ 120.7(5)°; $\text{C}-\text{H} \cdots \text{F}$ contacts: $\text{H25} \cdots \text{F1}$ 2.33 Å, $\text{H3} \cdots \text{F2}$ 2.48 Å, $\text{H15C} \cdots \text{F3}$ 2.41 Å, $\text{H8} \cdots \text{F4}$ 2.50 Å; $\text{C}-\text{H} \cdots \text{N}$ hydrogen bond: $\text{N1} \cdots \text{H5C}$ 2.66 Å.

3. X-RAY DIFFRACTION ANALYSIS OF POLYCRYSTALS

XPRD analysis of polycrystals was performed on Shimadzu XRD-7000 diffractometer (Cu- K_{α} radiation, Ni – filter, 5 – 60° 2θ range, 0.03° 2θ step, 5s per point). Most of the polycrystalline samples were slightly ground with hexane in an agate mortar, and the resulting suspension was deposited on the polished side of a standard quartz sample holder. A smooth thin layer was formed after drying. The samples $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ and $1^{E/LS} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ were slightly ground and fixed using a minimal amount of Vaseline.

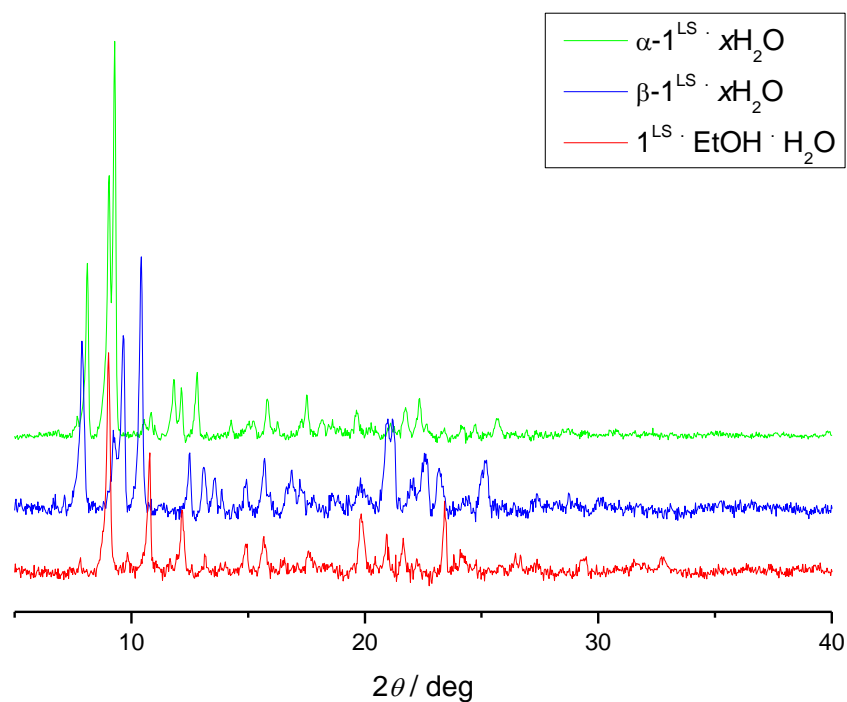


Figure S19. XRPD patterns of the parent phases $\alpha\text{-}1^{\text{LS}} \cdot x\text{H}_2\text{O}$, $\beta\text{-}1^{\text{LS}} \cdot x\text{H}_2\text{O}$ and $1^{\text{LS}} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$.

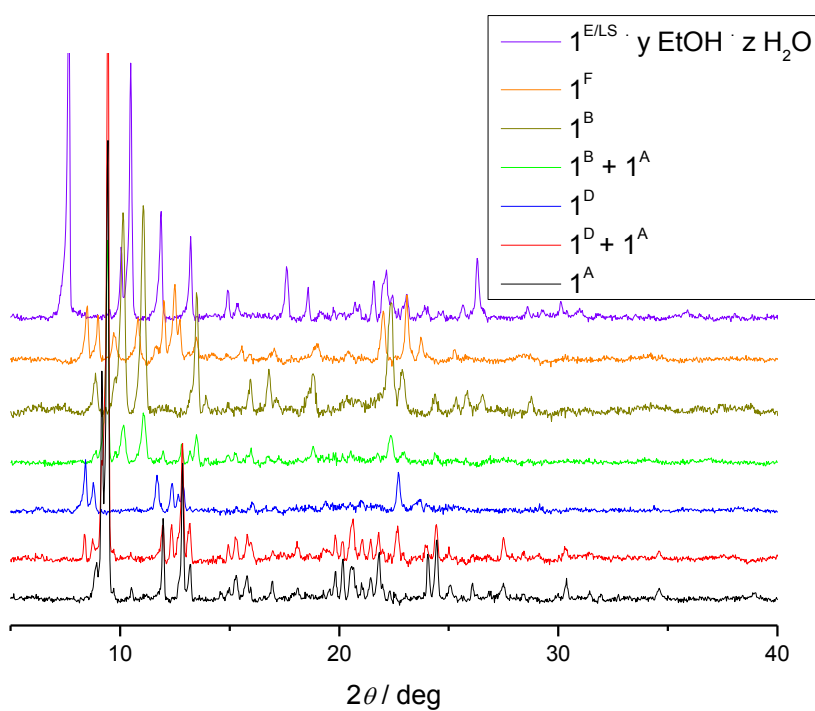


Figure S20. XRPD patterns of the phases $1^{\text{E/LS}} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$, 1^{F} , 1^{B} , 1^{D} , 1^{A} and the mixtures $1^{\text{B}} + 1^{\text{A}}$ and $1^{\text{D}} + 1^{\text{A}}$.

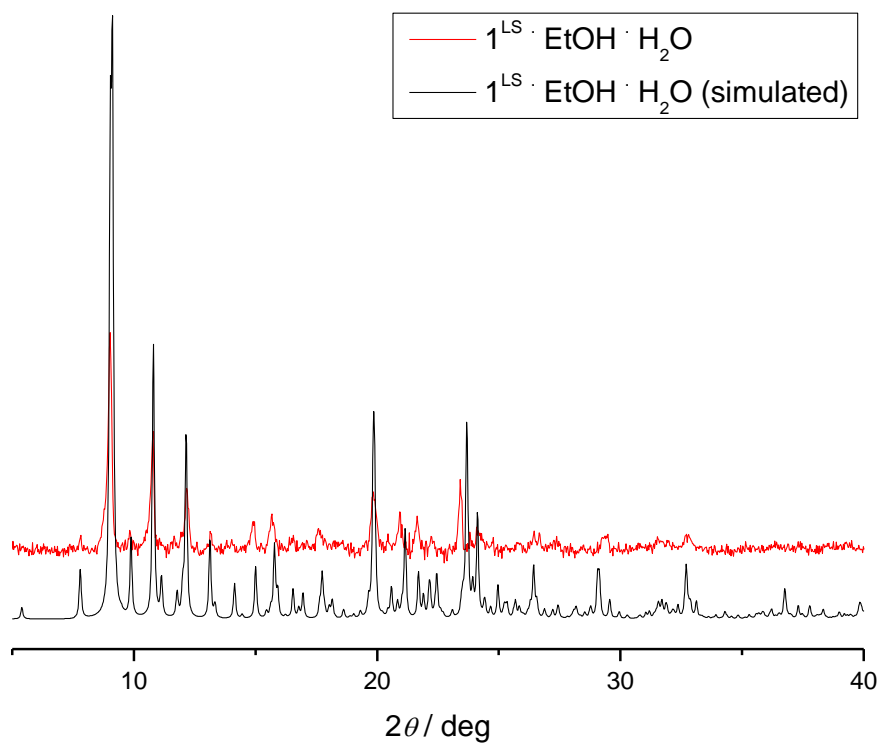


Figure S21. Comparison of XRPD pattern of the phase $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ with simulated pattern.

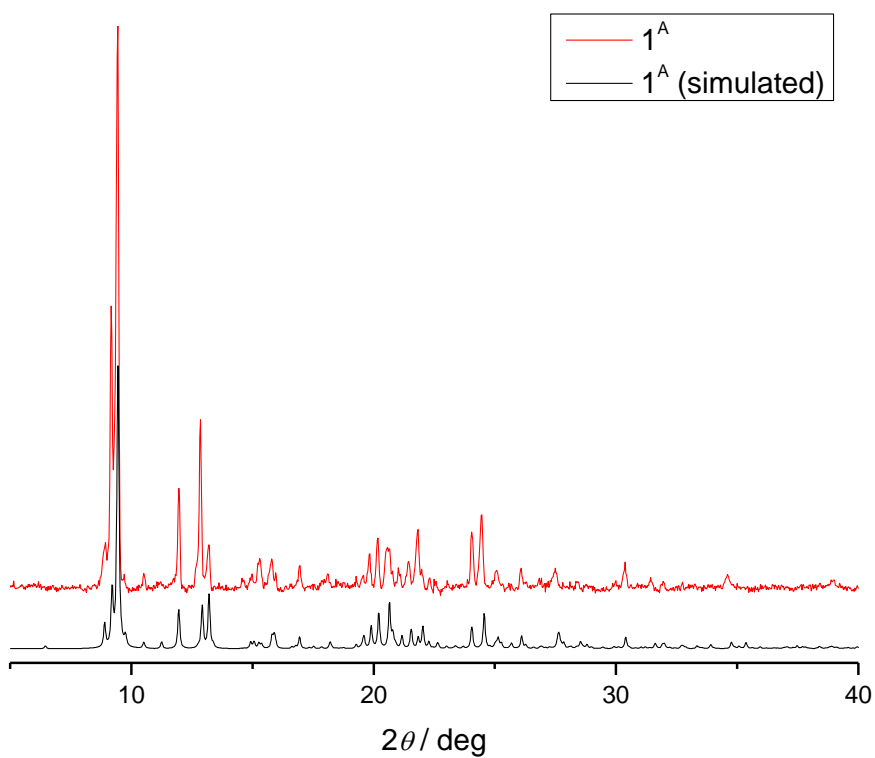


Figure S22. Comparison of XRPD pattern of the phase $1^{A/LS}$ with simulated pattern.

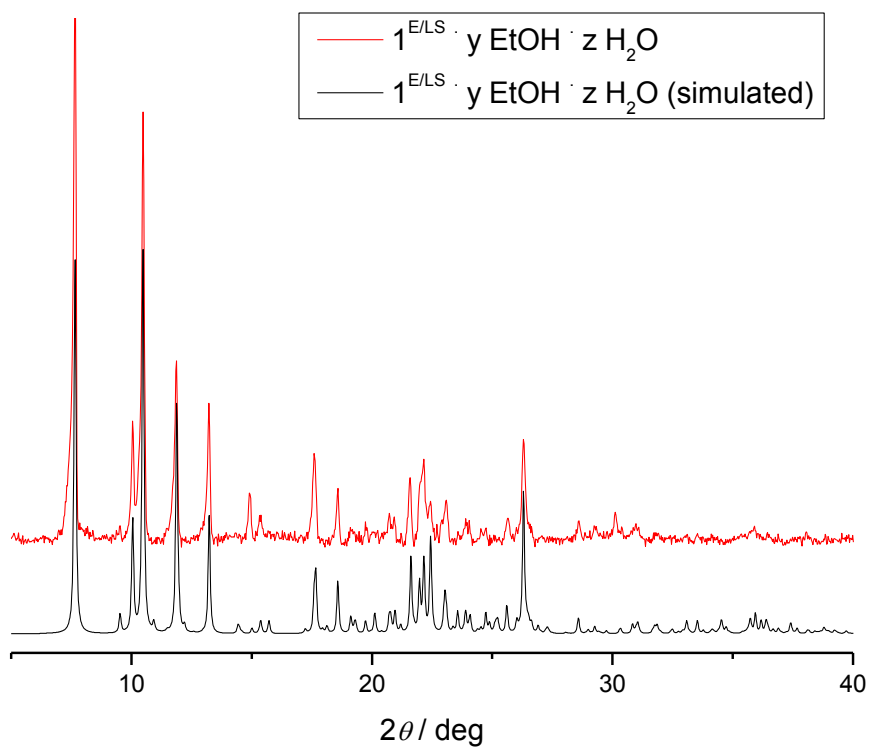


Figure S23. Comparison of XRPD pattern of the phase $1^{E/LS} \cdot y \text{EtOH} \cdot z \text{H}_2\text{O}$ with simulated pattern.

4. DIFFERENTIAL SCANNING CALORIMETRY

Thermodynamic properties were studied using differential scanning calorimeter NETZSCH DSC 204 F1 Phoenix. DSC measurements of the samples were performed by heat flow measurement method at heating/cooling rate 6 K min^{-1} in 25 ml min^{-1} Ar flow. The baseline signal obtained by heating two empty crucibles was subtracted from the experimental results for the samples. The sensitivity calibration of the sample carrier sensors and temperature scale graduation included melting peak area measurements of six melting standard samples from calibration set 6.239.2–91.3 supplied by Netzsch. The transition temperatures were defined from the resulting heat flow as intersections of the peak onset with the corresponding baseline. Netzsch Proteus Analysis software was used to determine DSC peak area and transition temperatures and for further averaging the results of 3 experiments. Thermodynamic properties have been investigated in sealed aluminum crucibles. Differential scanning measurements were carried out over the temperature range $293 - 500 \text{ K}$ at warming and cooling modes. Molar enthalpy of transition, ΔH , was calculated as the area of the DSC peak. The excess entropy of the transition was calculated by the formula $\Delta S = \Delta H/T$, which is valid for the first order phase transitions.

Cycle 1: 1st day. After the first cycle had been done the sample was allowed to stay at room temperature.

Cycles 2, 3: 22nd day

Cycles 4, 5: 23rd day

Cycles 6, 7: 26th day

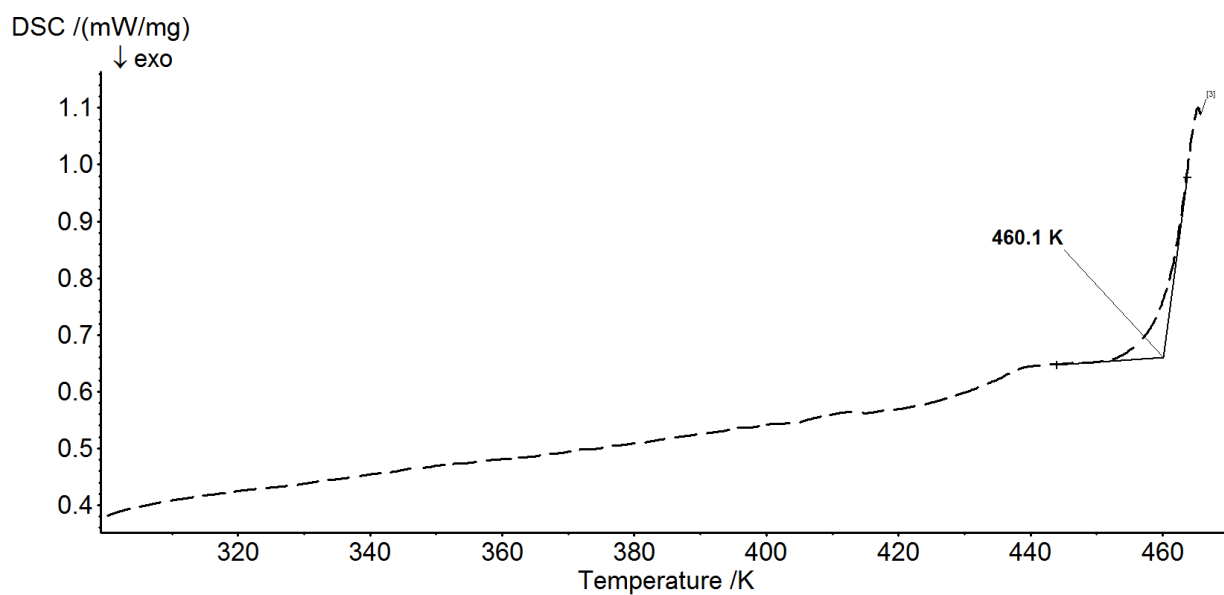


Figure S24. DSC curve for the first heating run.

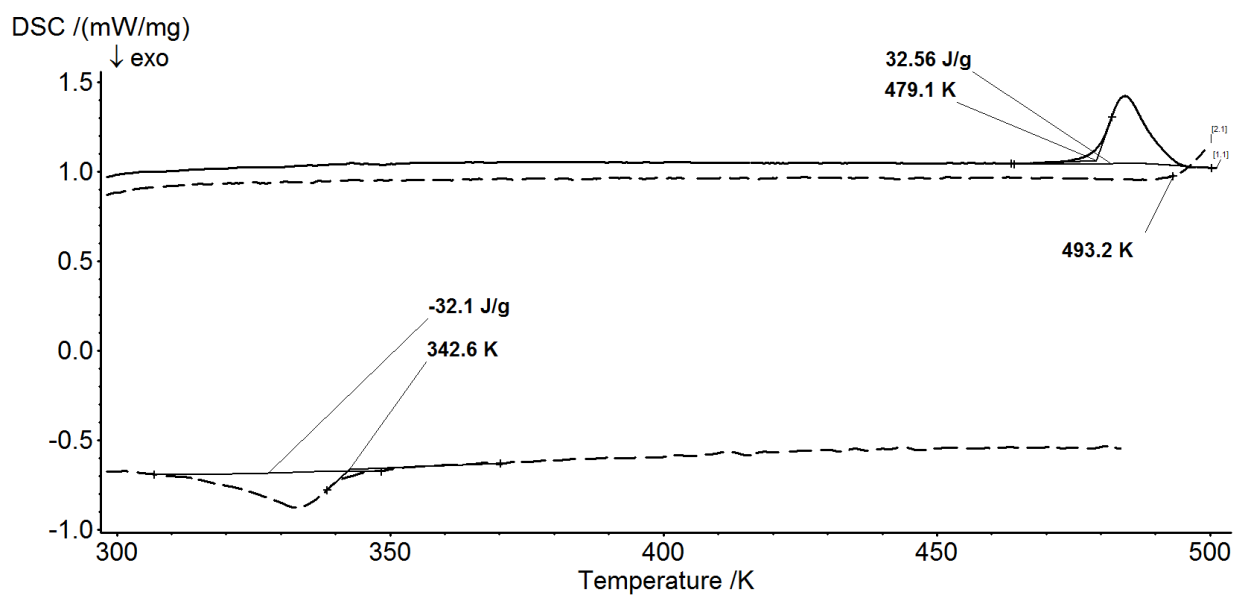


Figure S25. DSC curves for the transition $1^{A/LS} \leftrightarrow 1^{A/HS}$ (2^{nd} (dashed line) and 3^{rd} (solid line) cycles).

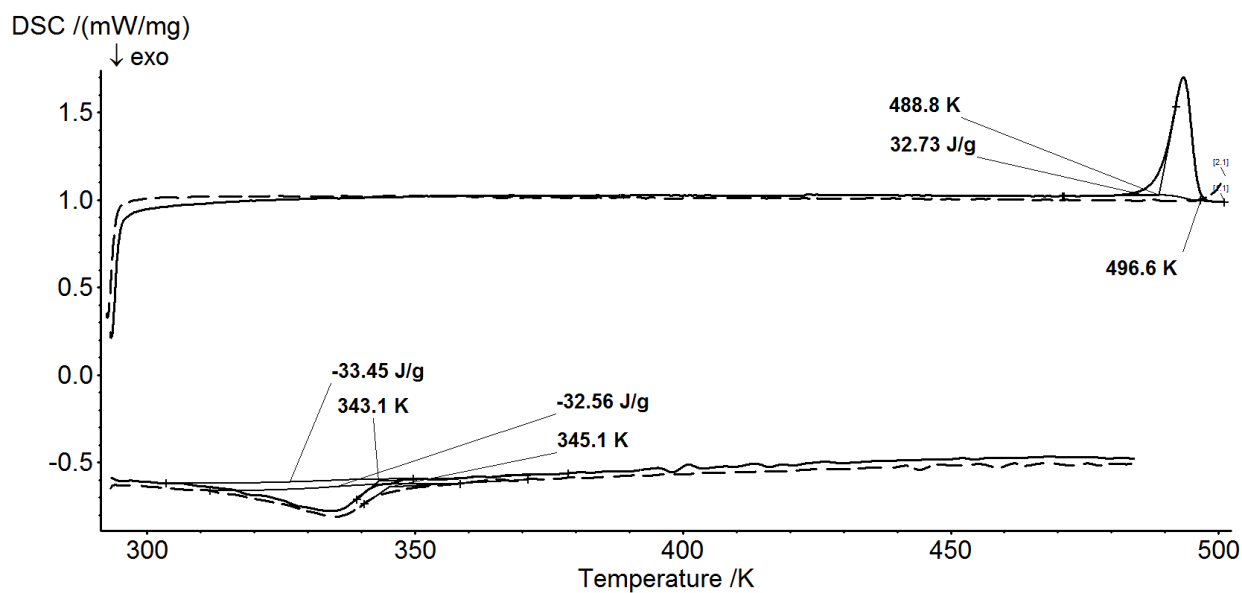


Figure S26. DSC curves for the transition $1^{A/LS} \leftrightarrow 1^{A/HS}$ (4th (dashed line) and 5th (solid line) cycles).

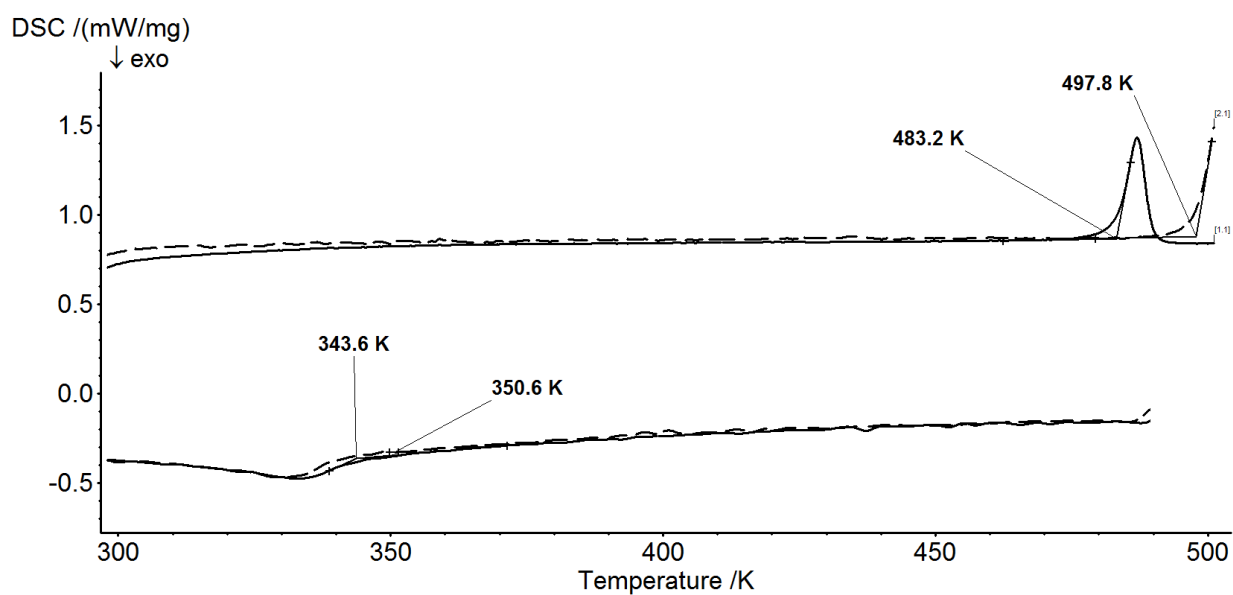


Figure S27. DSC curves for the transition $1^{A/LS} \leftrightarrow 1^{A/HS}$ (6th (dashed line) and 7th (solid line) cycles).

5. IR SPECTROSCOPY

IR absorption spectra were recorded on a Scimitar FTS 2000 spectrometer.

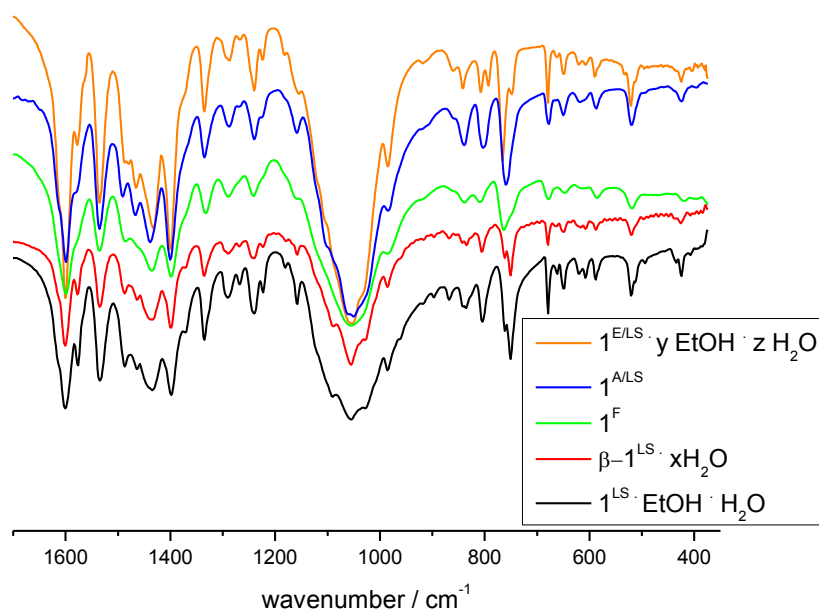


Figure S28. IR spectra of $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, $\beta\text{-}1^{LS} \cdot x \text{H}_2\text{O}$, $1^{A/LS}$, $1^{E/LS} \cdot y \text{EtOH} \cdot z \text{H}_2\text{O}$ and 1^F (1700 – 350 cm⁻¹, KBr).

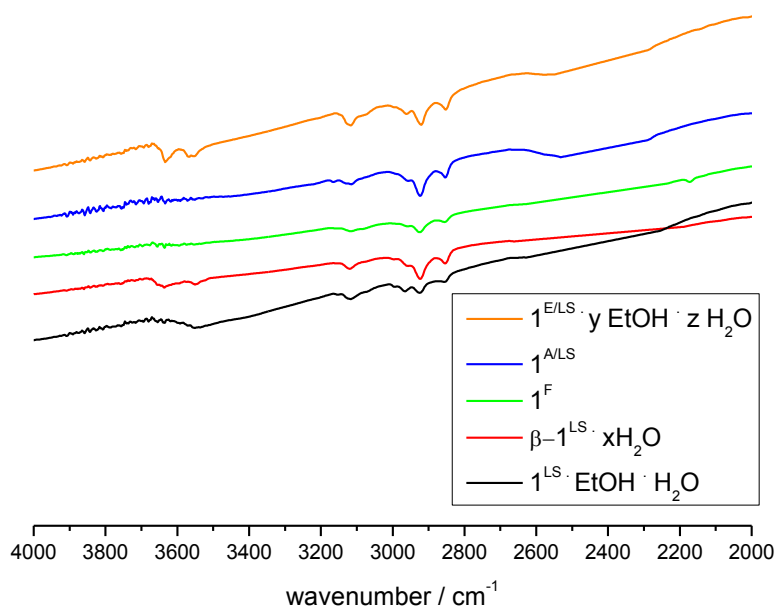


Figure S29. IR spectra of $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, $\beta\text{-}1^{LS} \cdot x \text{H}_2\text{O}$, $1^{A/LS}$, $1^{E/LS} \cdot y \text{EtOH} \cdot z \text{H}_2\text{O}$ and 1^F (4000 – 2000 cm⁻¹, fluorinated oil). IR spectra of the phases $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, $\beta\text{-}1^{LS} \cdot x \text{H}_2\text{O}$ and $1^{E/LS} \cdot y \text{EtOH} \cdot z \text{H}_2\text{O}$ contain $\nu(\text{OH})$ bands of low intensity. This means that the phases contain outerspheric ethanol and water molecules.

6. THERMAL ANALYSIS

Simultaneous thermal analysis (STA) of $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$, $\beta\text{-}1^{LS} \cdot x\text{H}_2\text{O}$, $1^{A/LS}$, 1^D , $1^{E/LS} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ and 1^F , including thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements, was performed on NETZSCH instruments (NETZSCH TG 209 F1, NETZSCH STA 449F1, NETZSCH STA 409 PC/PG; open Al crucible, heating rate 10 K min^{-1}).

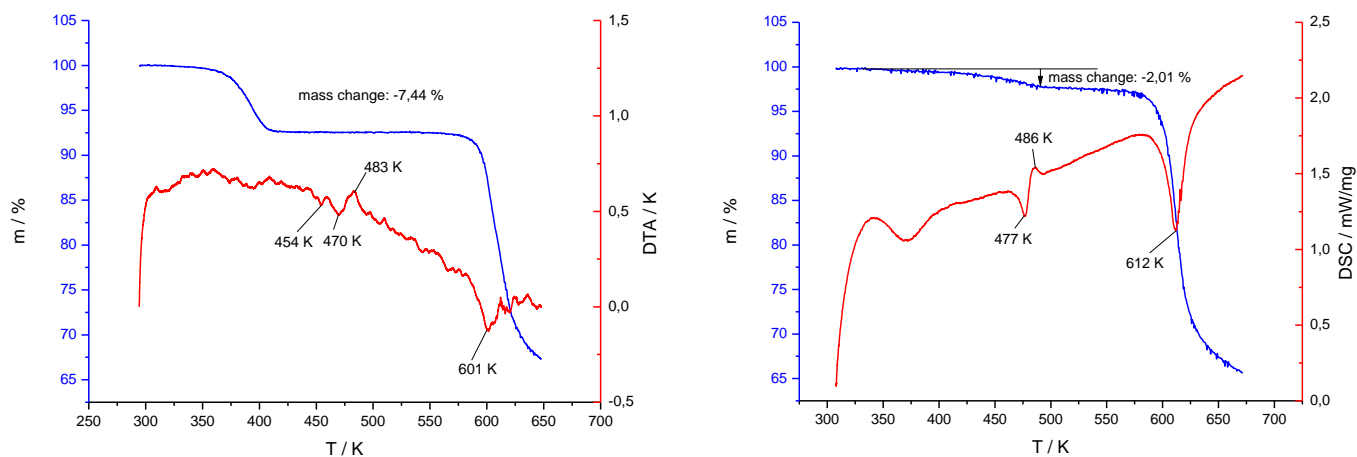


Figure 30. TG and DTA/DSC curves for the complex $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ (sample #1, just after filtration, left) and $\beta\text{-}1^{LS} \cdot x\text{H}_2\text{O}$ (sample #1, 10 days after filtration, right).

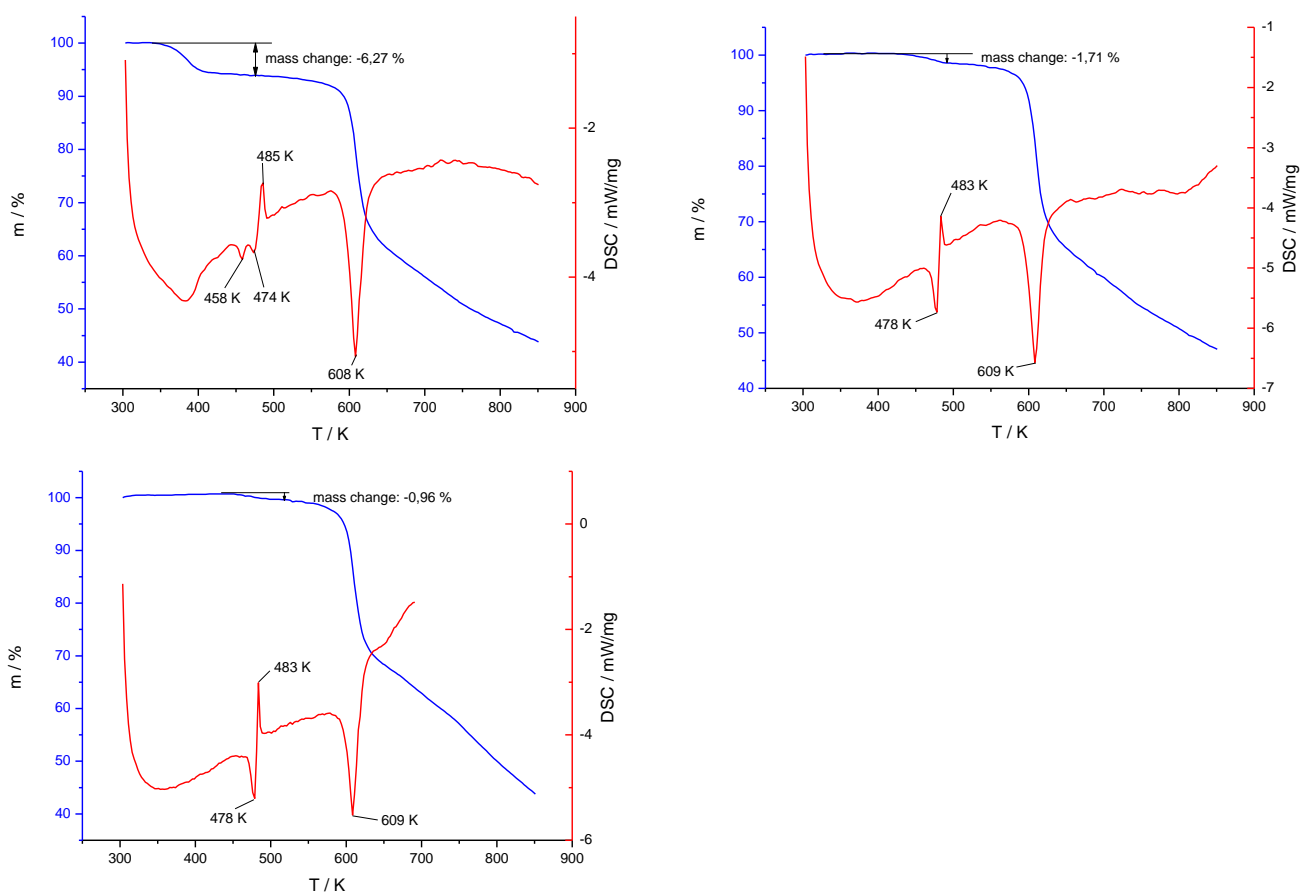


Figure S31. TG and DSC curves for the complex $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ (sample #2, *ca.* 2 h after filtration, top, left), $\beta\text{-}1^{LS} \cdot x\text{H}_2\text{O}$ (sample #2, 20 days after filtration, top, right) and $\beta\text{-}1^{LS} \cdot x\text{H}_2\text{O}$ (sample #2, two months after filtration, bottom).

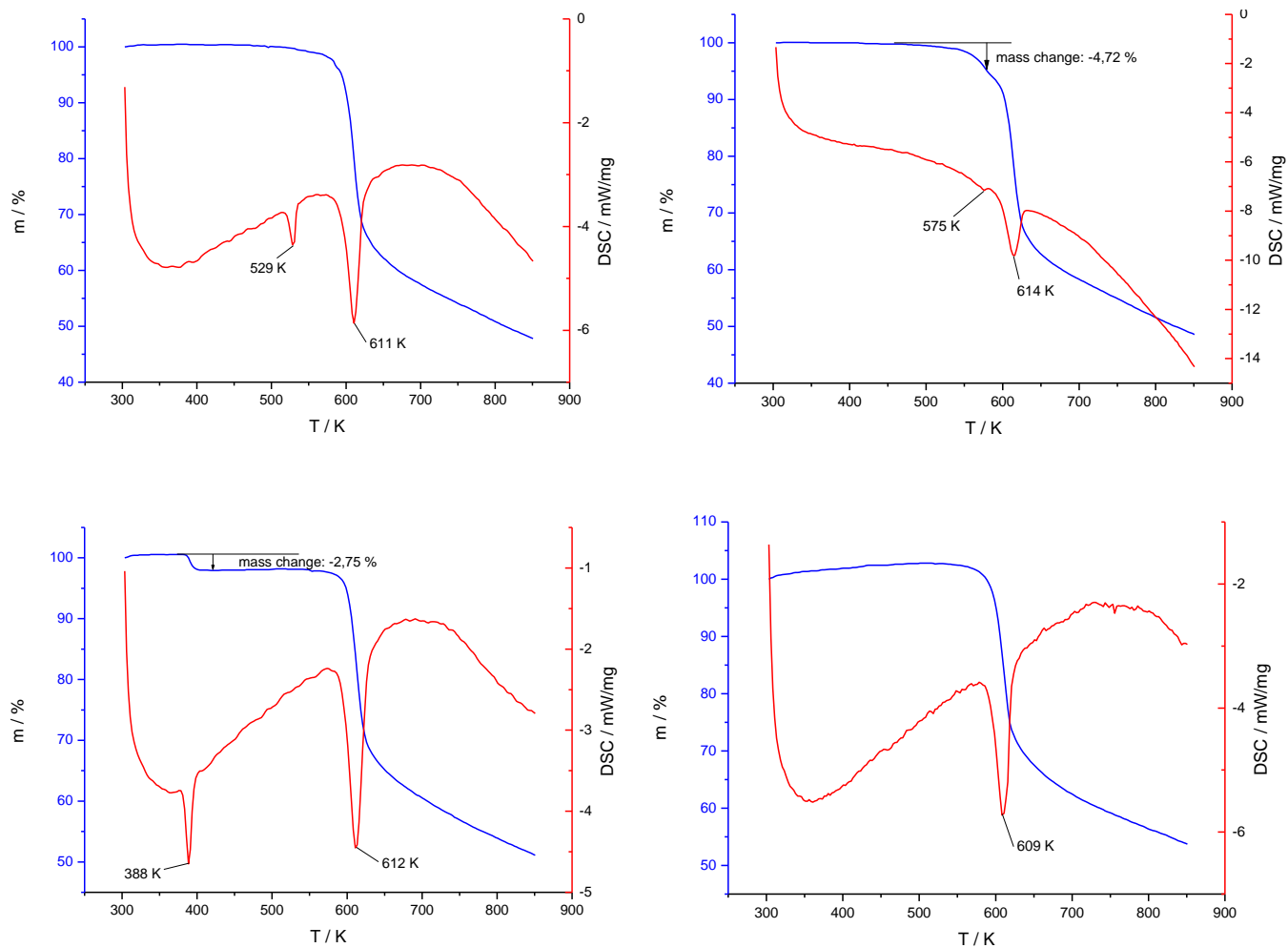


Figure S32. TG and DSC curves for the complex $1^{A/LS}$ (top, left), 1^D (top, right), $1^{E/LS} \cdot yEtOH \cdot zH_2O$ (bottom, left) and 1^F (bottom, right).

7. MAGNETIC DATA: EXPERIMENTS AND FITTING

Experimental details

The study of magnetic properties of the complexes was performed on a Faraday balance in the temperature range 80 – 500 K in the magnetic fields from 5.8 to 10.9 kOe. The measurements showed that magnetic susceptibility of the samples did not depend on the magnetic field strength proving the absence of ferromagnetic impurities. Further measurements of the magnetic susceptibility were performed in the field of 9.09 kOe. Magnetic measurements on the samples **19** and **20** were performed in open quartz ampoules under vacuum. All the other samples were placed into quartz ampoules and sealed. The molar magnetic susceptibility (χ_M) was calculated taking into account the diamagnetism of the atoms using the Pascal additive scheme and a correction for the sample holder was applied. Details on the parent phases are given below. The values of the m/V ratio are collected in Table S2.

