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Articles

Highly Ordered Smectic Phases from Polar Calix[4]arene Derivatives

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A novel series of highly luminescent end-functionalized tetra-oligophenylene substituted calix[4]-arenes have been synthesized by palladium-catalyzed Suzuki cross-coupling of arylboronic acid and tetraiodocalix-[4]arene as a key step. It is important to find that liquid crystallinity can easy be induced by introducing the polarity or enhancing the polarizability of the three-dimensional phenylene-substituted calix[4]arene rigid segment. In contrast to the classical one-dimensional 4-cyano-4′-alkoxybiphenyl mesogens, which exhibit nematic and/or smectic A phases, cyano-phenyl-calix[4]arene and methyl-biphenyl-calix[4]arene derivatives exhibit highly ordered smectic supramolecular organization as evidenced by the polarized optical microscopy and X-ray diffraction studies. On the basis of the results of X-ray diffraction, an interdigitated antiparallel packing mode is proposed for the ordered smectic mesophase. The presence of the strong dipoles in the rigid calixarene segments not only facilitates and stabilizes the formation of the highly ordered lamellar smectic structure but also enhances the optical properties of calix[4]arene derivatives. Our findings provide a new guideline to design interesting three-dimensional luminescent mesogenic materials.

Introduction

Liquid crystals, a condensed state of soft matter possessing unique functional and physical properties due to the anisotropic geometry of molecules, have already found practical uses in flat-panel displays technology, light modulators and gates for photonics, soaps and detergents, high yield strength polymers, artificial muscle, and drug delivery systems. More recently, their applications in light emitting diodes,[1] photovoltaic cells,[2] and field effect transistors[3] have also been explored. Structure−functional property correlations of rod-like (one-dimensional) mesogens have been very well established over the past several decades.[4] Even though numerous nonconventional mesophase morphologies have been realized either by controlling the molecular topology or by tailoring the shape of rigid segments and changing the volume fractions of the incompatible segments,[5] the guidelines for designing higher dimensional mesogens, particularly three-dimensional mesogens, are still scarce. This knowledge would be important and useful for the discovery of new mesophases and for the synthesis of new materials with novel properties.

Calix[4]arene has been extensively used as molecular scaffolds in the design of supramolecular guest−host systems[6] and in the construction of novel molecular architectures[7] because of its tunable and unique three-dimensional

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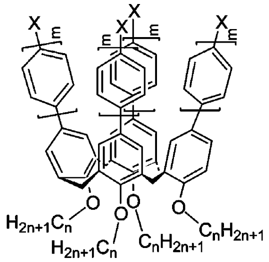
structures together with the ease of functionalizations. Recently, it has also been used as a building block for liquid crystalline materials.[8] Shinkai and Swager independently demonstrated the use of cone-shaped calix[4]arene skeleton as a rigid core with flexible alkyl chains incorporated at the upper rim to induce the bowlic (columnar) liquid crystal phase.[9] Recently, the extended styrylstyrylcalix[4]arene skeleton has also been used as a rigid core to form a new liquid crystalline material when attached with long alkyl chains at the upper rim.[7c] On the other hand, the oligophenylenecalix[4]arene skeleton, which is photochemically and thermally stable, has never been used as a three-dimensional rigid segment for LC formation. By altering the length of the rigid segments of phenylenecalix[4]arene or modifying the polarity or polarizability of the rigid segments or changing the length of the alkoxy groups at the lower rim, unusually highly ordered smectic (Sm) supramolecular organization was obtained from a novel series of cone-conformed end-functionalized oligophenylene (OPP)-substituted calix[4]-arenes, C_n-Calix-OPP(*m*)-X. In contrast to the corresponding monomers, they could only exhibit nematic and/or less ordered smectic A phases. We present herein the synthesis of a novel series of end-functionalized OPP-substituted calix[4]-arenes and the investigation of the structure factor(s) that are useful to enhance the formation of ordered LC phases of oligophenylenecalix[4]arene derivatives. To modify the polarity or polarizability of the rigid oligophenylenecalix[4]arene cores, we incorporated various electron-donating or electron-withdrawing groups, which include fluoro, cyano, methyl, hexylsulfanyl, and hexylsulfonyl as end-substituents. It is important to find that these end-substituents play an important role in the exhibition of LC phases.



C_n-Calix-OPP(m)-X
m = 1, X = H, F, CN, CH_3, SC_6H_{13}, $SO_2C_6H_{13}$
m = 2, X = CH_3

Results and Discussion

Synthesis. The synthesis of end-functionalized OPP-substituted calix[4]-arene derivatives, C_n-Calix-OPP(*m*)-X is summarized in Scheme 1. The tetra-oligophenylene skeleton was constructed by a convergent approach using palladium-catalyzed Suzuki cross-coupling of arylboronic acid and tetraiodocalix[4]arene as a key step.[7d,f] Removal of *tert*-butyl groups from readily available *p*-*tert*-butylcalix[4]arene **1** in the presence of phenol and $AlCl_3$ as a catalysis afforded calix[4]arene **2**, which was then alkylated to the exclusive cone-conformed tetraalkylated calix[4]arene by means of NaH in DMF because of the chelation effect.[10] Iodination of the corresponding tetraalkylated calix[4]arene with silver trifluoroacetate and I_2 in chloroform gave tetraiodocalix[4]-arenes **3a**−**i**. Palladium-catalyzed Suzuki cross-coupling of tetraiodocalix[4]arenes **3a**−**i** with various arylboronic acid, which was generally prepared by lithium−bromide exchange of the corresponding aryl bromide, followed by reaction with trimethyl borate and subsequently acid hydrolysis, afforded the corresponding C_n-Calix-OPP(*m*)-X in moderate to good yields. All of the newly synthesized OPP-substituted calix-[4]arenes were fully characterized by ^{1}H NMR, ^{13}C NMR, and low/high-resolution mass spectroscopy and found to be in good agreement with the expected structures. For those end-functionalized OPP-calix[4]arene derivatives that exhibit LC properties, their corresponding biphenyl monomers were also synthesized using the same approach for comparison.

