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Preparation of Mesogen-Functionalized Dendrimers for Second-Order Nonlinear Optics

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ABSTRACT: Liquid crystalline dendrimers with peripheral mesogen-containing units have been prepared. Multistep synthesis with several selective reactions was used in the preparation of the mesogen-containing molecules, 4″-[10-(hydroxycarbonyl)decyloxy]phenyl 4-[4′-(2-(*R*)-octyloxy)-3′-nitrophenyl]benzoate and 4″-[10-(hydroxycarbonyl)decyloxy]biphenyl 4-[4′-(2-(*R*)-octyloxy)-3′-nitrophenyl]benzoate. Both molecules possessed an electron-accepting nitro group placed perpendicular to the long axis of the molecules in order to enhance the nonlinear optical activity. A second generation hydroxyl functional aliphatic dendrimer based on the dihydroxy acid, 2,2-bis(hydroxymethyl)propionic acid, was used as dendritic scaffold and was subsequently functionalized with the aforementioned groups. The purity and structure of the two liquid crystalline dendrimers were determined by ^{1}H NMR spectroscopy, size exclusion chromatography, and elemental analysis. The synthesis of both the mesogen-containing units and the liquid crystalline dendrimers is described in detail. Investigation of the liquid crystalline properties of the materials by differential scanning calorimetry and optical microscopy showed that they exhibited different mesophases, including the chiral smectic C phase. Ferroelectric switching was observed in this tilted phase, and electrooptical properties, including tilt angle and spontaneous polarization measurements, were investigated. Finally, the nonlinear optical properties of one of the materials were preliminary characterized.

Introduction

During the past decade, there has been a growing effort in developing organic and polymeric materials for second-order nonlinear optics (NLO).[1] However, a common problem with organic and polymeric materials is their low degree of polar order. Liquid crystalline (LC) materials have shown to be promising candidates for the preparation of NLO materials. Unfortunately, although they can form highly ordered phases, they possess an intrinsic quadrupolar order but in general not a dipolar one.[2] In chiral smectic C (SmC*) liquid crystals or ferroelectric liquid crystals (FLCs), however, the molecular symmetry allows a local dipolar order perpendicular to the tilt plane[3] which can be extended to the whole sample either by orienting all the molecular dipoles in an external electric field or by surface constraints like the one used in surface-stabilized FLCs (SSFLCs).[4] Early experiments performed on a classic FLC molecule, (*S*)-2-methylbutyl *N*-(4-*n*-decyloxybenzylidene)-4′-aminocinnamate (DOBAMBC),[3] confirmed the potential use of FLCs for nonlinear optics, although the NLO susceptibility turned out to be extremely small.[5] Walba and co-workers[6] were the first to realize that FLCs with enhanced NLO effects could be obtained if a NLO chromophore was aligned in the direction of the polarization, perpendicular to the long axis of the molecule. Therefore, they synthesized a low molecular weight FLC **I** (Figure 1), in which an electron-accepting nitro group was introduced in the ortho position of the chiral moiety, with the specific purpose of increasing the second-order optical nonlinearity. This compound showed a second harmonic generation (SHG) coefficient (d_{22}) of 0.6 pm/V.[7] In 1993, Schmitt et al.,[8] in an attempt to increase the SHG signal, synthesized a four-ring compound in which an electron-donating amino group was introduced in the molecule in the para position to the electron-accepting nitro group (Figure 1, compound **II**). Their NLO properties were studied, and a large SHG coefficient (d_{22}) of 5pm/V was obtained.[9] Based on the work of Walba and Schmitt, several liquid crystal-

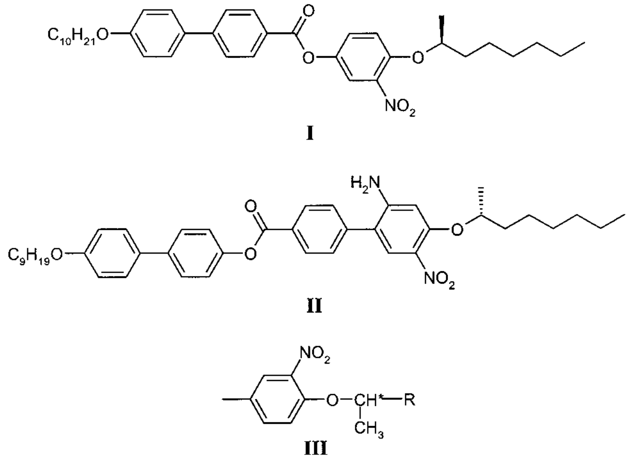

Figure 1. Ferroelectric liquid crystals designed for nonlinear optics (**I** and **II**) and the NLO active part 4-((*R* or *S*)-1-methylalkoxy)-3-nitrophenyl (**III**).

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line systems containing the NLO moiety **III**, 4-((*R* or *S*)-1-methylalkoxy)-3-nitrophenyl, have been prepared. Thus, dimers,[10] dimesogenic oligosiloxanes,[11] cyclic oligomers,[12] side-chain polymers,[8b,13] and main-chain polymers,[14] including **III**, have been synthesized for NLO purposes. In addition, partially cross-linked[15] and densely cross-linked[16] pyroelectric polymers, based on ferroelectric acrylate monomers of type **I**, have been prepared by our group in order to improve the mechanical properties and long-term stability of the NLO materials.

Lately, thermotropic LC materials with dendritic architecture have received a lot of attention, and both LC hyperbranched polymers[17] and LC dendrimers[18] have been prepared by several groups. Dendritic liquid crystalline polymers (DLCPs) offer new synthetic and structural alternatives to side-chain and main-chain liquid crystalline polymers. Recently, we presented the preparation of ferroelectric LC dendrimers[19] based on aliphatic dendritic scaffolds functionalized with mesogen-containing units. Although there are some examples of hyperbranched polymers[20] and dendrimers[21] with NLO properties in the literature, to our knowledge, no other ferroelectric dendritic liquid crystalline systems designed for NLO purposes have been prepared so far.

Herein, we report the functionalization of a second generation dendritic aliphatic polyester, bearing 12 hydroxyl groups on its surface, with two different mesogen-containing units incorporating the NLO active group **III**. The preparation and characterization of both the mesogen-containing units and the mesogen-functionalized dendrimers are described in detail. In addition, the liquid crystalline properties of the dendrimers are reported, and initial results concerning the electrooptical and nonlinear optical properties are shortly presented.

Results and Discussion

Synthesis. Both mesogen-functionalized dendrimers were prepared according to a general strategy described earlier.[18a,19] Their preparation is divided into three parts: (a) synthesis of the dendritic scaffold, G#2-$(OH)_{12}$, with 12 terminal hydroxyl groups; (b) preparation of the mesogen-containing units possessing a carboxylic acid terminal group; (c) coupling of the respective mesogen-containing units to the dendritic scaffold via acid chloride reaction yielding the mesogen-functionalized dendrimers **NitroAG#2** and **NitroBG#2**.

Both mesogen-containing units, 4″-[10-(hydroxycarbonyl)decyloxy]phenyl 4-[4′-(2-(*R*)-octyloxy)-3′-nitrophenyl]benzoate (**10a**) and 4″-[10-(hydroxycarbonyl)decyloxy]biphenyl 4-[4′-(2-(*R*)-octyloxy)-3′-nitrophenyl]benzoate (**10b**), incorporating the NLO active group **III**, are expected to exhibit a chiral smectic C mesophase and promising nonlinear optical properties.[6,8]

(a) Synthesis of the Hydroxyl Functional Dendrimer. The second generation hydroxyl functional aliphatic dendrimer, G#2-$(OH)_{12}$, was prepared according to a previously described procedure.[22] In our previous work on ferroelectric LC dendrimers,[19b] we underlined that the electrooptical properties of the materials were independent of the generation number. However, electrooptical measurements were easier to perform on ferroelectric LC dendrimers of higher generation (generations 2 and 3) as compared to the first generation LC dendrimer. Moreover, the preparation of the third generation aliphatic dendritic scaffold requires more synthetic steps than the preparation of the second generation dendrimer. For these reasons, G#2-$(OH)_{12}$ was used as dendritic scaffold in this study.

