

Electronic Supporting Information

Azo-containing asymmetric bent-core liquid crystals with modulated smectic phases

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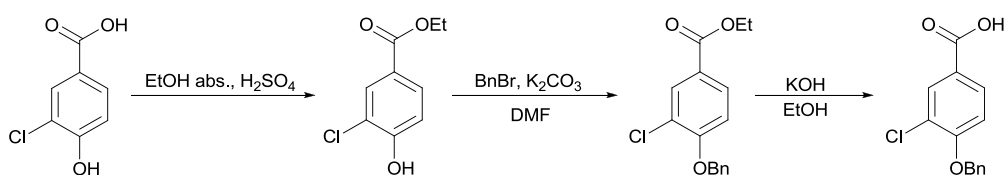
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Synthesis of the intermediates and the target bent-core compounds

The reagents were purchased from Sigma Aldrich and were used without further purifications. All the solvents were dried and distilled using general standard procedures. The chemical structures and the purities of the synthesized compounds were confirmed by melting points, elemental analysis, FT-IR, ^1H and ^{13}C NMR spectra.

The preparation and characterization of intermediates **8–11**, **14–17**, **32** and acids **25**, **26** and **30** has been reported previously^{1–4}.

The synthesis of 3-chloro-4-hydroxybenzoic acid is shown in Scheme S1. The synthesis of this compound was done using similar methods to that reported in literature⁵.



3-Chloro-4-benzyloxybenzoic acid. a) 3-Chloro-4-hydroxy benzoic acid (5.00 g, 29.0 mmol) was dissolved in 100 mL of absolute ethanol and 4 mL of conc. H_2SO_4 was added and the reaction mixture was refluxed overnight. The excess of ethanol was evaporated and the residue was poured into ice cold water. Ethyl 4-hydroxy benzoate was isolated as a white powder. Yield: 85%; b) Potassium carbonate (4.45 g, 32.20 mmol) was added to a solution of ethyl 3-chloro-4-hydroxybenzoate (4.20 g, 20.94 mmol) in DMF (150 mL). The reaction mixture was stirred for 30 min, following which benzyl bromide (2.55 ml, 21.46 mmol) was added and the solution was stirred for 48 h. The reaction mixture was poured into water and the precipitate was filtered off, washed with water and recrystallized from ethanol. Yield: 70%. c) Ethyl 3-chloro-4-benzyloxy benzoate (4.00 g, 13.75 mmol) was refluxed for 4 h with KOH (2.30 g, 40.95 mmol) in 100 mL of ethanol. The reaction mixture was poured into ice cold water, acidified with dilute HCl, and the precipitate was filtered, washed, dried and recrystallized from an ethanol/chloroform mixture. Yield: 73%; FTIR (KBr) ν (cm^{-1}) = 3463, 2932, 2526, 1683, 1596, 1566, 1501, 1456, 1430, 1384, 1321, 1276, 1156, 1331, 1066, 999, 985, 931, 905, 822, 767, 740, 718; ^1H NMR (200 MHz, CCl_3D) δ : 5.29 (s, 2H, CH_2 , 2H), 7.32–7.51 (comp, 6H, Ar), 7.88 (dd, $J = 2.2$ and 8.4 Hz, 1H, Ar), 7.93 (d, $J = 2.0$ Hz, Ar); ^{13}C NMR (50 MHz, CDCl_3): δ 70.6 (CH_2), 114.0 (Ar), 121.8 (Ar), 124.4 (Ar), 127.9 (Ar), 128.4 (Ar), 128.8 (Ar), 130.2 (Ar), 131.1 (Ar), 136.3 (A), 157.4 (Ar), 166.3 (C=O). Elemental analysis, found: C, 48.75; H, 3.04. Calc. for $\text{C}_7\text{H}_5\text{ClO}_3$: C, 48.72; H, 2.92%.

Dodecyl 3-chloro-4-hydroxybenzoate (7). Lauryl alcohol (2.60 g, 14.0 mmol) and TsOH (150 mg) were added to a solution of 3-chloro-4-hydroxybenzoic acid (14.0 mmol) in toluene (30 mL) and the reaction mixture was refluxed overnight. Toluene was evaporated and the residue was taken in chloroform. The chloroform solution was washed with sodium bicarbonate solution, water, dried over anhydrous magnesium sulfate and chloroform was then evaporated. The crude product was purified by recrystallization from an ethanol/water mixture. Yield: 60 %; FTIR (KBr) ν (cm⁻¹) = 3497, 2958, 2919, 2849, 1696, 1635, 1600, 1469, 1428, 1385, 1299, 1268, 1123, 1056, 981, 956, 902, 837, 769, 719, 637; ¹H NMR (200 MHz, CCl₃D) δ : 0.87 (t, J = 6.4 Hz, 3H, CH₃), 1.25–1.57 (m, 18H, CH₂), 1.74 (quin, J = 6.8 Hz, 2H, CH₂), 4.28 (t, J = 6.6 Hz, 2H, CH₂), 6.50 (s, 1H, OH), 7.04 (d, J = 8.4 Hz, 1H, Ar), 7.87 (dd, J = 2.0 and 8.6 Hz, 1H, Ar), 8.02 (d, J = 2.2 Hz, 1H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.0 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 28.6 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.4 (CH₂), 116.0 (Ar), 120.0 (Ar), 123.8 (Ar), 130.2 (Ar), 130.9 (Ar), 155.5 (Ar), 165.6 (C=O). Elemental analysis, found: C, 66.93; H, 8.69. Calc. for C₁₉H₂₉ClO₃: C, 66.94; H, 8.57%

4-Dodecyloxycarbonylphenyl 3-chloro-4-benzyloxybenzoate (12). 3-Chloro-4-benzyloxybenzoic acid (2.82 g, 10.74 mmol) in oxalyl chloride (25 mL) in the presence of catalytic amount of DMF was stirred under reflux for 4 hours. The excess of oxalyl chloride was removed and the obtained solid was further dried under vacuum for 2 hours. To a solution of dodecyl 4-hydroxybenzoate (3.00 g, 9.76 mmol) and triethylamine (1.50 mL, 10.74 mmol) in dichloromethane (35 mL), 3-chloro-4-benzyloxybenzoyl chloride previously dissolved in dichloromethane (10 mL) was added and the reaction mixture was stirred for 48 h. Afterwards, it was washed with 10% HCl (2 × 20 mL) and several times with cold water and finally dried over anhydrous sodium sulphate. The crude product was purified by crystallisation from an ethanol/ethyl acetate mixture. Yield: 58%; FTIR (KBr) ν (cm⁻¹) = 2960, 2923, 2850, 1720, 1596, 1506, 1465, 1409, 1384, 1262, 1228, 1208, 1165, 1119, 1086, 1057, 1021, 992, 955, 922, 905, 859, 811, 751, 724, 698; ¹H NMR (200 MHz, CCl₃D) δ : 0.91 (t, J = 6.4 Hz, 3H, CH₃), 1.15–1.50 (m, 18H, CH₂), 1.80 (quin, J = 6.8 Hz, 2H, CH₂), 4.35 (t, J = 6.6 Hz, 2H, CH₂), 5.28 (s, 2H, CH₂), 7.08 (d, J = 8.8 Hz, 1H, Ar), 7.30 (d, J = 8.8 Hz, 2H, Ar), 7.37–7.53 (m, 5H, Ar), 8.07 (dd, J = 2.2 and 8.6 Hz, 1H, Ar), 8.14 (d, J = 8.8 Hz, 2H, Ar), 8.26 (d, J = 2.2 Hz, 1H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.2 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.2 (CH₂), 70.8 (CH₂), 112.9 (Ar), 121.6 (Ar), 122.3 (Ar), 123.4 (Ar), 127.0 (Ar), 128.2 (Ar), 128.3 (Ar), 128.7 (Ar), 130.5 (Ar), 131.2 (Ar), 132.3 (Ar), 135.5 (Ar), 154.4 (Ar), 158.5 (Ar), 163.3 (C=O), 165.9 (C=O). Elemental analysis, found: C, 71.90; H, 7.30. Calc. for C₃₃H₃₉ClO₅: C, 71.92; H, 7.13%.

