



Columnar catenar bisoxazoles and bisthiazoles



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ABSTRACT

Three new series of catenar liquid crystals **1a–c** derived from heterocyclic bisoxazoles and bisthiazoles exhibiting columnar phases were reported. All compounds **1a–c** exhibited hexagonal columnar phases, which were confirmed by powder XRD diffractometer. Compounds **1a** have a slightly wider temperature range of columnar phases than that of compounds **1b**, which might be attributed to higher dipole polarized in **1a**. A N_{cell} and R_{af} value equal to 2.54–2.76 and 19.99–20.45 Å² within a slice of 9.0 Å thick were obtained for three derivatives **1a–c** (all $n_s=12$), indicating that a single molecule was packed within columns in Col_h phases. All derivatives showed good stabilities at temperature below $T=408$ °C on TGA. The PL spectra of all compounds **1a–c** showed one intense peak at $\lambda_{\text{max}}=505$ –510 nm, and these photoluminescent emissions originated from quinoxaline moiety.

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1. Introduction

Benzoxazoles, considered as an important member among heterocyclic family have demonstrated many unique properties in the area of materials chemistry.¹ Most of these known structures were highly or/and extended conjugated, and efficient π -stacking and strong intermolecular interactions resulted in some novel physicochemical and mechanical properties engaged in such materials. Heterocyclic derivatives incorporated with higher electronegativity atoms (N, O, and S) were also considered as electron-deficient moieties, and intermolecular dipoles were easily polarized and induced by donor–acceptor (D–A; aromatic as donor, heterocycle as acceptor) interactions when structurally fused to aromatic rings. An efficient light-emitting diode (LED) material² derived from heterocyclic benzoxazoles or benzobisazoles has been studied. The positions or arrangements of the oxygen atoms of the core structure from the cis to trans orientation of benzobisazole copolymers changed their stabilities and hole mobilities on heterojunction photovoltaic devices.³ Theoretical studies on the n-type organic semiconducting materials using thiazole or oxazole as core frameworks indicated that the empty d-orbitals of the sulfur atoms can contribute to the molecular π -orbitals, decreasing the energy of the π – π transitions. Replacing oxygen atom with the less

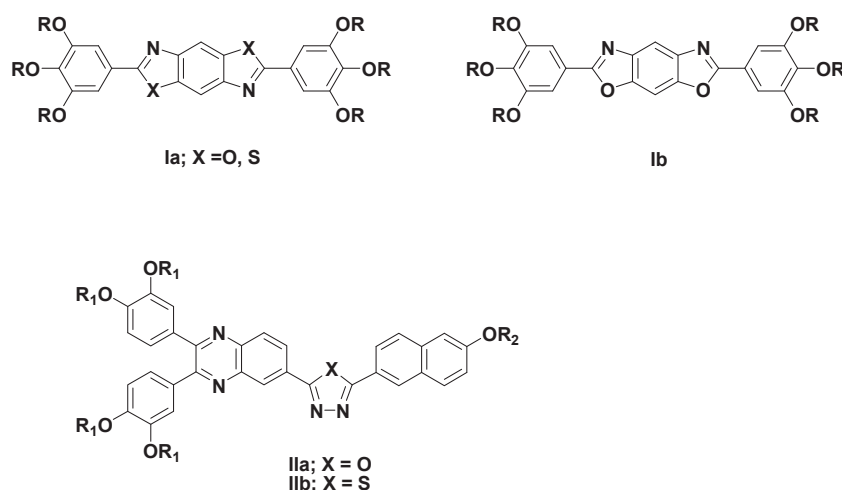
electronegative sulfur atom increased the delocalization with the π -orbitals.

Quinoxalines, considered as highly π -conjugated backbones or frameworks have been widely applied to generate practical materials, such as dyes, organic light-emitting diodes, electroluminescence, organic thin film transistors (TFT), and organic photovoltaics.⁴ Their conformation shapes were considered as half-disc, elliptical or round molecules, which could easily or spontaneously self-assemble into columns when π – π interaction or dipole–dipole interactions are accessible between neighboring molecules. These molecules capable of forming columnar stacking arrangements might have a dramatic impact propensity. A few mesogenic examples⁵ constructed by use of quinoxalines were studied and investigated in this group.

Polycatenar liquid crystals,⁶ represented as a new structural motif in exploring new mesogenic materials. Recently, more and more catenar LCs showing interesting mesophases have been continuously reported. In general, the structures of such mesogens are virtually based on calamitic molecules; constituted by a relatively long central aromatic core surrounded by more-than-two terminal aliphatic chains on both ends. The core structures of known examples are composed of rigid elongated polyaromatic or highly conjugated heterocyclic fused rings, for example, 1,3,4-oxadiazole,⁷ oxazolines,⁸ bipyridines,⁹ and others. Many polymers¹⁰ derived from bisoxazoles and bisthiazoles showing conducting or hole transporting properties were reported.