Mesogenic Properties. The thermal behavior of various aryl-calix[4]arenes, C_{10}-Calix-OPP(1)-X, where X = H, F, Me, CN, SC_6H_{12}, and $SO_2C_6H_{12}$, was initially studied by differential scanning calorimetry (DSC). It was interesting to find that only C_{10}-Calix-OPP(1)-CN showed an enantiotropic mesophase, indicating the importance of polarity or polarizability of the three-dimensional rigid phenyl-calix[4]-arene segment. To understand and characterize the structure−property correlations of this mesophase in detail, a series of C_n-Calix-OPP(1)-CNs where $n = 8-16$ by varying the length of the alkyoxy chains at the lower rim of calix[4]arene were prepared accordingly as shown in Scheme 1.

All of the cyano-end functionalized phenyl-calix[4]arenes exhibited typical thermotropic LC phase transitions, mainly exhibiting two endothermic peaks on the heating cycle and two corresponding exothermic peaks on the cooling cycle, with the exception of C_8-Calix-OPP(1)-CN, which only gave crystalline phase. In addition, C_{12}-Calix-OPP(1)-CN and C_{13}-Calix-OPP(1)-CN showed additional subtle phase transitions within the LC temperature range (Table 1).

The optical textures of C_n-Calix-OPP(1)-CN were examined by the polarized optical microscopy (POM), and they generally exhibited typical fanlike or mosaic texture, which suggest the ordered smectic mesophases.[11] Several representative POM textures of C_n-Calix-OPP(1)-CN are shown in Figure 1. Furthermore, the coexistence of the homeotropic dark areas was often observed, which implies the perpendicular orientation of molecules to the layer plane. With an extension of the alkoxy tails at the lower rim such as going from C_{15}-Calix-OPP(1)-CN to C_{16}-Calix-OPP(1)-CN, grass-like textures that partially developed into organized fanlike textures were observed. Despite very viscous LC states, all

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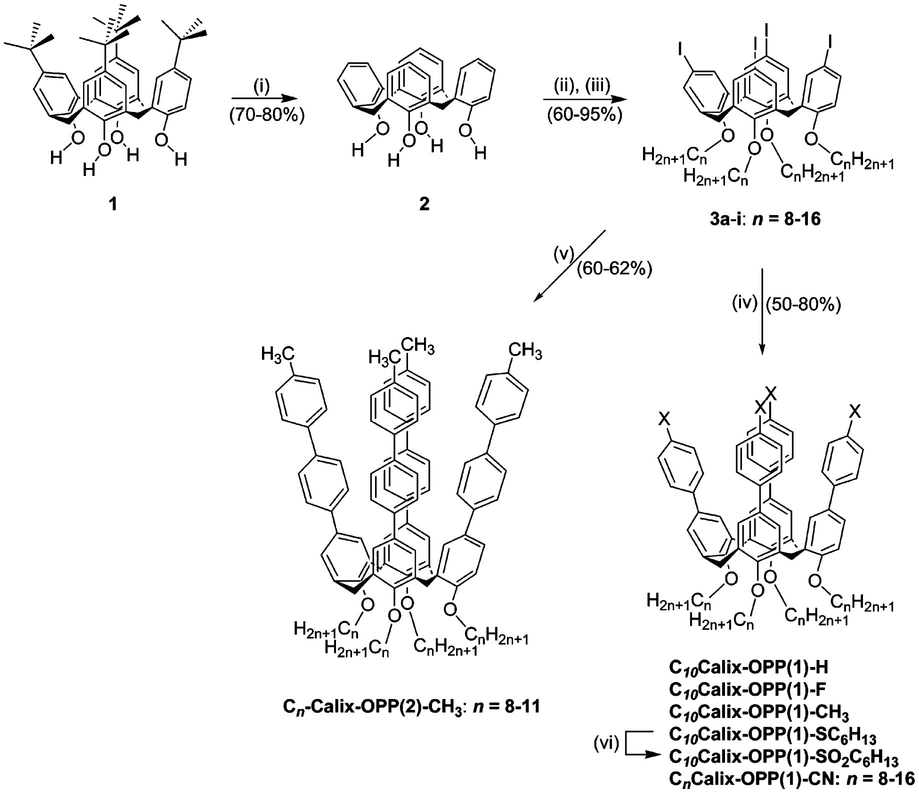
Scheme 1. Synthesis of End-Functionalized OPP-Calix[4]arene Derivatives, C_n-Calix-OPP(m)-X



Conditions and Reagent: (i) phenol, $AlCl_3$, toluene, rt , 3-4 h; (ii) a) NaH, DMF, 0 °C, 1 h, b) C_nH_{2n+1}-Br, 75 °C, overnight; (iii) a) $AgCF_3COO$, $CHCl_3$, 75 °C, 30 min, b) I_2, 75 °C, 2 h; (iv) X-C_6H_4-$B(OH)_2$, $Pd(OAc)_2$/2P(o-tol)$_3$, K_2CO_3, toluene and methanol, 75 °C, overnight, N_2; (v) CH_3-$(C_6H_4)_2$-$B(OH)_2$, $Pd(OAc)_2$/2P(o-tol)$_3$, K_2CO_3, toluene and methanol, 75 °C, overnight, N_2; (vi) *m*CPBA, CH_2Cl_2, rt, 1 h.

