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## Gallic Esters of 4,5-Dinitrocatechol as Potential Building Blocks for Thermotropic Liquid Crystals

Roxana Judele,<sup>a</sup> Sabine Laschat,<sup>a,\*</sup> Angelika Baro<sup>a</sup> and Manfred Nimitz<sup>b</sup>

<sup>a</sup> *Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany*

<sup>b</sup> *Gesellschaft für Biotechnologische Forschung, Mascheroder Weg 1, D-38124 Braunschweig, Germany*

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**Abstract**—A series of unsubstituted and 1,4-disubstituted gallic catecholates **1**, **6**, and **7** as possible candidates for wedge-shaped mesogens were prepared starting from the respective benzene derivatives **2a–c** and gallic esters **5a–h**. The mesomorphic properties were investigated by DSC. However, only the 4,5-dinitro derivatives **1d,f–h** with C<sub>8</sub>H<sub>17</sub> and C<sub>10</sub>H<sub>21</sub> to C<sub>12</sub>H<sub>25</sub> alkyl side chains displayed mesophases, as evaluated by fluidity and optical anisotropy.

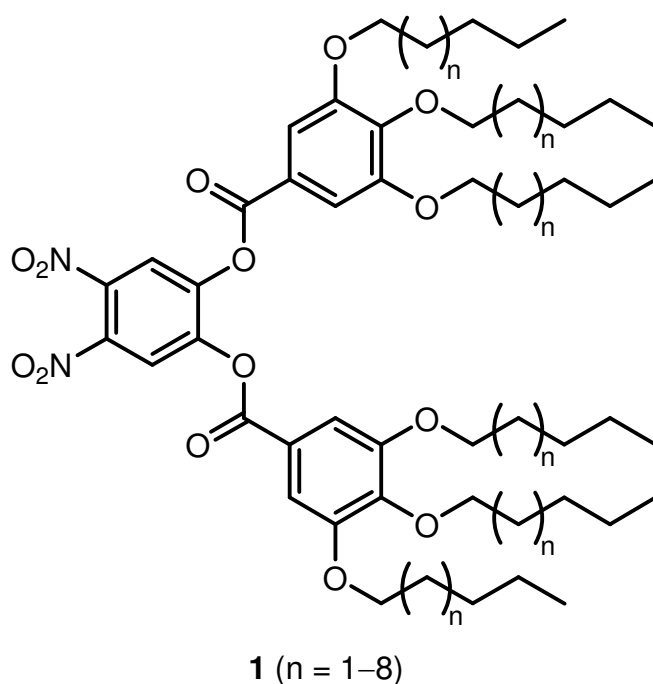
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\*Corresponding author. Fax: +49-711-685-64285; e-mail: sabine.laschat@oc.uni-stuttgart.de

## 1. Introduction

The effect of nitro groups on the mesomorphic and optical properties of low molecular weight thermotropic liquid crystals has been studied by several groups during the last couple of years.<sup>1</sup> In most cases molecules exhibiting smectic, nematic and banana phases have been investigated, whereas wedge-shaped systems were not considered. Bushby<sup>2,3</sup> and Kumar<sup>4</sup> observed that nitration of hexaalkoxy-substituted triphenylenes leads to enhanced mesophase behaviour. This prompted us to prepare gallic esters **1** of 4,5-dinitrocatechol as potential candidates for wedge-shaped mesogens (Scheme 1). Herein we report their synthesis and the study of mesomorphic properties.

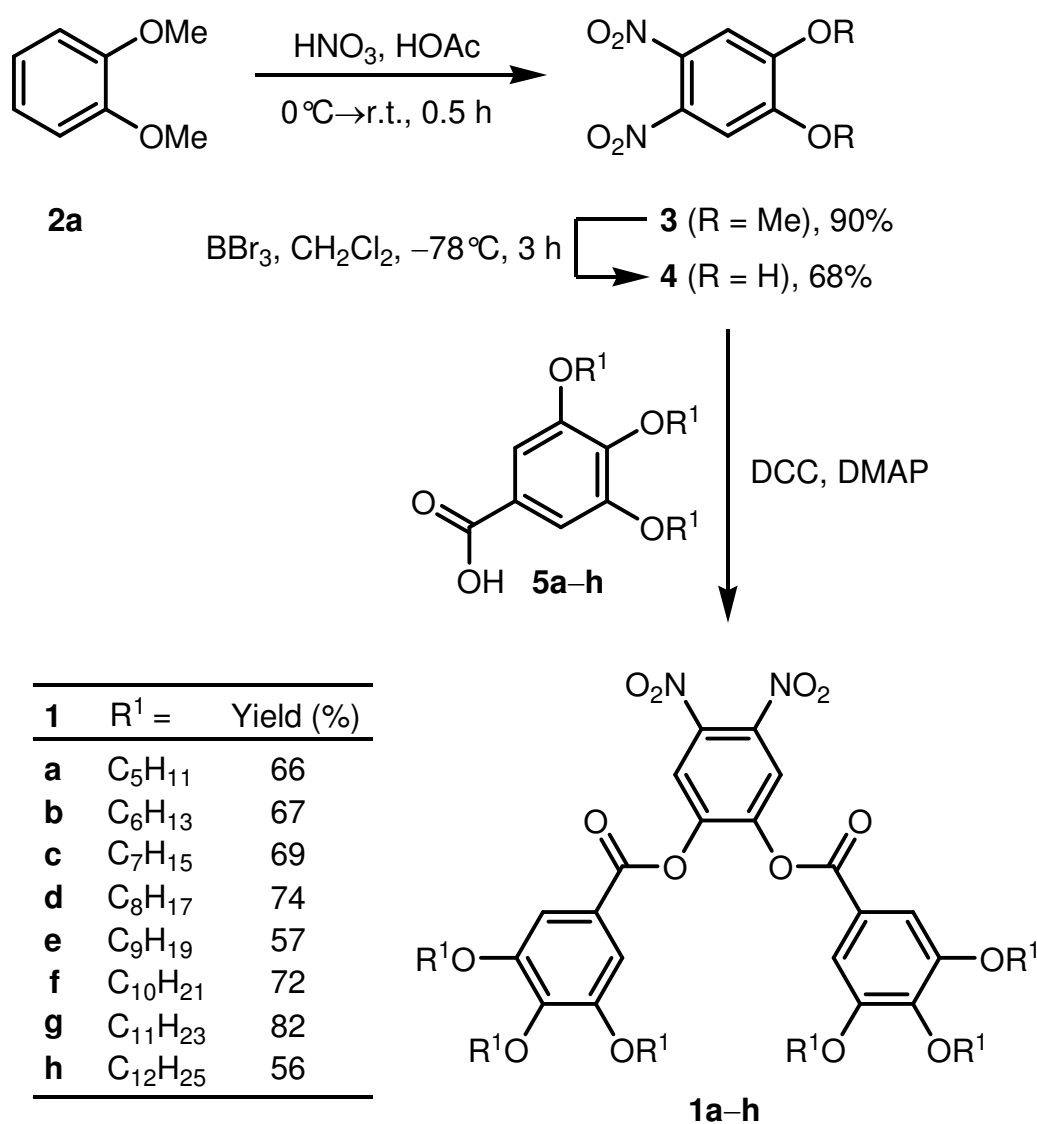


**Scheme 1.** Gallic esters **1** derived from 4,5-dinitrocatechol.

## 2. Results and discussion

As shown in Scheme 2, target compounds **1** were accessible via three-step reaction. 1,2-Dimethoxybenzene **2a** was treated with nitric acid to give 1,2-dimethoxy-4,5-dinitrobenzene **3** in 80% yield following a procedure by Marquet.<sup>5</sup> Compound **3** was subsequently deme-

thylated with  $\text{BBr}_3$  at  $-78^\circ\text{C}$  in  $\text{CH}_2\text{Cl}_2$  to afford 4,5-dinitrocatechol **4** in 68% yield.<sup>6</sup> The latter was esterified with tris(alkyloxy)gallic acids **5a–h** in the presence of DCC and DMAP<sup>7</sup> to yield the target gallic esters **1a–h** in 56–82% (Scheme 2). Compounds **5** were prepared from ethyl 3,4,5-trihydroxybenzoate via *O*-alkylation and subsequent saponification.<sup>7</sup> Slight modification of this protocol by replacing DMF with acetonitrile as the solvent and slow addition of the alkyl bromide<sup>8</sup> markedly improved the yields up to 99%.



