# CHEMISTRY OF MATERIALS

## Janus-Type Dendromesogens: A Tool to Control the Nanosegregation and Polar Organization of Bent-Core Structures

Nélida Gimeno,<sup>†</sup> Jorge Vergara,<sup>†</sup> Miguel Cano,<sup>†</sup> José Luis Serrano,<sup>‡</sup> M. Blanca Ros,<sup>\*,†</sup> Josu Ortega,<sup>§</sup> César L. Folcia,<sup>⊥</sup> Sofía Rodríguez-Conde,<sup>⊥</sup> Gerardo Sanz-Enguita,<sup>⊥</sup> and Jesús Etxebarria<sup>⊥</sup>

<sup>†</sup>Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

<sup>‡</sup>Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Nanociencia de Aragón, Universidad de Zaragoza, 50009-Zaragoza, Spain

<sup>§</sup>Departamento de Física Aplicada II, Facultad de Ciencia y Tecnología, and <sup>⊥</sup>Departamento de Física de la Materia Condensada, Facultad de Ciencia y Tecnología, UPV/EHU, 48080 Bilbao, Spain

**Supporting Information** 

**ABSTRACT:** Several first- or second-generation Janus-type codendrimers that combine promesogenic bent-core and rodlike molecular segments have been synthesized by the versatile CuAAC reaction and the materials have been characterized by POM, DSC, XRD, and SHG studies. Depending on the ratio between the number of rod- and bent-core units, these compounds form mesophases ranging from nematic to a



complex polar smectic mesophase in which the two types of mesogenic moieties are segregated on a nanometric scale. In the case of a 1:1 bent/rod ratio, the materials form ferroelectric mesophases and the macroscopic polarization is stable in the absence of an applied electric field. The appearance of the different mesophases is explained in terms of the relative values of the transverse areas of the mesogenic cores.

KEYWORDS: Janus codendrimers, bent-shaped molecules, liquid crystals, ferroelectric material, bent-core liquid crystals

#### INTRODUCTION

In the search for functional or smart materials with tunable properties, organized molecular assemblies represent a key area.<sup>1,2</sup> It has been demonstrated in numerous studies that liquid crystals are excellent candidates for organizing active units and a variety of mesophases have been successfully used with this aim in recent decades.<sup>3</sup> In the work described here we focused on unconventional liquid crystals, the so-called bentcore liquid crystals.<sup>4</sup> These materials are a type of mesogen that has compact molecular packing in the mesophase, thus restricting the molecular rotational freedom. This packing leads to strong polar order within layers or columns and many interesting phenomena have been observed in these systems. Among other properties, we can highlight the manifestation of supramolecular chirality in the absence of chiral molecules<sup>4</sup> and the appearance of high macroscopic polarization values and piezoelectric, flexoelectric, or nonlinear optical responses.<sup>4,5</sup>

Current research interest in this area is focused on the structural characterization and understanding of the new types of mesophases<sup>4-6</sup> and the modulation of their physical properties. In this sense, it is especially important to understand how to control this kind of supramolecular packing through appropriate molecular design for both  $low^{4-6}$  and high<sup>7-10</sup> molecular weight compounds.

An efficient strategy to control or modify supramolecular arrangements of bent-core molecules involves the incorporation

in the same material of bent molecules and other structures, a design that allows the unique properties derived from both systems to be combined. For this purpose, two different approaches have been employed. In most cases, new materials are prepared by physical blending of bent-shaped molecules with the other components. This approach has provided new mesophases and/or phase sequences that depend on the concentrations of the components.<sup>11-15</sup> For example, mixtures with a small amount of achiral bent-core molecules have been successfully used to enhance chiral effects<sup>12</sup> or to induce antiferroelectric behavior.<sup>13</sup> Moreover, it has recently been reported that the doping of nematic bent-core liquid crystals with a small percentage of chiral additive yields blue phases<sup>14,15</sup> (namely BPI and BPIII). Unfortunately, in many cases, the limited molecular miscibility seriously limits the possibilities for this kind of approach.

A different strategy has been proposed that involves the use of dimeric molecules, where the bent-core structures are covalently linked to another moiety to form nonsymmetric molecules. Despite the fact that very few examples have been reported to date, this approach offers the possibility of obtaining interesting physical properties.<sup>16–19</sup> For example,

Received:July 9, 2012Revised:December 14, 2012Published:December 24, 2012

Scheme 1. Schematic Representation of the Different Units Selected to Build up the Janus-Type Dendrimers (top) and the Six Codendrimers Prepared from These Units (bottom)



Yelamaggad et al.<sup>17,18</sup> reported the induction of a biaxial nematic phase or broad blue mesophases in dimers based on bent core-calamitic hybrids, and Weissflog et al.<sup>16a,19</sup> studied the structure–property relationships for these kinds of bent-core based dimers.

Numerous attractive possibilities still remain unexplored in the combination of bent-core and rod-like structures. One such example is the case of block codendrimers, sometimes known as hybrid or "Janus" dendrimers.<sup>20</sup> Janus-like structures represent a useful tool to exploit the cooperative nature of the mesomorphism and, whereas dimers offer a fixed 1:1 bent/ rod ratio, Janus-like structures allow the manipulation of the bent/rod ratio through the appropriate dendron combinations among other possibilities.

Janus dendrimers have recently attracted a great deal of attention as a new class of compounds since they combine two differently functionalized segments on opposite sides of a single molecule, thus yielding bifunctionalized products with a perfectly controlled disposition of the peripheral groups. This approach has been used to produce outstanding examples of amphiphilic self-assembling materials or materials for medical applications.<sup>21,22</sup> Janus-type dendrimers can also present mesomorphism<sup>20a,b,g,23</sup> and this has proven to be a very powerful and promising feature to control the supramolecular organization of dissimilar chemical structures in which either calamitic or discotic moieties have been incorporated.<sup>23f-h,24-29</sup>

We describe here the synthesis and characterization of the first series of low generations Janus-type dendrimers that bear rodlike and bent-shaped cores (Scheme 1). The work mainly focuses on the different mesomorphism and physical properties, which depend on the bent/rod ratio of the constituent cores of the dendrimers. We concentrated on what we consider to be a representative selection of structural motifs from the many possibilities that exist. Our aim was to gain a better understanding of the general rules that govern the mesomorphic behavior of this kind of block dendrimer depending on the bent/rod core ratio. Moreover, we also report the first series of dendrons bearing bent-core units in their periphery.

