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Effect of the *Ortho* Alkylation of Perylene Bisimides on the Alignment and Self-Assembly Properties

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The effect of the *ortho* alkylation of perylene bisimides on the alignment and self-assembly properties has been studied. It was found that the dichroic properties of perylene bisimides in a liquid crystal host can be reversed with a single synthetic step by *ortho* alkylation. Furthermore, a solvent-induced growth of ultralong organic n-type semiconducting fibrils from non-*ortho*-alkylated perylene bisimide was observed. *Ortho* substitution of the perylene bisimide core alters the mode of fibrillar growth, leading to isotropic crystallization.

In the last few decades, there has been significant research focused on the potential of employing organic dyes in optoelectronic devices such as organic light-emitting diodes,^[1] field-effect transistors,^[2] and photovoltaic cells.^[3] Organic dyes have also been applied in a variety of other devices including liquid crystal displays, thin-film polarizers, solar systems, microelectrical mechanical systems, lenses, imaging, lighting, microlasers, and smart windows.^[4,5] In these devices, the supramolecular organization of the dye in the active layer of the devices plays a crucial role.^[6,7] Furthermore, in many of these applications, the alignment of the dichroic chromophore, which is mainly determined by the shape of the chromophore, in the host matrix, often a liquid crystal (LC), is decisive.^[8]

Perylene bisimides (PBs) constitute a unique class of organic dyes with high extinction coefficients, thermal and photochemical stability and n-type semiconducting properties.^[9,10,11] However, the low solubility of perylene bisimides restricts their application. In order to increase solubility, perylene bisimides

have been substituted with side chains. Such a modification often leads to different molecular, supramolecular and macroscopic properties.^[11,12] It is therefore key to understand how side chains affect the molecular, self-assembly, optical and optoelectronic properties of organic dyes.^[11–13] Recently, a facile method was adopted to increase the solubility of perylene bisimides by using styrene tails via a ruthenium-catalyzed C–H activation reaction in a single step.^[14] We have used this methodology to alkylate a commonly used perylene bisimide PB-1 (see PB-2 in Figure 1) to investigate the influence of *ortho* substitution on the alignment of this dye in LC matrixes and on the self-assembly into nanofibers.^[15,16]

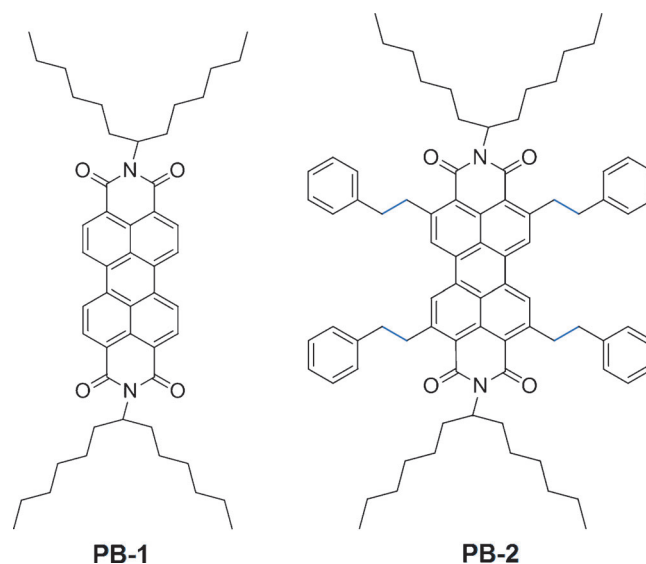


Figure 1. Chemical structures of swallow-tail-substituted perylene bisimide (PB-1) and its phenylethyl analogue (PB-2).

PB-1 was synthesized according to a reported method^[17] and was functionalized with four phenylethyl groups by using $\text{Ru}(\text{H}_2)(\text{CO})(\text{PPh}_3)_3$ as catalyst yielding PB-2 (Figure 1). The styrylation was confirmed by ^1H NMR and MALDI-TOF mass spectroscopy (Supporting Information, figures 1,2). It must be noted that no isomeric products having 1-phenylethyl substituents were observed.^[16]

To evaluate the dye alignment in an anisotropic LC medium, ~0.5% PB-1 and PB-2 were each dissolved in a nematic LC E7 (Supporting Information, figure 3), and the solutions were used to fill 20 μm thick LC cells made of glass (2 cm \times 2 cm) coated with rubbed polyimide alignment layers by capillary action.