Table 1. DSC Thermal Analysis Data for C_n-Calix-OPP(1)-CN (n = 8−16)

n	heating[a]				cooling[a]			
8				224.7 (18.8)				196.4 (−16.3)
9	94.1 (1.54)			216.4 (17.9)	77.7 (−1.18)			200.9 (−17.3)
10	57.2 (5.61)			208.9 (14.6)	25.9 (−7.25)			185.1 (−13.6)
11	59.4 (9.78)			204.6 (12.5)	47.6 (−10.1)			191.4 (−12.5)
12	46.6 (9.32)		107.7 (0.89)	201.2 (12.9)	41.3 (−8.24)		94.6 (−1.11)	188.8 (−12.9)
13	17.8 (6.82)	36.4 (3.92)	109.7 (0.41)	197.3 (13.5)	11.8 (−6.34)	29.0 (−3.59)	107.0 (−0.53)	186.0 (−12.7)
14	28.0 (8.77)			182.0 (6.46)	20.4 (−7.68)			155.3 (−5.45)
15	39.0 (22.7)			179.1 (6.71)	30.2 (−21.5)			165.5 (−6.93)
16	43.9 (23.6)			172.6 (6.23)	35.9 (−22.7)			154.7 (−6.25)

[a] Thermal transition temperature in °C (in parentheses, transition enthalpy in J/g, positive value stands for endothermic, negative value means exothermic); data from the second heating and first cooling cycles.

of the samples could be sheared between the cover glass slides. On the contrary, the corresponding one-dimensional monomeric series, 4-cyano-4′-alkoxybiphenyl, C_n-OPP(2)-CNs where $n = 9-12$ exhibited smectic A phase with typical focal conic textures, and C_9-OPP(2)-CN also exhibited a narrow temperature range (76−78 °C) of nematic phase with schlieren texture (see Supporting Information).

The X-ray diffraction (XRD) measurements of C_n-Calix-OPP(1)-CN with n = 9−16, carried out on the frozen mesophase samples quenched by dry ice, displayed up to six orders of reflections (00n) (Figure 2), which further confirms the formation of the smectic layered structure. The XRD measurements at 160 °C for C_{12}-Calix-OPP(1)-CN and at 130 °C for C_{16}-Calix-OPP(1)-CN showed diffraction patterns and results similar to those obtained from the frozen LC samples (see Supporting Information). More importantly, the intensity ratios of the second and third harmonic to the first (I_{002}/I_{001} and I_{003}/I_{001}) were found to be greater than 10%, which is in sharp contrast to the smectic A phase where the ratio is 2−3 orders of magnitude less. Thus, the smectic layers formed from these cyano-phenyl-calix[4]arene deriva-

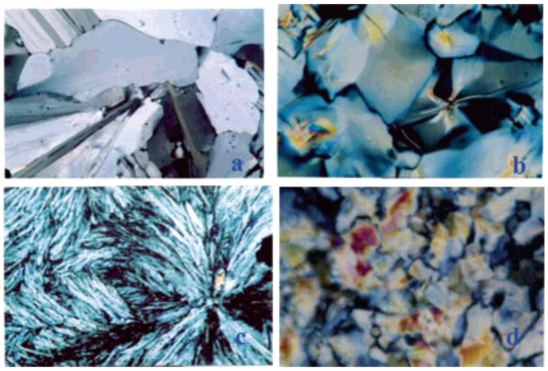


Figure 1. Some representative polarized optical microscope textures (magnification 200×) (a) C_{11}-Calix-OPP(1)-CN at 168 °C, mosaic and lancet texture with some homeotropic area; (b) C_{14}-Calix-OPP(1)-CN at 148 °C, mosaic texture; (c) C_{15}-Calix-OPP(1)-CN at 153 °C, grasslike and fanlike texture; (d) C_9-Calix-OPP(2)-CH_3 at 150 °C, mosaic texture.

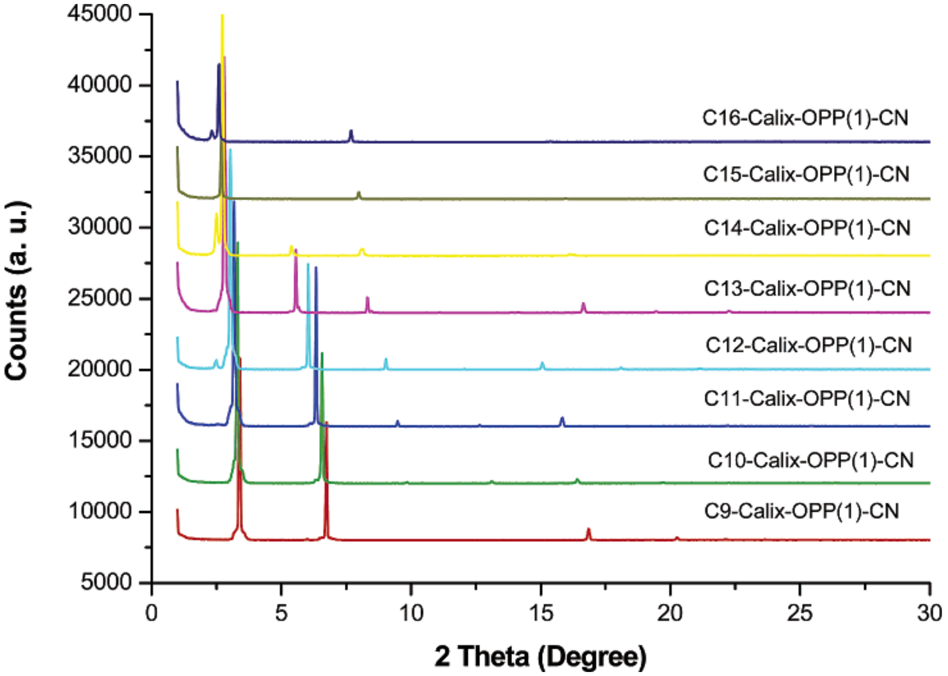


Figure 2. XRD patterns of frozen LC samples of C_n-Calix-OPP(1)-CN with $n = 9-16$ exhibiting multiple higher order reflections in the small angle area.

tives, C_n-Calix-OPP(1)-CNs, are more well-organized and well-defined than smectic A phase formed from the monomeric 4-cyano-4′-alkoxybiphenyl series, reminiscent of the unusual smectic ordering from the long alkoxy-substituted binuclear metallohelicates[12] or the highly ordered smectic phase from guanidium alkanesulfonates.[13] It is interesting to note that, although there is no significant odd−even effect observed in either the melting temperature or the Sm-isotropic phase transition temperature (Table 1), a weak reflection at 2θ of ca. 2.5° for longer even-numbered alkoxy-substituted C_n-Calix-OPP(1)-CN ($n = 12, 14, 16$) in the XRD patterns was found. This may arise from the molecular packing of the alkyl chains within the smectic layers. The CH_2 units at the end of the longer even-numbered alkoxy chains, which are less deviated from the all-trans conformation in the presence of the oxygen atom,[14] may develop partial interdigitated crystal-like order upon cooling[15] and superpose a little longer long-range order on the smectic structure.

