

Synthesis of New Chiral Chromonic Lyotropic Liquid Crystal Based on Perylenebis(dicarboximide)

Jaishri J. Naidu, Yun-Ju Bae, Kwang-Un Jeong, Seung Hee Lee, Shinwoong Kang,[†] and Myong-Hoon Lee*

Department of Polymer/Nano Science Technology, Chonbuk National University, Chonju, Chonbuk 561-756, Korea. *E-mail: mhlee2@chonbuk.ac.kr

[†]Liquid Crystal Institute, Kent State University, Kent, Ohio 44242, USA

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Lyotropic chromonic liquid crystals (LCLCs) represent a special class of lyotropic mesophases markedly different from the conventional amphiphilic mesogens.¹⁻³ LCLCs are composed of plank-like molecules with polyaromatic central core and hydrophilic ionic groups at the periphery. Because of the hydrophobic nature of the aromatic central core and the hydrophilic periphery, the molecules assemble into stacks with degenerated molecular orientation in the molecular plane to form chromonic nematic (N) phase. In the N phase, the columnar aggregates align parallel to each other but show no long-range positional correlations. The variety of possible geometries of aggregations is enriched by the fact that the molecular planes can adopt different orientations with respect to the axis of the aggregates.

Applications of chromonic liquid crystals are relatively unexplored. Potential applications reported for chromonic liquid crystals include the fabrication of light-harvesting devices⁴ and coatable polarizers which are fabricated by aligning liquid crystals *via* photo-alignment or mechanical shearing techniques.⁵ In both cases, an important criterion for generating high performance polarizing films is the self-organization of dichroic dyes into a highly ordered orientation. Chromonic liquid-crystalline phase is subsequently dried to give an anisotropically oriented solid phase. The structure-property relationships of chromonic liquid crystals are not clearly understood despite the identification of many chromonic mesogens. Furthermore, despite the importance of the LCLCs in various applications such as optically oriented films, bio-sensors and mimicking of nucleic acids, chromonic mesogens having optically active center have been studied rarely. Besides, the most of studies concerns a chiral phase attained by doping a chromonic N phase with a chiral dopant⁶ rather than a chiral group directly attached to a mesogenic core.⁷

Perylene dyes cover the whole range of the visible spectrum and find applications in conventional uses as well as in high-tech applications.⁸⁻¹² Especially, 3,4:9,10-perylenebis(dicarboximides) are generally referred as a functional dye due to their electro-optic nature such as photo-conductivity and fluorescence in addition to the unique optical absorption property. The perylene dyes find wide applications in optical films, photo-conducting materials, sensors and electroluminescent displays. Recently, LCLCs based on perylene core have attracted much attention because the anisotropic

orientation of molecules with π - π stacking of aromatic core can exploit their intrinsic properties most efficiently.

In this paper, we report the first synthesis of a perylene-based chiral mesogen for LCLC as shown in Figure 1, and discuss its lyotropic chromonic liquid crystalline behavior. The synthesis of (S)-(-)-2-aminomethyl-1-ethylpyrrolidine 3,4:9,10-perylenebis(dicarboximide) (**1**) was carried out by refluxing perylene-3,4:9,10-tetracarboxylic anhydride with chiral (S)-(-)-2-aminomethyl-1-ethylpyrrolidine in dimethylsulfoxide (DMSO) to give a dark red perylene diimide solid in high yield after purification.¹³ Dihydrochloride salt (**2**) of **1** was prepared by addition of excess amount of conc. HCl with subsequent removal of remnant HCl. The compound **1** was not soluble in most of organic solvents, slightly soluble in methylene chloride and chloroform, and only soluble in acids such as CF₃COOH and HCl. When converted to a salt form

