Electronic Supplementary Information (ESI)

for

**Crystal Structures of Ordered and Plastic-Crystalline Phases
of *iso*-Butyllithium by X-Ray Powder Diffraction**

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Experimental and NMR

All sample preparations and manipulations were carried out under Ar (99.999%) using Schlenk techniques.[1,2] Solutions of *i*-BuLi (16% in heptane, technical) were obtained from Rockwood/Albemarle Lithium. After preconcentration to 2.3 mol · L^{-1} (titrated with Ph_2Te_2 [3]), the solvent was removed *in vacuo*. The crude *i*-BuLi was supended in a small amount of pentane, dried *in vacuo* and sublimated (70–75 °C, 3 · 10^{-3} mbar, 2 h) to yield colorless plastic crystalline *i*-BuLi. The capillaries were filled by application of glass trousers and a special capillary station (Fig. 1 - 3) and then flame-sealed. All samples were checked for their stability during the measurements.

Pentane and C_6D_6 were dried and stored over activated molecular sieves (4 Å) and degassed with three *freeze-pump-thaw* cycles. NMR spectra were recorded from samples, dissolved in C_6D_6 in flame-sealed borosilicate glas tubes, on a Bruker *Avance*-300 (^{1}H 300.03 MHz; ^{7}Li 116.60 MHz; ^{13}C 75.45 MHz) spectrometer. The chemical shifts were referred to Me_4Si and LiCl in H_2O as external standards and, if possible, calibrated on the residual signal of the incomplete deuterated solvent C_6D_6 ($\delta(^1H)$ = 7.16, $\delta(^{13}C)$ = 128.06). The multiplicities are given with common abbreviations (s = singulet, d = doublet, m = multiplet, br = broad). The values of the *J*-couplings are given in Hz.

^{1}H NMR (300 MHz, C_6D_6) δ/ ppm = 1.63 (m, *J* = 6.3 Hz, 1H, CH), 1.09 (d, *J* = 6.3 Hz, 6H, CH_3), -0.79 (d, *J* = 6.8 Hz, 2H, Li-CH_2).

^{13}C NMR (75 MHz, C_6D_6) δ/ ppm = 30.0, 29.5, 27.4 (br).

^{7}Li NMR (117 MHz, C_6D_6) δ/ ppm = 2.37 (s).
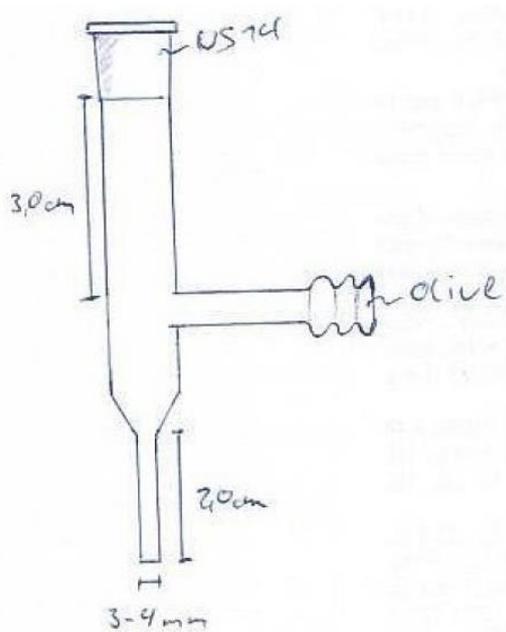
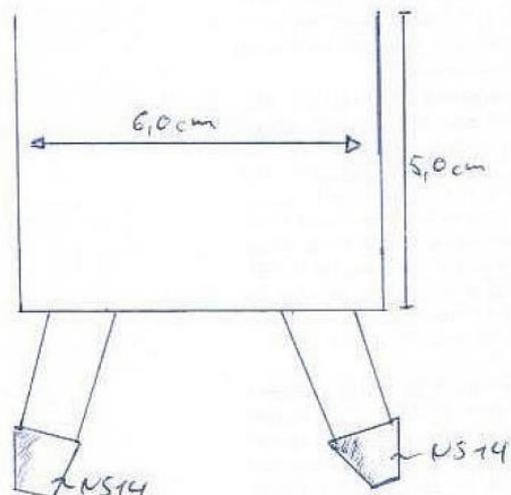Figure S 1: Sketch of the applied capillary station.

