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Synthesis and Electropolymerization of a Perylenebisimide-Functionalized 3,4-Ethylenedioxythiophene (EDOT) Derivative

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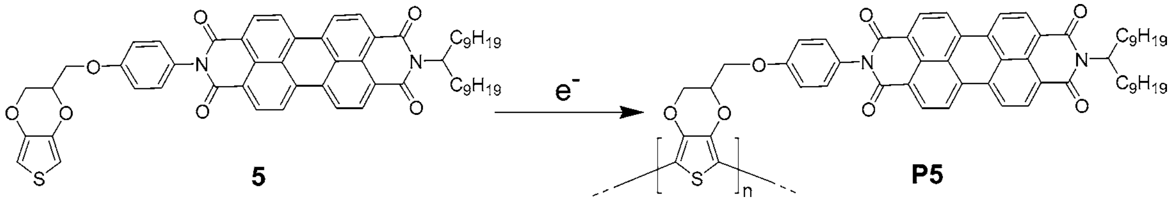
ABSTRACT



We have developed a convenient and straightforward procedure for the preparation of functionalized 3,4-ethylenedioxythiophene (EDOT) systems by using a new chloromethyl-EDOT derivative as a versatile synthon. Based on this procedure, novel suitably functionalized perylenetetracarboxylic diimide (PDI) dye derivatives covalently linked to 3,4-ethylenedioxythiophene moieties have been synthesized and electrochemically polymerized to yield a donor–acceptor PEDOT derivative with an enhanced absorption cross-section.

A great deal of interest has been devoted in recent years to the synthesis and investigation of conjugated oligomers and polymers because of their potential as active materials in applications such as light-emitting diodes (OLEDs),[1,2] plastic lasers,[3] field-effect transistors,[4] and photovoltaic devices (solar cells).[5,6] On the other hand, conjugated polymers that show both p-type (hole) and n-type (electron) conductivity might behave as intrinsic and uniform p/n-type semiconductors with suitable properties for organic photovoltaics.[7,8] Among numerous conducting polymers that have been developed and studied over the past decades, poly(3,4-ethylenedioxythiophene), also known as PEDOT,[9] has developed into one of the most successful materials from both a fundamental and practical perspective.[10] Very recently, the first functionalized PEDOTs bearing pendant groups, e.g., tetrathiafulvalene or viologen, were disclosed.[11] Perylenetetracarboxylic diimide (PDI) dyes have been also the subject of study during recent years because of their high absorbance in the visible, good electron mobility, and good thermal and

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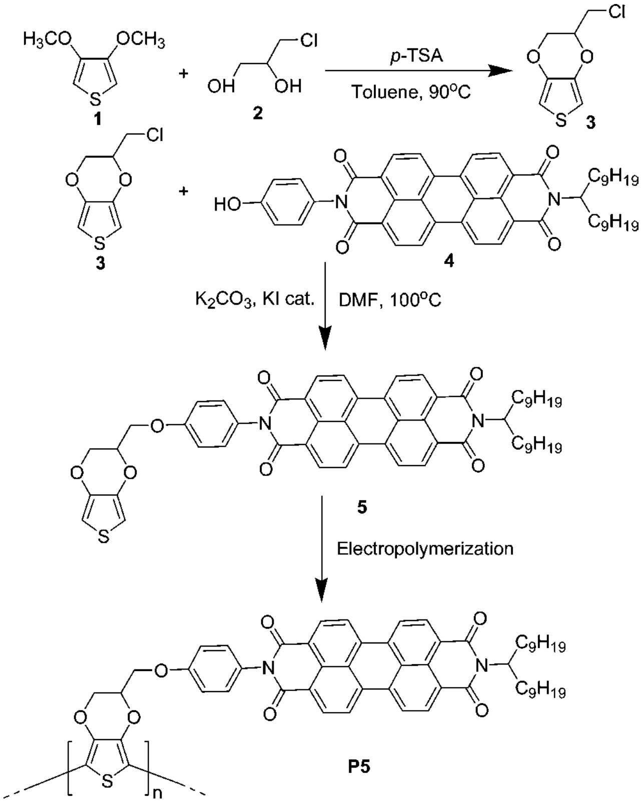
photostability.[12] Conjugated polymers bearing PDI moieties have been recently reported to exhibit photoinduced electron transfer,[13] while oligothiophene derivatives covalently linked to PDI moieties have shown promising results as an active layer in organic photovoltaic devices.[14]

In this communication we report the synthesis and electrochemical polymerization of an EDOT functionalized with an electron-accepting PDI bearing solubilizing swallowtail alkyl side chains. Subsequent electropolymerization of the EDOT monomer yields a conjugated hybrid polymer that might combine high p-type charge carrier mobility along the PEDOT backbone and n-type behavior of the covalently linked PDI dye units. The complementary absorption properties of both moieties now leads to a coverage of a wide range of the solar spectrum (Figure 2).

To functionalize the basic EDOT unit we have prepared chloromethyl-substituted EDOT **3** as a versatile synthon to further react the EDOT system (Scheme 1).

