Photosensitive bent-core liquid crystals based on methyl substituted 3-hydroxybenzoic acid

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Electronic Supporting Information

The ESI file summarizes experimental data for the synthesis of intermediates and target bent-core materials as well as additional information and comments on mesomorphic and photochemical behaviour of the studied materials.

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1. Synthesis

1.1 Characterisation

The structures of intermediates and products were confirmed by $^1$H NMR and $^1$H-$^1$H correlation spectroscopy (Varian Gemini 300 HC instrument), deuteriochloroform was used as a solvent and the signals of the solvent served as an internal standard, $J$ values being given in Hz. The elemental analyses were carried out on a Perkin-Elmer 2400 instrument. The purity of all final compounds was confirmed by HPLC analysis (Luna Silica 150×4.5 column) and found >99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60-100 μm).

1.2 Experimental

1.2.1 Materials of series I

(E)-4-((4-Hexadecyloxyphenyl)diazenyl)phenyl 3-(tert-butyl(dimethyl)silyloxy)-4-methylbenzoate (7). A solution of acid 1 (150 mg, 0.56 mmol), phenol 5 (260 mg, 0.59 mmol), DCC (120 mg, 0.58 mmol) and a catalytic amount of DMAP (25 mg, 0.20 mmol) in dry dichloromethane (25 ml) was stirred for 24 h at room temperature in an inert atmosphere of argon. The precipitated dicyclohexylurea was filtered off and washed with dichloromethane (5 ml). The filtrate was evaporated and the crude product purified by column chromatography (toluene/tert-butyl methyl ether, 20/1) yielding 270 mg (71%) of 7 as an orange solid, m.p. 98-99°C.

$^1$H NMR (CDCl$_3$): 0.27 (s, 6 H, 2×CH$_3$), 0.87 (t, 3 H, CH$_3$), 1.03 (s, 9 H (CH$_3$)$_3$), 1.25-1.36 (m, 24 H, (CH$_2$)$_{12}$), 1.47 (m, 2 H, CH$_2$), 1.82 (m, 2 H, CH$_2$), 2.30 (s, 3 H, CH$_3$), 4.04 (m, 2 H, OCH$_2$), 7.00 (d, 2 H, $J$ = 9.0, 2 × CH), 7.12 (d, 1 H, $J$ = 9.1, H-5), 7.34 (d, 2 H, $J$ = 8.6, 2 × CH), 7.57 (d, 1 H, $J$ = 1.6, H-2), 7.72 (dd, 1 H, $^3J$ = 7.8, $^4J$ = 1.6, H-6), 7.90 (d, 2 H, $J$ = 8.6, 2 × CH), 7.94 (d, 2 H, $J$ = 8.6, 2 × CH).

$^{13}$C NMR (CDCl$_3$): 164.8 (C=O), 161.8 (C$_q$), 154.1 (C$_q$), 152.5 (C$_q$), 150.4 (C$_q$), 146.8 (C$_q$), 136.0 (C$_q$), 131.0 (CH), 127.9 (C$_q$), 124.8 (CH), 123.7 (CH), 123.0 (CH), 122.3 (CH), 119.7 (CH), 114.7 (CH), 68.4 (CH$_2$), 31.9 (CH$_2$), 29.7-29.2 (CH$_2$)$_n$, 26.0 (CH$_2$), 25.7 (CH$_3$), 22.7 (CH$_2$), 18.3 (C$_q$), 17.3 (CH$_2$), 14.1 (CH)$_3$ $\square$4.2 (CH$_3$). Elemental analysis: for C$_{42}$H$_{62}$N$_2$O$_4$Si (686.45), calculated C 73.42, H 9.10, N 4.08; found C 73.50, H 9.02, N 4.15%.

4-(4-Hexadecyloxybenzoyl)oxyphenyl 3-benzyloxy-4-methylbenzoate (8). A mixture of acid 2 (260 mg, 0.84 mmol), phenol 5 (400 mg, 0.88 mmol), DCC (180 mg, 0.88 mmol) and a catalytic amount of DMAP (50 mg, 0.41 mmol) in dry dichloromethane (50 ml) was stirred for 24 h at room temperature in an inert atmosphere of argon. The precipitated dicyclohexylurea was filtered off and washed with dichloromethane (5 ml). The filtrate was evaporated and the crude product purified by column chromatography (toluene/tert-butyl methyl ether, 20/1) yielding 270 mg (71%) of 8 as a white solid, m.p. 98-118°C.

