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Electronic Supporting Information

Original polymorphism in a naphthalene bisimide π-conjugated organogelator : a complex interplay between hydrogen bonding and heterocycle π-stacking

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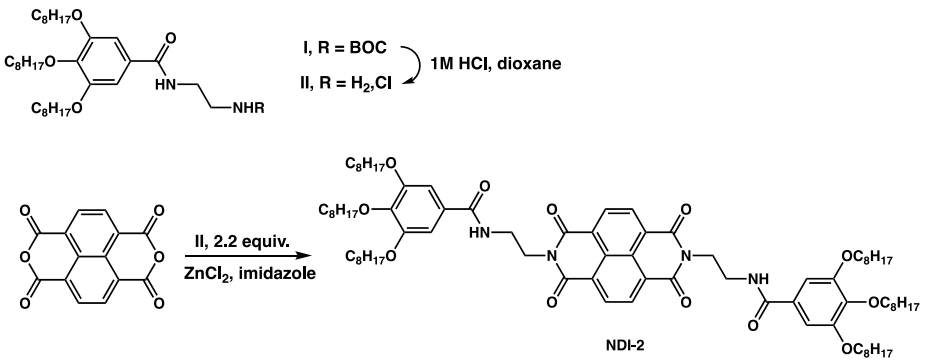
Synthesis of NDI-2

NDI-2 was synthesized according to the synthetic method described in ref. 1 or by a modified procedure (Scheme 1). Compound I was synthesized according to ref. 2.



Scheme 1. Modified procedure for the synthesis of NDI2

N,N'-di(2-(3,4,5-trioctyloxybenzamido))eth-1-yl naphthalene-1,4,5,8 tetracarboxylic acid bisimide (NDI2) : compound I (250 mg, 370 µmol) was mixed with a solution of HCl in dioxane (1 M, 10 mL) and the mixture was stirred for 3 hrs. The solution was evaporated under vacuum and the solid residue mixed with 1,4,5,8-naphthalenetetracarboxylic dianhydride (50.6 mg, 188 µmol), $Zn(OAc)_2$ (130.2 mg, 470 µmol) and imidazole (2 g) in a sealed tube. The mixture was heated at 140 °C for 12 hrs, cooled at 25 °C, dissolved in $CHCl_3$ (200 mL), washed with aqueous HCl (1 M, 4 x 100 mL) and with brine (3 x 100 mL). The organic layer was dried ($MgSO_4$) and the solvent evaporated under vacuum. The solid residue was dissolved in $CHCl_3$ and precipitated in MeOH. The solid was purified by chromatography (SiO_2, $CHCl_3$/MeOH: 98.5/1.5) to afford pure NDI2 as a yellow solid (yield 55%). ^{1}H NMR (400 MHz, CDCl3): δ [ppm] 8.63 (4H, s, naphthalene H), 6.81 (4H, s, phenyl **H**), 6.68 (2H, t, *J* = 5.1 Hz, N**H**), 4.45 (4H, m, $CH_2N(CO)_2$), 3.89 (12H, m, OCH_2), 3.76 (4H, q, *J* = 5.3 Hz, C**H**$_2$NHCO), 1.72 (8H, p, *J* = 7.39 Hz, *m*OCH_2C**H**$_2$), 1.63 (4H, m, *p*OCH_2C**H**$_2$), 1.38 (12H, m, *J* = 7.7 Hz, OCH2CH2C**H**2), 1.30-1.18 (48H, m, (C**H**$_2$)$_4CH_3$), 0.81 (18H, t, *J* = 6.83 Hz, C**H3**); ^{13}C NMR (100 MHz, CDCl3): δ [ppm] 167.6, 163.4, 153, 141, 131.1, 129, 126.9, 126.6, 105.4, 73.5, 69.2, 40.2, 39.8, 31.9, 31.8, 30.3, 29.5, 29.4, 29.3, 26.1, 26.0, 22.7, 14.1.

Anal. Found : C,72.61; H, 9.38; N, 3.91. Calcd for $C_{80}H_{120}N_4O_6$: C, 72.25; H, 9.10; N, 4.21.

References

(1) Molla, M. R.; Ghosh, S., *Chem. Mater.* **2011**, *23*, 95–105.Sarbu, A.; Biniek, L.; Guenet, J.-M.; Mésini, P. J.; Brinkmann, M. *J. Mater. Chem. C* **2015**, *3*, 1235–1242.

(2) Sarbu, A.; Biniek, L.; Guenet, J.-M.; Mésini, P. J.; Brinkmann, *J. Mater. Chem. C* **2015**, *3*, 1235–1242.

Table S1. Structures formed (sol, precipitate, gel) in various solvents.

