Self-Organizing Liquid Crystal Perylene Diimide Thin Films: Spectroscopy, Crystallinity, and Molecular Orientation

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Three different liquid crystal (LC) perylene diimides were investigated with respect to the optical and physical characteristics of their thin films. Films were prepared by spin-coating, vacuum evaporation, and Langmuir–Blodgett (LB) techniques on substrates such as microscope glass, indium–tin oxide-coated glass and highly oriented pyrolytic graphite. Films were characterized by polarized optical microscopy, absorption and fluorescence emission spectroscopy, and X-ray diffraction. The self-organizing ability of the LC perylene diimides allows them to rapidly reach a stable, low-energy configuration, unlike many thin film materials, and reveals that they are driven to organize and orient in a highly specific fashion, independent of substrate or deposition method. The molecules tend to form a slipped stack arrangement that maximizes attractive π–π electronic interactions, with the π–π stacking axis oriented parallel to the substrate. Relative to the substrate plane, the LC **1** perylene cores are tilted ~47° along the stacking axis and ~58° perpendicular to this direction. The two other LCs have similar structures. An analysis of the intermolecular electronic and steric interactions, and of the interactions between the molecules and the substrates, is proposed to explain why this is such a strongly preferred orientation. The implications for the potential use of such molecules in electronic and photovoltaic applications is discussed.

Introduction

Perylene diimide derivatives are promising candidates for applications in molecular electronic devices and organic photovoltaic solar cells such as those reported in 1986 based on a perylene compound and a phthalocyanine (Pc).[1] Much attention has been focused on this kind of solar cell,[2] but the energy conversion efficiencies (η) are still rather low (ca. 1%). Attempts to improve the η value of the p–n junction include an increase of the exciton diffusion length and an improvement of the transport of charge carriers in the organic material. It has already been shown that increased ordering of perylene molecules leads to an increase in exciton diffusion length[3] and stabilizes the charge separated states, which slows down charge recombination.[4] In addition, increased ordering will also favor the transport of charge carriers in organic materials. Therefore, obtaining highly ordered perylene molecules on substrates is important, and liquid crystals possess the ability to self-organize spontaneously into highly ordered structures. For this purpose, a number of liquid crystalline (LC) perylene materials were reported recently and some of their physical or photophysical properties were studied.[2a,5a,6] However, a comprehensive understanding of the behavior of LC perylene materials on substrates, such as their morphology, spectroscopy, crystallinity, and molecular orientation, is still lacking. Understanding these factors is key to evaluating their potential use in photovoltaic cells and other electronic applications.

Thus, we have undertaken a multifaceted study of LC perylene thin films. The compounds studied are shown in Chart 1. We focus our attention on the role played by the preparation methods and conditions of the thin films on different solid substrates (microscope slide glass, indium–tin oxide (ITO)-coated glass, and highly oriented pyrolytic graphite (HOPG)) in determining their morphology and their spectroscopic and crystalline characteristics as well as their molecular orientation on the substrates. By using molecules that can self-organize, the irreproducibile factors often associated with film preparation methods are minimized, revealing that such perylene diimides are driven to organize in a highly specific fashion. We demonstrate here that (i) all LC perylene molecules **1**–**3** form highly ordered structures on the substrates by either spin-coating or vacuum deposition and (ii) changing the preparation methods or conditions, or using different substrates, does not significantly change the properties of the resulting thin films. Furthermore, we have determined the orientation of the molecules on the substrates and we discuss why this orientation is so strongly preferred and how it affects the utility of this class of molecules for fundamental studies and for electronic applications.

Experimental Section

Synthesis of LC3. The syntheses of compounds **1**, **2**, and **4** were previously reported.[3a,5a] The synthesis of LC3 described here is based on the previously developed procedures[5a] and is shown schematically in Scheme 1.
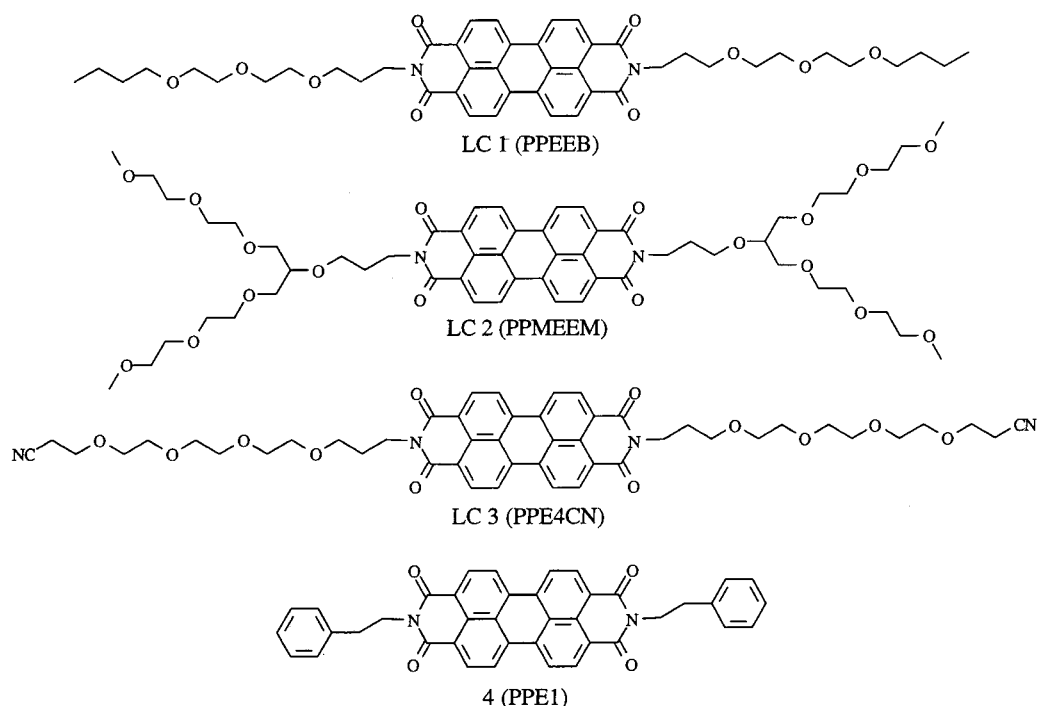
3-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]propanenitrile (HOE4CN). Sodium methoxide (100 mg) was added in one portion to a stirred reaction mixture composed of triethylene glycol (75 g, 0.50 mol) and acrylonitrile (26.5 g, 0.50 mol). The reaction mixture warmed spontaneously to approximately
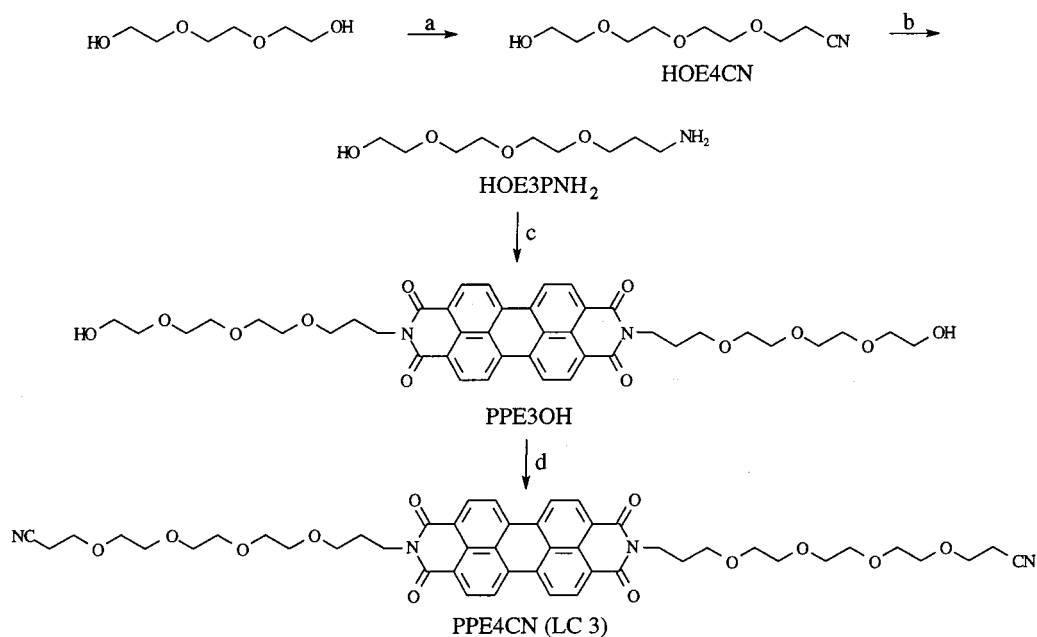
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CHART 1

