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

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 CDCl₃ using a Bruker AMX-400 (400 MHz) / AMX-500 (500 MHz) spectrometer. All chemical shifts are reported in δ (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 acidsS¹ were prepared according to reported standard procedures. Compounds 1 – 4 and B1-B3 were synthesized as described in reference.² 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 S1.³
Scheme S1. Synthesis of the bent-core based dimesogens and intermediates: Reagents and conditions: i) DCC, DMAP (catalytic), CH2Cl2, 4 h; ii) 10% Pd-C, H2 (2.7 bar), dry THF, 12 h;  iii) 3-bromo-propene, anhyd. K2CO3, butanone, reflux, 10 h; iv) 200 °C, neat, 1 h; v) n-bromohexane, anhyd. K2CO3, butanone, reflux, 10 h; vi) 10 % NaOH (aq), EtOH, reflux, 4 h; vii) 4-hydroxy benzaldehyde, DCC, DMAP (catalytic), CH2Cl2, 20 °C, 4 h; viii) resorcinol, NaClO2, NaH2PO4, H2O, tert-butanol, 20 °C, 12 h; ix) 1,1,3,3-tetramethyl disiloxane, Karstedt's catalyst, toluene, 20 °C, 12 h.

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 K2CO3 (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, Rf = 0.79) to yield 6.1 g (24.24 mmol, 98%) of (6) as pale yellow liquid. 1H-NMR (CDCl3, 400MHz): δ 7.96 (d, 2H, J = 2.0, Ar-H), 7.01 (d, 2H, J = 2.0, Ar-H), 6.05 (m, 1H, CH=CH2), 5.44 (m, 2H, CH=CH2), 4.64 (d, 2H, J = 2.0, OCH2-CH=CH2 ), 4.30 (m, 2H, OCH2CH3), 1.32 (t, 3H, J = 7.2, CH3).
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, Rf = 0.34) confirmed complete reaction and then was subjected to the next step without further purification. \(^1\)H-NMR (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, O\(\text{CH}_2\)\(\text{CH}_3\)), 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 K\(_2\)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, \(R_f = 0.81\)). \(^1\)H-NMR (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, O\(\text{CH}_2\)\(\text{CH}_3\)), 4.01 (t, 2H, \(J = 6.4\), O\(\text{CH}_2\)), 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 (4.25 g, 16.2 mmol). \(^1\)H-NMR (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, \(J = 6.4\), O\(\text{CH}_2\)), 3.38 (m, 2H, \(\text{CH}_2\)-\(\text{CH} = \text{CH}_2\)), 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 CH\(_2\)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, \(R_f = 0.75\)). \(^1\)H-NMR (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, \(J = 6.4\), O\(\text{CH}_2\)), 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 NaClO\(_4\) (0.75 g, 8.3 mmol) and NaH\(_2\)PO\(_4\)\(-\)H\(_2\)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 (0.41 g, 1.1 mmol) in 79% yield; TLC (40% EtOAc/n-hexane, \(R_f = 0.35\)): \(^1\)H-NMR (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, \(J = 6.4\), O\(\text{CH}_2\)), 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-Hexyloxyphenoxycarbonyl)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 CH₂Cl₂ (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 Rf = 0.78) to obtain (R1) in 80% yield: ¹H-NMR (CDCl₃, 400MHz): δ 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, CH=CH₂), 5.08 (m, 2H, CH=C₃H₂), 4.06 (t, 2H, J = 6.4, OCH₂), 3.95 (t, 2H, J = 6.4, OCH₂), 3.44 (m, 2H, C₂H₂-CH=CH₂), 1.87 – 1.24 (m, 16H, CH₂ × 8), 0.92 (m, 6H, CH₃× 2).

**B1**: Colorless solid (79 %); ¹H-NMR (CDCl₃, 400MHz): δ 8.32 (d, 2H, J = 8.8, Ar-H), 8.26 (d, 2H, J = 8.8, Ar-H), 8.14 (q, 4H, J = 2.0, 8.1, Ar-H), 7.88 (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), 5.16 (m, 2H, CH=C₃H₂), 4.07 (t, 4H, J = 6.4, OCH₂ × 2), 1.82 – 1.30 (m, 24H, CH₂ × 12), 0.92 (t, 3H, J = 6.8, CH₃); EA, calc. for C₅₀H₄₉O₁₀N, 823.92 g/mol:, C 72.89, H 5.99, N 1.70, found: 72.64, 5.70, 1.67.

**B2**: Colorless solid (61%); ¹H-NMR (CDCl₃, 400MHz): δ 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), 5.87 (m, 1H, CH=CH₂), 5.07 (m, 2H, CH=C₃H₂), 4.06 (t, 4H, J = 6.4, OCH₂ × 2), 1.82 – 1.30 (m, 24H, CH₂ × 12), 0.92 (t, 3H, J = 6.8, CH₃); EA, calc. for C₅₂H₅₃O₁₀N, 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)

The appropriate olefin (B1/B2/B3, 1 equiv.) was dissolved in dry toluene (4 mL) under argon atmosphere, to this solution tetramethyl disiloxane (HMe₂SiOMe₂SiH) (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 CH₂Cl₂ as eluent.