Dodecyl 3-chloro-4-(4-benzyloxybenzoyloxy)benzoate (13). The synthesis of **13** was carried out according to the method described for **12**. Yield: 74%; m.p. 72–74 °C; FTIR (KBr) ν (cm⁻¹) = 2951, 2925, 2916, 2850, 1728, 1721, 1609, 1578, 1513, 1471, 1403, 1385, 1278, 1247, 1221, 1174, 1150, 1124, 1073, 1013, 912, 892, 840, 760, 741, 728, 698; ¹H NMR (200 MHz, CCl₃D) δ : 0.89 (t, J = 6.4 Hz, 3H, CH₃), 1.15–1.47 (m, 18H, CH₂), 1.78 (quin, J = 6.8 Hz, 2H, CH₂), 4.34 (t, J = 6.6 Hz, 2H, CH₂), 5.18 (s, 2H, CH₂), 7.09 (d, J = 9.0 Hz, 2H, Ar), 7.37 (d, J = 8.4 Hz, 1H, Ar), 7.38–7.48 (m, 5H, Ar), 8.01 (dd, J = 2.0 and 8.6 Hz, 1H, Ar), 8.19 (d, J = 9.0 Hz, 3H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 28.6 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.6 (CH₂), 70.2 (CH₂), 114.9 (Ar), 120.9 (Ar), 123.9 (Ar), 127.4 (Ar), 127.5 (Ar), 128.3 (Ar), 128.7 (Ar), 129.1 (Ar), 129.3 (Ar), 131.7 (Ar), 132.7 (Ar), 132.8 (Ar), 136.0 (Ar), 150.9 (Ar), 163.4 (C=O), 165.0 (C=O). Elemental analysis, found: C, 71.95; H, 7.10. Calc. for C₃₃H₃₉ClO₅: C, 71.92; H, 7.13%.

4-Dodecyloxycarbonylphenyl 3-chloro-4hydroxybenzoate (18). Palladium on activated carbon (10% Pd/C, 0.25 g) was added to a solution of compound **12** (2.50 g, 4.54 mmol) in cyclohexene (25 mL) and the mixture was vigorously stirred under reflux for 12 h. The insoluble part was removed by filtration and the solvent was evaporated. The crude product was recrystallized from toluene. Yield: 80%; FTIR (KBr) ν (cm⁻¹) = 3474, 2954, 2916, 2852, 1721, 1611, 1591, 1518, 1491, 1479, 1472, 1450, 1384, 1278, 1246, 1225, 1168, 1118, 1074, 955, 898, 845, 761, 733, 715, 691, 614; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, J = 6.4 Hz, 3H, CH₃), 1.13–1.46 (m, 18H, CH₂), 1.78 (quin, J = 6.8 Hz, 2H, CH₂), 4.34 (t, J = 6.6 Hz, 2H, CH₂), 6.93 (d, J = 8.8 Hz, 2H, Ar), 7.37 (d, J = 8.6 Hz, 2H, Ar), 8.01 (dd, J = 2.0 and 8.4 Hz, 1H, Ar), 8.12 (d, J = 8.8 Hz, 2H, Ar), 8.16 (d, J = 2.0 Hz, 1H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 28.6 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.9 (CH₂), 115.7 (Ar), 120.2 (Ar), 124.0 (Ar), 127.5 (Ar), 129.2 (Ar), 131.7 (Ar), 132.9 (Ar), 151.0 (Ar), 161.6 (Ar), 164.0 (C=O), 165.4 (C=O). Elemental analysis, found: C, 67.81; H, 7.30. Calc. for C₂₆H₃₃ClO₅: C, 67.74; H, 7.22%.

Dodecyl 3-chloro-4-(4-benzyloxybenzoyloxy)benzoate (19). The synthesis of **19** was carried out according to the method described for **18**. Yield: 60%; FTIR (KBr) ν (cm⁻¹) = 3360, 2956, 2923, 2850, 1724, 1702, 1602, 1582, 1508, 1469, 1412, 1292, 1274, 1203, 1166, 1120, 1091, 1058, 1020, 952, 912, 832, 763, 755, 720, 610; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, J = 6.5 Hz, 6H, CH₃), 1.27–1.48 (m, 18H, CH₂), 1.78 (quin, J = 6.4 Hz, 2H, CH₂), 4.33 (t, J = 6.7 Hz, 2H, CH₂), 6.25 (s, 1H, OH), 7.13 (d, J = 8.6 Hz, 1H, Ar), 7.29 (d, J = 8.6 Hz, 2H, Ar), 8.05 (dd, J = 2.2 and 8.8 Hz, 1H, Ar), 8.13 (d, J = 8.8 Hz, 2H, Ar), 8.21 (d, J = 2.0 Hz, 1H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 26.0

(CH₂), 28.7 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.4 (CH₂), 116.3 (Ar), 120.3 (Ar), 121.7 (Ar), 122.5 (Ar), 128.2 (Ar), 131.1 (Ar), 131.2 (Ar), 131.6 (Ar), 154.4 (Ar), 156.1 (Ar), 163.3 (C=O), 166.0 (C=O). Elemental analysis, found: C, 67.81; H, 7.30. Calc. for C₂₆H₃₃ClO₅: C, 67.74; H, 7.22%.

4-(Dodecyloxycarbonyl)phenyl 4-(3-(benzyloxy)benzoyloxy)-3-chlorobenzoate (37). 3-Benzyloxybenzoic acid (0.65 g, 2.86 mmol) in oxalyl chloride (25 mL) in the presence of catalytic amount of DMF was stirred under reflux for 4 hours. The excess of oxalyl chloride was removed and the obtained solid was further dried under vacuum for 2 hours. To a solution of compound **18** (1.20 g, 2.60 mmol) and triethylamine (0.40 mL, 2.86 mmol) in dichloromethane (35 mL), 3-benzyloxybenzoyl chloride previously dissolved in dichloromethane (10 mL) was added and the reaction mixture was stirred for 48 h. Afterwards, it was washed with 10% HCl (2 × 20 mL) and several times with cold water and finally dried over anhydrous sodium sulphate. The crude product was purified by crystallisation from an ethanol/ethyl acetate mixture. Yield: 50% ¹H NMR (200 MHz, CCl₃D) δ: 0.89 (t, *J* = 6.5 Hz, 3H, CH₃), 1.15–1.60 (m, 18H, CH₂), 1.78 (quin, *J* = 6.6 Hz, 2H, CH₂), 4.34 (t, *J* = 6.6 Hz, 2H, CH₂), 5.16 (s, 2H, CH₂), 7.27–7.50 (comp, 11H, Ar), 7.84 – 7.90 (m, 2H, Ar), 8.15 (d, *J* = 8.6 Hz, 2H, Ar), 8.21 (d, *J* = 2.0 Hz, 1H, Ar), 8.36 (d, *J* = 1.8 Hz, 1H); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 26.0 (CH₂), 28.8 (CH₂), 29.3 (CH₂), 29.8 (CH₂), 31.9 (CH₂), 65.3 (CH₂), 70.3 (CH₂), 115.9 (Ar), 121.6 (Ar), 123.1 (Ar), 124.2 (Ar), 127.6 (Ar), 127.8 (Ar), 128.0 (Ar), 128.2 (Ar), 128.5 (Ar), 128.7 (Ar), 129.6 (Ar), 129.9 (Ar), 131.3 (Ar), 132.4 (Ar), 136.3 (Ar), 151.6 (Ar), 154.2 (Ar), 159.0 (Ar), 162.9 (C=O), 163.5 (C=O), 165.8 (C=O). Elemental analysis, found: C, 71.61; H, 6.43. Calc. for C₄₀H₄₃ClO₇; C, 71.58; H, 6.46%

