Supporting Information

Mirror symmetry breaking in cubic phases and isotropic liquids driven by hydrogen bonding

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1. Synthesis and Analytical Data

1.1. Characterization methods

Thin layer chromatography (TLC) was performed on aluminium sheet precoated with silica gel. Analytical quality chemicals were obtained from commercial sources and used as obtained. The solvents were dried using the standard methods when required. The purity and the chemical structures of all compounds synthesized were confirmed by the spectral data. The structure characterization of the synthesized compounds is based on ¹H-NMR and ¹³C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in CDCl₃ or DMSO-d₆ solutions, with tetramethylsilane as internal standard). Microanalyses were performed using a Leco CHNS-932 elemental analyzer.

1. 2. Synthesis of the new liquid crystalline hydrogen-bonded compounds ABn

All chemical reactions were carried out under argon gas. The proton acceptors 4-(4-alkoxyphenylazo)pyridine **B***n* were synthesized according to the same procedure described in references^{S1,S2} and the analytical data of 4-(4-octyloxyphenylazo)pyridine **B**8 is given below as an example. The intermediate compound 4'-hydroxybiphenyl-3,4,5-trihexyloxyphenylbenzoate **5** was synthesized using similar method to that reported in reference, ^{S3} while the intermediate 4- (benzyloxycarbonyl)benzoic acid **4** was prepared as described in reference. ^{S4} The synthesis details of the benzoic acid **A**, as well as the final hydrogen-bonded complexes (**AB***n*) are described below.

1.2.1. 4-(4-Octyloxyphenylazo)pyridine B8

Yield 83 %; m.p. 70.6 °C (Lit. 68 °C);^{S1 1}H-NMR (400 MHz, CDCl₃): δ 8.77 (d, *J* = 4.6 Hz, 2H, Ar-H), 7.95 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.67 (d, *J* = 4.6 Hz, 2H, Ar-H), 7.02 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.06 (t, *J* = 6.6 Hz, 2H, -O<u>CH</u>₂CH₂), 1.89 – 1.73 (m, 2H, -OCH₂<u>CH</u>₂), 1.58 – 1.20 (m, 10H, CH₂), 0.89 (t, *J* = 6.9 Hz, 3H, CH₃).

Comp.	m.p. (<i>T</i> /°C)	m.p. (<i>T</i> /°C) in ref. S1
B8	71	67.9
B10	66	65.9
B12	73	72.9
B14	74	73.3

Table S1. Melting points of the 4-(4-alkyloxyphenylazo)pyridines Bn.



Scheme S1. Synthesis of the azopyridines **B***n*, the benzoic acid derivative **A** and the hydrogenbonded complexes **AB***n*.

1.2.2. Compound 6

4-(Benzyloxycarbonyl)benzoic acid 4^{S4} (0.43 g, 1.67 mmol) and 4'-hydroxybiphenyl-3,4,5-tri(hexyloxy)phenylbenzoate 5^{S3} (0.99 g, 1.67 mmol) and a catalytic amount of DMAP were dissolved in dichloromethane with stirring and to this reaction mixture DCC (0.35 g, 1.67 mmol) previously dissolved in DCM was added and the stirring was continued for 48 hours. The reaction progress was checked with TLC and at the end of the reaction the white solid formed was filtered out and washed three times with DCM. The solvent was then removed under vacuum and the crude white material obtained was purified with column chromatography using DCM as an eluent followed by recrystallization from ethanol to give 1.05 g, 66.04 % yield of compound **6** as colourless crystals. M.p. = 85 °C, ¹H-NMR (400 MHz, CDCl₃): δ 8.29 (d, J = 8.9 Hz, 2H, Ar-H), 8.22 (d, J = 8.8 Hz, 2H, Ar-H), 7.71 – 7.57 (m, 4H, Ar-H), 7.53 – 7.24 (m, 11H, Ar-H overlapped with CDCl₃), 5.42 (s, 2H, , Ph-<u>CH₂-</u>), 4.16 – 3.93 (m, 6H, -O<u>CH₂CH₂</u>), 1.92 – 1.70 (m, 6H, -OCH₂<u>CH₂</u>), 1.60 – 1.23 (m, 18H, CH₂), 1.00 – 0.77 (m, 9H, CH₃).

