

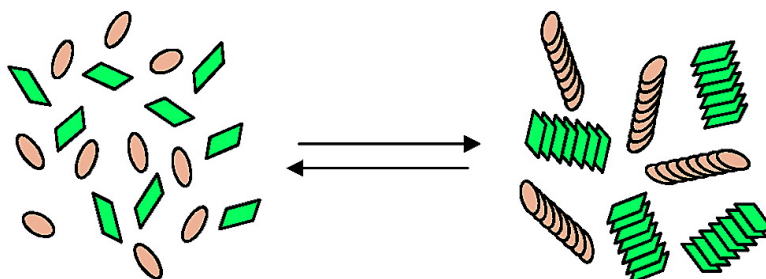
Article

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Jeroen van Herrikhuyzen, Asha Syamakumari, Albertus P. H. J. Schenning, and E. W. Meijer

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Synthesis of n-Type Perylene Bisimide Derivatives and Their Orthogonal Self-Assembly with p-Type Oligo(*p*-phenylene vinylene)s

Jeroen van Herrikhuyzen, Asha Syamakumari,[†] Albertus P. H. J. Schenning,* and E. W. Meijer*

Contribution from the Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Received March 2, 2004; E-mail: A.P.H.J.Schenning@tue.nl; E.W.Meijer@tue.nl

Abstract: Four different (chiral) electron-deficient (n-type) perylene bisimides containing aliphatic, aromatic, or ethyleneoxide side chains have been synthesized and fully characterized. All of them form supramolecular stacks in apolar methylcyclohexane (MCH) solution as demonstrated by concentration- and temperature-dependent absorption, circular dichroism, and fluorescence studies. One derivative was investigated in more detail in the solid state and proven to be liquid crystalline and capable of forming nanometer-sized fiberlike networks when drop-cast from MCH. Optical spectroscopy techniques show that perylene bisimide and an oligo(*p*-phenylene vinylene) (p-type) derivative orthogonally self-assemble into separate nanosized p- and n-type stacks in MCH. In contrast in toluene only molecularly dissolved species are present. In films deposited from MCH as well as from toluene photoinduced electron transfer takes place from the p-type material to the n-type material. As a result of the orthogonal self-assembly process, in films from MCH an ordered network of fibers was formed, whereas in films from toluene no ordering was observed. However, probably due to the lateral orientation on the surface and the presence of long aliphatic chains pointing toward the electrodes, efficient bulk heterojunction solar cells could not be constructed.

Introduction

Organic solar cells consist of an electron-deficient and an electron-rich organic semiconductor (n- and p-type material, respectively).^{1,2} When irradiated by light (photons), charge transfer occurs yielding a negatively charged n-type and a positively charged p-type material. Subsequently, the resulting charges migrate through the materials and reach the cathode and anode to create a photocurrent. Organic solar cells can be constructed by using either a traditional p–n junction¹ or bulk heterojunctions.² The traditional p–n junction is disadvantageous as it has a small contact area between the two materials, which results in a limited participation in the charge separation process. Many excitations will decay to the ground state before they can reach the depletion layer, since they have limited lifetimes and have to migrate through the bulk material. As this phenomenon decreases the efficiency of the solar cell, it is believed that bulk heterojunctions are needed that are highly self-ordered at the nanoscopic scale, for instance, via a liquid-crystalline mesophase.³ So far, promising efficiencies of 2.5%⁴

to 3.0%⁵ have been achieved for bulk heterojunction solar cells, although the charge carrier mobility is still low.

Separate nanosized pathways of p- and n-type material with a high charge carrier mobility would be ideal architectures for solar cells. An attractive approach to achieve this objective is the separate self-assembly of electron acceptor and donor building blocks to create independently nanosized p- and n-type fibers that coexist within a single system. Recently such an orthogonal approach has been used in organogels in liquid crystalline phases⁶ and in the self-assembly of gelators and surfactant to create fibrillar networks with encapsulated micelles.⁷ Furthermore, self-sorting systems have been reported for small molecular systems based on different noncovalent interactions.⁸ However, orthogonal self-assembly of donor and acceptor molecules has not been reported so far and was focused on donor–acceptor alternating complexes rather than separate n- and p-type stacks.⁹

[†] Current address: Polymer Science Division, Regional Research Laboratory, Thiruvananthapuram 695019, India.

