Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Fine-tuning effect of π–π Interactions on the stability of the N_{TB} phase

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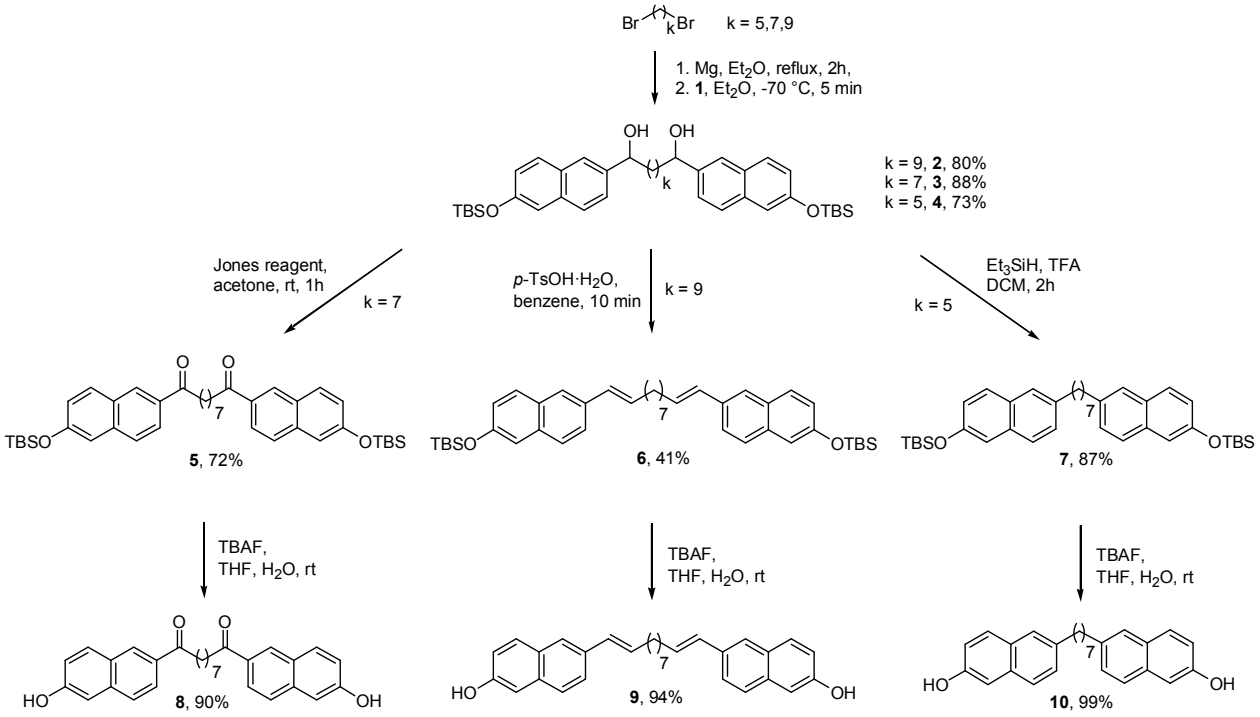
1. General Information

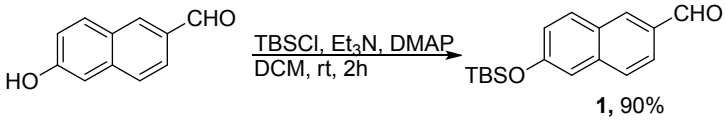
All the solvents were either *puriss p.a.* quality or distilled over appropriate drying reagents. Reagents were used directly as supplied by Aldrich, Alfa Aesar or Acros. Flash column chromatography was carried out using silica gel (Merck, 40−63 μm particle size). Analytical thin-layer chromatography was carried out on Fluka Kieselgel 60 F_{254} 0.25 mm precoated aluminium plates. Visualization was carried out under ultra-violet irradiation (254 nm). NMR spectra were recorded on Bruker AV 600 MHz and 300 MHz spectrometers, operating at 150.92 or 75.47 MHz for ^{13}C and 600.13 or 300.13 MHz for ^{1}H nuclei. Chemical shifts are quoted in ppm, and are referenced to $SiMe_4$ as internal standard unless stated otherwise. Multiplets are abbreviated as follows: br – *broad*; s – *singlet*; d – *doublet*; t – *triplet*; q – *quartet*; m – *multiplet*. CHN analyses were done on Perkin Elmer 2400 Series II CHNS analyser. Phase transition temperatures and textures were determined using an Olympus BX51 polarizing microscope equipped with a Linkam TH600 hot stage and PR600 temperature controller. Enthalpies of transition were determined from thermograms recorded on Perkin-Elmer Diamond DSC, operated at scanning rates of 5 °C min^{-1}.

2. Synthesis of 6,6'-alkyl-bis(naphthalen-2-ol)s (8-10)

Scheme 1



2.1. 6-((*tert*-Butyldimethylsilyl)oxy)-2-naphthaldehyde (1)



To a solution of 6-hydroxy-2-naphthaldehyde (2.06 g, 12 mmol, 1 equiv) in DCM (40 mL) *tert*-butyldimethylsilyl chloride (1.73 g, 13 mmol, 1.1 equiv) was added followed by Et_3N (1.8 mL, 1,1 equiv) and DMAP (57 mg, 0.04 equiv). The mixture was stirred for 2 h at room temperature. Water (100 mL) was added and the mixture extracted with DCM (2x30 mL). Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Product was purified by column chromatography on silica gel using DCM (R_f = 0.50). The product was obtained as a yellow solid (3.02 g, 90%).