Figure S 2: Sketch of the applied glass trousers.

Figure S 3: Picture of the glass trousers and the capillary station for the transfer of the sample from the Schlenk apparatus to the capillary.
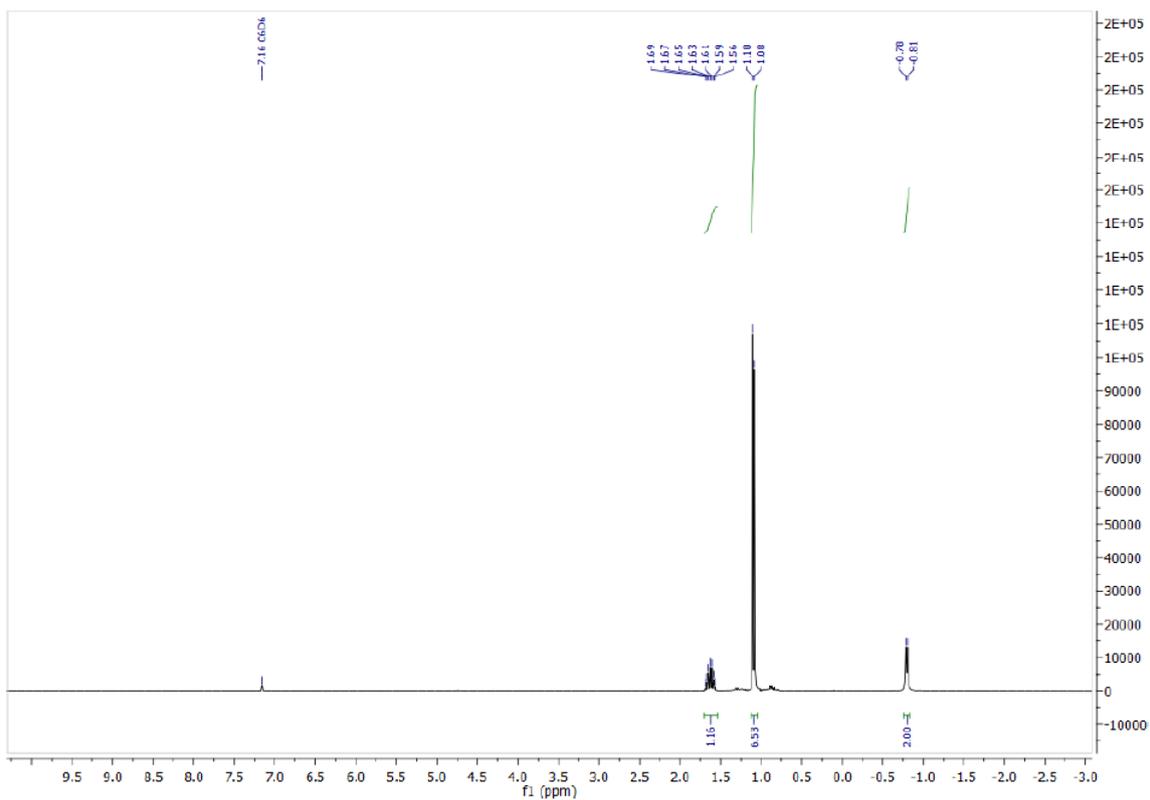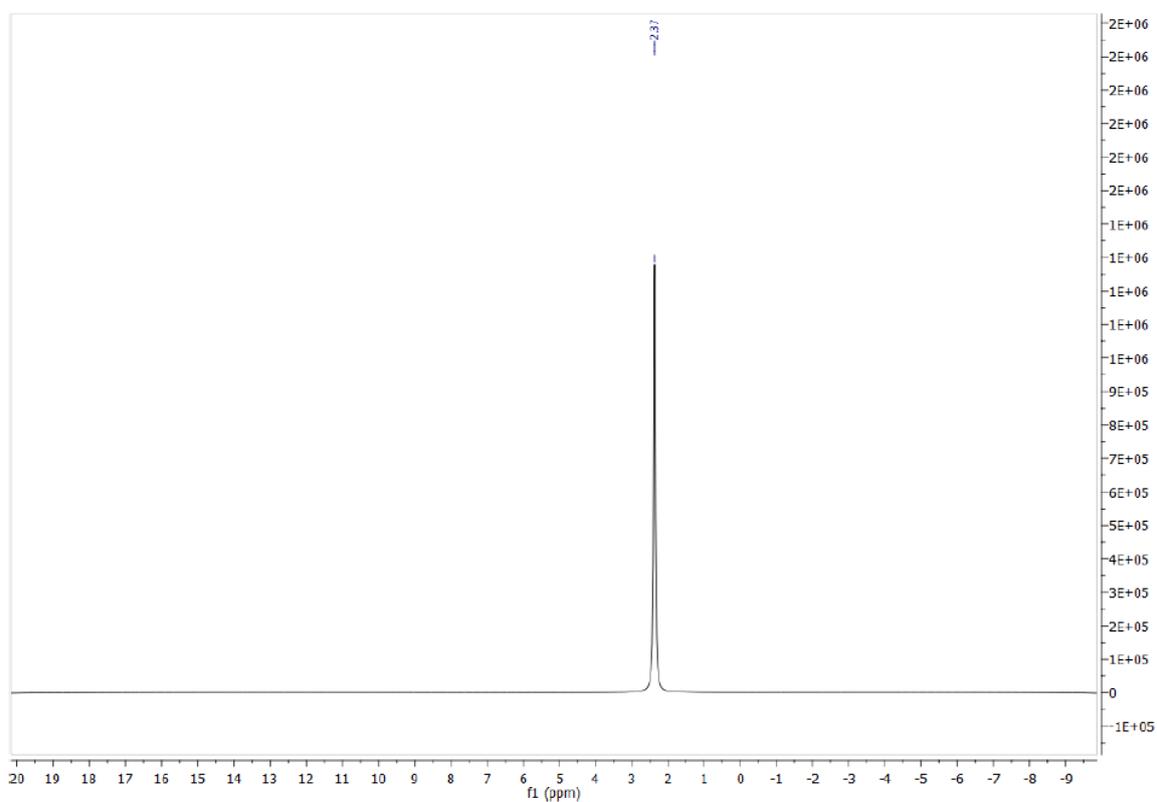
Figure S 4: ^{1}H spectrum of i-BuLi in C_6D_6.

