

## **A reversible isothermal twist-bend nematic – nematic phase transition driven by the photoisomerisation of an azobenzene-based nonsymmetric liquid crystal dimer**

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## Section 1: Materials/ General methods/ Instrumentation

### Materials

All reagents and solvents were available commercially and used as received unless otherwise stated.

### General methods and instrumentation

All compounds were characterised using a combination of  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and FTIR spectroscopies.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian Unity INOVA 400 MHz NMR spectrometer with pulsed field gradients and waveform generator. Infrared spectra were recorded on a diamond tip Perkin Elmer UATR two spectrometer with an ATR diamond cell.

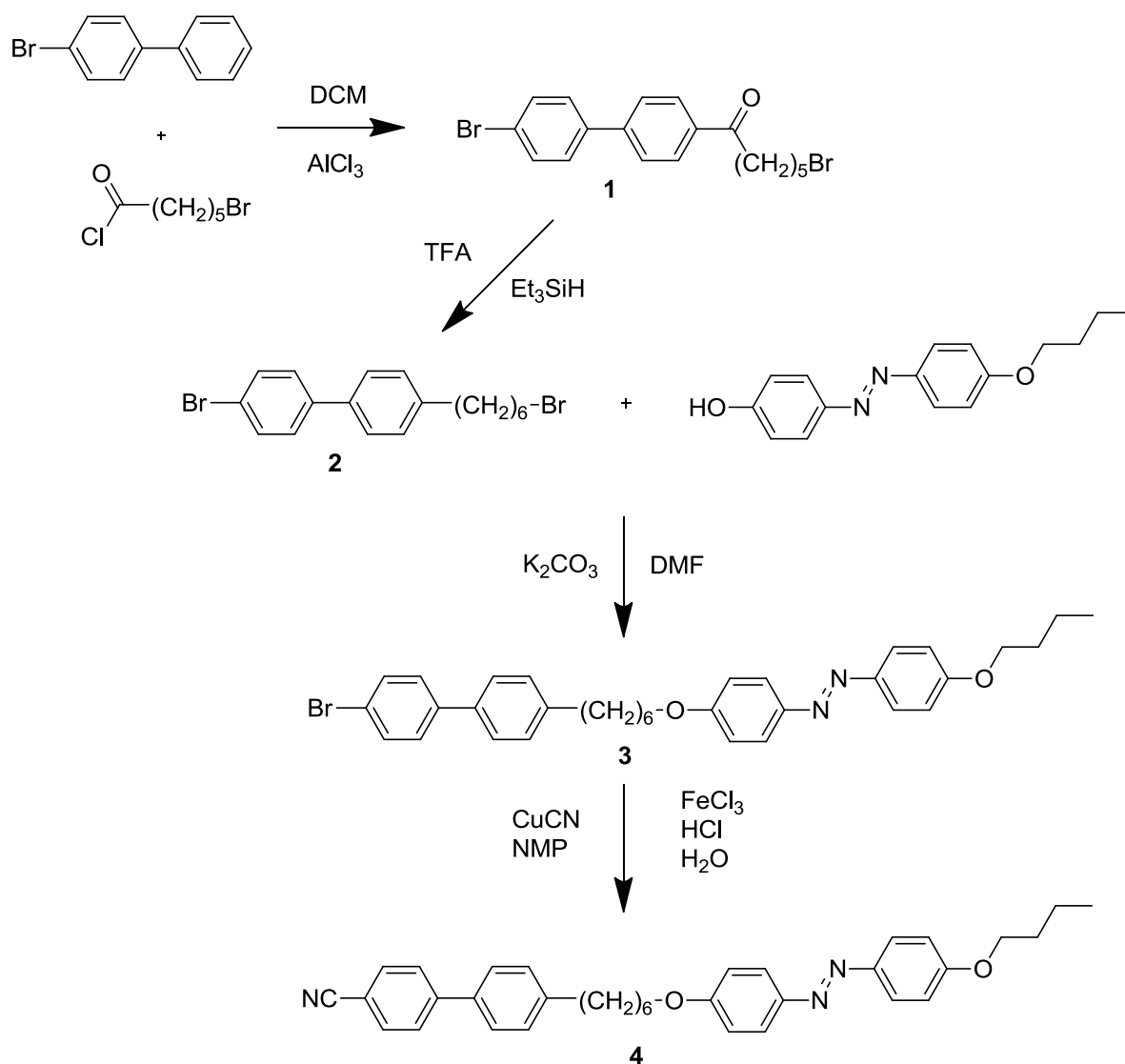
Purity was confirmed by elemental analysis performed at the Micro Analytical Laboratory in the School of Chemistry at the University of Manchester.