It is important to find that similar liquid crystalline phases could also be obtained by elongating the phenylene-calix[4]arene rigid segment without incorporating the polar cyano end-groups. However, among C_n-Calix-OPP(2)-CH_3's where $n = 8-11$ synthesized, only C_9-Calix-OPP(2)-CH_3 and C_{10}-Calix-OPP(2)-CH_3 exhibited mosaic or platelet textures as shown in Figure 1d, implying ordered smectic layered structure, which was further supported by the higher order (00n) reflections on the XRD patterns (see Supporting Information).

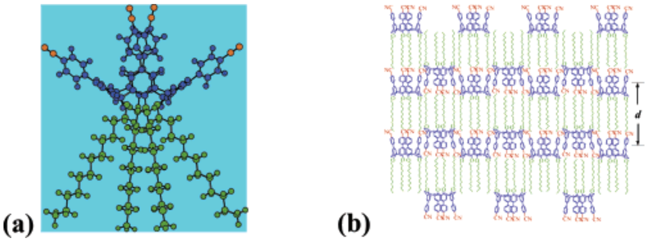


Figure 3. (a) MM2-optimized pinched cone conformation of C_{12}-Calix-OPP(1)-CN; (b) schematic representation of the smectic layered molecular arrangement (dark blue, OPP high electron cloud density layer; green, alkyl low electron cloud density layer; orange, strong dipole −CN).

The period (lattice spacing d) of the lamellar structure of C_n-Calix-OPP(1)-CN ($n = 9-16$) increases linearly with the number of carbon n of the alkoxy tails according to the equation (least-squares fit, $R = 0.99$):

$$d\ (\text{Å}) = [14.72 \pm 0.96] + [1.229 \pm 0.076]n$$

For C_n-Calix-OPP(1)-CN, the lamellar period $d = 1.2-1.3 \times$ the molecular length (L), and for C_n-Calix-OPP(2)-CH_3 homologues, $d = 1.4-1.5 \times L$. Considering the relationship between d and L together with the slope of 1.23 from the d/n equation (very near $2.54/2 = 1.27$ Å for the all-trans alkyl conformation), an interdigitated antiparallel packing arrangement as shown in Figure 3b is proposed for the ordered smectic mesophase. According to the MM2 geometry optimizations, the C_n-Calix-OPP(m)-X derivatives often adopt a pinched cone conformation as shown in Figure 3a, in which two co-facial aryl rings of calix[4]arene arrange in a parallel fashion while the other two lean outward. The pinched cone-conformed mesogens orient alternatively up and down adhered by the $\pi-\pi$ interactions between the arylene segments and by the weak van der Waals interactions among the interdigitated alkyl chains forming a highly ordered two-dimensional layered structure, which thus gives rise to sharp electron cloud density contrast.

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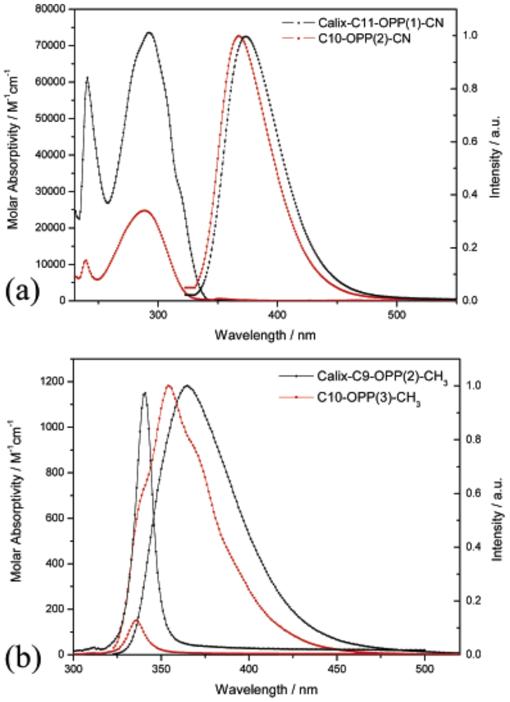

Figure 4. Absorption and emission spectra measured in chloroform of (a) C_n-Calix-OPP(1)-CN and 4-cyano-4′-alkoxy-3′,5′-dimethylbiphenyl and (b) C_n-Calix-OPP(2)-CH_3 and 4-methyl-4′-alkoxy-3′,5′-dimethylterphenyl.

In contrast to the reproducible and stable thermal behavior of the polar C_n-Calix-OPP(1)-CN series, the phase behavior of C_n-Calix-OPP(2)-CH_3's showed nonconventional thermotropic behavior but well-developed textures after annealing. This phenomenon suggests that the antiparallel arrangement of the dipoles in the C_n-Calix-OPP(1)-CN series exerts a positive reinforcement for the mesophase formation. The relatively strong dipole−dipole interactions facilitate the ordered packing of the phenylene-calix[4]arene rigid segments and also stabilize the lamellar structure thus formed. On the other hand, the anisotropic hard-core $\pi-\pi$ interactions and the weak van der Waals interactions present in the C_n-Calix-OPP(2)-CH_3 series do not guarantee stable liquid crystallinity. It should also be stressed that the long alkoxy groups at the lower rim of phenylene-calix[4]arene rigid segment are crucial to render the transformation of the condensed state into a genuine smectic phase. With alkoxy tails shorter than nonyloxy groups, no mesophase was observed. At the present time, the absence of supplementary reflection peaks on the XRD patterns limits the precise structure order determination within the smectic layer, which together with the investigation of the subtle phase transition as in C_{12}- and C_{13}-Calix-OPP(1)-CN would be the subject of forthcoming work.