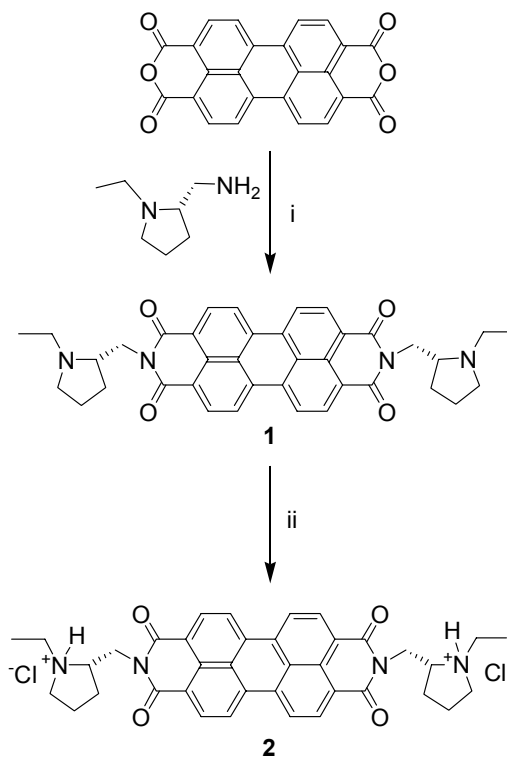


Figure 1. Synthetic scheme of new chiral LCLC. i) in DMSO, 70 °C, 26 h; ii) conc. HCl.

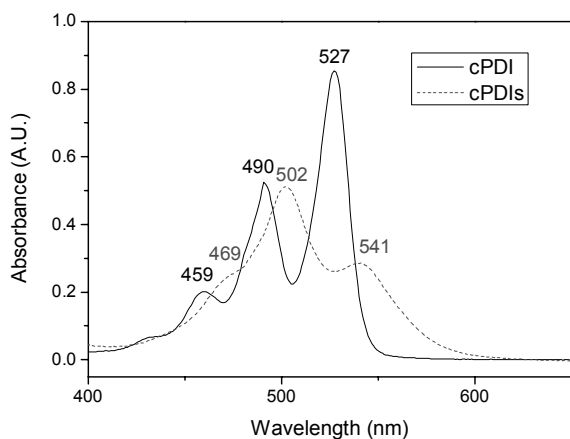


Figure 2. Visible spectra of **1** (solid) in CHCl_3 (2×10^{-7} M), and **2** (dot) in water (1.7×10^{-6} M).

with HCl, however, it became soluble in water. Compound **1** exhibited strong fluorescence with violet color in methylene chloride or chloroform solution. The structure of compound **1** was characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, IR and UV/vis spectroscopy. The results of $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectroscopic characterization are listed in reference 13. High resolution mass spectroscopic result also confirmed the structure of compound **1**. IR peaks at 1692 and 1664 cm^{-1} indicated the complete formation of imide bond. The visible absorption spectra for compound **1** (2×10^{-7} M) in chloroform and **2** (1.7×10^{-6} M) in distilled water are shown in Figure 3. Compound **1** showed a λ_{max} at 527 nm with two smaller absorptions at 490 and 459 nm , which are characteristic of

free perylenebis(dicarboximide).¹³ For corresponding salt **2**, we observed the peak at 527 nm which is most likely due to absorption of the monomeric dye molecules¹⁴ shifted to red with significantly decreased intensity. The relative intensity of the other two peaks at 490 and 459 nm increased with red-shift. This suggests that the salt form exists as a dimer and higher aggregates in aqueous solution even at dilute concentration, which is referred as isodemic.

Aqueous solutions of compound **2** under polarized optical microscope (POM) exhibited various liquid-crystalline textures as shown in Figure 3. A cholesteric fingerprint texture was observed at $35.8\text{ }^\circ\text{C}$ for the sample of $9\text{ wt } \%$ concentration (Fig. 1a). This clearly indicates a formation of chiral nematic (N^*) phase due to helical stacking of chiral mesogens. The spacing of the bands was measured to be *ca.* $2.6\text{ }\mu\text{m}$ which corresponds to half of the pitch. When the sample was slightly heated, the cholesteric fingerprint texture mixed with the isotropic phase as shown in Figure 1b, which is defined as a biphasic state where a nematic phase and an isotropic phase coexist. Oily streaks texture which is another characteristic of chiral nematic (N^*) phase was also observed (Fig. 1c). In addition, ribbons and herringbone textures were found for samples with high concentration indicating the existence of hexagonal (M) phase (Fig. 1d and 1e). Marbled texture of nematic (N^*) phase was also noticed as shown in Fig. 1f.

