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Columnar Liquid Crystal with a Spontaneous Polarization along the Columnar Axis

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Ferroelectric materials are those having a spontaneous polarization that can be reversed by an applied electric field. Ferroelectric liquid crystals (FLCs) have attracted much attention in material sciences because of their potential utility for piezoelectric, pyroelectric, and second-order nonlinear optical (NLO) devices as well as displays.[1] However, it is essentially difficult to realize polar orders in fluidic media, because molecules prefer to align symmetrically so as to cancel their dipole moments. While a variety of FLCs have so far been reported since the pioneering work of Meyer et al.,[2] they are smectic and composed of chiral rod-shaped or bent-core molecules[3] capable of breaking the symmetry of the systems. Because of the presence of an in-layer macroscopic polarization in such FLCs, each layer in principle may serve as a 1-bit memory if the in-layer polarization can be switched individually. However, this idea might not be realistic. A more feasible approach would be to make use of the geometry of columnar liquid crystals. If each column has a spontaneous polarization along its column axis, and the columns are oriented in such a way that their polarizations align unidirectionally, the resulting LC materials are promising for the development of high-density ferroelectric memory devices, given that the polarization switching is possible in each column.[4] Despite such a prospect for columnar FLCs, the absence of a rational design strategy has made progress extremely difficult. As the first step toward this goal, we report here fan-shaped **2** (Figure 1a) is the first LC molecule that forms a columnar mesophase (Figure 1b) with a spontaneous polarization along the columnar axis.

Percec et al. have reported that certain fan-shaped molecules self-assemble conically into an umbrella, which stacks up to form a columnar LC structure (Figure 1b).[5] We expect that introduction of a large dipole into the focal core of such fan-shaped molecules might result in spontaneous macroscopic polarization in the resulting LC mesophase. For this purpose, 4,5-dithiaphthalonitrile derivatives **2** and **3** were synthesized and unambiguously characterized by NMR and MALDI-TOF-MS analyses.[6] These compounds commonly possess two H-bonding amide groups with a view to ensure their umbrella-shaped assemblies, essential for polarized columns. By means of differential scanning calorimetry (DSC) and polarizing optical microscopy (POM), we confirmed that **2** and **3** both form an LC mesophase (Figure 1c, d).[6] Although compound **3** in its LC state showed an X-ray diffraction (XRD) pattern typical of a hexagonal columnar (Col$_h$) geometry (Figure 2b), that of **2** suggested the existence of a 3D lattice, in which 10.7 nm long columns form a 2D hexagonal lattice (Figure 2a, e).[6,7] Intercolumnar distances of the LC mesophases of **2** and **3** were evaluated as 4.2 and 3.4 nm, respectively, suggesting that four and three molecules of **2** and **3** assemble concentrically into expected umbrellas.

Note that the structural difference between **2** and **3** lies only in that the former has a one-carbon shorter spacer than the latter between the Ar−S and amide groups. In regard to a question why **2** and **3** assemble into such different mesophase structures, we found that their H-bonding modes are totally different from one another. In variable-temperature infrared (VT-IR) spectroscopy, **2** at 120 °C showed characteristic stretching vibrational bands due to H-bonded amide CO and NH groups at 1644 and 3330 cm^{-1}, respectively (Figure 2c). Of interest, these bands shifted discontinuously to lower wavenumbers at the isotropic melt-to-LC phase transition,[6] indicating that the molecules of **2** are tightly connected together by a strong H-bonding interaction in each column. In sharp contrast, **3** displayed a much less explicit H-bonding nature (Figure

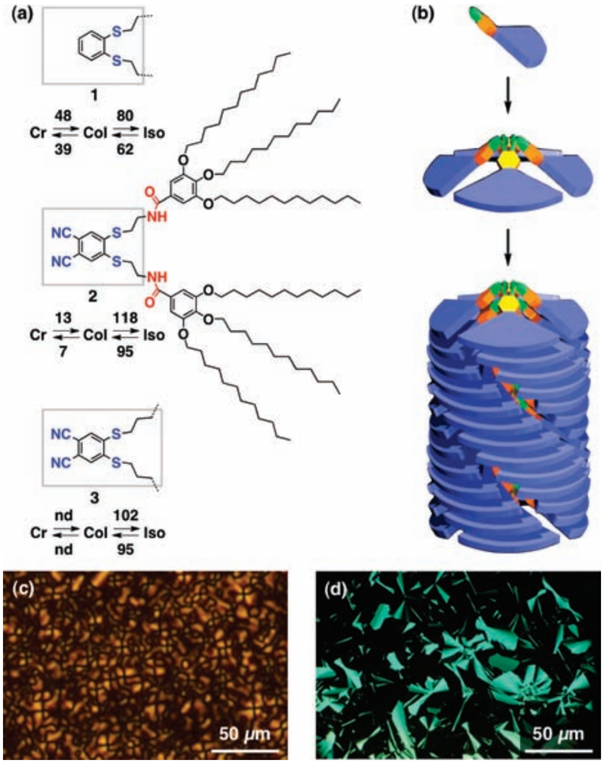

Figure 1. (a) Structures of compounds **1**−**3** (phase transition temperatures in °C) and (b) illustration of their columnar assembly. POM images of (c) **2** and (d) **3** at 90 and 80 °C, respectively.