Scheme 1



In contrast to previous studies, where we synthesized a 2,5-dimethoxycarbonyl-substituted analogue of chloromethyl-EDOT **3** by Mitsunobu reaction (65% yield),[15] this time we used the more convenient acid-catalyzed transetherification reaction[16] of 3,4-dimethoxythiophene (**1**) and 3-chloro-1,2-propanediol (**2**) in refluxing toluene (58% yield, Scheme 1). The coupling of the PDI subunit to the EDOT moiety was carried out by a Williamson ether synthesis from EDOT **3** and the hydroxyphenyl-derivatized PDI **4**, prepared by condensation of the corresponding monoimide-monoanhydride and *p*-aminophenol under standard conditions.[17] Thus, the asymmetric-perylenebisimide functionalized EDOT **5** has been obtained in 34% yield.

The swallowtail alkyl group in the perylene unit provides sufficient solubility to the monomer to allow full spectroscopic and electrochemical characterization.[18]

Cyclic voltammetry of PDI-functionalized EDOT **5** reveals the redox transitions of the individual subunits. Thus, a cyclic voltammogram of **5** (5×10^{-3} M in dichloromethane/tetrabutylammonium hexafluorophosphate (TBAHFP, 0.1 M), 100 mV s^{-1}, Figure 1, dotted line) shows characteristic reversible reduction waves of the perylenebisimide moiety involving two successive one-electron transfers ($E°_{red1} = -1.11$ V and $E°_{red2} = -1.33$ V vs Fc/Fc$^+$), indicating stable radical anions and dianions. These values are directly comparable to those of a *N*,*N*-dialkyl-substituted perylenebisimide reference ($E°_{red1} = -1.15$ V and $E°_{red2} = -1.37$ V vs Fc/Fc$^+$), as well as to those of a recently reported

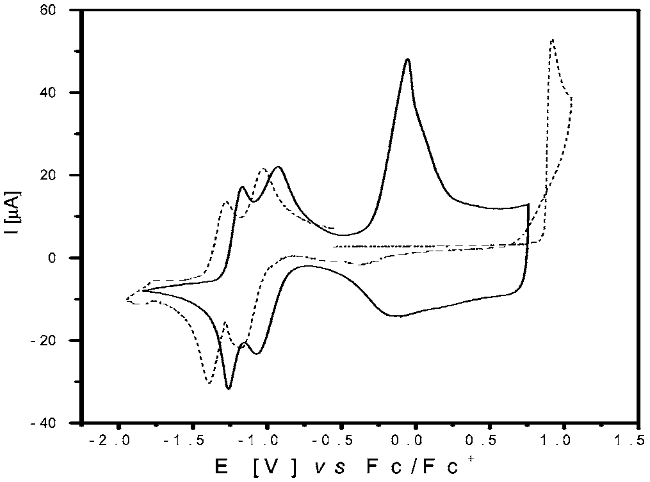


Figure 1. Cyclic voltammograms of PDI-EDOT monomer **5** (dashed line) in dichloromethane/TBAHFP (0.1 M) at a scan rate of 100 mV/s and electrochemical characterization of polymer **P5** (solid line) in a monomer-free solution, in CH_3CN/TBAHFP (0.1 M) at a scan rate of 100 mV/s on a Pt disk electrode.

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terthiophene-derivatized PDI.[19] In the positive potential regime, the typical irreversible oxidation of the EDOT moiety was determined at $E^{\mathrm{p}}_{\mathrm{ox1}} = 0.91$ V, which is cathodically shifted in comparison with 2-methyl-2,3-dihydro-thieno[3,4-*b*][1,4]dioxine (Me-EDOT, 1.03 V), which is a suitable reference.[20] Oxidative polymerization of the PDI-functionalized EDOT **5** was carried out by potentiodynamic cycling in the range of −0.2 to 1.4 V (see Supporting Information). The growth of the conducting polymer is reflected by gradually increasing currents in subsequent potential cycles and an electroactive polymer film at the working electrode, whose thickness regularly increases with the number of cycles. The polymers obtained exhibited homogeneous morphologies and were strongly adhering to the electrode. The PDI-functionalized PEDOT **P5** was electrochemically characterized in an electrolyte free of monomer (see Supporting Information). The CVs were taken at different scan rates and clearly exhibit the characteristic broad redox wave of the PEDOT backbone ($E^{\circ}_{\mathrm{pa}} = -0.06$ V), which is 670 mV more positive compared to poly(2-methyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxine) [p(Me-EDOT), $E^{\circ}_{\mathrm{pa}} = -0.73$ V].[17] By scanning to the negative potential regime, the two characteristic reduction waves of the appended PDI moieties at $E^{\circ}_{\mathrm{red1}} = -1.08$ V and $E^{\circ}_{\mathrm{red2}} = -1.26$ V are visible. In comparison to the monomer, these values are shifted positively and the conjugated backbone is still sufficiently conducting to allow electron transfer to the PDI side groups. Typically, in polythiophenes functionalized with redox active groups the electron transfer at potentials where the conjugated backbone is semiconducting is strongly hampered.[21] In this respect, the use of an EDOT unit seems to be clearly superior to use of a normal thiophene.