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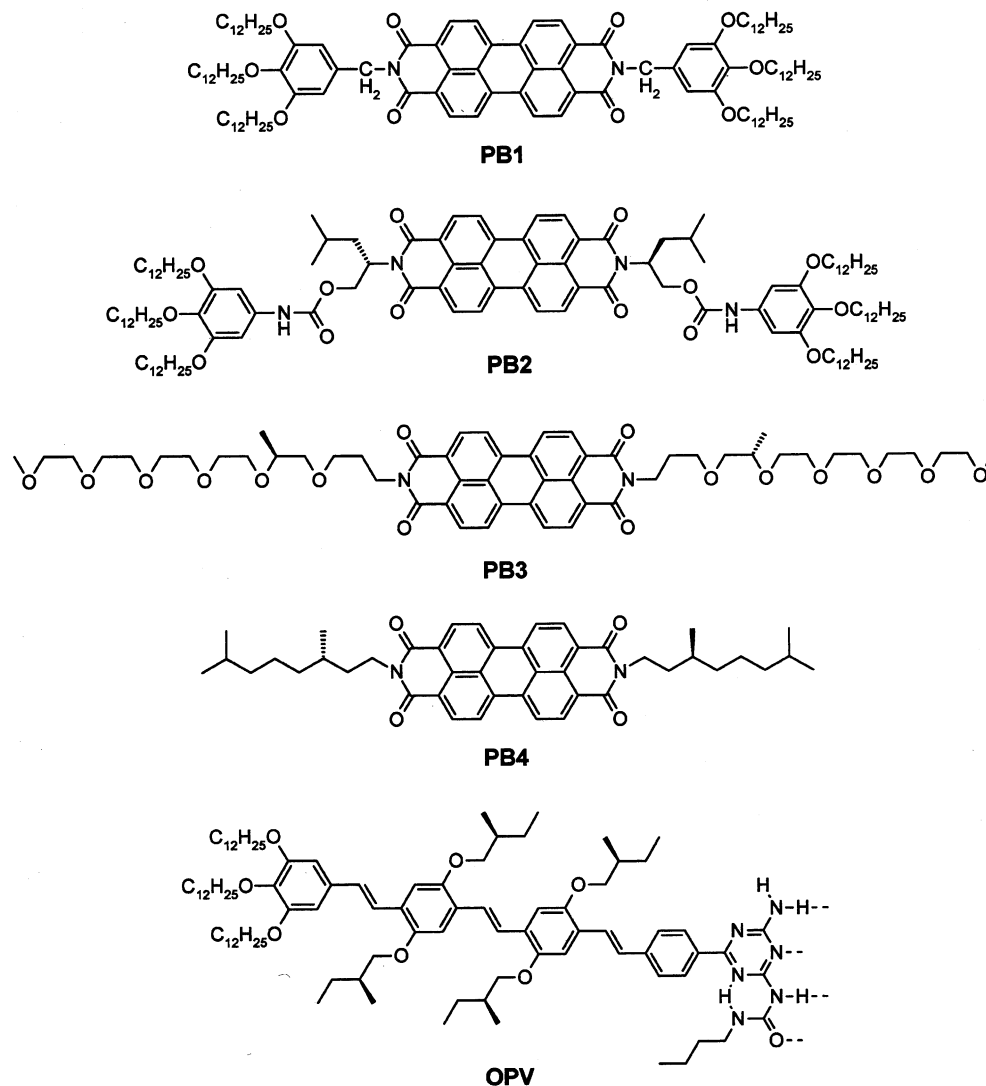


Figure 1. Four perylene bisimides with different substituents at the N-position (**PB1-4**) and the oligo(*p*-phenylene vinylene) derivative **OPV**.

We recently have reported p-type fibers of hydrogen-bonded oligo(*p*-phenylene vinylene)s (**OPV**, Figure 1),¹⁰ as well as fibers containing both p-type and n-type strands.¹¹ To create an ordered network of p–n junctions, we have now used the orthogonal self-assembly of electron-donor and -acceptor molecules. Since p-type fibers already exist,¹⁰ we have first synthesized four different electron-deficient (n-type) perylene bisimides (Figure 1) and investigated the stacking behavior in apolar solvent.¹² Subsequently we have orthogonally self-assembled perylene bisimides and OPVs in apolar solvent and

in the solid state. Finally, the mixed films were tested in a photovoltaic device.

Results and Discussion

Synthesis. The perylene bisimide derivatives **PB1**, **PB3**, and **PB4** were synthesized from the corresponding amine-terminated chains (Scheme 1, Figure 1) with 3,4,9,10-perylenetetracarboxy anhydrides at 160 °C in imidazole in the presence of zinc acetate. Ethyleneoxide derivative **3** was synthesized from alcohol **1** followed by a Michael addition of acrylonitril and subsequent reduction with BH_3 . Benzylamine derivative **5** was obtained after a reduction of benzonitrile derivative **4** with H_2 in the presence of PtO_2 . Perylene bisimide **PB2** was synthesized by coupling trialkoxybenzene isocyanate with *N,N'*-di(1-isobutyl-2-hydroxyethyl)-3,4,9,10-perylenebis(dicarboximide) using a catalytic amount of dibutyltin dilaurate. All compounds were fully characterized by ^1H , ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis.