Typically, heating/cooling rate in “dynamic” magnetic measurements was 0.9 K min⁻¹. Magnetic properties of the samples **5-1** and **12-1** were studied at rates 0.9, 0.4 and 0.25 K min⁻¹. To study SCO kinetics in “static” measurements, the samples were rapidly cooled or heated (at 4 K min⁻¹) to the temperature of annealing. Any deviation from this is stated below.

Fitting

Fitting of sigmoidal curves has been done according to the Johnson–Mehl–Avrami–Kolmogorov (JMAK) model using the equation

$$\gamma = 1 - \exp(-kt^n),$$

where γ is the fraction transformed at time t ($0 \leq \gamma \leq 1$), n is the Avrami exponent and k is the overall rate constant (s⁻ⁿ). The fractions γ_{HS} and γ_{LS} were normalized using the equations

$$\gamma_{HS} = \frac{(\chi_M T)_t - (\chi_M T)_{min}}{(\chi_M T)_{max} - (\chi_M T)_{min}}$$

and

$$\gamma_{LS} = 1 - \frac{(\chi_M T)_t - (\chi_M T)_{min}}{(\chi_M T)_{max} - (\chi_M T)_{min}}$$

where $(\chi_M T)_t$ is the $\chi_M T$ value at time t , $(\chi_M T)_{min}$ is a minimal $\chi_M T$ value at a given temperature T and $(\chi_M T)_{max}$ is a maximal $\chi_M T$ value at a given temperature T .

Fitting of exponential curves has been done in the frame of bi- or tri-exponential approximation using the equations

$$\chi_M T = (\chi_M T)_1 e^{(-\frac{t}{\tau_1})} + (\chi_M T)_2 e^{(-\frac{t}{\tau_2})} + (\chi_M T)_0$$

and

$$\chi_M T = (\chi_M T)_1 e^{(-\frac{t}{\tau_1})} + (\chi_M T)_2 e^{(-\frac{t}{\tau_2})} + (\chi_M T)_3 e^{(-\frac{t}{\tau_3})} + (\chi_M T)_0$$

where $(\chi_M T)_i$ are the initial $\chi_M T$ values for each exponent and τ_i are lifetimes of each exponent.

Cooperative effect for the transition $1^{A/LS} \rightarrow 1^{A/HS}$

The Slichter-Drickamer model (SDM) describes an SCO system in terms of mean field theory as a regular solution of HS and LS molecules. It uses a phenomenological parameter of cooperative interaction, Γ , which reflects the tendency of SCO molecule in a certain spin state to be surrounded by SCO molecules of the same spin state ($\Gamma > 0$). The SDM reproduces various forms of SCO curves as well as hysteresis effect. A first-order phase transition as well as a possibility for hysteretic bistable behavior are predicted when $\Gamma > 2RT_c$. The SDM uses the following equation for the HS molar fraction γ_{HS} :

$$\ln\left(\frac{1-\gamma_{HS}}{\gamma_{HS}}\right) = \frac{\Delta H + \Gamma(1-2\gamma_{HS})}{RT} - \frac{\Delta S}{R}, \quad (1)$$

where ΔH and ΔS are the enthalpy and entropy changes associated with spin transition.

We calculated the $\gamma_{HS}(T)$ values and the value of Γ as follows.

1) Magnetic contributions of HS and LS fractions were extracted from magnetic susceptibility data above and below the transition region.

2) The $\gamma_{HS}(T)$ values were calculated at different temperatures from magnetic data using the equation $\chi'_M = \gamma_{HS}\chi'_M(\text{HS}) + (1-\gamma_{HS})\chi'_M(\text{LS})$, where $\chi'_M(\text{HS})$ and $\chi'_M(\text{LS})$ stand for magnetic contributions of HS and LS fractions at high and low temperature limits, respectively.

3) Parameter Γ was determined by the least squares method, by minimizing numerically the sum

$$\sum_T \left[\ln\left(\frac{1-\gamma_{HS}(T)}{\gamma_{HS}(T)}\right) - \frac{\Delta H + \Gamma(1-2\gamma_{HS}(T))}{RT} + \frac{\Delta S}{R} \right]^2. \quad (2)$$

The Sorai-Seki model (SSM) assumes that the crystal lattice consists of N non-interacting domains of equal size containing n molecules and that the spin transition in each domain occurs

simultaneously. The SSM does not describe the hysteresis effects. The equation to calculate model value of γ_{HS} can be written as

$$\gamma_{HS}^{\text{mod}} = \frac{1}{1 + \exp\left(\frac{-n\Delta H}{R} \left(\frac{1}{T} - \frac{1}{T_{1/2}}\right)\right)}, \quad (3)$$

where $T_{1/2}$ is the temperature at which the number of domains in the HS and LS forms is equal. The parameter n was determined by minimizing the sum

$$\sum_T [\gamma_{HS}^{\text{mod}}(T) - \gamma_{HS}(T)]^2. \quad (4)$$

Sample 1
Parent phase $1^{LS} \cdot EtOH \cdot H_2O$.

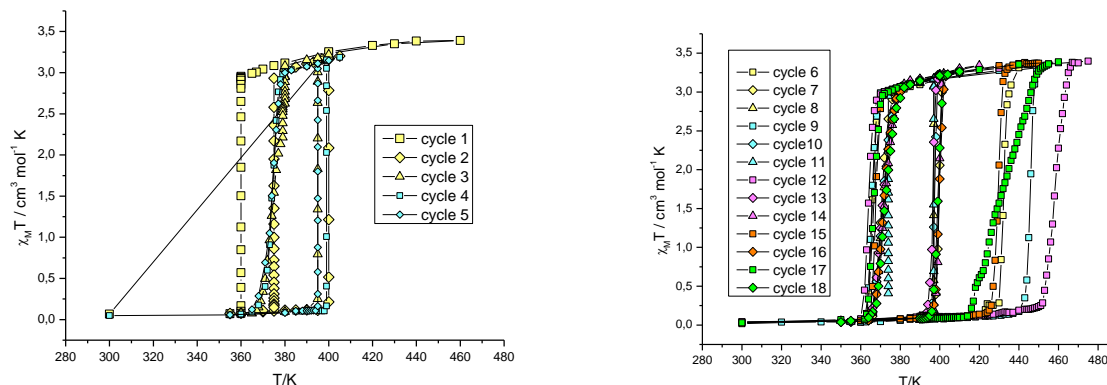


Figure S33. Sample 1. Thermal cycles 1 – 5 (left) and 6 – 18 (right). Heating rate in the cycle 1 (300 – 400 K) was 10 K/min.

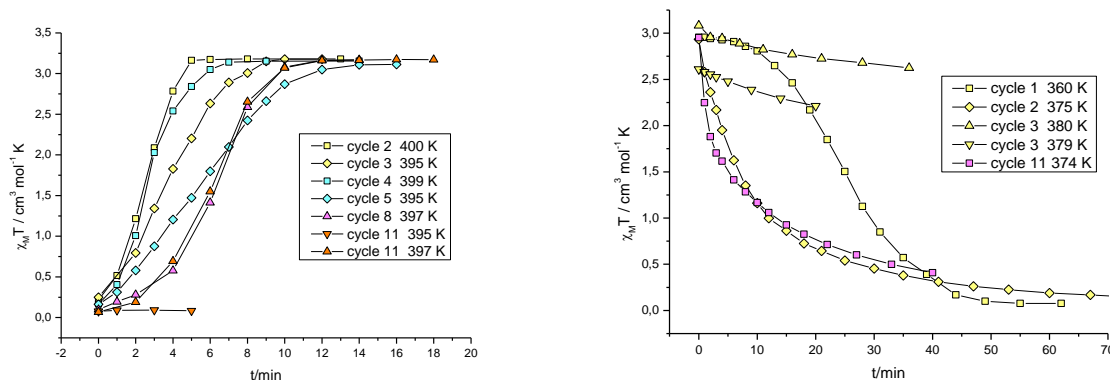


Figure S34. Sample 1. Kinetic curves for the cycles 2 – 5, 8, 11 (LS → HS transformation, left) and 1 – 3 and 11 (HS → LS transformation, right).

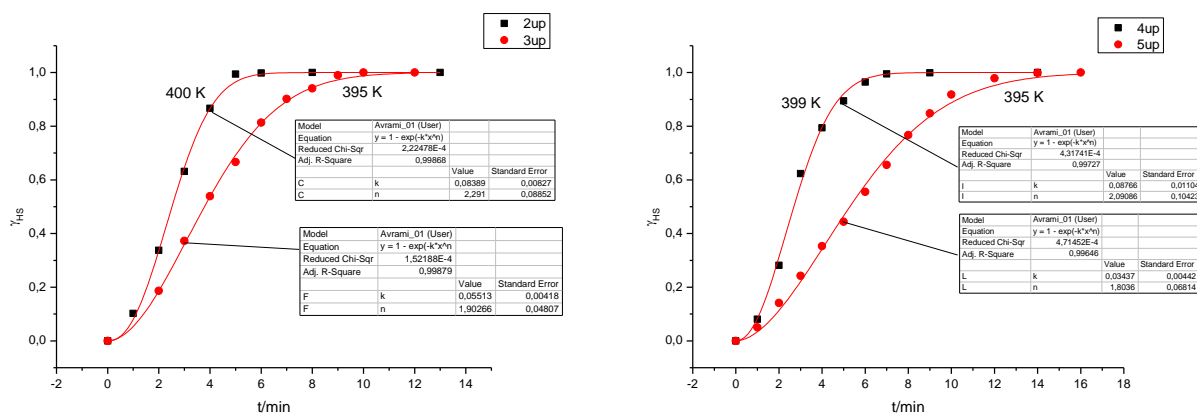


Figure S35. Fitting of kinetic curves for **1** using the JMAK model (LS → HS transformation; left: cycles 2 and 3, right: cycles 4 and 5).

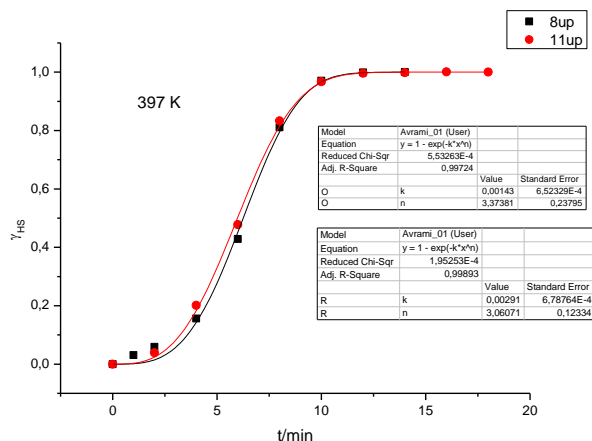


Figure S36. Fitting of kinetic curves for **1** using the JMAK model (LS \rightarrow HS transformation; cycles 8 and 11).

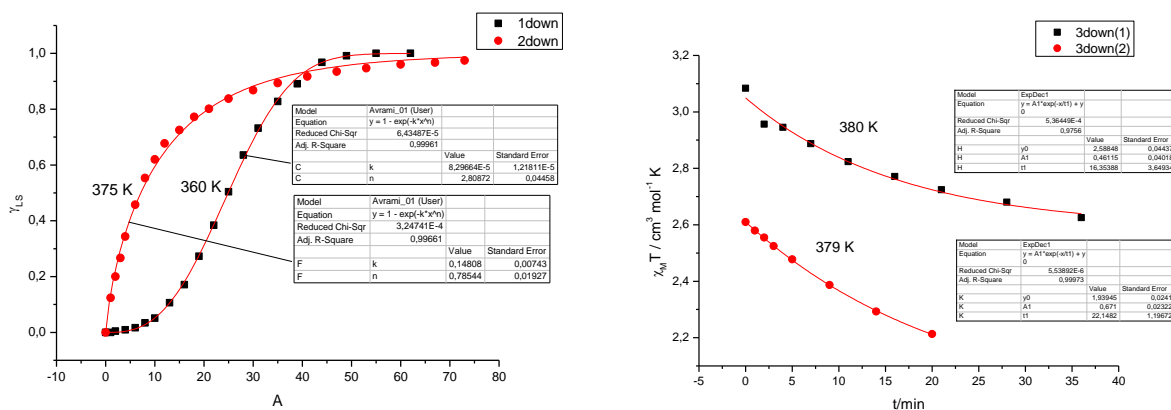


Figure S37. Fitting of kinetic curves for **1** using the JMAK model (right: cycles 1 and 2, HS \rightarrow LS transformation) and the monoexponential law (left: cycle 3, LS \rightarrow HS transformation).

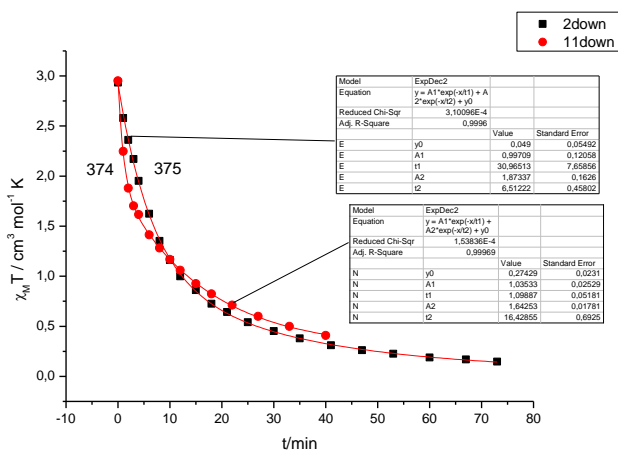


Figure S38. Fitting of kinetic curves for **1** in the bi-exponential approximation (cycles 2 and 11, LS \rightarrow HS transformation).

Samples 2, 2-1, 2-2 and 2-3

Sample 2

Cycles 1 – 3. Parent phase $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$.

Sample 2-1

Cycles 4 – 6. Parent phase 1^{ALS} . This sample was taken from the experiment 2, placed in a new ampoule, dried in the ambient air for 3 days and sealed.

Sample 2-2

Cycles 7 – 11. Parent phases: a mixture of 1^{ALS} and 1^{BLS} . This sample was exposed to water vapor for 48 h. This was followed by the increase in the mass of the sample by 1.9 % and by a drop in the magnetic moment. This sample was sealed and subjected to thermal cycling.

Sample 2-3

Cycles 12 - 14. Parent phase 1^{ALS} . This sample of the phase 1^{ALS} was taken from the experiment 2-2, exposed to water vapor for 1 h (no change in the mass was observed) and sealed.

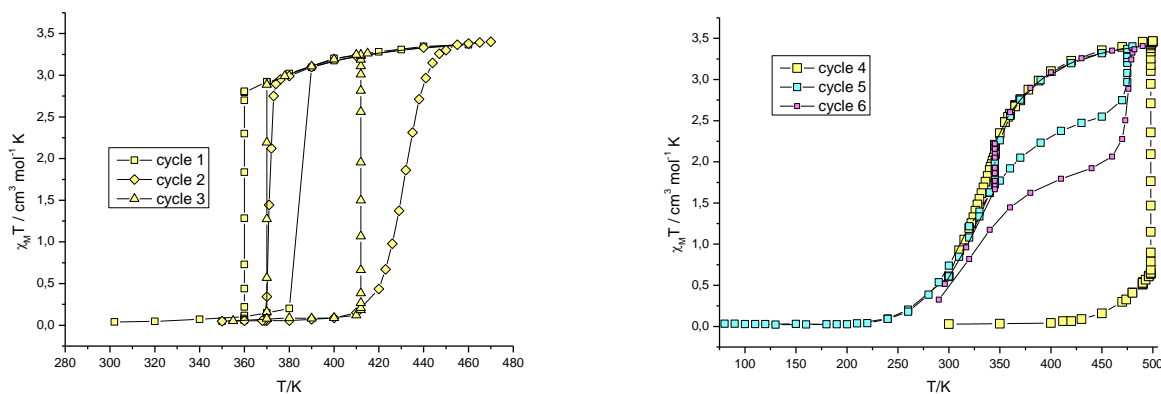


Figure S39. Left: sample 2, thermal cycles 1 – 3. Right: sample 2-1 thermal cycles 4 – 6.

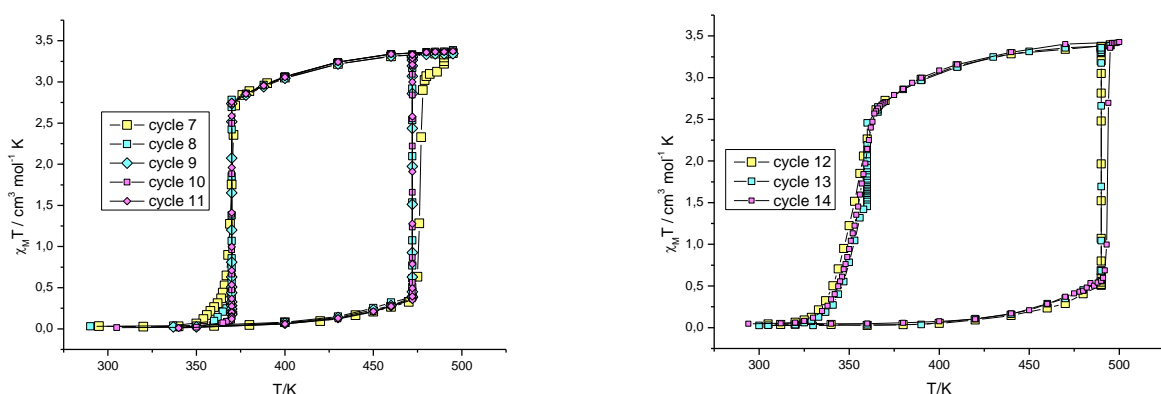


Figure S40. Left: sample 2-2, thermal cycles 7 – 11. Right: sample 2-3, thermal cycles 12 – 14.

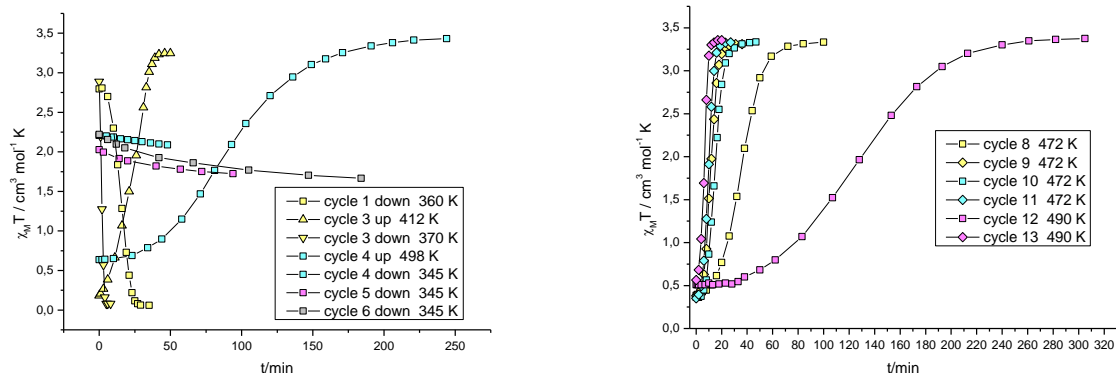


Figure S41. Left: samples **2**, **2-1** and **2-2**. Kinetic curves for the cycles 1, 3 – 6 (LS \rightarrow HS and HS \rightarrow LS transformations). Right: sample **2-3**. Kinetic curves for the cycles 8 – 13 (LS \rightarrow HS transformation).

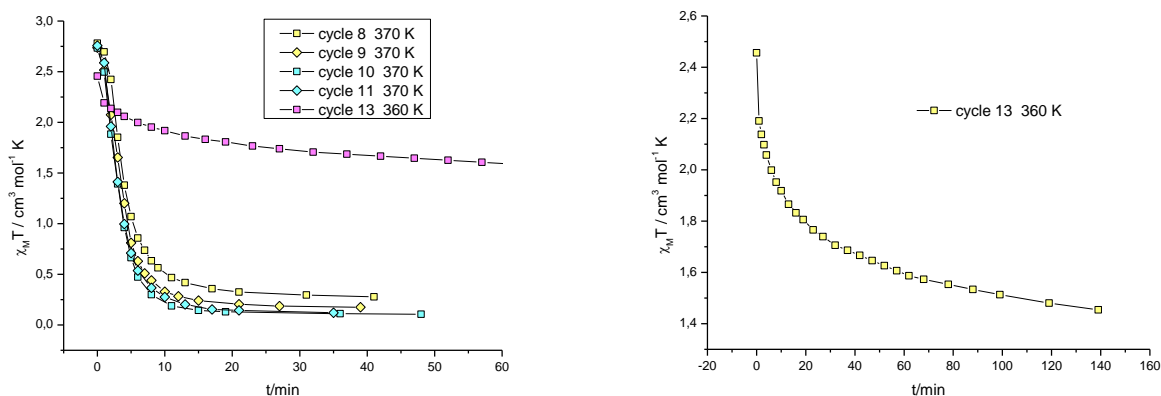


Figure S42. Samples **2-2** and **2-3**. Kinetic curves for the cycles 8 – 11 and 13 (HS \rightarrow LS transformation).

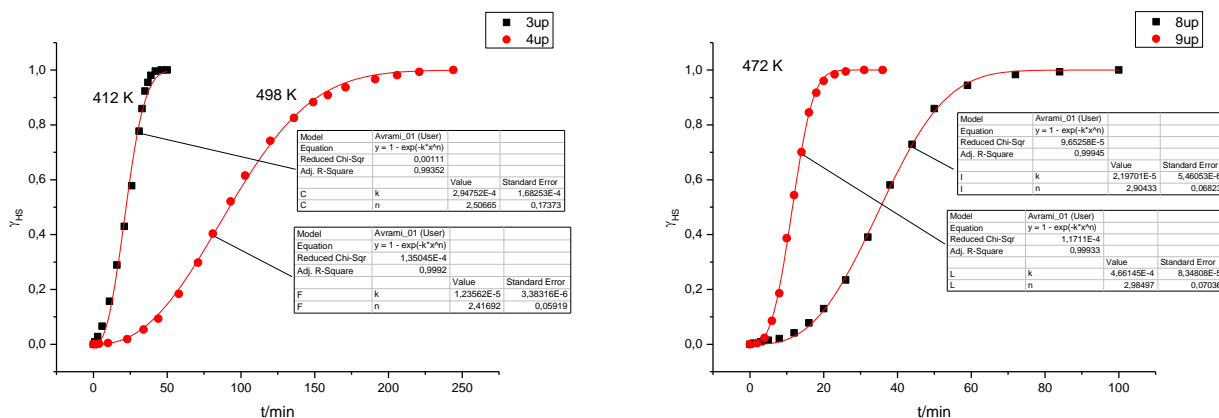


Figure S43. Fitting of kinetic curves for **2**, **2-1** and **2-2** using the JMAK model (LS \rightarrow HS transformation; left: cycles 3 and 4; right: cycles 8 – 9).

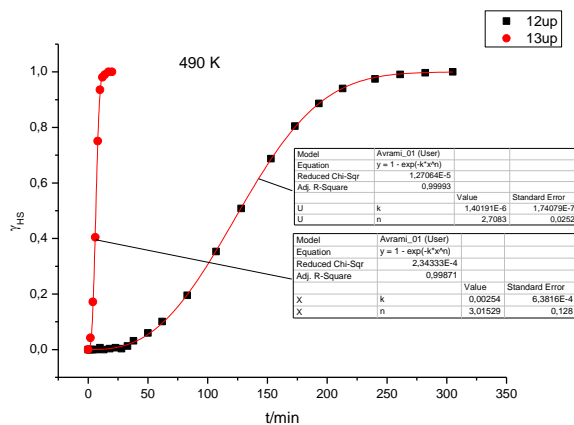
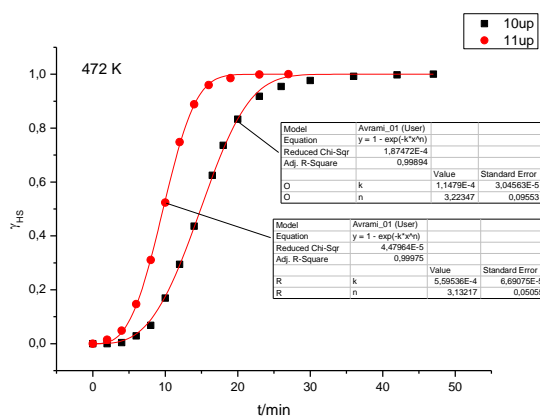


Figure S44. Fitting of kinetic curves for 2-2 and 2-3 using the JMAK model (LS \rightarrow HS transformation; left: cycles 10 and 11; right: cycles 12 and 13).

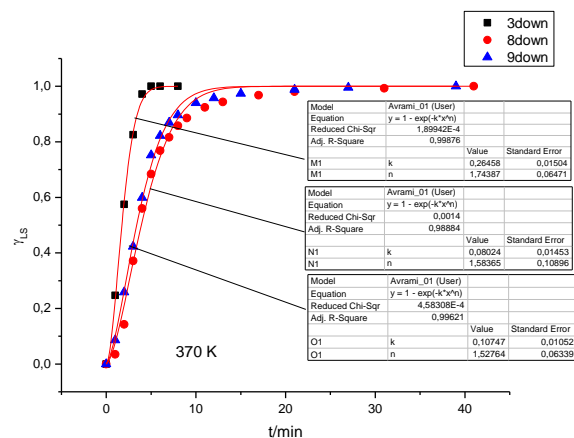
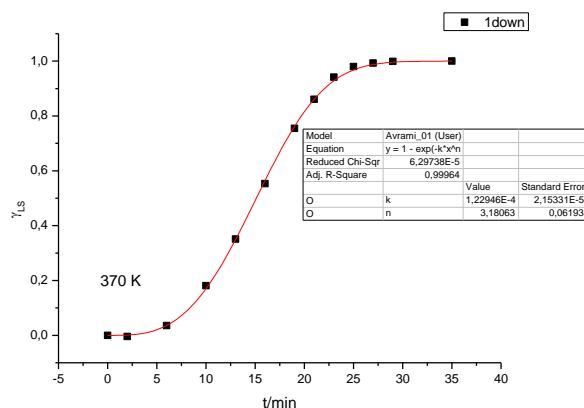


Figure S45. Fitting of kinetic curves for 2 and 2-2 using the JMAK model (HS \rightarrow LS transformation; left: cycle 1; right: cycles 3, 8 and 9).

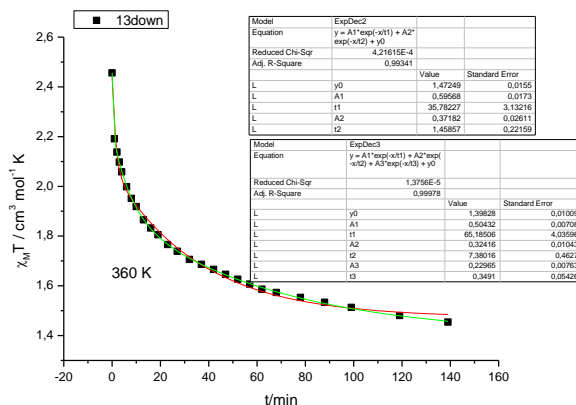
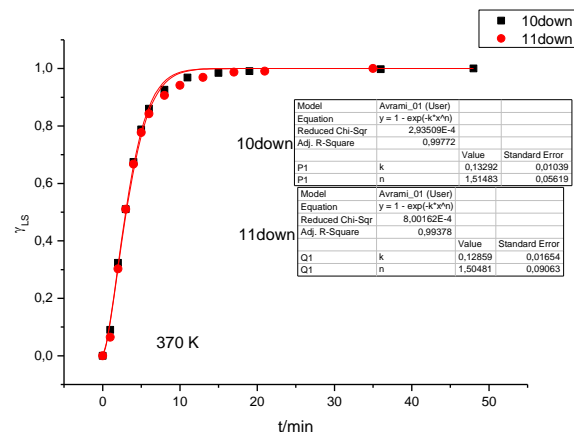


Figure S46. Left: fitting of kinetic curves for 2-2 using the JMAK model (HS \rightarrow LS transformation; cycles 10 and 11). Right: fitting of a kinetic curve for 2-3 in bi- and tri-exponential approximations (HS \rightarrow LS transformation; cycle 13).

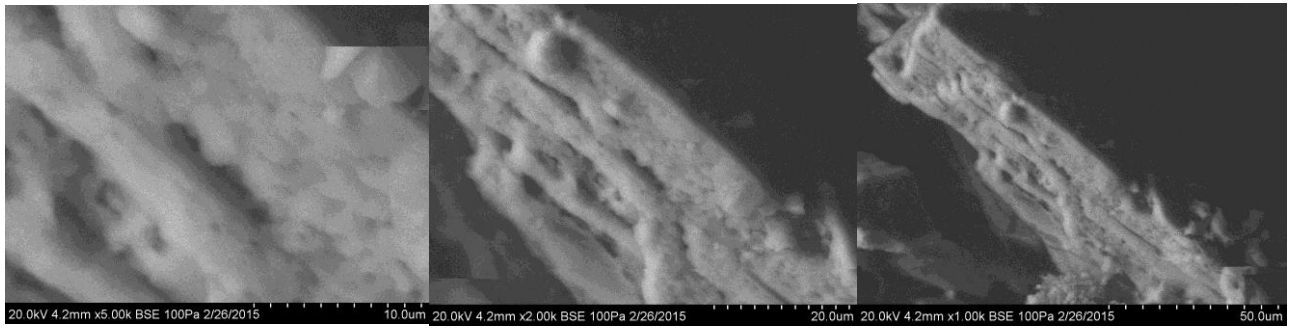


Figure S47. SEM images of the sample **2-3** after thermal cycling.

Sample 2-4

Parent phase $1^{A/LS}$. This sample of the phase $1^{A/LS}$ was taken from the experiment 2-2, vigorously ground with pestle and mortar, exposed to water vapor for 1 h (no change in the mass was observed) and sealed.

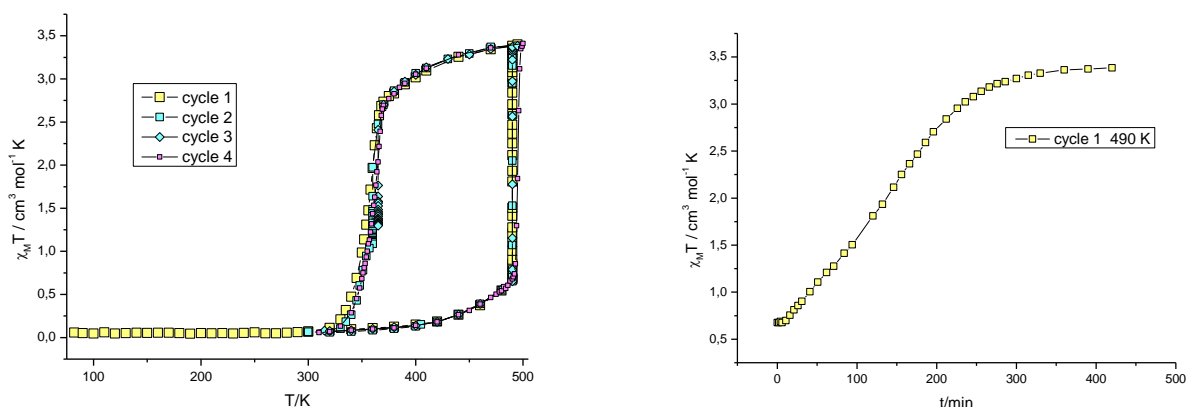


Figure S48. Sample 2-4. Thermal cycles 1 – 4 (left) and a kinetic curve for the cycle 1 (LS → HS, right).

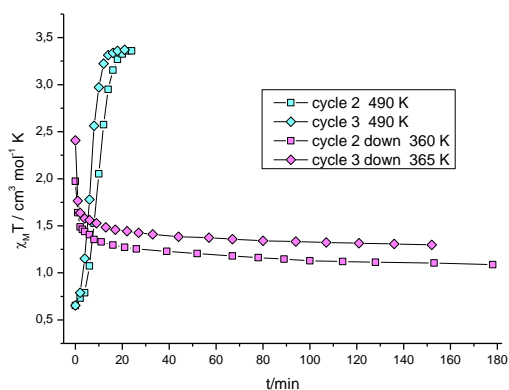


Figure S49. Sample 2-4. Kinetic curves for the cycles 2 and 3 (LS → HS and HS → LS transformations).

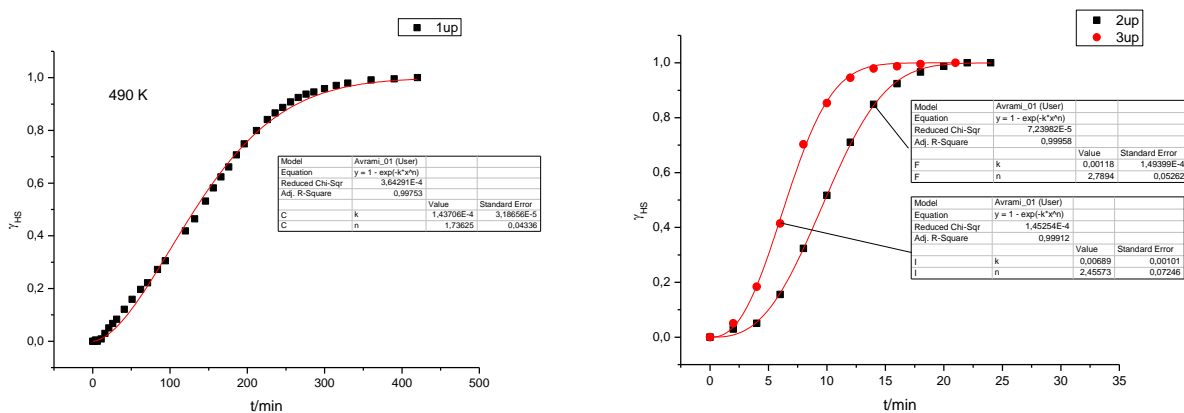


Figure S50. Fitting of kinetic curves for 2-4 using the JMAK model (LS → HS; left: cycle 1; right: cycles 2 and 3).

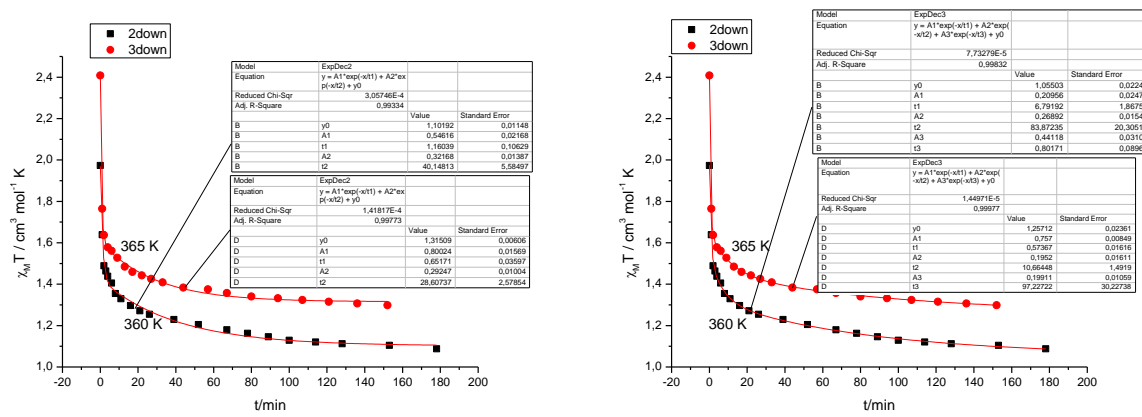


Figure S51. Fitting of kinetic curves for **2-4** (HS → LS; cycles 2 and 3) in bi- and tri-exponential approximations.

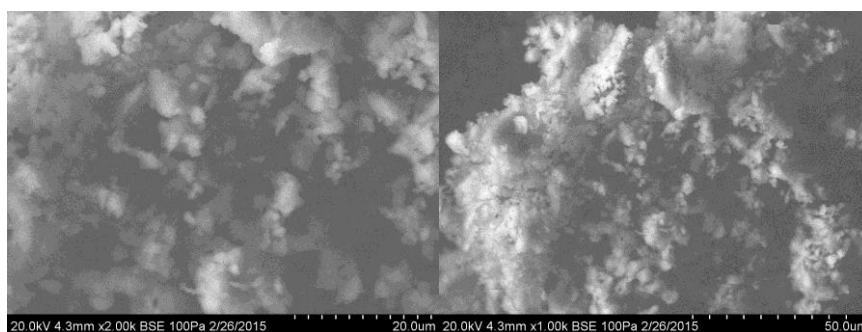


Figure S52. SEM images of the sample **2-4** after thermal cycling.

Sample 3
Parent phase $1^{LS} \cdot EtOH \cdot H_2O$.

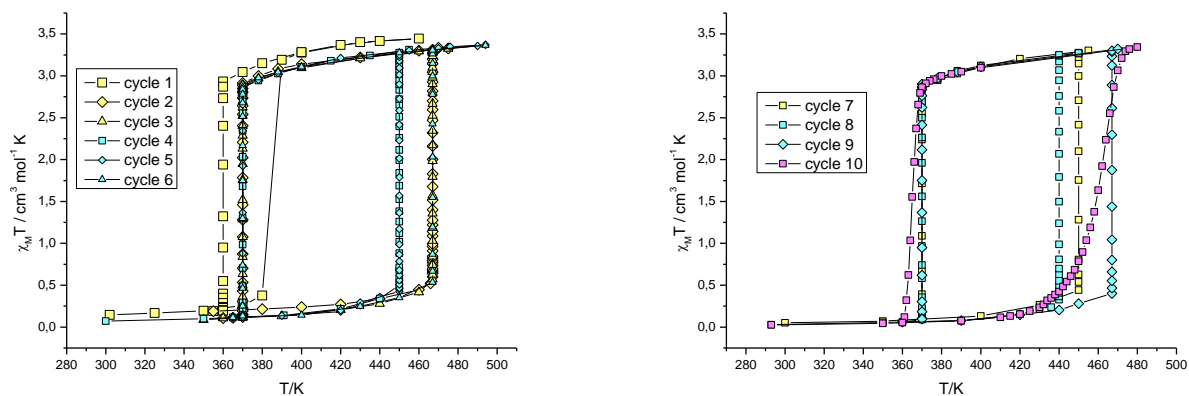


Figure S53. Sample 3. Thermal cycles 1 – 6 (left) and 7 – 10 (right). Cycles 2, 3, 6 and 9: heating rate 6 K min^{-1} .