**Scheme 2.** Synthesis of target gallic esters **1** starting from 1,2-dimethoxybenzene **2a**.

The mesomorphic properties of esters **1** were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The results are summarized in Table 1. Whereas the derivatives **1a–c** with  $R^1 = C_5H_{11}$  to  $C_7H_{15}$  side chain displayed only isotropic melting during the DSC heating scans, a melting transition at 37°C and a clearing transition at 55°C was observed for octyloxy ester **1d**. Surprisingly, only isotropic melting was found for the homologous nonyloxy ester **1e**. In contrast, derivatives **1f–h** with longer alkyl chains ( $R^1 = C_{10}H_{21}$  to  $C_{12}H_{25}$ ) again displayed a mesophase. The high clearing enthalpies of compounds **1d,f–h** deserve some additional comment. Although they may be taken as evidence for plastic crystals,<sup>9</sup> we have previously reported high clearing enthalpies for both columnar<sup>10,11</sup> and smectic mesophases.<sup>11</sup>

Table 1. Phase transition temperatures [°C] and enthalpies [ $\text{kJ mol}^{-1}$ ] of gallic esters **1a–h**

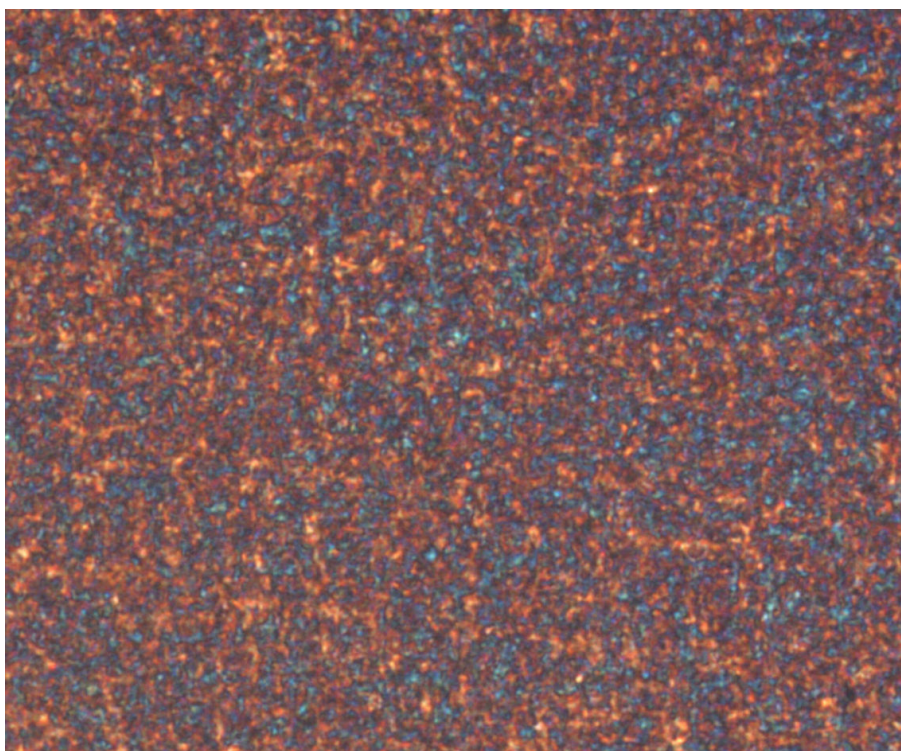
Compd	$R^1$	Cr <sub>1</sub>	$T$ ( $\Delta H$ )	I	$T$ ( $\Delta H$ )	
<b>1a</b>	$C_5H_{11}$	Cr	69 (65.8)	I		
<b>1b</b>	$C_6H_{13}$	Cr	75 (51.7)	I		
<b>1c</b>	$C_7H_{15}$	Cr	63 (85.9)	I		
<b>1d</b>	$C_8H_{17}$	Cr	37 (10.6)	$M_x$	55 (28.1)	I
<b>1e</b>	$C_9H_{19}$	Cr	62 (71.5)	I		
<b>1f</b>	$C_{10}H_{21}$	Cr	44 (42.0)	$M_x$	61 (66.4)	I
<b>1g</b>	$C_{11}H_{23}$	Cr	46 (49.1)	$M_x$	63 (77.0)	I
<b>1h</b>	$C_{12}H_{25}$	Cr	61 (63.5)	$M_x$	65 (13.0)	I

Cr = crystalline,  $M_x$  = mesophase, I = isotropic

Under the polarizing optical microscope small, poorly defined textures were observed for compounds **1d** and **1f–h** upon cooling from the isotropic liquid. Typical examples are shown in Figure 1. Unfortunately, we were not able to obtain suitable X-ray diffraction data. Thus, a crystal to crystal transition instead of a crystal to mesophase (i.e. smectic) transition cannot be completely excluded. However, the fluidity of the birefringent phase, which was obtained upon cooling from the isotropic liquid, was proven by mechanically shearing the sample

between the cover slip and the slide. The combination of fluidity and optical anisotropy gives clear evidence of a liquid crystalline state.

(a)



(b)

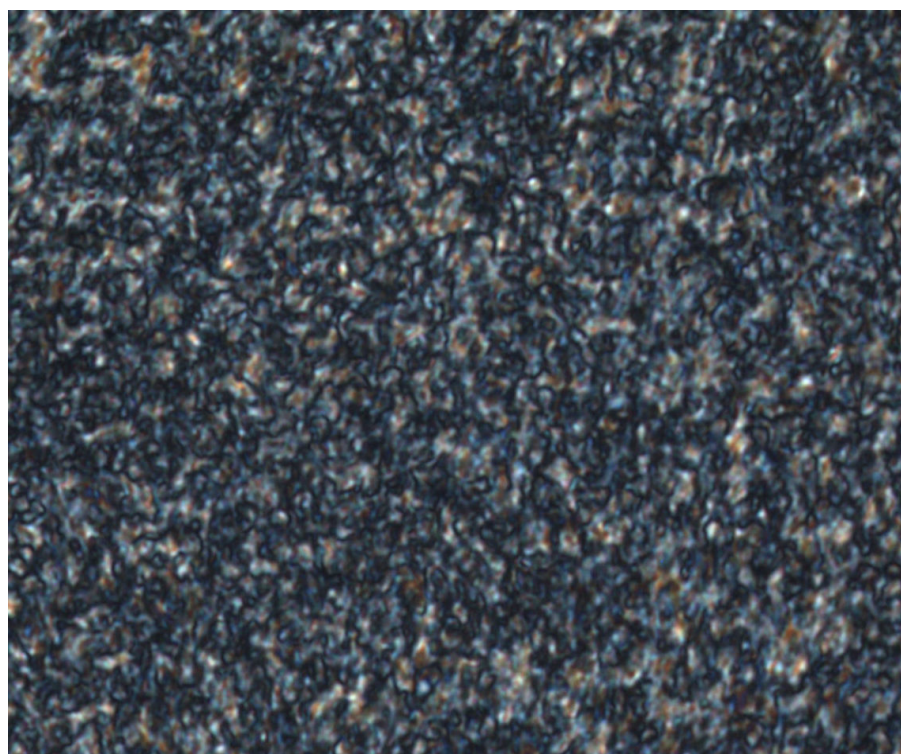
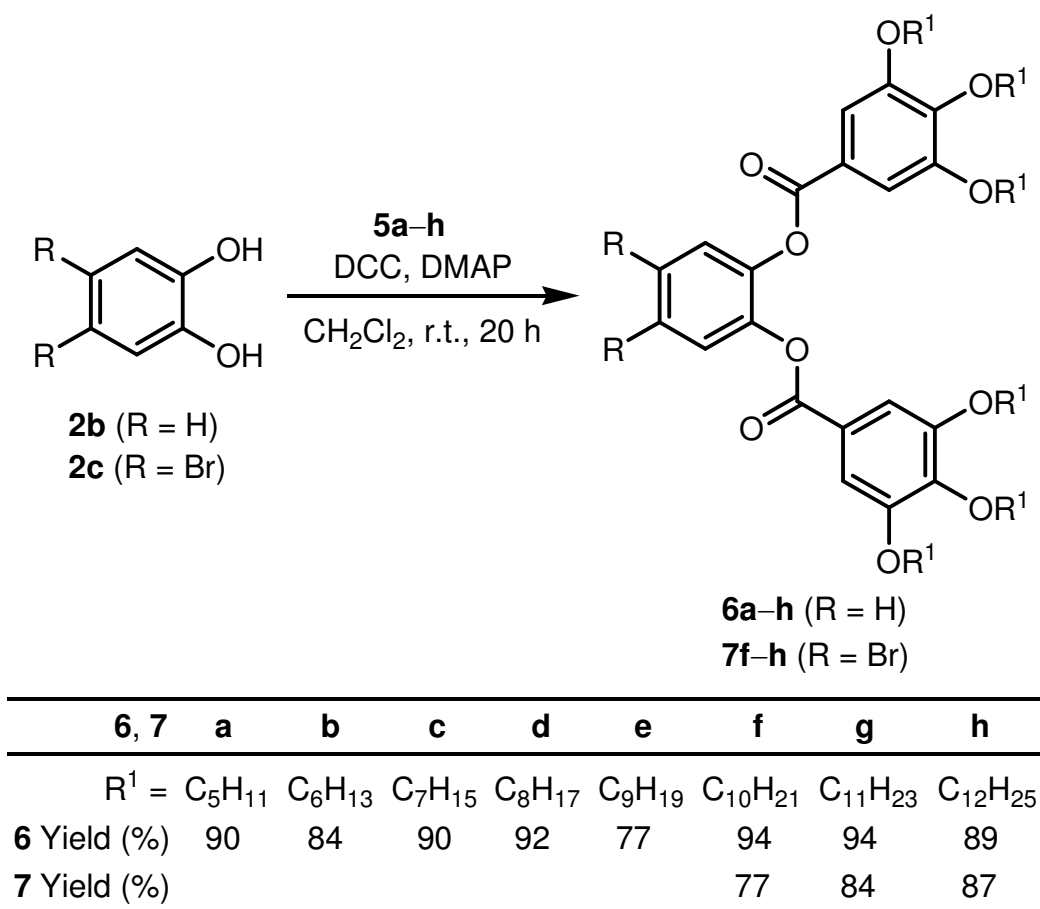