$^1$H NMR (CDCl$_3$): 0.88 (t, 3 H, $J$ = 6.7, CH$_3$), 1.25-1.36 (m, 24 H, (CH$_2$)$_{12}$), 1.48 (m, 2 H, CH$_2$), 1.83 (m, 2 H, CH$_2$), 2.38 (s, 3 H, CH$_3$), 4.05 (t, 2 H, $J$ = 6.6, OCH$_2$), 5.18 (s, 2 H, OCH$_2$Ph), 6.98 (d, 2 H, $J$ = 9.2, 2 × CH), 7.27 (s, 4 H, 4 × CH), 7.30 (d, 1 H, $J$ = 7.8, H-5), 7.34-7.50 (m, 5 H, Ph), 7.71 (d, 1 H, $J$ = 1.2, H-2), 7.76 (dd, 1 H, $^3J$ = 7.8, $^4J$ = 1.6, H-6), 8.15 (d, 2 H, $J$ = 9.0, 2
stirred under reflux in an inert argon atmosphere for 3 h. The reaction mixture was filtered while hot. The filtrate was evaporated and the crude product was purified by column chromatography (toluene/isobutyl methyl ketone) yielding 160 mg (82%) of a yellow solid, m.p. 140-142 °C. 1H NMR (CDCl₃): 1.23 (t, 3 H, CH₃), 1.37-1.64 (m, 26 H, (CH₂)₁₃), 1.98 (m, 2 H, CH₂), 2.41 (s, 3 H, CH₃), 4.21 (m, 2 H, OCH₂), 7.17 (d, 2 H, J = 8.6, 2 × CH), 7.39 (d, 1 H, J = 7.8, 1 H, H-5), 7.49 (d, 2 H, J = 8.5, 2 × CH), 7.70 (m, 1 H, H-2), 7.79 (m, 1 H, H-6), 8.28 (m, 4 H, 4 × CH). 13C NMR (CDCl₃): 164.8 (C=O), 162.1 (C₉), 155.1 (C₉), 152.6 (C₉), 150.0 (C₉), 146.9 (C₉), 136.1 (C₉), 130.6 (CH), 127.9 (C₉), 124.8 (CH), 123.7 (CH), 123.0 (CH), 122.3 (CH) 114.5 (CH), 111.9 (CH), 68.4 (CH₂), 31.9 (CH₂), 29.7-29.4 (CH₂n), 26.1 (CH₂), 22.3 (CH₂), 17.0 (CH₂), 14.1 (CH₃). Elemental analysis: for C₅₄H₄₇O₆ (678.39), calculated C 77.84, H 8.02; found C 77.84, H 7.94%.

(E)-4-((4-Hexadecyloxyphenyl)diazaneryl)phenyl 3-hydroxy-4-methylbenzoate (9). To a solution of 7 (200 mg, 0.29 mmol) in aqueous 90% tetrahydrofuran (22 ml), TBAF·3 H₂O (23 mg, 0.07 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The reaction was poured into water (50 ml) and the resulting suspension was extracted with ethyl acetate (2×25 ml). The combined organic solution was washed with water and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (toluene/isobutyl methyl ketone) yielding 230 mg (64%) of a white solid, m.p. 170-172 °C. 1H NMR (CDCl₃+CD₃OD): 1.23 (t, 3 H, CH₃), 1.37-1.64 (m, 26 H, (CH₂)₁₃), 1.98 (m, 2 H, CH₂), 2.41 (s, 3 H, CH₃), 4.21 (m, 2 H, OCH₂), 7.17 (d, 2 H, J = 8.6, 2 × CH), 7.39 (d, 1 H, J = 7.8, 1 H, H-5), 7.49 (d, 2 H, J = 8.5, 2 × CH), 7.70 (m, 1 H, H-2), 7.79 (m, 1 H, H-6), 8.28 (m, 4 H, 4 × CH). 13C NMR (CDCl₃): 164.8 (C=O), 162.1 (C₉), 155.1 (C₉), 152.6 (C₉), 150.0 (C₉), 146.9 (C₉), 136.1 (C₉), 130.6 (CH), 127.9 (C₉), 124.8 (CH), 123.7 (CH), 123.0 (CH), 122.3 (CH) 114.5 (CH), 111.9 (CH), 68.4 (CH₂), 31.9 (CH₂), 29.7-29.4 (CH₂n), 26.1 (CH₂), 22.3 (CH₂), 17.0 (CH₂), 14.1 (CH₃). Elemental analysis: for C₃₆H₄₈N₂O₄ (572.36), calculated C 75.49, H 8.45, N 4.89; found C 75.60, H 8.45, N 4.81%.

