

## Supporting Information

### Laterally Connected Bent-Core Dimers and Bent-Core-Rod-Couples with Nematic Liquid Crystalline Phases

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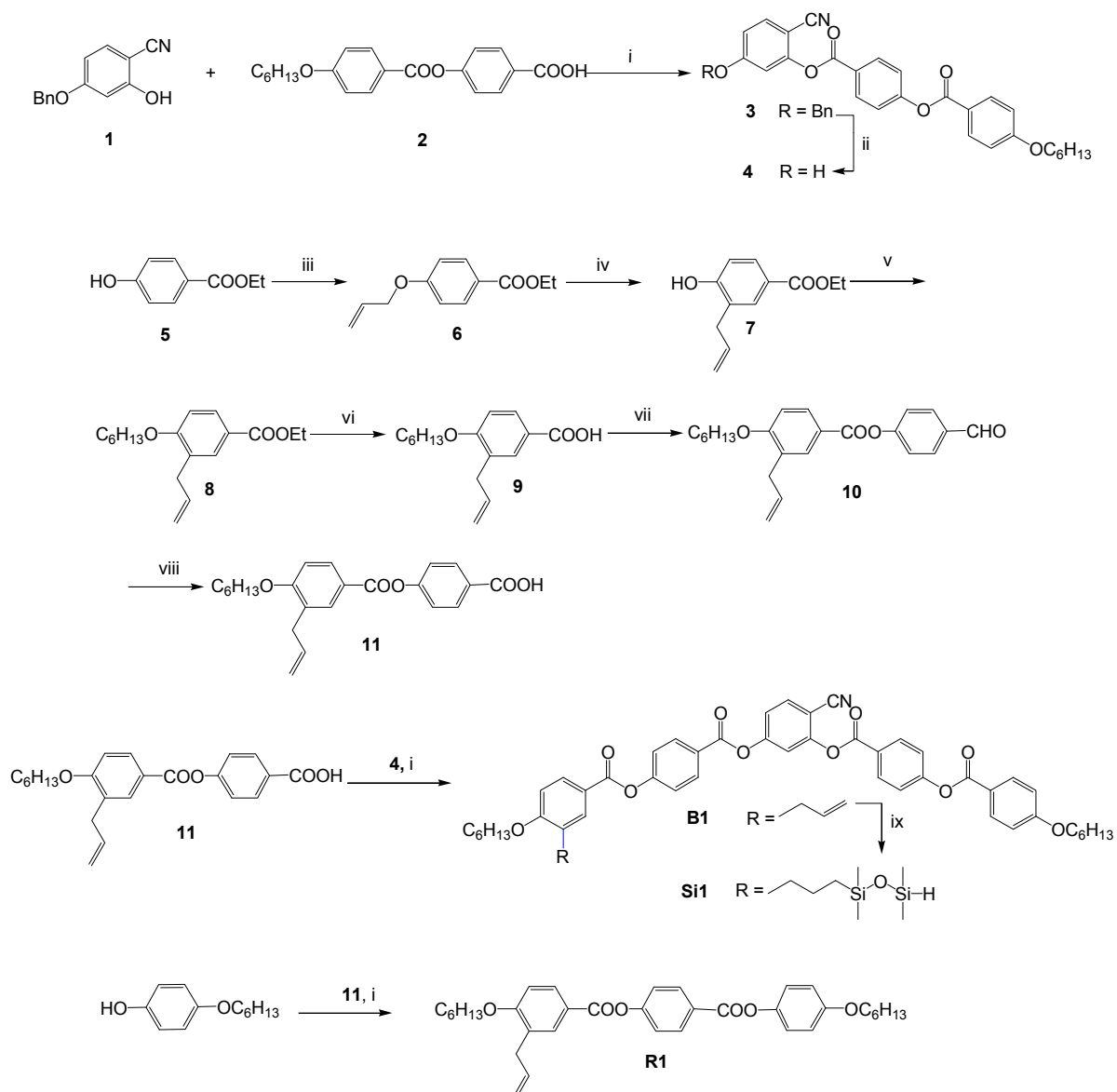
1. Syntheses and analytical data
2. Additional DSC and XRD data
3. Electro-optical investigations

#### 1. Syntheses and analytical data

Starting materials were obtained from Aldrich, Alfa Aesar, Fluka or ABCR companies and used as received. Solvents were purified and dried by standard methods prior to use. The crude samples were purified by column chromatographic technique using silica gel (230-400 mesh) as a stationary phase. Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). NMR spectra were recorded in CDCl<sub>3</sub> using a Bruker AMX-400 (400 MHz) / AMX-500 (500 MHz) spectrometer. All chemical shifts are reported in  $\delta$  (ppm) using TMS as an internal reference and  $J$  values are expressed in Hz.

##### 1.1 General

2,4-Dihydroxybenzaldehyde (Alfa Aesar) and 4-benzyloxy-2-hydroxybenzaldehyde (ABCR) were obtained from commercial sources and were used as received. 4-(4-*n*-alkylbenzoyloxy)benzoic acids<sup>S1</sup> were prepared according to reported standard procedures. Compounds **1** – **4** and **B1-B3** were synthesized as described in reference.<sup>S2</sup> The bent-core dimesogens (**BB1**, **BB2**) and bent-core-rod couples (**BR1-BR4**) were accomplished by the synthetic procedures shown in Scheme 2 of the main text and in Scheme S1.<sup>S3</sup>