LC 1 (PPEEB)

LC 2 (PPMEEM)

LC 3 (PPE4CN)

4 (PPE1)

SCHEME 1

HOE4CN

HOE3PNH$_2$

PPE3OH

PPE4CN (LC 3)

(a) CH$_2$=CHCN / NaOMe (catalytic), 25-60 °C
(b) H$_2$ / PtO$_2$ in EtOH / CHCl$_3$, 50 psi, 25 °C.
(c) PTCDA / pyridine, 125 °C.
(d) CH$_2$=CHCN / NaOMe (catalytic), pyridine, 60 °C.

60 °C within 20 min and then cooled to ambient temperature over a period of about 30 min. After stirring overnight (18 h) at room temperature, a 0.5 mL portion of acetic acid was added to the pale yellow mixture, and unreacted acrylonitrile was removed under reduced pressure. The crude product was diluted with methylene chloride and passed through a silica extraction column (methylene chloride eluent) to remove most of the yellow color and some insoluble solid. Failure to perform this latter procedure resulted in retro-cyanoethylation during the subsequent distillation. Distillation through a 10 cm Vigreux column afforded 22.05 g of forerun (bp < 165/0.7 Torr (93 Pa)) consisting of mostly triethylene glycol and 48.80 g of impure product as a colorless oil (bp 167−171/0.7 Torr). A second distillation yielded a small forerun (bp < 150/0.4 Torr) and 36.56 g (36% yield) of pure product (bp < 153−155/0.4 Torr). ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.47 (br t, J = 6.3 Hz, 1 H, OH), 2.64 (t, J = 6.7 Hz, 2 H, CH_2CN), 3.61−3.75 (m with br s at δ 3.68, 14 H, CH_2O).

3-[2-[2-(2-Hydroxyethoxy)ethoxy]ethoxy]-1-propanamine (HOE3PNH₂). The previously described general procedure for hydrogenation of cyanoethylation products[5a] afforded a 72% yield of pure amine from HOE4CN. ^{1}H NMR (300 MHz, CDCl₃): δ 1.73 (quintet, $J = 6.0$ Hz, 2 H, OCH₂CH_2CH₂N), 2.56 (br s, 3 H, NH_2, OH), 2.85 (t, $J = 6.0$ Hz, 2 H, OCH₂-CH₂CH_2N), 3.57−3.73 (m with br s at δ 3.65, 14 H, CH_2O).

N,N′-Bis[3-[2-[2-(2-hydroxyethoxy)ethoxy]ethoxy]propyl]-perylene-3,4:9,10-tetracarboxyldiimide (PPE3OH). Following the previously described general procedure for preparing perylene diimides,[5a] this compound was obtained in 89% yield as a dark red solid, which melted at 258−261 °C after recrystallization from methanol. ^{1}H NMR (300 MHz, CDCl₃): δ 2.08 (quintet, $J = 6.6$ Hz, 4 H, OCH₂CH_2CH₂N), 2.66 (br s, 2 H, OH), 3.59−3.75 (m with br s at δ 3.64 and 3.65, 28 H, CH_2O), 4.32 (br t, $J = 7.2$ Hz, 4 H, OCH₂CH₂CH_2N), 8.52 (d, $J = 7.9$ Hz, 4 H, Ar-H), 8.62 (d, $J = 7.9$ Hz, 4 H, Ar-H).