4-(4-Hexadecyloxybenzoyloxy)phenyl 3-hydroxy-4-methylbenzoate (10). To a hot solution of benzyl derivative 8 (420 mg, 0.62 mmol) and Pd/C (50 mg, 10% w/w) in dry 2-pentanone (20 ml), ammonium formate (120 mg, 1.90 mmol) was added and the reaction mixture was stirred under reflux in an inert argon atmosphere for 3 h. The reaction mixture was filtered while hot. The filtrate was evaporated and the crude product was purified by column chromatography (toluene/isobutyl methyl ketone) yielding 230 mg (64%) of a white solid, m.p. 140-142 °C. 1H NMR (CDCl₃): 0.88 (t, 3 H, J = 6.6, CH₃), 1.25-1.36 (m, 24 H, (CH₂)₁₂), 1.48 (m, 2 H, CH₂), 1.82 (m, 2 H, CH₂), 2.35 (s, 3 H, CH₃), 4.05 (t, 2 H, J = 6.4, OCH₂), 4.97 (s, 1 H, OH), 6.97 (d, 2 H, J = 8.6, 2 × CH), 7.25-7.27 (m, 5 H, 4 × CH, H-5), 7.58 (s, 1 H, H-2), 7.71 (dd, 1 H, ²J = 7.2, ³J = 1.7, H-6), 8.14 (d, 2 H, J = 8.2, 2 × CH). 13C NMR (CDCl₃+CH₃OH): 166.7 (C=O), 166.2 (C=O), 164.7 (C₉), 156.1 (C₉), 149.2 (C₉), 149.1 (C₉), 133.0 (CH), 132.7 (C₉), 131.6 (CH), 128.2 (C₉), 128.0 (CH), 123.3 (CH), 123.2 (CH), 122.1 (CH), 121.7 (C₉), 116.2 (CH), 115.0 (CH), 68.7 (CH₂), 32.0 (CH₂), 29.7-29.4 (CH₂n), 26.0 (CH₂), 22.7 (CH₂), 16.3 (CH₃), 14.0 (CH₃). Elemental analysis: for C₄₇H₄₆O₆ (588.35), calculated C 75.48, H 8.22; found C 75.46, H 8.15%.

4-[3-(4-Hexadecyloxybenzoyloxy)benzoyloxy]-4-methylbenzoxylovynylphenyl 4-hexadecyloxybenzoate (Ia). From a boiling solution of 10 (100 mg, 0.17 mmol) and DMAP (22 mg, 0.18 mmol) in toluene (20 ml), approximately 3 ml of the solvent were distilled off in order to remove traces of water. The heating bath was removed and to the still hot solution, a solution of acid chloride 12 (90 mg, 0.18 mmol) in dry toluene (5 ml) was added at once via syringe. The reaction mixture was stirred under inert argon atmosphere and
left to cool down to room temperature. Then it was poured into 2% aqueous hydrochloric acid (30 ml) and the resulting suspension was extracted with chloroform (3 × 30 ml). The combined organic solution was washed with water (15 ml), brine (10 ml) and dried with anhydrous magnesium sulphate. The solvent was evaporated, and the crude product purified by column chromatography (toluene/tert-butyl methyl ether) providing 140 mg (78%) of Ia. The target material was further purified by multiple crystallisation from an ethyl acetate/ethanol mixture. $^1$H NMR (CDCl$_3$): 0.88 (t, 6 H, $J$ = 6.8, 2 × CH$_3$), 1.26-1.34 (m, 48 H, 2 × (CH$_2$)$_{12}$), 1.48 (m, 4 H, 2 × CH$_2$), 1.83 (m, 4 H, 2 × CH$_2$), 2.35 (s, 3 H, CH$_3$), 4.05 (m, 4 H, 2 × OCH$_2$), 6.98 (m, 4 H, 4 × CH), 7.27 (s, 4 H, 4 × CH), 7.40 (d, 2 H, $J$ = 9.0, 2 × CH), 7.45 (d, 1 H, $J$ = 8.2, H-5), 8.00 (dd, 1 H, $J$ = 1.6, H-2), 8.05 (dd, 1 H, $J$ = 7.8, $J$ = 1.6, H-6), 8.15 (m, 4 H, 4 × CH), 8.32 (d, 2 H, $J$ = 8.6, 2 × CH). $^{13}$C NMR (CDCl$_3$): 164.8 (C=O), 164.4 (C=O), 164.3 (C=O), 164.0 (C=O), 163.9 (C$_q$), 163.6 (C$_q$), 155.6 (C$_q$), 149.5 (C$_q$), 148.6 (C$_q$), 148.2 (C$_q$), 137.1 (C$_q$), 132.4 (CH), 132.3 (CH), 131.9 (CH), 131.5 (CH), 128.6 (C$_q$), 128.0 (CH), 126.3 (C$_q$), 123.9 (CH), 122.7 (CH), 122.6 (CH), 122.3 (CH), 121.4 (C$_q$), 120.9 (C$_q$), 114.4 (CH), 114.3 (CH), 68.4 (CH$_2$), 68.3 (CH$_2$), 31.9 (CH$_2$), 29.7 - 29.1 (CH$_2$)$_n$, 26.0 (CH$_2$), 22.7 (CH$_2$), 16.7 (CH$_3$), 14.1 (CH$_3$). Elemental analysis: for C$_{67}$H$_{88}$O$_{10}$ (1052.64), calculated C 76.39, H 8.42; found C 76.51, H 8.45%.

Similarly, the other materials of the series I were prepared.