As far as the bent-core units are concerned, two structures based on the 3,4'-dihydroxybiphenyl core, a well-known promoter of bent-core mesophases, were selected.<sup>4</sup> The first part of our research was focused on the use of a long promesogenic unit (B2) that contained six aromatic rings, an ntetradecyloxy chain as the outer terminal tail and a long  $[-(CH_2)_{10}-]$  flexible spacer – a system that was previously used by us to produce bent-core dendrimers.<sup>30</sup> Based on the results obtained we decided to extend our study to a shorter system  $(B1)^{30}$  that contained five aromatic rings, an n-octyloxy terminal chain and a short  $\left[-(CH_2)_4-\right]$  spacer. These bentcore moieties were attached to dendritic structures based on bis-MPA<sup>31</sup> dendrons of the first (G1) and second (G2) generations functionalized at the focal point with an alkyne group. A well-known rod-shaped promesogenic core, namely the photoactive cyanoazobenzene (R), was chosen as a rod-like unit and this was attached to the same type of dendron (G1 and G2) functionalized at the focal point as an azide. Calamitic dendrons were attached to bent-core-based dendrons through a triazole ring (TA) by applying a "click chemistry" approach (CuAAC reaction).<sup>32</sup> This methodology was used to prepare six first- or second-generations Janus-dendrimers with different

OBr

G1-Bn

<u>Route 1</u>

B2-OH

Route 2

ΗΟ

но -

HO **B2**O B2-CH<sub>2</sub>C≡CH DCC/DPTS/DCM но **B2**O **B2**() B2-OH **B2**O Pd(OH)<sub>2</sub>/C OBn C . EtOH DCC/DPTS/DCM **B2**O DCC/DPTS/DCM **B2**O **B2**() B2G1-Bn B2G1-H в2G1-СН₂С≡СН





Scheme 3. General Synthesis of the Dendrons Based on the B1 Structure (Route 3), the R Moiety (Route 4) and Janus-Type Codendrimers (Route 5)

Route 3



bent-core/rod-core ratios and the properties of these compounds were studied. Four molecules based on the longer

bent-core structure (B2) [B2-TA-RG1 (1:2 bent/rod units), B2G1-TA-RG1 (2:2 bent/rod units), B2G1-TA-RG2 (2:4

compd	phase transitions (°C) (kJ mol <sup>-1</sup> ) <sup><math>a,b</math></sup>	measured spacings (Å)	Miller indices hkl	layer thickness c (Å)	theoretical molecular length (Å)
B2-CH <sub>2</sub> C≡CH	Cr 84 [17.8] SmCP 118 [14.1] I	40.0	002	80.0	72.4
B2G1-Bn	Cr 79 [2.6] SmCP 140 [34.7] I	92.9	001		
		46.0	002	92.1	75.6
		30.4	003		
B2G1-H	Cr 83 [18.1] SmCP 152 [35.6] I	42.3	002	84.0	70.8
		27.8	003		
B2G1-CH <sub>2</sub> C≡CH	Cr 82 [8.3] SmCP 143 [37.7] I	43.0	002	86.0	73.2
B2G2-Bn	Cr 62 [26.0] SmCP 141 [73.0] I	89.6	001	89.7	
		44.8	002		79.2
		29.9	003		
B2G2-H	Cr 81 [10.4] SmCP 166 [71.6] I	42.8	002	87.7	74.3
		29.9	003		
B2G2-CH <sub>2</sub> C≡CH	Cr 87 [12.2] SmCP 158 [77.1] I	89.6	001	89.6	
		44.8	002		76.9
		29.4	003		
B1G1-CH₂C≡CH	Cr 76 [3.7] Col <sub>r</sub> 104 [30.2] I	53.3	100	a:22.1	
		26.1	200	b:52.2	59.7
		20.4	110		
		17.3	120		
B1G2-CH <sub>2</sub> C≡CH	Cr 70 [23.0] Col <sub>r</sub> 124 [61.7] I <sup>c</sup>	53.3	100	a:22.4	
		26.5	200	b:53.1	59.7
		20.7	110		
		174	120		

Table 1. Thermal and XRD Data for the Intermediate Compounds and the First- and Second-Generations Dendrons Derived from the Bent-Core Units B1 and B2

<sup>a</sup>Data determined by DSC, from second scans at a scanning rate of 10 °C/min. <sup>b</sup>Cr, crystal; SmCP, smectic C polar mesophase; Col., rectangular columnar phase; I, isotropic liquid. <sup>c</sup>Data from the first heating scan.

bent/rod units), and B2G2-TA-RG2 (4:4 bent/rod units)] and two codendrimers containing the shorter bent-shaped structure (B1) [B1G1-TA-RG2 (2:4 bent/rod units) and B1G2-TA-**RG2** (4:4 bent/rod units)] were prepared.

## LIQUID CRYSTALLINE BEHAVIOR

#### RESULTS

Synthesis of the Compounds. Details of the synthetic routes followed to prepare the dendrons and Janus-type dendrimers are provided in Schemes 2 and 3. The nondendritic bent-shaped alkyne B2-CH<sub>2</sub>C≡CH was prepared by functionalization of the previously reported acid B2-OH<sup>33</sup> with propargylic alcohol, as shown in Route 1. Two alternative synthetic routes were assessed in order to prepare the alkynefunctionalized dendrons. In the case of bent-core dendrons based on B2, the synthetic scheme shown in Route 2 was employed and this provided several intermediate dendrons (B2G1-Bn, B2G1-H, B2G1-CH<sub>2</sub>C≡CH, B2G2-Bn, B2G2-H, and  $B2G2-CH_2C\equiv CH$ ). However, a simplified synthetic pathway (Route 3) allowed us to obtain bent-core unit B1derived dendrons (B1G1-CH<sub>2</sub>C≡CH and B1G2-CH<sub>2</sub>C≡CH) in a straightforward manner. On the other hand, dendrons containing the calamitic units were prepared by Route 4, as reported previously.<sup>34</sup> All of the codendrimers were synthesized using an alkyne and azide Huisgen cycloaddition with CuBr as catalyst, N,N,N',N',N"-pentamethyldiethylenetriamine (PMDETA) as ligand and DMF as solvent (Route 5, Scheme 3). The combination of bent-core and rod-like functionalized dendrons gave access to codendrimers with a 1:1 or 1:2 bent/ rod ratio and allowed perfect control of the number of bentcore and rod-like units on each side of the block codendrimer. Further synthetic details and full characterization data for all these compounds are gathered in the Supporting Information.

The mesomorphic properties of the dendrons and the Janustype dendrimers were investigated by polarized light optical microscopy (POM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD).

Bent-Core-Based Dendrons. Bent-core-based dendrons have not been described previously and we present the dendritic molecules under investigation here due to their novelty. All of the bent-core first- and second-generations dendrons described here form liquid crystalline phases and their thermal and XRD data are gathered in Table 1. More detailed information on the mesomorphic properties of these dendrons, as well as data for the dendrons based on calamitic molecules, is gathered in the Supporting Information. A schematic representation of some of the mesophases that are typical of bent-core molecules is also provided in Figure S1 in the Supporting Information.