(b) Synthesis of the Mesogen-Containing Units. Two different molecules were prepared, both possessing a carboxylic acid terminal group required for the coupling to the dendritic scaffold. The mesogenic core of 4″-[10-(hydroxycarbonyl)decyloxy]phenyl 4-[4′-(2-(*R*)-octyloxy)-3′-nitrophenyl]benzoate (**10a**) consists of a three-aromatic-ring system, whereas 4″-[10-(hydroxycarbonyl)decyloxy]biphenyl 4-[4′-(2-(*R*)-octyloxy)-3′-nitrophenyl]benzoate (**10b**) contains four aromatic rings. The mesogen-functionalized dendrimer **NitroBG#2** is therefore expected to show higher phase transition temperatures than **NitroAG#2**.[8] The synthesis of **10a** and **10b** involves several selective reactions, described in detail in the next paragraph.

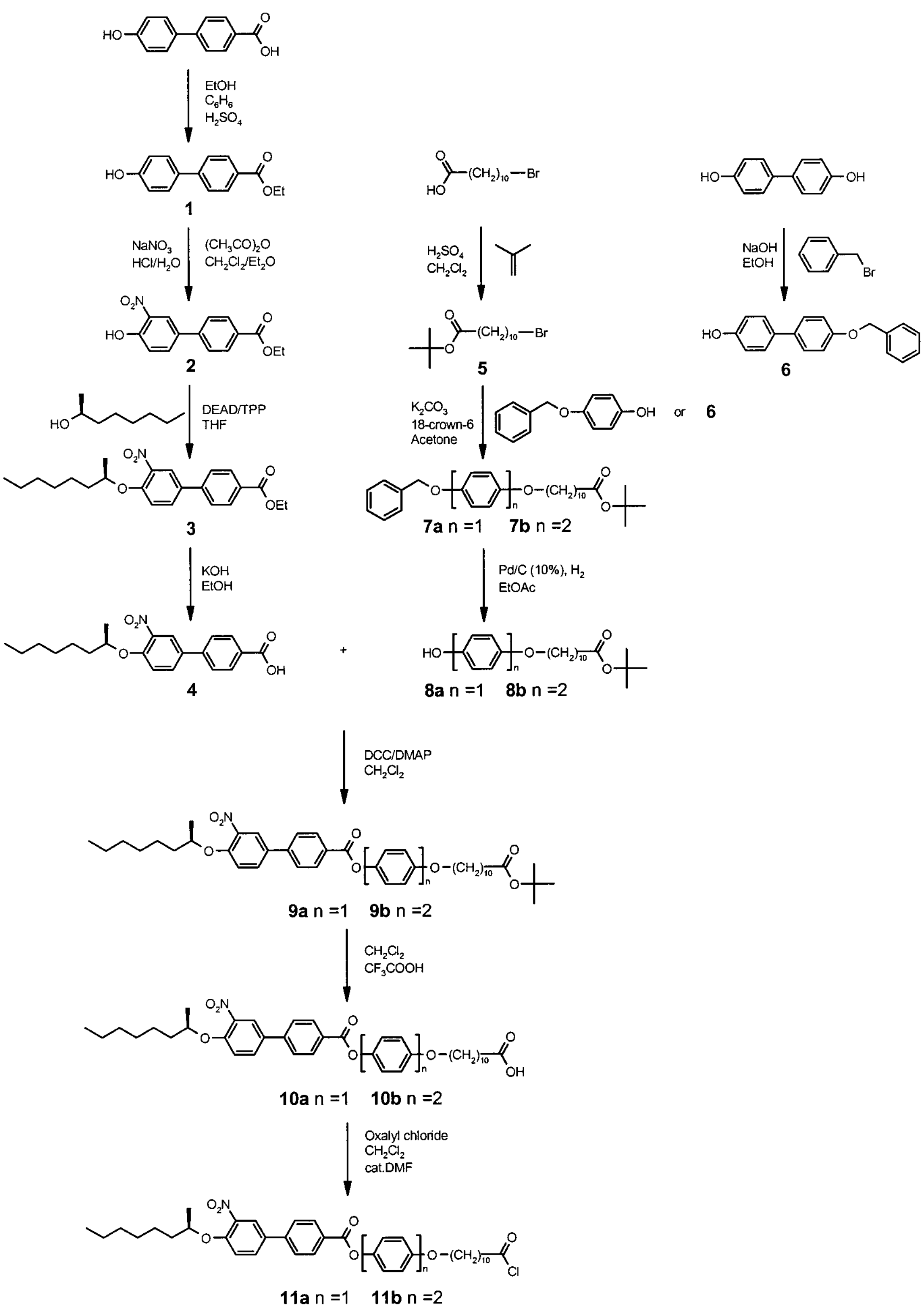
The synthetic pathways used in the preparation of **10a** and **10b** are shown in Scheme 1.

Compounds **10a** and **10b** were synthesized according to the same procedure. Therefore, only the preparation of **10b** is described in detail. The synthesis of **10b** was divided into two parts **4** and **8b**, which were coupled in a low-temperature esterification procedure using *N*,*N*′-dicyclohexylcarbodiimide (DCC) and 4-(dimethylamino)pyridine (DMAP) to yield the intermediate **9b**. Compound **4** was synthesized in four steps starting by the protection via esterification of 4′-hydroxy-4-biphenylcarboxylic acid with ethanol to give **1**. Nitration of the para-substituted phenol **1** using a two-phase system described by Keller gave exclusively the ortho-nitrated compound **2**.[23] **2** was etherified by (*S*)-2-octanol in the presence of diethylazodicarboxylate (DEAD) and triphenylphosphine (TPP) using the Mitsunobu reaction to yield the intermediate **3**.[24] This step proceeds by inversion of configuration of the chiral center, changing the *S*-alcohol to a *R*-ether. Compound **3** was subsequently deprotected by saponification with KOH to give **4**.

The synthesis of the other half of the molecule was also divided into two parts **6** and **5**. 4,4′-Dihydroxybiphenyl was mono protected with benzyl bromide under basic conditions to give **6**. The *tert*-butyl ester **5** was prepared by reaction of 11-bromoundecanoic acid with isobutylene according to the procedure described by Anderson and Callahan.[25] Attempts to prepare **5** from 11-bromoundecanoic acid and *tert*-butyl alcohol using standard esterification procedures failed to give the desired compound in reasonable yields. **7b** was obtained by etherification of **6** with **5** in the presence of potassium carbonate and a catalytic amount of 18-crown-6. This reaction proceeded without affecting the *tert*-butyl ester group of **5**. Finally, the benzyl ether protective group of **7b** was removed by catalytic hydrogenolysis to yield compound **8b**. This method did not affect the ester function in **7b**. **9b** was obtained by coupling **4** with **8b**, and the *tert*-butyl group was removed by acid-catalyzed hydrolysis using trifluoroacetic acid to finally give the meson-containing unit **10b**.[26] This reaction proceeded without any adverse effects on the central ester bond and other functional groups. **10a** was prepared in a similar way. However, commercially available 4-benzyloxyphenol was used instead of **6**.

(c) Synthesis of the Mesogen-Functionalized Dendrimers (Scheme 2). These compounds were prepared according to a previously described method.[19] Coupling of the mesogen-containing units to the dendritic scaffolds was performed via acid chloride reaction in the presence of triethylamine (TEA) and DMAP.

