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Self-assembled discotic liquid crystals formed by hydrogen bonding of alkoxystilbazoles

Jun Hyup Lee,[a] Man-Jae Han,[a] Sook Hee Hwang,[a] Ihwa Jang,[a] Seung Jun Lee,[a]
Seung Hoo Yoo,[a] Jae Young Jho[a,*] and Soo-Young Park[b]

[a]*Hyperstructured Organic Materials Research Center and School of Chemical and Biological Engineering,*
Seoul National University, Seoul 151-744, South Korea
[b]*Department of Polymer Science, Kyungpook National University, Daegu 702-701, South Korea*

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Abstract—A series of discotic liquid crystals formed by simple hydrogen bonding between phloroglucinol core and alkoxystilbazole peripheral units was prepared. Nematic columnar and hexagonal columnar mesophases were observed depending on the length of alkyl chains around the aromatic core.

Since their discovery by Chandrasekhar et al. in 1977,[1] discotic liquid crystals (DLCs) have attracted increasing attention due to their remarkable charge transport properties including electronic conductivity,[2] photoconductivity,[3] and photovoltaic properties.[4] In general, DLC molecules consist of a disk-shaped aromatic core surrounded by peripheral arms with a sufficient number of flexible alkyl or alkoxy groups. It has been shown that such molecules can form nematic or columnar mesophases through self-assembly. Columnar mesophases further associate to form a two-dimensional network leading to various types of columnar arrangements including hexagonal, rectangular, and oblique arrays.

While DLC materials formed through covalent bondings have been extensively studied,[5] those by non-covalent bondings were reported only in recent years.[6–11] In particular, discotic complexes by intermolecular hydrogen bonding between non-identical components were prepared only in a few cases.[9–11] All of these studies utilized double hydrogen bonding of benzoic acid derivatives. The need to incorporate the double hydrogen bonding units, however, restricts the structure of the counterpart component for hydrogen bonding and requires considerable synthetic effort.

Here, we report a simple way to prepare self-assembled discotic liquid crystals formed by single hydrogen bonding between phenol and pyridine moieties. While there are some examples of calamitic mesogens formed by phenol–pyridine interaction,[12–14] no discotic mesogens formed by such interaction have been reported. For the construction of DLC structure, we used 1,3,5-trihydroxybenzene (phloroglucinol, PG) as a core molecule and *trans*-4-alkoxy-4′-stilbazoles (AS*n*) with systematically varied alkyl chain lengths (*n*) as peripheral units. PG and AS*n* would form 1:3 three-armed complexes (PG/AS*n*) by intermolecular hydrogen bonding (Scheme 1). The previous work by Matsunaga et al. showed that this type of three-armed molecules composed of a small core exhibits the columnar phase.[15] In our system, it was expected that PG core and three stilbazole arms could be assembled into hydrogen-bonded disks and subsequently the disks stack to form columnar phases through π–π interaction.

AS*n* ($n = 4$–10 and 12) were prepared according to a known method.[16–18] The DLC complexes were obtained by mixing PG with AS*n* in anhydrous acetone in a 1:3 molar ratio and subsequent slow evaporation of the acetone at reduced pressure.

The formation of these hydrogen-bonded complexes was confirmed by FTIR spectroscopy. For pure PG, a broad stretching band of O–H, which is intermolecular hydrogen-bonded, was observed at 3377 cm^{-1}. For PG/AS*n*

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* Corresponding author. Tel.: +82 2 880 8346; fax: +82 2 884 7355; e-mail: jyjho@snu.ac.kr

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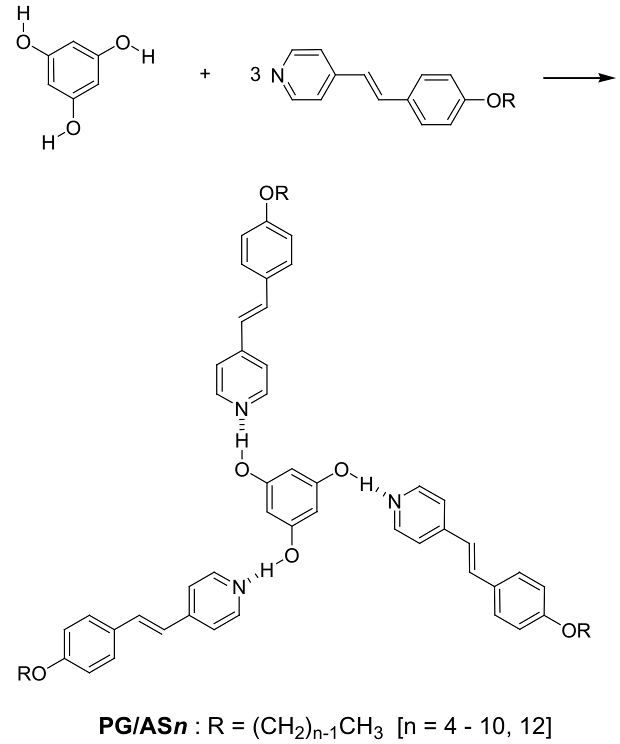

Scheme 1. Preparation of self-assembled discotic liquid crystals.