The liquid crystalline behavior of the four perylene bisimides was investigated by optical polarization microscopy (OPM) and

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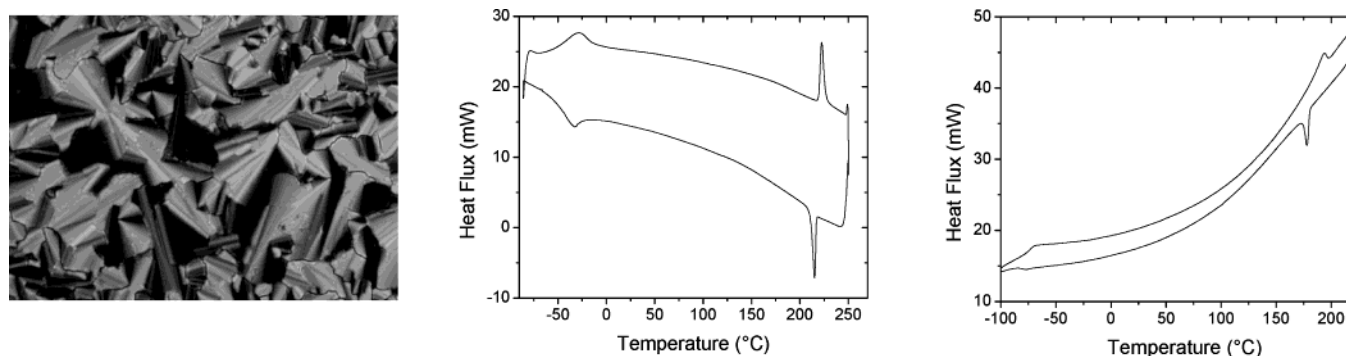
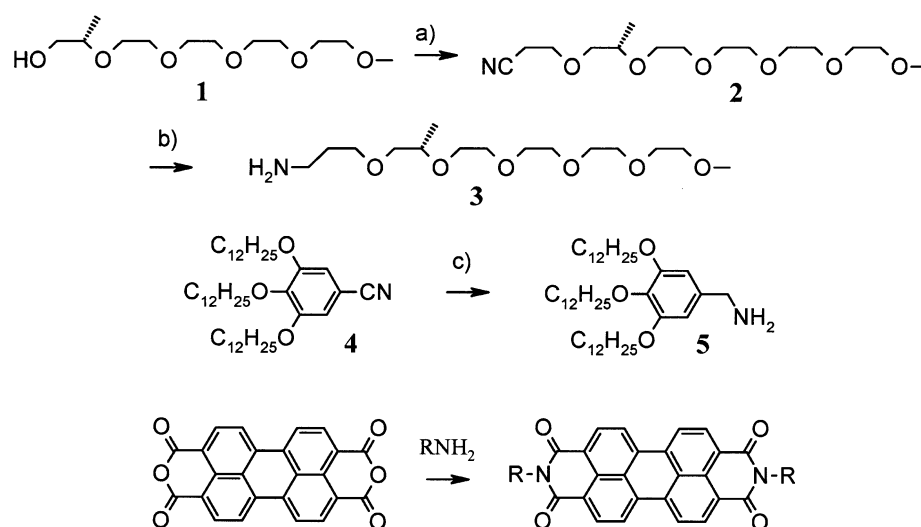


Figure 2. Optical polarization microscopy image ($0.43 \times 0.32 \text{ mm}^2$) of **PB1** (crossed polarizers) at $198 \text{ }^\circ\text{C}$ showing a hexagonal columnar mesophase (left) and DSC curves of **PB1** (middle) and **PB3** (right).

Scheme 1



differential scanning calorimetry (DSC) (Figure 2 and Experimental Section in the Supporting Information). DSC measurements showed that **PB1** is liquid crystalline between $-46 \text{ }^\circ\text{C}$ ($\Delta H = 0.95 \text{ kJ/mol}$) and $219 \text{ }^\circ\text{C}$ ($\Delta H = 17.8 \text{ kJ/mol}$). By OPM, a hexagonal columnar mesophase could be detected for perylene bisimide **PB1**.^{12c} For **PB2**, no liquid crystallinity was observed. Perylene bisimide **PB3** showed birefringent fernlike textures upon cooling from the isotropic melt. A clearing temperature of $185 \text{ }^\circ\text{C}$ ($\Delta H = 8.27 \text{ kJ/mol}$) was determined by means of DSC.

