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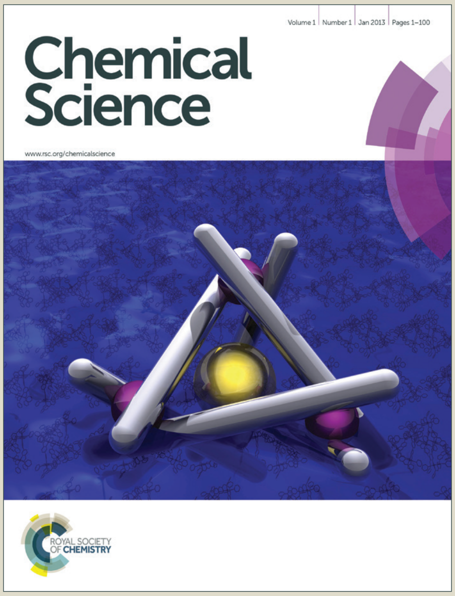

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Ferroelectric and Antiferroelectric Odd-Even Behavior in a Tricarbosilane-Terminated Liquid Crystal Homologous Series

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A new class of polyphilic mesogens composed of a tolanphenyl carboxylate core, a chiral alkoxy tail, and a tricarbosilane terminated alkoxy tail was synthesized, and shown to self-organize into nanophase segregated, smectic liquid crystalline (LC) phases. It was found that the number of carbons in the alkyl spacer between the tricarbosilane and the core controlled the observed phase with perfect fidelity: odd-carbon spacers gave antiferroelectric phases, and even-carbon spacers gave ferroelectric phases. Even more interestingly, homologues with odd carbon number show the rare and useful chiral orthoconic antiferroelectric SmC_A* phase, where the optic axis tilt alternates from layer to layer between +45° and -45°, making the molecular directors in adjacent layers orthogonal. The even-carbon homologues exhibit the SmC* phase with close to 45° tilt. The findings demonstrate that the supramolecular self-organization of polyphilic mesogens may be controlled by the length of hydrocarbon spacers.

Introduction

Understanding liquid crystal (LC) structure-property relationships, and in particular, how the molecular structures determine the observed LC phases, is of fundamental importance, yet represents a challenge, since very small variations of free energy per molecule can have a dominating effect on the collective free energy of the supramolecular self-organization. In this regard, nanophase segregation is currently under active investigation as an important contributor to LC phase energetics and structure.[1] In this context, nanophase segregation occurs when the mesogen structure incorporates certain "polyphilic"[1a,2] moieties in addition to the traditional aromatic/aliphatic units. Such polyphilic mesogens have been shown to provide novel and complex self-organized structures,[1i, 2b] and in some cases allow dramatic tailoring of phase properties.[3,4,5]

In the present case, we focus on the factors driving formation of the ferroelectric (FE) SmC* phase and antiferroelectric (AF) SmC_A* phase from chiral calamitic (composed of rod-shaped molecules) mesogens. As illustrated in **Fig. 1**, the FE SmC* structure has synclinic (molecules in adjacent layers are tilted in the same direction) layer interfaces, while the rare AF[6] structure possesses anticlinic (molecules in adjacent layers are tilted in opposite directions) layer interfaces. Due to the suppression of interlayer fluctuations occurring at the molecular length scale, polyphilic molecules containing fluorinated units are known to provide the SmC_A* phase in calamitics.[5] In bent-core mesogens, where the relationship between clinicity and polarity are reversed relative to calamitics, oligosiloxanes and oligocarbosilanes have been shown to produce the rare synclinic SmC_SP_F[4] and untilted $SmAP_F$ phases.[3f]