N,N′-Bis[3-[2-[2-[2-(2-cyanoethoxy)ethoxy]ethoxy]ethoxy]-propyl]perylene-3,4:9,10-tetracarboxyldiimide (PPE4CN, LC 3). Into a 50 mL pressure tube (Ace Glass #8648) equipped with a magnetic stirring bar were placed PPE3OH (0.77 g, 1 mmol), acrylonitrile (1 mL, 0.81 g, 15 mmol), pyridine (5 mL) and sodium methoxide (50 mg). The sealed reaction mixture was heated with stirring in an oil bath at approximately 60 °C. After 20 h, the resulting deep red mixture was cooled, and a 0.4 mL portion of acetic acid was added. Pyridine and excess acrylonitrile were removed under reduced pressure. The crude product was chromatographed on a silica extraction column (2−5% methanol in methylene chloride eluent) to yield 0.67 g of crude product. Recrystallization from 95% ethanol yielded 0.52 g (59%) of purified product as a brown-red, waxy solid, mp 223−225 °C. ^{1}H NMR (300 MHz, CDCl₃): δ 2.08 (quintet, $J = 6.6$ Hz, 4 H, OCH₂CH_2CH₂N), 2.63 (t, $J = 6.4$ Hz, 4 H, CH_2CN), 3.62−3.75 (m, 32 H, CH_2O), 4.32 (br t, $J = 7.2$ Hz, 4 H, OCH₂-CH₂CH_2N), 8.57 (d, $J = 8.1$ Hz, 4 H, Ar-H), 8.22 (d, $J = 8.1$ Hz, 4 H, Ar-H).

Film Preparation. Films were prepared either by spin-coating (2000 rpm) from a CHCl₃ solution or a THF solution of the compounds (15−30 mg/mL) onto different solid substrates or by vacuum deposition at $(2−5) \times 10^{-6}$ Torr $((3−7) \times 10^{-4}$ Pa) at an average rate of 3−4 Å/s. The substrates used in this study were glass microscope slides (Fisher), indium−tin oxide (ITO)-coated glass (Delta Technologies), and freshly cleaved highly oriented pyrolytic graphite (HOPG). Before preparation of the films, the glass or ITO-coated glass was cleaned according to normal procedures and dried under a nitrogen flow.

Fabrication of Langmuir and LB films of LC perylene compounds **1**−**3** was carried out on a KSV-2000 (KSV, Finland) minitrough. Each compound was spread onto a water subphase (Continental Water System Corp., San Antonio, TX) from a chloroform solution. The purified water had a resistivity of 18 MΩ cm and a surface tension of 72.6 mN/m at 20.0 ± 0.5 °C. The concentrations employed were 1.290×10^{-3}, 1.010×10^{-3}, and 1.186×10^{-3} M for LC perylene compounds **1**−**3**, respectively. After the solvent had been allowed to evaporate completely, the floating layer at the air−water interface was compressed at a speed of 20 Å² molecule^{-1} min^{-1} to obtain the surface pressure−area isotherm. Monolayers of **1** and **3** could be transferred onto quartz or microscope slide glass substrates at a surface pressure of 12 mN/m. The upstroke speeds used for this Z-type model deposition were approximately 15 mm/min. The best transfer ratio of near unity was obtained by adjusting the upstroke speeds. However, in the case of **2**, it was very difficult to transfer the monolayer onto substrates by either Z- or Y-type deposition.

Instrumentation. The phase and crystallinity of the film materials were determined using a 4-circle Scintag X-ray diffractometer with a Cu Kα source operated at 45.0 kV and 40.0 mA at a scan speed of 2°/min. Micrography was performed with a Nikon Labophot 2 polarizing microscope. Absorption and fluorescence spectra were measured with a HP 8543 Spectrometer and a SLM AMINCO AB2 Luminescence Spectrometer, respectively.

Results and Discussion

Materials, Thin Film Preparation, and Morphology. Chart 1 presents the structures of LC perylene diimides **1**−**3** and a related non-LC perylene compound **4**. The solid to LC phase transition temperature for **1** is 67 °C,[5a] for **2** is −37 °C,[5a,6] and for **3** is 80 °C. Thus, only **2** is a liquid crystal at room temperature. The phase behavior and film-forming properties of **1** and **2** have been described.[5a,6] The LC compounds were spin-coated onto different substrates from CHCl₃ or THF solutions forming solid films with thickness of 70−140 nm. For comparison, thin films of compounds **1** and **4** were also prepared by vacuum deposition with similar thickness.

We first investigated the effects of the two different solvents (CHCl₃ and THF) on the spin-coated thin films of LCs **1**−**3** as observed in an optical microscope between crossed polarizers. In the case of **2**, there were no significant differences in the morphology upon spin-coating from either THF or CHCl₃ solution. The films initially consisted of 5−20 μm (liquid) crystalline regions.[6] However, in the case of **1**, if the film was spin-coated from CHCl₃ solution, it appeared amorphous, in agreement with the XRD analysis discussed below. But, if the film was spin-coated from THF solution, it was as highly crystalline as those made from **2**. It is possible that aggregates exist in the THF solutions of **1**. Due to the low solubility of **3** in THF ($<10^{-4}$ M), only results for thin films of **3** prepared from CHCl₃ solution are discussed below. However, there was no significant difference in spectroscopy between thin films spin-coated from either CHCl₃ or THF solution for **3**. Eventually, all the films spontaneously transform under ambient conditions into a more ordered phase with longer wavelength absorption. We usually refer to these phases by their color: **1** and **2** change spontaneously from red to black,[5a,6] and **3** changes from brown to green.

Since the morphology of the films made from **1** is dependent, to some extent, on the preparation conditions, we also investigated the effects of vacuum deposition on the morphology of the films of **1**. As evidenced by optical micrography and XRD analysis (see below), the vacuum-deposited films were similar to the spin-coated films from THF solution, being highly crystalline. So, the different initial morphology for the CHCl₃ solution spin-coated films of **1** may result from the greater solvating effect of CHCl₃.

Solution and Thin Film Spectroscopy. The absorption and fluorescence emission spectra of LC perylene diimide **1** in CHCl₃ are shown in Figure 1. LC derivatives **2** and **3** (**4** is insoluble) showed the same absorption and emission spectra as **1** in CHCl₃ solution: three well-resolved, relatively narrow absorption peaks at 458, 489, and 526 nm are matched by the corresponding emission peaks at 540, 576, and 624 nm, respectively. The almost mirror image relationship of the emission and absorption spectra is obvious, but the relative intensity of the emission peaks is slightly different from that of the absorption peaks. Changing the solvent from CHCl₃ to THF
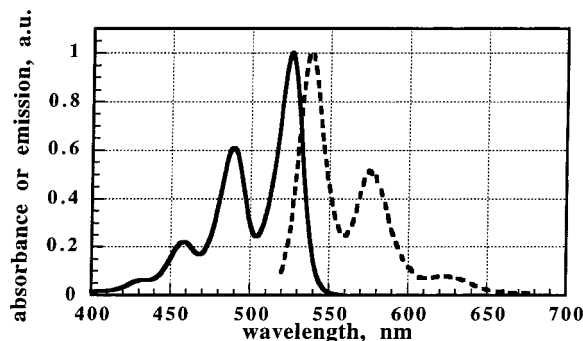
Figure 1. Absorption (solid curve) and corrected fluorescence emission (dashed) spectra of **1** in CHCl$_3$, [**1**] $\approx 1.7 \times 10^{-5}$ M for absorption and $\approx 1.0 \times 10^{-5}$ M for emission spectra measurements. Emission was recorded at an excitation wavelength of 489 nm.

causes a blue shift of about 4−6 nm for all peaks in both absorption and emission spectra for **1-3**.

