Electronic Supporting Information

Cybotactic Nematic phases of photoisomerizable hockey-stick liquid crystals

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1. Synthesis and analytical data

Thin layer chromatography (TLC) was performed on aluminium sheet pre-coated 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 materials is based on ¹H-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in CDCl₃ solutions, with tetramethylsilane as internal standard). Microanalyses were performed using a Leco CHNS-932 elemental analyser. The synthesis details for the intermediate compound 4-(4'-n-octyloxyphenylazo(4''-benzoyloxy)benzoic acid as an example for the azobenzene derived benzoic acids **3/n** and **3F12** as well as the synthesis details for 4-bromo-3-hydroxyphenyl-4'-dodecyloxybenzoate (**6**) and for the final hockey-stick molecules **An** and **AF12** are given below.

1.1. Synthesis of 4-(4'-*n*-octyloxyphenylazo(4''-benzoyloxy)benzaldehyde **2/8**

The acid **1/8** [S1] (3.54 g, 1.0 mmol) was heated under reflux with thionyl chloride (3 mL) and a catalytic amount of *N,N*-Dimethylformamide (DMF) for one hour. The excess of thionyl chloride was removed by distillation under reduced pressure. The obtained acid chloride was then dissolved in dry dichloromethane (DCM, 20 mL) followed by addition of 4-hydroxybenzaldehyde (1.22g, 1.0 mmol) previously dissolved in DCM, triethylamine (TEA, 1.66 mL, 1.2 mmol) and a catalytic amount of pyridine (pyr.) and the reaction mixture was then refluxed for 6 hours under argon atmosphere. The reaction progress was checked with TLC and at the end of the reaction the solution was cooled to room temperature and the solvent was removed under vacuum. The crude product was purified with column chromatography using dichloromethane as eluent followed by recrystallization from ethanol to give the desired aldehyde as orange powder. The analytical data for the aldehyde **2/8** are:

Orange powder, yield 3.29 g, 71.85 %, phase transitions: Cr 113 °C SmA 175 °C isotropic, ¹H-NMR (400 MHz, CDCl₃): δ 10.04 (s, 1H, -CHO), 8.33 (d, *J* = 8.6 Hz, 2H, Ar-H), 8.04 – 7.88 (m, 6H, Ar-H), 7.45 (d, *J* = 8.8 Hz, 2H, Ar-H), 7.02 (d, *J* = 8.7 Hz, 2H, Ar-H), 4.06 (t, *J* = 6.6 Hz, 2H, Ar-OCH₂CH₂), 1.92 – 1.73 (m, 2H, Ar-OCH₂CH₂), 1.62 – 1.17 (m, 10H, CH₂), 0.90 (t, *J* = 6.6 Hz, 3H, CH₃).

1.2. Synthesis of 4-(4'-*n*-octyloxyphenylazo(4''-benzoyloxy)benzoic acid **3/8**

This was synthesized using an oxidation procedure similar to that reported in Ref. [S1] as following: the aldehyde **2/8** (2.04 g, 4.44 mmol) and resorcinol (0.53 g, 4.75 mmol) were dissolved in *tert*-butyl alcohol (50 mL). A previously prepared solution of sodium chlorite (1.56 g, 17.28 mmol) and sodium dihydrogenphosphate (1.28 g, 10.70 mmol) in water (20 mL) was added in a drop wise manner over a 10-min period. The reaction mixture was stirred at room temperature overnight. Volatile components were removed under vacuum and the residue was dissolved in water (100 mL). 1 N Aqueous HCl was added till pH 3 and the obtained orange precipitate was isolated, washed successively with water and hexane, and dried in air. The obtained acid **3/8** was used for the next step without further purification (2.07 g, yield 98 %).