Solvent	Structure formed in solution
Toluene	Sol
Chloroform	Sol
1,2-dichlorobenzene	Sol
Dichloromethane	Sol
Benzene	Precipitate
Acetone	Precipitate
Methanol	Precipitate
Ethanol	Precipitate
Tetrachloroethane	Gel
Cyclohexane	Gel
Decaline	Gel
Methylcyclohexane	Gel
o-xylene	Gel
p-xylene	Gel
trans-decaline	Gel
Tetrachloroethylene	Gel

Table S2. Summary of phase transition temperatures and associated enthalpies determined from the DSC scans in Figure 3 for different T_{max} temperatures.

DSC scan - (T_{max})	Transitions (phases, temperatures and enthalpies)	
	Heating	Cooling
a) 250°C	II (Hex.) – (177°C, -30kJ/mol) – III (Lam.) – (210°C, 72 kJ/mol) - Iso	Iso – (187°C, -39kJ/mol) – II (Hex.)
b) 210°C	IV (Cr.) – (99°C 24kJ/mol) – III (Lam.) – (210°C, 72kJ/mol) - Iso	Iso – (198°C, -62 kJ/mol) – III (Lam.) – (93°C, -28kJ/mol) – IV (Cr.)
c) 180°C	IV (Cr.) – (99°C 24kJ/mol) – III (Lam.)	III (Lam.) – (91°C, -28kJ/mol) – IV (Cr.)

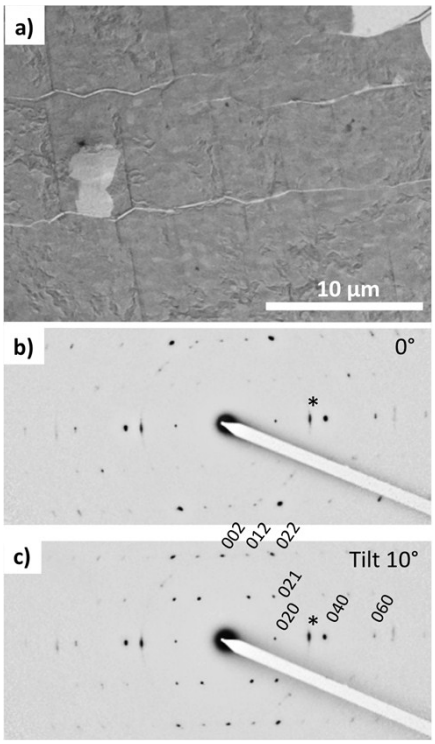


Figure S1. *Morphology of a form IV thin film of NDI2 oriented on PTFE. a) Bright field, b) diffraction pattern and c) diffraction pattern obtained for a 10° tilt around the b* axis. The asterisk points at the 100 reflection of the PTFE substrate.*