It can be seen that all of the bent-core dendrons present mesophases with broad temperature ranges (more than  $\overline{60}$  °C). This fact confirms that dendritic molecules tend to stabilize bent-core-type mesomorphism, not only for dendrimeric structures<sup>30,35</sup> but also for these bis-MPA-derived dendrons. Once again, the supramolecular arrangement depends strongly on the nature of the bent-core promesogenic unit. On the basis of POM and XRD studies, a lamellar arrangement has been assigned to the dendrons with the longest bent-core moiety (B2) regardless of the generation of the dendron (G1 or G2) or the focal point structure (-Bn, -H, or -CH<sub>2</sub>C $\equiv$ CH), which only modulates the transition temperatures slightly. On the other hand, a columnar mesophase is proposed for the two dendrons derived from the shortest bent-core unit B1. Furthermore, concerning the clearing enthalpies, there is an additive contribution of each mesogenic structure to the



Figure 1. (a) X-ray pattern of B2G2-Bn at small angles, (c, d) structural models deduced from (b) one of the electron density distributions compatible with the experimental diagram. In c and d, the molecular tilt of the bent-core molecular segments has been omitted for clarity and an antiferroelectric structure is represented by the antiparallel orientation of the dipole moments of the bent-core units.

transition enthalpy. Thus, the enthalpy for the first generation (~35 kJ/mol) is approximately double that of the bent-shaped acid (18.4 kJ/mol) and half the enthalpy measured for the second-generation dendron (~70 kJ/mol). This phenomenon has also been reported for other liquid crystalline dendritic systems.<sup>30,34,36</sup>

The results obtained for dendron B2G2-Bn will be discussed in detail as this material showed the most attractive properties, reasonable transition temperatures and better chemical stability. On cooling from the isotropic phase B2G2-Bn showed schlieren textures of very low birefringence, which are typical of the SmCP phase. The existence of a lamellar arrangement was confirmed by the X-ray diffractograms, which showed up to three reflections in the small-angle region in addition to the diffuse wide-angle scattering. For this compound the theoretical length (79.2 Å) calculated by Chemsketch<sup>37</sup> is significantly smaller than the layer spacing (89.7 Å). This finding indicates that there are at least two dendrons per smectic layer. Similar behavior was found for the other SmCP structures (Table 1). The X-ray pattern (see Figure 1) contains a large (002) peak and two small (001) and (003) reflections. Different models consistent with the observed intensities could be proposed either dendrons in an elongated conformation with two mesogenic cores on both sides of the focal point (presumably the most stable conformation), or alternatively, completely folded dendrons. In both cases, the molecules are tilted within the layers.

In a first approximation, the smectic phase has a periodicity equal to c/2 since the (002) peak is by far the most dominant. However, the existence of the (001) and (003) peaks implies a real periodicity of c. These reflections account for the small difference in electronic density between the terminal chains with and without the linking unit. A schematic representation of the structures is shown in Figure 1 along with a possible profile for the electronic density obtained by an inverse Fourier transform that is compatible with the observed X-ray intensities.<sup>4h,38</sup>

The SmCP mesophase of dendron **B2G2-Bn** was studied under electric fields and it showed electrooptic switching. The polarization curves indicate antiferroelectric behavior (see the Supporting Information). In this case, the birefringence was observed to increase on applying the electric field and, on removal of the field, a dark texture with chiral domains appeared on uncrossing the polarizers (see Figure 2). This observation indicates that the material has a homochiral character (dark conglomerate without field and SmCP under field).  $^{39}$ 

**Janus-Type Dendromesogens.** All of the first- and second-generation Janus-type codendrimers described here showed mesomorphism. Remarkably, the liquid crystal phases remained on cooling below 100 °C. The phase sequences and corresponding enthalpy values for the compounds are summarized in Table 2. The XRD data are gathered in Table 3. It can be seen that, in general, the higher the generation the broader the stabilization of the mesophase range (**B2G1-TA-RG1** vs **B2G2-TA-RG2**), which is not the trend reported for the dendrons or homodendrimers.<sup>30</sup>

One can clearly distinguish between the mesogenic behavior displayed by the codendrimers with 1:2 and 1:1 bent/rod ratios. Two of the three codendrimers with a 1:2 bent/rod ratio (**B2-TA-RG1** and **B1G1-TA-RG2**) show diffuse reflections at small angles (see Figure 3a), whereas the third (**B2G1-TA-RG2**) presents a sharp peak in that region. The first kind of pattern can be attributed to a nematic phase and that for the third compound is consistent with a smectic mesophase. The important fact, however, is that in all three cases the corresponding distances (about 40 Å) are much smaller than the molecular sizes. This indicates that the bent-cores and rodcores are homogeneously mixed in both the nematic and smectic mesophases; i.e. there is no nanophase segregation – as described in b and d in Figure 3.

The structure shown in Figure 3e is another possibility that is compatible with the XRD pattern of the smectic material. In this case nanosegregation of both types of mesogenic segments takes place. The single reflection observed would be the (003), and the smaller angle reflections are assumed to be very weak. In this case, the material would have a pseudoperiodicity of c/3 because of the similar electronic density of two calamitic cores and one bent-core. Further analysis of this structure will be presented in the Discussion section.

The electric field responses of **B2-TA-RG1** and **B1G1-TA-RG2**, both of which show the N mesophase, were investigated in 5  $\mu$ m glass cells. As expected, ferroelectric switching was not detected. However, under a strong low-frequency electric field (20 V/ $\mu$ m) an electrooptic response was observed due to the dielectric anisotropy. The smectic mesophase of **B2G1-TA-RG2** also responded to the field. In this case the material showed antiferroelectric switching for fields above 20 V/ $\mu$ m



Figure 2. Microphotographs of the SmCP-DC mesophase of B2G2-Bn: (a) in the absence of an electric field, (b) under an electric field between crossed polarizers; (c, d) after removing the electric field and uncrossing the polarizers, showing the chiral domains. Arrows indicate transmission directions of the polarizers. (e, f) Textures of the SmC<sub>s</sub>P<sub>F</sub> phase of compound B2G2-TA-RG2 at 113 °C under opposite electric field polarity (10 V  $\mu$ m<sup>-1</sup>). After field removal the textures remain unaltered in both cases, indicating a bistable ferroelectric ground state.

when the field was applied during the cooling process from the isotropic phase. The smectic mesophase can thus be identified as  $SmC_AP_A$  (see Figure S3 in the Supporting Information). The lamellar mesomorphism of this codendrimer, which contains a similar number of mesogenic units as **B1G1-TA-RG2**, should be ascribed to a layer-ordering preference favored by the presence of the more extended rigid core (**B2**) increasing the intermolecular interactions.

The X-ray patterns of the codendrimers with a 1:1 bent/rod ratio were completely different. Up to five Bragg peaks were

#### Table 2. Transition Temperatures and Enthalpies Determined by DSC for Janus-Like Compounds B2-TA-RG1, B2G1-TA-RG1, B2G1-TA-RG2, B2G2-TA-RG2, B1G1-TA-RG2 and B1G2-TA-RG2

codendrimer	phase transition (°C) (kJ mol <sup>-1</sup> ) <sup><math>a,b</math></sup>
B2-TA-RG1	Cr 71.6 [28.7] N 77.2 [12.8] I
B2G1-TA-RG1	Cr 89.9 [4.9] SmC <sub>s</sub> P <sub>F</sub> 104.2 [42.4] I
B2G1-TA-RG2	Cr 85.1 [58.6] SmC <sub>A</sub> P <sub>A</sub> 99.5 [46.3] I
B2G2-TA-RG2	Cr 89.5 [12.4] SmC <sub>S</sub> P <sub>F</sub> 130.9 [83.5] I
B1G1-TA-RG2	Cr 46.5 [11.7] N 78.9 [10.3] I
B1G2-TA-RG2	Cr 66.3[23.0] SmC <sub>s</sub> P <sub>F</sub> 92.5 [65.5] I

<sup>*a*</sup>Data determined in the second scans at a scanning rate of 10 °C/min. <sup>*b*</sup>Cr, crystal; SmC<sub>S</sub>P<sub>F</sub>, polar smectic C synclinic ferroelectric mesophase; SmC<sub>A</sub>P<sub>A</sub>, polar smectic C anticlinic antiferroelectric mesophase; N, nematic phase; I, isotropic liquid.

