Supporting Information

New room temperature dark conglomerate mesophase formed by bent-core molecules combining 4-iodoresorcinol with azobenzene units

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1. Syntheses and analytical data

The synthetic procedure for the new bent-core compounds (A12 and Bn) is shown in Scheme S1. Ethyl 4-aminobenzoate (Fluka), sodium nitrite (BDH), 2-fluoro phenol (Fluka), 1-bromoalkane (Aldrich), potassium carbonate (Fluka), potassium iodide (Riedel-de Haen), potassium hydroxide (Merck), 1,3-dicycloxylcarbodiimide (DCC; Merck), 4-(N,N-dimethylamino) pyridine (DMAP) (Aldrich), resorcinol (Aldrich) and iodine monochloride (ABCR). 4-Iodoresorcinol was synthesized according to the procedure described in Ref.^{S1} 2-Butanone (Merck) and dichloromethane (Merck) were dried separately over calcium chloride (Merck) and distilled before use. Other solvents and chemicals were used without further purification.

The spectral data and the microanalyses obtained for all the compounds were in agreement with their chemical structures

The preparation procedure for Ethyl 4-(3-fluoro-4-hydroxyphenylazo) benzoate (1) is given in Ref.^{S2} The preparation and the analytical data obtained for the intermediate

compounds 2/14, 3/14 as examples for compounds 2/n and 3/n, respectively and for the final bent core molecules (A12 and Bn) are given below.



Scheme S1. Synthesis of bent core molecules under investigation.

1.1 Ethyl 4-(3-fluoro-4-tetradecyloxyphenylazo) benzoate (2/14)

18.5 mmol of **A**, anhydrous K_2CO_3 (5.11 g, 37.0 mmol) and KI (0.100 g) were dissolved in 100 mL of 2-butanone, under argon atmosphere. After 10 minutes stirring, 1-bromotetradecane (6.15 g, 22.2 mmol) were added drop wise via syringe while the solution

was refluxing. The mixture was stirred overnight under reflux. After cooling down to room temperature, 200 mL of water were added. The product was extracted with dichloromethane. The organic layer was dried with MgSO₄ and filtered, and then the solvent was evaporated. The product was recrystallized with ethanol. Yield: 90 %. m.p. 90 °C. The product was an orange powder. ¹H-NMR (500 MHz, CDCl₃) δ 8.16 (d, 2H, *J* = 8.3 Hz, 2H, Ar-H), 7.89 (d, 2H, *J* = 8.3 Hz, 2H, Ar-H), 7.77 (d, *J* = 8.7, 1H, Ar-H), 7.70 (dd, *J* = 12.0, 2.3 Hz, 1H, Ar-H), 7.07 (t, *J* = 8.6 Hz, 1H, Ar-H), 4.39 (q, *J* = 7.1 Hz, 2H, $-\text{COOCH}_2$), 4.11 (t, *J* = 6.6 Hz, 2H, OCH₂), 1.90–1.80 (m, 2H), 1.54–1.18 (m, 25H, -CH₂- and $-\text{COOCH}_2$ CH₃), 0.86 (t, *J* = 7.0 Hz, 3H, CH₃).

1.2. 4-(3-Fluoro-4-tetradecyloxyphenylazo) benzoic acid (3/14)

2/14 (6.25 g, 12.9 mmol) is dissolved in ethanol (150 mL), and (5.8 g, 90 mmol) of KOH were added. The reaction mixture was heated to reflux, and stirred overnight. Then, the mixture was cooled to room temperature. 0.5 L of water was added and the mixture was subsequently acidified with 35% HCl until pH = 2. The solid was filtered off and then it was recrystallized twice from glacial acetic acid and washed with methanol. The product was a bright orange solid. Yield = 95 %. Phase transition: Cr 137 SmC 204 N 244 °C Isotropic liquid. ¹H-NMR (500 MHz, Acetone): δ 8.21 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.97 (d, *J* = 8.7 Hz, 2H, Ar-H), 7.87 (d, *J* = 9.8 Hz, 1H, Ar-H), 7.73 (dd, *J* = 12.1, 2.3 Hz, 1H, Ar-H), 7.38 (t, *J* = 8.7 Hz, 1H, Ar-H), 4.24 (t, *J* = 6.5 Hz, 2H, O<u>CH</u>₂), 1.90–1.82 (m, 2H, OCH₂<u>CH</u>₂), 1.57–1.18 (m, 22H, CH₂), 0.86 (t, *J* = 6.9 Hz, 3H, CH₃).

