Novel smectic liquid crystals based on benzo[c]cinnoline: their synthesis, mesomorphism, opto- and electro-chemical properties

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ABSTRACT

A series of novel calamatic liquid crystals based on a polar benzo[c]cinnoline moiety were efficiently prepared through a facile route. Rich smectic mesophases were induced by the monoalkylated and dialkylated molecular design, including highly ordered smectic mesophases in the rectangular and hexagonal orders. Dialkylated phenylbenzocinnoline derivatives showed a very wide temperature range over 150°C for smectic C (SmC) phase, while the monoalkylated ones only presented the low-ordered mesophases, which exhibited a bilayer structure in crystalline phase. From pronounced reversible redox waves in a cyclic voltammogram and low-lying lowest unoccupied molecular orbital level of about $-3.2$ eV indicated possible electron-transporting behaviour. In addition, a switching behaviour originating from ferroelectricity in SmC* induced by chiral dopant was observed.

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Introduction

Liquid crystals (LCs) exhibit unique properties distinguished from those in either liquids or crystals, and provide us with unique applications. In fact, dielectric properties in fluidic nematic LCs [1,2] are utilised for LC displays, selective reflection of visible light in cholesteric LCs is applied to thermometer [3] and rewritable colour recordings [4]. In addition, tribological properties of LCs have been interested in lubricant applications [5,6].

Apart from these conventional view point of LCs described earlier, it is worth describing that LCs could be a material platform for developing a new property from a molecule when the molecules are condensed into an orderly molecular aggregate: chiral smectic C (SmC*) LCs express ferroelectricity in that phase [7,8], but other way round it is no doubt that this ferroelectricity is a new property that polar and chiral molecules do not express until they are properly aligned in tilted layers; another example is enhanced charge carrier transport in discotic and smectic mesophases [9,10], which does not appear until an aromatic $\pi$-conjugate system as a core, that is, a chromophore for charge carrier transport, is aligned closely in columns or layers.

In this way, it would be quite interesting to liquid-crystallise a functionality molecule for exploring a new property in mesophases, which motivates us to design a new LC and look at the new property. From this point of view, we paid our attention to a benzo[c]cinnoline (BC) for a core moiety: BC is an analogue of phenanthrene in chemical structure whose benzene unit in the centre is replaced with a pyrazine; it is an electron-deficient aromatic system and gives a large dipole moment perpendicular to the long molecular axis; in addition, its linear molecular shape favours expression of mesophases when chemically modified with long alkyl chains. Furthermore, there is no reported calamitic LCs based on BC backbone before.

Hence herein, a series of novel calamitic LCs based on a BC framework were designed, whose specific molecular structures are shown in Figure 1, and synthesised with...
facile and rational synthetic routes for both symmetrically and unsymmetrically structured LCs.

In this article, we report their synthesis, phase transition behaviours and optical properties in detail, which were systematically investigated by differential scanning calorimetry (DSC), polarisation optical microscopy (POM) and X-ray diffraction studies (XRD). All the derivatives synthesised exhibited smectic mesophases. A noteworthy LC feature found in this system was a wide temperature range of over 150°C for SmC phase in dialkylated derivatives. Moreover, the preliminary results on a switching behaviour originating from ferroelectricity in a SmC* induced by a chiral dopant is shortly described.

**Experimental**

**Preparation of materials**

Unless otherwise noted, all the reagents and solvents were used as received from Aldrich Chemical, Tokyo Chemical Industry and Wako Pure Chemical Industries. Compounds 1 and 2 were prepared according to already reported procedures [7,8]. Other intermediates 3–8 were obtained under the typical Suzuki-coupling reaction. The modified last-step syntheses of the targeted products were reported. All products have been purified by column chromatography and recrystallisation, and their structures were characterised by 1-hydrogen nuclear magnetic resonance (1H NMR) and high-resolution mass spectrometry (HRMS). 1H NMR spectra were recorded in CDCl₃ on 400 MHz Bruker nuclear magnetic resonance spectrometers and HRMS were obtained on a double-focusing magnetic sector mass spectrometer JEOL JMS-700.

