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Remarkable Miscibility between Disk- and Lathlike Mesogens

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π-conjugated liquid crystals have recently attracted much attention because of their semiconducting properties.[1] A particular field of interest is their use as active components in solar cells because some of them have proven to carry charges and excitons more efficiently than conventional conjugated polymers.[2] A crucial aspect of photovoltaic devices is the miscibility of their active components, which could dramatically impact charge separation processes.[3] There are many examples of bulk heterojunction solar cells known for polymers. Efficient solar cells have recently been demonstrated for blends of hexabenzocoronene discotics with a crystalline perylene tetracarboxydiimide derivative.[4] However, photovoltaic devices made of liquid crystals as active components are less known.

Blends of conjugated polymers are generally not miscible at the molecular scale for obvious entropic reasons. The case of low molecular weight mesogens is closer to that of liquids: partial or even full miscibility, that is, over the composition range, commonly occurs. Mesogens of similar shape likely tend to self-organize into phases of the same structures and are, thus, expected to be potentially miscible.[5]

The presence of specific interactions, such as hydrogen bonding, donor−acceptor, acid−base, electrostatic, or halo-bonded interactions, creates new situations.[6−8] For instance, molecular miscibility is observed for molecules of dissimilar shape or having different phase structures; for example, systems comprising both an electron donor and an electron acceptor having disk- or rodlike shapes give homogeneous blends as a result of the formation of donor−acceptor complexes.[8] For example, the use of an electron acceptor such as 2,4,7-trinitrofluorenone (TNF) with triphenylene disklike mesogens leads to a stabilized columnar mesophase.[9] This stabilization is due to the intercalation of the acceptor within columns of disks, which is allowed by the small size of TNF. Such miscibility may be explained by the formation of donor−acceptor complexes, which is not restricted to the example given above.[10,11]

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Complementary polytopic interactions are nonspecific interactions. They originate from complimentary-shaped molecules and result from the sum of van der Waals interactions between atoms in close contact. Complementary polytopic interactions have been documented for 1:1 blends of disklike molecules of different sizes, forming different phases. It has been observed that such phases are more ordered than the phases formed by the single compounds (i.e., extension of a regular stacking over a long distance of correlation) and, consequently, are stabilized over a greater temperature range.[12]

Much less is known about blends made of differently shaped mesogens such as calamitics and discotics. Atomic force microscopy has shown that a perylene diimide derivative with short C_3 aliphatic chains and an octasubstituted phthalocyanine bearing C_{12} thioether chains form a solid solution without any phase segregation for a blend containing 20 mol % of the phthalocyanine.[13] The thermotropic properties of such a blend have, however, not yet been reported. In particular, miscibility has not been investigated as a function of temperature and composition.

To force miscibility at the molecular scale, covalently linked molecules made of two differently shaped moieties have been synthesized.[14−17] Molecules combining rod- and disk-shape moieties have been found to be fully miscible with both rods and disks, respectively. However, X-ray diffraction studies have evidenced the absence of ordered mesophases in such compounds, and mainly nematic phases were observed, as well as, in one case, a disordered type of lamellar phase.[18] Another important result was that of a mesogen containing both an electron acceptor (TNF) and a flat aromatic electron donor [hexa(pentyloxy)triphenylene] linked with a flexible spacer has the same thermotropic behavior as the 1:1 mixture of the noncovalently bound moieties.[19]

Encouraged by the efficient discotic-based solar cells reported by Schmidt-Mende et al[4] and the hope to further increase the external quantum efficiency by the control of miscibility, morphology, and alignment, we have launched a research program with the aim of studying blends made of donor and acceptor mesogens.