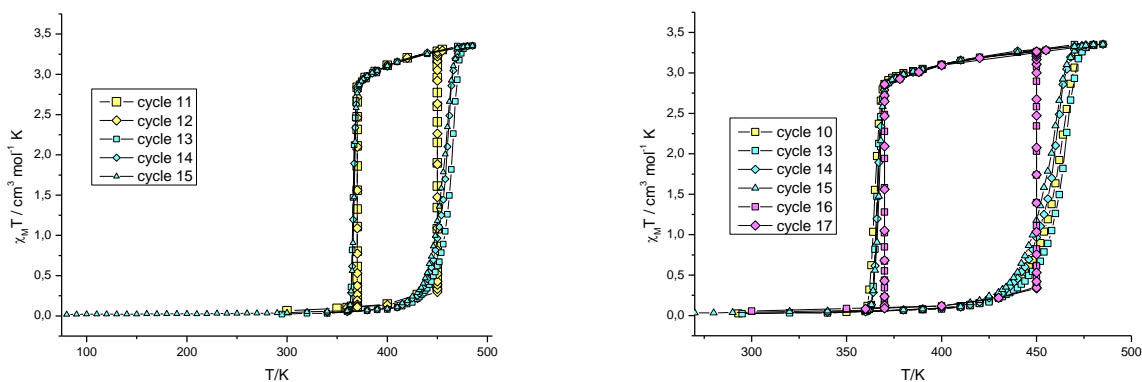


Figure S54. Sample 3. Thermal cycles 11 – 15 (left) and 10, 13 – 17 (right).

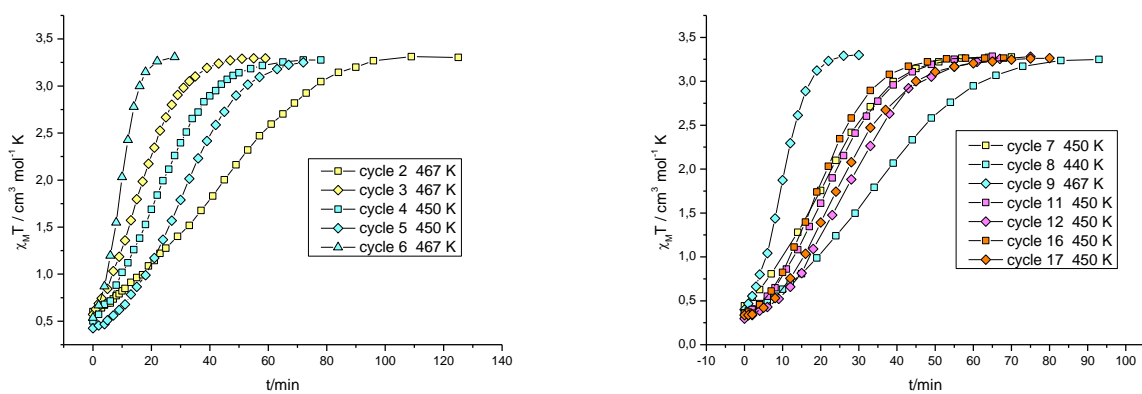


Figure S55. Sample 3. LS \rightarrow HS transformation. Kinetic curves for the cycles 2 – 6 (left) and 7 – 9, 11, 12, 16 and 17 (right).

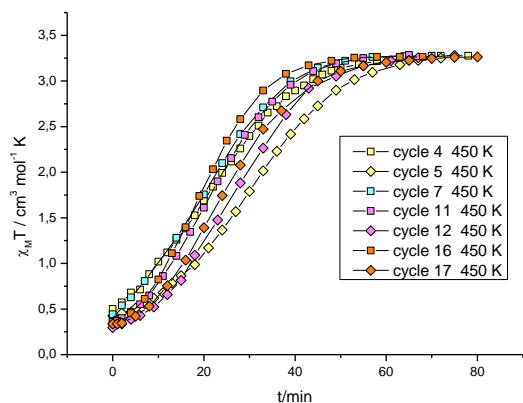


Figure S56. Sample 3. Kinetic curves for LS \rightarrow HS transformation at 450 K.

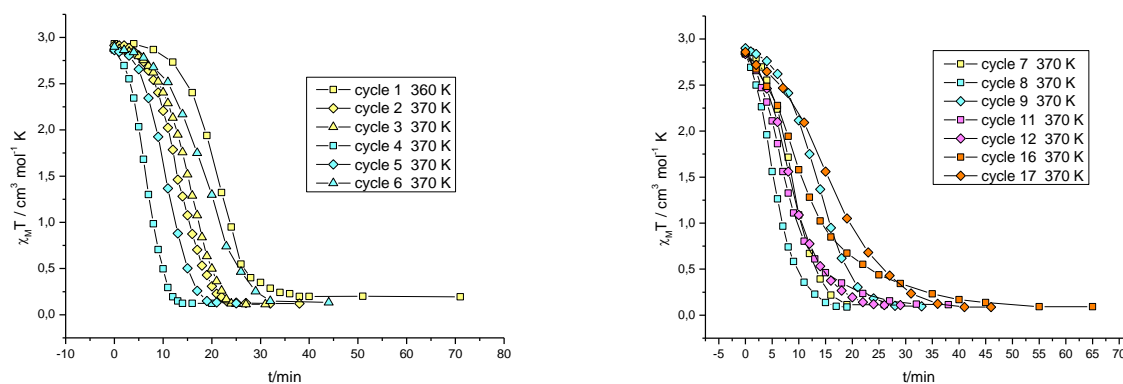


Figure S57. Sample 3. HS \rightarrow LS transformation. Kinetic curves for the cycles 1 – 6 (left) and 7 – 9, 11, 12, 16 and 17 (right).

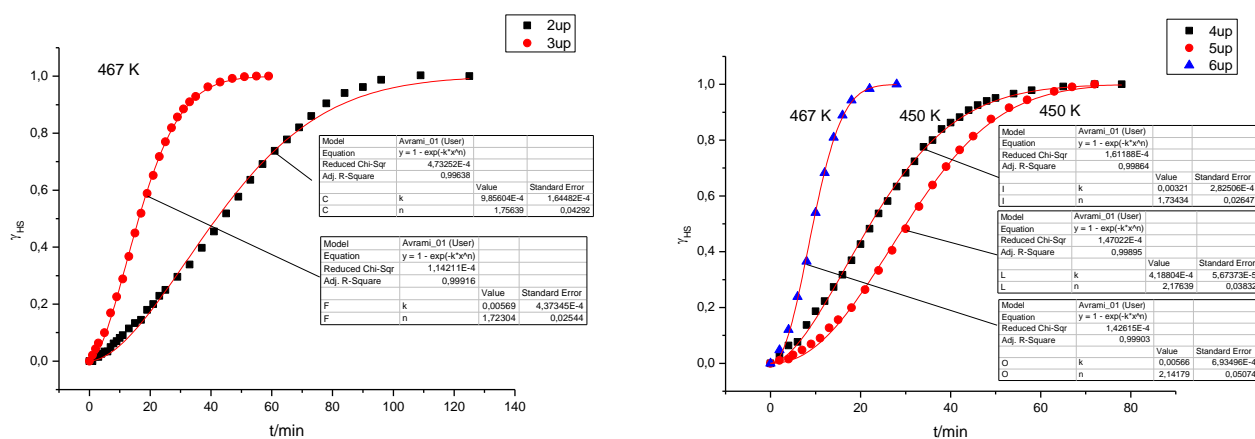


Figure S58. Fitting of kinetic curves for 3 using the JMAK model (LS \rightarrow HS transformation; left: cycles 2 and 3; right: cycles 4 – 6).

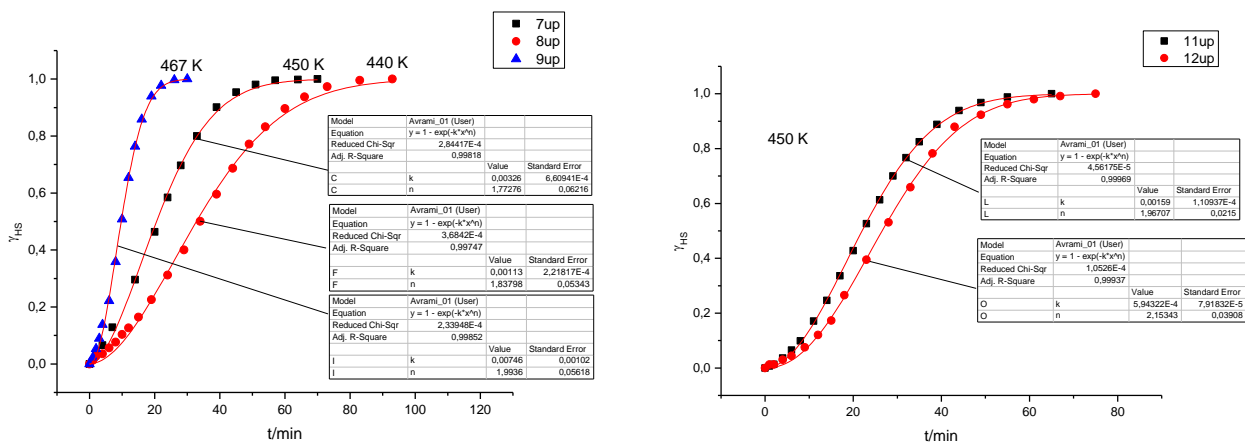


Figure S59. Fitting of kinetic curves for **3** using the JMAK model (LS → HS transformation; left: cycles 7 – 9; right: cycles 11 and 12).

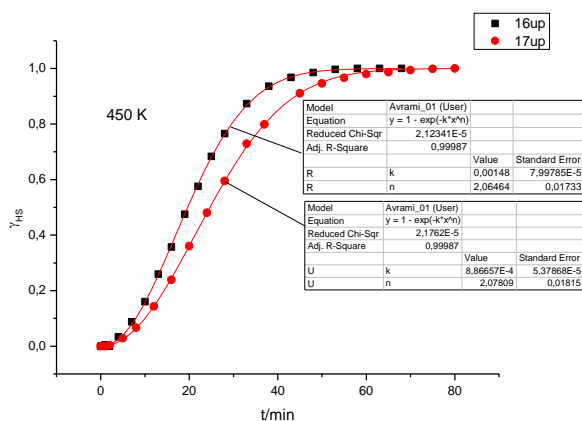


Figure S60. Fitting of kinetic curves for **3** using the JMAK model (LS → HS transformation; cycles 16 and 17).

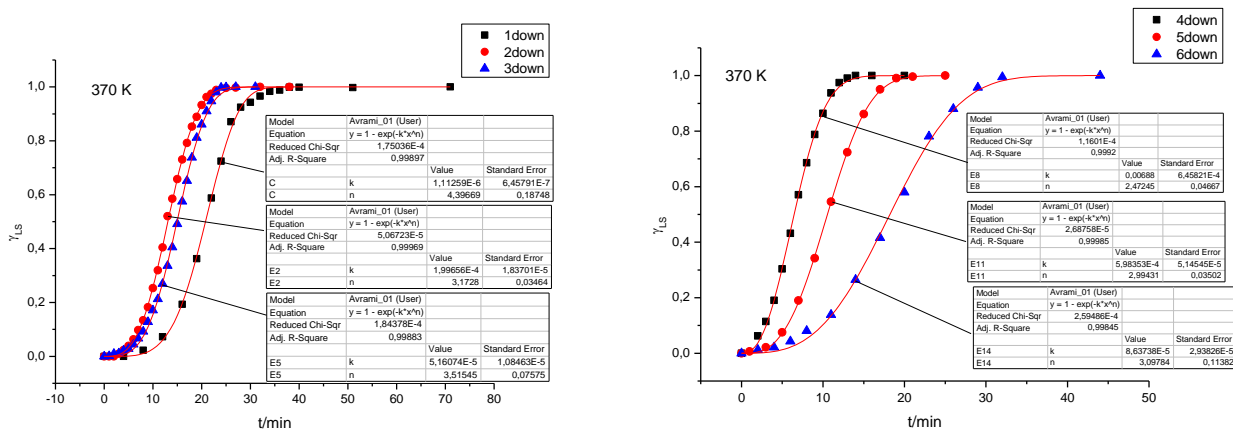


Figure S61. Fitting of kinetic curves for **3** using the JMAK model (HS → LS transformation left: cycles 1 – 3; right: cycles 4 – 6).

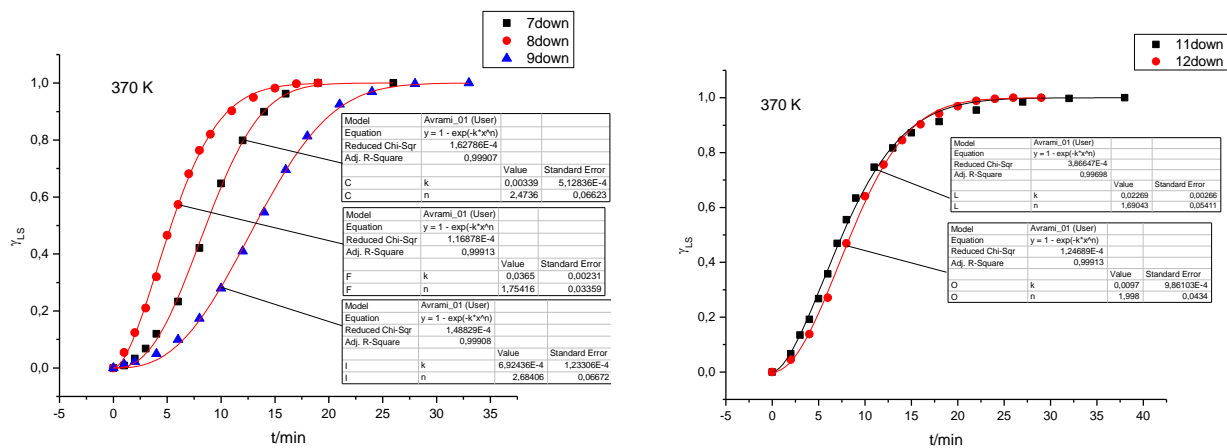


Figure S62. Fitting of kinetic curves for **3** using the JMAK model (HS \rightarrow LS transformation; left: cycles 7 – 9; right: cycles 11 – 12).

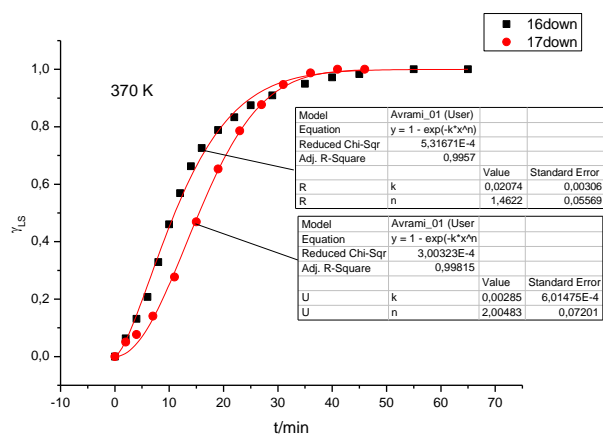


Figure S63. Fitting of kinetic curves for **3** using the JMAK model (HS \rightarrow LS transformation; cycles 16 and 17).

Sample 4
Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$.

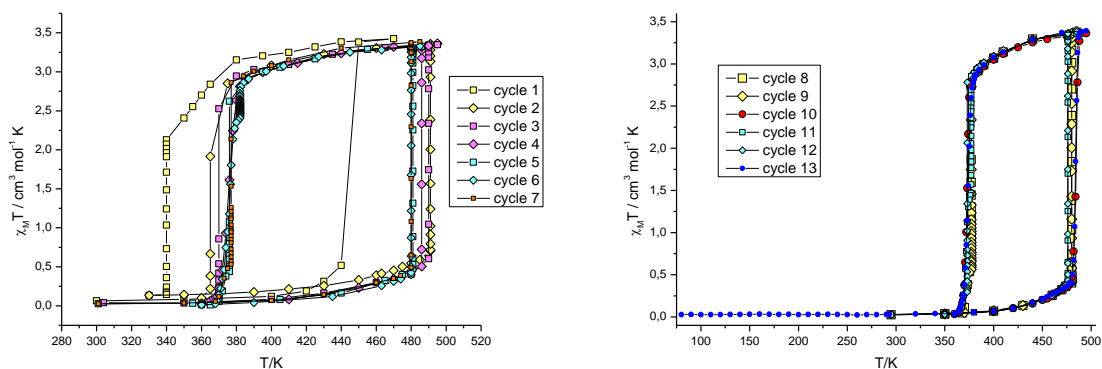


Figure S64. Sample 4. Thermal cycles 1 – 7 (left) and 8 – 13 (right).

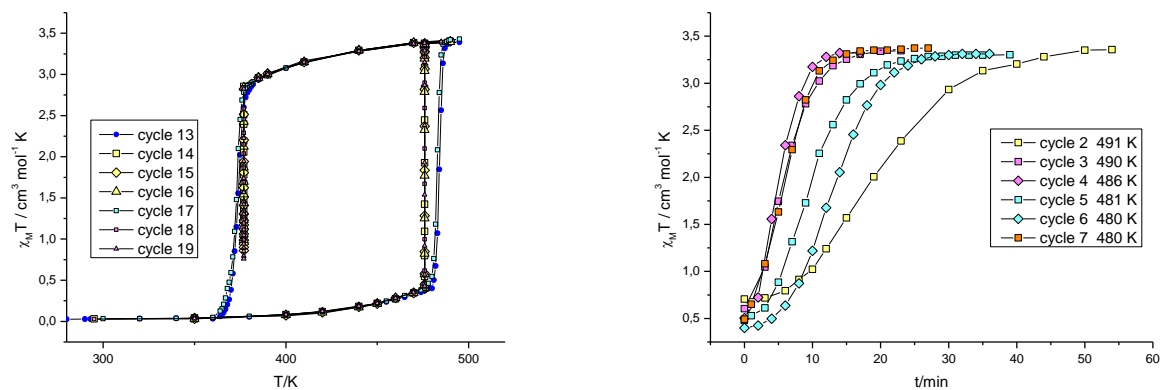


Figure S65. Sample 4. Thermal cycles 13 – 19 (left) and kinetic curves for the cycles 2 – 7 (LS → HS; right).

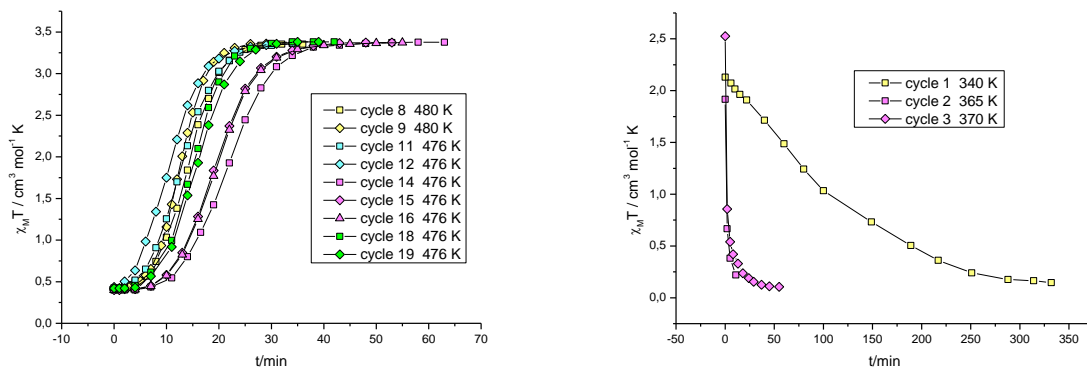


Figure S66. Sample 4. Kinetic curves for the cycles 8, 9, 11, 12, 14 – 16, 18 and 19 (LS → HS; left) and for the cycles 1 – 3 (HS → LS; right).

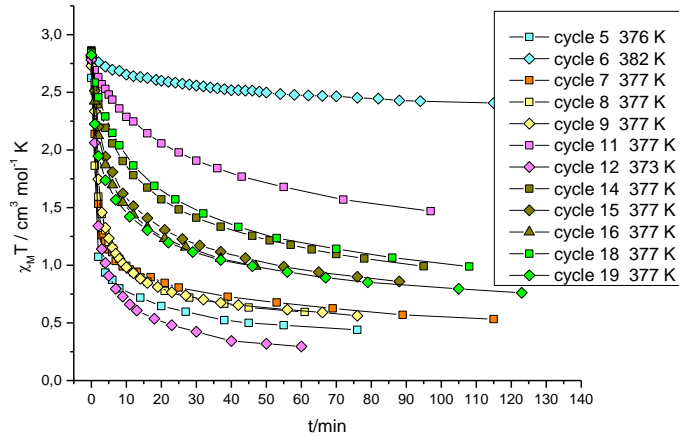


Figure S68. Sample 4. Kinetic curves for the cycles 5 – 9, 11, 12, 14 – 16, 18 and 19 (HS \rightarrow LS).

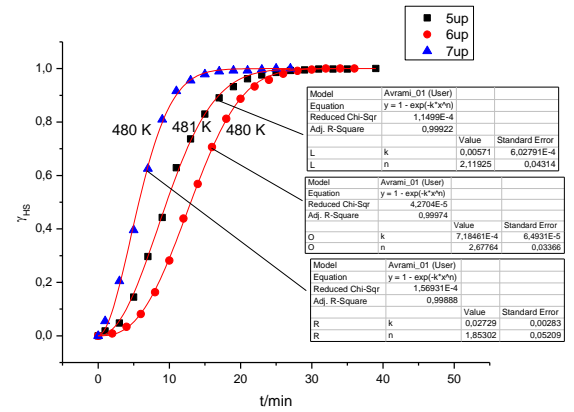
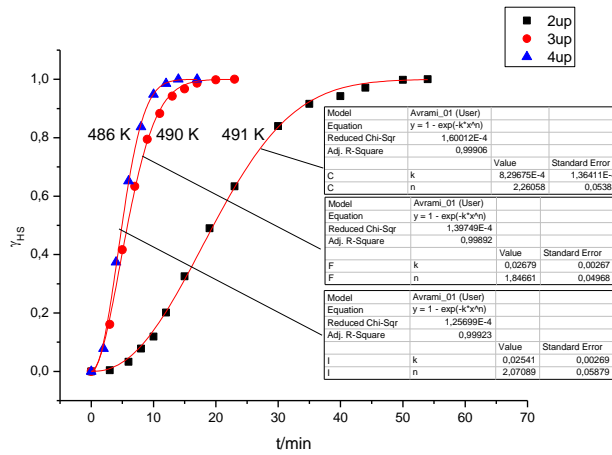


Figure S69. Fitting of kinetic curves for 4 using the JMAK model (LS \rightarrow HS; left: cycles 2 – 4; right: cycles 5 and 7).

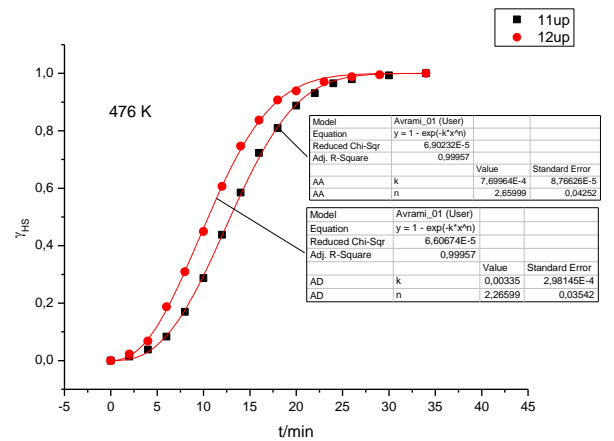
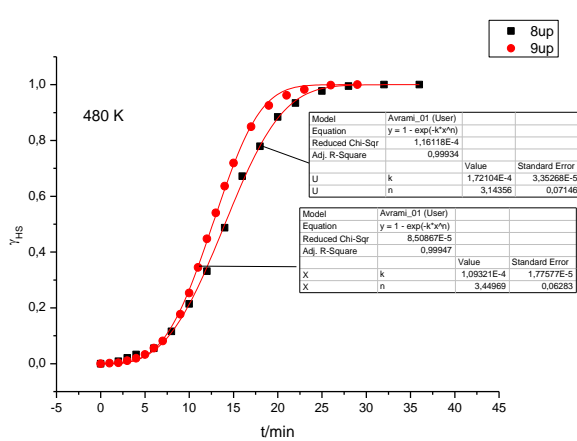


Figure S70. Fitting of kinetic curves for 4 using the JMAK model (LS \rightarrow HS; left: cycles 8 and 9; right: cycles 11 and 12).

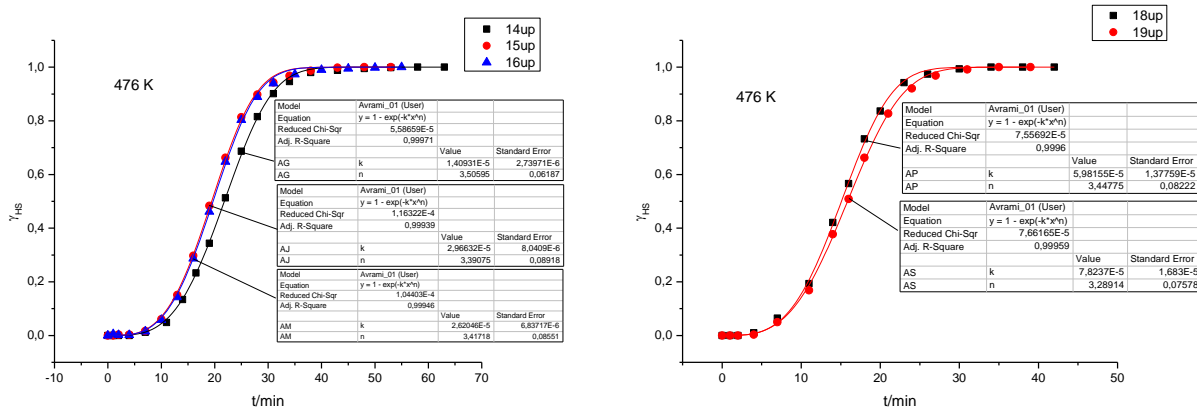


Figure S71. Fitting of kinetic curves for **4** using the JMAK model (LS → HS; left: cycles 14 – 16; right: cycles 18 and 19).

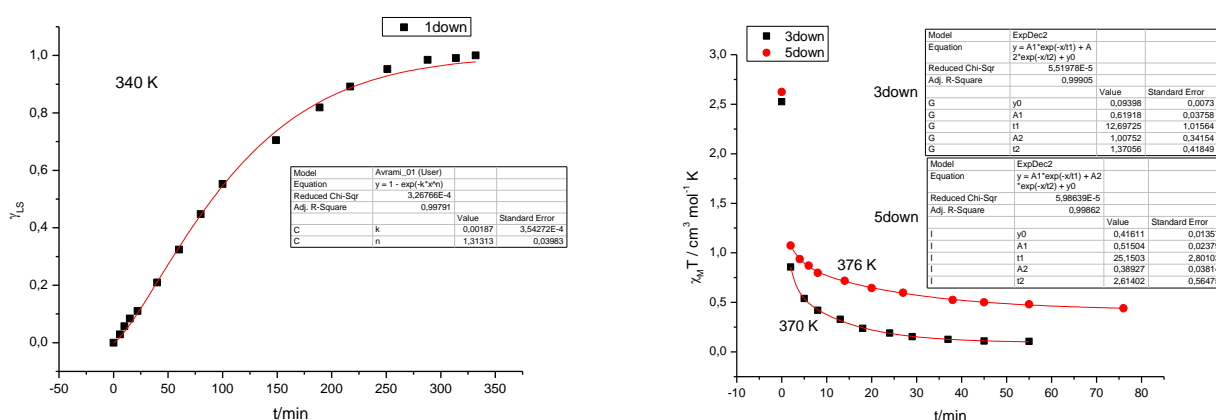


Figure S72. Fitting of kinetic curves for **4** using the JMAK model (left: cycle 1, HS → LS) and bi-exponential approximation (right: cycles 3 and 5, HS → LS).

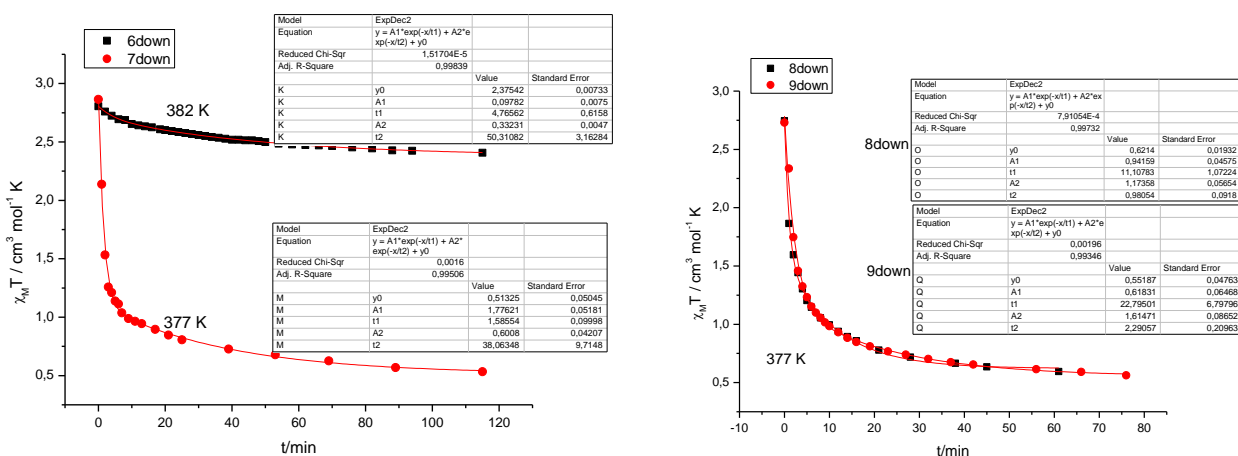


Figure S73. Fitting of kinetic curves for **4** in bi-exponential approximation (HS → LS; right: cycles 6 and 7; left: cycles 8 and 9).

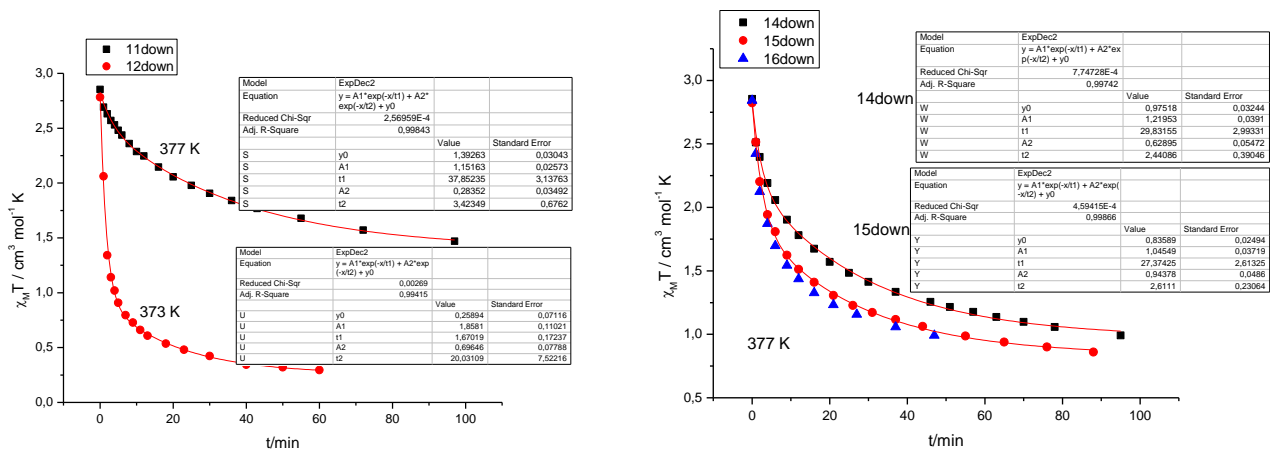


Figure S74. Fitting of kinetic curves for **4** in bi-exponential approximation (HS \rightarrow LS; right: cycles 11 and 12; left: cycles 14 – 16).

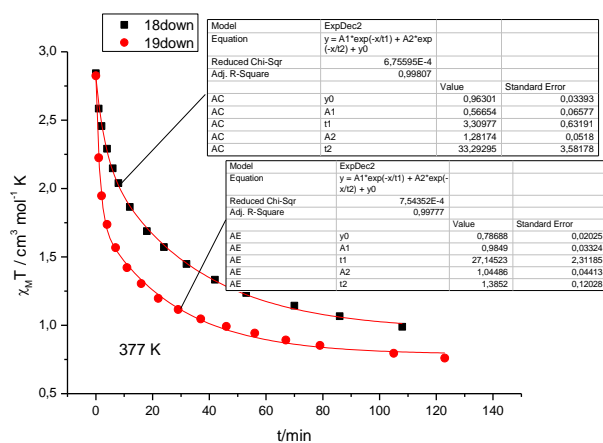


Figure S75. Fitting of kinetic curves for **4** in bi-exponential approximation (cycles 18 and 19, HS \rightarrow LS).

Elemental analysis of the sample after thermal cycling (%), calcd for $C_{30}H_{30}N_{10}B_2F_8Fe$ (760.10): C 47.4, H 4.0, N 18.4; found C 47.2, H 4.1, N 18.4.

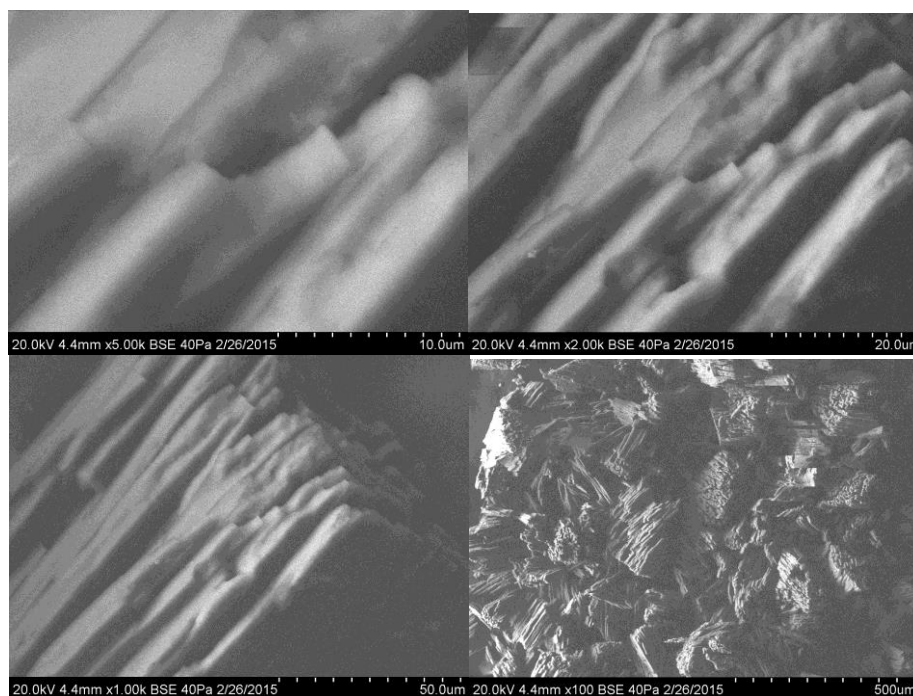


Figure S76. SEM images of the sample **4** after thermal cycling.

Samples 5 and 5-1

Sample 5

Cycles 1 and 2. Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$. The SCO regime in the cycles 1 and 2 is typical for the phase 1^{D} .

Sample 5-1

Cycles 3 – 12. After the cycles 1 and 2 had been done the sample was taken off the ampoule, exposed to water vapor for 48 h (the value of $\chi_{\text{M}}T$ dropped to *ca.* $0.1 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$; no change in the mass was detected) followed by ampoule sealing.

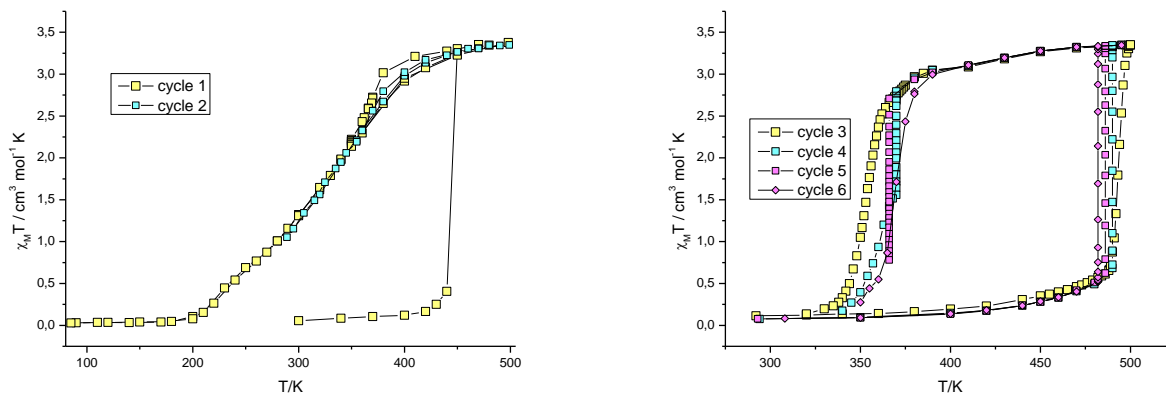


Figure S77. Left: sample 5. Thermal cycles 1 and 2. Right: sample 5-1. Thermal cycles 3 – 6.

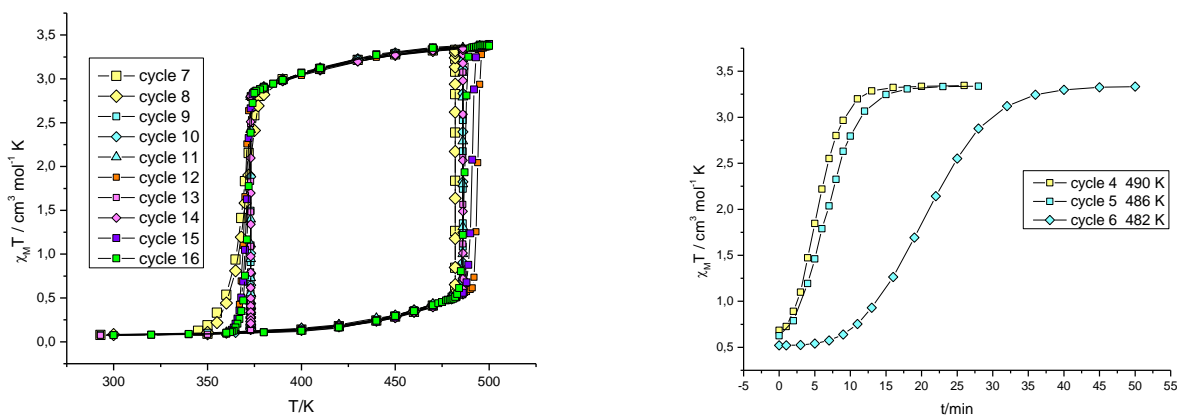


Figure S78. Sample 5-1. Thermal cycles 8 – 16 (left; cycle 12, 0.9 K min^{-1} ; cycle 15, 0.4 K min^{-1} ; cycle 16, 0.25 K min^{-1}) and kinetic curves for the cycles 4 – 6 (LS \rightarrow HS transformation, right).