The color in dilute solution is mainly determined by the electronic properties of the individual molecules. However, in the solid state, perylene derivatives can form several polymorphs or phases having different colors due to the significant intermolecular electronic interactions of the close-packed molecules. Thus, the color is an indication of different crystal packing of the molecules in the solid state.[7] Coupled with theory,[4] electronic spectroscopy can provide useful information about the structure of the thin films of perylene derivatives. We previously described two different phases (red and black) for both **1** and **2** in spin-coated thin films from THF solution.[5a,6] As-prepared **3** films were initially brown and eventually turned into a green phase. The absorption and emission spectra of thin films of **1−3** are shown in Figure 2. The brown phase of **3** is spectroscopically similar to the red phases of **1** and **2** and the green phase of **3** is similar to the black phases of **1** and **2**.[5a,6] The differences between the spectra of the three compounds reflect slight differences in the molecular packing or orientation, in agreement with the XRD analysis (see below). It is noteworthy that **3**, which is a more highly polar compound than **1** and **2**, has the most red-shifted absorption and emission spectra. This may indicate an increased intermolecular charge-transfer character in the excited state,[4] stabilized by the higher dielectric constant.

The spontaneous improvement (red shift) in the absorption spectra of LC **1−3** thin films indicates that the black/green phase is more thermodynamically stable than the originally formed red/brown phase. The as-prepared films of **1−3**, both spin-coated and vacuum-deposited, turn black (**1** and **2**) or green (**3**) in times varying from hours (**1**) to a few days (**2**) to a week or so (**3**).

XRD Analysis. The XRD patterns of the red and black phases of **1** are shown in Figure 3. The films were spin-coated from a CHCl$_3$ solution on ITO-coated glass. The red phase shows only one diffraction peak at $2\theta = 3.18°$ (corresponding to 27.76 Å). The black phase shows a comparatively strong and narrow peak at $2\theta = 3.91°$ (22.55 Å) along with 5 weaker higher order diffraction peaks corresponding to $22.55/n$ Å where $n = 2, 3, 4, 5$ and 7. The existence of only a single diffraction peak with its higher order diffractions indicates the films are highly ordered in a layered structure with the layer planes running parallel to the substrate. The XRD results are consistent with the black phase being highly ordered and the red phase, where the single peak is very weak and broad, being quite disordered. These results are in agreement with the optical measurements discussed above.

The initial phase of **3** (Figure 4a) shows a major diffraction peak at $2\theta = 3.09°$ (28.57 Å), near the peak for **1** in the red
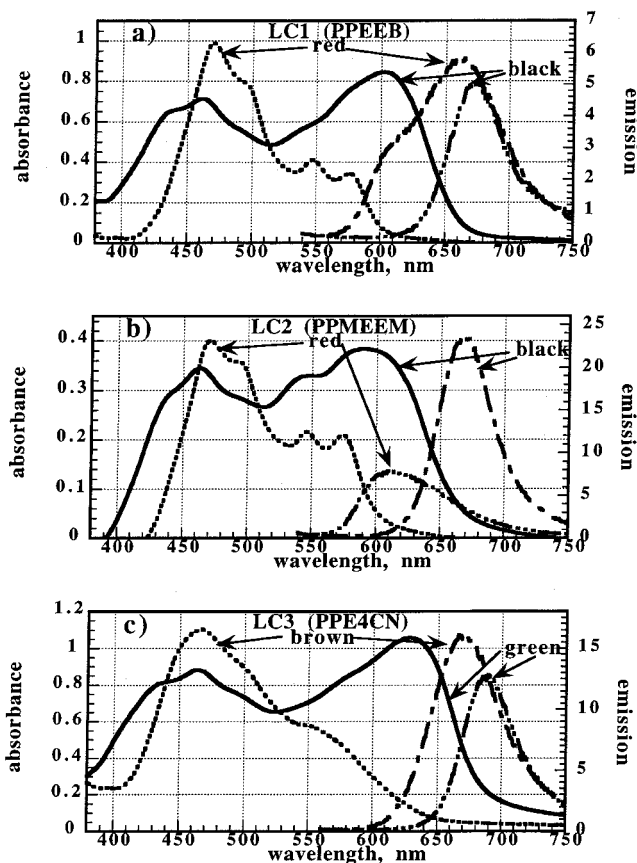

Figure 2. Absorption and fluorescence emission spectra of thin films of **1** (a), **2** (b), and **3** (c). The films were spin-coated on microscope slides from CHCl$_3$ solution. For the emission spectra, excitation was at the isosbestic point.
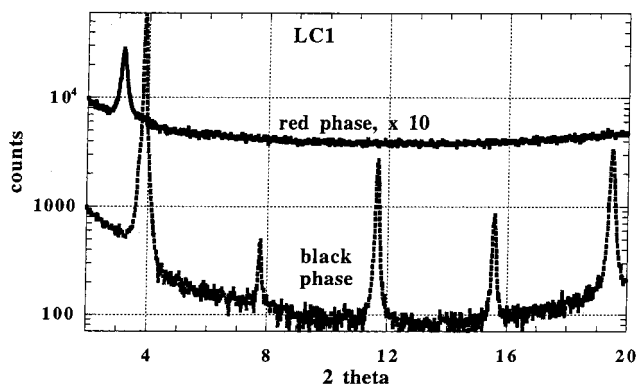

Figure 3. XRD patterns of thin films of **1** in the red and black phases. The traces are offset for clarity.