^{1}H NMR ($CDCl_3$) δ/ppm: 0.28 (s, 6H), 1.03 (s, 9H), 7.16 (dd, 1H, *J* = 13.8 Hz, 4.9 Hz), 7.23 (d, 1H, *J* = 4.8 Hz), 7.76 (d, 1H, *J* = 13.5 Hz), 7.89 (m, 2H), 8.25 (s, 1H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.35, 18.26, 25.71, 115.08, 123.32, 127.76, 128.21, 131.20, 132.50, 134.43, 138.18, 156.55, 192.03.

Mp 32-34 °C

2.2. General procedure A: Grignard reaction

Magnesium turnings (3 equiv) were suspended in dry diethyl ether (5 mL), flushed with argon and activated by addition of a single iodine crystal. Dibromoalkane (1 equiv) was added and the reaction mixture was refluxed for another 1-2 h. Reaction mixture was then cooled to -20 °C and 6-((*tert*-butyldimethylsilyl)oxy)-2-naphthaldehyde (1.6-1.8 equiv) solution in diethyl ether was added. After 5 min the reaction mixture became dense and the stirring stopped. 5% Aqueous solution of NH_4Cl (20 mL) was added and the mixture extracted with ethyl acetate (2x20 mL). Combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Product was purified by column chromatography on silica gel using DCM/MeOH (98:2). Yield was calculated according to aldehyde.

2.2.1. 1,11-Bis(6-hydroxynaphthalen-2-yl)undecane-1,11-diol (2)

Prepared from 1,9-dibromononane (1.35 g, 0.95 ml, 5 mmol) and **1** (2.25 g, 7.8 mmol) according to general procedure A. Yield: 2.19 g (80%)

^{1}H NMR ($CDCl_3$) δ/ppm: 0.24 (s, 12H), 1.01, (s, 18H), 1.20-1.26 (m, 14H), 1.70-1.92 (m, 4H), 4.76 (t, *J* = 6.5 Hz, 2H), 7.06 (dd, *J* = 8.2 Hz, 2.3 Hz, 2H), 7.17 (d, *J* = 2.3 Hz, 2H), 7.41 (dd, *J*= 8.7 Hz, 1.3 Hz, 2H), 7.63-7.73 (m, 6H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.29, 18.30, 25.76, 25.90, 29.52, 38.91, 74.85, 114.86, 122.36, 124.47 (2C), 127.08, 128.99, 129.33, 134.13, 140.17, 153.48.

2.2.2. 1,9-Bis(6-hydroxynaphthalen-2-yl)nonane-1,9-diol (3)

Prepared from 1,7-dibromoheptane (2.3 g, 1.7 ml, 10 mmol) and **1** (4.60 g, 16 mmol) according to general procedure A. Yield: 4.75 g (88%)

^{1}H NMR ($CDCl_3$) δ/ppm: 0.24 (s, 12H), 1.01, (s, 18H), 1.20-1.36 (m, 10H), 1.70-1.90 (m, 4H), 4.75 (t, *J* = 6.5 Hz, 2H), 7.05 (dd, *J* = 8.2 Hz, 2.3 Hz, 2H), 7.17 (d, *J* = 2.3 Hz, 2H), 7.40 (dd, *J* = 8.7 Hz, 1.3 Hz, 2H), 7.63-7.73 (m, 6H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.30, 18.29, 25.75, 25.83, 29.41, 38.88, 74.80, 114.82, 122.32, 124.45 (2C), 127.06, 129.01, 129.31, 134.16, 140.17, 153.51.

2.2.3. 1,7-Bis(6-hydroxynaphthalen-2-yl)heptane-1,7-diol (4)

Prepared from 1,5-dibromopentane (1.18 g, 0.70 ml, 5 mmol) and **1** (2.30 g, 8 mmol) according to general procedure A. Yield: 1.90 g (73%)

^{1}H NMR ($CDCl_3$) δ/ppm: 0.24 (s, 12H), 1.01, (s, 18H), 1.32-1.38 (m, 6H), 1.75-1.82 (m, 4H), 4.73 (t, *J* = 6.5 Hz, 2H), 7.06 (dd, *J* = 8.2 Hz, 2.3 Hz, 2H), 7.16 (d, *J* = 2.3 Hz, 2H), 7.37 (dd, *J* = 8.7 Hz, 1.3 Hz, 2H), 7.63-7.73 (m, 6H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.31, 18.28, 25.75, 29.40, 38.76, 74.75, 114.82, 122.33, 124.42, 124.46, 127.08, 129.07, 129.31, 134.17, 140.08, 153.52.

