

A Room-Temperature Liquid-Crystalline Phase with Crystalline π Stacks**

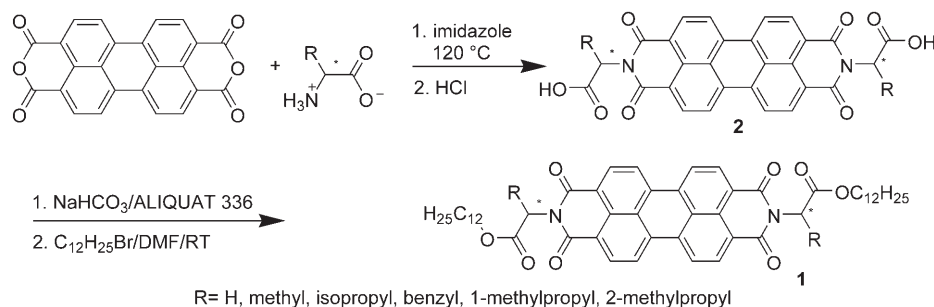
Yijin Xu, Siwei Leng, Chenming Xue, Runkun Sun, Jie Pan, Jason Ford, and Shi Jin*

Charge-transport liquid-crystalline (LC) materials have attracted considerable attention because of their potential applications in devices such as field-effect transistors, electroluminescent displays, and photovoltaic cells.^[1] By seamlessly combining molecular mobility with order, they offer excellent processability with respectable charge-carrier mobility. Liquid-crystalline materials with π stacks are particularly promising candidates, as charge migration along the stacking direction is accelerated as a result of significant orbital overlap between adjacent π systems. For example, discotic columnar LC (DCLC) materials exhibit mobilities as high as $0.46 \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ because of the presence of columnar π stacks.^[2] Charge transport along π stacks can be further improved if the stacks crystallize. For example, a sudden increase in charge-carrier mobility is always observed when a DCLC phase becomes ordered into a crystalline phase with a π stack.^[3] Therefore, a LC phase with crystalline π stacks would be ideal as it combines the maximal charge-carrier mobility of crystalline π stacks with the unique processability of LC materials. Here we report the molecular design, synthesis, and structural characterization of the first such LC material.

The intracolumnar order of a DCLC phase must be short-range since one-dimensional (1D) crystalline order does not exist.^[4] In contrast, quasi-long-range 2D intralayer crystalline order exists in thin films with highly ordered smectic LC phases such as the smectic B phase, although weak interlayer coupling converts the 2D order into genuine 3D crystalline order in thick films.^[5] If π -

stacking order is built in as a part of the 2D intralayer crystalline order, and measures are taken to decouple the interlayer correlation, a LC phase with crystalline π stacks could be generated. A series of perylene-3,4,9,10-tetracarboxylic diimides (PDIs) **1** has been synthesized to obtain such an LC phase. Their design was based on *N,N'*-di-*n*-alkyl PDIs, which are excellent n-type semiconductors that exhibit a high-temperature smectic LC phase with disordered π stacks.^[6] The *N,N'*-di-*n*-alkyl PDIs crystallize into a layered structure with alternating crystalline π stacks and crystalline alkyl chains at room temperature (RT).^[7] Substituents R of various sizes were introduced into **1** to eliminate crystallinity in the alkyl chain while retaining the crystalline π stacks, which is successfully achieved when R = methyl (**1a**).

Compound **1a** was prepared according to Scheme 1 (details of the synthesis can be found in the Supporting



Scheme 1. Synthesis of **1**. DMF = *N,N*-dimethylformamide.

Information). To avoid diastereomeric complications optically pure L-alanine was employed as a starting material to ensure that both chirality centers in **1a** possess the *S* configuration. The differential scanning calorimetry (DSC) traces of **1a** are illustrated in Figure 1 and the transition temperatures

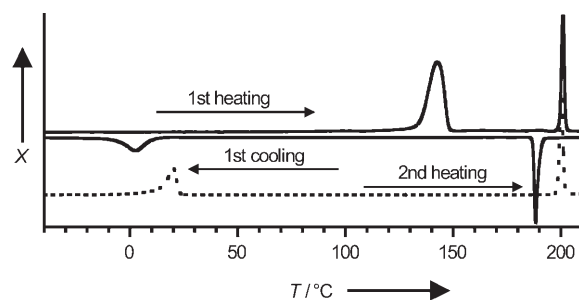


Figure 1. DSC traces of **1a** at a ramp rate of $10^\circ \text{C min}^{-1}$. X = heat flow, the arrow direction is endothermic.