1.2.3. The benzoic acid derivative A

A suspension of compound **6** (0.90 g, 1.08 mmol) and Pd/C (10% Pd, 0.3 g) in 80 mL THF was flushed with hydrogen. The mixture was stirred at 45 °C at normal pressure for 24 hours, checked with TLC and at the end of the reaction the solid material was removed by filtration and solvent was evaporated under reduced pressure. The crude white product was purified by flash chromatography (silica gel, THF/n-hexane 1:1) to give 0.76 g of **A** as a white powder, yield = 95 %, transition temperatures: Cr 162 °C Col_{hex} 246 °C Iso, ¹H-NMR (400 MHz, DMSO-d₆): δ 8.25 (d, *J* = 8.2 Hz, 2H, Ar-H), 8.13 (d, *J* = 8.2 Hz, 2H, Ar-H), 7.90 – 7.65 (m, 4H, Ar-H), 7.52 – 7.24 (m, 6H, Ar-H), 4.16 – 3.83 (m, 6H, , -O<u>CH₂CH₂</u>), 1.85 – 1.54 (m, 6H, -OCH₂<u>CH₂</u>), 1.55 – 1.15 (m, 18H, CH₂), 0.99 – 0.74 (m, 9H, CH₃). ¹³C-NMR (126 MHz, DMSO-d₆): δ 166.97, 164.73, 164.48, 153.01, 150.77, 150.56, 142.64, 137.73, 137.47, 135.97, 132.93, 130.49, 130.18, 128.34, 128.29, 124.01, 122.90, 122.82, 108.48, 73.10, 69.08, 31.52, 31.40, 30.17, 29.18, 25.65, 25.61, 22.56, 22.53, 14.32, 14.29. Elemental Analysis: Calc. for C₄₅H₅₄O₉ C, 73.15; H, 7.37. Found C, 72.98; H, 7.31 %.

1.2.4. Hydrogen-bonded complexes ABn

The hydrogen-bonded complexes were prepared by mixing any of the azopyridine derivatives **B***n* with the acid **A** in 1:1 molar ratios and melting them together in DSC pans (30 μ l) with stirring to give an intimate blend, then cooling the mixture to room temperature. After crystallization the materials was grinded, and this process was repeated to obtain a homogeneous mixture. For example, to prepare the hydrogen-bonded complex **AB8**, 0.135 mg of the acid **A** was melted together with 0.042 mg of 4-(4-octyloxyphenylazo)pyridine **B8** in the same way described above. As a representative example, the ¹H-NMR data of the complex **AB8** are given below.

¹H-NMR (400 MHz, CDCl₃): δ 8.83 (d, J = 4.7 Hz, 2H, Ar-H), 8.40 – 8.22 (m, 4H, Ar-H), 7.97 (d, J = 8.7 Hz, 2H, Ar-H), 7.74 (d, J = 4.6, 2H, Ar-H), 7.71 – 7.59 (m, 4H, Ar-H), 7.44 (s, 2H, Ar-H), 7.38 – 7.24 (m, 4H, Ar-H, overlapped with CDCl₃), 7.02 (d, J = 8.6 Hz, 2H, Ar-H), 4.16 – 3.99 (m, 8H, -O<u>CH₂CH₂</u>), 1.98 – 1.71 (m, 8H, -O<u>CH₂CH₂</u>), 1.61 – 1.19 (m, 28H, CH₂), 1.02 – 0.81 (m, 12H, CH₃).

2. NMR Spectra



Figure S1. ¹H-NMR Spectrum of B8 (CDCl₃, 400 MHz).



