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Helical Perylene Polymers for Application in Photovoltaic Devices

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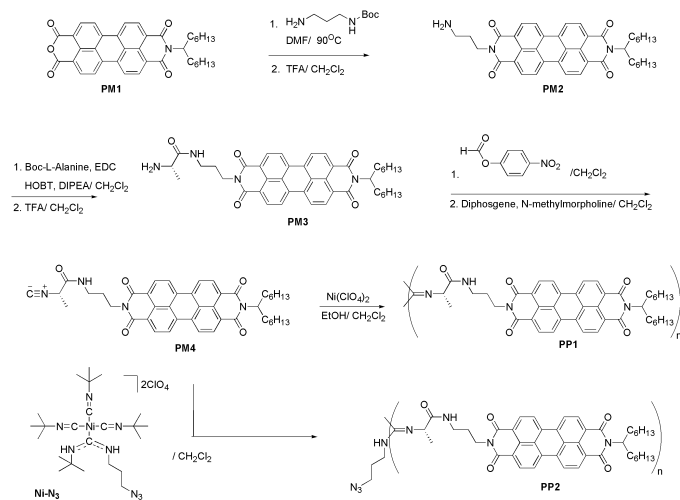
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INTRODUCTION

Application of dyes in optical materials requires high thermal and photochemical stability of these compounds. Perylenes possess these features and combine them with absorption in the visible part of the spectrum, high fluorescence quantum yields and high electron affinities.^{1,2} High electron mobilities have been found in perylene crystals³ and for this reason perylenes are very promising chromophores for application in organic solar cells, although the energy conversion efficiency (η) of perylene-based solar cells so far has remained low. Increasing the order in the arrangement of perylenes is expected to enhance this efficiency. As a continuation of previous studies on perylene functionalized polyisocyanides⁴ we present here the synthesis of more soluble analogues in which the perylene units are well-organized in four stacks around the polymer backbone. The performance of these polymers was tested in an organic solar cell.

RESULTS AND DISCUSSION

Synthesis and Characterization. Scheme 1 shows the synthetic route to perylene polymers **PP1** and **PP2**. Perylene monoanhydride was reacted with mono-Boc-1,3 diaminopropane and after deprotection of the product with trifluoroacetic acid (TFA) **PM2** was obtained. The amine functionalized perylene was then coupled to boc-L-alanine using (3-dimethylamino-propyl)-ethyl-carbodiimide (EDC) and hydroxybenzotriazol (HOBT) as coupling reagents. **PM3** was obtained after removal of the boc-group with TFA.



Scheme 1. Synthetic route to the perylene functionalized polyisocyanides **PP1** and **PP2**.

Formylation of **PM3** using the *p*-nitrophenol ester of formic acid, followed by dehydration of the formamide product with diphosgene and *N*-methylmorpholine, yielded isocyanide **PM4**. Polymer **PP1** was finally obtained by reacting this monomer with nickel perchlorate. By using Ni-N_3 as the initiator complex, **PP2** was obtained, which has an azide end-

functionality. This opens the possibility to functionalize the end of the polymer at a later stage, using "click"-chemistry.

During polymerization of isocyanides derived from alanine, a 4₁-helix is formed in which the (n+4)th repeat unit is placed above the nth repeat unit (see the schematic drawing in Figure 1a) at approximately 4.2 Å distance⁵. As can be expected when the alanine units are equipped with chromophores⁶, polymerization of **PM4** was accompanied by a color change of the reaction mixture from yellow to red, which is indicative for exciton coupling between the perylenes in the side-chains (Figure 1b). This exciton coupling is also reflected in the absorption, fluorescence and circular dichroism (CD)-spectra of the polymer in chloroform (see Figure 1c). Compared to the monomer, the absorption spectrum of the polymer is broadened and has a lower intensity. The broadening can be interpreted as a combination of a blue and red shift. Whereas the blue shift of the spectrum can be explained by face-to-face interactions between the perylenes within the stacks, the red shift is probably caused by interactions between different perylene stacks within one helix and by slightly off-set face-to-face orientations. The fluorescence spectrum of the polymer (excitation at 492 nm) reveals a broad, structureless band at 608 nm with a quantum yield of 5%, as compared to the emissions for the monomer at 535 and 575 nm. The appearance of such a large shift in emission unaccompanied by a similar shift in absorption suggests that excimer-like species are being formed. The CD-spectrum shows Cotton effects in the absorption region of the perylene, whereas no CD-signal is observed for the monomer. Figure 1d shows an AFM picture of **PP1** spin-coated from a chloroform solution on a mica surface. Analysis of the AFM pictures gave a value of the average length of 261 nm corresponding to an M_n of 1.6 · 10⁶.

