Control of Film Morphology by Folding Hydrogen-Bonded Oligo(*p*-phenylenevinylene) Polymers in Solution

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ABSTRACT: The film morphology of π-conjugated oligomers has been controlled by self-assembly in solution. To this end supramolecular hydrogen-bonded systems of oligo(*p*-phenylenevinylene) (OPV) carrying ureido-*s*-triazine hydrogen-bonding groups are used. Neutron scattering experiments in dodecane solutions show that columnar stacks are formed. Films with thicknesses on the order of 100 nm are made that have a supramolecular organization resembling the organization present in solution. Uniform rodlike morphological domains range over several hundreds of nanometers as shown by atomic force microscopy. The rodlike morphology of the OPVs was also preserved when blended with a C_{60} derivative, producing stable photovoltaic devices.

Introduction

The performance characteristics of optoelectronic devices based on π-conjugated polymers, such as light-emitting diodes (LEDs),[1] field-effect transistors (FETs),[2] and photovoltaic cells (PVs),[3] are set by the proper choice of the chemical structure and the supramolecular organization in thin films.[4] Similar devices can also be constructed from small organic molecules, e.g., π-conjugated oligomers. The ability to vacuum evaporate these molecules often results in highly ordered crystalline films, and mobilities are generally 1 order of magnitude higher than those observed in solution processed materials because of the low amount of impurities and defects. However, especially for large area plastic electronics, solution processing is preferred since vacuum deposition techniques are more expensive.

Exciting results have been obtained in electronic devices based on polymers and small organic molecules; however, it remains a challenge to create materials that will give highly ordered films by less expensive means such as spin-coating or inkjet printing. Because of the viscosity of polymer solutions, π-conjugated polymers can be processed from solution and therefore offer low-cost manufacture. Processing conditions dictate the morphology and interchain interactions.[5] Moreover, small impurities in the polymer backbone can have a negative influence on the device performance. An attractive strategy would be applying the principles of supramolecular self-assembly to organize π-conjugated oligomers into well-defined supramolecular structures. The groups of Müllen and Friend reported the use of liquid crystalline molecules, hexabenzocoronenes and perylenebisimides, to control the film morphology in photovoltaic cells.[6]

Previously, we reported a supramolecular hydrogen-bonded random coil polymer consisting of oligo(*p*-phenylenevinylene) (OPV) carrying ureido-pyrimidinone as hydrogen-bonding groups.[7] These supramolecular π-conjugated polymers were successfully applied in photovoltaic devices.[8] Furthermore, we developed a similar hydrogen-bonded random-coil OPV system based on a different quadruple hydrogen-bonding system, i.e., the ureido-*s*-triazine unit.[9] This system folds supramolecularly in apolar solutions.[9] In this article, we describe how the thin-film morphology of such OPVs systems is controlled by aggregation in solution prior to spin-coating. The material is applied as an electron donor in photovoltaic devices using a well-known electron methanofullerene acceptor, PCBM (Scheme 1). A few literature examples show the application of oligo(*p*-phenylenevinylene)s and PCBM in photovoltaic devices; these films were either vacuum-deposited[10] or solution-processed.[8,11] Recently, the co-self-organization and orthogonal self-assembly of OPVs and perylenes (acceptor) into well-organized two-component systems in solution were reported; however, the photovoltaic devices based on these structures did not work.[12]

Results and Discussion

Aggregation in Solution. Previously, we observed that compound **1** (Scheme 1) is present as a random coiled polymer in chloroform (0.05 g L^{-1}); the shapes of the absorption and emission spectra are similar to that of the molecularly dissolved tetrameric OPVs (Figure 1).[9] In dodecane (0.05 g L^{-1}), **1** is present as so-called frustrated stacks.[9a] The absorption and emission exhibit a small but distinct red shift upon changing the solvent from chloroform to dodecane, indicative of $\pi-\pi$ interactions in this less polar solvent (Figure 1). A small Cotton effect was found in the circular dichroism spectrum of **1** dissolved in dodecane.[9a] Interestingly, concentrated toluene solutions (10 g L^{-1}) also reveal aggregated species similar as dodecane as concluded from the red-shifted UV spectrum (λ_{max} = 467 nm) and the emission maximum (λ_{max} = 560 nm) (Figure 1), whereas the dilute solutions show similar spectra as for chloroform.