Figure S2. ¹H-NMR Spectrum of compound 6 (CDCl₃, 400 MHz).



Figure S3a. ¹H-NMR Spectrum of the benzoic acid **A** (DMSO-d₆, 400 MHz); due to insolubility, even at elevated temperature, the spectrum could not be recorded in CDCl₃.



Figure S3b. ¹³C-NMR Spectrum of the benzoic acid A (DMSO-d₆, 126 MHz).



Figure S4. ¹H-NMR Spectrum of the complex **AB8** (CDCl₃, 400 MHz), confirming the complex formation between the acid **A** and the azopyrindine derivative **B8** (see Figs. S1 and S3a).

3. Additional data

3.1 Additional DSC traces



Figure S5. First DSC heating traces (10 K min⁻¹) a) of the benzoic acid **A** and b) of the 4-(4-octyloxyphenylazo)pyridine **B8**; none of the peaks of the two components is found in the DSC traces of the complex **AB8** (Fig. 1) indicating complete complex formation.

3.2 Additional textures



Figure S6. Texture of the Col_{hex} of the acid **A** at T = 170 °C: a) without lambda plate and b) with lambda plate; c) shows the indicatrix orientation; the fans aligned bottom-right to top-left are blue shifted whereas those oriented bottom-left to top right are yellow; the columns are aligned perpendicular to the fan direction, thus indicating that the main π -conjugation pathway is perpendicular to the column long axis.



Figure S7. Textures of the chiral crystalline phase $Cr^{[*]}$ of compound **AB8** on cooling from the $Cub^{[*]}/I432$ phase at T = 60 °C: a) after rotating one polarizer from the crossed position by -7° i, b) under crossed polarizers and c) after rotating one polarizer from the crossed position by +7°, showing dark and bright domains, indicating the presence of areas with opposite chirality sense.



Figure S8. Textures of the chiral Cub^[*]/*I*432 phase of compounds: a,b) **AB12** at T = 125 °C and c,d) **AB14** at T = 130 °C after rotating one polarizer from the crossed position by ±12, respectively.

3.3. Additional XRD patterns



Figure S9. XRD investigation of the Col_{hex} of the benzoic acid **A**: a) small angle and b) diffuse wide angle scattering at T = 180 °C.



Figure S10. a) Powder SAXS pattern of Cub/ $Im\overline{3}m$ of **AB10** recorded at 140 °C and b) diffuse wide angle scattering of **AB8** at T = 150 °C on cooling.

3.4. Numerical XRD data

20	<i>d</i> /nm	$d_{\rm calc}/{\rm nm}$	hk	<i>d-d</i> _{calc} /nm
1.881	4.70	4.70	10	0.00
3.244	2.72	2.71	11	0.01
3.741	2.36	2.35	20	0.01
4.943	1.79	1.78	21	0.01
19.212	0.46		diff	
$\operatorname{Col}_{\operatorname{hex}}/p6mm, a_{\operatorname{hex}} = 5.4 \text{ nm}$				

Table S2. Numerical XRD data of the Col_{hex} phase of A with indexation.

Table S3. Experimental and calculated *d*-spacing of the observed SAXS reflection of the Cub/ $Ia\overline{3}d$ phase of **AB8** at 150 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\rm obs.}$ – spacing (nm)	$d_{\text{cal.}}$ – spacing (nm)	intensity	Phase	
(211)	5.35	5.35	100.0	π	
(220)	4.63	4.63	52.1	π	
(321)	3.50	3.50	0.2	π	
(400)	3.27	3.27	2.8	π	
(420)	2.93	2.93	1.1	π	
(332)	2.79	2.79	1.3	0	
(422)	2.68	2.67	0.3	0	
(440)	2.32	2.32	0.1	0	
(611)	2.12	2.12	0.04	/	
(532)	2.13	2.12	0.02	/	
(444)	1.89	1.89	1.0	/	
(543)	1.85	1.85	0.2	/	
$a_{\rm cub} = 13.10 \text{ nm}$					