[*] Dr. Y. Xu, S. Leng, C. Xue, R. Sun, J. Pan, J. Ford, Prof. S. Jin
Center for Engineered Polymeric Materials
Department of Chemistry
College of Staten Island and
Graduate Center of the City University of New York
Staten Island, NY 10314 (USA)
Fax: (+1) 718-982-3910
E-mail: jin@mail.csi.cuny.edu
Homepage: <http://163.28.8.169/jin.htm>

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and enthalpies are summarized in Table 1. The first heating trace is significantly different from the second heating scan, but no further changes were observed upon subsequent cooling and heating. There are two endothermic transitions in

Table 1: Phase transition temperatures (onset, °C) and enthalpies (kJ mol⁻¹).

Phase transitions of 1a					
1st heating	Cr	134.8 (62.4)	LC	199.6 (22.5)	Iso
1st cooling	Iso	190.7 (19.7)	LC	8.0 (14.4)	O ^[a]
2nd heating	O*	14.6 (19.0)	LC	198.7 (21.2)	Iso

[a] An unidentified ordered phase. Cr = crystalline phase, Iso = isotropic phase.

the first heating: The first corresponds to the melting of crystalline **1a** into the LC phase while the second suggests isotropization of **1a**, based on polarized light microscopy (PLM) observations. The original crystalline phase never reforms during subsequent scans, as evidenced by the absence of a corresponding melting peak, even with a ramp rate as low as 1 °C min⁻¹. Isothermal annealing at 100 °C for 12 h was employed to promote crystallization; however, no crystallization could be detected by DSC. Since the fusion of the more ordered phase formed by subambient cooling occurs at 14.6 °C, **1a** is in an LC phase at RT after the melting of the as-prepared crystalline form. This finding is confirmed by 1D wide-angle X-ray diffraction (WAXD) analysis (Figure 2).

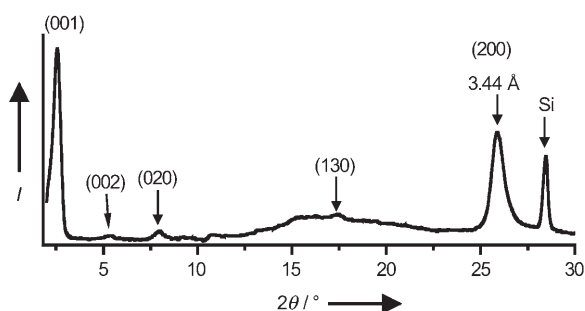


Figure 2. 1D WAXD pattern of **1a** in the RT LC form (The peak marked Si corresponds to the diffraction from crystalline silicon powders that were added as the calibration standard. Indexation was based on 2D patterns).

The pattern contains multiple sharp diffractions at both small and wide angles which testify to the ordered nature of the phase. However, the *n*-alkyl chains are in a disordered state, as indicated by the absence of sharp diffractions between 3.7 and 4.8 Å, and is supported by the CH₂ stretching region in the FTIR spectrum (Figure 3). It is known that the frequencies of asymmetric stretching $\nu_{as}(\text{CH}_2)$ and symmetric stretching $\nu_s(\text{CH}_2)$ of *n*-alkyl chains depend on their conformation.^[8] The $\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ values for an all-anti alkyl chain are typically in the ranges of 2846 to 2850 and 2916 to 2920 cm⁻¹, respectively. These ranges shift to 2854–2856 and 2924–2928 cm⁻¹ for liquid *n*-alkanes. The $\nu_{as}(\text{CH}_2)$ and $\nu_s(\text{CH}_2)$ frequencies of **1a** in the RT LC phase are 2923 and 2853 cm⁻¹. Given that these two modes appear at 2925 and 2854 cm⁻¹ for