(E)-4-((4-Hexadecyloxybenzoyloxy)benzoyloxy)-3-(4-(4-Hexadecyloxybenzoyloxy)benzoyloxy)diazenylphenyl (Ib). Yield 89%. $^1$H NMR (CDCl$_3$): 0.88 (t, 6 H, $J$ = 6.8, 2 × CH$_3$), 1.26-1.39 (m, 48 H, 2 × (CH$_2$)$_{12}$), 1.48 (m, 4 H, 2 × CH$_2$), 1.82 (m, 4 H, 2 × CH$_2$), 2.35 (s, 3 H, CH$_3$), 4.05 (m, 4 H, 2 × OCH$_2$), 7.00 (m, 4 H, 4 × CH), 7.36 (d, 2 H, $J$ = 8.8, 2 × CH), 7.40 (d, 2 H, $J$ = 8.7, 2 × CH), 7.46 (d, 1 H, $J$ = 7.9, H-5), 7.91 (d, 2 H, $J$ = 8.9, 2 × CH), 7.96 (d, 2 H, $J$ = 8.8, 2 × CH), 8.01 (d, 1 H, $J$ = 1.7, H-2), 8.06 (dd, 1 H, $J$ = 7.9, $J$ = 1.7, H-6), 8.16 (d, 2 H, $J$ = 8.9, 2 × CH), 8.32 (d, 2 H, $J$ = 8.7, 2 × CH). $^{13}$C NMR (CDCl$_3$): 164.4 (C=O), 164.1 (C=O), 164.0 (C=O), 163.9 (C$_q$), 163.6 (C$_q$), 155.6 (C$_q$), 149.5 (C$_q$), 148.6 (C$_q$), 148.2 (C$_q$), 137.1 (C$_q$), 132.4 (CH), 132.3 (CH), 131.9 (CH), 131.5 (CH), 128.6 (C$_q$), 128.0 (CH), 126.3 (C$_q$), 123.9 (CH), 122.7 (CH), 122.6 (CH), 122.3 (CH), 121.4 (C$_q$), 120.9 (C$_q$), 114.4 (CH), 114.3 (CH), 68.4 (CH$_2$), 68.3 (CH$_2$), 31.9 (CH$_2$), 29.7 - 29.1 (CH$_2$)$_n$, 26.0 (CH$_2$), 22.7 (CH$_2$), 16.7 (CH$_3$), 14.1 (CH$_3$). Elemental analysis: for C$_{67}$H$_{88}$N$_2$O$_8$ (1036.65), calculated C 76.41, H 8.55, N 2.70; found C 76.43, H 8.50, N 2.72.

4-(4-Hexadecyloxybenzoyloxy)phenyl (E)-3-[(4-(4-hexadecyloxybenzoyloxy)benzoyloxy)-4-methylbenzoato (Ic). Yield 84%. $^1$H NMR (CDCl$_3$): 0.88 (t, 6 H, $J$ = 6.8, 2 × CH$_3$), 1.26-1.36 (m, 48 H, 2 × (CH$_2$)$_{12}$), 1.47 (m, 4 H, 2 × CH$_2$), 1.83 (m, 4 H, 2 × CH$_2$), 2.37 (s, 3 H, CH$_3$), 4.05 (m, 4 H, 2 × OCH$_2$), 6.97 (d, 2 H, $J$ = 9.0, 2 × CH), 7.03 (d, 2 H, $J$ = 9.0, 2 × CH), 7.27 (s, 4 H, 4 × CH), 7.46 (d, 1 H, $J$ = 7.8, H-5), 7.99 (m, 5 H, 4 × CH, H-2), 8.06 (dd, 1 H, $J$ = 7.8, $J$ = 1.6, H-6), 8.14 (d, 2 H, $J$ = 9.0, 2 × CH), 8.37 (d, 2 H, $J$ = 7.9, 2 × CH). $^{13}$C NMR (CDCl$_3$): 165.7 (C$_q$), 165.2 (C$_q$), 164.5 (C$_q$), 163.5 (C$_q$), 156.9 (C$_q$), 150.4 (C$_q$), 149.4 (C$_q$), 149.0 (C$_q$), 147.7 (C$_q$), 137.9 (C$_q$), 133.0 (CH), 132.2 (CH), 132.0 (CH), 130.5 (C$_q$), 129.4 (C$_q$), 126.0 (CH), 123.9 (CH), 123.4 (CH), 123.3 (CH), 123.2 (CH), 122.1 (C$_q$), 115.5 (CH), 115.0 (CH), 68.9 (CH$_2$), 68.7 (CH$_2$), 32.1 (CH$_2$),
29.8-29.5 (CH$_2$)$_n$, 29.3 (CH$_2$), 29.2 (CH$_2$), 26.2 (CH$_2$), 26.1 (CH$_2$), 22.8 (CH$_2$), 16.4 (CH$_3$), 13.9 (CH$_3$). Elemental analysis: for C$_{68}$H$_{88}$N$_2$O$_8$ (1036.65), calculated C 76.41, H 8.55, N 2.70; found C 76.32, H 8.52, N 2.74.