**Scheme S1** . Synthesis of the bent-core based dimesogens and intermediates: Reagents and conditions: i) DCC, DMAP (catalytic),  $\text{CH}_2\text{Cl}_2$ , 4 h;<sup>S1</sup> ii) 10% Pd-C,  $\text{H}_2$  (2.7 bar), dry THF, 12 h;<sup>S3a</sup> iii) 3-bromo-propene, anhyd.  $\text{K}_2\text{CO}_3$ , butanone, reflux, 10 h;<sup>S2</sup> iv) 200 °C, neat, 1 h; v) *n*-bromohexane, anhyd.  $\text{K}_2\text{CO}_3$ , butanone, reflux, 10 h;<sup>S2</sup> vi) 10 % NaOH (aq), EtOH, reflux, 4 h;<sup>S3a</sup> vii) 4-hydroxy benzaldehyde, DCC, DMAP (catalytic),  $\text{CH}_2\text{Cl}_2$ , 20 °C, 4 h;<sup>S1</sup> viii) resorcinol,  $\text{NaClO}_2$ ,  $\text{NaH}_2\text{PO}_4$ ,  $\text{H}_2\text{O}$ , *tert*-butanol, 20 °C, 12 h;<sup>S3a</sup> ix) 1,1,3,3-tetramethyl disiloxane, Karstedt's catalyst, toluene, 20 °C, 12 h.<sup>S3a-d,f</sup>

## 1.2 Intermediates

**Ethyl 4-allyloxybenzoate (6):** Ethyl 4-hydroxybenzoate (**5**) (2.0 g, 12 mmol) was refluxed with 3-bromoprop-1-ene (1.6 g, 13.2 mmol) and  $\text{K}_2\text{CO}_3$  (3.3 g, 24.1 mmol) in dry butanone (20 mL) for 10 h and the crude product was filtered, butanone was evaporated followed by column chromatography (silica gel, 20% EtOAc/*n*-hexanes,  $R_f = 0.79$ ) to yield 6.1 g (24.24 mmol, 98%) of (**6**) as pale yellow liquid.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  7.96 (d, 2H,  $J = 2.0$ , Ar-H), 7.01 (d, 2H,  $J = 2.0$ , Ar-H), 6.05 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.44 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.64 (d, 2H,  $J = 2.0$ ,  $\text{OCH}_2-\text{CH}=\text{CH}_2$ ), 4.30 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 1.32 (t, 3H,  $J = 7.2$ ,  $\text{CH}_3$ ).

**Ethyl 3-allyl-4-hydroxybenzoate (7):** Neat compound (6) (3.0 g, 14.5 mmol) was heated to 200 °C for 1 h until TLC (20% EtOAc/*n*-hexane,  $R_f = 0.34$ ) confirmed complete reaction and then was subjected to the next step without further purification.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  7.97 (d, 2H,  $J = 8.4$ , Ar-H), 6.89 (d, 1H,  $J = 8.4$ , Ar-H), 6.01 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.15 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.32 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 3.42 (m, 2H,  $\text{CH}_2\text{-CH}=\text{CH}_2$ ), 1.35 (t, 3H,  $J = 6.8$ ,  $\text{CH}_3$ ).

**Ethyl 3-allyl-4-hexyloxybenzoate (8):** A mixture of (7) (3g, 14.5 mmol), *n*-bromohexane (2.6 g, 16 mmol) and  $\text{K}_2\text{CO}_3$  (4.0 g, 29.1 mmol) was refluxed in dry butanone for 10 h. Solids were filtered off and the solution was concentrated in vacuum, followed by column chromatography to yield 91% of compound as a yellow liquid (3.8 g, 13.1 mmol); TLC (20% EtOAc/*n*-hexane,  $R_f = 0.81$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  7.89 (d, 2H,  $J = 7.4$ , Ar-H), 6.82 (d, 1H,  $J = 8.8$ , Ar-H), 5.97 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.03 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.33 (m, 2H,  $\text{OCH}_2\text{CH}_3$ ), 4.01 (t, 2H,  $J = 6.4$ ,  $\text{OCH}_2$ ), 3.39 (m, 2H,  $\text{CH}_2\text{-CH}=\text{CH}_2$ ), 1.81 – 1.28 (m, 11H,  $\text{CH}_2 \times 4$ ,  $\text{CH}_3 \times 1$ ), 0.91 (t, 3H,  $J = 6.8$ ,  $\text{CH}_3$ ).

**3-Allyl-4-hexyloxybenzoic acid (9):** 10% aq NaOH (5 mL) was added to compound (8) (5 g, 17.2 mmol) in ethanol (40 mL) and refluxed for 4 h, the reaction mixture was concentrated followed by neutralization with 5% HCl till pH = 2. The white solid separated was filtered, dried and crystallized from EtOAc/EtOH (1:9) to obtain 94% of compound 9 (4.25 g, 16.2 mmol).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  7.95 (d, 2H,  $J = 6.8$ , Ar-H), 6.86 (d, 1H,  $J = 8.4$ , Ar-H), 5.96 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.09 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.00 (t, 2H,  $J = 6.4$ ,  $\text{OCH}_2$ ), 3.38 (m, 2H,  $\text{CH}_2\text{-CH}=\text{CH}$ ), 1.82 – 1.24 (m, 8H,  $\text{CH}_2 \times 4$ ), 0.92 (t, 3H,  $J = 6.8$ ,  $\text{CH}_3$ ).

**4-Formylphenyl 3-allyl-4-hexyloxybenzoate (10):** A mixture of compound (9) (0.5 g, 1.9 mmol), 4-hydroxybenzaldehyde (0.25 g, 2.0 mmol) and a catalytic amount DMAP were taken up in dry  $\text{CH}_2\text{Cl}_2$  (15 mL) and stirred for 5 min. To the above clear solution, DCC (0.59 g, 2.8 mmol) was added and the mixture was stirred for 4 h at room temperature, followed by solvent evaporation. The crude mass was then column chromatographed to obtained 85% of 10 (0.6g, 0.98 mmol); TLC (20% EtOAc/*n*-hexane  $R_f = 0.75$ ):  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  10.01 (s, 1H, CHO), 8.05 (d, 2H,  $J = 8.8$ , Ar-H), 7.96 (d, 2H,  $J = 2.0$ , Ar-H), 7.39 (d, 2H,  $J = 8.4$ , Ar-H), 6.91 (d, 1H,  $J = 8.8$ , Ar-H), 5.98 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.07 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.07 (t, 2H,  $J = 6.4$ ,  $\text{OCH}_2$ ), 3.43 (m, 2H,  $\text{CH}_2\text{-CH}=\text{CH}_2$ ), 1.86 – 1.24 (m, 8H,  $\text{CH}_2 \times 4$ ), 0.93 (t, 3H,  $J = 6.4$ ,  $\text{CH}_3$ ).