#### Table 3. XRD Data for the Mesophases of Janus-Like Compounds B2-TA-RG1, B2G1-TA-RG1, B2G1-TA-RG2, B2G2-TA-RG2, B1G1-TA-RG2 and B1G2-TA-RG2

codendrimer	mesophase <sup><i>a</i></sup>	measured spacings (Å)	Miller indices <i>hkl</i>	layer thickness c (Å)	theoretical molecular length (Å)
B2-TA-RG1	Ν	30-40			116
B2G1-TA-	SmC <sub>s</sub> P <sub>F</sub>	137.0	001	136.7	124
RG1		69.0	002		
		45.4	003		
		34.2	004		
		27.1	005		
B2G1-TA- RG2	$SmC_AP_A$	44.6	001	44.7	126
B2G2-TA-	SmC <sub>s</sub> P <sub>F</sub>	137.0	001	136.5	128
RG2		68.0	002		
		45.9	003		
		34.0	004		
		27.3	005		
B1G1-TA- RG2	Ν	30-40			102
B1G2-TA-	$SmC_{S}P_{F}$	108.7	001	108.7	107.2
RG2		54.5	002		
		36.2	003		
		27.7	004		
		21.7	005		

<sup>*a*</sup>N, nematic phase;  $SmC_SP_F$ , polar smectic C synclinic ferreoelectric mesophase;  $SmC_AP_A$ , polar smectic C anticlinic antiferreoelectric mesophase.

observed at low angles in addition to the wide-angle diffuse halo. The mesophases are smectic because all the sharp reflections can be indexed as (00l). The structure periodicities are larger than the corresponding molecular lengths. In addition, the intensity of the peaks follows a characteristic sequence, with a dominant (003) reflection, a significant (002) intensity and a small (001) peak (see Figure 4a). All of these findings can be explained by the structural model proposed and depicted in Figure 4b. As can be seen, the rod-core segments are completely interdigitated, whereas the bent-core moieties segregate in pairs between two consecutive layers of calamitic structures. The peculiar pattern for the reflection intensities is due to the complex structure of the smectic layers. A possible electronic density consistent with the experimental intensities is shown in Figure 4c and this was obtained by following the Fourier transform procedure mentioned previously.<sup>4h,38</sup> The narrow density peaks account for the rod-core part and the



Figure 3. (a) XRD diagram and (b) proposed structure for the nematic phase of B2-TA-RG1. (c) XRD diagram and (d, e) proposed structures for the SmC<sub>A</sub>P<sub>A</sub> phase of B2G1-TA-RG2.



**Figure 4.** (a) X-ray pattern of **B2G1-TA-RG1** at small angles, and (b) structural model deduced from (c) the electron density distributions compatible with the experimental X-ray diagram. In b, the molecular tilt of the bent-core molecular segments has been omitted for clarity and the ferroelectric structure is represented by the parallel orientation of the dipole moments of the bent-core units.

broader peaks are due to the bent-core moieties. The bent-core part should be tilted by an angle of about  $50^{\circ}$  to fit the observed spacing, and this is consistent with tilt angles within SmCP phases.

Rather remarkably, the three 1:1 compounds exhibit ferroelectric smectic phases ( $SmC_SP_F$ ). This point was proved by the textures observed under an electric field and by SHG measurements. Representative textures for this kind of mesogen (**B2G2-TA-RG2**) are shown in panels e and f in Figure 2. Under an electric field of 10 V  $\mu$ m<sup>-1</sup>, molecular switching around the tilt cone (see Figure S1 in the Supporting Information) was observed over the whole mesophase range. The POM images indicate a synclinic arrangement under an electric field. On removing the field the texture remained unaltered regardless of the field polarity, which indicates that the ferroelectric state is truly bistable. In order to ascertain whether the mesophase is intrinsically ferroelectric, second-harmonic generation (SHG) experiments were carried out (see the Supporting Information for experimental details). In the three 1:1 codendrimers, an SHG signal was detected in the absence of a field just below the clearing point. A plot of SHG intensity versus temperature for **B2G1-TA-RG1** is shown in Figure 5 as an example.



Figure 5. SHG intensity of compound B2G1-TA-RG1 vs temperature. The experiment was carried out in the absence of a field.

SHG interferometry experiments were carried out in an effort to gain a further insight into the ferroelectric behavior of the ground state of these materials. A schematic representation of the experiment is shown in Figure 6. Further experimental details can be found in the Supporting Information. The resulting SHG interference fringes are shown in Figure 6b. The different curves were obtained in compound **B2G1-TA-RG1** under electric fields with different polarity (+ open, - solid circles) and after removal of the field (+ open, - solid squares). The electric field was applied perpendicular to the sample



**Figure 6.** (a) Schematic representation of the SHG interferometry experiment. (b) SHG intensity of the interferometric experiment in the same compound under an electric field with different polarity (+ open, - solid circles) and after field removal (+ open, - solid squares). Fringes are in phase after field removal and a phase shift of  $\pi$  is observed when the polarity is inverted. Lines connecting points are to guide the eye.

substrate. The results shown in Figure 6b can be interpreted as follows: If full circles (squares) represent  $|E_1^{2\omega} + E_2^{2\omega}|^2$  then open circles (squares) represent  $|E_1^{2\omega} - E_2^{2\omega}|^2$ . In other words, a phase shift of  $\pi$  in the SHG field generated by the sample is observed after inverting the polarity, which indicates that the ferroelectric state is fully switched by the field. Furthermore, because a shift in the fringes was not observed on removing the field, the bistability of the material is again confirmed. Therefore, the ground state can be classified as SmC<sub>S</sub>P<sub>F</sub>. Similar experiments were carried out on previous chiral bent-core liquid crystals that exhibit ferroelectric smectic phases.<sup>40,41</sup>