Figure 1. Optical textures of compounds **1d** at 50°C (a) and **1f** at 64°C (b) upon cooling from the isotropic liquid (cooling rate 1 K min<sup>-1</sup>, magnification ×200).

In order to study the effect of the nitro groups on the mesomorphic properties, the unsubstituted gallic esters **6a–h** (R = H) were prepared as described above by esterification of 1,2-dihydroxybenzene **2b** with gallic acids **5a–h** in the presence of DCC and DMAP in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.<sup>7</sup> In an analogous manner, the corresponding 4,5-dibromo gallic esters **7f–h** were obtained in 77–87% yield starting from 4,5-dibromo-1,2-dihydroxybenzene **2c**<sup>12</sup> and gallic ester derivatives **5f–h** (Scheme 3).



**Scheme 3.** Preparation of gallic esters **6a–h** and 4,5-dibromo derivatives **7f–h**.

In contrast to the dinitro esters **1** the corresponding unsubstituted derivatives **6** did not display any mesophases. Only crystal to crystal transitions and isotropic melting was observed (Table 2). All melting points were much lower than those of the dinitro compounds **1**, resulting from the decreased polarity. As can be seen from Table 2, even the dibromo derivatives **7f–h** with

long alkyl chains ( $R^1 = C_{10}H_{21}$  to  $C_{12}H_{25}$ ) did not show any mesophases but crystal to crystal transitions.

Table 2. Phase transition temperatures [ $^{\circ}C$ ] and enthalpies [ $kJ\ mol^{-1}$ ] of gallic ester derivatives **6a–h** and **7f–h**

Compd	$R^1$	Cr <sub>1</sub>	$T(\Delta H)$	I	$T(\Delta H)$	
<b>6a</b>	$C_5H_{11}$	Cr	4 (12.4)	I		
<b>6b</b>	$C_6H_{13}$	Cr	-5 (9.7)	I		
<b>6c</b>	$C_7H_{15}$	Cr <sub>1</sub>	3 (0.8)	Cr <sub>2</sub>	9 (1.5)	I
<b>6d</b>	$C_8H_{17}$	Cr <sub>1</sub>	8 (1.3)	Cr <sub>2</sub>	11 (2.3)	I
<b>6e</b>	$C_9H_{19}$	Cr	18 (3.6)	I		
<b>6f</b>	$C_{10}H_{21}$	Cr <sub>1</sub>	-56 (8.2)	Cr <sub>2</sub>	22 (12.0)	I
<b>6g</b>	$C_{11}H_{23}$	Cr <sub>1</sub>	-22 (26.3)	Cr <sub>2</sub>	25 (12.7)	I
<b>6h</b>	$C_{12}H_{25}$	Cr <sub>1</sub>	5 (28.9)	Cr <sub>2</sub>	28 (8.7)	I
<b>7f</b>	$C_{10}H_{21}$	Cr	33 (71.2)	I		
<b>7g</b>	$C_{11}H_{23}$	Cr <sub>1</sub>	-2 (49.0)	Cr <sub>2</sub>	42 (47.1)	I
<b>7h</b>	$C_{12}H_{25}$	Cr <sub>1</sub>	5 (28.9)	Cr <sub>2</sub>	42 (64.2)	I

Cr = crystalline, I = isotropic

In conclusion, substituent effects on the phase behavior of gallic catecholates **1**, **6**, and **7** were evaluated. While some of the dinitro derivatives **1** displayed mesophases, both the corresponding unsubstituted gallic esters **6** and the dibromo-substituted derivatives **7** are certainly not mesomorphic. However, in the case of **1** it cannot be differentiated undoubtedly between true mesophases or just soft crystal phases. In general, phase transition temperatures decrease in the order **1** > **7** > **6** with an approximate temperature difference of  $20^{\circ}C$  between the different series. Although compounds **6** and **7** did not show any mesomorphic properties, they are useful building blocks for the convergent preparation of larger mesogenic subunits via oxidative coupling (Schöll reaction)<sup>13</sup> or Pd-catalyzed cross coupling.<sup>14</sup>



### 3. Experimental

#### 3.1. General

Column chromatography was accomplished using SiO<sub>2</sub> 60, grain size 0.063–0.200 mm (Merck) with hexanes (PE, bp 30–60°C), EtOAc, and dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>) as eluents. Starting materials **2a,b** are commercially available. <sup>13</sup>C NMR multiplicities were determined with DEPT experiments. DSC was performed on a Mettler Toledo DSC822. Compounds **2c, 3** and **4** were prepared according to literature procedures.<sup>5,6,12</sup>

**3.1.1. General procedure for the preparation of gallic esters 5a–h.** A mixture of K<sub>2</sub>CO<sub>3</sub> (9 equiv.) and ethyl 3,4,5-trihydroxybenzoate (1 equiv.) in MeCN (30–60 mL) was refluxed for 30 min under N<sub>2</sub> atmosphere. A solution of the respective alkyl bromide (4 equiv.) in MeCN (6–12 mL) was added dropwise to the slurry, maintaining reflux and stirring for 20 h. The reaction was cooled to room temp. and filtered. The inorganic residue was washed with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The filtrate was concentrated under vacuum, the residue dissolved in CH<sub>2</sub>Cl<sub>2</sub> (75 mL) and washed with a 0.5 M NaOH solution (50 mL) and water (2 × 50 mL), dried (MgSO<sub>4</sub>), and concentrated, yielding an oil. A solution of KOH (14 equiv.) in EtOH (75 mL) was added to the gained oil and the mixture was refluxed for 6 h. After evaporation of the solvent, the oily solid was cooled at 0°C, then treated with H<sub>2</sub>O (50 mL) followed by 36.5% HCl (20 mL) after 10 min. The white precipitate was isolated by filtration, washed with water and dried under vacuum. In the case of **5g, 5h**, the mixture was treated with cold MeOH (20 mL), stirred for 30 min at 0°C, filtrated and dried. The spectroscopic data of products **5** are in accordance with those in the literature.<sup>7</sup>