**4-(3-Allyl-4-hexyloxybenzoyloxy)benzoic acid (11):** Aldehyde (10) (0.5 g, 1.4 mmol), and resorcinol (0.21 g, 1.9 mmol) was dissolved in *tert*-butanol (15 mL). A mixture of  $\text{NaClO}_4$  (0.75 g, 8.3 mmol) and  $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$  (0.60 g, 4.3 mmol) dissolved in a min. quantity of water was added to the above clear *tert*-butanol solution and stirred at room temperature for 12 h. The reaction mixture was neutralized with 5% HCl till pH = 2 to get a white solid, which was filtered off and dried followed by crystallization from EtOAc and EtOH (1: 9) to afford pure compound 11 (0.41 g, 1.1 mmol ) in 79% yield; TLC (40% EtOAc/*n*-hexane  $R_f = 0.35$ ):  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.16 (d, 2H,  $J = 8.8$ , Ar-H), 7.97 (d, 2H,  $J = 2.0$ , Ar-H), 7.32 (d, 2H,  $J = 6.8$ , Ar-H), 6.91 (d, 1H,  $J = 8.8$ , Ar-H), 5.99 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.07 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.06 (t, 2H,  $J = 6.4$ ,  $\text{OCH}_2$ ), 3.43 (m, 2H,  $\text{CH}_2\text{-CH}=\text{CH}_2$ ), 1.86 – 1.24 (m, 8H,  $\text{CH}_2 \times 4$ ), 0.92 (t, 3H,  $J = 6.8$ ,  $\text{CH}_3$ ).

**4-(4-Hexyloxyphenoxy)phenyl 3-allyl-4-hexyloxybenzoate (R1):** A mixture of compound (11) (0.5 g, 1.3 mmol), 4-hexyloxyphenol (0.27 g, 1.3 mmol) and catalytic amount

of DMAP were taken up in dry  $\text{CH}_2\text{Cl}_2$  (20 mL) and stirred for 5 minutes. To the above clear solution DCC (0.40, 1.9 mmol) was added and stirring was continued for 4 h at room temperature followed by solvent evaporation and column chromatography (20% EtOAc/n-hexanes  $R_f = 0.78$ ) to obtain (**R1**) in 80% yield:  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.25 (d, 2H,  $J = 8.4$ , Ar-H), 8.06 (d, 1H,  $J = 8.4$ , Ar-H), 7.97 (d, 1H,  $J = 2.4$ , Ar-H), 7.35 (d, 2H,  $J = 8.4$ , Ar-H), 7.11 (d, 2H,  $J = 8.8$ , Ar-H), 6.92 (m, 3H, Ar-H), 5.98 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.08 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.06 (t, 2H,  $J = 6.4$ ,  $\text{OCH}_2$ ), 3.95 (t, 2H,  $J = 6.4$ ,  $\text{OCH}_2$ ), 3.44 (m, 2H,  $\text{CH}_2\text{-CH}=\text{CH}_2$ ), 1.87 – 1.24 (m, 16H,  $\text{CH}_2 \times 8$ ), 0.92 (m, 6H,  $\text{CH}_3 \times 2$ ).

**B1**<sup>S2</sup>: Colorless solid (79 %);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.32 (d, 2H,  $J = 8.8$ , Ar-H), 8.26 (d, 2H,  $J = 8.8$ , Ar-H), 8.15 (d, 2H,  $J = 8.4$ , Ar-H), 8.1 (d, 1H,  $J = 8.0$ , Ar-H), 7.90 (d, 1H,  $J = 2.0$ , Ar-H), 7.70 (d, 1H,  $J = 8.4$ , Ar-H), 7.50 (d, 1H,  $J = 2.0$ , Ar-H), 7.40 (m, 4H, Ar-H), 7.30 (d, 1H,  $J = 2.4$ , Ar-H), 7.0 (d, 2H,  $J = 8.8$ , Ar-H), 6.9 (d, 1H,  $J = 8.6$ , Ar-H), 5.98 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.17 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.07 (t, 4H,  $J = 6.4$ ,  $\text{OCH}_2 \times 2$ ), 3.40 (d, 2H,  $J = 6.8$ ,  $\text{CH}_2\text{-CH}=\text{CH}_2$ ), 1.85 – 1.24 (m, 16H,  $\text{CH}_2 \times 8$ ), 0.93 (t, 6H,  $J = 7.2$ ,  $\text{CH}_3 \times 2$ ); EA, calc. for  $\text{C}_{50}\text{H}_{49}\text{O}_{10}\text{N}$ , 823.92 g/mol.; C 72.89, H 5.99, N 1.70, found: 72.64, 5.70, 1.67.