Characterization in Solution. The stacking behaviors of the four perylene bisimides were first studied by temperature-dependent UV-vis and CD measurements (the latter not for **PB1**) ($1 \times 10^{-5} \text{ M}$ in methylcyclohexane (MCH), see Figure 3). Upon cooling, a clear red shift was observed in the UV-vis measurements for all perylene bisimides, indicating the formation of J-type aggregates,^{12c} a process which was proven to be reversible. The melting temperature T_m (the transition temperature from stacked to molecularly dissolved species) increases in the order of **PB1**, $T_m = 43 \text{ }^\circ\text{C}$; **PB3**, $T_m = 45 \text{ }^\circ\text{C}$; **PB4**, $T_m = 55 \text{ }^\circ\text{C}$; and **PB2**, $T_m = 64 \text{ }^\circ\text{C}$. The fluorescence of perylene bisimides **PB1** and **PB2** (at an optical density of approximately 0.1) was completely quenched at room temperature, indicating the formation of stacked species (data not shown). At $80 \text{ }^\circ\text{C}$ the fluorescence of **PB1** was still largely quenched. UV-vis clearly revealed that no stacks are present at high temperatures. Therefore, the quenching is probably

caused by electron transfer from the tridodecyloxybenzyl substituents to the perylene moiety.^{12c} For perylene bisimide **PB2**, the fluorescence returned at elevated temperatures, whereas a CD effect was still present. This behavior is in agreement with the observed UV-vis with the high melting temperature obtained from CD and to similar perylene bisimide systems having the same urethane spacer. These data suggest strong binding of perylene molecules as a result of the formation of hydrogen-bonded dimers as earlier found for similar compounds.¹³ Probably, these hydrogen-bonded dimers, which are present at high temperatures, subsequently form larger stacks at room temperature. For **PB3** and **PB4**, the CD effect has already disappeared between $40 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$ and $50 \text{ }^\circ\text{C}$ and $60 \text{ }^\circ\text{C}$, respectively. This points out weaker stacking interactions as a result of less π - π stacking interactions, which is due to the presence of two single tails instead of two phenyl wedges with three tails.

The stacking behavior in methylcyclohexane (MCH) of the four different perylene bisimides was further investigated by concentration-dependent UV-vis measurements (from 10^{-3} M to 10^{-7} M). Perylene bisimide **PB1** showed a transition from aggregated state to monomeric species (Figure 4). At high concentrations J-type stacks are formed, whereas at low concentrations the spectrum was similar to the one in chloroform where no stacking takes place.^{12c} When the fraction of ag-

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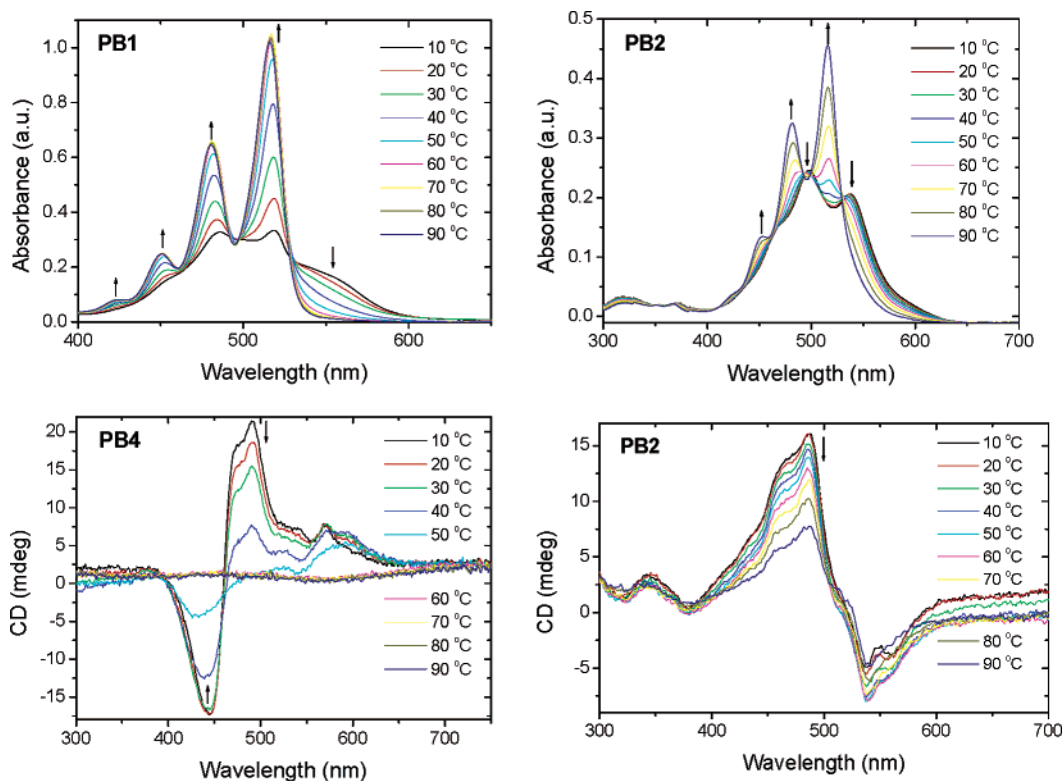


Figure 3. Temperature-dependent UV–vis measurements of perylene bisimide **PB1** (top left) and **PB2** (top right) and temperature-dependent CD measurements of perylene bisimide **PB2** (bottom right) and **PB4** (bottom left), all 1×10^{-5} M in MCH upon heating.

