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Pronounced Supramolecular Order in Discotic Donor-Acceptor Mixtures**

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Dedicated to the memory of Tadeusz Pakula

An approach to tuning the properties of materials is the blending of two different discotic compounds. In analogy to the mixing of two linear polymers, various effects can be expected, ranging from a phase separation in the blend to the formation of a homogenous one-phase system. In the case of two polymers, the blending enthalpy determines whether the mixture will be homogenous or phase separated.^[1] The mixing of two macromolecules that self-assemble into superstructures is complex, since additional interactions between the different components complicate the description of the system.^[2] As illustrated in Figure 1, several different supramolecular assemblies can be formed in the mixture. For discotic molecules, which self-assemble in columnar super-



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Communications

structures by π stacking, this ranges from a heterogeneous phase to micro- and even nanoseparation.

Intensive investigations of mixtures containing triphenylene as the donor compound have been carried out, whereby trinitrofluorenone,^[2,3] azatriphenylenes,^[4,5] and mellitic trimides^[6] have been used as acceptor molecules. For equimolar mixtures, alternating stacking of the acceptor and donor molecules has been observed, leading to an enhanced columnar stability. Time-of-flight experiments verified an enhanced columnar organization and revealed considerably higher charge-carrier mobilities for the blends.^[7–9]

In this study, the effect of blending two discotic materials, which differ significantly in their electronic properties, was examined. While hexa-*peri*-hexabenzocoronene substituted by long, branched alkyl chains (HBC- $C_{10,6}$, **1**; Figure 2) is an electron-donating agent, perylenediimide^[10] (PDI, **2**) and terrylenediimide derivatives (TDI, **3**) are strong acceptors. Semiemperical calculations (AM1) indicate that there is a weak electronic interaction between the two components, which should lead to alternating stacking in the columnar structure and therefore to increased stabilization and a higher level of order in this donor–acceptor mixture. In addition, the

blended molecules are compatible in size, permitting matched intracolumnar packing and leading to a different self-assembly on surfaces.

The substitution of the HBC aromatic core with bulky, branched side chains led to a considerable lowering of the isotropization temperature (T_i) to 93 °C for 1 in comparison to those of HBC derivatives with linear side chains. Twodimensional wide-angle X-ray diffraction (2D-WAXS) experiments indicated a herringbone arrangement (Figure 3a) of the HBC discs in the room-temperature plastic crystalline phase, whereby heating beyond the phase transition at 24 °C (second differential calorimetry scan at a rate of 10°Cmin⁻¹) resulted in a disordered columnar liquidcrystalline (LC) phase. Highly birefringent dendritic structures appeared when the material was cooled from the isotropic phase between glass slides, implying defect structures with columns predominately parallel to the surface (Figure 2a). During crystallization of 2 from the isotropic phase ($T_i = 130$ °C), optical textures with pseudofocal conical fan shapes (Figure 2b) were observed, indicating the formation of a mesophase in which the molecules are orthogonally arranged with respect to the stacking axis. Such intracolumnar



Figure 2. Chemical structures and polarized optical microscopic images of a) 1, b) 2, and c) 3 (the arrow indicates the columnar orientation); in the inset the same section of the sample was rotated relative to the direction of polarization of the light, and it indicates a high level of optical anisotropy. The crossed arrows indicate the orientation of the polarization filters in the optical microscope. The images were recorded during crystallization from the isotropic phase at the cooling rate of 1° C min⁻¹.



Figure 3. Room-temperature 2D-WAXS patterns of a) 1 b) 2, and c) and an equimolar mixture of 1 and 2 (inset shows the sample directly after extrusion). The Miller's indexes describe the periodicity along the columnar structures. All samples were prepared by filament extrusion, and the filament axis was oriented vertically in the diffraction experiment.

packing of **2** was also confirmed by the 2D-WAXS experiments.

Mixtures of **1** with **2** or **3** were first prepared at set molar ratios in solution and afterwards blended in the isotropic phase to avoid demixing due to different solubilities. The investigation of the thermal behavior by differential scanning calorimetry (DSC) revealed that all prepared mixtures formed a macroscopic, homogeneous phase.