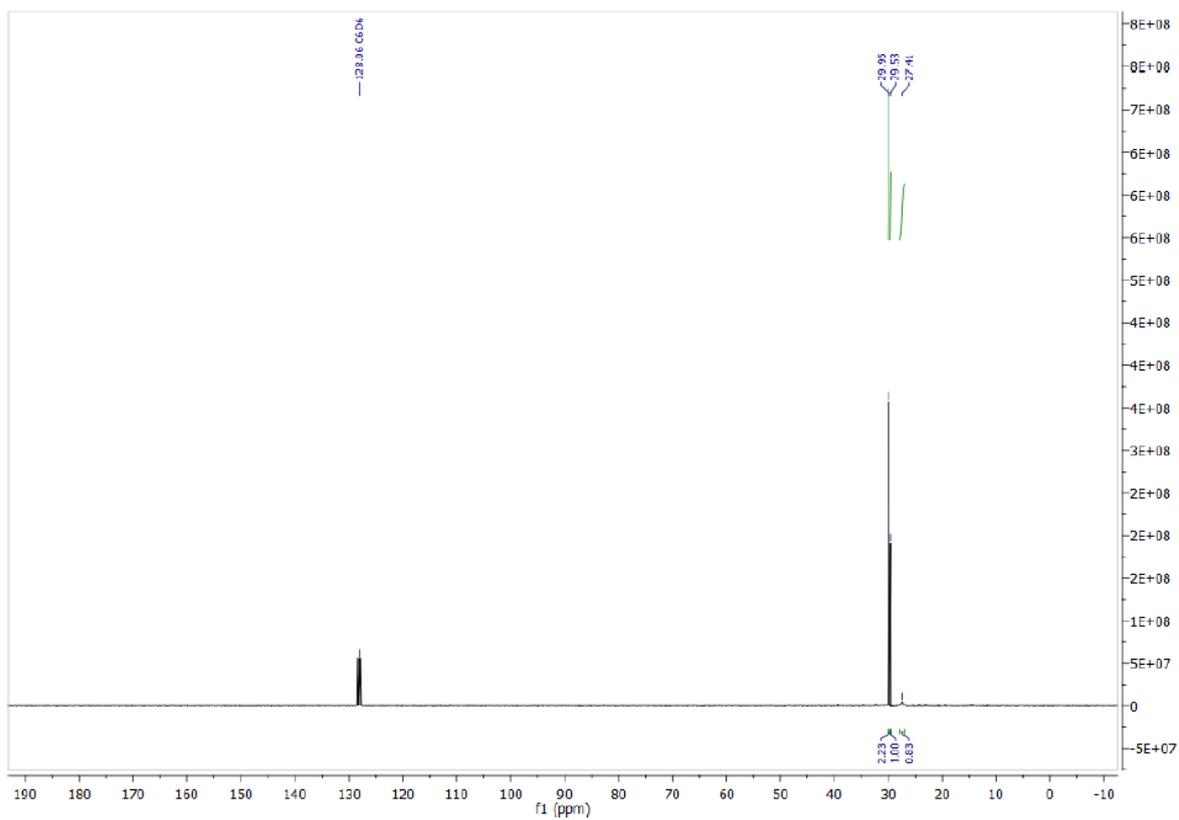Figure S 5: ^{7}Li spectrum of i-BuLi in C_6D_6.