We report on the full miscibility between two differently shaped molecules of similar dimensions, namely, the electron donor tetra-alkyloxy-phthalocyanine, **1**, and the electron acceptor perylene diimide derivative bearing two flexible side chains, **2**.[20] They have been chosen because they both strongly absorb in the solar spectrum and they have complementary absorption spectra. Phthalocyanines have been shown to exhibit good charge carrier mobilities,[21] and perylenes are known to allow a very efficient electronic conduction.[22] Besides their functional character, the interest in **1** and **2** arises from their disk- and lath-shapes, respectively (Figure 1). The miscibility at the molecular scale extends up to 60 mol % of **1**. We have chosen to document it for a **1**−**2** molar ratio of 3:1 by a comprehensive experimental study combining differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD).

The synthesis of **1** will be described elsewhere.[23] The new perylene derivative **2** is obtained in a one-step condensation reaction[24] between the two commercially available compounds perylene-3,4,9,10-tetracarboxilicdianhydride and oleylamine.[20] Blend **3** is prepared by a "neat method" from the melt as follows. **1** (180 mg, 0.09 mmol) and **2** (28 mg, 0.03 mmol) are stirred in the dark at 300 °C for 1 h under an inert atmosphere of argon. At this temperature, both compounds are in the isotropic phase (see Table 1) and form a homogeneous liquid mixture. The latter is then allowed to cool to room temperature to yield a dark pasty material. Usually, mixtures are prepared by covapor deposition[25] or by mixing two solutions of each compound.[26] We chose the latter for the preparation of the blend because **2** was poorly soluble in common organic solvents and both **1** and **2** are stable at 300 °C in these conditions. Thus, no phase separation due to the different solubilities of **1** and **2** could occur upon solvent evaporation. The blend was kept in the dark. No difference in the thermotropic behavior has been observed depending on the cooling rate during the preparation of **3**. This means that no phase separation occurs and the blend is thermodynamically stable. No degradation or phase separation was detected by DSC or POM after a 6-month period under storage in the dark. In addition, thermogravimetric analysis (TGA) measurements have demonstrated the thermal inertness of **1**, **2**, and **3** up to 300 °C.

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(20) Perylene oleylamine **2** was synthesized by heating, at 200 °C in quinoline, 2.28 g (5.8 mmol) of perylene-3,4,9,10-tetracarboxilicdianhydride, 4.66 g (17.4 mmol) of oleylamine, and 1.06 g (5.8 mmol) of zinc acetate for 18 h under an inert atmosphere of argon. After filtration, Soxhlet extraction with dichloromethane yielded pure **2** in 55% yield. **2** gave satisfactory mass and ^{1}H NMR spectra: 891 (M^+), 641, 404, 391. ^{1}H NMR {300 MHz, $CDCl_3$, 25 °C}: δ (ppm) 8.63 (d, $J = 8.1$ Hz, 4H, Ar), 8.56 (d, $J = 8.1$ Hz, 4H, Ar), 5.34 (t, $J = 4.7$ Hz, 4H, HC=CH), 4.20 (t, $J = 7.7$ Hz, 4H, N−CH_2), 2.00 (m, 8H, HC=CH−CH_2), 1.76 (m, 4H, NCH_2CH_2), 1.50−1.15 (44H, other CH_2), 0.87 (t, 6H, CH_3).