2.3. 1,9-Bis(6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)nonane-1,9-dione (5)

Jones reagent was added dropwise to a solution of **3** (2.30 g, 3.4 mmol) in acetone (40 mL) until the red color persisted in the mixture. During the addition the temperature was kept under 20 °C. The mixture was stirred for another 0.5 h. Solvent was evaporated, water was added, and the mixture extracted with DCM. Combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The product **5** (1.65 g, 72%) was obtained after column chromatography on silica gel using DCM gradient to DCM/MeOH (97:3).

^{1}H NMR ($CDCl_3$) δ/ppm: 0.27 (s, 12H), 1.02, (s, 18H), 1.42-1.46 (m, 6H), 1.75-1.82 (m, 4H), 3.06 (t, *J* = 7.5 Hz, 4H), 7.12 (dd, *J* = 8.8 Hz, 2.3 Hz, 2H), 7.20 (d, *J* = 2.0 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 2H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.98 (dd, *J* = 8.6 Hz, 1.3 Hz, 2H), 8.40 (s, 2H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.29, 18.28, 24.58, 25.67, 29.29, 29.37, 38.50, 114.82, 122.94, 124.41, 127.03, 128.15, 129.55, 131.20, 132.64, 137.12, 155.83, 200.27.

2.4. (1*E*,10*E*)-1,11-Bis(6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)undeca-1,10-diene (6)

p-TsOH Monohydrate (20-30 mg) was refluxed in benzene until dissolved. Solution of diol **2** (1.52 g, 2.3 mmol) in benzene (1-2 mL) was added and the mixture is refluxed for another 15 min. After cooling MTBE is added and the mixture washed with aqueous solution of $NaHCO_3$. Organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Product **6** (590 mg, 41%) was purified by column chromatography on silica gel using toluene/hexane (15:85) and obtained as (*E*,*E*) isomer exclusively.

^{1}H NMR ($CDCl_3$) δ/ppm: 0.24 (s, 12H), 1.01, (s, 18H), 1.35-1.52 (m, 10H), 2.20-2.28 (m, 4H), 6.23-6.33 (m, 2H), 6.49 (d, *J* = 16.1 Hz, 2H), 7.02 (dd, *J* = 8.7 Hz, 2.5 Hz, 2H), 7.13 (d, *J* = 2.0 Hz, 2H), 7.45-7.62 (m, 8H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.33, 18.26, 25.72, 29.17, 29.38, 29.43, 33.13, 114.88, 122.20, 123.90, 125.06, 126.83, 129.19, 129.43, 129.86, 130.67, 133.49, 133.76, 153.23.

2.5. 1,7-Bis(6-((*tert*-butyldimethylsilyl)oxy)naphthalen-2-yl)heptane (7)

The mixture of TFA (3 mL) and triethylsilane (6 mL) was stirred for 20 min at room temperature. The solution of diol **4** (1.70 g, 2.6 mmol) in DCM (5 mL) was added and stirred for 2 h at room temperature. The solvent was evaporated. After purification by column chromatography on silica gel using DCM/hexane (15:85) to DCM/MeOH (99:1), product **7** (1.40 g, 87%) was obtained.

^{1}H NMR ($CDCl_3$) δ/ppm: 0.26 (s, 12H), 1.05, (s, 18H), 1.35-1.42 (m, 6H), 1.65-1.72 (m, 4H), 2.74 (t, *J* = 6.5 Hz, 4H), 7.04 (dd, *J* = 9.2 Hz, 2.6 Hz, 2H), 7.15 (d, *J* = 1.8 Hz, 2H), 7.26 (dd, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.53 (s, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR ($CDCl_3$) δ/ppm: -4.29, 18.31, 25.79, 29.29, 29.45, 31.48, 35.95, 114.80, 122.04, 126.07, 126.58, 127.75, 128.77, 129.43, 132.98, 138.24, 152.85.

2.6. General procedure B: deprotection of TBS group

TBS protected compounds **5**-**7** (1.5-2.5 g) were dissolved in THF (30-40 mL). TBAF (1M solution in THF, 0.1-0.2 equiv) and water (0.5-0.8 mL) were added. The mixture was stirred overnight. Solvent was evaporated, and EtOAc was added. The mixture was washed with 1M NaH_2PO_4 or NH_4Cl. Organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. Products were purified by column chromatography of recrystallization.

2.6.1. 1,9-Bis(6-hydroxynaphthalen-2-yl)nonane-1,9-dione (8)

Prepared from **5** (1.65 g, 2.5 mmol) according to general procedure B, and obtained after recrystallization from EtOH. Yield: 975 mg (90%).

^{1}H NMR (DMSO) δ/ppm: 1.33-1.38 (m, 6H), 1.65-1.69 (m, 4H), 3.09 (t, *J* = 7.0 Hz, 4H), 7.15-7.19 (m, 4H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.86 (dd *J* = 8.5 Hz, 1.5 Hz, 2H), 7.97 (d, *J* = 9 Hz, 2H), 8.54 (s, 2H), 10.18 (s, 2H).

^{13}C NMR (DMSO) δ/ppm: 24.56, 29.14, 29.31, 38.09, 109.20, 119.94, 124.40, 126.76, 127.08, 130.31, 131.70, 131.95, 137.52, 158.22, 200.04.