To investigate the shape of the supramolecular assemblies formed by **1** in dodecane, SANS experiments were performed, covering a range of scattering vectors from 7×10^{-4} Å^{-1} < Q < 0.3 Å^{-1} (Figure 2). The results showed a broad region in which the intensity $I(Q)$ correlates with Q^{-1}. This linear dependence together with the appearance of a side maximum is representative for cylindrical aggregates. Excellent fits to the data were based on a model assuming an isotropic distribution of homogeneous rigid cylindrical structures, yielding columns

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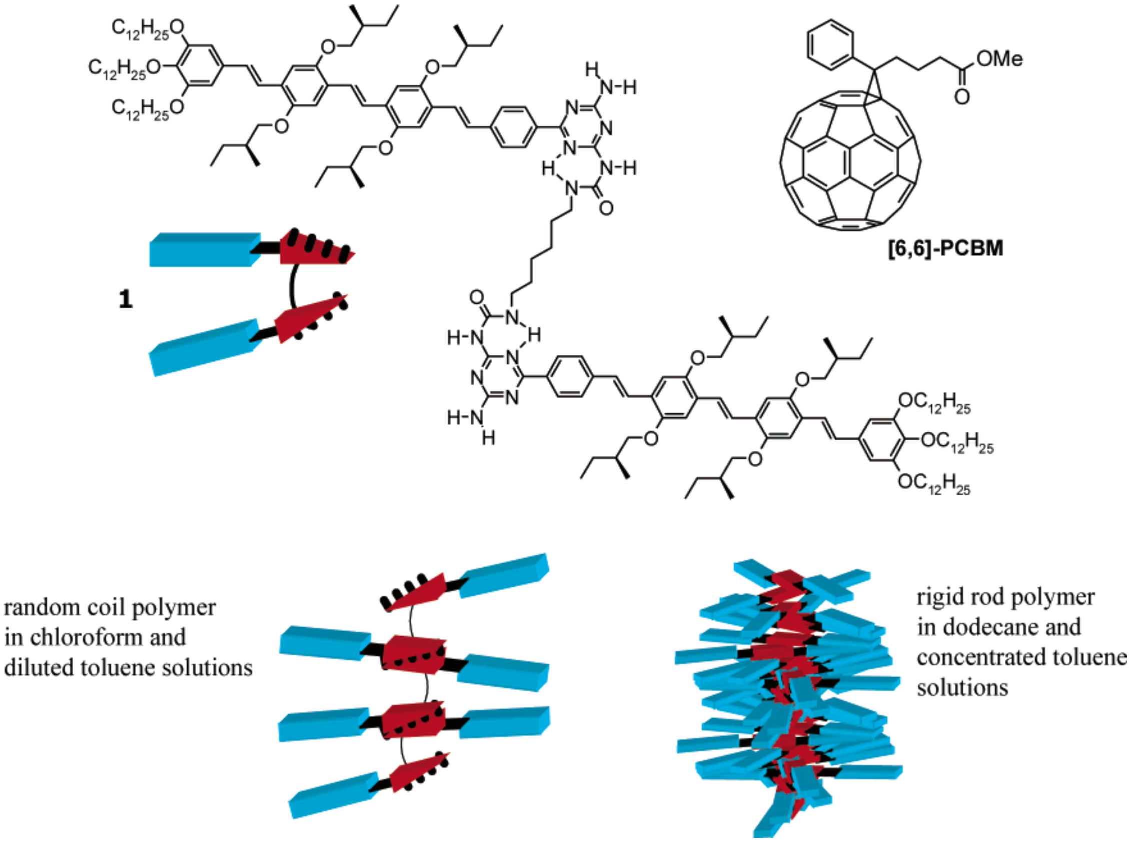
Scheme 1. Molecular Structures of 1 and PCBM[a]



[a] The blue blocks represent the oligo(*p*-phenylenevinylene) parts, and the red triangles represent the quadruple hydrogen-bonding ureido-*s*-triazine units. The self-assembly process of **1** into random coiled and rigid rod polymer is depicted. The random coiled polymer of **1** is present in chloroform and dilute toluene solutions. Folded rigid-rod polymer of **1** exists in dodecane and concentrated toluene solutions.