(hkl)	$d_{\rm obs.}$ – spacing (nm)	$d_{\text{cal.}}$ – spacing (nm)	intensity	Phase	
(310)	6.18	6.17	/	/	
(222)	5.66	5.65	/	/	
(321)	5.22	5.22	/	/	
(400)	4.89	4.88	/	/	
(330)	1.62	4.60	/	/	
(411)	4.02	4.00	/	/	
420)	4.40	4.38	/	/	
$a_{\rm cub} = 19.53 \text{ nm}$					

Table S4. Experimental and calculated *d*-spacings of the observed SAXS reflections of the Cub/ $Im\overline{3}m$ phase of **AB8** at 160 °C on cooling.^{*a*}

^{*a*} because only domain-like pattern was observed for $Cub/Im\overline{3}m$ phase, so no intensities were given here.

Table S5. Experimental and calculated *d*-spacings of the observed SAXS reflections of the Cub/ $Im\overline{3}m$ phase of **AB10** at 140 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\rm obs.}$ – spacing (nm)	$d_{\text{cal.}}$ – spacing (nm)	intensity	phase
(211)	7.93	7.93	0.1	0
(310)	6.14	6.14	0.3	0
(222)	5.61	5.61	4.4	0
(321)	5.19	5.19	41.5	π
(400)	4.86	4.86	100.0	0
(330)	1 59	1 5 9	13.7	/
(411)	4.58	4.38	6.8	π
(420)	4.34	4.34	19.2	0
(422)	3.97	3.97	0.8	π
(431)	2.91	2.91	0.5	0
(510)	3.81	5.61	1.0	/
(521)	3.55	3.55	0.2	/
(440)	3.44	3.44	0.1	/

(433)	2.22	2.22	0.1	/
(530)	5.55	5.55	0.1	/
(442)	2.25	2.24	0.1	/
(600)	5.25	5.24	0.4	/
(532)	2.15	2.15	0.2	/
(611)	5.15	5.15	0.5	/
(541)	3.00	3.00	0.1	/
(631)	2.87	2.86	0.1	/
(444)	2.80	2.80	1.4	/
(543)			0.03	/
(550)	2.75	2.75	0.1	/
(710)			0.06	/
(640)	2.70	2.69	0.5	/
(552)			0.4	/
(633)	2.64	2.64	0.4	/
(721)			0.2	/
(642)	2.60	2.60	0.04	/
(730)	2.55	2.55	0.18	/
(651)	2.47	2.47	0.04	/
(732)	2.47	2.47	0.04	/
(554)			0.05	/
(741)	2.39	2.39	0.03	/
(811)			0.05	/
(644)	2.20	2.20	0.02	/
(820)	2.30	2.36	0.02	/
(653)	2.32	2.32	0.04	/
(743)	2.26	2.26	0.02	/
(750)			0.05	/

(831)			0.02	/
(662)	2.23	2.23	0.04	/
(833)	2.15	2.15	0.08	/
(910)		2.13	0.08	/
(842)	2.12	2.12	0.04	/
(655)			0.04	/
(761)	2.10	2.10	0.02	/
(921)			0.02	/
(664)	2.07	2.07	0.04	/
(754)			0.03	/
(851)	2.05	2.05	0.05	/
(930)			0.05	/
(763)	2.00	2.00	0.03	/
(932)		2.00	0.03	/
(770)			0.04	/
(853)	1.96	1.96	0.01	/
(941)			0.01	/
(860)	1.05	1.04	0.02	/
(10 0 0)	1.95	1.94	0.08	/
(772)	1.02	1.02	0.02	/
(10 1 1)	1.92	1.92	0.02	/
(862)	1.01	1.01	0.03	/
(10 2 0)	1.91	1.91	0.05	/
(943)	1.80	1.90	0.02	/
(950)	1.89	1.89	0.04	/
(765)			0.03	/
(952)	1.85	1.85	0.03	/
(10 3 1)			0.03	/