Photoluminescence excitation spectra for an equimolar mixture of 1 and 2 in solution showed a superposition of the spectra of the pure components. In contrast, drop-cast films of the blend showed a shift of the fluorescence signal of 2 by 60 nm accompanied by a strong quenching, which was expected because of energy-transfer processes. The significant change of the electronic environment of the chromophore was supported by the differential pulse voltammetry measurements. These displayed an additional peak for the mixture which was shifted by 0.18 eV in comparison to measurements with pure 2.

The 2D-WAXS pattern of the equimolar mixture of 1 and 2 indicated a considerable difference of the supramolecular arrangement in the blend (Figure 3c). The X-ray pattern changed significantly when the extruded sample was annealed for 48 h at ambient conditions, whereby the number of distinct reflections increased dramatically. A set of new higher order reflections appeared, indicating an exceptional long-range order and a complex helical arrangement of the two discotic species within the columnar stacks. The transformation of the first equatorial reflection, which converted from an isotropic shape (Figure 3c) to three sharp peaks, was particularly impressive. This implied not only a simple intracolumnar reorganization but also a rearrangement of entire columnar segments.

The layered distribution of the reflections in the meridional direction in the WAXS pattern in Figure 3c was identified by the Miller's indices (*hkl*), which were assigned to the intracolumnar packing.^[11] The smallest intracolumnar repeating distance between single building blocks is 0.34 nm. This distance is in relation to the (hkl) reflection lines indicating strong correlations over long ranges between ten molecules per helical pitch (helical pitch distance: 3.4 nm). The suggested model for the supramolecular arrangement is illustrated in Figure 4. It is assumed that an alternating molecular packing results in the helical organization. In this



Figure 4. Schematic packing model of an alternating intracolumnar arrangement for the binary mixture. Molecules of **2** are intercalated between units of **1**, which are displaced by 12° with respect to each other, resulting in a helical pitch of 3.4 nm.

structure, PDI (2) is intercalated between the HBC discs (1), which are rotated with respect to each other by 12° thus providing the necessary repeat unit for the helical arrangement. This rotation is induced by the space demand of the alkyl side chains in both derivatives. In 2003 helical columnar arrangements were observed for HBC derivatives with rigid substituents.^[12] Electronic donor–acceptor interactions were thought to cause the observed pronounced alternating intracolumnar ordering. A similar situation was reported for single crystals consisting of hexafluorobenzene and fullerene; the interactions were confirmed by fluorescence and differential pulse voltammetry measurements.^[13]

To gain more detailed insight into the supramolecular arrangement of other mixtures, complementary compositions with ratios of 1:2 and 2:1 were investigated. All extruded samples showed significantly higher order after annealing. The 2D-WAXS pattern of both blends displayed reflections at positions identical to those observed for the 1:1 blend, but with different reflection intensities, which depended on the composition ratio. The additional reflections reached their maximum intensity for the 1:1 molar ratio, possibly due to sequences of identical molecules of the excess components in the nonequimolar mixtures.

The new supramolecular structure in the blends significantly affected the thermal behavior and the morphology. When a 2:1 mixture of HBC (1) and PDI (2) was cooled down from the isotropic phase between two glass slides, a homogenous film was obtained that did not display significant birefringence in polarized light; this would be characteristic for a homeotropic phase (Figure 5a). The transmission 2D-WAXS pattern of the film confirmed the proposed orientation (Figure 5b), whereby the lateral arrangement of the lattice differed considerably between the domains. This

Communications



Figure 5. Example for a homeotropically aligned sample based on the 2:1 mixture of 1 and 2. a) Image from the optical microscope (polarizer and analyzer at a 45° angle with respect to each other; inset recorded with crossed polarizers). b) Characteristic 2D-WAXS pattern of the film with homeotropic order (identical hexagonal lattice in different small domains leads to the appearance of multiple reflections).

morphology stands in contrast to those of the individual components. A similar morphology was also obtained for mixtures of other compositions; however, the number of birefringent defects increased significantly.