**3.1.2. General procedure for the preparation of 4,5-dinitro-2-[[3,4,5-tris(alkyloxy)-benzoyl]oxy}phenyl 3,4,5-tris(alkyloxy)benzoates 1a–h.** DCC (3.1 equiv.) was added to a cooled solution of the appropriate acid **5** (2.2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (14 mL) at 0 °C, and the

reaction mixture was stirred for 10 min. Then DMAP (1.0 equiv.) and **3** (1.0 equiv.) were added and after stirring for 5 d, the reaction mixture was treated with CH<sub>2</sub>Cl<sub>2</sub> (20 mL), washed with 1 M HCl (3 × 30 mL) and H<sub>2</sub>O (30 mL), dried (MgSO<sub>4</sub>), and concentrated. The oily residue was treated with PE (30 mL) and the white solid was filtered off. The filtrate was evaporated and the residue purified by repeated flash chromatography on SiO<sub>2</sub> with PE/CH<sub>2</sub>Cl<sub>2</sub> [1 : 3, then 10 : 27 (**1a**), 2 : 2.3 (**1b**), 2 : 2.1 (**1c**), 2 : 2.2 (**1d**), 11 : 1 (**1e**), 20 : 23 (**1f**), 13 : 10 (**1g,h**)] to give products **1** as bright yellow solids.

**4,5-Dinitro-2-[[3,4,5-tris(pentyloxy)benzoyl]oxy]phenyl 3,4,5-tris(pentyloxy)benzoate**

(**1a**). Mp 69°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.92 (t, *J* = 6.8 Hz, 18H; 6 CH<sub>3</sub>), 1.30–1.51 (m, 24H; 6 (CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 1.70–1.80 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.4 Hz, 8H; 4 OCH<sub>2</sub>), 4.02 (t, *J* = 6.4 Hz, 4H; 2 OCH<sub>2</sub>), 7.23 (s, 4H, Ar-H), 8.07 (s, 2 H, Ar-H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 13.9 (4 CH<sub>3</sub>), 14.0 (2 CH<sub>3</sub>), 22.41 (2 CH<sub>3</sub>CH<sub>2</sub>), 22.47 (CH<sub>3</sub>CH<sub>2</sub>), 28.1 (2 CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.2 (CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>), 28.8 (2 CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), 29.9 (CH<sub>3</sub>(CH<sub>2</sub>)<sub>3</sub>), 69.1 (2 OCH<sub>2</sub>), 73.5 (OCH<sub>2</sub>), 108.5 (4 CH), 120.7 (2 CH), 121.0, 140.0, 144.0, 145.8, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2954 (m), 2932 (vs), 2870 (vs), 1746 (vs), 1732 (vs), 1588 (m), 1540 (vs), 1430 (m), 1333 (vs), 1270 (vs), 1180 (vs), 1157 (vs), 1084 (s), 934 (m), 743 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 309 (3.29), 276 (3.42), 229 (0.74), 213 (0.61). MS (EI), *m/z* (%): 924.5 (40) [M<sup>+</sup>], 880.8 (100) [M<sup>+</sup> – CO<sub>2</sub>], 809.8 (20), 742.6 (15), 696.4 (100), 626.5 (15), 562.3 (25), 517.3 (40), 380.2 (45), 310.2 (28), 170.0 (100), 43 (75). MS (ESI), *m/z* (%): 947.5 (100) [M<sup>+</sup> + Na], 942.6 (25) [M<sup>+</sup> + NH<sub>4</sub>], 925.6 (10) [M<sup>+</sup> + H]. Anal. calcd for C<sub>50</sub>H<sub>72</sub>N<sub>2</sub>O<sub>14</sub> (924.5): C, 64.91; H, 7.84; N, 3.03. Found: C, 64.70; H, 7.81; N, 2.98.

**4,5-Dinitro-2-[[3,4,5-tris(hexyloxy)benzoyl]oxy]phenyl 3,4,5-tris(hexyloxy)benzoate (1b).**

Mp 75°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.90 (t, *J* = 6.6 Hz, 18H; 6 CH<sub>3</sub>), 1.30–1.57 (m, 36H; 6 (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.69–1.80 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.3 Hz, 8H; 6 CH<sub>3</sub>), 4.02 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.23 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm. <sup>13</sup>C NMR (75 MHz,

CDCl<sub>3</sub>):  $\delta$  = 13.9 (4 CH<sub>3</sub>), 14.0 (2 CH<sub>3</sub>), 22.5, 22.6, 25.6, 25.7, 29.1, 30.2, 31.5, 31.6 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>), 69.1 (4 OCH<sub>2</sub>), 73.6 (2 OCH<sub>2</sub>), 108.5 (4 CH), 120.7 (2 CH), 121.0, 140.0, 144.0, 145.8, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2926 (vs), 2855 (vs), 1747 (vs), 1735 (vs), 1552 (s), 1540 (vs), 1430 (s), 1332 (vs), 1276 (vs), 1187 (vs), 1159 (vs), 1113 (vs), 930 (m), 744 (m), 631(m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 282 (3.37), 229 (0.67), 208 (0.51). MS (ESI),  $m/z$  (%): 1031.6 (100) [M<sup>+</sup> + Na], 1026.7 (15) [M<sup>+</sup> + NH<sub>4</sub>], 1009.6 (8) [M<sup>+</sup> + H], 1008.6 (5) [M<sup>+</sup>]. Anal. calcd for C<sub>56</sub>H<sub>84</sub>N<sub>2</sub>O<sub>14</sub> (1008.6): C, 66.64; H, 8.39; N, 2.78. Found: C 66.73; H, 8.38; N, 2.75.

**4,5-Dinitro-2-[[3,4,5-tris(heptyloxy)benzoyl]oxy]phenyl 3,4,5-tris(heptyloxy)benzoate**

(1c). Mp 63°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.89 (t,  $J$  = 6.6 Hz, 18H; 6 CH<sub>3</sub>), 1.30–1.57 (m, 48H; 6 (CH<sub>2</sub>)<sub>4</sub>CH<sub>3</sub>), 1.70–1.80 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t,  $J$  = 6.3 Hz, 8H; 4 OCH<sub>2</sub>), 4.01 (t,  $J$  = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.22 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.0 (6 CH<sub>3</sub>), 22.6, 22.7, 25.9, 26.0, 29.0, 29.1, 29.2, 30.3, 31.8, 31.9 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>), 69.1 (4 OCH<sub>2</sub>), 73.6 (2 OCH<sub>2</sub>), 108.5 (4 CH), 120.7 (2 CH), 121.0, 140.0, 144.0, 145.8, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2924 (vs), 2854 (vs), 1746 (vs), 1735 (vs), 1589 (m), 1552 (vs), 1539 (vs), 1466 (m), 1429 (vs), 1332 (vs), 1276 (vs), 1186 (vs), 1159 (vs), 1113 (vs), 930 (m), 744 (m) cm<sup>-1</sup>. UV/VIS (CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{\max}$  (log  $\epsilon$ ) = 277 (3.42), 229 (0.74). MS (ESI),  $m/z$  (%): 1115.7 (100) [M<sup>+</sup> + Na], 1110.7 (35) [M<sup>+</sup> + NH<sub>4</sub>], 1093.7 (12) [M<sup>+</sup> + H], 1092.7 (10) [M<sup>+</sup>]. Anal. calcd for C<sub>62</sub>H<sub>96</sub>N<sub>2</sub>O<sub>14</sub> (1092.7): C, 68.10; H, 8.85; N, 2.56. Found: C, 68.01; H, 8.70; N, 2.48.