Si₁-Si₃: Soft solid, (90 %); ¹H-NMR (CDCl₃, 400MHz): δ 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, OCH₂ × 2), 2.70 (t, 2H, J = 6.8, CH₂), 1.85 – 1.06 (m, 18H, CH₂ × 9), 0.93 (t, 6H, J = 6.8, CH₃ × 2), 0.39 (m, 2H, SiCH₂), 0.06 (m, 12H, SiCH₃ × 4).
Figure S1: $^1$H-NMR (CDCl$_3$, 400 MHz) of compound Si1.

Si$_2$$^{3a-d}$: Soft solid (90%); $^1$H-NMR (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, $J = 6.7$, OCH$_2 \times 2$), , 2.02 – 1.21 (m, 26H, CH$_2 \times 13$), 0.93 (t, 3H, $J = 6.7$, CH$_3$), 0.41 (m, 2H, SiCH$_2$), 0.02 (m, 12H, SiCH$_3 \times 4$).

Si$_3$$^{3a-d}$: Soft solid (89%); $^1$H-NMR (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, $J = 6.8$, OCH$_2 \times 2$), , 2.03 – 1.24 (m, 26H, CH$_2 \times 13$), 0.92 (t, 3H, $J = 6.8$, CH$_3$), 0.40 (m, 2H, SiCH$_2$), 0.03 (m, 12H, SiCH$_3 \times 4$).

BB$_1$$^{3a-d}$: Colorless solid (62%); $^1$H-NMR (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, $J = 8.0$, OCH$_2 \times 4$), 2.65 (m, 4H, CH$_2 \times 2$), 1.82 – 1.23 (m, 36H, CH$_2 \times 18$), 0.93 (t, 12H, $J = 8.0$, CH$_3 \times 4$), 0.60 (m, 4H, SiCH$_2 \times 2$), 0.03 (m, 12H, SiCH$_3 \times 4$); $^{13}$C-NMR (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) $^1$H-NMR (CDCl$_3$, 400 MHz) and (b) $^{13}$C-NMR (CDCl$_3$, 125 MHz) of dimer BB1.
BB2S3a-d: Colorless solid (60 %); ¹H-NMR (CDCl₃, 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 = 2.4, Ar-H), 3.58 (m, 2H, CH₂), 1.83 – 1.34 (m, 44H, CH₂× 22), 0.92 (t, 9H, J = 6.8, CH₃ × 3), 0.60 (m, 4H, SiCH₂ × 2), 0.02 (m, 12H, SiCH₃ × 4).

BR1S3a-d: Colorless solid (58 %); ¹H-NMR (CDCl₃, 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 = 1.6, Ar-H), 7.94 (d, 2H, J = 2.4, Ar-H), 7.53 (d, 1H, J = 2.4, Ar-H), 7.40-7.30 (m, 10H, Ar-H), 4.06 (m, 8H, OCH₂ × 4), 2.68 (m, 2H, CH₂), 1.81 – 1.24 (m, 36H, CH₂× 18), 0.90 (m, 12H, CH₃ × 4), 0.62 (m, 4H, SiCH₂ × 2), 0.03 (m, 12H, SiCH₃ × 4).

BR2S3a-d: Colorless solid (59 %); ¹H-NMR (CDCl₃, 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, 1H, J = 2.4, Ar-H), 7.40-7.30 (m, 4H, Ar-H), 6.98 – 6.86 (m, 7H, Ar-H), 4.04 (m, 10H, OCH₂ × 5), 2.67 (m, 2H, CH₂), 1.83 – 1.23 (m, 44H, CH₂× 22), 0.92 (t, 9H, J = 6.8, CH₃ × 3), 0.47 (m, 4H, SiCH₂ × 2), 0.03 (m, 12H, SiCH₃ × 4).

BR3S3a-d: Colorless solid (48 %); ¹H-NMR (CDCl₃, 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, OCH₂ × 5), 2.67 (m, 2H, CH₂), 1.82 – 1.15 (m, 52H, CH₂× 26), 0.92 (m, 12H, CH₃ × 4), 0.39 (m, 4H, SiCH₂ × 2), 0.03 (m, 12H, SiCH₃ × 4).

BR4S3a-d: Colorless solid (49 %); ¹H-NMR (CDCl₃, 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, OCH₂ × 5), 1.83 – 1.24 (m, 60H, CH₂× 30), 0.91 (m, 9H, CH₃ × 3), 0.49 (m, 4H, SiCH₂ × 2), 0.01 (m, 12H, SiCH₃ × 4).

2. Additional DSC and XRD data

![Figure S3](image-url)
Figure S4. X-ray diffraction patterns of an oriented samples of compound BR1 under a magnetic field; (a) N_{cybC} phase at 45 °C (shows the pattern after subtraction of the scattering in the isotropic liquid state T = 80 °C); (b) χ-scans over the diffused small angle scattering (for 2θ = 1.5-4.°) at 65, 55 and 45 °C, I_{rel} = I(T)/I(80 °C, Iso).

Table S1 Crystallographic data of dimer BR1

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

Table S2 Crystallographic data of dimer BR4

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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

References