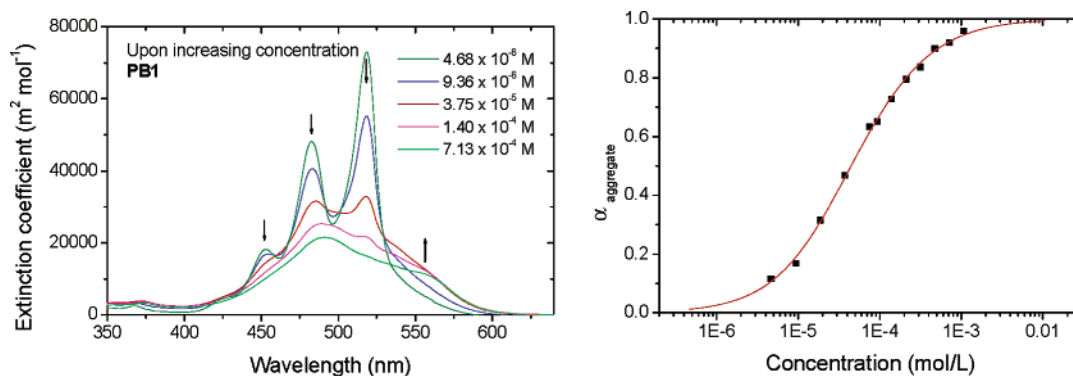


Figure 4. Concentration-dependent UV–vis measurements of perylene bisimide **PB1** in MCH (left) and a plot of the fraction of aggregates versus concentration and the fitting of these data to the isodesmic or equal K model (right).

gregates was plotted as a function of the concentration, the data could be fitted to the isodesmic or equal K model¹⁴ revealing a binding constant of $(13.0 \pm 0.5) \times 10^3 \text{ M}^{-1}$. In this model the binding constant for each binding step is the same. The binding constant of **PB1** is 3 orders of magnitude lower than that for a comparable perylene bisimide lacking the methylene spacer earlier reported by Würthner et al.^{12c} Thus, due to the presence of this small spacer, the rigidity of the molecule is drastically decreased resulting in a lower binding constant. For perylene bisimide **PB2**, a strong binding between the perylene molecules was observed over a broad concentration range (from 10^{-3} M to 10^{-7} M). Similar behavior was observed for circular dichroism (CD) measurements. The strong stacking can be attributed to the formation of hydrogen-bonded dimers similar to those found in the temperature-dependent measurements.¹³

For **PB3** and **PB4**, no concentration-dependent UV–vis and CD measurements were performed due to the low solubility of the molecules in MCH (highest possible concentration is approximately 10^{-5} M).¹⁵

From the four perylene bisimides, **PB1** was chosen to be investigated in more detail in the solid state and in the orthogonal self-assembly with **OPV**. It has shown to have promising stacking behavior in solution, whereas **PB2** has the difficulty of forming hydrogen-bonded dimers¹³ and **PB3** and **PB4** have a lower solubility.

Characterization in the Solid State. The aggregation behavior in the solid state of **PB1** was studied by tapping mode AFM. A highly intertwined network of stacked perylene bisimides was observed in the concentration range from 1×10^{-3} M to 5×10^{-5} M after drop-casting a MCH solution on

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(15) Temperature- and concentration-dependent UV–vis measurements showed that perylene bisimide **3** also stacks in water (data not shown).