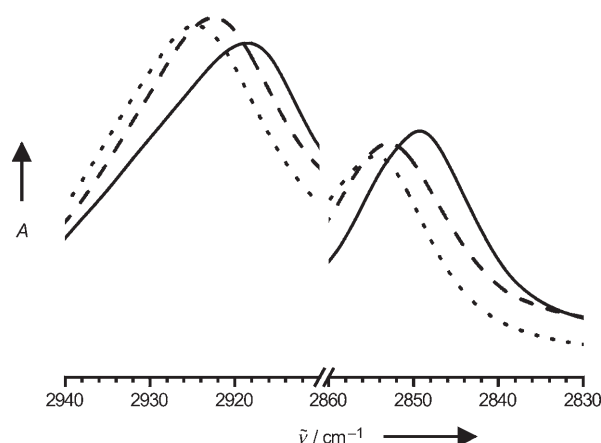


Figure 3. FTIR spectra of **1a** in the crystalline form (—) and LC form (---), as well as liquid dodecane (.....).

liquid *n*-dodecane and 2918 and 2849 cm⁻¹ for the **1a** crystalline phase, it is clear that the alkyl chains of **1a** are in a liquidlike conformation. The diffraction peak at 3.44 Å is indicative of π stacking of the PDI cores. The intrastack correlation length is 12 nm, which is equivalent to about 35 molecules of **1a**—as estimated from the peak width and using the Scherrer equation. This value is greater than the correlation lengths of π stacks found in other LC PDIs^[6,9] and typical highly ordered columnar LC phases such as LC hexabenzocoronene derivatives.^[10] The π stacking is confirmed by fluorescence spectroscopy (Figure 4). The wave-

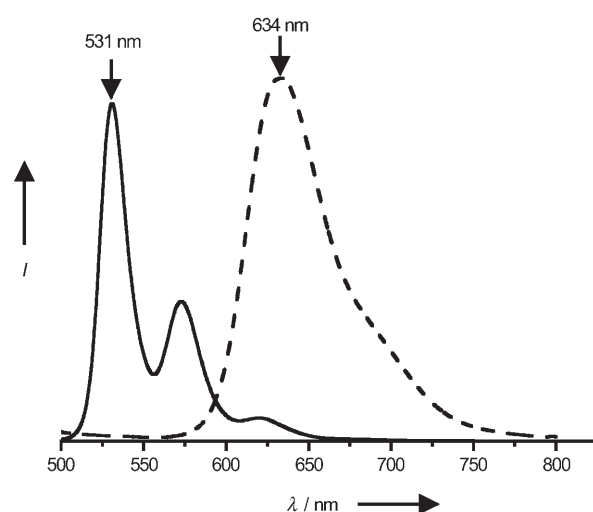


Figure 4. Fluorescence spectra of **1a**: in chloroform ($c = 10^{-6}$ M; —), LC form (---).

length of maximum absorption (λ_{max}) of **1a** in dilute solution is 531 nm, but red-shifts by more than 100 nm to 634 nm in the LC phase, thus indicating a strong π -stacking interaction.^[11]

To obtain more structural information on the LC phase, 2D WAXD analysis was performed on an oriented sample with monodomain characteristics generated by mechanical shearing at RT. The RT stability of the LC phase allows for X-rays to be directed along three orthogonal directions: through

direction (TD), edge direction (ED), and shear direction (SD, Figure 5). The TD, ED, and SD patterns approximately represent [001], [100], and [010] zones, respectively. A summary of the diffraction peaks and their indexation can

