

# Naphthalene System as the Origin of Unconventionally Shaped Ferroelectric Liquid Crystals

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On the basis of the possibilities of disubstitutions that the naphthalene ring offers, the liquid-crystal and ferroelectric properties of new chiral [1,5]-, [1,6]-, [2,3]-, [2,5]-, [2,6]-, and [2,7]naphthyl benzoates are reported. These new structures have molecular shapes of different linearity which significantly influences both the liquid-crystal behavior (only the [2,6] derivatives form a liquid crystal) and the ferroelectric response of the products that were evaluated in binary mixtures. While the stepped [1,5]- and [2,6]naphthalene structures can be considered useful alternatives to the linear biphenyl ones for ferroelectric blends, the behavior of the angled compounds ([1,6], [2,3], [2,5], and [2,7]) strongly depends on the chiral tail position: on the benzoate ring or on the naphthyl one. For the latter, as well as a worse dipolar coupling, the bending structure obliges the chiral tail to adopt conformations that lead to a significant lowering of the macroscopic polarization of the material.

## Introduction

Since the theoretical prediction and experimental verification of ferroelectricity in chiral liquid phases,<sup>1</sup> many efforts have been devoted to theory,<sup>2-6</sup> synthesis,<sup>7-14</sup> experimental investigation of physical properties,<sup>6,15-20</sup> and practical applications<sup>21</sup> of ferroelectric liquid crystal (FLC).<sup>22</sup>

Moreover, these efforts, particularly the synthetic and experimental ones, have been especially fruitful because

they have allowed researchers to discover new exciting and different phenomena in liquid crystals: the electroclinic effect<sup>23</sup> and the chiral smectic A phase,<sup>24</sup> also termed twist grain boundary structures (TGB\*<sub>A</sub>) or antiferroelectric and ferroelectric mesophases.<sup>25,26</sup>

Interest in molecular structure-activity correlations has therefore increased and consequently in the synthesis of new compounds, so chemical structure is mainly responsible for the properties of a liquid crystal. Thus research on both new chiral tails<sup>27-30</sup> and new central cores<sup>14,30-34</sup> to obtain new FLC materials is being carried out. Most of this work is with rodlike molecules.

As far as central cores are concerned, structures based on three aromatic rings<sup>11,32,34</sup> are proving to be of great

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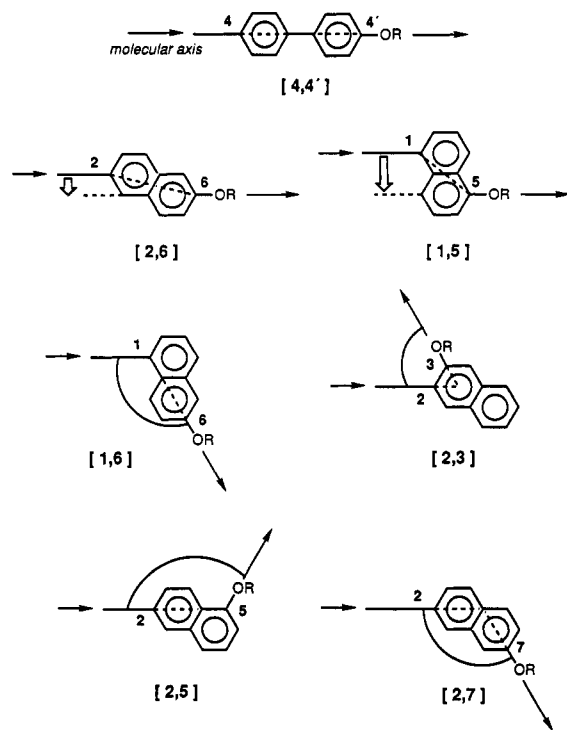
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**Figure 1.** Schematic representation of the structural modification introduced by the different substitutions on the naphthalene system.

interest in order to obtain the potentially ferroelectric SmC\* phase. Of all these FLC, those based on the biphenyl system which provides long and linear central structures, have been widely studied.<sup>19,30,34,35</sup>

We have recently reported<sup>29,36</sup> the good ferroelectric behavior of several chiral series derived from 6-(2-hydroxynaphthyl) benzoates, with a three-ring central core scarcely studied.<sup>37,38</sup> Most of these compounds exhibited the SmC\* phase below 90 °C in an I–Ch–Sm–A–SmC\* phase sequence, increasing the interest in the structure of naphthalene in the FLC field. But we also consider very interesting the attractive possibilities of disubstituted structures the naphthalene ring enables us to study.

In comparison with the linear geometry of the 4,4'-biphenyl system, the naphthalene ring, depending on the substitution, allows us to introduce steps ([2,6] and [1,5]) or angles ([1,6], [2,3], [2,5], and [2,7]) that significantly alter the linearity of the molecule (see Figure 1).

The influence of similar changes on the mesophase arrangement has been studied elsewhere,<sup>39</sup> but it has never been studied as far as the ferroelectric behavior of liquid crystals is concerned.

In this paper, we report the synthesis and the physical behavior of new chiral naphthalene–benzoates. They show the same conjugated central core that defines the main axis of the molecule, but their molecular shapes are different. To evaluate the possibilities of these structures in the FLC field, two representative chiral

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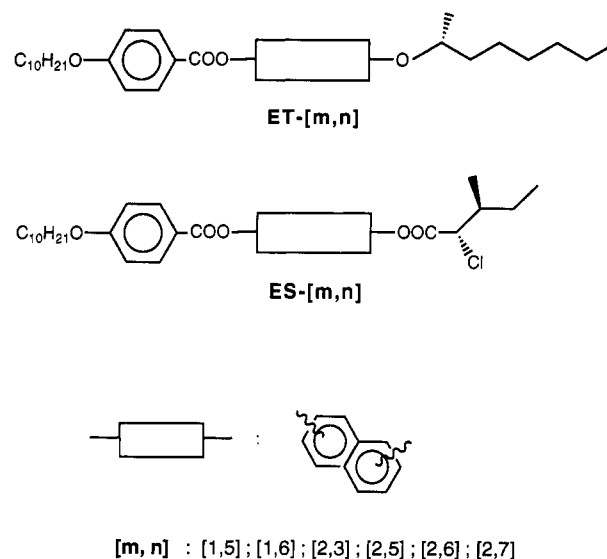
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**Chart 1**



tails, the (*R*)-1-methylheptyloxy group and the  $\alpha$ -chloro acid derived from L-isoleucine, have been chosen (see Chart 1).

For the sake of simplicity, each (*n*-decyloxy)benzoate derivative is named by ET or ES to denote the type of chiral chain (ether or ester, respectively) and with the two numbers in brackets corresponding to the substitution; the first number always indicates the benzoate group position.

To make a comparative study with a linear three aromatic ring structure, the homologous biphenyl benzoates, named ET-[4,4'] and ES-[4,4'],<sup>40</sup> have also been synthesized and characterized. ET-[4,4'] is reported for the first time even though similar ethers were described by Inukai et al. in 1986.<sup>35</sup>

The analysis of the behavior of the proposed compounds obliged us to study six new naphthalene benzoates which have permitted us to draw the conclusions proposed in this paper. They differ only in the chiral tail position, in the benzoic ring instead of the naphthalene one, so we have called them as ET-[2\*,3], ET-[2\*,6], ET-[2\*,7], ES-[2\*,3], ES-[2\*,6], and ES-[2\*,7].

## Results and Discussion

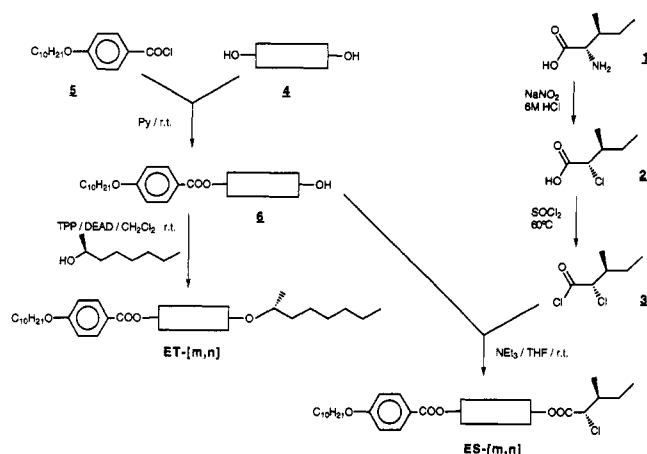
**Synthesis.** The general reaction pathways followed to obtain the target materials are shown in Schemes 1 and 2.

The commercially available (*S*)-(+)-2-octanol (Aldrich Chemie) served as enantiomerically enriched starting material for the ET compounds. L- $\alpha$ -Isoleucine, available in high enantiomeric purity, provided the chiral source for the ES derivatives.

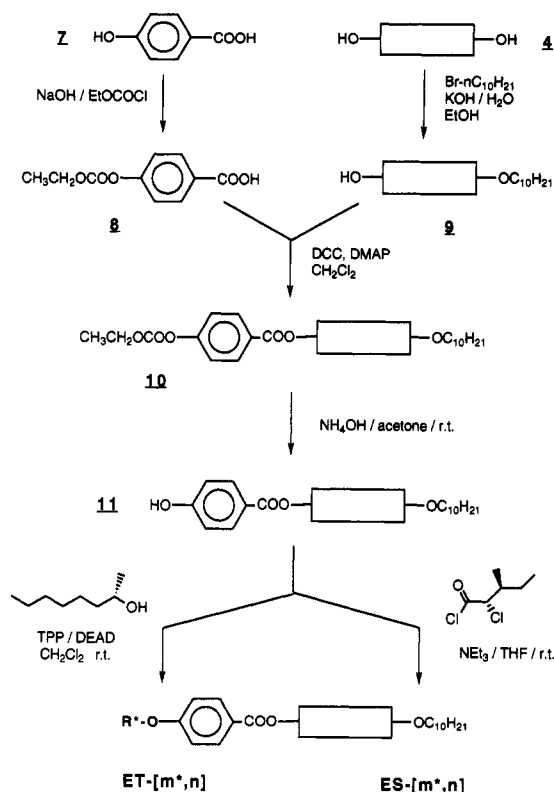
To obtain the (*n*-decyloxy)benzoate derivatives (Scheme 1), commercial dihydroxynaphthalenes and 4,4'-dihydroxybiphenyl were esterified with 4-(*n*-decyloxy)benzoyl chloride in pyridine following the synthetic method described elsewhere<sup>29</sup> which afforded the corresponding monoesters **6**. From this reaction mixture the diester derivatives were also isolated and characterized, and liquid-crystal behavior was observed in some cases (see Experimental Section).