Figure S 6: ^{13}C spectrum of *i*-BuLi in C_6D_6.

X-Ray Powder Diffraction

Powder samples were measured in sealed glass capillaries (d = 1.0mm) in Debye-Scherrer geometry on a STOE STADI-P diffractometer within several days. X-rays were generated by a classical sealed tube with a Cu anode. Cu-Kα_1 radiation (λ = 1.5406 Å) was selected with a curved Ge(111) monochromator. The scattered intensities were recorded by a linear position sensitive detector (lin. PSD, filled with Kr/CH$_4$). The samples were cooled or heated with an Oxford Cryostream 700Plus cooling device.

Structure solution and Rietveld refinement

The structures of both phases were solved with the real-space method using simulated annealing with the program DASH[4]. All Rietveld refinements were carried out with TOPAS[5-6] (TOPAS Academic, Version 4.2).

The temperature-dependent XRPD data in the main paper were plotted with Origin, while Fig. S8 was plotted with the STOE WinXPOW[7] software package. Molecular models and packing motifs were generated with SCHAKAL[8]. Plots of the Rietveld[9-10] and LeBail[11] refinements were plotted with ORIGIN[12].

<u>α-phase</u>
The structure solution was challenging. We tested different space groups (*P*1 and *P*-1), and tetramers as well as hexamers. The hexamers show a molecular symmetry with inversion centres; hence in *P*-1, Z = 2, the hexamers could be located on two symmetrically independent inversion centres. Correspondingly, the positioning of two independent hexamers on two of the eight inversion centres in *P*-1 had to be tried. Surprisingly, tetrameric as well as hexameric models gave promising results. Only the subsequent Rietveld refinements with TOPAS[5-6], using restraints on bond lengths and angles, revealed that the correct structure has space group *P*-1 and is built from hexamers. The final Rietveld refinement converged with good confidence values and a smooth difference curve (See Fig. 1, 2, 3 in the main manuscript; Tab. S1, see below).
The Rietveld refinement of the α-phase was carried out using two half hexamers. To ensure a sensible molecular geometry, dummy atoms placed on the positions of the corresponding Li and C positions, according to the inversion symmetry were used to restrain the Li-C and Li-Li distances within the hexamer. The z-matrix/rigid body for the refinement of the γ-phase was generated from the refined structure of the α-phase by ToolKit within DASH[4], torsion angles were not refined.

Remark on the Li-Li and Li-C distances:
The Li-Li and Li-C distances of the α-phase given in the paper were determined from a Rietveld refinement with unrestrained Li atoms. In the final refinements, restraints were used for Li–Li and Li–C bond lengths.