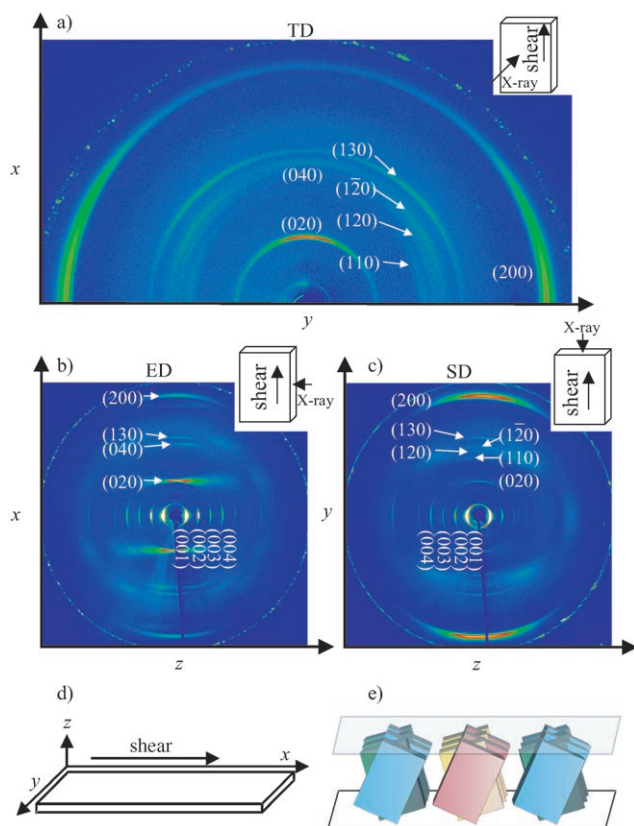


Figure 5. 2D WAXD patterns along TD (a), ED (b), and SD (c). The shear geometry (d) and the packing model (e) are also shown. Different colors in (e) represent crystallographically non-equivalent molecules.

be found in the Supporting Information. The TD pattern shows seven diffractions that can be indexed based on a 2D oblique lattice: $a = 6.88 \text{ \AA}$, $b = 22.0 \text{ \AA}$, $\gamma = 87.6^\circ$. The large number of $(hk0)$ diffractions, particularly those with h and $k \neq 0$, confirms the crystalline nature of the 2D lattice. A maximum of four orders of $(00l)$ diffractions were observed at the equator of the ED and SD patterns, thus indicating a long-range ordered layer structure with a periodicity of $d = 32.4 \text{ \AA}$. The layer normal c^* is along the TD. In the ED pattern, (020) and (040) diffractions can be observed 8° away from the meridian. Weak (200) and (130) diffractions with respective periodicities of 3.44 and $5.04 \text{ \AA}$ also appear because of the imperfect orientation. The SD pattern shows the intense (200) diffraction on the meridian. Weak (130) , $(1\bar{2}0)$, (120) , (110) , and (020) diffractions also appear as a result of a nonideal alignment.

These three diffraction patterns substantiate a putative molecular packing model as shown in Figure 5e. A long-range ordered layer structure forms along the TD as a consequence of microsegregation between the rigid PDI cores and the flexible alkyl chains. A 2D crystalline order exists within a

layer. The cell parameter a originates from the π stacking of PDI cores. The π stacks must be crystalline because π stacking is a part of the 2D crystalline order. Typical intrastacking spacing ranges from 3.4 to $3.6 \text{ \AA}$, thus it is reasonable to assume that two crystallographically non-equivalent molecules of **1a** are cofacially stacked along the a axis in the unit cell. The probable cause of this is a 40° rotation of the PDI core, with respect to the neighboring molecules in the same stack, around its plane normal. The direction of rotation alternates along the a axis. The possible causes of rotations may be concurrent steric and electrostatic interactions between adjacent molecules, as suggested by our molecular simulation results. The observed cell parameter b of $22.0 \text{ \AA}$ stems from the edge-edge organization of the PDI cores. Since the width of a PDI core is approximately $9.2 \text{ \AA}$,^[6] there must be two molecules of **1a** laterally packed along the b axis. α^* and β^* are estimated to be 98° and 90° , respectively, based on the ED and SD patterns.