**General procedure for the synthesis of targeted products by reduction-cyclisation reaction**

To a three-necked round-bottomed flask equipped with a condenser was added LiAlH₄ (8eq.) in anhydrous ether under argon atmosphere. Intermediates 3–8 (1eq.) in anhydrous ether and toluene were added into the reaction mixture. After stirred for 2 h at room temperature, the reaction mixture was heated at 50°C for 30 min. Water was then slowly added to the reaction mixture to decompose excess LiAlH₄. The reaction mixture was filtered and solvents were evaporated. The yellow solid was collected and purified by column chromatography using dichloromethane as the eluent as the eluent to afford final products.

**10-Ph-BC-Ph-10**: 1H NMR (CDCl₃, 400 MHz): 8.97 (d, 2H), 8.65 (d, 2H), 8.20 (d, 1H), 8.18 (d, 1H), 7.78 (d, 4H), 7.38 (d, 4H), 2.72 (t, 4H), 1.69 (m, 4H), 1.28–1.48 (m, 28H), 0.93 (t, 6H). HRMS: Calcd. For C₄₄H₅₆N₂ [M⁺]: 612.4443; Found: 612.4439.

**12-Ph-BC-8**: 1H NMR (CDCl₃, 400 MHz): 8.93 (d, 1H), 8.49–8.60 (m, 3H), 8.17 (m, 1H), 7.74–7.78 (m, 3H), 7.37 (d, 2H), 2.96 (t, 2H), 2.71 (t, 2H), 1.83 (m, 2H), 1.70 (m, 2H), 0.9 (t, 3H). HRMS: Calcd. For C₃₈H₅₂N₂ [M⁺]: 536.4130; Found: 536.4125.

**Ph-BC-8**: 1H NMR (CDCl₃, 400 MHz): 8.96 (d, 1H), 8.63 (d, 1H), 8.50–8.55 (m, 2H), 8.18 (m, 1H), 7.77–7.89 (m, 3H), 7.48–7.58 (m, 3H), 2.97 (t, 2H), 1.83 (m, 2H), 1.28–1.78 (m, 10H), 1.26–1.44 (m, 28H), 0.87 (t, 6H). HRMS: Calcd. For C₂₆H₂₈N₂ [M⁺]: 368.2252; Found: 368.2250.

**BC-Ph-8**: 1H NMR (CDCl₃, 400 MHz): 8.59 (d, 1H), 8.75 (m, 1H), 8.65 (m, 2H), 8.18–8.20 (m, 1H), 7.90–7.93 (m, 3H), 7.78 (d, 2H), 7.38 (d, 2H), 2.72 (t, 2H), 1.71 (m, 2H), 1.70 (m, 2H); 1.29–1.39 (m, 10H), 0.90 (t, 3H). HRMS: Calcd. For C₂₆H₂₈N₂ [M⁺]: 368.2252; Found: 368.2250.

**Analytical methods**

In this research, DSC 220C system, Seiko Elec., was used. The polarised light microscope of Optiphot2-pol,
Nikon, the hot-stage of FP900 thermo-system, was employed for taking optical graphs. X-ray diffraction equipment (Rigaku RAD-2B) was used to determine the phase structure.

**Computational method**

Molecular length and dipole moment in this article were estimated by MOPAC 2012. MOPAC (Molecular Orbital PACkage) is a semiempirical quantum chemistry program based on Dewar and Thiel’s Neglect of Diatomic Differential Overlap approximation. MOPAC 2012 employed the semiempirical method Parameterized Model 7 (PM7).

**Results and discussion**

**Synthesis**

Efficient and straightforward synthetic strategies were employed to achieve the targeted BC-based derivatives, and their specific synthetic routes for both symmetrical and unsymmetrical derivatives in structures are shown in Scheme 1. Dinitrobiphenyls, 1 and 2, were key starting materials, which were obtained by Cu-catalysed Ullmann-coupling reaction of dibromodinitrobenzene and o-nitorbromobenzene according to the literatures reported [7,8].