2.6.2. 6,6'-((1*E*,10*E*)-Undeca-1,10-diene-1,11-diyl)bis(naphthalen-2-ol) (9)

Prepared from **6** (590 mg, 0.89 mmol) according to general procedure B, and obtained after chromatography on silica gel using DCM/EtOAc/MeOH (50:45:5). Yield: 360 mg (94%).

^{1}H NMR (DMSO) δ/ppm: 1.33-1.36 (m, 6H), 1.44 -1.47 (m, 4H), 2.18-2.22 (m, 4H), 6.25-6.33 (m,2H), 6.46 (d, *J* = 16.1 Hz, 2H), 7.03 (dd, *J* = 8.5 Hz, 2.1 Hz, 2H), 7.07 (d, *J* = 1.8 Hz, 2H), 7.51 (dd, *J* = 7.5 Hz, 1.5 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.61 (s, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 9.67 (s, 2H).

^{13}C NMR (DMSO) δ/ppm: 29.05, 29.19, 29.37, 32.97, 109.22, 119.22, 124.18, 125.46, 126.73, 128.29, 129.71,130.13, 130.27, 132.31, 134.24, 155.66.

2.6.3. 6,6'-(Heptane-1,7-diyl)bis(naphthalen-2-ol) (10)

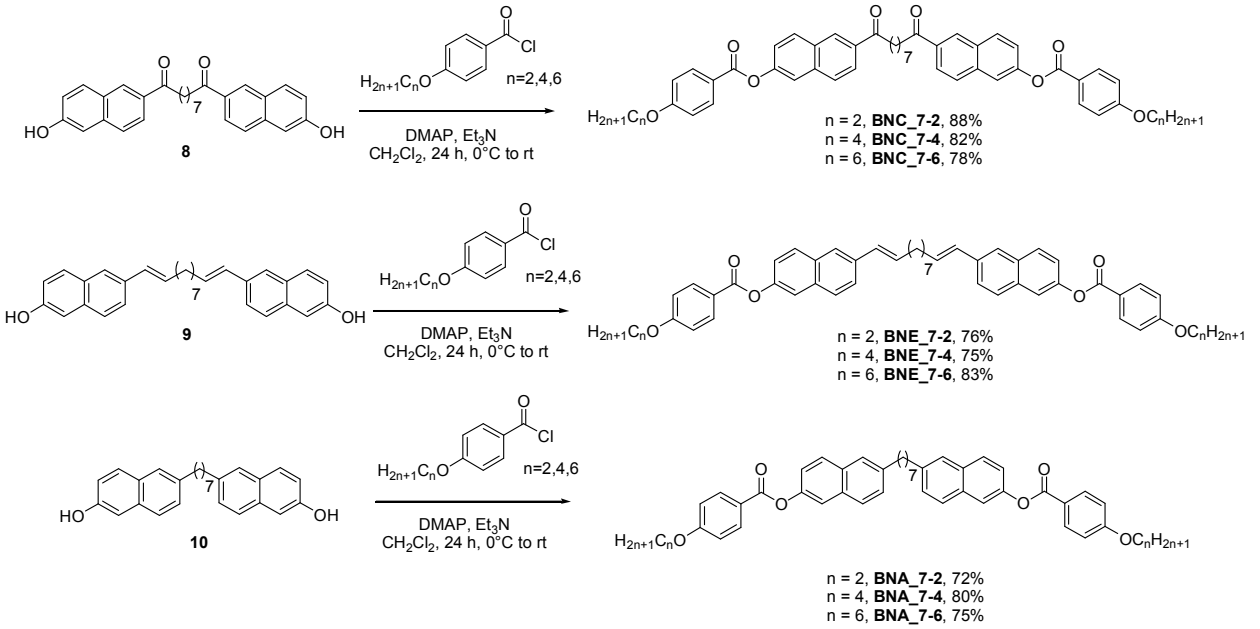
Prepared from **7** (1.40 g, 2.3 mmol) according to general procedure B, and obtained after recrystallization from 2-PrOH/H_2O (1:1) following by column chromatography on silica gel using DCM/EtOAc (9:1). Yield: 870 mg, 99%.

^{1}H NMR (DMSO) δ/ppm: 1.17-1.32 (m, 6H), 1.50-1.64 (m, 4H), 2.63 (t, *J* = 6.5 Hz, 4H), 7.00-7.09 (m, 4H), 7.21 (dd, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.50 (s, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (DMSO) δ/ppm: 29.05, 29.14, 31.33, 35.50, 108.96, 118.94, 126.30, 126.38, 127.97, 128.30, 129.18, 133.43, 136.87, 155.12.

2.7. General procedure C: synthesis of BNA, BNE and BNC dimers

Scheme 2



4-*O*-substituted benzoic acid (5 equiv according to diol) was suspended in toluene. Oxalyl chloride (6.5 equiv according to diol) was added followed by a single drop of DMF. The mixture was stirred for 1.5 h. Solvent was evaporated and acyl chloride was used immediately in the next step without purification. Crude acyl chloride was dissolved in dichloromethane (2 mL) and added dropwise to a mixture of diol (100 mg, 1 equiv), Et_3N (10 equiv) and DMAP (0.15 equiv) in dichloromethane (5 mL) cooled to 0 °C. The mixture was stirred overnight at room temperature and then concentrated. The product was purified by flash column chromatography on silica gel using DCM to DCM/MeOH (95 : 5), followed by recrystallization from acetone or acetone/DCM.