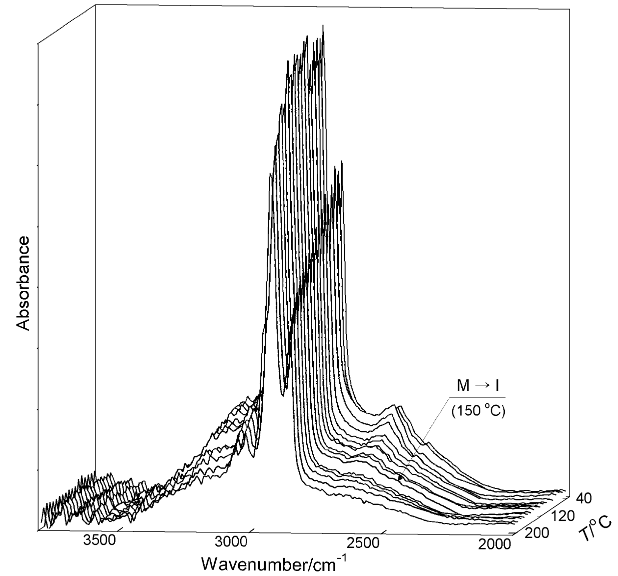

Figure 1. Temperature-dependent FTIR spectra for PG/AS10 complex in the range of 2000–3800 cm^{-1} from 40 to 200 °C. M, mesophase; I, isotropic phase.

complexes, O–H stretching band was found at a lower wavenumber of around 2900 cm^{-1}, which is attributed to the stronger hydrogen bonding between O–H and nitrogen in the complexes. These results show that the intermolecular hydrogen bonds between PG and AS*n* are formed to a large extent. Similar results were obtained for both other complexes and hydrogen-bonded polymer blends involving phenol–pyridine interaction.[13]

The stability of the hydrogen bond was investigated for PG/AS10 by temperature-dependent FTIR spectroscopy. PG/AS10 complex showed a mesophase between 84.8 and 146.5 °C on heating in a differential scanning calorimetry (DSC) experiment. Figure 1 shows that absorbance of the broad band near 2900 cm^{-1} is maintained over the mesophase range without significant change, and decreases abruptly above the clearing temperature (150 °C). These results suggest that the hydrogen bonding is stable in the liquid crystalline phase and the stability of the hydrogen bond is strongly influenced by molecular ordering.[14]

The mesomorphic properties of PG/AS*n* complexes were studied by DSC, polarized optical microscopy (POM), and X-ray diffraction (XRD) measurements. AS*n* with longer alkyl chains ($n = 6$–10 and 12) showed narrow temperature ranges of smectic phase, typically between 75 and 91 °C, while no liquid crystalline behavior was observed for AS4 and AS5.[19] The phase transition behaviors of PG/AS*n* complexes, summarized in Table 1, were different from those of the peripheral AS*n*. The complexes generally showed a wider range of mesophases than AS*n*. While PG/AS4 and PG/AS5 complexes exhibited monotropic mesophases, enantiotropic mesophases were formed in the other complexes. In PG/AS10 and PG/AS12 complexes, the temperature range of the mesophase was wider than that in the other complexes. The enthalpy of clearing transition was relatively high (17–18 J g^{-1}), indicating highly ordered mesophase in these complexes. In POM experiments, Schlieren textures characteristic of nematic phases were observed for PG/AS*n* complexes with $n = 4$–9 (Fig. 2a).

Table 1. Phase transition temperatures (°C) and enthalpies (J g^{-1}, in parentheses) of PG/AS*n* complexes[a]

Complex	Heating	Cooling
PG/AS4	Cr 49.6 (2.8) Cr′ 128.7 (67.2) I	I 124.1 (4.1) N_{Col} 91.0 (31.5) Cr
PG/AS5	Cr 89.1 (8.4) Cr′ 117.9 (57.3) I	I 114.1 (3.1) N_{Col} 92.0^{b} (33.3) Cr
PG/AS6	Cr 109.2 (60.4) N_{Col} 133.1 (5.0) I	I 120.9 (5.0) N_{Col}
PG/AS7	Cr 87.7^{b} (74.2) N_{Col} 131.7 (6.5) I	I 119.2 (7.1) N_{Col}
PG/AS8	Cr 79.8^{b} (61.2) N_{Col} 124.3 (4.4) I	I 109.4 (4.4) N_{Col} 53.7 (2.1) Cr
PG/AS9	Cr 75.4 (52.5) N_{Col} 121.5 (6.1) I	I 113.1 (6.3) N_{Col} 73.0 (5.8)^{b} Cr
PG/AS10	Cr 84.8 (52.1) Col_h 146.5 (17.2) I	I 131.7 (18.3) Col_h
PG/AS12	Cr 81.3 (56.9) Col_h 139.4 (18.6) I	I 131.9 (17.3) Col_h 52.1 (2.6) Cr

Cr, Cr′ = crystalline phase; N_{Col} = nematic columnar phase; Col_h = hexagonal columnar phase; I = isotropic phase.

