# Liquid crystalline dimers composed of bent-core mesogenic units

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## Supporting Information

## Synthesis

*General procedure A:* Esterification via acylchloride

The carboxylic acid (10 mmol) was solved or suspended in dichloromethane (100 ml) and a solution of oxalylchloride in dichloromethane (20 ml 2molar = 40 mmol) was added to the suspension, followed by a drop of pyridine. The obtained mixture was heated to reflux and stirred until the suspension cleared out. The mixture was cooled to room temperature, solvent and excess of oxalylchloride were removed under reduced pressure, dry toluene was added and removed with traces of reagent in vacuum. The obtained crude acylchloride was dissolved in dichloromethane (100 ml) and the corresponding phenol (10 mmol) was added, followed by pyridine (0.8 ml, 12 mmol) and DMAP (750 mg, 6 mmol). The reaction was stirred at room temperature and observed via TLC. To the reaction mixture was added a 5% aqueous solution of HCl, the resulting layers were separated, aqueous layers washed 2x with dichloromethane and combined organic fractions washed successively with 5% aqueous solution of HCl, 5% aqueous solution of NaOH (2x, only in cases where low molecular acid or phenol was used in excess in the reaction) and brine. The resulting solution was dried with anhydrous $NaSO_4$, solvent was removed in vacuum. The ratio of the reactants was varied in limits depending on their molar mass to allow a better reaction and purification. The detailed

amounts of the reactants used and the method of purification is described for each compound separately.

*General procedure B:* Deprotection of benzyl ethers and benzyl esters

The corresponding benzyl protected compound was suspended or dissolved in acetone (40 ml pro 1 g of starting material) and ammonium formate (4 mol pro 1 mol of protected compound) was added, followed by 5% Pd/C (0.1 g pro 1 g of starting material). The reaction mixture was stirred and heated to reflux under nitrogen atmosphere and observed by means of TLC. The reaction was stopped when all starting material disappeared, usually after 1 h. The hot mixture was 2x filtered to remove the catalyst (in case of products with low solubility in acetone, hot THF was used to wash the filter). In case of deprotection of phenols, the solvent was removed in vacuum, in case of acids the amount of solvent was reduced by half and the solution poured into a mixture of 5% aqueous solution of HCl and ice. The crude solids are filtered and washed twice with water. The remaining crude materials were purified as described for each compound.

*Compounds **1a-d, 2a-d, 3a-d** (see Scheme 1)*

**Ib:** 3-Hydroxyphenyl-4-(3-chloro-4-n-dodecyloxybenzoyloxy)benzoate

The 4-(3-chloro-4-n-octyloxybenzoyloxy)benzoic acid (9.65 g, 21.7 mmol) was converted into the corresponding acylchloride according to the general procedure A by means of oxalylchloride (4 ml, d=1.5 g/ml, 96 %, 45.4 mmol) in dichloromethane (100 ml) and reacted with resorcinol monobenzylether (4.4 g, 22.0 mmol) in presence of pyridine (2 ml, d=0.97 g/ml, 24.5 mmol) in dichloromethane (100 ml). The crude product (10.3 g, 16.0 mmol, 77 %) was without further purification deprotected according to the procedure B and purified by

double recrystallization from ethanol. The yield of the reaction was 6.83 g (77 %) of white solid.

$^{1}$H-NMR: 8.24 d, 2 H, $^{3}J$ = 8.9 (ArH); 8.10 d, 1 H, $^{4}J$ = 2.2 (ArH); 8.06 dd, 1 H, $^{4}J$ = 2.2, $^{3}J$ = 8.7 (ArH); 7.32 d, 1 H, $^{3}J$ = 8.7 (ArH); 7.34 d, 2 H, $^{3}J$ = 8.7 (ArH); 7.25 t, 1 H, $^{3}J$ = 8.5 (ArH); 6.78-6.71 m, 3 H (ArH); 4.16 t, 2 H, $^{3}J$ = 6.5 ($OCH_2$); 1.85-1.78 m, 2 H ($CH_2$); 1.52-1.43 m, 2 H ($CH_2$); 1.37-1.25 m, 16 H (8x$CH_2$); 0.87 t, 3 H, $^{3}J$ = 6.6 ($CH_3$).

**Ic:** 3-Hydroxyphenyl-4-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy)]benzoate

4-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]benzoic acid (4.0 g, 7.32 mmol) and 3-benzyloxyphenol (1.57 g, 7.84 mmol) was reacted using prodedures A. The intermediate was purified by crystallization from a mixture of methanol and acetone to give 3.98 g (75 %) of the benzyl protected compound which was directly deprotected according to the general procedure B. Yield 2.96 g (86 %) of white crystals (propan-2-ol and ethyl acetate)

$^{1}$H-NMR (DMSO): 9.77 s, 1 H (OH); 8.21 d, 2 H, *J* = 8.7 (ArH); 8.25 d, 2 H, *J* = 8.7 (ArH); 8.09 d, 2 H, *J* = 8.9 (ArH); 7.53 d, 2 H, *J* = 8.9 (ArH); 7.55 d, 2 H, *J* = 8.9 (ArH); 7.24 t, 1 H, *J* = 8.1 (ArH); 7.12 d, 2 H, *J* = 8.9 (ArH); 6.72-6.67 m, 3 H (ArH); 4.09 t, 2 H, *J* = 6.4 ($OCH_2$); 1.76-1.72 m, 2 H ($CH_2$); 1.42-1.23 m, 18 H ($CH_2$); 0.84 t, 3 H, *J* = 6.7 ($CH_3$).