2.7.1. 1,9-Bis(6-(4-ethyloxybenzoyloxy)naphthalene-2-yl)nonane-1,9-dione (BNC_7-2)

Yield: 147 mg (88%) starting from compound **8**.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.45 (m, 12H), 1.84 (m, 4H), 3.12 (t, *J* = 7.4 Hz, 4H), 4.15 (q, *J* = 7.0 Hz, 4H), 7.00 (d, *J* = 9.0 Hz, 4H), 7.45 (dd, *J* = 8.9 Hz, 2.2 Hz, 2H), 7.74 (d, *J* = 2.2 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 8.05 (m, 4H), 8.20 (d, *J* = 9.0 Hz, 4H), 8.51 (s, 2H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.71, 24.46, 29.28, 29.38, 38.67, 63.89, 114.41, 118.80, 121.34, 122.48, 124.73, 128.19, 129.44, 130.55, 132.44, 134.30, 136.20, 150.77, 163.56, 164.88, 200.29.

Anal. Calcd. for $C_{47}H_{44}O_8$: C, 76.61; H, 6.02; found: C, 76.48; H, 6.04.

2.7.2. 1,9-Bis(6-(4-butyloxybenzoyloxy)naphthalene-2-yl)nonane-1,9-dione (BNC_7-4)

Yield: 150 mg (82%) starting from compound **8**.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.00 (t, *J* = 7.5 Hz, 6H), 1.44-1.72 (m, 10H), 1.76-1.88 (m, 8H), 3.10 (t, *J* = 7.4 Hz, 4H), 4.06 (t, *J* = 6.4 Hz, 4H), 6.99 (d, *J* = 8.7 Hz, 4H), 7.42 (dd, *J* = 8.9 Hz, 2.2 Hz, 2H), 7.72 (d, *J* = 2.2 Hz, 2H), 7.86 (d, *J* = 8.7 Hz, 2H), 8.03 (m, 4H), 8.18 (d, *J* = 8.9 Hz, 4H), 8.49 (s, 2H).

^{13}C NMR ($CDCl_3$) δ/ppm: 13.83, 19.21, 24.44, 29.25, 29.36, 31.14, 38.64, 68.06, 114.40, 118.78, 121.24, 122.45, 124.70, 128.16, 129.41, 130.52, 131.07, 132.39, 134.27, 136.17, 150.75, 163.75, 164.87, 200.26.

Anal. Calcd. for $C_{51}H_{52}O_8$: C, 77.25; H, 6.61; found: C, 76.97; H, 6.38.

2.7.3. 1,9-Bis(6-(4-hexyloxybenzoyloxy)naphthalene-2-yl)nonane-1,9-dione (BNC_7-6)

Yield: 152 mg (78%) starting from compound **8**.

^{1}H NMR ($CDCl_3$) δ/ppm: 0.93 (m, 6H), 1.31-1.41 (m, 8H), 1.43-1.54 (m, 10H) 1.77-1.89 (m, 8H), 3.11 (t, *J* = 7.5 Hz, 4H), 4.06 (t, *J* = 6.7 Hz, 4H), 6.99 (d, *J* = 8.9 Hz, 4H), 7.43 (dd, *J* = 8.8 Hz, 2.1 Hz, 2H), 7.72 (d, *J* = 2.1 Hz, 2H), 7.87 (d, *J* = 8.5 Hz, 2H), 8.04 (m, 4H), 8.18 (d, *J* = 8.9 Hz, 4H), 8.49 (s, 2H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.04, 22.60, 24.43, 25.67, 29.07, 29.25, 29.36, 31.56, 38.64, 68.38, 114.40, 118.78, 121.23, 122.46, 124.70, 128.16, 129.42, 130.52, 131.07, 132.39, 134.27, 136.17, 150.75, 163.75, 164.87, 200.26.

Anal. Calcd. for $C_{55}H_{60}O_8$: C, 77.80; H, 7.12; found: C, 77.65; H, 7.07.

2.7.3. (1*E*,10*E*)-1,11-Bis(6-(4-ethyloxybenzoyloxy)naphthalene-2-yl)undeca-1,10-diene (BNE_7-2)

Yield: 128 mg (76%) starting from compound **9**.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.37-1.58 (m, 16H), 2.28 (m, 4H), 4.13 (q, *J* = 6.9 Hz, 4H), 6.36 (dt, *J* = 15.8 Hz, 6.8 Hz, 2H), 6.54 (d, *J* = 15.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 4H), 7.31 (dd, *J* = 8.2 Hz, 2.2 Hz, 2H), 7.57-7.63 (m, 4H), 7.67-7.76 (m, 4H), 7.81 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 8.9 Hz, 4H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.81, 29.31, 29.49, 33.29, 63.94, 114.42, 118.70, 121.73, 121.80, 124.43, 125.25, 127.91, 129.34, 129.83, 131.86, 131.91, 132.46, 133.10, 135.40, 148.59, 163.48, 165.25.