Scheme 1. Synthesis of Mesogen-Containing Units 10a and 10b and Its Acid Chloride Derivatives 11a and 11b

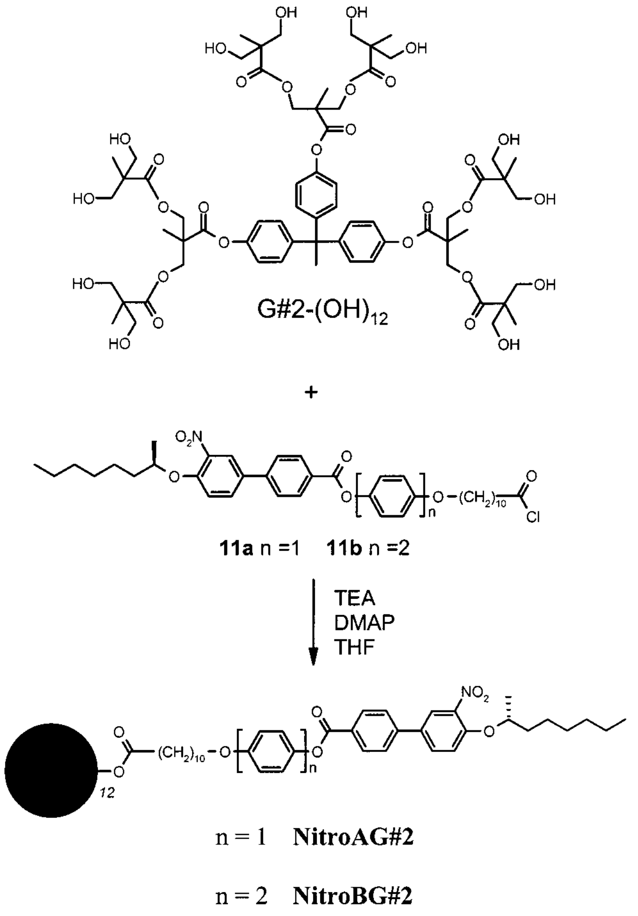


Compound **10a** (**10b**) was reacted with oxalyl chloride in the presence of a catalytic amount of DMF to give the corresponding acid chloride **11a** (**11b**). For every terminal hydroxyl function, a 1.15 molar excess amount of **11a** (**11b**) was used to ensure full substitution of the second generation dendritic scaffold. The products, **NitroAG#2** and **NitroBG#2**, were highly soluble in dichloromethane, chloroform, and THF but insoluble in methanol, ethanol, and water. The final purification was performed by precipitation of a solution of the dendrimer in dichloromethane into a large volume of methanol. This procedure was repeated until no starting mesogen-containing unit was detected by ^{1}H NMR spectroscopy. Both materials were isolated as slightly yellow powders.

General Characterization. The chemical structures of **NitroAG#2** and **NitroBG#2** were confirmed by ^{1}H NMR, size exclusion chromatography (SEC), and elemental analysis.

^{1}H NMR spectroscopic data of all compounds were in agreement with the structures proposed (see Experimental Section). Figure 2 shows the ^{1}H NMR spectrum of **NitroAG#2**. The disappearance of the signal around

Scheme 2. Synthesis of Mesogen-Functionalized Dendrimers NitroAG#2 and NitroBG#2; The Circle Represents the Dendritic Scaffold



3.6 ppm in the ^{1}H NMR spectrum of **NitroAG#2** (which corresponds to the methylene group close to the hydroxyl function of the partially substituted dendrimer) and the appearance of a signal at 4.22 ppm (which corresponds to the methylene group **f** of the fully substituted dendrimer) confirmed that all hydroxyl groups were functionalized. Moreover, the lack of a signal at 2.35 ppm in the ^{1}H NMR spectrum (which corresponds to the methylene group close to the carboxylic acid function in **10a**) proved that the final product was not contaminated with no unreacted mesogen-containing unit. Instead, a signal appeared at 2.28 ppm (**h**) in the fully substituted dendrimer. Finally, it is important to note that the signals corresponding to the mesogenic aromatic protons in **NitroAG#2** shifted upfield as compared to the corresponding signals in the mesogen-containing unit **10a**. Such subtle changes could be attributed to the intramolecular and steric interactions between the mesogen-containing units in the dendrimer. Similar observations have been made in other mesogen-functionalized dendrimers.[19b]

A similar ^{1}H NMR spectrum was obtained for **NitroBG#2**. However, it showed two additional signals (two doublets) corresponding to the aromatic protons of the fourth aromatic ring present in the mesogen.

SEC analyses showed that only narrow monodisperse peaks were shown for both LC dendrimers. The obtained data are reported in Table 1. The molar masses of **NitroAG#2** and **NitroBG#2** determined by SEC were not in agreement with the theoretical molar masses. Such behavior is common for dendrimers and is related to the differences in the hydrodynamic volume of linear polystyrene standards and dendrimers. At present, it is known that dendrimers, because of their compact globular shape, have smaller hydrodynamic volume as compared to that of linear polymers.[27]

Finally, additional information from elemental analysis confirmed the high purity and individuality of **NitroAG#2** and **NitroBG#2** (see Experimental Section).

Liquid Crystalline Properties. The mesomorphic and thermal properties of **NitroAG#2** and **NitroBG#2** were investigated by differential scanning calorimetry (DSC) and optical microscopy. The transition temperatures of the compounds are listed in Table 2.

The DSC scans of the two materials showed a second-order phase transition (glass transition) and two first-order phase transitions. Both dendrimers exhibit liquid crystalline behavior. As can be seen from the data in Table 2, **NitroBG#2** showed a higher glass transition temperature (T_g) than **NitroAG#2**. Moreover, it appeared that the temperature corresponding to the transition between the liquid crystalline state and the isotropic phase, T_{LC-I}, was dramatically higher in the case of **NitroBG#2** than in the case of **NitroAG#2**. It is known that an increase in the length of the mesogens elevates both the transition from the glass to the liquid crystalline phase and the transition from the liquid crystalline to the isotropic phase. The upper transition is usually affected more, and thereby the stability of the liquid crystalline phase region is enhanced. Such changes have also been observed in side-chain liquid crystalline polyacrylates obtained from monomers similar to **10a** and **10b**.[8b]

The optical textures of both compounds were examined by optical microscopy by preparing thin liquid crystal films sandwiched between a clean glass slide and a coverslip. In the case of **NitroAG#2**, coexistence of focal–conic fan and homeotropic textures appeared at 82 °C when slowly cooling (0.5 °C/min) the sample from the isotropic state. These macroscopic textures suggest that a smectic A* (SmA*) phase is formed.[28] Those textures were unchanged until 69 °C. At this temperature, a different liquid crystalline phase was formed. The focal–conic fan and homeotropic textures were replaced by broken focal–conic fan and sanded schlieren textures. These optical textures are characteristic of the chiral smectic C (SmC*) phase. According to these observations, one can suppose that **NitroAG#2** displays the following phase transitions: g ↔ SmC* ↔ SmA* ↔ I. **NitroBG#2** displayed comparable liquid crystalline properties. However, as mentioned before, the phase transition temperatures were higher. Parts a and b of Figure 3 show the optical textures of **NitroBG#2** in the smectic A* and smectic C* phase, respectively. It is important to note that, in both cases, large monodomains could be obtained between the glass plates by slowly cooling the samples from the isotropic state.

Observation of both smectic A* and smectic C* phases in the materials indicates that the mesogen-containing units are not oriented radially around the dendritic scaffold but form a cylinder-like structure with the mesogens oriented upward and downward. A possible model explaining the formation of smectic layers by such dendritic structures has recently been proposed by others and us.[19b,29]

To get additional information on the properties of the SmC* phase displayed by **NitroAG#2** and **NitroBG#2**,