1.3. 4-Bromo-3-benzyloxyphenyl-4'-dodecyloxybenzoate, **5**

Compound **4** [S2] (2.79 g, 1.0 mmol) was esterified with 4-dodecyloxybenzoic acid (3.06 g, 1.0 mmol) in the presence of DCC (2.06 g, 1.0 mmol) and a catalytic amount of DMAP. The crude product was purified by recrystallization from ethanol to give 4.24 g, yield 74.8 % of **5** as colourless crystals. M.p. 82 °C, ¹H-NMR (500 MHz, CDCl₃): δ 8.12 (d, *J* = 8.6, 2H, Ar-H), 7.60 (d, *J* = 8.6 Hz, 1H, Ar-H), 7.53 – 7.30 (m, 5H, Ar-H), 7.02 – 6.95 (m, 2H, Ar-H), 6.88 (d, *J* = 2.5 Hz, 1H, Ar-H), 6.76 (dd, *J* = 8.6, 2.5 Hz, 1H, Ar-H), 5.16 (s, 2H, Ph-CH₂), 4.06 (t, *J* = 6.6 Hz, 2H, Ar-OCH₂CH₂), 1.89 – 1.75 (m, 2H, Ar-OCH₂CH₂), 1.65 – 1.16 (m, 18H, CH₂), 0.90 (t, *J* = 6.9 Hz, 3H, CH₃).

1.4. 4-Bromo-3-hydroxyphenyl-4'-dodecyloxybenzoate, **6**

A suspension of compound **5** (1.98 g, 3.50 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, followed by filtration and evaporation of the solvent. The crude product was purified by flash chromatography (silica gel, CHCl₃/PE 8:2) to give 1.59 g, yield 95.6 % of **6** as a white powder. M.p. 84 °C, ¹H-NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 8.7, 2H, Ar-H), 7.48 (d, *J* = 8.7 Hz, 1H, Ar-H), 6.96 (d, *J* = 8.5, 2H, Ar-H), 6.92 (d, *J* = 2.6 Hz, 1H, Ar-H), 6.72 (dd, *J* = 8.7, 2.6 Hz, 1H, Ar-H), 5.59 (s, 1H, Ar-H), 4.04 (t, *J* = 6.6 Hz, 2H, Ar-OCH₂CH₂), 1.88 – 1.74 (m, 2H, Ar-OCH₂CH₂), 1.61 – 1.13 (m, 18H, CH₂), 0.88 (t, *J* = 6.9 Hz, 3H, CH₃).

1.5. Hockey-stick molecules **An** and **AF12**

General procedure: 1.0 mmol of the corresponding acid **3/n** was esterified with 4-bromoresorcinol monobenzoate **6** (1.0 mmol) using the esterification procedure described above for the synthesis of the aldehyde **2/8**. At the end of the reaction the solution was cooled to room temperature, washed with 10% HCl (2 × 50 mL) and three times with cold water followed by extraction with dichloromethane (3 × 50 mL) and finally dried over anhydrous sodium sulphate. The crude residue was chromatographed on silica gel using DCM followed by recrystallization from chloroform/ethanol mixture.

A8. - Orange crystals, yield 63 %. ¹H-NMR (500 MHz, CDCl₃): δ 8.39 – 8.33 (m, 4H, Ar-H), 8.14 (d, *J* = 8.9 Hz, 2H, Ar-H), 8.04 – 7.96 (m, 4H, Ar-H), 7.71 (d, *J* = 8.7 Hz, 1H, Ar-H), 7.45

(d, $J = 8.7$ Hz, 2H, Ar-H), 7.30 (d, $J = 2.6$ Hz, 1H, Ar-H), 7.12 (dd, $J = 8.8, 2.6$ Hz, 1H, Ar-H), 7.05 (d, $J = 6.0$ Hz, 2H, Ar-H), 6.99 (d, $J = 8.9$ Hz, 2H, Ar-H), 4.11 – 4.02 (m, 4H, Ar-OCH₂CH₂), 1.89 – 1.79 (m, 4H, Ar-OCH₂CH₂), 1.58 – 1.22 (m, 28H, CH₂), 0.95 – 0.86 (m, $J = 7.0$ Hz, 6H, CH₃). Elemental Analysis: Calc. for **C₅₃H₆₁BrN₂O₈** C, 68.16; H, 6.58; N, 3.00. Found C, 68.10; H, 6.49; N, 2.93 %.