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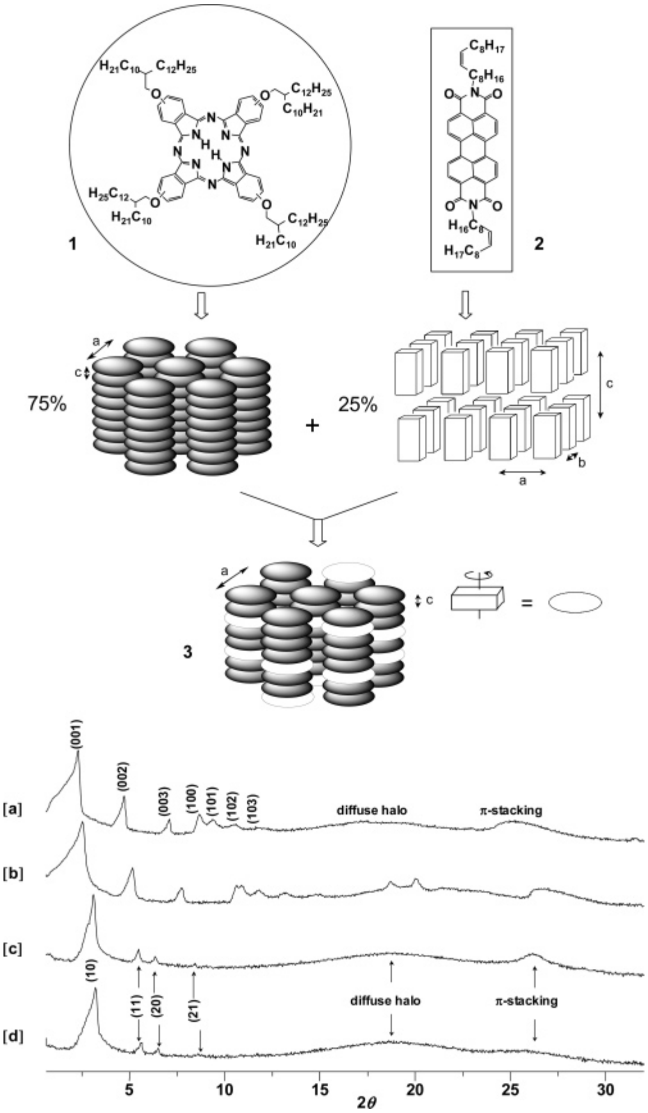

Figure 1. Molecular structures of **1** and **2** (top); supramolecular arrangement of **1**, **2**, and **3** (middle); and diffractograms of **2** at 200 °C [a] and 100 °C [b], **3** at 100 °C [c], and **1** at 100 °C [d].

Table 1. Thermotropic Properties of 1, 2, and 3

compound	phase behavior[a,b]	cell parameters[c]	
1	$\mathrm{Col_r}$ 60 (0.05) $\mathrm{Col_h}$ 180 (3.3) I I 174 (−3.2) $\mathrm{Col_h}$ 57 (−0.05) $\mathrm{Col_r}$	$\mathrm{Col_r}$ $a = 52.1$ $b = 32.5$	$\mathrm{Col_h}$ $a = 31.7$
2	Cr 178 (12.8) $\mathrm{L_{Col}}$ 292 (21.6) I I 282 (−20.1) $\mathrm{L_{Col}}$ 152 (−12.3) Cr	$\mathrm{L_{Col}}$ $a = 10.2$ $b = 3.5$ $c = 38.1$ $\beta = 100.85°$	
3	$\mathrm{Col_h}$ 260 (5.0) I I 258 (−3.2) $\mathrm{Col_h}$	$\mathrm{Col_h}$ $a = 32.0$	

[a] Phase transition temperatures measured for the second heating and cooling runs in °C (10 °C/min) and normalized transition enthalpy values in kJ/mol between parentheses (±5%). [b] Phase assignment: Cr = crystalline phase; $\mathrm{Col_r}$ = columnar rectangular phase; $\mathrm{Col_h}$ = columnar hexagonal phase; $\mathrm{L_{Col}}$ = lamello-columnar phase; I = isotropic liquid. [c] a, b, and c are in Å.

The thermotropic behavior of **1**, **2**, and **3** has been investigated with DSC and POM.

