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Face-on Oriented Bilayer of Two Discotic Columnar Liquid Crystals for Organic Donor−Acceptor Heterojunction

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Organic solar cells are based on a heterojunction resulting from the association of a donor and an acceptor material. Absorption of photons creates excitons which diffuse to the donor−acceptor interface, where they are dissociated into free charge carriers (holes and electrons respectively) by the local electric field. Donor−acceptor heterojunctions in organic photovoltaic devices can be created with two types of architectures, namely, bilayer (also called planar) heterojunctions and bulk heterojunctions.[1a] The main advantage of bulk heterojunction cells is to exhibit a wide donor−acceptor contact area, increasing the power conversion efficiency. However, such a geometry of interpenetrated networks is difficult to achieve and is not thermodynamically stable,[1b] suffering therefore from sensitivity toward aging. The lack of direct control of the bulk heterojunction morphology leads also in most cases to the formation of random-shaped domains within the photovoltaic device. An alternative approach to improve the conversion efficiency by the increase of both the exciton diffusion length and the charge carrier mobility is to significantly expand the structural order at large scales inside the heterojunction via the self-organization of two electronically complementary discotic compounds into liquid-crystalline phases.[2] Discotic columnar liquid crystals (CLCs) are known for their high exciton diffusion lengths and charge carrier mobilities along the columns when compared to conventional disordered materials used in organic solar cells.[3] Notably, the exciton diffusion length along the columns in typical triphenylene-based CLCs has been found to be of the order of 200 molecules, or 70 nm,[4] similar to the average thickness of an absorptive layer in an organic solar cell. In this work, we describe the realization of an *oriented bilayer heterojunction* by annealing-induced macroscopic self-assembly of two discotic materials. Our approach using ordered liquid-crystalline structures aims to eliminate the task to interdigitate the donor and acceptor domains by the stacking of two face-on (or homeotropically oriented) hexagonal columnar liquid crystals. This morphology is structurally favorable in terms of electronic properties and is invariant over time. Based on a pair of discotic CLCs which exhibit antagonist solubility and adjusted transition temperatures, we present here how homeotropic bilayers of such pairs of materials have been obtained by sequential thermal annealing of their codeposited mixtures.

Recently, a quite diverse family of materials exhibiting an appropriate hexagonal columnar liquid-crystalline phase at room temperature, namely arene-oligocarboxylic alkyl esters with racemic branched alkyl chains,[5] have been synthesized, and we have shown that homogeneous thin films of such materials can be obtained with the desired face-on alignment via a thermal annealing process through the liquid-to-CLC phase transition.[6] As a functional organic solar cell has to include not only one active layer of an appropriately oriented CLC but also both a columnar donor and a columnar acceptor layer in homeotropic orientation, we have set out to develop pairs of columnar materials which are essentially not miscible and whose alignment behavior can be managed. Despite a few approaches developed during the past few years, control of the phase separation between two discotic compounds remains challenging.[7] For instance, it has been shown that oligooxyethylene side chains are able to render columnar liquid crystals soluble in polar solvents such as methanol or water and to induce microphase segregation within liquid-crystalline phases of materials that bear also apolar alkyl chains within the same molecules.[8] Although the water-soluble perylene-3,4,9,10-tetracarboxylic tetra-2-(2-(methoxy)ethoxy)-ethyl ester is not liquid-crystalline,[9] we found that the shorter chain ester **1** not only is soluble in methanol and insoluble in alkanes but also shows a hexagonal CLC phase at room temperature and up to a clearing transition to the isotropic liquid phase at approximately $T_{\mathrm{CLC}\mathbf{1}\text{-}\mathrm{Iso}\mathbf{1}} = 148$ °C (see Supporting Information (SI)). We obtained **1** as a regioisomer mixture from perylene-3,4,9,10-tetracarboxylic dianhydride by 2-fold anhydride ring-opening with diethyleneglycol monomethylether followed by a 2-fold base catalyzed alkylation of the resulting diester-diacid with 2-bromoethyl methyl ether. Contact preparations of **1** with a room temperature hexagonal CLC material bearing conventional apolar alkyl chains such as pyrene-1,3,6,8-tetracarboxylic tetra-(2-ethyl)hexyl ester **2** ($T_{\mathrm{CLC}\mathbf{2}\text{-}\mathrm{Iso}\mathbf{2}} = 91$ °C)[5a] shows that the two materials are almost immiscible even at an elevated temperature where both are in the isotropic liquid phase (Figure 1), as also confirmed by X-ray scattering and calorimetric studies (see SI). Moreover, **1** and **2** exhibit antagonist solubility, **2** being soluble in *n*-heptane, whereas **1** is completely insoluble. This specific solubility allows a *sequential* solution-processed deposition of the two discotic materials (on bare or ITO-covered glass slides or on silicon wafers with their oxide). After the successive deposition by spin-coating of **1** and **2** using chloroform and *n*-heptane respectively (see SI), each layer of a few hundred nanometers thick exhibits a degenerate planar alignment.[6] The bilayer is then heated up to ~150 °C, where **1** and **2** are in the isotropic liquid phase (Iso**1** and Iso**2**, respectively, in Figure 2a), before being cooled down at 5 °C/min. At ~135 °C, dendritic domains of **1** in the homeotropic orientation appear (CLC**1** in Figure 2b), whereas the upper layer of **2** is still in the isotropic liquid phase. Note that the decrease of $T_{\mathrm{CLC}\mathbf{1}\text{-}\mathrm{Iso}\mathbf{1}}$ of a few degrees can be attributed to some supercooling at this cooling rate and also to the tiny amount of **2** mixed with **1** (see SI). At 89 °C, the second columnar mesophase (CLC**2** in Figure 2d) nucleates on the top of the CLC**1** layer. The hexagonal germ of CLC**2** characteristic of a face-on orientation expands