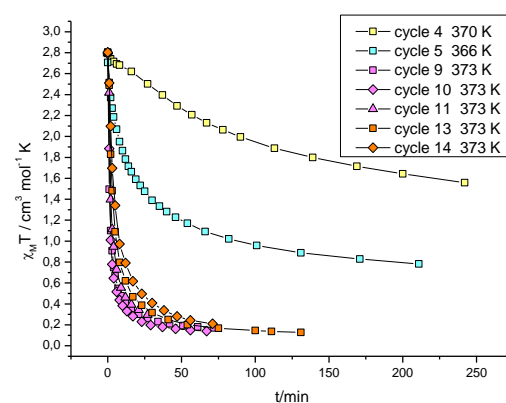
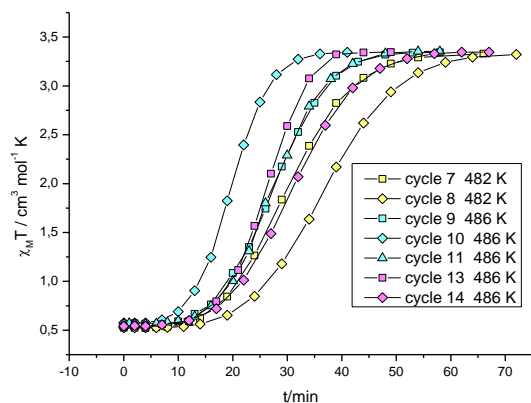


Figure S79. Sample 5-1. Kinetic curves for the cycles 7 – 11, 13, 14 (LS → HS transformation, left) and 4, 5, 9 – 11, 13 and 14 (HS → LS transformation, left).

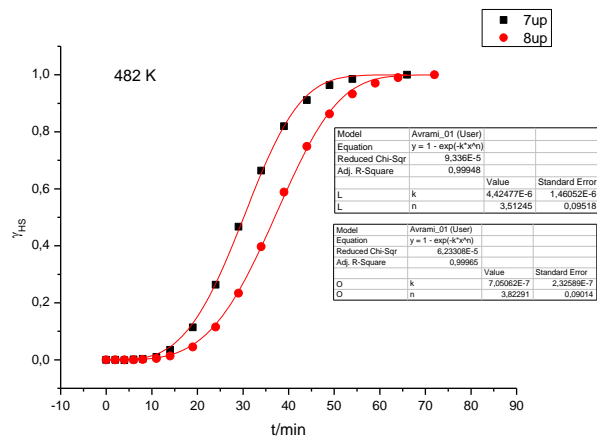
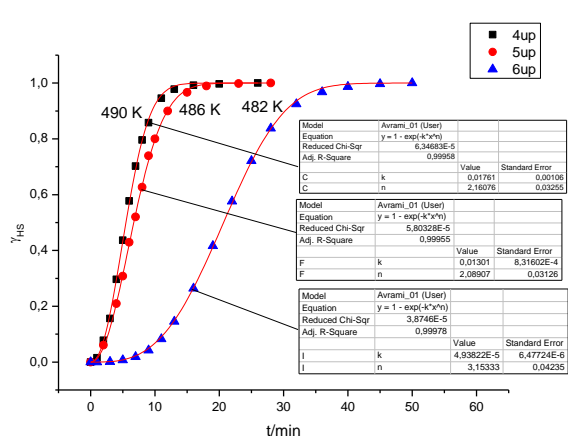


Figure S80. Fitting of kinetic curves for 5-1 using the JMAK model (LS → HS; left: cycles 4 – 6; right: cycles 7 and 8).

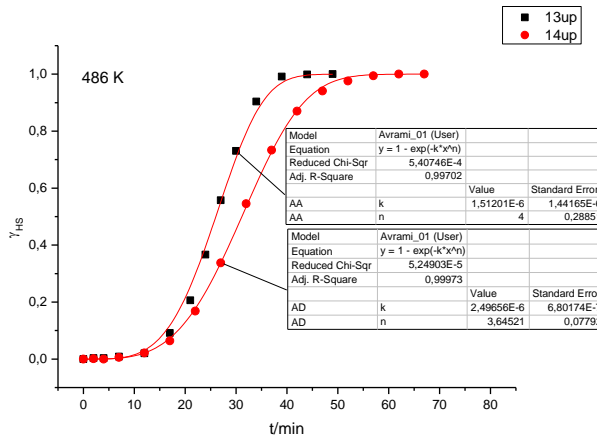
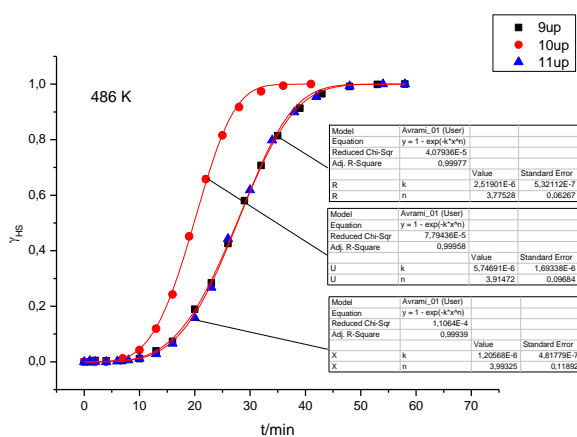


Figure S81. Fitting of kinetic curves for 5-1 using the JMAK model (LS → HS; left: cycles 9 – 11; right: cycles 13 and 14).

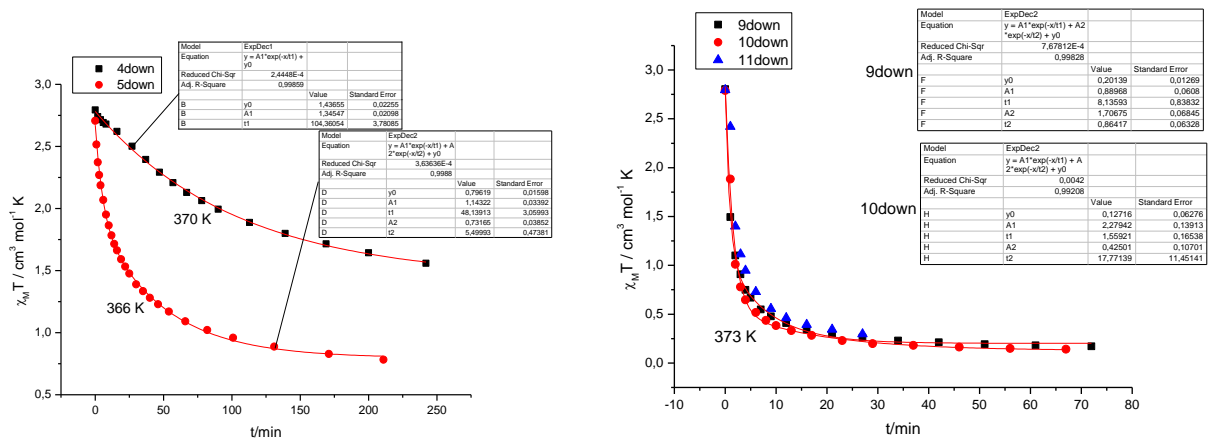


Figure S82. Fitting of kinetic curves for **5-1** in mono- and bi-exponential approximations (HS \rightarrow LS; left: cycles 4 and 5; right: cycles 9 and 10).

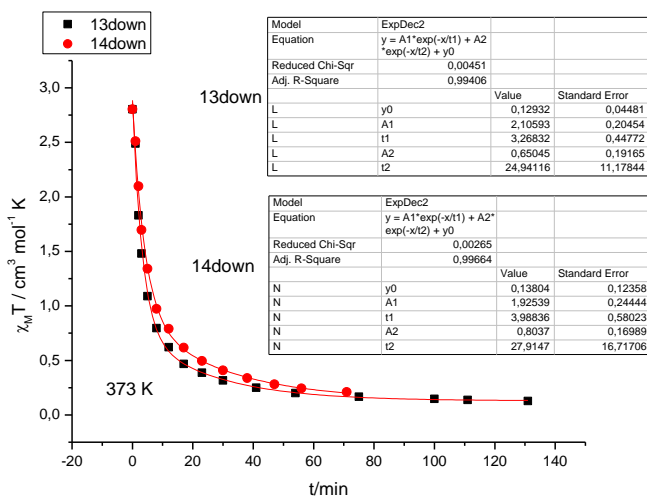


Figure S83. Fitting of kinetic curves for **5-1** in bi-exponential approximation (HS \rightarrow LS; cycles 13 and 14).

Sample 6

Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$. The phase was exposed to water and ethanol vapors for 48 h (mass increase: 4.6 %).

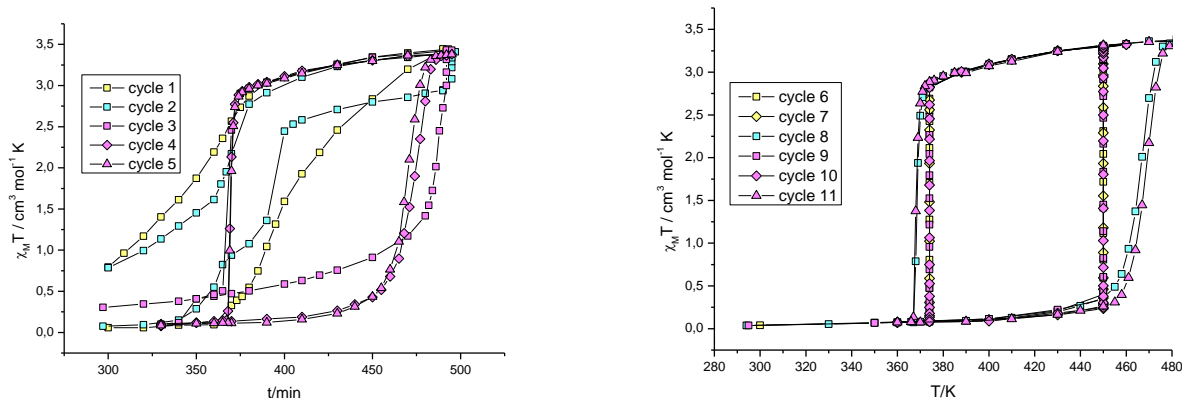


Figure S84. Sample 6. Thermal cycles 1 – 5 (left) and 6 – 11 (right).

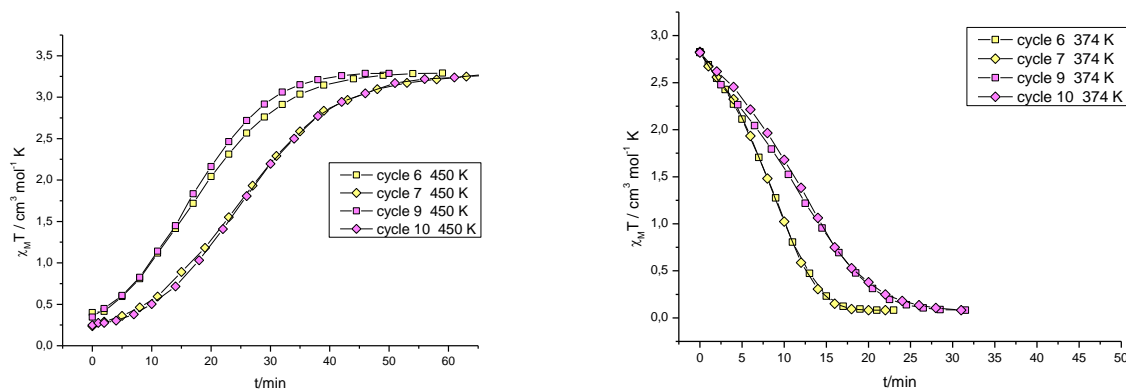


Figure S85. Sample 6. Kinetic curves for the cycles 6, 7, 9, 10 (left: LS → HS transformation, right: HS → LS transformation).

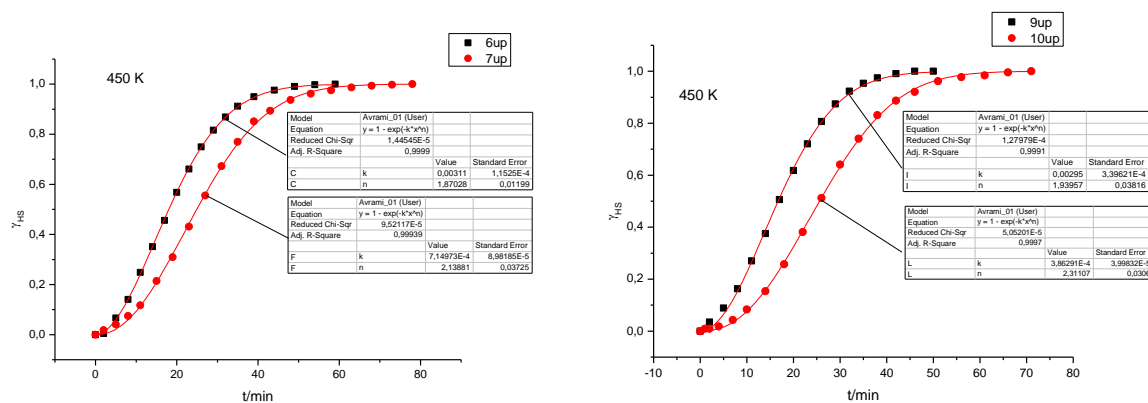


Figure S86. Fitting of kinetic curves for 6 using the JMAK model (LS → HS; left: cycles 6 and 7; right: cycles 9 and 10).

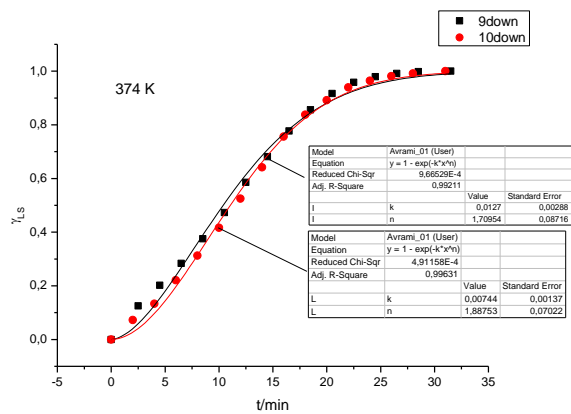
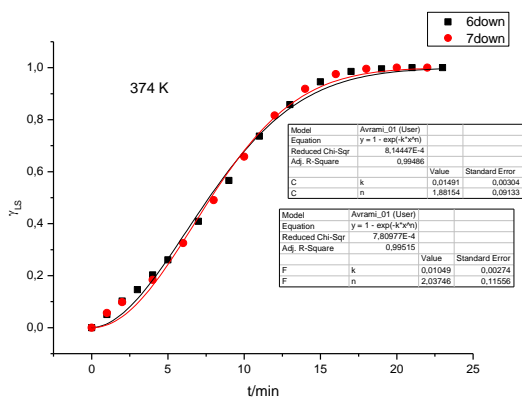


Figure S87. Fitting of kinetic curves for **6** using the JMAK model (HS → LS; left: cycles 6 and 7; right: cycles 9 and 10).

Sample 7
Parent phase $1^{LS} \cdot EtOH \cdot H_2O$.

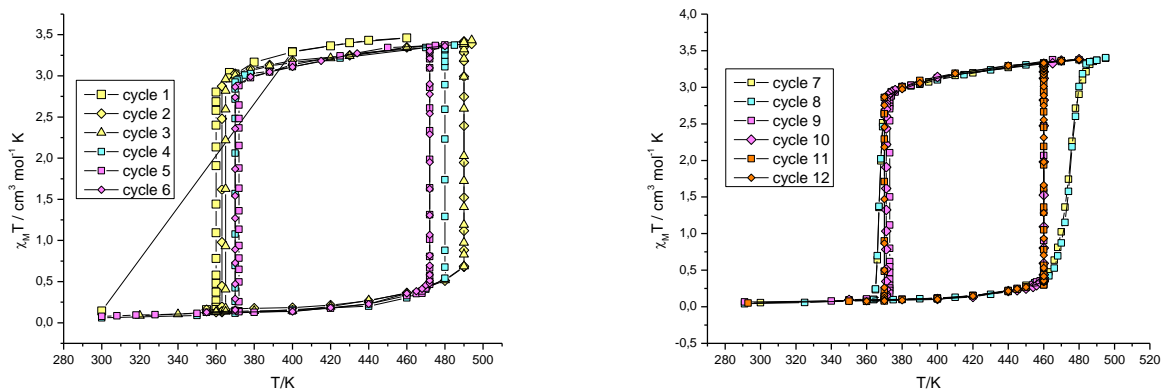


Figure S88. Sample 7. Thermal cycles 1 – 6 (left) and 7 – 12 (right). Cycle 1: heating rate 10 K/min (300 – 400 K). Cycles 2, 3, 4, 11, 12: heating rate 6 K/min. Cycles 5, 6, 9, 10: heating rate 2 K min⁻¹.

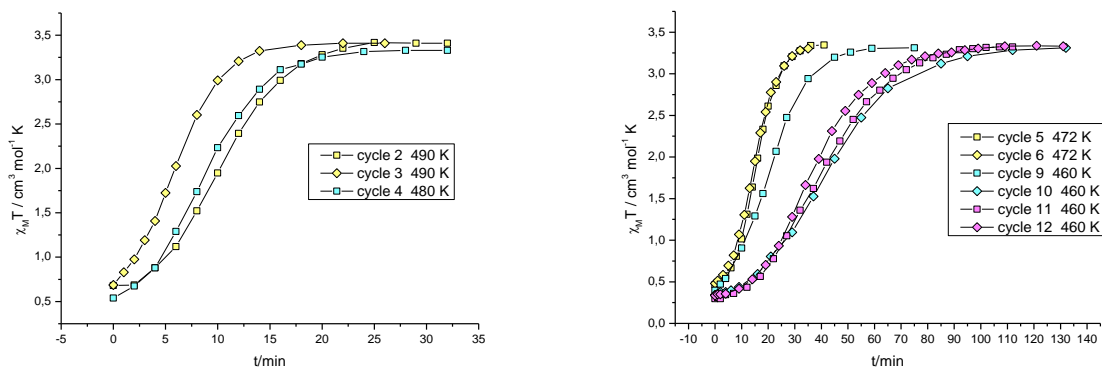


Figure S89. Sample 7. LS → HS transformation. Kinetic curves for the cycles 2 – 4 (left) and 5, 6, 9 – 12 (right).

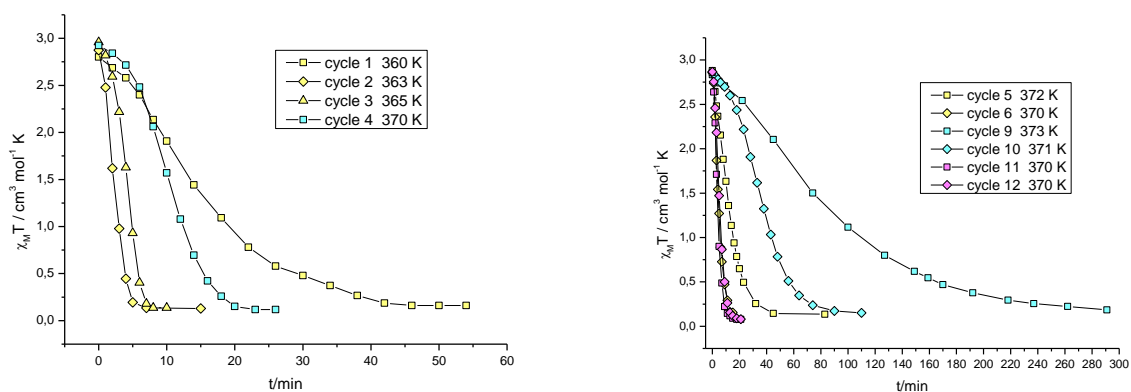


Figure S90. Sample 7. HS → LS transformation. Kinetic curves for the cycles 1 – 4 (left) and 5, 6, 9 – 12 (right).

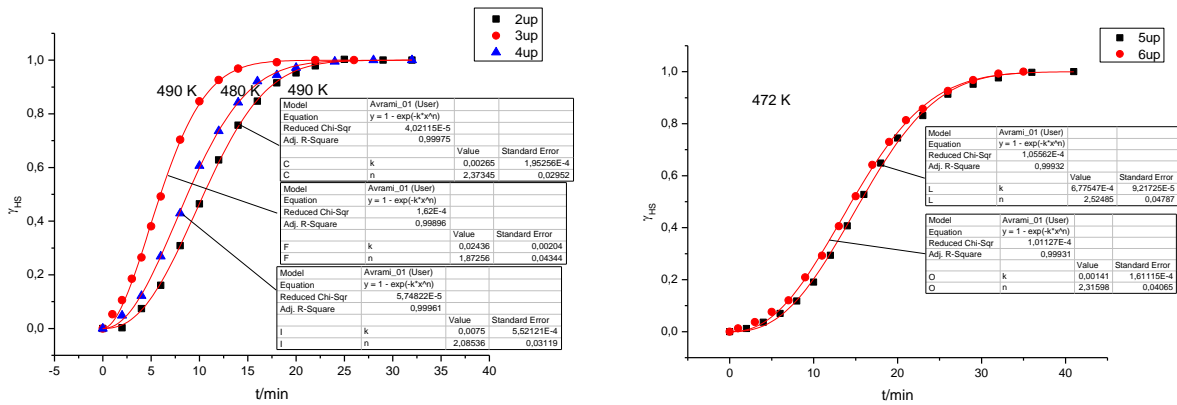


Figure S91. Fitting of kinetic curves for 7 using the JMAK model (LS → HS; left: cycles 2 – 4; right: cycles 5 and 6).

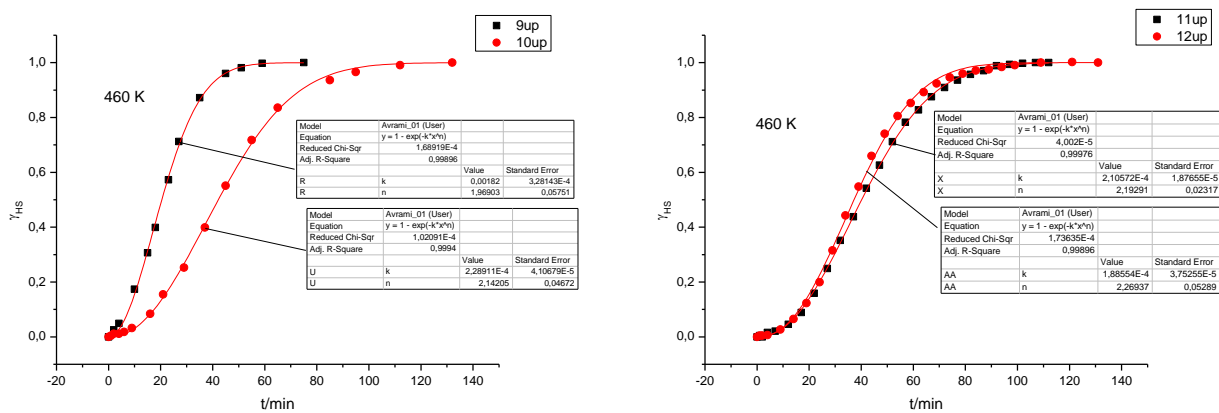


Figure S92. Fitting of kinetic curves for 7 using the JMAK model (LS → HS; left: cycles 9 and 10; right: cycles 11 and 12).

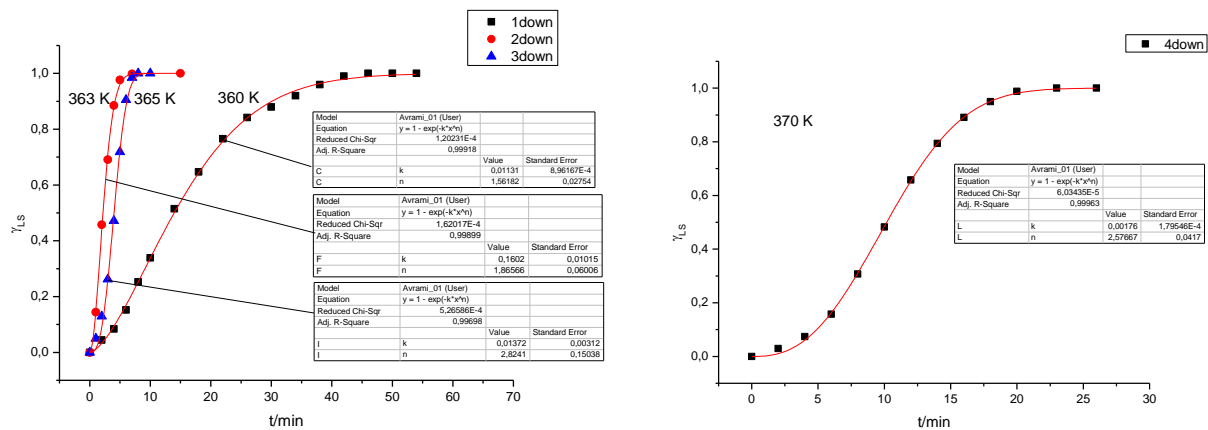


Figure S93. Fitting of kinetic curves for 7 using the JMAK model (HS → LS; left: cycles 1 – 3; right: cycle 4).

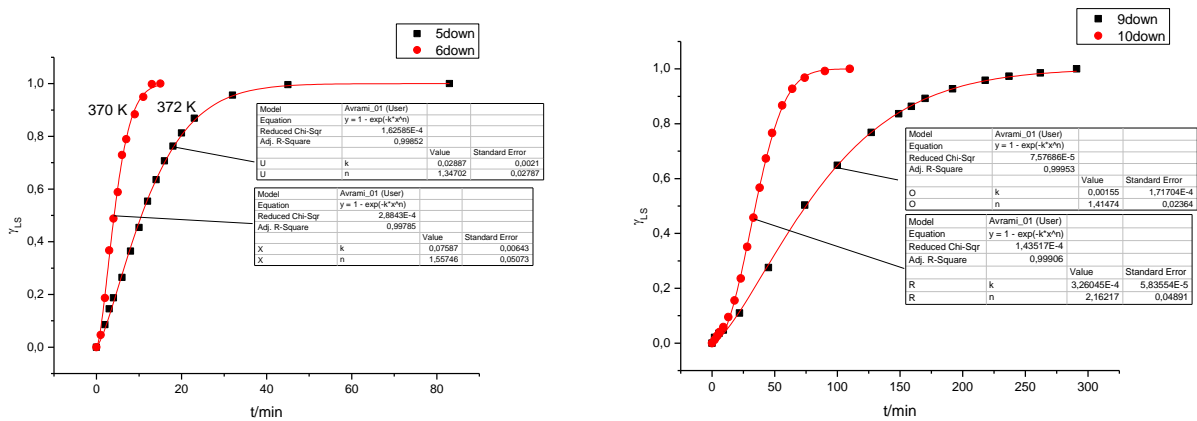


Figure S94. Fitting of kinetic curves for 7 using the JMAK model (HS → LS; left: cycles 5 and 6; right: cycles 9 and 10).

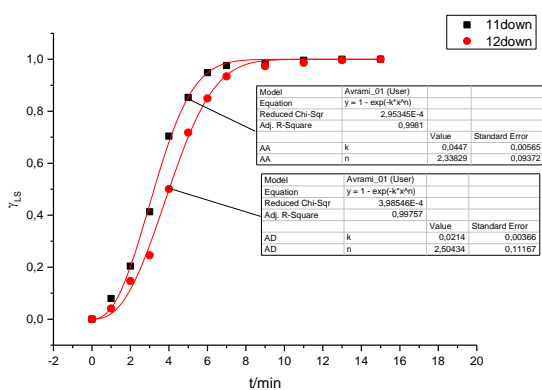


Figure S95. Fitting of kinetic curves for 7 using the JMAK model (HS → LS; cycles 11 and 12).

Sample 8

Parent phase $1^{LS} \cdot EtOH \cdot H_2O$.

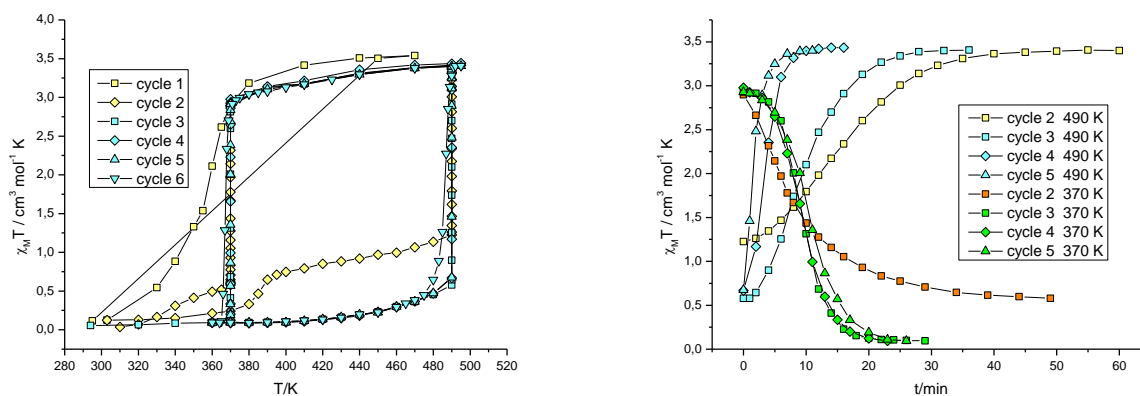


Figure S96. Sample 8. Thermal cycles 1 – 6 (left) and kinetic curves for the cycles 2 – 5 (right). Heating rate in the cycle 1 was 10 K/min (300 – 450 K).

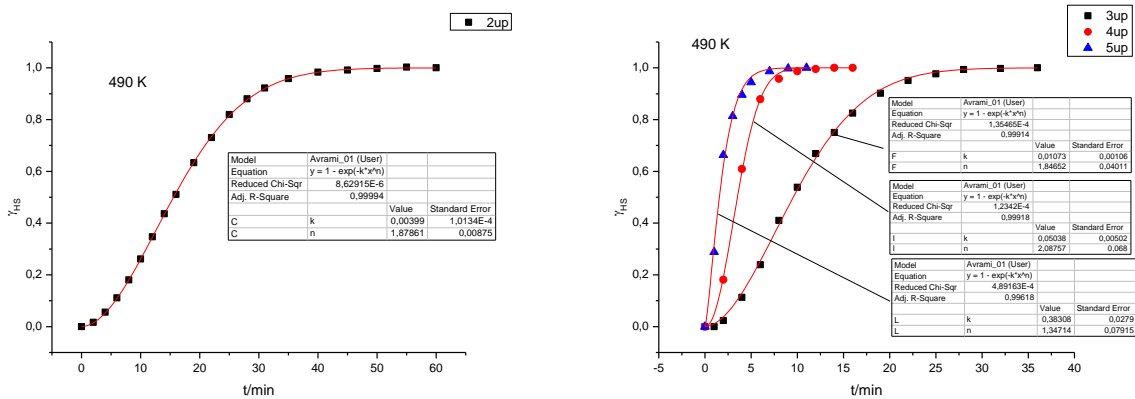


Figure S97. Fitting of kinetic curves for 8 using the JMAK model (LS \rightarrow HS; left: cycle 2; right: cycles 3 – 5).

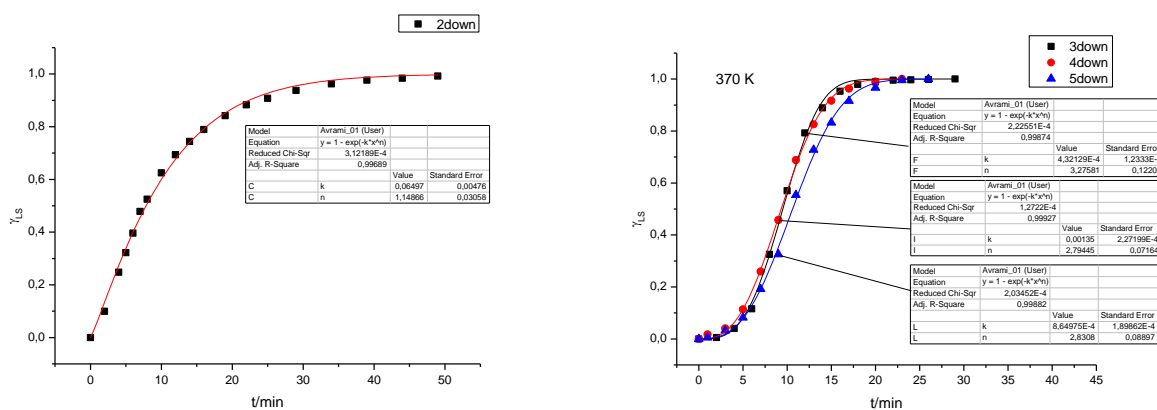


Figure S98. Fitting of kinetic curves for 8 using the JMAK model (HS \rightarrow LS; left: cycle 2; right: cycles 3 – 5).

Sample 9
Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$.

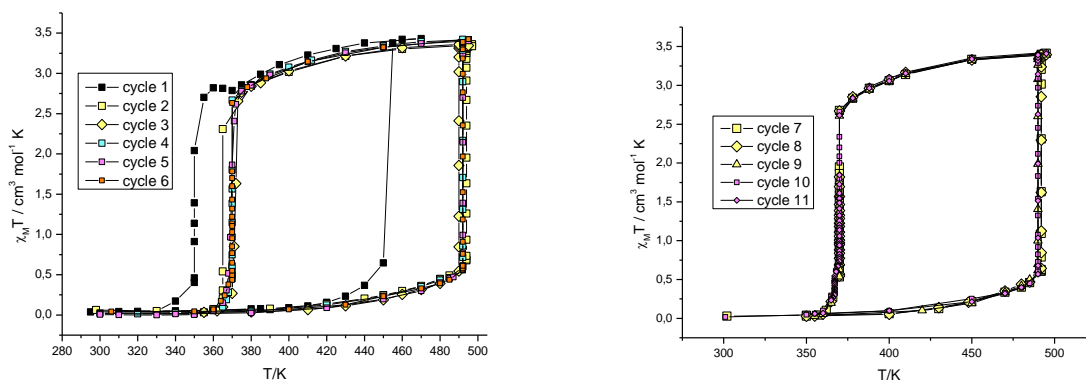


Figure S99. Sample 9. Thermal cycles 1 – 6 (left) and 7 – 11 (right).

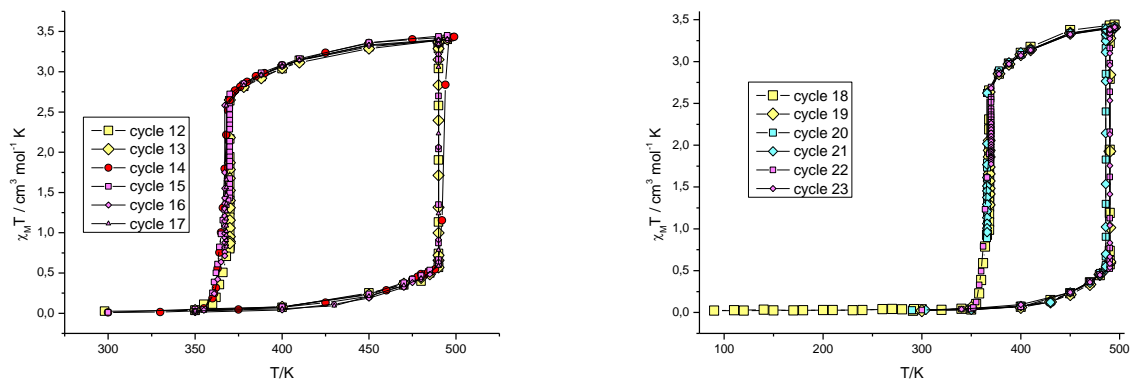


Figure S100. Sample 9. Thermal cycles 12 – 17 (left) and 18 – 23 (right)

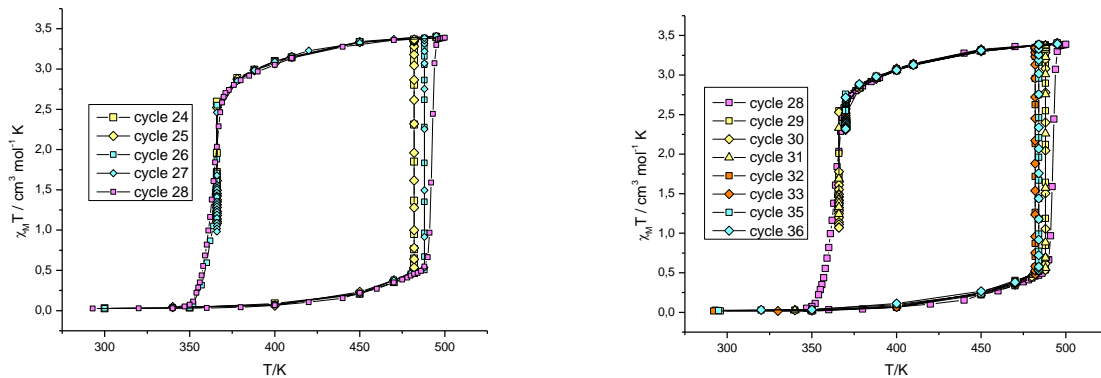


Figure S101. Sample 9. Thermal cycles 24 – 28 (left) and 28 – 36 (right).

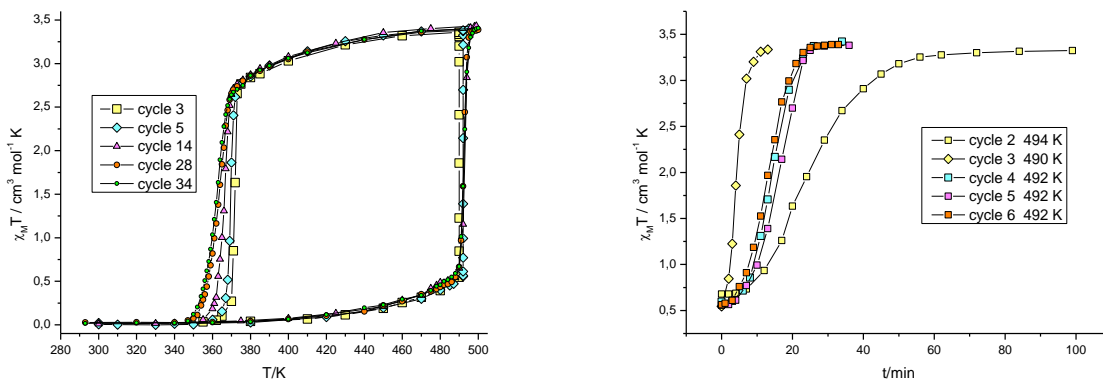


Figure S102. Sample 9. Thermal cycles 3, 5, 14, 28 and 34 (left) and kinetic curves for the cycles 2 – 6 (right, LS \rightarrow HS).