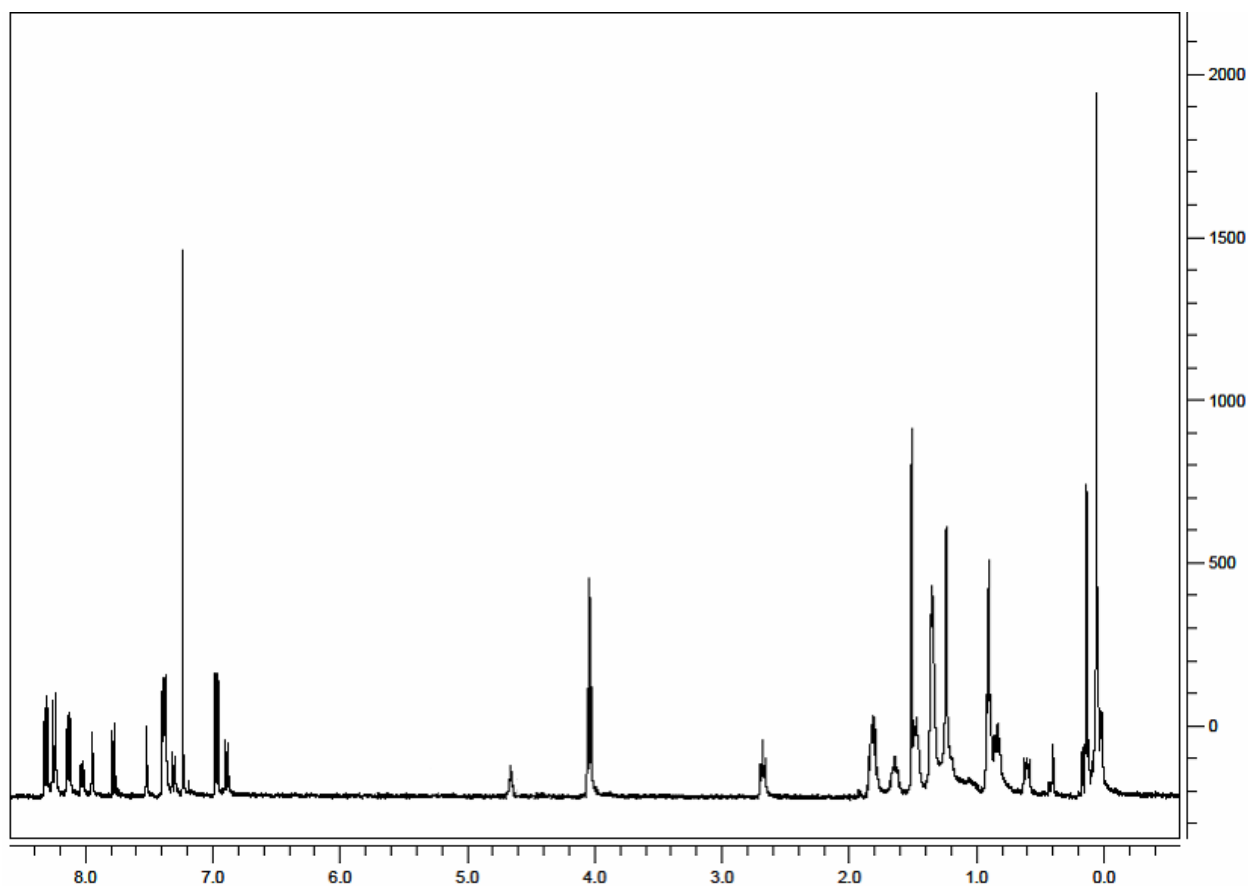
**B2**<sup>S1</sup>: Colorless solid (61%);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.32 (d, 2H,  $J = 8.8$ , Ar-H), 8.26 (d, 2H,  $J = 8.6$ , Ar-H), 8.14 (q, 4H,  $J = 2.0$ ,  $J = 8.1$ , Ar-H), 7.78 (d, 1H,  $J = 8.4$ , Ar-H), 7.52 (d, 1H,  $J = 2.0$ , Ar-H), 7.39 – 7.36 (m, 4H, Ar-H), 7.32 (dd, 1H,  $J = 2.0$ ,  $J = 2.4$ , Ar-H), 6.96 (d, 4H,  $J = 8.8$ , Ar-H), 5.87 (m, 1H,  $\text{CH}=\text{CH}_2$ ), 5.07 (m, 2H,  $\text{CH}=\text{CH}_2$ ), 4.06 (t, 4H,  $J = 6.4$ ,  $\text{OCH}_2 \times 2$ ), 1.82 – 1.30 (m, 24H,  $\text{CH}_2 \times 12$ ), 0.92 (t, 3H,  $J = 6.8$ ,  $\text{CH}_3$ ); EA, calc. for  $\text{C}_{52}\text{H}_{53}\text{O}_{10}\text{N}$ , 851.98 g/mol.; C 73.31, H 6.27, N 1.64, found: 73.34, 6.34, 1.44.

### 1.3 General procedure for the synthesis of bent-core dimesogens (**BB1** and **BB2**) and bent-core rod couples (**BR1-BR4**)<sup>S3</sup>

The appropriate olefin (**B1/B2/B3**, 1 equiv.) was dissolved in dry toluene (4 mL) under argon atmosphere, to this solution tetramethyl disiloxane ( $\text{HMe}_2\text{SiOMe}_2\text{SiH}$ ) (2 equiv.) and two drops of Karstedt's catalyst (in xylene, 2% Pt) were added and the mixture was stirred at room temperature for 12 h. The solvent was evaporated and the crude product was purified by flash chromatography, the intermediates **Si1-Si3** (see Schemes 2 and S1) were isolated and further subjected for next step reactions immediately.

Intermediates (**Si1 / Si2 / Si3**) dissolved in dry toluene (4 mL) under an argon atmosphere, the appropriate olefin **B1**, **B2**, **B3**, **R1** or **R2** (1 equiv.), 2 drops of Karstedt's catalyst were added and the solution was stirred at room temperature for 12 h. The solvent was evaporated and the crude product was purified by chromatography on silica gel using dry  $\text{CH}_2\text{Cl}_2$  as eluent.

**Si1**<sup>S3a-d</sup>: Soft solid, (90 %),  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.32 (d, 2H,  $J = 8.8$ , Ar-H), 8.25 (d, 2H,  $J = 8.8$ , Ar-H), 8.15 (d, 2H,  $J = 2.0$ , Ar-H), 8.12 (d, 1H,  $J = 2.0$ , Ar-H), 8.04 (d, 1H,  $J = 8.4$ , Ar-H), 7.94 (d, 1H,  $J = 8.4$ , Ar-H), 7.52 (d, 1H,  $J = 2.0$ , Ar-H), 7.39 (m, 4H, Ar-H), 7.37 (d, 1H,  $J = 2.4$ , Ar-H), 6.98 (d, 2H,  $J = 8.8$ , Ar-H), 6.90 (d, 1H,  $J = 8.8$ , Ar-H), 4.66 (m, 1H, SiH), 4.01 (t, 4H,  $J = 6.4$ ,  $\text{OCH}_2 \times 2$ ), 2.70 (t, 2H,  $J = 6.8$ ,  $\text{CH}_2$ ), 1.85 – 1.06 (m, 18H,  $\text{CH}_2 \times 9$ ), 0.93 (t, 6H,  $J = 6.8$ ,  $\text{CH}_3 \times 2$ ), 0.39 (m, 2H,  $\text{SiCH}_2$ ), 0.06 (m, 12H,  $\text{SiCH}_3 \times 4$ ).



