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Liquid Crystalline Corannulene Responsive to Electric Field

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Corannulene is a bowl-shaped π-conjugated molecule, whose carbon network skeleton is equivalent to a partial structure of fullerenes.[1,2] Because of this nonplanar geometry, corannulene can provide some unique properties that are not provided by planar π-conjugated analogues. For example, corannulene in solution undergoes inversion of its bowl-shaped skeleton at a rate of greater than 2×10^5 s^{-1} at 25 °C.[3] The electron densities of corannulene on its concave and convex faces are different from one another, so that this polycyclic aromatic hydrocarbon has a dipole moment.[4] Therefore, if one can assemble this molecule into a one-dimensional columnar array, the resulting ordered material might display ferroelectric properties.[5] Despite such an interesting potential, columnar π-stacking has been realized only in the crystalline state with a few corannulene derivatives.[6] Here we report the first corannulene derivatives **2** and **3** (Figure 1) that are able to form a liquid crystalline (LC) assembly. In particular, compound **3** forms a hexagonal columnar LC assembly over a wide temperature range including room temperature. We also found that this LC assembly responds to an applied electric field, giving rise to a homeotropic alignment of the hexagonal columns with respect to the electrode surface.

Reported polycyclic aromatic hydrocarbons, forming LC assemblies, bear long paraffinic side chains in their periphery. So, we initially investigated the assembling properties of reported corannulene derivative **1** having 10 thiododecyl side chains,[7] with an expectation that a multivalent intermolecular sulfur−sulfur interaction might operate and help the corannulene core to π-stack columnarly. However, as studied by differential scanning calorimetry (DSC; Figure 1) and X-ray diffraction (XRD) analysis, **1**, over a wide temperature range, remained amorphous and did not show any sign of the formation of LC mesophases. Having these results in mind, we newly synthesized **2** and **3** bearing 10 peripheral amide functionalities, since these amide groups, located concentrically around the corannulene core, are expected to form multiple hydrogen bonds[8] and therefore assist the formation of a stable columnar structure. While **2** carries linear paraffinic side chains, corannulene **3** with a molecular weight of 7572 possesses tri-branched paraffinic side chains,[9] which are known to lower the crystalline nature of amidated discotic molecules.[8a]

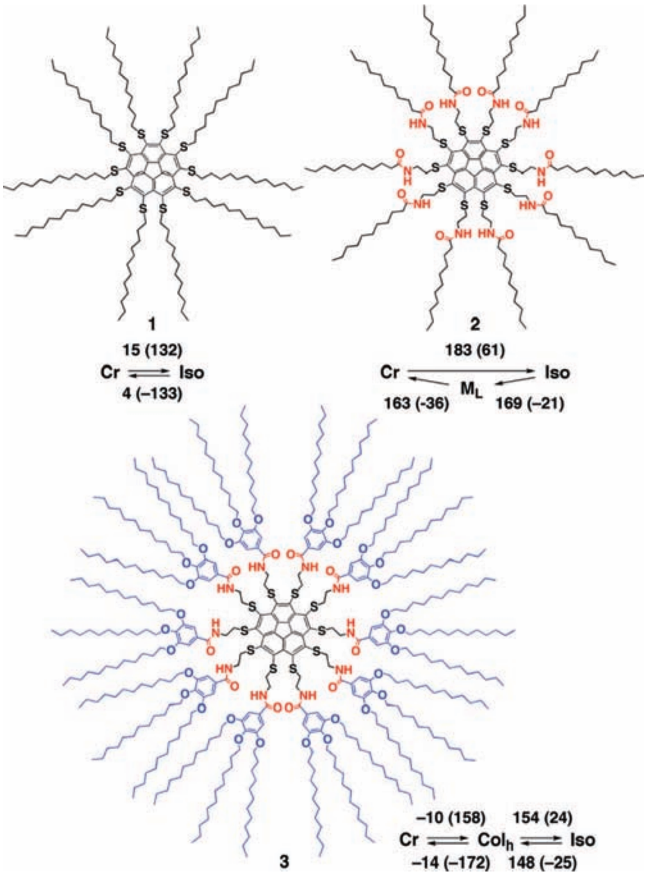

Figure 1. Schematic structures of corannulenes **1**−**3** and their phase transition profiles determined by DSC and XRD. Numeric values represent phase transition temperatures (°C) and enthalpy changes (kJ mol^{-1}) in parentheses.[10] Cr, Col_h, M_L, and Iso denote crystalline, hexagonal columnar, lamellar, and isotropic phases, respectively.

1 was synthesized according to a method reported by Scott et al., using decachlorocorannulene and the sodium salt of dodecane thiolate.[7] For the synthesis of **2** and **3**, the synthetic protocol for **1** had to be modified in such a way that the thiol species of the corresponding paraffinic components are ionized in situ by using DBU for the reaction with decachlorocorannulene.[10] In sharp contrast with **1**, these corannulenes assembled into a LC mesophase, where **3** behaved much better than **2** in various aspects. DSC analysis of **3** showed a phase transition behavior, where a LC mesophase, on second heating, appeared at −10 °C and then disappeared at 154 °C to form an isotropic melt (Figure 1).[10] On cooling from the isotropic melt, the resulting fluidic LC material in polarized optical microscopy (POM) at, e.g., 115 °C clearly showed a fan texture (Figure 2c), characteristic of hexagonal columnar LC assemblies. In fact, XRD analysis of **3** at 70 °C showed diffraction peaks with *d*-spacings of 35.0, 20.2, and 17.5