phase, but it also shows a second-order peak at 6.17°. In contrast to these two, the red phase of **2** shows five diffraction peaks starting at $2\theta = 3.03°$ (29.13 Å) and continuing up to the fifth harmonic at $2\theta = 15.12°$. Thus, in the initial phase, **2** seems to be the most regularly ordered of the three materials, possibly because it is a LC at room temperature,[6] which allows it to self-organize more rapidly than the other two materials. In the thermodynamically stable phases (Figure 4b), the first peak of all three compounds is shifted toward a greater angle (smaller layer spacing) and multiple, higher order reflections are seen. Both **1** and **3** show a single harmonic series of higher order reflections, but **2** has two series. The diffraction intensity of the brown or green phase of **3** was substantially less than that of the corresponding red or black phase of **1** and **2**. We also investigated the XRD patterns of **1−3** films prepared by
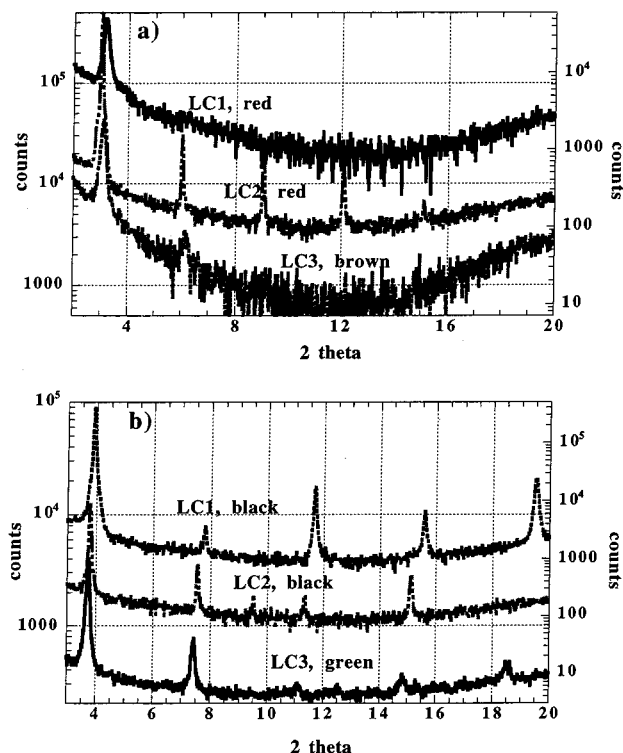
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Figure 4. XRD patterns of thin films of **1**−**3** spin-coated onto microscope slides from CHCl₃ solution. (a) Initial phases: red (**1** and **2**) and brown (**3**). (b) Final, thermodynamically stable phases: black (**1** and **2**) and green (**3**). The traces are offset for clarity.

Figure 5. XRD patterns of a film of perylene **4** in the black phase after 10 h CH₂Cl₂ vapor annealing (top trace), black powder (middle) and the theoretical X-ray diffractions generated by CrystalDiffract[14] (lower) for black powders of perylene **4**. The traces are offset for clarity.

Figure 6. Surface pressure−area isotherms of the three LC perylene diimides at 20 ± 0.5 °C.

different methods (spin-coating and vacuum deposition) or prepared under similar conditions on different substrates (microscope slide glass, ITO, and HOPG). We observe (i) both the diffraction position and peak shape are independent of the preparation methods and solvents, (ii) for all the spin-coated films, **1** showed much higher diffraction intensity if spin-coated from THF solution than from CHCl₃ solution, but **2** and **3** did not show a significant solvent effect, and (iii) the diffraction intensity of the spin-coated film of **1** from THF is similar to that of the vacuum deposited film. Finally, the most unexpected observation was that the film structure was independent of the substrate. We obtained identical diffraction results on glass, ITO and freshly cleaved HOPG, even though the latter surface is very different from the first two, consisting of an almost perfectly uniform and planar sheet of graphite. Apparently, *the intermolecular forces control the orientation and crystallinity of the film, while the film−substrate interactions are comparatively weak.*

Thin films of a non-LC perylene derivative PPEI, **4**, have been studied for the past few years regarding the morphology, crystalline phases and spectroscopic properties.[3,8−12] It is known that PPEI can form several different polymorphs in thin solid films. They can be produced by changing film evaporation conditions[9] or by solvent vapor annealing of an evaporated film in order to induce crystallization.[3,10] Both the spectroscopy and the photocharge generation efficiency of PPEI thin films depend on the crystalline phase of the films.[3a,11] A single-crystal structure of the black phase of PPEI has been solved;[5b] thus we compared the XRD patterns of PPEI films to those of the LC perylene diimide films in order to get more structural information for the LCs. The evolution of the absorption spectra of PPEI films during solvent vapor annealing to form a highly crystalline black phase has been reported.[3a] This phase is spectrally indistinguishable from the black phase of **1**. The
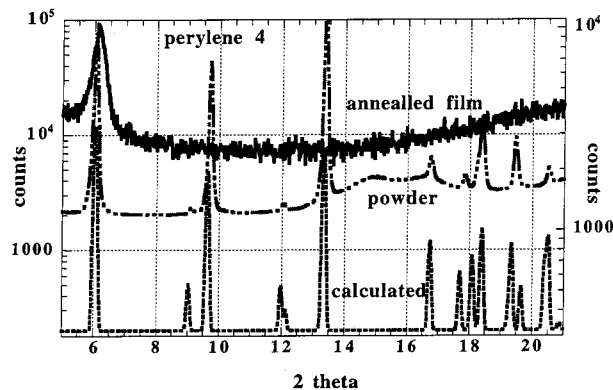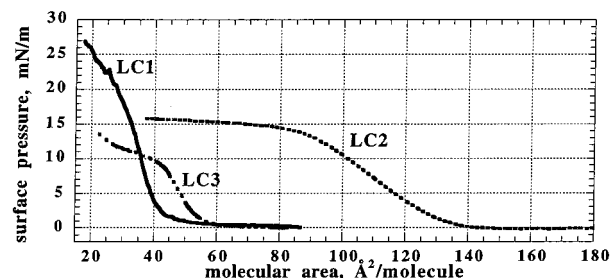
emission spectrum of PPEI does not change significantly during annealing but the emission intensity increases by ∼10× over 10 h. To get a clear picture of the orientation of PPEI molecules in the black phase, we performed an XRD analysis for both the black films and black powder,[13] shown in Figure 5.