Dodecyl 3-chloro-4-(4-(3-(benzyloxy)benzoyloxy)benzoyloxy)benzoate (38). The synthesis of **38** was carried out according to the method described for **37**. Yield: 50% ¹H NMR (200 MHz, CCl₃D) δ: 0.90 (t, *J* = 6.6 Hz, 3H, CH₃), 1.16–1.55 (m, 18H, CH₂), 1.79 (quin, *J* = 6.8 Hz, 2H, CH₂), 4.35 (t, *J* = 6.6 Hz, 2H, CH₂), 5.16 (s, 2H, CH₂), 7.25–7.28 (overlapped with the CDCl₃ signal, 1H, CH₂), 7.30 (dd, *J* = 1.0 and 2.6 Hz, 1H, Ar), 7.33–7.53 (comp, 8H, Ar), 7.82–7.87 (m, 2H), 8.04 (dd, *J* = 2.0 and 8.5 Hz, 1H, Ar), 8.20 (d, *J* = 2.0 Hz, 1H, Ar), 8.32 (d, *J* = 8.8 Hz, 2H, Ar). ¹³C NMR (50 MHz, CDCl₃): δ 14.0 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 28.6 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.7 (CH₂), 70.2 (CH₂), 115.8 (Ar), 121.1 (Ar), 122.2 (Ar), 122.9 (Ar), 123.8 (Ar), 126.0 (Ar), 127.3 (Ar), 127.5 (Ar), 128.2 (Ar), 128.7 (Ar), 129.2 (Ar), 129.6 (Ar), 129.8 (Ar), 130.2 (Ar), 131.7 (Ar), 132.1 (Ar), 132.1 (Ar), 136.3 (Ar), 150.7 (Ar), 155.5 (Ar), 158.9 (Ar), 163.0 (C=O), 164.3 (C=O), 164.8 (C=O). Elemental analysis, found: C, 71.62; H, 6.42. Calc. for C₄₀H₄₃ClO₇; C, 71.58; H, 6.46%

Dodecyl 4'-(3-(benzyloxy)benzoyloxy)biphenyl-4-carboxylate (39). The synthesis of **39** was carried out according to the method described for **37**. Yield: 60 %; FTIR (KBr) ν (cm⁻¹) = 3415, 2915, 2850, 1725, 1710, 1608, 1598, 1492, 1440, 1384, 1324, 1273, 1189, 1171, 1121, 1086, 1004, 989, 927, 875, 855, 770, 751, 692, 716, 680; ¹H NMR (200 MHz, CCl₃D) δ : 0.90 (t, J = 6.5 Hz, 3H, CH₃), 1.17–1.65 (m, 18H, CH₂), 1.81 (quin, J = 6.8 Hz, 2H, CH₂), 4.36 (t, J = 6.6 Hz, 2H, CH₂), 5.18 (s, 2H, CH₂), 7.26–7.52 (comp, 9H, Ar), 7.68 (d, J = 8.4 Hz, 2H, Ar), 7.70 (d, J = 8.6 Hz, 2H, Ar), 7.84–7.89 (m, 2H, Ar), 8.14 (d, J = 8.6 Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.2 (CH₂), 70.2 (CH₂), 115.7 (Ar), 120.9 (Ar), 122.2 (Ar), 122.9 (Ar), 127.0 (Ar), 127.6 (Ar), 128.2 (Ar), 128.4 (Ar), 128.7 (Ar), 129.4 (Ar), 129.7 (Ar), 130.1 (Ar), 130.7 (Ar), 136.4 (Ar), 137.9 (Ar), 144.6 (Ar), 151.0 (Ar), 158.9 (Ar), 165.0 (C=O), 166.5 (C=O). Elemental analysis, found: C, 78.95; H, 7.49. Calc. for C₃₉H₄₄O₅: C, 79.02; H, 7.48%.

4-(Dodecyloxycarbonyl)phenyl 3-chloro-4-(3-hydroxybenzoyloxy)benzoate (44). Palladium on activated carbon (10% Pd/C, 0.15 g) was added to a solution of compound **37** (0.76 g, 1.13 mmol) in a mixture of cyclohexane (30 mL) and cyclohexene (30 mL) and the reaction mixture was vigorously stirred under reflux until the starting material disappeared (TLC control). The reaction mixture is then left to cool down under stirring and acetone was added (15 ml). The resulting mixture was again heated to boil and filtered while hot. The solvents were evaporated and the crude product was recrystallized from toluene. Yield: 42 %; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, J = 6.6 Hz, 3H, CH₃), 1.14–1.52 (m, 18H, CH₂), 1.79 (quin, J = 6.8 Hz, 2H, CH₂), 4.34 (t, J = 6.6 Hz, 2H, CH₂), 5.64 (s, 2H, CH₂), 7.17 (ddd, J = 1.0, 2.6 and 8.2 Hz, 1H, Ar), 7.29 (d, J = 8.8 Hz, 2H, Ar), 7.36–7.48 (m, 2H, Ar), 7.71 (dd, J = 1.8 and 2.4 Hz, 1H, Ar), 7.82 (dt, J = 1.2 and 7.8 Hz, 1H, Ar), 8.15 (d, J = 8.8 Hz, 2H, Ar), 8.20 (d, J = 2 Hz, 1H, Ar), 8.35 (d, J = 2 Hz, 1H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.3 (CH₃), 22.6 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.5 (CH₂), 117.0 (Ar), 121.6 (Ar), 122.9 (Ar), 124.8 (Ar), 127.8 (Ar), 128.1 (Ar), 128.4 (Ar), 129.6 (Ar), 129.9 (Ar), 130.1 (Ar), 131.3 (Ar), 132.0 (Ar), 132.4 (Ar), 151.6 (Ar), 154.2 (Ar), 156.1 (Ar), 162.6 (C=O), 163.7 (C=O), 166.7 (C=O). Elemental analysis, found: C, 68.19; H, 6.45. Calc. for C₃₃H₃₇ClO₇: C, 68.21; H, 6.42%.