**4,5-Dinitro-2-[[3,4,5-tris(octyloxy)benzoyl]oxy]phenyl 3,4,5-tris(octyloxy)benzoate (1d).**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  = 0.88 (t,  $J$  = 6.3 Hz, 18H; 6 CH<sub>3</sub>), 1.28–1.56 (m, 60H; 6 (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.68–1.79 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t,  $J$  = 6.3 Hz, 8H; 4 OCH<sub>2</sub>), 4.01 (t,  $J$  = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.22 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta$  = 14.0 (6 CH<sub>3</sub>), 22.6, 26.1, 29.2, 29.3, 29.5, 30.3, 31.8, 31.9 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>), 69.1 (4

OCH<sub>2</sub>), 73.6 (2 OCH<sub>2</sub>), 108.5 (4 CH), 120.7 (2 CH), 121.0, 140.0, 144.0, 145.8, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2918 (vs), 2851 (s), 1740 (vs), 1735 (vs), 1591 (m), 1534 (vs), 1430 (m), 1333 (vs), 1276 (vs), 1193 (vs), 1166 (vs), 1115 (vs), 743 (m), 633 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 282 (3.37), 229 (0.67), 208 (0.51). MS (ESI), *m/z* (%): 1199.8 (100) [M<sup>+</sup> + Na], 1194.8 (35) [M<sup>+</sup> + NH<sub>4</sub>], 1177.8 (37) [M<sup>+</sup> + H]. HRMS (EI) calcd 1176.7801 (for C<sub>68</sub>H<sub>108</sub>N<sub>2</sub>O<sub>14</sub>), found 1176.7838 [M<sup>+</sup>]. Anal. calcd for C<sub>68</sub>H<sub>108</sub>N<sub>2</sub>O<sub>14</sub> (1176.8): C, 69.36; H, 9.24; N, 2.38. Found: C, 69.19; H, 9.11; N, 2.40.

**4,5-Dinitro-2-[[3,4,5-tris(nonyloxy)benzoyl]oxy]phenyl 3,4,5-tris(nonyloxy)benzoate (1e).**

Mp 62°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.3 Hz, 18H; 6 CH<sub>3</sub>), 1.27–1.56 (m, 72H; 6 (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 1.68–1.79 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.3 Hz, 8H; 4 OCH<sub>2</sub>), 4.01 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.22 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 14.0 (6 CH<sub>3</sub>), 22.6, 29.2, 29.32, 29.37, 29.4, 29.61, 29.68, 30.3, 31.91, 31.94 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>), 69.1 (4 OCH<sub>2</sub>), 73.6 (2 OCH<sub>2</sub>), 108.6 (4 CH), 120.7 (2 CH), 121.1, 140.0, 144.0, 145.9, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2918 (vs), 2849 (vs), 1743 (vs), 1735 (vs), 1590 (m), 1535 (vs), 1430 (vs), 1332 (vs), 1277 (vs), 1193 (vs), 1166 (vs), 1115 (vs), 742 (m), 722 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 286 (1.16), 230 (0.45), 221 (0.42), 208 (0.35). MS (ESI), *m/z* (%): 1284.0 (100) [M<sup>+</sup> + Na], 1278.9 (18) [M<sup>+</sup> + NH<sub>4</sub>], 1262.0 (35) [M<sup>+</sup> + 2H], 1260.8 (8) [M<sup>+</sup>]. Anal. calcd for C<sub>74</sub>H<sub>120</sub>N<sub>2</sub>O<sub>14</sub> (1260.9): C, 70.44; H, 9.59; N, 2.22. Found: C, 70.22; H, 9.48; N, 2.10.

**4,5-Dinitro-2-[[3,4,5-tris(decyloxy)benzoyl]oxy]phenyl 3,4,5-tris(decyloxy)benzoate (1f).**

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.4 Hz, 18H; 6 CH<sub>3</sub>), 1.27–1.56 (m, 84H; 6 (CH<sub>2</sub>)<sub>7</sub>CH<sub>3</sub>), 1.68–1.79 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.3 Hz, 8H; 4 OCH<sub>2</sub>), 4.01 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.22 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm. <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ = 14.0 (6 CH<sub>3</sub>), 22.6, 26.0, 26.1, 29.3, 29.4, 29.5, 29.6, 29.66, 29.74, 30.3, 31.9 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 69.1 (4 OCH<sub>2</sub>), 73.6 (2 OCH<sub>2</sub>), 108.6 (4 CH), 120.7 (2 CH), 121.0, 140.0, 144.0,

145.9, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2917 (vs), 2849 (vs), 1743 (vs), 1590 (m), 1535 (vs), 1430 (vs), 1334 (vs), 1277 (vs), 1192 (s), 1167 (vs), 1117 (vs), 784 (s), 743 (m), 633 (m)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 276 (3.42), 229 (0.70), 205 (0.53). MS (ESI),  $m/z$  (%): 1367.9 (100) [ $\text{M}^+ + \text{Na}$ ], 1362.9 (20) [ $\text{M}^+ + \text{NH}_4$ ], 1345.9 (10) [ $\text{M}^+ + \text{H}$ ]. Anal. calcd for  $\text{C}_{80}\text{H}_{132}\text{N}_2\text{O}_{14}$  (1345.0): C, 71.39; H, 9.89; N, 2.08. Found: C, 71.47; H, 9.95; N, 2.05.

**4,5-Dinitro-2-[[3,4,5-tris(undecyloxy)benzoyl]oxy]phenyl 3,4,5-tris(undecyloxy)benzoate**

(**1g**).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.2 Hz, 18H; 6  $\text{CH}_3$ ), 1.26–1.58 (m, 96H; 6  $(\text{CH}_2)_8\text{CH}_3$ ), 1.68–1.79 (m, 12H; 6  $\text{OCH}_2\text{CH}_2$ ), 3.81 (t,  $J$  = 6.3 Hz, 8H; 4  $\text{OCH}_2$ ), 4.01 (t,  $J$  = 6.5 Hz, 4H; 2  $\text{OCH}_2$ ), 7.22 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 (6  $\text{CH}_3$ ), 22.6, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9 (6  $\text{CH}_3(\text{CH}_2)_9$ ), 69.1 (4  $\text{OCH}_2$ ), 73.6 (2  $\text{OCH}_2$ ), 108.6 (4 CH), 120.7 (2 CH), 121.1, 140.0, 144.0, 145.9, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2917 (vs), 2849 (vs), 1743 (vs), 1590 (m), 1535 (vs), 1430 (vs), 1334 (vs), 1277 (vs), 1192 (vs), 1167 (vs), 1118 (vs), 930 (m), 742 (m), 721 (m)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 285 (3.17), 229 (0.66), 207 (0.51). MS (MALDI-TOF),  $m/z$  (%): 1431.0 (92) [ $\text{M}^+ + \text{H}$ ], 1430.0 (100) [ $\text{M}^+$ ]. Anal. calcd for  $\text{C}_{86}\text{H}_{144}\text{N}_2\text{O}_{14}$  (1429.1): C, 72.23; H, 10.15; N, 1.96. Found: C, 71.59; H, 9.96; N, 1.89.

**4,5-Dinitro-2-[[3,4,5-tris(dodecyloxy)benzoyl]oxy]phenyl 3,4,5-tris(dodecyloxy)benzoate**

(**1h**).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.2 Hz, 18H; 6  $\text{CH}_3$ ), 1.26–1.56 (m, 108H; 6  $(\text{CH}_2)_9\text{CH}_3$ ), 1.68–1.76 (m, 12H; 6  $\text{OCH}_2\text{CH}_2$ ), 3.81 (t,  $J$  = 6.3 Hz, 8H; 4  $\text{OCH}_2$ ), 4.01 (t,  $J$  = 6.4 Hz, 4H; 2  $\text{OCH}_2$ ), 7.22 (s, 4H; Ar-H), 8.08 (s, 2H; Ar-H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 (6  $\text{CH}_3$ ), 22.6, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9 (6  $\text{CH}_3(\text{CH}_2)_{10}$ ), 69.1 (4  $\text{OCH}_2$ ), 73.6 (2  $\text{OCH}_2$ ), 108.5 (4 CH), 120.7 (2 CH), 121.0, 140.0, 144.0, 145.9, 153.0, 162.5 (2 CO) ppm. FT-IR (ATR): 2917 (vs), 2849 (vs), 1742 (vs), 1591 (m), 1534 (vs), 1430 (vs), 1334 (s), 1277 (vs), 1192 (vs), 1167 (s), 1116 (vs), 933 (m), 825 (m), 742 (m), 721 (m), 606 (m)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 229 (0.74), 216 (0.64),

208 (0.59), 202 (0.54). MS (MALDI-TOF),  $m/z$  (%): 1515.1 (100) [ $M^+ + 2H$ ], 1514.1 (100) [ $M^+ + H$ ], 1513.0 (10) [ $M^+$ ]. Anal. calcd for  $C_{92}H_{156}N_2O_{14}$  (1513.2): C, 72.97; H, 10.38; N, 1.85. Found: C, 72.95; H, 10.14; N, 1.87.