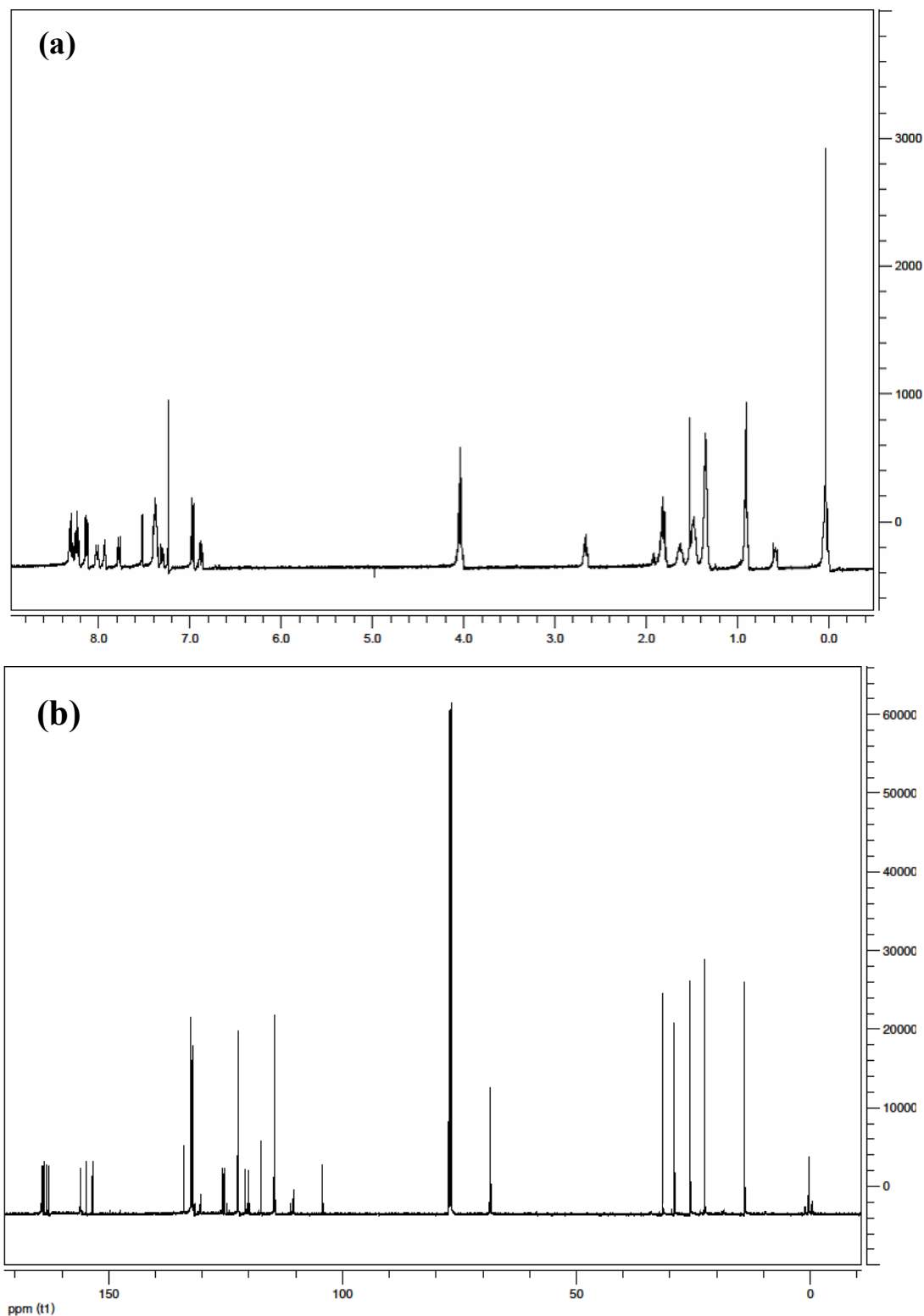
**Figure S1:**  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400 MHz) of compound **Si1**.

**Si2**<sup>S3a-d</sup>: Soft solid (90 %);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.34 (d, 2H,  $J = 8.7$ , Ar-H), 8.26 (d, 2H,  $J = 8.8$ , Ar-H), 8.13 (d, 2H,  $J = 2.0$ , Ar-H), 8.14 (d, 1H,  $J = 2.0$ , Ar-H), 8.11 (d, 2H,  $J = 8.9$ , Ar-H), 8.01 (d, 1H,  $J = 8.8$ , Ar-H), 7.80 (d, 1H,  $J = 8.6$ , Ar-H), 7.43 (m, 4H, Ar-H), 7.01 (d, 2H,  $J = 8.8$ , Ar-H), 6.92 (d, 2H,  $J = 8.6$ , Ar-H), 4.67 (m, 1H, SiH), 4.05 (t, 4H,  $J = 6.7$ ,  $\text{OCH}_2 \times 2$ ), 2.02 – 1.21 (m, 26H,  $\text{CH}_2 \times 13$ ), 0.93 (t, 3H, t,  $J = 6.7$ ,  $\text{CH}_3$ ), 0.41 (m, 2H,  $\text{SiCH}_2$ ), 0.02 (m, 12H,  $\text{SiCH}_3 \times 4$ ).