Phase characterisation was performed by polarising light microscopy using an Olympus BH2 polarizing light microscope equipped with a Linkam TMS 92 hot stage. The transitional properties were measured by differential scanning calorimetry using a Mettler Toledo DSC 820 differential scanning calorimeter equipped with a TS0801RO sample robot. The heating profile in all cases was heat, cool, reheat at  $10\text{ }^\circ\text{Cmin}^{-1}$  with a 3 min isotherm between heating and cooling. All samples were heated to at least  $30\text{ }^\circ\text{C}$  above their clearing temperatures. Thermal data was extracted from the reheat trace where possible, duplicate samples of each dimer were recorded and the data averaged.

## Section 2: Synthetic procedures

### Synthesis of 1-(4-butoxyazobenzene-4'-yloxy)-6-(4-cyanobiphenyl-4'yl)hexane

The synthesis of 1-(4-butoxyazobenzene-4'-yloxy)-6-(4-cyanobiphenyl-4'yl)hexane **4**, is shown in scheme 1.



**Scheme 1.**

**2.1. 4-Bromo-4'-(6-bromohexanoyl)biphenyl, 1**

A solution of 6-bromohexanoyl chloride (24.18 g, 0.11 mol) and 4-bromobiphenyl (25.05 g, 0.11 mol) in dichloromethane (50 ml) was added dropwise to a stirred suspension of aluminium(III) chloride (14.68 g, 0.11 mol) in dichloromethane (50 ml) cooled to 0 °C in an ice bath. This mixture was warmed to room temperature and stirred overnight. The reaction mixture was added to H<sub>2</sub>O (250 ml) and extracted using dichloromethane (2 x 80 ml). The organic fractions were combined and dried over anhydrous magnesium sulphate before the solvent was removed under vacuum. The crude product was purified using silica gel chromatography with a petroleum ether (40/60) and dichloromethane, 50:50 mixture as eluent. The crude product thus obtained was recrystallised from ethanol to give the title compound as a white solid. Yield: 22.70 g, 50%. M.p. 77.0 °C. Infrared  $\nu$  cm<sup>-1</sup>: 2925, 1679 1603, 1258, 1184, 971, 807, 665. <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>) $\delta$ : 7.96 (2H, d, *J* 8.6, Ar), 7.57 (2H, d, *J* 8.6, Ar), 7.52 (2H, d, *J* 9.0, Ar), 7.42 (2H, d, *J* 8.6, Ar), 3.37 (2H, t, *J* 6.7, BrCH<sub>2</sub>CH<sub>2</sub>), 2.95 (2H, t, *J* 7.40, COCH<sub>2</sub>CH<sub>2</sub>), 1.87 (2H, quin, *J* 6.70, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.73 (2H, quin, *J* 7.40, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.49 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>) $\delta$ : 199.45, 144.39, 138.78, 135.94, 132.10, 128.81, 128.72, 127.06, 122.64, 38.35, 38.81, 33.61, 32.62, 32.37, 27.87, 23.35.