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Scheme 1



Scheme 2



The hydroxy esters **6** were etherified with (*S*)-(+)-2-octanol using diethylazodicarboxylate (DEAD) and triphenylphosphine following the procedure described by Mitsunobu.<sup>41</sup> This is a redox reaction which proceeds with net inversion of configuration in the chiral center.

The  $\alpha$ -halo acid **2** was prepared as described by Fu and co-workers<sup>42</sup> with a modification of the procedure<sup>43</sup> in order to increase the yield and chemical and enantiomeric purity. The conversion of the amino group of the  $\alpha$ -amino acid is known to proceed with neat retention of configuration which is ascribed to a sequence of two  $S_N2$  inversion steps.

The coupling of the hydroxyesters **6** with (2*S*,3*S*)-2-chloro-3-methylpentanoic acid was carried out by esterification of **6**, in soft conditions, with the previously

Table 1. Phase Transition Temperatures of Pure Compounds

compound	phase transition temp (°C) <sup>a,b</sup>
ET-[1,5]	X <sub>1</sub> -23.1 X <sub>2</sub> 16.8 I
ET-[1,6]	I <sup>c</sup>
Et-[2,3]	X 53.8 I
ET-[2,5]	X 10.2 I
ET-[2,6]	X 68.7 I
	I 59.2 Ch 55.3 SmA 48 <sup>d</sup> SmC* 31.5 X
ET-[2,7]	X 10.8 I
Et-[4,4']	X 74.8 SmC* 107.0 Ch 124.6 I
	I 119.4 Ch 106.2 SmC* 67.9 Scryst 40.0 X
ET-[2*,3]	X 53.0 I
ET-[2*,6]	X 42.9 Ch 51.7 I
	I 53.3 <sup>d</sup> BP 51.5 <sup>d</sup> Ch 14.2 SmC* 11.5 X
ET-[2*,7]	X 45.8 I
ES-[1,5]	X 52.0 I
ES-[1,6]	X 37.8 I
ES-[2,3]	X 84.0 I
ES-[2,5]	X 34.5 I
ES-[2,6] <sup>29</sup>	X 68.1 SmC* 75 <sup>d</sup> SmA 95.0 Ch 99.5 I
ES-[2,7]	X 60.5 I
ES-[4,4'] <sup>40</sup>	X 85.0 SmC* 138 <sup>d</sup> SmA 142.5 Ch 158.8 I
	I 158.6 <sup>d</sup> BP 157.3 <sup>d</sup> Ch 142.0 SmA 138 <sup>d</sup> SmC*
	60.3 SmI* 55.4 C
ES-[2*,3]	X 51.0 I
ES-[2*,6]	X 79.2 Ch 91.0 I
	I 90.8 Ch 66.5 SmC* 45.5 X
ES-[2*,7]	X 68.4 I

<sup>a</sup> Data referring to the second DSC cycle. <sup>b</sup> I = isotropic liquid, X = crystal, BP = blue phase, Ch = cholesteric phase, SmA = smectic A phase, SmC\* = chiral smectic C phase, Scryst = crystal smectic phase, SmI\* = chiral smectic I phase. <sup>c</sup> At temperatures up to -20 °C. <sup>d</sup> Optical microscopic data.

prepared acid chloride, using triethylamine. Owing to the existence of a second asymmetric carbon in the chiral tail, we were able to examine the diastereomeric purity by means of <sup>1</sup>H NMR technique. In some of the final products, namely, ES-[1,6], ES-[2,3], and ES-[2,7], partial racemization was found but the diastereomeric excess was always higher than 94%.

A different synthetic route was chosen to obtain the (*n*-decyloxy)naphthyl derivatives (Scheme 2). In this case, the (*n*-decyloxy)naphthyl [(ethoxycarbonyl)oxy]benzoates **10** were prepared as intermediates which after a deprotective reaction afforded the (*n*-decyloxy)naphthyl 4-hydroxybenzoates **11**. These intermediates were etherified or esterified in conditions similar to those previously mentioned. For the ES-[2\*,6] partial racemization (d.e. 95%) was detected by <sup>1</sup>H NMR.

**Liquid-Crystal Properties.** The thermal data of the final compounds are gathered in Table 1. As can be seen, only those naphthalene derivatives with the substituents in the 2 and 6 positions as well as the biphenyl analogues, showed mesogenic properties.

The liquid crystals based on naphthalene exhibit the potentially ferroelectric SmC\* mesophase below 70 °C. But the low melting points of the nonmesogenic compounds are also noteworthy, and this makes them very attractive from the FLC mixtures point of view. In general, the ether derivatives melt at lower temperatures than the ester ones.

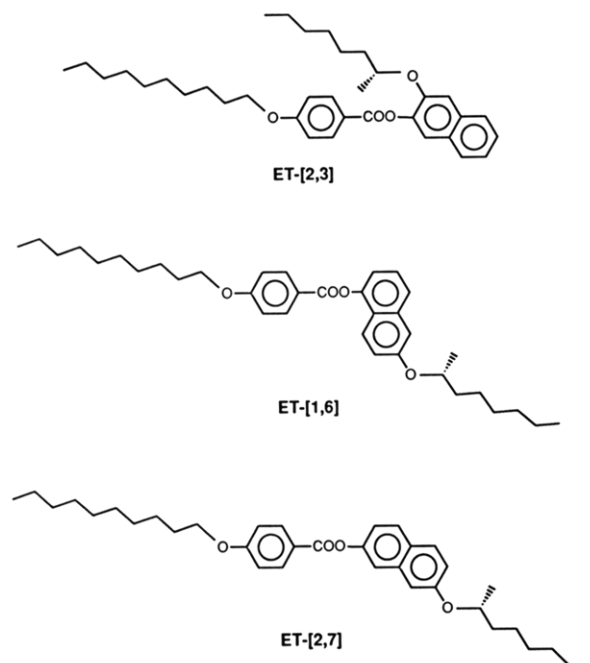
These data clearly show that molecular shape strongly influences the molecular arrangement in both the solid and the liquid-crystal phases.

The linear biphenyl structures we have considered as models favor attractive forces. X-ray data in the solid state reported for some chiral biphenyl benzoates have revealed a neat lateral overlapped packing in smectic-

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**Figure 2.** Schematic representation of the different terminal chain alignment proposed considering their all-trans conformations.

like layer order.<sup>44</sup> Furthermore, these authors conclude that these crystal structures are closely related to the LC phase sequence exhibited by the compounds.

For the naphthalene structures, this linearity is altered by steps or bends that change the length-to-broad ratio which undoubtedly will affect molecular packing.<sup>45</sup>

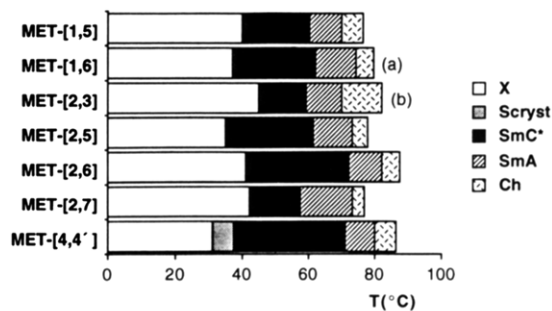
The different arrangement in the solid state is first reflected at the melting point, and thus most of these compounds melt at rather lower temperatures than the biphenyl analogues. To explain the high melting points of the [2,3] derivatives, we propose two different molecular models at the crystal: a V-shaped structure for these compounds and an elongated one for the rest of the naphthalene structures (see Figure 2).

Unfortunately, we have no X-ray data to support our proposal; neither are there any in the literature. However, Matsunaga has recently reported<sup>46</sup> the liquid-crystal behavior of a series of phenyl 4-((4-alkoxyphenyl)iminomethyl)benzoates and its 2-folded homologous 1,2-phenylene bis[4-((4-alkoxyphenyl)iminomethyl)benzoates]. In both series, with the same terminal chain length the transition temperatures are similar, and furthermore, X-ray data in the mesophase revealed very close layer spacing, concluding a V-shaped molecular core for the latter.

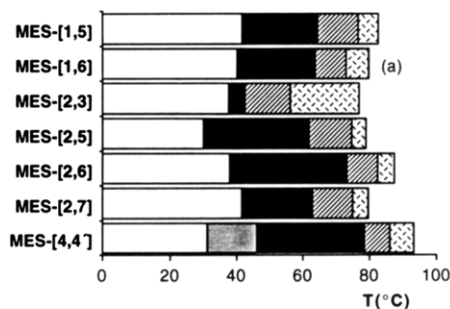
As far as the liquid-crystal formation is concerned, we can see that small variations, as is the case with the [2,6] derivatives, lead to a worsening of the mesogenic properties. Thus, ET-[2,6] forms only a monotropic liquid crystal and ES-[2,6] exhibits a rather shorter mesophase range than ES-[4,4']. This effect is more remarkable for the rest of the substitutions, compounds for which a complete lack of liquid-crystal order was determined.

These differences in molecular packing can be explained by taking into account that these structural

#### MESOGENIC PROPERTIES OF MIXTURES MET-[m,n]



#### MESOGENIC PROPERTIES OF MIXTURES MES-[m,n]



**Figure 3.** Mesophase ranges on the cooling processes of the binary mixtures with 4'-(n-hexyloxy)phenyl 4-(n-decyloxy)benzoate. (a) The components of the mixture did not mix well, so these data do not correspond to a well-known proportion. (b) 5 mol % mixture.

modifications cause a molecular broadening effect that reduces the anisotropy of the molecular polarizability as well as increasing axial separation, thus decreasing intermolecular attractions. Other authors have reported that 1,5- or even 2,3-substituted naphthalenes<sup>39,46,47</sup> are capable of supporting mesogeneity. However, we could say that for the systems here studied, the less linear the worse the molecular packing.

To evaluate the ferroelectric behavior of all the compounds synthesized, we prepared binary mixtures to induce the ferroelectric phase SmC\*. For this purpose, the achiral host 4'-(n-hexyloxy)phenyl 4-(n-decyloxy)benzoate [X 62.5 °C SmC 78.2 °C SmA 84.5 °C N 90.5 °C I] was doped with ca. 10 mol % of chiral component.

Figure 3 shows the mesogenic properties of these mixtures we have denoted as MET-[m,n] and MES-[m,n]. All of them showed the sequence I-Ch-SmA-SmC\* with ranges for the SmC\* mesophase between 20 and 90 °C. Compounds ET-[1,6] and ES-[1,6] did not mix well in any proportion, which prevented the evaluation of the physical and mesogenic properties of the mixtures.