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The alignment of a dye molecule can be expressed by the order parameter " S_a ", which is defined as

$$S_a = \frac{(A_{\text{par}} - A_{\text{per}})}{(A_{\text{par}} + 2A_{\text{per}})} \quad (1)$$

where A_{par} and A_{per} are the absorbance of the sample when exposed to light polarized along the alignment direction of the host LC and to light polarized perpendicular to the alignment of the host LC, respectively. Figure 2 represents the polarized

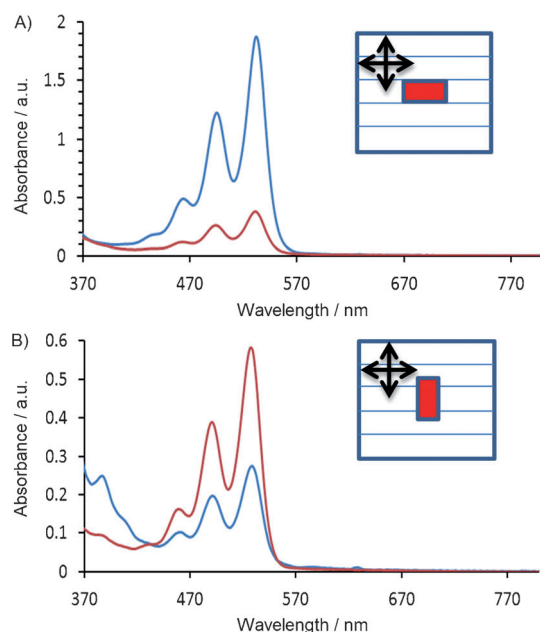


Figure 2. Absorption spectra of A) PB-1 and B) PB-2 exposed to light polarized parallel to the E7 (A_{par} —) and perpendicular to the E7 alignment (A_{per} —). The red bars in the insets represent the PB core, lines represent the alignment direction of E7, and the arrows show the polarization direction of the incoming light.

absorption spectra for the non-alkylated and alkylated perylene bisimide dye. These spectra represent the characteristic vibronic absorption bands with maxima at $\lambda = 456, 487,$ and 523 nm originating from perylene bisimide chromophore.^[11] For PB-1, the main axis of the dye is aligned along the LC director since the absorption parallel to the molecular director is higher than that perpendicular. The order parameter was determined to be 0.57 at 532 nm, which is similar to results found earlier.^[8] Remarkably, alkylated PB-2 shows a higher absorption perpendicular to the LC director, revealing that the orientation of the main perylene bisimide core is opposite to PB-1. The order parameter is now -0.27 at 527 nm. Apparently, the orientation of the dye has been changed due to the phenylethyl units, and the longest part of the molecule is now aligned opposite to the molecular axis of the host LC.^[8] These results show that the dichroic properties of perylene bisimide dyes can be reversed with a single synthetic modification.

In the next step, we investigated the aggregation behavior of PB-1 and the effect of alkylation of the PB core (PB-2) on the supramolecular organization in solution and in the solid state. In the first experiments, the dyes were dissolved in dodecane and drop cast on a glass surface. Field emission scanning electron microscopic (FESEM) images of the dried samples show that, in case of PB-1, highly anisotropic needle-shaped fibers are formed having an average width of $4 \mu\text{m}$ and length of several hundred micrometers, some even as long as 1.5 mm (Figure 3; top left). Moreover, the growth appears to be regulated, as there is no evidence of branching. The production of

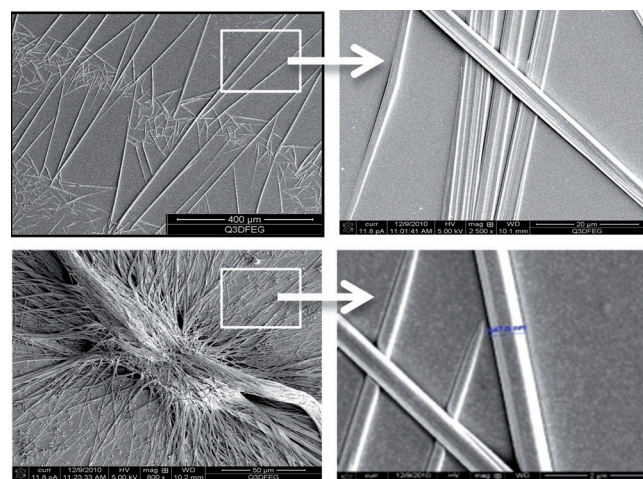


Figure 3. FESEM images of PB-1 (top) and PB-2 (bottom) solvent dried films (cast from 5 mm dodecane solutions). Scale bars: top left : $500 \mu\text{m}$; top right: $20 \mu\text{m}$; bottom left: $50 \mu\text{m}$; bottom right: $2 \mu\text{m}$.