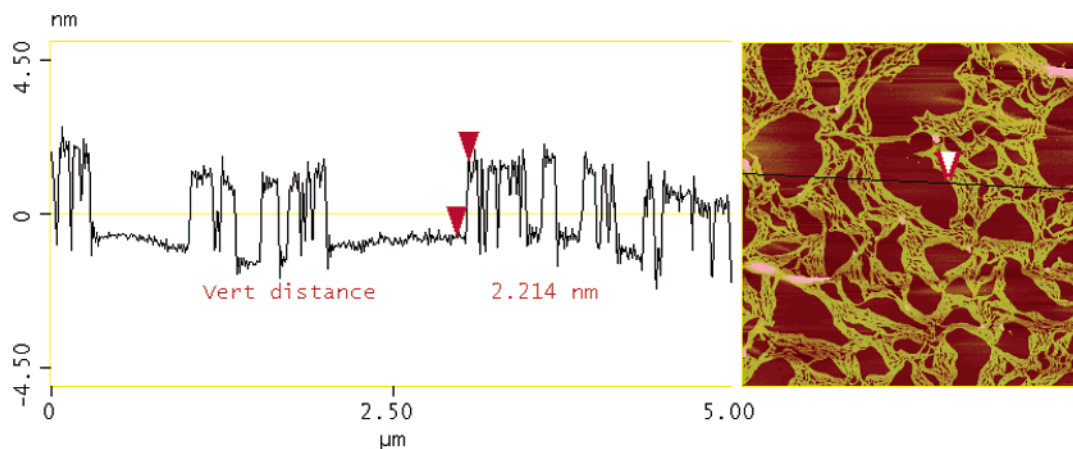


Figure 5. Tapping mode AFM height image of perylene bisimide **PB1** (right) and a cross section (left) after dropcasting on a MICA substrate from a 2.5×10^{-5} M solution in MCH.

a MICA substrate. In this concentration range, a single-layered network of perylene bisimides is formed with an occasional second, top layer.¹⁶ After drop-casting in 2.5×10^{-5} M MCH, a single-layered network is formed (Figure 5), and at lower concentrations (1×10^{-5} M to 5×10^{-6} M), the network structure is lost. At this concentration, only molecular dissolved species are present in solution (Figure 4). This concentration-dependent behavior is similar to that observed recently for OPV (Figure 1).¹⁰ On a glass substrate, the same network was detected. Typically, over the whole concentration range, a layer thickness of approximately 2.2 to 2.5 nm is observed (based on the height). According to CPK models, this distance corresponds to the length of the perylene bisimide (i.e., from chain end to chain end).

Orthogonal Self-Assembly of Perylene Bisimides with Oligo(*p*-phenylene vinylene)s. Since perylene bisimide **PB1** (n-type) and hydrogen-bonded oligo(*p*-phenylene vinylene) **OPV**^{10,17} (p-type) both form stacks in apolar solvents and nanometer-sized fibers in the solid state, mixed films can be promising for use in photovoltaic devices. For that reason, the stacking behavior in solution as well as in the solid state of a 1:1 mixture of **PB1** and **OPV** was studied. The compounds were mixed in methylcyclohexane (MCH), a solvent in which both form stacks, and, as comparison, in toluene in which both components are molecularly dissolved (for both solvents, a concentration of 10^{-5} M was used).

Temperature-dependent UV-vis, fluorescence (PL), and circular dichroism (CD) studies were carried out in MCH and toluene of a 1:1 mixture of **PB1** and **OPV**. In MCH, **PB1** and **OPV** form separate stacks at low temperatures, since the spectra are summations of the spectra of the two separate compounds (Figure 6). At elevated temperatures, the compounds are molecularly dissolved, since the spectra are similar to those found for the separate compounds at this temperature. Heating and cooling cycles show that the self-assembly process is reversible (data not shown). Based on the optical data, both compounds are, as expected, molecularly dissolved in toluene. From the UV-vis measurement of the mixture in MCH, a similar melting temperature ($T_m = 44$ °C) to that for **PB1** itself ($T_m = 43$ °C) was determined, indicating separate stacks of

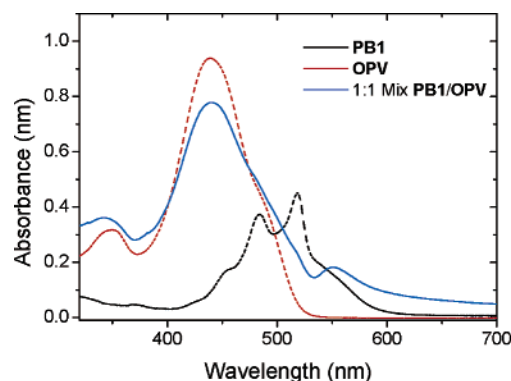


Figure 6. Comparison between UV-vis data of **OPV** and **PB1** in methylcyclohexane (MCH) and toluene at room temperature of separate and mixed samples at concentrations of 1×10^{-5} M.

perylene bisimides and OPVs (Figure 7). Moreover the CD spectrum is similar to that observed for **OPV** itself showing that there is no interaction between the oligo(*p*-phenylene vinylene) and the perylene bisimide molecules.

UV-vis measurements at room temperature of both spin-coated and drop-cast mixed films (**OPV/PB1**, 1:1) from MCH and toluene resulted in all cases in similar, broadened spectra with red-shifted peaks (data not shown). Upon annealing, less defined spectra were obtained. For the films made from MCH, a CD effect was observed unlike the films made from toluene where no CD effect was present. This points out that, in MCH, ordered stacks (of **OPV**) and, in toluene, no ordering are obtained. Interestingly, for both films the fluorescence of both **OPV** and perylene bisimide **PB1** was highly quenched. This indicates that electron transfer occurs from the OPV to the perylene bisimide (vide infra).