A12. - Orange crystals, yield 64.7 %. ¹H-NMR (500 MHz, CDCl₃): δ 8.41 – 8.30 (m, 4H, Ar-H), 8.14 (d, $J = 8.9$ Hz, 2H, Ar-H), 8.05 – 7.96 (m, 4H, Ar-H), 7.71 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.45 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.30 (d, $J = 2.6$ Hz, 1H, Ar-H), 7.12 (dd, $J = 8.7, 2.6$ Hz, 1H, Ar-H), 7.05 (d, $J = 6.1$ Hz, 2H, Ar-H), 6.98 (d, $J = 8.9$ Hz, 2H, Ar-H), 4.11 – 4.01 (m, 4H, Ar-OCH₂CH₂), 1.89 – 1.79 (m, 4H, Ar-OCH₂CH₂), 1.59 – 1.20 (m, 36H, CH₂), 0.96 – 0.84 (m, 6H, CH₃). Elemental Analysis: Calc. for **C₅₇H₆₉BrN₂O₈** C, 69.15; H, 7.02; N, 2.83. Found C, 69.11; H, 7.00; N, 2.74 %.

A20. - Orange crystals, yield 67.3 %. ¹H-NMR (500 MHz, CDCl₃): δ 8.41 – 8.32 (m, 4H, Ar-H), 8.13 (d, $J = 9.3$, 2H, Ar-H), 8.04 – 7.95 (m, 4H, Ar-H), 7.71 (d, $J = 8.8$ Hz, 1H, Ar-H), 7.45 (d, $J = 8.7$ Hz, 2H, Ar-H), 7.30 (d, $J = 2.6$ Hz, 1H, Ar-H), 7.12 (dd, $J = 8.7, 2.6$ Hz, 1H, Ar-H), 7.05 (d, $J = 6.1$ Hz, 2H, Ar-H), 6.98 (d, $J = 8.9$ Hz, 2H, Ar-H), 4.11 – 4.01 (m, 4H, Ar-OCH₂CH₂), 1.90 – 1.76 (m, 4H, Ar-OCH₂CH₂), 1.61 – 1.20 (m, 52H, CH₂), 0.95 – 0.83 (m, 6H, CH₃). Elemental Analysis: Calc. for **C₆₅H₈₅BrN₂O₈** C, 70.83; H, 7.77; N, 2.54. Found C, 70.79; H, 7.69; N, 2.51 %.

AF12. - Orange powder, yield 68.0 %. ¹H-NMR (500 MHz, CDCl₃): δ 8.41 – 8.32 (m, 4H, Ar-H), 8.13 (d, $J = 6.7, 4.8$ Hz, 2H, Ar-H), 8.01 (d, $J = 8.5$ Hz, 2H, Ar-H), 7.84 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.76 (dd, $J = 11.8, 2.3$ Hz, 1H, Ar-H), 7.71 (d, $J = 8.7$ Hz, 1H, Ar-H), 7.45 (d, 2H, Ar-H), 7.30 (d, $J = 2.6$ Hz, 1H, Ar-H), 7.16 – 7.08 (m, 2H, Ar-H), 6.99 (d, $J = 8.9$ Hz, 2H, Ar-H), 4.16 (t, $J = 6.6$ Hz, 2H, Ar-OCH₂CH₂), 4.06 (t, $J = 6.5$ Hz, 2H, Ar-OCH₂CH₂), 1.94 – 1.78 (m, 4H, Ar-OCH₂CH₂), 1.58 – 1.19 (m, 36H, CH₂), 0.94 – 0.84 (m, 6H, CH₃). Elemental Analysis: Calc. for **C₅₇H₆₈BrFN₂O₈** C, 67.91; H, 6.80; N, 2.78. Found C, 67.90; H, 6.76; N, 2.74 %.

2. ^1H -NMR Spectra

Figure S1. ^1H -NMR Spectrum of **A8** in CDCl_3 .

Figure S2. ^1H -NMR Spectrum of **A12** in CDCl_3 .

Figure S3. ¹H-NMR Spectrum of **A20** in CDCl₃.

Figure S4. ¹H-NMR Spectrum of **AF12** in CDCl₃.

3. References

[S1] Alaasar M, Prehm M, Poppe M, Nagaraj M, Vij JK, Tschierske C. Development of polar order and tilt in lamellar liquid crystalline phases of a bent-core mesogen. *Soft Matter*. 2014;10: 5003-5016.

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