Dodecyl 3-chloro-4-(4-(3-hydroxybenzoyloxy)benzoyloxy)benzoate (45). The synthesis of **45** was carried out according to the method described for **44**. Yield: 70 %; FTIR (KBr) ν (cm⁻¹) = 3341, 2953, 2920, 2850, 1752, 1736, 1720, 1697, 1604, 1505, 1488, 1471, 1456, 1413, 1385, 1294, 1281, 1245, 1200, 1162, 1116, 1093, 1054, 1015, 999, 923, 882, 759, 727, 692, 678, 600; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, J = 6.4 Hz, 6H, CH₃), 1.27–1.47 (m, 18H, CH₂), 1.78 (quin, J = 6.8 Hz, 2H, CH₂),

4.34 (t, $J = 6.7$ Hz, 2H, CH₂), 5.67 (s, 1H, OH), 7.14 (ddd, $J = 1.0, 2.6$ and 8.1 Hz, 1H, Ar), 7.38 (d, $J = 8.6$ Hz, 2H, Ar), 7.39 (d, $J = 8.8$ Hz, 1H, Ar), 7.68 (dd, $J = 1.6$ and 2.5 Hz, 1H, Ar), 7.79 (dt, $J = 1.2$ and 7.8 Hz, 1H, Ar), 8.03 (dd, $J = 2.0$ and 8.4 Hz, 1H, Ar), 8.18 (d, $J = 2.0$ Hz, 1H, Ar), 8.32 (d, $J = 8.8$ Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 25.9 (CH₂), 28.6 (CH₂), 29.2 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.8 (CH₂), 116.8 (Ar), 121.3 (Ar), 122.2 (Ar), 122.7 (Ar), 123.8 (Ar), 126.0 (Ar), 127.4 (Ar), 129.4 (Ar), 129.6 (Ar), 130.0 (Ar), 130.2 (Ar), 131.8 (Ar), 132.2 (Ar), 150.7 (Ar), 155.5 (Ar), 156.0 (Ar), 163.1 (Ar), 164.4 (C=O), 165.1 (C=O). Elemental analysis, found: C, 68.24; H, 6.38. Calc. for C₃₃H₃₇ClO₇: C, 68.21; H, 6.42%.

Dodecyl 4'-(3-hydroxy)benzoyloxy)biphenyl-4-carboxylate (46). The synthesis of **46** was carried out according to the method described for **44**. Yield: 77 %; FTIR (KBr) ν (cm⁻¹) = 3440, 2952, 2917, 2850, 1730, 1689, 1602, 1520, 1495, 1473, 1451, 1398, 1384, 1294, 1211, 1201, 1174, 1125, 1099, 1079, 1009, 1000, 922, 882, 869, 851, 817, 801, 771, 748; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, $J = 6.4$ Hz, 3H, CH₃), 1.15–1.49 (m, 18H, CH₂), 1.79 (quin, $J = 6.8$ Hz, 2H, CH₂), 4.35 (t, $J = 6.6$ Hz, 2H, CH₂), 5.54 (s, 1H, OH), 7.14 (ddd, $J = 0.8, 2.5$ and 8.0 Hz, 1H, Ar), 7.30 (d, $J = 8.6$ Hz, 2H, Ar), 7.40 (t, $J = 8.0$ Hz, 1H, Ar), 7.68 (d, $J = 8.4$ Hz, 2H, Ar), 7.70 (d, $J = 8.6$ Hz, 2H, 7.70 (dd, $J = 1.6$ and 2.5 Hz, 1H, Ar), 7.80 (dt, $J = 1.0$ and 7.82 Hz, 1H, Ar), 8.13 (d, $J = 8.4$ Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.3 (CH₂), 116.8 (Ar), 121.0 (Ar), 122.2 (Ar), 122.7 (Ar), 127.0 (Ar), 128.4 (Ar), 129.3 (Ar), 130.0 (Ar), 130.2 (Ar), 130.8 (Ar), 137.9 (Ar), 144.7 (Ar), 151.0 (Ar), 155.9 (Ar), 164.9 (C=O), 166.8 (C=O). Elemental analysis, found: C, 76.49; H, 7.58. Calc. for C₃₂H₃₈O₅: C, 76.46; H, 7.62%.

Compound Ia (4-((4-(octyloxycarbonyl)phenoxy)carbonyl)phenyl 3-(4-((4-(undecyloxy)phenyl)diazanyl)benzoyloxy)benzoate) A mixture of 4-(4-undecyloxyphenylazo)benzoic acid (0.37 g, 0.94 mmol), oxalyl chloride (0.12 mL, 1.4 mmol) and few drops of DMF in dry toluene (45 mL) was stirred at room temperature for 16 hours. When the reaction mixture became a red solution, the solvent was removed and the obtained orange solid was dried under vacuum for 2 hours. To a solution of the acid chloride in dry dichloromethane (20 mL), compound **40** (0.42 g, 0.86 mmol) previously dissolved in dichloromethane (10 mL) was added, followed by the addition of triethylamine (0.19 mL, 1.4 mmol). The reaction mixture was stirred at the room temperature for 48 h. It was washed with 10% HCl (2 × 10 mL) and several times with cold water and finally dried over anhydrous sodium sulphate. The crude residue obtained after removal of solvent was chromatographed on silica gel using chloroform as eluent. Removal of solvent from the eluate afforded an orange material which was recrystallized from a hexane/toluene mixture to give the target bent-core compound. Yield: 60%; FTIR

(KBr) ν (cm^{-1}) = 2920, 2851, 1740, 1707, 1602, 1503, 1471, 1439, 1384, 1309, 1257, 1205, 1162, 1141, 1116, 1066, 1016, 914, 863, 847, 763, 743, 688, 548; ^1H NMR (200 MHz, CCl_3D) δ : 0.89 (t, J = 6.2 Hz, 6H, CH_3), 1.16–1.57 (m, 26H, CH_2), 1.69–1.91 (m, 4H, CH_2), 4.07 (t, J = 6.5 Hz, 2H, CH_2), 4.33 (t, J = 6.6 Hz, 2H, CH_2), 7.03 (d, J = 9.0 Hz, 2H, Ar), 7.31 (d, J = 8.8 Hz, 2H, Ar), 7.41 (d, J = 8.8 Hz, 2H, Ar), 7.60 (t, J = 2 Hz, 1H, Ar), 7.64 (t, J = 7.8 Hz, 1H, Ar), 7.98 (d, J = 9.0 Hz, 2H, Ar), 8.00 (d, J = 8.6 Hz, 2H, Ar), 8.12–8.16 (comp, 3H, Ar), 8.18 (dd, J = 1.6 and 4.0 Hz, 1H, Ar), 8.30 (d, J = 8.8 Hz, 2H, Ar), 8.36 (d, J = 8.6 Hz, 2H, Ar); ^{13}C NMR (50 MHz, CDCl_3): δ 14.1 (CH_3), 22.7 (CH_2), 26.0 (CH_2), 28.7 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 31.8 (CH_2), 31.9 (CH_2), 65.3 (CH_2), 68.5 (CH_2), 114.9 (Ar), 121.7 (Ar), 122.1 (Ar), 122.6 (Ar), 123.7 (Ar), 125.4 (Ar), 126.9 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.8 (Ar), 130.0 (Ar), 130.6 (Ar), 131.2 (Ar), 131.3 (Ar), 132.0 (Ar), 146.9 (Ar), 151.1 (Ar), 154.4 (Ar), 155.2 (Ar), 156.0 (Ar), 162.6 (Ar), 163.7 (C=O), 163.9 (C=O), 164.6 (C=O), 165.9 (C=O). Elemental analysis, found: C, 73.23; H, 6.98; N, 3.18. Calc. for $\text{C}_{53}\text{H}_{60}\text{N}_2\text{O}_9$: C, 73.25; H, 6.96; N, 3.22%.