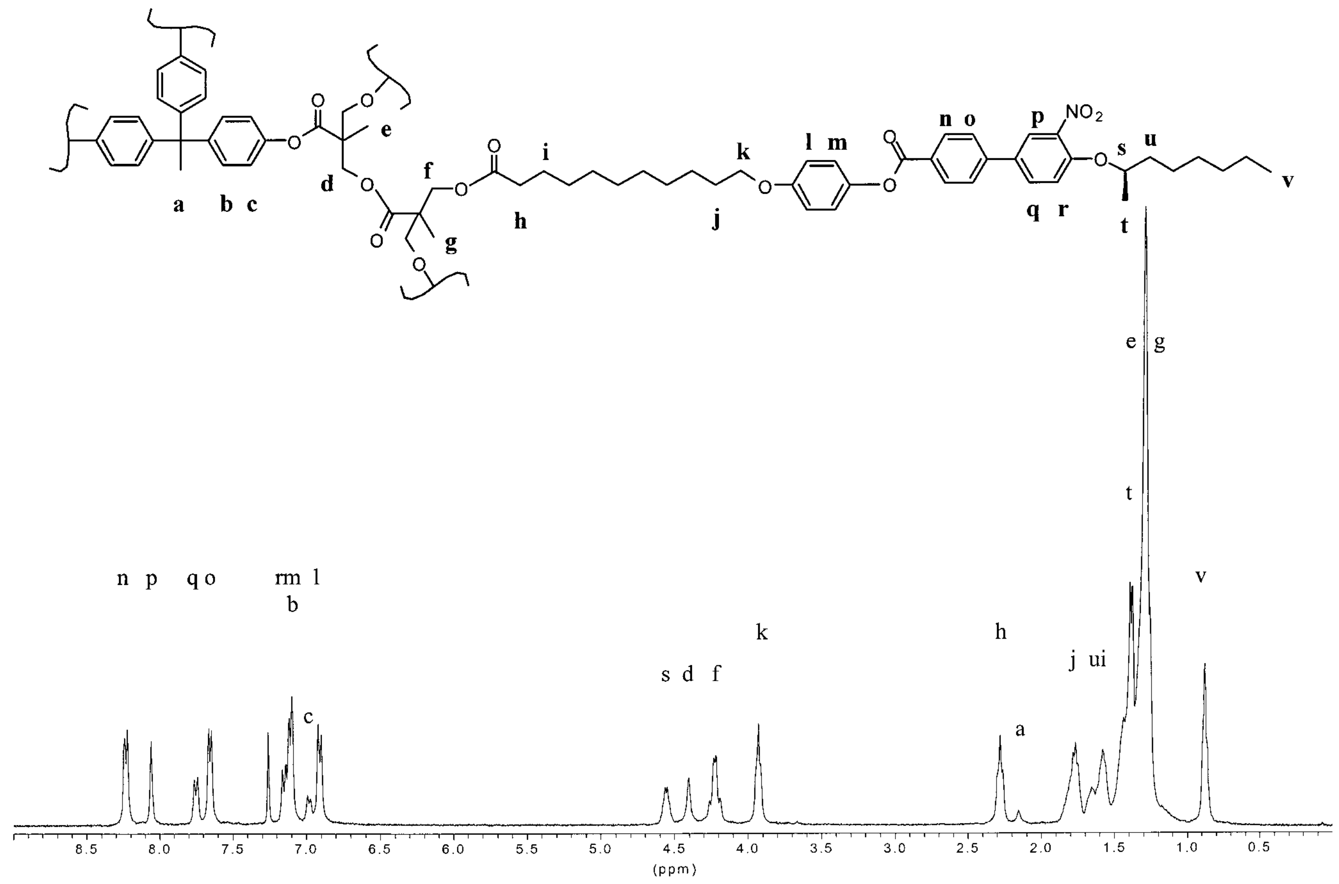


Figure 2. ^{1}H NMR spectrum of **NitroAG#2**.

Table 1. SEC Data of the LC Dendrimers

LC dendrimer	M(calcd) (g/mol)	$\bar{M}$(SEC) (g/mol)	$\bar{M}$(SEC) (g/mol)	$\bar{M}/\bar{M}$
NitroAG#2	8898	10 900	10 000	1.09
NitroBG#2	9810	13 100	12 000	1.09

Table 2. Phase Transition Temperatures of the LC Dendrimers[a]

LC dendrimer	T_g (°C)	transition temp (°C)
NitroAG#2	34	SmC* 69 SmA* 82 I
NitroBG#2	70	SmC* 152 SmA* 208 I

[a] T_g = glass transition temperature, SmA* = chiral smectic A phase, SmC* = chiral smectic C phase, I = isotropic liquid.

the compounds were subjected to electrooptical studies. Moreover, nonlinear optical properties of **NitroBG#2** were preliminarily characterized.

Ferroelectric and Nonlinear Optical Properties. The setups and methods used in the characterization of the electrooptical and nonlinear optical properties of the LC dendrimers have been previously described.[30,31] Commercial 4 μm glass cells (EHC, Japan) with both sides pretreated with indium tin oxide (ITO) and rubbed polyimide were used in the determination of the aforementioned properties. Each compound was heated to a temperature region close the isotropization temperature and was subsequently soaked into the glass cell by capillary forces. It is worth noting that below the narrow temperature region we used filling of the cells did not occur, and above this temperature region wetting of the surfaces was poor, leaving large air bubbles in the film. In fact, the two materials turned out to be extremely viscous, and good parallel-aligned samples were difficult to obtain. The presence of a strong lateral polar group in the LC dendrimers increases the viscosity of the materials. Similar effects have also been observed in side-chain and main-chain liquid crystalline polymers. However, initial measurements were performed on the films of best optical quality.

(a) Ferroelectric Properties. After filling of the cells, the films were cooled to the temperature region corresponding to the SmC* phase. Both LC dendrimers showed ferroelectric switching. Typical current and optical responses to an applied triangular electric field in the SmC* phase of **NitroBG#2** are depicted as an example in Figure 4.

The materials were subjected to electrooptical studies, including spontaneous polarization (P_s) and tilt angle (θ) measurements. As we observed in ferroelectric dendrimers previously reported,[19b] determination of the electrooptical properties of the materials was not possible in the full temperature range of the SmC* phase. Both spontaneous polarization and tilt angle measurements were affected by the high viscosity of the materials. In fact, measurements could only be performed in a narrow temperature region under the transition from the SmA* to the SmC* phase. Herein, we report the maximal values obtained at a given reduced temperature T_r defined as

$$T_r = T - T_{tr} \tag{1}$$

where T_{tr} corresponds to the SmA*–SmC* transition temperature in **NitroAG#2** and **NitroBG#2**. T is the temperature at which the spontaneous polarization and tilt angle measurements were performed. **NitroAG#2** showed a maximal spontaneous polarization P_s of 18 nC/cm^2 at $T_r = -6$ °C. However, determination of the tilt

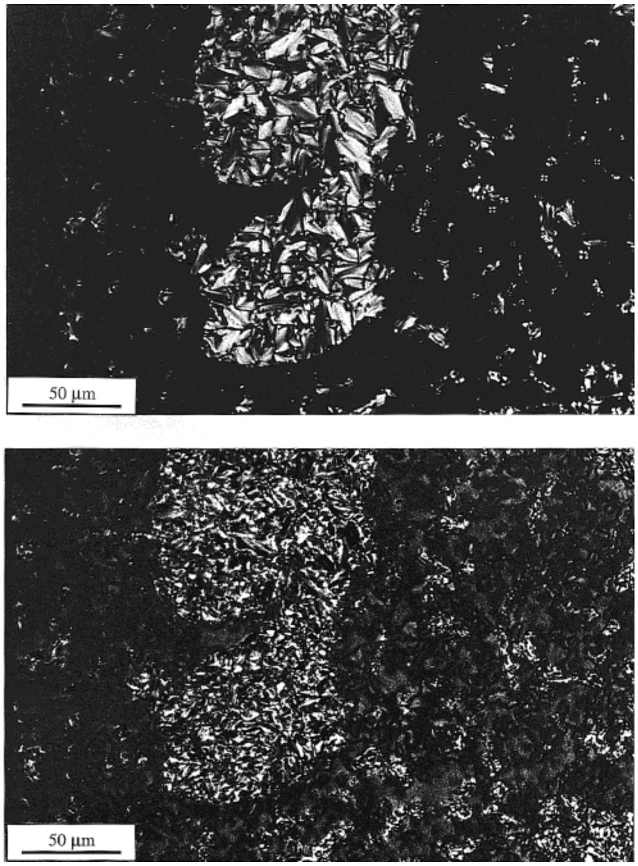


Figure 3. (a, top) Polarized photomicrograph of **NitroBG#2** in the SmA* at $T = 160$ °C. (b, bottom) Polarized photomicrograph of **NitroBG#2** in the SmC* at $T = 138$ °C.