(E)-4-(4-Hexadecyloxybenzoyloxy)phenyl 3-butyl(dimethyl)silyloxy)-6-methylbenzoate (14). In the same way as for 8, reaction of protected acid 4 (200 mg, 0.84 mmol) with hydroxy ester 6 (400 mg, 0.88 mmol) provided protected intermediate 14, 360 mg (63%), m.p. 92-93 °C. 1H NMR (CDCl$_3$): 0.88 (t, 3 H, J = 6.7, CH$_3$), 1.25-1.36 (m, 24 H, (CH$_2$)$_n$), 1.48 (m, 2 H, CH$_2$), 1.83 (m, 2 H, CH$_2$), 2.60 (s, 3 H, CH$_3$), 4.05 (t, 2 H, J = 6.7, OCH$_2$), 5.12 (s, 2 H, OCH$_2$Ph), 6.98 (d, 2 H, J = 9.0, 2 × CH), 7.11 (dd, 1 H, J = 8.6, 4 J = 2.7, H-4), 7.23 (d, 1 H, H-3), 7.26 (s, 4 H, 4 × CH), 7.34-7.47 (m, 5 H, Ph), 7.78 (d, 1 H, J = 2.7, H-6), 8.15 (d, 2 H, J = 8.6, 2 × CH).

13C NMR (CDCl$_3$): 165.4 (C=O), 164.8 (C=O), 163.6 (C$_q$), 156.7 (C$_q$), 148.4 (C$_q$), 148.2 (C$_q$), 136.6 (C$_q$), 133.6 (C$_q$), 133.0 (CH), 132.3 (CH), 129.0 (C$_q$), 128.6 (CH), 128.1 (CH), 127.6 (CH), 122.7 (CH), 122.6 (CH), 121.3 (C$_q$), 119.9 (CH), 116.9 (CH), 114.3 (CH), 70.3 (CH$_2$), 68.4 (CH$_2$), 31.9 (CH$_2$), 29.7-29.4 (CH$_2$)$_n$, 29.2 (CH$_2$), 26.0 (CH$_2$), 22.7 (CH$_2$), 21.1 (CH$_3$),
14.1 (CH₃). Elemental analysis: for C₄₄H₅₄O₆ (678.39), calculated C 77.84, H 8.02; found C 77.92, H 7.95%.

(E)-4-((4-Hexadecyloxyphenyl)diazenyl)phenyl 3-hydroxy-6-methylbenzoate (15). Using the same synthetic pathway as for 9, deprotection of 13 (200 mg, 0.29 mmol) afforded hydroxy ester 15 as a yellow solid, 160 mg (94%), m.p. 127-128 °C. ¹H NMR (CDCl₃): 0.88 (t, 3 H, CH₃), 1.26-1.33 (m, 24 H, (CH₂)₁₂), 1.48 (m, 2 H, CH₂), 1.83 (m, 2 H, CH₂), 2.60 (s, 3 H, CH₃), 4.05 (m, 2 H, OCH₂), 5.00 (s, 1 H, OH), 7.00 (m, 3 H, 2 × CH, H-4), 7.20 (d, 1 H, J = 8.2, H-3), 7.34 (d, 2 H, J = 8.8, 2 × CH), 7.65 (d, 1 H, H-6), 7.92 (d, 2 H, J = 9.1, 2 × CH), 7.96 (d, 2 H, J = 8.8, 2 × CH). ¹³C NMR (DMSO): 164.0 (C=O), 162.0 (Cₓ), 155.9 (Cₓ), 152.8 (Cₓ), 150.2 (Cₓ), 146.5 (Cₓ), 133.3 (CH), 130.7 (Cₓ), 128.9 (Cₓ), 125.0 (CH), 123.8 (CH), 123.3 (CH), 120.7 (CH), 117.5 (CH₃), 115.4 (CH), 68.4 (CH₂), 31.7 (CH₂), 29.5 - 29.4 (CH₂)ₙ, 29.1 (CH₂), 29.0 (CH₂), 25.8 (CH₂), 22.5 (CH₂), 20.7 (CH₃), 14.2 (CH₃). Elemental analysis: for C₃₈H₄₈N₂O₄ (572.36), calculated C 75.49, H 8.45, N 4.89; found C 75.61, H 8.39, N 4.93%.