**Mesophase Characterization.** The previously mentioned mesophases were assigned on the basis of their optical textures<sup>48</sup> and X-ray measurements.

By optical microscopy, the mesophases were mainly identified in the cooling process, and due to the fact that both the pure compounds and the mixtures showed similar textures, we will discuss them together.

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**Table 2. Ferroelectric Properties of Pure Compounds**

compound	$P_{s,max}$ (nC/cm <sup>2</sup> )	$P_s$ (nC/cm <sup>2</sup> ) <sup>a</sup>	$\phi^a$ (deg)	$\tau E^a$ ( $\mu$ sV/ $\mu$ m)	$\gamma_0^a$ (Pa s)	$P_0^{a,b}$ (nC/cm <sup>2</sup> )
ET-[2,6]	+33	+31	20	1240	0.223	91
ES-[2,6] <sup>c</sup>	-135	-54	18	437	0.136	175
ET-[4,4']	+60	+51	32	455	0.130	96
ES-[4,4']	-214	-80	23	279	0.130	205
ES-[2*,6]	-100	-80	28	2272	1.040	170

<sup>a</sup> Data measured at  $T_c - T = 10$  °C ( $T_c$  SmA-SmC\* phase transition temperature). <sup>b</sup>  $P_0 = P_s/\sin \phi$ . <sup>c</sup> Variations with regard to the previous data reported by us<sup>29</sup> are attributed to the different cells used in the measurement.

The cholesteric phase was identified from its focal conic and Grand-Jean plane textures and also by observing the typical fingerprints. The SmA phase appears from the cholesteric one in a focal conic and homeotropic coexisting textures. Further cooling produced a transition to a chiral smectic C mesophase (SmC\*) which exhibited both broken focal conic and Schlieren textures. Dechiralization lines of variable pitch were observed only for MET samples, with the exceptions of MET-[2\*,7] and MET-[2\*,3].

Compound ET-[4,4'] and the mixtures based on the biphenyl system showed an unidentified highly ordered smectic phase when the SmC\* mesophase cooled.

In compounds ES-[4,4'] and ET-[2\*,6] transitions to blue phases were detected, showing blue-green platelet and blue plane textures, respectively.

A SmI phase, not reported for this compound by other authors,<sup>40</sup> was also observed for ES-[4,4'] when the SmC\* phase cooled.

**Ferroelectric Properties.** Table 2 shows the most relevant data determined for the pure compounds that exhibit the ferroelectric SmC\* mesophase.

According to the dipolar moments associated with both chiral tails, compounds with the (R)-1-methylheptyloxy group show lower values of  $P_s$  and higher switching times than those with (2S,3S)-(2-chloro-3-methylpentanoyl)oxy chain. Likewise, a positive sign of  $P_s$  for the ET compounds was established, while that for the ES compounds was negative. These results are in good agreement with the ones reported in the literature for both tails.<sup>29,31,49</sup>

The more representative ferroelectric properties of the chiral binary mixtures prepared are given in Table 3.

As far as the mixtures based on the (*n*-decyloxy)-benzoates (MET-[*m,n*] and MES-[*m,n*]) are concerned, it is possible to differentiate between two groups of blends.

One group is formed by those materials for which significant  $P_s$  values were measured, i.e., the blends containing compounds derived from [2,6]- and [1,5]-naphthalene, as well as the biphenyl-based structures. The switching times, reorientational viscosities (termed as rotational viscosity), and polarizations independent of temperature ( $P_0$ ) were determined.

The naphthalene materials display the usual ferroelectric behavior with properties very similar to those measured for the homologous biphenyl blends.

Figure 4 shows the trends of some of the ferroelectric properties of these mixtures as a function of temperature. As can be seen in Figure 4a, the  $P_s$  gradually increase as the temperature decreases until saturation values are reached.

**Table 3. Ferroelectric Properties of Binary Mixtures**

mixture	sign $P_s$	$P_{s,max}$ (nC cm <sup>-2</sup> )	$P_s^a$ (nC cm <sup>-2</sup> )	$\phi^a$ (deg)	$\tau E^a$ ( $\mu$ s V $\mu$ m <sup>-1</sup> )	$\gamma_c^a$ (Pa s)	$P_0^a$ (nC cm <sup>-2</sup> )
MET-[1,5]	+	3.1	2.9	16	273	0.004	11
MET-[2,6]	+	2.0	1.9	18	267	0.003	6
MET-[4,4']	+	2.7	2.2	17	154	0.002	8
MET-[2,3] <sup>c</sup>	-	<1		16			
MET-[2,5]	-	<0.5		17			
MET-[2,7]	+	<0.5		15			
MET-[2*,6]	+	4.0	3.2	24	852	0.016	8
MET-[2*,3]	+	2.3	2.0	18	1700	0.018	7
MET-[2*,7]	+	1.5	1.2	21	1465	0.010	3
MES-[1,5]	-	7.0	5.4	18	218	0.006	18
MES-[2,6]	-	9.8	7.1	18	190	0.008	23
MES-[4,4']	-	7.8	6.5	18	160	0.006	21
MES-[2,3]	+	d		e			
MES-[2,5]	-	d		18			
MES-[2,7]	-	d		16			
MES-[2*,6]	-	10.5	5.1	18	308	0.010	17
MES-[2*,3]	-	6.7	4.5	16	760	0.020	16
MES-[2*,7]	-	5.5	3.5	18	764	0.015	11

<sup>a</sup> Data measured at  $T_c - T = 10$  °C ( $T_c =$  SmA-SmC\* phase transition temperature). <sup>b</sup>  $P_0 = P_s/\sin \phi$ . <sup>c</sup> 5 mol % of chiral dopant. <sup>d</sup> The sample showed electrooptic response, but no signal of polarization was detected. <sup>e</sup> The crystallization of the sample prevented its evaluation.

As far as the response times and the tilt angles are concerned, only slight differences were observed (Figure 4b,c) and all of them showed values within similar ranges.

Well after the SmC\*-SmA transition, the rotational viscosity  $\eta$  ( $\gamma_c = \eta/\sin^2 \phi$ )<sup>18</sup> of these mixtures exhibits an Arrhenius-type dependence in the range 0.02–0.07 Pa s; however, the slopes of the graphs are nearly the same, which means that, regardless of the guest chiral tail, the activation energy in the switching process between the two states<sup>50</sup> is almost the same in these mixtures.

The second group of blends gathers those materials based on the rest of the (*n*-decyloxy)benzoates we were able to study: [2,3], [2,5], and [2,7] derivatives. All mixtures exhibited an electrooptic response, and their tilt angles were similar to those of previous blends (see Figure 4d). However, very low polarization values were measured for the MET materials, and what is more remarkable, no peak corresponding to polarization was experimentally detected for the mixtures based on the  $\alpha$ -chloro ester (MES). This tail usually gives rise to high values of  $P_s$  (100–200 nC cm<sup>-2</sup> in pure compounds).<sup>51–53</sup>

With regard to the sign of  $P_s$ , most of the mixtures studied showed the  $P_s$  sign expected, positive for ET-based mixtures and negative for the MES-[*m,n*]. However, abnormal behavior was detected in MET-[2,3], MES-[2,3], and MET-[2,5], all of which showed a sign opposite to that expected according to their chiral tail.

To confirm the results determined for the  $\alpha$ -chloro ester blends and to study the ferroelectric behavior of the [1,6] compounds, we prepared a set of new binary mixtures. In this case, we selected the naphthalene benzoate **11** (X 64.8 °C SmC 87.9 °C N 122.3 °C I) as a racemic host, to lessen the influence of the achiral component and to ensure good mixing.

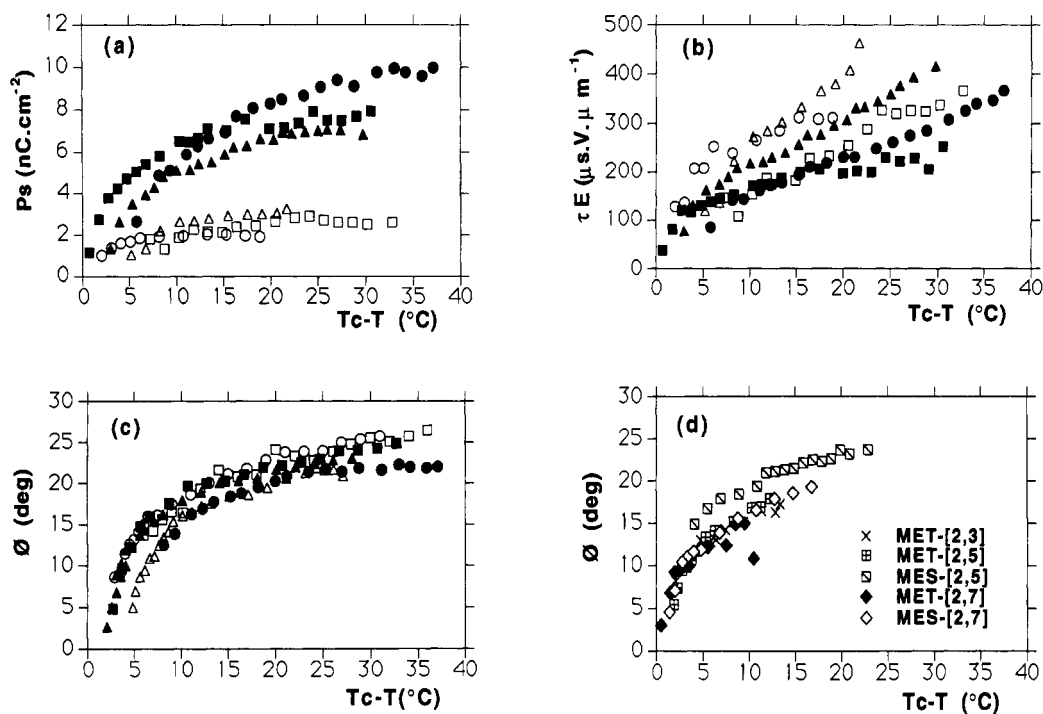
(50) Fujisawa, K.; Sekine, C.; Uemura, Y.; Higashii, T.; Minai, M.; Dohgane, T. *Ferroelectrics* **1991**, *121*, 167.

(51) Bahr, Ch.; Heppke, G. *Mol. Cryst. Liq. Cryst.* **1987**, *148*, 29.