**2.2. 1-Bromo-6-(4'-bromobiphenyl-4-yl)hexane, 2**

Compound **2** was prepared by reduction of the carbonyl group on **1** using triethylsilane in trifluoroacetic acid. Triethylsilane (22 ml, 0.14 mol) was added dropwise to a stirred solution of **1** (22.70 g, 0.057 mol) in trifluoroacetic acid (33.5 ml, 0.44 mol) cooled in an ice bath, maintaining the temperature below 20 °C. The reaction mixture was stirred overnight at room temperature before being added to a mixture of dichloromethane (100 ml) and H<sub>2</sub>O (300 ml). The layers were separated and the aqueous layer was washed with dichloromethane (2 x 100 ml). The organic layers were combined and dried over anhydrous magnesium sulphate before removing the solvent under vacuum. The crude product thus obtained was recrystallised from ethanol to give the title compound as a white solid. Yield: 11.13 g, 51%. M.p 77.0 °C. Infrared  $\nu$  cm<sup>-1</sup>: 2928, 2854, 1479, 1077, 1000, 804, 646, 503. <sup>1</sup>H NMR (400

MHz CDCl<sub>3</sub>) $\delta$ : 7.54 (2H, d, *J* 8.6, Ar), 7.47 (2H, d, *J* 8.2, Ar), 7.44 (2H, d, *J* 8.6, Ar), 7.25 (2H, d, *J* 8.4, Ar), 3.41 (2H, t, *J* 6.6, BrCH<sub>2</sub>CH<sub>2</sub>), 2.65 (2H, t, *J* 7.3, ArCH<sub>2</sub>CH<sub>2</sub>), 1.87 (2H, quin, *J* 7.8, BrCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.67 (2H, quin, *J* 7.4, ArCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.48 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.39 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>) $\delta$ : 142.18, 140.02, 137.41, 131.79, 128.94, 128.55, 126.81, 121.20, 35.41, 33.93, 32.71, 31.18, 28.28, 28.01.

### 2.3. 1-(4-butoxyazobenzene-4'-yloxy)-6-(4-bromobiphenyl-4'-yl)hexane, **3**

A mixture of **2** (1.20 g, 0.003 mol), 4-butoxy-4'-hydroxyazobenzene (0.77 g, 0.003 mol) and potassium carbonate (0.80 g, 0.006 mol) in dimethylformamide (50 ml) was heated at reflux overnight. The reaction mixture was cooled to room temperature, poured into H<sub>2</sub>O (150 ml), acidified with dilute HCl (0.5 M) and the orange precipitate collected by vacuum filtration. The crude product was purified using silica gel chromatography with a petroleum ether (40/60) and dichloromethane, 40:60 mixture as eluent before being recrystallised from ethanol and ethyl acetate (2:1 mix) to give the title compound as an orange solid. Yield: 0.99 g, 56%. M.p. 152 °C. Infrared  $\nu$  cm<sup>-1</sup>: 2928, 2868, 1600, 1578, 1480, 1389, 1241, 1146, 1001, 843, 806, 553. <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>)  $\delta$ : 7.85 (4H, d, *J* 8.9, Ar), 7.54 (2H, d, *J* 8.6, Ar), 7.46 (2H, d, *J* 8.5, Ar), 7.44 (2H, d, *J* 8.5, Ar), 7.25 (2H, d, *J* 7.5, Ar), 6.99 (2H, d, *J* 9.0, Ar), 6.98 (2H, d, *J* 9.0, Ar), 4.05 (2H, d, *J* 6.5, OCH<sub>2</sub>), 4.02 (2H, d, *J* 6.3, OCH<sub>2</sub>), 2.67 (2H, t, *J* 7.4, ArCH<sub>2</sub>), 1.82 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.70 (2H, quin, *J* 7.4, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.53 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.45 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.00 (3H, t, *J* 7.4 CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>) $\delta$ : 161.43, 161.32, 146.44, 142.26, 140.00, 137.36, 131.78, 128.95, 128.53, 126.78, 124.52, 121.48, 121.16, 115.17, 114.73, 109.99, 68.22, 68.05, 35.44, 31.28, 31.24, 29.09, 28.92, 25.86, 19.22, 13.84.