(774)			0.03	/	
(855)	1.82	1.82	0.03	/	
(871)			0.01	/	
(864)	1.80	1.80	0.01	/	
(10 4 0)	1.80	1.80	0.02	/	
(961)	1.70	1 70	0.02	/	
(10 3 3)	1.79	1.79	0.04	/	
(10 4 2)	1.77	1.77	0.01	/	
(873)			0.01	/	
(954)	1.76	1.76	0.01	/	
(11 1 0)			0.02	/	
(963)			0.01	/	
(10 5 1)	1.73	1.73	0.01	/	
(11 2 1)			0.01	/	
	$a_{\rm cub} = 19.43 \text{ nm}$				

Table S6. Experimental and calculated *d*-spacings of the observed SAXS reflections of the Cub/ $Im\overline{3}m$ phase of **AB14** at 140 °C. All intensity values are Lorentz and multiplicity corrected.

(hkl)	$d_{\rm obs.}$ – spacing (nm)	$d_{\text{cal.}}$ – spacing (nm)	intensity	phase
(211)	7.94	7.94	0.1	0
(310)	6.15	6.15	0.2	0
(222)	5.62	5.62	2.9	0
(321)	5.20	5.20	42.2	π
(400)	4.86	4.86	100.0	0
(330)	4.50	4.50	15.7	/
(411)	4.39	4.39	7.8	π
(420)	4.35	4.35	16.6	0
(422)	3.97	3.97	0.5	π

(431)	2.92	2.82	0.5	0
(510)	5.82	5.82	0.3	/
(521)	3.55	3.55	0.2	/
(440)	3.44	3.44	0.1	/
(433)	2.24	2.24	0.2	/
(530)	5.34	5.34	0.1	/
(442)	2.25	2.24	0.1	/
(600)	3.25	3.24	0.4	/
(532)	2.16	2.17	0.2	/
(611)	5.10	3.10	0.4	/
(620)	3.08	3.08	0.03	/
(541)	3.00	3.00	0.13	/
(631)	2.87	2.87	0.07	/
(444)	2.81	2.81	1.00	/
(543)			0.00	/
(550)	2.75	2.75	0.01	/
(710)			0.01	/
(640)	2.70	2.70	0.31	/
(552)			0.30	/
(633)	2.65	2.65	0.30	/
(721)			0.15	/
(651)	2.47	2.47	0.04	/
(732)	2.47	2.47	0.04	/
(554)			0.04	/
(741)	2.40	2.40	0.02	/
(811)	1		0.04	/
(644)	2.24	2.24	0.01	/
(820)	2.36	2.36	0.01	/

(743)			0.02	/
(750)	2.26	2.26	0.04	/
(831)			0.02	/
(662)	2.23	2.23	0.04	/
(833)	2.15	2.15	0.04	/
(910)	2.13	2.13	0.04	/
(842)	2.12	2.12	0.02	/
(655)			0.03	/
(761)	2.10	2.10	0.01	/
(921)			0.01	/
(851)			0.02	/
(754)	2.05	2.05	0.03	/
(930)			0.03	/
(763)	2.01	2.01	0.02	/
(932)	2.01	2.01	0.02	/
(770)			0.02	/
(853)	1.97	1.97	0.01	/
(941)			0.01	/
(862)	1.01	1.01	0.01	/
(10 2 0)	1.91	1.91	0.02	/
(871)			0.02	/
(952)	1.86	1.85	0.02	/
(10 3 1)			0.02	/
(774)			0.02	/
(855)	1.82	1.82	0.02	/
(871)			0.01	/
(961)	1.70	1.70	0.01	/
(10 3 3)	1./9	1./9	0.02	/

(873)			0.00	/
(954)	1.76	1.76	0.00	/
(11 1 0)			0.01	/
$a_{\rm cub} = 19.46 \text{ nm}$				

4. References

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