SUPPLEMENTARY INFORMATION

Towards understanding the N_{TB} phase: a combined experimental, computational and spectroscopic study

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X-Ray measurements

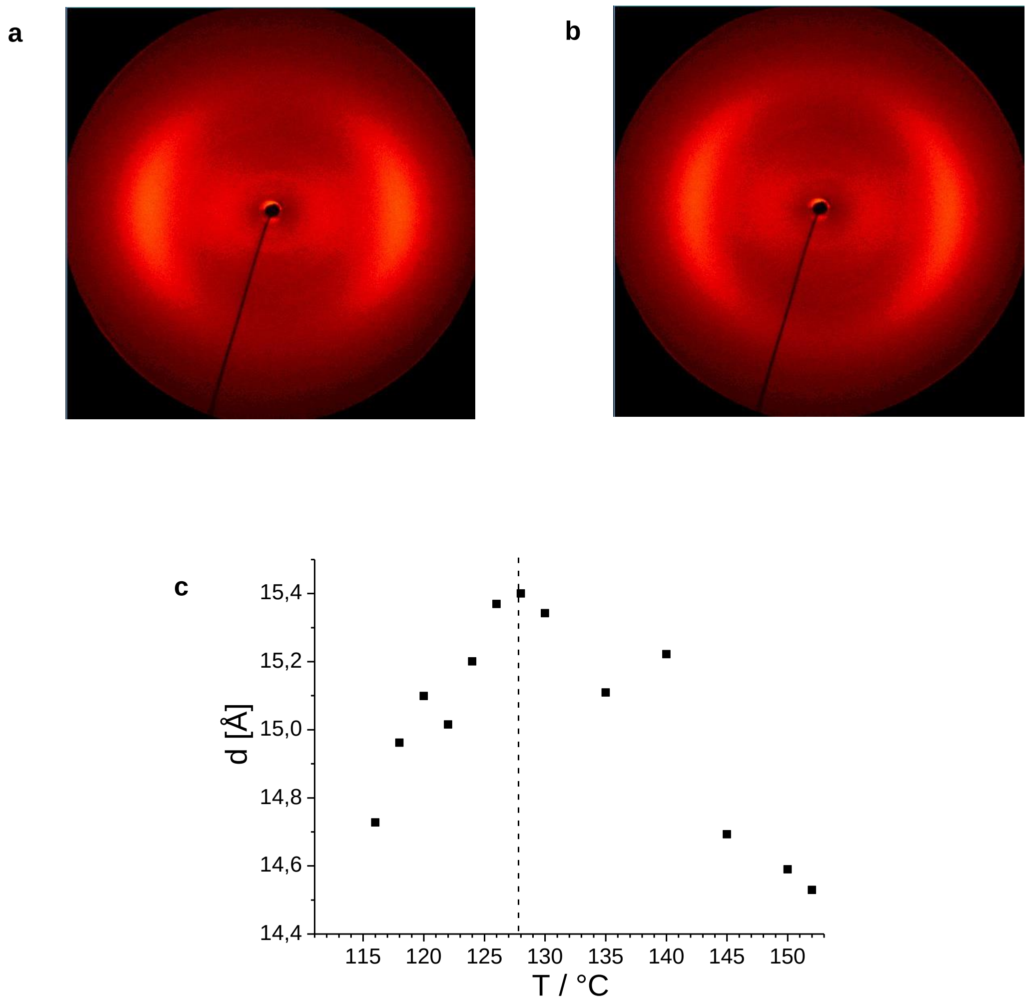

Figure S1. 2D XRD pattern of **CBI-9-ICB**; (a) in the N phase at 150 °C, (b) in the N_{TB} phase at 116 °C, (c) d value of the intensity maximum of the inner scattering at about 15 Å depending on the temperature

Table S1: Diffraction angles 2θ and d values for the intensity maxima of the small and wide angle X-ray diffraction of **CBI-7-ICB** and **CBI-9-ICB**