Compound Ib *4-((4-(decyloxy)phenyl)phenoxy)carbonyl)phenyl 3-(4-((4-(undecyloxy)phenyl)diazanyl)benzoyloxy)benzoate*. The synthesis of **Ib** was carried out according to the method described for **Ia**. Yield: 46 %; FTIR (KBr) ν (cm^{-1}) = 2955, 2919, 2851, 1738, 1714, 1639, 1603, 1502, 1476, 1384, 1312, 1266, 1253, 1216, 1164, 1067, 1016, 865, 842, 760, 737, 689; ^1H NMR (200 MHz, CCl_3D) δ : 0.88 (t, J = 6.4 Hz, 6H, CH_3), 1.28–1.60 (m, 30H, CH_2), 1.71–1.90 (m, 4H, CH_2), 4.06 (t, J = 6.5 Hz, 2H, CH_2), 4.33 (t, J = 6.6 Hz, 2H, CH_2), 7.03 (d, J = 9.2 Hz, 2H, Ar), 7.31 (d, J = 8.6 Hz, 2H, Ar), 7.41 (d, J = 8.8 Hz, 2H, Ar), 7.60 (t, J = 2 Hz, 1H, Ar), 7.64 (t, J = 7.8 Hz, 1H, Ar), 7.98 (d, J = 9.0 Hz, 2H, Ar), 8.00 (d, J = 8.6 Hz, 2H, Ar), 8.11–8.16 (comp, 3H, Ar), 8.18 (dd, J = 1.6 and 4.0 Hz, 1H, Ar), 8.30 (d, J = 8.8 Hz, 2H, Ar), 8.36 (d, J = 8.6 Hz, 2H, Ar); ^{13}C NMR (50 MHz, CDCl_3): δ 14.1 (CH_3), 22.7 (CH_2), 26.0 (CH_2), 28.7 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 65.3 (CH_2), 68.5 (CH_2), 114.9 (Ar), 121.7 (Ar), 122.1 (Ar), 122.6 (Ar), 123.7 (Ar), 125.4 (Ar), 126.8 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.8 (Ar), 130.0 (Ar), 130.6 (Ar), 131.2 (Ar), 131.3 (Ar), 132.0 (Ar), 146.8 (Ar), 151.1 (Ar), 154.4 (Ar), 155.2 (Ar), 156.0 (Ar), 162.6 (Ar), 163.7 (C=O), 163.9 (C=O), 164.6 (C=O), 165.9 (C=O). Elemental analysis, found: C, 73.64; H, 7.19; N, 3.12. Calc. for $\text{C}_{55}\text{H}_{64}\text{N}_2\text{O}_9$: C, 73.64; H, 7.19; N, 3.12%.

Compound Ic *4-((4-(dodecyloxy)phenyl)phenoxy)carbonyl)phenyl 3-(4-((4-(undecyloxy)phenyl)diazanyl)benzoyloxy)benzoate*. The synthesis of **Ic** was carried out according to the method described for **Ia**. Yield: 65%; FTIR (KBr) ν (cm^{-1}) = 2954, 2917, 2850, 1737, 1712, 1602, 1502, 1472, 1281, 1266, 1252, 1216, 1164, 1067, 1015, 865, 843, 760, 735, 550, 513; ^1H NMR (200

MHz, CCl₃D) δ : 0.88 (t, J = 6.2 Hz, 6H, CH₃), 1.15–1.60 (m, 34H, CH₂), 1.71–1.90 (m, 4H, CH₂), 4.06 (t, J = 6.8 Hz, 2H, CH₂), 4.33 (t, J = 6.8 Hz, 2H, CH₂), 7.03 (d, J = 9.0 Hz, 2H, Ar), 7.31 (d, J = 8.4 Hz, 2H, Ar), 7.41 (d, J = 8.4 Hz, 2H, Ar), 7.60 (t, J = 2 Hz, 1H, Ar), 7.64 (t, J = 7.8 Hz, 1H, Ar), 7.98 (d, J = 9.0 Hz, 2H, Ar), 7.98 (d, J = 9.0 Hz, 2H, Ar), 7.99 (d, J = 8.4 Hz, 2H, Ar), 8.11–8.17 (m, 4H, Ar), 8.30 (d, J = 9.0 Hz, 2H, Ar), 8.35 (d, J = 8.6 Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.3 (CH₂), 68.5 (CH₂), 114.9 (Ar), 121.7 (Ar), 122.1 (Ar), 122.6 (Ar), 123.7 (Ar), 125.4 (Ar), 126.9 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.8 (Ar), 129.9 (Ar), 130.6 (Ar), 131.2 (Ar), 131.3 (Ar), 132.0 (Ar), 146.9 (Ar), 151.1 (Ar), 154.4 (Ar), 155.2 (Ar), 156.0 (Ar), 162.6 (Ar), 163.7 (C=O), 163.9 (C=O), 164.6 (C=O), 165.9 (C=O). Elemental analysis, found: C, 73.93; H, 7.42; N, 3.04. Calc. for C₅₇H₆₈N₂O₉: C, 74.00; H, 7.41; N, 3.03%.

Compound Id 4-((4-(tetradecyloxy)phenyl)phenoxy)carbonyl)phenyl 3-(4-((4-(undecyloxy)phenyl)diazenyl)benzoyloxy)benzoate. The synthesis of **Id** was carried out according to the method described for **Ia**. Yield: 35 %. FTIR (KBr) ν (cm⁻¹) = 2954, 2917, 2850, 1737, 1713, 1603, 1503, 1472, 1281, 1266, 1252, 1216, 1165, 1068, 1016, 865, 842, 760, 737, 689; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, J = 6.2 Hz, 6H, CH₃), 1.15–1.59 (m, 38H, CH₂), 1.71–1.91 (m, 4H, CH₂), 4.06 (t, J = 6.6 Hz, 2H, CH₂), 4.33 (t, J = 6.6 Hz, 2H, CH₂), 7.03 (d, J = 9.0 Hz, 2H, Ar), 7.32 (d, J = 8.8 Hz, 2H, Ar), 7.41 (d, J = 8.6 Hz, 2H, Ar), 7.60 (t, J = 2.0 Hz, 1H, Ar), 7.64 (t, J = 8.0 Hz, 1H, Ar), 7.97 (d, J = 9.0 Hz, 2H, Ar), 7.99 (d, J = 8.6 Hz, 2H, Ar), 8.12–8.16 (comp, 3H, Ar), 8.18 (dd, J = 1.8 and 3.2 Hz), 8.30 (d, J = 8.8 Hz, 2H, Ar), 8.36 (d, J = 8.6 Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.3 (CH₂), 68.5 (CH₂), 114.9 (Ar), 121.7 (Ar), 122.1 (Ar), 122.6 (Ar), 123.7 (Ar), 125.4 (Ar), 126.9 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.8 (Ar), 129.9 (Ar), 130.6 (Ar), 131.2 (Ar), 131.3 (Ar), 132.0 (Ar), 146.9 (Ar), 151.1 (Ar), 154.4 (Ar), 155.2 (Ar), 156.0 (Ar), 162.6 (Ar), 163.7 (C=O), 163.9 (C=O), 164.6 (C=O), 165.9 (C=O). Elemental analysis, found: C, 74.36; H, 7.59; N, 2.95. Calc. for C₅₉H₇₂N₂O₉: C, 74.34; H, 7.61; N, 2.94%.