**3.1.3 General procedure for the preparation of 2-[[3,4,5-tris(alkyloxy)benzoyl]oxy]-phenyl 3,4,5-tris(alkyloxy)benzoates 6a–h.** DCC (3.1 equiv.) was added to a cooled solution of the appropriate **5** (2.2 equiv.) in  $CH_2Cl_2$  (7–10 mL) at 0 °C. After stirring for 10 min, DMAP and **2b** (1.0 equiv. each) were added and the reaction mixture stirred at room temp. for 20 h. The reaction mixture was treated with  $CH_2Cl_2$  (10 mL), washed with 1 M HCl (2 × 20 mL) and  $H_2O$  (20 mL), dried ( $MgSO_4$ ) and concentrated. The oily solid was treated with PE (30 mL) and the white solid was filtered off. The filtrate was evaporated and the residue purified by flash chromatography on  $SiO_2$  with PE/ $CH_2Cl_2$  [20 : 29 (**6a**), 20 : 27 (**6b**), 20 : 24 (**6c**), 20 : 22 (**6d**), 1 : 1 (**6e,f**), 22 : 20 (**6g**), 26 : 20 (**6h**)] to give the products **6a–h** as yellowish to white oils, which were dried for 1 h under freezing conditions (liquid  $N_2$ ) and vacuum ( $10^{-3}$  mbar).

**2-[[3,4,5-Tris(pentyloxy)benzoyl]oxy}phenyl 3,4,5-tris(pentyloxy)benzoate (6a).** Mp 4°C.  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 0.92 (t,  $J$  = 7.0 Hz, 18H; 6  $CH_3$ ), 1.32–1.50 (m, 24H; 6  $(CH_2)_2CH_3$ ), 1.71–1.78 (m, 12H; 6  $OCH_2CH_2$ ), 3.83 (t,  $J$  = 6.4 Hz, 8H; 4  $OCH_2$ ), 3.99 (t,  $J$  = 6.4 Hz, 4H; 2  $OCH_2$ ), 7.26 (s, 4H; Ar-H), 7.32–7.40 (2 m, 4H; Ar-H) ppm.  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 13.9 (4  $CH_3$ ), 14.0 (2  $CH_3$ ), 22.4 (2  $CH_3CH_2$ ), 22.5 ( $CH_3CH_2$ ), 28.1 (2  $CH_3CH_2CH_2$ ), 28.2 ( $CH_3CH_2CH_2$ ), 28.94 (2  $CH_3CH_2CH_2CH_2$ ), 29.98 ( $CH_3CH_2CH_2CH_2$ ), 69.0 (2  $OCH_2$ ), 73.4 ( $OCH_2$ ), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.5, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2954 (s), 2930 (vs), 2870 (vs), 1738 (vs), 1585 (vs), 1495 (s), 1428 (s), 1334 (vs), 1241 (m), 1192 (vs), 1102 (vs), 948 (m), 748 (w)  $cm^{-1}$ . UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 257 (3.39), 210 (0.63). MS (ESI),  $m/z$  (%): 853.5 (50) [ $M^+ + NH_4 +$

H], 852.5 (100) [ $M^+ + NH_4$ ], 836.5 (20), 835.5 (32) [ $M^+ + H$ ]. Anal. calcd for  $C_{50}H_{74}O_{10}$  (834.6): C, 71.91; H, 8.93. Found: C, 72.07; H, 8.94.

**2-[[3,4,5-Tris(hexyloxy)benzoyl]oxy]phenyl 3,4,5-tris(hexyloxy)benzoate (6b).** Mp  $-5^\circ C$ .

$^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 0.90 (t,  $J$  = 6.3 Hz, 18H; 6  $CH_3$ ), 1.28–1.50 (m, 36H; 6  $(CH_2)_3CH_3$ ), 1.70–1.77 (m, 12H; 6  $OCH_2CH_2$ ), 3.83 (t,  $J$  = 6.4 Hz, 8H; 4  $OCH_2$ ), 3.98 (t,  $J$  = 6.5 Hz, 4H; 2  $OCH_2$ ), 7.26 (s, 4H; Ar-H), 7.32–7.40 (2 m, 4 H; Ar-H) ppm.  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 14.0 (4  $CH_3$ ), 14.1 (2  $CH_3$ ), 22.6, 22.7, 25.6, 25.7, 29.2, 30.2, 31.5, 31.7 (6  $CH_3(CH_2)_4$ ), 69.0 (4  $OCH_2$ ), 73.4 (2  $OCH_2$ ), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.5, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2927 (vs), 2858 (vs), 1738 (vs), 1585 (vs), 1495 (s), 1428 (s), 1334 (vs), 1241 (m), 1192 (vs), 1102 (vs), 957 (m), 748 (w)  $cm^{-1}$ . UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 260 (3.33), 236 (2.54), 209 (0.63). MS (ESI),  $m/z$  (%): 937.6 (50) [ $M^+ + NH_4 + H$ ], 936.6 (90) [ $M^+ + NH_4$ ], 919.6 (100) [ $M^+ + H$ ], 918.6 (5) [ $M^+$ ]. Anal. calcd. for  $C_{56}H_{86}O_{10}$  (918.6221): C, 73.17; H, 9.43. Found: C, 73.40; H, 9.44.

**2-[[3,4,5-Tris(heptyloxy)benzoyl]oxy]phenyl 3,4,5-tris(heptyloxy)benzoate (6c).**  $^1H$  NMR (500 MHz,  $CDCl_3$ ):  $\delta$  = 0.89 (t,  $J$  = 6.5 Hz, 18H; 6  $CH_3$ ), 1.27–1.50 (m, 48H; 6  $(CH_2)_4CH_3$ ), 1.70–1.77 (m, 12H; 6  $OCH_2CH_2$ ), 3.82 (t,  $J$  = 6.4 Hz, 8H; 4  $OCH_2$ ), 3.98 (t,  $J$  = 6.5 Hz, 4H; 2  $OCH_2$ ), 7.26 (s, 4H; Ar-H), 7.31–7.40 (2 m, 4 H; Ar-H) ppm.  $^{13}C$  NMR (125 MHz,  $CDCl_3$ ):  $\delta$  = 14.08 (4  $CH_3$ ), 14.09 (2  $CH_3$ ), 22.6, 22.7, 25.9, 26.0, 29.1, 29.2, 29.3, 30.3, 31.8, 31.9 (6  $CH_3(CH_2)_5$ ), 69.0 (4  $OCH_2$ ), 73.4 (2  $OCH_2$ ), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.5, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2924 (vs), 2855 (vs), 1738 (vs), 1585 (vs), 1495 (s), 1428 (s), 1334 (vs), 1241 (m), 1196 (vs), 1103 (vs), 937 (m), 861 (m), 748 (m)  $cm^{-1}$ . UV/Vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) = 255 (3.39), 210 (0.60). MS (ESI),  $m/z$  (%): 1022.7 (10), 1021.7 (25), 1020.7 (30) [ $M^+ + NH_4$ ], 1005.7 (22), 1004.7 (65), 1003.7 (100) [ $M^+ + H$ ], 1002.6 (5) [ $M^+$ ]. Anal. calcd for  $C_{62}H_{98}O_{10}$  (1002.7): C, 74.21; H, 9.84. Found: C, 73.20; H, 9.81.