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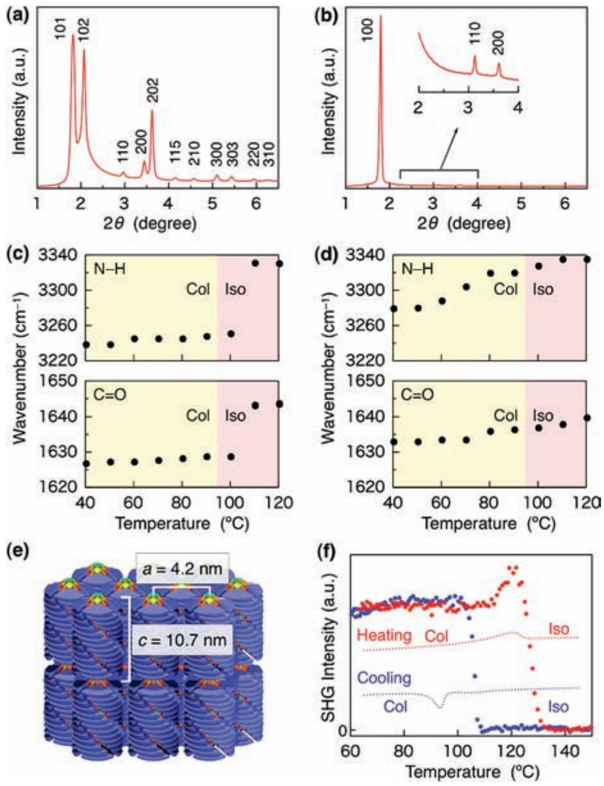

Figure 2. XRD patterns of (a) **2** and (b) **3** at 90 and 80 °C, respectively. IR spectral change profiles of the N—H and C═O stretching vibrational bands of (c) **2** and (d) **3** on cooling from 120 to 40 °C, where the pink- and yellow-colored regions represent temperature ranges for the isotropic melt and columnar mesophase, respectively. (e) Schematic representation of the columnar assembly of **2**. (f) SHG signal intensity profiles of **2** on cooling (blue) followed by heating (red) in a temperature range of 60−150 °C (broken curves represent the corresponding DSC thermograms).

2d), where its CO and NH stretching vibrations did not display an abrupt change upon phase transition.

Second harmonic generation (SHG), observable for molecular assemblies with a noncentrosymmetric geometry, has been utilized as a probe for the existence of polar structures.[8] Compound **3** in its LC state as well as in other temperature ranges showed no detectable SHG signal. In sharp contrast, the columnar mesophase of **2** clearly displayed an SHG signal with a hysteresis nature in accord with that of the phase transition profile (Figure 2f). Noteworthy, the SHG signal was more pronounced as the material was allowed to cool more slowly from its isotropic melt. Furthermore, use of a substrate covered with an aligned polyimide film did not cause any change in the signal intensity. Considering the hexagonal symmetry, all the above observations allow us to conclude that the columnar LC mesophase of **2** possesses a spontaneous macroscopic polarization along the columnar axis (*c* axis). The observed polarization originates from the large dipole in the aromatic core of **2**, since reference compound **1** without cyano groups (Figure 1a), though adopting an LC geometry identical to that of **2**,[6] was SHG-silent over a wide temperature range.

Spontaneous polarization is a prerequisite for ferroelectric liquid crystals. Although a few LC materials with a columnar geometry have been claimed to be ferroelectric based on their switchable current profiles,[4b] reinvestigations using SHG as a probe have revealed that they do not possess a spontaneous polarization.[8a] With that in mind, we inveastigated the ferroelectric response of **2** in its LC state. However, the polarity did not switch in response to an applied electric field, most likely due to an insufficient flexibility of the LC mesophase. Nevertheless, fan-shaped **2** is the first LC molecule whose columnar mesophase possesses a spontaneous macroscopic polarization and, therefore, provides useful design strategies toward the realization of columnar FLCs. Considering the VT-IR profile (Figure 2c), the polar aromatic core of **2** is highly constrained due to a short spacing from the tightly H-bonded amide groups, so that the umbrella-shaped conical assembly of **2**, essential for the polar columnar assembly, seems to be quite stable against thermal fluctuations. The absence of spontaneous polarization in the mesophase of loosely H-bonded **3** supports the importance of a strong H-bonded network around the assembled aromatic cores. We also consider that the larger intercolumnar distance in the LC mesophase of **2** than that of **3** may be advantageous for polarized columns to align unidirectionally.

In summary, we developed a fan-shaped **2** having H-bonding amide groups in proximity to its polar aromatic core as the first LC molecule that self-assembles into a columnar geometry with a spontaneous macroscopic polarization along the columnar axis. Although this LC is not ferroelectric because its polarization does not respond to the applied electric field, further elaboration of this molecular design may lead to the realization of ferroelectric columnar LC materials.

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Supporting Information Available: Details of synthesis and characterization, POM, XRD, DSC, and IR spectral profiles of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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