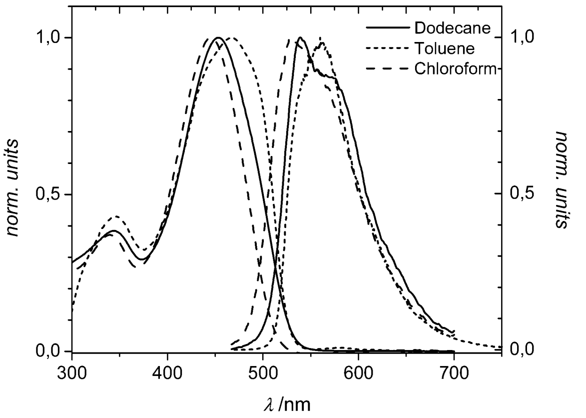


Figure 1. Normalized absorption and emission spectra of **1** in dodecane (0.05 g L^{-1}) (solid lines), chloroform (0.05 g L^{-1}) (dashed lines), and toluene (10 g L^{-1}) (short dashed lines) solutions at room temperature.

with lengths of ~180 nm and a diameter of about 4 nm (Figure 2). Remarkably, the diameter for columns of **1** is reduced with respect to the full oligomeric length which presumably indicates that the OPVs adopt a tilted orientation. The shape of these supramolecular structures is comparable to monofunctional ureido-*s*-triazine OPVs that lack the alkyl spacer.[8b]

Aggregation in Films. First, we have spin-cast different solutions of only **1** onto glass. The resulting films are fluorescent with an emission maximum at about $\lambda = 572$ nm when cast from toluene and dodecane, which is red-shifted compared to the solutions (Figure 3). The time-resolved emission measurements show comparable kinetics of the OPV emission at $\lambda = 650$ nm for the films ($\tau = 0.6$ and 2 ns).

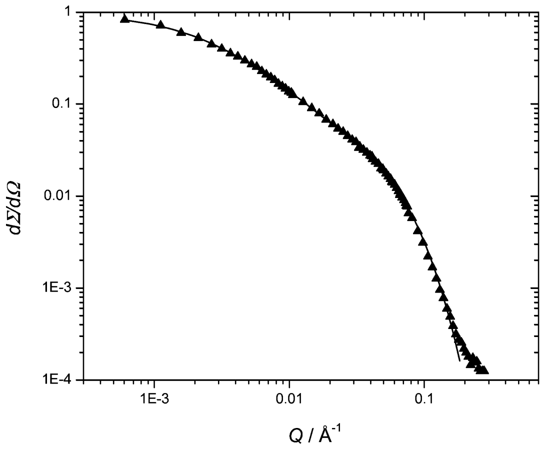


Figure 2. SANS data intensity decay data vs *Q* for 1 in d_{26}-dodecane and fit according to cylindrical form factor.

TM-AFM images showed that the spin-cast films from toluene are smooth with no pinholes or defects (Figure 4a). The supramolecular polymer films have a rms roughness of 1.4 nm and peak-to-peak variations in height of less than 10 nm. Phase imaging[13] (Figure 4b) reveals elongated rodlike textures having a constant width of about 4−5 nm as deduced from the line scan. The lengths of the rods are in agreement with the SANS data for dodecane solutions. This behavior shows that in concentrated toluene presumably the same type of rod is formed as in dodecane. The rods form ordered domains of on average 200 nm in size. In contrast, the films spun from chloroform did not reveal specific textures and were less smooth. Hence, the (lack of) supramolecular architectures present in solution is preserved in the film after spin-coating.