Compound Ie 4-((4-(dodecyloxy)phenyl)phenoxy)carbonyl)phenyl 3-(4-((4-(undec-10-enyloxy)phenyl)diazenyl)benzoyloxy)benzoate. The synthesis of **Ie** was carried out according to the method described for **Ia**. Yield: 55 %; FTIR (KBr) ν (cm⁻¹) = 2918, 2850, 1738, 1713, 1602, 1502, 1473, 1312, 1281, 1267, 1252, 1216, 1165, 1068, 1017, 913, 865, 843, 760, 737, 689, 551; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, J = 6.4 Hz, 3H, CH₃), 1.27–1.60 (m, 30H, CH₂), 1.71–1.90 (m, 4H, CH₂), 2.05 (q, J = 6.6 Hz, 2H, CH₂), 4.06 (t, J = 6.5 Hz, 2H, CH₂), 4.33 (t, J = 6.6 Hz, 2H, CH₂), 4.90–

5.06 (m, 2H, =CH₂), 5.72–5.93 (m, 1H, –CH=), 7.03 (d, *J* = 9.0 Hz, 2H, Ar), 7.31 (d, *J* = 8.6 Hz, 2H, Ar), 7.41 (d, *J* = 8.8 Hz, 2H, Ar), 7.59 (t, *J* = 1.8 Hz, 1H, Ar), 7.64 (t, *J* = 8 Hz, 1H, Ar), 7.97 (d, *J* = 9.0 Hz, 2H, Ar), 7.99 (d, *J* = 8.6 Hz, 2H, Ar), 8.12–8.16 (comp, 3H, Ar), 8.18 (dd, *J* = 1.8 and 3.4 Hz), 8.30 (d, *J* = 8.8 Hz, 2H, Ar), 8.36 (d, *J* = 8.6 Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 28.9 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 33.8 (CH₂), 65.3 (CH₂), 68.4 (CH₂), 114.2 (=CH₂), 114.8 (Ar), 121.7 (Ar), 122.1 (Ar), 122.6 (Ar), 123.7 (Ar), 125.4 (Ar), 126.9 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.8 (Ar), 129.9 (Ar), 130.6 (Ar), 131.2 (Ar), 131.3 (Ar), 132.0 (Ar), 139.2 (–CH=), 146.9 (Ar), 151.1 (Ar), 154.4 (Ar), 155.2 (Ar), 156.0 (Ar), 162.6 (Ar), 163.7 (C=O), 163.9 (C=O), 164.6 (C=O), 165.9 (C=O). Elemental analysis, found: C, 74.13; H, 7.20; N, 3.07. Calc. for C₅₇H₆₆N₂O₉: C, 74.16; H, 7.21; N, 3.03%.

Compound If (4-((4-(tetradecyloxycarbonyl)phenoxy)carbonyl)phenyl 3-(4-((4-(undec-10-enyloxy)phenyl)diazanyl)benzoyloxy)benzoate). The synthesis of **If** was carried out according to the method described for **Ia**. Yield: 35 %; FTIR (KBr) ν (cm⁻¹) = 2918, 2850, 1737, 1714, 1602, 1502, 1473, 1414, 1384, 1280, 1267, 1252, 1216, 1165, 1068, 1017, 913, 865, 842, 761, 737, 689, 551; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, *J* = 6.4 Hz, 3H, CH₃), 1.26–1.56 (m, 34H, CH₂), 1.71–1.91 (m, 4H, CH₂), 2.05 (q, *J* = 6.8 Hz, 2H, CH₂), 4.07 (t, *J* = 6.5 Hz, 2H, CH₂), 4.33 (t, *J* = 6.6 Hz, 2H, CH₂), 4.91–5.06 (m, 2H, =CH₂), 5.72–5.92 (m, 1H, –CH=), 7.03 (d, *J* = 9.0 Hz, 2H, Ar), 7.31 (d, *J* = 8.8 Hz, 2H, Ar), 7.41 (d, *J* = 8.6 Hz, 2H, Ar), 7.60 (t, *J* = 2 Hz, 1H, Ar), 7.64 (t, *J* = 8.0 Hz, 1H, Ar), 7.97 (d, *J* = 8.8 Hz, 2H, Ar), 7.99 (d, *J* = 8.6 Hz, 2H, Ar), 8.12–8.16 (comp, 3H, Ar), 8.18 (dd, *J* = 1.6 and 3.4 Hz, 1H, Ar), 8.30 (d, *J* = 8.6 Hz, 2H, Ar), 8.36 (d, *J* = 8.4 Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 28.9 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 33.8 (CH₂), 65.3 (CH₂), 68.4 (CH₂), 114.2 (=CH₂), 114.8 (Ar), 121.7 (Ar), 122.1 (Ar), 122.6 (Ar), 123.7 (Ar), 125.4 (Ar), 126.9 (Ar), 127.6 (Ar), 127.9 (Ar), 128.3 (Ar), 129.8 (Ar), 130.0 (Ar), 130.6 (Ar), 131.2 (Ar), 131.3 (Ar), 132.0 (Ar), 139.2 (–CH=), 146.9 (Ar), 151.1 (Ar), 154.4 (Ar), 155.2 (Ar), 156.0 (Ar), 162.6 (Ar), 163.7 (C=O), 163.9 (C=O), 164.6 (C=O), 165.9 (C=O). Elemental analysis, found: C, 74.47; H, 7.45; N, 2.96. Calc. for C₅₉H₇₀N₂O₉: C, 74.50; H, 7.42; N, 2.95%.

Compound Ig (4-((4-(dodecyloxycarbonyl)phenoxy)carbonyl)phenyl 3-(4-((4-(dec-9-enyloxy)carbonyl)phenyl)diazanyl)benzoyloxy)benzoate). The synthesis of **Ig** was carried out according to the method described for **Ia**. Yield: 35%; FTIR (KBr) ν (cm⁻¹) = 2918, 2850, 1737, 1715, 1603, 1506, 1468, 1447, 1414, 1384, 1277, 1224, 1207, 1165, 1077, 1015, 914, 862, 759, 740, 688, 548; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, *J* = 6.4 Hz, 3H, CH₃), 1.27–1.57 (m, 28H, CH₂), 1.78 (q, *J* = 6.8 Hz, 4H, CH₂), 2.06 (q, *J* = 6.8 Hz, 2H, CH₂), 2.61 (t, *J* = 7.4 Hz, 2H, CH₂), 4.33 (t, *J* = 6.6 Hz,

2H, CH₂), 4.90–5.06 (m, 2H, =CH₂), 5.72–5.93 (m, 1H, –CH=), 7.28 (d, *J* = 9.2 Hz, 2H, Ar), 7.31 (d, *J* = 8.8 Hz, 2H, Ar), 7.41 (d, *J* = 8.8 Hz, 2H, Ar), 7.60 (t, *J* = 2 Hz, 1H, Ar), 7.65 (t, *J* = 7.8 Hz, 1H, Ar), 8.02 (d, *J* = 9.0 Hz, 2H, Ar), 8.03 (d, *J* = 8.6 Hz, 2H, Ar), 8.12–8.16 (comp, 3H, Ar), 8.18 (dd, *J* = 1.4 and 3.2 Hz, 1H, Ar), 8.30 (d, *J* = 8.8 Hz, 2H, Ar), 8.38 (d, *J* = 8.6 Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.6 (CH₂), 24.8 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 28.7 (CH₂), 29.0 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 33.7 (CH₂), 34.4 (CH₂), 65.3 (CH₂), 114.2 (=CH₂), 121.7 (Ar), 122.1 (Ar), 122.4 (Ar), 122.9 (Ar), 123.7 (Ar), 124.5 (Ar), 126.9 (Ar), 127.5 (Ar), 127.9 (Ar), 128.3 (Ar), 130.0 (Ar), 130.6 (Ar), 131.2 (Ar), 131.4 (Ar), 132.0 (Ar), 139.2 (–CH=), 150.1 (Ar), 151.1 (Ar), 153.5 (Ar), 154.4 (Ar), 155.2 (Ar), 155.6 (Ar), 163.7 (Ar), 163.9 (C=O), 164.4 (C=O), 165.9 (C=O), 171.9 (C=O). Elemental analysis, found: C, 73.08; H, 6.81; N, 3.02. Calc. for C₅₇H₆₄N₂O₁₀: C, 73.05; H, 6.88; N, 2.99%.

