Preferential formation of columnar mesophases via peripheral modification of discotic π-systems with immiscible side chain pairs†

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When sufficient volume of dodecyl chains are attached at one imide position of a perylenediimide (PDI) or naphthalenediimide (NDI) core and triethyleneglycol (TEG) chains on the other side, the resulting molecules PDIC12/TEG G0, PDIC12/TEG G1, and NDIR12/TEG G0 self-assemble into a rectangular columnar mesophase with p2mg symmetry, forming hydrophobic/hydrophilic nano-segregation of side chains. The driving force of PDIC12/TEG G0 to form preferentially the rectangular columnar mesophase is given by the immiscibility between the side chain pairs—exclusion of other phases such as cubic, crystalline and amorphous phases, where thermodynamically unstable contacts between hydrophobic and hydrophilic chains considerably take place. In contrast, this preference is less found in the analogous molecules decorated with either dodecyl or TEG chains at both termini. PDIC12/TEG G0 and PDIR12/TEG G0 form a hexagonal columnar mesophase because of the optimized chain/core volume. However, if the side chain volume grows, PDITEG/TEG G1 does not form a mesophase but undergoes a soft crystalline–isotropic phase transition, while PDIC12/C12 G1 was revealed to destabilize its columnar mesophase but forms a micellar cubic phase. NDIR12/C12 G0 resulted in a strong crystallization, while NDIR12/TEG G0 formed amorphous liquid. The molecular design strategy using immiscible side chain pairs potentially enables a variety of π-systems to stack up to form a columnar phase rather than other ordered phases, regardless of the chain/core volume balance.

Introduction

Columnar liquid crystals (LCs) based on discotic π-systems have attracted interest due to their potential use as soft organic semiconductors with unidirectional charge carrier transporting properties.1–3 If the methodology to obtain columnar mesophases with largely π-conjugated cores by rational molecular design strategies is established, we can use various active π-systems as photo and electronic devices. For discotic LC molecules, the major driving force to enable columnar structures via self-assembly is mostly given by the peripheral modification of disc-shaped cores with long paraffinic chains,4–7 where rigid π-systems and flexible side chains are segregated in a nanoscopic scale. Nevertheless, the volume balance between a discotic core and peripheral chains has a remarkable impact on the stable phase structures,8 leading to the formation of other phases such as micelle cubic,9–11 bicontinuous cubic,12–14 crystalline,15,16 and amorphous phases.17,18 Therefore, in order to obtain columnar LC materials, the try-and-error in the synthesis process is required for every discotic π-system such as changing the number and length of chains. Here we demonstrate a potentially general molecular design strategy using an immiscible side chain pair19–26 (Fig. 1) that preferentially induces the formation of a rectangular columnar mesophase rather than other non-columnar phases. As a proof of this strategy, we selected typical n-type semiconducting cores, perylenediimide (PDI)27,28 and naphthalenediimide (NDI),29,30 that are easily available for site-specific introduction of different side chain functionalities.31,32 As an immiscible chain pair, dodecyl (hydrophobic) and triethyleneglycol (hydrophilic) chains were adopted and introduced into the imide positions of the PDI or NDI cores. Since contact between hydrophobic and hydrophilic chains is thermodynamically unfavorable, PDIC12/TEG G0, a PDI molecule having the immiscible side chain pair (Fig. 1), allows discotic cores to avoid the phase structures containing large intermolecular paraffinic-oxyethylene contacts and thus eventually
form a columnar structure with hydrophobic/hydrophilic nano-segregated layers (Fig. 2). Of interest, we found that this preference was also confirmed when the volume balance between the core and side chains is changed as seen in PDIC12/C12 G0 and NDI C12/TPEG G0 series (Fig. 1). These results support our concept and propose a potentially general molecular design strategy to realize self-assembled columnar structures from a variety of large planar \( \pi \)-systems.

**Results and discussion**

**Synthesis**

The PDI derivatives PDIC12/C12 G0, PDIC12/TPEG G0, PDIC12/C12 G1, PDIC12/TPEG G1, and PDIC12/TPEG G1 (Fig. 1) were newly synthesized through the reaction using perylenetetracarboxylic dianhydride and taper-shaped amine compounds having dodecyl or TEG chains (see ESI†). PDIC12/C12 G0 was synthesized according to the reported procedures with a slight modification. The NDI derivatives were also prepared by following the similar synthetic schemes used in the PDI synthesis. Isolation and purification were successfully carried out by column chromatography using silica gel, followed by the recycling preparative size-exclusion chromatography, and then reprecipitation (see ESI†). All the PDI and NDI compounds were fully characterized by \(^1\)H and \(^{13}\)C NMR spectroscopy and MALDI-TOF-MS spectrometry (see ESI†).

