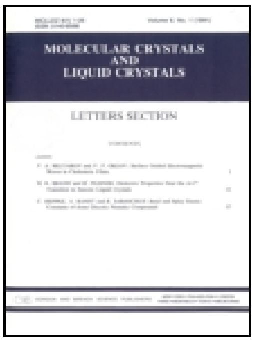

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Preparation and Photoluminescent Properties of Hydrogen-bonded Discotic Liquid Crystals

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Photoluminescent discotic liquid crystals (DLCs) have been prepared through intermolecular hydrogen bonding between core and peripheral units. 1,3,5-Trihydroxybenzene was employed as core molecule and peripheral stilbazole derivatives containing linearly conjugated moieties were complexed to form hydrogen-bonded DLCs. Their structures, mesophases, and optical properties were investigated. The complexation of core and peripherals made some discotic complexes form photoluminescent DLCs. The prepared luminescent DLCs exhibited columnar mesophases with strong blue or sea green photoluminescence. These findings may contribute to the development of luminescent supramolecular liquid crystals for emitting materials in light emitting devices.

Keywords Columnar order; discotic liquid crystal; hydrogen bonding; mesophase; photoluminescence

Introduction

Since the discovery of discotic mesophase from disc-shaped molecules [1], discotic liquid crystals (DLCs) have been a wide research interest because of their unique physical properties related to electron and hole transport phenomena [2]. Generally, DLCs consist of π-conjugated aromatic core surrounded by several alkyl chains to give rise to discotic mesophases such as columnar and nematic phases. In particular, discotic columnar mesophases have attracted much attention due to their electronic and photonic applications including electronic conductors, photovoltaics, and organic light emitting diodes (OLED) [3–5]. The organized columnar structure increases the conductivity along the column direction and allows tailoring of the electro-optical properties in the device applications [2]. Besides the charge transport properties of these DLCs, the luminescent properties can offer the possibility of simple layer structure in OLED device involving a combination of transporting and light-emitting properties within one single molecule.

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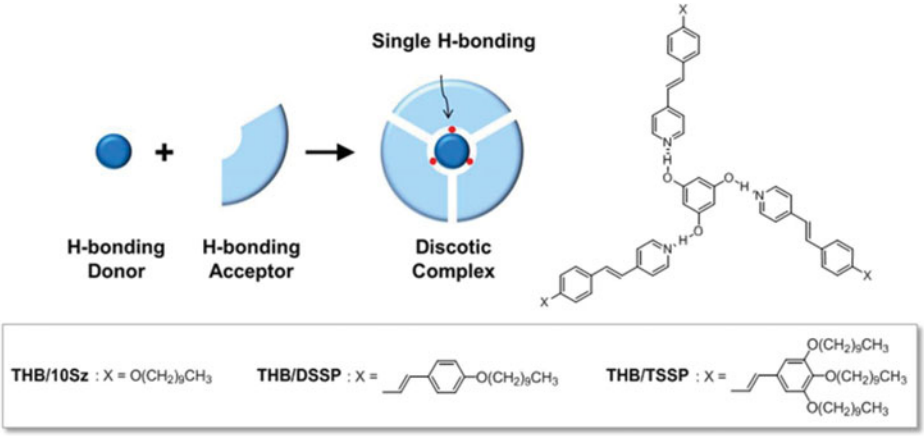

Figure 1. Preparation of photoluminescent self-assembled discotic liquid crystals.

Among the noncovalent interactions, hydrogen bonding is an ideal and powerful tool to build supramolecular structure since it is strong and directional [6]. Recently, DLC materials have been readily prepared by single hydrogen bonding between non-identical components [7]. This type of hydrogen bonding could be advantageous for preparation of novel functional organic materials having discotic and luminescent properties. In this study, we report the preparation and characterization of photoluminescent self-assembled DLCs formed by single hydrogen bonding between core and peripheral units. For the construction of discotic structure, we employed 1,3,5-trihydroxybenzene (THB) as core molecule and stilbazole derivatives containing linearly conjugated moieties as peripheral units, as shown in Fig. 1. The mesomorphic and photoluminescent properties of self-assembled DLCs were examined and discussed in detail in order to investigate their structure–property relationship.

Experimental

Measurements

NMR spectroscopy was performed on JEOL JNM-LA 300 spectrometer. FTIR spectra were measured with JASCO FT/IR-200 spectrometer. Differential scanning calorimetry (DSC) was conducted on TA DSC 2010 under a nitrogen atmosphere with the scan rate of $10^\circ\mathrm{C\ min^{-1}}$. Polarized optical microscopy (POM) was carried out with Leica LABORLUX 12 POLS microscope fitted with Mettler FP82HP hot stage and Mettler FP90. X-ray diffraction (XRD) patterns were measured with Bruker AXS X-ray diffractometer fitted with HI-STAR detector and heating unit. UV-visible spectra were obtained from Agilent 8453 spectrophotometer. Photoluminescence (PL) experiment was performed on PL measurement system equipped with a He:Cd laser source ($\lambda = 325$ nm, continuous wave) and an integrating sphere.