**IIa**: 3-(4-Hydroxybenzoyloxy)phenyl-4-(4-dodecyloxybenzoyloxy)benzoate

Reaction of 3-hydroxyphenyl-4-(4-dodecyloxybenzoyloxy)benzoate (**Ia**) (2.54 g, 4.90 mmol) and 4-benzyloxybenzoic acid (1.23 g, 5.39 mmol) was carried out according to the general procedure A. Yield 3.52 g (99 %) of crude benzyl protected product that was immediately used in deprotection reaction according to general procedure B. Yield 2.8 g (91 %) **IIa** white crystals (methanol), mp. 186 °C.

$^{1}$H-NMR (DMSO): 10.52 s, 1 H (OH); 8.22 d, 2 H, *J* = 8.7 (ArH); 8.09 d, 2 H, *J* = 8.9 (ArH); 7.99 d, 2 H, *J* = 8.9 (ArH); 7.56-7.50 m, 3 H (ArH); 7.30-7.21 m, 3 H (ArH); 7.12 d, 2 H, *J* =

8.9 (ArH); 6.92 d, 2 H, *J* = 8.7 (ArH); 4.08 t, 2 H, *J* = 6.5 ($OCH_2$); 1.74-1.71 m, 2 H ($CH_2$); 1.41-1.23 m, 18 H ($CH_2$); 0.84 t, 3 H, *J* = 6.7 ($CH_3$).

**IIb:** 3-(4-hydroxybenzoyloxy)phenyl-4-(3-chloro-4-octyloxybenzoyloxy)benzoate

4-Benzyloxybenzoic acid (2.5 g, 11.0 mmol) reacted with phenol **Ib** (5.0 g, 9.04 mmol) according to procedure A and B. Column chromatography on silica gel (230 g, solvent dichloromethane + 5% ethyl acetate) followed by crystallization from toluene (2x) and mixture of propan-2-ol and toluene resulted in 4.53 g (74 % overall) of white crystals, mp. 187 °C.

$^1$H-NMR (DMSO): 10.49 s, 1 H (OH); 8.20 d, 2 H, *J* = 8.5 (ArH); 8.1 d, 1 H, *J* = 2.1 (ArH); 8.06 dd, 1 H, *J* = 2.1, *J* = 8.7 (ArH); 7.96 d, 2 H, *J* = 8.7 (ArH); 7.54-7.47 m, 3 H (ArH); 7.32 d, 1 H, *J* = 8.7 (ArH); 7.27-7.18 m, 3 H (ArH); 6.89 d, 2 H, *J* = 8.7 (ArH); 4.16 t, 2 H, *J* = 6.4 ($OCH_2$); 1.78-1.68 m, 2 H ($CH_2$); 1.43-1.38 m, 2 H ($CH_2$); 1.35-1.20 m, 16 H ($CH_2$); 0.81 t, 3 H, *J* = 6.6 ($CH_3$).

**IIc:** 3-(4-hydroxybenzoyloxy)phenyl-4-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy)]-benzoate

4-Benzyloxybenzoic acid (1.2 g, 5.26 mmol) reacted with phenol **Ic** (2.9 g, 4.54 mmol) The crude intermediate was used directly in deprotection reaction according to the general procedure B. Crystallization from a mixture of propan-2-ol and ethyl acetate afforded 2.70 g (79 % overall) of white crystals, mp. 214 °C.

$^1$H-NMR (DMSO): 10.52 s, 1 H (OH); 8.27-8.24 m, 4 H (ArH); 8.09 d, 2 H, *J* = 8.9 (ArH); 7.99 d, 2 H, *J* = 8.9 (ArH); 7.53 d, 2 H, *J* = 8.7 (ArH); 7.55 t, 1 H, *J* = 8.3 (ArH); 7.58 d, 2 H, *J* = 8.7 (ArH); 7.31 t, 1 H, *J* = 2.1 (ArH); 7.22 dd, 1 H, *J* = 2.1, *J* = 8.3 (ArH); 7.27 dd, 1 H, *J* = 2.1, *J* = 8.3 (ArH); 7.12 d, 2 H, *J* = 8.9 (ArH); 6.92 d, 2 H, *J* = 8.9 (ArH); 4.09 t, 2 H, *J* = 6.6 ($OCH_2$); 1.76-1.72 m, 2 H ($CH_2$); 1.42-1.23 m, 18 H ($CH_2$); 0.85 t, 3 H, *J* = 6.6 ($CH_3$).

**IId:** 3-(4-Hydroxybenzoyloxy)phenyl-4-(4-dodecyloxyphenylcabonyloxy)benzoate

4-Benzylbenzoic acid (1.15 g, 5.04 mmol) was reacted with phenol **Id** (2.0 g, 3.86 mmol) using procedure A followed by direct deprotection according to procedure B. Double crystallization from ethanol, column chromatography on silica gel (eluent dichloromethane + 5% ethyl acetate) and final crystallization from ethanol yield in 1.68 g (68 % overall) of white crystals, mp. 163 °C.

$^1$H-NMR (DMSO): 10.53 s, 1 H (OH); 8.31 s, 4 H (ArH); 7.99 d, 2 H, *J* = 8.7 (ArH); 7.56 t, 1 H, *J* = 8.1 (ArH); 7.34 t, 1 H, *J* = 2.3 (ArH); 7.25-7.20 m, 3 H (ArH); 7.29 dd, 1 H, *J* = 2.3, *J* = 8.1 (ArH); 6.95 d, 2 H, *J* = 8.9 (ArH); 6.99 d, 2 H, *J* = 9.1 (ArH); 3.97 t, 2 H, *J* = 6.4 ($OCH_2$); 1.74-1.67 m, 2 H ($CH_2$); 1.41-1.20 m, 18 H ($CH_2$); 0.85 t, 3 H, *J* = 6.7 ($CH_3$).

