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Macrocycle-Based Liquid Crystals: A Study of Topological Effects on Mesomorphism

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A liquid-crystalline molecule based on a macrocycle and a forklike mesogen forms smectic A phases over a wide temperature range. This thermal behavior of the macrocycle-based compound has been compared with that of the corresponding catenane molecule.

Keywords: catenane; macrocycle; smectic liquid crystal; topological effect

INTRODUCTION

Intensive studies have been focused on the structure-property relationships of liquid crystals [1–9]. New chemical structures of liquid-crystalline (LC) molecules have been designed and prepared. Recently, induction of liquid crystallinity for topological interlocked molecules such as rotaxanes and catenanes has attracted attention [10–14] due to their potentials as dynamically functional molecular machines. For example, LC [2]catenane **1** and its copper complex **2** were reported in our previous communication [10]. These compounds

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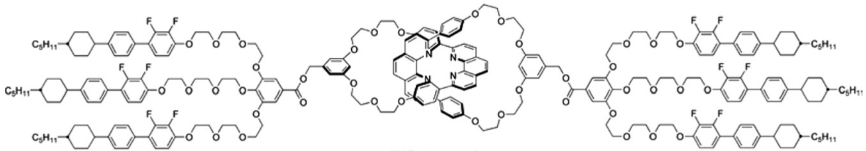
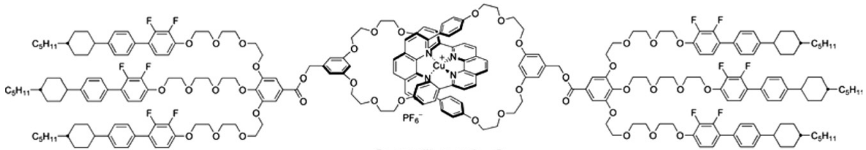
exhibit smectic A phases over wide temperature ranges. Dynamic control over the topology of the macrocyclic compounds in the condensed state is intriguing; however, it has been mainly demonstrated in solutions [15–20] and in polymer networks [21–23].

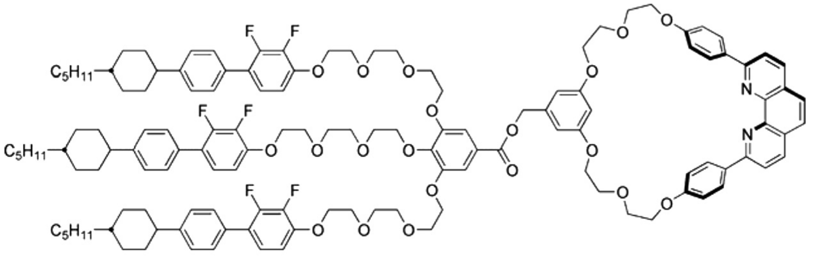


[2]Catenane **1**



Copper(I) complex **2**

It is of interest to examine how the interlocked catenane structure affects the LC properties. In the present study, the corresponding monomeric macrocycle **3** has been prepared, and its self-assembled behavior has been examined. Compound **3** can be regarded as a new macrocyclic liquid crystal, while a number of liquid crystals having macrocyclic moieties have been developed [24–26].



Macrocycle **3**

RESULTS AND DISCUSSION

The molecular design (Fig. 1) is based on the use of a fluoro-substituted cyclohexylbiphenyl core, which tends to show a wide range of smectic LC phases with a low melting point [27–29]. The syntheses of **1, 2, 4, 5**, and **6** were reported earlier [10]. Macrocycle **3** was