The origin of the quenching in the solid state was investigated in more detail by means of transient photoinduced absorption (femtosecond pump-pulse spectroscopy). Drop-cast films from 10^{-3} M solutions of MCH and toluene showed that in both cases charges had been created within 1 ps (Figure 8, left). When excited at 450 or 520 nm, where mainly **OPV** or perylene bisimide **PB1** absorbs, respectively, the OPV radical cation became visible at a wavelength of 1450 nm. This indicates in both films charge transfer is occurring from **OPV** to perylene bisimide **PB1**. The decay times are 400 and 600 ps for films drop-cast from MCH and toluene, respectively (Figure 8, right). Finally, both systems were tested in a photovoltaic

(16) See Supporting Information.

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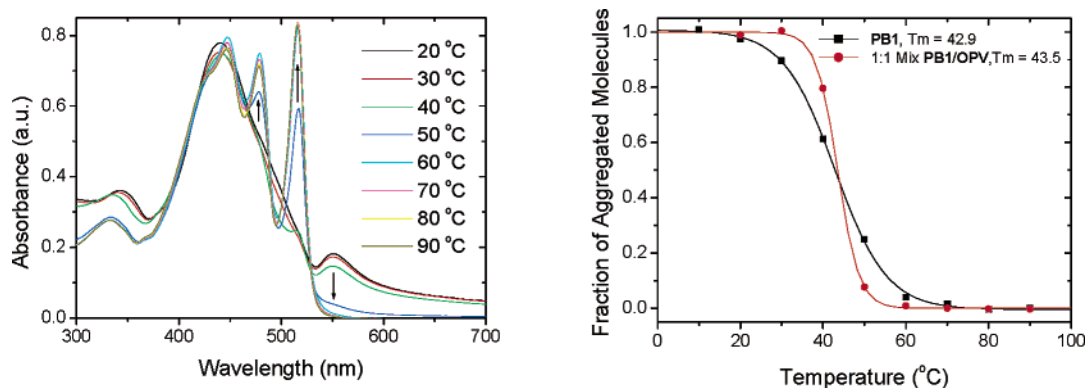


Figure 7. Temperature-dependent UV-vis measurements of a 1:1 mixture of perylene bisimide **PB1** and oligo(*p*-phenylene vinylene) **OPV** in methylcyclohexane (MCH) at 10^{-5} M upon heating (left) and the melting temperature of **PB1** solely in solution and as a mixture (right).

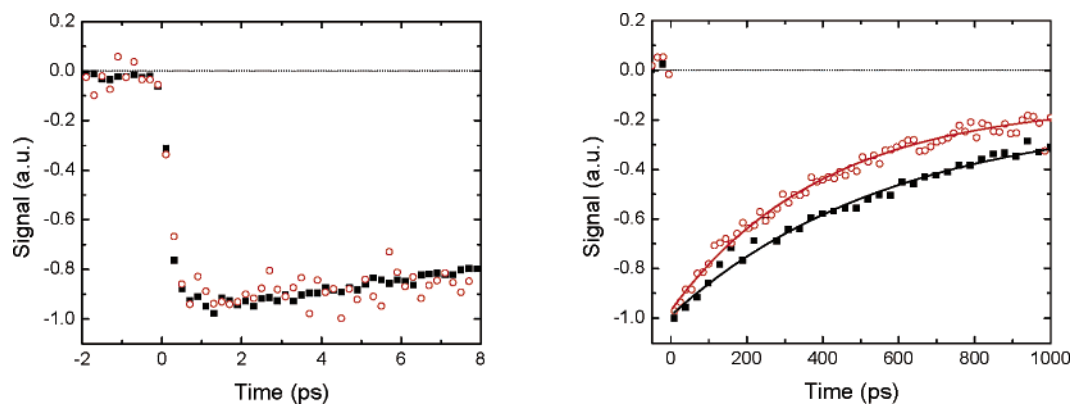


Figure 8. Formation of charges (left) and their decay and the corresponding exponential decay curve fit (right) of a 1:1 mixture of **OPV** and perylene bisimide **PB1** in films drop-cast from methylcyclohexane (○) and toluene (■) as recorded by femtosecond pump-pulse spectroscopy.