**Liquid crystalline property of G0-PDI derivatives**

Differential scanning calorimetry (DSC) revealed that PDIC12/C12 G0 showed a mesophase from \( -30 \) to \( 220 \) °C in the second cooling process at a rate of \( 10 \) °C min\(^{-1}\) (Table 1 and Fig. S1, ESI†). In the mesophase, birefringent textures were observed in polarized optical microscopy (POM) (Fig. 3a) 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.\(^{33,34}\) From the (100) diffraction peak in the XRD pattern, a lattice parameter \( a = 30.9 \) Å at \( 70 \) °C was disclosed, and one relatively broad peak was assigned to a \( \pi \)-stacking periodicity of \( c = 3.4 \) Å (Fig. 4a). In the solid state below \( ca. -30 \) °C, the observed diffraction peaks in its XRD pattern became obviously broad (Fig. S3, ESI†) though the set of the peaks was still assigned to a hexagonal lattice, indicating that the material was in a LC-glass phase\(^{35}\) (Table 1). The diffraction corresponding to the \( \pi-\pi \) plane was confirmed at all the measured temperatures below the clearing point. In fact, spin-coated thin films of PDIC12/C12 G0 afforded electronic absorption spectra typical of H-type \( \pi \)-stacked PDI aggregates (Fig. 5a),\(^{36}\) displaying a blue shift and broadening of the absorption bands at around 500 nm compared to that in a good solvent such as CHCl\(_3\).

With these results in mind, the other compounds were characterized in the identical manner. When cooled down from its isotropic melt, PDIC12/C12 G0 exhibited a phase transition into a mesophase at 168 °C in which the dendritic texture developed in POM (Fig. 3c). The lower clearing point than that of PDIC12/C12 G0 probably originates from the more flexible
sharp diffraction peaks that did not appear at 80°. For example, the XRD pattern at 20° (Fig. S1, ESI†) for PDIC12/TEG, PDIC12/C12, and PDITEG/TEG G0 shows narrow peaks in XRD, and thus showing broad peaks in XRD. On the other hand, TEG G0, PDIC12/C12 G0, and NDIC12/C12 G0 have high melting temperature mesophase assigned to a hexagonal columnar phase with a π–π distance of c = 3.4 Å (Fig. 4d). The lattice parameter a was calculated as 26.5 Å for PDITEG/TEG G0, which agrees with the shorter chain length of TEG than that of dodecyl. One notable behavior of PDITEG/TEG G0 is that the phase transition at 46°C detected by DSC measurements at 10°C min⁻¹ upon cooling (Fig. 4b) and (h) PDIC12/TEG G0 at 78°C. Scale bars indicate 200 µm.

As discussed above, dodecyl chains represent stronger interchain interactions upon freezing (larger ΔH: 13.0 kJ mol⁻¹). At the same time, they show a larger entropy loss (larger ΔS: 26.3 J mol⁻¹) than that of dodecyl chains, which was often seen in the previous reports. In addition, XRD analysis revealed that the observed mesophase was a hexagonal columnar phase with a π–π distance of c = 3.4 Å (Fig. 4e). The lattice parameter a was calculated as 26.5 Å for PDITEG/TEG G0, which agrees with the shorter chain length of TEG than that of dodecyl. One notable behavior of PDITEG/TEG G0 is that the phase transition at 46°C detected by DSC measurements at 10°C min⁻¹ upon cooling (Fig. 4b) and (g) PDIC12/TEG G0 at 78°C. Scale bars indicate 200 µm.

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layers (Fig. 6). Consequently, a rectangular columnar LC phase with \( p2mg \) symmetry is realized. This mesophase structure, upon elevating the temperature, undergoes phase transition into the hexagonal columnar mesophase at 113°C, which is probably due to the partially mixed dodecyl and TEG chains that lead to the higher-symmetry phase (Fig. 6). The above possible mechanism was also supported by another PDIderivative carrying dodecyl and semifluoroalkyl chains reported recently.39,40 We believe that the combined use of two immiscible chains as peripheral substituents generally enables a variety of \( \pi \)-conjugated motifs to form columnar mesophases. It should be noted that both PDIC12/TEG G0 and PDITEG/TEG G0 displayed absorption spectra similar to that of PDIC12/C12 G0 in their spin-coated films (Fig. 5). We concluded that the actual \( \pi \)-stacking geometry of PDI units within a columnar structure is not essentially different among the three materials. We should mention the previous work by Thelakkat et al.,32 where the modification by a pair of two-blanced immiscible chains results in the formation of hexagonal columnar mesophases. It suggested the importance of core/chain volume balances on the selection of hexagonal/rectangular geometry.26

