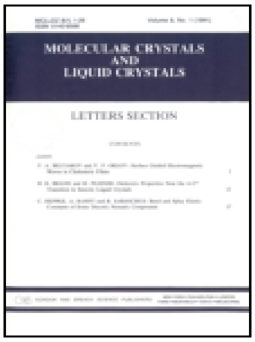

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Supramolecular Discotic Columnar Liquid Crystals Built through Single Hydrogen Bonding between Carboxylic Acid and Pyridine Moieties

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New self-assembled discotic columnar liquid crystals were prepared via single hydrogen bonding between the core molecule of 1,3,5-cyclohexanetricarboxylic acid and the peripheral units of stilbazole derivatives. The hydrogen-bonded liquid crystals exhibited rectangular columnar and hexagonal columnar mesophases depending on the number of alkyl chains in three arms of the discotic mesogen through dipole-dipole interactions between carbonyl groups along the column axis. The intermolecular hydrogen bonding between carboxylic acid and pyridine moieties provides an effortless methodology to prepare the ordered columnar liquid crystals for electronic applications.

Keywords Carboxylic acid; discotic columnar; liquid crystal; self-assembly; single hydrogen bonding

Introduction

Since the discovery of disc-shaped molecules by Chandrasekhar et al. [1], discotic liquid crystals (DLCs) have received considerable attention due to their potential applications in electronic conductors, photovoltaic cells, and organic light emitting diodes [2–4]. Discotic molecules typically comprising a disc-shaped core and peripheral alkyl groups give rise to columnar mesophases. In these columnar phases, disc-shaped molecules would tend to interact with one another to build up two-dimensional lattices leading to the columnar arrangements such as hexagonal (Col_h), rectangular (Col_r), and oblique (Col_{ob}) arrays.

For optoelectronic applications, DLCs are required to form organized columnar structures resulting in excellent electrical conductivity or photoconductivity along the column axis [5]. The conductive discotic cores surrounded by insulating alkyl chains would exhibit high charge transport properties. In general, these columnar DLCs have been prepared by

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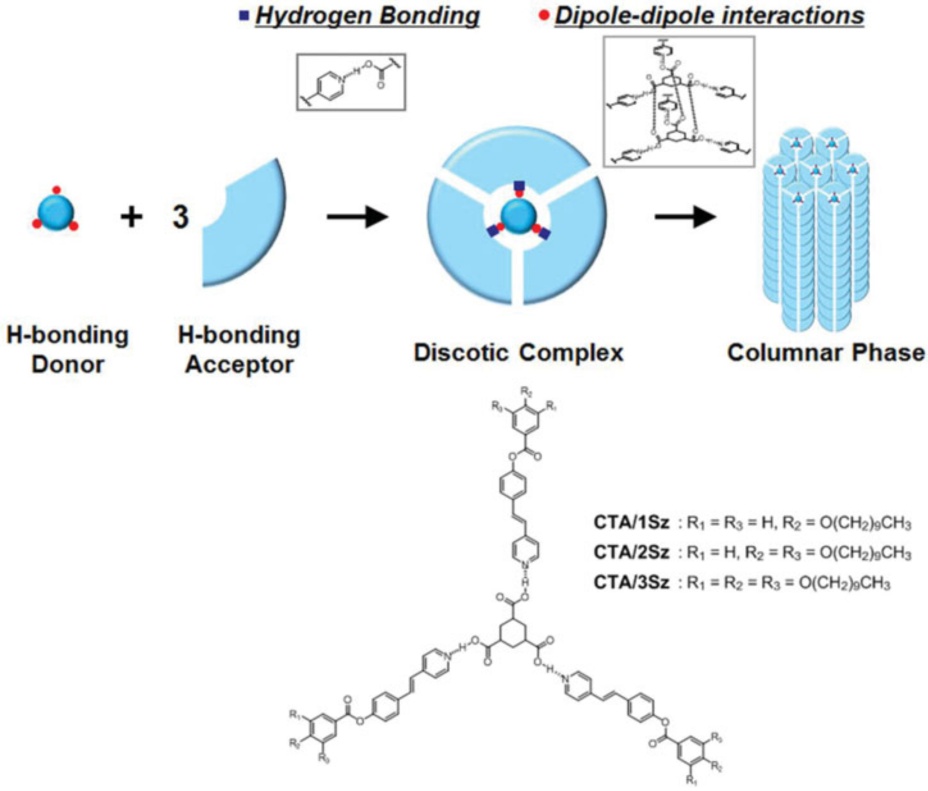

Figure 1. Schematic illustration of supramolecular discotic columnar liquid crystals.

a conventional synthetic route using covalent bonding. However, the need to incorporate many aromatic rings into the discotic cores restricts the structural variation of DLCs and requires substantial synthetic effort.