Using CrystalDiffract[14] and the published structural data for a black PPEI (**4**) crystal,[5b] we generated the theoretical XRD pattern for PPEI black powder (lower line in Figure 5). The experimental XRD pattern for the black powder is in good agreement with the theoretical one. The black film annealed under CH₂Cl₂ for 10 h shows only one diffraction peak at 2θ = 6.14° originating from the (002) direction by comparison to the black powder. The black film, which was only annealed under CH₂Cl₂ for 0.5 h (not shown), exhibited the same XRD pattern (one peak at around 2θ=6.14°), but the intensity is about 130 times lower than for the film with a longer annealing time. This indicates a much better crystallinity with longer annealing time, as expected. However, the films are still relatively disordered compared to the LC perylenes in the black (green) phase. Knowing the crystal structure of PPEI allowed us to calculate its molecular orientation in the film: the long axis of the PPEI molecules is tilted at ∼47° from the substrate plane. The tilted end-on, or edge-on orientation of molecules on substrates is a common structural motif in organic semiconductor thin films.[15]

Langmuir Blodgett Films of LC Perylenes. As a result of having two somewhat hydrophilic polyoxyethylene-like chains attached to the perylene diimide core, **1**−**3** are suitable for fabrication of ultrathin films by the LB technique. Figure 6 shows the surface pressure−area isotherms of **1**−**3**. For each case, a steeply inclining trace shows the formation of a solid monolayer at the air−water interface. The surface pressure of the collapse point of the monolayer of **1** is higher than that of **2**, showing the better film forming ability of **1**. A detailed surface
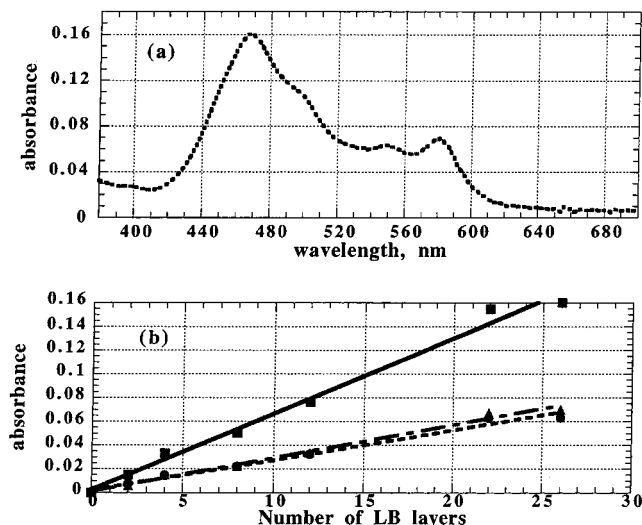
Figure 7. (a) Absorption spectrum of an as-prepared 26-layer LB film of **1**. (b) Relationships between the absorbance and the number of LB layers: (■) at 470 nm; (●) at 548 nm;(▲) at 582 nm. The lines show the best linear fits.

chemistry study of **1**-**3** will be published elsewhere, especially for **1** and **3**. We focus our attention on the molecular orientation of **1** and **2** at the air−water interface and on solid substrates.

The Langmuir films of **2** were very difficult or even impossible to transfer to solid substrates, though we tried different conditions and techniques. In contrast, Langmuir films of **1** were capable of being transferred and deposited onto quartz, mica, or glass substrates. The transfer ratio was around 0.8− 1.0 by adjusting the upstroke speeds. UV−vis absorbance measurements were used to assess the transfer behavior to solid substrates of the floating Langmuir films at the air−water interface. Figure 7a shows the absorption spectrum of an as-prepared 26-layer LB film of **1**. It is very similar to that of as-prepared spin-coated or vacuum deposited films of **1** (see Figure 2a). This suggests that the molecular packing and orientation in both the LB film and the spin-coated or vacuum deposited films are similar. The spectrum consists of three absorption bands in the visible region at 470, 548, and 582 nm, respectively. The absorbance values at these peaks are plotted in Figure 7b, showing the linear relationships between the absorbance and the number of transferred layers. This indicates that each monolayer contributes, on average, an equal amount to the absorbance, meaning the monolayers were reproducibly and uniformly transferred onto the substrate.

Structure and Orientation of PPEEB Thin Films. The best way to obtain the molecular structure and orientation in the thin films of the LC perylene compounds would be to solve the single-crystal structure and compare its powder pattern to the XRD of the film, as we did for the film of **4**. However, it is very difficult to prepare single crystals suitable for XRD analysis of LC compounds in general, and we have not been able to grow such crystals of **1**−**3**. But with the XRD, LB and optical studies, along with knowledge of the π−π stacking motif that results in the black phase in other perylene diimides,[4,7] we can determine the structure of these films within certain limits. The exact tilt angles of molecules in the films cannot be uniquely determined, nor can we determine the relative orientation of perylenes in neighboring stacks (which determines the number of molecules in a unit cell[7]). Nevertheless, our studies reveal a clear picture of the film structure as well as some general rules for packing these types of molecules on surfaces.
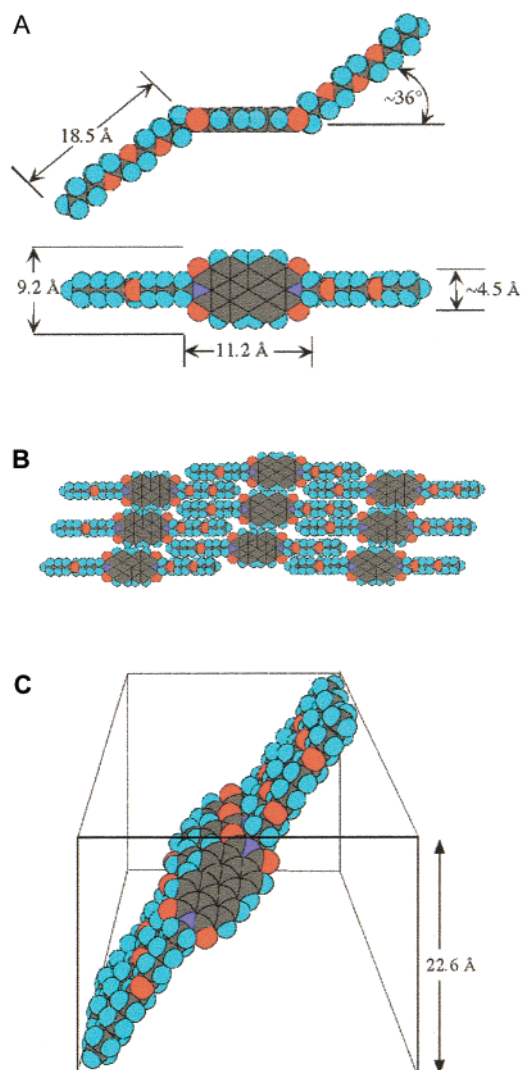

Figure 8. (a) Space-filling model of LC **1** and its relevant dimensions and angles. (b) Model showing the interdigitation of the side chains. (c) Three molecules of **1** in a π−π stack shown schematically (this is not a unit cell); the top and bottom surfaces of the cube shown enclosing the molecules are parallel to the substrate plane.