Anal. Calcd. for $C_{49}H_{48}O_6$: C, 80.30; H, 6.60; found: C, 80.04; H, 6.90.

2.7.4. (1*E*,10*E*)-1,11-bis(6-(4-butyloxybenzoyloxy)naphthalene-2-yl)undeca-1,10-diene (BNE_7-4)

Yield: 135 mg (75%) starting from compound **9**.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.00 (t, *J* = 7.4 Hz, 6H), 1.36-1.58 (m, 14H), 1.81 (m, 4H), 2.27 (m, 4H), 4.04 (t, *J* = 6.5 Hz, 4H), 6.36 (dt, *J* = 15.8 Hz, 6.8 Hz, 2H), 6.53 (d, *J* = 15.8 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 4H), 7.30 (dd, *J* = 8.8 Hz, 2.2 Hz, 2H), 7.55-7.62 (m, 4H), 7.66-7.74 (m, 4H), 7.80 (d, *J* = 8.8 Hz, 2H), 8.17 (d, *J* = 8.8 Hz, 4H).

^{13}C NMR ($CDCl_3$) δ/ppm: 13.96, 19.33, 29.31, 29.49, 31.27, 33.29, 68.13, 114.44, 118.70, 121.73, 124.43, 125.25, 127.91, 129.33, 129.83, 131.85, 131.90, 132.43, 133.10, 135.39, 148.60, 163.69, 165.26.

Anal. Calcd. for $C_{53}H_{56}O_6$: C, 80.68; H, 7.15; Found: C, 80.69; H, 7.25.

2.7.5. (1*E*,10*E*)-1,11-Bis(6-(4-hexyloxybenzoyloxy)naphthalene-2-yl)undeca-1,10-diene (BNE_7-6)

Yield: 161 mg (83%) starting from compound **9**.

^{1}H NMR ($CDCl_3$) δ/ppm: 0.92 (m, 6H), 1.33-1.57 (m, 22H), 1.83 (m, 4H), 2.28 (m, 4H), 4.05 (t, *J* = 6.5 Hz, 4H), 6.36 (dt, *J* = 15.7 Hz, 6.7 Hz, 2H), 6.54 (d, *J* = 15.7 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 4H), 7.30 (dd, *J* = 8.8 Hz, 2.2 Hz, 2H), 7.57-7.62 (m, 4H), 7.67-7.75 (m, 4H), 7.81 (d, *J* = 8.8 Hz, 2H), 8.18 (d, *J* = 8.8 Hz, 4H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.17, 22.73, 25.81, 29.22, 29.32, 29.50, 31.69, 33.29, 68.48, 114.45, 118.71, 121.74, 124.44, 125.25, 127.92, 129.35, 129.83, 131.87, 131.92, 132.45, 133.11, 135.40, 148.61, 163.70, 165.28.

Anal. Calcd. for $C_{57}H_{64}O_6$: C, 81.01; H, 7.63; found: C, 81.06; H, 8.01.

2.7.6. 1,7-Bis(6-(4-ethyloxybenzoyloxy)naphthalene-2-yl)heptane (BNA_7-2)

Yield: 143 mg (81%) starting from compound **10**.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.34-1.42 (m, 6H), 1.47 (t, *J* = 7.0 Hz, 6H), 1.70 (m, 4H), 2.77 (t, *J* = 7.6 Hz, 4H), 4.13 (q, *J* = 7.0 Hz, 4H), 6.98 (d, *J* = 8.9 Hz, 4H), 7.32 (m, 4H), 7.62 (m, 4H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 8.19 (d, *J* = 8.7 Hz, 4H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.70, 29.18, 29.35, 31.29, 36.00, 63.82, 114.29, 118.47, 121.33, 121.75, 126.23, 127.52, 128.14, 128.82, 131.66, 132.25, 132.33, 140.22, 148.17, 163.33, 165.20.

Anal. Calcd. for $C_{45}H_{44}O_6$: C, 79.39; H, 6.51; found: C, 79.35; H, 6.79.

2.7.7. 1,7-bis(6-(4-butyloxybenzoyloxy)naphthalene-2-yl)heptane (BNA_7-4)

Yield: 153 mg (80%) starting from compound **10**.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.01 (t, *J* = 7.3 Hz, 6H), 1.36-1.42 (m, 6H), 1.48-1.58 (m, 4H), 1.67-1.75 (m, 4H), 1.77-1.87 (m, 4H), 2.77 (t, *J* = 7.5 Hz, 4H), 4.05 (q, *J* = 6.5 Hz, 4H), 6.98 (d, *J* = 9.0 Hz, 4H), 7.32 (m, 4H), 7.63 (m, 4H), 7.74 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 4H).

^{13}C NMR ($CDCl_3$) δ/ppm: 13.86, 19.23, 29.19, 29.37, 31.17, 31.30, 36.01, 68.02, 114.32, 118.48, 121.35, 121.68, 126.24, 127.53, 128.14, 128.82, 131.67, 132.26, 132.32, 140.22, 148.18, 163.55, 165.21.