[a] Transition temperatures and enthalpies were determined by DSC (scan rate, 10 °C min^{-1}).

[b] Determined at onset temperature.

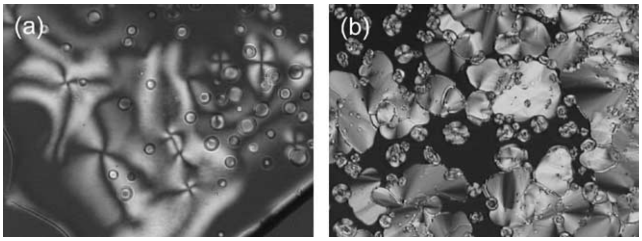

Figure 2. Polarized optical micrographs of (a) PG/AS7 at 118 °C and (b) PG/AS10 at 151 °C on cooling (200×).

On the other hand, PG/AS10 and PG/AS12 complexes exhibited a pseudo-focal conic texture (Fig. 2b) and a focal conic texture, respectively, which are typical observations for columnar mesophases.

The difference in mesophases of PG/ASn ($n = 4$–9) and PG/ASn ($n = 10$ and 12) complexes was examined in detail by X-ray diffraction. The PG/AS10 complex showed a sharp high-intensity peak (44.8 Å) and two lower-intensity peaks (26.2 and 22.1 Å) in the small-angle region (Fig. 3a), with a reciprocal spacings ratio of $1{:}3^{1/2}{:}2$. These peaks were indexed as (1 0), (1 1), and (2 0) reflections, respectively, from the two-dimensional hexagonal lattice with a lattice constant of 51.7 Å. A broad halo was observed at 4.2 Å in the wide-angle region, resulting from the average distance between alkoxy chains. These are characteristic of a hexagonal columnar ($\mathrm{Col_h}$) mesophase. A similar diffraction pattern containing the (1 0) and (1 1) reflections was also obtained for the PG/AS12 complex. For the PG/AS7 complex, in addition to a broad halo (4.2 Å), a single intense peak was observed at 40.1 Å (Fig. 3b). The peak is less sharp than that for the PG/AS10 complex, which reflects a less-ordered columnar structure in the mesophase. This diffraction pattern of the PG/AS7 complex indicates the formation of a nematic columnar ($\mathrm{N_{Col}}$) phase.[20,21] These XRD results suggest that the three-armed system formed by simple hydrogen bonding is capable of forming columnar phases through self-assembly.

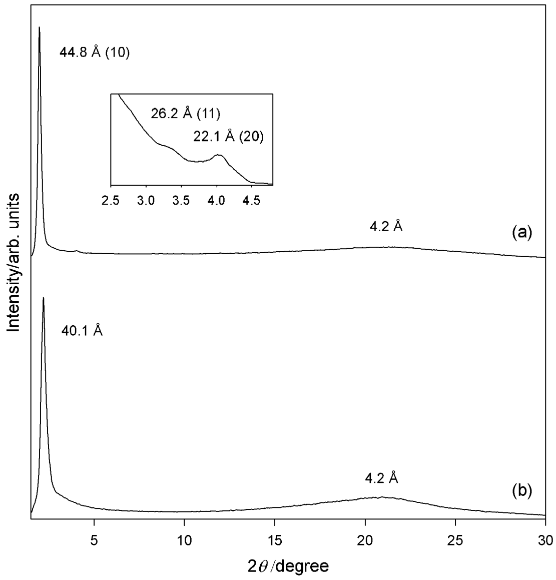

Figure 3. X-ray diffraction patterns of (a) PG/AS10 at 140 °C and (b) PG/AS7 at 100 °C.

In summary, discotic liquid crystals were prepared simply through hydrogen bonding between a non-mesogenic phloroglucinol and alkoxystilbazoles, and their self-assembly behavior was investigated. The PG/AS10 and PG/AS12 complexes showed hexagonal columnar mesophases, while the other PG/ASn ($n = 4$–9) complexes formed nematic columnar mesophases. These results indicate that the type of mesophase structure was strongly dependent on the alkyl chain length around the aromatic core. The discotic complexes with hexagonal columnar mesophases may serve as dynamic charge transport materials using reversibility of the hydrogen bonding.

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