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New liquid crystals based on calixarenes

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New liquid crystals based on calixarenes (**7** and **8**) were prepared by the reaction of calixarene, *tert*-butylcalix[8]arene and *C*-methyloctakis(2-hydroxyethyl)calix[4]resorcinarene, and 11-[(4′-cyano-1,1′-biphenyl-4-yl)oxy]undecanoyl chloride in the presence of triethylamine. The structures of **7** and **8** were characterized by IR, ^{1}H NMR, ^{13}C NMR, and MALDI-TOF mass spectroscopies. Compounds **7** and **8** had glass transitions at approximately –30 and 25 °C, respectively. Both of them exhibited smectic liquid crystals. Compound **8** was found to adopt a specific molecular structure due to the rigid bowl calix[4]resorcinarene core, *i.e.*, a cone-like structure with mesogenic units aligned within the molecule. Moreover, the smectic A phase of **8** was transformed to nematic. The supercooling of **8** for the phase transition was very small due to the molecular structure.

Introduction

Liquid crystals (LCs) are materials with potential for use as active media in optical applications. Their quick response to changes in electric fields enables them to be used to produce liquid crystal displays. Therefore, LCs have attracted interest as materials for photo-recording devices.[1–4] However, such optical devices require a very fast response.

Recently, the synthesis and the characterization of liquid crystals having unique structural properties, such as cyclosiloxane-based liquid crystalline materials[5] and liquid crystalline dendrimers (LCDs),[6] have received much attention owing to their similarity to side chain liquid crystalline polymers (SCLCPs). LCDs into which mesogenic units are introduced *via* long alkyl chains were reported to display thermotropic nematic and smectic liquid crystalline phases. Their low viscosity as well as their relatively low phase-transition temperature are advantageous for fast switching materials.

On the other hand, composite films, in which micrometre-sized domains of LCs with low molecular weights are dispersed in an amorphous polymer matrix, are relevant for electro-optical applications such as light shutters, information displays, and optical nonlinear materials.[7] However, control of the domain size is not easy.

Shirota and co-workers have recently suggested a new method for the molecular design of low molecular weight amorphous materials, called "amorphous molecules", which involves increasing the number of conformers by lowering the symmetry of nonplanar molecules.[8] In addition, a definite molecular weight and good processability of the "amorphous molecules" are advantageous for casting a transparent and tough film. We have found that calixarenes can act as "amorphous molecules" with bulky substituents on their hydroxy groups and were thus applied as a new positive-type photoresist.[9,10] Therefore, the introduction of LC side chains into calixarenes would provide "amorphous molecules" with LC properties. In fact, mesogenic materials with a calix[4]arene central unit were reported and some of them exhibit film-forming ability.[11] Furthermore, the unique structures of such LC calixarenes include the possibility of inducing the intermolecular orientation of the mesogenic units. Calixarenes having LC chains are expected to be useful as optical switching materials with a fast response.

In this study, we prepared LC calixarenes by the attachment of cyanobiphenyl mesogenic groups to hydroxy groups on calixarenes, *tert*-butylcalix[8]arene and calix[4]resorcinarene, *via* ester groups having alkyl spacers. Their LC properties were revealed by thermal analyses and polarizing microscopic and X-ray diffraction methods.

Experimental

Materials

tert-Butylcalix[8]arene (C8-A) was prepared by the base-catalyzed condensation of *p*-*tert*-butylphenol with formaldehyde according to the reported procedure.[12] Calix[4]resorcinarene (C4-RA) was prepared by the reaction of resorcinol with acetaldehyde according to the reported procedure and was crystallized from methanol.[13]

11-{[4′-Cyano-1,1′-biphenyl-4-yl]oxy}undecanoic acid **3** as an LC side chain was obtained according to the procedure reported by Hölter *et al.*[14] *C*-Methyloctakis(2-hydroxyethyl)-C4-RA **5** was also prepared by the procedure reported by Fujimoto *et al.*[15]

Solvents were dried and purified in the usual manner, and stored under an atmosphere of argon. Most manipulations were carried out either under dry, oxygen-free argon or nitrogen or *in vacuo* in Schlenk-type flasks.

Ethyl 11-bromoundecanoate 1

A solution of 11-bromoundecanoic acid (10.0 g, 0.075 mol) and a few drops of conc. H_2SO_4 in a mixture of ethanol (7.5 mL) and toluene (4 mL) was refluxed for 2 h. The residue formed after evaporation of the solvent was dissolved in toluene (20 mL) and washed with a saturated aqueous $NaHCO_3$ solution (20 mL). The organic layer was dried over $MgSO_4$ and filtered, and the filtrate was concentrated. The residue was passed through a short silica column (toluene) to yield a clear liquid. Yield: 9.01 g (81%). IR (KBr) ν 1735 cm^{-1} (C=O). ^{1}H NMR (270 MHz, $CDCl_3$) δ 4.16 (q, OCH_2, 2H), 3.41

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(t, $BrCH_2$, 2H), 2.29 (t, $C(O)CH_2$, 2H), 2.02 (m, CH_2, 2H), 1.62 (m, CH_2, 2H), 1.42 (m, CH_2, 2H), 1.28 (m, CH_2, 12H), 1.26 (t, CH_3, 3H).