We have previously described that supramolecular DLCs are readily obtained through hydrogen bonding between phenol and pyridine moieties [6–8]. Such hydrogen-bonded discotic complexes could exhibit discotic mesophases [9]. Here, we report a new type of supramolecular discotic columnar liquid crystals based on the single hydrogen bonds between carboxylic acid and pyridine moieties. For the construction of discotic columnar structure, we used 1,3,5-cyclohexanetricarboxylic acid (CTA) as a core molecule and stilbazole derivatives (*n*Sz) with different number of alkyl chains (*n*) as peripheral arms, as shown in Fig. 1. It is expected that CTA core and three peripheral stilbazole derivatives could be held together by hydrogen bonding, and subsequently the hydrogen-bonded discs stack to form columnar mesophases through dipole-dipole interactions between carbonyl groups along the column axis. The LC properties of supramolecular DLCs were studied by using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD) measurements.

Experimental

Measurements

Fourier transform infrared (FTIR) spectroscopy was carried out on JASCO FT/IR-200 spectrometer. DSC was performed on TA DSC 2010 under nitrogen atmosphere at scan rate of 10°C min^{-1}. The phase transitions were determined as the temperature at the peak maximum. POM was conducted on Leica LABORLUX 12 POLS microscope fitted with Mettler FP82HP hot stage. XRD patterns were recorded on Bruker AXS X-ray diffractometer provided with heating accessory using Cu Kα radiation ($\lambda = 1.54$ Å).

Preparation of Hydrogen-bonded Discotic Complexes

The three stilbazole derivatives with different number of alkyl chains, which were 4-(4-decyloxybenzoyloxy)-4′-stilbazole (1Sz), 4-(3,4-didecyloxybenzoyloxy)-4′-stilbazole (2Sz), and 4-(3,4,5-tridecyloxybenzoyloxy)-4′-stilbazole (3Sz), were prepared by procedures described in the literature [6]. The discotic complexes were prepared by mixing CTA core and stilbazole derivatives (1/3 mol/mol) in anhydrous tetrahydrofuran and subsequent slow evaporation of the solvent under reduced pressure.

Results and Discussion

Formation of Supramolecular Discotic Complexes

The complexation between a CTA core and peripheral stilbazole derivatives was confirmed by FTIR spectroscopy. Figure 2 shows the FTIR spectra of CTA, 1Sz peripheral, and CTA/1Sz complex in KBr discs of neat powders at room temperature. For CTA, two broad stretching bands of O-H corresponding to self-hydrogen bonding between carboxylic acid groups were found at around 3000 cm^{-1} and 2700 cm^{-1}. For CTA/1Sz complex, two new stretching bands of O-H were appeared at about 2500 cm^{-1} and 1950 cm^{-1}, lower wavenumbers than those in the spectrum of CTA, which indicates the existence of stronger hydrogen bonds between carboxylic acids of CTA and pyridine moieties of 1Sz. The blue shift of the absorption band for pyridine ring from 1591 cm^{-1} in pure 1Sz to 1600 cm^{-1} in CTA/1Sz complex also indicated the formation of hydrogen bond [8]. These results suggest that intermolecular hydrogen bonding between CTA core and peripheral stilbazole derivatives is favored, and their discotic complexes are successfully prepared. Similar FTIR results were observed for other discotic complexes and analogous spectral features were reported in the literature [10].