*Compounds **1a-d, 2a-d, 3a-d** (see Scheme 1; melting behaviour see Table 1)*

Compound **1a**: The diacid **III-1** (70 mg, 0.169 mmol) was converted into the corresponding acylchloride according to the general procedure A by means of oxalylchloride (0.35 ml of 2M solution in dichloromethane, 0.7 mmol) in dichloromethane (3 ml) and reacted with phenol **IIa** (220 mg, 0.344 mmol) in presence of pyridine (0.03 ml, d=0.97 g/ml, 0.368 mmol) and DMAP (10 mg, 0.082 mmol) in dichloromethane (6 ml). The crude product was purified by means of column chromatography on silica gel (20 g, solvent dichloromethane + 1% of ethyl acetate) and crystallization from ethyl acetate to give 210 mg (75 %) of white crystals.

$^1$H-NMR: 8.25 d, 8 H, $^3J$ = 8.3 (ArH); 8.13 d, 8 H, $^3J$ = 8.9 (ArH); 7.47 t, 2 H, $^3J$ = 8.7 (ArH); 7.35 d, 8 H, $^3J$ = 8.7 (ArH); 7.19-7.15 m, 6 H (ArH); 6.96 d, 8 H, $^3J$ = 8.9 (ArH); 4.06-4.02 m, 8 H ($OCH_2$); 1.85-1.78 m, 8 H ($CH_2$); 1.52-1.43 m, 8 H ($CH_2$); 1.37-1.25 m, 40 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.7 ($CH_3$).

Compound **1b:** Diacid **III-1** (90 mg, 0.217 mmol) reacted with phenol **IIb** (300 mg, 0.452 mmol) in analogy to **1a** to give 200 mg (53 %) of white crystals (crystallization from toluene and ethyl acetate)

$^1$H-NMR: 8.21 d, 2 H, $^3J$ = 2.3 (ArH); 8.28-8.24 m, 8 H (ArH); 8.13 d, 4 H, $^3J$ = 8.9 (ArH); 8.06 dd, 2 H, $^4J$ = 2.3, $^3J$ = 8.6 (ArH); 7.48 t, 2 H, $^3J$ = 8.1 (ArH); 7.36 d, 8 H, $^3J$ = 8.5 (ArH); 7.20-7.15 m, 6 H (ArH); 7.03-6.95 m, 6 H (ArH); 4.12 t, 4 H, $^3J$ = 6.4 ($OCH_2$); 4.04 t, 4 H, $^3J$ = 6.5 ($OCH_2$); 1.89-1.78 m, 8 H ($CH_2$); 1.59-1.42 m, 8 H ($CH_2$); 1.40-1.20 m, 40 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.6 ($CH_3$).

Compound **1c:** Diacid **III-1** (70 mg, 0.169 mmol) reacted with phenol **IIc** (250 mg, 0.329 mmol) in analogy to **1a.** Recrystallization from ethyl acetate gave 230 mg **1c** (74 %).

$^1$H-NMR: 8.29-8.24 m, 12 H (ArH); 8.13 d, 8 H, $^3J$ = 8.9 (ArH); 7.40-7.34 m, 12 H (ArH); 7.48 t, 2 H, $^3J$ = 8.2 (ArH); 7.20-7.16 m, 6 H (ArH); 6.97 d, 8 H, $^3J$ = 8.9 (ArH); 4.06-4.02 m, 8 H ($OCH_2$); 1.85-1.77 m, 8 H ($CH_2$); 1.50-1.43 m, 8 H ($CH_2$); 1.38-1.23 m, 40 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.6 ($CH_3$).

Compound **1d:** Diacid **III-1** (80 mg, 0.193 mmol) reacted with phenol **IId** (250 mg, 0.391 mmol) to give 220 mg **1d** (68 %), recrystallized from ethyl acetate.

$^1$H-NMR: 8.3 s, 8 H (ArH); 8.25 d, 4 H, $^3J$ = 8.9 (ArH); 8.13 d, 4 H, $^3J$ = 8.9 (ArH); 7.49 t, 2 H, $^3J$ = 8.1 (ArH); 7.36 d, 4 H, $^3J$ = 8.7 (ArH); 7.22-7.17 m, 6 H (ArH); 7.12 d, 4 H, $^3J$ = 8.9 (ArH); 6.92 d, 4 H, $^3J$ = 9.1 (ArH); 6.97 d, 4 H, $^3J$ = 8.9 (ArH); 4.04 t, 4 H, $^3J$ = 6.4 ($OCH_2$); 3.95 t, 4 H, $^3J$ = 6.6 ($OCH_2$); 1.85-1.74 m, 8 H ($CH_2$); 1.48-1.41 m, 8 H ($CH_2$); 1.36-1.24 m, 40 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.6 ($CH_3$).

Compound **2a:** Diacid **III-2** (70 mg, 0.161 mmol) reacted with phenol **IIa** (220 mg, 0.344 mmol). Chromatography on silica gel (dichloromethane + 5% of ethyl acetate) and crystallization from ethanol yielded 190 mg (70 %) of white crystals.

$^{1}$H-NMR: 8.25 d, 4 H, $^{3}J$ = 8.9 (ArH); 8.25 d, 4 H, $^{3}J$ = 8.7 (ArH); 8.13 d, 8 H, $^{3}J$ = 8.9 (ArH); 7.47 t, 2 H, $^{3}J$ = 8.2 (ArH); 7.35 d, 4 H, $^{3}J$ = 8.9 (ArH); 7.34 d, 4 H, $^{3}J$ = 8.7 (ArH); 7.19-7.15 m, 6 H (ArH); 7.00 d, 4 H, $^{3}J$ = 8.9 (ArH); 6.96 d, 4 H, $^{3}J$ = 8.9 (ArH); 4.21 t, 4 H, $^{3}J$ = 4.9 ($OCH_2$); 4.04 t, 4 H, $^{3}J$ = 6.7 ($OCH_2$); 3.89 t, 4 H, $^{3}J$ = 4.9 ($CH_2O$); 3.75-3.68 m, 8 H ($OCH_2CH_2O$); 1.85-1.78 m, 4 H ($CH_2$); 1.52-1.43 m, 4 H ($CH_2$); 1.37-1.25 m, 32 H ($CH_2$); 0.87 t, 6 H, $^{3}J$ = 6.7 ($CH_3$).