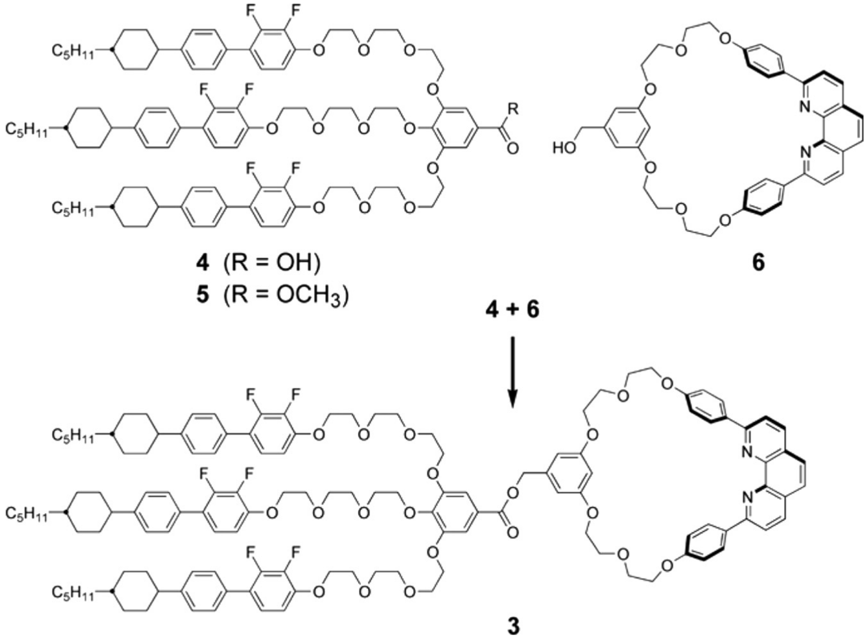


FIGURE 1 Structures of forklike dendrons (**4, 5**) and macrocycles (**3, 6**). The catenane corresponding to two interlocked **3** is named **1**.

prepared by esterification of **4** with **6** mediated by EDC in 44% yield. This new compound was characterized by mass spectrometry (MALDI-TOF) as well as one- and two-dimensional NMR spectroscopy. The spectroscopic properties are in accordance with previous results on related molecules [15–18,27–29].

The thermal properties of **1, 2, 4**, and **5** were reported previously [10], but no self-assembling properties of **4** and **5** were discussed. The LC properties of **1–5** were examined by polarized optical microscopy, differential scanning calorimetry (DSC), and small-angle X-ray scattering (SAXS) measurements (Table 1). All these compounds show smectic LC phases over wide temperature ranges. The glass transition and the isotropization of macrocycle **3** occur at 46 and 109°C, whereas for catenane **1** they occur at 69 and 117°C, respectively. This observation suggests that the topological dimerization enhances thermal stabilization of the glassy and liquid-crystalline states. Moreover, macrocycle **3** exhibits an additional phase transition at 97°C. The polarized optical microscopic images (Fig. 2a, c) and the SAXS patterns (Fig. 2b, d) for **3** reveal that both phases are different

TABLE 1 Thermal Properties of **1–5**

Compound	Phase transition behavior[a]										
1	G	69	S_X	83	S_{A1}	117	Iso				
2	G	68	S_{A1}	147	Iso						
3	G	46	S_{A2}	97	S_{Ad}	109	Iso				
4	G	2	S_{A2}	176	Iso						
5	G	−5	S_C	40	S_{A2}	129	S_{Ad}	136	N	141	Iso

[a] Transition temperature (°C) determined by DSC (second cooling; 5°C $\min^{-1}$). G: glassy, S_{A1}: monolayered smectic A, S_{A2}: bilayered smectic A, S_{Ad}: interdigitated smectic A, S_C: smectic C, S_X: unidentified smectic phase, N: nematic, and Iso: isotropic.

types of smectic A phases. The peaks at 77.5, 38.7, and 25.7 Å corresponding to the (100), (200), and (300) reflections are observed in the SAXS pattern of **3** at 65°C (Fig. 2b). The interlayer spacing of 77.5 Å is almost identical to that of **1** (78.7 Å) in the smectic A_1 phase (Fig. 3). These results suggest that the molecular organization in this phase is mostly controlled by the relative volume of the macrocycle compared to the mesogenic dendron, which is the same in the