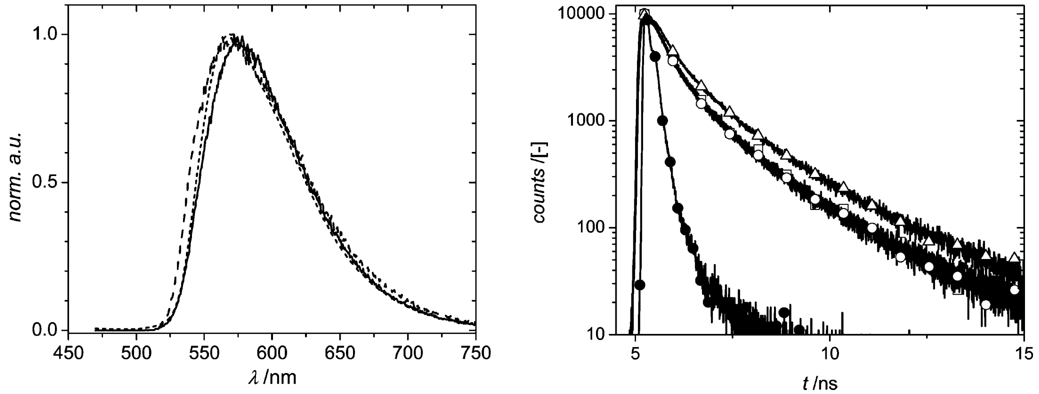


Figure 3. Emission spectra (left) of films **1** spin-cast from dodecane (solid line), toluene (short dashed line), and chloroform (dashed line). Emission decay curves at 650 nm of films of **1** spin-cast from dodecane (squares), toluene (open circles), and chloroform (triangle) and of films of **1**/PCBM spin-cast from toluene (closed circles).

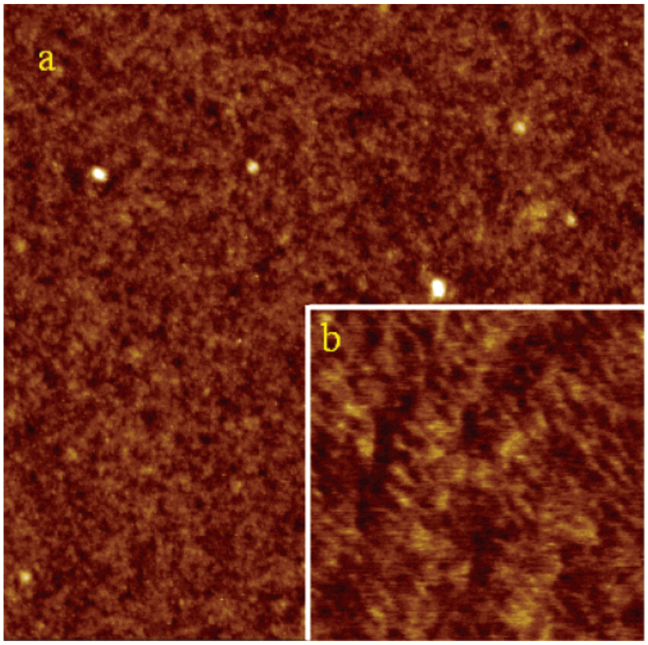


Figure 4. (a) Height image (a) 10 × 10 μm^2, *z*-scale 10 nm and (b) close-up phase image, 200 × 200 nm^2, *z*-scale of spin-cast films of **1** from toluene onto glass.

Aggregation in Mixed Films. The folded OPVs in combination with a C_{60} derivative, PCBM (Scheme 1), have been applied in photovoltaic cells in an attempt to create films having a controlled morphology. In such composite films, OPV acts as electron donor and PCBM as electron acceptor after absorption of light, and as a result charge carriers are created at the interface of the two materials.[8,14] Since PCBM is poorly soluble in chloroform and dodecane, toluene was used as a solvent because it allows **1** to form rigid cylindrical aggregates.

The morphology of films of **1** spin-cast from toluene on the device substrate, i.e., ITO/PEDOT:PSS, revealed also very smooth surfaces with a fibrillar network consisting of typical features of about 5−6 nm wide (data not shown), in agreement with the morphology obtained on films of **1** spin-cast on glass (Figure 4). Also, pure PCBM films appear as smooth films (data not shown). The hydrophilicity of the surface has negligible influence on the supramolecular organization in thick films since the fibrillar structures are formed in solution. This contrasts with our earlier observations that the deposition process depends highly on the nature of the substrate.[9] However, in that case we reported the controlled deposition from solution to surfaces of individual single supramolecular structures based on monofunctional ureido-*s*-triazine OPVs instead of making 100 nm thick films.