4-(4-Hexadecyloxybenzoyloxy)phenyl 3-hydroxy-6-methylbenzoate (16). Similarly as for compound 10, deprotection of 14 (350 mg, 0.52 mmol) provided 200 mg (67%) of hydroxy ester 16, m.p. 108-109 °C. ¹H NMR (CDCl₃): 0.88 (t, 3 H, J = 6.8, CH₃), 1.26-1.36 (m, 24 H, (CH₂)₁₂), 1.48 (m, 2 H, CH₂), 1.83 (m, 2 H, CH₂), 2.60 (s, 3 H, CH₃), 4.05 (t, 2 H, J = 6.6, OCH₂), 4.95 (s, 1 H, OH), 6.98 (m, 3 H, 2 × CH, H-4), 7.19 (d, 1 H, J = 8.2, H-3), 7.25 (s, 4 H, 4 × CH), 7.63 (d, 1 H, J = 3.1, H-6), 8.15 (d, 2 H, J = 8.6, 2 × CH). ¹³C NMR (CDCl₃): 166.8 (C=O), 164.9 (C=O), 163.6 (Cₓ), 153.5 (Cₓ), 148.5 (Cₓ), 148.1 (Cₓ), 133.4 (Cₓ), 133.2 (CH), 132.3 (CH), 129.1 (Cₓ), 122.7 (CH), 122.6 (CH), 121.3 (Cₓ), 120.1 (CH), 117.6 (CH), 114.3 (CH), 68.3 (CH₂), 31.8 (CH₂), 29.7-29.6 (CH₂)ₙ, 29.5 (CH₂), 29.4 (CH₂), 26.0 (CH₂), 22.7 (CH₂), 21.0 (CH₃), 14.1 (CH₃). Elemental analysis: for C₃₇H₄₇O₆ (588.35), calculated C 75.48, H 8.22; found C 75.51, H 8.23%.

Using the same synthetic pathway as for series I, the materials of series II were prepared.

4-(4-Hexadecyloxybenzoyloxy)phenyl 3-(4-(4-hexadecyloxybenzoyloxy)benzoyloxy)-6-methylbenzoate (IIa). Yield 76%. ¹H NMR (CDCl₃): 0.88 (t, 6 H, J = 6.8, 2 × CH₃), 1.26-1.36 (m, 48 H, 2 ×(CH₂)₁₂), 1.48 (m, 4 H, 2 ×CH₂), 1.83 (m, 4 H, 2 ×CH₂), 2.71 (s, 3 H, CH₃), 4.05 (m, 4 H, 2 ×OCH₂), 6.98 (m, 4 H, 4 ×CH), 7.27 (s, 4 H, 4 ×CH), 7.39 (m, 4 H, 2 ×CH, H-3, H-4), 8.04 (d, 1 H, J = 1.6, H-6), 8.15 (m, 4 H, 4 ×CH), 8.30 (d, 2 H, J = 8.7, 2 ×CH). ¹³C NMR (CDCl₃): 164.8 (C=O), 164.7 (C=O), 164.3 (2 ×C=O), 163.6 (Cₓ), 155.6 (Cₓ), 148.7 (Cₓ), 148.6 (Cₓ), 148.0 (Cₓ), 139.2 (Cₓ), 133.1 (CH), 132.4 (CH), 132.3 (CH), 131.9 (CH), 129.3 (Cₓ), 126.5 (Cₓ), 126.3 (CH), 124.3 (CH), 122.74 (CH), 122.6 (CH), 122.2 (CH), 121.4 (Cₓ), 121.0 (Cₓ), 114.4 (CH), 114.3 (CH), 68.4 (CH₂), 68.3 (CH₂), 31.9(CH₂), 29.7-29.6 (CH₂)ₙ, 29.4 (CH₂), 29.1 (CH₂), 26.0 (CH₂), 22.7 (CH₂), 21.5 (CH₃), 14.1 (CH₃). Elemental analysis: for C₆₇H₉₈O₁₀ (1052.64), calculated C 76.39, H 8.42; found C 76.31, H 8.40%. 