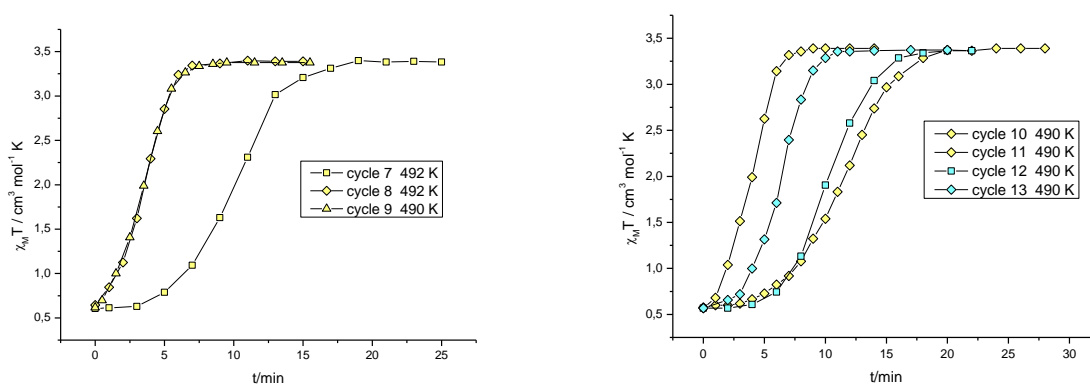


Figure S103. Sample 9. Kinetic curves for the cycles 7 – 9 (LS \rightarrow HS; right) and 10 – 13 (LS \rightarrow HS; left).

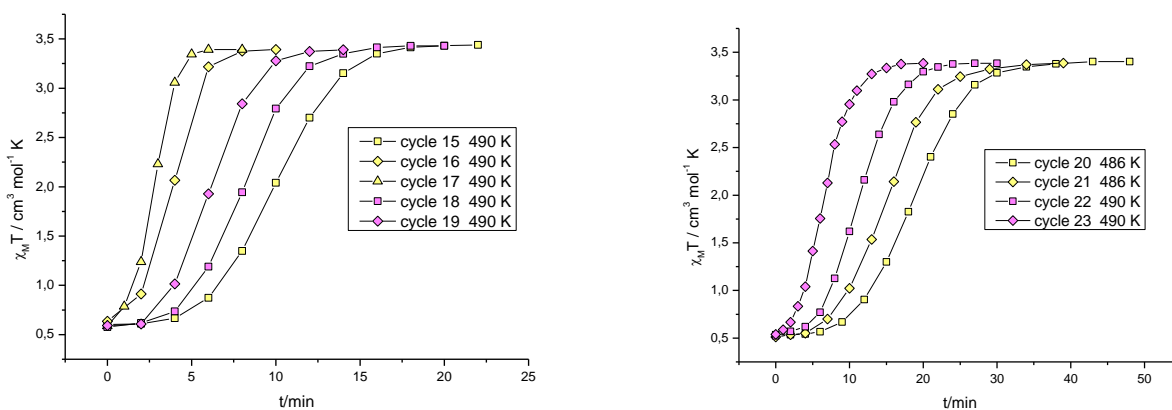


Figure S104. Sample 9. Kinetic curves for the cycles 15 – 19 (LS \rightarrow HS; right) and 20 – 23 (LS \rightarrow HS; left).

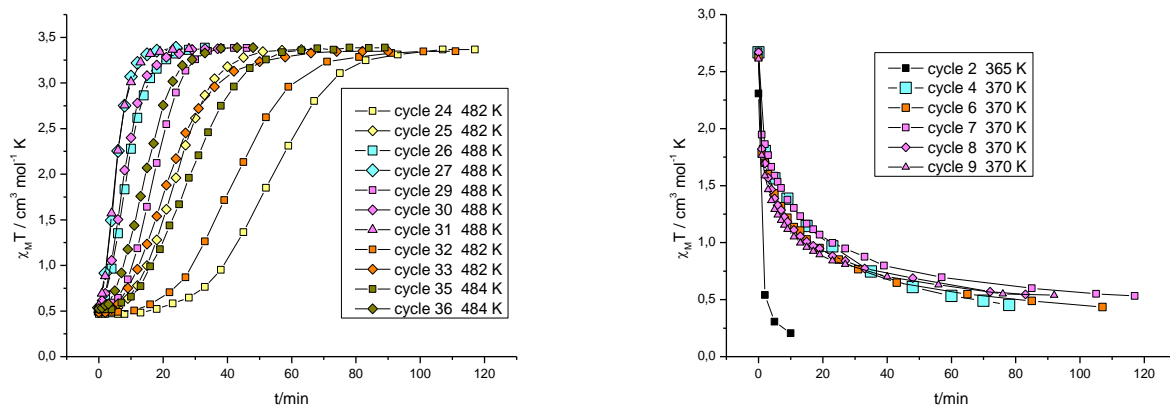


Figure S105. Sample 9. Kinetic curves for the cycles 24 – 27, 29 – 33, 35 and 36 (LS → HS; left) and 2, 4, 6 – 9 (HS → LS; right).

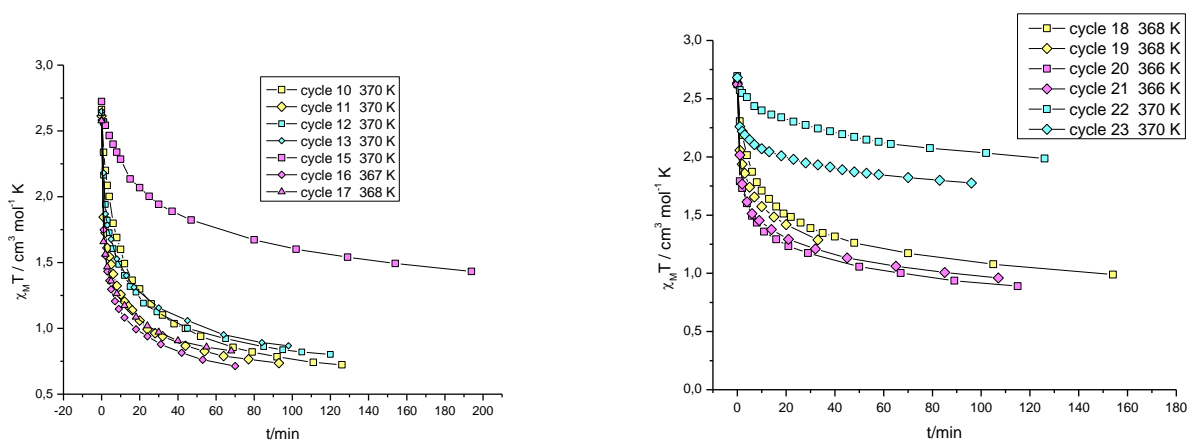


Figure S106. Sample 9. Kinetic curves for the cycles 10 – 13 and 15 – 16 (HS → LS; left) and 18 – 23 (HS → LS; right).

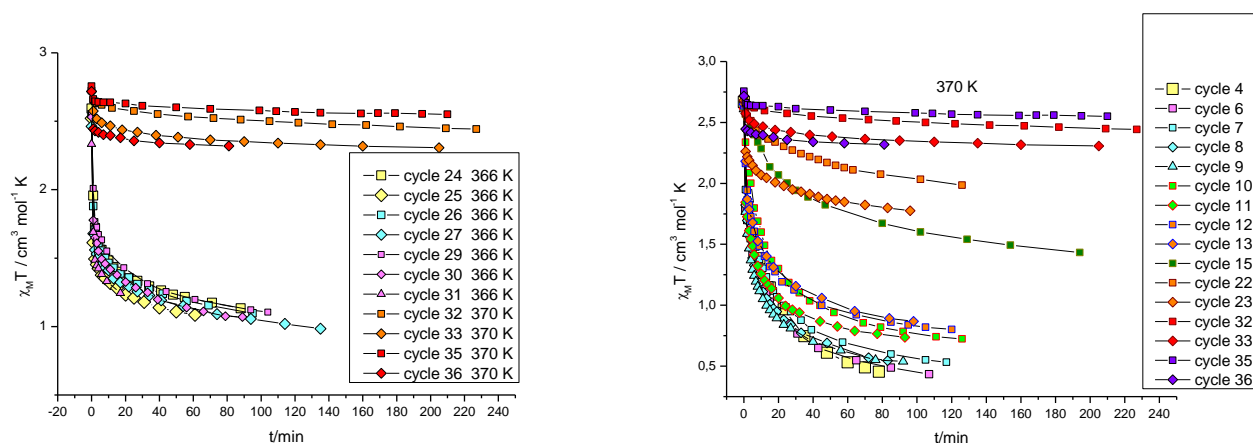


Figure S107. Sample 9. Kinetic curves for the cycles 24 – 27, 29 – 33, 35 and 36 (HS → LS; left) and all kinetic curves at 370 K (HS → LS; right).

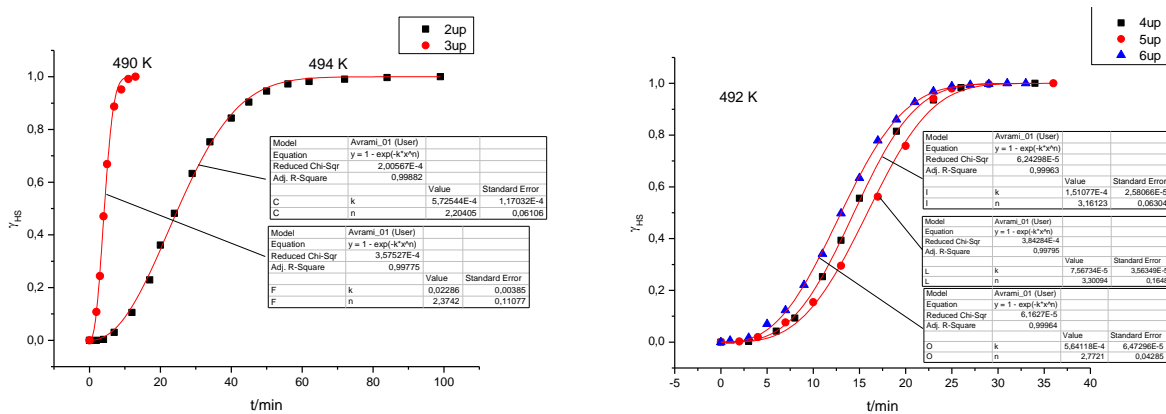


Figure S108. Fitting of kinetic curves for 9 using the JMAK model (LS → HS; left: cycles 2 and 3; right: cycles 4 - 6).

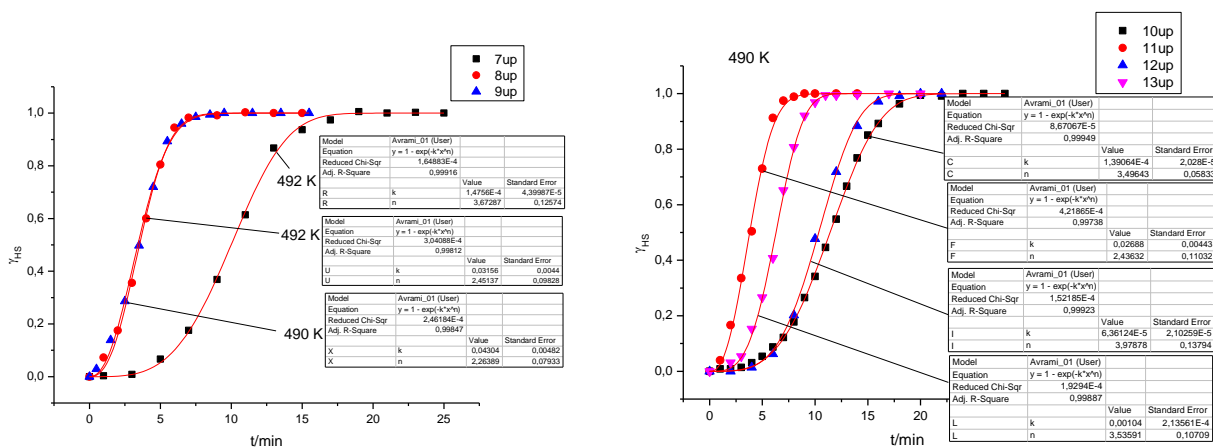


Figure S109. Fitting of kinetic curves for 9 using the JMAK model (LS → HS; left: cycles 7 - 9; right: cycles 10 - 13).

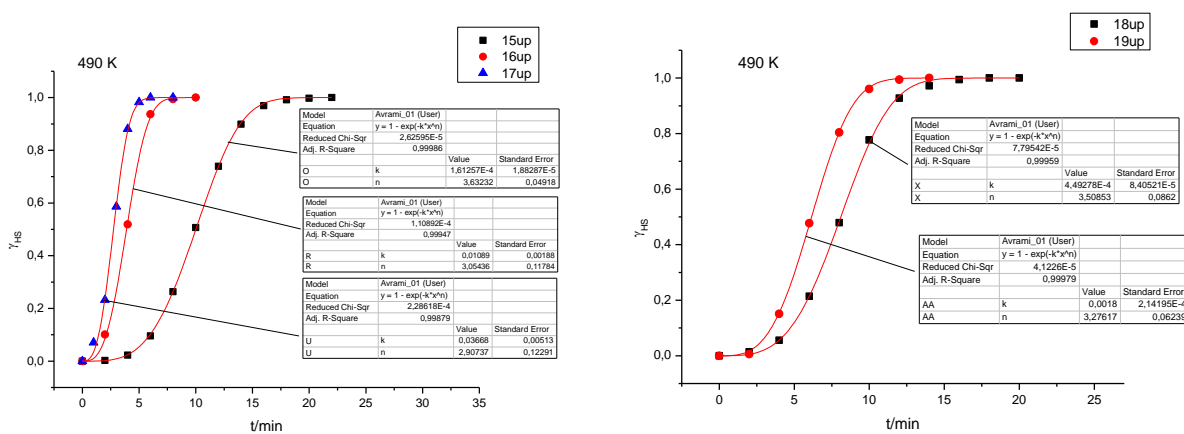


Figure S110. Fitting of kinetic curves for 9 using the JMAK model (LS → HS; left: cycles 15 - 17; right: cycles 18 and 19).

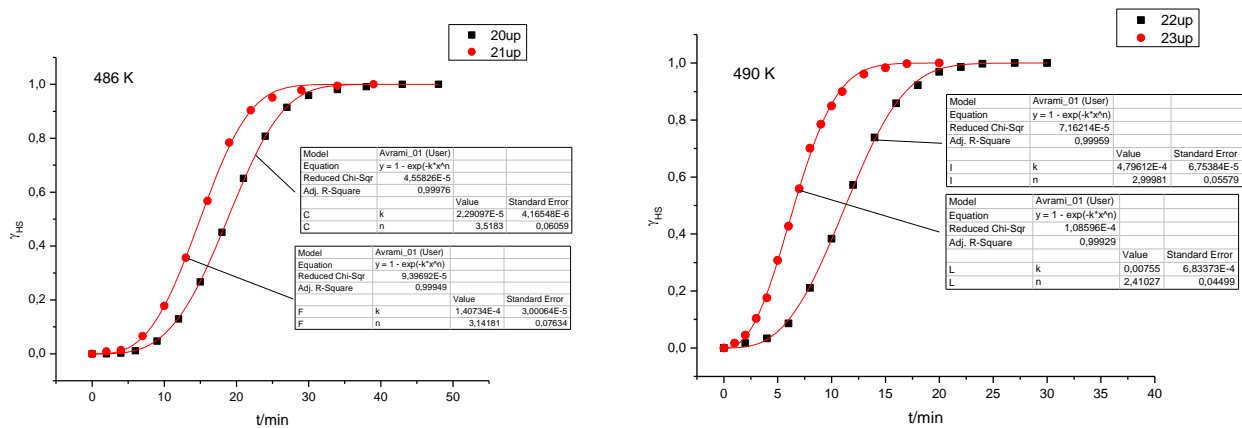


Figure S111. Fitting of kinetic curves for **9** using the JMAK model (LS → HS; left: cycles 20 and 21; right: cycles 22 and 23).

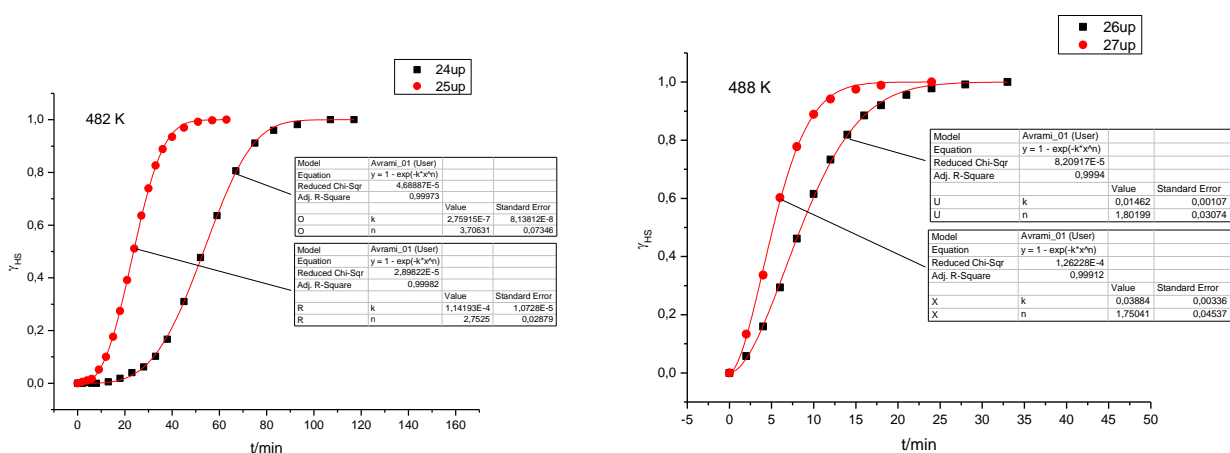


Figure S112. Fitting of kinetic curves for **9** using the JMAK model (LS → HS; left: cycles 24 and 25; right: cycles 26 and 27).

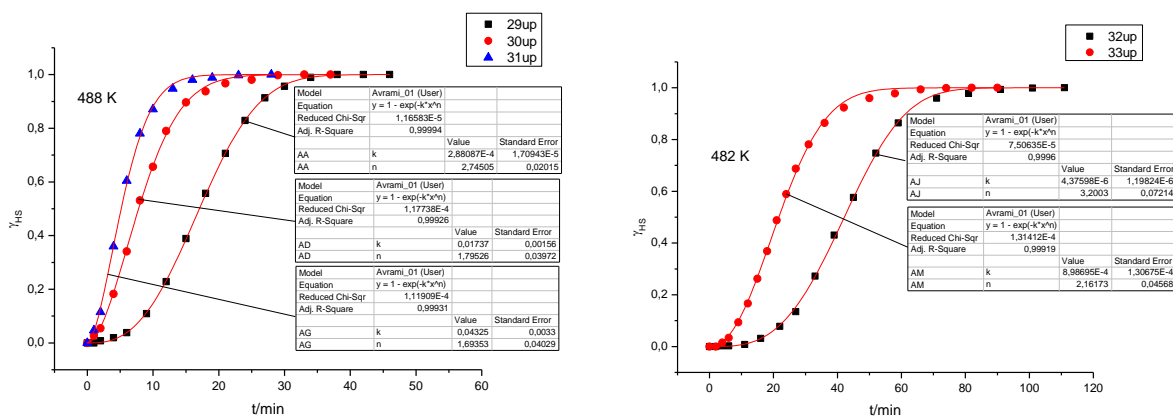


Figure S113. Fitting of kinetic curves for **9** using the JMAK model (LS → HS; left: cycles 29 – 31; right: cycles 32 and 33).

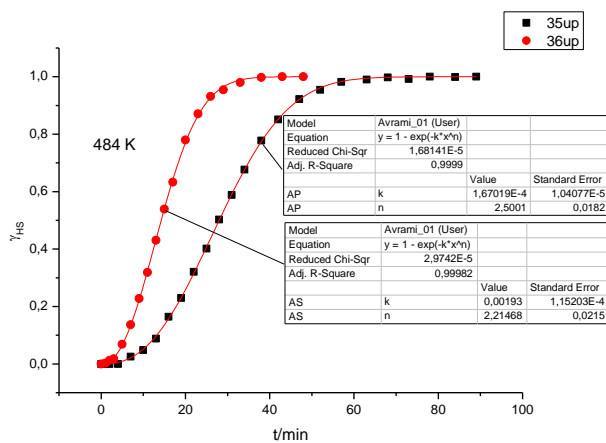


Figure S114. Fitting of kinetic curves for **9** using the JMAK model (LS → HS; cycles 35 and 36).

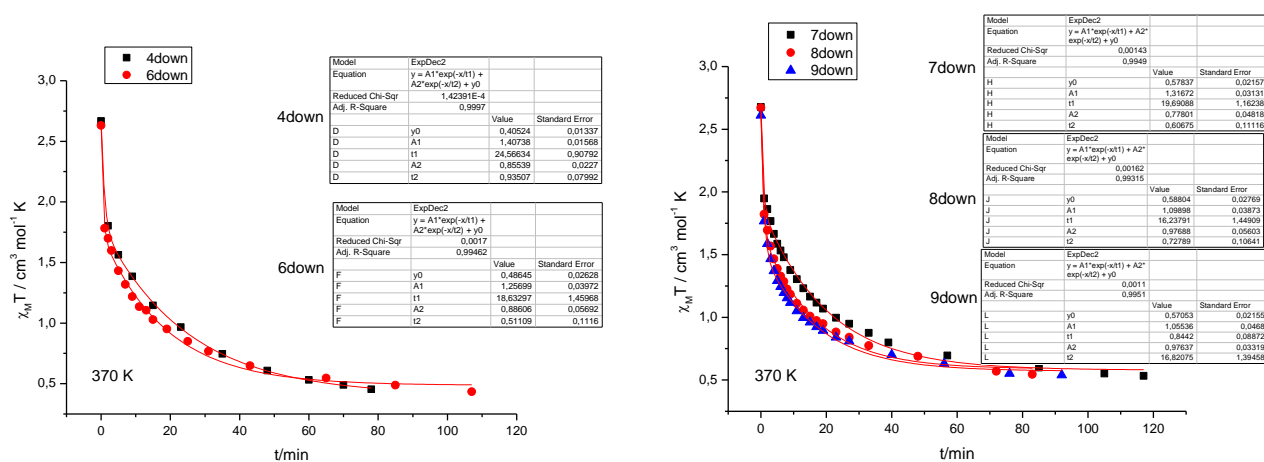


Figure S115. Fitting of kinetic curves for **9** in bi-exponential approximations (HS → LS; left: cycles 4 and 6; right: cycles 7 – 9).

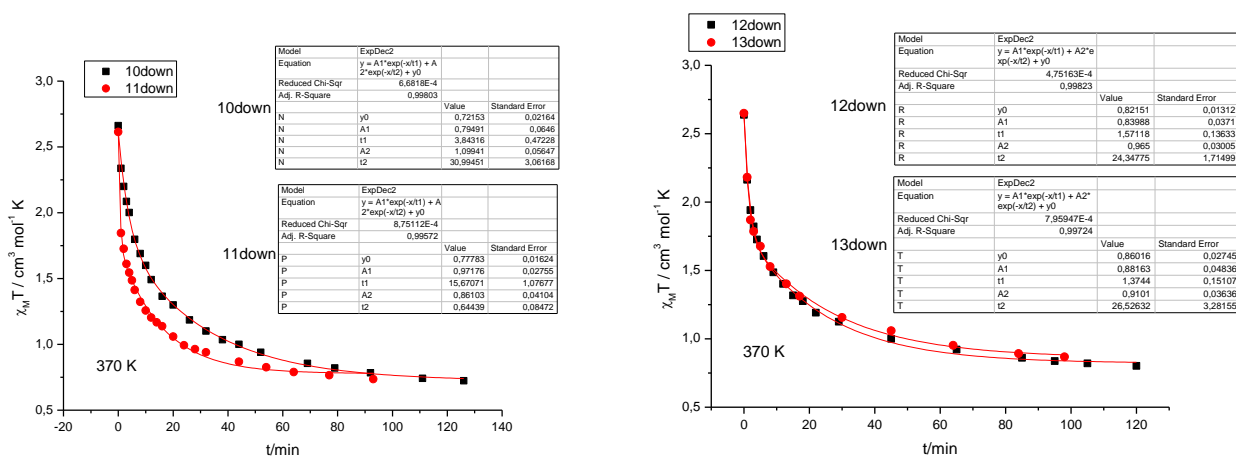


Figure S116. Fitting of kinetic curves for **9** in bi-exponential approximations (HS → LS; left: cycles 10 and 11; right: cycles 12 and 13).

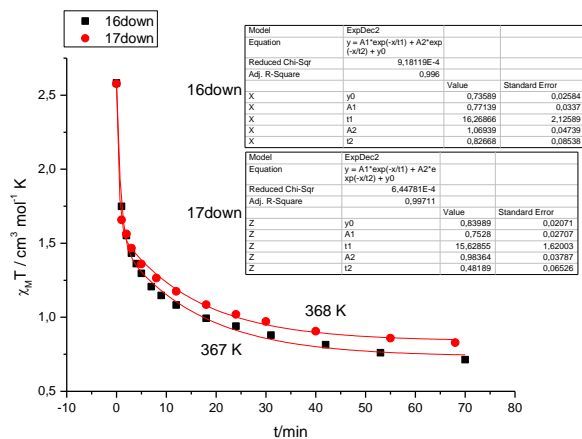
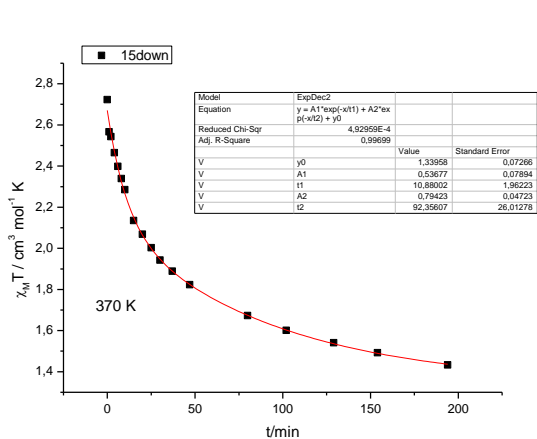


Figure S117. Fitting of kinetic curves for **9** in bi-exponential approximations (HS \rightarrow LS; left: cycle 15; right: cycles 16 and 17).

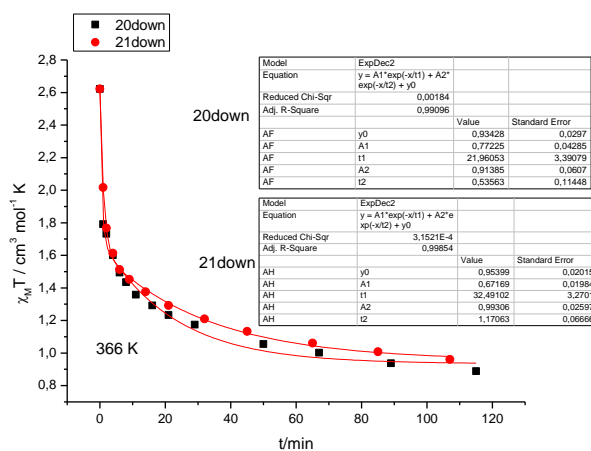
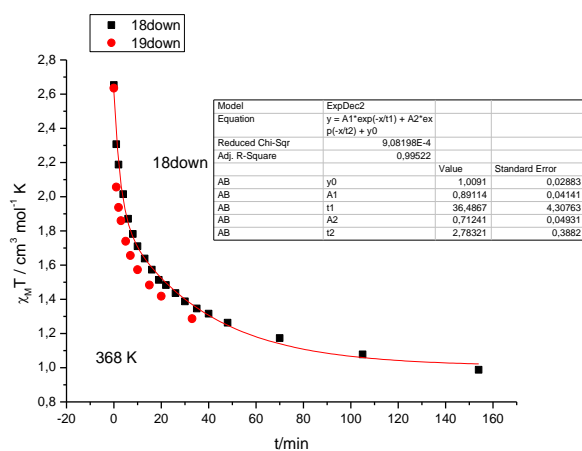


Figure S118. Fitting of kinetic curves for **9** in bi-exponential approximations (HS \rightarrow LS; left: cycle 18; right: cycles 20 and 21).

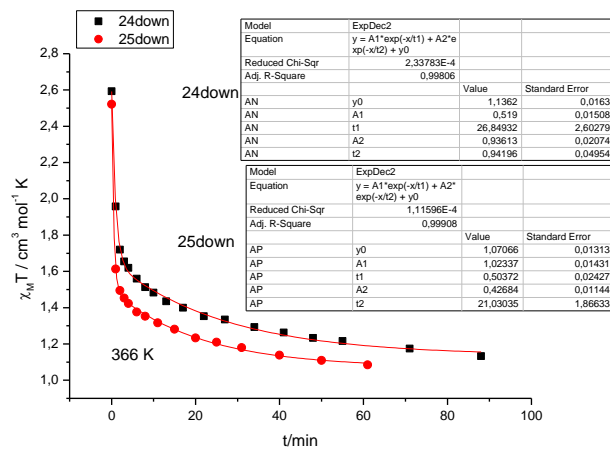
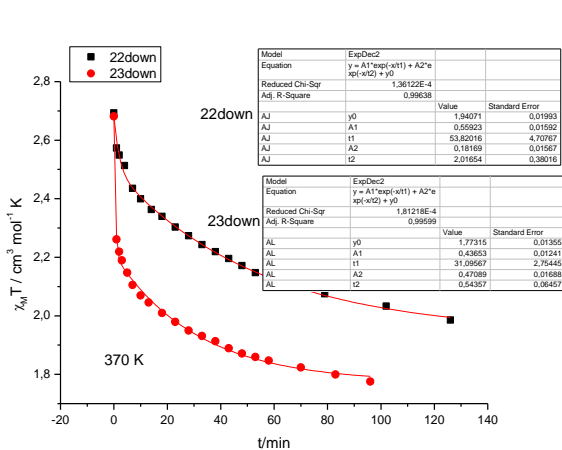


Figure S119. Fitting of kinetic curves for **9** in bi-exponential approximations (HS \rightarrow LS; left: cycles 22 and 23; right: cycles 24 and 25).

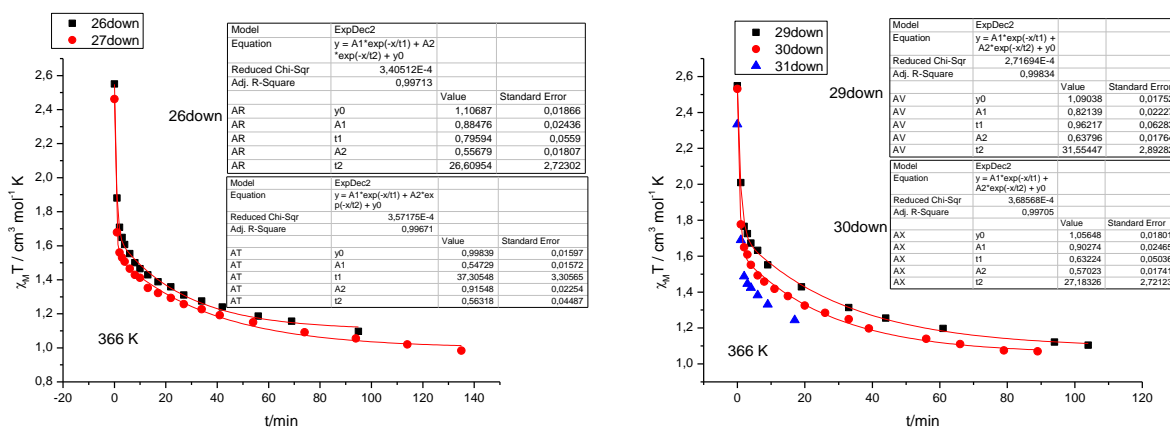


Figure S120. Fitting of kinetic curves for **9** in bi-exponential approximations (HS → LS; left: cycles 26 and 27; right: cycles 29 and 30).

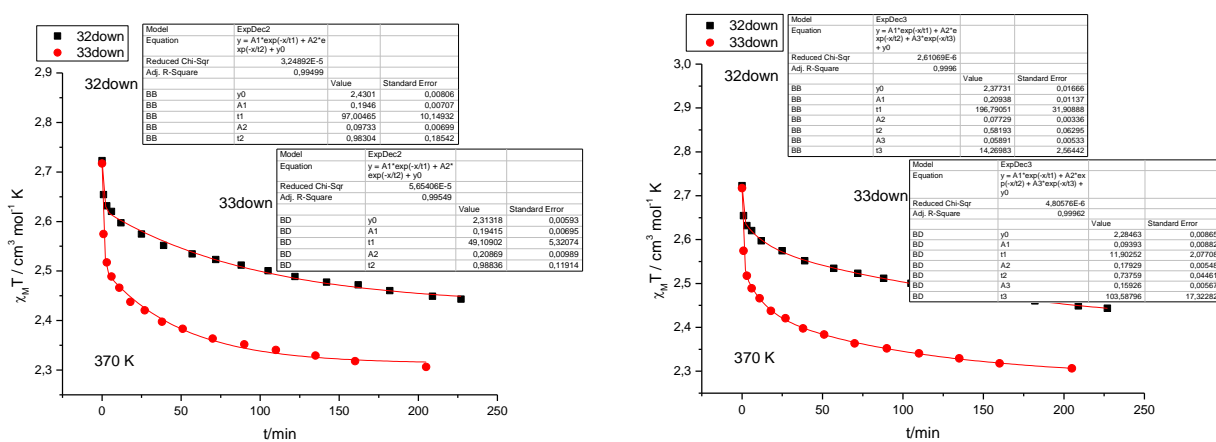


Figure S121. Fitting of kinetic curves for **9** in bi- and tri-exponential approximations (HS → LS; cycles 32 and 33; left: bi-exponential fitting, right: tri-exponential fitting).

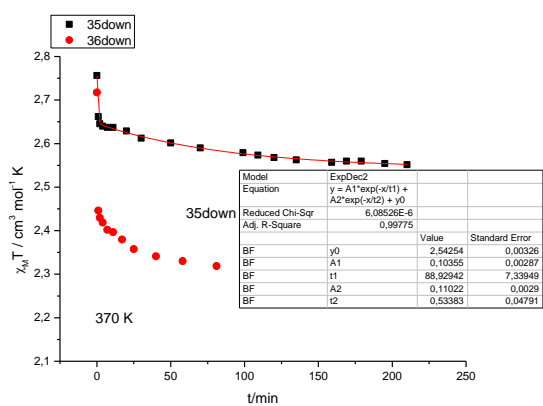


Figure S122. Fitting of a kinetic curve for **9** in bi-exponential approximations (HS → LS; cycle 35).

Samples 10 and 10-1

Sample 10

Cycles 1 – 3. Parent phase $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$. Crystals of the phase $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$ were exposed to ethanol vapor overnight and sealed. SCO regime typical for the phase $1^{E/LS} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ was observed in the cycles 1 – 3. X-ray powder pattern of the sample agrees with the pattern obtained for the sample **21** (see below).

Sample 10-1

Cycles 4 – 10. Main part of the sample **10** (the phase $1^{E/LS} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$) was placed in a new ampoule and exposed to water vapor for 2 days. The mass of the sample slightly decreased (2.1 %) and the ampoule was sealed.

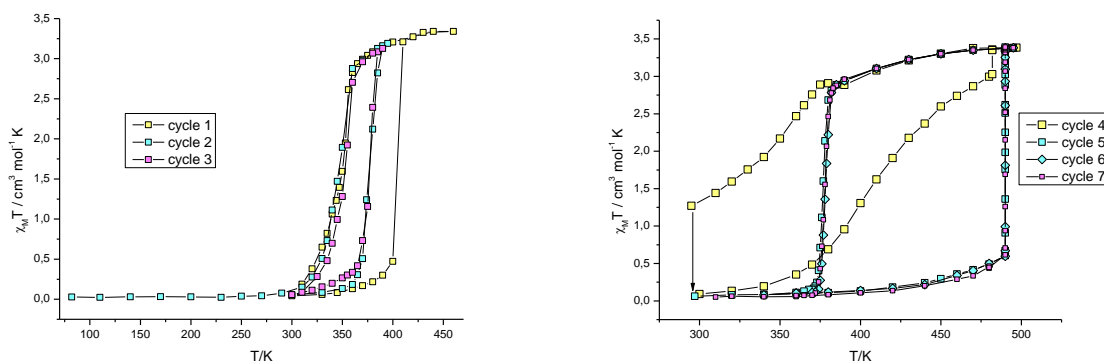


Figure S123. Left: sample **10**. Thermal cycles 1 – 3. Right: sample **10-1**. Thermal cycles 4 – 7.

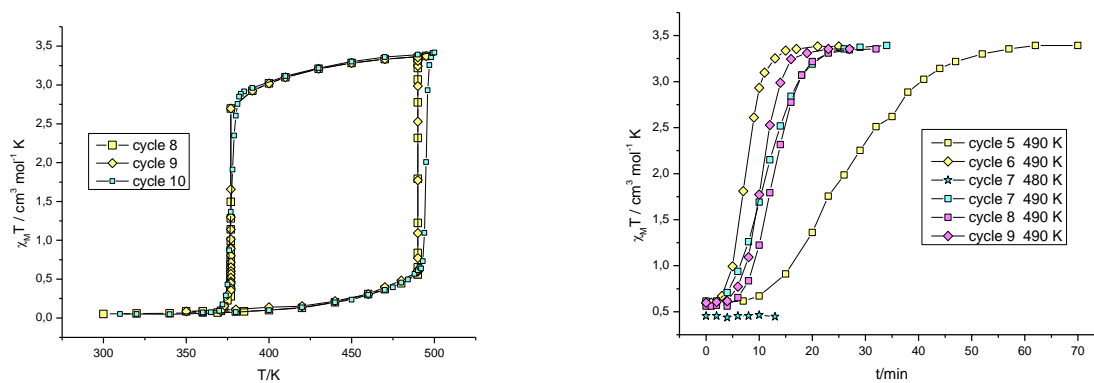


Figure S124. Left: sample **10-1**. Thermal cycles 8 – 10. Right: sample **10-1**. Kinetic curves for the cycles 5 – 9 (LS \rightarrow HS).

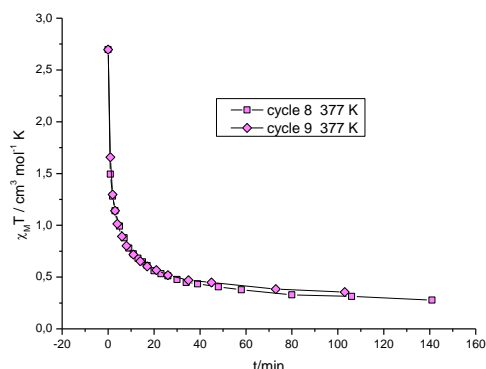


Figure S125. Sample 10-1. Kinetic curves for the cycles 8 and 9 (LS → HS transformation).