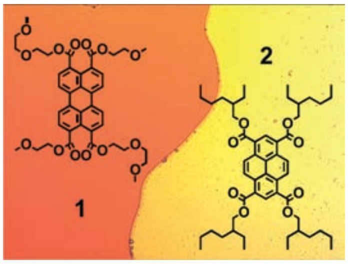

Figure 1. Schematic structure of the two compounds **1** (where only one of the two regioisomers is sketched) and **2**. Their low degree of miscibility is shown by a contact preparation between coverslip and glass slide in the isotropic liquid phase. Observation performed by bright field microscopy. The image size is 440 μm × 325 μm.

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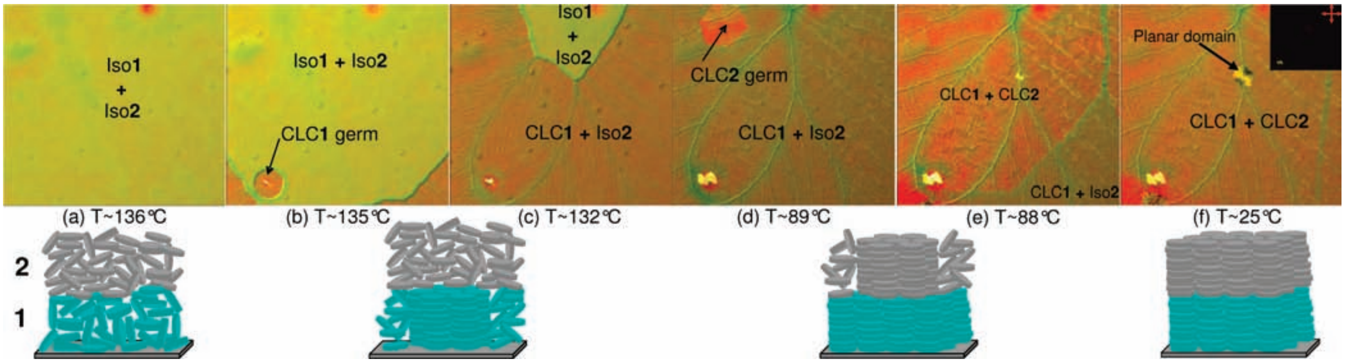