(E)-4-((4-Hexadecyloxybenzoyloxy)diazeyenyl)phenyl 3-(4-(4-hexadecyloxybenzoyloxy)benzoyloxy)-6-methylbenzoate (IIb). Yield 81%. ¹H NMR (CDCl₃): 0.88 (t, 6 H, J = 6.8, 2 × CH₃), 1.25-1.39 (m, 48 H, 2 ×(CH₂)₁₂), 1.49 (m, 4 H, 2 ×CH₂), 1.82 (m, 4 H, 2 ×CH₂), 2.72 (s, 3 H, CH₃), 4.05 (m, 4 H, 2 ×OCH₂), 7.00 (m, 4 H, 4 ×
mesophases, no other organization in layers has been found. Details of textures observed under polarizing microscope are presented. For compound 129.2 (C\textsubscript{12}H\textsubscript{26}O\textsubscript{6}N\textsubscript{2}), 7.35 (d, 2 H, J = 8.9, 2 × CH), 8.30 (d, 2 H, J = 8.7, 2 × CH). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): 164.5 (C=O), 164.4 (C=O), 164.3 (C=O), 163.9 (C\textsubscript{6}), 161.8 (C\textsubscript{7}), 155.6 (C\textsubscript{8}), 152.2 (C\textsubscript{9}), 150.5 (C\textsubscript{10}), 148.7 (C\textsubscript{11}), 146.8 (C\textsubscript{12}), 139.4 (C\textsubscript{13}), 133.1 (CH), 132.4 (CH), 131.9 (CH), 129.2 (C\textsubscript{14}), 126.5 (C\textsubscript{15}), 126.4 (CH), 124.8 (CH), 124.4 (CH), 123.8 (CH), 122.3 (CH), 122.2 (CH), 120.8 (C\textsubscript{16}), 114.7 (CH), 114.5 (CH), 68.4 (CH\textsubscript{2}), 31.9 (CH\textsubscript{2}), 29.7 - 29.4 (CH\textsubscript{2}a\textsubscript{n}), 29.2 (CH\textsubscript{2}), 29.1 (CH\textsubscript{2}), 26.0 (CH\textsubscript{2}), 25.9 (CH\textsubscript{2}), 22.7 (CH\textsubscript{2}), 21.5 (CH\textsubscript{3}), 14.3 (CH\textsubscript{3}). Elemental analysis: for C\textsubscript{66}H\textsubscript{88}N\textsubscript{2}O\textsubscript{8} (1036.65), calculated C 76.41, H 8.55, N 2.70; found C 76.57, H 8.58, N 2.63%.

(E)-4-(4-Hexadecyloxybenzoyloxy)phenyl (E)-3-[(4-(4-hexadecyloxyphenyl)diazenyl)benzoyloxy]-6-methylbenzoate (IId). Yield 83%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 0.88 (t, 6 H, J = 6.8, 2 × CH\textsubscript{3}), 1.27-1.36 (m, 48 H, 2 × (CH\textsubscript{2})\textsubscript{12}), 1.48 (m, 4 H, 2 × CH\textsubscript{2}), 1.83 (m, 4 H, 2 × CH\textsubscript{2}), 2.72 (s, 3 H, CH\textsubscript{3}), 4.06 (m, 4 H, 2 × OCH\textsubscript{2}), 6.97 (d, 2 H, J = 9.0, 2 × CH), 7.03 (d, 2 H, J = 9.0, 2 × CH), 7.27 (s, 4 H, 4 × CH), 7.41 (m, 2 H, 2 × CH), 7.98 (m, 4 H, 4 × CH), 8.07 (s, 1 H, H-6), 8.14 (d, 2 H, J = 8.6, 2 × CH), 8.35 (d, 2 H, J = 8.6, 2 × CH). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): 164.8 (C=O), 164.7 (C=O), 164.6 (C=O), 162.5 (C\textsubscript{6}), 155.9 (C\textsubscript{7}), 148.7 (C\textsubscript{8}), 148.6 (C\textsubscript{9}), 148.0 (C\textsubscript{10}), 146.9 (C\textsubscript{11}), 139.3 (C\textsubscript{12}), 133.1 (CH), 132.3 (CH), 131.3 (CH), 130.0 (C\textsubscript{14}), 129.3 (C\textsubscript{15}), 126.3 (CH), 125.3 (CH), 124.3 (CH), 122.8 (CH), 122.6 (CH), 122.5 (CH), 121.3 (C\textsubscript{16}), 114.8 (CH), 114.3 (CH), 68.5 (CH\textsubscript{2}), 68.3 (CH\textsubscript{2}), 31.9 (CH\textsubscript{2}), 29.7 - 29.1 (CH\textsubscript{2}a\textsubscript{n}), 26.0 (CH\textsubscript{2}), 25.9 (CH\textsubscript{2}), 22.7 (CH\textsubscript{2}), 21.5 (CH\textsubscript{3}), 14.1 (CH\textsubscript{3}). Elemental analysis: for C\textsubscript{66}H\textsubscript{88}N\textsubscript{2}O\textsubscript{8} (1036.65), calculated C 76.41, H 8.55, N 2.70; found C 76.29, H 8.48, N 2.71%.

