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

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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/triethyleneglycol-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/oxyethyleneglycol nano-domains, resulting in high stability of the mesophases with the wide temperature range over 100°C. 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-assembly.^{2–5)} 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

Fig. 1. Molecular structures of perylenediimide (PDI) derivatives having semi-fluoroalkyl side chains together with a reference PDI having alkyl chains.

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 triethyleneglycol 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

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.²⁻⁵⁾ However, when incompatible side chain pairs were introduced to large π -conjugated cores, structural changes⁹⁻¹³⁾ were also observed, leading to the unique properties including enhancement of charge carrier mobility,⁹⁾ switching of dominant charge carriers,¹¹⁾ photoluminescence color change¹³⁾, 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.^{14,15)} 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 BL44B2¹⁶⁾ 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 0.01° 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 10°C 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

Scheme 1. Synthetic schemes of perylenediimide derivatives. (a) 1-bromododecane, K₂CO₃, DMF, 80°C, 36 h; (b) TsO(CH₂CH₂O)₃Me, K₂CO₃, DMF, 80°C, 24 h; (c) Br(CH₂)₄(CF₂)₈F, K₂CO₃, DMF, 80°C, 36 h; (d) H₂N-NH₂·H₂O, EtOH, reflux, 3 h; (e) **3C12**, imidazole, pyridine, 90°C; (f) **3F**, imidazole, pyridine, 90°C, 18 h; (g) **3C12**, **3F**, imidazole, benzonitrile, pyridine, 90°C, 18 h; (h) **3TEG**, **3F**, imidazole, benzonitrile, pyridine, 90°C, 18 h.

procedure of 2-(3,4,5-tris(benzyloxy)benzyl)isindoline-1,3-dione.¹⁷⁾

3. Results and discussion

The three compounds **PDI_{F/F}**, **PDI_{F/C12}**, and **PDI_{F/TEG}** were newly synthesized according to the reported procedures with a slight modification. **PDI_{C12/C12}**^{18,19)} 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/C12}** showed a mesophase from -31 to 220°C on the second cooling process at a rate of 10 °C 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 280°C, **PDI_{F/F}** showed one solid-solid phase transition at around 242°C (Fig. 2a). **PDI_{F/F}** appeared as powder, did not melt into isotropic liquid (IL) even over 300°C, 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 **PDI_{F/F}** may be the major driving force to form crystalline phases rather than usual columnar LC phases as seen in **PDI_{C12/C12}**.

In contrast, **PDI_{F/C12}** behaves as a typical columnar LC but the phase structure is quite unique. **PDI_{F/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 **PDI_{F/C12}** became dark while dendritic textures were seen in the optical micrograph (Fig. 2d). These features are characteristic of homeotropically oriented columnar LC phases.^{20,21)} 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.^{20,21)} Based on the XRD pattern, we noticed that the structure of Col_{r2} phase of **PDI_{F/C12}** (Table 1) was not a typical rectangular columnar phase with *p2mm* symmetry. For example, (100) peak, usually not detected in common rectangular phases with high symmetry, was observed as seen in Fig. 3d. After complete assignment of all the obvious diffraction peaks, we found that the LC phase at 170°C was assigned to be a rectangular columnar lattice with *p2mg* symmetry, where the lattice parameters of *a* and *b* are 60.7 and 34.1 Å, respectively. This structure can be explained as a result of side-chain immiscibility.^{10,11,22)} Namely, dodecyl chains prefer to assemble with themselves and *vice versa* for the semifluoroalkyl chains. Therefore, to minimize the contact between dodecyl and fluoroalkyl domains, **PDI_{F/C12}** molecules stack up to form columnar structures that further integrate into alternate immiscible nano-scale layers (Fig. 4a). When further cooled

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, Col_h, Col_r, Col_x, and IL denote crystalline, grassy, hexagonal columnar liquid crystalline, rectangular columnar liquid crystalline, unidentified columnar, and isotropic liquid phases, respectively.