**Liquid crystalline properties of G1-PDI derivatives**

Then our motivation moved on to the acceptable range of the proposed effect by immiscible side chains. We wondered that...
which type of mesophases appeared if the volume of the side chains get larger or smaller. For this purpose, PDLG series were prepared (Fig. 1). PDLC exhibited two mesophases at −3--90 °C and 90--186 °C on second cooling (Table 1 and Fig. S1, ESI†). However, no optical texture was appeared in POM above ca. 90 °C, even though the isotropic melt of PDLC was cooled down. The fact possibly reflects the presence of an optically-isotropic but structurally-ordered mesophase. By means of XRD analysis, PDLC at 110 °C gave a set of diffractions at 2θ = 1.64, 2.32, 2.85 and 3.28° that are not assignable to common columnar phases (Fig. 4e). In fact, the higher-temperature mesophase was assigned to a micellar cubic phase with the Im3m symmetry. Considering the lattice parameter a = 53.4 Å at that temperature, the probable molecular arrangement is composed of several stacks of PDI cores that are covered with a shell of dodecyl chains (Fig. 2 and 7). The reason of the higher transition temperature of PDLC than that of PDLC is attributed to the crowded environment of dodecyl chains. Upon melting of the chains along the glass-LC transition, dodecyl chains get a smaller degree of freedom as compared to the case of PDLC. Namely, the entropic gain per single chain is smaller for PDLC, whereas the enthalpic penalty may be comparable (Table S1, ESI†), resulting in a higher transition temperature (Tg-LC = ΔHg-LC/ΔSg-LC) for PDLC.

On the other hand, PDTEG/TEG showed a simple DSC curve basically containing one phase transition upon both heating and cooling processes (Table 1 and Fig. S1, ESI†). Although birefringent textures appeared in POM at 93 °C (Fig. 3f), the lower-temperature phase is not liquid crystalline. For example, the obtained XRD pattern at 90 °C includes several notable diffraction peaks (Fig. 4h and Fig. S8, ESI†) that however were not assignable to simple columnar, lamellar, or cubic phases. We gave up clarifying the detailed phase structure and denoted it as an unidentified crystalline phase. In this solid phase, PDTEG/TEG contains π-stacked aggregates, which was proved by absorption spectral study in the film state (Fig. 5b). The absence of LC phase for PDTEG/TEG is most likely due to the bulky substituents with too fluidic TEG chains. TEG chains in this crowded environment do not receive the entropic gain enough for stabilizing the LC phase as a thermodynamically stable phase. This issue is delicate and difficult to discuss in a general manner.

PDTC showed two mesophases at −3--147 °C and 147--154 °C (Table 1 and Fig. S1, ESI†). Upon cooling from its isotropic melt, PDTC at 148 °C afforded birefringent focal-conic textures in POM, indicative of a columnar mesophase (Fig. 3e). Indeed, XRD measurements disclosed that the dominant diffraction peaks were assigned to (100), (200), and (110) in a rectangular lattice with the p2mg symmetry, where the lattice parameters of a and b are 79.3 and 38.9 Å at 149 °C, respectively (Fig. 4g). Moreover, though the XRD patterns involved unidentified crystal-like peaks upon cooling in this mesophase (Fig. S7, ESI†), still (100), (200) and (110) peaks in a rectangular lattice mainly appeared. Taking into account the π-stacking interactions among PDI units (Fig. 5), PDTC was found to behave similar to PDLC because of the modification with immiscible side chains. One distinct difference is the absence of a hexagonal columnar phase. If the PDTC molecules move significantly in translational or rotational directions, the mixing of large volume of dodecyl and TEG chains takes place, leading to a considerable enthalpic penalty. Therefore, PDTC maintains the rectangular columnar structure even
upon elevating the temperature. Unfortunately, we could not obtain information of a higher-temperature mesophase at 147–154 °C (on cooling) despite the detailed VT-XRD measurements. The other interesting matter to note is that XRD patterns in the temperature region of the Col phase showed broad diffraction at 2θ = ca. 14 and 16° (Fig. S7, ESI†). These diffraction peaks strongly indicate the halo of dodecyl and TEG chains, respectively, which proves the presence of nanoscale immiscible domains.

Through the above experimental results, the peripheral modification of immiscible side chain pairs seems to extend the acceptable range of core/chain volume balance for columnar LC formation, whose driving force was given by the unstabilization of other possible mesophase candidates (Fig. 2 and 7).