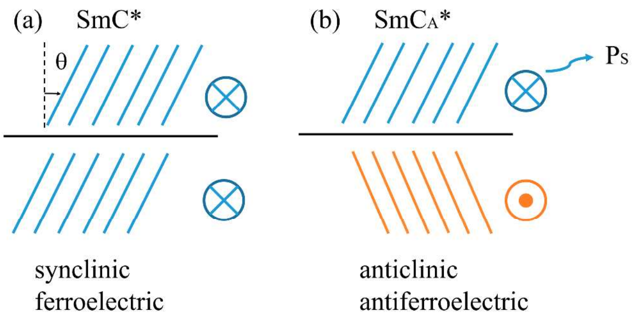


Fig.1 (a) Illustration of the structures of the SmC*; and (b) SmC_A* in the polar smectic phases. A spontaneous polarization is denoted by Ps, and Ps points perpendicular to the plane of the page (cross circle indicates pointing inside; dot circle indicates pointing outside). The layer interface (horizontal line) in the uniformly tilted SmC structure is denoted as synclinic, while the layer interface in the alternately tilted SmC_A* is denoted as anticlinic.

It is reported that an odd-even effect with perfect fidelity for alternating between ferroelectric and antiferroelectric bent-core phases can be obtained adjusting by the polymethylene spacer length between a simple 1-methylethyl terminating group and the aromatic core.[7] This was not considered to be a manifestation of nanophase segregation by the authors of that work, but rather a molecular-level steric interaction occurring at the layer interfaces.

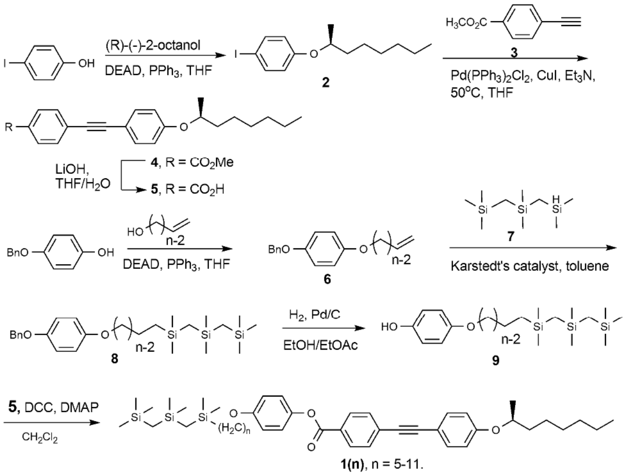
Here, we describe a new calamitic LC system allowing control the synclinic and anticlinic layer interfaces by varying the number of methylene groups between the aromatic core and a tricarbosilane-terminated alkoxy chain. Introducing the tricarbosilane group is expected to suppress the interlayer fluctuations by forming a nanophase segregated tricarbosilane sublayer.[3f] Thus, the LC homologous **1(n) (Scheme 1)**, possessing a mesogenic tolanphenyl carboxylate core, a chiral 1-methylheptyloxy alkyl chain, and a tricarbosilane-terminated alkoxy tail, were synthesized, where **n** is the number of methylene groups between the core and the tricarbosilane moiety. And these homologous exhibit a dramatic odd-even effect, alternating between the chiral ferroelectric SmC* phase with close to 45° tilt, and the rare and potentially useful chiral orthoconic antiferroelectric SmC$_A$* phase. These results are surprising, since isolation of the layers from each other would seemingly make the number of methylenes in the spacer effectively irrelevant as a determinant of layer interface clinicity. Observation of such an effect with perfect fidelity in a nanophase segregated system has not been reported previously, and serves as an interesting data point in understanding of the structure and energetics of nanophase segregated supramolecular self-organizations.

Orthoconic antiferroelectric LCs (OAFLCs), namely 45° tilted antiferroelectrics, not only exhibit the interesting properties of AF LCs for electro-optic applications, such as fast switching, a wide viewing angle, and excellent gray scale, but also provide higher optical contrast due to the unique optical behavior of the dark state.[8] So far, most OAFLCs reported are mixtures comprised of multiple components, and typically require a cell gap of about 1 μm in order to achieve a perfect dark state.[9] LC cells with such small cell gaps are difficult to manufacture, and typically lead to strong surface-stabilization of the field induced ferroelectric state, degrading electro-optic performance. Thus, the development of new room temperature orthoconic mesogens that allow a cell thickness to be 2-3 μm is under active investigation.