Then one- or two-step Suzuki-coupling reaction under the presence of Pd(PPh$_3$)$_4$ and K$_2$CO$_3$ was applied to furnish the corresponding dinitrophenyl intermediates 3, 4, 5, 6, 7 and 8. The resulting coupling products were easily isolated by column chromatography with SiO$_2$. Eventually, they were reduced by LiAlH$_4$ in anhydrous toluene and Et$_2$O, leading to the final BC derivatives. All of products were solid, pale yellow in colour, and highly soluble in common organic solvents such as chloroform, tetrahydrofuran (THF) and toluene. The above-mentioned newly synthesised molecules were determined by the $^1$HNMR spectra and HRMS.

**Mesomorphic and self-organisation properties**

Mesomorphic behaviours of the BC-based derivatives were investigated by a combination of DSC and POM measurements. Additionally, the molecular order within the observed mesophases was determined by XRD diffraction patterns at various temperatures. All DSC thermogramms of BC-based LCs are presented in Supplemental data.

The phase-transition temperatures and enthalpies are summarised in Table 1. Two mesophases and three exothermic peaks for 10-Ph-BC-Ph-10 were observed in its DSC curves at 319°C ($\Delta H = 11.1$ kJ/mol), 136.1°C ($\Delta H = 8.8$ kJ/mol) and 48.2°C ($\Delta H = 37.0$ kJ/mol) upon cooling. In the high-temperature phase, POM image at 220°C in Figure 2a showed a broken fan-shaped texture, which is characteristic of a SmC phase. Furthermore, the XRD patterns in
In the low-temperature phase, the POM texture of 10-Ph-BC-Ph-10 at 130°C in Figure 2b changed into the banded fingerprint pattern suggesting the formation of a highly ordered mesophase. The XRD patterns at 130°C showed two low-angle peaks at $\theta = 2.64°$ and $\theta = 5.14°$, which were originated from the (001) and (002) diffraction planes, indicating the formation of more well-ordered layer structure. In addition, two small wide-angle peaks at $\theta = 18.6°$ and $\theta = 20.7°$ can be well assigned to be the (110) and (200) diffraction planes, and the corresponding d-spacings were estimated to be 4.51 Å (110) and 3.78 Å (200). The d-spacings of the (110) and (200) reflections exhibited the characteristic ratio approximately $1:\sqrt{3}/2$, which revealed that molecules were hexagonally packed with the lattice constant $a = 9.52$ Å according to Equation (1) in Table 2. Additionally, the layer spacing (33.4 Å) was shorter than the extended molecular length (37.6 Å). Therefore, this low-temperature mesophase should be a SmG (or J) phase in hexagonal array referring to the textbook of LCs [11] and some literatures reported [12,13]. The X-ray diffraction angles and the corresponding lattice constants for 10-Ph-BC-Ph-10 are listed in Table 2.

For 12-Ph-BC-8, DSC curves presented two exothermic peaks at 206.4°C (ΔH = 8.6 kJ/mol) and 49.6°C (ΔH = 8.2 kJ/mol) during cooling. In the high-temperature range for 12-Ph-BC-8 should be a SmC phase similar to 10-Ph-BC-Ph-10. In the XRD diffraction patterns at 25°C, the low-angle peaks at $\theta = 2.64°$ and $\theta = 5.08°$ were designated to be the

$$\frac{1}{d_{hkl}} = \frac{1}{h^2a^2} + \frac{1}{k^2b^2} (1).$$

$$\frac{1}{d_{hkl}} = \frac{1}{l^2c^2} + \frac{1}{k^2b^2} (2).$$

**Table 2.** X-ray diffraction angles and lattice constants for 10-Ph-BC-Ph-10 and 12-Ph-BC-8.

| Compound     | Phase transition T/°C (ΔH/kJ mol$^{-1}$) | Phase (lattice constants) |
|--------------|------------------------------------------|----------------------------|
| 10-Ph-BC-Ph-10 | 180°C: SmC (32.4 Å, 001) | Hexagonal lattice ($a = 9.52$ Å) |
|              | 130°C: SmG (33.4 Å, 001) | SmG (or J) |
| 12-Ph-BC-8   | 150°C: SmC (30.0 Å, 001) | Hexagonal lattice ($a = 9.02$ Å) |
|              | 25°C: SmG (33.4 Å, 001) | SmG (or K) |