Ethyl 11-[(4′-cyano-1,1′-biphenyl-4-yl)oxy]undecanoate 2

A mixture of K_2CO_3 (0.995 g, 7.2 mmol) and 4′-hydroxy-1,1′-biphenyl-4-carbonitrile (1.17 g, 6 mmol) in butan-2-one (24 mL) was refluxed for 1.5 h and then compound **1** (2.02 g, 6.9 mmol) was added to the solution. The mixture was refluxed for 24 h. After the solvent was evaporated, the solid was washed with water and dried under reduced pressure to give the crude product **2** (2.36 g, 99%). IR (KBr) ν 2230 (C≡N), 1730 cm^{-1} (C=O). ^1H NMR (270 MHz, $CDCl_3$) δ 7.66 (q, Ar-H, 4H), 7.58 (d, Ar-H, 2H), 7.00 (d, Ar-H, 2H), 4.14 (q, OCH_2, 2H), 4.00 (t, OCH_2, 2H), 2.29 (t, $C(O)CH_2$, 2H), 1.81 (m, CH_2, 2H), 1.62 (m, CH_2, 2H), 1.42 (m, CH_2, 2H), 1.31 (m, CH_2, 12H), 1.26 (t, CH_3, 3H).

11-[(4′-Cyano-1,1′-biphenyl-4-yl)oxy]undecanoic acid 3

To a solution of compound **2** (2.42 g, 6.2 mmol) in acetone (8 mL) was added 1.5 M aqueous potassium hydroxide solution (4 mL) over a 20 min period. The solution was refluxed for 2 h and cooled to room temperature. The reaction mixture was diluted with water (10 mL) and acidified with 1.2 M hydrochloric acid. The precipitate was collected through a glass filter, washed with water, and dried under reduced pressure. Pure product **3** (1.69 g, 75%) was obtained by recrystallization from propan-2-ol. IR (KBr) ν 3400–2000 (OH), 1710 cm^{-1} (C=O). ^1H NMR (270 MHz, DMSO-d_6) δ 7.84 (q, Ar-H, 4H), 7.69 (d, Ar-H, 2H), 7.03 (d, Ar-H, 2H), 4.14 (q, OCH_2, 2H), 2.16 (t, $C(O)CH_2$, 2H), 1.71 (m, CH_2, 2H), 1.46–1.24 (m, CH_2, 14H).

4,6,10,12,16,18,22,24-Octakis(ethoxycarbonylmethoxy)-2,8,14,20-tetramethylcalix[4]arene 4

A mixture of calix[4]resorcinarene (C4-RA) (1.09 g, 2.0 mmol) and potassium carbonate (2.65 g, 19.2 mmol) in acetone (20 mL) was refluxed for 30 min. To this mixture was added ethyl bromoacetate (3.21 g, 19.2 mmol) and the mixture was refluxed for 12 h. A precipitate was filtered off and the filtrate was evaporated. The residue was recrystallized from propan-2-ol The yield of pure C4-RA derivative **4** was 1.65 g (67%). Mp 139–140 °C. IR (KBr) ν 1750 cm^{-1} (C=O). ^1H NMR (270 MHz, $CDCl_3$) δ 6.56 (br, ArH, 4H), 6.25 (s, ArH, 4H), 4.73 (q, CH, 4H), 4.32 (br, CH_2, 16H), 4.21 (m, CH_2, 16H), 1.48 (d, CH_3 12H), 1.28 (t, CH_3, 24H).

4,6,10,12,16,18,22,24-Octakis(2-hydroxyethoxy)-2,8,14,20-tetramethylcalix[4]arene 5

To a mixture of lithium aluminium hydride (1.52 g, 40 mmol) in dry THF (100 mL) was added dropwise a solution of **4** (3.08 g, 2.5 mmol) in THF (20 mL). The mixture was then refluxed for 20 h. Water (12 mL) was added dropwise to the mixture and the precipitate was filtered off. The filtrate was evaporated and a white solid appeared. The product was recrystallized from propan-2-ol to give **5** (1.03 g, 46%). Mp > 300 °C (decomp.). IR (KBr) ν 3415 cm^{-1} (O–H). ^1H NMR (270 MHz, DMSO-d_6, 100 C) δ 6.54 (s, ArH, 4H), 6.44 (s, ArH, 4H), 4.59 (q, CH, 4H), 4.17 (t, OH, 8H), 3.87 (m, CH_2, 8H), 3.71 (m, CH_2 8H), 3.59 (q, CH_2, 16H), 1.32 (d, CH_3, 12H).

11-[(4′-Cyano-1,1′-biphenyl-4-yl)oxy]undecanoyl chloride 6

A solution of **3** (1.90 g, 5 mmol) in $SOCl_2$ (6.6 mL) was refluxed for 5 h. The excess of $SOCl_2$ was removed *in vacuo* and a yellow solid was obtained (1.90 g, 100%). ^1H NMR spectra of the solid showed that **3** was completely converted to the corresponding acid chloride **6**. ^1H NMR (270 MHz, $CDCl_3$) δ 7.64 (q, Ar-H, 4H), 7.51 (d, Ar-H, 2H), 6.98 (d, Ar-H, 2H), 3.99 (t, OCH_2, 2H), 2.87 (t, $C(O)CH_2$, 2H), 1.82 (m, CH_2, 2H), 1.70 (m, CH_2, 2H), 1.47–1.31 (m, CH_2, 12H).

5,11,17,23,29,35,41,47-Octakis(*tert*-butyl)-49,50,51,52,53,54,55,56-octakis{11-[(4′-cyano-1,1′-biphenyl-4-yl)oxy]undecanoyloxy}calix[8]arene 7

Acid chloride **6** (1.90 g, 5 mmol) was dissolved in dry THF (3.3 mL) and was slowly added to a solution of *tert*-butylcalix[8]arene (C8-A) (0.406 g, 0.31 mmol) and triethylamine (0.52 mL, 3.75 mmol) in THF (3.3 mL). The reaction mixture was stirred at room temperature for 12 h and refluxed for 5 h. After evaporation of the solvent, the reaction mixture was dissolved in ethyl acetate (10 mL) and the solution was extracted with two portions of aqueous Na_2CO_3 solution (10 mL). The organic phase was dried over $MgSO_4$ and evaporated. The residue was washed in refluxing propan-2-ol and purified by Soxhlet extraction with methanol to yield the yellow solid **7** (0.722 g, 55%).