The shape and relevant molecular dimensions of **1** are shown in Figure 8a. These results come from a calculated structure of **1** optimized with the MM2 force field using the Chem3D program (CambridgeSoft Corp.) and are similar to those obtained by other groups investigating perylene diimides.[2a,7] Salient features of the molecular structure are (1) the ∼36° angle between the side chain and the plane of the perylene core that is enforced by steric crowding at the imide nitrogen position, (2) the extended, all-anti orientation of the atoms in the side chain, which is the energetically most favorable conformation and which is also the conformation observed in the known crystal structures of perylene diimides with (shorter) alkyl or alkyl ether side chains,[7] and (3) the width of the side chain (∼4.5 Å) being almost exactly half the width of the perylene core (9.2 Å), suggesting that, if at all possible, the side chains of one perylene diimide column will interdigitate with those of a neighboring column in order to fill space most efficiently. Such interdigitation was recently confirmed by Sudhölter et al. in LC perylene diimides with long alkyl side chains.[2a]

The crystal structures of a number of perylene diimides are known, and a great deal is understood about the relationship between the color of the crystal and the geometry of the

LC Perylene Diimide Thin Films

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perylene−perylene interactions.[4,5b,7,16] These studies show a strong tendency of perylene diimides to stack in a manner that minimizes steric repulsion while maximizing the in-phase overlap between the π orbitals of adjacent molecules, resulting in an intermolecular charge-transfer absorption band around 600−630 nm.[4] This produces a black, or green, crystal phase, like those shown in Figure 2. The π−π stacking structure that leads to this phase in a number of compounds is well-defined: (i) the perylene diimide core is offset longitudinally, in a slipped stack arrangement, from its two neighbors in the stack by ∼3.1 Å; (ii) it is offset laterally by ∼0.8 Å; (iii) the π−π stacking distance is ∼3.4 Å. The strong intermolecular electronic interactions, and therefore the color of the crystals, is determined by the π−π stacking of the molecules in a single column; the intercolumnar interactions play no appreciable role.[7] The orientations of perylene diimides in adjacent columns may be identical (one molecule per unit cell) or different (two or four molecules per unit cell), but this does not affect the optical properties.[7] (The splitting of the monomer absorption into a high and a low energy band in the solid is thus not a consequence of having two molecules per unit cell, in contrast to the prediction of simple exciton theory.[17]) If perylene diimides for steric or kinetic reasons cannot achieve the optimal π−π stacking arrangement, they exist in a red to reddish brown phase with weaker intermolecular interactions.[4,7]

Taking into account these known perylene−perylene interactions, our data lead to a clear understanding of the orientation of the LC perylenes on surfaces. We first consider the results from the LB films. From the surface pressure−area isotherms (Figure 6), the limiting molecular area can be estimated: for **1**, it is about 44 Å² and for **2**, it is around 137 Å². These values and the known dimensions of the compounds (Figure 8a) allow us to estimate the configuration of the molecules at the air−water interface, as has been done with LB films of phthalocyanines.[18,19] The area of the perylene diimide core, looking straight down on the π-system, is about 103 Å² (11.2 Å x 9.2 Å). If the molecule were lying flat on the water surface, it would take up at least this much area, and probably more because the first part of the side chains must extend away from the core. This consideration shows that **1** cannot be lying flat on the water surface, while **2** probably is. This is reasonable since the side chains of **2** are much more hydrophilic than those of **1** (in fact, **2** is slightly water soluble). Thus, the interaction energy of the side chains with water in an LC **2** monolayer is enough to overcome the stabilizing electronic interactions that occur when the perylene diimide cores form π−π stacks. In **1**, however, the side chains are less water soluble and the π−π stacking energy apparently prevails, leading to an end-on orientation of the molecule to the water with only one of the side chains in the water. If the molecules were oriented perpendicularly to the water surface, the effective molecular area would be ∼31 Å² (9.2 Å x 3.4 Å) Since the observed area is 44 Å², the molecules are probably tilted relative to the surface, similar to the phthalocyanines,[18,19] and as expected for perylene diimide π−π stacks (see below).

The strong tendency of perylene diimides to form π−π stacks with a ∼3.1 Å longitudinal offset between the cores forces the side chains to be displaced on opposite sides of the perylene core, one "up" and one "down", as shown in Figure 8a. If both are on the same side of the core, as apparently occurs in the LB films of **2**, this prevents close approach of neighboring perylenes in a π−π bonding orientation. This may explain why multilayer films of **2** cannot be transferred from the LB trough to a solid substrate: the molecules are not in the correct

orientation for attractive π−π interactions between the perylenes in multilayer films. But LB films of **1** are already in an orientation where they interact strongly with neighboring molecules; thus, they readily form multilayer stacks when transferred to solid substrates. These considerations, and those discussed below, show that the attractive π−π interactions can force specific orientations of the molecules relative to the substrate.

To review the XRD results of **1:** in the black phase it organizes into a highly ordered, layered structure on all substrates tested (glass, ITO and HOPG). The uniform progression of six peaks at spacings corresponding to 22.55 Å times $1/n$ where $n = 1−5$ and 7, and the absence of any other peaks, demonstrate that the films are almost perfectly ordered in the direction perpendicular to the plane of the substrate. This ordering is independent of substrate and method of deposition, showing that molecules of **1** have the conformational mobility necessary to achieve an energetic minimum, and that the intermolecular forces are stronger than the interfacial forces.