### DISCUSSION

As mentioned previously, the Janus-type codendrimers under investigation can be classified into two different families according to their mesogenic behavior. On the one hand, for compounds with a 1:2 bent/rod ratio segregation did not occur between bent- and rod-shaped cores. On the other hand, segregation was observed for the group with a 1:1 bent/rod ratio. This peculiar behavior can be explained in terms of the different effective cross sections that the cores present. First, we will assume that a rod-like core has a similar transverse area to the lateral structures (arms) of a bent-shaped molecule. However, it is clear that for the geometry of a bent-core smectic material the arms are tilted with respect to the layer normal even in the absence of a molecular tilt. This arrangement increases the effective cross-section of the arm, as depicted in Figure 7a. The enhancement is given by a factor  $1/\cos\phi$ , where  $\phi$  is the angle of the molecular segment with respect to the smectic layer normal. This angle is related to the molecular tilt  $\theta$  according to  $\cos\phi = \cos\theta \sin(\gamma/2)$ , where  $\gamma$  is the bend angle (about 120°). For typical values of  $\theta$  and  $\gamma$ , the effective area becomes enlarged by a factor close to 2. In this case the difference between the in-plane areas per molecular moiety could give rise to conflict when accommodating the different cores in the mesophase. In the case of the 1:2 bent/ rod ratio, the cross-section of the bent cores, which in principle is smaller, can be increased to match that of the rod-like cores simply by means of a suitable molecular tilt. Once the molecule is tilted, both bent-shaped and rod-shaped core groups will have the same cross section and these would be be indistinguishable when packed within the layers - a situation that does not give rise to core segregation (see Figure 7b). In contrast, in the case of the 1:1 bent/rod ratio, the cross-section of the bent-core part is inevitably higher due to the molecular bend. This undesirable situation can be resolved if core segregation is assumed. The



Figure 7. (a) Schematic comparison between the effective crosssection of a rod-like core and the lateral part (arm) of a bent-shaped molecule. (b) Smectic layer of a compound with a 1:2 bent/rod ratio in which the matching of the in-layer areas is represented schematically. (c) The same scheme for a codendrimer with 2 rodlike molecules and 2 bent-core molecules (1:1 bent/rod ratio). In this case, segregation of rod and bent cores takes place and the rods become interdigitated.

proposed model implies that rod-like structures of different codendrimers interdigitate and form a sublayer, whereas bentcore molecules are suitably tilted to match the cross section of the rodlike units (see Figure 7c). In both families of compounds, the required tilts of the bent cores are compatible with the layer spacings measured by XRD.

An apparent exception to this general behavior is the structure proposed for B2G1-TA-RG2 (Figure 3e), where there is core segregation for a 1:2 bent/rod ratio compound. However, arguments based on the calculation of the mass density of the material allow us to rule out this possibility. The density of the structure is given by  $\rho = (2M)/(cA)$ , where M is the molecular mass and A is the transverse area of 4 calamitic segments  $(A = 4\pi (d/2)^2)$ . If we take d = 4.6 Å, the well-known typical diameter of a calamitic molecule, and c = 134 Å, we obtain  $\rho = 1.58$  g/cm<sup>3</sup>, which is rather high for a purely organic liquid crystal. The alternative structure (Figure 3d) is more realistic. In this case,  $\rho = M/(2cA)$  and c = 134/3 Å = 44.7 Å. This gives  $\rho = 1.18 \text{ g/cm}^3$ , which is more in keeping with the expected value (in fact, the same density  $\rho = 1.18 \text{ g/cm}^3$  also results for the structure shown in Figure 4b for a 1:2 bent/rod ratio dendrimer). We can therefore conclude that nanosegregation does not occur in this material.

A very interesting feature of the family with the 1:1 bent/rod ratio is the appearance of true ferroelectricity. There are very few examples of this kind of behavior in bent-core liquid crystals<sup>6b,40-42</sup> and it is even more unusual if the materials are composed of achiral molecules, as in the present case. In the smectic mesophases of bent-core compounds antiferroelectricity is usually favored. However, in the present family of codendrimers the appearance of the rodlike sublayer partially inhibits the interaction between bent-core layers and allows the appearance of ferroelectricity. A similar origin for the ferroelectricity in bent-core compounds attached to bulky oligosiloxane units has been proposed.<sup>41b</sup> In those cases, it is

the siloxane groups that are assumed to decouple the bent-core molecular layers and prevent the appearance of antiferroelectricity.

#### CONCLUSIONS

A variety of liquid crystalline phases can be formed by first- or second-generation Janus-type codendrimers that combine bentshaped and rodlike units. Depending on the bent/rod-core ratio, the mesophases obtained are different as a result of different supamolecular segregation processes that can be attributed to the difference in the cross sections of the rod- and bent-shaped cores. In the compounds with a 1:2 bent/rod ratio, nematic phases have been found in two cases but a third codendrimer, with larger promesogenic units, is able to induce an antiferroelectric smectic phase. In this kind of codendrimer, the rod and bent cores do not segregate. In contrast, compounds with a 1:1 ratio exhibited well-defined SmCP phases in all cases, with the bent- and rod-shaped cores separated in different sublayers. Remarkably, in compounds with a 1:1 ratio this difference also gives rise to intrinsically bistable ferroelectric phases  $(SmC_SP_F)$ .

The preparation of low-generation Janus-type codendrimers based on bent-core moieties is a very interesting synthetic strategy to control the nanosegregation and polar organization of bent-core units and to combine such attractive promesogenic structures with different promesogenic cores or with even more varied functional structures. This approach can lead to ferroelectric liquid crystals, interestingly in the absence of electric fields, and has great potential as a route to a variety of multifunctional materials. This kind of material opens new and stimulating possibilities for both bent-core-based and dendritic supramolecular materials. Such materials have rarely been reported in the literature and are of interest in basic and applied supramolecular chemistry, materials science and technological scenarios.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

Experimental section: Synthesis of the compounds. DSC and X-ray data for the dendrons derived from calamitic units. DSC diagrams and POM for codendrimers, and polarization switching current curves of representative dendrons and codendrimers. This information is available free of charge via the Internet at http://pubs.acs.org/.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*Tel.: +34 976762277. E-mail: bros@unizar.es.

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

The authors greatly appreciate financial support from the Spanish Government (MICINN-FEDER projects MAT2009-14636-C03) and the Aragón-FSE (project E04) and Basque (project GIC10/45) Governments. The authors are also grateful to Juan de la Cierva-MICINN, JAE-DOC-CSIC (N.G.), to the BSCH-UZ and Aragón Government (project E04) (J.V.) and Aragón Government (M.C.) fellowship programs for support. S.R.C. and G.S.E. thank the MEC of Spain and the Basque Government for grants. Thanks are given to Nuclear Magnetic Resonance, Mass Spectra and Thermal

Analysis Services from the Instituto de Ciencia de Materiales de Aragón (ICMA), Universidad de Zaragoza-CSIC (Spain).

#### REFERENCES

(1) (a) Chem. Soc. Rev. 2007, 36, 125–440. (b) Steed, J. W.; Atwood, J. L. In Supramolecular Chemistry; John Wiley and Sons: Chichester, U.K., 2009.

(2) Proc. Natl. Acd. Sci. U.S.A. 2005, 102, 8800; Chem. Soc. 2010, 110.
(3) (a) Pena dos Santos, E.; Santilli, C. V.; Pulcinelli, S. H.; Prouzet, E. Chem. Mater. 2004, 16, 4187. (b) Aldred, M. P.; Eastwood, A. J.; Kelly, S. M.; Vlachos, P.; Contoret, A. E. A.; Farrar, S. R.; Mansoor, B.; O'Neill, M.; Tsoi, W. C. Chem. Mater. 2004, 16, 4928. (c) DePierro, M. A.; Carpenter, K. G.; Guymon, C. A. Chem. Mater. 2006, 18, 5609. (d) Woon, K. L.; Aldred, M. P.; Vlachos, P.; Mehl, G. H.; Stirner, T.; Kelly, S. M.; O'Neill, M. Chem. Mater. 2006, 18, 2311. (e) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hagele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. Angew.Chem., Int. Ed. 2007, 46, 4832. (f) Kaafarani, B. R. Chem. Mater. 2011, 23, 378.