Phase-transition temperatures and their associated transition enthalpies are reported in Table 1. They all exhibit perfectly reproducible enantiotropic behavior. It has been established that, upon cooling from the isotropic melt, **1** presents a columnar hexagonal phase from 174° down to 57 °C (Figure 1, [d]) and a columnar rectangular phase below 57 °C.[23] One interesting feature of the $\mathrm{Col_h}$ phase is given by the presence of the signal observed at ca. 3.5 Å. Its relative broadness suggests that the flat cores are either slightly tilted with respect to the hexagonal plane or the stacking is not correlated over a long length. Both possibilities ought to be considered, and they likely coexist. Such an imperfection of the molecular stacking is likely due to the presence of the bulky branched chains and to their nonhomogeneous distribution around the core, which leads to a mixture of four different regioisomers with different molecular symmetry. **2** presents a mesophase characterized by a lamellar structure between 282 and 152 °C and a crystalline phase below 152 °C (Table 1 and Figure 1). Both phases of **2** have been identified and characterized by XRD. At 200 °C (Figure 1, [a]), the XRD pattern resembles that of a lamello-columnar mesophase, $\mathrm{L_{Col}}$, as those described for similar perylene derivatives with fully saturated alkyl chains.[27] Three intense reflections are observed in the small-angle region at 37.4, 18.7, and 12.45 Å, with the reciprocal spacings being in the ratio $1{:}{}^{1}/_{2}{:}{}^{1}/_{3}$, respectively, consistent with a layered phase and assigned as (001), (002), and (003) reflections, respectively. This observation is of interest and indicates sharp interfaces and a very regular repetition of these layers, that is, good microsegregation of the aliphatic and aromatic parts over a long distance of correlation length. Two halos are observed in the wide angle part, a broad one at 4.6 Å corresponding to the liquidlike order of the molten chains and a sharper one at 3.35 Å arising from the $\pi-\pi$ interactions between aromatic cores, indicative of the development of an intermolecular stacking into columns within the layer planes (ribbons of columns). Finally, additional sharp reflections are seen in the middle-angle range and are indexed in a monoclinic system as ($h0l$) with $h = 1$ and 2 and $l = 0$, 1, 2, and 3. As for the related perylene derivatives,[27] we use the same structural model to describe the intermolecular ordering in this $\mathrm{L_{Col}}$ phase. Therefore, a monoclinic cell has been considered, with the parameters at 200 °C equal to 10.2, 3.5, and 38.1 Å for a, b, and c, respectively; a represents the smallest distance between two neighboring columns of stacked molecules (intercolumnar distance), b represents the value of the distance between two consecutive molecules cofacially stacked, and c represents the layer periodicity. Each layer is, thus, formed by columns and is two-dimensionally ordered along a and b (Figure 1).

At 100 °C, the X-ray diffraction pattern evidences the transformation of the $\mathrm{L_{Col}}$ into a crystalline phase (Figure 1, [b]), with a structure reminiscent of the one described at 200 °C; it preserves the lamellar character of the mesophase only.

Surprisingly, blend **3** shows a very simple thermotropic behavior. Only one phase transition, though broad, occurring between 265 and 245 °C (peak at 258 °C) is detected by DSC upon cooling from 300 to 25 °C. This phase transition marks the beginning of a temperature range in which **3** forms

