Side Chain-Directed Assembly of Large Discotic π-Conjugated Molecules: Toward Tuning and Stabilization of Mesophases

Yusuke Tsutsui,1 Tsuneaki Sakurai,1* Kenichi Kato,2 Masaki Takata,2 and Shu Seki1*

1 Department of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan. 2 RIKEN SPring-8 Center, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5148, Japan. E-mail: t-sakurai@chem.eng.osaka-u.ac.jp, seki@chem.eng.osaka-u.ac.jp

A representative π-conjugated motif, perylenediimide (PDI), when functionalized with taper-shaped semi-fluoroalkyl chains at one of its imide positions, self-assembled into various ordered phase structures depending on the type of side chains at the other imide position. Asymmetrical substitution by semi-fluoroalkyl/alkyl chains allowed the PDI molecule to form a rectangular columnar liquid crystalline mesophase while semi-fluoroalkyl/triethylene glycol-substitution resulted in a lamellar-packed crystalline mesophase. In both mesophases, the immiscible nature of superhydrophobic/hydrophobic or superhydrophobic/hydrophilic segments works as the major driving force to lead semi-fluoroalkyl/alkyl or semi-fluoroalkyl/oxyethylene glycol nano-domains, resulting in high stability of the mesophases with the wide temperature range over 100ºC. The compound decorated with tapered semi-fluoroalkyl chains at the both imide positions exhibited complicated crystalline ordered phases with high thermal stability.

keywords: liquid crystal, columnar phase, perylenediimide, immiscible chains

1. Introduction

Large π-conjugated molecules are of great interest because of their potential use as functional materials with optical, electrical, and magnetic properties. Such unique properties depend on not only the structure of π-systems itself but also their assembled structures. In particular, when focusing on their application as organic semiconductors, it is quite important how π-systems stack up to form long-range charge carrier transport pathways.1 One of the promising approaches includes the peripheral modification of large π-systems with flexible chains that allows the formation of one-dimensional discotic columns via self-assembly2–5. Although the diversity of central π-conjugated molecules has grown rapidly, long alkyl chains have been mostly utilized for large π-systems. Considering the fine-tuning of the π-stacking mode, morphology, and dimension of the structures to control the semiconducting property, there is still plenty room for improvement hopefully given by side-chain engineering.

The strategy of side chain-directed assembly have been often reported for small aromatic compounds. Functionalization by long alkyl, fluoroalkyl, dimethylsiloxane, and triethylene glycol chains triggers nano-segregation between the aromatic cores and respective chains, resulting in the formation of highly-ordered phase structures.6–8 In contrast, large π-system can

![Molecular structures of perylenediimide (PDI) derivatives having semi-fluoroalkyl side chains together with a reference PDI having alkyl chains.](image-url)
form, without such additional interactions, columnar structures with two-dimensional periodic packing since strong π-π stacking interaction operates together with the core/chain nano-segregation. However, when incompatible side chain pairs were introduced to large π-conjugated cores, structural changes were also observed, leading to the unique properties including enhancement of charge carrier mobility, switching of dominant charge carriers, photoluminescence color change, and so on. Here we report that perylenediimide (PDI) molecules carrying taper-shaped semi-fluoroalkyl chains at one imide position self-assembled into various type of ordered structures due to the strong self-aggregation character of fluoroalkyl segments. By tuning the type of chains at the other imide position of PDI (Fig. 1), we demonstrated both liquid crystalline (LC) and crystalline materials that show different macroscopic orientation capability.

2. Experimental
2.1. General
Unless otherwise noted, all commercial reagents were used as received. 1H-NMR spectra were recorded in CDCl3 on a JEOL model AL-400 spectrometer operating at 400 MHz. Polarized optical micrographs were recorded on a Nikon model ECLIPSE E600FN polarized optical microscope equipped with a hand-made hot stage and KPI model TC02 temperature controller. Differential scanning calorimetry measurements were performed on a Mettler model DSC 822e differential scanning calorimeter. Cooling and heating profiles were recorded and analyzed with a Mettler model STARe system. X-ray diffraction measurements were carried out using a synchrotron radiation X-ray beam with a wavelength of 0.108 nm on BL44B2 at the Super Photon Ring (SPring-8, Hyogo, Japan). During the measurements, samples were put into a 0.5-mm thick glass capillary and rotated and all diffraction patterns were recorded with a 0.01º step in 2θ. The exposure time to the X-ray beam was 3 min. The temperature was controlled by high-temperature N2 gas flow. Heating and cooling process was controlled at a rate of 10ºC min⁻¹ and the sample was annealed at the target temperature for 2 min prior to the beam exposure.