***T*/°C**	**CBI-7-ICB**				**CBI-9-ICB**			
	inner halo		**outer halo**		**inner halo**		**outer halo**	
	2*θ*/°	***d*/Å**	**2*θ*/°**	***d*/Å**	**2*θ*/°**	***d*/Å**	**2*θ*/°**	***d*/Å**
114	6.530	13.54	20.35	4.36				
116	6.528	13.54	20.31	4.37	6.001	14.73	20.33	4.37
118	6.443	13.72	20.31	4.37	5.907	14.96	20.24	4.39
120	6.330	13.96	20.27	4.38	5.853	15.10	20.26	4.38
122	6.294	14.04	20.27	4.38	5.886	15.02	20.26	4.38
124	6.303	14.02	20.31	4.37	5.814	15.20	20.24	4.39
126	6.252	14.14	20.25	4.38	5.750	15.37	20.24	4.39
128					5.739	15.40	20.20	4.39
130	6.319	13.99	20.21	4.39	5.760	15.34	20.22	4.39
135	6.310	14.01	20.17	4.40	5.849	15.11	20.13	4.41
140	6.355	13.91	20.12	4.41	5.806	15.22	20.06	4.43
145	6.402	13.81	20.06	4.43	6.015	14.69	20.07	4.42
148	6.469	13.66	20.00	4.44				
150					6.058	14.59	19.95	4.45
152					6.083	14.53	20.00	4.44

Liquid state NMR measurements.

Complete assignment of the compound **BB_7-4** is based on 1D and 2D homo- and heteronuclear NMR spectra and shown in Table S2. The spectra were taken at 50 °C due to low solubility of compound in DMSO-d_6 at room temperature.

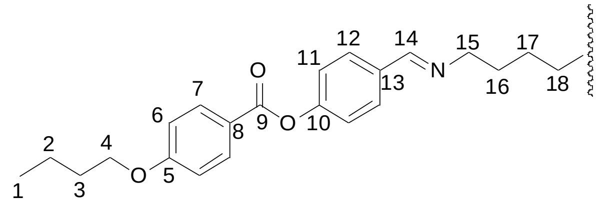

Table S2. ^{1}H and ^{13}C NMR chemical shifts (δ/ppm)[a] recorded in DMSO-d$_6$ solution, H-H and C-H coupling constants[b] of compound **BB_7-4** in (50 °C) and ^{1}H chemical shifts of the neat compound at 117 °C.

Atom		**^{1}H** (δ/ppm)		**^{13}C** (δ/ppm)	**^{1}H** (δ/ppm)	**Δ**δ/ppm[c]
1	δ $^{3}J_{HH}$	0.95 (6) 7.38 (t)	δ J_{CH}	13.25 125.25 (q)	0.13	0.82
2	δ $^{3}J_{HH}$	1.46 (4) 7.42 (sextet)	δ J_{CH}	18.33 125.34 (t)	0.60	0.86
3	δ $^{3}J_{HH}$	1.74 (4) 6.97 (pentet)	δ J_{CH}	30.29 125.31 (t)	0.85	0.89
4	δ $^{3}J_{HH}$	4.09 (4) 6.48 (t)	δ J_{CH}	67.55 144.52 (t)	3.00	1.09
5	--	---	δ	163.06 s	---	---
6	δ $^{3}J_{HH}$	7.09 (4) 8.88 (d)	δ J_{CH}	114.49 162.92 (d)	6.02	1.07
7	δ $^{3}J_{HH}$	8.05 (4) 8.88 (d)	δ J_{CH}	131.71 163.08 (d)	7.20	0.85
8	--	---	δ	120.54 s	---	---
9	--	---	δ	163.69 s	---	---
10	--	---	δ	152.11 s	---	---
11	δ $^{3}J_{HH}$	7.30 (4) 8.58 (d)	δ J_{CH}	121.80 164.50 (d)	6.43	0.87
12	δ $^{3}J_{HH}$	7.79 (4) 8.58 (d)	δ J_{CH}	128.59 162.92 (d)	6.91	0.88
13	--	---	δ	133.71 s	---	---
14	δ	8.34 (2) s	δ J_{CH}	159.07 158.54 (d)	7.37	0.97
15	δ $^{3}J_{HH}$	3.57 (4) 6.84 (t)	δ J_{CH}	60.06 131.27 (t)	2.79	0.70
16	δ $^{3}J_{HH}$	1.64 (4) 6.76 (pentet)	δ J_{CH}	30.10 126.32 (t)	0.96	0.68
17 and 18	δ	1.34-1.40 (6) m	δ	26.38 and 28.21	0.67	0.70