Results and discussion

The synthesis of homologues **1(n)** (n = 5 – 11) is showed in Scheme 1. It started with Mitsunobu coupling of 4-iodophenol and (R)-(-)-2-octanol to provide ether **2** with a stereocenter. Subjecting **2** and terminal alkyne **3**[10] under Sonigashira reaction conditions furnished di-substituted alkyne **4**, of which the methyl ester was converted to the corresponding carboxylic acid **5** via saponification. Compound **5** served as the common intermediate for all the homologues **1(n)**. Synthesis of the other fragment of **1(n)** also began with Mitsunobu coupling of the mono-benzyl-protected hydroquinone and the vinyl alcohol with the carbon number **(n)** corresponding for **1(n)** to provide ether **6**. Installing the tricarbosilane functional group onto ether **6** relied on hydrosilylation catalyzed by Karstedt's catalyst in toluene to provide compound **8**. After removing the benzyl protecting group of **8** by hydrogenolysis, the resulting phenol **9** was coupled with carboxylic acid **5** under Steglich esterification reaction conditions to provide **1(n)**.

All new LC materials are characterized by differential scanning calorimetry (DSC), polarized optical microscopy and electro-optics (POM and EO), X-ray diffraction, and depolarized reflected light microscopy on freely suspended thin films (DRLM)[11]. The phase sequences on heating and on cooling, transition temperatures, and clearing enthalpies are summarized in **Table 1**. As indicated, all **1(n)** show enantiotropic smectic phases over a broad temperature range including room temperature. There is, however, no clear trend, or odd-even effect in the clearing points or clearing enthalpies. However, mesogens **1** do show a striking odd-even effect with remarkable fidelity: All n = odd members of the series exhibit the 45° (± 2°) orthoconic AF LC phase, while all n = even members exhibit ferroelectric SmC* phases with close to 45° tilt. Only one LC phase is observed for each compound. There are some unidentified phases (denoted as X in **Table 1**) at temperatures below the smectic phases (see DSC curves in Supporting Information, **Fig. S1**). These are likely crystal phases, or partially crystallized glasses at low temperatures. The temperature dependence of spontaneous polarization in this series of mesogens is shown in **Fig. S2**. The values of spontaneous polarization of these mesogens are between 47 and 59 nC/cm^2. There are no significant fluctuations in the values of spontaneous polarization as the temperature changes for the whole series.



Scheme 1. Synthesis of tricarbosilane-terminated **1(n)**.

Table 1. Phase sequence and transition temperatures, and clearing enthalpy of **1(n)** from a combination of DSC, XRD, POM, EO and DRLM data.

n	phases, transition temperatures (°C), and enthalpies (kJ mol^{-1}) in parentheses[a]
5	X 7.7 → SmC$_A$* 54.5 (4.1) → Iso X ← 0.86-SmC$_A$* ← 53.6-Iso
6	X 2.87 → SmC* 54.1 (4.3) → Iso X ← -1.61-SmC* ← 53.81-Iso
7	X 12.2 → SmC$_A$* 67.7 (4.7) → Iso X ← 11.5-SmC$_A$* ← 66.9-Iso
8	X 12.9 → SmC* 71.5 (5.3) → Iso X ← 12.4-SmC* ← 70.8-Iso
9	X 12.6 → SmC$_A$* 74.1 (5.7) → Iso X ← 12.3-SmC$_A$* ← 72.7-Iso
10	X 15.1 → SmC* 74.1 (4.2) → Iso X ← 11.7-SmC* ← 73.4-Iso
11	X 13.8 → SmC$_A$* 79.8 (6.3) → Iso X ← 13.5-SmC$_A$* ← 79.3-Iso

[a] X, SmC*, SmC$_A$*, and Iso denote unidentified phases, ferroelectric, antiferroelectric, and isotropic phases, respectively.