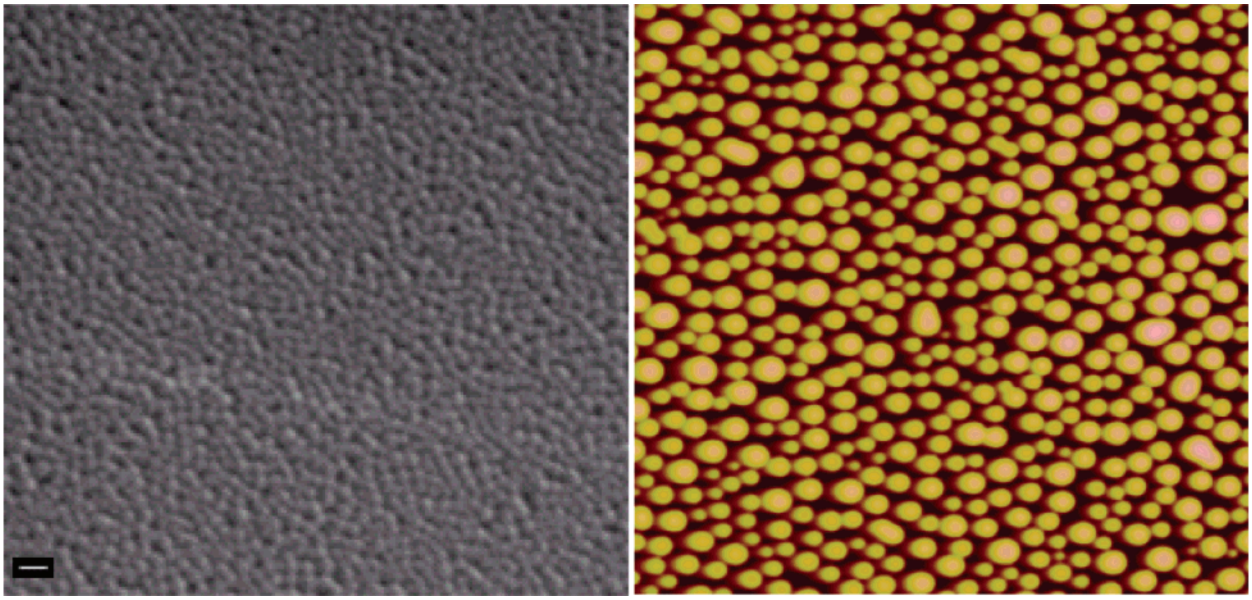


Figure 5. SEM picture (left, bar represents 1 μm) and TM-AFM height image (right, z-scale is 90 nm, 10 × 10 μm^2) on blend films of **1** and PCBM spin-cast from toluene.

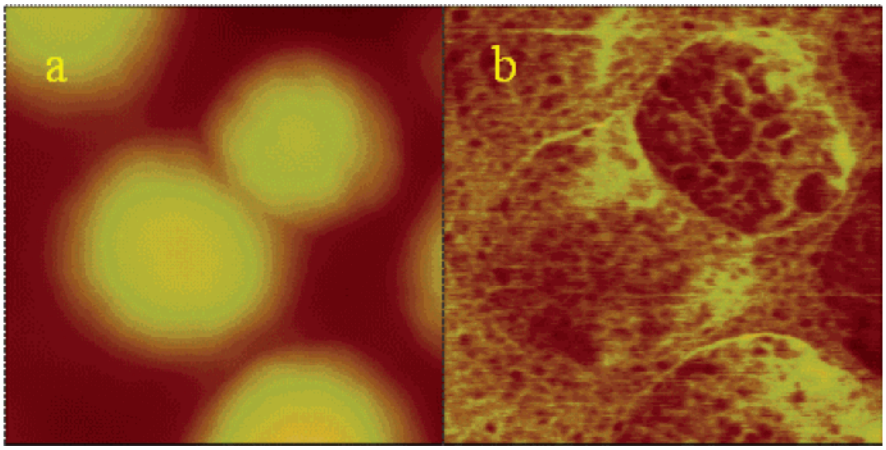


Figure 6. TM-AFM images (760 × 760 nm^2) of films of blends of **1** and PCBM spin-cast from toluene with in (a) the topography (z-scale is 100 nm) and in (b) the simultaneously recorded phase image at a set point ratio of 0.7.