Hexagonal lattice: $1/d_{hkl}^2 = h^2 + k^2 + hl/3a^2 (1)$. Rectangular lattice: $1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 (2)$. BC: benzo[c]cinnoline.
(001) and (002) diffraction planes. Four diffraction peaks appeared in the wide-angle region and their d-spacings 4.51 Å (19.64°), 4.26 Å (20.82°), 3.78 Å (23.46°) and 3.18 Å (28°) can be well assigned to be the (200), (010), (110) and (210) diffraction planes, respectively, following Equation (2) in Table 2, which demonstrated a rectangular order of the molecular position within the smectic layers, although the lattice constant of (210) should be 3.05 Å in a perfectly rectangular lattice. The layer spacing (33.4 Å) was shorter than the extended molecular length (34.5 Å). Therefore, the phase in the low-temperature region could be identified as a SmH (or K) in rectangular array according to the textbook of LCs [11] and reported literatures [14–16]. The specific lattice constants are exhibited in Table 2.

For the monoalkylated Ph-BC-8, two small transition enthalpies (1.1 and 0.4 kJ/mol) and a big transition enthalpy (24.5 kJ/mol) in sequence were observed at the first cooling run in the DSC curves (Supplemental data), revealing the existence of two low-ordered mesophases. Typical schlieren texture at 148°C as shown in Figure 4(a) was attributed to the nematic phase and fan-shaped texture at 130°C as shown in Figure 4(b) to the SmA phase. In fact, the layer spacing corresponded to the sharp diffraction at 4° in Figure 4(c) was 22.6 Å, which was slightly bigger than the molecular length of 20.6 Å, indicating that molecules are perpendicular within the smectic layer. Likewise, the SmA phase appeared in the analogous compound, BC-Ph-8. Specific phase analysis of this compound by DSC, POM and XRD was shown in the Supplemental data.

Although similar mesomorphic behaviours were observed for BC-Ph-8 and Ph-BC-8, different self-organisation features occurred on cooling from SmA to crystal phase. For Ph-BC-8, it was noted that the first diffraction peak in Figure 4(c) shifted a lot from 4° to 2.6°, which indicated a remarkable change in the layer distance from 22.6 Å to 33.9 Å, in the phase transition from SmA phase to crystal phase. Based on these, a possible conclusion was drawn that a titled bilayer structure was generated, as illustrated in Figure 5. Recently some literatures on the asymmetric monoalkylated [1] Benzothieno[3,2-b]benzothiophene [17] and Thiophene/phenylene co-oligomers [18] derivatives also reported the same results. Interestingly, such phenomenon was not observed for BC-Ph-8, and only normal interspacing transformation happened, while the molecules kept sitting perpendicular to the layers. The XRD results of BC-Ph-8 are presented in the Supplemental data. One reason may be that the terminal phenyl groups played an important role, more specifically, enhanced intermolecular interactions between
layers more effectively than the alkyl chains, thus leading to the appearance of a bilayer structure.

**Photophysical and electrochemical properties**

UV-vis spectra in Figure 6 of the BC derivatives were measured in chloroform solution. All four compounds presented almost similar spectral features with an intense absorption at around from 300 to 330 nm and relatively a weak absorption from 330 to 425 nm except for 10-Ph-BC-Ph-10. It showed much broader absorption at the wavelength from 300 to 350 nm resulted from additional phenyl core introduced into the BC scaffold. Nearly uniform edge absorption wavelength around 420 nm was recorded, and thus, optical gaps were estimated to be approximately 2.96 eV.