**Si3**<sup>S3a-d</sup>: Soft solid (89 %);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.32 (d, 2H,  $J = 8.8$ , Ar-H), 8.25 (d, 2H,  $J = 8.8$ , Ar-H), 8.14 (d, 2H,  $J = 2.0$ , Ar-H), 8.12 (d, 1H,  $J = 2.0$ , Ar-H), 8.10 (d, 2H,  $J = 8.8$ , Ar-H), 8.03 (d, 1H,  $J = 8.8$ , Ar-H), 7.79 (d, 1H,  $J = 8.4$ , Ar-H), 7.40 (m, 4H, Ar-H), 6.98 (d, 2H,  $J = 8.8$ , Ar-H), 6.89 (d, 2H,  $J = 8.8$ , Ar-H), 4.64 (m, 1H, SiH), 4.06 (t, 4H,  $J = 6.8$ ,  $\text{OCH}_2 \times 2$ ), 2.03 – 1.24 (m, 26H,  $\text{CH}_2 \times 13$ ), 0.92 (t, 3H, t,  $J = 6.8$ ,  $\text{CH}_3$ ), 0.40 (m, 2H,  $\text{SiCH}_2$ ), 0.03 (m, 12H,  $\text{SiCH}_3 \times 4$ ).

**BB1**<sup>S3a-d</sup>: Colorless solid (62%);  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 400MHz):  $\delta$  8.32 (d, 4H,  $J = 8.0$ , Ar-H), 8.26 (d, 4H,  $J = 8.8$ , Ar-H), 8.12 (d, 4H,  $J = 8.4$ , Ar-H), 8.0 (d, 2H,  $J = 8.0$ , Ar-H), 7.93 (d, 2H,  $J = 2.0$ , Ar-H), 7.78 (d, 2H,  $J = 8.0$ , Ar-H), 7.52 (d, 2H,  $J = 2.0$ , Ar-H), 7.39-7.38 (m, 8H, Ar-H), 7.31 (d, 2H,  $J = 2.4$ , Ar-H), 6.98 (d, 4H,  $J = 8.0$ , Ar-H), 6.88 (d, 2H,  $J = 8.0$ , Ar-H), 4.04 (t, 8H,  $J = 8.0$ ,  $\text{OCH}_2 \times 4$ ), 2.65 (m, 4H,  $\text{CH}_2 \times 2$ ), 1.82 – 1.23 (m, 36H,  $\text{CH}_2 \times 18$ ), 0.93 (t, 12H,  $J = 8.0$ ,  $\text{CH}_3 \times 4$ ), 0.60 (m, 4H,  $\text{SiCH}_2 \times 2$ ), 0.03 (m, 12H,  $\text{SiCH}_3 \times 4$ );  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 125MHz):  $\delta$  164.46, 164.19, 164.15, 163.88, 163.85, 163.27, 162.88, 161.79, 160.93, 160.11, 156.04, 155.90, 154.77, 153.46, 133.93, 132.43, 132.42, 132.23, 132.06, 131.98, 131.85, 131.59, 130.52, 130.30, 128.72, 128.04, 127.46, 125.69, 125.30, 124.69,

122.37, 122.32, 122.21, 122.18, 120.84, 120.79, 120.25, 120.19, 119.98, 120.01, 117.38, 114.76, 114.44, 114.42, 111.19, 110.50, 104.23, 68.65, 68.39, 68.38, 68.20, 34.03, 31.51, 29.10, 29.02, 25.75, 25.70, 25.62, 23.52, 22.55, 18.92, 18.53, 18.40, 13.99, 1.16, 1.04, 0.34.



**Figure S2:** (a) <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400 MHz) and (b) <sup>13</sup>C-NMR (CDCl<sub>3</sub>, 125 MHz) of dimer **BB1**.

**BB2**<sup>S3a-d</sup>: Colorless solid (60 %); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 8.31 (d, 4H, *J* = 8.8, Ar-H), 8.25 (d, 4H, *J* = 8.4, Ar-H), 8.14 (d, 4H, *J* = 2.0, Ar-H), 8.12 (d, 2H, *J* = 2.4, Ar-H), 8.01 (d, 2H, *J* = 8.4, Ar-H), 7.79 (d, 2H, *J* = 8.0, Ar-H), 7.52 (d, 1H, *J* = 2.0, Ar-H), 7.40-7.365 (m, 8H, Ar-H), 7.32 (d, 2H, *J* = 2.4, Ar-H), 6.98 (d, 4H, *J* = 8.0, Ar-H), 6.88 (d, 4H, *J* = 8.0, Ar-H), 4.04 (t, 8H, *J* = 6.8, OCH<sub>2</sub> × 4), 2.58 (m, 2H, CH<sub>2</sub>), 1.83 – 1.34 (m, 44H, CH<sub>2</sub> × 22), 0.92 (t, 9H, *J* = 6.8, CH<sub>3</sub> × 3), 0.60 (m, 4H, SiCH<sub>2</sub> × 2), 0.02 (m, 12H, SiCH<sub>3</sub> × 4).

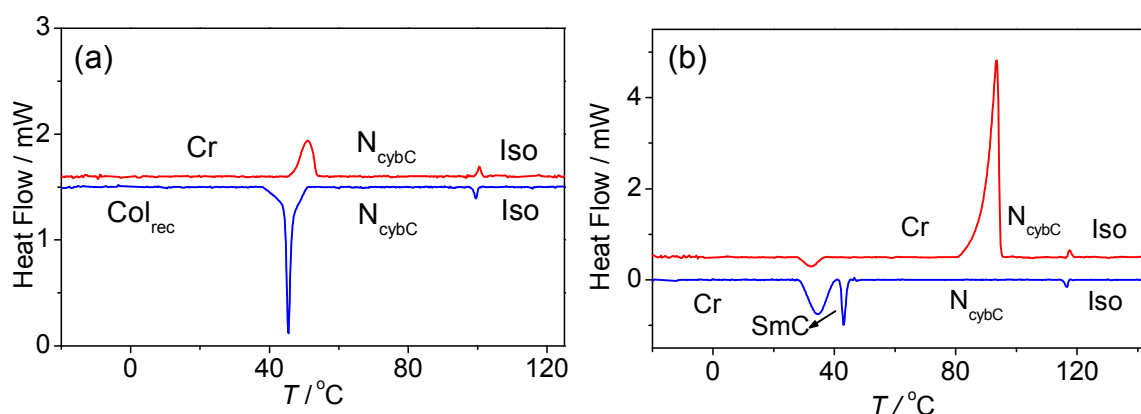
**BR1**<sup>S3a-d</sup>: Colorless solid (58 %); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 8.33 (d, 4H, *J* = 8.4, Ar-H), 8.28 (d, 4H, *J* = 9.0, Ar-H), 8.14 (d, 4H, *J* = 2.0, Ar-H), 8.12 (d, 2H, *J* = 2.4, Ar-H), 8.03 (d, 2H, *J* = 2.0, Ar-H), 7.79 (d, 2H, *J* = 2.0, Ar-H), 7.52 (d, 1H, *J* = 2.4, Ar-H), 7.39-6.89 (m, 10H, Ar-H), 4.06 (m, 8H, OCH<sub>2</sub> × 4), 2.68 (m, 4H, CH<sub>2</sub> × 2), 1.81 – 1.24 (m, 36H, CH<sub>2</sub> × 18), 0.90 (m, 12H, CH<sub>3</sub> × 4), 0.62 (m, 4H, SiCH<sub>2</sub> × 2), 0.03 (m, 12H, SiCH<sub>3</sub> × 4).