Optical Properties. In addition to the unique mesogenic properties, end-functionalized aryl-substituted calix[4]arenes show optical properties significantly different from those of the corresponding monomers. Interestingly, the cyano end-capped series show much stronger absorption (absorptivity) than those of the methyl end-capped series even though the methyl-substituted series have a longer conjugated core, which indicates the importance of the polar cyano functionality (Figure 4). Generally, both absorption and emission spectra of end-functionalized aryl-substituted calix[4]arenes (C_n-Calix-OPP(1)-CN, $\lambda_{max}^{abs} = 292$ nm, $\lambda_{max}^{em} = 374$ nm, and $\Phi_{FL} = 99\%$; and C_n-Calix-OPP(2)-CH_3, $\lambda_{max}^{abs} = 340$ nm, $\lambda_{max}^{em} = 365$ nm, and $\Phi_{FL} = 98\%$) are relatively red-shifted with an enhanced fluorescence quantum efficiency as compared to those of the corresponding monomers (4-cyano-4′-alkoxy-3′,5′-dimethylbiphenyl, $\lambda_{max}^{abs} = 289$ nm, $\lambda_{max}^{em} = 368$ nm, and $\Phi_{FL} = 94\%$; and 4-methyl-4′-alkoxy-3′,5′-dimethylterphenyl, $\lambda_{max}^{abs} = 336$ nm, $\lambda_{max}^{em} = 354$ nm, and $\Phi_{FL} = 92\%$). These results suggest that covalently linking the chromophores in a proximate and preorganized fashion leading to the interchromophoric interactions could be an alternative and useful means to modify and enhance the optical properties of a chromophore.

Conclusions

In summary, a novel series of highly luminescent end-functionalized tetra-oligophenylene-substituted calix[4]-arenes have been synthesized by palladium-catalyzed Suzuki cross-coupling of arylboronic acid and tetraiodocalix[4]arene as a key step. We have demonstrated that enhancing the polarity or polarizability of the three-dimensional rigid oligophenylene-calix[4]arene segment would lead to liquid crystallinity. In contrast to the smectic A phase exhibited by the corresponding monomeric mesogens, cyano-phenyl-calix[4]arene and methyl-biphenyl-calix[4]arene derivatives exhibited highly ordered smectic supramolecular organization. In addition, the presence of the strong dipoles in the rigid phenylenecalix[4]arene segments is important to enhance and stabilize the formation of the highly ordered smectic structure as well as to enhance the optical properties of the mesogen. Our findings provide a new guideline and approach to design three-dimensional mesogenic materials.

Experimental Procedures

The differential scanning calorimetry thermograms were recorded on a Perkin-Elmer Pyris 1 instrument equipped with a cooling accessory and under nitrogen atmosphere. The temperatures and heat flows were calibrated using standard sample indium. Usually ~5 mg of powder sample was encapsulated in a sealed aluminum pan with an identical empty pan as the reference. The heating and cooling rate was 10 °C/min. The liquid crystalline textures were observed and photographed using a polarized optical microscope equipped with a Leitz-350 heating stage. The films cast from dichloromethane solution with thickness of ~0.1 mm on clean glass substrate or melt-pressed sandwiched preparations between a glass slide and a cover glass were used for the investigation of morphological changes at different temperatures.

X-ray diffraction (XRD) experiments were performed on an ARL X'TRA diffractometer, using Cu Kα 1.5406 Å as the radiation source with 40 kV, 20 mA power. Film samples were set horizontally on the sample stage. The films with a thickness of ~0.1 mm on glass slides cast from dichloromethane solution were first heated to isotropic state and then slowly cooled to LC state and annealed for 30 min, and then quenched, and the XRD patterns were recorded at room temperature. The reflection peak positions were calibrated with standard silicon powder ($2\theta > 15°$) and silver behenate ($2\theta < 10°$), respectively. The elevated temperature XRD patterns were recorded on a PANalytical X'Pert diffractometer with an Anton Paar HTK 1200 high-temperature oven camera system.

Calix[4]arene 2. A slurry of *p-tert*-butylcalix[4]arene (**1**) (2.50 g, 3.9 mmol), phenol (1.79 g, 19.1 mmol), and $AlCl_3$ (2.63 g, 19.6

mmol) was stirred in 21 mL of toluene at 25 °C under N_2. After being stirred for 4 h, the mixture was poured into 35 mL of 0.2 M HCl and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with water four times, dried over anhydrous Na_2SO_4, and evaporated to dryness. Upon addition of MeOH, the precipitate formed was filtered. The crude product was recrystallized from MeOH/$CHCl_3$, affording 1.2 g of a white solid (80% yield). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 10.16 (d, $J = 5.94$ Hz, 4H), 7.03 (d, $J = 7.56$ Hz, 8H), 6.71 (t, $J = 14.85$ Hz, 4H), 3.88 (d, 4H), 3.48 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 148.7, 128.9, 128.2, 122.2, 31.7. MS (FAB): m/z 424.3 (M^+).