(E)-4-(4-Hexadecyloxybenzoyloxy)phenyl (E)-3-[(4-(4-(2-hexadecyloxyphenyl)diazenyl)benzoyloxy)-6-methylbenzoate (IId). Yield 69%. \textsuperscript{1}H NMR (CDCl\textsubscript{3}): 0.88 (t, 6 H, J = 6.7, 2 × CH\textsubscript{3}), 1.20-1.43 (m, 48 H, 2 × (CH\textsubscript{2})\textsubscript{12}), 1.48 (m, 4 H, 2 × CH\textsubscript{2}), 1.82 (m, 4 H, 2 × CH\textsubscript{2}), 2.73 (s, 3 H, CH\textsubscript{3}), 4.05 (m, 4 H, 2 × OCH\textsubscript{2}), 7.02 (m, 4 H, 4 × CH), 7.35 (d, 2 H, J = 8.8, 2 × CH), 7.41 (m, 2 H, 2 × CH), 7.91 (d, 2 H, J = 8.8, 2 × CH), 7.94-7.99 (m, 6 H, 6 × CH), 8.09 (bs, 1 H, CH), 8.35 (d, 2 H, J = 8.8, 2 × CH). \textsuperscript{13}C NMR (CDCl\textsubscript{3}): 164.7 (C=O), 164.2 (C=O), 162.5 (C\textsubscript{6}), 161.8 (C\textsubscript{7}), 155.9 (C\textsubscript{8}), 152.2 (C\textsubscript{9}), 150.5 (C\textsubscript{10}), 148.8 (C\textsubscript{11}), 146.9 (C\textsubscript{12}), 146.8 (C\textsubscript{13}), 139.4 (C\textsubscript{14}), 133.1 (CH), 131.3 (CH), 130.0 (C\textsubscript{15}), 129.2 (C\textsubscript{16}), 126.4 (CH) 125.3 (CH), 124.9 (CH), 124.4 (CH), 123.8 (CH), 122.6 (CH), 122.3 (CH), 114.8 (CH), 68.5 (CH\textsubscript{2}), 68.4 (CH\textsubscript{2}), 31.9 (CH\textsubscript{2}), 29.7-29.4 (CH\textsubscript{2}a\textsubscript{n}), 29.2 (CH\textsubscript{2}), 29.1 (CH\textsubscript{2}), 26.0 (CH\textsubscript{2}), 22.7 (CH\textsubscript{3}), 16.7 (CH\textsubscript{3}). Elemental analysis: for C\textsubscript{66}H\textsubscript{88}N\textsubscript{4}O\textsubscript{6} (1020.67), calculated C 76.43, H 8.68, N 5.49; found C 76.41, H 8.68, N 5.55%.

2. Mesomorphic behaviour
For compound Ib, x-ray measurements confirmed the tilted SmC\textsubscript{s} phase for all smectic mesophases, no other organization in layers has been found. Details of textures observed under polarizing microscope are presented. For compound Ib only small textural details allow us to distinguish between different smectic SmC\textsubscript{s} mesophases (Fig. S1). In Fig. S2 for Id the
texture with the transition bars at the phase transition from the nematic to SmC phase is shown.

Fig.S1 Textures of the smectic C phases of compound Ib as observed by polarizing microscopy between crossed polarizers: a-c) in a homeotropic cell (left column) a) SmC$_{s1}$ phase, b) SmC$_{s2}$ phase and c) in the SmC$_{s3}$ phase; d-f) shows the corresponding textures in in a planar cell, namely d) SmC$_{s1}$ phase, e) SmC$_{s2}$ phase and f) in the SmC$_{s3}$ phase;
**Fig.S2** Texture for Id at the phase transition from the nematic to smectic SmC$_s$ (T=106 °C) observed by polarizing microscope. The width of the figure is about 200 µm.

3. **Photochemical properties**

In the following figures, the thermal relaxation of UV-irradiation-induced Z-isomer back to more stable E-isomer is depicted.
**Fig.S3** Overlay of $^1$H NMR spectra of thermal relaxation of the $Z$-isomer of Ib formed under UV-irradiation at 50 °C in the dark. Diagnostic signals of the $Z$-isomer are marked with an arrow.

![Overlay of $^1$H NMR spectra](image)

**Fig.S4** Overlay of $^1$H NMR spectra of thermal relaxation of the $Z$-isomer of Iib formed under UV-irradiation at 50 °C in the dark. Diagnostic signals of the $Z$-isomer are marked with an arrow.

### 4. Ab initio calculations

All calculations were performed in Gaussian 03W®, initial geometries were designed and results visualized in GaussView 3.0®. The optimization procedure followed the same procedure, we previously described for laterally substituted 3-hydroxybenzoic acid-based bent-core liquid crystals.\(^1\)

In brief, the geometry of side wings 6 and 12 as well as intermediate 16 was adopted from reference 1 and re-calculated with the method used in this publication. Since azobenzene-based side arm is a planar fragment, $E$-isomer of which is much more stable than corresponding $Z$-isomer, planar alignment in $E$-configuration of the azo bond was the only considered arrangement. Additionally, it has already been described that the carbonyl unit connected to the aromatic ring lies in the same plane as the corresponding aromatic unit.\(^2\) Therefore, for the intermediate 9, only the orientation of connecting ester unit was considered (**Figure S5**). Similarly, different conformations of the side wing 11 have not been considered and only the orientation of the ester linkage was studied in the final material IIC.
Fig. S5 Assumed conformations with the lowest energy of intermediate 9. Due to the length of the terminal alkyl chain, part of it is omitted in the structures.

Since there was small difference in total energy for conformers a and c (Figure 5), conformer c showing even lower total energy than conformer a, both of them were used for modelling the target material Ib. The resulting geometry of Ib is depicted in the main text.

5. References