Preparation of Hydrogen-bonded DLCs

The three stilbazole derivatives, which were *trans*-4-decyloxy-4′-stilbazole (10Sz), 4-(4-(4-(decyloxy)styryl)-styryl)pyridine (DSSP), and 4-(4-(3,4,5-tris(decyloxy)styryl)-styryl)pyridine (TSSP), were prepared as described in the literature [8,9]. The selected analytical data for DSSP are given below.

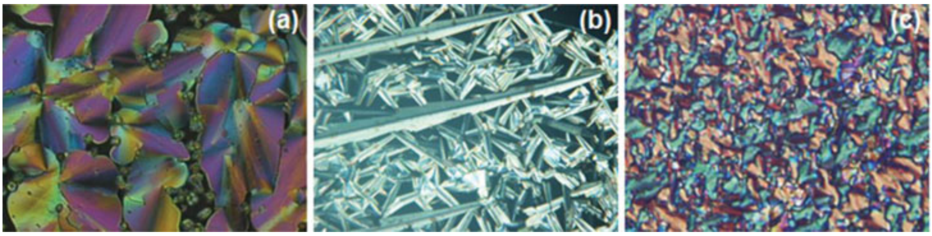

Figure 2. Polarized optical micrographs of (a) THB/10Sz at 145°C, (b) THB/DSSP at 235°C, and (c) THB/TSSP at 69°C (200×).

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (d, 2H), 7.59-7.30 (m, 9H), 7.17-6.87 (m, 5H), 3.98 (t, 2H), 1.86-1.72 (m, 2H), 1.53-1.18 (m, 14H), 0.88 (t, 3H). MS (*m/z*): 439.3 (M^+).

The hydrogen-bonded DLCs were prepared by mixing THB core and stilbazole derivatives in a molar ratio of 1 : 3 in anhydrous acetone or tetrahydrofuran and then slow evaporation of the solution under reduced pressure.

Results and Discussion

Liquid Crystalline Properties of Hydrogen-bonded DLCs

The formation of hydrogen-bonded DLC complexes was identified by FTIR experiment. The THB core showed a broad OH stretching band at about 3370 cm^{-1} corresponding to self-hydrogen bonding, whereas the DLC complexes displayed a new OH stretching band at a lower wavenumber of about 2900 cm^{-1}, which is ascribed to the strong hydrogen bonding between hydroxyl group of THB and nitrogen of stilbazole derivatives. Similar results were obtained for other study using phenol-pyridine interaction [10].

The mesomorphic properties of hydrogen-bonded DLCs were investigated by DSC, POM, and XRD. The THB/10Sz complex showed wide temperature range of discotic mesophase between 85 and 147°C on heating [11]. Moreover, a pseudo-focal conic texture characteristic of columnar phases was observed upon slow cooling, as shown in Fig. 2(a). The XRD pattern of THB/10Sz at room temperature showed numerous reflections characteristic of crystalline phase, while elevation of the temperature to 140°C in the mesophase region left only characteristic reflections corresponding to hexagonal columnar mesophase (Fig. 3(a)). These reflections disappeared at 170°C in the isotropic region. In the case of THB/DSSP complex, no transitions indicative of mesophases were observed in DSC experiment. As shown in Fig. 2(b), POM revealed that the complex decomposed at 235°C above the melting point of THB (218°C) to give rise to crystalline needles floated on an isotropic melt. This result is probably due to the existence of stable crystalline phase of DSSP (melting point = 271°C), rendering the formation of mesophase thermodynamically unfavorable. For THB/TSSP complex, a discotic mesophase was observed below 73°C on heating [9]. A fan-shaped texture typically found in columnar mesophases was exhibited at 69°C, as shown in Fig. 2(c). In XRD pattern of THB/TSSP, four reflections corresponding to (100), (110), (210), and (120) of rectangular columnar phase were observed at 50°C in the mesophase region, and maintained at room temperature (Fig. 3(b)). The sharp reflection of (100) did not disappear above the clearing temperature (Tc) of 73°C, and broadened as

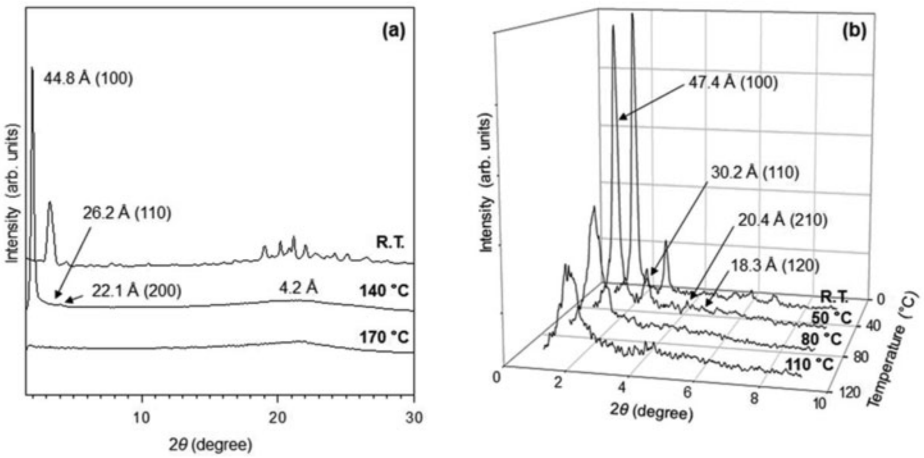

Figure 3. Temperature-dependent XRD patterns of (a) THB/10Sz complex and (b) THB/TSSP complex.

the temperature increased, which indicates the local ordering of columns above Tc. Similar observations were reported for DLC formed by a dimer of phenanthridinones [12].