such ultralong fibrillar organization has not been reported previously for these perylene bisimides.^[12] The use of dodecane as solvent, which has a high boiling point, might have influenced the self-organization due to its slow evaporation rate. In contrast, PB-2 only yielded small bundles of thin fibers growing in all directions from central nucleation points without having global anisotropic domains. The individual fibrils widths measured between 300 and 550 nm with a highly entangled morphology.

It was also observed that in a 5 mm solution in dodecane, PB-2 is completely soluble at 140°C and that aggregates start to appear upon quenching to 20°C (Figure 4, top). Unlike PB-2, PB-1 does not seem to dissolve completely in dodecane, even at elevated temperature (approx. 160°C), as the dispersion lacks transparency (Figure 4, bottom). Most likely a small fraction of associated perylene bisimide nanocrystals act as seeds to nucleate the unidirectional growth of ultralong fibers. As earlier reported, most likely so-called H-type aggregates are formed in which the fluorescence is quenched.^[14]

The solution shape of the perylene bisimide aggregates was studied by small angle X-ray scattering (SAXS). Figure 5 represents the SAXS profiles taken at ambient temperature for the two perylene bisimide solutions, revealing the presence of cylindrical objects. The nature of the scattering profiles suggests

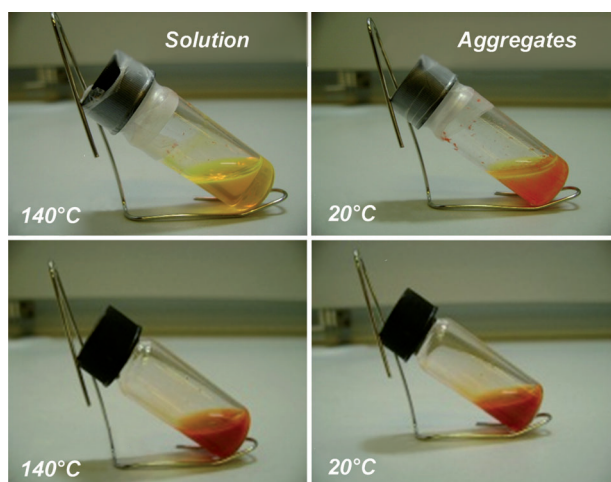


Figure 4. Photographs of perylene bisimide dodecane solutions (5 mM) at the indicated temperatures taken under normal light for PB-2 (top) and PB-1 (bottom).

that the one dimensional objects have a significant polydispersity in cross-sectional diameter (fibrillar crystallites were seen in electron microscopy images as well). The SAXS profiles of the two solutions are not identical: the average fibrillar diameter of PB-1 aggregates were remarkably high compared to the PB-2 aggregates, which is in agreement with the FESEM data. Note that the scattering profiles of Figure 5 are corrected for solvent background as well as for dark current. The simulation curve is constructed using the “form factor” equation for infinitely long cylinders.^[18]

$$I(q) = \frac{\phi r^2 \Delta \rho^2}{2q} \left[\frac{J_1(qr)}{qr} \right]^2 \quad (2)$$

Therein, q is the module of the scattering vector ($q = 4\pi \sin \theta / \lambda$, with θ half of the scattering angle and λ the X-ray wavelength), r is the radius of the cylinder's scatter, J_1 represents the Bessel function of first order and $\Delta \rho$ represents the contrast factor, that is, the difference between the electron density of the aggregates and the solvent. The reason for the different fibrillar growth patterns is most likely due to the enhanced