Compound **2b:** Diacid **III-2** (100 mg, 0.230 mmol) reacted with phenol **IIb** (300 mg, 0.467 mmol) in analogy to **1a.** Column chromatography on silica gel (dichloromethane + 5% ethyl acetate) followed by crystallization from a mixture of ethanol and ethyl acetate yielded 210 mg (52 %) **2b**.

$^{1}$H-NMR: 8.20 d, 2 H, $^{4}J$ = 2.3 (ArH); 8.28-8.24 m, 8 H (ArH); 8.13 d, 4 H, $^{3}J$ = 8.9 (ArH); 8.06 dd, 2 H, $^{4}J$ = 2.3, $^{3}J$ = 8.7 (ArH); 7.47 t, 2 H, $^{3}J$ = 8.3 (ArH); 7.36-7.34 m, 8 H (ArH); 7.24-7.15 m, 6 H (ArH); 7.00-6.96 m, 6 H (ArH); 4.21 t, 4 H, $^{3}J$ = 4.6 ($OCH_2$); 4.12 t, 4 H, $^{3}J$ = 6.6 ($OCH_2$); 3.89 t, 4 H, $^{3}J$ = 4.6 ($CH_2O$); 3.75-3.69 m, 8 H ($OCH_2CH_2O$); 1.76-1.72 m, 4 H ($CH_2$); 1.40-1.20 m, 32 H ($CH_2$); 1.42-1.40 m, 4 H ($CH_2$); 0.87 t, 6 H, $^{3}J$ = 6.7 ($CH_3$).

Compound **2c:** Diacid **III-2** (70 mg, 0.161 mmol) reacted with phenol **2c** (250 mg, 0.329 mmol). Column chromatography on silica gel (20 g, eluent dichloromethane + 5% ethyl acetate) followed by double recrystallization from mixture of ethanol and ethyl acetate resulted in 130 mg (42 %) of **2c**.

$^{1}$H-NMR: 8.28-8.24 m, 12 H (ArH); 8.13 d, 4 H, $^{3}J$ = 8.9 (ArH); 8.13 d, 4 H, $^{3}J$ = 8.9 (ArH); 7.47 t, 2 H, $^{3}J$ = 8.2 (ArH); 7.39-7.34 m, 12 H (ArH); 7.20-7.16 m, 6 H (ArH); 6.97 d, 4 H, $^{3}J$

= 8.9 (ArH); 6.99 d, 4 H, $^3J$ = 8.9 (ArH); 4.21 t, 4 H, $^3J$ = 4.7 ($OCH_2$); 4.04 t, 4 H, $^3J$ = 6.6 ($OCH_2$); 3.89 t, 4 H, $^3J$ = 4.7 ($CH_2O$); 3.76-3.69 m, 8 H ($OCH_2CH_2O$); 1.85-1.78 m, 4 H ($CH_2$); 1.40-1.24 m, 32 H ($CH_2$); 1.49-1.42 m, 4 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.6 ($CH_3$).

Compound **2d:** Diacid **III-2** (85 mg, 0.196 mmol) reacted with phenol **IId** (250 mg, 0.391 mmol). Column chromatography on silica gel (eluent dichloromethane + 5% ethyl acetate) followed by double recrystallization from mixture of ethanol and ethyl acetate yielded 170 mg (52 %) of product **2d**.

$^1$H-NMR: 8.3 s, 8 H (ArH); 8.25 d, 4 H, $^3J$ = 8.7 (ArH); 8.13 d, 4 H, $^3J$ = 8.7 (ArH); 7.49 t, 2 H, $^3J$ = 8.2 (ArH); 7.35 d, 4 H, $^3J$ = 8.7 (ArH); 7.22-7.17 m, 6 H (ArH); 7.12 d, 4 H, $^3J$ = 8.9 (ArH); 6.92 d, 4 H, $^3J$ = 8.9 (ArH); 6.99 d, 4 H, $^3J$ = 8.9 (ArH); 4.21 t, 4 H, $^3J$ = 4.8 ($OCH_2$); 3.95 t, 4 H, $^3J$ = 6.4 ($OCH_2$); 3.89 t, 4 H, $^3J$ = 4.8 ($CH_2O$); 3.75-3.69 m, 8 H ($OCH_2CH_2O$); 1.81-1.74 m, 4 H ($CH_2$); 1.45-1.41 m, 32 H ($CH_2$); 0.87 t, 6 H, $J$ = 6.6 ($CH_3$).

Compound **3a:** Diacid **III-3** (160 mg, 0.165 mmol) reacted with phenol **IIa** (210mg, 0.329 mmol) in analogy to **1a.** Column chromatography on silica gel (dichloromethane + 2% ethyl acetate) followed by recrystallization from a mixture of ethanol and ethyl acetate resulted in 240 mg (54 %) of product **3a**.

$^1$H-NMR: 8.25 d, 8 H, $^3J$ = 8.3 (ArH); 8.13 d, 8 H, $^3J$ = 8.9 (ArH); 7.47 t, 2 H, $^3J$ = 8.7 (ArH); 7.35 d, 8 H, $^3J$ = 8.7 (ArH); 7.19-7.15 m, 6 H (ArH); 6.96 d, 8 H, $^3J$ = 8.9 (ArH); 4.03 t, 8 H, $^3J$ = 6.5 ($OCH_2$); 1.84-1.77 m, 8 H ($CH_2$); 1.50-1.43 m, 8 H ($CH_2$); 1.40-1.20 m, 60 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.6 ($CH_3$); 0.52 t, 4 H, $^3J$ = 7.3 ($SiCH_2$); 0.0 s, 6 H ($SiCH_3$); -0.05 s, 9 H ($SiCH_3$).