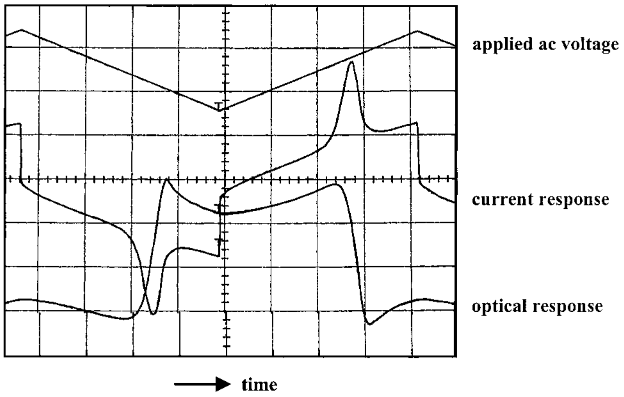


Figure 4. Typical optical and current responses (bottom and middle, respectively) to an applied triangular electric field (top) in the SmC* phase of **NitroBG#2** ($T = 143$ °C).

angle of this material was not possible due to poor alignment. The maximal spontaneous polarization obtained for **NitroBG#2** was 66 nC/cm^2 at $T_r = -11$ °C. Moreover, a tilt angle value of 32.5° was obtained at $T_r = -36$ °C. These initial results confirm that the presence of an electron-accepting nitro group placed perpendicular to the long axis of the molecule improves the electrooptical properties of the materials. In fact, for the second generation ferroelectric liquid crystalline dendrimer reported previously (LC dendrimer without polar nitro group in the mesogen), the value of the spontaneous polarization determined at $T_r = -11$ °C was approximately 25 nC/cm^2.

Further investigation of the electrooptical properties may be achieved by realizing a better parallel alignment of the samples. One alternative could be the use of glass cells pretreated with a uniaxial Teflon monolayer.[14a]

NitroBG#2, which appeared as the most promising material, was subjected to second-harmonic generation (SHG) measurements.

(b) Nonlinear Optical Properties. A film of **NitroBG#2** was prepared as mentioned above and was cooled to 150 °C, where appropriate switching of the ferroelectric liquid crystalline dendrimer was established. A complete unwinding of the helix axis of the ferroelectric phase could not be induced by surface forces alone, and at low electric fields the switching originated mainly from the deflection of the optic axis. This deflection was attributed to the deformation of the helix. Above a critical electric field (the threshold field) a sharp shift in birefringence color occurred, and this was taken as a confirmation of the unwinding of the helix axis (ferroelectric switching mode). An electric field with an amplitude of 6.5 V/μm (square wave, 5 Hz) gave a purple-pink birefringence color at 150 °C (birefringence 0.14, ferroelectric switching mode) and a yellowish color at 140 °C (birefringence 0.08, deformed helix switching mode). The birefringence was estimated from the Michel−Levy chart and was correct within approximately 20%. The lowering of the temperature was accompanied by a sharp shift in birefringence color due to increased viscosity, which caused the threshold field to increase above 6.5 V/μm. After these findings, a static electric field of 20 V/μm was applied at 150 °C, and the heating of the oven was turned off. The birefringence color changed from purple-pink at high temperature to light blue-cyan on reaching room temperature (birefringence 0.18). The tilt angle was close to 45° at room temperature. The electric field was then removed, and the SHG measurements were performed at room temperature without external electric field.

The unwound SmC* liquid crystal phase belongs to the C_2 symmetry group in which the second-order reduced susceptibility tensor, $\boldsymbol{d}$, contains four independent coefficients under the assumption of Kleinman symmetry conditions:[32]

$$\boldsymbol{d} = \begin{bmatrix} 0 & 0 & 0 & d_{14} & 0 & d_{16} \\ d_{16} & d_{22} & d_{23} & 0 & d_{14} & 0 \\ 0 & 0 & 0 & d_{23} & 0 & d_{14} \end{bmatrix} \tag{2}$$

Values obtained for the second harmonic coefficients d_{23} and d_{16} were of the same order of magnitude, which is in agreement with data reported on nitro-substituted ferroelectric liquid crystals.[33] d_{23} and d_{16} were estimated to be 0.03 pm/V and 0.025 pm/V, respectively. The inaccuracy of the given values of d_{23} and d_{16} due to the weak contribution of d_{22} is approximately 20%. In addition, the accuracy is decreased by the lack of information on the dispersion relation of the refractive index (inaccuracy estimated to 10%). However, from the measurements and the analysis accounted for here, we conclude that the d coefficients on the ferroelectric liquid crystalline dendrimer **NitroBG#2**, as determined by SHG, are $d_{23} = 0.03 \pm 0.007$ pm/V and $d_{16} = 0.025 \pm 0.006$ pm/V.

Conclusions

Novel liquid crystalline dendrimers have been successfully prepared. Two different mesogen-containing units incorporating a nitro group perpendicular to their long axis were synthesized and subsequently coupled to a second generation aliphatic dendrimer possessing 12 terminal hydroxyl groups. The two compounds, **NitroAG#2** and **NitroBG#2**, showed SmA* and SmC* phases, and ferroelectric response was observed in the SmC* phase. Moreover, the second harmonic generation coefficients d_{23} and d_{16} of **NitroBG#2** were measured at room temperature, and the values obtained were 0.03 pm/V and 0.025 pm/V, respectively. Thus, mesogen-functionalized dendrimers offer a new alternative for the preparation of NLO active materials.

Experimental Section

General Procedures. All the chemicals were purchased from Aldrich, Lancaster, and Acros Organics and used without further purification. ^{1}H NMR spectra were recorded on a Bruker AM 400 at 400 MHz using $\mathrm{CDCl_3}$ and DMSO-d_6 as solvents. The solvent signal was used as internal standard. All purifications were performed by medium-pressure liquid chromatography as described by Baeckström et al.,[34] unless specified. Size exclusion chromatography (SEC) measurements were performed on a Waters GPC system using a solvent delivery system (M510), automatic injector (WISP 710B), and a differential refractometer (Waters 410) as a detector. All measurements were made at 25 °C with a 10 μm mixed B column from Polymer Labs. THF was used as eluent at a flow rate of 1.0 mL/min. The molecular weights were computed using a calibration curve constructed by linear polystyrene standards with narrow molecular weight distribution. Elemental analysis was performed at the Analytische Laboratorien GmbH, Lindlar, Germany. Transition temperatures were determined by differential scanning calorimetry on a Mettler Toledo DSC 820 under a nitrogen atmosphere (80 mL/min). In all cases, heating and cooling rates were 10 °C/min. Optical texture studies were made using a Leitz Ortholux POL BK II polarized optical microscope equipped with a Mettler Hot Stage FP 82 and a FP 80 central processor. Equipment and techniques used to determine the electrooptical[30] and the NLO[31] properties have been previously described.

Synthesis. Ethyl 4-(4′-Hydroxyphenyl)benzoate (1). 4′-Hydroxy-4-biphenylcarboxylic acid (5 g, 23.36 mmol), concentrated sulfuric acid (few drops), ethanol (99,5%) (41 mL), and benzene (13 mL) were charged in a single-necked 250 mL round-bottom flask equipped with a Dean–Stark trap. The mixture was stirred under reflux for 36 h. After cooling to room temperature, most of the solvent was evaporated under vacuum. The residue was dissolved in $\mathrm{CH_2Cl_2}$, and the organic phase washed with aqueous $\mathrm{NaHCO_3}$ solution (10%) and then with water. The organic phase was dried over $\mathrm{MgSO_4}$ and filtered, and the solvent was evaporated to give a white crystalline powder. Yield: 5.2 g (92%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta =$ 1.42 (t, 3H, $-\mathrm{OCH_2C}H_3$), 4.42 (q, 2H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 6.07 (b, 1H, $-\mathrm{O}H$), 6.97 (d, 2H, 3′-*H* and 5′-*H*), 7.52 (d, 2H, 2′-*H* and 6′-*H*), 7.61 (d, 2H, 3-*H* and 5-*H*), 8.09 (d, 2H, 2-*H* and 6-*H*).

Ethyl 4-(3′-Nitro-4′-hydroxyphenyl)benzoate (2). Compound **1** (3.3 g, 13.64 mmol) dissolved in $\mathrm{Et_2O}$ (60 mL) and $\mathrm{CH_2Cl_2}$ (30 mL) was added to a stirred solution of $\mathrm{NaNO_3}$ (1.16 g, 13.64 mmol), water (20 mL), and concentrated HCl (10 mL). Acetic anhydride (0.5 mL) was then added. The reaction mixture was stirred for 4 h, and the organic layer was separated off. The aqueous phase was extracted once with $\mathrm{Et_2O}$. The combined etheral phases were extracted once with brine, and the solvent was evaporated. The brown crystalline product was dissolved in a minimum amount of EtOH (95%) at 60 °C, and water was added to the mixture. The voluminous precipitate was filtered off, washed well with water, and dried under vacuum to give a yellow crystalline solid. Yield: 3.83 g (98%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta =$ 1.42 (t, 3H, $-\mathrm{OCH_2C}H_3$), 4.42 (q, 2H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 7.27 (d, 1H, 5′-*H*), 7.63 (d, 2H, 3-*H* and 5-*H*), 7.86 (dd, 1H, 6′-*H*), 8.13 (d, 2H, 2-*H* and 6-*H*), 8.37 (d, 1H, 2′-*H*), 10.25 (b, 1H, $-\mathrm{ArArO}H$).