5,11,17,23-Tetrakisiodo-25,26,27,28-tetradecyloxycalix[4]-arene 3c. To a stirred solution of calix[4]arene (0.47 g, 1.1 mmol) in 30 mL of DMF was added NaH (0.11 g, 4.58 mmol) at 0 °C. After the mixture was stirred for 1 h, 1-bromodecane (1.4 mL, 6.6 mmol) was added, and then the reaction mixture was heated to 75 °C overnight. After being cooled to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with water four times to remove DMF, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was filtered by short silica gel column chromatography using petroleum ether/CH_2Cl_2 (v/v 8:1) as eluent, affording 25,26,27,28-tetradecyloxycalix[4]arene as a viscous liquid. To a stirred solution of 25,26,27,28-tetradecyloxycalix[4]arene (0.43 g, 0.4 mmol) in 20 mL of $CHCl_3$ was added silver trifluoroacetate (0.58 g, 2.6 mmol). After refluxing for 30 min under N_2, iodine (0.66 g, 2.6 mmol) was added. The reaction mixture was allowed to reflux for another 2 h under N_2. After being cooled to room temperature, the crude mixture was filtered via short silica gel column chromatography with Celite to remove the yellow AgI precipitate. The filtrate was washed with Na_2SO_3 solution and extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layer was washed with water four times, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether/CH_2Cl_2 (v/v 8:1) as eluent, affording 0.56 g (85%) of a viscous liquid. ^{1}H NMR (270 MHz, $CDCl_3$, δ): 6.91 (m, 8H), 4.20 (d, 4H, $J = 13.23$ Hz), 3.76 (t, $J = 7.29$ Hz, 8H), 2.97 (d, $J = 13.5$ Hz, 4H), 1.77 (m, 8H), 1.24 (bs, 56H), 0.81 (t, $J = 6.75$ Hz, 12H). ^{13}C NMR (66 MHz, $CDCl_3$, δ): 156.0, 136.7, 136.5, 86.1, 31.9, 30.3, 30.1, 29.9, 29.8, 29.7, 29.4, 29.2, 26.2. 22.7, 14.1. MS (FAB): m/z 1489.5 (M^+).

5,11,17,23-Tetrakis(4-cyanophenyl)-25,26,27,28-tetraoctyloxycalix[4]arene C_8-Calix-OPP(1)-CN. To a stirred solution of 5,11,17,23-tetrakisiodo-25,26,27,28-tetraoctyloxycalix[4]arene (0.45 g, 0.3 mmol), palladium(II) acetate (0.04 g, 0.1 mmol), and P(*o*-tol)$_3$ (0.1 g, 0.4 mmol) in 20 mL of toluene, 10 mL of methanol, and 3 mL of 2 M K_2CO_3 under N_2 was added 4-cyanobenzeneboronic acid (0.4 g, 2.7 mmol). The reaction mixture was heated to 75 °C overnight under N_2. After being cooled to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with water three times, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent. The pure product was obtained by recrystallization from petroleum ether, affording a slightly yellow solid of 0.32 g (75% yield). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.39−7.36 (m, 8H), 7.17−7.14 (m, 8H), 6.90 (s, 8H), 4.57 (d, $J = 13.50$ Hz, 4H), 3.98 (t, 8H), 3.30 (d, $J = 13.23$ Hz, 4H), 1.96 (m, 8H), 1.40−1.24 (bs, 48H), 0.90 (t, 12H). ^{13}C NMR (67.8 MHz, $CDCl_3$, δ): 157.3, 144.9, 135.5, 132.8, 132.0, 126.9, 126.7, 118.6, 110.0, 75.6, 32.0, 31.3, 30.4, 29.9, 29.6, 26.4, 22.7, 14.1. HRMS (MALDI-TOF) m/z calcd for $C_{88}H_{100}O_4N_4Na$, 1299.7642; found, 1299.7609 $[M + Na]^+$.

5,11,17,23-Tetrakis(4-cyanophenyl)-25,26,27,28-tetranonyloxycalix[4]arene C_9-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetranonyloxycalix[4]arene (0.32 g, 0.21 mmol), 4-cyanobenzeneboronic acid (187 mg, 1.27 mmol), Pd(OAc)$_2$ (28 mg, 0.12 mmol), and P(*o*-tol)$_3$ (78 mg, 0.26 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 50% (0.15 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39−7.37 (m, 8H), 7.16−7.15 (m, 8H), 6.90 (s, 8H), 4.57 (d, $J = 13.20$ Hz, 4H), 3.98 (t, 8H), 3.30 (d, $J = 13.60$ Hz, 4H), 1.96 (m, 8H), 1.41−1.29 (bs, 48H), 0.88 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.4, 145.0, 135.6, 132.9, 132.1, 126.9, 126.7, 118.7, 110.0, 75.6, 31.9, 31.3, 30.3, 29.9, 29.4, 26.3, 22.7, 14.1. HRMS (MALDI-TOF) m/z calcd for $C_{92}H_{108}O_4N_4Na$, 1356.8301; found, 1356.8267 $[M + Na]^+$.

5,11,17,23-Tetrakis(4-cyanophenyl)-25,26,27,28-tetradecyloxycalix[4]arene C_{10}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetradecyloxycalix[4]arene (0.40 g, 0.27 mmol), 4-cyanobenzeneboronic acid (0.24 g, 1.64 mmol), Pd(OAc)$_2$ (36 mg, 0.16 mmol), and P(*o*-tol)$_3$ (97 mg, 0.32 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 80% (0.30 g). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.39−7.37 (m, 8H), 7.16−7.14 (m, 8H), 6.90 (s, 8H), 4.56 (d, $J = 13.20$ Hz, 4H), 3.97 (t, $J = 7.20$ Hz, 8H), 3.30 (d, $J = 13.20$ Hz, 4H), 1.95 (m, 8H), 1.41−1.28 (bs, 56H), 0.87 (t, $J = 7.20$ Hz, 12H). ^{13}C NMR (67.8 MHz, $CDCl_3$, δ): 157.3, 144.8, 135.5, 132.8, 132.1, 126.9, 126.7, 118.6, 110.0, 75.7, 32.0, 31.4, 30.4, 30.1, 29.9, 29.5, 26.4, 22.8, 14.2. HRMS (MALDI-TOF) m/z calcd for $C_{96}H_{116}O_4N_4Na$, 1412.8927; found, 1412.8978 $[M + Na]^+$.