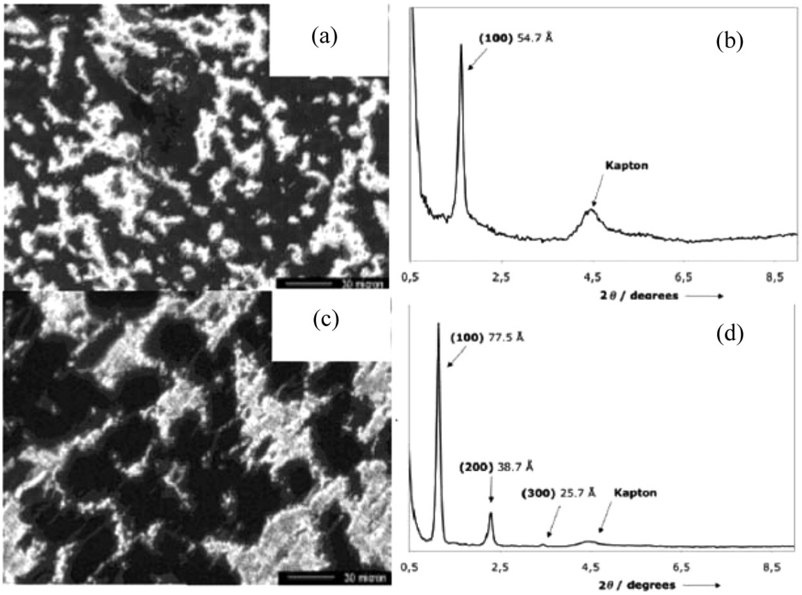


FIGURE 2 (a) Polarized optical micrograph and (b) SAXS pattern of **3** in the S_{Ad} phase at 107°C (c) Polarized optical micrograph at 88°C and (d) SAXS pattern of **3** in the S_{A2} phase at 65°C.

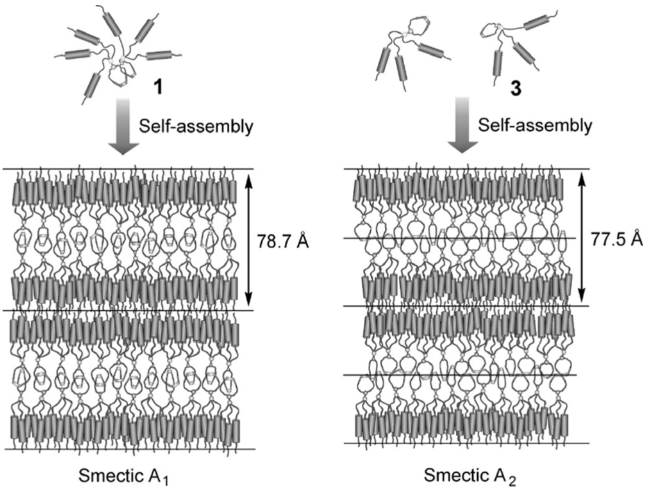


FIGURE 3 Possible organization of the layered structures for **1** in the S_{A1} phase and for **3** in the S_{A2} phase.

catenane **1**. The mechanically interlocked structure does not seem to have a strong influence on the molecular organization in this smectic A phase. The phase is smectic A_1 in the case of catenane **1**. In the case of macrocycle **3**, it should be called smectic A_2 because each layer is composed of two layers of the molecules [30]. As the temperature rises at 107°C, the SAXS pattern of macrocycle **3** exhibits only one peak at 54.7 Å corresponding to the (100) reflection of a smectic A_d phase. The interdigitation should take place in the layer of the macrocycles. This interdigitation is forbidden in catenane **1** due to the mechanically interlocked structure.

It is of interest to note the differences in the mesomorphic properties between dendrons **4** and **5**, which only differ in the substituent at the apex. For dendron **5**, the phase sequence smectic C–smectic A_2–smectic A_d–nematic is clearly observed on heating and cooling. While the smectic C–smectic A_2 transition is not detected on the DSC scans, the polarized optical microscopy clearly shows the phase transition from the textured smectic C to black, homeotropically aligned smectic A_2 phases around 40°C. The SAXS measurement shows that the interlayer spacing of **5** (56.4 Å) in the smectic A_2 phase is longer than its fully extended molecular length of 31 Å, suggesting the formation of a bilayer type smectic structure. A large decrease in the interlayer spacing to 44.4 Å is also observed for the smectic A_d due to the interdigitation of the forklike mesogenic moieties.