2.2 Synthesis
Synthetic schemes of PDI derivatives are described in Scheme 1. Compound 1 was synthesized in a similar way to the reported procedure of 2-(3,4,5-tris(benzyloxy)benzyl) isoindoline-1,3-dione.

3. Results and discussion
The three compounds PDI/F, PDI/C12, and PDI/TEG were newly synthesized according to the reported procedures with a slight modification. PDI/C12 was also synthesized as a reference material exhibiting a typical hexagonal columnar LC phase. All the four compounds were characterized by 1H NMR spectroscopy and MALDI-TOF-MS spectrometry. In differential scanning calorimetry (DSC), PDI/C12 showed a mesophase from −31 to 220ºC on the second cooling process at a rate of 10 ºC min –1 (Table 1). In the mesophase, birefringent textures were observed in polarized optical microscopy (POM) while the mesophase structure was assigned to a columnar hexagonal lattice by means of X-ray diffraction analysis (XRD), both of which are consistent with the previous reports. Having these in mind, the newly developed compounds were characterized in the identical methods. In the temperature region from −50 to 280ºC, PDI/F showed one solid-solid phase transition at around 242ºC (Fig. 2a). PDI/F appeared as powder, did not melt into isotropic liquid (IL) even over 300ºC, and exhibited poor solubility to common organic solvents. In addition, the powder showed birefringence in POM. Its XRD patterns at 300
and 200°C both displayed a set of sharp diffraction peaks (Fig. 3a). Although it is difficult to assign these peaks to a simple crystalline lattice, we can conclude, based on the above observations, that self-aggregation of fluoroalkyl segments in PDIF/F may be the major driving force to form crystalline phases rather than usual columnar LC phases as seen in PDIC12/C12.

In contrast, PDIF/C12 behaves as a typical columnar LC but the phase structure is quite unique. PDIF/C12 in DSC showed 4 and 3 times phase transitions on heating and cooling at 10 °C min⁻¹, respectively (Fig. 2b). The enthalpy changes at around 240°C indicated the phase transition between LC and IL phases, which was confirmed by microscopy and XRD measurements. Of interest, when cooled down from the IL to LC phase at 1 °C min⁻¹, the crossed polarized micrograph of PDIF/C12 became dark while dendritic textures were seen in the optical micrograph (Fig. 2d). These features are characteristic of homeotropically oriented columnar LC phases. In the slow-cooling condition, the LC nucleation may take place near the interface between LC and a glass substrate, and the columnar structures grow from each nucleus. Thus, the direction of the columns should be perpendicular to the glass substrates. In fact, birefringent textures appeared by the treatment of fast cooling at a rate of 20 °C min⁻¹ (Fig. 2e). In the fast-cooling condition, many nuclei form in bulk, thus resulting in the formation of randomly-oriented LC domains. The observed spontaneous homeotropic alignment capability is important for the device-scale application of LC materials.

Table 1. Phase behaviors with transition temperatures (°C) on the second heating/cooling process at a rate of 10 °C min⁻¹. Transition enthalpies (kJ mol⁻¹) are given in parentheses. Symbols Cr, G, Colh, Colr, Colx, and IL denote crystalline, grassy, hexagonal columnar liquid crystalline, rectangular columnar liquid crystalline, unidentified columnar, and isotropic liquid phases, respectively.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phase</th>
<th>T, / °C (ΔH / kJ mol⁻¹)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDIF/C12/C12</td>
<td>G</td>
<td>-26 (18.1)</td>
<td>Cr₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-31 (-16.3)</td>
<td>Cr₁</td>
</tr>
<tr>
<td>PDIF/C12/C12</td>
<td>Cr₁</td>
<td>243 (4.2)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>18 (6.2)</td>
<td>Colh</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-10 (-8.2)</td>
<td>Col₁</td>
</tr>
<tr>
<td>PDIF/C12/C12</td>
<td>G</td>
<td>56</td>
<td>Col₁</td>
</tr>
<tr>
<td>PDIF/C12/C12</td>
<td>G</td>
<td>211 (4.4)</td>
<td>Col₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>206 (-4.1)</td>
<td>IL</td>
</tr>
<tr>
<td>PDIF/TPEG</td>
<td>G</td>
<td>56</td>
<td>Col₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>Col₁</td>
</tr>
<tr>
<td></td>
<td></td>
<td>239 (-21.5)</td>
<td>IL</td>
</tr>
</tbody>
</table>