Now, we examine the film morphology of blends of **1** and PCBM (1:4 ratio by weight) spin-cast from toluene by TM-AFM, scanning electron microscopy (SEM), and optical spectroscopy. Surprisingly, these composite films gave a very rough surface with a rms roughness of 24 nm and a peak-to-peak distance of 88 nm (Figure 5). The globular structures observed on the blend films are ranging from tens to several hundreds of nanometers in diameter and are spread over the surface. SEM observations (Figure 5) also identified circularly shaped structures with a variety of dimensions and distributions in agreement with AFM.[15] Interestingly, related blends of poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) (MDMO−PPV) and PCBM can also lead to coarse demixing exhibiting similar globular structures, rich in PCBM, when spin-coated from toluene.[16,17] The phase image (Figure 6b) showed brighter and darker regions which can be attributed to regions with different compositions.[18] The semicontinuous network that is observed, throughout the surface, resembles the rods as seen in the AFM image in Figure 4. However, areas that lead to a phase shift (bright) appear less on the globules, whereas a more homogeneous closed network is observed in the areas between the globules. Apparently, the areas between the globules are **1**-rich, while the globules contain more PCBM. It should be noted, however, that these nanoscale structures, although of the same dimensions in both diameter and length, are qualitatively different from the structures observed in pure films of **1**; they are further apart and less aligned in domains. The existence of the supramolecular network of **1** in the blend films is supported by OPV fluorescence quenching despite the coarse demixing. Time-resolved PL measurements on a blend of **1** and PCBM showed an accelerated decay of the OPV emission at $\lambda = 650$ nm when excited at $\lambda = 488$ nm compared to films cast from pure **1**, showing that the donor and acceptor networks are in close contact (Figure 3b). Therefore, films of **1** and PCBM with its complicated phase behavior are used to fabricate photovoltaic devices.

Photovoltaic Devices. Photovoltaic devices were constructed by evaporating aluminum top electrodes on the films spin-cast from toluene. The devices were characterized in the dark and under white-light illumination of a halogen lamp (100 mW/cm^2, 400−800 nm). Figure 7a shows the semilogarithmic plot of the J/V curves of a typical device spun from toluene. The curves are completely reversible, and the device shows excellent diode behavior with a rectification ratio of ~10^3 at ±2 V, revealing little or no shunts. Under white-light illumination, a short circuit current of 0.64 mA/cm^2 and an open circuit voltage of 0.79 V was measured. The fill factor is 0.48 (defined as FF $= J_{\max}V_{\max}/J_{sc}V_{oc}$, with $V_{\max}$ and $J_{\max}$ as the voltage and current at maximal power). The incident photon-to-current conversion efficiency (IPCE, Figure 7b) reached a maximum of 12% at $\lambda = 430$ nm, which is lower when compared to blends (1:4) of MDMO−PPV and PCBM that show 50% at $\lambda = 500$ nm. This reduced performance is most likely the consequence of the large phase separation of donor and acceptor phases.[19] The overall power-conversion efficiency (η) is 0.25%.[20] Although difficult to compare, this efficiency is higher than reported for oligo(*p*-phenylenvinylene)s[8,10,11] but lower than those for poly(*p*-phenylenevinylene)s.[3]