IR (KBr) ν 1750 cm^{-1} (C=O). ^1H NMR (270 MHz, DMSO-d_6, 100 °C) δ 7.73 (q, Ar-H, 16H), 7.70 (q, Ar-H, 16H), 7.57 (d, Ar-H, 16H), 6.94 (d, Ar-H, 16H), 6.91 (s, Ar-H, 16H), 3.94 (t, OCH_2, 16H), 3.55 (s, $ArCH_2$, 16H), 2.37 (t, $C(O)CH_2$, 16H), 1.69–1.58 (m, CH_2, 32H), 1.40–1.25 (m, CH_2, 96H), 1.03 (s, CH_3, 72H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 170.8 (C-O), 159.4, 147.5, 145.0, 144.2, 132.4, 131.1, 127.9, 126.6, 125.2, 115.1 and 109.2 (ArC), 118.5 (CN), 67.7 (OCH_2), 33.5, 32.8, 30.5, 28.5, 28.4, 28.4, 28.3, 25.1, and 24.0 (alkyl). MALDI-TOF-MASS molecular weight calc. for $C_{280}H_{328}N_8O_{24}$: $m/z = 4212.6\ [M+Na]^+$. Found: $m/z = 4213.3\ [M+Na]^+$. Anal. calc. for $C_{280}0H_{328}N_8O_{24}$: C, 80.27; H, 7.89; N, 2.67%. Found: C, 79.84; H, 8.17; N, 2.48%.

4,6,10,12,16,18,22,24-Octakis(2-{11-[(4′-cyano-1,1′-biphenyl-4-yl)oxy]undecanoyloxy}ethoxy)-2,8,14,20-tetramethylcalix[4]-arene 8

A solution of **3** (0.607 g, 1.6 mmol) in $SOCl_2$ (2.2 mL) was refluxed for 5 h. The excess of $SOCl_2$ was removed *in vacuo* and a yellow solid was obtained. To a solution of acid chloride **6** in dry THF (1.1 mL) was slowly added a solution of **5** (0.090 g, 0.1 mmol) and triethylamine (0.17 mL, 1.2 mmol) in THF (1.1 mL). The reaction mixture was stirred at room temperature for 12 h and refluxed for 5 h. Ethyl acetate (10 mL) was added to the reaction mixture and the precipitate was filtered off. The filtrate was extracted with two portions of aqueous Na_2CO_3 solution (10 mL). The organic phase was dried over $MgSO_4$ and evaporated. The residue was washed in refluxing propan-2-ol to remove any unreacted **3** and dried over reduced pressure to give yellow solid **8** (0.235 g, 62%). IR (KBr) ν 1750 cm^{-1} (C=O). ^1H NMR (270 MHz, DMSO-d_6, 100 °C) δ 7.75 (q, Ar-H, 16H), 7.73 (q, Ar-H, 16H), 7.59 (d, Ar-H, 16H), 6.96 (d, Ar-H, 16H), 6.44 (s, Ar-H, 8H), 4.52 (q, CH, 4H), 4.35–3.62 (br, CH_2, 32H), 3.95 (t, OCH_2, 16H), 2.23 (t, $C(O)CH_2$, 16H), 1.72–1.62 (m, CH_2, 16H), 1.53–1.45 (m, CH_2, 16H), 1.40–1.10 (m, CH_2 and CH_3, 112H). ^{13}C NMR (67.5 MHz, DMSO-d_6, 100 °C) δ 169.5 (C=O), 144.3, 132.5, 130.4, 128.0, 126.7, 116.3, and 109.2 (ArC), 118.6 (CN), 67.7, 66.9, and 62.2 (OCH_2), 33.2, 28.5, 28.4, 28.3, 28.2, 28.1, 26.1, and 24.1 (alkyl). MALDI-TOF MS molecular weight calc. for $C_{240}H_{280}N_8O_{32}$: $m/z = 3811.8\ [M+Na]^+$. Found: $m/z = 3812.1\ [M+Na]^+$. Anal. calc. for $C_{240}H_{280}N_8O_{32}\cdot 7.3\ H_2O$: C, 73.50; H, 7.57; N, 2.86%. Found: C, 73.47; H, 7.04; N, 2.58%.

Measurements

Thermal analyses were performed under nitrogen on a Seiko SSS 5000 TG-DTA 220 thermal analyzer at a heating rate of 10 °C min^{-1} for thermogravimetry (TG) and a Seiko SSS5000 DSC 220 at a heating rate of 10 °C min^{-1} for differential scanning calorimetry (DSC). Optical textures of the samples were examined under nitrogen using a polarizing optical microscope (POM) equipped with a hot stage (Linkam Co., TH-600RMS).

X-Ray diffraction experiments were carried out on a RAD-rA diffractometer (Rigaku Denki Co. Ltd.) equipped with a heating device. Nickel-filtered Cu-Kα radiation was employed. Changes in the wide-angle X-ray diffraction (WAXD) traces were recorded by a scintillation counter system with a 1.0 mm diameter pin-hole collimator and 1 × 1° receiving slit. The diffractometry was performed in transmission. WAXD traces were obtained by a step-scanning method: the step width and fixed time were programmed in steps of 0.05° every 4 s. The WAXD photographs were taken with a flat Laue camera with a 0.5 mm diameter pin-hole collimator.