Compound **3b:** Diacid **III-3** (200 mg, 0.206 mmol) reacted with phenol **37-1b** (300 mg, 0.452 mmol). Column chromatography on silica gel (dichloromethane + 2% of ethyl acetate)

followed by crystallization from mixture of ethanol and ethyl acetate resulted in 280 mg (60 %) of white crystals of **3b**.

$^{1}$H-NMR: 8.2 d, 2 H, $^{4}J$ = 2.1 (ArH); 8.27-8.24 m, 8 H (ArH); 8.13 d, 4 H, $^{3}J$ = 9.1 (ArH); 8.06 dd, 2 H, $^{4}J$ = 2.1, $^{3}J$ = 8.7 (ArH); 7.48 t, 2 H, $^{3}J$ = 8.1 (ArH); 7.35 d, 8 H, $^{3}J$ = 8.9 (ArH); 7.19-7.15 m, 6 H (ArH); 7.00-6.95 m, 6 H (ArH); 4.11 t, 4 H, $^{3}J$ = 6.4 ($OCH_2$); 4.03 t, 4 H, $^{3}J$ = 6.4 ($OCH_2$); 1.89-1.77 m, 8 H ($CH_2$); 1.53-1.43 m, 8 H ($CH_2$); 1.35-1.20 m, 64 H ($CH_2$); 0.87 t, 6 H, $^{3}J$ = 6.5 ($CH_3$); 0.51 t, 4 H, $^{3}J$ = 7.9 ($SiCH_2$); 0.0 s, 6 H ($SiCH_3$); -0.05 s, 12 H ($SiCH_3$).

Compound **3c:** Diacid **III-3** (160 mg, 0.165 mmol) was reacted with phenol **IIc** (250 mg, 0.329 mmol). Double column chromatography on silica gel (dichloromethane + 2% ethyl acetate) followed by recrystallization from a mixture of ethanol and ethyl acetate resulted in 260 mg (64 %) of product **3c**.

$^{1}$H-NMR: 8.29-8.24 m, 12 H (ArH); 8.13 d, 4 H, $^{3}J$ = 8.9 (ArH); 8.13 d, 4 H, $^{3}J$ = 8.9 (ArH); 7.40-7.34 m, 12 H (ArH); 7.48 t, 2 H, $^{3}J$ = 8.1 (ArH); 7.20-7.16 m, 6 H (ArH); 6.96 d, 4 H, $^{3}J$ = 8.9 (ArH); 6.97 d, 4 H, $^{3}J$ = 8.9 (ArH); 4.06-4.02 m, 8 H ($OCH_2$); 1.85-1.78 m, 8 H ($CH_2$); 1.52-1.26 m, 68 H ($CH_2$); 0.87 t, 6 H, $^{3}J$ = 6.6 ($CH_3$); 0.52 t, 4 H, $^{3}J$ = 7.5 ($SiCH_2$); 0.0 s, 6 H ($SiCH_3$); -0.05 s, 12 H ($SiCH_3$).

Compound **3d:** Diacid **III-3** (190 mg, 0.196 mmol) reacted with phenol **IId** (250 mg, 0.391 mmol). Double column chromatography on silica gel (eluent dichloromethane + 2% ethyl acetate) followed by recrystallization from a mixture of ethanol and ethyl acetate yielded in 140 mg (32 %) of product **3d**.

$^{1}$H-NMR: 8.31 s, 8 H (ArH); 8.26 d, 4 H, $^{3}J$ = 8.7 (ArH); 8.13 d, 4 H, $^{3}J$ = 8.9 (ArH); 7.49 t, 2 H, $^{3}J$ = 8.1 (ArH); 7.36 d, 4 H, $^{3}J$ = 8.9 (ArH); 7.22-7.17 m, 6 H (ArH); 7.12 d, 4 H, $^{3}J$ = 8.9 (ArH); 6.92 d, 4 H, $^{3}J$ = 8.9 (ArH); 6.96 d, 4 H, $^{3}J$ = 9.1 (ArH); 4.03 t, 4 H, $^{3}J$ = 6.4 ($OCH_2$);

3.95 t, 4 H, $^3J$ = 6.6 ($OCH_2$); 1.83-1.76 m, 8 H ($CH_2$); 1.40-1.20 m, 60 H ($CH_2$); 1.48-1.43 m, 8 H ($CH_2$); 0.87 t, 6 H, $^3J$ = 6.6 ($CH_3$); 0.52 t, 4 H, $^3J$ = 7.5 ($SiCH_2$); 0.0 s, 6 H ($SiCH_3$); -0.05 s, 12 H ($SiCH_3$).

*Compound **1e** (see Scheme 2)*

**IV** 4-{3-[4-(4-n-dodecyloxybenzoyloxy)benzoyloxy]phenyloxycarbonyl}benzoic acid: The monobenzylester of terephthalic acid (280 mg, 1.09 mmol) was converted into the corresponding acylchloride according to the general procedure A and reacted with the phenol **Ia** (500 mg, 0.964 mmol). The crude product (690 mg, 95 %) was without further purification deprotected as described in the general procedure B and purified by crystallization from propan-2-ol to afford 440 mg (72 %) of white crystals.
$^1$H-NMR: 8.26-8.22 m, 4 H (ArH); 8.11 d, 2 H, $^3J$ = 8.7 (ArH); 8.09 d, 2 H, $^3J$ = 8.9 (ArH); 7.52 d, 2 H, $^3J$ = 8.7 (ArH); 7.59 t, 1 H, $^3J$ = 8.2 (ArH); 7.4 t, 1 H, $^4J$ = 2.3 (ArH); 7.31 dd, 2 H, $^4J$ = 2.3, $^3J$ = 8.9 (ArH); 7.12 d, 2 H, $^3J$ = 8.9 (ArH); 4.09 t, 2 H, $^3J$ = 6.4 ($OCH_2$); 1.76-1.72 m, 2 H ($CH_2$); 1.40-1.20 m, 16 H ($CH_2$); 1.42-1.40 m, 2 H ($CH_2$); 0.85 t, 3 H, $^3J$ = 6.6 ($CH_3$).