**BR2**<sup>S3a-d</sup>: Colorless solid (59 %); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 8.34 (d, 4H, *J* = 8.4, Ar-H), 8.25 (d, 4H, *J* = 8.0, Ar-H), 8.15 (d, 4H, *J* = 2.0, Ar-H), 8.12 (d, 2H, *J* = 2.4, Ar-H), 8.03 (d, 2H, *J* = 1.6, Ar-H), 7.94 (d, 1H, *J* = 2.4, Ar-H), 7.53 (d, 2H, *J* = 2.4, Ar-H), 7.40-7.30 (m, 4H, Ar-H), 6.98 – 6.86 (m, 7H, Ar-H), 4.04 (m, 8H, OCH<sub>2</sub> × 4), 2.67 (m, 2H, CH<sub>2</sub>), 1.83 – 1.23 (m, 44H, CH<sub>2</sub> × 22), 0.92 (t, 9H, *J* = 6.8, CH<sub>3</sub> × 3), 0.47 (m, 4H, SiCH<sub>2</sub> × 2), 0.03 (m, 12H, SiCH<sub>3</sub> × 4).

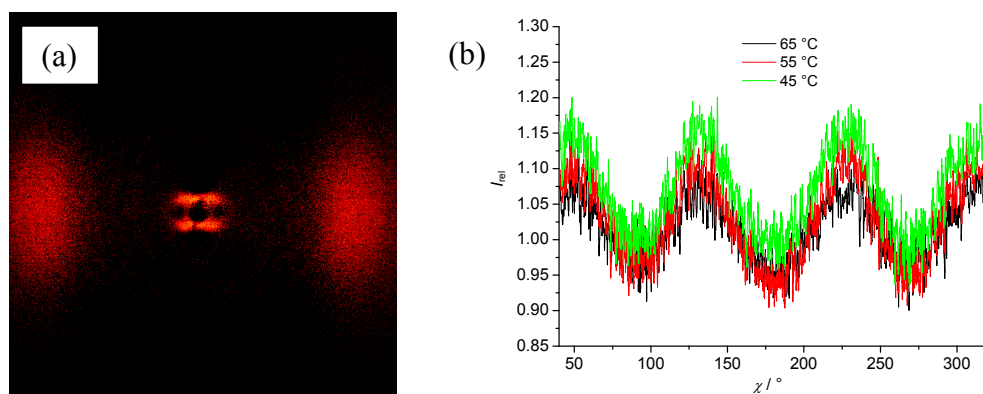
**BR3**<sup>S3a-d</sup>: Colorless solid (48 %); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 8.25 (d, 4H, *J* = 8.2, Ar-H), 8.14 (d, 4H, *J* = 8.8, Ar-H), 8.01- 7.83 (m, 6H, Ar-H), 7.52 (m, 1H, Ar-H), 7.43 (m, 1H, Ar-H), 7.41 – 7.28 (m, 10H, Ar-H), 7.02 – 6.96 (m, 4H, Ar-H), 6.89 (d, 1H, *J* = 8.6, Ar-H), 4.04 (m, 10H, OCH<sub>2</sub> × 5), 2.67 (m, 2H, CH<sub>2</sub>), 1.82 – 1.15 (m, 52H, CH<sub>2</sub> × 26), 0.92 (m, 12H, CH<sub>3</sub> × 4), 0.39 (m, 4H, SiCH<sub>2</sub> × 2), 0.03 (m, 12H, SiCH<sub>3</sub> × 4).

**BR4**<sup>S3a-d</sup>: Colorless solid (49 %); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 400MHz): δ 8.25 (d, 4H, *J* = 8.0, Ar-H), 8.14 (d, 4H, *J* = 8.4, Ar-H), 8.16- 7.83 (m, 6H, Ar-H), 7.50 (m, 1H, Ar-H), 7.49 – 7.25 (m, 12H, Ar-H), 7.01 – 6.94 (m, 4H, Ar-H), 6.89 (d, 1H, *J* = 8.6, Ar-H), 4.08 (m, 10H, OCH<sub>2</sub> × 5), 1.83 – 1.24 (m, 60H, CH<sub>2</sub> × 30), 0.91 (m, 9H, CH<sub>3</sub> × 3), 0.49 (m, 4H, SiCH<sub>2</sub> × 2), 0.01 (m, 12H, SiCH<sub>3</sub> × 4).