Ethyl 4-[3′-Nitro-4′-((*R*)-2-octyloxy)phenyl]benzoate (3). TPP (4.63 g, 17.66 mmol) was added all at once to a stirred solution of DEAD (3.07 g, 17.66 mmol), compound **2** (5.07 g, 17.66 mmol), and (*S*)-2-octanol (2.30 g, 17.66 mmol) in dry THF (40 mL). The reaction mixture was stirred for 12 h at room temperature, and the solvent was evaporated under vacuum. The remaining product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) to give a yellow oil. Yield: 5.91 g (84%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta =$ 0.89 (t, 3H, $-(\mathrm{CH_2})_5\mathrm{C}H_3$), 1.27–1.45 (m, 14H, $-\mathrm{ArArOCH(C}H_3)\mathrm{CH_2(C}H_2)_4$-$\mathrm{CH_3}$ and $-\mathrm{OCH_2C}H_3$), 1.60–1.88 (m, 2H, $-\mathrm{ArArOCH}-(\mathrm{CH_3})$-$\mathrm{C}H_2-$), 4.40 (q, 2H, $-\mathrm{OC}H_2\mathrm{CH_3}$), 4.55 (m, 1H, $-\mathrm{ArArOC}H(\mathrm{CH_3})$-$\mathrm{CH_2}-$), 7.14 (d, 1H, 5′-*H*), 7.60 (d, 2H, 3-*H* and 5-*H*), 7.74 (dd, 1H, 6′-*H*), 8.04 (d, 1H, 2′-*H*), 8.10 (d, 2H, 2-*H* and 6-*H*).

4-[3′-Nitro-4′-(2-(*R*)-octyloxy)phenyl]benzoic Acid (4). Compound **3** (7.04 g, 17.64 mmol) and KOH (85%) (2.32 g, 35.28 mmol) were stirred in ethanol (95%) (100 mL) under reflux for 3 h. The solution was allowed to cool, acidified by HCl (2 M), and poured into water. The mixture was extracted three times with $\mathrm{CH_2Cl_2}$, and the combined organic phases were washed with water, dried over $\mathrm{MgSO_4}$, and filtered. The solvent was evaporated to give a yellow solid. Yield: 6.41 g (98%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta = 0.88$ (t, 3H, $-(\mathrm{CH_2})_5\mathrm{C}H_3$), 1.30–1.50 (m, 11H, $-\mathrm{ArArOCH(C}H_3)\mathrm{CH_2(C}H_2)_4\mathrm{CH_3}$), 1.60–1.88 (m, 2H, $-\mathrm{ArArOCH(CH_3)C}H_2-$), 4.57 (m, 1H, $-\mathrm{ArArOC}H(\mathrm{CH_3})$-$\mathrm{CH_2}-$), 7.16 (d, 1H, 5′-*H*), 7.66 (d, 2H, 3-*H* and 5-*H*), 7.76 (dd, 1H, 6′-*H*), 8.07 (d, 1H, 2′-*H*), 8.19 (d, 2H, 2-*H* and 6-*H*).

***tert*-Butyl 11-Bromoundecanoate (5).** Isobutylene was passed through a stirred solution of 11-bromoundecanoic acid (10.6 g, 40 mmol) in $\mathrm{CH_2Cl_2}$ (50 mL) containing concentrated $\mathrm{H_2SO_4}$ (0.5 mL) for 3 h at room temperature. After standing an additional 12 h at room temperature, the solvent was evaporated, and the remaining crude product was dissolved in hexane and extracted with a mixture of saturated $\mathrm{NaHCO_3}$ and brine (1:1) and then with water. The organic phase was dried over $\mathrm{MgSO_4}$ and filtered, and the solvent was evaporated to afford a colorless oil. Yield: 11.56 g (90%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta =$ 1.27 (m, 12H, $-\mathrm{CH_2(C}H_2)_6\mathrm{CH_2}-$), 1.43 (s, 9H, $-\mathrm{COOC(C}H_3)_3$), 1.55 (m, 2H, $-\mathrm{OOCCH_2C}H_2-$), 1.84 (m, 2H, $\mathrm{BrCH_2C}H_2-$), 2.19 (t, 2H, $-\mathrm{OOCC}H_2-$), 3.40 (t, 2H, $\mathrm{BrC}H_2-$).

4′-Benzyloxy-4-hydroxybiphenyl (6). 4,4′-Dihydroxybiphenyl (3.72 g, 20 mmol) and sodium hydroxide (0.8 g, 20 mmol) were dissolved in EtOH (30 mL), and the solution was heated to boiling. Once the solution turned dark green, benzyl bromide (3.42 g, 20 mmol) was added all at once, and the reaction was refluxed for 3 h. The solution was allowed to cool to ambient temperature and subsequently acidified with HCl (2 M). The resulting precipitate was collected by filtration, washed with EtOH, dried in a vacuum, and recrystallized from a mixture of EtOH (95%)/acetic acid to give a white crystalline powder. Yield: 4.25 g (77%). ^{1}H NMR (DMSO-d_6): $\delta =$ 4.37 (bd, 1H, $-\mathrm{ArArO}H$), 5.13 (s, 2H, $-\mathrm{OC}H_2\mathrm{ArH}$), 6.81 (d, 2H, 3-*H* and 5-*H*), 7.04 (d, 2H, 3′-*H* and 5′-*H*), 7.33–7.50 (m, 9H, $-\mathrm{OCH_2Ar}H$, 2-*H*, 6′-*H*, 2-*H*, and 6-*H*).

***tert*-Butyl 11-(4-(Benzyloxy)phenyloxy)undecanoate (7a).** A mixture of 4-benzyloxyphenol (2.00 g, 10 mmol), anhydrous $\mathrm{K_2CO_3}$ (1.45 g, 10.5 mmol), and 18-crown-6 (catalytic amount) in acetone (100 mL) was stirred at 60 °C for 1 h. To the resulting white suspension was added a solution of compound **5** (3.53 g, 11 mmol) in dry acetone (10 mL), and stirring was continued at 60 °C for 36 h. The mixture was allowed to cool to room temperature, and the solvent was evaporated. The residue was dissolved in $\mathrm{CH_2Cl_2}$ and extracted three times with brine. The organic phase was dried over $\mathrm{MgSO_4}$ and filtered, and the solvent was evaporated. The resulting brown powder was recrystallized from EtOH (95%) to give white crystals. Yield: 4.05 g (92%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta =$ 1.29 (m, 12H, $-\mathrm{CH_2(C}H_2)_6\mathrm{CH_2}-$), 1.44 (s, 9H, $-\mathrm{COOC(C}H_3)_3$), 1.57 (m, 2H, $-\mathrm{OOCCH_2C}H_2-$), 1.74 (q, 2H, $-\mathrm{ArOCH_2C}H_2-$), 2.20 (t, 2H, $-\mathrm{OOCC}H_2-$), 3.89 (t, 2H, $-\mathrm{ArOC}H_2-$), 5.01 (s, 2H, $-\mathrm{OC}H_2\mathrm{Ar}$), 6.81 (d, 2H, 2-*H* and 6-*H*), 6.90 (d, 2H, 3-*H* and 5-*H*), 7.37 (m, 5H, $-\mathrm{OCH_2Ar}H$).