γ-phase

Indexing of the powder pattern of the γ-phase at room temperature with DICVOL[13] led to an orthorhombic unit cell with $Z = 2$ with a volume of 1625 Å^3, *i.e.* ~9% larger than the α-phase at -80°C. Such a volume increase is typical for plastic-crystalline phases, because rotating molecules need more space. The systematic extinctions indicated *Pnnn* as likely space group. The structure could be solved in *Pnnn* with DASH[4] using a rigid hexamer on a general position. The occupancy of all atoms is 1/4. In the subsequent Rietveld refinement with TOPAS, the hexamer was also treated as a rigid body, taking the geometry from the refined α-phase, and refining only the position and spatial orientation of the hexamers and one overall temperature factor. The final Rietveld plot is shown in Fig. 4 in the main paper. The unit cell contains two disordered hexameric units. Both exhibits a four-fold rotational disorder. The hexamers are located close to (¼, ¼, ¾) and (¾, ¾, ¼), which is a site with 222 (D_2) symmetry in *Pnnn* (Origin choice 2). The hexamers are arranged in a distorted face-centred cubic packing (Fig. 5 in the main paper, Fig. S9-S11 below).
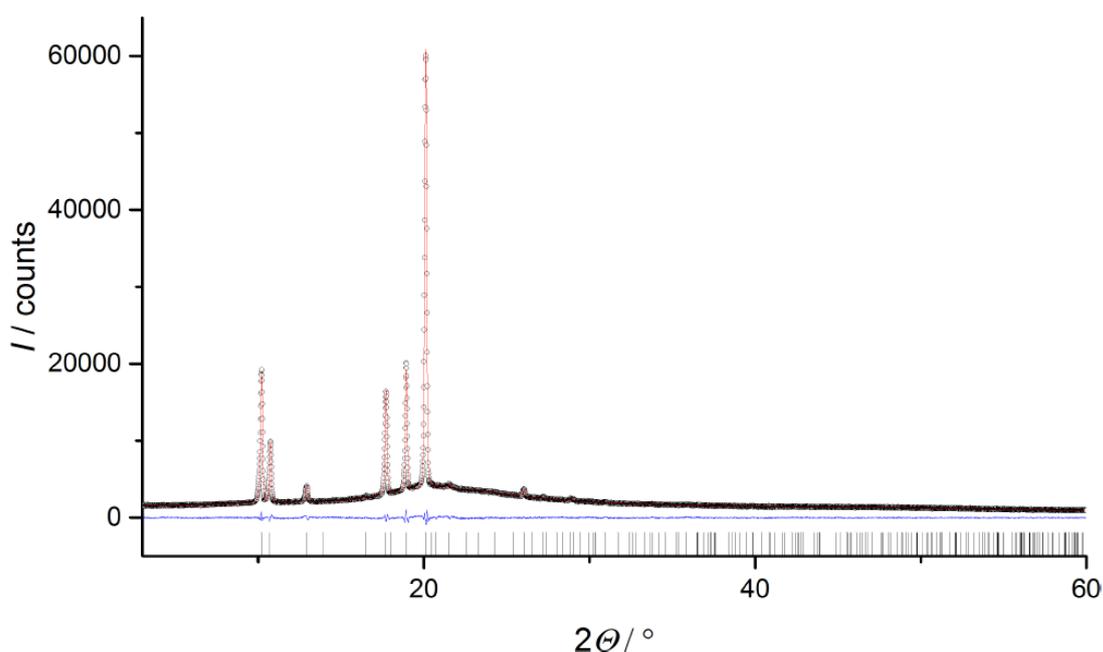

Figure S 7: Plot of the LeBail[7] refinement of the plastic crystalline phase of *i*-BuLi with space group *Pnnn*.

Table S1: Crystallographic data of *i*-BuLi. Results of the Rietveld refinements of the low-temperature α-phase and the room-temperature γ-phase. The last column shows the results of the LeBail[7] fit of the γ-phase.