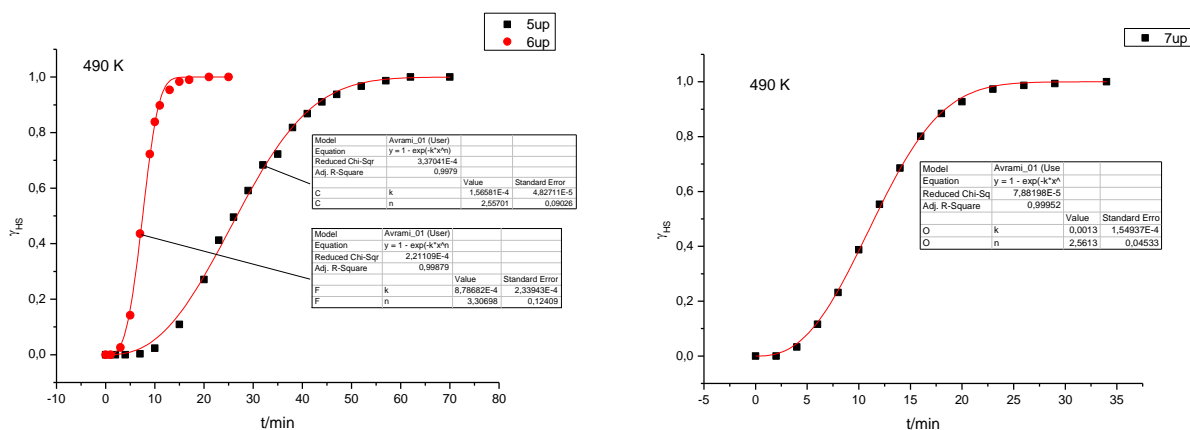


Figure S126. Fitting of kinetic curves for 10-1 using the JMAK model (LS → HS; left: cycles 5 and 6; right: cycle 7).

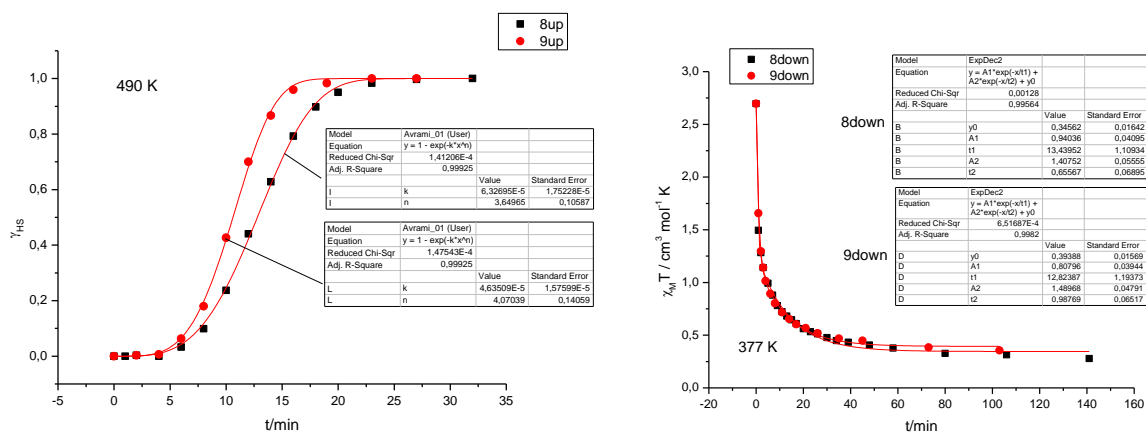


Figure S127. Fitting of kinetic curves for 10-1 using the JMAK model (left: cycles 8 and 9, LS → HS transformation) and bi-exponential approximation (right: cycles 8 and 9, HS → LS transformation).

Sample 11
Parent phase $1^{LS} \cdot EtOH \cdot H_2O$.

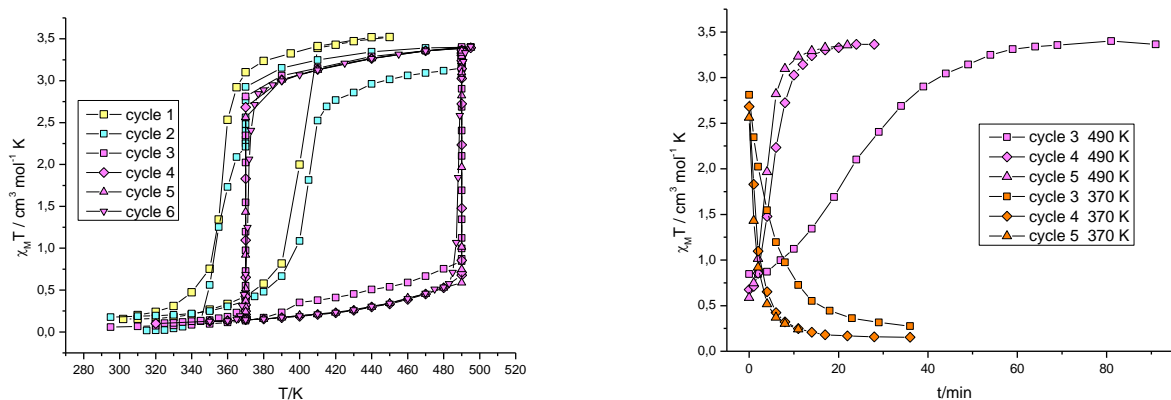


Figure S128. Sample 11. Thermal cycles 1 – 6 (left) and kinetic curves for the cycles 3 – 5 (LS → HS and HS → LS transformations, right).

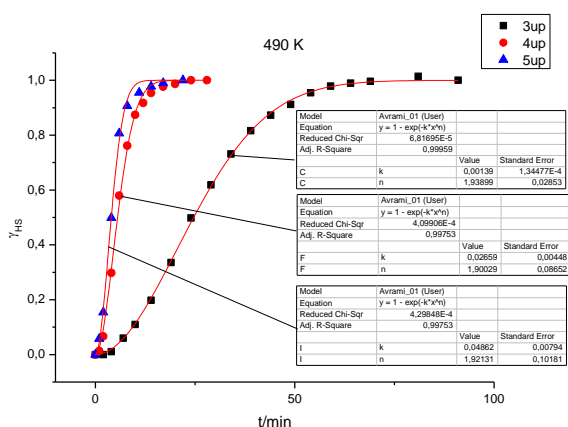


Figure S129. Fitting of kinetic curves for 11 using the JMAK model (LS → HS; cycles 3 – 5).

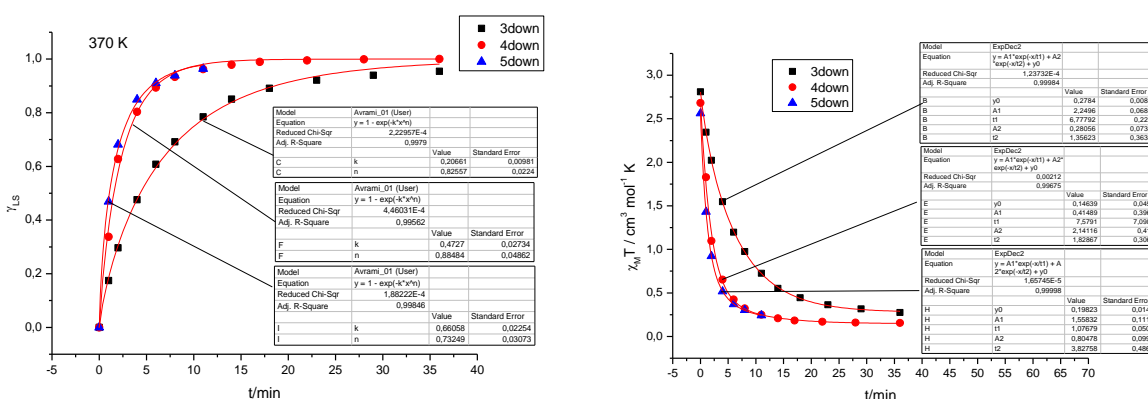


Figure S130. Fitting of kinetic curves for 11 using the JMAK model (left: cycles 3 – 5) and biexponential approximation; right: cycles 3 – 5). The JMAK model gives very small and non-typical values of $n < 1$.

Samples 12 and 12-1

Sample 12

Cycle 1. Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$.

Sample 12-1

Cycles 2 – 18. After the first cycle had been done the sample **12** was allowed to stand at room temperature in a sealed ampoule. X-ray powder diffraction pattern of the sample was recorded after *ca.* 9 months. The sample appeared to be the phase $1^{\text{A/LS}}$. It was placed in a new quartz ampoule, exposed to ethanol vapor for 1 h and sealed.

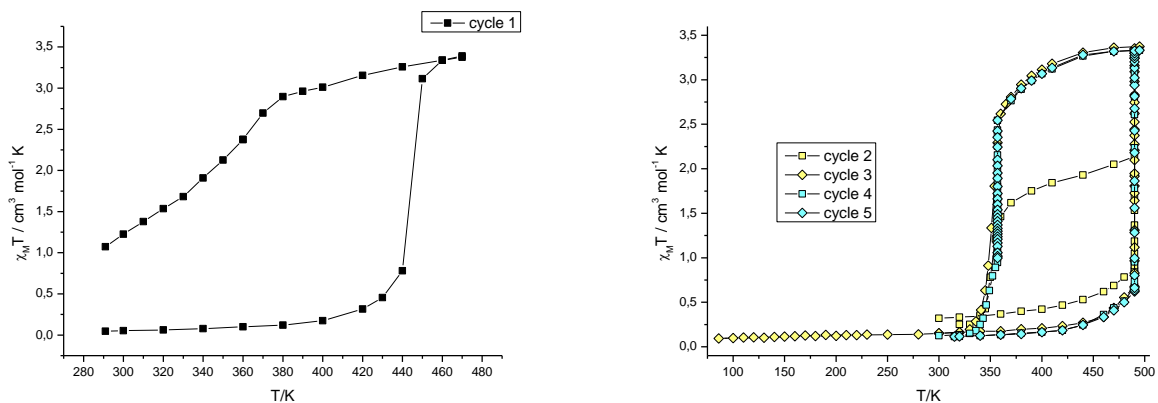


Figure S131. Thermal cycle 1 (left) and cycles 2 – 5 (right) for the samples **12** and **12-1**.

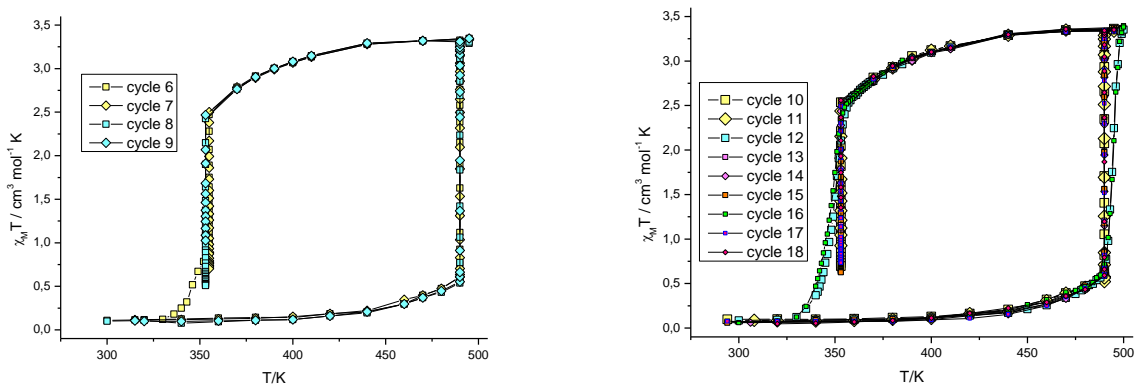


Figure S132. Sample **12-1**. Thermal cycles 6 – 9 (left) and 10 – 18 (right).

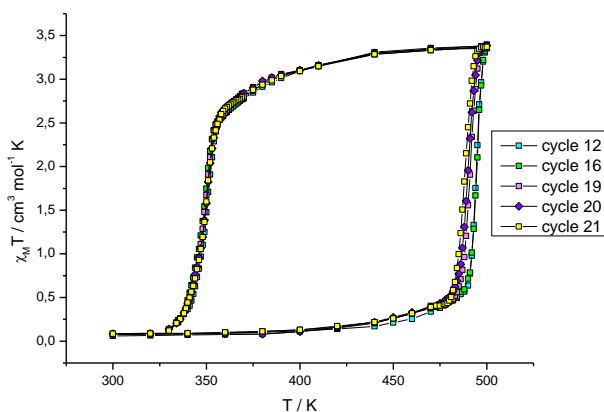


Figure S133. Sample 12-1. Thermal cycles at heating/cooling rate of 0.9 K min^{-1} (cycles 12 and 16), 0.4 K min^{-1} (cycles 19 and 20) and 0.25 K min^{-1} (cycle 21).

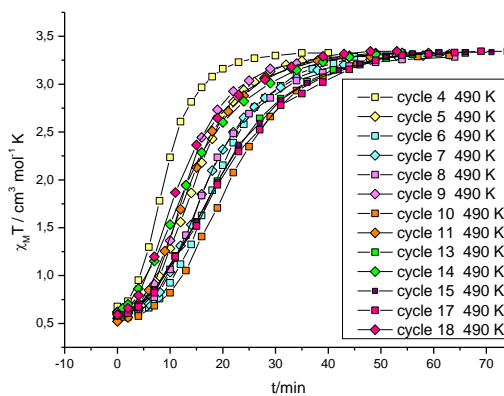
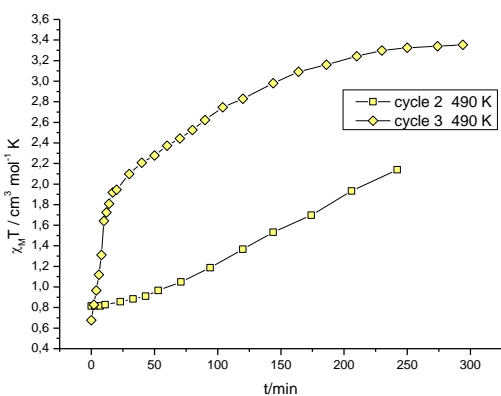


Figure S134. Sample 12-1. Kinetic curves (LS \rightarrow HS; left: cycles 2 and 3; right: cycles 4 – 18).

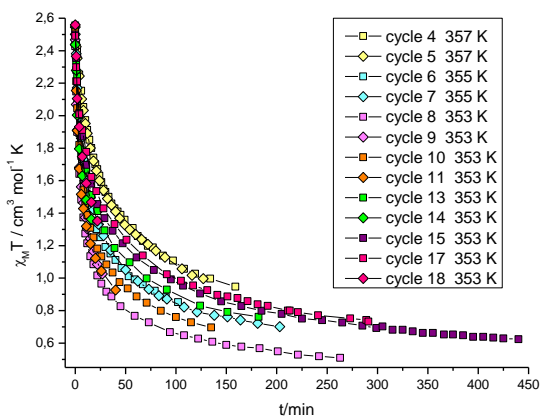


Figure S135. Sample 12-1. Kinetic curves (HS \rightarrow LS; cycles 4 – 10, 11, 13 – 15, 17, 18).

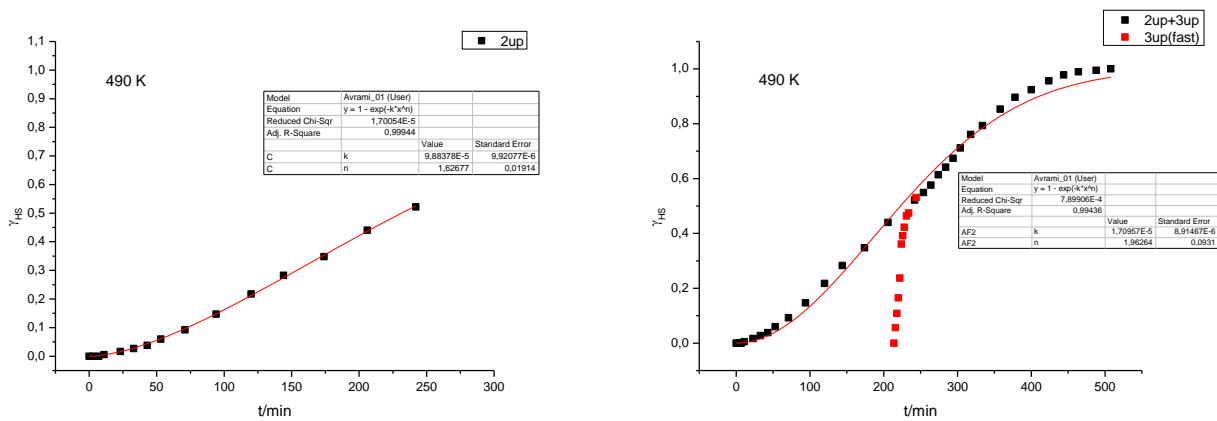


Figure S136. Fitting of kinetic curves for 12-1 using the JMAK model (LS → HS; cycles 2, 3 and fitting of the “combined” slow branch of the cycles 2 and 3, points of the fast branch of the cycle 3 (red squares) were not taken into the fitting).

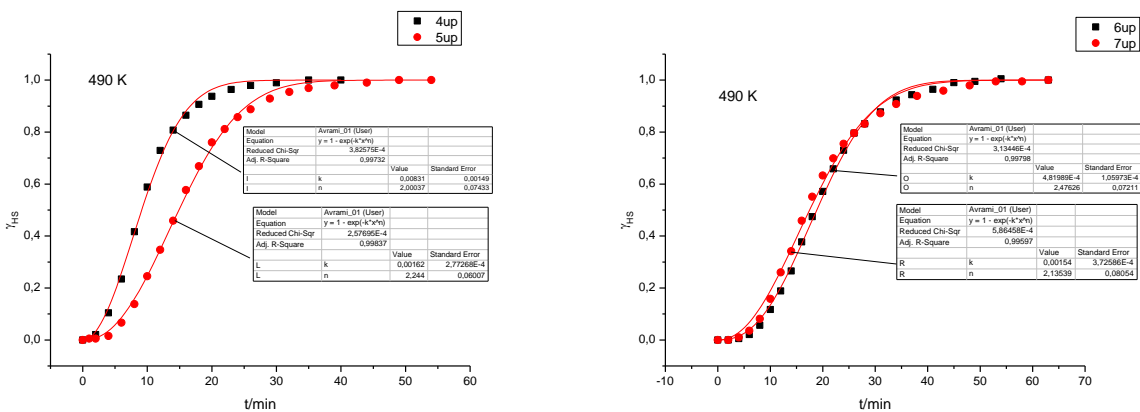


Figure S137. Fitting of kinetic curves for 12-1 using the JMAK model (LS → HS; left: cycles 4, 5; right: cycles 6, 7).

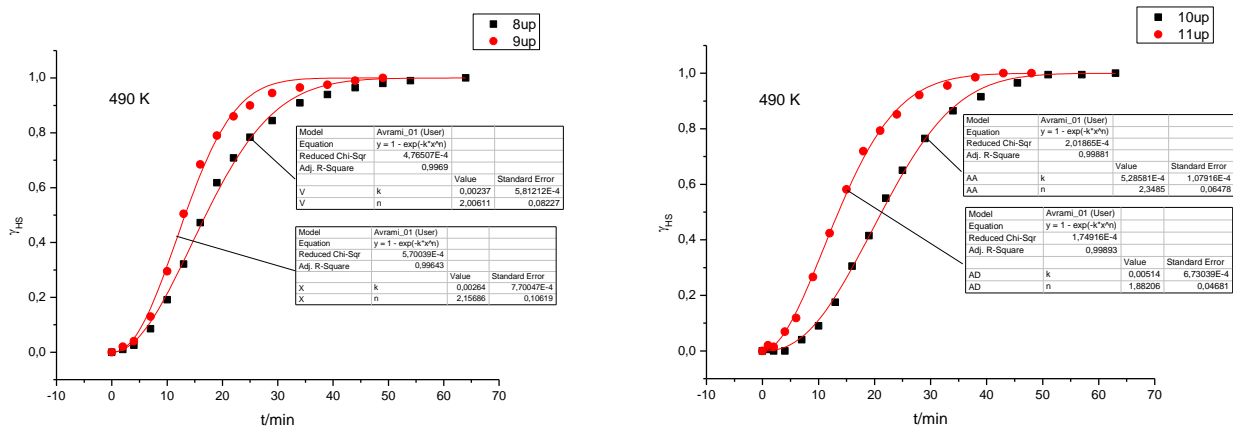


Figure S138. Fitting of kinetic curves for 12-1 using the JMAK model (LS → HS; left: cycles 8, 9; right: cycles 10, 11).

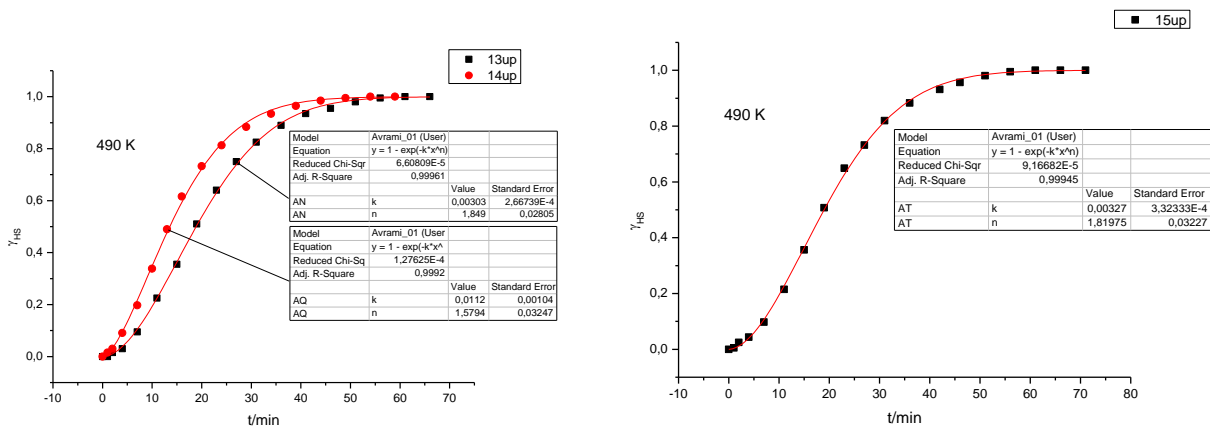


Figure S139. Fitting of kinetic curves for **12-1** using the JMAK model (left: cycles 13, 14; right: cycle 15).

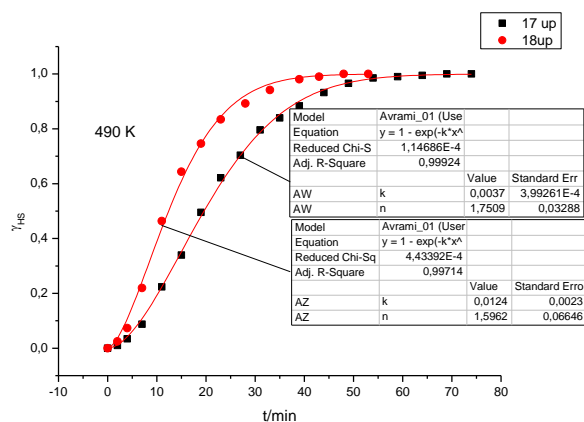


Figure S140. Fitting of kinetic curves for **12-1** using the JMAK model (LS → HS; cycles 17, 18).

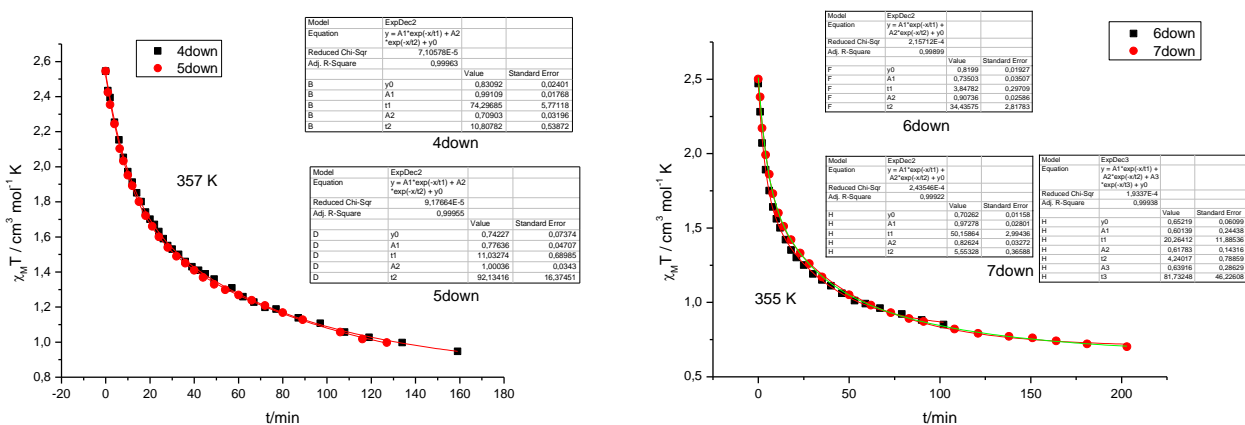


Figure S141. Fitting of kinetic curves for **12-1** using bi- and tri-exponential approximations (HS → LS; left: cycles 4, 5; right: cycles 6, 7).

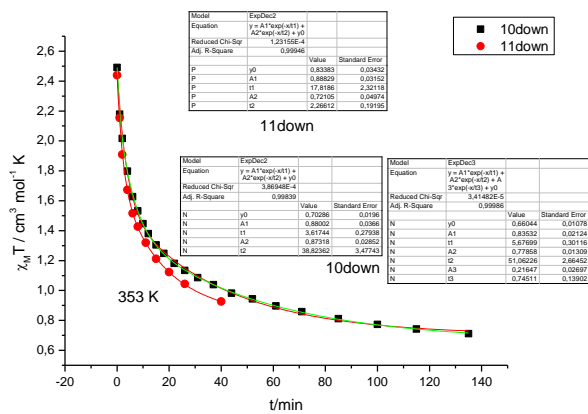
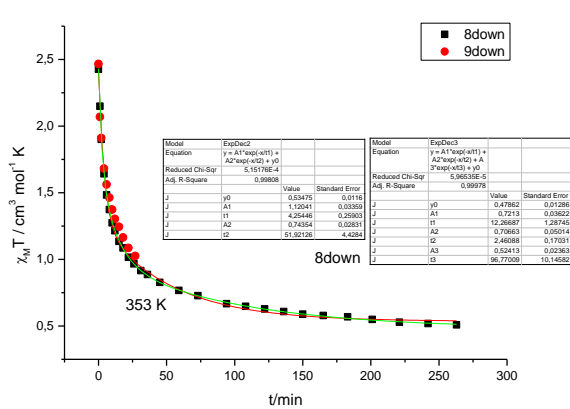


Figure S142. Fitting of kinetic curves for 12-1 using bi- and tri-exponential approximations (HS → LS; left: cycles 8, 9; right: cycles 10, 11).

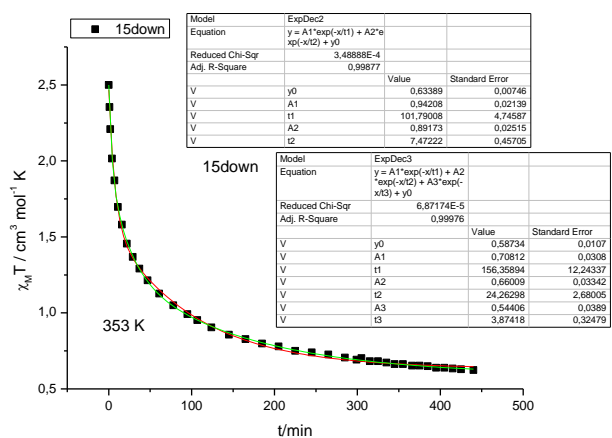
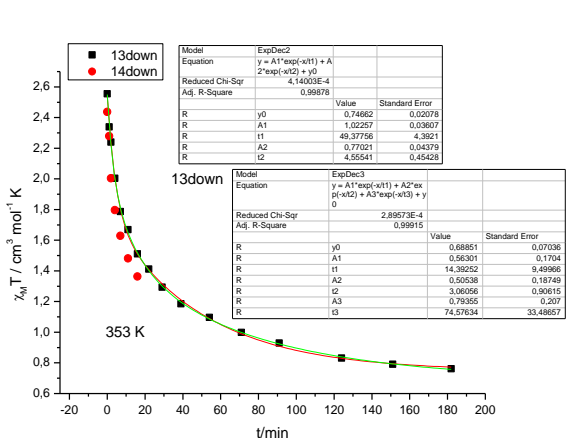


Figure S143. Fitting of kinetic curves for 12-1 using bi- and tri-exponential approximations (HS → LS; left: cycle 13; right: cycle 15).

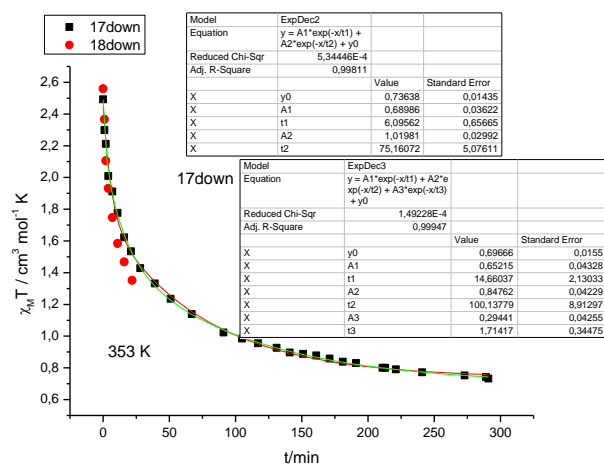


Figure S144. Fitting of kinetic curves for 12-1 using bi- and tri-exponential approximations (HS → LS; cycle 17).

Sample 13

Parent phase 1^{ALS} after XRPD. This sample of the phase 1^{ALS} was obtained from the phase $\alpha-1^{LS}$. xH_2O [see ref. 29, electronic supporting information, Figure S8]. The formation of the phase 1^{ALS} was confirmed by X-ray powder diffraction. This sample of the phase 1^{ALS} was placed in a quartz ampoule, exposed to water vapor for 1 h (mass of the sample did not change) and sealed.

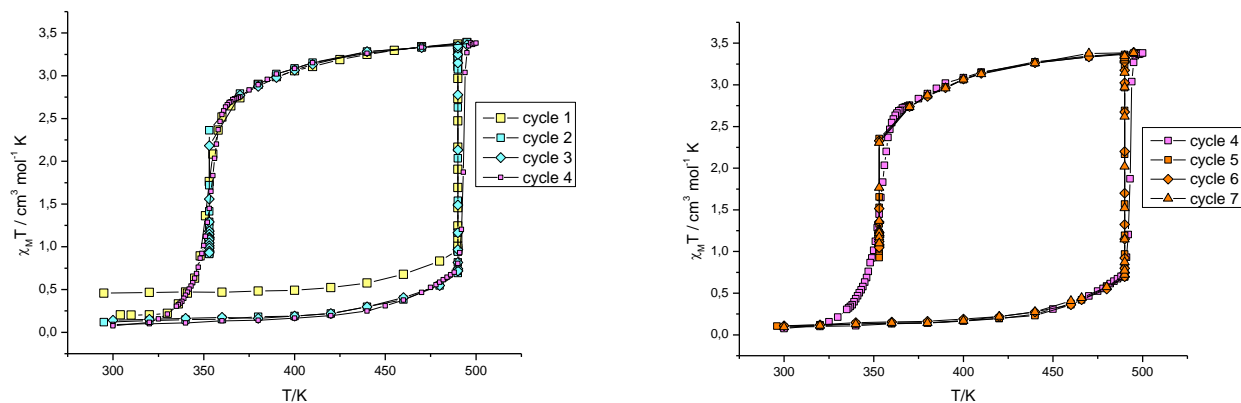


Figure S145. Sample 13. Thermal cycles 1 – 4 (left) and 4 – 7 (right).

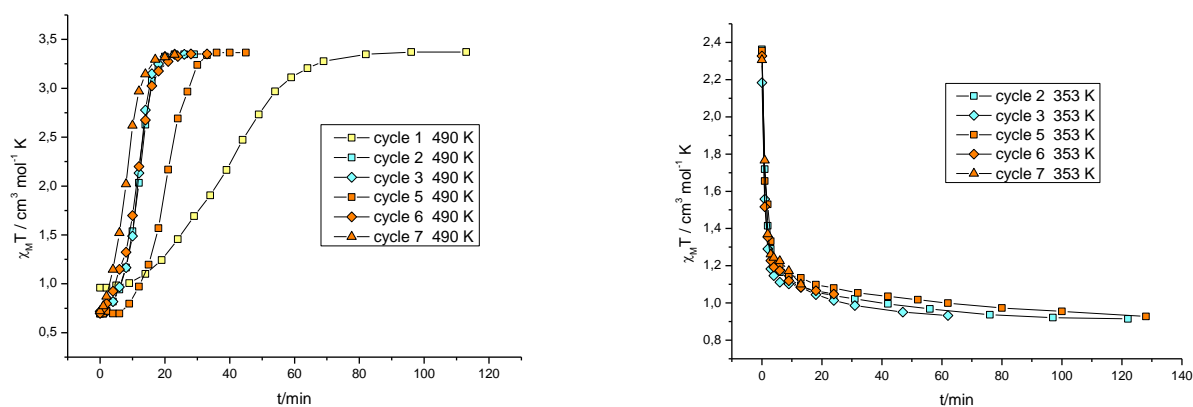


Figure S146. Sample 13. Left: kinetic curves for the cycles 1 – 3 and 5 – 7 (LS \rightarrow HS). Right: kinetic curves for the cycles 2, 3, 5 – 7 (HS \rightarrow LS).

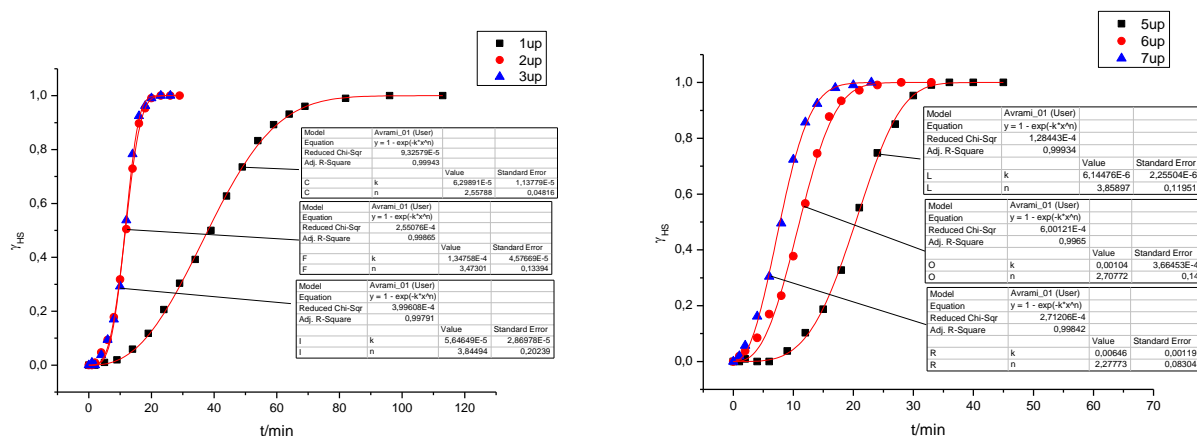


Figure S147. Fitting of kinetic curves for 13 using the JMAK model (LS \rightarrow HS; left: cycles 1 – 3; right: cycles 5 – 7).

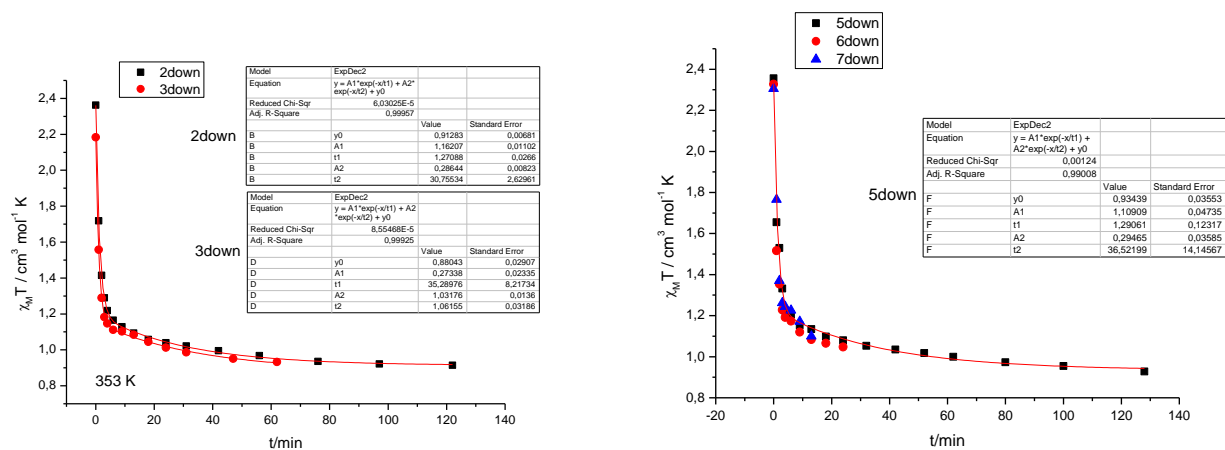


Figure S148. Fitting of kinetic curves for **13** in bi-exponential approximation (HS \rightarrow LS; left: cycles 2 and 3; right: cycle 5).

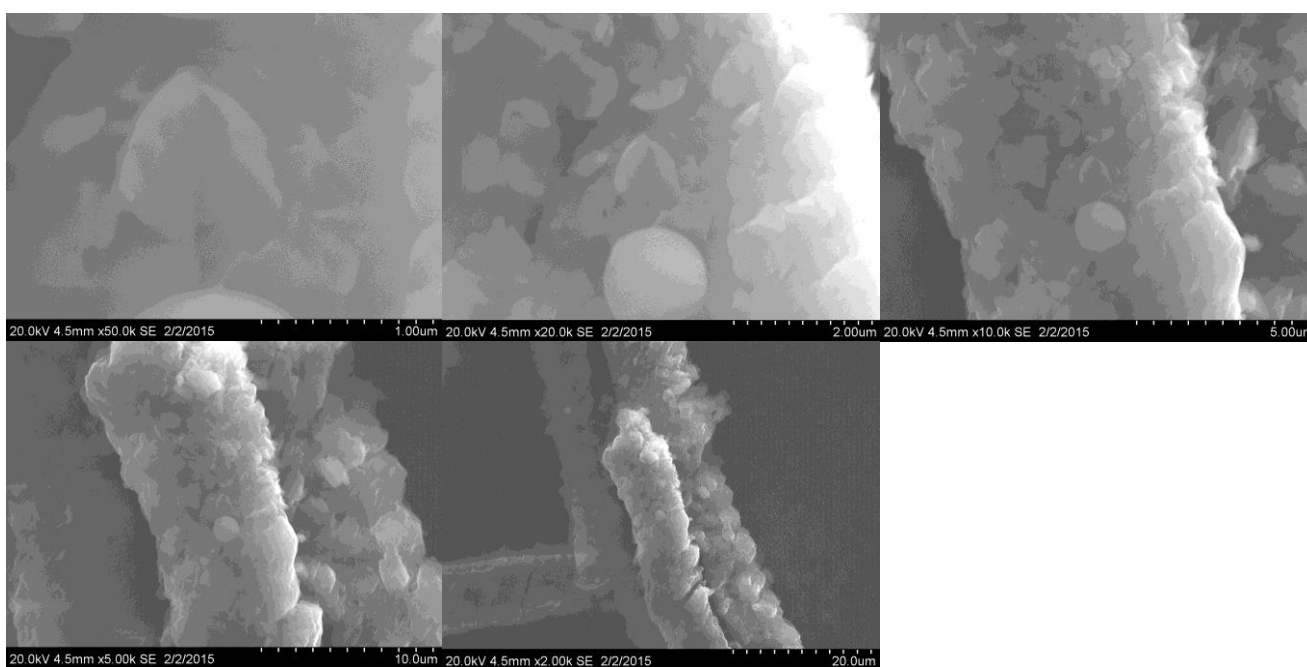


Figure S149. SEM images of the sample **13** after thermal cycling.