## 2. Additional DSC and XRD data



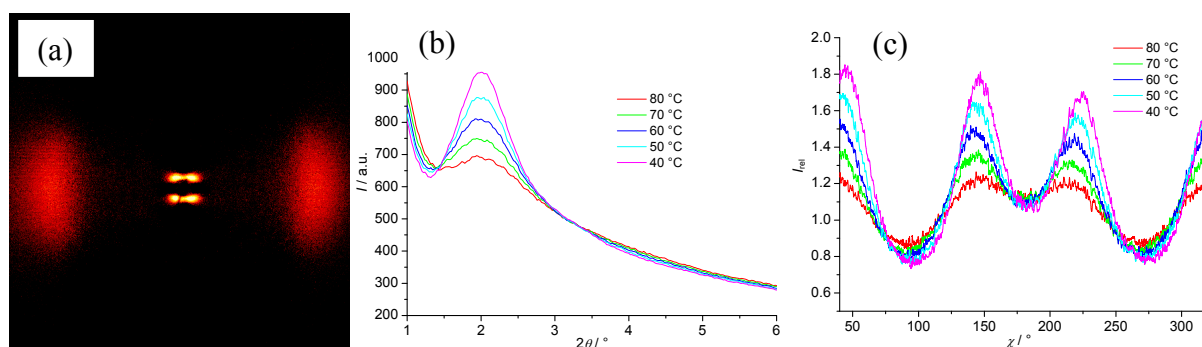
**Figure S3.** DSC thermograms obtained during second heating and cooling traces scanned at a rate of 10 Kmin<sup>-1</sup> of (a) **BR2** and (b) **BB2**.



**Figure S4.** X-ray diffraction patterns of an oriented samples of compound **BR1** under a magnetic field; (a)  $N_{\text{cybC}}$  phase at 45 °C (shows the pattern after subtraction of the scattering in the isotropic liquid state  $T = 80$  °C); (b)  $\chi$ -scans over the diffused small angle scattering (for  $2\theta = 1.5\text{--}4.^\circ$ ) at 65, 55 and 45 °C,  $I_{\text{rel}} = I(T)/I(80^\circ\text{C, Iso})$ .

**Table S1** Crystallographic data of dimer **BR1**

$T / ^\circ\text{C}$	Small angle scattering			Wide angle scattering	
	$\theta / ^\circ$	d/nm	$\Delta\chi/2 / ^\circ$	$\theta / ^\circ$	d/nm
65	1.40	3.16	50	9.41	0.47
55	1.42	3.12	50	9.46	0.47
45	1.43	3.10	49	9.51	0.47



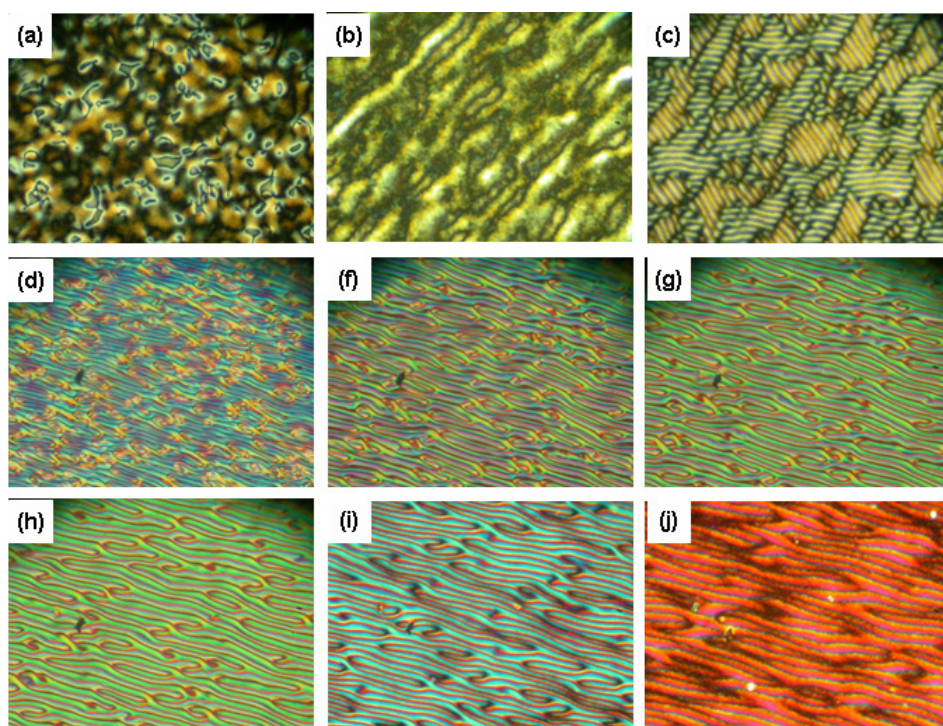
**Figure S5.** X-ray diffraction patterns of an oriented samples of compound **BR4** under a magnetic field; (a)  $N_{\text{cybC}}$  phase at 60 °C (shows the pattern after subtraction of the scattering in the isotropic liquid state  $T = 90$  °C); (b)  $\theta$ -scans of the  $N_{\text{cybC}}$  phase in the small angle region at different temperatures; (c)  $\chi$ -scans over the diffused small angle scattering (for  $2\theta = 1\text{--}3^\circ$ ) between 80 – 40 °C,  $I_{\text{rel}} = I(T)/I(90^\circ\text{C, Iso})$ .

**Table S2** Crystallographic data of dimer **BR4**

$T / ^\circ\text{C}$	Small angle scattering			Wide angle scattering	
	$\theta / ^\circ$	d/nm	$\Delta\chi/2 / ^\circ$	$\theta / ^\circ$	d/nm
80	1.07	4.14	35	9.51	0.47
70	1.03	4.29	37	9.58	0.46
60	0.99	4.47	38	9.61	0.46
50	1.00	4.43	38	9.65	0.46
40	1.00	4.41	39	9.74	0.46



### 3. Electro-optical investigations



**Figure S6:** Electrohydrodynamic instabilities as seen for the nematic phase of bent-core rod couple **BR2** (a) 2 Vpp, 10 Hz, 50 °C; (b) 100 Vpp, 10 Hz, 50 °C; (c) 180 Vpp, 10 Hz, 50 °C; (d) 190 Vpp, 10 Hz, 50 °C; (e) 200 Vpp, 10 Hz, 55 °C; (f) 200 Vpp, 10 Hz, 60 °C; (g) 200 Vpp, 10 Hz, 65 °C; (h) 200 Vpp, 10 Hz, 75 °C; (i) 200 Vpp, 10 Hz, 75 °C; (j) 200 Vpp, 10 Hz, 85 °C

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