Based on the temperature-controlled POM observation of aqueous solution of compound **2** in a sealed glass cell, we successfully obtained a phase diagram of the chiral LCLC in terms of concentration vs. temperature as shown in Figure 4. The concentration of aqueous solution was precisely determined by thermogravimetric analyses (TGA) from the

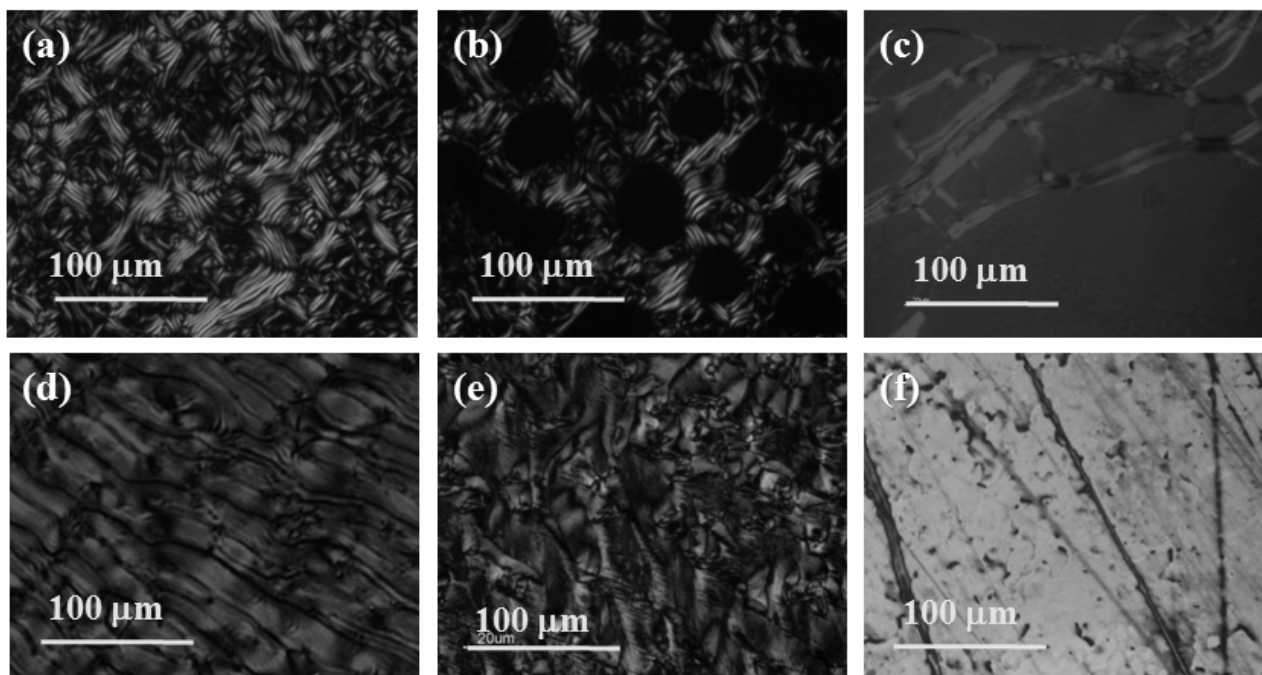


Figure 3. POM textures of compound **2** in aqueous solution: (a) Cholesteric fingerprint texture of cholesteric (N^*) phase ($9\text{ wt } \%$ at $35.8\text{ }^\circ\text{C}$); (b) Cholesteric fingerprint texture of cholesteric (N^*) phase mixed with isotropic phase observed at the same location of (a) ($9\text{ wt } \%$ at $45.7\text{ }^\circ\text{C}$); (c) Oily streaks texture of cholesteric (N^*) phase ($30\text{ wt } \%$); (d) Ribbons of hexagonal (M) phase ($15\text{ wt } \%$); (e) Herringbone texture of hexagonal (M) phase ($27\text{ wt } \%$); (f) Marbled texture (N^*) ($9\text{ wt } \%$).