Polymer films of different thicknesses formed after 5, 10, and 20 multisweep scans were investigated. CVs of the various polymer films revealed that expectedly the peak current for the redox process involving the PEDOT backbone is highly dependent on the number of scans used in the polymerization process and increases linearly with increasing thickness. In contrast, peak current for the reduction waves of the PDI moiety relatively decreases with increasing thickness, indicating a different charge transport mechanism. Whereas polaronic and bipolaronic delocalization on the conjugated chains is responsible for a band-like and p-type conductivity of the PEDOT backbone, thickness-dependent n-type electron hopping processes could determine the charge transport via the perylene redox centers. The optical properties of the novel PDI-PEDOT **P5** in various oxidation states were investigated by spectroelectrochemistry.[22] In the state where both the PEDOT backbone and the perylene unit are neutral, the absorption of **P5** (dashed line, Figure 2) completely covers the visible range and extends up to 850 nm, revealing the superimposition of the electronic properties of the individual π-systems. Thus, at shorter wavelengths the characteristic vibronic structured absorption of the PDI system (dotted line) can be identified, whereas at higher wavelengths can be identified the pattern corresponding to the p(Me-EDOT). At 750 nm can be also observed an absorption band that might be assigned to a charge-transfer process. Oxidation of the PEDOT moiety results in a decrease of the absorption corresponding to the PEDOT system in the neutral state and the simultaneous appearance of bands due to polaron and bipolaron formation. The formation of PDI radical anions and dianions can also be followed at negative potentials, and their characteristic bands coincide with these of PDI as reference compound.

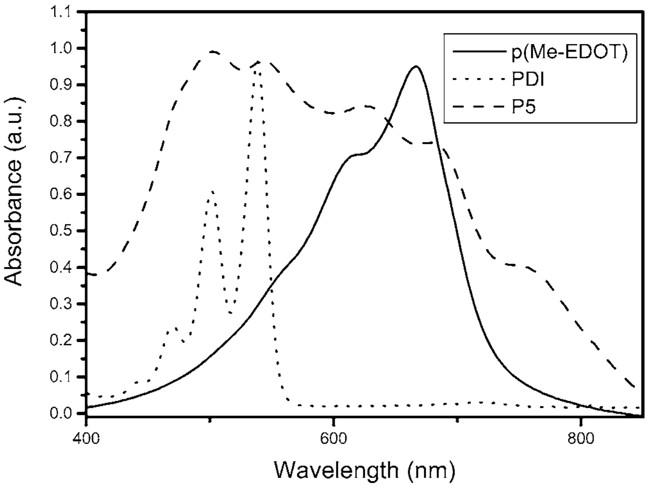

Figure 2. UV−vis−NIR spectra of a dichloromethane solution of reference PDI (dotted) and polymer films of **P5** (dashed) and reference p(Me-EDOT) (solid) electrochemically deposited on a platinum working electrode in a reflection mode.

In conclusion, the versatile chloromethyl-substituted EDOT derivative **3** has been synthesized, which provides easy access to EDOTs and their corresponding PEDOTs endowed with functional groups such as, for example, redox active units. In this line, we have prepared a novel donor−acceptor-type polymer, perylenetetracarboxylic diimide functionalized PEDOT **P5**. The absorption of the neutral polymer film covers a wide range of the solar spectrum, promoting this type of donor−acceptor-type polymer as an ideal candidate for organic photovoltaic devices. Work is in progress to investigate the photophysics of the system as well as its potential in organic solar cells.

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(18) **Selected Data for 5.** ^{1}H NMR (CDCl$_3$, 400 MHz) δ 8.75 (d, J = 8.04 Hz, 4H), 8.67−8.63 (m, 4H), 7.29 (d, J = 8.78 Hz, 2H), 7.11 (d, J = 8.78 Hz, 2H), 6.38 (AB system, J_{AB} = 3.89 Hz, 2H), 5.23 (m, 1H), 4.6−4.2 (m, 5H), 2.27 (m, 2H), 1.89 (m, 2H), 1.56−1.20 (m, 28H), 0.83 (t, 6H). ^{13}C NMR (CDCl$_3$, 100 MHz) δ 163.73, 158.31, 141.43, 141.11, 135.13, 131.84, 129.55, 128.35, 126.68, 126.42, 123.30, 123.04, 115.41, 100.04, 100.00, 99.82, 71.79, 66.40, 65.87, 54.85, 32.37, 31.85, 29.69, 29.25, 26.98, 22.72, 14.07. FT-IR (KBr) ν 2922, 2852, 1699, 1653, 1595, 1344, 1254 cm^{-1}. MS (MALDI-TOF) *m/z* 903 [M + H]$^{+}$. Anal. Calcd for $C_{56}H_{58}N_2O_7S$: C, 74.47; H, 6.47; N, 3.10. Found: C, 74.68; H, 6.59; N, 2.98.

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Supporting Information Available: Experimental details and electrochemical characterization of the polymer **P5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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