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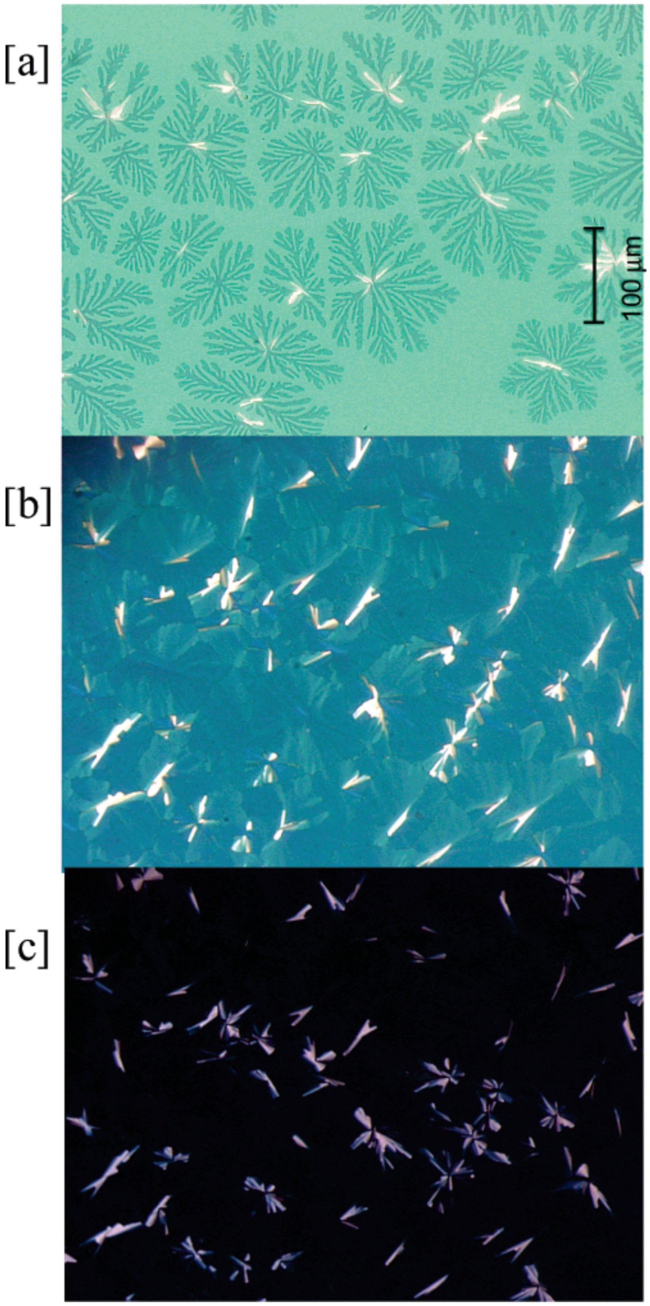

Figure 2. [a] Dendritic growth of the columnar hexagonal phase formed by **3** (257 °C). [b] Mosaic texture obtained at 25 °C. [c] The same picture taken under crossed polarizers; black areas testify to an homeotropic alignment.

a liquid crystalline columnar hexagonal phase, as assigned by the means of POM. The texture growing from the isotropic melt presents dendritic features typical of a columnar hexagonal phase (Figure 2, [a]).[28] Upon further cooling, the dendritic aggregates coalesce into a mosaic texture (Figure 2, [b]). Under crossed polarizers, black areas testify to a homeotropic alignment between the two glass slides (Figure 2, [c]). In this latter case, columns are perpendicularly oriented to the surface of the slides. In view of the residual birefringence beside the large black domains, it is more appropriate to consider the homeotropic alignment as “defective”.[29]