Fig. 2. Differential scanning calorimetry traces of (a) PDIF/F, (b) PDIF/C12, and (c) PDIF/TPEG on second heating and cooling processes at a rate of 10 °C min⁻¹. Optical (left) and crossed polarized (right) micrographs of (d) PDIF/C12 at 239°C, (e) PDIF/C12 at 230°C, and (f) PDIF/TPEG at 202°C in a sandwich-type glass cell. The samples were cooled from their isotropic liquid phase at a rate of 1 °C min⁻¹ for (d) and (f) and 20 °C min⁻¹ for (e), respectively.

down, PDIF/C12 undergoes a phase transition at around 90°C to exhibit Col₁ phase (Fig. 2b). According to the XRD pattern at 50°C, the basic structure of Col₁ phase is similar to that of Col₂ except the appearance of sharp diffraction peaks at around 2θ = 5, 12, and 18° (Fig. 3e). These
diffraction features may originate from the crystallization of fluoroalkyl chains that are known to interdigitate each other.  

As shown in Fig. 3h, PDIF/TEG indicated the \( \pi \)-stacking periodicity in its XRD pattern at 200\(^\circ\)C. Taking account of its DSC chart (Fig. 2c), PDIF/TEG has a columnar mesophase at 56–211\(^\circ\)C on heating and 206–50\(^\circ\)C on cooling. However, we discovered that the mesophase was not a typical LC but crystal-like mesophase. Although the several strong diffraction peaks were assigned to a lamellar-based periodic structure (Figs. 3i and 3j), there were still many minor diffractions that were difficult to assign. This mesophase was defined as Col\( \chi \). Nevertheless, the (100) diffraction (\( d = 60.1 \) Å) of PDIF/TEG at 200\(^\circ\)C should correspond to the layered distance similar to the case of PDIF/C\(_{12}\), giving the proposed packing structure as shown in Fig 4b. We thought that the extremely immiscible nature between the fluoroalkyl and triethyleneglycol chains would rule out the rectangular packing of the columnar structures and result in the lamellar-based structure without any contact between the fluoroalkyl and triethyleneglycol chains. Because of the absence of LC character, PDIF/TEG did not show homeotropic alignment capability even in the slow cooling condition at 1 °C min \(^{-1}\) from its IL phase (Fig. 2f).

4. Conclusion

Toward the fine-tuning of structures, morphology, and \( \pi \)-stacking mode of self-assembled perylenediimide (PDI) motifs, we have developed a side-chain strategy including taper-shaped semifluoroalkyl chains. When both imide positions were decorated with these chains, resulting PDIF/F formed crystalline phases having high thermal stability. By replacing one of the imide positions with tapered alkyl chains (PDIF/C\(_{12}\), columnar liquid crystalline mesophases with \( p2mg \) symmetry were appeared as a result of
minimizing the contact between dodecyl and fluoroalkyl domains. When a tapered semifluoroalkyl and triethyleneglycol pair was employed (PDIF/TEG), a lamellar-based crystalline mesophase was developed as an ultimate structure to avoid the contact between these incompatible chains. Interplay of π-stacking interactions and nano-segregation via introduction of immiscible side chain pairs in the orthogonal direction would be a general strategy to form stable mesophases from disc-shaped large π-conjugated molecules.

Acknowledgements
This work was partly supported by a Grant-in-Aid for Young Scientists (B) (26810049) from the Japan Society for the Promotion of Science. We thank Prof. Dr. Aida and Mr. Shibuya in The Univ. of Tokyo for DSC measurements. The synchrotron radiation experiments were performed at BL44B2 in SPring-8 with the approval of RIKEN (Proposal No. 20130021).

References