Compound Ih (*4-(dodecyloxycarbonyl)phenyl 3-chloro-4-(3-(4-((4-(undecyloxy)phenyl)diazenyl)benzoyloxy)benzoyloxy)benzoate*). The synthesis of **Ih** was carried out according to the method described for **Ia**. Yield: 45 %; FTIR (KBr) ν (cm⁻¹) = 2956, 2917, 2852, 1745, 1726, 1706, 1602, 1506, 1473, 1449, 1399, 1384, 1278, 1260, 1208, 1164, 1141, 1081, 1015, 902, 863, 836, 763, 737, 689; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, *J* = 6.4 Hz, 6H, CH₃), 1.27–1.60 (m, 34H, CH₂), 1.71–1.90 (m, 4H, CH₂), 4.06 (t, *J* = 6.6 Hz, 2H, CH₂), 4.33 (t, *J* = 6.6 Hz, 2H, CH₂), 7.03 (d, *J* = 9.0 Hz, 2H, Ar), 7.31 (d, *J* = 8.8 Hz, 2H, Ar), 7.48 (d, *J* = 8.6 Hz, 1H, Ar), 7.61 (t, *J* = 2.0 Hz, 1H, Ar), 7.65 (t, *J* = 8.0 Hz, 1H, Ar), 7.97 (d, *J* = 9.0 Hz, 2H, Ar), 7.99 (d, *J* = 8.6 Hz, 2H, Ar), 8.12–8.19 (comp, 4H, Ar), 8.22 (d, *J* = 2 Hz, 1H, Ar), 8.36 (d, *J* = 8.6 Hz, 2H, Ar), 8.36 (d, *J* = 2.2 Hz, 1H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.0 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.3 (CH₂), 68.5 (CH₂), 114.9 (Ar), 121.6 (Ar), 122.6 (Ar), 123.9 (Ar), 124.2 (Ar), 125.4 (Ar), 127.9 (Ar), 128.1 (Ar), 128.2 (Ar), 128.5 (Ar), 129.8 (Ar), 129.9 (Ar), 130.0 (Ar), 131.3 (Ar), 132.4 (Ar), 146.9 (Ar), 151.1 (Ar), 151.5 (Ar), 154.2 (Ar), 156.0 (Ar), 162.6 (Ar), 162.8 (C=O), 162.9 (C=O), 164.5 (C=O), 165.9 (C=O). Elemental analysis, found: C, 71.41; H, 7.12; N, 2.90. Calc. for C₅₇H₆₇ClN₂O₉: C, 71.34; H, 7.04; N, 2.92%.

Compound Ii (*dodecyl 3-chloro-4-(4-(3-(4-((4-(undecyloxy)phenyl)diazenyl)benzoyloxy)benzoyloxy)benzoyloxy)benzoate*). The synthesis of **Ii** was carried out according to the method described for **Ia**. Yield: 45 %; FTIR (KBr) ν (cm⁻¹) = 2957, 2917, 2852, 1736, 1721, 1603, 1504, 1472, 1440, 1405, 1384, 1283, 1269, 1253, 1218, 1161, 1148, 1077, 1015, 915, 859, 829, 758, 751, 737; ¹H NMR (200 MHz, CCl₃D) δ : 0.88 (t, *J* = 6.2 Hz, 6H, CH₃), 1.27–1.59 (m, 34H, CH₂), 1.71–1.90 (m, 4H, CH₂), 4.06 (t, *J* = 6.6 Hz, 2H, CH₂), 4.34 (t, *J* = 6.6 Hz,

2H, CH₂), 7.03 (d, $J = 9.0$ Hz, 2H, Ar), 7.39 (d, $J = 8.4$ Hz, 1H, Ar), 7.42 (d, $J = 8.6$ Hz, 2H, Ar), 7.60 (t, $J = 2$ Hz, 1H, Ar), 7.64 (t, $J = 7.8$ Hz, 1H, Ar), 7.98 (d, $J = 9.0$ Hz, 2H, Ar), 8.00 (d, $J = 8.4$ Hz, 2H, Ar), 8.05 (d, $J = 2$ Hz, 1H, Ar), 8.12 (d, $J = 2.0$ Hz, 1H, Ar), 8.15 (t, $J = 2$ Hz, 1H, Ar), 8.18 (d, $J = 1.8$ Hz, 1H, Ar), 8.34 (d, $J = 8.8$ Hz, 2H, Ar), 8.36 (d, $J = 8.4$ Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.6 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.7 (CH₂), 68.5 (CH₂), 114.9 (Ar), 122.2 (Ar), 122.6 (Ar), 123.7 (Ar), 123.8 (Ar), 125.4 (Ar), 126.2 (Ar), 127.4 (Ar), 127.6 (Ar), 127.9 (Ar), 129.2 (Ar), 129.6 (Ar), 129.8 (Ar), 130.0 (Ar), 130.6 (Ar), 131.3 (Ar), 131.8 (Ar), 132.3 (Ar), 146.9 (Ar), 150.7 (Ar), 151.1 (Ar), 155.4 (Ar), 156.0 (Ar), 162.6 (Ar), 163.0 (C=O), 163.7 (C=O), 164.6 (C=O), 164.9 (C=O). Elemental analysis, found: C, 71.27; H, 7.05; N, 3.00. Calc. for C₅₇H₆₇ClN₂O₉: C, 71.34; H, 7.04; N, 2.92%.

Compound Ij (dodecyl 4'-(3-(4-((4-(undecyloxy)phenyl)diazenyl)benzoyloxy)benzoyloxy)biphenyl-4-carboxylate). The synthesis of **Ij** was carried out according to the method described for **Ia**. Yield: 75 %; FTIR (KBr) ν (cm⁻¹) = 2955, 2917, 2849, 1733, 1713, 1602, 1585, 1470, 1397, 1276, 1252, 1193, 1117, 1085, 1026, 911, 841, 769, 552; ¹H NMR (200 MHz, CDCl₃) δ : 0.88 (t, $J = 5.8$ Hz, 6H, CH₃), 1.27–1.59 (m, 34H, CH₂), 1.72–1.90 (m, 4H, CH₂), 4.06 (t, $J = 6.5$ Hz, 2H, CH₂), 4.34 (t, $J = 6.6$ Hz, 2H, CH₂), 7.03 (d, $J = 9.0$ Hz, 2H, Ar), 7.33 (d, $J = 8.6$ Hz, 2H, Ar), 7.53–7.71 (m, 6H, Ar), 7.97 (d, $J = 9.0$ Hz, 2H, Ar), 7.99 (d, $J = 8.6$ Hz, 2H, Ar), 8.10–8.20 (m, 4H, Ar), 8.36 (d, $J = 8.6$ Hz, 2H, Ar); ¹³C NMR (50 MHz, CDCl₃): δ 14.1 (CH₃), 22.7 (CH₂), 26.0 (CH₂), 28.7 (CH₂), 29.1 (CH₂), 29.3 (CH₂), 29.6 (CH₂), 31.9 (CH₂), 65.2 (CH₂), 68.5 (CH₂), 114.8 (Ar), 122.2 (Ar), 122.6 (Ar), 123.6 (Ar), 125.4 (Ar), 127.0 (Ar), 127.3 (Ar), 127.8 (Ar), 128.5 (Ar), 129.4 (Ar), 129.9 (Ar), 130.1 (Ar), 131.0 (Ar), 131.3 (Ar), 138.0 (Ar), 144.6 (Ar), 146.8 (Ar), 150.8 (Ar), 151.1 (Ar), 156.0 (Ar), 162.6 (Ar), 164.3 (C=O), 164.6 (C=O), 166.5 (C=O). Elemental analysis, found: C, 76.36; H, 7.74; N, 3.16. Calc. for C₅₆H₆₈N₂O₇: C, 76.33; H, 7.78; N, 3.18%.