In LC cells composed of glass substrates spin-coated with a thin film of elvamide nylon, and one surface mechanically rubbed, the odd number homologues of the series exhibit typical, unique EO behavior of OAFLCs, due to surface-stabilized parallel alignment.[12] Without an applied electrical field, an almost perfectly black dark state observed by POM between crossed polarizer and analyzer in cells less than 3 μm thick (**Fig. 2a**), as expected for a typical OAFLC phase with close to 45° tilt. Application of an electric field causes soliton-wave mediated switching[6a] to the ferroelectric state with the expected bright birefringence color, which is attributed to the EO switching from SmC$_A$* to SmC* (**Fig. 2b**). In thicker cells (~ 3.5 μm), there is observable texture in the dark state (see SI, **Fig. S3**). For all the odd number homologues, the surface stabilized orthoconic texture can be obtained in cells up to 3 μm thick, which are considerably larger than cells of most OAFLCs composed of multi-components.[5,9] In contrast, all homologues with an even number of methylene units exhibit the synclinic SmC* ferroelectric phase with nominal domain-wall mediated,[13] FFLC electro-optics in parallel aligned cells, as shown in **Fig. 2c**.

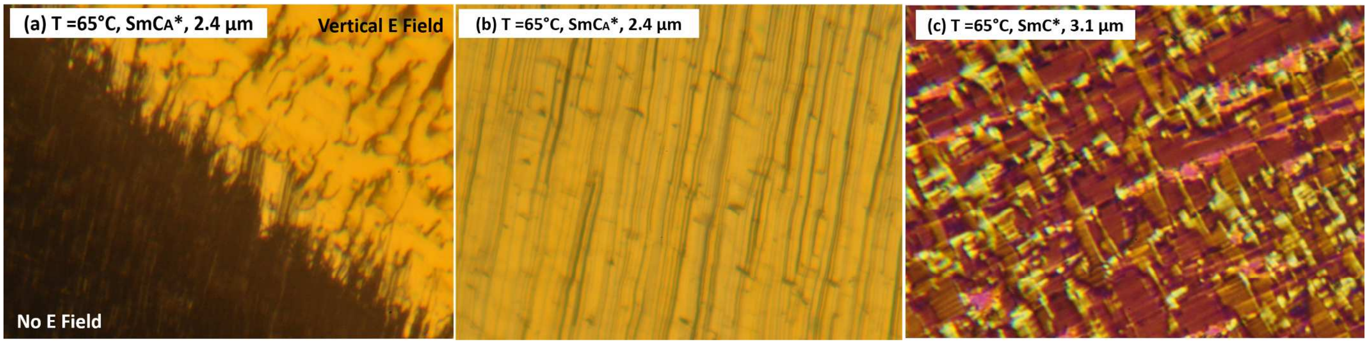


Fig. 2 (a) An electric field (+5 V/μm) was applied to the sample **1(11)** at 65 °C in a 2.4 μm-thick cell. A dark state can be seen on the left, off the electrode with no applied field, and on the right the bright birefringence was shown over the ITO-coated area. (b) The photomicrograph showing the soliton-wave mediated switching behavior of **1(11)** from SmC$_A$* to SmC* under the application of an electric field. (c) The photomicrograph showing domain-wall mediated behavior under application of an electric field +0.5 V/μm to a 3.1 μm-thick cell of **1(8)** at 65 °C.

In ~ 4 μm-thick commercial homeotropic cells, odd and even homologues of the series also exhibit totally different behavior. All homologues exhibit focal conic textures when cooling from the isotropic phase to the dark state. But, the odd number antiferroelectric homologues show an interesting dynamic texture not exhibited by the even homologues while evolving from the focal conic to the dark texture (see SI, **Videos**). It is proposed that this dynamic texture results from the helix pitch in the orthoconic phase changing with the temperature.