**2-[[3,4,5-Tris(octyloxy)benzoyl]oxy}phenyl 3,4,5-tris(octyloxy)benzoate (6d).**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.7 Hz, 18H; 6  $\text{CH}_3$ ), 1.25–1.50 (m, 60H; 6  $(\text{CH}_2)_5\text{CH}_3$ ), 1.70–1.77 (m, 12H; 6  $\text{OCH}_2\text{CH}_2$ ), 3.82 (t,  $J$  = 6.4 Hz, 8H; 4  $\text{OCH}_2$ ), 3.98 (t,  $J$  = 6.5 Hz, 4H; 2  $\text{OCH}_2$ ), 7.26 (s, 4H; Ar-H), 7.32–7.40 (2 m, 4 H; Ar-H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.0 (6  $\text{CH}_3$ ), 22.67, 22.69, 26.0, 26.1, 29.3, 29.38, 29.41, 29.5, 30.3, 31.8, 31.9 (6  $\text{CH}_3(\text{CH}_2)_6$ ), 69.0 (4  $\text{OCH}_2$ ), 73.4 (2  $\text{OCH}_2$ ), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.4, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2922 (vs), 2853 (vs), 1738 (vs), 1585 (vs), 1495 (s), 1429 (s), 1335 (vs), 1241 (m), 1196 (vs), 1104 (vs), 947 (w), 861 (m), 748 (m)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 256 (3.37), 212 (0.57). MS (ESI),  $m/z$  (%): 1104.8 (20) [ $\text{M}^+$  +  $\text{NH}_4$ ], 1089.8 (25), 1088.8 (60), 1087.7 (100) [ $\text{M}^+$  + H], 1086.7 (10) [ $\text{M}^+$ ]. Anal. calcd for  $\text{C}_{68}\text{H}_{110}\text{O}_{10}$  (1086.8): C, 75.09; H, 10.19. Found: C, 75.48; H, 10.27.

**2-[[3,4,5-Tris(nonyloxy)benzoyl]oxy}phenyl 3,4,5-tris(nonyloxy)benzoate (6e):** Mp 18°C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.8 Hz, 18H; 6  $\text{CH}_3$ ), 1.28–1.50 (m, 72H; 6  $(\text{CH}_2)_6\text{CH}_3$ ), 1.70–1.77 (m, 12H; 6  $\text{OCH}_2\text{CH}_2$ ), 3.82 (t,  $J$  = 6.4 Hz, 8H; 4  $\text{OCH}_2$ ), 3.98 (t,  $J$  = 6.5 Hz, 4H; 2  $\text{OCH}_2$ ), 7.26 (s, 4H; Ar-H), 7.32–7.40 (2 m, 4H; Ar-H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 (6  $\text{CH}_3$ ), 22.6, 26.0, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9, 32.0 (6  $\text{CH}_3(\text{CH}_2)_7$ ), 69.0 (4  $\text{OCH}_2$ ), 73.4 (2  $\text{OCH}_2$ ), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.5, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2921 (vs), 2852 (vs), 1738 (vs), 1585 (vs), 1495 (s), 1429 (s), 1335 (vs), 1241 (m), 1196 (vs), 1104 (vs), 748 (m)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 256 (3.37), 212 (0.57). MS (ESI),  $m/z$  (%): 1188.8 (18) [ $\text{M}^+$  +  $\text{NH}_4$ ], 1173.8 (30), 1172.8 (75), 1171.8 (100) [ $\text{M}^+$  + H], 1170.8 (20) [ $\text{M}^+$ ]. Anal. calcd for  $\text{C}_{74}\text{H}_{122}\text{O}_{10}$  (1170.9): C, 75.85; H, 10.49. Found: C, 76.19; H, 10.59.

**2-[[3,4,5-Tris(decyloxy)benzoyl]oxy}phenyl 3,4,5-tris(decyloxy)benzoate (6f):**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.5 Hz, 18H; 6  $\text{CH}_3$ ), 1.27–1.50 (m, 84H; 6  $(\text{CH}_2)_7\text{CH}_3$ ),



1.68–1.78 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.4 Hz, 8H; 4 OCH<sub>2</sub>), 3.98 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.26 (s, 4H; Ar-H), 7.31–7.40 (m, 4 H; Ar-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 14.0 (6 CH<sub>3</sub>), 22.6, 26.0, 26.1, 29.3, 29.38, 29.40, 29.5, 29.6, 29.7, 29.8, 30.3, 31.92, 31.93 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 69.0 (4 OCH<sub>2</sub>), 73.4 (2 OCH<sub>2</sub>), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.5, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2920 (vs), 2852 (vs), 1738 (vs), 1585 (vs), 1495 (s), 1429 (s), 1335 (vs), 1241 (m), 1196 (vs), 1105 (vs), 749 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 277 (2.74), 232 (1.58). MS (ESI), *m/z* (%): 1272.9 (15) [M<sup>+</sup> + NH<sub>4</sub>], 1257.9 (35), 1256.9 (80), 1255.9 (100) [M<sup>+</sup> + H]. Anal. calcd for C<sub>80</sub>H<sub>134</sub>O<sub>10</sub> (1255.0): C, 76.51; H, 10.75. Found: C, 76.79; H, 10.86.

**2-[[3,4,5-Tris(undecyloxy)benzoyl]oxy]phenyl 3,4,5-tris(undecyloxy)benzoate (6g).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.8 Hz, 18H; 6 CH<sub>3</sub>), 1.27–1.50 (m, 96H; 6 (CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.70–1.77 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.3 Hz, 8H; 4 OCH<sub>2</sub>), 3.98 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.26 (s, 4H; Ar-H), 7.33–7.40 (m, 4 H; Ar-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 14.1 (6 CH<sub>3</sub>), 22.6, 26.0, 26.1, 29.3, 29.39, 29.40, 29.5, 29.6, 29.69, 29.72, 29.8, 30.3, 31.93, 31.95 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>9</sub>), 69.0 (4 OCH<sub>2</sub>), 73.4 (2 OCH<sub>2</sub>), 108. (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.4, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2920 (vs), 2852 (vs), 1738 (vs), 1585 (vs), 1496 (s), 1466 (m), 1429 (s), 1336 (vs), 1241 (m), 1198 (vs), 1115 (vs), 1104 (vs), 750 (w) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 277 (2.74), 232 (1.58). MS (ESI), *m/z* (%): 1341.0 (80), 1340.0 (100) [M<sup>+</sup> + H], 1338.9 (20) [M<sup>+</sup>], 1338.0 (10). Anal. calcd for C<sub>86</sub>H<sub>146</sub>O<sub>10</sub> (1339.1): C, 77.08; H, 10.98. Found: C, 77.35; H, 11.03.

**2-[[3,4,5-Tris(dodecyloxy)benzoyl]oxy]phenyl 3,4,5-tris(dodecyloxy)benzoate (6h).** <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.8 Hz, 18H; 6 CH<sub>3</sub>), 1.26–1.50 (m, 108H; 6 (CH<sub>2</sub>)<sub>9</sub>CH<sub>3</sub>), 1.70–1.77 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.82 (t, *J* = 6.4 Hz, 8H; 4 OCH<sub>2</sub>), 3.98 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.26 (s, 4H; Ar-H), 7.32–7.40 (m, 4 H; Ar-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 14.1 (6 CH<sub>3</sub>), 22.7, 26.0, 26.1, 29.3, 29.39, 29.41, 29.5, 29.6, 29.69, 29.71,

29.75, 29.76, 29.78, 30.3, 31.9 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>), 69.0 (4 OCH<sub>2</sub>), 73.4 (2 OCH<sub>2</sub>), 108.3 (4 CH), 123.1 (2 CH), 123.5 (2 CH), 126.4, 142.5, 142.9, 152.8, 164.0 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2920 (vs), 2852 (vs), 1739 (vs), 1586 (vs), 1496 (s), 1430 (s), 1337 (vs), 1242 (m), 1199 (vs), 1105 (vs), 751 (m) cm<sup>-1</sup>. UV/Vis (CH<sub>2</sub>Cl<sub>2</sub>): λ<sub>max</sub> (log ε) = 276 (2.90), 232 (1.66). MS (ESI), *m/z* (%): 1426.1 (50), 1425.1 (90), 1424.1 (100) [M<sup>+</sup> + H], 1423.1 (15) [M<sup>+</sup>]. Anal. calcd for C<sub>92</sub>H<sub>158</sub>O<sub>10</sub> (1423.2): C, 77.58; H, 11.18. Found: C, 77.96; H, 11.14.