5,11,17,23-Tetrakis(4-cyanophenyl)-25,26,27,28-tetraundecyloxycalix[4]arene C_{11}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetraundecyloxycalix[4]arene (0.48 g, 0.31 mmol), 4-cyanobenzeneboronic acid (365 mg, 2.46 mmol), Pd(OAc)$_2$ (42 mg, 0.19 mmol), and P(*o*-tol)$_3$ (0.11 g, 0.37 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 77% (0.25 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.39−7.36 (m, 8H), 7.16−7.13 (m, 8H), 6.90 (s, 8H), 4.56 (d, $J = 13.23$ Hz, 4H), 3.98 (t, 8H), 3.30 (d, $J = 13.50$ Hz, 4H), 1.96 (m, 8H), 1.40−1.27 (bs, 64H), 0.87 (t, $J = 7.02$ Hz, 12H). ^{13}C NMR (67.8 MHz, $CDCl_3$, δ): 157.2, 144.8, 135.4, 132.7, 131.9, 126.8, 126.6, 118.6, 109.8, 75.5, 31.9, 31.3, 30.3, 30.0, 29.9, 29.8, 29.7, 29.4, 26.4, 22.7, 14.1. HRMS (MALDI-TOF) m/z calcd for $C_{100}H_{124}O_4N_4Na$, 1468.9553; found, 1468.9618 $[M + Na]^+$.

5,11,17,23-Tetra(4-cyanophenyl)-25,26,27,28-tetradodecyloxycalix[4]arene C_{12}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetradodecyloxycalix[4]arene (0.13 g, 0.08 mmol), 4-cyanobenzeneboronic acid (71 mg, 0.48 mmol), Pd(OAc)$_2$ (11 mg, 0.05 mmol), and P(*o*-tol)$_3$ (29 mg, 0.10 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 75% (0.09 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.39−7.36 (m, 8H), 7.15 (m, 8H), 6.89 (s, 8H), 4.56 (d, $J = 13.23$ Hz, 4H), 3.97 (t, 8H), 3.29 (d, $J = 12.69$ Hz, 4H), 1.96 (m, 8H), 1.39−1.26 (bs, 72H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.4, 145.0, 135.6, 132.9, 132.2, 127.0, 126.7, 118.6, 110.0, 75.7, 31.9, 31.3, 30.3, 30.0, 29.9, 29.8, 29.7, 29.4, 26.3, 22.7, 14.1. MS (MALDI-TOF) m/z calcd for $C_{104}H_{132}O_4N_4Na$, 1524.0101; found, 1524.0076 $[M + Na]^+$.

5,11,17,23-Tetra(4-cyanophenyl)-25,26,27,28-tetratridecyloxycalix[4]arene C_{13}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetratridecyloxycalix[4]arene (0.67 g, 0.40 mmol), 4-cyanobenzeneboronic acid (0.05 g, 3.30 mmol), $Pd(OAc)_2$ (11 mg, 0.24 mmol), and P(*o*-tol)$_3$ (29 mg, 0.49 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 49% (0.31 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.39−7.36 (m, 8H), 7.23−7.15 (m, 8H), 6.89 (s, 8H), 4.55 (d, $J = 13.50$ Hz, 4H), 3.97 (t, 8H), 3.29 (d, $J = 12.96$ Hz, 4H), 1.95 (m, 8H), 1.39−1.25 (bs, 88H), 0.86 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.4, 145.0, 135.6, 132.9, 132.2, 126.8, 126.7, 118.7, 110.1, 75.7, 31.9, 31.3, 30.3, 30.0, 29.9, 29.8, 29.7, 29.4, 26.3, 22.7, 14.1. MS (MALDI-TOF) *m*/*z* calcd for $C_{108}H_{140}O_4N_4Na$, 1581.0805; found, 1581.0785 $[M + Na]^+$.

5,11,17,23-Tetra(4-cyanophenyl)-25,26,27,28-tetratetradecyloxycalix[4]arene C_{14}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetratetradecyloxycalix[4]arene (0.84 g, 0.58 mmol), 4-cyanobenzeneboronic acid (0.68 g, 4.61 mmol), $Pd(OAc)_2$ (7.76 mg, 0.04 mmol), and P(*o*-tol)$_3$ (21 mg, 0.07 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 67% (0.62 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.46−7.43 (m, 8H), 7.15 (m, 8H), 6.89 (s, 8H), 4.56 (d, $J = 13.23$ Hz, 4H), 3.97 (t, 8H), 3.29 (d, $J = 12.69$ Hz, 4H), 1.96 (m, 8H), 1.39−1.26 (bs, 72H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.1, 144.7, 135.3, 132.7, 131.8, 126.8, 126.6, 118.5, 109.7, 75.5, 31.9, 31.3, 30.3, 30.0, 29.8, 29.7, 29.4, 26.3, 22.6, 14.1. MS (MALDI-TOF) *m*/*z* calcd for $C_{112}H_{148}O_4N_4Na$, 1637.1431; found, 1637.1475 $[M + Na]^+$.

5,11,17,23-Tetra(4-cyanophenyl)-25,26,27,28-tetrapentadecyloxycalix[4]arene C_{15}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetrapentadecyloxycalix[4]arene (0.41 g, 0.23 mmol), 4-cyanobenzeneboronic acid (0.27 g, 1.85 mmol), $Pd(OAc)_2$ (31.1 mg, 0.14 mmol), and P(*o*-tol)$_3$ (84.4 mg, 0.28 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 65% (0.25 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.39−7.36 (m, 8H), 7.15 (m, 8H), 6.89 (s, 8H), 4.56 (d, $J = 13.23$ Hz, 4H), 3.97 (t, 8H), 3.29 (d, $J = 12.69$ Hz, 4H), 1.96 (m, 8H), 1.39−1.26 (bs, 96H), 0.87 (t, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.2, 144.8, 135.4, 132.8, 132.0, 126.9, 126.6, 118.6, 110.0, 75.6, 31.9, 31.4, 30.4, 30.0, 29.9, 29.8, 29.7, 29.4, 26.4, 22.7, 14.2. HRMS (MALDI-TOF) *m*/*z* calcd for $C_{116}H_{156}O_4N_4Na$, 1693.2057; found, 1693.2076 $[M + Na]^+$.