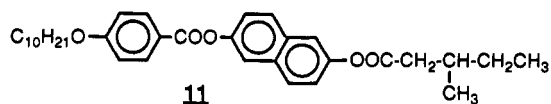
(52) Sakurai, T.; Mikami, N.; Higuchi, R.; Monma, M.; Yoshino, K. *Ferroelectrics* **1988**, *85*, 469.

(53) Krishna Prasad, S.; Khened, S. M.; Raja, V. N.; Shivkumar, B. *Ferroelectrics* **1991**, *121*, 319.

(49) Mohr, K.; Köhler, S.; Worm, K.; Pelze, G.; Diele, S.; Zschke, H.; Demus, D. *Mol. Cryst. Liq. Cryst.* **1987**, *146*, 151.



**Figure 4.** Temperature dependence of physical properties of the mixtures: (a) spontaneous polarization; (b) switching times, (c and d) tilt angles. For (a), (b), and (c): [ $\Delta$ ] MET-[1,5]; [ $\square$ ] MET-[2,6]; [ $\square$ ] MET-[4,4']; [ $\blacktriangle$ ] MES-[1,5]; [ $\bullet$ ] MES-[2,6]; [ $\blacksquare$ ] MES-[4,4'].



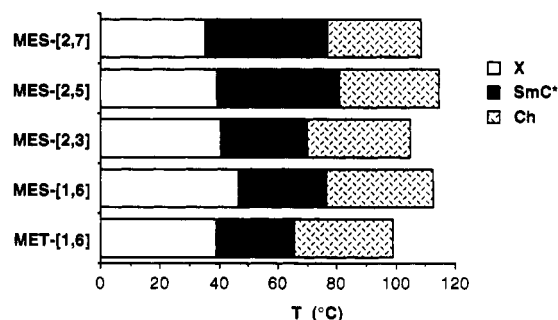
The 10 mol % mixtures prepared showed the I–Ch–SmC\* sequence on cooling (Figure 5).

Once again, all materials exhibited clear optoelectronic switching on an ac field, but no current peak was detected for any of these blends. However, with regard to the  $P_s$  sign, they provided the sign expected from their chiral tail. These results support those reported by other authors<sup>54</sup> that showed not only that the ferroelectric properties of blends depend on the chiral guest but, in some cases, they can be influenced by the host phase.

It is known that many times the  $P_s$  of FLC mixtures does not vary linearly with concentration, so low polarizations might be expected or even at low concentration the  $P_s$  peak may not occur. However, the significant differences observed for these groups of blends, so dramatic in the case of the ES samples, led us to try to understand where is the origin of such as differences.

The induction of SmC\* phases by mixing an achiral SmC host and a chiral guest implies that, through molecular interactions, the host compels the guest to adopt the tilted-layered arrangement characteristic of the SmC\* mesophase. Thus both central cores and terminal chains are involved in the guest–host interactions, allowing the coupling of the molecular dipoles which gives rise to new ferroelectric materials.

Different FLC molecular models suggest that the magnitude and sign of the spontaneous polarization derive from the dipolar moments and their orientation relative to the tilt plane of the molecules. Only the dipolar moment component perpendicular to this plane



**Figure 5.** Mesophase ranges of the cooling processes of the binary mixtures with compound 11.

will contribute.<sup>11,55</sup> Likewise, the good coupling of these dipoles has a decisive influence on ferroelectric behavior.<sup>29,36</sup>

For the majority of the binary mixtures here described, we can predict good core–core guest–host interactions, but with the chiral–achiral terminal chains interactions, some aspects should be borne in mind for the bending structures.

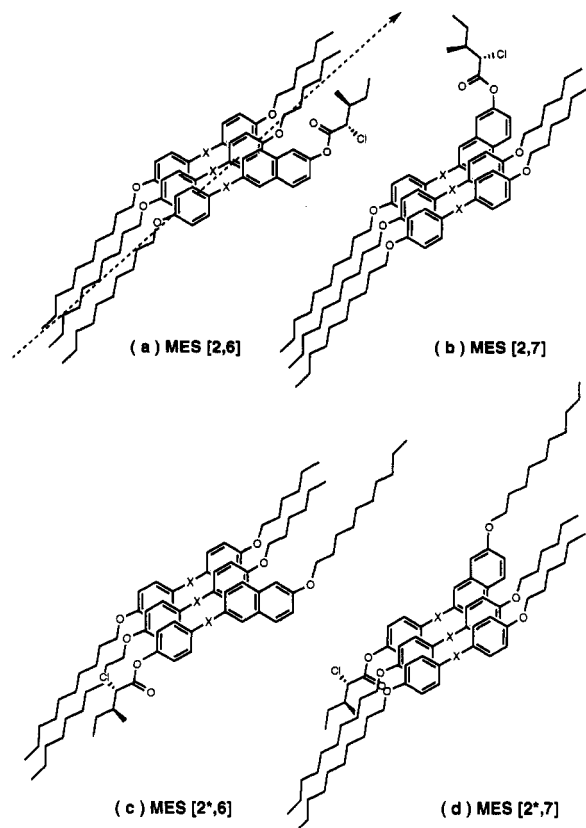
Due to the angled structure of these compounds, to allow the best tail interactions at the mesophase, the chiral tails should be orientated along the molecular axis determined by the host molecules rather than across it (see Figure 6a,b). Consequently, we might think about chiral tail conformations different from those shown in the more linear structures: [1,5], [2,6], and [4,4'].

If these new tail orientations have a low dipolar contribution at the macroscopic polarization direction and, because of the molecular shape, a presumably worse dipolar coupling occurs, we could satisfactorily explain the different ferroelectric properties determined within the series.

These negative effects would, in principle, decrease for compounds with the chiral tail on the benzoic ring

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(55) Koden, M.; Kuratate, T.; Funada, F.; Awane, K.; Sakaguchi, K.; Shiomi, Y. *Mol. Cryst. Liq. Cryst.* **1990**, *7*, 79.



**Figure 6.** Comparative schematic representation of one of the possible guest–host arrangements in the induced SmC\* phase using as example the zigzag-shaped conformers.

instead of the naphthalene structure, as chiral–achiral tail melting is favored (see Figure 6c,d).

To test this idea, we prepared the corresponding isomers of representative stepped and angular structures: ET-[2\*,6], ET-[2\*,3], ET-[2\*,7], ES-[2\*,6], ES-[2\*,6], and ES-[2\*,7].

These new compounds were obtained following the synthetic route shown in Scheme 2.

Once again, only the [2,6] derivatives form liquid crystals (see Table 1), so we evaluated their ferroelectric behavior in 10 mol % binary mixtures with 4'-(*n*-hexyloxy)phenyl 4-(*n*-decyloxy) benzoate.

In Tables 2 and 3 the ferroelectric properties of these compounds are gathered in the pure state (the fast crystallization of ET-[2\*,6] prevented its ferroelectric characterization) as in 10 mol % blends.

As can be seen in Table 3, this group of blends has a typically ferroelectric behavior. With slight variations, significant values of  $P_s$  were measured for all of them in the range of the ones shown by their [1,5], [2,6], and [4,4'] homologues.

Some years ago, different authors<sup>5,28,56</sup> pointed out an attractive possibility of the FLC: to use them as a tool to link macroscopic properties and microscopic structure in noncrystalline media such as the chiral tail conformations or the absolute configuration of chiral compounds. Our results could be considered as new examples in this line.

In this case, we can infer from the ferroelectric properties of the [ $m,n$ ] mixtures that in blends substantial differences exist between the chiral tail conforma-

tions for the stepped structures and the bending ones. However, in the [ $m^*,n$ ] combinations as well as in the [2,6] and [1,5] combinations, these chains adopt comparable orientations which thanks to good dipolar coupling, allow us to obtain alike macroscopic polarization.

Apart from this and taking into account the ferroelectric properties ( $P_0$  and response times) of the mixtures studied, we can also claim that several of the substituted naphthalene benzoates can be considered very interesting alternatives to the biphenyl structures, in ferroelectric blends. They have similar optoelectric behavior but, what is also important, they can help to lower temperatures.

## Experimental Section

**Synthesis.** *Preparation of (2S,3S)-2-Chloro-3-methylpentanoic Acid [2].* A flask containing 10 g (76 mmol) of L- $\alpha$ -isoleucine and 95 mL of 6 M HCl was cooled with an ice water bath to 0 °C. NaNO<sub>2</sub> (8.54 g, 123 mmol) was added in small portions with vigorous stirring for 3 h and the temperature kept at 0 °C. After the reaction was concluded, the mixture was stirred between 0 and -5 °C for another 5 h and then left to stand at room temperature overnight. The nitrous vapors are eliminated from the reaction flask by stirring for 1 h in the vacuum of the water suction pump. The aqueous solution is neutralized to pH 2–3 with solid sodium acid carbonate. The product is extracted four times with 120-mL portions of ether. The combined organic extracts were dried over anhydrous MgSO<sub>4</sub> filtered and the solvent was stripped by rotary evaporation. The crude product was distilled under reduced pressure affording 5.7 g (yield 50%) of (2S,3S)-2-chloro-3-methylpentanoic acid as a colorless liquid, bp 125 °C, 15 mmHg. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.9 (t,  $J$  = 7.4 Hz, 3H), 1.00 (d,  $J$  = 6.6 Hz, 3H), 1.32 (m, 1H), 1.6 (m, 1H), 2.0 (m, 1H), 4.20 (d,  $J$  = 6.3 Hz, 1H), 11.0 (s, 1H). IR (neat) 3200–2500, 1724 cm<sup>-1</sup>.

*Preparation of the (2S,3S)-2-Chloro-3-methylpentanoyl Chloride [3].* To a flask containing 230 mg (1.75 mmol) of (2S,3S)-2-chloro-3-methylpentanoic acid and 0.3 mL of dried toluene, 0.62 g (5.2 mmol) of SOCl<sub>2</sub> were added. The reaction was stirred at 60 °C for 5 h. The excess of SOCl<sub>2</sub> was removed by rotary evaporation. The product was used in the next step without further purification. IR (neat) 2970–2878, 1806 cm<sup>-1</sup>.

*Representative Procedure for Obtaining Compounds 6.* These intermediates were synthesized using the method previously described for 2'-(6'-hydroxy)naphthyl 4-(decyloxy)benzoate.<sup>29</sup> To an argon-flushed flask containing 71 mmol of dihydroxy derivatives and 90 mL of dried pyridine, 36 mmol of 4-(decyloxy)benzoyl chloride was added dropwise. The resulting mixture was stirred for 24 h. The reaction was quenched by addition of 230 mL of 2 M HCl/ice mixture, and the solid was filtered off and washed several times with water. The crude product was purified by flash chromatography on silica gel eluting with hexane/dichloromethane mixtures and recrystallized from ethanol.