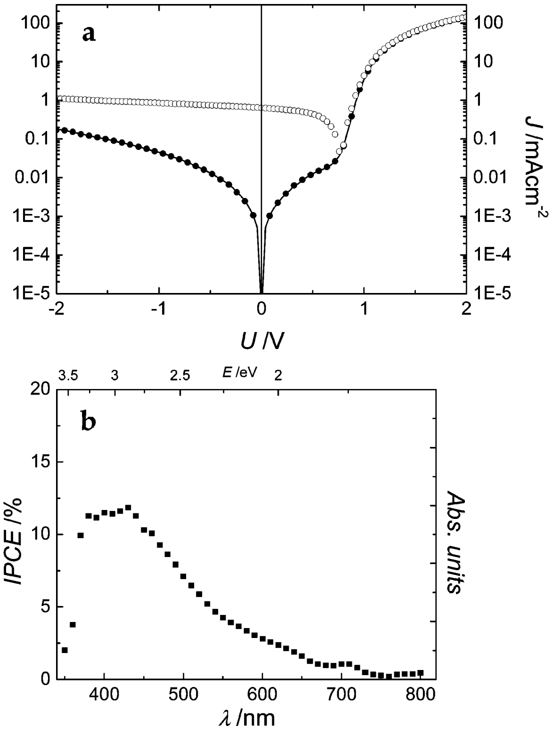


Figure 7. Photovoltaic properties of an ITO/PEDOT-PSS/**1**:PCBM/LiF/Al device with an active area of 1 cm^2 spin-coated from toluene: (a) semilogarithmic plot of current vs voltage in the dark (closed) and under illumination (open); (b) corresponding IPCE curve.

Conclusions

We have presented a strategy in which the film morphology in photovoltaic devices is controlled by self-assembly of π-conjugated oligomers in solution. In apolar solvents, such as dodecane and concentrated toluene, cylindrical aggregates of **1** are present, whereas in chloroform a random coiled polymer of **1** is present. The soluble supramolecular structures of **1** can be processed by spin-casting to give films of self-assembled columnar structures featuring ordered domains. In contrast, films spin-cast from chloroform showed an unstructured film morphology. The uniform rodlike domains of **1** were preserved when blended with PCBM, producing photovoltaic devices despite considerable phase separation.

The concept of controlling the morphology in the solid state by self-assembly in solution, in principle applicable to all kinds of π-conjugated oligomers, is an attractive strategy to improve the performance of devices. However, the homogeneous alignment of the supramolecular organized domains in the micrometer regime is still needed. This is not only an appealing challenge in the field of supramolecular chemistry but also in the area of materials science.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For a review: (a) Braun, D. *Mater. Today* **2002**, *5*, 32. (b) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Brédas, J. L.; Löglund, M.; Salaneck, W. R. *Nature (London)* **1999**, *397*, 121.

(2) For a review: Dimitrakopolous, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99.

(3) (a) Hoppe, H.; Sariciftci, N. S. *J. Mater. Res.* **2004**, *19*, 1924. (b) Coakley, K. M.; McGehee, M. D. *Chem. Mater.* **2004**, *16*, 4533.

(4) For a recent review: Hoeben, F. J. M.; Jonkheijm, P.; Meijer, E. W.; Schenning, A. P. H. J. *Chem. Rev.* **2005**, *105*, 1491−1546.

(5) See for example: (a) Schwartz, B. *Annu. Rev. Phys. Chem.* **2003**, *54*, 141. (b) Nguyen, T.-Q.; Yee, R. Y.; Schwartz, B. J. *J. Photochem. Photobiol. A* **2001**, *144*, 21. (c) Satrijo, A.; Swager, T. M. *Macromolecules* **2005**, *38*, 4054.

(6) Schmidt-Mende, L.; Fechtenkotter, A.; Müllen, K.; Moons, E.; Friend, R. H.; MacKenzie, J. D. *Science* **2001**, *293*, 1119−22.

(7) El-ghayoury, A.; Schenning, A. P. H. J.; Meijer, E. W. *Chem. Commun.* **2000**, 1969.

(8) El-ghayoury, A.; Schenning, A. P. H. J.; Hal, P. A. v.; Duren, J. K. J. v.; Janssen, R. A. J.; Meijer, E. W. *Angew. Chem., Int. Ed.* **2001**, *40*, 3660.

(9) (a) Schenning, A. P. H. J.; Jonkheijm, P.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2001**, *123*, 409. (b) Jonkheijm, P.; Hoeben, F. J. M.; Kleppinger, R.; Herrikhuyzen, J. v.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2003**, *125*, 15941.

(10) (a) Ouali, L.; Krasnikov, V. V.; Stalmach, U.; Hadziioannou, G. *Adv. Mater.* **1999**, *11*, 1515. (b) Melzer, C.; Krasnikov, V. V.; Hadziioannou, G. *J. Polym. Sci., Part B* **2003**, *41*, 2665.