Samples 14 and 14-1

Sample 14

Cycles 1 – 6. Parent phase $1^{LS} \cdot EtOH \cdot H_2O$. A single crystal of the phase $1^{A/LS}$ suitable for X-ray analysis was taken from the sealed ampoule after the cycles 1 – 6 had been done.

Sample 14-1

Cycles 7 – 14. Parent phase $1^{A/LS}$. This sample of the phase $1^{A/LS}$ was taken from the experiment 14, exposed to water vapor for 1 h (no change in the mass was observed) and sealed.

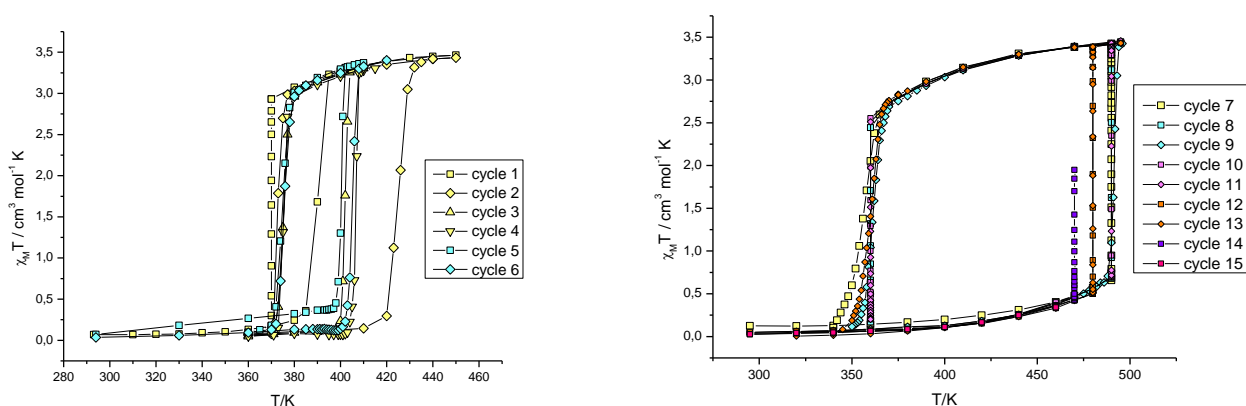


Figure S150. Left: sample 14. Thermal cycles 1 – 6. Right: sample 14-1. Thermal cycles 7 – 14.

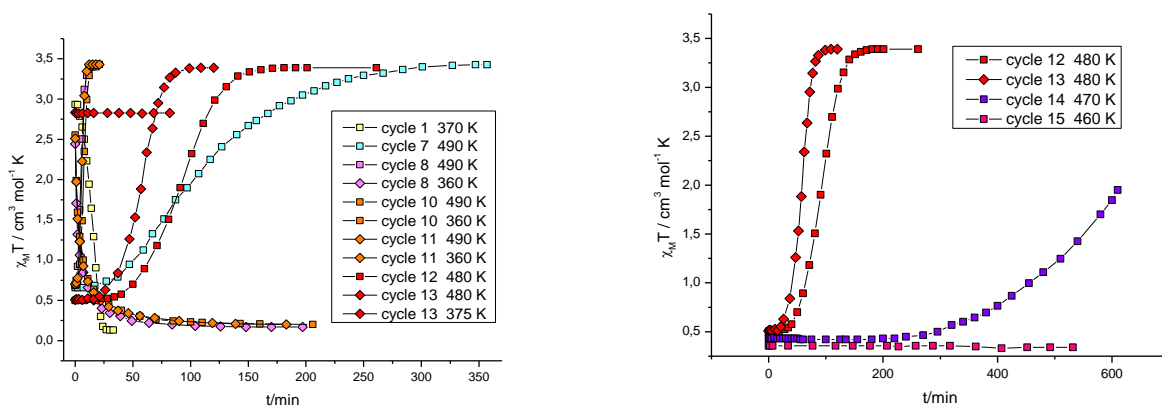


Figure S151. Kinetic curves for the samples 14 and 14-1 (LS → HS and HS → LS).

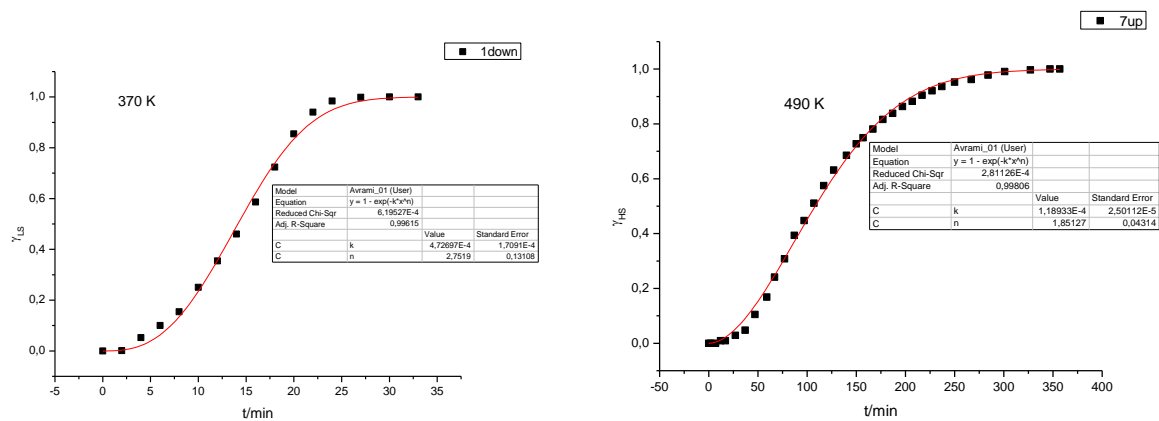


Figure S152. Fitting of kinetic curves for 14 and 14-1 using the JMAK model (LS → HS; left: cycle 1; right: cycle 7).

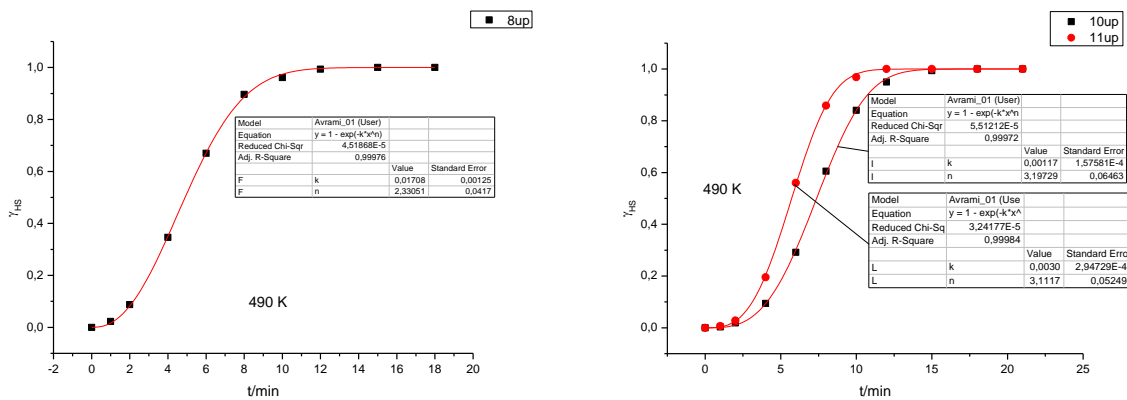


Figure S153. Fitting of kinetic curves for **14-1** using the JMAK model (LS \rightarrow HS; left: cycle 8; right: cycles 10 and 11).

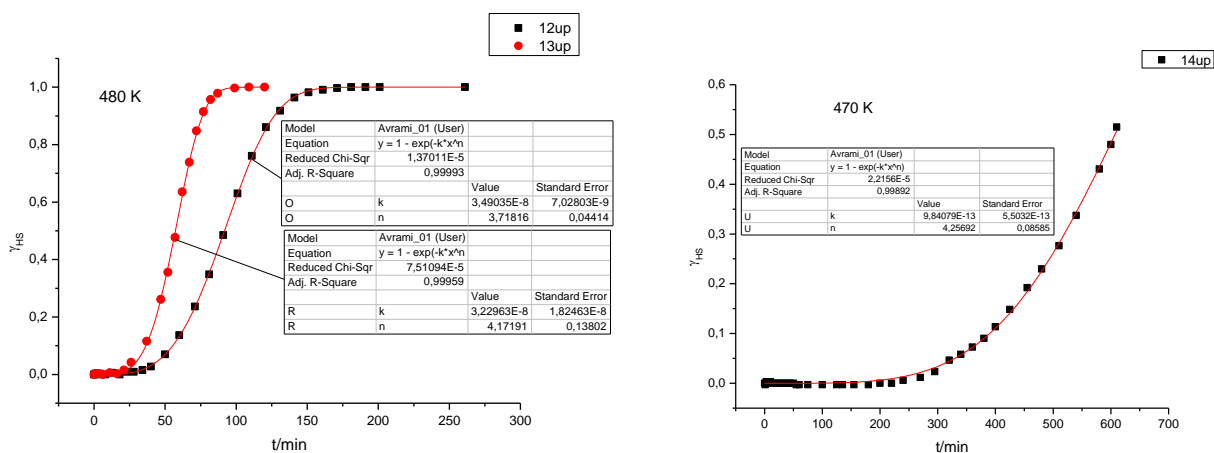


Figure S154. Fitting of kinetic curves for **14-1** using the JMAK model (LS \rightarrow HS; right: cycles 12 and 13; left: cycle 14).

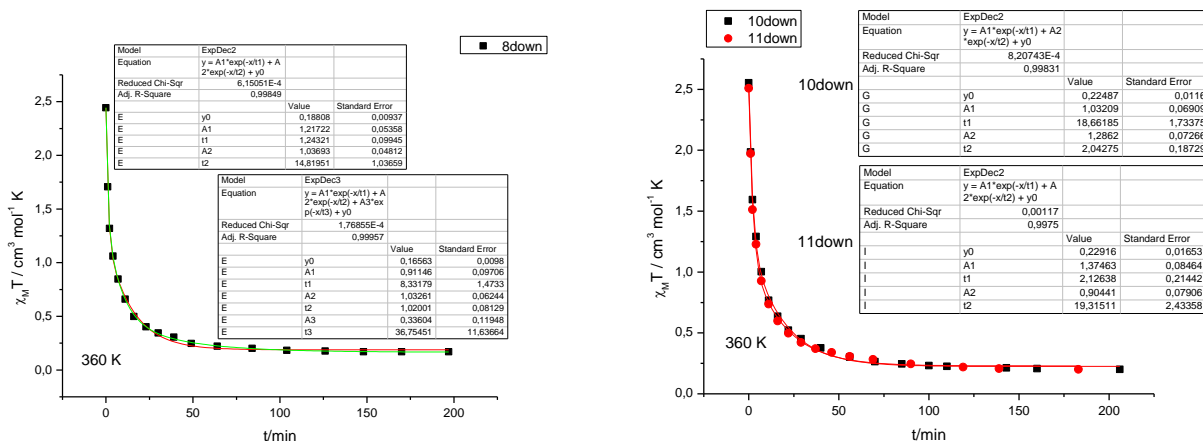


Figure S155. Fitting of kinetic curves for **9** in bi- and triexponential approximations (HS \rightarrow LS left: cycle 8; right: cycles 10 and 11).

Sample 15
Parent phase $1^{LS} \cdot EtOH \cdot H_2O$.

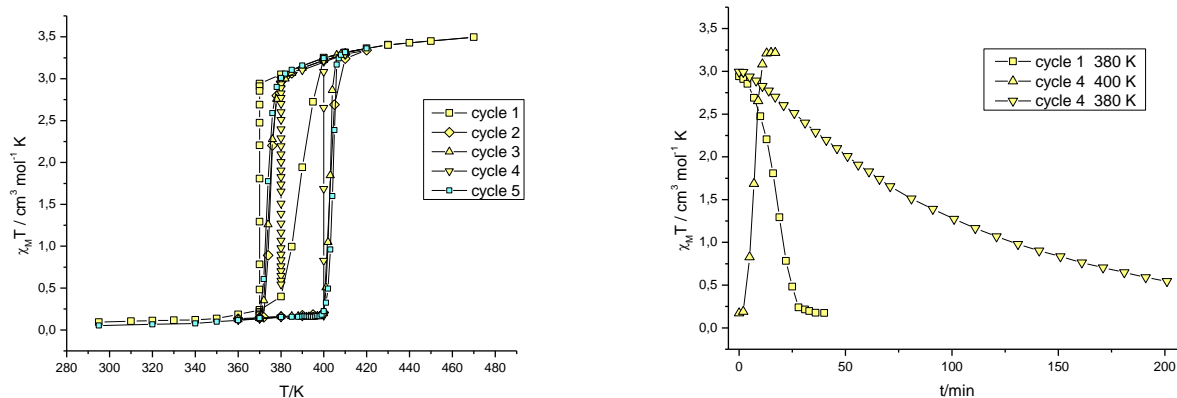


Figure S156. Sample 15. Thermal cycles 1 – 5 (left) and kinetic curves for the cycles 1 and 4 (LS → HS and HS → LS; right).

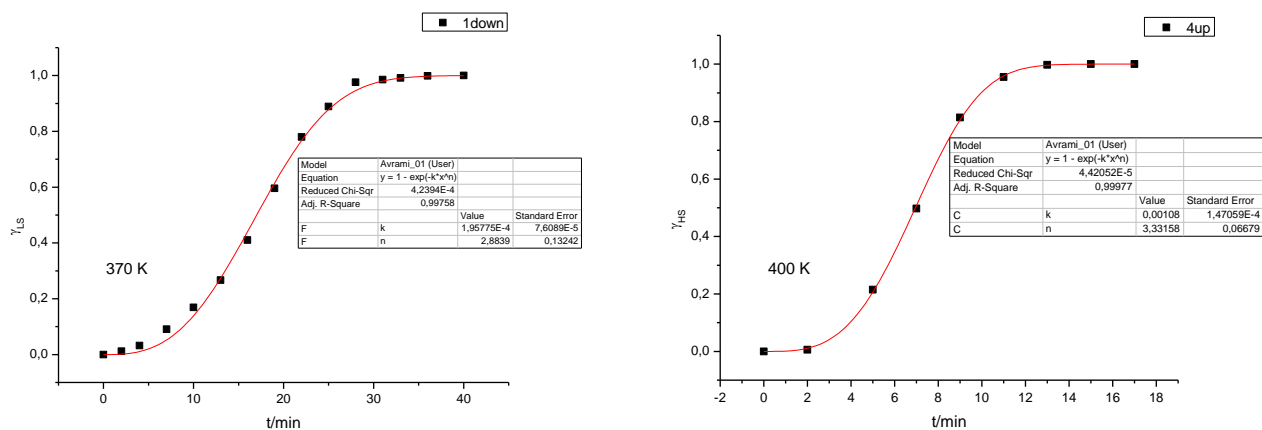


Figure S157. Fitting of kinetic curves for 15 using the JMAK model (left: cycle 1, HS → LS; right: cycle 4, LS → HS).

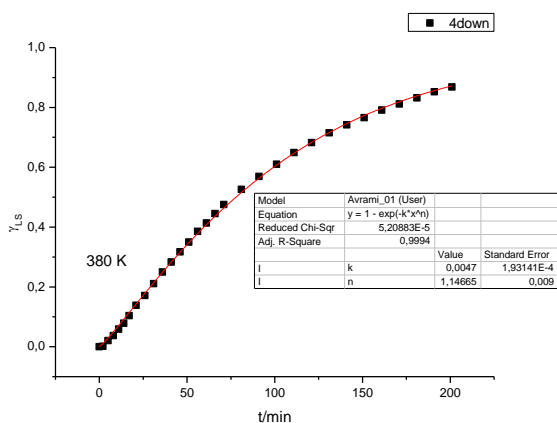


Figure S158. Fitting of a kinetic curve for 15 using the JMAK model (cycle 4, HS → LS).

Sample 16

Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$. The phase was exposed to water vapor for 2 days. Very slight increase of the mass was detected (*ca.* 1.0 %).

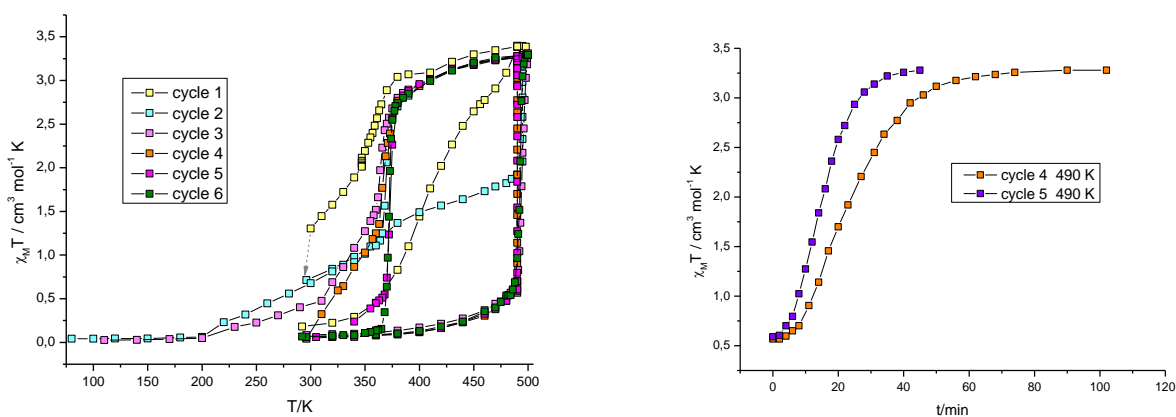


Figure S159. Sample 16. Thermal cycles 1 – 6 (left) and kinetic curves for the cycles 4 and 5 (LS → HS transformation, right).

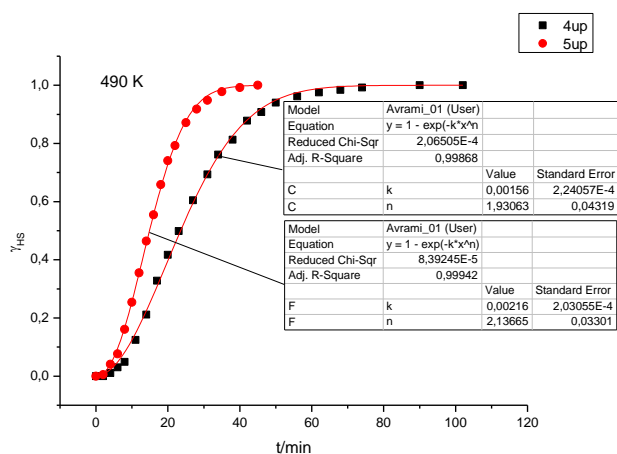


Figure S160. Fitting of kinetic curves for 16 using the JMAK model (LS → HS; cycles 4 and 5).

Sample 17

Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$. X-ray powder diffraction pattern of the product was recorded immediately after the cycle 1 had been done. It corresponds to the 1^{D} (see Figure S20).

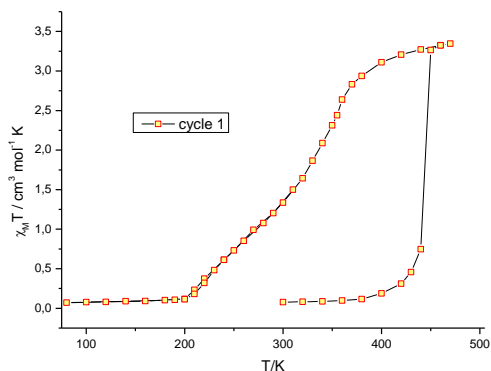


Figure S161. Sample 17. Thermal cycle 1.

Sample 18

Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$. X-ray powder diffraction pattern of the product was taken in two days after cycle 1 had been done. It corresponded to a mixture of phases 1^{D} and 1^{ALS} (see Figure S20).

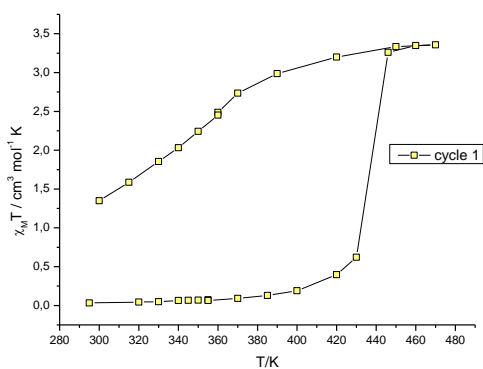


Figure S162. Sample 18. Thermal cycle 1.

Sample 19

Parent phase $1^{LS} \cdot EtOH \cdot H_2O$. Magnetic measurements were made under vacuum. X-ray powder diffraction pattern of the product corresponds to the phase 1^F (see Figure S20). Weight loss of 8.0 % is consistent with the removal of EtOH and H_2O molecules (calc. for $1^{LS} \cdot EtOH \cdot H_2O$: 7.8 %)

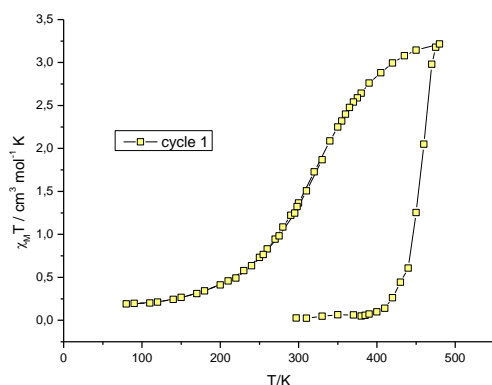


Figure S163. Sample 19. Thermal cycle 1.

Sample 20

Parent phase $\beta\text{-}1^{LS} \cdot xH_2O$. Magnetic measurements were made under vacuum. X-ray powder diffraction pattern of the product corresponds to the phase 1^F . Weight loss of 2.4 % is consistent with the H_2O molecules (calc. for $\beta\text{-}1^{LS} \cdot xH_2O$ ($x = 1$): 2.3 %)

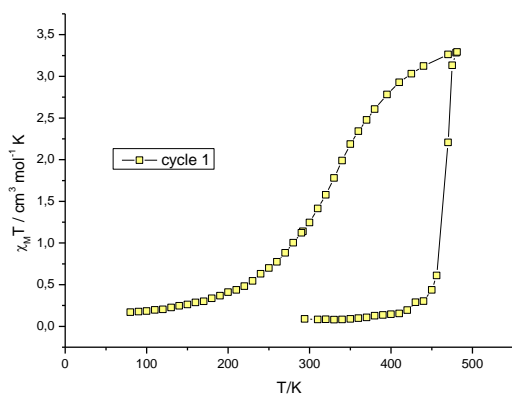


Figure S164. Sample 20. Thermal cycle 1.

Sample 21

Parent phase $\beta\text{-1}^{\text{LS}} \cdot x\text{H}_2\text{O}$. The phase was exposed to ethanol vapor for 48 h (mass increase: 4.5 %).

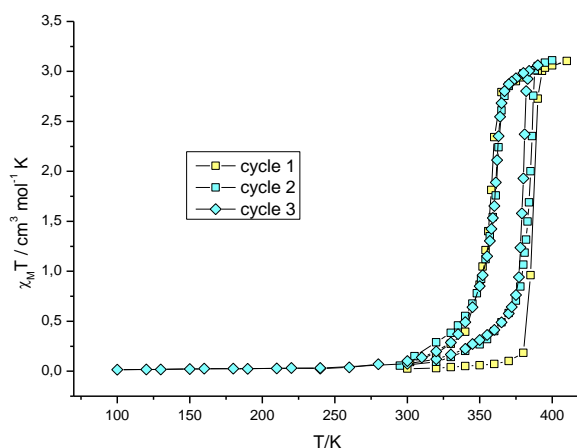


Figure S165. Sample **21**. Thermal cycles 1 – 3.

Elemental analysis of the sample after thermal cycling (%), calcd for $\text{C}_{30.8}\text{H}_{33.2}\text{N}_{10}\text{B}_2\text{F}_8\text{FeO}_{0.8}$ ($[\text{FeL}_2](\text{BF}_4)_2 \cdot 0.4\text{EtOH} \cdot 0.4\text{H}_2\text{O}$, 785.75): C 47.1, H 4.3, N 17.8; found C 46.5, H 4.0, N 17.3.

A single crystal of the phase $\mathbf{1}^{\text{E/LS}} \cdot y\text{EtOH} \cdot z\text{H}_2\text{O}$ ($y = 0.41$, $z = 0.40$) suitable for X-ray analysis was taken from this sample.

Sample 22

Parent phase $\mathbf{1}^{\text{A/LS}}$. Magnetic measurements were made under vacuum.

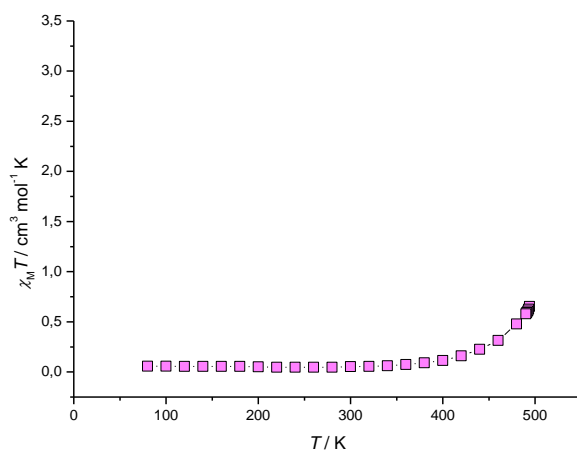


Figure S166. Thermal cycle for the sample **22**. This result agrees with the fact that in TGA experiments made under helium flow the phase $\mathbf{1}^{\text{A/LS}}$ shows an endothermic peak only at 529 K (Figure S32).

Sample 23

Parent phase $1^{A/LS}$. Phase purity of the sample was confirmed by XRPD. After that, this sample was kept in dry atmosphere. Measurements were performed in a sealed ampoule.

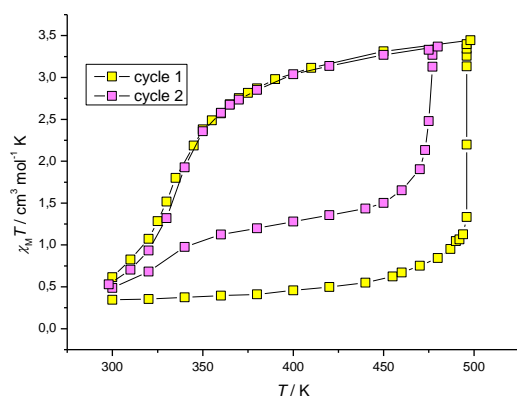


Figure S167. Sample 23. Thermal cycles 1 and 2. After that, a mixture of the phases $1^{A/LS}$ and 1^B was detected by XRPD. This behavior is analogous to the behavior of the sample 2-2. In the first cycle the sample shows high residual magnetic moment in the LS state due to X-ray irradiation (see also samples 12 and 13).

8. MAGNETIC DATA: MISCELLANEA

Table S2. The m/V values (mg/ μ L), information about thermal cycling, temperatures $T_c\uparrow$ and $T_c\downarrow$ (K), hysteresis loop width ΔT (K) and kinetic parameters for the LS \rightarrow HS and the HS \rightarrow LS transitions (JMAK model and biexponential approximation). The spin transition temperatures $T_c\uparrow$ and $T_c\downarrow$ were determined in “dynamic” experiments by the maximum value of $d(\chi_M T)/dT$; the temperatures at which kinetic measurements have been done are marked by “kin”. The hysteresis loop widths are given only for the cycles when both heating and cooling were done in “dynamic” mode.

Sample	m/V	cycle	day	$T_c\uparrow$, K	n	k , s^{-n}	k , s^{-1}	$T_c\downarrow$, K	$A_1\tau_1$, %	τ_1 , s	$A_2\tau_2$, %	τ_2 , s	n	k , s^{-n}	k , s^{-1}	ΔT	
1	0.0617	1	1st	-				360 kin					2.81	8.40×10^{-10}	5.88×10^{-4}		
		2	1st	400 kin	2.29	7.08×10^{-6}	5.65×10^{-3}	375 kin	28.3	3.91×10^2	71.7	1.86×10^3					
		3	1st	395 kin	1.90	2.28×10^{-5}	3.63×10^{-3}	380/379 kin									
		4	2nd	399 kin	2.09	1.68×10^{-5}	5.20×10^{-3}	374									
		5	2nd	395 kin	1.80	2.13×10^{-5}	2.57×10^{-3}	374									
		6	10th	432				366									66
		7	10th	400				370									30
		8	10th	397 kin	3.37	1.43×10^{-9}	2.39×10^{-3}	370									
		9	137th	446				365									81
		10	137th	397				370									27
		11	137th	397 kin	3.06	1.05×10^{-8}	2.47×10^{-3}	374 kin	4.0	6.59×10^1	96.0	9.85×10^2					
		12	259th	458				364									94
		13	259th	397				369									28
		14	259th	400				371									29
		15	343rd	430				367									63
		16	343rd	399				371									28
		17	343rd	ca. 433				366									67
		18	343rd	399				371									28
2	0.0482	1	1st	ca. 385				360 kin					3.18	2.71×10^{-10}	9.83×10^{-4}		
		2	1st	432				371								61	
		3	1st	412 kin	2.51	1.03×10^{-8}	6.50×10^{-4}	370 kin					1.74	2.10×10^{-4}	7.78×10^{-3}		
2-1	0.0374	4	7th	498 kin	2.42	6.25×10^{-10}	1.56×10^{-4}	345 kin									
		5	8th	475 kin				345 kin									
		6	54th	476				345 kin									
2-2	0.0330	7	56th	476				370								106	
		8	57th	472 kin	2.90	1.51×10^{-10}	4.15×10^{-4}	370 kin					1.58	1.22×10^{-4}	3.39×10^{-3}		
		9	57th	472 kin	2.98	2.29×10^{-9}	1.28×10^{-3}	370 kin					1.53	2.06×10^{-4}	3.87×10^{-3}		
		10	77th	472 kin	3.22	2.14×10^{-10}	9.99×10^{-4}	370 kin					1.52	2.69×10^{-4}	4.40×10^{-3}		
		11	77th	472 kin	3.13	1.51×10^{-9}	1.53×10^{-3}	370 kin					1.50	2.71×10^{-4}	4.27×10^{-3}		

2-3	0.0188	12	83rd	490 kin	2.71	2.14×10^{-11}	1.15×10^{-4}	356									
		13	84th	490 kin	3.02	1.11×10^{-8}	2.30×10^{-3}	360 kin	2.1	8.75×10^1	97.9	2.15×10^3					
		14	205th	494				359								135	
2-4	0.0152	1	97th	490 kin	1.74	1.18×10^{-7}	1.02×10^{-4}	360									
		2	98th	490 kin	2.79	1.30×10^{-8}	1.49×10^{-3}	360 kin	4.7	6.96×10^1	95.3	2.41×10^3					
		3	98th	490 kin	2.46	2.95×10^{-7}	2.19×10^{-3}	365 kin	5.9	3.91×10^1	94.1	1.72×10^3					
		4	204th	495				367								128	
3	0.0362	1	1st	ca. 385				360 kin					4.40	1.69×10^{-14}	7.37×10^{-4}		
		2	1st	467 kin	1.76	7.44×10^{-7}	3.24×10^{-4}	370 kin					3.17	4.56×10^{-10}	1.14×10^{-3}		
		3	1st	467 kin	1.72	4.91×10^{-6}	8.30×10^{-4}	370 kin					3.52	2.90×10^{-11}	1.00×10^{-3}		
		4	4th	450 kin	1.73	2.65×10^{-6}	6.08×10^{-4}	370 kin					2.47	2.77×10^{-7}	2.22×10^{-3}		
		5	4th	450 kin	2.18	5.66×10^{-8}	4.67×10^{-4}	370 kin					2.99	2.84×10^{-9}	1.40×10^{-3}		
		6	4th	467 kin	2.14	8.79×10^{-7}	1.49×10^{-3}	370 kin					3.10	2.68×10^{-10}	8.13×10^{-4}		
		7	9th	450 kin	1.77	2.29×10^{-6}	6.60×10^{-4}	370 kin					2.47	1.35×10^{-7}	1.67×10^{-3}		
		8	38th	440 kin	1.84	6.09×10^{-7}	4.15×10^{-4}	370 kin					1.75	2.78×10^{-5}	2.52×10^{-3}		
		9	38th	467 kin	1.99	2.12×10^{-6}	1.43×10^{-3}	370 kin					2.68	1.17×10^{-8}	1.11×10^{-3}		
		10	39th	464				365									99
		11	86th	450 kin	1.97	5.06×10^{-7}	6.30×10^{-4}	370 kin					1.69	2.24×10^{-5}	1.77×10^{-3}		
		12	86th	450 kin	2.15	8.82×10^{-7}	1.54×10^{-3}	370 kin					2.00	2.72×10^{-6}	1.64×10^{-3}		
		13	218th	466				366									100
		14	218th	460				366									94
		15	218th	460				367									93
		16	253rd	450 kin	2.06	3.15×10^{-7}	7.10×10^{-4}	370 kin					1.46	5.20×10^{-5}	1.17×10^{-3}		
		17	253rd	450 kin	2.08	1.79×10^{-7}	5.66×10^{-4}	370 kin					2.00	7.76×10^{-6}	2.83×10^{-3}		
4	0.0304	1	1st	ca.445				340 kin					1.31	8.65×10^{-6}	1.39×10^{-4}		
		2	1st	491 kin	2.26	7.92×10^{-8}	7.23×10^{-4}	365 kin									
		3	6th	490 kin	1.85	1.39×10^{-5}	2.35×10^{-3}	370 kin	14.9	8.23×10^1	85.1	7.62×10^2					
		4	6th	486 kin	2.07	5.28×10^{-6}	2.83×10^{-3}	376									
		5	11th	481 kin	2.12	9.74×10^{-7}	1.46×10^{-3}	376 kin	7.3	1.57×10^2	92.7	1.51×10^3					
		6	11th	480 kin	2.68	1.24×10^{-8}	1.12×10^{-3}	382 kin	2.7	2.86×10^2	97.3	3.02×10^3					
		7	12th	480 kin	1.85	1.38×10^{-5}	2.39×10^{-3}	377 kin	11.0	9.52×10^1	89.0	2.28×10^3					
		8	60th	480 kin	3.14	4.43×10^{-10}	1.06×10^{-3}	377 kin	9.9	5.88×10^1	90.1	6.67×10^2					
		9	60th	480 kin	3.45	7.99×10^{-11}	1.18×10^{-3}	377 kin	20.8	1.37×10^2	79.2	1.37×10^3					
		10	66th	484				373									111
		11	67th	476 kin	2.66	1.43×10^{-8}	1.13×10^{-3}	377 kin	2.2	2.05×10^2	97.8	2.27×10^3					
		12	67th	476 kin	2.27	3.13×10^{-7}	1.35×10^{-3}	377 kin	18.2	1.00×10^2	81.8	1.20×10^3					
		13	238th	484				374									110
		14	262nd	476 kin	3.51	8.22×10^{-12}	6.89×10^{-4}	377 kin	4.0	1.46×10^2	96.0	1.79×10^3					
		15	262nd	476 kin	3.39	2.49×10^{-11}	7.47×10^{-4}	377 kin	7.9	1.57×10^2	92.1	1.64×10^3					
		16	262nd	476 kin	3.42	2.20×10^{-11}	7.60×10^{-4}	377 kin									
		17	304th	483				373									110
		18	305th	476 kin	3.45	4.42×10^{-11}	9.93×10^{-4}	377 kin	4.2	1.99×10^2	95.8	2.00×10^3					

5	0.0388	19	305th	476 kin	3.29	1.11×10^{-10}	9.40×10^{-4}	377 kin	5.1	8.31×10^1	94.9	1.63×10^3						
		1	1st	ca. 440				ca. 320										
		2	18th	ca. 320				ca. 320										
5-1	0.0293	3	23rd	493				353								140		
		4	25th	490 kin	2.16	2.53×10^{-6}	2.57×10^{-3}	370 kin			100	6.26×10^3						
		5	26th	486 kin	2.09	2.51×10^{-6}	2.08×10^{-3}	366 kin	6.8	3.30×10^2	93.2	2.89×10^3						
		6	26th	482 kin	3.15	1.22×10^{-10}	7.17×10^{-4}	370										
		7	28th	482 kin	3.51	2.52×10^{-12}	4.98×10^{-4}	370										
		8	28th	482 kin	3.82	1.12×10^{-13}	4.10×10^{-4}	370										
		9	131st	486 kin	3.77	4.89×10^{-13}	5.48×10^{-4}	373 kin	16.9	5.19×10^1	83.1	4.88×10^2						
		10	131st	486 kin	3.92	6.28×10^{-13}	7.64×10^{-4}	373 kin	32.0	9.35×10^1	68.0	1.07×10^3						
		11	131st	486 kin	3.99	9.61×10^{-14}	5.49×10^{-4}	373 kin										
		12	168th	494				370								124		
		13	309th	486 kin	4.00	1.17×10^{-13}	5.84×10^{-4}	373 kin	29.8	1.96×10^2	70.2	1.50×10^3						
		14	309th	486 kin	3.65	8.24×10^{-13}	4.84×10^{-4}	373 kin	25.5	2.39×10^2	74.5	1.67×10^3						
		15	388th	491				371								120		
		16	393rd	487				372								115		
		6	0.0279	1	1st	ca. 400			-									
				2	2nd	-			-									
3	3rd			486				367								119		
4	3rd			477				369								108		
5	3rd			471				369								102		
6	34th			450 kin	1.87	1.47×10^{-6}	7.60×10^{-4}	374 kin				1.88	6.71×10^{-6}	1.78×10^{-3}				
7	34th			450 kin	2.14	1.12×10^{-7}	5.64×10^{-4}	374 kin				2.04	2.51×10^{-6}	1.78×10^{-3}				
8	152th			467				368								99		
9	153rd			450 kin	1.94	1.05×10^{-6}	8.27×10^{-4}	374 kin				1.71	1.16×10^{-5}	1.30×10^{-3}				
10	153rd			450 kin	2.31	3.00×10^{-8}	5.56×10^{-4}	374 kin				1.89	3.28×10^{-6}	1.24×10^{-3}				
11	153rd			470				368								102		
7	0.0273	1	1st	-				360 kin				1.56	1.89×10^{-5}	9.45×10^{-4}				
		2	1st	490 kin	2.37	1.60×10^{-7}	1.37×10^{-3}	363 kin				1.87	7.69×10^{-5}	6.24×10^{-3}				
		3	1st	490 kin	1.87	1.14×10^{-5}	2.30×10^{-3}	365 kin				2.82	1.30×10^{-7}	3.65×10^{-3}				
		4	3rd	480 kin	2.09	1.47×10^{-6}	1.59×10^{-3}	370 kin				2.58	4.60×10^{-8}	1.42×10^{-3}				
		5	4th	472 kin	2.52	2.19×10^{-8}	9.26×10^{-4}	372 kin				1.35	1.16×10^{-4}	1.20×10^{-3}				
		6	4th	472 kin	2.32	1.07×10^{-7}	9.79×10^{-4}	370 kin				1.56	1.29×10^{-4}	3.18×10^{-3}				
		7	11th	476				367								109		
		8	12th	475				367								108		
		9	13th	460 kin	1.97	5.74×10^{-7}	6.77×10^{-4}	373 kin				1.42	4.72×10^{-6}	1.72×10^{-4}				
		10	13th	460 kin	2.14	3.56×10^{-8}	3.33×10^{-4}	371 kin				2.16	4.67×10^{-8}	4.07×10^{-4}				
		11	210th	460 kin	2.19	2.66×10^{-8}	3.51×10^{-4}	370 kin				2.34	3.11×10^{-6}	4.41×10^{-3}				
		12	210th	460 kin	2.27	1.75×10^{-8}	3.81×10^{-4}	370 kin				2.50	7.55×10^{-7}	3.59×10^{-3}				
8	0.0226	1	1st	-				ca. 360										
		2	1st	490 kin	1.88	1.83×10^{-6}	8.80×10^{-4}	370 kin				1.15	5.88×10^{-4}	1.54×10^{-3}				