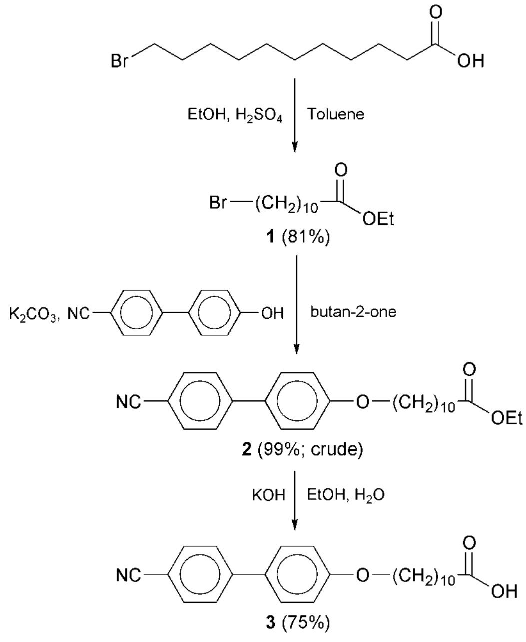
The oriented sample was prepared in a magnet field of 2.8 T using an Electromagnet TM-WV8615MRC-156 (Tamagawa Co.).

Results and discussion

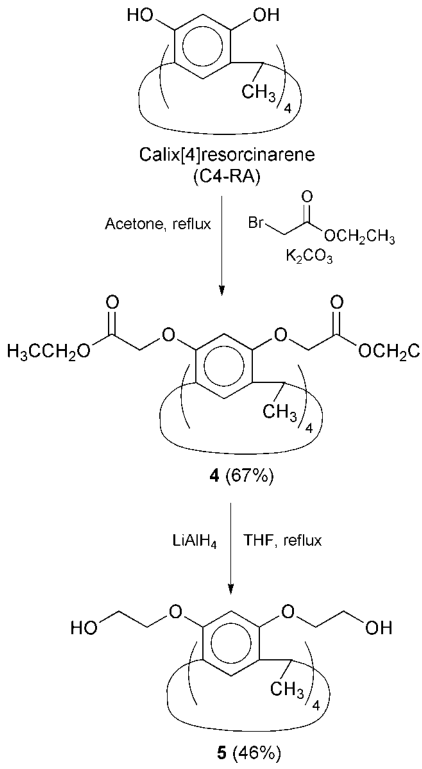
Synthesis of calixarene derivatives 7 and 8

The mesogen and the length of the spacer are the primary factors that determine the specific mesophases exhibited by a given side chain liquid crystalline polymer (SCLCP). A long spacer decouples the interaction between the mesogens and polymers, and makes the motions of mesogens free. On the basis of these considerations, the synthesis of calix[8]arene (C8-A) and calix[4]resorcinarene (C4-RA) with cyanobiphenyl groups as mesogens was carried out. The acid chloride method was chosen to introduce the mesogenic groups because the complete substitution of eight hydroxy groups on C8-A and C4-RA is not easy without high reactivity. The side chain group, 11-[(4′-cyano-1,1′-biphenyl-4-yl)oxy]undecanoyl chloride **6**, was prepared by modifying the procedure of Hölter *et al.*[14] First, the reaction of ethyl 11-bromoundecanoate **1** with 4′-hydroxy-1,1′-biphenyl-4-carbonitrile in the presence of potassium carbonate yielded corresponding ester **2**. Then, an alkaline hydrolysis of **2** produced acid **3** (Scheme 1), which was finally treated with thionyl chloride to give acid chloride **6**.

In order to facilitate the introduction of mesogen units into C4-RA, spacers were attached to C4-RA in advance by the Williamson reaction with ethyl bromoacetate, which was followed by reduction with lithium aluminium hydride (Scheme 2).[15] The modification of C8-A and C4-RA required two equivalents of acid chloride for the hydroxy groups, yielding 55 and 62% of products **7** and **8**, respectively (Scheme 3). The products obtained were purified by Soxhlet extraction with methanol and propan-2-ol, and characterized by IR, NMR, and MALDI-TOF-MASS.