[a] Referred to TMS. Number of protons in brackets. [b] (s) singlet, (d) doublet, (t) triplet, (q) quartet, (m) multiplet. [c] δ/ppm(solution) − δ/ppm at 117 °C

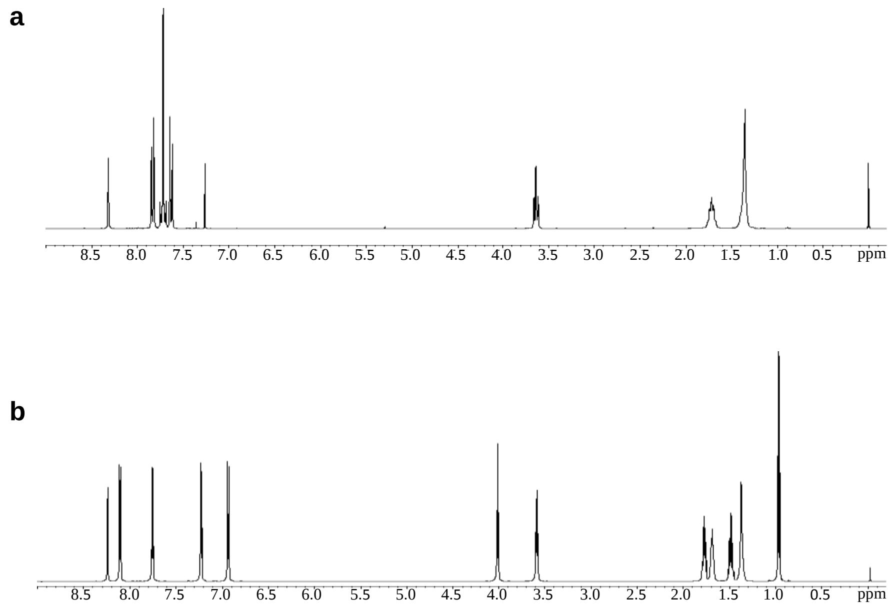

Figure S2. ^{1}H NMR spectra of (a) **CBI-7-ICB** and (b) **BB_7-4** in $CDCl_3$ solution.