*Analytical Data for Other Compounds.* 1-(5'-Hydroxynaphthyl) 4-(*n*-decyloxy)benzoate: mp 114 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.89 (t,  $J$  = 7.1 Hz, 3H), 1.20–1.55 (m, 14H), 1.80–1.87 (m, 2H), 4.07 (t,  $J$  = 6.6 Hz, 2H), 5.63 (s, 1H), 6.74 (dd,  $J$  = 7.6 Hz,  $J$  = 0.7 Hz, 1H), 7.02 (d,  $J$  = 8.8 Hz, 2H), 7.22 (d,  $J$  = 7.6 Hz, 1H), 7.24 (d,  $J$  = 7.6 Hz, 1H), 7.35 (dd,  $J$  = 7.6 Hz,  $J$  = 1.0 Hz, 1H), 7.47 (d,  $J$  = 8.3 Hz, 1H), 7.48 (t,  $J$  = 8.3 Hz, 1H), 8.06 (d,  $J$  = 8.3 Hz, 1H), 8.27 (d,  $J$  = 8.8 Hz, 2H). IR (Nujol) 3422, 1704, 1604, 1579, 1510, 1466, 1286, 1173 cm<sup>-1</sup>.

1-(6'-Hydroxynaphthyl) 4-(*n*-decyloxy)benzoate: mp 124 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.89 (t,  $J$  = 6.6 Hz, 3H), 1.20–1.39 (m, 14H), 1.83 (m, 2H), 4.06 (t,  $J$  = 6.6 Hz, 2H), 5.53 (s, 1H), 6.75 (dd,  $J$  = 7.6 Hz,  $J$  = 1Hz, 1H), 7.0 (d,  $J$  = 8.8 Hz, 2H), 7.28–7.40 (m, 3H), 7.61 (d,  $J$  = 2.2 Hz, 1H), 8.17 (d,  $J$  = 9.0 Hz, 1H), 8.20 (d,  $J$  = 8.8 Hz, 2H). IR (Nujol) 3362, 1698, 1602, 1504, 1465, 1277, 1211, 1172, 1148 cm<sup>-1</sup>.

2-(3-Hydroxynaphthyl) 4-(*n*-decyloxy)benzoate: mp 152 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  0.89 (t,  $J$  = 7.1 Hz, 3H), 1.20–

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1.50 (m, 14H), 1.80–1.90 (m, 2H), 4.06 (t,  $J = 6.6$  Hz, 2H), 5.66 (s, 1H), 7.00 (d,  $J = 9.0$  Hz, 2H), 7.32–7.46 (m, 2H), 7.39 (s, 1H), 7.68 (s, 1H), 7.70–7.78 (m, 2H), 8.20 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 3405, 1718, 1603, 1508, 1482, 1240, 1168  $\text{cm}^{-1}$ .

*2'-(5-Hydroxynaphthyl) 4-(n-decyloxy)benzoate*: mp 120 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.8$  Hz, 3H), 1.20–1.57 (m, 14H), 1.80–1.90 (m, 2H), 4.07 (t,  $J = 6.6$  Hz, 2H), 5.37 (s, 1H), 7.00 (d,  $J = 2.4$  Hz, 1H), 7.03 (d,  $J = 9.0$  Hz, 2H), 7.05 (dd,  $J = 10.5$  Hz,  $J = 2.2$  Hz, 1H), 7.17 (dd,  $J = 8.3$  Hz,  $J = 1.0$  Hz, 1H), 7.44 (dd,  $J = 8.0$  Hz,  $J = 8.0$  Hz, 1H), 7.54 (d,  $J = 8.3$  Hz, 1H), 7.78 (d,  $J = 9.0$  Hz, 1H), 8.27 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 3454, 1698, 1604, 1509, 1461, 1281, 1259, 1171  $\text{cm}^{-1}$ .

*2'-(7-Hydroxynaphthyl) 4-(n-decyloxy)benzoate*: mp 151 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 7.1$  Hz, 3H), 1.20–1.35 (m, 14H), 1.80–1.90 (m, 2H), 4.06 (t,  $J = 6.6$  Hz, 2H), 5.35 (s, 1H), 6.99 (d,  $J = 9.0$  Hz, 2H), 7.0–7.06 (m, 2H), 7.17 (dd,  $J = 8.7$  Hz,  $J = 2.4$  Hz, 1H), 7.46 (d,  $J = 1.9$  Hz, 1H), 7.71 (d,  $J = 8.8$  Hz, 1H), 7.78 (d,  $J = 8.8$  Hz, 1H), 8.18 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 3419, 1714, 1606, 1511, 1467, 1280, 1258, 1170  $\text{cm}^{-1}$ .

*4'-(4-Hydroxybiphenyl) 4-(n-decyloxy)benzoate*: X 175.5 °C N 205.5 °C I(N 171.9 °C SmC 159.7 °C X);  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.84 (t, 3H), 1.20–1.50 (m, 14H), 1.70–1.90 (m, 2H), 4.00 (t,  $J = 6.6$  Hz, 2H), 6.88 (d,  $J = 8.6$  Hz, 2H), 6.93 (d,  $J = 8.6$  Hz, 2H), 7.17 (d,  $J = 8.6$  Hz, 2H), 7.38 (d,  $J = 8.6$  Hz, 2H), 7.51 (d,  $J = 8.6$  Hz, 2H), 8.10 (d,  $J = 8.6$  Hz, 2H). IR (Nujol) 3354, 1727, 1610, 1509, 1257, 1083  $\text{cm}^{-1}$ .

*Analytical Data of the Diester Isolated. 1,5-Bis[[4-(n-decyloxy)benzoyloxy]oxy]naphthalene*: X 141 °C N 144 °C I; $^{47}$   $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.6$  Hz, 6H), 1.20–1.6 (m, 28H), 1.80–1.90 (m, 4H), 4.08 (t,  $J = 6.6$  Hz, 4H), 7.03 (d,  $J = 9.0$  Hz, 4H), 7.40 (dd,  $J = 7.5$  Hz,  $J = 0.9$  Hz, 2H), 7.52 (dd,  $J = 8.5$  Hz,  $J = 7.5$  Hz, 2H), 7.88 (d,  $J = 8.5$  Hz, 4H), 8.28 (d,  $J = 9.0$  Hz, 4H). IR (Nujol) 1726, 1602, 1509, 1260, 1235, 1167  $\text{cm}^{-1}$ .

*1,6-Bis[[4-(n-decyloxy)benzoyloxy]oxy]naphthalene*: mp 72 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 6.8$  Hz, 6H), 1.20–1.50 (m, 28H), 1.78–1.90 (m, 4H), 4.03 (t,  $J = 6.6$  Hz, 2H), 4.04 (t,  $J = 6.6$  Hz, 2H), 6.97 (d,  $J = 9.0$  Hz, 2H), 7.01 (d,  $J = 8.8$  Hz, 2H), 7.31–7.35 (m, 2H), 7.52 (dd,  $J = 7.5$  Hz,  $J = 7.5$  Hz, 1H), 7.72–7.78 (m, 2H), 7.97 (d,  $J = 9.3$  Hz, 1H), 8.16 (d,  $J = 9.2$  Hz, 2H), 8.25 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1727, 1605, 1510, 1259, 1272, 1170  $\text{cm}^{-1}$ .

*2,3-Bis[[4-(n-decyloxy)benzoyloxy]oxy]naphthalene*: mp 84 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t, 6H), 1.20–1.50 (m, 28H), 1.70–1.81 (m, 4H), 3.96 (t,  $J = 6.6$  Hz, 4H), 6.81 (d,  $J = 9.2$  Hz, 4H), 7.46–7.50 (m, 2H), 7.80–7.84 (m, 4H), 8.01 (d,  $J = 9.0$  Hz, 4H). IR (Nujol) 1733, 1605, 1510, 1242, 1166  $\text{cm}^{-1}$ .

*2,6-Bis[[4-(n-decyloxy)benzoyloxy]oxy]naphthalene*: X 135 °C SmC °C 170 °C N 220 °C I.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.6$  Hz, 6H), 1.20–1.55 (m, 28H), 1.80–1.86 (m, 4H), 4.06 (t,  $J = 6.6$  Hz, 4H), 7.00 (d,  $J = 9.0$  Hz, 4H), 7.38 (dd,  $J = 8.8$ ,  $J = 2.4$  Hz, 2H), 7.71 (d,  $J = 2.4$  Hz, 2H), 7.88 (d,  $J = 9.0$  Hz, 2H), 8.19 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1725, 1603, 1510, 1210, 1168  $\text{cm}^{-1}$ .

*2,7-Bis[[4-(n-decyloxy)benzoyloxy]oxy]naphthalene*: mp 111 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.6$  Hz, 6H), 1.20–1.50 (m, 28H), 1.78–1.90 (m, 4H), 4.05 (t,  $J = 6.6$  Hz, 2H), 6.99 (d,  $J = 9.1$  Hz, 4H), 7.35 (dd,  $J = 8.8$  Hz,  $J = 2.2$  Hz, 2H), 7.65 (d,  $J = 2.2$  Hz, 2H), 7.91 (d,  $J = 8.9$  Hz, 2H), 8.19 (d,  $J = 9.1$  Hz, 4H). IR (Nujol) 1726, 1604, 1511, 1286, 1253, 1237, 1169  $\text{cm}^{-1}$ .

*4,4'-Bis[[4''-(n-decyloxy)benzoyloxy]oxy]biphenyl*: X 134.5 °C SmC 216 °C N 262.6 °C I;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 6.96$  Hz, 6H), 1.20–1.50 (m, 28H), 1.78–1.90 (m, 4H), 4.04 (t,  $J = 6.6$  Hz, 4H), 6.96 (d,  $J = 8.9$  Hz, 4H), 7.25 (d,  $J = 8.4$  Hz, 4H), 7.61 (d,  $J = 8.4$  Hz, 4H), 8.14 (d,  $J = 8.8$  Hz, 4H). IR (Nujol) 1729, 1608, 1508, 1289, 1254, 1216, 1176  $\text{cm}^{-1}$ .

*Synthesis of Compounds 8 and 9*. These intermediates were synthesized following conventional method described in the literature $^{57,58}$  with satisfactory results.