Compound **1e:** The acid **IV** (300 mg, 0.450 mmol) reacted with the bisphenol **V** 4-[9-(4-hydroxyphenoxy)nonyloxy]phenol (75 mg, 0.218 mmol) in presence of DMAP (60 mg, 0.491 mmol) in dichloromethane (5 ml). Purification by column chromatography on silica gel (dichloromethane) followed by crystallization from ethyl acetate afforded 90 mg (25 %) of white crystals.
$^1$H-NMR: 8.31 s, 8 H (ArH); 8.26 d, 4 H, $^3J$ = 8.7 (ArH); 8.13 d, 4 H, $^3J$ = 8.9 (ArH); 7.49 t, 2 H, $^3J$ = 8.1 (ArH); 7.36 d, 4 H, $^3J$ = 8.7 (ArH); 7.24-7.17 m, 6 H (ArH); 7.13 d, 4 H, $^3J$ = 8.9 (ArH); 6.93 d, 4 H, $^3J$ = 9.1 (ArH); 6.97 d, 4 H, $^3J$ = 8.9 (ArH); 4.04 t, 4 H, $^3J$ = 6.7 ($OCH_2$);

3.96 t, 4 H, $^{3}J$ = 6.5 ($OCH_2$); 1.83-1.77 m, 8 H ($CH_2$); 1.50-1.25 m, 46 H ($CH_2$); 0.87 t, 6 H, $^{3}J$ = 6.6 ($CH_3$).

*Compound **5** (see Scheme 3)*

**VI:** 2-Hydroxy-4-benzyloxybenzonitril

11.0 g KOH in 25 ml water were added to a solution of 6.30 g (0.24 mol) 2-acetyloxy-4-benzyloxybenzonitril in 100 ml ethanol and refluxed for 2 hours. After cooling the mixture was added to 200 g ice and 200 ml diethylether and acidified with HCl to pH 3 under strong stirring. The organic layer was separated, washed with sodium hydrogenecarbonat solution (5%), water and brine. Drying by means of sodium sulfate and evaporation the solvent results in 4.3 g (74.5%) compound **VI** after recrystallization from a water ethanol mixture. mp. 145-147 °C.

$C_{14}H_{11}NO_2$ (Mm: 225.24) Elemental analysis: calculated: C 74.65; H 4.92; N 6.22; found: C 74.24; H 4.90; N 6.19 ; IR (KBr) ν [$cm^{-1}$]: 2228 (-CN)

$^{1}$H NMR (400 MHz) DMSO-$d_6$: 7.49 (d, $^{3}J$ = 8.5, 1H, ArH); 7.43-7.32 (m, 5H, ArH); 6.60-6.56 (m, 2H, ArH); 5.10 (s, 2H, $OCH_2$).

**VII**: 2-Cyano-5-benzyloxyphenyl 4-(4-n-octyloxybenzoyloxy)benzoate

5.55 g (1.5 mmol) 4-(4-n-octyloxybenzoyloxy)benzoic acid was esterificated with 4.3 g (1.5 mmol) **VI** according to procedure A. Yield 4.6 g (42%), mp. 107-109 °C (ethanol/DMF).

$^{1}$H-NMR ($CDCl_3$): 8.29 dd, 2 H, $^{3}J$ = 8.7, $^{4}J$ =1.9 (ArH); 8.13 d, 2 H, $^{3}J$ = 8.9, $^{4}J$=1.9, (ArH); 7.96 d, 2 H, $J$ = 8.7 (ArH); 7.60 d, 1 H, $^{3}J$ = 8.7 (ArH); 7.40-7.34 m, 7 H (ArH); 7.08 d, 1 H, $J$ = 2.3 (ArH); 6.97 d, 1 H, $^{3}J$ = 8.8, $^{4}J$=1.9 (ArH); 6.92 d, 2 H, $^{3}J$ = 9.1 (ArH); 5.10 s, 2H

($CH_2$); 4.04 t, 2 H, $^3J$ = 6.6 ($OCH_2$); 1.83-1.79 m, 2 H ($OCH_2\underline{CH_2}$); 1.41-1.23 m, 10 H ($CH_2$); 0.84 t, 3 H, $^3J$ = 6.7 ($CH_3$).

**VIII**: 2-Cyano-5-hydroxyphenyl 4-(4-n-octyloxybenzoyloxy)benzoate

Deprotection of **VII** was realized by means of hydrogen using Pd (5% on carbon) as catalyst. White product, mp. 184-188 °C (mixture ethanol – DMF). Yield: 87%. Elemental analyses: $C_{29}H_{29}NO_6$ (487.55. calc. C 71.44, H 6.00, N 2.87; found C 71.56, H 5.69, N 2.90;

IR (KBr) ν [$cm^{-1}$]: 2239 (-CN)

$^1$H-NMR (DMSO): 8.23 d, 2 H, $^3J$ = 8.7 (ArH); 8.09 d, 2 H, $^3J$ = 8.9 (ArH), 7.75 d, 1 H, $^3J$ = 8.5 (ArH); 7.54 dd, 2 H $^3$J=8.7, $^4$J=1.9 (ArH); 7.11 d, 2 H, $^3J$= 9.1 (ArH); 6.97 d, 1 H, $^4J$=2.0 (ArH); 6.87 dd, 1 H, $^3J$ = 8.5, $^4$J=2.3 (ArH); 4.08 t, 2 H, $^3J$ = 6.5 ($OCH_2$); 1.76-1.72 m, 2 H ($OCH_2\underline{CH_2}$); 1.43-1.26 m, 10 H ($CH_2$); 0.85 t, 3 H, $^3J$ = 6.7 ($CH_3$).