Scheme 1

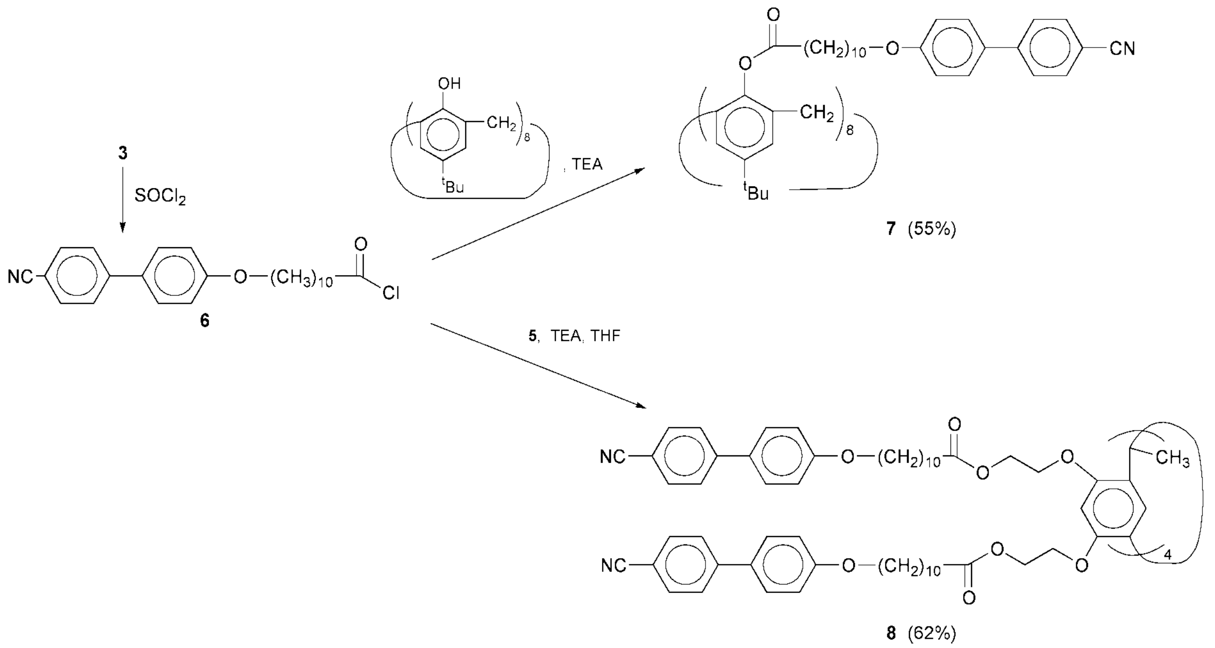


Scheme 2

Fig. 1 shows the ^{1}H NMR spectrum of the C8-A derivative **7** at 100 °C. The biphenyl units, which are *para*-substituted with an ether and a cyano group, give four doublet peaks at 6.94, 7.57, 7.70 and 7.73 and a sharp singlet signal assigned to the methyl protons of the *tert*-butyl groups of **7** is observed at δ 1.03 in the ^{1}H NMR spectrum. The methylene and phenyl protons on the calixarene ring were found at δ 3.55 and 6.91. All of the assignments are shown in Fig. 1. Compound **8** also showed a similar spectrum, and a characteristic quartet signal assigned to the methane protons of the C4-RA core was clearly observed at δ 4.52 (Fig. 2). These results confirmed that the modification of C8-A and C4-RA was complete. Generally, partially modified calixarenes exhibit multiple peaks and broad peaks due to their asymmetric shape even at high temperatures, whereas fully modified calixarenes eventually give well-resolved ^{1}H NMR spectra. The most conclusive molecular weights of compounds **7** and **8** were determined by MALDI TOF mass spectrometry. The MALDI-TOF mass spectra of **7** and **8** show one signal that is clearly shows the formation of the desired calixarenes with 8 mesogens. The *m*/*z* values of the signals for **7** (found: 4212.6) and **8** (found: 3812.1) correspond to the calculated values of 4212.6 and 3811.8 $[M+Na]^+$, respectively (Fig. 3). Products **7** and **8** are soluble in acetone, THF, $CHCl_3$ and ethyl acetate at room temperature.

Thermal properties and phase transition

Thermal gravimetric analyses (TGA) showed that **7** and **8** are stable up to 300 °C, as illustrated by the traces in Fig. 4. Fig. 5 shows the DSC traces of **7**: an endothermic peak was found at 75 °C after the 2nd heating, and its enthalpy change (ΔH) was approximately 18.5 kJ mol^{-1}. The cooling DSC trace shows a broad and small exothermic peak at 65 °C ($\Delta H = ca.$ 19 kJ



Scheme 3

mol^{-1}) and a base line shift corresponding to T_g around −30 °C.

Polarizing optical microscopy (POM) was employed to characterize the LC phase. The endothermic peak at 75 °C was an isotropization, as a dark field was observed under POM with crossed polarizers above this temperature. Small grain texture appeared in the dark field on cooling from the isotropic melt. On the other hand, the sample was put between two glass plates, and they were heated to 50 °C on the hot stage. When the sample was sheared by sliding the upper glass plate, the optical texture shown in Fig. 6 appeared. The stress induced larger liquid crystalline textures. The texture was almost unchanged on cooling to room temperature.

The XRD pattern of the sample indicated some reflections for small and wide angle areas, as illustrated in Fig. 7. The reflections for the small angle area correspond to a smectic layer structure. The *d*-spacings of the reflections observed at $2\theta = 2.7$, 5.2, and 7.6° are 3.27, 1.67, and 1.16 nm, respectively, and are associated with the 1st, 2nd, and 3rd reflections. The reflections for the wide angle area suggest a highly ordered smectic phase such as smectic E. Moreover, a very small exothermic peak was observed at 15.1 °C on the DSC cooling

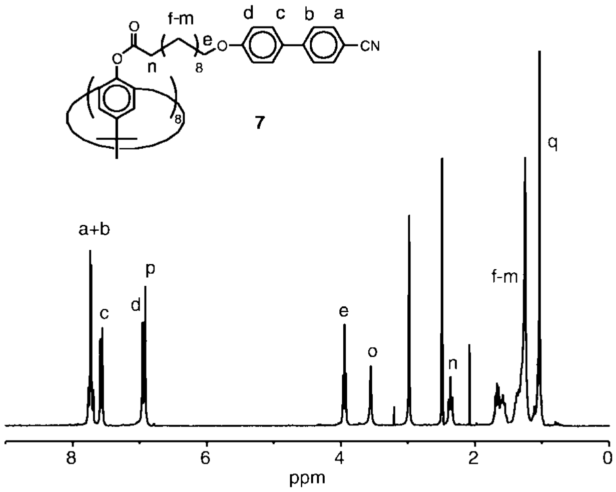


Fig. 1 ^{1}H NMR spectrum of **7** in DMSO-d_6 at 100 °C (270 MHz).

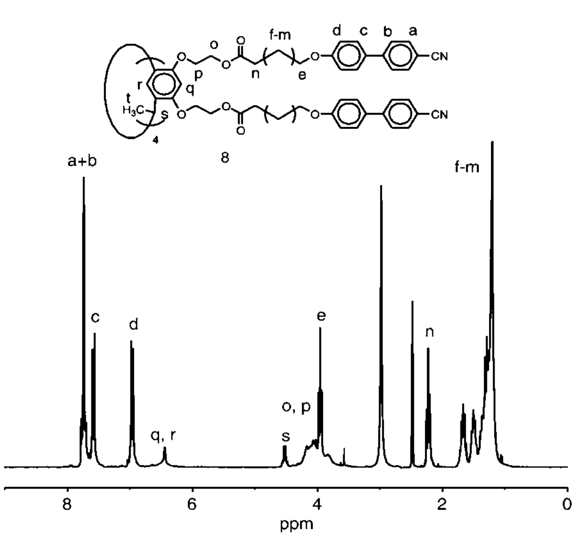


Fig. 2 ^{1}H NMR spectrum of **8** in DMSO-d_6 at 100 °C (270 Hz).