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However, known examples¹¹ derived from bisoxazoles and bisthiazoles exhibiting mesomorphic behavior were relatively rare. A rod-like structure¹² used as ordered organic semiconductors, showing SmA and N phase with a clearing temperature at 425 K was reported. In contrast, two series of tetra- and hexacatenar benzobisthiazoles exhibiting enantiotropic hexagonal columnar phases and also showing good photoluminescent properties in the visible region were described.¹³ In our previously report, two series of hexacatenar liquid crystals derived from heterocyclic bisthiazoles and bisoxazoles **1a–b** exhibiting columnar phases^{14a} were reported, and the formation of columnar phases was found to be strongly sensitive to central heteroatoms and/or their positions incorporated.



In this work, we report the preparation and mesomorphic studies of three new series of catenar mesogens derived from bisoxazoles and bisthiazoles **1a–c**. These were constructed by incorporating quinoxalines^{14b} to enhance the molecular polarization and/or supplementary shape effect needed to induce columnar phases. Also, increasing π – π interactions between the neighboring molecules might favor the molecules to be well stacked within the columns. All compounds **1a–c** exhibited hexagonal columnar phases (Col_h), which were also confirmed by powder XRD diffraction. The PL spectra of all compounds **1a–c** were examined.

2. Results and discussions

2.1. Synthesis and characterization

The synthetic routes applied to prepare the precursors **2** and final compounds **1a–c** were shown in Scheme 1. 1,2-Bis(3,4-alkoxy)phenyl-1,2-ethanediones were obtained by the reaction of 1,2-bis(dodecyloxy)benzene with oxalyl chloride in the presence of AlCl₃ stirring in carbon disulfide at ice bath temperature for 6 h, which was then condensed with 3,4-diaminobenzoic acid stirring in THF to give 2,3-bis-(3,4-bis(alkoxy)phenyl)quinoxaline-6-carboxylic acids **2**. On ¹H NMR spectra, a characteristic broad peak often appeared at δ 12.8–13.5 ppm assigned for –COOH was not observed for acids **2** due to its rapid exchange. However, a characteristic peak appeared at δ 170.92–171.03 ppm assigned for –COOH was indeed observed on ¹³C NMR spectra. The acid chlorides, obtained from acids **2** and thionyl chloride were directly reacted with 4,6-diaminoresorcinol dihydrochloride (for **1a**), 2,5-diaminobenzene-1,4-diol dihydrochloride (for **1b**), or 2,5-

diaminobenzene-1,4-dithiol dihydrochloride (for **1c**) in refluxing NMP for 48 h. All products, isolated as bright yellow solids were obtained by silica gel chromatography eluting with hexane/ethyl acetate. The yields were relatively lower, 23–45%. All final compounds **1a–c** were characterized by ¹H NMR, ¹³C NMR, mass spectrometry, and elemental analysis.

2.2. Mesomorphic properties and thermal stability

The mesomorphic behavior of compounds **1a–c** was studied and characterized by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The phase transitions and thermodynamic data for compounds **1a–c** are summarized in Table 1. All

compounds **1a–c** exhibited enantiotropic columnar phases, and the temperature range of columnar phases was slightly sensitive to central heteroatoms and/or their positions incorporated. For the series of compounds **1a**, a phase transition of crystal→columnar→isotropic (Cr→Col→I) was typically observed. Both melting and clearing temperatures were decreased when carbon chain length was decreased; the melting temperatures were ranged at $T_{mp}=121.6$ ($n=8$)> 106.0 ($n=12$)> 90.4 °C ($n=16$) and clearing temperatures were ranged at $T_{cl}=201.3$ ($n=8$)> 185.1 ($n=12$)> 166.9 °C ($n=16$). On the other hand, the temperature range of mesophases were decreasing with carbon chain length; $\Delta T_{Col}=90.0$ ($n=8$)> 84.1 ($n=12$)> 74.7 °C ($n=16$) on the cooling process. Under POM, a typically pseudo focal-conic or more leaf-like texture (see Fig. 1) with linear birefringent defects was clearly observed when cooling from their isotropic liquids. These observed textures, also accompanied by a large area of homeotropic domain were characteristic for hexagonal columnar phases. A few more transitions of crystal-to-crystal (Cr₁, Cr₂, and Cr₃) observed in this series might be due to the π – π interactions from the neighboring quinoxaline moieties.

All compounds **1b** showed similar phase transitions of compounds **1a**. Both melting and clearing temperatures in **1b** were slightly higher than those of compounds **1a** by $\Delta T_{Col}=15.7$ ($n=10$)– 26.9 °C ($n=16$) and $\Delta T_{cl}=0.5$ ($n=16$)– 3.9 °C ($n=10$). However, the temperature range of columnar phases was only slightly lower than those of compounds **1a**; $\Delta T_{Col}=67.1$ ($n=8$)> 64.2 ($n=12$)> 48.7 °C ($n=16$) on the cooling process (Fig. 2). A similar optical texture, focal-conic texture with linear birefringent defects when slowly cooled from their isotropic liquids was observed, as shown in Fig. 1. The mesophases of both compounds

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