### 2.4. 1-(4-butoxyazobenzene-4'yloxy)-6-(4-cyanobiphenyl-4'-yl)hexane, **4**

The cyanation of **3** was achieved using a modified Rosenmund-von Braun reaction. A mixture of **3** (1.00 g, 0.002 mol), copper(I) cyanide (0.44 g, 0.005 mol) and dry N-methyl-2-pyrrolidone (50 ml) was heated at 200 °C for 4 h. The reaction mixture was cooled to 80 °C and to this was added a solution of

## SUPPLEMENTARY INFORMATION

iron(III) chloride (6.99 g, 0.05 mol), H<sub>2</sub>O (15 ml) and 32% HCl (6 ml) at 60 °C. This was allowed to cool slowly to room temperature and stirred overnight, then added to a dichloromethane (200 ml) and H<sub>2</sub>O (200 ml) mix. The aqueous layer was washed with dichloromethane (100 ml). All organic fractions were combined and washed with H<sub>2</sub>O (3 x 100 ml) before drying over anhydrous magnesium sulphate. Solvent was removed under vacuum to yield a brown liquid which was added to H<sub>2</sub>O (200 ml). The resulting brown precipitate was collected by vacuum filtration and washed with H<sub>2</sub>O (400 ml). The crude product was purified by silica gel chromatography using dichloromethane and petroleum ether (40/60), 40:60 mix as eluent. The crude product thus obtained was recrystallised from ethanol to give the title compound as a yellow solid. Yield: 0.209 g, 26%. M.p. 153 °C. Elemental analysis: Calculated for C<sub>35</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub>: C, 79.06%, H, 7.01%, N, 7.90%. Found: C, 78.86%, H, 7.31%, N, 7.97%. Infrared  $\nu$  cm<sup>-1</sup>: 2939, 2868, 2228, 1599, 1579, 1495, 1471, 1243, 1149, 881, 877, 547, 519. <sup>1</sup>H NMR (400 MHz CDCl<sub>3</sub>)  $\delta$ : 7.87 (4H, d, *J* 8.2, Ar), 7.72 (2H, d, *J* 7.9, Ar), 7.68 (2H, d, *J* 8.6, Ar), 7.52 (2H, d, *J* 8.2, Ar), 7.31 (2H, d, *J* 8.2, Ar), 7.01 (2H, d, *J* 6.3, Ar), 6.99 (2H, d, *J* 6.2, Ar), 4.07 (2H, d, *J* 6.6, OCH<sub>2</sub>), 4.04 (2H, d, *J* 6.3, OCH<sub>2</sub>), 2.72 (2H, t, *J* 7.4, ArCH<sub>2</sub>), 1.84 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.71 (2H, quin, *J* 7.8 CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.54 (4H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.46 (2H, m, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 1.00 (3H, t, *J* 7.4 CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz CDCl<sub>3</sub>)  $\delta$ : 161.21, 161.06, 146.96, 146.90, 145.54, 143.48, 136.50, 132.55, 129.19, 127.46, 127.09, 124.31, 119.03, 114.67, 114.64, 114.68, 110.53, 68.13, 68.01, 35.47, 31.27, 31.22, 29.10, 28.89, 25.86, 19.25, 13.87.