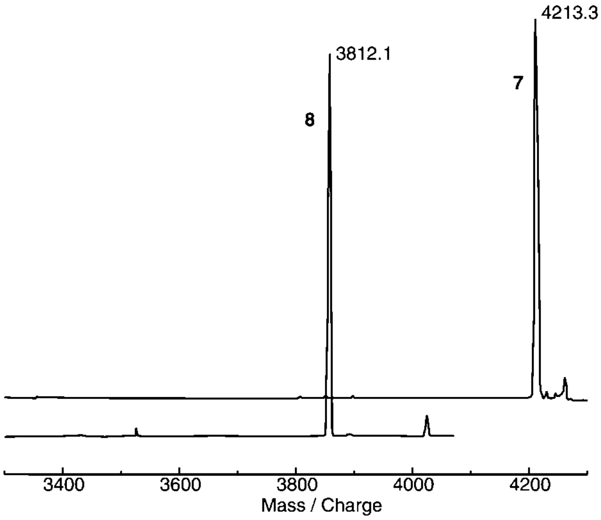


Fig. 3 MALDI-TOF mass spectra of **7** and **8**. The spectra were measured using 2,5-dihydroxybenzoic acid (DHBA) as the matrix.

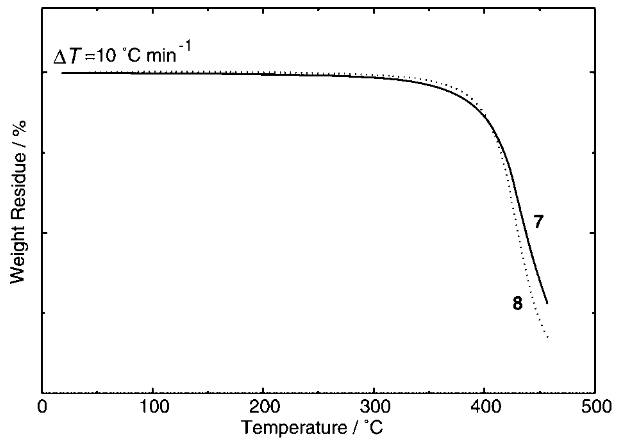


Fig. 4 TGA traces of **7** and **8** at a heating rate of 10 °C min^{-1} in N_2.

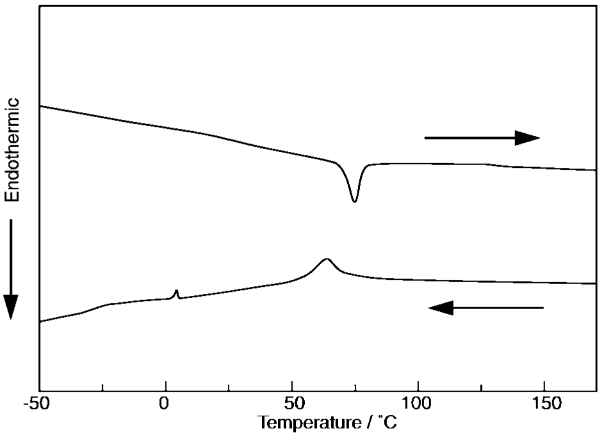


Fig. 5 DSC traces of **7** for heating and cooling processes.

trace. This phase transition could not be assigned, since the optical texture and XRD pattern remained almost unchanged.

T_g points clearly appeared around 25 °C on both the heating and cooling DSC traces of **8** as shown in Fig. 8. A comparatively large endothermic peak and a small shoulder peak were observed at 76.3 and 84.7 °C, respectively, on heating. An isotropization occurred above the higher endothermic peak. The cooling scan exhibited an exothermic peak at 74.5 °C. There was also a small shoulder, but no peak was observed at higher temperatures. The degree of supercooling was very low. Moreover, the total ΔH value of the endothermic

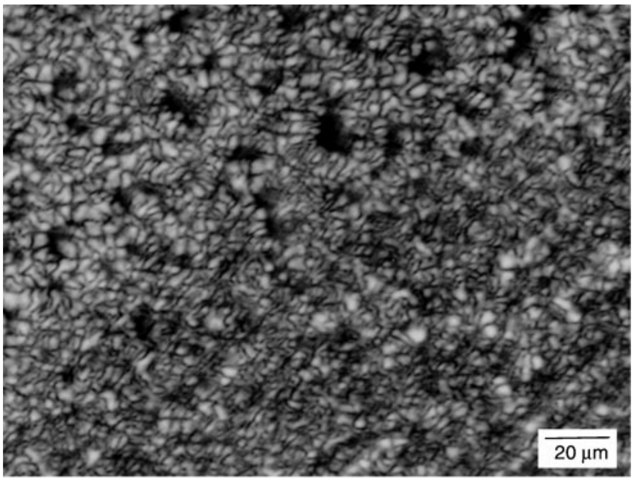


Fig. 6 Optical texture of **7** observed using POM with crossed polarizers. The sample was sheared at 50 °C.

