

## Supporting information

### Theoretical model for the Frank elastic moduli in the intercalated SmA<sub>b</sub> phase of bent-shaped dimers

Claire Meyer<sup>1\*</sup>, Tatiana Sergan<sup>2</sup>, Vassili Sergan<sup>2</sup>, Daniel Stoenescu<sup>3</sup>, Patrick Davidson<sup>4</sup>, Anamarija Knežević<sup>5</sup>, Irena Dokli<sup>5</sup>, Andreja Lesac<sup>5</sup> and Ivan Dozov<sup>1,4</sup>

<sup>1</sup>Physique des Systèmes Complexes, Université de Picardie Jules Verne, 80039 Amiens, France

<sup>2</sup>California State University, Sacramento, 6000 J Street, Sacramento, California 95608, USA

<sup>3</sup>Optics Department, IMT Atlantique, CS 83818, 29238 Brest cedex, France

<sup>4</sup>Laboratoire de Physique des Solides, Université Paris-Saclay, CNRS, 91405 Orsay, France

<sup>5</sup>Ruđer Bošković Institute, Bijenička 54, 10000 Zagreb, Croatia

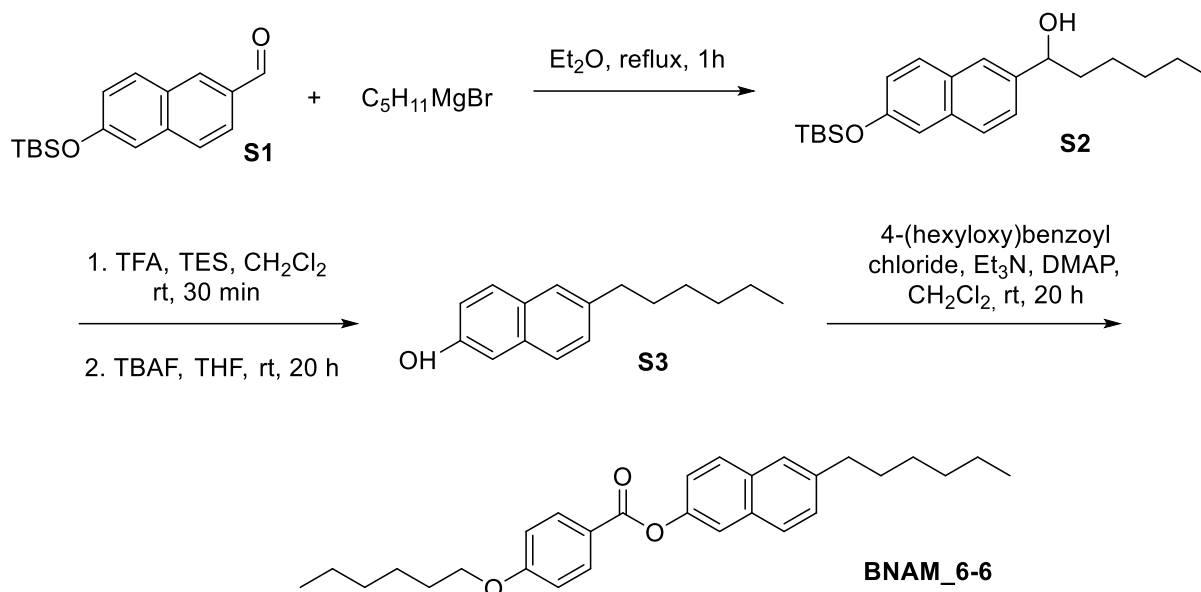
## Synthesis

### General Methods

All reactions were conducted under argon atmosphere unless stated otherwise. THF and Et<sub>2</sub>O were dried following standard methods. The commercial grade reagents and solvents were used without further purification. TLC was performed on aluminum-baked silica plates (60 F254, Merck). UV light (254 nm) or phosphomolybdic acid reagent was used for visualizing. Column chromatography was performed on silica gel (Silicagel 60, 70–230 mesh, Merck) or flash silica gel (Silicagel 60, 230-400 mesh, Merck). Transition temperatures were determined from thermograms recorded on Perkin-Elmer Diamond DSC, operated at scanning rates of 5 °C min<sup>-1</sup>. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV 300 and 600 spectrometers in CDCl<sub>3</sub> or d<sub>6</sub>-DMSO. Chemical shifts ( $\delta$ ) are given in ppm referenced to TMS or solvent. Coupling constants are given in Hz. Chemical purity and reaction progress were monitored by HPLC on an Agilent 1260 Infinity instrument on an InfinityLab Poroshell 120 EC-C18, 4.6 x 100 mm, 2.7  $\mu$  column with DAD detector, 0.5 mL/min flow. CHN analyses were done on Perkin Elmer 2400 Series II CHNS analyser.