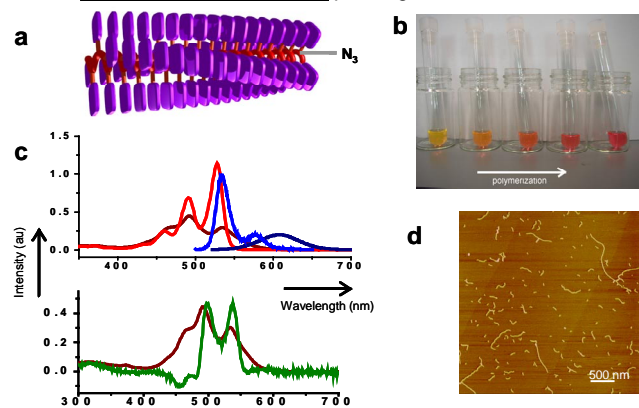


Figure 1. a) Schematic representation of polymer **PP2**. b) Color changes observed during polymerization of **PM4**. c) Upper graph: absorption (—) and fluorescence (—) spectra of **PP2** compared to absorption (—) and fluorescence (—) characteristics of **PM4** (—); Lower graph: CD (—) and absorption (—) spectra of **PP2**. d) AFM image of a diluted solution of **PP1** spin-coated on mica.

Photovoltaics. Because of the high ordering of the perylene chromophores, polymers **PP1** and **PP2** are very interesting acceptor (*n*-type) materials for applications in photovoltaic cells. For such devices it is expected that ordering of the perylenes in well-defined arrays facilitates efficient exciton transport from the acceptor (perylene) to the donor (e.g. polythiophene) site, resulting in a more efficient charge separation. More importantly, it is expected that the perylene arrays create an easier pathway for the electrons to reach the electrode, thereby improving the photovoltaic yield.

Solutions of perylene functionalized polyisocyanide **PP2** (7mg/ml) in chloroform were mixed in different weight ratios with chloroform solutions of regioregular poly(3-hexylthiophene) **PT** (7mg/ml) as a donor material. The polymer mixtures were spin cast at different rotation speeds (1500, 2500 and 4000 rpm) on a glass plate equipped with transparent front electrodes of indium tin oxide (ITO) covered with a layer of polyethylenedioxythiophene polystyrenesulfonate (PEDOT:PSS). In this way different thicknesses of the active layer (indicated as thick, medium and thin, see Figure 2a) were created. On

the active polymer layer, back electrodes of lithium fluoride (1nm) and aluminum (100nm) were deposited in vacuum. The current-voltage (J-V) characteristics of the cells were measured in the dark and under illumination with a tungsten halogen lamp at 75 mW/cm². The power outputs for the different cells are depicted in Figure 2a. The best performances were obtained for (PP2:PT=1:1) cells. Compared to the performance of a (1:1) cell made of PT and a monomeric perylenebisimide PM5 with two hexylheptyl tails, the power output showed at least a 20-fold increase. For the (PT-PP2=1:1) cell of medium thickness the following characteristics were measured (see Figure 2b,c): an open circuit voltage V_{oc} and a short circuit current density J_{sc} of 0.621 V and 0.537 mA/cm², respectively and a fill factor FF of 0.338. In Figure 2d the external quantum efficiency (EQE) of this cell is shown.

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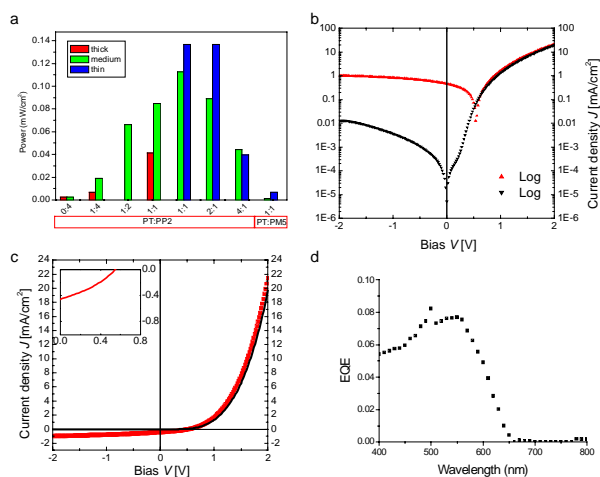


Figure 2. Performance of photovoltaic cells constructed from various blends of polythiophene PT and PP2. a) Power outputs for cells constructed from different ratio's of PT:PP2 spin cast with different layer thicknesses; For comparison a blend of PT and di(hexylheptyl) perylenebisimide (PM5) was measured b) Semi-logarithmic J-V plot in the dark (—) and under illumination (---) of the (1:1) cell (medium thickness). c) Linear J-V plot, inset shows the fourth quadrant. d) External quantum efficiency versus wavelength.

CONCLUSIONS

Perylene functionalized polyisocyanides PP1 and PP2 have been synthesized and from PP2 photovoltaic devices were prepared with a 20-fold improved power output compared to cells constructed from a low molecular weight perylene.

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