On the Crystal forms of NDI-C6: annealing and deposition procedures to access elusive polymorphs

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Supplementary information

Table S1 - List of Solvents used for solubility screening

S.	Solvent	abbreviation	Soluble	
No				
1	isopropanol	2PR	No	
2	acetonitrile	ACN	No	
3	acetone	ACT	No	
4	chloroform	CHF	> 100g/L	
5	dichloromethane	DCM	> 100g/L	
6	dimethylformamide	DMF	~10 g/L @	
			50°C	
7	dimethyl sulfoxide	DMSO	~10 g/L @	
			75°C	
8	ethyl acetate	ETA	No	
9	water	H2O	No	
10	methanol	MET	No	
11	p-xylene	PXY	~28mg/ml	
12	toluene	TOL	~25mg/ml	



Figure S1 - Hot stage microscopy during the heating of a single crystal NDI-C6, a) Form α at 170°C, b) Form γ at 178°C, c) Form δ at 184°C.



Figure S2 - Hot stage microscopy during the heating until before the melting of a single crystal NDI-C6, a) Form α at 175°C, b) Form $\alpha \rightarrow$ Form δ transition starting at 180°C, c) transition into Form δ complete. Cooling starting from Form δ d) Form δ at 190°C, e) transition Form $\delta \rightarrow$ Form γ occurring at 168°C, f) transition into Form γ complete, g) Form γ at 70°C, h) Form β at 58°C



Figure S3 – VT-XRPD of NDI-C6, in green Form α at RT before heating, in red Form δ at 185°C before melting, in blue Form δ at 195°C at cooling after melt and in black Form α at RT after cooling from the melt.

More information about the transitions observed by DSC, such as temperature and enthalpy are summarized in Table S2.

Table S2 – Transitions observed in the DSC curves.

	Transition	Temperature (°C)	Enthalpy (kJ.mol ⁻¹)	
	Form $\alpha \rightarrow$ Form γ	178 7	15 7	
	Form $\gamma \rightarrow$ Form δ	178.7	10.7	
	Form δ → Form γ	163.2	-9.6	
Without molting	Form $\gamma \rightarrow$ Form β	56.4	-6.3	
without menting	Form $\beta \rightarrow$ Form γ	68.8	7.0	
	Form $\gamma \rightarrow$ Form $\gamma + \alpha$	100.3	-2.3	
	Form $\alpha \rightarrow$ Form γ	1767	15 7	
	Form $\gamma \rightarrow$ Form δ	170.7	13.7	
	Form $\alpha \rightarrow$ Form γ	178.2	14.0	
	Form $\gamma \rightarrow$ Form δ	178.2	14.7	
	Form $\delta \rightarrow$ Liquid	207.1	22.0	
	Liquid → Form δ	204.7	-21.7	
With melting	Form $\delta \rightarrow$ Form γ	164.9	-8.7	
	Form $\gamma \rightarrow$ Form α	143.0	-3.6	
	Form $\alpha \rightarrow$ Form γ	175 1	15 4	
	Form $\gamma \rightarrow$ Form δ	1/3.1	13.4	
	Form $\delta \rightarrow$ Liquid	207.0	21.9	



Figure S4 – Form ε on thin films produced with a DCM solution and Form ε obtained from quenching of the melt

Form	<i>T_m</i> (°C)	Lattice parameters	Volume (ų)	Space group	Z, Z'	Density (gcm ⁻³)	
Form α	RT	a=4.89482(5) Å b=8.2672 (2) Å c=14.5209 (1) Å α =96.293 (1)° β =98.064 (1)° γ =93.589 (2)°	577	P-1	1/0.5	1.25	Pawley refinement of the cell parameter of KEKJIU01
Form β	RT	a=22.855 ^Å (8) b=4.818 (1) ^Å c=32.052 ^Å (2) α=90° β=91.833° (2) γ=90°	3528	P21	6/3	1.22	Pawley refinement of the cell parameter reported by Milita et al.
Form y	54	a= 4.85556(6) Å b= 6.47166(7) Å c= 19.94656(13) Å α = 92.1464(13)° β = 95.834(2)° γ = 104.2269(12)°	603	P-1	1/0.5	1.20	Structure determination from Powder
Form δ	196.85	a=8.7946(1) Å b=8.0212(2) Å c=37.9396(4) Å α=90° β=90° γ=95.180(3)°	2665	P112 ₁ /b	4/1	1.05	Pawley refinement of the cell parameter reported by Milita et al.



Figure S5 – Pawley Refinement of Form α at RT, with a Rwp of 3.43



Figure S6 - Pawley Refinement of Form 6 at RT, with a Rwp of 10.66



Figure S7 – Rietveld Refinement of Form γ at 54°C with a Rwp of 3.45, an interval of 2 ϑ was excluded from the refinement since it was present peaks related to impurities.



Figure S8 - Pawley Refinement of Form δ at 197°C, with a Rwp of 6.52



Figure S9 – Thermal expansion indicatrix with positive thermal expansion shown in red and NTE in blue. Crystal packing of each phase superimposed on the corresponding indicatrix to visualize the direction of the expansion regarding the crystal packing. a) Form α , b) Form γ