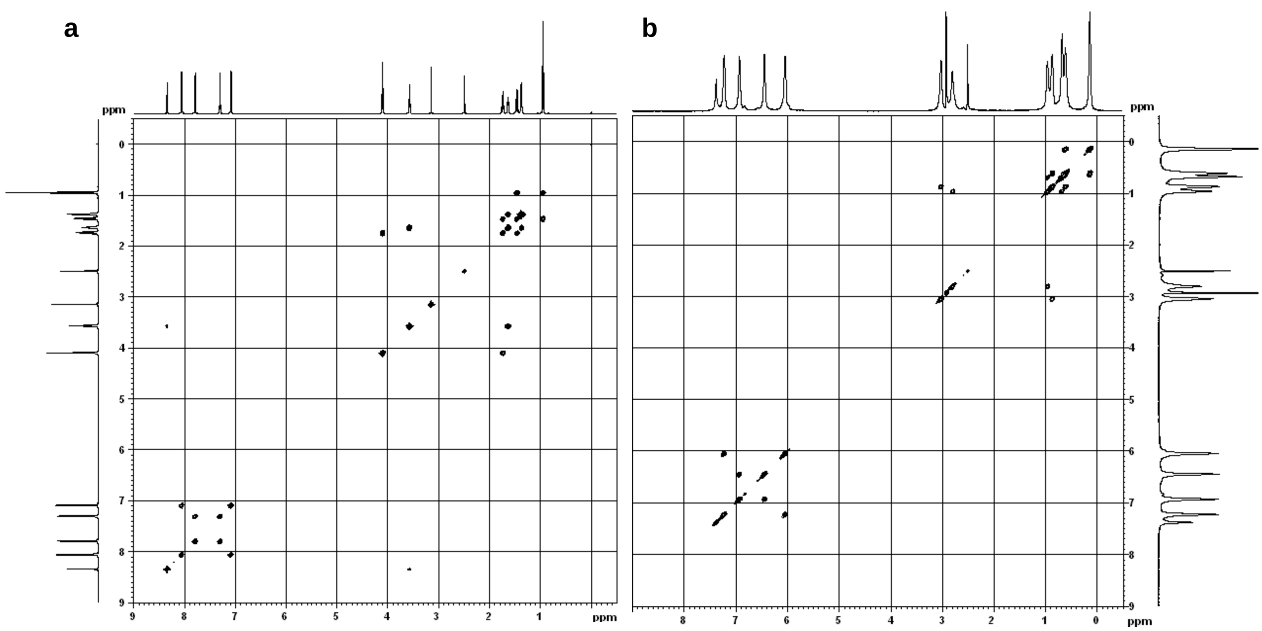

Figure S3. (a) COSY spectrum of **BB_7-4** in DMSO-d_6 solution, (b) COSY spectrum of the neat **BB_7-4** at 117 °C.

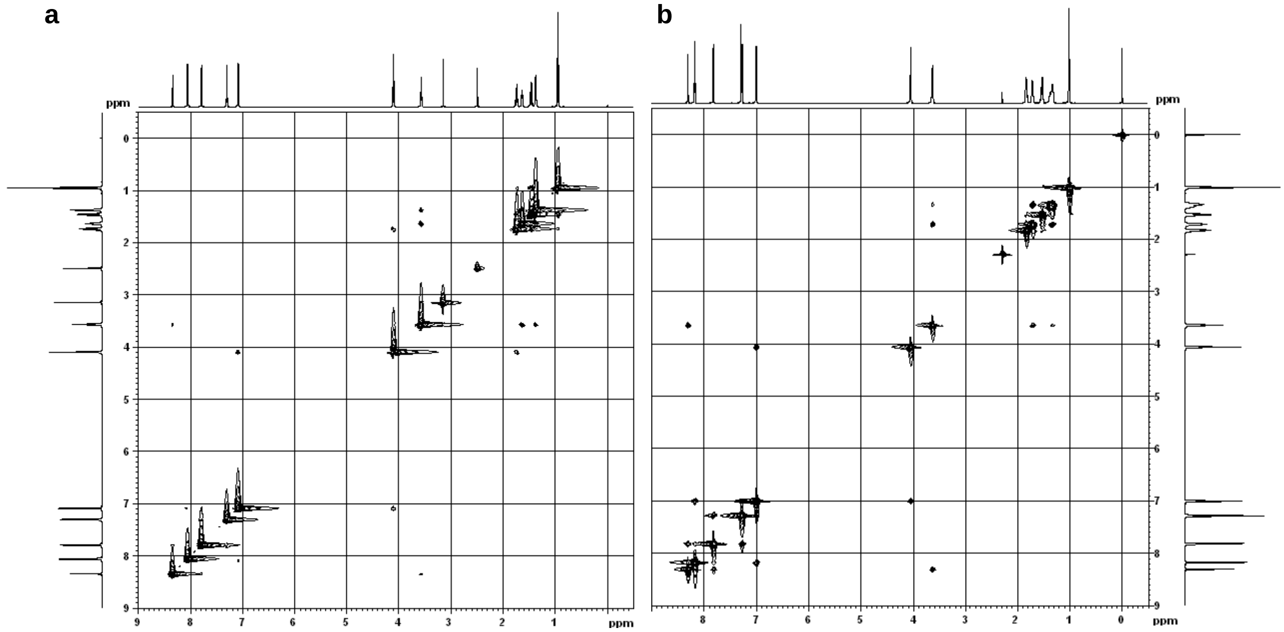

Figure S4. NOESY spectrum of **BB_7-4** dissolved in (a) DMSO-d_6 at 50 °C (b) $CDCl_3$ at -40 °C