The ferroelectric and antiferroelectric assignments for all of the homologues of **1(n)** are fully confirmed by DRLM. This experiment involves application of electric fields parallel to the layers in freely-suspended films with a small integer number of smectic layers, and observation of the response of the samples by DRLM. **Fig. 3a** shows DRLM accomplished on **1(11)**. Regions with an even number of layers have a longitudinal polarization parallel to the tilt plane, while regions with odd number of layers possess a transverse polarization normal to the tilt plane. This behavior is characteristic of the SmC$_A$* phase. In **Fig. 3b**, A freely suspended thin film sample of even homologue **1(10)** shows domains with layer numbers determined to be 3, 4, 6 and 7 by laser reflectivity measurements. All regions appear to be bright when the analyzer is decrossed away from the electric field. Therefore, the mesogen in these layers must have a transverse polarization. Because regions of either odd or even numbers of smectic layers all have transverse polarizations, **1(10)** is identified to be a ferroelectric smectic phase (SmC*).

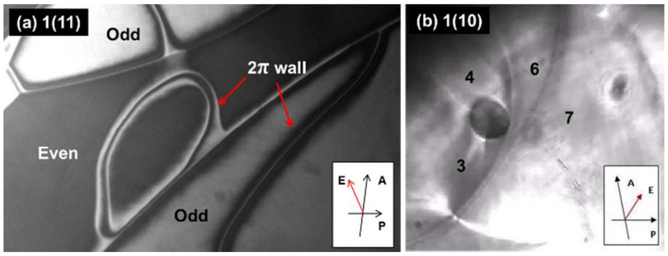


Fig. 3 Typical inhomogeneous films of **1(11)** and **1(10)** in an applied electric field viewed between decrossed polarizers.

X-ray diffraction experiments[14] in **Fig. 4** confirm the presence of a relatively well-defined smectic layer structure by observation of a clear second harmonic peak of the smectic layer reflection.[15] Harmonics of the layer reflection are either absent or, down three or four orders of magnitude in intensity from the first-order peak in conventional smectic LCs.[1b,15] In our cases, the ratios of the peak intensity of the second harmonic to that of the first order peak for **1(11)** and **1(10)** are almost the same (about 1%) (**Fig. 4S**). The observation of the same ratios of the second-harmonic peak intensity to the first-order one for **1(11)** and **1(10)** is consistent with interlayer nanophase segregation of the tricarbosilane units, which might contribute to the suppression of interlayer fluctuations in both ferroelectric and antiferroelectric phases. The temperature dependence of the layer thickness in this series of homologues (**Fig. 5**) was studied by synchrotron X-ray diffraction experiments. Overall, there is a remarkable dependence of the layer thickness on the length of the spacer unit. Upon a decrease in the spacer length, the layer thickness decreases from d = 4.0 nm (n = 11) to d = 3.3 nm (n = 5). The layer thickness, for example d ~ 4 nm for compound **1(11),** is always significantly smaller than the fully extended molecular length estimated from the "long" conformational local minima in gas phase. For **1(11)** the fully extended molecular length is about 5 nm,[16] which is in line with a strongly tilted arrangement of the molecules with an optic axis tilt close to 45°. For in-depth discussion, as the number of alkyl chain spacer decreases, there seems to be almost no change in the layer thickness from odd number to even number (from **1(11)** to **1(10)** and from **1(7)** to **1(6)**), but a big jump from even number to odd number (from **1(10)** to **1(9)** and from **1(6)** to **1(5)**). Similar observations of odd-even effect in layer thickness have been reported in bent-core LCs.[4b,7] In our case, as shown in **Fig. 6** which is discussed in more details later, the layer thickness is determined by the combined lengths of the aliphatic spacer, aromatic core, and the tricarbosilane unit. As for the homologues with varying the number of the spacer unit, there are many factors that could contribute to the layer thickness, such as the accommodation of the alkyl spacer between the aromatic core and the tricarbosilane unit to the terminal chiral alkyl chains, small variations in the tilt of the aromatic cores, the degree of interdigitation of the tricarbosilane units, and the direction of the tricarbosilane units. Therefore, the layer thickness is a subtle function of chemical structures, conformations, tilt angles, and so on, and is difficult to interpret at the molecular level.