(4) (a) Pelzl, G.; Diele, S.; Weissflog, W. Adv. Mater. 1999, 11, 707.
(b) Tschierske, C.; Dantlgraber, G. Pramana. J. Phys. 2003, 61, 455.
(c) Walba, D. M. Top. Stereochem. 2003, 24, 457. (d) Ros, M. B.; Serrano, J. L.; De la Fuente, M. R.; Folcia, C. L. J. Mater. Chem. 2005, 15, 5093. (e) Reddy, R. A.; Tschierske, C. J. Mater. Chem. 2006, 16, 907. (f) Takezoe, H.; Takanishi, Y. Jpn. J. Appl. Phys. 2006, 45, 597.
(g) Weissflog, W.; Sheenivasa Murthy, H. N.; Diele, S.; Pelzl, G. Phil. Trans. R. Soc. A 2006, 364, 2657. (h) Folcia, C. L.; Alonso, I.; Ortega, J.; Etxebarria, J.; Pintre, I.; Ros, M. B. Chem. Mater. 2006, 18, 4617.
(i) Pelzl, G.; Weissflog, W. In Thermotropic Liquid Crystals. Recent Advances; Ramamoorthy, A., Ed.; Springer: Amsterdam, The Netherlands, 2007; Chapter 1. (j) Zhang, Y.; Baumeister, U.; Tschierske, C.; O'Callaghan, M. J.; Walker, C. Chem. Mater. 2010, 22, 2869.

(5) (a) Jákli, A.; Bailey, C.; Harden, J. in *Thermotropic Liquid Crystals. Recent Advances*; Ramamoorthy, A., Ed.; Springer: Amsterdam, The Netherlands, 2007; Chapter 2. (b) Keith, C.; Dantlgraber, G.; Reddy, R. A.; Baumeister, U.; Tschierske, C. *Chem. Mater.* 2007, *19*, 694. (c) Etxebarria, J.; Ros, M. B. *J. Mater. Chem.* 2008, *18*, 2919. (d) van Le, K.; Araoka, F.; Fodor-Csorba, K.; Ishikawa, K.; Takezoe, H. *Liq. Cryst.* 2009, *36*, 1119. (e) Jákli, A.; Pintre, I. C.; Serrano, J. L.; Ros, M. B.; De La Fuente, M. R. *Adv. Mater.* 2009, *21*, 3784. (f) Pintre, I. C.; Serrano, J. L.; Ros, M. B.; Martínez-Perdiguero, J.; Alonso, I.; Ortega, J.; Folcia, C. L.; Etxebarria, J.; Alicante, R.; Villacampa, B. *J. Mater. Chem.* 2010, *20*, 2965. (g) Harden, J.; Chambers, M.; Verduzco, R.; Luchette, P.; Gleeson, J. T.; Sprunt, S.; Jákli, A. *App. Phys. Lett.* 2010, *96*, 102907.

(6) (a) Dantlgraber, G.; Eremin, A.; Diele, S.; Hauser, A.; Kresse, H.; Pelzl, G.; Tschierske, C. Angew. Chem., Int. Ed. 2002, 41, 2408.
(b) Hough, L. E.; Jung, H. T.; Krüerke, D.; Heberling, M. S.; Nakata, M.; Jones, C. D.; Chen, D.; Link, D. R.; Zasadzinski, J.; Heppke, G.; Rabe, J. P.; Stocker, W.; Körblova, E.; Walba, D. M.; Glaser, M. A.; Clark, N. A. Science 2009, 325, 456. (c) Lagerwall, J. P. F.; Giesselmann, F. ChemPhysChem 2010, 11, 975.

(7) (a) Dantlgraber, G.; Baumeister, U.; Diele, S.; Kresse, H.; Luhmann, B.; Lang, H.; Tschierske, C. J. Am. Chem. Soc. 2002, 124, 14852. (b) Dantlgraber, G.; Diele, S.; Tschierske, C. Chem. Commun. 2002, 2768. (c) Hahn, H.; Keith, C.; Lang, H.; Reddy, R. A.; Tschierske, C. Adv. Mater. 2006, 18, 2629.

(8) Kardas, D.; Prehm, M.; Baumeister, U.; Pociecha, D.; Reddy, R. A.; Mehl, G. H.; Tschierske, C. J. Mater. Chem. **2005**, *15*, 1722.

(9) Keith, C.; Dantlgraber, G.; Reddy, R. A.; Baumeister, U.; Prehm,
M.; Hahn, H.; Lang, H.; Tschierske, C. J. Mater. Chem. 2007, 17, 3796.
(10) Pan, Q. W.; Chen, X. F.; Fan, X. G.; Shen, Z. H.; Zhou, Q. F. J.
Mater. Chem. 2008, 18, 3481.

(11) (a) Pratibha, R.; Madhusudana, N. V.; Sadashiva., B. K. Science
2000, 288, 2184. (b) Schroder, M. W.; Diele, S.; Pelzl, G.; Pancenko, N.; Weissflog, W. Liq. Cryst. 2002, 29, 1039. (c) Majumdar, K. C.; Sinha, R. K.; Chakravorty., S. J. Phys. Chem. Sol. 2009, 70, 1171.
(c) Madhusudana, N. V. Liq. Cryst. 2009, 36, 1173 and references therein..

(12) Gorecka, E.; Cepic, M.; Mieczkowski, J.; Nakata, M.; Takezoe, H.; Zecks., B. *Phys. Rev. E* **2003**, *67*, 061704.

(13) (a) Gorecka, E.; Nakata, M.; Mieczkowski, J.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H.; Eichhorn, S. H.; Swager., T. M. *Phys. Rev. Lett.* **2000**, *85*, 2526. (b) Goc, F.; Selbmann, C.; Rauch, S.; Heppke, G.; Dabrowski, R. *Mol. Cryst. Liq. Cryst.* **2005**, *439*, 147.

(14) (a) Coles, H. J.; Pivnenko, M. N. Nature 2005, 436, 997.
(b) Kitzerow, H. S. ChemPhysChem 2006, 7, 63. (c) Kitzerow, H. S. Ferroelectrics 2010, 395, 66.

(15) (a) Lee, M.; Hur, S.-T.; Higuchi, H.; Song, K.; Choi, S.-W.; Kikuchi., H. J. Mater. Chem. **2010**, 20, 5813. (b) Taushanoff, S.; Van Le, K.; Williams, J.; Twieg, R. T.; Sadashiva, B. K.; Takezoe, H.; Jakli., A. J. Mater. Chem. **2010**, 20, 5893.