It is clear that the RT LC phase is highly ordered in all three dimensions. However, since the alkyl chains themselves are disordered, there is no long-range interlayer correlation of the molecules and, as a result, 3D crystalline order does not exist. The absence of (hkl) diffractions with l and h or $k \neq 0$ confirms the LC nature of this phase. This finding, together with the fact that only diffuse scatterings can be found in the quadrants signifies the decoupling of the intralayer 2D crystalline order and the long-range lamellar order. The phase can be considered as a molecular composite consisting of alternating 2D crystalline PDI cores monolayers and liquidlike alkyl layers. As a result, the PDI core layers are able to slip along the layer plane under moderate shear stress, which is in accord with **1a** being oriented by mechanical shearing in the RT LC phase, with the layers parallel to the shearing direction.

Note that it is possible that the interlayer correlation of molecules existed in the as-prepared state but was lost in the mechanical shearing process by which the oriented sample was obtained. The fact that all the diffractions in the 1D WAXD pattern can be found in the 2D WAXD patterns suggests that shearing did not change the type of structure. To further clarify the relationship between the shearing and the interlayer molecular correlation, the oriented sample was annealed at 170°C for 0.5 h , and then 2D WAXD patterns were again acquired at RT with the X-rays aligned along the three orthogonal directions. The 2D patterns did not change significantly after annealing. No new diffractions appeared. This result suggests that the decoupling of the intralayer 2D lattice and the long-range ordered smectic order is intrinsic for the RT LC phase.

This phase is different from those already reported for LC PDIs, which are either columnar,^[9,12c,d] smectic,^[12a,b] or lamellar columnar phases.^[6] The phase is related to lamellar columnar phases^[6,13] and can be considered as a more ordered version of a biaxial smectic phase.^[14] It is best described as a highly ordered columnar smectic phase, which typifies its long-range lamellar order, with 2D-crystalline in-layer positional order including π stacking order.

In summary, we have designed and synthesized the first LC material with crystalline π stacks. The design principle

could also apply to other LC materials. Crystalline π stacks in this highly ordered columnar smectic phase should lead to substantially improved charge-carrier mobility than found in conventional LC materials. This property, in combination with the RT liquid crystallinity and inherent optoelectronic properties of the PDI core, makes **1a** a promising material for use in optoelectronic devices.

Experimental Section

Synthesis procedure of *N,N'*-di((S)-1-carboxylethyl)-3,4:9,10-perylene-tetracarboxyldiimide (**2a**, R = CH₃): L-alanine (1.9 g, 21 mmol), 3,4:9,10-perylene-tetracarboxyldianhydride (PTCDA; 3.92 g, 10 mmol), and imidazole (28 g) were placed into a 50-mL Schlenk flask. The mixture was purged with argon for 15 minutes before being heated at 120 °C for 30 minutes. The reaction mixture was then cooled to 90 °C and deionized water was added under argon. The dark red solution was filtered to remove the trace amount of PTCDA. The solution was then acidified with an aqueous 2 M solution of HCl to pH 3–4, the precipitate was collected by suction-filtration, and washed thoroughly with deionized water until the filtrate had a neutral pH value. The red solid was then collected and dried at 75 °C in a vacuum oven to constant weight. Yield: 5.15 g (96.4 %).

Synthesis procedure of *N,N'*-di((S)-2-dodecyloxy-1-methyl-2-oxoethyl)-3,4:9,10-perylene-tetracarboxyldiimide (**1a**): Compound **2a** (1 mmol) was dissolved in an aqueous solution of 5 % NaHCO₃ (10 mL). ALIQUAT 336 (0.9 g, ca. 2 mmol) was dissolved in a 2:1 (v/v) ethanol/water mixture (10 mL). The two solutions were mixed and stirred at room temperature for 30 minutes. The mixture was then extracted three times with petroleum ether (3 × 10 mL) and the combined petroleum ether solution evaporated to dryness. The residue was further dried at 75 °C for 2 h in a vacuum oven and then dissolved in DMF (10 mL). 1-Bromododecane (0.6 g, 2.4 mmol) was added and the mixture was stirred at room temperature for 12 h. The mixture was then poured into methanol (40 mL). The product was collected as an orange powder by suction-filtration and washed thoroughly with methanol. After drying the product at 75 °C in a vacuum oven to constant weight, it was purified by column chromatography on silica gel using 40:1 (v/v) CHCl₃/acetone as the eluent. Yield: 0.700 g (81 %).

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