The diffractogram of **3** at 100 °C, representative of the diffractograms over the whole temperature range (Figure 1, [c]), confirms the presence of a unique columnar hexagonal lattice, and thus the full miscibility between **1** and **2**, since the L_{Col} phase of **2** has totally disappeared. This miscibility was not expected a priori because **1** forms a columnar hexagonal phase of discotic molecules and **2** forms a lamellar-columnar phase with a very well-defined smectic organization, and compounds forming such different types of mesophases usually do not mix.[8] The X-ray pattern of the mesophase presents a set of sharp and small angle reflections whose reciprocal spacings follow the ratio $1:\sqrt{3}:2:\sqrt{7}$. They correspond to the indexation $(hk) = (10), (11), (20)$, and (21), respectively, of a 2D hexagonal system. In the wide-angle region, the diffractogram shows a broad halo with a maximum at 4.60 Å, being the average distance between side chains in a column, representative of the liquidlike order of the molten chains. A sharp signal with a maximum at 3.40 Å is seen at larger angles. This value is attributed to the average stacking distance between two molecules in a column. The remarkable thinness and the relatively high intensity of this signal is indicative of a long-range stacking order along the columns, in contrast to **1**. Using Sherrer’s equation,[30] we have calculated the magnitude of the correlation length for the stacking cores to be close to 100 Å, that is, about 30 stacked molecules. We try to explain the relative higher order inside the columns of **3** by the intercalation of molecules of **2** inside columns of **1**, as in the TNF−mesogen mixtures.[8] For this 3:1 composition, there is room enough for the chains of the two compounds to fill in the space around the aromatic cores, particularly if the hard disks of **1** are not tilted (vide supra). Thus, in this blend, two possibilities may be envisaged: (i) perylenes can stack within columns of phthalocyanines or (ii) they can be randomly distributed between columns of **1**. In the first case, two models can be described. On one hand, **2** intercalates between the disklike molecules **1** without disturbing the packing due to the space available; however, this arrangement does not necessarily occur with a long-range order of orientation with respect to the hexagonal plane. Indeed, the random distribution of these orientations is such that after a certain periodicity, the perylene derivatives give rise to an apparent disk-shaped cross section compatible with the area of the columns of the Col_h phase. On the other hand, the perylene derivatives aggregate together into disklike clusters (2 or 3 molecules) as in polycatenar liquid crystals[31] in order to compensate the cross section of the columns, those disklike clusters then intercalating within the discotic compounds **1**. Note that these molecular clusters would be stabilized by the specific core−core interactions, as those present in the L_{Col} phase of the pure perylene derivative **2**. We believe the reality is probably a compromise between these two models. We might envisage that perylenes could be randomly

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distributed between the columns of phthalocyanines. However, strong $\pi-\pi$ stacking interactions between the perylene cores prevent such a random distribution, especially for such a relatively high amount of **2**. In addition, **2** is very poorly soluble in alkanes, so it would be surprising that the alkyl chains of **1** could serve as a solvent for **2**. Finally, if **2** was randomly distributed between the columns, the cell parameters for the $\mathrm{Col_h}$ phase of **3** should be higher than those of pure **1**, and this is not the case.

Thus, and quite remarkably, the columnar mesophase stability has been considerably enhanced compared to that of **1**, and not only has the clearing been raised by about 100 K but the $\mathrm{Col_r}$ phase has disappeared at the expense of the $\mathrm{Col_h}$ phase. The intercalation of **2** within columns of **1** is not only evidenced by the columnar hexagonal mesophase of **3** but is also emphasized by the value of the cell parameters of that phase. They are very close to those found for **1** (Table 1). In fact, the length of the aromatic part of **2** is comparable to the diameter of the Pc ring of **1**, the chains of both compounds filling homogeneously and efficiently the soft aliphatic crown around the hard columnar core, as in **1**.

In summary, we have found that there is a full miscibility between the disk- and lathlike mesogens used for mixtures comprising at least 60 mol % of **1**. We have shown that covalent linkage is not necessary to prevent phase separation between two structurally different molecules. The simultaneous DSC, POM, and XRD studies are all in a good agreement and allowed us a precise assignment of the phases. **1** presents a $\mathrm{Col_r}$ phase below 57 °C and a $\mathrm{Col_h}$ phase between 57 and 174 °C, while **2** is a crystalline solid below 152 °C and presents a $\mathrm{L_{Col}}$ mesophase between 152 and 282 °C (clearing temperature). Blend **3** presents a unique $\mathrm{Col_h}$ phase with a long-range stacking order. This mesophase exists up to 260 °C and is highly stabilized (by more than 100 K) compared to that of pure **1**. The good miscibility, and, as a consequence, the stabilization of the columnar mesophase, probably occurs by specific donor−acceptor interactions between **1** and **2**. Furthermore, POM has evidenced that a high proportion of the columns are spontaneously homeotropically aligned between two glass slides without any external intervention such as annealing.

This example could be of great interest for the (supra)-molecular design and engineering of new photovoltaic devices. Further studies as a function of blend composition and chain substitution are currently underway in our laboratory to discover the nature of the interactions that give rise to miscibility.

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Supporting Information Available: X-ray data for **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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