Novel Anthracene-Core Molecule for the Development of Efficient PCBM-Based Solar Cells

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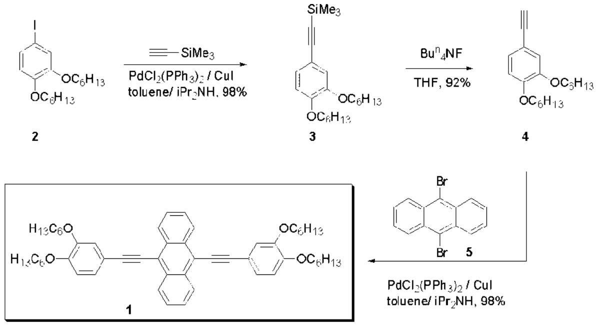
There has been a great deal of interest in the field of photovoltaic devices for organic semiconductors such as π-conjugated molecules[1–3] because of their solution processability, their compatibility with plastic substrates, and use in low temperature processes such as, for example, roll-to-roll and ink-jet manufacturing technologies. The principle of bulk heterojunction solar cells[4–10] based on the spontaneous phase separation between donor and acceptor materials has become popular, leading to the development of high-performance devices. Recently, a power conversion efficiency (PCE) of up to 5.2% has been reached by using a dispersion of [6,6]-phenyl C_{61}-butyric acid methyl ester (PCBM) as the acceptor material within regioregular poly(3-hexylthiophene).[6]

Behind the polymeric heterojunction solar cells, now it is widely accepted that also low-dimensional highly π-conjugated molecular systems can play an important role in the development of organic solar cells.[11–15] However, for photovoltaic devices soluble molecules are needed because they must be blended with a complementary acceptor to achieve a bulk heterojunction.[16] One possibility to make conjugated molecules soluble is to introduce flexible side chains as reported here.

Scheme 1



In continuation of our efforts[17] on the study of synthesis and photoresponsive properties of diarylanthracenes we report in this article the preparation of the novel compound **1** containing hexyloxy groups in the benzene rings (Scheme 1) and its use as donor material for the realization of PCBM based heterojunction solar cells. The hexyloxy groups have been chosen both to increase the solubility in the most common organic solvents and to enhance the dispersion of the molecule with PCBM electron acceptor. We report here how a photovoltaic cell using such a blend is able to reach a PCE of 1.12%.

The synthesis of compound **1** outlined in Scheme 1 is based on the Sonogashira[18] reaction starting from the known dihexyloxyiodobenzene **2**[19] (see Supporting Information). The structure analysis of all new compounds was based on extensive NMR investigation.

The absorption spectrum for the film of neat **1** shows four peaks centered at 333, 441, 464, and 498 nm, respectively (Figure 1a). When films of **1**/PCBM blends were examined (1:0.88, 1:1.17, 1:1.46 molar weight ratios), the peak at 333 nm increases its intensity with increasing the PCBM content as a result of the overlapping of the absorption peak of compound **1** and the absorption peak of PCBM (339 nm; inset of Figure 1a). Moreover when the PCBM was added the onset of absorption of the neat molecule at 365 nm shows a red shift, and a modification of the fine structure was observed, this effect being dependent on the **1**/PCBM weigth ratio. In particular, for a 1:1.46 ratio the fine structure was lost (Figure 1b); this finding is generally attributed to the formation of an amorphous phase.[9] Moreover the tail at about 630 nm was more evident than in the other blends. This

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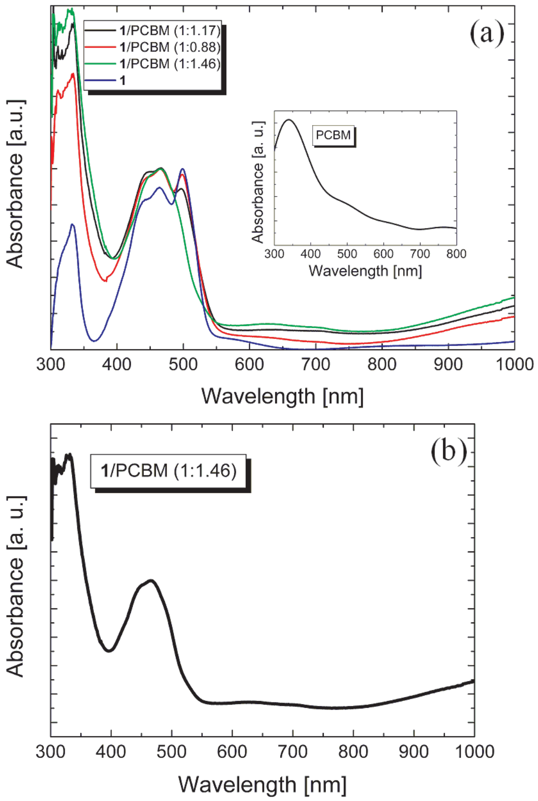

Figure 1. (a) UV–vis spectra of **1** and **1**/PCBM films with different weight ratios. The inset shows the UV–vis spectrum of the PCBM film. (b) UV–vis spectrum of **1**/PCBM film with 1:1.46 weight ratio.

feature attributed to the PCBM phase[20] indicates presumably areas of increased PCBM concentration due to its aggregation. These results indicate a difference in **1**/PCBM dispersion in a bulk heterojunction thin film.

To support this hypothesis, scanning electron microscopy (SEM) analysis of thin films consisting of the neat molecule and the blends have been reported in Figure 2. The film **1** consists of grains (Figure 2a) that appear to have many ridges and gaps (inset of Figure 2a). Whereas films containing 1:0.88 and 1:1.17 weight ratios are homogeneous and morphologically similar to the neat molecule (Figure 2b,c), the 1:1.46 blend (Figure 2d) shows a network of isolated crystallites dispersed in an amorphous matrix (inset of Figure 2d).