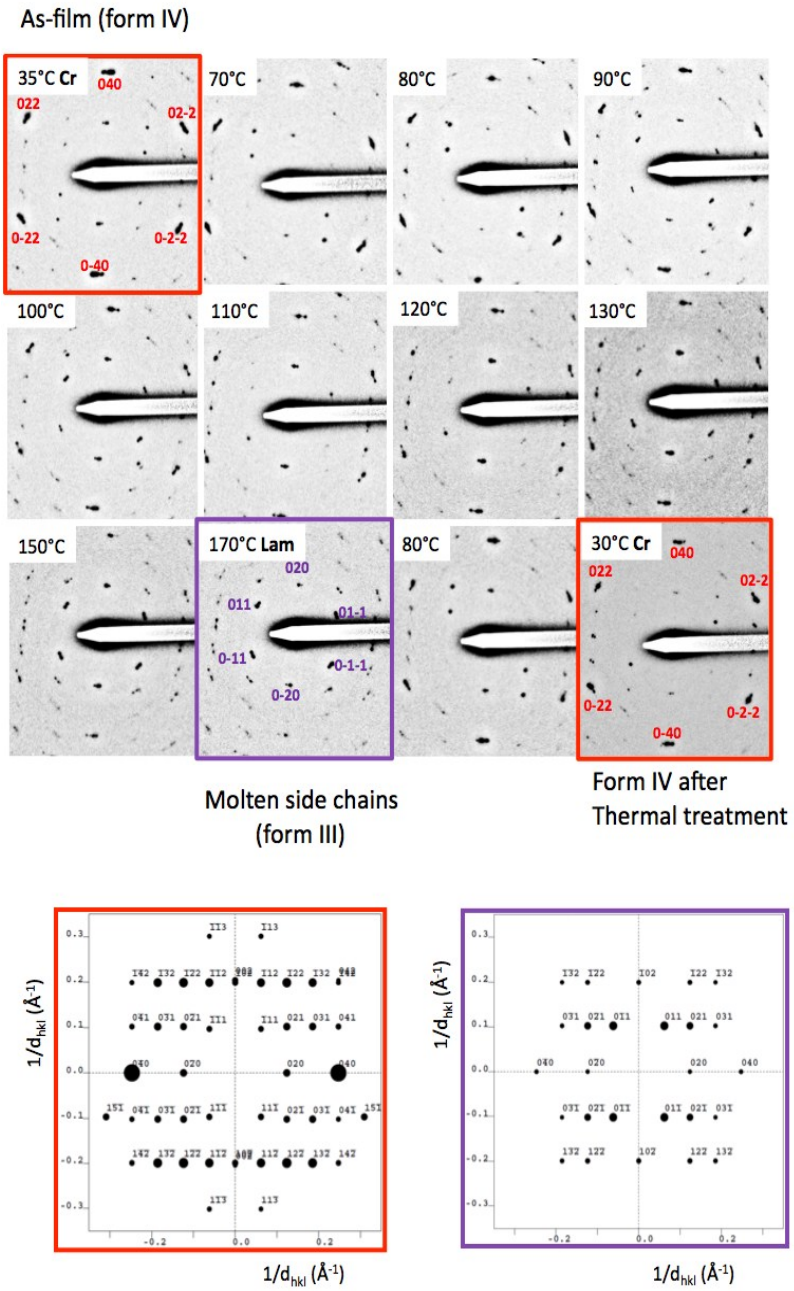


Figure S2. In situ TEM experiment showing the evolution of the electron diffraction (ED) pattern of form IV (crystalline form) as a function of temperature upon heating and upon cooling back to room temperature. The two diffractograms at the bottom correspond to the calculated ED patterns [100] zone for the crystalline form (red) and for the same structure without taking into account the alkyl side chains (violet).

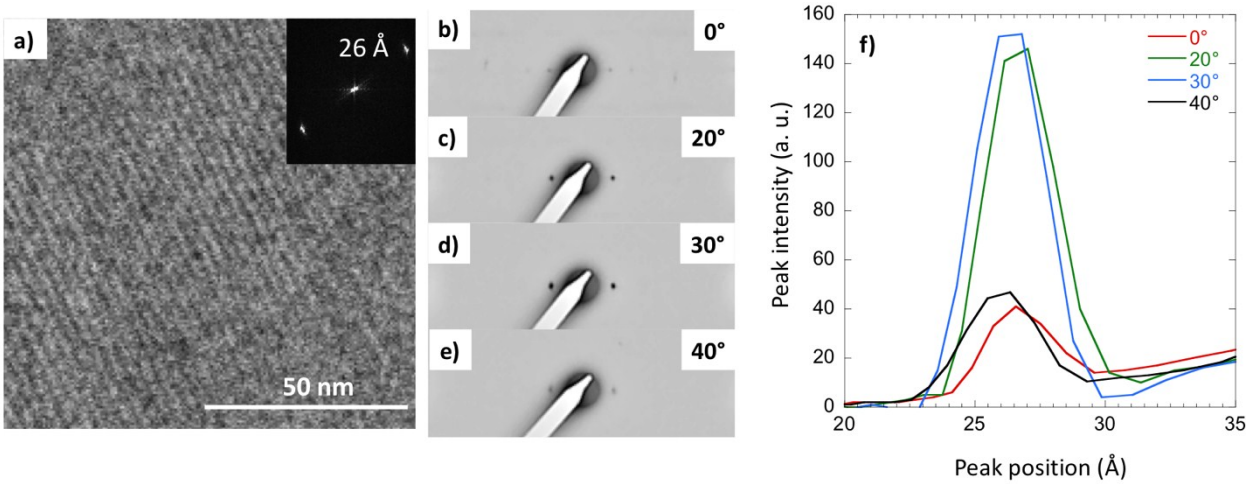


Figure S3. (a) HRTEM image showing columnar arrangements of NDI2 in form II. The inset represents the FFT of the HRTEM image. (b)– (e) Evolution of the (210) peak intensity with tilt angle after rotating a thin film of form II (hex. col. phase) in the TEM along the c axis (PTFE chain direction). (f) The section profile of the (210) peak as a function of tilt angle indicates maximum intensity for a tilt angle close to 30°, indicating that the unit cell is trigonal.

Cif file of crystalline form IV of NDI2.

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#              Cambridge Crystallographic Data Centre
#                          CCDC
#
##################################################################################
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_symmetry_equiv_pos_as_xyz

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3 -x,-y,-z

4 x,1/2-y,1/2+z

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