By contrast, dendron **4** with the free carboxylic acid group presents significantly different LC behavior. The isotropic phase of **4** is attained at a much higher temperature (ca. 180°C) and the range of the smectic A_2 phase is much wider than **5** because of the formation of hydrogen-bonded dimers. The interlayer spacing of **5** (57.1 Å) in the smectic A_2 phase is comparable to that of **4**. The supramolecular dimerization that occurred in **4** via hydrogen-bonding may prevent the interdigitation of the forklike mesogenic moieties, which is evident from the absence of the smectic A_d phase. The LC properties of the couple macrocycle **3**/catenane **1** is similar to the couple dendron ester **5**/dendron acid **4**. It should be noted that more stable LC phases can be induced when supramolecular dimers are formed via catenation or hydrogen bonds, in which the interdigitation of the layers is not observed anymore.

EXPERIMENTAL

Synthesis of Macrocycle 3

To a solution of **4** (40 mg, 0.025 mmol) in dry CH_2Cl_2 (3 mL) were added 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC, 60 mg, 0.31 mmol) and 4-dimethylaminopyridine (DMAP, 140 mg, 1.15 mmol). After stirring at room temperature for 20 minutes, **6** (15 mg, 0.023 mmol) was added as a solid, and the suspension was sonicated in an ultra-sound bath until a clear solution is obtained. The solution was stirred for one week at room temperature under an Ar atmosphere. A saturated aqueous solution of $NaHCO_3$ (30 mL) was added to the reaction mixture, and the product was extracted with $CHCl_3$. The combined organic layers were dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified with recycling GPC to afford **3** as a slightly yellowish amorphous solid (yield = 23 mg, 44%). ^1H NMR ($CDCl_3$, 400 MHz): δ 8.40 (d, $^3J = 8.8$ Hz, 4H), 8.24 (d, $^3J = 8.4$ Hz, 2H), 8.05 (d, $^3J = 8.4$ Hz, 2H), 7.73 (s, 2H), 7.38 (d, $^3J = 8.0$ Hz, 6H), 7.27-7.23 (m, 8H), 7.13 (d, $^3J = 8.8$ Hz, 4H), 7.06-7.00 (m, 3H), 6.78-6.70 (m, 3H), 6.60 (d, $^4J = 1.6$ Hz, 1H), 6.57 (d, $^4J = 1.6$ Hz, 1H), 5.18 (s, 2H), 4.32 (t, $^3J = 4.8$ Hz, 4H), 4.23-4.10 (m, 18H), 3.95-3.89 (m, 6H), 3.87-3.79 (m, 12H), 3.71 (s, 12H), 2.52-2.44 (m, 3H), 1.93-1.85 (m, 12H), 1.51-1.41 (m, 6H), 1.34-1.17 (m, 27H), 1.10-0.99 (m, 6H), 0.90 (t, $^3J = 6.8$ Hz, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 165.7 160.1 160.0 156.2 152.2 150.1 (m) 147.4 147.3 (m) 146.0 143.1 142.6 140.6 138.3 136.6 132.6 132.2 129.0 128.6 (d) 127.4 127.0 125.5 124.8 123.5 123.3 (m) 119.1 115.5 109.9 109.3 106.5 102.0 72.4 71.0 70.9 70.8 70.6 70.5

69.9 69.6 69.5 69.4 68.9 67.8 67.5 66.6 44.3 37.4 37.3 34.3 33.6 32.2 26.6 22.7 14.1. MS (MALDI): m/z 2214.51 (calcd $[M\text{+H}]^+ = 2214.11$), 2236.48 (calcd $[M\text{+Na}]^+ = 2236.09$).

CONCLUSION

In conclusion, we have prepared the LC macrocycle, and compared the thermal properties with the LC catenane. It shows that catenation can be used as a new tool for making dimeric LC molecules and tuning the thermal behavior. For the first time, topological effects induced by non-trivial interlocked molecule are shown for the LC phase. The combination of supramolecular association [1,2,31,32] and nanosegregation [3,33,34] of liquid crystals with molecular design of interlocked molecules would provide new functional materials.

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