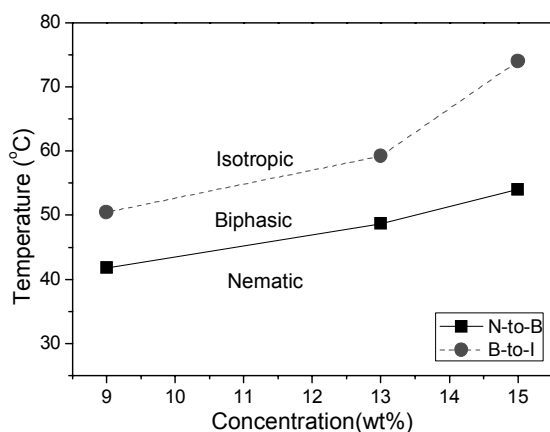


Figure 4. Phase diagram of compound 2 in aqueous solution.

amount of evaporated water when heated up to 250 °C. Phase transitions of LCLC with respect to temperature change can be observed in the range of 9 – 15 wt %. As the temperature increased from room temperature, nematic phase (N^*) turned into a biphasic state in which a nematic (N^*) phase coexists with isotropic phase, and subsequently changed to isotropic phase. At higher concentration than 20 wt %, further phase transition from nematic phase was not detected up to the boiling temperature of water (>100 °C).

In summary, we report the first example of chiral lyotropic chromonic liquid crystal (LCLCs) based on perylenebis(dicarboximide) core. Structure of chiral LCLC was characterized by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, UV-vis spectrometer and POM. Aqueous solution of the chiral salt exhibited characteristic textures of chiral nematic (N^*) phase such as cholesteric fingerprint and oily streaks under POM. We derived a phase diagram based on the phase transitions monitored by POM at various concentrations and temperature. Further structural analyses including high-resolution synchrotron X-ray diffraction studies are now in progress, which will be published in due course.

Experimental Section

(S)-(-)-2-Aminomethyl-1-ethylpyrrolidine 3,4:9,10-perylenebis(dicarboximide) (1). In a 100 mL round bottom flask, (S)-(-)-2-aminomethyl-1-ethylpyrrolidine (3.40 mL, 22.95 mmol) was added to 3.0 g (7.65 mmol) of perylene-3,4:9,10-tetracarboxylic anhydride dissolved in 50 mL of DMSO. The mixture was stirred at 70 °C for 26 h. After cooling, the reaction mixture was filtered, and the dark red solid washed with MeOH and ethyl acetate repeatedly. The solid was dried under vacuum to obtain compound 1 in 89.4% yield. $^1\text{H-NMR}$ (400MHz, in CF_3COOD): δ 8.01 (d, 4H, $J = 8.2$ Hz), 7.83 (d, 4H, $J = 8.1$ Hz), 4.92- 4.78 (dd, 4H), 4.52 (m, 2H), 4.02 (d, 4H), 3.65 (q, 4H), 2.6 (t, 4H), 2.2 (t, 4H), 1.65 (t, 6H); $^{13}\text{C-NMR}$ (400MHz, in CF_3COOD): δ 159.4, 133.9, 133.0,

130.9, 129.2, 126.5, 124.5, 57.8, 55.4, 46.7, 38.0, 29.3, 23.4, 13.6; FT-IR (KBr): 2957, 2789, 1692, 1664, 1593, 1351, 1245 cm^{-1} ; HRMS-FAB [MH^+] calcd. m/z (612.27), found m/z (612.28).

Dihydrochloride salt (2) of compound 1. Compound 2 was prepared by completely dissolving compound 1 in conc. HCl, with subsequent evaporation of remaining HCl by rotary evaporator under reduced pressure. The resulting solid was dried in vacuum oven at room temperature for 24 h.

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