In general, HBCs with nonbulky alkyl substituents align homeotropically when cooled down from the isotropic phase. When the π -stacking interactions between the aromatic cores are significantly reduced in the isotropic phase, the molecules arrange with their planes parallel to the surface. This arrangement is assumed to be the most thermodynamically favored, since interactions (e.g. van der Waals interactions) between the molecule and the surface are maximized. On the other hand, the high steric demand of the alkyl chains close to the aromatic core might hinder the approach the disc to the surface, as seen for HBC-C_{10,6} **1** and previously for HBC-C_{14,10}.^[14] In both cases, the high degree of rotational freedom at the β position of the side chains results in the increase of the steric requirements, which lead the formation of defect structures

The steric influence of the substituents on the columnar packing can be reduced synthetically^[15] or, as described in this work, by packing effects of the donor–acceptor molecules. The electronic interaction between **1** and **2** resulted in the strictly alternating stacking of the donor and acceptor species. The distance between the HBC discs in the columns increased, whereby the steric influence of the long, branched $C_{10,6}$ alkyl chains on the stacking was significantly reduced. Consequently, the mixture formed a homeotropic phase. Additionally, the intracolumnar packing was enhanced by the helical arrangement of the molecules. Analogous behavior was observed for mixtures of **1** and **3** with molar ratios of 1:1 and 2:1 (Figure 6). Both blends revealed a homeotropic alignment suggesting an identical intracolumnar packing of the two discotics as described above.

In conclusion, we have shown that supramolecular organization in a binary mixture differs strongly from that of the individual components. Strictly alternating stacks formed spontaneously when the mixture was cooled from the isotropic state, because of the weak donor-acceptor interactions between the electron-rich 1 and the electron-poor rylene dyes 2 and 3. These interactions, proved by



Figure 6. Example of a homeotropically aligned sample based on the 2:1 mixture of 1 and 3. a) Image from the optical microscope (polarizer and analyzer at a 45° angle with respect to each other; lower inset recorded with crossed polarizers, upper inset image recorded during crystallization of the dendritic structure). b) Characteristic 2D-WAXS pattern of the film with homeotropic order.

photoluminescence and differential pulse voltammetry, lead to a significantly higher level of order within the selfassembled columnar stacks. The molecules in the mixture assume a homeotropic orientation, due to an auxiliary effect of the smaller aromatic molecule, while forming the first monolayer of the sterically demanding HBCs on the surface.

Experimental Section

The blends were first prepared in tetrachlormethane and were then used in the isotropic phase. To ensure an intermixture of both compounds, the blends were processed in an ultrasonic bath under nitrogen atmosphere.

The 2D-WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimation and a Siemens 2D detector. A double graphite monochromator for the Cu_{Ka} radiation ($\lambda = 0.154$ nm) was used. The samples were oriented by filament extrusion. The optical textures were investigated using a Zeiss microscope with polarizing filters equipped with a Hitachi KP-D50 color digital CCD camera. The samples were sandwiched between two glass slides and then thermally treated (first heated to the isotropic phase and then slowly cooled down) on a Linkam hotstage regulated with a Linkam TMS 91 temperature controller.

Electrochemical measurements were performed on a voltametric analyzer (AutoLab PGSTAT-30, potentiostat/galvanostat) in a threeelectrode cell with a gold working electrode (3 mm diameter), a silver quasi-reference electrode (AgQRE, calibrated with the Fc/Fc⁺ redox couple $E^{\circ} = 4.8 \text{ eV}$) and a platinum counterelectrode. Films were dropcast from a solution of toluene. Tetrabutylammonium perchlorate (TBACIO₄, 0.1M) and acetonitrile were used as electrolyte and solvent, respectively. Differential pulse voltammetry was measured with 15-mV, 50-ms pulses at 100-ms intervals.

The photoluminescence was recorded on a SPEX Fluorolog 2 type 212 steady-state fluorometer at a concentration of 10^{-3} M and dropcast films on quartz substrates. DSC was measured with a Mettler DSC 30 at a heating rate of 10 K min⁻¹ from -100 °C to 200 °C. The electronic potential density distribution was calculated by means of Spartan for Windows (AM1 of ground state). The synthesis of HBC-C_{10.6} **1** has been described elsewhere;^[12] the syntheses of PDI **2** and TDI **3** are described in the Supporting Information.

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