(16) (a) Kosata, B.; Tamba, G.-M.; Baumeister, U.; Pelz, K.; Diele, S.; Pelzl, G.; Galli, G.; Samaritani, S.; Agina, E. V.; Boiko, N. I.; Shibaev, V. P.; Weissflog, W. *Chem. Mater.* **2006**, *18*, 691. (b) Stannarius, R.; Heuer, J. *Eur. Phys. J. E* **2007**, *24*, 27. (c) Stannarius, R.; Eremin, A.; Tamba, M.-G.; Pelzl, G.; Weissflog, W. *Phys. Rev. E* **2007**, *76*, 061704. (c) Heuer, J.; Stannarius, R.; Tamba, M.-G.; Weissflog, W. *Phys. Rev. E* **2008**, *77*, 056206. (d) Shanker, G.; Prehm, M.; Tschierske, C. J. *Mater. Chem.* **2012**, *22*, 168. (e) Wang, Y.; Yoon, H. G.; Bisoyi, H. K.; Kumar, S.; Li, Q. J. *Mater. Chem.* **2012**, *22*, 20363.

(17) (a) Yelamaggad, C. V.; Prasad, S. K.; Nair, G. G.; Shashikala, I.; Shankar Rao, D. S.; Lobo, C. V.; Chandrasekhar, S. Angew. Chem., Int. Ed. 2004, 43, 3429. (b) Prasad, S. K.; Nair, G. G.; Shankar Rao, D. S.; Lobo, C. V.; Shashikala, I.; Yelamaggad., C. V. Mol. Cryst. Liq. Cryst. 2005, 437, 211. (c) Yelamaggad, V. C.; Shashikala, I. S.; Liao, G.; Shankar Rao, D. S.; Prasad, S. K.; Li, Q.; Jakli, A. Chem. Mater. 2006, 18, 6100. (d) Yelamaggad, V. C.; Shashikala, I. S.; Li, Q. Chem. Mater. 2007, 19, 6561.

(18) Jakli, A.; Liao, G.; Shashikala, I.; Hiremath, U. S.; Yelamaggad., C. V. *Phys. Rev. E* **2006**, *74*, 041706.

(19) (a) Tamba, M. G.; Kosata, B.; Pelzl, K.; Diele, S.; Pelzl, G.; Vakhovskaya, Z.; Kresse, H.; Weissflog, W. Soft Matter 2006, 2, 60.
(b) Tamba, M. G.; Baumeister, U.; Pelzl, G.; Weissflog, W. Liq. Cryst. 2010, 853.

(20) Recent books and reviews on dendrimers and Janus-dendrimers and references therein: (a) *Dendrimers. Towards Catalytic, Material and Biomedical Uses;* Caminade, A. M., Turrin, C. O., Laurent, R., Ouali, A., and Delavaux-Nicot, B., Eds.; Wiley: New York, 2011. (b) . Nierengarten, J. F.; Holler, M. and Deschenaux, R.Fullerene-Containing Dendrimers: Synthesis and Properties. In *Fullerenes: Principles and Applications*; Langa De La Puente, F., Nierengarten, J.-F., Eds.; RSC Publishing: London, 2012; Chapter 5. (c) Khandare, K.; Calderón, M.; Dagiaa, N. M.; Haag, R. *Chem. Soc. Rev.* **2012**, *41*, 2824. (d) Twibanire, J. K.; Bruce Grindley, T. *Polymers* **2012**, *4*, 794. (e) Walter, M. V.; Malkoch, M. *Chem. Soc. Rev.* **2012**, *41*, 4593. (f) Wang, Y.; Grayson, S. M. *Adv. Drug Delivery Rev.* **2012**, *64*, 852. (g) Caminade, A. M.; Laurent, R.; Delavaux-Nicot, B.; Majoral, J. P. *New. J. Chem.* **2012**, *36*, 217.

(21) (a) Joester, D.; Losson, M.; Pugin, R.; Heinzelmann, H.; Walter, E.; Merkle, H. P.; Diederich, F. Angew. Chem., Int. Ed. 2003, 42, 1486.
(b) Guillot, M.; Eisler, S.; Weller, K.; Merkle, H. P.; Gallani, J.; Diederich, F. Org. Biomol. Chem. 2006, 4, 766. (c) Bury, I.; Donnio, B.; Gallani, J.; Guillon, D. Langmuir 2007, 23, 619. (d) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. Chem. Rev. 2010, 110, 1857. (a) Percec, V.; Wilson, D. A.; Leowanawat, P.; Wilson, C. J.; Hughes, A. D.; Kaucher, M. S.; Hammer, D. A.; Levine, D. H.; Kim, A. J.; Bates, F. S.; Davis, K. P.; Lodge, P. T.; Klein, M. L.; DeVane, R. H.; Aqad, E.; Rosen, B. M.; Argintaru, A. O.; Sienkowska, M. J.; Rissanen, K.; Nummelin, S.; Ropponen, J. Science 2010, 328, 1009.

(22) (a) Lee, C. C.; Gillies, E. R.; Fox, M. E.; Guillaudeu, S. J.; Frechet, J. M. J.; Dy, E. E.; Szoka, F. C. *Proc. Natl. Acad. Sci.* **2006**, *103*, 16649. (b) Gillies, E. R.; Dy, E.; Frechet, J. M. J.; Szoka, F. C. *Mol. Pharm.* **2005**, *2*, 129. (c) Astruc, D. *Chem. Rev.* **2009**, *109*, 6275.

(23) Reviews on liquid crystal dendrimers and references therein : (a) Ponomarenko, S. A.; Boiko, N. I.; Shibaev, V. P. *Polym. Sci., Ser. C* **2001**, 43, 1. (b) Donnio, B.; Guillon, D. *Adv. Polym. Sci.* **2006**, 201, 45. (c) Donnio, B.; Buathong, S.; Bury, I.; Guillon, D. Chem. Soc. Rev. 2007, 36, 1495.
(d) Marcos, M.; Martín-Rapún, R.; Omenat, A.; Serrano, J. L. Chem. Soc. Rev. 2007, 36, 1889.
(e) Deschenaux, R.; Donnio, B.; Guillon, D. New J. Chem. 2007, 31, 1064.
(f) Saez, I. M.; Goodby, J. W. Struct. Bonding (Berlin) 2008, 128, 1.
(g) Rosen, B. M.; Wilson, C. J.; Wilson, D. A.; Peterca, M.; Imam, M. R.; Percec, V. Chem. Rev. 2009, 109, 6275.
(h) Saez, I.; Goodby, J. W.Supramolecular and Dendritic Liquid Crystals. In Supramolecular Soft Matter; John Wiley and Sons: New York, 2011; Chapter 15.

(24) (a) Saez, I.; Goodby., J. W. Chem.—Eur. J. 2003, 9, 4869.
(b) Saez, I.; Goodby., J. W. Chem. Commun. 2003, 1726.