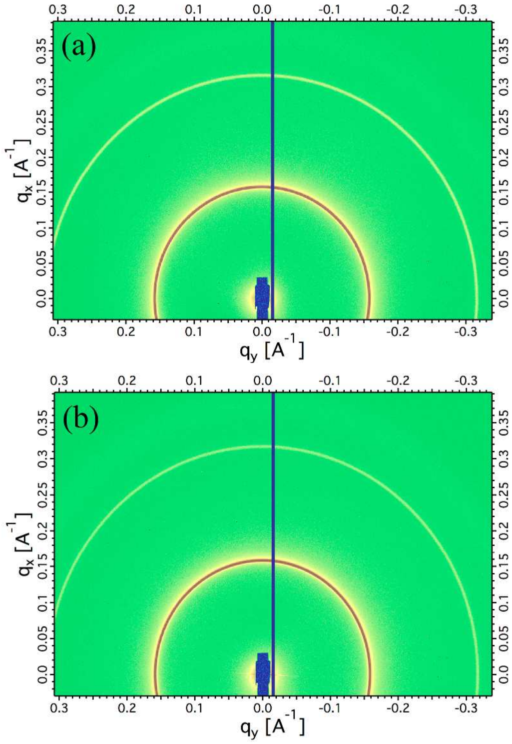


Fig. 4 X-ray diffraction patterns obtained from powder samples of **1(11)** at 45 °C (a) and **1(10)** at 44 °C (b). The red reflection (q = 0.16 A^{-1}) shown is the first-order smectic peak for the mesophases of **1(11)** and **1(10)**. The light yellow reflection (q = 0.32 A^{-1}) observed is the second harmonic peak from smectic layers for the mesophases of **1(11)** and **1(10)**.

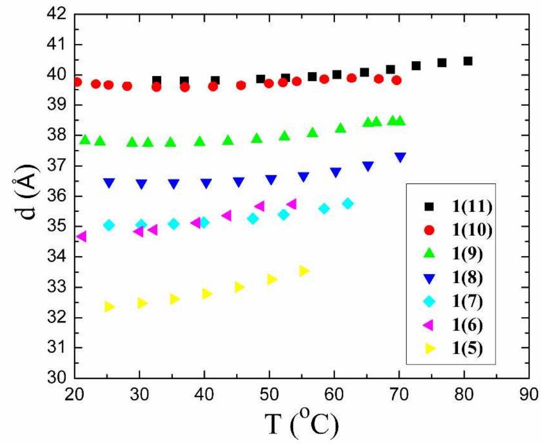


Fig. 5 X-ray measurements of layer thickness of all mesogens **1(n)** of the series, denoted by d, as a function of T.

The antiferroelectric and ferroelectric phases appear alternatively when the number of methylene groups between the aromatic core and terminating tricarbosilane group is odd and even, respectively. This unexpected and interesting odd-even effect prompts speculation regarding a mechanism explaining these results. As illustrated in **Fig. 6**, we first assume that the tricarbosilane moieties build up their own nanophase segregated sublayers at the smectic layer interfaces.[17] The current working hypothesis for the origins of the odd-even effect is described as follows. First, the tricarbosilane units in the silane sublayer are in an all-anti, elongated conformation, and more or less parallel to each other. If the "nematic director" of the tricarbosilane sublayer is oriented more or less parallel to the axis of the aromatic cores, synclinic layer interfaces are expected (**Fig. 6a**). If the "nematic director" in the tricarbosilane sublayer is normal to the layer interfaces, making a large angle with respect to the axis of the aromatic cores, then anticlinic layer interfaces would be possible, though not necessary, as illustrated in **Fig. 6b**.

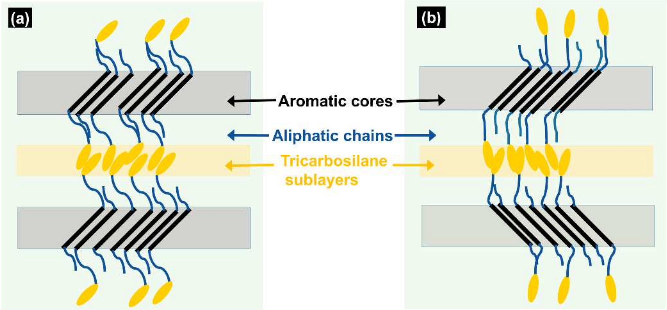


Fig. 6 Proposed model of the organization of **1(n)** when n is even number (a) and when n is odd number (b) in the triply segregated smectic layer.