1.3. Bent core molecules An

General procedure. The mixture of 1.2 mmol of 4-iodoresorcinol, 2.4 mmol of the corresponding 3/n, 2.4 mmol of dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) as catalyst in 40 ml of dry dichloromethane was stirred at room temperature under an argon atmosphere for 24 h. The precipitate was filtered, the solvent was evaporated. The crude products were purified by column chromatography on silica gel using dichloromethane as eluent and crystallized twice from ethanol/ CHCl₃ mixture. The analytical data obtained for A12 and **B***n* are as fellow:

1.3.1. 4-Iodo-1,3-phenylene bis-[4-(4-dodecyloxyphenylazo)benzoate] (A12)

Yield = 35 %. ¹H-NMR (400 MHz, CDCl₃): δ 8.46–8.35 (m, 4H, Ar-H), 8.32 (d, J = 8.8 Hz, 1H, Ar-H), 8.05–7.86 (m, 8H, Ar-H), 7.38 (s, 1H, Ar-H), 7.33 (d, J = 2.6 Hz, 1H, Ar-H), 7.02 (t, J = 8.5 Hz, 4H, Ar-H), 4.06 (t, J = 6.6 Hz, 4H, O<u>CH₂</u>), 1.93–1.70 (m, 4H, OCH₂<u>CH₂</u>), 1.58–1.14 (m, 36H, CH₂), 0.88 (t, J = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₅₆H₆₉IN₄O₆ C, 65.87; H, 6.81; N, 5.49. Found C, 65.88; H, 6.79; N, 5.45 %.

1.3.2. 4-Iodo-1,3-phenylene bis-[4-(3-fluoro-4-octyloxyphenylazo)benzoate] (B8)

Yield = 35 %. ¹H-NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 8.5 Hz, 2H, Ar-H), 8.32 (d, J = 8.5 Hz, 2H, Ar-H), 8.05–7.91 (m, 5H, Ar-H), 7.82 (d, J = 8.6 Hz, 2H, Ar-H), 7.78–7.70 (m, 2H, Ar-H), 7.33 (d, J = 2.5 Hz, 1H, Ar-H), 7.10 (t, J = 8.1 Hz, 2H, Ar-H), 7.04 (dd, J = 8.7, 2.5 Hz, 1H, Ar-H), 4.14 (t, J = 6.6 Hz, 4H, O<u>CH₂</u>), 1.95–1.82 (m, 4H, OCH₂<u>CH₂</u>), 1.58–1.21 (m, 20H, CH₂), 0.90 (t, J = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₄₈H₅₁IF₂N₄O₆ C, 61.02; H, 5.44; N, 5.93. Found C, 61.00; H, 5.42; N, 5.94 %.

1.3.3. 4-Iodo-1,3-phenylene bis-[4-(3-fluoro-4-decyloxyphenylazo)benzoate] (B10)

Yield = 33 %. ¹H-NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 8.7 Hz, 2H, Ar-H), 8.32 (d, J = 8.7 Hz, 2H, Ar-H), 8.05–7.91 (m, 5H, Ar-H), 7.82 (d, J = 8.6 Hz, 2H, Ar-H), 7.78–7.70 (m, 2H, Ar-H), 7.33 (d, J = 2.6 Hz, 1H, Ar-H), 7.10 (t, J = 8.1 Hz, 2H, Ar-H), 7.04 (dd, J = 8.7, 2.6 Hz, 1H, Ar-H), 4.14 (t, J = 6.6 Hz, 4H, O<u>CH₂CH₂</u>), 1.95–1.82 (m, 4H, OCH₂<u>CH₂</u>), 1.58–1.19 (m, 28H, CH₂), 0.89 (t, J = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₅₂H₅₉IF₂N₄O₆ C, 62.40; H, 5.94; N, 5.60. Found C, 62.38; H, 5.93; N, 5.55 %.