## Experimental procedures

### Scheme 1



### 1-(6-((*tert*-Butyldimethylsilyloxy)naphthalen-2-yl)hexan-1-ol (S2)

Magnesium turnings (510 mg, 20.9 mmol) were suspended in dry diethyl ether (10 mL), flushed with argon, and activated by addition of a single iodine crystal. 1-Bromopentane (1.3 mL, 10.5 mmol) was added, and the reaction mixture was refluxed for 4 h. A solution of 6-((*tert*-butyldimethylsilyloxy)naphthalen-2-yl)hexanal (S1) (2 g, 7.0 mmol) in diethyl ether (10 mL) was added dropwise and the mixture was refluxed for another 1 h. After cooling, a 5% aqueous solution of  $NH_4Cl$  (30 mL) was added and the mixture extracted with  $CH_2Cl_2$  (3 x 40 mL). Combined organic layers were washed with brine, dried over  $Na_2SO_4$ , filtered, and concentrated under reduced pressure. Product was purified by column chromatography on silica gel ( $CH_2Cl_2$ ) to obtain 2.29 g (92 %) of compound S2 as a white solid.  $^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  7.73-7.65 (m, 3H), 7.42 (dd,  $J = 8.5, 1.7$  Hz, 1H), 7.17-7.18 (m, 1H), 7.07 (dd,  $J = 8.8, 2.4$  Hz, 1H), 4.80-4.75 (m, 1H), 1.93-1.82 (m, 2H), 1.82-1.72 (m, 1H), 1.49-1.38 (m, 1H), 1.35-1.24 (m, 5H), 1.02 (s, 9H), 0.92-0.78 (m, 3H), 0.24 (s, 6H).  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  153.5, 140.2, 134.2, 129.3, 129.0, 127.1, 124.5, 122.3, 114.8, 74.9, 38.9, 31.8, 25.7, 25.6, 22.6, 18.3, 14.0, -4.3.

### 6-Hexylnaphthalen-2-ol (S3)

The mixture of trifluoroacetic acid (5 ml) and triethylsilane (10 ml) was stirred for 20 min at rt. Compound S2 (2.2 g, 6.1 mmol) in  $CH_2Cl_2$  (15 ml) was added dropwise, and the mixture

was stirred for another 0.5 h at rt. Solvent was evaporated. TBAF solution (1M in THF, 7 mL) was added and the mixture stirred overnight at rt. Water was added (30 mL) and the mixture extracted to EtOAc (3 x 30 mL). Combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Product was purified by column chromatography on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to obtain 1.15 g (82 % over two steps) of compound **S3** as a white solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 8.8 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.57-7.52 (m, 1H), 7.30 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.12 (d, *J* = 2.6 Hz, 1H), 7.08 (dd, *J* = 8.8, 2.5 Hz, 1H), 5.07 (s, 1H), 2.77-2.65 (m, 2H), 1.77-1.59 (m, 2H), 1.45-1.24 (m, 6H), 0.95-0.78 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 152.8, 138.3, 133.0, 129.4, 129.3, 128.3, 126.4, 126.3, 117.7, 109.5, 36.1, 31.9, 31.5, 29.2, 22.8, 14.2.

### **6-Hexylnaphthalen-2-yl 4-(hexyloxy)benzoate (BNAM\_6-6)**

4-(Hexyloxy)benzoic acid (0.98 g, 4.4 mmol) was suspended in dry toluene (10 mL) under argon, and at 0 °C. Oxalyl chloride (1.9 mL, 22 mmol) was added followed by DMF (1 drop). The mixture was stirred for 1 hour at room temperature, solvent was evaporated, and the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (15 mL). This solution was added dropwise to a premixed solution of compound **S3** (1.1 g, 4.8 mmol), Et<sub>3</sub>N (6.1 mL, 44 mmol) and DMAP (270 mg, 2.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL). Reaction mixture was stirred overnight at room temperature. Water (30 mL) was added, and the mixture extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 20 mL). Organic extracts were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. Crude product was purified using silica gel column chromatography (CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane = 2:1) to obtain ester **BNAM\_6-6** (1.81 g, 97%) as a white solid which was further crystalized from acetone (1.52 g, 80%). PT (°C): Cr 84 N 118 Iso. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 8.9 Hz, 2H), 7.81 (d, *J* = 9.5 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.63-7.61 (m, 2H), 7.34 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.30 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.98 (d, *J* = 8.9 Hz, 2H), 4.04 (t, *J* = 6.6 Hz, 2H), 2.79-2.74 (m, 2H), 1.85-1.78 (m, 2H), 1.73 – 1.66 (m, 2H), 1.51-1.44 (m, 2H), 1.40-1.27 (m, 10H), 0.94-0.90 (m, 3H), 0.90-0.87 (m, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 165.3, 163.7, 148.3, 140.4, 132.44, 132.37, 131.8, 128.9, 128.3, 127.6, 126.3, 121.8, 121.5, 118.6, 114.4, 68.5, 36.2, 31.9, 31.7, 31.5, 29.2, 29.1, 25.8, 22.8, 22.7, 14.25, 14.17. Anal. Calcd. for C<sub>29</sub>H<sub>36</sub>O<sub>3</sub>: C, 80.52; H, 8.39; Found: C, 80.95; H, 8.50.