(11) (a) Nierengarten, J.-F.; Eckert, J.-F.; Nicoud, J.-F.; Ouali, L.; Krasnikov, V. V.; Hadziioannou, G. *Chem. Commun.* **1999**, 617. (b) Peeters, E.; Hal, P. A. v.; Knol, J.; Brabec, C.; Sariciftci, N. S.; Hummelen, J. C.; Janssen, R. A. J. *J. Phys. Chem. B* **2000**, *104*, 10174. (c) Schenning, A. P. H. J.; Fransen, M.; Duren, J. K. J. v.; Hal, P. A. v.; Janssen, R. A. J.; Meijer, E. W. *Macromol. Rapid Commun.* **2002**, *23*, 271.

(12) (a) Würthner, F.; Chen, Z.; Hoeben, F. J. M.; Osswald, P.; You, C.-C.; Jonkheijm, P.; Herrikhuyzen, J. v.; Schenning, A. P. H. J.; Schoot, P. P. A. M. v. d.; Meijer, E. W.; Beckers, E. H. A.; Meskers, S. C. J.; Janssen, R. A. J. *J. Am. Chem. Soc.* **2004**, *126*, 10611. (b) Herrikhuyzen, J. v.; Syamakumari, A.; Schenning, A. P. H. J.; Meijer, E. W. *J. Am. Chem. Soc.* **2004**, *126*, 10021.

(13) Kemerink, M.; van Duren, J. K. J.; Jonkheijm, P.; Pasveer, W. F.; Koenraad, P. M.; Janssen, R. A. J.; Salemink, H. W. M.; Wolter, J. H. *Nano Lett.* **2003**, *3*, 1191.

(14) Spin-coating a 1:2 (wt %) blend of **1**:PCBM from toluene resulting in device characteristics that are typically $J_{SC} = 0.11$ mA cm^{-2}, $V_{OC} = 0.50$ V, and $FF = 0.35$.

(15) To investigate the morphology in more detail, films were spin-cast from chlorobenzene and *o*-xylene. These films have a much smoother surface; the rms roughness decreased to 15 and 9 nm respectively, with a peak-to-peak distance of 73 and 48 nm, respectively (see Supporting Information). However, the semicontinuous fibrillar network was not observed on larger AFM magnifications. Apparently, polarity and boiling point affect both the supramolecular organization in solution and the phase separation in the solid state: toluene (111 °C, $\epsilon = 2.4$), chlorobenzene (132 °C, $\epsilon = 5.6$), and *o*-xylene (140 °C, $\epsilon = 2.6$).

(16) Martens, T.; D'Haen, J.; Munters, T.; Beelen, Z.; Goris, L.; Manca, J.; D'Olieslaeger, M.; Vanderzande, D.; De Schepper, L.; Andriessen, R. *Synth. Met.* **2003**, *138*, 243.

(17) Yang, X.; Duren, J. K. J. v.; Janssen, R. A. J.; Michels, M. A. J.; Loos, J. *Macromolecules* **2004**, *37*, 2151−8.

(18) AFM images at different amplitude set points are shown in the Supporting Information.

(19) (a) Shaheen, S. E.; Brabec, C. J.; Padinger, F.; Fromherz, T.; Hummelen, J. C.; Sariciftci, N. S. *Appl. Phys. Lett.* **2001**, *78*, 841. (b) Wienk, M. M.; Kroon, J. M.; Verhees, W. J. H.; Knol, J.; Hummelen, J. C.; Van Hal, P. A.; Janssen, R. A. J. *Angew. Chem., Int. Ed.* **2003**, *42*, 3371.

(20) The differences in morphology induced by the choice of processing solvent influence the performance of the photovoltaic cells. Whereas cells spun from *o*-xylene, which lack the supramolecular network of **1**, show comparable V_{OC} (0.84 V), and the J_{SC} drops significantly to 0.47 mA cm^{-2} (see Supporting Information). This is reflected in the decline of the FF to 0.28, resulting in $\eta = 0.06\%$.

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