(a) T~136 °C (b) T~135 °C (c) T~132 °C (d) T~89 °C (e) T~88 °C (f) T~25 °C

Figure 2. Growth by thermal annealing of a homeotropically oriented open bilayer (cooling rate: 5 °C/min) observed by differential interference contrast microscopy. In a preliminary step, both compounds **1** and **2** have been sequentially deposited by spin-coating before (a) being heated up to their isotropic liquid phase (Iso**1** and Iso**2**, respectively). (b, c) Nucleation of the compound **1** in the columnar liquid-crystalline phase (CLC**1**) with a dendritic texture, while the upper layer (compound **2**) is still in its isotropic liquid phase (Iso**2**). (d, e) Growth of CLC**2** above CLC**1**. Note the apex angle of the CLC**2** growing domain of ~120° characteristic of a face-on alignment. (f) Both layers exhibit a homeotropic alignment, as confirmed in the inset by the lack of birefringence between crossed polarizers. The layer thicknesses are approximately 350 and 200 nm for compounds **1** and **2**, respectively. The image size is 715 μm × 650 μm.

over all the sample area (Figure 2e). This demonstrates good wetting of the upper layer of CLC**2** on CLC**1** and leads to the following relation between the anisotropic surface tensions associated with the homeotropic anchoring, $\gamma^{\perp}$:

$$\gamma^{\perp}_{\mathrm{CLC\mathbf{1}\text{-}air}} > \gamma^{\perp}_{\mathrm{CLC\mathbf{1}\text{-}CLC\mathbf{2}}} + \gamma^{\perp}_{\mathrm{CLC\mathbf{2}\text{-}air}} \tag{1}$$

This shows the stabilizing role of the upper discotic layer of **2** for managing a continuous face-on aligned CLC**1** film. Moreover, the realization of the inverse heterojunction (with CLC**2** as first layer and CLC**1** as top layer) leads to strong dewetting with the formation of droplets. The existence of a few small birefringent side-on domains evidenced by polarizing microscopy (inset of Figure 2f) emphasizes the lack of optical anisotropy associated with the face-on orientation of each layer in the heterojunction. The homeotropic alignment of the bilayer is confirmed by transmission X-ray diffraction, with the presence of two X-ray patterns exhibiting a 6-fold symmetry (Figure 3), which are the signature of the homeotropic orientation of each layer. To increase X-ray transmission, very thin glass (80 μm tick, Corning Inc.) has been used as a solid substrate. The more intense signal at smaller wavevector $q = 3.5\ \mathrm{nm}^{-1}$ corresponds to CLC**2**. The lower intensity at larger $q = 4.1\ \mathrm{nm}^{-1}$ associated with CLC**1** stems from partial absorption of the scattered X-ray signal by the upper layer **2** of the heterojunction. Note that no epitaxial relations leading to a correlated orientation between the two compounds within the plane of the sample have to be inferred from Figure 3 (see SI).

In summary, the present work reports the achievement of a face-on oriented bilayer heterojunction formed by a pair of discotic materials designed with specific properties: selective solubility, low degree of miscibility, adjusted transition temperatures, and room temperature hexagonal columnar liquid-crystalline phase. The homeotropic orientation of the open bilayer formed by these two compounds of only a few hundred nanometers thick has been demonstrated by both optical microscopy and X-ray scattering. This represents the first proof of principle of an organic heterojunction based on two *oriented* columnar liquid crystal layers.

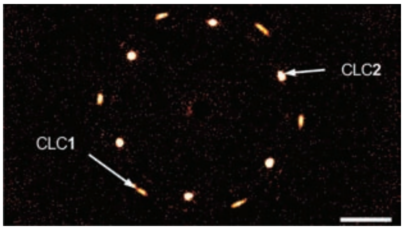

Figure 3. X-ray diffraction pattern of the homeotropically oriented bilayer in the geometry of an open supported thin film. The two 6-fold symmetries are the signature of the face-on (homeotropic) alignment of the two hexagonal columnar mesophases. Experiment performed in transmission with the X-ray beam normal to the plane of the substrate. The scale bar indicates 2 nm^{-1}.

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Supporting Information Available: Synthesis of **1**, physical characterizations of **1** and **2** and of their blend (X-ray diffraction and differential scanning calorimetry), film preparation, calibration of layer thicknesses, and optical absorption of the aligned heterojunction. This material is available free of charge via the Internet at http://pubs.acs.org.

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