*Representative Procedure for Obtaining Compounds 10. 2'-(3'-(n-Decyloxy)naphthyl) 4-[(Ethoxycarbonyloxy)benzoate*. To a flask containing a solution of 2.5 g (8.3 mmol) of 2-(n-decyloxy)-6-naphthol and 1.75 g (8.3 mmol) of 4-[(ethoxycarbonyloxy)benzoic acid in 75 mL of dry dichloromethane, 1.88 g (9.1 mmol) of DCC, and a catalytic amount of DMAP were added. The reaction was left to stand at room temperature for 20 h. The *N,N*-dicyclohexylurea was filtered off, and the filtrate evaporated. The crude product was purified by flash chromatography on silica gel eluting with hexane/dichloromethane 1/1 and recrystallized from ethanol (yield 56%): mp 67 °C;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (m, 3H), 1.20–1.36 (m, 14H), 1.43 (t,  $J = 7.0$  Hz, 3H), 1.70–1.80 (m, 2H), 4.08 (t,  $J = 6.4$  Hz, 2H), 4.37 (q,  $J = 7.0$  Hz, 2H), 7.25 (d,  $J = 8.2$  Hz, 2H), 7.32–7.48 (m, 3H), 7.61 (s, 1H), 7.75 (d,  $J = 8.0$  Hz, 2H), 8.29 (d,  $J = 8.7$  Hz, 2H). IR (neat) 1766, 1743, 1604, 1508, 1220, 1153, 1112, 1064  $\text{cm}^{-1}$ .

*Analytical Data for Other Compounds. 2-(6'-(n-Decyloxy)naphthyl) 4-[(Ethoxycarbonyloxy)benzoate*. X 92.2 °C N 133.7 °C I.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 6.8$  Hz, 3H), 1.27–1.49 (m, 14H), 1.40 (t,  $J = 7.1$  Hz, 3H), 1.81–1.86 (m, 2H), 4.06 (t,  $J = 6.6$  Hz, 2H), 4.35 (q,  $J = 7.1$  Hz, 2H), 7.14–7.18 (m, 2H), 7.27 (dd,  $J = 8.8$  Hz,  $J = 2.2$  Hz, 1H), 7.34 (d,  $J = 8.8$  Hz, 2H), 7.57 (d,  $J = 2.2$  Hz, 1H), 7.70 (d,  $J = 8.8$  Hz, 1H), 7.75 (d,  $J = 9.0$  Hz, 1H), 8.27 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1758, 1732, 1603, 1510, 1259, 1217  $\text{cm}^{-1}$ .

*2-(7'-(n-Decyloxy)naphthyl) 4-[(Ethoxycarbonyloxy)benzoate*. Mp 69 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (m, 3H), 1.20–1.55 (m, 14H), 1.40 (t,  $J = 7.1$  Hz, 3H), 1.78–1.90 (m, 2H), 4.03 (t,  $J = 6.6$  Hz, 2H), 4.35 (q,  $J = 7.1$  Hz, 2H), 7.07–7.12 (m, 1H), 7.13–7.16 (m, 1H), 7.17–7.19 (d,  $J = 2.2$  Hz, 1H), 7.34 (d,  $J = 9.0$  Hz, 2H), 7.52 (d,  $J = 2.2$  Hz, 1H), 7.73 (d,  $J = 8.8$  Hz, 1H), 7.79 (d,  $J = 8.8$  Hz, 1H), 8.27 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1768, 1736, 1604, 1512, 1275, 1248, 1214  $\text{cm}^{-1}$ .

*Representative Procedure for Obtaining Compounds 11. 2-((7'-(n-Decyloxy)naphthyl) 4-Hydroxybenzoate*. To a flask containing a solution of 2.2 g (5 mmol) of 2'-((7'-n-decyloxy)naphthyl)-4-[(ethoxycarbonyloxy)benzoate in 50 mL of acetone, 30 mL of a solution of  $\text{NH}_3$  in water (20%) were added slowly. The resulting slurry was left to stand at room temperature for 2 h and then poured into water and cooled dry ice. The white precipitate was filtered off and recrystallized from acetonitrile (yield 90%). Mp 117 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (t, 3H), 1.20–1.50 (m, 14H), 1.70–1.90 (m, 2H), 4.04 (t,  $J = 6.6$  Hz, 2H), 6.90 (d,  $J = 8.8$  Hz, 2H), 7.07–7.18 (m, 3H), 7.51 (d,  $J = 1.6$  Hz, 1H), 7.72 (d,  $J = 9.0$  Hz, 1H), 7.77 (d,  $J = 8.8$  Hz, 1H), 8.12 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 3371, 1733, 1609, 1512, 1283, 1248, 1213, 1196  $\text{cm}^{-1}$ .

*Analytical Data for Other Compounds. 2-(3'-(n-Decyloxy)naphthyl) 4-Hydroxybenzoate*. Mp 90 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t, 3H), 1.18–1.40 (m, 14H), 1.65–1.80 (m, 2H), 4.08 (t,  $J = 6.4$  Hz, 2H), 5.45 (s, 1H), 6.91 (d,  $J = 8.7$  Hz, 2H), 7.23 (s, 1H), 7.33–7.46 (m, 2H), 7.60 (s, 1H), 7.74 (d,  $J = 8.2$  Hz, 2H), 8.15 (d,  $J = 8.5$  Hz, 2H). IR (Nujol) 3378, 1631, 1606, 1510, 1280, 1231, 1213, 1113, 1070  $\text{cm}^{-1}$ .

*2-(6'-(n-Decyloxy)naphthyl) 4-Hydroxybenzoate*. Mp 159 °C.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86 (t, 3H), 1.26–1.50 (m, 14H), 1.80–1.85 (m, 2H), 4.05 (t,  $J = 6.6$  Hz, 2H), 5.37 (s, 1H), 6.90 (d,  $J = 8.4$  Hz, 2H), 7.13–7.17 (m, 2H), 7.25–7.29 (m, 1H), 7.56 (d,  $J = 1.8$  Hz, 1H), 7.68 (d,  $J = 9.0$  Hz, 1H), 7.73 (d,  $J = 9.0$  Hz, 1H), 8.13 (d,  $J = 8.4$  Hz, 2H). IR (Nujol) 3389, 1699, 1605, 1511, 1278, 1223  $\text{cm}^{-1}$ .

*Representative Procedure for Etherification of Phenols 6 and 11 with (S)-(+)-2-Octanol [ET-[*m,n*] and Et-[*m\*,n*]]*. (R)-2-[(6'-(1''-Methylheptyloxy)naphthyl) 4-(n-Decyloxy)benzoate. To an argon-flushed flask containing a solution of 0.8 g (1.8 mmol) of 2'-[(6'-hydroxy)naphthyl]-4-(decyloxy)benzoate and 0.58 g (2.2 mmol) of triphenylphosphine in 20 mL of dry dichloromethane, a solution of 0.23 g (1.8 mmol) of (S)-(+)-2-octanol in 5 mL of dry dichloromethane was added via syringe. A solution of 0.37 g (2.13 mmol) of diethyl azodicarboxylate in 20 mL of dry dichloromethane was added dropwise. The reaction mixture was stirred at room temperature for 23 h. Five drops of water were added and the reaction was stirred for another 1 h. The solvent was removed by rotary evaporation and the residual solid suspended in a mixture of hexane/ethyl acetate (7:3) and stirred for 1 h. The white solid is

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filtered off through a silica gel pad. After the solvent is removed, the product was purified by flash chromatography on silica gel eluting with hexane/dichloromethane (1:1). The product was twice recrystallized from absolute ethanol (yield 70%).  $R_f$  (50:50 hexane:dichloromethane) = 0.52.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.89 (m, 6H), 1.20–1.60 (m, 22H), 1.37 (d,  $J = 6.1$  Hz, 3H), 1.60 (m, 1H), 1.80–1.90 (m, 3H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.5 (m, 1H), 6.98 (d,  $J = 9.0$  Hz, 2H), 7.13–7.18 (m, 2H), 7.29 (dd,  $J = 8.8$  Hz,  $J = 2.2$  Hz, 1H), 7.58 (d,  $J = 2.2$  Hz, 1H), 7.73 (d,  $J = 8.8$  Hz, 1H), 7.74 (d,  $J = 8.8$  Hz, 1H), 8.18 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1729, 1606, 1512, 1274, 1222, 1177  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.16; H, 9.36.

**Analytical Data for Other Compounds.** (R)-1-[5'-(1''-(Methylheptyloxy)naphthyl)-4-(n-Decyloxy)benzoate].  $R_f$  (50:50 hexane:dichloromethane) = 0.63.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.83–0.89 (m, 6H), 1.20–1.60 (m, 22H), 1.38 (d,  $J = 6.1$  Hz, 3H), 1.65 (m, 1H), 1.70–1.90 (m, 3H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.55 (m, 1H), 6.82 (d, 1H), 7.0 (d,  $J = 9.0$  Hz, 2H), 7.31–7.36 (m, 2H), 7.42–7.48 (m, 2H), 8.2 (d,  $J = 8.3$  Hz, 1H), 8.24 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1736, 1603, 1510, 1167, 1079  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.00; H, 9.21.

(R)-1-[6'-(1''-(methylheptyloxy)naphthyl)-4-(n-Decyloxy)benzoate].  $R_f$  (50:50 hexane-dichloromethane) = 0.41.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.89 (m, 6H), 1.20–1.59 (m, 22H), 1.6 (m, 1H), 1.70–1.90 (m, 3H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.43 (m, 1H), 7.0 (d,  $J = 8.8$  Hz, 2H), 7.09 (dd,  $J = 9.0$  Hz,  $J = 2.4$  Hz, 1H), 7.12–7.18 (m, 2H), 7.42 (dd,  $J = 7.5$  Hz,  $J = 7.5$  Hz, 1H), 7.60 (d,  $J = 8.4$  Hz, 1H), 7.79 (d,  $J = 9.3$  Hz, 1H), 8.23 (d,  $J = 9.0$  Hz, 2H). IR (neat) 1734, 1604, 1578, 1509, 1088, 1256, 1214, 1163  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.11; H, 9.31.

(R)-2-[3'-(1''-(Methylheptyloxy)naphthyl)-4-(n-Decyloxy)benzoate].  $R_f$  (50:50 hexane:dichloromethane) = 0.58.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.83 (t,  $J = 6.6$  Hz, 3H), 1.15–1.80 (m, 24H), 1.31 (d,  $J = 6.1$  Hz, 3H), 1.83 (m, 2H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.5 (m, 1H), 6.98 (d,  $J = 8.9$  Hz, 2H), 7.22 (s, 1H), 7.3–7.45 (m, 2H), 7.6 (s, 1H), 7.73 (d,  $J = 8.4$  Hz, 2H), 8.18 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1734, 1606, 1508, 1275, 1231, 1173  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.11; H, 9.20.