Entry	Phase	$T_i / ^\circ\text{C}$ ($\Delta H / \text{kJ mol}^{-1}$)	Phase
PDI_{C12/C12}	G	$\xrightarrow{-26 (18.1)}$	Col _h
	Col _h	$\xrightarrow{223 (13.7)}$	IL
PDI_{F/F}	Cr ₁	$\xrightarrow{243 (4.2)}$	Cr ₂
	Cr ₂	$\xrightarrow{242 (-3.3)}$	Cr ₁
PDI_{F/C12}	G	$\xrightarrow{18 (6.2)}$	Col _{r1}
	Col _{r1}	$\xrightarrow{10 (-8.2)}$	G
	Col _{r1}	$\xrightarrow{92 (13.4)}$	Col _{r2}
	Col _{r2}	$\xrightarrow{114 (3.3)}$	Col _{r1}
PDI_{F/C12}	Col _{r2}	$\xrightarrow{240 (15.4)}$	IL
	IL	$\xrightarrow{239 (-21.5)}$	Col _{r2}
PDI_{F/TEG}	G	$\xrightarrow{56}$	Col _x
	Col _x	$\xrightarrow{211 (4.4)}$	IL
PDI_{F/TEG}	IL	$\xrightarrow{206 (-4.1)}$	Col _x
	Col _x	$\xrightarrow{50}$	G

Fig. 2. Differential scanning calorimetry traces of (a) **PDI_{F/F}**, (b) **PDI_{F/C12}**, and (c) **PDI_{F/TEG}** on second heating and cooling processes at a rate of 10 °C min⁻¹. Optical (left) and crossed polarized (right) micrographs of (d) **PDI_{F/C12}** at 239°C, (e) **PDI_{F/C12}** at 230°C, and (f) **PDI_{F/TEG}** 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, **PDI_{F/C12}** undergoes a phase transition at around 90°C to exhibit Col_{r1} phase (Fig. 2b). According to the XRD pattern at 50°C, the basic structure of Col_{r1} phase is similar to that of Col_{r2} except the appearance of sharp diffraction peaks at around $2\theta = 5, 12,$ and 18° (Fig. 3e). These

Fig. 3. X-ray diffraction patterns of **PDI_{F/F}** at (a) 300 °C, and (b) 200 °C, **PDI_{F/C12}** at (c) 280 °C, (d) 170 °C, (e) 50 °C, and (f) -30 °C, and **PDI_{F/TEG}** at (g) 250 °C, (h) 200 °C, (i) 80 °C, and (j) -30 °C.

diffraction features may originate from the crystallization of fluoroalkyl chains that are known to interdigitate each other.¹⁵⁾

As shown in Fig. 3h, **PDI_{F/TEG}** indicated the π -stacking periodicity in its XRD pattern at 200°C. Taking account of its DSC chart (Fig. 2c), **PDI_{F/TEG}** has a columnar mesophase at 56–211°C on heating and 206–50°C on cooling. However, we discovered that the mesophase was not a typical

Fig. 4. Schematic illustration of molecular arrangement in (a) rectangular columnar liquid crystalline phase of **PDI_{F/C12}** and (b) crystalline phase of **PDI_{F/TEG}**.

LC but crystal-like mesophase. Although the several strong diffraction peaks were assigned to a lamellar-based periodic structure (Figs. 3h and 3i), there were still many minor diffractions that were difficult to assign. This mesophase was defined as Col_X. Nevertheless, the (100) diffraction ($d = 60.1$ Å) of **PDI_{F/TEG}** at 200°C should correspond to the layered distance similar to the case of **PDI_{F/C12}**, 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, **PDI_{F/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 π -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 **PDI_{F/F}** formed crystalline phases having high thermal stability. By replacing one of the imide positions with tapered alkyl chains (**PDI_{F/C12}**), 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 ($\text{PDI}_{\text{F/TEG}}$), 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.

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