(25) (a) Campidelli, S.; Lenoble, J.; Barberá, J.; Paolucci, F.; Marcaccio, M.; Paolucci, D.; Deschenaux., R. *Macromolecules* **2005**, *38*, 7915–7925. (b) Lenoble, J.; Campidelli, S.; Maringa, N.; Donnio, B.; Guillon, D.; Yevlampieva, N.; Deschenaux, R. *J. Am. Chem. Soc.* **2007**, *129*, 9941. (c) Campidelli, S.; Bourgun, P.; Guintchin, B.; Furrer, J.; Stoeckli-Evans, H.; Saez, I. M.; Goodby, J. W.; Deschenaux, R. *J. Am. Chem. Soc.* **2010**, *132*, 3574.

(26) (a) Choi, J. W.; Ryu, H.; Lee, E.; Cho, B. K. Chem.—Eur. J.
2010, 16, 9006. (b) Choi, J. W.; Choi, B. K. Soft Matter 2011, 7, 4045.
(27) (a) Kouwer, P. H. J.; Mehl., G. H. Angew. Chem., Int. Ed. 2003, 42, 6015. (b) Kouwer, P. H. J.; Mehl., G. H. J. Am. Chem. Soc. 2003, 125, 11172. (c) Kouwer, P. H. J.; Welch, C. J.; McRobbie, G.; Dodds, B. J.; Priest, L.; Mehl, G. H. J. Mater. Chem. 2004, 14, 1798.
(d) Kouwer, P. H. J.; Mehl, G. H. J. Mater. Chem. 2004, 14, 1798.
(e) Kouwer, P. H. J.; Mehl, G. H. J. Mater. Chem. 2004, 16. (e) Kouwer, P. H. J.; Mehl, G. H. J. Mater. Chem. 2009, 19, 1564.
(28) Yamaguchi, A.; Uehara, N.; Yamamoto, J.; Yoshizawa, A. Chem. Mater. 2007, 19, 6445.

(29) (a) Bury, I.; Heinrich, B.; Bourgogne, C.; Guillon, D.; Donnio., B. Chem.—Eur. J. 2006, 12, 8396. (b) Tuutila, T.; Lahtinen, M.; Kuuloja, N.; Huuskonen, J.; Rissanen, K. Thermochim. Acta 2010, 497, 101. (c) Tuutila, T.; Lahtinen, M.; Huuskonen, J.; Rissanen, K. Thermochim. Acta 2010, 497, 109. (g) Bury, I.; Heinrich, B.; Bourgogne, C.; Mehl, G. H.; Guillon, D.; Donnio, B. New J. Chem. 2012, 36, 452.

(30) Vergara, J.; Gimeno, N.; Cano, M.; Barberá, J.; Romero, P.; Serrano, J. L.; Ros, M. B. *Chem. Mater.* **2011**, *23*, 4931 ; wWe have maintained the nomenclature used for the same bent-core structures.. (31) Ihre, H.; Hult, A.; Frechet, J. M. J.; Gitsov, I. *Macromolecules* **1998**, *31*, 4061.

(32) Golas, P. L.; Tsarevsky, N. V.; Sumerlin, B. S.; Matyjaszewski. *Macromolecules* **2006**, *39*, 6451.

(33) Giner, I.; Gascón, I.; Vergara, J.; López, M. C.; Ros, B.; Royo, F. M. Langmuir **2009**, 25, 12332.

(34) del Barrio, J.; Oriol, L.; Sánchez, C.; Serrano, J. L.; Di Cicco, A.; Keller, P.; Li, M.-H. J. Am. Chem. Soc. **2010**, *132*, 3762.

(35) Kardas, D.; Prehm, M.; Baumeister, U.; Pociecha, D.; Reddy, R. A.; Mehl, G. H.; Tschierske, C. J. Mater. Chem. **2005**, *15*, 1722.

(36) Marcos, M.; Omenat, A.; Serrano., J. L. Compt. Rend. Chemie 2003, 6, 947.

(37) All the theoretical molecular lengths were calculated using ACD Labs Chemsketch.

(38) Gorecka, E.; Vaupotič, N.; Pociecha, D. Chem. Mater. 2007, 19, 3027.

(39) (a) Hough, L. E.; Spannuth, M.; Nakata, M.; Coleman, D. A.; Jones, C. D.; Dantlgraber, G.; Tschierske, C.; Watanabe, J.; Körblova, E.; Walba, D. M.; Maclennan, J. E.; Glaser, M. A.; Clark, N. A. *Science* **2009**, 325, 452. (b) Ortega, J.; Folcia, C. L.; Etxebarria, J.; Martínez-Perdiguero, J.; Gallastegui, J. A.; Ferrer, P.; Gimeno, N.; Ros, M. B. *Phys. Rev. E* **2011**, 84, 021707.

(40) (a) Nakata, M.; Link, D. R.; Araoka, F.; Thisayukta, J.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. *Liq. Cryst.* **2001**, 28, 1301. (b) Lee, S. K.; Heo, S.; Lee, J. G.; Kang, K.; Kumazawa, K.; Nishida, K.; Shimbo, Y.; Takanishi, Y.; Watanabe, J.; Doi, T.; Takahashi, T.; Takezoe, H. *J. Am. Chem. Soc.* **2005**, *127*, 11085.

(41) (a) Reddy, R. A.; Sadashiva, B. K. J. Mater. Chem. 2002, 12, 2627. (b) Dantlgraber, G.; Eremin, A.; Diele, S.; Hauser, A.; Kresse, H.; Pelzl, G.; Tschierske, C. Angew. Chem., Int. Ed. 2002, 41, 2408.

#### **Chemistry of Materials**

(42) (a) Park, B.; Kinoshita, Y.; Takezoe, H.; Watanabe, J. Jpn. J. Appl. Phys. 1998, 37, L136. (b) Walba, D. M.; Korblova, E.; Shao, R.; Maclennan, J. E.; Link, D. R.; Glaser, M, A.; Clark, N. A. Science 2000, 288, 2181. (c) Gorecka, E.; Pociecha, D.; Araoka, F.; Link, D. R.; Nakata, M.; Thisayukta, J.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. Phys. Rev. E 2000, 62, R4524. (d) Kresse, H.; Pelzl, G.; Tschierske, C. Angew. Chem., Int. Ed. 2002, 41, 2408. (e) Rauch, S.; Bault, P.; Sawade, G.; Heppke, G. G.; Nair, A. Jakli Phys. Rev. E 2002, 66, 021706. (f) Nishida, K.; Kim, W. J.; Lee, S. K.; Heo, S.; Gun Lee, J.; Kang, K.; Takanishi, Y.; Ishikawa, K.; Watanabe, J.; Takezoe, H. Jpn. J. Appl. Phys. 2006, 45, L329. (g) K. Nishida, M.; Cepic, W. J.; Kim, S. K.; Lee, S.; Heo, H.; Lee, J. G.; Takanishi, Y.; Ishikawa, K.; Kang, K.; Watanabe, J.; Takezoe, H. Phys. Rev. E 2006, 74, 021704. (h) Niigawa, Y.; Nishida, K.; Kim, W. J.; Lee, S. K.; Heo, S.; Lee, J. G.; Araoka, F.; Takanishi, Y.; Ishikawa, K.; Kang, K. T.; Cepic, M.; Takezoe, H. Phys. Rev. E 2007, 76, 031702.