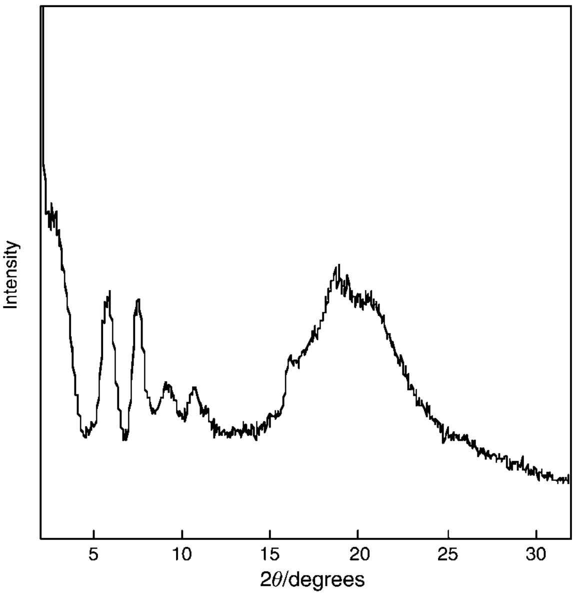


Fig. 7 XRD traces of **7** measured at room temperature.

peaks is 20.0 kJ mol^{-1}, and it agreed fairly well with that of the exothermic peak (20.2 kJ mol^{-1}).

The sample **8** was sheared in a similar way to **7**. A typical schlieren texture indicating $s = \pm 1$ and $+1/2$ disclinations was induced by shearing, as shown in Fig. 9(a), which was taken at 76 °C on cooling. Thus, the endothermic peak of the DSC curve can be assigned to a nematic–isotropic phase transition. When the sample was cooled, stripes appeared immediately on the schlieren texture, and the stripe pattern became clear, as shown in Fig. 9(b), which was taken at room temperature. Fig. 10(A) shows the XRD pattern of **8** taken at room temperature. The sample was cooled from the melt and annealed at 70 °C for 1 h. It exhibited two diffuse halos at 2θ = approximately 5 and 20°. The *d*-spacings of the two halos at low and wide angles are about 1.5 and 0.43 nm, respectively. The halo at wide angle corresponds to the average distance between the neighboring mesogens. However, it is hard to assign the halo observed at low angle from above data. The rings for the small angle area can be associated with the smectic layer structure. The layer spacing is estimated as 5.11 nm. Accordingly, **8** exhibited nematic and smectic phases. The large peak shown in Fig. 8 can

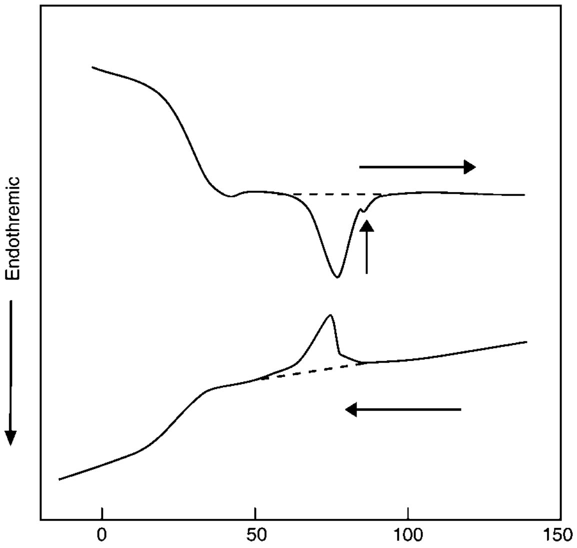


Fig. 8 DSC traces of **8** for heating and cooling processes.

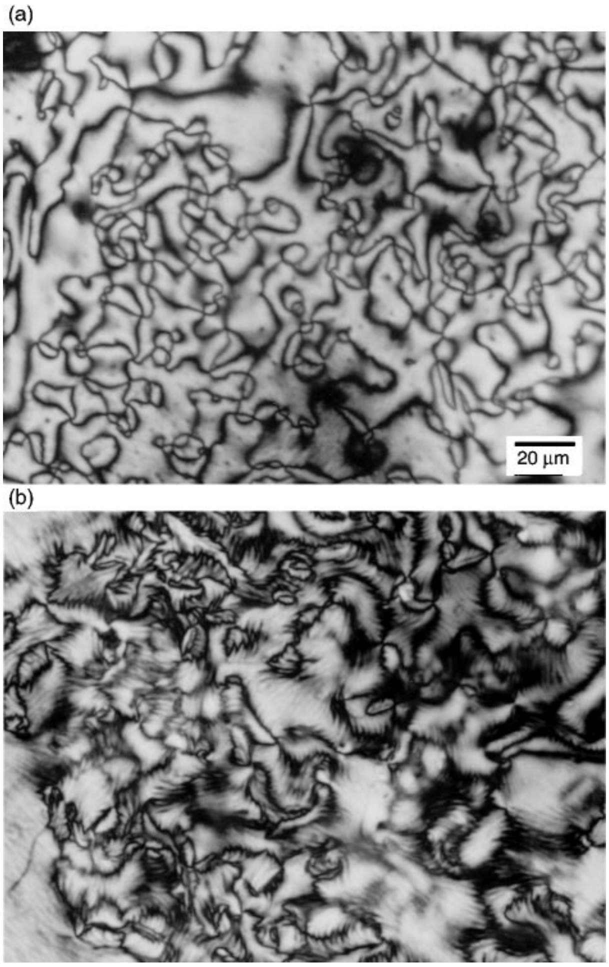


Fig. 9 Optical textures of **8** taken at (a) 76 °C and (b) RT on cooling using POM with crossed polarizers.