**Liquid crystalline properties of G0-NDI derivatives**

For tuning the core/chains volume balance, there is another approach using smaller π-conjugated motifs than PDI without changing the G0-type peripheral units. For this purpose, we synthesized NDI-G0 series (Fig. 1) and investigated their phase transition behaviors and structural information. Based on the DSC curves scanned at a rate of 10 °C min⁻¹, NDI_{C12/C12-G0} has three solid and one isotropic liquid phases (Table 1 and Fig. S1, ESI†). Upon cooling from its isotropic melt, NDI_{C12/C12-G0} obviously crystallizes at 140 °C (Fig. 3g). The typical XRD patterns indicate the high crystallinity of all the three solid phases, though we only denote the highest-temperature mesophase as Col, (Fig. 4i, j and Fig. S9, ESI†). In addition, judging from the XRD patterns (Fig. S9, ESI†), the diffraction peak corresponding to the π-stacking periodicity, if any, was quite weak.

In contrast, NDI_{TEG/TEG-G0} forms isotropic liquid even at a room temperature. Its POM images are dark and only broad peaks were observed in its XRD patterns (Fig. 4j), while its DSC curves are almost planar (Fig. S1, ESI†). Considering the behavior of NDI_{C12/C12-G0} and NDI_{TEG/TEG-G0}, the π-stacking capability of the NDI system is so weak that the properties of side chains are dominant for the whole molecule—NDI_{C12/C12-G0} strongly crystallizes due to the interdigitation of dodecyl chains while NDI_{TEG/TEG-G0} is an isotropic liquid due to the flexibility of TEG chains.

Similar to PDI_{C12/TEG-G0} and PDI_{C12/TEG-G1}, NDI_{C12/TEG-G0} forms a rectangular columnar phase with the p2mg symmetry, which was confirmed by the presence of the 100 diffraction peak in XRD (Fig. 4k). Meanwhile, some hysteresis was observed in its DSC curves (Fig. S1, ESI†) and minor but sharp diffractions were appeared in XRD (Fig. 4k and Fig. S10, ESI†), both of which imply the crystalline nature of the materials. However, NDI_{C12/TEG-G0} has characteristic features from those of NDI_{C12/C12-G0}-, NDI_{C12/TEG-G0} in a glass cell showed fan-shaped textures at 140 °C in POM (Fig. 3h). Furthermore, it displayed a clear π-stacking periodicity of c = 3.46 Å in XRD patterns (Fig. 4k and Fig. S10, ESI†). Overall, immiscible chains play a role in forcing the NDI core to stack up in a columnar fashion, affording p2mg rectangular columnar structures. When looking at the thermodynamic parameters, different behaviors of NDI series are obvious. By plotting the entropy and enthalpy values upon the LC–Iso phase transition (Fig. S2, ESI†), the entropy–enthalpy compensation was confirmed. However, the linear correlation is different between the PDI and NDI compounds having mesophases. The fact implies the large contribution of inter-chain interactions to the Col–Iso transitions that is not commonly observed for LC–Iso transitions. However, what we would like to emphasize here is that the immiscible side chain pairs work to develop the columnar mesophase with a periodically-stacked π-system in both LC (PDI_{C12/TEG-G0} and PDI_{C12/TEG-G1}) and crystalline (NDI_{C12/TEG-G0}) cases.

**Conclusions**

Motivated by our previous findings, where the modification with a immiscible side chain pair makes a π-system form a columnar liquid crystalline phase, here we have investigated the effect of immiscible side chain pairs on the mesomorphism of discotic π-systems in a more systematic and general way. We prepared two types of discotic cores, PDI and NDI, two types of peripheral units, three-branched G0- and six-branched G1-type dendronized chains, and immiscible chain pairs, alkyl and TEG chains. After recognizing that the combination of PDI and G0 chains, PDI_{C12/C12-G0}, PDI_{C12/TEG-G0}, and PDI_{TEG/TEG-G0} all form columnar mesophases, we studied PDI_{G1} and NDI_{G0} systems having larger volumes of side chains to the cores. As a result, when the side chain volume becomes much larger, the derivatives having one type of (dodecyl or TEG) peripheral chains adopt micellar cubic, crystalline, or isotropic liquid phases. In sharp contrast, all three compounds having the immiscible side chain pair form rectangular columnar mesophases involving π-stacked arrays. The dominant reason of the observed preferential formation of columnar phases is the consequence of the exclusion of other phases, where a thermodynamically unfavorable contact between hydrophobic and hydrophilic chains considerably takes place. The molecular design strategy demonstrated here would extend the acceptable range of core/chain volume balance for columnar LC formation and would enable a variety of π-conjugated motifs to form columnar mesophases by side-chain directed assembly.

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**Notes and references**