Anal. Calcd. for $C_{49}H_{52}O_6$: C, 79.86; H, 7.11; found: C, 79.59; H, 7.38.

2.7.8. 1,7-Bis(6-(4-hexyloxybenzoyloxy)naphthalene-2-yl)heptane (BNA_7-6)

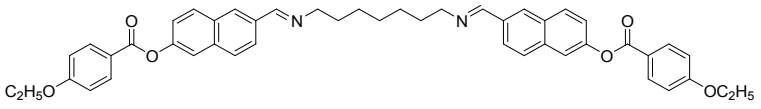
Yield: 155 mg (75%) starting from compound **10**.

^{1}H NMR ($CDCl_3$) δ/ppm: 0.93 (m, 6H), 1.32-1.42 (m, 14H), 1.44-1.54 (m, 4H), 1.66-1.75 (m, 4H), 1.78-1.88 (m, 4H), 2.77 (t, *J* = 7.6 Hz, 4H), 4.05 (q, *J* = 6.5 Hz, 4H), 6.99 (d, *J* = 8.8 Hz, 4H), 7.32 (m, 4H), 7.62 (m, 4H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 4H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.04, 22.60, 25.68, 29.09, 29.18, 29.35, 31.29, 31.56, 36.00, 68.34, 114.31, 118.47, 121.33, 121.67, 126.23, 127.51, 128.13, 128.81, 131.65, 132.24, 132.31, 140.21, 148.16, 163.54, 165.22.

Anal. Calcd. for $C_{53}H_{60}O_6$: C, 80.27; H, 7.63; found: C, 80.24; H, 7.96.

2.8. *N*,*N*'-Bis[6'-(4''-ethoxybenzoyloxy)naphthalen-2'-ylmethylene]-heptane-1,7-diamine (BNI_7-2)



BNI_7-2 was prepared following the procedure reported previously.[1]

Yield: 175 mg (77%) starting from 6-(4'-ethoxybenzoyloxy)naphthalen-2-yl carbaldehyde.

^{1}H NMR ($CDCl_3$) δ/ppm: 1.42-1.50 (m, 12H), 1.71-1.82 (m, 4H), 3.67 (t, *J* = 6.9 Hz, 4H), 4.13 (q, *J* = 6.9 Hz, 4H), 6.98 (d, *J* = 8.9 Hz, 4H), 7.37 (dd, *J* = 8.9 Hz, 2.2 Hz, 2H), 7.68 (d, *J* = 2.2 Hz, 2H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.9 Hz, 2H), 7.99 (dd, *J* = 8.6 Hz, 1.4 Hz, 2H), 8.04 (s, 2H), 8.18 (d, *J* = 8.9 Hz, 4H), 8.41 (s, 2H).

^{13}C NMR ($CDCl_3$) δ/ppm: 14.69, 27.33, 29.25, 30.92, 61.88, 63.84, 114.34, 118.86, 121.49, 122.02, 124.67, 128.17, 129.37, 130.03, 131.12, 132.38, 133.91, 135.14, 149.69, 160.64, 163.45, 164.98.

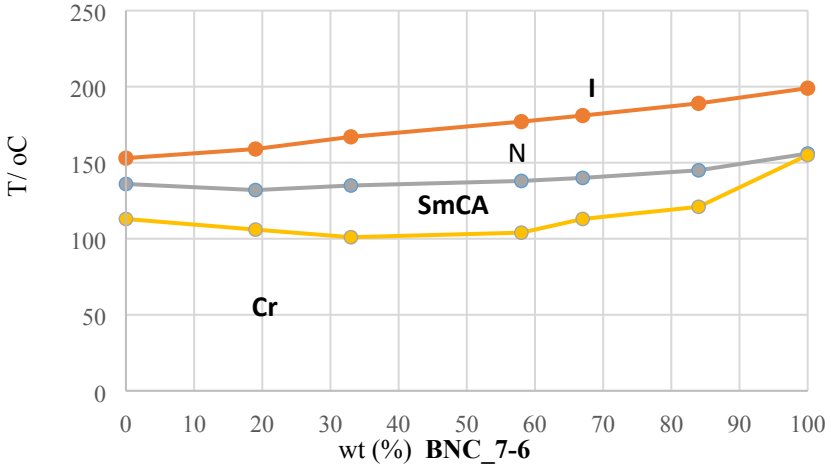
Anal. Calcd. for $C_{47}H_{46}N_2O_6$: C, 76.82; H, 6.31; N, 3.81; found: C, 76.79; H, 6.46; N, 3.70.

2.9. Literature

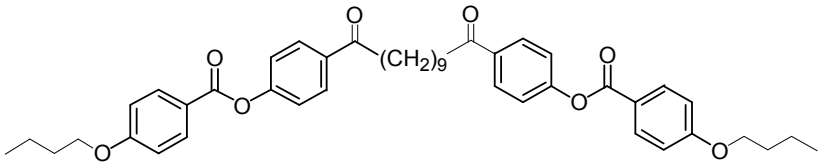
(1) Šepelj, M.; Baumeister, U.; Ivšić, T.; Lesac, A. Effects of Geometry and Electronic Structure on the Molecular Self-Assembly of Naphthyl-Based Dimers. *J. Phys. Chem. B* **2013**, *117* (29), 8918–8929.