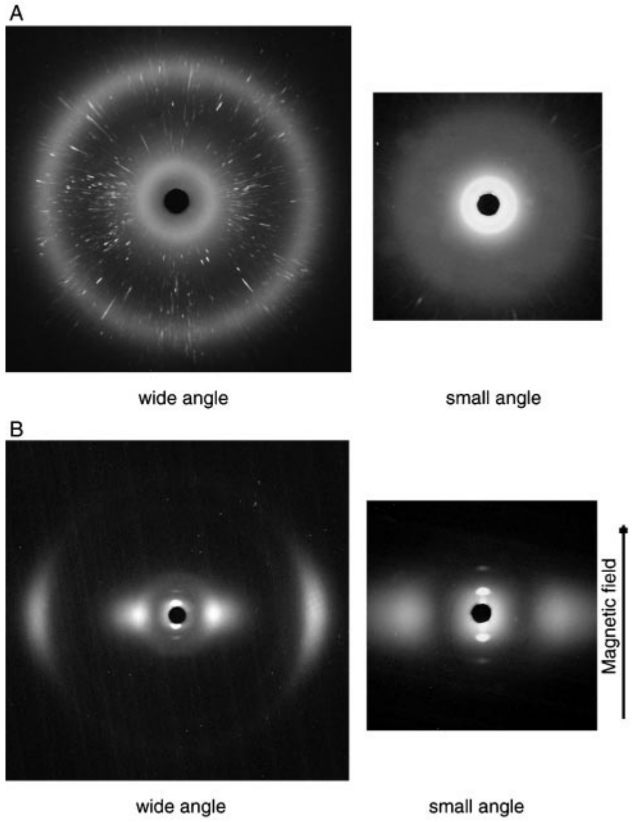


Fig. 10 XRD pattern of **8** (a) annealed at 70 °C and (b) oriented in a magnetic field of 2.8 T.

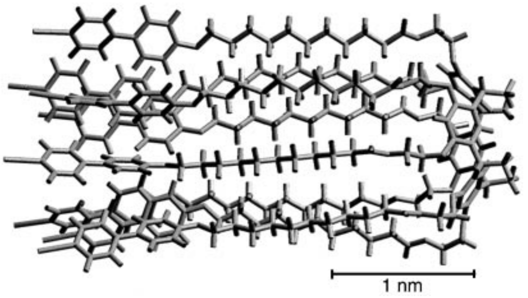


Fig. 11 Molecular model of **8** built by Cerius^2.

be associated with the nematic–smectic phase transition on the basis of these findings.

The nematic–isotropic phase transition was reversibly induced by heating and cooling; the nematic texture quickly appeared in the dark field on cooling. The degree of supercooling is very small. This suggests that **8** has a lack of entanglements and thus a quick response LC would be expected. The oriented film of **8** was prepared in a magnetic field in order to elucidate the liquid crystalline structure. Compound **8** was dissolved in DMF and the solution was cast on the glass plate and then placed in a magnetic field of 2.8 T at 25 °C for 2 h during the drying process. The film exhibited an oriented XRD pattern, as shown in Fig. 10(B). The diffused arcs were observed at low and wide angle areas on the equator. Both arcs were associated with the diffuse halos observed in Fig. 10(A). In addition, comparatively sharp reflections were observed at small angle area on the meridian. This pattern reveals a smectic A phase with a layer spacing of 5.11 nm.

Molecular modelling of **8** was carried out in Cerius^2 (Molecular Simulation Inc.). The all-*cis*-configuration of C4-RA was maintained after minimization using the force field pcff 300. The starting model of **8** was built such that the mesogens were arranged parallel, and then it was minimized using pcff 300. The estimated geometry of **8** was a cone-like structure, as illustrated in Fig. 11, where the mesogenic units are readily orientated within the molecule. On the other hand, molecular modelling for **7** exhibited diversity because of the various configurations of C8-A. It is possible that the C8-A core hardly affects the alignment of the mesogens within a molecule.

From the molecular model of **8**, the width and length of **8** could be estimated as approximately 1.5 and 3.5 nm, respectively, which corresponds with the *d*-spacing of the diffuse arc observed at low angle ($2\theta = 5°$) on the equator in Fig. 10(B). Thus, the scattering corresponds to the intermolecular distance between molecules of **8** within the smectic layer. It confirms that **8** has a similar conformation to the above cone-like structure model in the SA phase. The diffuse halo was also observed at 78 °C in the nematic phase. Thus, the corn-like structure of **8** was formed in the nematic phase.

The molecular length of **8** is shorter than the layer spacing (5.11 nm). Thus, the SA of **8** comprises an overlap layer. The SA structure of **8** is depicted in Fig. 12 using the molecular model on the basis of the above results. The structure is one of the possible smectic A structures, where a partial overlapping of the cyanobiphenyl units occurs and the alkyl spacers display

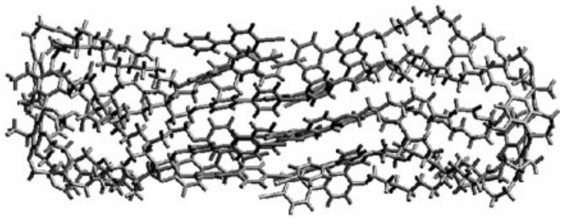


Fig. 12 Molecular modelling of overlapped **8** molecules using Cerius^2.

an increased conformational disorder because of the small width of the corn-like molecule.

Conclusions

The attachment of LC chains to calixarenes has been successfully carried out. Characterization of the products by MALDI-TOF-MASS and NMR supported the formation of completely modified calixarenes **7** and **8**. Compounds **7** and **8** had glass transitions at approximately −30 and +25 °C, respectively. They also exhibited liquid crystalline behaviour. The smectic structures of both samples were quite different; **7** exhibited a highly ordered smectic phase, whereas **8** possessed a smectic A phase. The difference between the two compounds comes from the molecular structures of the calixarenes. The configuration of the C4-RA core was found to be helpful in aligning the mesogens in a molecule. On the other hand, the C8-A core hardly affects the alignment of the mesogens. Furthermore, **8** exhibits a nematic phase in which a corn-like structure is formed. The degree of supercooling is comparatively small and the nematic texture rapidly appears on cooling. Thus, **8** is expected to act as a high response LC in its nematic phase. Additionally, it is possible to demonstrate a memory effect owing to the high glass transition temperature as in side-chain liquid crystalline polymers.

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