		3	3rd	490 kin	1.85	5.58×10^{-6}	1.43×10^{-3}	370 kin					3.28	6.46×10^{-10}	1.57×10^{-3}		
		4	3rd	490 kin	2.09	9.76×10^{-6}	3.98×10^{-3}	370 kin					2.79	1.45×10^{-8}	1.57×10^{-3}		
		5	3rd	490 kin	1.35	1.54×10^{-3}	8.18×10^{-3}	370 kin					2.83	8.00×10^{-9}	1.38×10^{-3}		
		6	3rd	487				367								120	
9	0.0181	1	1st	ca. 450				350									
		2	2nd	494 kin	2.20	6.89×10^{-8}	5.63×10^{-4}	365 kin									
		3	2nd	490 kin	2.37	1.38×10^{-6}	3.40×10^{-3}	372									
		4	8th	492 kin	3.16	3.62×10^{-10}	1.03×10^{-3}	370 kin	2.3	5.61×10^1	97.7	1.47×10^3					
		5	9th	492 kin	3.30	1.03×10^{-10}	9.40×10^{-4}	367									
		6	116th	492 kin	2.77	6.64×10^{-9}	1.12×10^{-3}	370 kin	1.9	3.07×10^1	98.1	1.12×10^3					
		7	117th	492 kin	3.67	4.34×10^{-11}	1.51×10^{-3}	370 kin	1.8	3.64×10^1	98.2	1.18×10^3					
		8	117th	492 kin	2.45	1.38×10^{-6}	4.07×10^{-3}	370 kin	3.8	4.37×10^1	96.2	9.74×10^2					
		9	117th	490 kin	2.26	4.05×10^{-6}	4.15×10^{-3}	370 kin	5.1	5.07×10^1	94.9	1.01×10^3					
		10	118th	490 kin	3.50	8.44×10^{-11}	1.31×10^{-3}	370 kin	8.2	2.31×10^2	91.8	1.86×10^3					
		11	118th	490 kin	2.44	1.25×10^{-6}	3.78×10^{-3}	370 kin	3.5	3.87×10^1	96.5	9.40×10^2					
		12	123rd	490 kin	3.98	5.35×10^{-12}	1.47×10^{-3}	370 kin	5.3	9.43×10^1	94.7	1.46×10^3					
		13	123rd	490 kin	3.56	4.80×10^{-10}	2.42×10^{-3}	370 kin	4.8	8.24×10^1	95.2	1.59×10^3					
		14	171st	494					367								127
		15	173rd	490 kin	3.63	5.61×10^{-11}	1.50×10^{-3}	370 kin	7.4	6.53×10^2	92.6	5.54×10^3					
		16	173rd	490 kin	3.05	4.05×10^{-8}	3.80×10^{-3}	367 kin	6.6	4.96×10^1	93.4	9.76×10^2					
		17	173rd	490 kin	2.91	2.49×10^{-7}	5.35×10^{-3}	368 kin	3.9	2.89×10^1	96.1	9.38×10^2					
		18	174th	490 kin	3.51	2.60×10^{-10}	1.85×10^{-3}	368 kin	5.7	1.67×10^2	94.3	2.19×10^3					
		19	174th	490 kin	3.28	2.69×10^{-9}	2.42×10^{-3}	368 kin									
		20	175th	486 kin	3.52	1.27×10^{-11}	8.00×10^{-4}	366 kin	2.8	3.21×10^1	97.2	1.32×10^3					
		21	175th	486 kin	3.14	3.66×10^{-10}	9.91×10^{-4}	366 kin	5.1	7.03×10^1	94.9	1.95×10^3					
		22	203th	490 kin	3.00	2.23×10^{-9}	1.30×10^{-3}	370 kin	1.2	1.21×10^2	98.8	3.23×10^3					
		23	203th	490 kin	2.40	4.08×10^{-7}	2.18×10^{-3}	370 kin	1.9	3.26×10^1	98.1	1.87×10^3					
		24	208th	482 kin	3.71	7.10×10^{-14}	2.83×10^{-4}	366 kin	6.0	5.65×10^1	94.0	1.61×10^3					
		25	208th	482 kin	2.75	1.47×10^{-9}	6.14×10^{-4}	366 kin	5.4	3.02×10^1	94.6	1.26×10^3					
		26	211th	488 kin	1.80	9.12×10^{-6}	1.60×10^{-3}	366 kin	4.5	4.78×10^1	95.5	1.60×10^3					
		27	211th	488 kin	1.75	3.00×10^{-5}	2.60×10^{-3}	366 kin	2.5	3.38×10^1	97.5	2.24×10^3					
		28	327th	493					364								129
		29	373rd	486 kin	2.75	3.79×10^{-9}	8.55×10^{-4}	366 kin	3.8	5.77×10^1	96.2	1.89×10^3					
		30	373rd	486 kin	1.80	1.11×10^{-5}	1.75×10^{-3}	366 kin	3.6	3.79×10^1	96.4	1.63×10^3					
		31	373rd	486 kin	1.69	4.21×10^{-5}	2.61×10^{-3}	366 kin									
		32	450th	482 kin	3.20	8.94×10^{-12}	3.53×10^{-4}	370 kin	0.5	5.90×10^1	99.5	5.82×10^3					
		33	450th	482 kin	2.16	1.29×10^{-7}	6.49×10^{-4}	370 kin	2.1	5.93×10^1	97.9	2.95×10^3					
		34	491st	493	2.75	3.79×10^{-9}			363								130
		35	527th	484 kin	2.50	5.99×10^{-9}	5.14×10^{-4}	370 kin	0.6	3.20×10^1	99.4	5.34×10^3					
		36	527th	484 kin	2.21	2.22×10^{-7}	9.92×10^{-4}	370 kin									
10	0.0354	1	1st	ca. 405				353								52	
		2	3rd	374				350								24	

10-1	0.0162	3	5th	378				355								23	
		4	30th	ca. 420				ca. 320									
		5	37th	490 kin	2.56	4.46×10^{-9}	5.42×10^{-4}	377									
		6	37th	490 kin	3.31	1.16×10^{-9}	1.98×10^{-3}	378									
		7	39th	490 kin	2.56	3.63×10^{-8}	1.24×10^{-3}	378									
		8	40th	490 kin	3.65	2.05×10^{-11}	1.18×10^{-3}	377 kin	6.8	3.93×10^1	93.2	8.06×10^2					
		9	40th	490 kin	4.07	2.69×10^{-12}	1.44×10^{-3}	377 kin	12.4	5.93×10^1	87.6	7.69×10^2					
		10	45th	495			377									118	
11	0.0137	1	1st	ca. 395				ca. 355									
		2	5th	ca. 405				ca. 360									
		3	6th	490 kin	1.94	4.96×10^{-7}	5.60×10^{-4}	370 kin	2.4	8.14×10^1	97.6	4.07×10^2	0.83	7.03×10^{-3}	2.47×10^{-3}		
		4	6th	490 kin	1.90	1.11×10^{-5}	2.47×10^{-3}	370 kin	56.3	1.14×10^2	43.7	4.55×10^2	0.88	1.26×10^{-2}	7.15×10^{-3}		
		5	6th	490 kin	1.92	1.87×10^{-5}	3.45×10^{-3}	370 kin	35.3	6.46×10^1	64.7	2.30×10^2	0.73	3.29×10^{-2}	9.46×10^{-3}		
		6	6th	488				371									117
12		1	1st	ca. 455			ca. 330										
12-1	0.0128	2	281st	490 kin	1.63	1.23×10^{-7}	5.76×10^{-5}	350									
		3	282nd	490 kin	1.96	5.55×10^{-9}	6.20×10^{-5}	354									
		4	283rd	490 kin	2.00	2.31×10^{-6}	1.52×10^{-3}	357 kin	9.4	6.49×10^2	90.6	4.46×10^3					
		5	283rd	490 kin	2.24	1.66×10^{-7}	9.51×10^{-4}	357 kin	8.5	6.62×10^2	91.5	5.53×10^3					
		6	284th	490 kin	2.48	1.91×10^{-8}	7.62×10^{-4}	355 kin	8.3	2.31×10^2	91.7	2.07×10^3					
		7	284th	490 kin	2.13	2.46×10^{-7}	8.03×10^{-4}	355 kin	8.6	3.33×10^2	91.4	3.01×10^3					
		8	290th	490 kin	2.01	6.42×10^{-7}	8.19×10^{-4}	353 kin	11.0	2.55×10^2	89.0	3.12×10^3					
		9	290th	490 kin	2.16	3.86×10^{-7}	1.06×10^{-3}	353 kin									
		10	369th	490 kin	2.35	3.52×10^{-8}	6.71×10^{-4}	353 kin	8.6	2.17×10^2	91.4	2.33×10^3					
		11	369th	490 kin	1.88	2.31×10^{-6}	1.01×10^{-3}	353 kin									
		12	393rd	495				350									145
		13	409th	490 kin	1.85	1.56×10^{-6}	7.24×10^{-4}	353 kin	6.5	2.73×10^2	93.5	2.96×10^3					
		14	409th	490 kin	1.58	1.74×10^{-5}	9.69×10^{-4}	353 kin									
		15	466th	490 kin	1.82	1.90×10^{-6}	7.18×10^{-4}	353 kin	6.5	4.48×10^2	93.5	6.11×10^3					
		16	473rd	495				350									145
		17	553rd	490 kin	1.75	2.85×10^{-6}	6.81×10^{-4}	353 kin	5.2	3.66×10^2	94.8	4.51×10^3					
		18	553rd	490 kin	1.60	1.80×10^{-5}	1.06×10^{-3}	353 kin									
		19	609th	491				351									140
		20	609th	490				351									139
		21	613th	488				350									138
		13	0.0075	1	1st	490 kin	2.56	1.78×10^{-9}	3.80×10^{-4}	353							
2	2nd			490 kin	3.47	9.01×10^{-11}	1.28×10^{-3}	353 kin	14.4	7.63×10^1	85.6	1.85×10^3					
3	2nd			490 kin	3.84	8.22×10^{-12}	1.31×10^{-3}	353 kin	10.2	6.37×10^1	89.8	2.12×10^3					
4	29th			493				355									138
5	42nd			490 kin	3.86	8.44×10^{-13}	7.44×10^{-4}	353 kin	11.7	7.75×10^1	88.3	2.19×10^3					
6	42nd			490 kin	2.71	1.59×10^{-8}	1.32×10^{-3}	353 kin									
7	42nd			490 kin	2.28	5.75×10^{-7}	1.82×10^{-3}	353 kin									

14	0.0545	1	1st	ca. 390				370 kin					2.75	6.04×10^{-9}	1.03×10^{-3}		
		2	1st	425				372									53
		3	1st	402				375									27
		4	1st	407				375									32
		5	134th	401				374									27
		6	134th	405				375									30
14-1	0.0177	7	179th	490 kin	1.85	6.08×10^{-8}	1.26×10^{-4}	358									
		8	180th	490 kin	2.33	1.22×10^{-6}	2.91×10^{-3}	360 kin	9.2	7.46×10^1	90.8	8.89×10^2					
		9	180th	492				361								131	
		10	187th	490 kin	3.20	2.42×10^{-9}	2.02×10^{-3}	360 kin	12.0	1.23×10^2	88.0	1.12×10^3					
		11	187th	490 kin	3.11	8.78×10^{-9}	2.58×10^{-3}	360 kin	14.3	1.28×10^2	85.7	1.16×10^3					
		12	242nd	480 kin	3.72	8.54×10^{-15}	1.64×10^{-4}										
		13	242nd	480 kin	4.17	1.23×10^{-15}	2.67×10^{-4}	362									
		14	256th	470 kin	4.26	2.65×10^{-20}	2.52×10^{-5}										
		15	263rd	460 kin													
15	0.0521	1	1st	390				380 kin					2.88	1.46×10^{-9}	8.63×10^{-4}		
		2	1st	403				375								28	
		3	1st	403				374								29	
		4	1st	400 kin	3.33	1.28×10^{-9}	2.15×10^{-3}	380 kin					1.15	4.31×10^{-5}	1.55×10^{-4}		
		5	14th	405				374								31	
16	0.0217	1	1st	ca. 400													
		2	7th	495				368								127	
		3	10th	495				364								131	
		4	11th	490 kin	1.93	5.75×10^{-7}	5.86×10^{-4}	366									
		5	12th	490 kin	2.14	3.42×10^{-7}	9.43×10^{-4}	372									
		6	282nd	493				372								121	

Table S3. HS → LS transitions. Triexponential approximation. Selected curves.

Sample	Cycle	$A_1\tau_1$, %	τ_1 , s	$A_2\tau_2$, %	τ_2 , s	$A_3\tau_3$, %	τ_3 , s
12-1	7	3.9	2.54×10^2	18.2	1.22×10^3	77.9	4.90×10^3
	10	0.4	4.47×10^1	10.6	3.41×10^2	89.0	3.06×10^3
	13	2.2	1.84×10^2	11.8	8.63×10^2	86.0	4.47×10^3
	15	1.6	2.30×10^2	12.4	1.46×10^3	85.9	9.38×10^3
	17	0.5	1.03×10^2	10.1	8.80×10^2	89.4	6.01×10^3
9	32	0.1	3.49×10^1	2.0	8.56×10^2	97.9	1.18×10^4
	33	0.1	4.43×10^1	6.3	7.14×10^2	93.6	6.22×10^3
2-3	13	0.2	2.09×10^1	6.8	4.43×10^2	93.0	3.91×10^3
2-4	2	1.5	4.81×10^1	5.9	4.08×10^2	92.7	5.03×10^3
	3	2.0	3.44×10^1	9.5	6.40×10^2	88.5	5.83×10^3

Evolution of the Avrami exponent

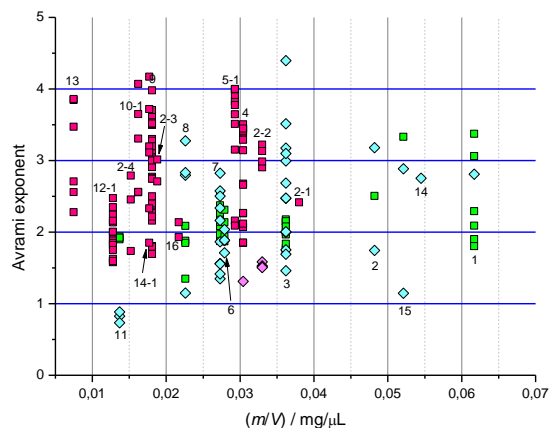


Figure S168. Values of the Avrami exponent n for the $1^{A/LS} \rightarrow 1^{A/HS}$ (squares) and $1^{A/HS} \rightarrow 1^{A/LS}$ (diamonds) transitions. Pink and light pink: parent phases $\beta\text{-}1^{LS} \cdot x\text{H}_2\text{O}$ and 1^{ALS} . Green and cyan: parent phase $1^{LS} \cdot \text{EtOH} \cdot \text{H}_2\text{O}$.

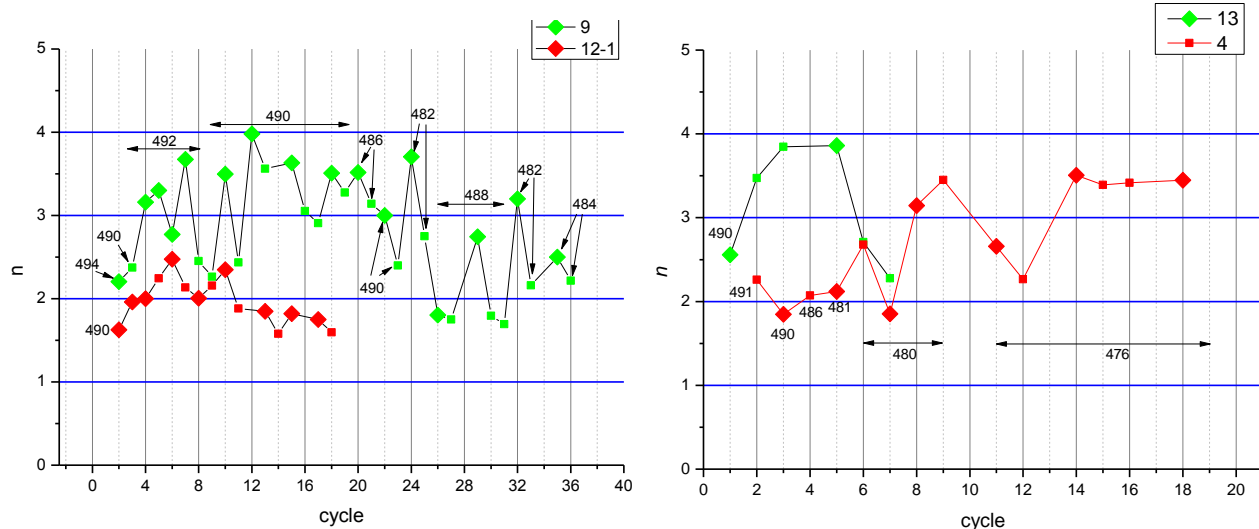


Figure S169. Evolution of the Avrami exponent n for the $1^{A/LS} \rightarrow 1^{A/HS}$ transition (samples 9, 12-1, 13 and 4; diamonds: the first cycle a day (or the sole cycle)).

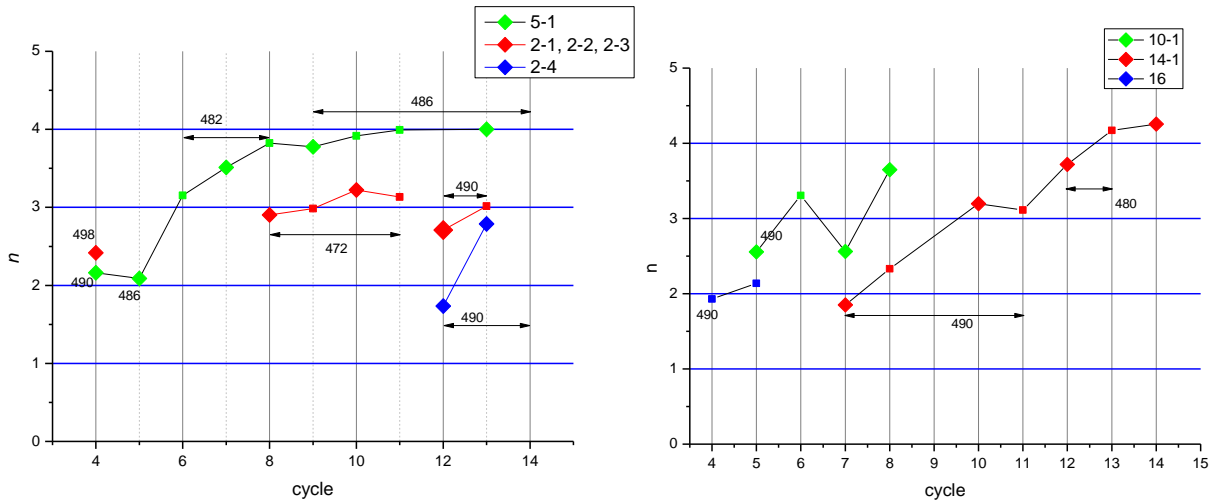


Figure S170. Evolution of the Avrami exponent n for the $1^{A/LS} \rightarrow 1^{A/HS}$ transition (samples 5-1, 2-1, 2-2, 2-3, 2-4, 10-1, 14-1 and 4; diamonds: the first cycle a day (or the sole cycle)).

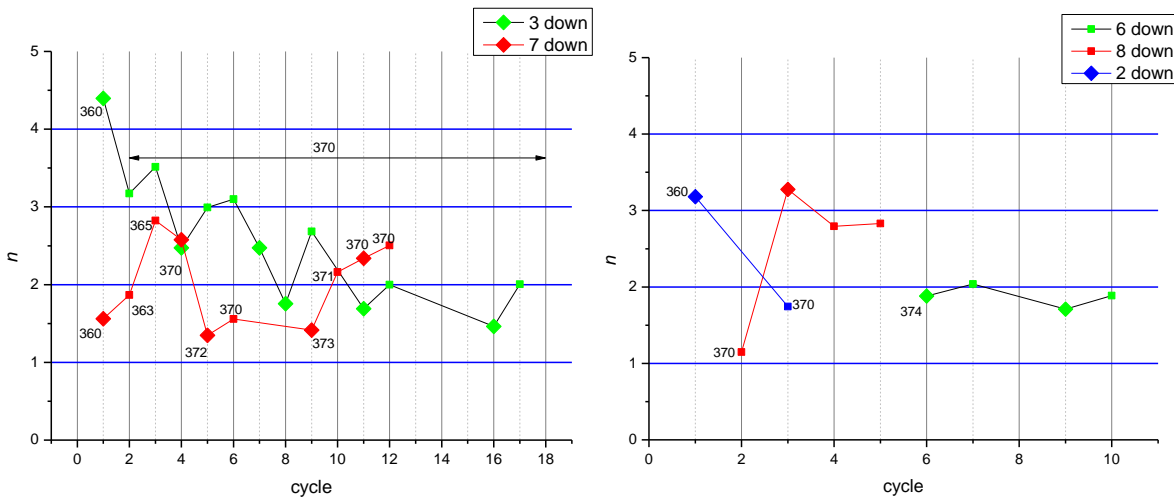


Figure S171. Evolution of the Avrami exponent n for the $1^{A/HS} \rightarrow 1^{A/LS}$ transition (samples 3, 7, 2-2, 6, 8 and 2; diamonds: the first cycle a day (or the sole cycle)).

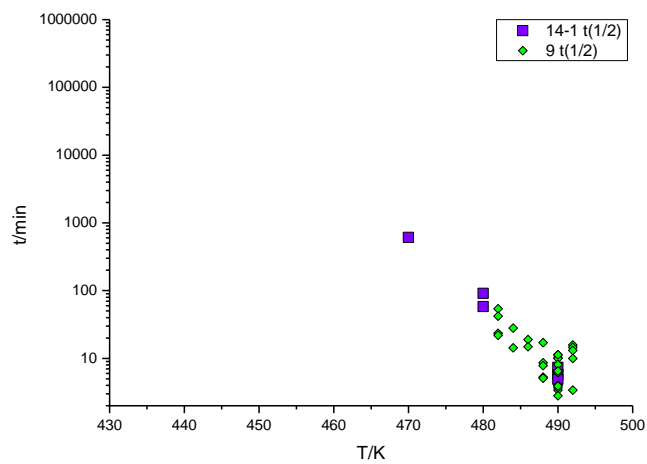


Figure S172. Half-time–Temperature–Transformation diagram for the $1^{A/LS} \rightarrow 1^{A/HS}$ conversion (the samples **9** and **14-1**).

Activation energy

1) Magnetochemistry: Kinetic analysis under isothermal conditions

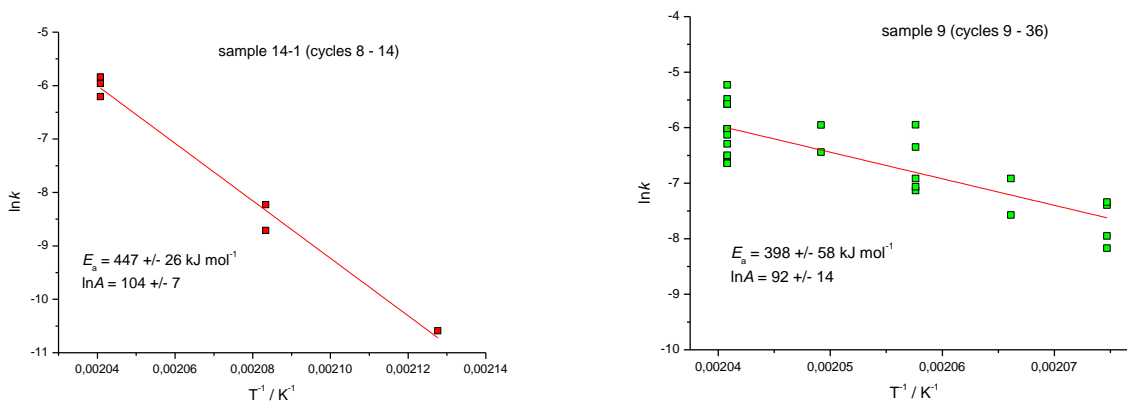


Figure S173. Left: Arrhenius plot for the sample 14-1. Right: Arrhenius plot for the sample 9.

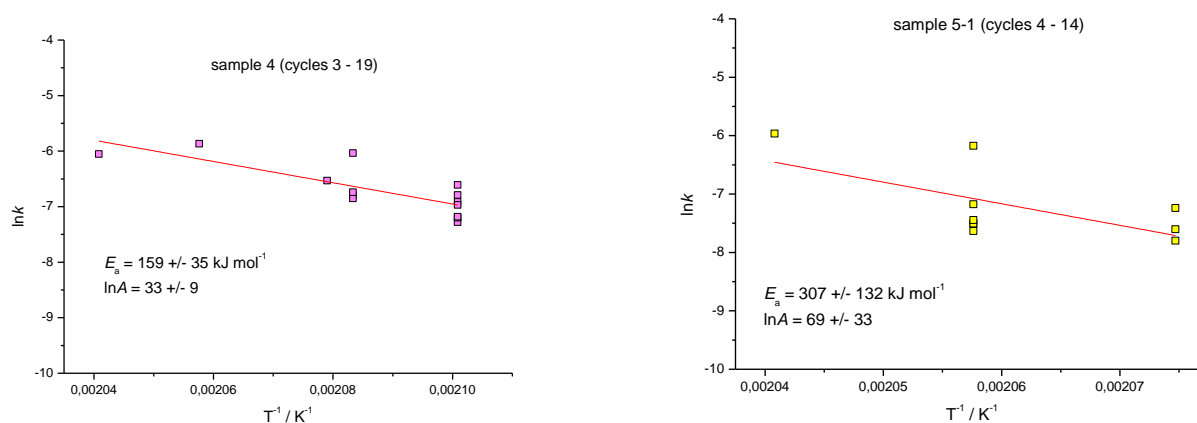


Figure S174. Left: Arrhenius plot for the sample 4. Right: Arrhenius plot for the sample 5-1.

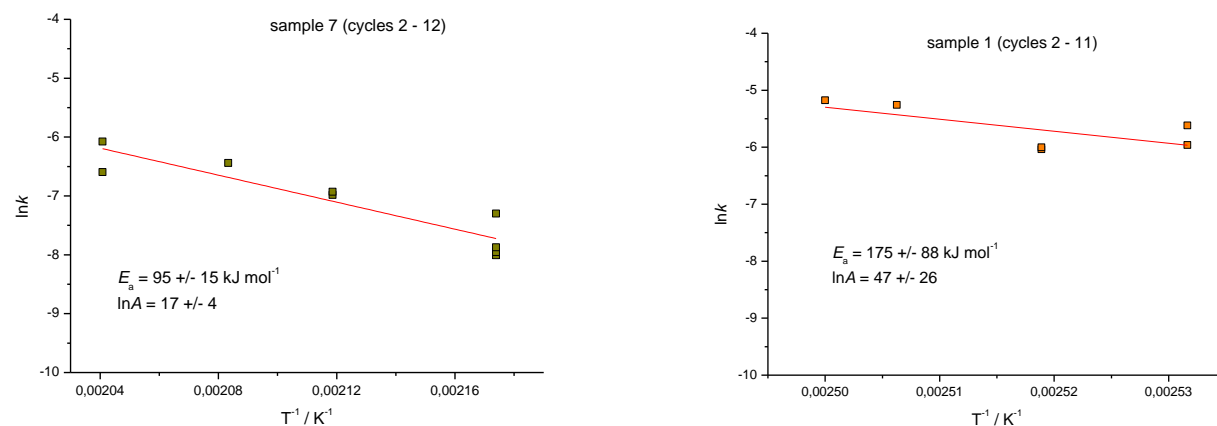


Figure S175. Left: Arrhenius plot for the sample 7. Right: Arrhenius plot for the sample 1.

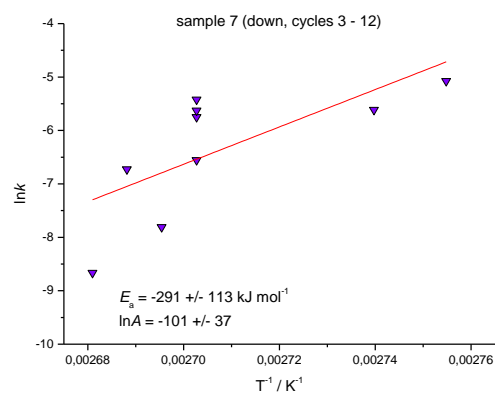
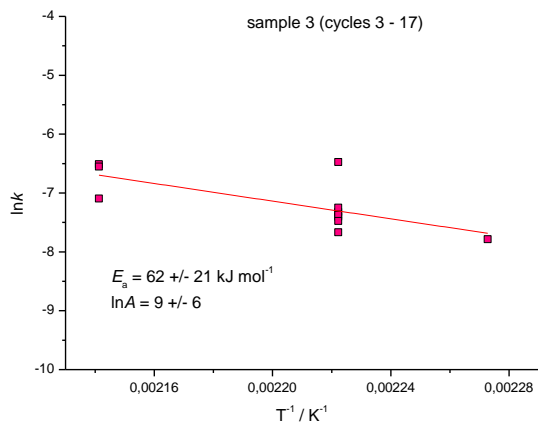


Figure S176. Left: Arrhenius plot for the sample **3**. Right: Arrhenius plot for the sample **7** (HS \rightarrow LS).

2) Magnetochemistry: Kinetic analysis under non-isothermal conditions

In principle, the activation energy of the spin transition can be estimated using various methods of kinetic analysis of non-isothermal data (*e.g.* the Ozawa model, the Kissinger model, the Friedman model, *etc.*). In this case the heating runs should be performed at several different heating rates varying from slow (from *ca.* 1 K min⁻¹) to fast ones (up to 10 – 40 K min⁻¹). Although we made a series of measurements at three different slow scan rates not exceeding 0.9 K min⁻¹ only (which may lead to high errors when estimating the activation barrier height) we roughly estimated the activation energy of the $1^{A/LS} \rightarrow 1^{A/HS}$ transition for the samples **5-1** and **12-1** using the Ozawa equation^{S3}

$$\ln\beta = \text{const} - 1.052 \frac{E_a}{R} \frac{1}{T_c}$$

where β is heating rate and T_c is the spin transition temperature determined by the maximum value of $d(\chi_M T)/dT$. The activation energy appeared to be *ca.* 340 – 350 kJ mol⁻¹ for both samples. This value is in good agreement with the values calculated using isothermal magnetic data.

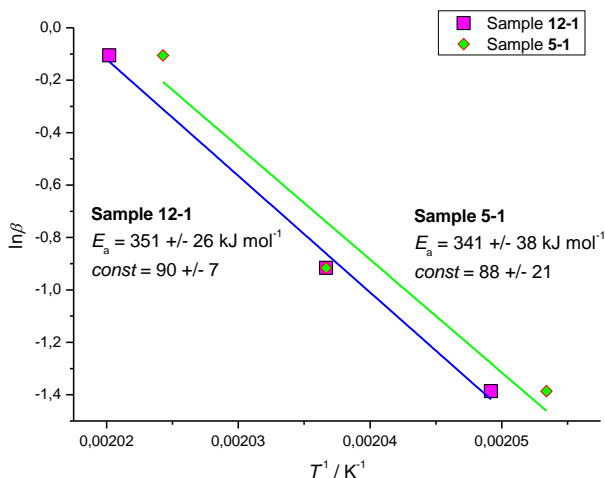


Figure S177. Ozawa plot for the samples **5-1** and **12-1**.

S3 T. Ozawa, *J. Therm. Anal.*, 1970, **2**, 301 – 324.

3) DSC: Kinetic analysis under non-isothermal conditions

DSC data were processed with the computer program Netzsch Thermokinetics 2 (Version 2004.05).^{S3} We used the experimental DSC data to search for the corresponding topochemical equation (the selection was made from different equations: chemical reaction at the interface, nucleation and diffusion). This calculation was made by the improved differential procedure of Borchardt–Daniels.^{S4,S5} The F test^{S4} was used to search for the best kinetic description and for statistical control of the obtained equation. It tests the residual variance of individual models against one another and answers the question of whether the models differ significantly (statistically) or not. The statistical quantile F_{crit} is obtained for a level of significance of 0.05.

The first three equations: CnB, C1B and B1 (Table S4) describe the processes with the acceleration.

Table S4.

F_{crit}	F_{exp}	F_{act}	Equation
1.23	1.00	260	CnB
1.23	1.16	261	C1B
1.23	2.45	260	Bna
1.23	3.63	261	Fn
1.23	3.65	261	An
1.23	6.56	262	D3
1.23	6.88	262	B1
1.23	14.78	262	D4
1.23	51.18	262	D1

The used topochemical equations are: reactions with autocatalysis (CnB and C1B), different type of diffusion (D1, D3, D4), n -th order (Fn), Avrami-Erofeev (An), Prout–Tompkins (BnA and B1) equations.^{S4}

Data on the F test of fit quality was considered and partially used to identify the best kinetic description.

The best description is the equation CnB:

$$f(\alpha) = (1-\alpha)^{0.9} \cdot (1 + 14 \cdot \alpha). E = 427 \pm 1 \text{ kJ mol}^{-1}; \lg A = 42.9 \pm 1.$$

Corr. coeff. = 0.998770.

The best description is the equation C1B:

$$f(\alpha) = (1-\alpha) \cdot (1 + 7 \cdot \alpha). E = 552 \pm 1 \text{ kJ mol}^{-1}; \lg A = 56.5 \pm 1.$$

Corr. coeff. = 0.998564.

We observed high values of the pre-exponential factor. In this context it should be noted that for such phase transformations as the phase transformation monoclinic sulfur \rightarrow rhombic sulfur or the recrystallization of Al the amount of instantly reacting molecules is estimated as 10^7 , and the reacting crystal volume is estimated as 10^{-15} cm^3 .^{S6} This can explain the high values of calculated pre-exponential factors for the phase transformation $\mathbf{1}^{\text{A/LS}} \rightarrow \mathbf{1}^{\text{A/HS}}$.

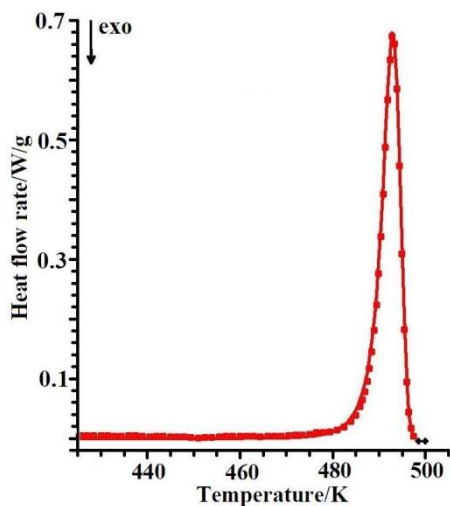


Figure S178. Data processing for the thermal phase transformation. DSC curve fitting of linear regression, simulated with single-step reaction (CnB). The *points* are the experimental data; the *lines* are the calculated data. The heating rate was 6 K min^{-1} .

S4 Netzsch Thermokinetics. <http://www.netzsch-thermal-analysis.com/us/products-%20%20solutions/advanced-software/thermokinetics.html>

S5 H. J. Borchard and F. Daniels, The application of differential thermal analysis to the study of reaction kinetics. *J. Am. Chem. Soc.*, 1957, **79**, 41–46.

S6 N. N. Hartshorne, *Discuss. Faraday Soc.*, 1945, **5**, 149.

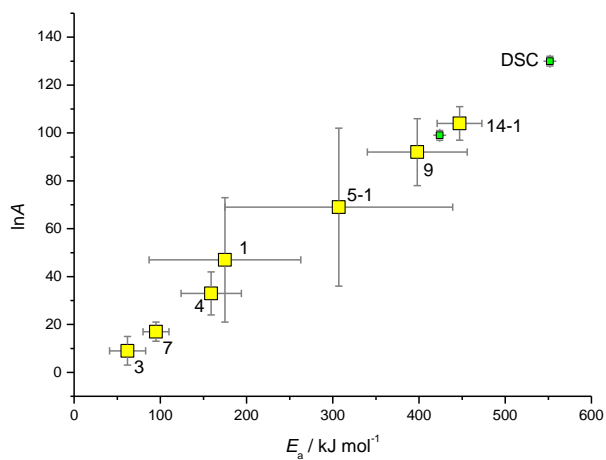


Figure S179. Compensation effect for the transition $1^{A/LS} \rightarrow 1^{A/HS}$. Yellow: isothermal magnetic data. Green: non-isothermal DSC data.

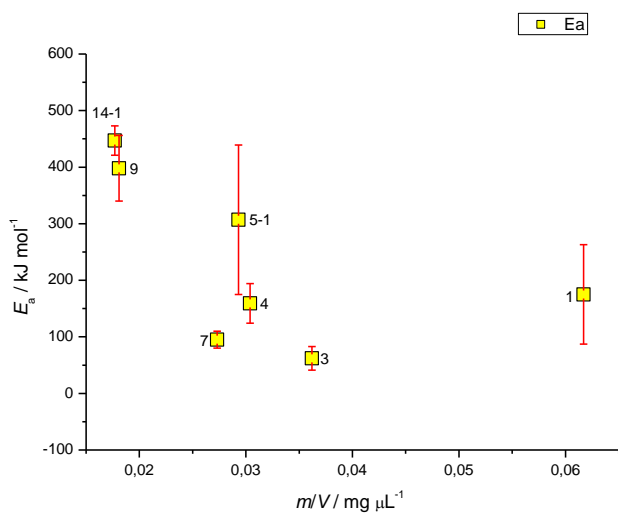


Figure S180. Dependence of the activation energy on the m/V ratio.