The cyclic voltammograms (CVs) measured in THF solution, which is shown in Figure 7, exhibited two clear reversible redox waves, uncovering the obvious electron deficiency and potential n-type charge transport nature of the BC-based LCs. The energy levels of the highest occupied molecular orbital and the lowest unoccupied molecular orbital (LUMO), were estimated from cyclic voltammetry and optical gaps, and were estimated to be about −6.10 and −3.2 eV, respectively. All photophysical and electrochemical data was shown in Table 3.

As described, 12-Ph-BC-8 has exhibited large dipole perpendicular to the long molecular axis, which is estimated to be 3.45 Debye from MOPAC method, so that switching behaviour is expected under applied biases when SmC* phase is induced. Figure 8b and 8c showed POM textures of a cell capillary filled with 12-BC-Ph-8 and a small amount of 5 wt% chiral dopant (R)-2,3-difluoro-4-(octan-2-yloxy)-4′-octyloxyterphenyl, whose chemical structure is shown in the Supplemental data, under positive and negative bias of 10 V, respectively. These textures in opposite brightness indicates a switching behaviour originating from ferroelectricity induced in the SmC* doped with this chiral dopant.

**Table 3. Photophysical and electrochemical data of BC LCs.**

| Compound      | \(E_{1/2}^{\text{red}}\) [eV] \(^a\) | \(E_{1/2}^{\text{red}}\) [eV] \(^b\) | \(E_{\text{LUMO}}\) [eV] \(^c\) | \(E_{\text{HOMO}}\) [eV] \(^d\) | \(\lambda_{\text{edge}}\) [nm] \(^e\) |
|---------------|--------------------------------------|--------------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 10-Ph-BC-Ph-10| −1.65                                | 2.94                                 | −3.15                           | −6.09                           | 421                             |
| 12-Ph-BC-8    | −1.66                                | 2.96                                 | −3.14                           | −6.10                           | 419                             |
| Ph-BC-8       | −1.64                                | 2.96                                 | −3.16                           | −6.12                           | 419                             |
| BC-Ph-8       | −1.62                                | 2.96                                 | −3.18                           | −6.13                           | 419                             |

HOMO: highest occupied molecular orbital; LUMO: lowest unoccupied molecular orbital; BC: benzo[c]cinnoline.

\(^a\)Half-wave potentials, determined by cyclic voltammetric measurement in 0.1 M solution of TBAP in THF vs. Fc/Fc+.  
\(^b\)Estimated vs. vacuum level from \(E_{\text{LUMO}} = E_{1/2}^{\text{red}} - 4.8\) eV.  
\(^c\)Optical bandgap, calculated from the maximum absorption wavelength.  
\(^d\)Estimated from \(E_{\text{HOMO}} = E_{\text{LUMO}} - E_{1/2}^{\text{red}}\).  
\(^e\)Estimated from UV-vis absorption spectra.
Therefore, a wide temperature range of over 150°C for SmC phase in the present BC derivatives are very attractive for ferroelectric application.

**Conclusion**

A series of BC-based LCs were prepared through facile and versatile synthetic strategies with moderate yields. Dialkylated BC derivatives of 10-Ph-BC-Ph-10 and 12-Ph-BC-8 showed SmC phase over a wide temperature range (>150°C) and highly ordered SmG (or J) and SmH (or K) phases, while mono-alkylated derivatives of Ph-BC-8 and BC-Ph-8 showed only low-ordered mesophases of nematic and SmA phases. The low-lying LUMO levels of these derivatives were estimated to be approximately ~3.2 eV, suggesting their potential for n-type charge transport behaviour. Moreover, in particular, it is noteworthy that the wide temperature range of the SmC phase in dialkylated BC derivatives made them become promising candidates for ferroelectric LCs if the chiral moieties were incorporated. Therefore, liquid crystallisation of BC moiety may result in a new material of ferroelectric liquid crystal-line organic semiconductor yellow in colour. Its ferroelectric and charge transport properties will be reported elsewhere in detail.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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