	α-phase Rietveld ref.	γ-phase Rietveld ref.	γ-phase LeBail fit
Chemical formula	$(C_4H_9Li)_6$	$(C_4H_9Li)_6$	$(C_4H_9Li)_6$
MW / g·mol^{-1}	204.36	204.36	204.36
Crystal system	triclinic	orthorhombic	orthorhombic
Space group (No.)	$P\bar{1}$ (No. 2)	*Pnnn* (No. 48)	*Pnnn* (No. 48)
T / °C	-80	20	20
a / Å	10.58463(15)	17.3368(5)	17.333(1)
b / Å	10.79287(13)	10.0113(3)	10.0100(5)
c / Å	15.14807(19)	9.3692(3)	9.3679(5)
α / °	79.9009(12)	90	90
β / °	84.3582(14)	90	90
γ / °	61.2763(11)	90	90
V / Å^3	1493.84(4)	1627.24(8)	1625.38(1)
Z	2	2	
Z'	2 · ½	¼	
ρ_{calc} /Mg·m^{-3}	0.854	0.785	
Radiation type	Cu-Kα$_1$	Cu-Kα$_1$	Cu-Kα$_1$
λ / Å	1.5406	1.5406	1.5406
2θ range / °	3-80	3-60	3-60
Data points	7700	5700	5700
Parameters	313	31	33
Restraints	221	Rigid body	
R_p / %	1.52	3.85	
R_{wp} / %	1.95	5.01	2.73
R_{exp} / %	1.44	2.17	2.09
R'_p / % ^{a}	5.76	23.41	
R'_{wp} / % ^{a}	7.11	20.45	8.20
R'_{exp} / % ^{a}	5.24	8.86	6.31
R_{Bragg} / %	0.757	8.05	
gof	1.36	2.31	1.30
B_{iso}	4.10(7)	17.5(5)	

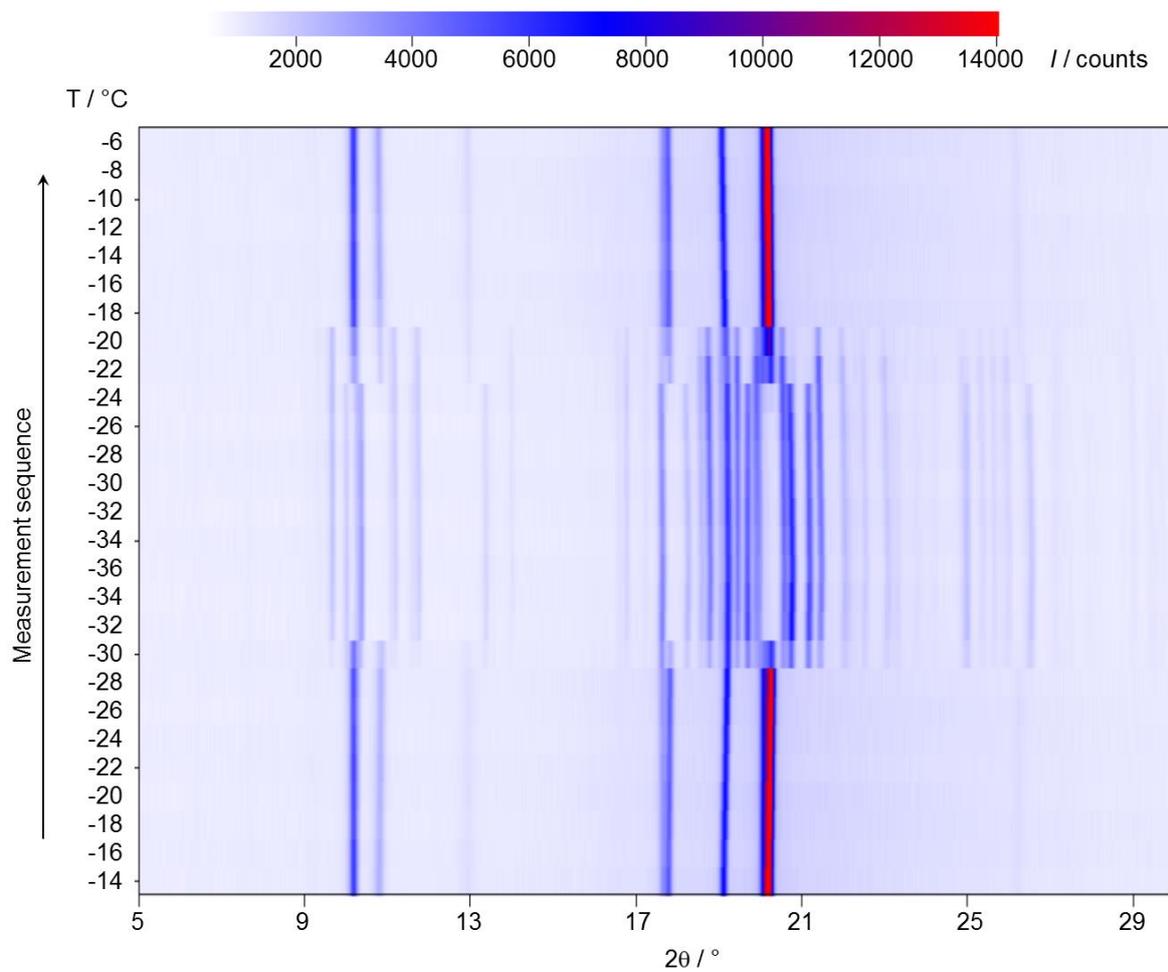a) R'_p, R'_{wp}, and R'_{exp} denote background-corrected values[5-6].