(R)-2-[5'-(1''-(Methylheptyloxy)naphthyl)-4-(n-Decyloxy)benzoate].  $R_f$  (50:50 hexane:dichloromethane) = 0.49.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.89 (m, 6H), 1.20–1.56 (m, 22H), 1.40 (d,  $J = 5.9$  Hz, 3H), 1.63 (m, 1H), 1.80–1.90 (m, 3H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.58 (m, 1H), 6.80 (dd,  $J = 6.6$ ,  $J = 2.2$  Hz, 1H), 6.99 (d,  $J = 9.0$  Hz, 2H), 7.29 (dd,  $J = 9.0$ ,  $J = 2.2$  Hz, 1H), 7.32–7.42 (m, 2H), 7.6 (d,  $J = 2.2$  Hz, 1H), 8.19 (d,  $J = 9.0$  Hz, 2H), 8.33 (d,  $J = 9.3$  Hz, 1H). IR (neat) 1734, 1605, 1580, 1509, 1258, 1210, 1166, 1067  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.27; H, 9.09.

(R)-2-[7'-(1''-(Methylheptyloxy)naphthyl)-4-(n-Decyloxy)benzoate].  $R_f$  (50:50 hexane:dichloromethane) = 0.56.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.92 (m, 6H), 1.2–1.52 (m, 22H), 1.8–1.85 (m, 3H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.5 (m, 1H), 6.99 (d,  $J = 8.7$  Hz, 2H), 7.08–7.20 (m, 2H), 7.17 (dd,  $J = 8.8$  Hz,  $J = 2.2$  Hz, 1H), 7.53 (d,  $J = 2.2$  Hz, 1H), 7.75 (d,  $J = 9.6$  Hz, 1H), 7.79 (d,  $J = 8.8$  Hz, 1H), 8.18 (d,  $J = 8.5$  Hz, 2H). IR (Nujol) 1733, 1605, 1511, 1245, 1192, 1166, 1065  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.07; H, 9.19.

(R)-4-[4'-(1''-(Methylheptyloxy)biphenyl)-4-(n-Decyloxy)benzoate].  $R_f$  (50:50 hexane:dichloromethane) = 0.38.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.86–0.90 (m, 6H), 1.20–1.65 (m, 23H), 1.32 (d,  $J = 6.1$  Hz, 3H), 1.70–1.90 (m, 3H), 4.05 (t, 2H), 4.4 (m, 1H), 6.96 (d,  $J = 8.8$  Hz, 2H), 6.98 (d,  $J = 9.0$  Hz, 2H), 7.24 (d,  $J = 8.8$  Hz, 2H), 7.5 (d,  $J = 9.0$  Hz, 2H), 7.58 (d,  $J = 9.0$  Hz, 2H), 8.16 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1729, 1610, 1511, 1170  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{37}\text{H}_{50}\text{O}_4$ : C, 79.51; H, 9.04. Found: C, 79.10; H, 9.54.

(R)-2-[3'-n-Decyloxy)naphthyl]-4-(1'-Methylheptyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.67.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.83–0.89 (t, 6H), 1.10–1.40 (m, 22H), 1.33 (d,  $J = 7.2$  Hz, 3H), 1.60–1.80 (m, 4H), 4.06 (t,  $J = 6.63$  Hz, 2H), 4.45 (m,  $J = 6.0$  Hz, 1H), 6.93 (d,  $J = 8.7$  Hz, 2H), 7.24 (s, 1H), 7.30–7.43 (m, 2H), 7.58 (s, 1H), 7.71 (d,  $J = 8.7$

hz, 2H), 8.15 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1741, 1605, 1508, 1257, 1233, 1180, 1058  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 78.85; H, 9.25.

(R)-2-[6'-(n-Decyloxy)naphthyl]-4-(1'-Methylheptyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.49.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t, 6H), 1.28–1.42 (m, 23H), 1.33 (d,  $J = 6.0$  Hz, 3H), 1.80–1.86 (m, 3H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.47 (m,  $J = 6.0$  Hz, 1H), 6.94 (d,  $J = 8.8$  Hz, 2H), 7.13–7.17 (m, 2H), 7.27 (dd,  $J = 8.8$ ,  $J = 2.2$  Hz, 1H), 7.56 (d,  $J = 2.2$  Hz, 1H), 7.69 (d,  $J = 8.8$  Hz, 1H), 7.73 (d,  $J = 9.0$  Hz, 1H), 8.15 (d,  $J = 8.6$  Hz, 2H). IR (Nujol) 1736, 1604, 1508, 1254, 1227  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.19; H, 9.18.

(R)-2-[7'-(n-Decyloxy)naphthyl]-4-(1'-Methylheptyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.50.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.82–0.92 (m, 6H), 1.20–1.65 (m, 23H), 1.33 (d,  $J = 6.0$  Hz, 3H), 1.70–1.88 (m, 3H), 4.04 (t,  $J = 6.6$  Hz, 2H), 4.42–4.52 (m,  $J = 6.0$  Hz, 1H), 6.95 (d,  $J = 8.8$  Hz, 2H), 7.08 (m, 1H), 7.11–7.17 (m, 1H), 7.16 (m, 1H), 7.51 (d, 1H), 7.72 (d,  $J = 8.9$  Hz, 1H), 7.77 (d,  $J = 8.6$  Hz, 1H), 8.15 (d,  $J = 8.9$  Hz, 2H). IR (Nujol) 1728, 1605, 1513, 1272, 1247  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{48}\text{O}_4$ : C, 78.89; H, 9.10. Found: C, 79.13; H, 9.35.

**Representative Procedure for Coupling of Phenols [6] and [11] with (2S,3S)-2-Chloro-3-methylpentanoyl Chloride [ES-[m,n] and ES-[m\*,n]].** (2''S,3''S)-2'-[6'-(2''-Chloro-3''-methylpentanoyloxy)naphthyl]-4-(n-Decyloxy)benzoate. To an argon-flashed flask containing a stirring solution of 0.6 g (1.62 mmol) of 2'-(6'-hydroxynaphthyl)-4-(decyloxy)benzoate in 7 mL of dried tetrahydrofuran and 0.2 g (1.98 mmol) of freshly distilled triethylamine, a solution of (2S,3S)-2-chloro-3-methylpentanoyl chloride in 3 mL of dried tetrahydrofuran was added dropwise via syringe. After this stirred for 16 h at room temperature, the solvent was removed and the product purified by flash chromatography on silica gel eluting with 1:2 hexane:dichloromethane. The pure product was twice recrystallized from absolute ethanol (yield 70%).  $R_f$  (50:50 hexane:dichloromethane) = 0.35.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t, 3H), 1.01 (t,  $J = 8.0$  Hz, 3H), 1.17 (d,  $J = 6.8$  Hz, 3H), 1.28–1.53 (m, 15H), 1.80–1.85 (m, 3H), 2.25 (m, 1H), 4.06 (t,  $J = 6.6$  Hz, 2H), 4.42 (d,  $J = 6.9$  Hz, 1H), 6.98 (d,  $J = 9.0$  Hz, 2H), 7.26 (dd,  $J = 9.0$  Hz,  $J = 2.0$  Hz, 1H), 7.38 (dd,  $J = 8.8$  Hz,  $J = 2.2$  Hz, 1H), 7.61 (t,  $J = 2$  Hz, 1H), 7.98 (d, 1H), 7.68 (d,  $J = 2.2$  Hz, 1H), 7.85 (d,  $J = 9$  Hz, 1H), 7.86 (d,  $J = 8.8$  Hz, 1H), 8.17 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1761, 1746, 1606, 1580, 1511, 1261, 1238, 1174, 1074  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.30; H, 7.75.

Optical purity (d.e.) of all ES derivatives were determined by integration of the doublet signals in the  $\delta$  4.4–4.6 ppm range, which correspond to the protons  $-\text{*CHCl}-$ .

**Analytical Data for Other Compounds.** (2''S,3''S)-1-[5'-(2''-Chloro-3''-methylpentanoyloxy)naphthyl]-4-(n-Decyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.41.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t,  $J = 6.6$  Hz, 3H), 1.02 (t,  $J = 7.3$  Hz, 3H), 1.20 (d,  $J = 6.8$  Hz, 3H), 1.23–1.60 (m, 15H), 1.80–1.85 (m, 3H), 2.35 (m, 1H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.5 (d,  $J = 7.5$  Hz, 1H), 7.01 (d,  $J = 8.9$  Hz, 2H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.41 (d,  $J = 7.6$  Hz, 1H), 7.47 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H), 7.56 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H), 8.24 (d,  $J = 8.9$  Hz, 2H). IR (Nujol) 1761, 1746, 1606, 1580, 1511, 1261, 1238, 1174, 1074  $\text{cm}^{-1}$ . IR (Nujol) 1761, 1746, 1606, 1580, 1511, 1261, 1238, 1174, 1074  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.39; H, 7.70.

(2''S,3''S)-1-[6'-(2''-Chloro-3''-methylpentanoyloxy)naphthyl]-4-(n-Decyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.31.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 7$  Hz, 3H), 1.00 (t,  $J = 7.6$  Hz, 3H), 1.37 (d,  $J = 6.8$  Hz, 3H), 1.20–1.60 (m, 15H), 1.70–1.87 (m, 3H), 2.26 (m, 1H), 4.07 (t,  $J = 6.6$  Hz, 2H), 4.43 (d,  $J = 7.6$  Hz, 1H), 4.58 (d,  $J = 50$  Hz, 1H) [corresponding to the 2''R,3''S diastereoisomer], 7.03 (d,  $J = 9.0$  Hz, 2H), 7.24 (dd,  $J = 9.0$  Hz,  $J = 2.4$  Hz, 1H), 7.37 (dd,  $J = 7.6$  Hz,  $J = 1$  Hz, 1H), 7.54 (dd,  $J = 7.6$  Hz,  $J = 7.6$  Hz, 1H), 7.65 (d,  $J = 2.1$  Hz, 1H), 7.74 (d,  $J = 8.1$  Hz, 1H), 7.98 (d, 1H), 8.26 (d,  $J = 8.8$  Hz, 2H). IR (neat) 1768, 1734, 1604, 1604, 1598, 1509, 1249, 1214, 1164, 1140, 1086  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.53; H, 7.72.