***tert*-Butyl 11-(4′-(Benzyloxy)biphenyloxy)undecanoate (7b).** Compound **7b** was synthesized according to the procedure described for compound **7a** starting from **6** and **5**. Yield: 2.27 g (88%). ^{1}H NMR ($\mathrm{CDCl_3}$): $\delta =$ 1.29 (m, 12H, $-\mathrm{CH_2}$-$(\mathrm{C}H_2)_6\mathrm{CH_2}-$), 1.44 (s, 9H, $-\mathrm{COOC(C}H_3)_3$), 1.55 (m, 2H,

$-OOCCH_2CH_2-$), 1.79 (q, 2H, $-ArArOCH_2CH_2-$), 2.20 (t, 2H, $-OOCCH_2-$), 3.98 (t, 2H, $-ArArOCH_2-$), 5.10 (s, 2H, $-OCH_2$-ArH), 6.94 (d, 2H, 3-*H* and 5-*H*), 7.03 (d, 2H, 3′-*H* and 5′-*H*), 7.33−7.50 (m, 9H, $-OCH_2ArH$, 2′-*H*, 6′-*H*, 2-*H*, and 6-*H*).

***tert*-Butyl 11-[4-(Hydroxy)phenyloxy]undecanoate (8a).** 0.53 g of Pd/C (10%) was added to a solution of compound **7a** (5.3 g, 12.04 mmol) in EtOAc (150 mL). The round-bottom flask was evacuated from air and filled with H_2. The mixture was stirred overnight at room temperature. The Pd/C was filtered off and carefully washed with EtOAc. The filtrate was evaporated to give white crystals. Yield: 4.11 g (98%). ^{1}H NMR ($CDCl_3$): δ = 1.28 (m, 12H, $-CH_2(CH_2)_6CH_2-$), 1.44 (s, 9H, $-COOC(CH_3)_3$), 1.57 (m, 2H, $-OOCCH_2CH_2-$), 1.74 (m, 2H, $-ArOCH_2CH_2-$), 2.20 (t, 2H, $-OOCCH_2-$), 3.89 (t, 2H, $-ArOCH_2-$), 4.79 (b, 1H, $-ArOH$), 6.76 (s, 4H, 2-*H*, 6-*H*, 3-*H*, and 5-*H*).

***tert*-Butyl 11-[4′-(Hydroxy)biphenyloxy]undecanoate (8b).** Compound **8b** was synthesized according to the procedure described for compound **8a**. Yield: 1.85 g (99%). ^{1}H NMR ($CDCl_3$): δ = 1.29 (m, 12H, $-CH_2(CH_2)_6CH_2-$), 1.46 (s, 9H, $-COOC(CH_3)_3$), 1.59 (m, 2H, $-OOCCH_2CH_2-$), 1.81 (q, 2H, $-ArArOCH_2CH_2-$), 2.22 (t, 2H, $-OOCCH_2-$), 3.98 (t, 2H, $-ArArOCH_2-$), 5.50 (b, 1H, $-ArArOH$), 6.89 (d, 2H, 3′-*H* and 5′-*H*), 6.94 (d, 2H, 3-*H* and 5-*H*), 7.42 (d, 2H, 2′-*H* and 6′-*H*), 7.45 (d, 2H, 2-*H* and 6-*H*).

4″-[10-(*tert*-Butyloxycarbonyl)decyloxy]phenyl 4-[4′-(2-(*R*)-Octyloxy)-3′-nitrophenyl]benzoate (9a). A solution of compound **8a** (3.5 g, 10 mmol), compound **4** (3.71 g, 10 mmol), DCC (2.47 g, 12 mmol), and DMAP (0.12 g, 1 mmol) in CH_2Cl_2 (50 mL) was stirred at room temperature for 24 h. The reaction mixture was then cooled to −5 °C, and the white precipitate of 1,3-dicyclohexylurea was filtered from the solution. The solvent was evaporated, and the resulting product was purified by column chromatography (silica gel, hexane/EtOAc as eluent) to give a yellow liquid crystalline material. Yield: 5.06 g (72%). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 3H, $-(CH_2)_5CH_3$), 1.30−1.45 (m, 32H, $-ArArOCH(CH_3)CH_2(CH_2)_4$-$CH_3$, $-CH_2(CH_2)_6CH_2-$, and $-COOC(CH_3)_3$), 1.51−1.85 (m, 6H, $-ArArOCH(CH_3)CH_2-$, $-ArOCH_2CH_2-$, and $-OOCCH_2$-CH_2-), 2.20 (t, 2H, $-OOCCH_2-$), 3.96 (t, 2H, $-ArOCH_2-$), 4.57 (m, 1H, $-ArArOCH(CH_3)CH_2-$), 6.93 (d, 2H, 3″-*H* and 5″-*H*), 7.13 (d, 2H, 2″-*H* and 6″-*H*), 7.17 (d, 1H, 5′-*H*), 7.68 (d, 2H, 3-*H* and 5-*H*), 7.77 (dd, 1H, 6′-*H*), 8.08 (d, 1H, 2′-*H*), 8.26 (d, 2H, 2-*H* and 6-*H*).

4″-[10-(*tert*-Butyloxycarbonyl)decyloxy]biphenyl 4-[4′-(2-(*R*)-Octyloxy)-3′-nitrophenyl]benzoate (9b). Compound **9b** was synthesized according to the procedure described for compound **9a** starting from **8b** and **4**. Yield: 2.57 g (65%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.30−1.45 (m, 32H, $-ArArOCH(CH_3)CH_2(CH_2)_4CH_3$, $-CH_2(CH_2)_6CH_2-$, and $-COOC(CH_3)_3$), 1.52−1.85 (m, 6H, $-ArArOCH(CH_3)CH_2-$, $-ArArOCH_2CH_2-$, and $-OOCCH_2CH_2-$), 2.21 (t, 2H, $-OOC$-CH_2-), 4.00 (t, 2H, $-ArArOCH_2-$), 4.57 (m, 1H, $-ArArOCH$-$(CH_3)CH_2-$), 6.97 (d, 2H, 3″-*H* and 5″-*H*), 7.17 (d, 1H, 5′-*H*), 7.28 (d, 2H, 3‴-*H* and 5‴-*H*), 7.52 (d, 2H, 2″-*H* and 6″-*H*), 7.60 (d, 2H, 2‴-*H* and 6‴-*H*), 7.70 (d, 2H, 3-*H* and 5-*H*), 7.78 (dd, 1H, 6′-*H*), 8.09 (d, 1H, 2′-*H*), 8.29 (d, 2H, 2-*H* and 6-*H*).

4″-[10-(Hydroxycarbonyl)decyloxy]phenyl 4-[4′-(2-(*R*)-Octyloxy)-3′-nitrophenyl]benzoate (10a). Compound **9a** (4.78 g, 6.8 mmol) was dissolved in CH_2Cl_2 (20 mL) and cooled in an ice bath, whereupon trifluoroacetic acid (TFA) (10.5 mL, 136 mmol) was added dropwise with stirring. The resulting solution was stirred at this temperature for 1 h and allowed to warm to ambient temperature over 12 h. The solution was then concentrated in a vacuum, and the residual TFA was removed by coevaporation with CH_2Cl_2 (10 mL) and benzene (20 mL). Repeating twice this coevaporation procedure gave a slightly yellow solid. Yield: 4.17 g (95%). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 3H, $-(CH_2)_5CH_3$), 1.30−1.45 (m, 23H, $-ArArOCH$-$(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6CH_2-$), 1.51−1.85 (m, 6H, $-ArArOCH(CH_3)CH_2-$, $-ArOCH_2CH_2-$, and $HOOCCH_2$-CH_2-), 2.35 (t, 2H, $HOOCCH_2-$), 3.96 (t, 2H, $-ArOCH_2-$), 4.57 (m, 1H, $-ArArOCH(CH_3)CH_2-$), 6.93 (d, 2H, 3″-*H* and 5″-*H*), 7.13 (d, 2H, 2″-*H* and 6″-*H*), 7.17 (d, 1H, 5′-*H*), 7.68 (d, 2H, 3-*H* and 5-*H*), 7.77 (dd, 1H, 6′-*H*), 8.08 (d, 1H, 2′-*H*), 8.26 (d, 2H, 2-*H* and 6-*H*).