Figure S8: Temperature-dependent XRPD data of *i*-BuLi. Intensity by colour.
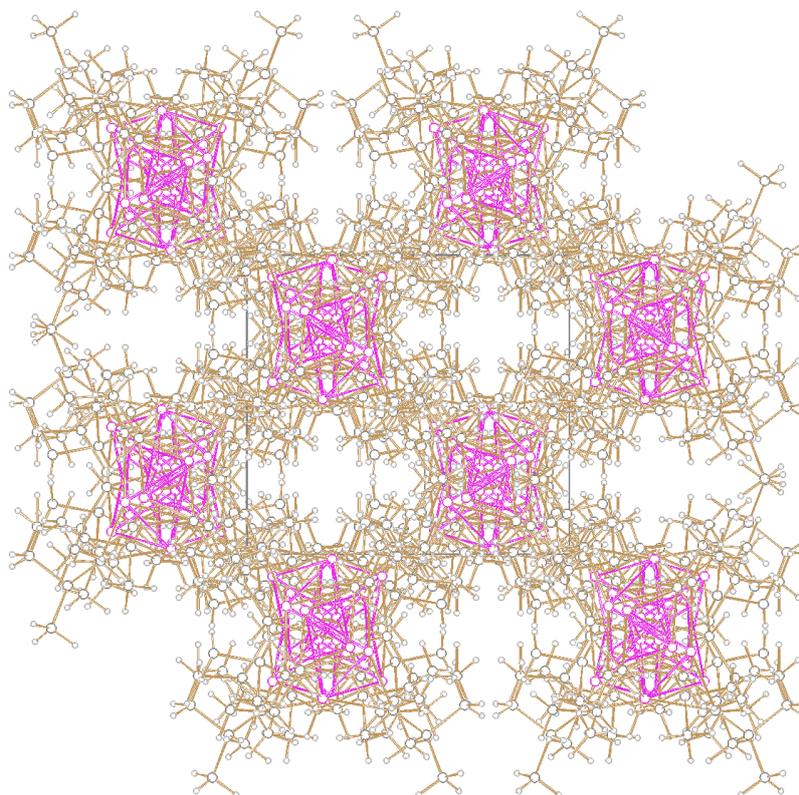
Crystal structure of the γ-phase