1.3.4. 4-Iodo-1,3-phenylene bis-[4-(3-fluoro-4-dodecyloxyphenylazo)benzoate] (B12)

Yield = 33 %. ¹H-NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 8.7 Hz, 2H, Ar-H), 8.32 (d, J = 8.7 Hz, 2H, Ar-H), 8.05–7.90 (m, 5H, Ar-H), 7.82 (d, J = 8.7 Hz, 2H, Ar-H), 7.78–7.70 (m, 2H, Ar-H), 7.33 (d, J = 2.6 Hz, 1H, Ar-H), 7.10 (t, J = 8.6 Hz, 2H, Ar-H), 7.04 (dd, J = 8.7, 2.6 Hz, 1H, Ar-H), 4.14 (t, J = 6.6 Hz, 4H, O<u>CH₂CH₂</u>), 1.94–1.83 (m, 4H, OCH₂<u>CH₂</u>), 1.58–1.18 (m, 36H, CH₂), 0.88 (t, J = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₆₄H₆₇F₂IN₄O₆ C, 66.66; H, 5.86; N, 4.86. Found C, 66.63; H, 5.90; N, 4.82 %.

1.3.5. 4-Iodo-1,3-phenylene bis-[4-(3-fluoro-4-tetradecyloxyphenylazo)benzoate] (B14)

Yield = 32 %. ¹H-NMR (400 MHz, CDCl₃): δ 8.41 (d, J = 8.5 Hz, 2H, Ar-H), 8.32 (d, J = 8.5 Hz, 2H, Ar-H), 8.04–7.92 (m, 5H, Ar-H), 7.82 (d, J = 8.7 Hz, 2H, Ar-H), 7.78–7.70 (m, 2H, Ar-H), 7.33 (d, J = 2.6 Hz, 1H, Ar-H), 7.10 (t, J = 8.0 Hz, 2H, Ar-H), 7.04 (dd, J = 8.7, 2.6 Hz, 1H, Ar-H), 4.14 (t, J = 6.5 Hz, 4H, OCH₂CH₂), 1.93–1.82 (m, 4H, OCH₂CH₂), 1.57–1.19 (m, 44H, CH₂), 0.88 (t, J = 6.8 Hz, 6H, CH₃). Elemental Analysis: Calc. for C₆₀H₇₅F₂IN₄O₆ C, 64.74; H, 6.79; N, 5.03. Found C, 64.70; H, 6.78; N, 5.01 %.

2. Techniques

The structure characterization of the synthesized bent-core compounds 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 analyzer.

The mesophase behaviour and transition temperatures of the bent-core molecules with central 4-iodoresorcinol core were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Nikon Optiphot-2 polarizing microscope. The associated enthalpies were obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10 K min⁻¹.

The X-ray diffraction patterns were recorded with a 2D detector (Vantec-500, Bruker). Ni filtered and pin hole collimated CuK_{α} radiation was used. The exposure time was 30 min and the sample to detector distance was 8.6 cm or 26.6 cm respectively. Alignment was tried to achieve by slow cooling (rate: 1 K min⁻¹ – 0.1 K min⁻¹) of a small droplet of the sample on a glass plate and takes place at the sample–glass or at the sample–air interface, with domains fibre-like disordered around an axis perpendicular to the interface. The aligned samples were held on a temperature-controlled heating stage.

3. Additional data



Figure. S1 DSC heating and cooling curves (10 K min-1) observed for B14 after six weeks.



Figure S2. XRD pattern of the DC phase of **B**14 at T = 90 °C (small angle pattern, attempted alignment on a glass surface; b) θ -scan of the diffraction pattern.



Figure S3. 1:1 mixture of **B**14 with 5-CB: a-c) at T = 60 °C showing the dark conglomerate phase and d) at T = 25 °C after crystallization.

4. References

- S1. I. Thomsen and K. B. G. Torssell, Acta Chemica, 1991, 24, 539.
- S2. M. Alaasar, M. Prehm and C. Tschierske, Liq. Cryst., 2013, 40, 656.