4″-[10-(Hydroxycarbonyl)decyloxy]biphenyl 4-[4′-(2-(*R*)-Octyloxy)-3′-nitrophenyl]benzoate (10b). Compound **10b** was synthesized according to the procedure described for compound **10a**. Yield: 2.15 g (98%). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.30−1.45 (m, 23H, $-ArArOCH$-$(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6CH_2-$), 1.52−1.85 (m, 6H, $-ArArOCH(CH_3)CH_2-$, $-ArArOCH_2CH_2-$, and HOO-CCH_2CH_2-), 2.35 (t, 2H, $HOOCCH_2-$), 4.00 (t, 2H, −ArAr-OCH_2-), 4.57 (m, 1H, $-ArArOCH(CH_3)CH_2-$), 6.97 (d, 2H, 3″-*H* and 5″-*H*), 7.17 (d, 1H, 5′-*H*), 7.28 (d, 2H, 3‴-*H* and 5‴-*H*), 7.52 (d, 2H, 2″-*H* and 6″-*H*), 7.60 (d, 2H, 2‴-*H* and 6‴-*H*), 7.70 (d, 2H, 3-*H* and 5-*H*), 7.78 (dd, 1H, 6′-*H*), 8.09 (d, 1H, 2′-*H*), 8.29 (d, 2H, 2-*H* and 6-*H*).

4″-[10-(Chlorocarbonyl)decyloxy]phenyl 4-[4′-(2-(*R*)-Octyloxy)-3′-nitrophenyl]benzoate (11a). Oxalyl chloride (0.51 g, 4 mmol) was added drop by drop to a solution of **10a** (1.29 g, 2 mmol) and 3 drops of DMF in CH_2Cl_2 (20 mL). The reaction was allowed to reach completion for 3 h at room temperature. The excess of oxalyl chloride was removed on the rotary evaporator to give a slightly yellow solid that was used without any further purification. Yield: 1.33 g (quantitative). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 3H, -$(CH_2)_5CH_3$), 1.30−1.45 (m, 23H, $-ArArOCH(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6$-CH_2-), 1.51−1.85 (m, 6H, $-ArArOCH(CH_3)CH_2-$, $-ArOCH_2$-CH_2-, and $ClOCCH_2CH_2-$), 2.89 (t, 2H, $ClOCCH_2-$), 3.96 (t, 2H, $-ArOCH_2-$), 4.57 (m, 1H, $-ArArOCH(CH_3)CH_2-$), 6.93 (d, 2H, 3″-*H* and 5″-*H*), 7.13 (d, 2H, 2″-*H* and 6″-*H*), 7.17 (d, 1H, 5′-*H*), 7.68 (d, 2H, 3-*H* and 5-*H*), 7.77 (dd, 1H, 6′-*H*), 8.08 (d, 1H, 2′-*H*), 8.26 (d, 2H, 2-*H* and 6-*H*).

4″-[10-(Chlorocarbonyl)decyloxy]biphenyl 4-[4′-(2-(*R*)-Octyloxy)-3′-nitrophenyl]benzoate (11b). Compound **11b** was synthesized according to the procedure described for compound **11a**. Yield: 1.48 g (quantitative). ^{1}H NMR ($CDCl_3$): δ = 0.89 (t, 3H, $-(CH_2)_5CH_3$), 1.30−1.45 (m, 23H, $-ArArOCH(CH_3)CH_2(CH_2)_4CH_3$ and $-CH_2(CH_2)_6CH_2-$), 1.61−1.85 (m, 6H, $-ArArOCH(CH_3)CH_2-$, $-ArArOCH_2CH_2-$, and $ClOCCH_2CH_2-$), 2.89 (t, 2H, $ClOCCH_2-$), 4.00 (t, 2H, −ArAr-OCH_2-), 4.57 (m, 1H, $-ArArOCH(CH_3)CH_2-$), 6.97 (d, 2H, 3″-*H* and 5″-*H*), 7.17 (d, 1H, 5′-*H*), 7.28 (d, 2H, 3‴-*H* and 5‴-*H*), 7.52 (d, 2H, 2″-*H* and 6″-*H*), 7.60 (d, 2H, 2‴-*H* and 6‴-*H*), 7.70 (d, 2H, 3-*H* and 5-*H*), 7.78 (dd, 1H, 6′-*H*), 8.09 (d, 1H, 2′-*H*), 8.29 (d, 2H, 2-*H* and 6-*H*).

NitroAG#2. Compound **11a** (1.294 g, 2 mmol), diluted in a small amount of THF, was added dropwise to a solution of G#2-$(OH)_{12}$ dendrimer (0.195 g, 0.145 mmol), DMAP (0.106 g, 0.87 mmol), and TEA (0.264 g, 2.609 mmol) in THF (10 mL) at 0 °C. After stirring at 0 °C for 1 h, the mixture was allowed to reach ambient temperature and stirred for a further 24 h. The solvent was then evaporated under vacuum, and the brown residue was dissolved in CH_2Cl_2. The solution was first extracted three times with saturated $NaHCO_3$, then three times with HCl (2 M), and finally with brine. The organic phase was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Finally, the solid was dissolved in a minimum amount of CH_2Cl_2 and precipitated from methanol. The precipitated powder was filtered off and dried under vacuum. This procedure was repeated until no starting mesogen-containing units were detected on by ^{1}H NMR. Yield: 1.21 g (68%). ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 36H, $-(CH_2)_5CH_3$), 1.24−1.49 (m, 303H, $-ArArOCH(CH_3)CH_2(CH_2)_4CH_3$, $-CH_2(CH_2)_6$-CH_2-, and $-CH_3$), 1.51−1.66 (m, 48H, $-ArArOCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.78 (m, 24H, $-ArOCH_2CH_2-$), 2.15 (s, 3H, $-CH_3$), 2.28 (t, 24H, $-OOCCH_2-$), 3.93 (t, 24H, $-ArOCH_2-$), 4.22 (q, 24H, $-CH_2C-$), 4.40 (s, 12H, $-CH_2C-$), 4.56 (m, 12H, $-ArArOCH(CH_3)CH_2-$), 6.90 (d, 24H, 3″-*H* and 5″-*H*), 6.98 (d, 6H, Ar*H*), 7.11 (d, 30H, Ar*H*, 2″-*H*, and 6″-*H*), 7.15 (d, 12H, 5′-*H*), 7.65 (d, 24H, 3-*H* and 5-*H*), 7.75 (d, 12H, 6′-*H*), 8.06 (s, 12H, 2′-*H*), 8.23 (d, 24H, 2-*H* and 6-*H*). Anal. Calcd for $C_{521}H_{654}O_{114}N_{12}$: C, 70.24; H, 7.4; N, 1.89. Found: C, 70.32; H, 7.60; N, 1.79.

NitroBG#2. This compound was prepared from **11b** (1.446 g, 2 mmol), G#2-$(OH)_{12}$ (0.195 g, 0.145 mmol), DMAP (0.106 g, 0.87 mmol), and TEA (0.264 g, 2.609 mmol) according to the method described for **NitroAG#2**. Yield: 1.27 g (65%). ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 36H, $-(CH_2)_5CH_3$), 1.24−1.49 (m, 303H, $-ArArOCH(CH_3)CH_2(CH_2)_4CH_3$, $-CH_2(CH_2)_6CH_2-$, and $-CH_3$), 1.51−1.66 (m, 48H, $-ArArOCH(CH_3)CH_2-$ and $-OOCCH_2CH_2-$), 1.78 (m, 24H, $-ArArOCH_2CH_2-$), 2.15 (s, 3H, $-CH_3$), 2.28 (t, 24H, $-OOCCH_2-$), 3.93 (t, 24H, $-ArArOCH_2-$), 4.22 (q, 24H, $-CH_2C-$), 4.40 (s, 12H, $-CH_2C-$), 4.55 (m, 12H, $-ArArOCH(CH_3)CH_2-$), 6.94 (d, 24H, 3″-*H* and 5″-*H*), 6.98 (d, 6H, Ar*H*), 7.11 (d, 6H, Ar*H*), 7.15 (d, 12H, 5′-*H*), 7.24 (d, 24H, 3‴-*H* and 5‴-*H*), 7.48 (d, 24H, 2″-*H* and 6″-*H*), 7.57 (d, 24H, 2‴-*H* and 6‴-*H*), 7.67 (d, 24H, 3-*H* and 5-*H*), 7.75 (dd, 12H, 6′-*H*), 8.06 (d, 12H, 2′-*H*), 8.25 (d, 24H, 2-*H* and 6-*H*). Anal. Calcd for $C_{593}H_{702}O_{114}N_{12}$: C, 72.52; H, 7.21; N, 1.71. Found: C, 72.61; H, 7.34; N, 1.67.

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