5,11,17,23-Tetra(4-cyanophenyl)-25,26,27,28-tetrahexadecyloxycalix[4]arene C_{16}-Calix-OPP(1)-CN. The above coupling procedure was followed using 5,11,17,23-tetraiodo-25,26,27,28-tetrahexadecyloxycalix[4]arene (0.64 g, 0.35 mmol), 4-cyanobenzeneboronic acid (0.41 g, 2.79 mmol), $Pd(OAc)_2$ (4.68 mg, 0.02 mmol), and P(*o*-tol)$_3$ (12.7 mg, 0.04 mmol). The crude product was purified by silica gel column chromatography using CH_2Cl_2/EtOAc (v/v 100:1) as eluent, affording a slightly yellow solid with an isolated yield of 60% (0.36 g). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.39−7.36 (m, 8H), 7.15−7.12 (m, 8H), 6.89 (s, 8H), 4.55 (d, $J = 13.23$ Hz, 4H), 3.97 (t, $J = 7.56$ Hz, 8H), 3.29 (d, $J = 13.50$ Hz, 4H), 1.95 (m, 8H), 1.39−1.24 (bs, 104H), 0.86 (t, $J = 6.75$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 157.3, 144.9, 135.5, 132.8, 132.0, 126.9, 126.7, 118.6, 110.0, 75.6, 32.0, 31.4, 30.4, 30.1, 30.0, 29.9, 29.8, 29.7, 29.4, 26.4, 22.8, 14.2. HRMS (MALDI-TOF) *m*/*z* calcd for $C_{116}H_{156}O_4N_4Na$, 1749.2683; found, 1749.2649 $[M + Na]^+$.

5,11,17,23-Tetrakis(4′-methylbiphenyl)-25,26,27,28-tetradecyloxycalix[4]arene C_{10}-Calix-OPP(2)-CH_3. To a stirred solution of 5,11,17,23-tetrakisiodo-25,26,27,28-tetradecyloxycalix[4]arene (0.24 g, 0.2 mmol), palladium(II) acetate (0.02 g, 0.09 mmol), and P(*o*-tol)$_3$ (0.06 g, 0.2 mmol) in 20 mL of toluene, 10 mL of methanol, and 3 mL of 2 M K_2CO_3 under N_2 was added 4′-methylbiphenylboronic acid (0.20 g, 1.0 mmol). The reaction mixture was heated to 75 °C overnight under N_2. After being cooled to room temperature, the reaction mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was washed with water three times, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by silica gel column chromatography using petroleum ether as eluent. The pure product was obtained by recrystallization from petroleum ether, affording a white solid of 0.17 g (62% yield). ^{1}H NMR (270 MHz, $CDCl_3$, δ): 7.37−7.01 (m, 40H), 4.61 (d, $J = 12.96$ Hz, 4H), 3.02 (t, 8H), 3.33 (d, $J = 13.23$ Hz, 4H), 2.36 (s, 12H), 2.05 (m, 8H), 1.44−1.32 (bs, 56H), 0.90 (t, $J = 6.75$ Hz, 12H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 156.3, 139.8, 138.8, 137.8, 136.4, 135.1, 134.7, 129.3, 127.0, 126.9, 126.8, 126.6, 75.6, 32.0, 31.4, 30.4, 30.1, 29.9, 29.5, 26.5, 22.7, 21.1, 14.1. HRMS (MALDI-TOF) *m*/*z* calcd for $C_{120}H_{144}O_4Na$, 1672.0967; found, 1673.1011 $[M + Na]^+$.

5,11,17,23-Tetrakis(4′-methylbiphenyl)-25,26,27,28-tetranonyloxycalix[4]arene C_9-Calix-OPP(2)-CH_3. The above coupling procedure was followed using 5,11,17,23-tetrakisiodo-25,26,27,-28-tetranonyloxycalix[4]arene (0.81 g, 0.57 mmol), 4′-methylbiphenylboronic acid (734 mg, 3.46 mmol), $Pd(OAc)_2$ (76.2 mg, 0.34 mmol), and P(*o*-tol)$_3$ (207 mg, 0.68 mmol). The crude product was purified by silica gel column chromatography using petroleum ether as eluent. The pure product was obtained by recrystallization from petroleum ether, affording a white solid of 0.60 g (66% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.37−7.02 (m, 40H), 4.61 (d, $J = 13.20$ Hz, 4H), 4.03 (t, $J = 6.80$ Hz, 8H), 3.34 (d, $J = 13.20$ Hz, 4H), 2.36 (s, 12H), 2.04 (m, 8H), 1.45−1.33 (bs, 48H), 0.92 (t, $J = 7.20$ Hz, 12H). ^{13}C NMR (66 MHz, $CDCl_3$, δ): 156.1, 139.7, 138.7, 137.7, 136.3, 135.0, 134.6, 129.2, 127.0, 126.8, 126.7, 126.5, 75.6, 32.1, 30.5, 30.1, 29.6, 26.5, 22.8, 21.1, 14.2. HRMS (MALDI-TOF) *m*/*z* calcd for $C_{116}H_{136}O_4Na$, 1617.0370; found, 1617.0352 $[M + Na]^+$.

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Supporting Information Available: Characterization data for C_n-Calix-OPP(*m*)-X and monomers as well as results of DSC, POM, XRD patterns, and proposed indexing. This material is available free of charge via the Internet at http://pubs.acs.org.

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