Photoluminescent Properties of Hydrogen-bonded DLCs

To investigate the influence of conjugated moieties and hydrogen bonding on the photoluminescent properties of hydrogen-bonded DLCs, we measured UV-vis and PL spectra in solution of chloroform or film. The UV absorption of THB/10Sz complex in solution is about 330 nm, while the photoluminescence (PL) in solution is at around 380 nm, which is the edge of the visible area (Fig. 4(a)). Compared with PL spectrum in solution, THB/10Sz complex in the film exhibited an emission band with a maximum at 423 nm, which is strongly red-shifted emission relative to the solution. This spectral shift points to the formation of excimers derived from π–π stacking and molecular aggregation of conjugated moieties of DLC complex in the solid state. In comparison with THB/10Sz complex containing peripheral stilbazole units, it is expected that more conjugated styryl stilbazole arms in THB/DSSP complex induce bathochromic shifts in the absorption and emission spectra. As shown in Fig. 4(b), the UV absorption as well as the PL maximum in comparison to THB/10Sz complex are strongly shifted to the red (40–75 nm). This complex showed strong blue photoluminescence by extending the π-conjugated length in the peripheral arms.

As displayed in Fig. 4(c), THB/TSSP complex exhibited the emission peak at about 500 nm in sea green color, which is a longer wavelength than that in the PL spectrum of THB/DSSP. This appears to be the result of the existence of excimers coming from the J-type aggregations of DLC complex with a number of long alkyl chains [13]. Compared with peripheral TSSP, the emission peak of THB/TSSP complex has approximately 30 nm red-shift (*i.e.* from 470 nm to 500 nm). This bathochromic shift might be due to the slight expansion of π-conjugation length resulting from intermolecular hydrogen bonding involving the protonation of the pyridine group [14]. Therefore, intermolecular single hydrogen bonding between core molecules and peripheral units played a major role in the induction of photoluminescence and mesophase in these supramolecular DLCs

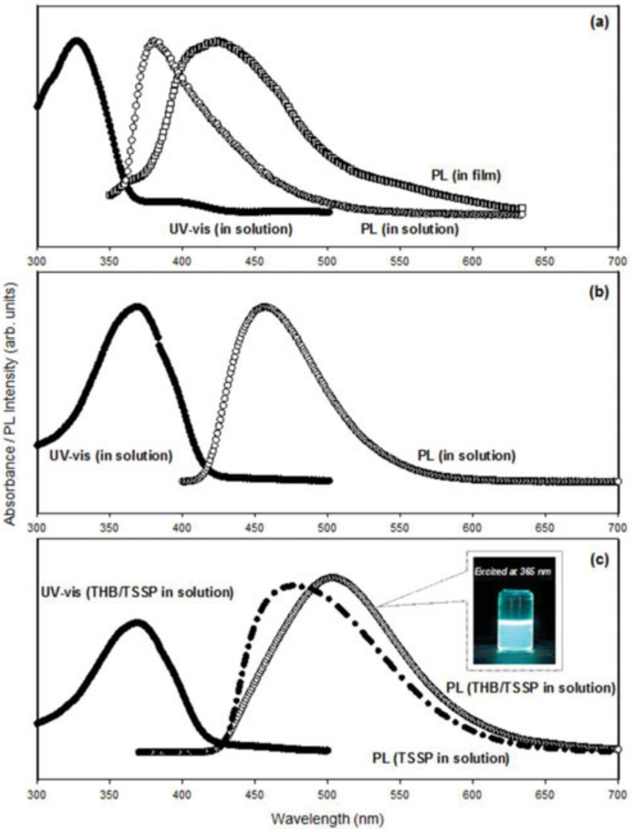

Figure 4. UV-vis absorption and photoluminescence spectra of (a) THB/10Sz complex, (b) THB/DSSP complex, and (c) THB/TSSP complex.

Conclusions

We have prepared photoluminescent self-assembled discotic liquid crystals simply through intermolecular hydrogen bonding between the core of 1,3,5-trihydroxybenzene and the peripheral units of stilbazole derivatives containing linearly conjugated moieties. The columnar mesophases with strong blue or sea green photoluminescence could be readily formed by introducing several hydrogen bonding building blocks. Our simple methodology may offer an efficient way to fabricate light-emitting liquid crystalline materials possessing solution processability for OLEDs.

Acknowledgments

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