Physical investigations

To confirm the chemical structure of the synthesized compounds, the following analytical methods were applied. Elemental analysis was realized using an Elemental Vario EL III microanalyzer, their results were found to be in good agreement ($\pm 0.3\%$) with the calculated values. FT-IR spectra were recorded on a Bomem MB 100 spectrophotometer (ν_{\max} in cm⁻¹) on KBr pellets. ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 200 spectrometer at 200 MHz for ¹H NMR and 50 MHz for ¹³C NMR spectra. NMR spectra were recorded in CDCl₃, or DMSO-*d*₆, using TMS as the internal standard (chemical shift δ in ppm).

The temperatures and enthalpies of the phase transitions were determined by differential scanning calorimetry (DSC) on a METTLER FP89 using cooling and heating runs at a rate of 5 °C min⁻¹. The samples of 3–5 mg were sealed in aluminium pans. For electro-optical investigations the materials were filled in home made 5 mm thick films with transparent indium tin oxide (ITO) electrodes and an antiparallel rubbed polyimide alignment layer. The electro-optical measurements were done using an Olympus BX51 microscope equipped with 90° crossed polarizers, an HCS402 hot stage from Instec Inc., and a digital camera (14.2 Mp Color Mosaic Model from Diagnostic Instruments, Inc.). The images were captured using a Hitachi CCD camera under transmitted light between crossed polarizers. The electric signals were applied using a HP function generator and FLC voltage amplifier.

Small angle X-ray scattering (SAXS) measurements were performed at beamline 7.3.3 of the Advanced Light Source of Lawrence Berkeley National Lab (10keV incident beam energy (1.24 Å wavelength), utilizing a Pilatus 2M detector) and at Structural Research Laboratory of University of Warsaw (Bruker NanoStar system with Vantec2000 detector, Cu K_a radiation (1.54 Å), equipped with heating stage). The materials were filled into 1 mm diameter quartz X-ray tubes, which were then mounted into a custom-built aluminum cassette that allowed X-ray detection with ±13.51° angular range. The cassette fits into a standard hot stage (Instec model HCS402) that allowed temperature control with ±0.05 °C precision. The stage also included two cylindrical neodymium iron boron magnets that supplied a magnetic induction of $B = 1.5$ T perpendicular to the incident X-ray beam.

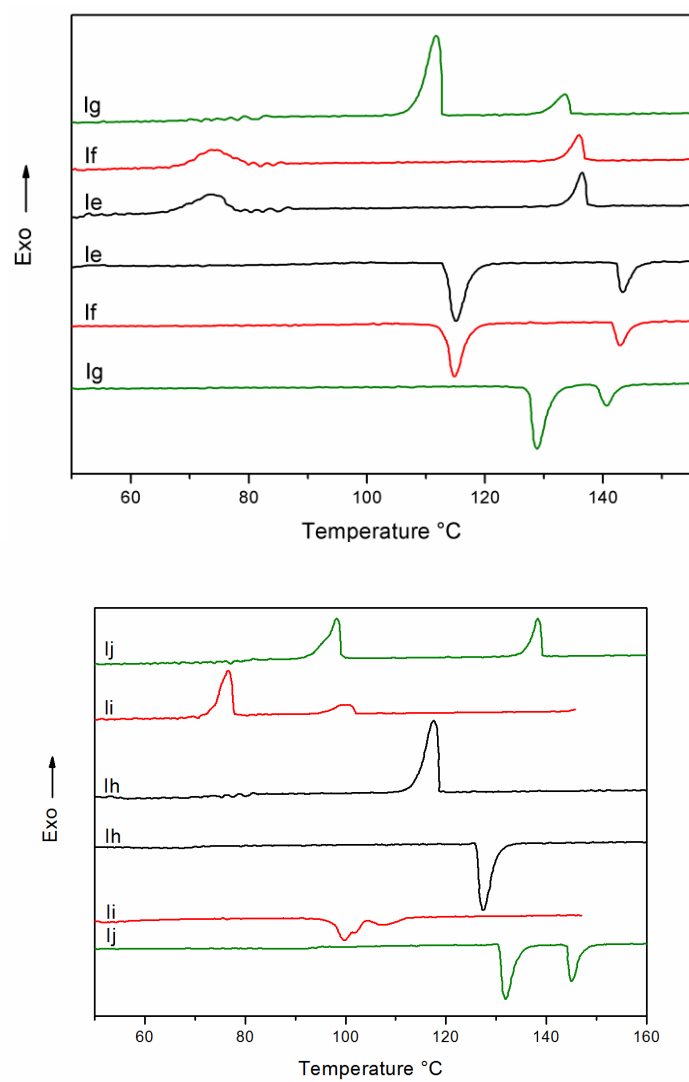


Fig. S1 DSC heating and cooling curves of compounds a) **Ig–Ie** and b) **Ih–Ij** at 5 °C min^{-1} .

Table S1 Experimental peak positions and intensities of the investigated compounds

Compound	Temp. (°C)	(hk) signal position (\AA^{-1}) and normalized intensity in parenthesis				
		(01)	(02)	(10)	(11)	(20)
Ia	151	0.0437 (14.3)	0.0869 (2.7)	0.1368 (100)	0.1443 (6.4)	0.275 (3.6)
	103	0.022 (4.4)	0.0441 (0.8)	0.1227 (100)	0.1243 (22.3)	0.2458 (1.8)
Ib	145	0.0441 (9.9)	0.0890 (2.8)	0.1317 (100)	0.1367 (31.8)	0.2648 (2.9)
	110	0.0320 (14.1)	0.0626 (3.2)	0.1303 (100)	-	0.2606 (2.7)
Ic	148	0.0441 (5.6)	0.0897 (14.3)	0.1274 (100)	0.1538 (2.9)	0.2570 (1.8)
	112	0.0313 (5.7)	0.0634 (11.9)	0.1253 (100)	0.1403 (4.4)	0.2520 (1.7)
Id	139	0.0461 (100)	0.0917 (21.1)	0.1270 (91.7)	0.1354 (21.2)	0.2583 (7.8)
	91	0.0274 (100)	0.0544 (29.2)	0.1242 (72.7)	0.1289 (17)	0.2508 (7)
Ie	137	0.0465 (4.9)	0.0935 (1.3)	0.1274 (100)	0.1349 (15.3)	0.2552 (1.1)
	80	0.0258 (6.8)	0.0522 (1.2)	0.1245 (100)	0.1283 (29.7)	0.02486 (0.3)
If	141	0.0469 (2.5)	-	0.1239 (100)	0.1317 (11.1)	0.2485 (1.3)
	107	0.03418 (2.8)	0.06836 (1.1)	0.12034 (100)	0.12603 (11.3)	0.2435 (0.9)
Ig	134	0.0386 (3.2)	0.0777 (0.4)	0.1252 (100)	0.1315 (10.9)	0.2508 (0.4)
	117	0.0293 (3.2)	0.0591 (0.5)	0.1252 (100)	0.1289 (11.3)	0.2505 (1.1)
Ii	100	0.0591 (8.6)	0.1187 (2.1)	0.1261 (100)	0.141 (4.7)	0.2527 (1.3)
	91	0.0563 (7)	0.1131 (1.5)	0.1261 (100)	0.141 (3)	0.2517 (0.8)
Ij	143	0.0555 (2.3)	-	0.1303 (100)	0.1459 (2.9)	0.2648 (1.7)
	113	0.0434 (2.5)	-	0.1274 (100)	0.1331 (4.8)	0.2584 (1.6)

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