Optical microscopy between crossed polarizers shows that the films are polycrystalline in the plane of the substrate and that the crystallites are highly birefringent. The optical axis of each crystallite appears to be randomly oriented relative to that of other crystallites. To be consistent with the XRD results (in which the measured spot size encompasses many crystallites), the differences between crystallites observed optically must occur only in the plane of the substrate, not perpendicular to it. Consistent with the measured orientation of compound **4** on substrates, these results suggest that the molecules of **1** are oriented in layers with the perylene cores tilted relative to the substrate plane, and that the direction of the tilt, but not the tilt angle (which would change the layer spacing), varies randomly between crystallites.

The LB results show that films of **1** closely resembling the spin-coated or vacuum-evaporated films can be deposited monolayer by monolayer on glass substrates, reinforcing the conclusion that the molecules are arranged in layers parallel to the substrate. The pressure versus area curves show that the aromatic cores of the molecules in each monolayer are tilted: they cannot be either perpendicular or parallel to the substrate. Again, this is consistent with both XRD and optical microscopy results.

From the density (1.27 g/cm³) and the molecular weight (795), we calculate a volume per molecule of **1** in the black phase of 1040 Å³. Using molecular models, the volume of an isolated molecule is ∼920 Å³. So the packing fraction in the solid film is quite high, about 88%, requiring that the side chains of adjacent layers be interdigitated (or folded, which is much less likely),[2a,7] as shown in Figure 8b. This is supported by the geometric considerations discussed earlier.

Given these results, along with the molecular dimensions shown in Figure 8a and basic physical principles, it is possible to calculate the approximate structure of the LC **1** film in the black phase. The black phase requires a longitudinal offset of ∼3.1 Å and a transverse offset of ∼0.8 Å; together with a molecular thickness of 3.4 Å, this results in a tilt of the perylene core relative to the π−π stacking axis of ∼47°. The XRD and LB results show that the repeating molecular planes, and therefore the π−π stacking axis, are parallel to the substrate. Taking just this tilt angle into account together with the other distances and angles shown in Figure 8a, and assuming fully interdigitated side chains results in a calculated repeat distance perpendicular to the substrate of 26.6 Å. The experimentally determined distance is 22.6 Å, meaning that the perylene

molecules must also be tilted along the only other available degree of freedom: that is, they are also tilted along a direction perpendicular to the $\pi-\pi$ stacks. Therefore, none of the angles in the unit cell can be 90° and the unit cell must be triclinic, as expected from the XRD powder pattern (not shown). To account for the known repeat distance of 22.6 Å, a minimum tilt angle in this direction of 58° from the substrate plane is required. If the interdigitation is less than maximal (though it cannot be much less, given the density of the phase), the tilt angle in this direction will be <58°. The results of these considerations are shown in Figure 8c where a $\pi-\pi$ stack of perylene diimides, appropriately offset longitudinally and laterally, is shown on a solid substrate. Although our data cannot provide information about the relative orientation between perylene cores in neighboring stacks (and therefore, about the number of molecules in a unit cell), we know that this uncertainty is confined to the intralayer regime; the thickness of the layers, and therefore the approximate tilt angles of the molecules, are fixed.

LC **3** has a chemical structure very similar to **1**, and its optical and XRD patterns are also very similar. This suggests that its film structure and molecular orientation resemble those of **1**. The molecular shape of **2** is somewhat different due to the branched side chains, and its XRD patterns are also slightly different from the other two. Nevertheless, the similarities are substantial and it most likely has a structure closely related to the other two.

The conductivity in molecular semiconductors is highly anisotropic,[15,20] and it becomes much more so when insulating side chains are included in the molecular structure.[15b] The $\pi-\pi$ stacking axis is usually the axis of highest electrical conductivity,[15,20] so the conductivity in the LC perylene diimide films is expected to be maximal parallel to the substrate and orders of magnitude smaller in the direction perpendicular to the substrate. It would be important for some applications to be able to align the highly conducting axis perpendicular to the substrate. Thus, we consider why the orientation of LC **1** molecules shown in Figure 8c is so rigorously maintained that it occurs on substrates so chemically and physically different as highly polar glass and very low-polarity, almost perfectly planar HOPG. One reason, of course, is that as the film gets thicker, the ratio of molecules involved in surface interactions relative to those involved in purely intermolecular interactions decreases, so the role of intermolecular interactions dominates above a certain thickness. But also, as discussed earlier, the longitudinal offset between perylene rings in the black phase requires the LC side chains to be on opposite sides of the perylene core (see the "side-on" view of **1** in Figure 8a). The only way this molecular shape can fill most space while conforming to a planar surface is to align end-on or edge-on to the surface; if it were to align with the perylene plane parallel to the surface, it would inevitably leave empty space between it and the surface: an energetically unfavorable situation. Therefore, these types of molecules probably cannot align with their highest conductivity axis perpendicular to the substrate, at least not when they are in the common slipped $\pi-\pi$ stacking arrangement such as the black phase of the perylene diimides. Even organic semiconductors that suffer no obvious constraints on their orientation often align end-on or edge-on to substrates.[15] We conclude that molecules such as the LC perylene diimides are best suited for applications such as field effect transistors where conductivity parallel to the surface is desired, and they may be less appropriate for applications such as solar cells where conductivity perpendicular to the surface is usually required. Nevertheless, their strong tendency to spontaneously self-organize into crystalline films,

and their ability to be controllably "doped" with similar molecules, makes the LC perylene diimides an excellent model system for studying processes such as electronic doping[21] and energy transfer in molecular semiconductors.

Conclusions

A series of LC perylene diimide thin films was deposited by three different methods onto several types of substrates and characterized by optical micrography, absorption and emission spectroscopy and X-ray diffraction measurements. By using molecules that can self-organize, the irreproducibile factors often associated with film preparation methods are alleviated, revealing that such perylene diimides are driven to organize in a very specific fashion. All three LCs formed highly ordered thin films with similar spectroscopic properties on all substrates independent of deposition method. The compounds formed a layered structure in which the perylene diimides self-assembled in $\pi-\pi$ stacks running parallel to the substrate plane. The strong tendency of the perylene diimides to form this specific $\pi-\pi$ stacking arrangement, and the geometry of the side chains that are constrained to be out of the plane of the perylene core, enforce this molecular orientation on all substrates studied, even on highly oriented pyrolytic graphite. The axis of highest electrical conductivity, the $\pi-\pi$ stacking axis, thus lies parallel to the substrate in the LC perylene diimide films.

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