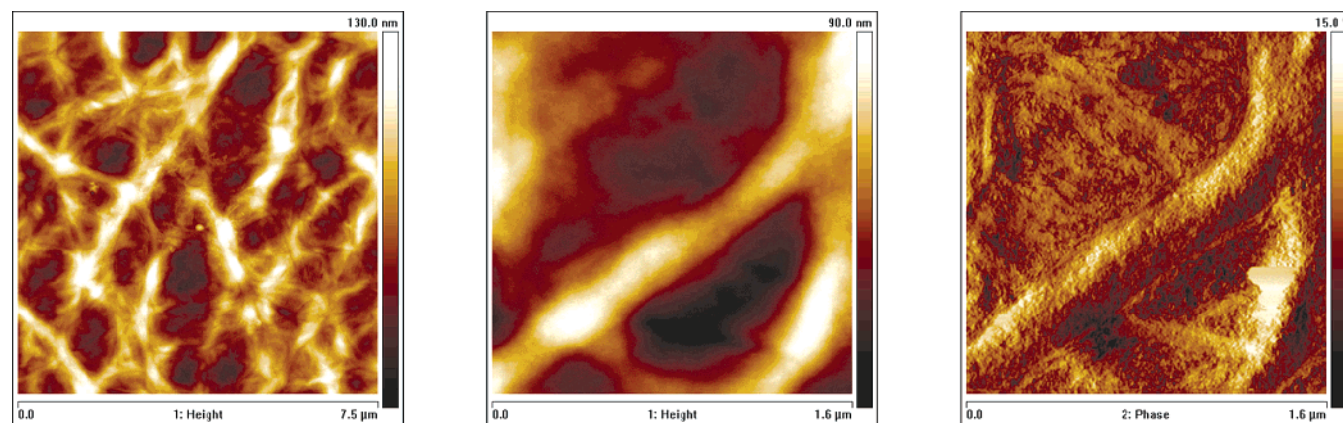


Figure 9. Tapping mode AFM height image of $7.5 \times 7.5 \mu\text{m}^2$ (left) and a height and phase image of $1.6 \times 1.6 \mu\text{m}^2$ (middle and right, respectively) of spin-coated films from MCH of a 1:1 mixture of **OPV** and perylene bisimide **PB1** of a glass/ITO/PEDOT:PSS/**OPV**:**PB1**/Al device.

glass/indium tin oxide(ITO)/polyethylenedioxythiophene: polystyrenesulfonate(PEDOT:PSS)/**OPV**:**PB1**/Al device. From films of 1:1 mixtures, a photovoltaic device was made (from MCH) with very low short-circuit currents of approximately $7 \mu\text{A}/\text{cm}^2$ and open-circuit voltages of approximately 1 V. Annealing did not improve the performance. Since from experience it is known that 4:1 mixtures of, respectively, n- and p-type material often result in improved devices,^{4,18} films were spin-coated from MCH and toluene in a 4:1 ratio of perylene bisimide **PB1** and **OPV**, respectively. This time, reproducible devices were obtained, but still very low short-circuit currents were measured: approximately $2 \mu\text{A}/\text{cm}^2$ and

$10 \mu\text{A}/\text{cm}^2$ for mixed films from MCH and toluene, respectively. Remarkably, although charges are created and ordered structures can be obtained in the solid state, efficient organic solar cells are not obtained. To obtain some insight in the poor solar cell performance, the films of the photovoltaic devices were investigated by tapping mode AFM. Height and phase images of spin-coated films from MCH revealed the presence of large bundles lying lateral at the surface (Figure 9). Films spin-coated from toluene were flatter but less ordered.¹⁶ Although the morphology in the films is different, preorganization in solution has hardly any effect on the charge formation and recombination. A reason for the poor efficiency in our solar cells could be that

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the active layer–electrode interface is not optimal, since the stacking direction of the assembly is parallel to the electrodes.

Conclusions

Supramolecular stacks of perylene bisimides have been obtained in apolar solution as demonstrated by concentration- and temperature-dependent absorption, circular dichroism, and fluorescence studies in methylcyclohexane (MCH). Furthermore these derivatives are capable of forming nanometer-sized fiberlike networks when drop-cast from MCH. By optical spectroscopy techniques, it was demonstrated that in MCH separate stacks of perylene bisimides and oligo(*p*-phenylene vinylene) (p-type) can be formed, whereas in toluene only molecularly dissolved species are present. In the solid state, charges were created in films deposited from MCH as well as from toluene. In films from MCH an ordered network of fibers was formed, whereas in films from toluene no ordering was observed. Bulk heterojunction solar cells of these mixed films show poor performance, which is probably due to the lateral orientation of the stacks on the surface. Therefore, for improving

the device characteristics, it seems essential to vertically align the supramolecular stacks in thin films.

Acknowledgment. We like to thank Jochem Langeveld for the synthesis of the amine derivative **3**, Martijn Wienk for the construction of the solar cell devices, Edwin Beckers for performing the photoinduced absorption measurements, and Pascal Jonkheijm for the AFM measurements. Henk Eding and Joost van Dongen are acknowledged for the elemental analysis and mass spectrometry.

Note Added after ASAP Publication: There were errors in Figure 1 and Scheme 1 in the version published on the Web July 13, 2004. Figure 1 and Scheme 1 are correct in the final Web version published on July 21, 2004 and in the print version.

Supporting Information Available: Additional experimental results (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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