(2''S,3''S)-2'-[3''-(2''-Chloro-3''-methylpentanoyloxy)naphthyl] 4-(n-Decyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.44.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.82 (t,  $J = 7.3$  Hz, 3H), 0.89 (t,  $J = 7.0$  Hz, 3H), 1.0 (d,  $J = 6.8$  Hz, 3H), 1.20–1.55 (m, 15H), 1.64 (m, 1H), 1.81 (m, 2H), 2.2 (m, 1H), 4.04 (t,  $J = 6.6$  Hz, 2H), 4.28 (d,  $J = 7.1$  Hz, 1H), 4.45 (d,  $J = 5.0$  Hz, 1H) [corresponding to the 2''R,3''S diastereoisomer], 6.97 (d,  $J = 8.8$  Hz, 2H), 7.50 (m, 2H), 7.71 (s, 1H), 7.83 (m, 2H), 7.76 (s, 1H), 8.15 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1773, 1730, 1603, 1511, 1249, 1223, 1166, 1089  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 72.06; H, 7.67.

(2''S,3''S)-2'-[5''-(2''-Chloro-3''-methylpentanoyloxy)naphthyl] 4-(n-Decyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.36.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.6$  Hz, 3H), 1.03 (7.6, 3H), 1.22 (d,  $J = 6.8$  Hz, 3H), 1.28–1.51 (m, 15H), 1.80–1.86 (m, 3H), 2.37 (m, 1H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.52 (d,  $J = 7.6$  Hz, 1H), 6.99 (d,  $J = 8.8$  Hz, 2H), 7.27 (dd,  $J = 8.1$  Hz,  $J = 1.2$  Hz, 1H), 7.41 (dd,  $J = 9.1$  Hz,  $J = 2.2$  Hz, 1H), 7.50 (dd,  $J = 8.0$  Hz,  $J = 8.0$  Hz, 1H), 7.73 (s, 1H), 8.02 (d,  $J = 9.0$  Hz, 1H), 8.18 (d,  $J = 8.8$  Hz, 2H). IR (neat) 1778, 1734, 1602, 1578, 1510, 1288, 1253, 1227, 1210, 1266, 1083, 1062  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.66; H, 7.65.

(2''S,3''S)-2'-[7''-(2''-Chloro-3''-methylpentanoyloxy)naphthyl] 4-(n-Decyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.31.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t,  $J = 6.6$  Hz, 3H), 1.00 (7.4, 3H), 1.17 (d,  $J = 6.6$  Hz, 3H), 1.20–1.53 (m, 15H), 1.74–1.90 (m, 3H), 2.27 (m, 1H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.43 (d,  $J = 7.2$  Hz, 1H), 4.60 (d,  $J = 5.5$  Hz, 1H) [corresponding to the 2''R,3''S diastereoisomer], 6.99 (d,  $J = 9.0$  Hz, 2H), 7.24 (dd,  $J = 2.2$  Hz, 1H), 7.36 (dd,  $J = 8.8$  Hz,  $J = 2.2$  Hz, 1H), 7.57 (d,  $J = 1.9$  Hz, 1H), 7.65 (d,  $J = 1.8$  Hz, 1H), 7.90 (dd,  $J = 9.0$  Hz,  $J = 1.8$  Hz, 2H), 8.18 (d,  $J = 9.0$  Hz, 2H). IR (Nujol) 1764, 1720, 1608, 1514, 1239, 1203, 1172  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.20; H, 7.38.

(2''S,3''S)-4-[4''-(2''-Chloro-3''-methylpentanoyloxy)biphenyl] 4-(n-Decyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.31.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (t,  $J = 7.1$  Hz, 3H), 1.00 (t,  $J = 7.3$  Hz, 3H), 1.15 (d,  $J = 6.6$  Hz, 3H), 1.28–1.55 (m, 15H), 1.70–1.90 (m, 3H), 2.30 (m, 1H), 4.05 (t,  $J = 6.6$  Hz, 2H), 4.41 (d,  $J = 7.1$  Hz, 1H), 6.98 (d,  $J = 9.0$  Hz, 2H), 7.20 (d,  $J = 9.0$  Hz, 2H), 7.27 (d,  $J = 8.8$  Hz, 2H), 7.60 (d,  $J = 9.0$  Hz, 4H), 8.16 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1762, 1729, 1610, 1204, 1166  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{35}\text{H}_{43}\text{O}_5\text{Cl}$ : C, 72.56; H, 7.50. Found: C, 72.83; H, 7.43.

(2''S,3''S)-2-(3''-(n-Decyloxy)naphthyl) 4-[(2'-Chloro-3'-methylpentanoyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.57.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85 (t,  $J = 6.6$  Hz, 3H), 0.98 (t,  $J = 7.5$  Hz, 3H), 1.14 (d,  $J = 6.9$  Hz, 3H), 1.10–1.50 (m, 15H), 1.60–1.80 (m, 3H), 2.23 (m, 2H), 4.06 (t,  $J = 6.6$  Hz, 2H), 4.39 (d,  $J = 7.2$  Hz, 1H), 7.22 (s, 1H), 7.27 (d,  $J = 9.0$  Hz, 2H), 7.30–7.45 (m, 2H), 7.59 (s, 1H), 7.73 (d,  $J = 8.7$  Hz, 2H), 8.28 (d,  $J = 9.0$  Hz, 2H), 7.75 (d,  $J = 9.0$  Hz, 1H), 8.28 (d,  $J = 8.6$  Hz, 2H). IR (Nujol) 1769, 1738, 1600, 1508, 1260, 1239, 1163, 1134, 1065  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.75; H, 7.35.

(2''S,3''S)-2-(6''-(n-Decyloxy)naphthyl) 4-[(2'-Chloro-3'-methylpentanoyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.41.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (t, 3H), 0.98 (t, 3H), 1.14 (d, 3H), 1.27–1.49 (m, 15H), 1.81–1.84 (m, 3H), 4.06 (t,  $J = 6.6$  Hz, 2H), 4.39 (d,  $J = 7.1$  Hz, 1H), 4.58 (d,  $J = 5.3$  Hz, 1H) [corresponding to the 2''R,3''S diastereoisomer], 7.15–7.18 (m, 2H), 7.26–7.30 (m, 3H), 7.58 (d,  $J = 2$  Hz, 1H), 7.70 (d,  $J = 8.8$  Hz, 1H), 7.75 (d,  $J = 9.0$  Hz, 1H), 8.28 (d,  $J = 8.6$  Hz, 2H). IR (Nujol) 1698, 1604, 1509, 1281, 1259, 1171  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 72.07; H, 7.75.

(2''S,3''S)-2-(7''-(n-Decyloxy)naphthyl) 4-[(2'-Chloro-3'-methylpentanoyloxy)benzoate.  $R_f$  (50:50 hexane:dichloromethane) = 0.41.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.89 (t, 3H), 1.01 (t, 3H), 1.16 (d, 3H), 1.24–1.55 (m, 15H), 1.74–1.92 (m, 3H), 2.20–2.32 (m, 1H), 4.07 (t,  $J = 6.6$  Hz, 2H), 4.42 (d,  $J = 7.2$  Hz, 1H), 7.10–7.17 (m, 2H), 7.20 (d,  $J = 2.2$  Hz, 1H), 7.31 (d,  $J = 8.8$  Hz, 2H), 7.55 (d, 1H), 7.76 (d,  $J = 8.8$  Hz, 1H), 7.82 (d,  $J = 8.8$  Hz, 1H), 8.31 (d,  $J = 8.8$  Hz, 2H). IR (Nujol) 1765, 1732, 1604, 1504, 1271, 1250, 1197, 1149, 1073  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{33}\text{H}_{41}\text{O}_5\text{Cl}$ : C, 71.64; H, 7.48. Found: C, 71.68; H, 7.57.

**Experimental Details of the Ferroelectric Measurements.** The values of spontaneous polarization ( $P_s$ ) were determined by integrating the displacement current peak which appears due to the reversal of  $P_s$ , as a response to an applied triangular voltage.<sup>59</sup> Polyimide-coated unidirectional rubbed cells of 4 and 10- $\mu\text{m}$  thickness and planar configuration were used. The maximum amplitude and frequency were 40 Vpp and 50 Hz respectively. A good alignment was obtained by slowly cooling (0.5 or 1  $^\circ\text{C}/\text{min}$ ) of the filled cell from the isotropic to the SmA phase. Most of the samples showed zigzag defects suggesting a chevron layer structure.<sup>60</sup>

Rotational viscosity  $\gamma_c$  was obtained from the parameters of the current peak calculated in the measure of the  $P_s$ . From both values we calculate the response time using the equation  $\tau = 1.75 \gamma_c / P_s E$ .<sup>61</sup>

The sign of  $P_s$  was determined by the field reversal method through optical observation of the extinction direction by rotating the stage according to Lagerwall's convection.<sup>62</sup>

The tilt angles were measured as a function of temperature under crossed Nikol, as half of the rotation angle between the two extinction positions, associated with the oppositely directed polarization. The detection was performed by a photomultiplier tube and the applied electrical dc field was of 5 V/ $\mu\text{m}$ .

**Techniques.** Microanalysis was performed with a Perkin-Elmer 240 B microanalyzer. Infrared spectra were recorded with a Perkin-Elmer 1600 (series FTIR) Spectrometer in the 400–4000- $\text{cm}^{-1}$  spectral range. All  $^1\text{H NMR}$  spectra were recorded on a Varian Unity-300 operating at 300 MHz for  $^1\text{H}$ .

The textures of the mesophases were studied with either a Nikon and an Olympus BH-2 polarizing microscope, equipped with a Mettler hot-stage FP82 and a control unit FP80 or a LINKAM hot-stage THMS600 with a central processor TMS91 and a CS196 cooling system.

Temperatures of transition were determined by differential scanning calorimetry using a Perkin-Elmer DSC-7 calorimeter with a heating and cooling rate of 5  $^\circ\text{C}/\text{min}$ . The apparatus was calibrated with indium at 5  $^\circ\text{C}/\text{min}$  (156.6  $^\circ\text{C}$ , 28.45 J/g).

Polarization and tilt angle studies were carried out using commercial cells with ITO electrodes coated with polyamide. The triangular wave voltage was supplied by a HP3325 A function generator, the current-voltage cycles were recorded by a digital acquisition system HP7090A. All the equipment was interfaced to a microcomputer.

Powder X-ray diffraction patterns were obtained in a Guinier diffractometer (Huber 644) operating with a Cu  $\text{K}\alpha_1$  beam issued from a germanium monochromator. The samples were held in rotating Lindemann glass capillaries (0.7-mm o.d.) and heated with a variable-temperature attachment. The diffraction patterns were registered with a scintillation counter.

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