Thermotropic Behaviours of Supramolecular Discotic Complexes

The mesophase properties of DLC complexes were examined by DSC and POM, and their thermal properties are summarized in Table 1. The CTA molecule is nonmesogenic and melts at 211°C. The stilbazole derivative of 1Sz exhibited smectic phases, while no transitions indicative of mesophases were observed for the 2Sz and 3Sz peripherals [6,11]. The phase transition behaviours of discotic complexes were different from those of the peripheral *n*Sz. All of the complexes exhibited mesophases. For CTA/1Sz and CTA/2Sz

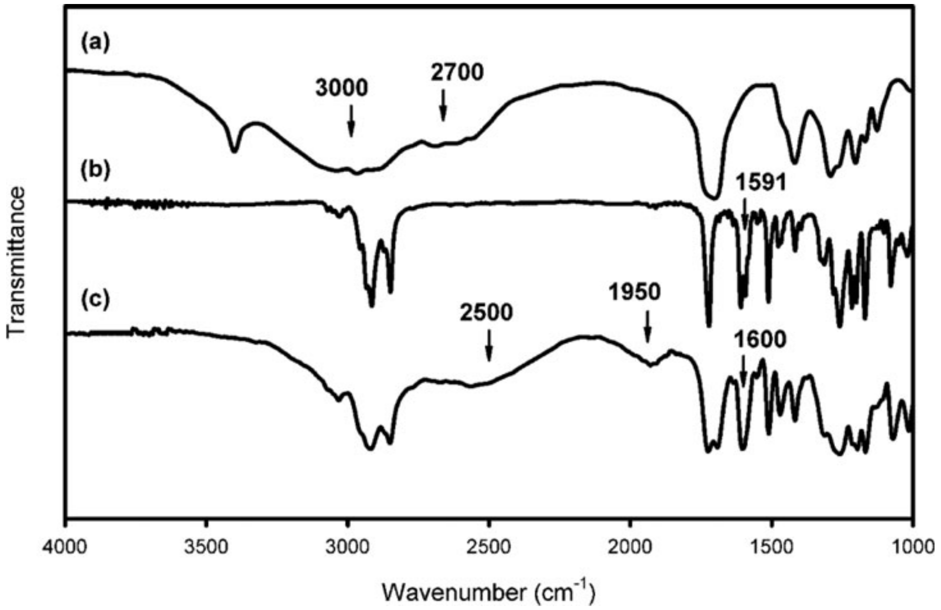

Figure 2. FTIR spectra of (a) CTA core, (b) 1Sz peripheral, and (c) CTA/1Sz complex.

complexes, monotropic mesophases with high enthalpy changes were observed, which indicates ordered columnar phases. In the case of CTA/3Sz complex, enantiotropic mesophase was formed. Interestingly, the enthalpy of clearing transition was relatively low compared to those of other complexes. It is supposed that a number of flexible alkyl chains in the CTA/3Sz complex would reduce π–π interactions of stilbazole arms in the discotic mesogen, which results in small enthalpy change. Figure 3 showed clearly birefringent textures of the discotic complexes in POM. A small fan-like or mosaic-like texture characteristic of columnar phases was observed for CTA/1Sz and CTA/2Sz complexes. For CTA/3Sz complex, a fine texture of small domains was observed upon cooling, which will be further characterized by XRD.

Table 1. Thermal properties of stilbazole derivatives and DLC complexes

	Phase transition behavior[a]	
Compounds	Heating	Cooling
1Sz	Cr 108 (59) Sm 176 (7.7) I	I 167 (5.8) Sm 78 (1.7) Cr
CTA/1Sz	Cr 94 (38) I	I 123 (10) Col 57 (14) Cr
2Sz	Cr 125 (143) I	I 105 (129) Cr
CTA/2Sz	Cr 118 (174) I	I 108 (18) Col 91 (106) Cr
3Sz	Cr 45 (35) Cr 72 (68) I	I 55 (55) Cr
CTA/3Sz	Col 66 (1.9) I	I 59 (2.8) Col

[a] Transition temperatures (°C) and enthalpies of transition (J g^{-1}, in parentheses) on heating and cooling at the scan rate of 10°C min^{-1}. Cr, crystalline; Sm, Smectic; Col, columnar; I, isotropic.

Figure 3. Polarized optical micrographs of (a) CTA/1Sz at 80°C, (b) CTA/2Sz at 100°C, and (c) CTA/3Sz at 25°C on cooling (200×).