This model then requires that the orientation of tricarbosilane units in their sublayers must be controlled to some extent by the number of methylene groups in the alkyl spacers. In order to gain some insights into the odd-even behavior, conformational analysis on single molecules in the gas phase was conducted. It was found that the orientation of the tricarbosilane units relative to the core axis changes depending upon the presence of odd or even carbon numbers in the alkyl spacer. For an all-anti chain, the odd carbon homologues have the tricarbosilane unit almost parallel to the core, and even carbon spacer chains have the carbosilane making a large angle with respect to the core axis. This result is inconsistent with the experimental observations. However, adding a guache bend at the C1-C2 bond in the alkoxy tail flips the relative orientation of the carbosilane unit relative to the core for odd and even spacers, as shown in **Fig. 7** (red circles).[16] We have used this kind of gauche bend to interpret the sign and rough magnitude of the ferroelectric polarization of SmC* materials containing a 1-methylheptyoxy chiral tail,[18] and suggest the same conformational preference is occurring in the present case. Gauche conformers of an unsubstituted n-alkyl chain have also been reported previously in the liquid crystal state of a macrocyclic phosphate.[19]

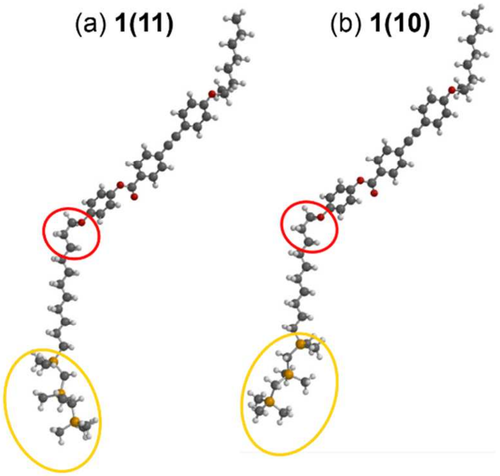


Fig. 7 One conformer of **1(11)** (a) and **1(10)** (b) for illustration of the models in Fig 6.

Conclusion

In conclusion, a new homologous series of smectic mesogens **1(n)**, possessing a tolanphenyl carboxylate core, a chiral alkoxy chain, and a tricarbosilane-terminated achiral alkoxy chain is reported. The phases obtained for mesogens **1(n)** have been identified unequivocally by POM and electro-optics, DRLM, and X-ray diffraction. It is found that an odd-even behavior with perfect fidelity for the alternative appearance of ferroelectric and antiferroelectric LC phases occurs. Also, all odd mesogens exhibit the rare and useful orthoconic antiferroelectric LC phase. Thus, the hydrocarbon spacer separating nanophase segregated tricarbosilane sublayers from the aromatic core controls the clinicity of the layer interfaces. Further investigation of such odd-even behavior in a variety of tricarbosilane-terminated mesogens is currently under way in our group. The strategy of using segregation of aliphatic chains and polyphilic moieties, such as tricarbosilane units, to control the supramolecular self-assembly can guide new molecular design leading to self-organizations exhibiting desired properties in bulk. These findings may provide an approach for dramatic control of supramolecular structure by simply varying the lengths of alkyl chains.

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Notes and references

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D.M.W. and N.A.C. directed the project. N.H. and D.M.W. designed the experiments, analyzed the data, and wrote the paper. N.H. discovered the odd-even behavior, synthesized, and characterized all the compounds. R.S. and N.H. did the POM and EO characterization. Y.S and C.Z.did the XRD measurements. C.Z. and C. P. did the DRLM experiments. E.K., C.G. and J.R. synthesized the first batches of **1(11)**. A. H. designed the beam line of 2D-XRD measurements.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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