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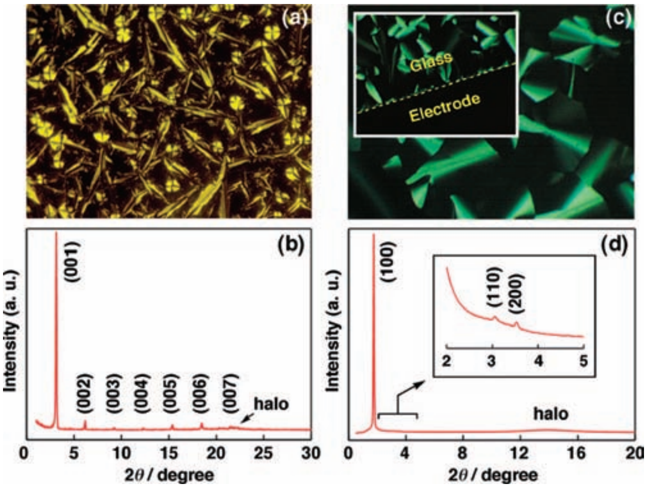

Figure 2. (a, c) Polarized optical micrographs (POM) of **2** at 165 °C and **3** at 115 °C. Inset in (c) shows POM at 125 °C of **3**, sandwiched by glass plates with patterned ITO electrodes (5-μm separation) under an applied electric field of 15 V μm^{-1}. (b, d) X-ray diffraction (XRD) patterns of **2** at 165 °C and **3** at 70 °C. Inset in (d) shows a magnified XRD pattern at 2θ = 2°−5°.

Å (Figure 2d), which can nicely be indexed as the (100), (110), and (200) reflections of a hexagonal columnar mesophase. A broad halo centered at 4.3 Å is typical of paraffinic domains in the molten state. Compared with **3**, corannulene **2** bearing linear paraffinic side chains formed a LC mesophase only in a very narrow and much higher temperature range. Namely, in DSC upon second cooling, **2** showed two endothermic peaks at 169 and 163 °C (Figure 1).[10] In POM at 165 °C, the resulting fluidic material showed a LC texture (Figure 2a), which was distinctively different from that of **3**. XRD analysis of **2** at 165 °C showed a periodic pattern composed of an intense peak with a *d*-spacing of 28.3 Å, indexed as the (001) reflection, followed by other peaks due to higher order reflections up to (007) (Figure 2b). From this characteristic XRD pattern, **2** most likely adopts a lamellar structure in the LC state.

The large difference in the assembling behaviors of amide-appended **2** and **3** from that of **1** suggests that a multivalent H-bonding interaction is crucial for the LC assembly. In fact, in variable-temperature infrared spectroscopy (VT-IR) of **2**, stretching vibrational bands due to the CO and NH groups shifted discontinuously toward lower wavenumber regions at around the temperatures for the isotropic melt-to-LC and LC-to-crystal phase transitions.[10] Likewise, liquid crystalline **3** displayed its CO and NH stretching vibrations in lower-wavenumber regions than those typically observed for non-H-bonded amide groups.[10] However, the spectral change, associated with the phase transition, was much less explicit or abrupt than in the case of **2**. This might be due to an intrinsic spectral feature of aromatic ester carbonyls or suggests that the peripheral amide groups of **3** prefer to remain H-bonded in the molten state even after the columnar π-stacking of the corannulene core is thermally broken.

One of the appealing aspects of LC materials is their potential capability of responding to external stimuli. In the course of the above study, we noticed that the LC columns of assembled **3**, under an applied electric field, can be aligned homeotropically to an ITO electrode surface.[11] For a clear demonstration of this phenomenon, **3** was sandwiched by glass plates (5-μm separation) patterned with ITO electrodes and allowed to assemble into the LC state by slow cooling from its isotropic melt. When the sample at 125 °C in an applied alternating electric field of 15 V μm^{-1} was continuously monitored by POM, the birefringent image, initially observed in the entire view of the sample, gradually changed and eventually displayed a certain pattern with a dark field only in a section sandwiched by the electrodes (Figure 2c, inset). This patterning was accomplished within 30 min. Interestingly, even after the electric field was switched off, the pattern developed electrically was maintained for a long period of time at 125 °C. However, once heated above the clearing temperature and allowed to cool subsequently without such an electric stimulus, the LC sample retrieved the birefringent texture in its entire view. This observation is noteworthy, considering that most discotic LC materials so far reported are hard to align electrically, mainly because of their excessive stiffness.[12]

In summary, we succeeded in developing the first liquid crystalline corannulenes **2** and **3** by incorporating multiple amidated paraffinic side chains into their bowl-shaped core. Because of a multivalent H-bonding interaction between the peripheral amide groups, along with a van der Waals interaction of the branched paraffinic wedges, **3** forms a hexagonal columnar mesophase over a wide temperature range including room temperature. Of further interest, the π-stacked columns of **3** are aligned in response to an applied electric field, whereas those of planar π-conjugated analogues are hardly responsive. These new LC materials, tailored with molecularly engineered corannulenes, are expected to open a new door to a variety of interesting applications.

Supporting Information Available: Details of synthesis and characterization, DSC, and VT-IR spectral profiles of **2** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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