**IX**: 2-Cyano-5-(4-hydroxybenzoyloxy)phenyl-4-(4-n-octyloxybenzoyloxy)benzoate

4-Benzyloxybenzoic acid (280 mg, 1.23 mmol) was converted into the corresponding acylchloride according to the general procedure A by means of oxalylchloride (2 ml of 2M solution in dichloromethane, 4.0 mmol) in dichloromethane (5 ml) and reacted with 2-cyano-5-hydroxyphenyl 4-(4-octyloxybenzoyloxy)benzoate (500 mg, 1.03 mmol) in presence of pyridine (0.1 ml, d=0.97 g/ml, 1.23 mmol) and DMAP (30 mg, 0.250 mmol) in dichloromethane (5 ml). The crude product was purified by column chromatography on silica gel (dichloromethane + 2% of ethyl acetate) to give 550 mg (77 %) of the benzyl protected crude material which was immediately deprotected using hydrogen (Pd 5% on carbon). The crude product was purified by means chromatography on silica gel (15 g, solvent dichloromethane + 5% ethyl acetate) followed by crystallization from ethanol to give 250 mg (53 %) of white crystals.

$^{1}$H-NMR (DMSO): 8.24 d, 2 H, *J* = 8.9 (ArH); 8.13 d, 2 H, *J* = 8.9 (ArH); 7.96 d, 2 H, *J* = 8.7 (ArH); 7.77 d, 1 H, *J* = 8.5 (ArH); 7.52 d, 1 H, *J* = 2.3 (ArH); 7.3 dd, 1 H, *J* = 2.3, *J* = 8.5 (ArH); 7.34 d, 2 H, *J* = 8.9 (ArH); 6.89 d, 2 H, *J* = 8.7 (ArH); 6.76 d, 2 H, *J* = 8.9 (ArH); 4.08 t, 2 H, *J* = 6.5 ($OCH_2$); 1.74-1.71 m, 2 H ($CH_2$); 1.41-1.23 m, 10 H ($CH_2$); 0.84 t, 3 H, *J* = 6.7 ($CH_3$).

*Compound **5***: The diacid **III-2** (90 mg, 0.207 mmol) was converted into the corresponding acylchloride according to the general procedure A and reacted with the phenolic compound **IX** (250 mg, 0.418 mmol). Column chromatography on silica gel (dichloromethane + 5% of ethyl acetate) followed by crystallization from mixture of ethanol and ethyl acetate yielded in 210 mg (66 %) of white crystals.

$^{1}$H-NMR: 8.31 d, 8 H, *J* = 8.9 (ArH); 8.23 d, 8 H, *J* = 8.7 (ArH); 8.15-8.11 m, 8 H (ArH); 7.77 d, 2 H, *J* = 8.5 (ArH); 7.52 d, 2 H, *J* = 2.3 (ArH); 7.40-7.36 m, 8 H (ArH); 7.3 dd, 2 H, *J* = 2.3, *J* = 8.5 (ArH); 7.00-6.96 m, 8 H (ArH); 4.21 t, 4 H, *J* = 4.6 ($OCH_2$); 4.04 t, 4 H, *J* = 6.4 ($OCH_2$); 3.89 t, 4 H, *J* = 4.6 ($CH_2O$); 3.75-3.68 m, 8 H ($OCH_2CH_2O$); 1.83-1.78 m, 4 H ($CH_2$); 1.49-1.22 m, 20 H ($CH_2$); 0.88 t, 6 H, *J* = 6.8 ($CH_3$).

*Compound **6** (see Scheme 4)*

4-Undec-10-en-1-yloxybenzoic acid (1.5 g, 3.45 mmol reacted with phenol **IIa** (3 g, 3.13 mmol) according to the general procedure A. The crude product was purified by double recrystallization from a mixture of ethanol and ethyl acetate to give 3.85 g (90 %) of white crystals.

$^{1}$H-NMR: 8.26 d, 4 H, $^{3}J$ = 8.7 (ArH); 8.13 d, 4 H, $^{3}J$ = 8.8 (ArH); 7.48 t, 1 H, $^{3}J$ = 8.5 (ArH); 7.33 d, 4 H, $^{3}J$ = 8.7 (ArH); 7.20-7.15 m, 3 H (ArH); 6.96 d, 4 H, $^{3}J$ = 8.9 (ArH); 5.85-5.75 m,

1 H (CH=C); 5.00-4.90 m, 2 H ($C=CH_2$); 4.04 t, 4 H, $^3J$ = 6.5 ($2xOCH_2$); 2.03 q, 2 H, $^3J$ = 6.6 ($CH_2C=C$); 1.85-1.78 m, 4 H ($2xCH_2$); 1.52-1.26 m, 30 H ($15xCH_2$); 0.87 t, 3 H, $^3J$ = 6.7 ($CH_3$).

*Compound **7** (see Scheme 4)*

600 mg (0.66 mmol) of the monomer compound **6** was dissolved in 5 ml dry toluene under a nitrogen atmosphere in a pyrex tube that was than sealed with a rubber septum. 36 mg (0.60 mmol repeat unit) of poly(methylhydro)siloxane (number average degree of polymerisation = 35) was added. After addition of 3 μl of a 2.5 wt% solution of platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex in xylene, the tube was placed in a sonicator and heated for 5 h to 40 °C. The polymer was finally precipitated in methanol , separated by centrifugation and further purified by repeated precipitation from chloroform or dichloromethane solutions in methanol, yield 88%.