Because bulk heterojunction organic photovoltaic performance is known to be a strong function of donor/acceptor ratio,[6,21] a series of devices were fabricated using the **1**/PCBM blends reported above.

The photovoltaic properties were tested through a device fabricated with the structure of indium tin oxide/poly(3,4-ethylenedioxythiophene/poly(styrene sulfonate)/active layer/LiF/Al under a halogen tungsten lamp with an intensity of 41 mW/cm^2 (see Supporting Information).

Figure 3 shows the current density–voltage characteristics for the prepared devices; the results are summarized in Table 1. A typical current density–voltage curve of the organic solar

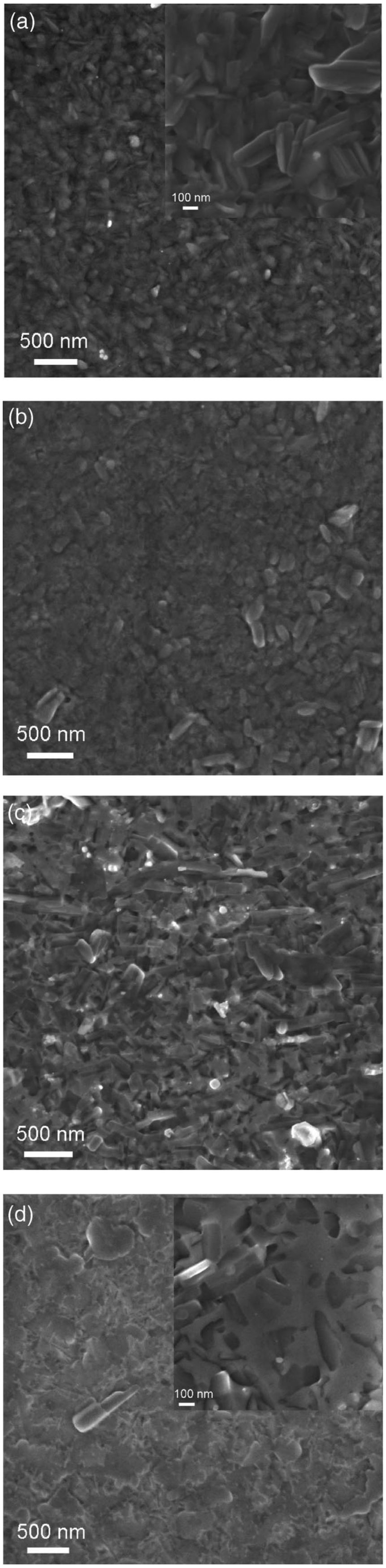

Figure 2. SEM images of (a) **1** and **1**/PCBM with different weight ratios: (b) 1:0.88, (c) 1:1.17, and (d) 1:1.46. The insets show a higher magnification views of parts a and d.

cells in the dark reported as the inset of Figure 3 shows a good quality of the diode. A short-circuit current density of

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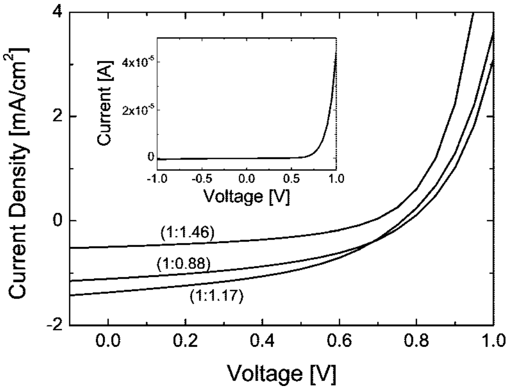

Figure 3. Current density–voltage curves (under illumination) of the organic solar cells based on **1**/PCBM films with different weight ratios. The inset shows a typical current density–voltage curve of the organic solar cells in the dark.

Table 1. Solar Cell Characteristics: Open-Circuit Voltage (V_{oc}), Short-Circuit Current Density (J_{sc}), Fill Factor (FF), and PCE (η) for the Prepared Films

1/PCBM	V_{OC} [mV]	J_{SC} [mA/cm^2]	FF	η [%] ± 0.05
1:0.88	780	1.109	0.44	0.92
1:1.17	762	1.37	0.44	1.12
1:1.46	687	0.556	0.44	0.40

1.37 mA/cm,^{2} an open-circuit voltage of 762 mV, and a fill factor of 0.44 result for the 1:1.17 blend in a PCE of 1.12%.

This value of PCE is encouraging if compared with those recently reported for small molecule based bulk heterojunction solar cells: 0.01,[22] 0.8,[23] and 1%.[24] It should be mentioned that higher efficiencies have been obtained with some of these materials when used in bilayer cells (i.e., 1.17[25] and 1.85%[26]). Attempts to use compound **1** in bilayer cells as well as work to modify the molecular architecture to extend the absorption spectrum of the donor toward longer wavelengths are ongoing.

In summary, the synthesis of a novel diarylanthracene bearing two dihexyloxysubstituted benzene rings has been reported, and the influence as donor material on the solar cell performance has been investigated. The presence of hexyloxy chains in the molecule imparts a high solubility in the most common organic solvents and improves its dispersion in PCBM for the preparation of bulk heterojunctions solar cells. Devices fabricated with this new compound exhibit a PCE of up to 1.12%.

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Supporting Information Available: Experimental details of synthesis and characterization of compounds **1**, **3**, and **4** and solar cell fabrication (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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