Mesophase Structures of Supramolecular Discotic Complexes

The structural differences in mesophases of discotic complexes were investigated in detail by XRD. The CTA/1Sz complex displayed two strong peaks at 36.8 and 31.3 Å, and three weak reflectios at 25.4, 20.8, and 18.5 Å in the small-angle region, as shown in Fig. 4(a). The two intense peaks assigned to the (110) and (200) reflections are typically observed for rectangular columnar mesophases [12,13]. Thus, these five peaks were indexed as (110), (200), (210), (300), and (220) reflections of *p2mm* symmetry, respectively, from the rectangular arrangement. A broad halo at around 4.3 Å corresponding to the flexible alkyl chains was detected in the wide-angle region. These are characteristic of rectangular columnar mesophase (Col_r) with lattice constants of $a = 62.6$ Å and $b = 45.4$ Å.

The XRD patterns of CTA/2Sz and CTA/3Sz complexes in the small-angle region were different from that of the CTA/1Sz. For CTA/3Sz complex, a sharp high-intensity peak (47.2 Å) and two lower-intensity peaks (27.2 and 23.6 Å) were detected, with a reciprocal spacings ratio of $1{:}3^{1/2}{:}2$, as shown in Fig. 4(c). These peaks were indexed as (100), (110), and (200) reflections, respectively, from the hexagonal arrangement with a

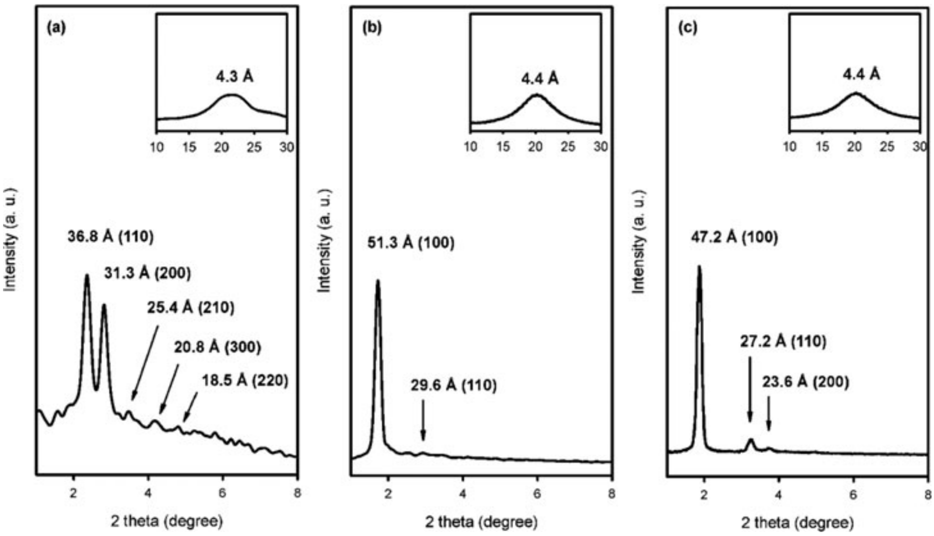

Figure 4. Small-angle and wide-angle X-ray diffractograms of (a) CTA/1Sz at 80°C, (b) CTA/2Sz at 100°C, and (c) CTA/3Sz at 25°C.

lattice constant of 54.4 Å. This XRD pattern is characteristic of hexagonal columnar ($\mathrm{Col_h}$) mesophase. A similar XRD result with a lattice constant of 59.2 Å was also obtained for CTA/2Sz complex. Interestingly, the intercolumnar distance of CTA/3Sz complex was a little smaller than that of CTA/2Sz. It is assumed that a large number of long alkyl chains with symmetric wedge shape in the CTA/3Sz complex would interact with one another in the manner of interdigitation, leading to small lattice constant of the hexagonal columnar phase. The XRD results suggest that the supramolecular discotic system formed by single hydrogen bonding between carboxylic acid and pyridine moieties is capable of forming columnar mesophases through dipole-dipole interactions between carbonyl groups along the column axis.

Conclusions

We have prepared new supramolecular discotic columnar liquid crystals simply through single hydrogen bonding between the CTA core and the peripheral arms of stilbazole derivatives with different number of alkyl chains. The rectangular columnar and hexagonal columnar mesophases could be readily obtained by dipole-dipole interactions between carbonyl groups along the column axis. Our controlled methodology will be helpful for providing a convenient and effective way to prepare more elaborate discotic columnar liquid crystals for future electronic devices.

Acknowledgments

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