$^1$H NMR ($CDCl_3$) δ in ppm: 8.26 d, 4 H, $^3J$ = 8.7 (ArH); 8.13 d, 4 H, $^3J$ = 8.8 (ArH); 7.48 t, 1 H, $^3J$ = 8.5 (ArH); 7.33 d, 4 H, $^3J$ = 8.7 (ArH); 7.20-7.15 m, 3 H (ArH); 6.96 d, 4 H, $^3J$ = 8.9 (ArH); 4.04 t, 4 H, $^3J$ = 6.5 ($2xOCH_2$); 1.85-1.78 m, 4 H ($2xCH_2$); 1.52-1.26 m, 34 H ($17xCH_2$); 0.87 t, 3 H, $^3J$ = 6.7 ($CH_3$); 0.5 t, 2H, $SiCH_2$; 0.1, s, 3 H, $SiCH_3$.

*Compound **8** (see Scheme 4)*

Compound **X**: A solution of the monomer compound **6** (2.0 g, 2.20 mmol) and dimethylchlorosilane (0.72 ml, 6.69 mmol) in anhydrous toluene (50 ml) was thoroughly dried, and a solution of platinum complex with cyclovinylmethylsiloxane (PC-085) (5.0 μl) was added in a flow of argon. The reaction mixture was heated in a closed vessel under argon at 34 °C for 72 H. The reaction completeness was checked by the disappearance of the NMR

resonance assigned to the protons of a terminal carbon-carbon double bond (δ = 4.95, 5.80). The product was not isolated because of strong hygroscopicity of chlorosilane derivatives. $^{1}$H NMR ($CDCl_3$, 250 MHz), δ in ppm: 8.26 d, 4 H, $^{3}J$ = 8.7 (ArH); 8.15 d, 4 H, $^{3}J$ = 8.8 (ArH); 7.47 t, 1 H, $^{3}J$ = 8.5 (ArH); 7.36 d, 4 H, $^{3}J$ = 8.7 (ArH); 7.20-7.15 m, 3 H (ArH); 6.98 d, 4 H, $^{3}J$ = 8.9 (ArH); 4.05 t, 4 H, $^{3}J$ = 6.5 (2x$OCH_2$); 1.85-1.78 m, 4 H (2x$CH_2$); 1.55-1.20 m, 34 H (17x$CH_2$); 0.88 t, 3 H, $^{3}J$ = 6.7 ($CH_3$); 0.53 t, 2H, $SiCH_2$; 0.07 s, 6H, $SiCH_3$.

A solution of pyridine (4.83 ml, 60.1 mmol) and water (0.83 ml, 46.2 mmol) in THF (25 ml) was added dropwise to a stirred solution of the crude intermediate prepared before (2.21 g, 2.20 mmol) and dimethylchlorosilane (8.86 ml, 81.33 mmol) in dry THF (25 ml) at 0 °C. After the reaction mixture was stirred for 30 min at room temperature, chloroform (500 ml) and water (50 ml) were added. The chloroform was washed several times by water until the reaction was neutral. The produced mixture was dried by calcium chloride, and the solvent was evaporated in vacuum. The isolated compound was chromatographically purified two times by being passed through a column packed with silica gel (Merck, 40-60 mesh), eluent: toluene – ethyl acetat (20 : 1). Yield of compound **X**: 1.2 g (52 %).
$^{1}$H NMR ($CDCl_3$, 250 MHz), δ in ppm: 8.26 d, 4 H, $^{3}J$ = 8.7 (ArH); 8.15 d, 4 H, $^{3}J$ = 8.8 (ArH); 7.47 t, 1 H, $^{3}J$ = 8.5 (ArH); 7.36 d, 4 H, $^{3}J$ = 8.7 (ArH); 7.20-7.15 m, 3 H (ArH); 6.98 d, 4 H, $^{3}J$ = 8.9 (ArH); 4.69, m, 1H OSiH; 4.05 t, 4 H, $^{3}J$ = 6.5 (2x$OCH_2$); 1.85-1.78 m, 4 H (2x$CH_2$); 1.55-1.20 m, 34 H (17x$CH_2$); 0.87 m, 3 H, ($CH_3$); 0.52 t, 2H, $SiCH_2$; 0.15-0.07 m, 12 H, $SiCH_3$.

Compound **8:** A reaction mixture composed of the dendritic carbosilane matrix G-1$(All)_8$ (0.034 g, 0.0495 mmol), the compound **X** (0.620 g, 0.594 mmol), platinum complex with divinyltetramethylsiloxane in xylene (PC-072) (5 μl ) and dry toluene (30 ml) was stirred in a closed vessel under argon at 35 °C for 72 h. The reaction mixture was passed through a

column packed with silica gel to deactivate the catalyst (eluent: toluene). The final purification of the product from the high molar-mass admixture and from excess initial silane was performed by preparative GPC. M = 8945 g/mol; Yield of compound **8**: 0.275 g (61%). $^{1}$H NMR ($CDCl_3$, 250 MHz), δ in ppm: 8.25 d, 4 H, $^{3}J$ = 8.3 (ArH); 8.14-8.11 m, 4 H (ArH); 7.47 t, 1 H, $^{3}J$ = 8.5 (ArH); 7.36 d, 4 H, $^{3}J$ = 8.7 (ArH); 7.18-7.14 m, 3 H (ArH); 6.97-6.94, m, 4 H, (ArH); 4.03 t, 4 H, $^{3}J$ = 6.4 (2x$OCH_2$); 1.80-1.78 m, 4 H (2x$CH_2$); 1.53-1.26 m, 34 H (17x$CH_2$); 0.87 m, 3 H, ($CH_3$); 0.59-0.49m, 7.5 H, $SiCH_2$; 0.19-0.00 m, 12 H, $OSiCH_3$.