### Section 3: Freeze-fracture transmission electron microscopy (FF-TEM)

Freeze-fracture transmission electron microscopy (FF-TEM) was used to confirm the formation of the  $N_{tb}$  phase of CB6OABOBu. The procedure adopted is similar to the one described previously in detail elsewhere and is briefly outlined here<sup>1,2</sup>. To prepare the replica specimens of CB6OABOBu for FF-TEM,  $\sim 0.6$   $\mu\text{l}$  of material was put on top of a copper planchette. The sample was first heated to  $170$   $^{\circ}\text{C}$  to obtain the isotropic phase and then cooled to  $90$   $^{\circ}\text{C}$  at a rate of  $2$   $^{\circ}\text{Cmin}^{-1}$ , and kept at  $90$   $^{\circ}\text{C}$  (a temperature within the  $N_{tb}$  phase) for  $5$  min. The sample was then quenched by rapidly freezing in liquid  $\text{N}_2$  (rate  $> 1000$   $^{\circ}\text{Cs}^{-1}$ ) to avoid further phase transitions and quickly transferred to a freeze-fracture vacuum chamber (BalTec BAF060), where the sample was kept at  $-165$   $^{\circ}\text{C}$ . In order to ensure no photoisomerisation during sample preparation, the entire sample preparation process was performed in a dark environment. Only low intensity of light with  $\lambda > 650$  nm was used to observe the sample. Inside the chamber, a built in microtome was used to cut the sample and expose a fractured surface.  $4$  nm thick of Pt was then deposited onto the fractured surface at an angle of  $45^{\circ}$  to create a shadowing of the surface structure, followed by a  $20$  nm thick carbon deposition from the top to form a supporting film. Samples were then slowly warmed to room temperature and removed from the freeze fracture chamber. Liquid crystalline material was removed by dissolving in chloroform and the replica film was placed onto the carbon coated TEM grid and observed at room temperature with TEM (FEI Tecnai F20).



## Section 4: X-ray diffraction

For X-ray diffraction measurements, the sample was filled into a 1 mm diameter quartz capillary which was flame sealed. The capillary was placed inside the Linkam hot stage equipped with temperature controller (HFSX350-CAP) with a temperature stability of  $\pm 0.1$  °C. A pair of rare-earth permanent magnets produced a field of  $\sim 2.5$  kG at the sample. The sample was aligned by heating it to the isotropic phase and then slowly cooling at a rate of  $0.5$  °Cmin<sup>-1</sup>. X-ray diffraction measurements were carried out using a micro-focused (diameter  $\sim 100$   $\mu$ m) beam of Cu K $\alpha$  ( $\lambda = 1.5418$  Å) radiation on the Rigaku Screen Machine. For UV exposure, Single-Pole LED UV Curing System 72005 from Electro-Lite Corporation with maximum operating power of  $2.5$  Wcm<sup>-2</sup> and wavelength of 365 nm was used. UV source was placed at a distance of 25 mm from the sample and the effect of UV exposure on the N<sub>tb</sub> phase determined at  $0.25$  mWcm<sup>-2</sup>. Seeing no effect, UV power was gradually raised to  $0.63$ ,  $1.25$ ,  $1.88$  and  $2.5$  mWcm<sup>-2</sup> while taking data in the N<sub>tb</sub> phase where the transition to N phase and a large change in the order parameters is expected. UV exposures and data acquisition lasted for 15 min at each temperature. The diffraction patterns were recorded by a high-resolution Mercury 3 CCD detector positioned at a distance of  $\sim 76.60$  mm from the sample. The 2D diffraction patterns were analysed by using FIT2D software<sup>3</sup> after subtracting the background measured with an empty capillary in the sample position. The data was calibrated against silver behenate standards traceable to the National Institute of Standards and Technology.

## Section 5: Electro-optic cells

Experimental cells were assembled from parallel glass plates with transparent indium tin oxide electrodes. For planar (tangential) alignment, the substrates were spin coated with polyimide PI2555 (HD Microsystems), and homeotropic alignment was achieved using an inorganic passivation layer NHC AT720-A (Nissan Chemical Industries, Ltd).

## Section 6: UV-Vis spectroscopy

The UV-vis spectra of CB6OABOBu in the 550-325 nm region was measured using a Cary 50-Vis Spectrophotometer in transmission mode. The sample was contained in a 1.7  $\mu\text{m}$  quartz cell, and the spectra collected at 90 °C. The sample was initially in the  $N_{\text{tb}}$  phase and the spectra collected for several light/dark cycles.

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