3. Miscibility test

a)



b)



Iso 154 N 136 SmC_A 104 Cr

Figure 1S. a) Miscibility phase diagram between **S** and **BNC_7-6**. b) Structure of the compound **S** and its phase transition temperatures obtained on cooling.

4. Conformational analysis:

Table 1S. Minima of BNA_7-2, BNC_7-2, BNI_7-2 and BNE_7-2 obtained by rotations of the α and τ angles of one half of the molecule. The minima of each molecule are given with respect to the lowest minimum for that molecule.

Molecule	Min	α	τ	Energy/ kcalmol^{-1}
BNA_7-2	1	-102	/	0.00
	2	107	/	0.01
	3	4	/	0.94
BNC_7-2	1	6	173	0.00
	2	-174	175	0.16
	3	-3	-89	0.48
	4	7	80	0.72
	5	180	-84	1.07
	6	-164	75	1.45
BNI_7-2	1	-178	-123	0.00
	2	-178	123	0.02
	3	-1	125	0.88
	4	2	125	0.95
BNE_7-2	1	-176	-119	0.00
	2	-176	123	0.02
	3	15	119	0.76
	4	-19	117	0.77
	5	13	-119	0.81
	6	-21	-122	0.83

	7	179	-1	0.84
	8	-21	-2	1.72
	9	16	0	1.73

Table 2S. Bending angles (β) and relative populations (in parentheses) of all minima obtained by rotations of the α angle of both sides of BNA. The columns/rows represent the conformations (corresponding to those in Table S1) of the first/second half.

	1	**2**	**3**
1	119 (19%)	117 (18%)	111 (6%)
2	117 (18%)	117 (17%)	110 (6%)
3	111 (6%)	110 (6%)	103 (2%)

Table 3S. Bending angles (β) and relative populations (in parentheses) of all minima obtained by rotations of the α and τ angles of both sides of BNC. The columns/rows represent the conformations (corresponding to those in Table 1S) of the first/second half.

	1	**2**	**3**	**4**	**5**	**6**
1	110 (9.4%)	122 (7.8%)	129 (5.3%)	98 (3.9%)	138 (2.6%)	110 (1.7%)
2	122 (7.8%)	133 (6.5%)	123 (4.4%)	100 (3.3%)	129 (2.2%)	110 (1.4%)
3	129 (5.3%)	123 (4.4%)	51(3.0%)	138 (2.2%)	55 (1.5%)	130 (0.9%)
4	98 (3.9%)	100 (3.3%)	138 (2.2%)	15 (1.7%)	127 (1.1%)	25 (0.5%)
5	138 (2.6%)	129 (2.2%)	55 (1.5%)	127 (1.1%)	50 (0.7%)	126 (0.5%)
6	110 (1.7%)	110 (1.4%)	130 (0.9%)	25 (0.5%)	117 (0.5%)	28.8 (0.3%)

Table 4S. Bending angles (β) and relative populations (in parentheses) of all minima obtained by rotations of the α and τ angles of both sides of BNI. The columns/rows represent the conformations (corresponding to those in Table 1S) of the first/second half.

	1	2	3	4
1	122 (14.2%)	127 (13.9%)	114 (5.0%)	118 (4.6%)
2	127 (13.9%)	140 (13.6%)	124 (4.9%)	129 (4.5%)
3	114 (5.0%)	124 (4.9%)	108 (1.8%)	112 (1.6%)
4	118 (4.6%)	129 (4.5%)	112 (1.6%)	119 (1.5%)

Table 5S. Bending angles (β) and relative populations (in parentheses) of all minima obtained by rotations of the α and τ angles of both sides of BNE. The columns/rows represent the conformations (corresponding to those in Table 1S) of the first/second half. The two highest energy conformations from Table 1S are omitted as the populations of minima containing those conformations are all approx. 1% or less.

	1	2	3	4	5	6	7
1	120 (5.9%)	125 (5.7%)	111 (2.4%)	117 (2.4%)	119 (2.3%)	112 (2.2%)	107 (2.2%)
2	125 (5.7%)	140 (5.4%)	121 (2.0%)	124 (2.0%)	131 (2.2%)	123 (2.2%)	117 (2.2%)
3	111 (2.4%)	121 (2.0%)	105 (1.0%)	110 (1.0%)	114 (0.9%)	105 (0.8%)	100 (0.8%)
4	117 (2.4%)	124 (2.0%)	110 (1.0%)	113 (0.9%)	116 (0.9%)	108 (0.8%)	102 (0.8%)
5	119 (2.3%)	131 (2.2%)	114 (0.9%)	116 (0.9%)	123 (0.9%)	116 (0.8%)	111 (0.9%)
6	112 (2.2%)	123 (2.2%)	105 (0.8%)	108 (0.8%)	116 (0.8%)	110 (0.8%)	105 (0.8%)
7	107 (2.2%)	117 (2.2%)	100 (0.8%)	102 (0.8%)	111 (0.9%)	105 (0.8%)	96 (0.7%)