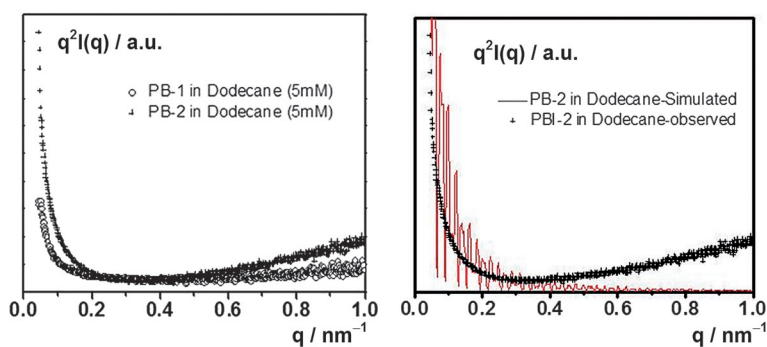


Figure 5. 5 mM solution SAXS profiles of PB-1 and PB-2 in dodecane as indicated (left). Solution SAXS profile of PB-2 in dodecane (5 mM) is compared with a calculated scattering curve for fibres with a polydisperse diameter (right).

steric crowding around the planar perylene π -core of PB-2, that is, the alkylation is arresting the fibrillar growth faces.^[19–21]

In conclusion, we have shown that the dichroic properties of perylene bisimides can be reversed with a single synthetic step. Such a finding is interesting for the fabrication of perylene bisimide dyes having a negative dichroic ratio. Furthermore, we have explored the solvent-induced growth of ultralong organic n -type semiconducting fibrils with n -alkylated perylene cores. Such ultralong fiber deposition might be of interest for organic field-effect transistor (OFET) systems, since the charge carrier properties for such fibrillar assemblies are dependent on fibrillar connectivity lying between the pair of deposited electrodes.^[22] We also demonstrated that *ortho* substitution of perylene cores alters the mode of fibrillar growth, leading to isotropic crystallization. In general, our results indicate that a single synthetic step modification of a perylene bisimide with commercially available side chains can significantly alter both the alignment and self-assembly properties of a perylene bisimide, which is interesting for the tuning the properties of optoelectronic devices.

Experimental Section

Materials: All solvents, purchased from Acros Chimica or Sigma–Aldrich–Fluka, were of p. a. quality. E7 was obtained from Merck. Deuterated solvents were from Cambridge Isotope Laboratories. All other chemicals were commercially available and were used without further purification. *N*-Hexyl-heptyl substituted perylene bisimide (PB-1) was synthesized and characterized by following the literature procedures described by Langhals et al.^[17]

PB-2 was synthesized based on a literature procedure (see Supporting Information).^[16] ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.69 (s, 4H), 7.40–7.31 (m, 6H), 7.17–6.88 (m, 8H), 6.75–6.35 (m, 6H), 5.32–5.21 (m, 2H), 3.76 (t, J = 7.6 Hz, 8H), 3.11 (t, J = 7.5 Hz, 8H), 2.49–2.12 (m, 4H), 2.12–1.68 (m, 4H), 1.48–1.03 (m, 16H), 0.82 (t, J = 6.9 Hz, 12H); ¹³C NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 141.80, 131.64, 128.97, 128.42, 127.43, 126.11, 124.21, 54.37, 36.97, 32.44, 31.82, 29.27, 27.00, 22.62, 14.06; MS (MALDI-TOF): m/z calcd for C₈₂H₉₄N₂O₄: 1170.72 [M]⁺, found: 1170.61.

Preparation of the dye/liquid crystalline mixtures: Each of the dyes were dissolved at 0.5% (w/w) in the liquid crystal blend E7. Custom made 5 × 5 cm² indium tin oxide (ITO)-coated glass cells with a 20 μ m spacing (LCTec, Pfronten, Germany) were filled with the dye solutions via capillary action. The polarized absorbance of the filled cells was measured on a UV-3102 spectrophotometer (Shimadzu, Kyoto, Japan) and determined by exposing the cells to light polarized both parallel and perpendicular to the alignment direction of the polyimide within the cells, with the absorbance of a cell filled with the LC E7 alone as a reference.

Field emission scanning electron microscopy: FESEM experiments were carried out on a Technai G2

Sphera FEI instrument (Hillsboro, Oregon, USA). Prior to microscopy, the samples were gold coated with a 20 nm thickness in a sputter coater.

Small angle X-ray scattering: SAXS experiments were carried out at DUBBLE BM-26B beamline at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The 2D images are collected using a 2D FReLoN CCD camera with pixel size of 46.9×46.9 microns in 2×2 binning mode.

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