Figure S 9: Plastic-crystalline γ-phase. View direction [100]. *b* axis to the right, *c* axis up. 8 molecules shown. Li atoms violet, C dark grey, H light grey.
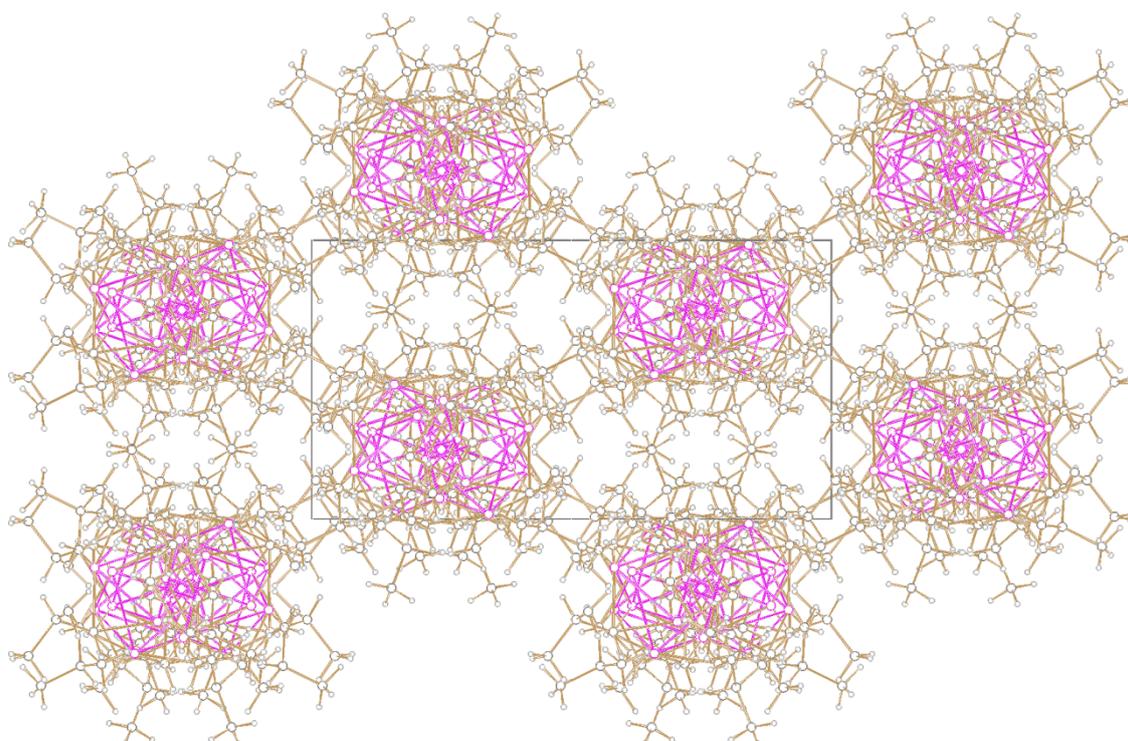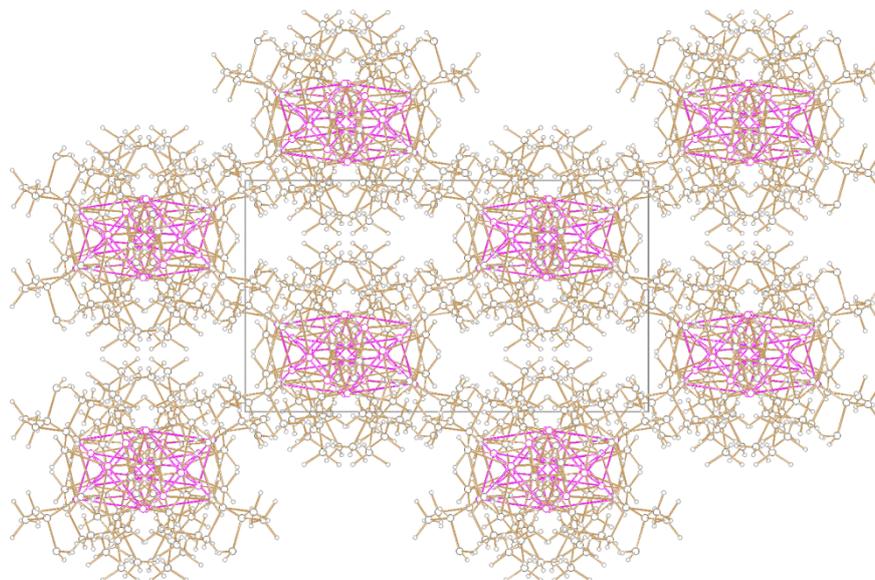

Figure S 10: Plastic-crystalline γ-phase. View direction [010]. *a* axis to the right, *c* axis down. 8 molecules shown.

SCHAKAL

Figure S 11: Plastic-crystalline γ-phase. View direction [001]. *a* axis to the right, *b* axis up. 8 molecules shown.

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