**3.1.4 General procedure for the preparation of 4,5-dibromo-2-[[3,4,5-tris(alkyloxy)benzoyl]oxy}phenyl 3,4,5-tris(alkyloxy)benzoates 7f–h.** DCC (3.1 equiv.) was added to a cooled solution of the appropriate **5** (2.2 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0°C and after stirring for 10 min, DMAP and **2c** (1 equiv. each) were added and the reaction mixture stirred at room temp. for a further 20 h. The reaction mixture was treated with CH<sub>2</sub>Cl<sub>2</sub> (30 mL), washed with 1 M HCl (2 × 30 mL) and H<sub>2</sub>O (30 mL), dried (MgSO<sub>4</sub>) and concentrated. The oily solid was treated with PE (30 mL) and the white solid was filtered off. The filtrate was evaporated and the residue purified by flash chromatography on SiO<sub>2</sub> with PE/CH<sub>2</sub>Cl<sub>2</sub> (15 : 10) to give products **7** as white solids, which were dried for 1 h under freezing conditions (liquid N<sub>2</sub>) and high vacuum (10<sup>-3</sup> mbar).

**4,5-Dibromo-2-[[3,4,5-tris(decyloxy)benzoyl]oxy}phenyl 3,4,5-tris(decyloxy)benzoate (7f).** Mp 33°C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 0.88 (t, *J* = 6.4 Hz, 18H; 6 CH<sub>3</sub>), 1.27–1.50 (m, 84 H; 6 (CH<sub>2</sub>)<sub>8</sub>CH<sub>3</sub>), 1.69–1.76 (m, 12H; 6 OCH<sub>2</sub>CH<sub>2</sub>), 3.81 (t, *J* = 6.3 Hz, 8H; 4 OCH<sub>2</sub>), 3.98 (t, *J* = 6.5 Hz, 4H; 2 OCH<sub>2</sub>), 7.21 (s, 4H; Ar-H), 7.69 (s, 2H; Ar-H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ = 14.0 (6 CH<sub>3</sub>), 22.6, 26.0, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 30.3, 31.9 (6 CH<sub>3</sub>(CH<sub>2</sub>)<sub>8</sub>), 69.0 (4 OCH<sub>2</sub>), 73.5 (2 OCH<sub>2</sub>), 108.3 (4 CH), 121.3 (2 CBr), 122.3, 128.1 (2 CH), 142.1, 143.1, 152.9, 163.6 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2917 (vs), 2849 (vs), 1743 (vs), 1589 (s), 1468 (s), 1430 (s), 1335 (vs), 1256 (m), 1196 (vs), 1112 (vs), 944 (m),

740 (w), 720 (w), 637 (w), 609 (w)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 283 (2.94), 229 (0.52). MS (ESI),  $m/z$  (%): 1436.1 (45) [ $\text{M}^+ + \text{Na} + \text{H}$ ], 573.7 (100), 433.6 (35). Anal. calcd for  $\text{C}_{80}\text{H}_{132}\text{Br}_2\text{O}_{10}$  (1410.8): C, 67.97; H, 9.41. Found: C, 67.97; H, 9.37.

**4,5-Dibromo-2-[[3,4,5-tris(undecyloxy)benzoyl]oxy]phenyl 3,4,5-tris(undecyloxy)benzoate (7g).**  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.4 Hz, 18H; 6  $\text{CH}_3$ ), 1.21–1.50 (m, 96H; 6  $(\text{CH}_2)_8\text{CH}_3$ ), 1.67–1.78 (m, 12H; 6  $\text{OCH}_2\text{CH}_2$ ), 3.81 (t,  $J$  = 6.3 Hz, 8H; 4  $\text{OCH}_2$ ), 3.98 (t,  $J$  = 6.5 Hz, 4H; 2  $\text{OCH}_2$ ), 7.21 (s, 4H; Ar-H), 7.69 (s, 2H; Ar-H) ppm.  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 (6  $\text{CH}_3$ ), 22.6, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 31.9 (6  $\text{CH}_3(\text{CH}_2)_9$ ), 69.0 (2  $\text{OCH}_2$ ), 73.5 (2  $\text{OCH}_2$ ), 108.3 (4 CH), 121.3 (2 CBr), 122.3, 128.1 (2 CH), 142.1, 143.1, 152.9, 163.6 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2916 (vs), 2849 (vs), 1744 (vs), 1589 (s), 1471 (s), 1463 (s), 1429 (s), 1336 (vs), 1259 (m), 1196 (vs), 1113 (vs), 944 (m), 739 (w), 720 (w)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 276 (3.36), 229 (0.54), 211 (0.47), 208 (0.47). MS (ESI),  $m/z$  (%): 1520.1 (100) [ $\text{M}^+ + \text{Na}$ ], 615.5 (90), 461.4 (35). Anal. calcd for  $\text{C}_{86}\text{H}_{144}\text{Br}_2\text{O}_{10}$  (1497.9): C, 68.96; H, 9.69. Found: C, 68.95; H, 9.69.

**4,5-Dibromo-2-[[3,4,5-tris(dodecyloxy)benzoyl]oxy]phenyl 3,4,5-tris(dodecyloxy)benzoate (7h).**  $^1\text{H}$  NMR (250 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 0.88 (t,  $J$  = 6.1 Hz, 18H; 6  $\text{CH}_3$ ), 1.20–1.52 (m, 108H; 6  $(\text{CH}_2)_9\text{CH}_3$ ), 1.61–1.80 (m, 12H; 6  $\text{OCH}_2\text{CH}_2$ ), 3.81 (t,  $J$  = 6.2 Hz, 8H; 4  $\text{OCH}_2$ ), 3.98 (t,  $J$  = 6.4 Hz, 4H; 2  $\text{OCH}_2$ ), 7.21 (s, 4H; Ar-H), 7.69 (s, 2H; Ar-H) ppm.  $^{13}\text{C}$  NMR (62.9 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 14.1 (6  $\text{CH}_3$ ), 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.6, 29.7, 29.8, 30.3, 31.9 (6  $\text{CH}_3(\text{CH}_2)_{10}$ ), 69.0 (4  $\text{OCH}_2$ ), 73.5 (2  $\text{OCH}_2$ ), 108.3 (4 CH), 121.3 (2 CBr), 122.3, 128.1 (2 CH), 142.1, 143.1, 152.9, 163.6 (2 CO) ppm. FT-IR (ATR): 2953 (s), 2916 (vs), 2849 (vs), 1744 (vs), 1589 (s), 1464 (s), 1430 (s), 1336 (vs), 1258 (m), 1197 (vs), 1113 (vs), 945 (m), 739 (w), 720 (w), 607 (w)  $\text{cm}^{-1}$ . UV/Vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) = 277 (3.37), 229 (0.60), 219 (0.56). MS (Micro Tof),  $m/z$  (%): 1604.0 (75) [ $\text{M}^+ + \text{Na} - \text{H}$ ], 711.5 (12). Anal. calcd for  $\text{C}_{92}\text{H}_{156}\text{Br}_2\text{O}_{10}$  (1579.0): C, 69.85; H, 9.94. Found: C, 70.21; H, 10.02.

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## Graphical Abstract

### Gallic Esters of 4,5-Dinitrocatechol as Potential Building Blocks for Thermotropic Liquid Crystals

Roxana Judele, Sabine Laschat,\* Angelika Baro and Manfred Nimtz

*Institut für Organische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70569 Stuttgart, Germany; Gesellschaft für Biotechnologische Forschung, Mascheroder Weg 1, D-38124 Braunschweig, Germany*

