

Spectroscopic properties of PEDOTEHIITN, a novel soluble low band-gap conjugated polymer

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Abstract

Polymers with narrow band gap are expected to possess appreciably high RT conductivities, luminescence in the NIR and improved solar energy harvesting properties. Here we report the spectroscopic properties of a soluble and environmentally stable copolymer (PEDOTEHIITN) with a band-gap of *ca.* 1.1 eV. The combination of this outstandingly narrow band gap, processability and stability are promising for future electronic and optoelectronic applications.

Keywords: low band-gap conjugated polymers, UV-Vis-NIR absorption, photoinduced absorption spectroscopy, organic photovoltaics

1. Introduction

Low band-gap conjugated polymers are attracting attention due to their interesting electronic and optical properties, which make them promising candidates for several applications.[1] For instance, low band-gap conjugated polymers are expected to possess appreciably high conductivities, luminescence in the NIR, and absorption spectra that match the solar photon flux spectrum. The latter property makes them especially interesting as materials for organic photovoltaics. Most of the low band-gap conjugated polymers prepared so far presented severe limitations as high instability of the monomeric compounds, intrinsic instability towards oxygen, and low or even no solubility.[1] Recently, poly(3,4-ethylenedioxythiophene)-*N*-2'-ethylexyl-4,5-dicarboxylic imide-benzo[*c*]thiophene (PEDOTEHIITN, Fig. 1), a soluble and stable novel conjugated polymer with a band-gap of about 1.1 eV, has been synthesized.[2] Here, we report its spectroscopic and photophysical properties, studied by photoinduced Vis-NIR-MIR absorption (PIA) spectroscopy. In addition, a preliminary characterization of photovoltaic devices made of PEDOTEHIITN in blend

with a soluble fullerene derivative is reported.

2. Experimental

The synthesis of PEDOTEHIITN will be reported elsewhere.[2] For electrochemistry, the material was cast from CHCl₃ solution onto a Pt disk. The supporting electrolyte was 0.1 M Bu₄NPF₆ in CH₃CN. For photoinduced absorption, carried out with the set-up described in 3, the 476 nm line of an Ar⁺ has been used as excitation source. Photocurrent spectra were measured with a lock-in technique under illumination by monochromatized light from a Xe lamp.

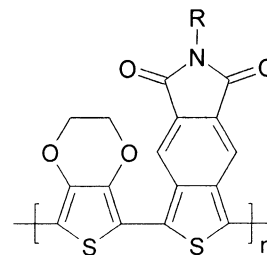


Fig. 1: Chemical structure of PEDOTEHIITN

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3. Results and discussion

The recent preparation of a highly stable ITN derivative, benzo[c]thiophene-N-2'-ethylexyl-4,5-dicarboxylic imide, allowed the synthesis of a family of robust and soluble low band-gap materials. Among them, PEDOTEHIITN shows excellent stability, solubility and film forming properties. Fig. 2 displays the cyclic voltammogram of a PEDOTEHIITN film. As can be seen the polymer is electrochemically active in both the anodic and the cathodic regions. From the onset of both reversible waves, the band-gap is estimated to be about 1.1 eV. The photoinduced IR absorption of a polymer film is shown in Fig. 3. Two broad electronic absorption bands, with maxima at about 7000 (~ 0.9) and 2000 cm^{-1} (~ 0.25 eV), are observed. These two features can be assigned to the typical allowed transitions of polarons, indicating that

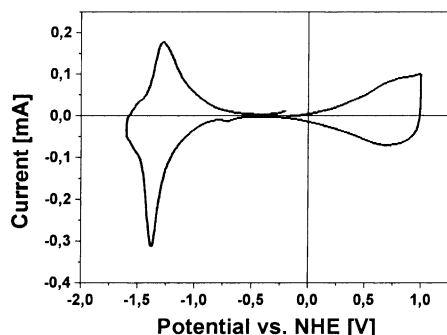


Fig. 2: Cyclic voltammogram of a PEDOTEHIITN film, drop cast from CHCl_3 . Working and counter electrodes: Pt disk. Potential is given versus NHE.

photoinduced charge generation occurs in PEDOTEHIITN solid films. It is worth to note that the electronic band with maximum at about 2000 cm^{-1} overlaps the infrared active vibration (IRAV) bands, giving a complicated pattern due to the occurrence of a resonance between electronic and vibrational transitions.[4]

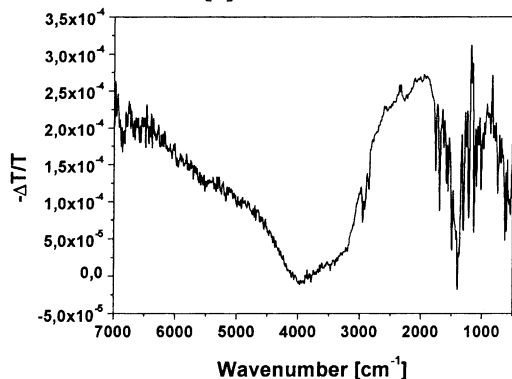


Fig. 3: Photoinduced IR absorption of PEDOTEHIITN films. Excitation at 476 nm. $T = 100$ K.

The band with maximum at about 0.9 eV is also seen in the Vis-NIR photoinduced spectrum (Fig. 4), along with a bleaching of the ground-state absorption (onset at ca. 1.2 eV). Mixing PEDOTEHIITN with a soluble

methanofullerene derivative (PCBM) enhances the photoinduced features by an order of magnitude, indicating a photoinduced electron transfer from the conjugated polymer to the fullerene component (Fig. 4).

The incident photon to current efficiency (IPCE) of PEDOTEHIITN:PCBM composites is depicted, along with the absorption spectrum, in Fig. 5. It can be seen that PEDOTEHIITN absorbs photons well above 700 nm, the region where the maximum solar photon flux occurs. A photocurrent with onset above 900 nm demonstrates the light harvesting properties of PEDOTEHIITN.

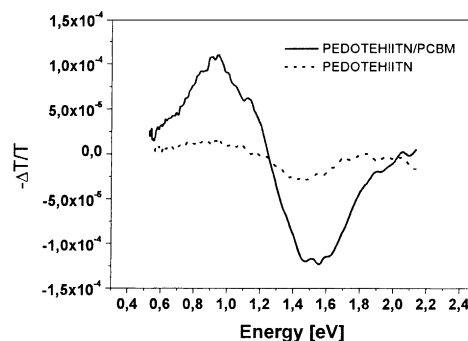


Fig. 4: Photoinduced Vis-NIR absorption of PEDOTEHIITN (dashed) and PEDOTEHIITN:PCBM blends (solid). Excitation at 476 nm. $T = 100$ K.

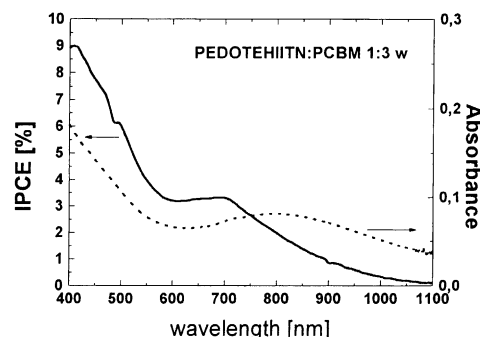


Fig. 5: IPCE (solid) and absorption (dashed) spectra of PEDOTEHIITN:PCBM composites.

4. Conclusions

We have reported the spectroscopic properties of a novel soluble low band-gap conjugated polymer. The observation of a photoinduced electron transfer from the polymer onto a fullerene derivative is promising for the preparation of photovoltaic devices.

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