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An Ambipolar Peryleneamidine Monoimide-Fused Polythiophene with Narrow Band Gap

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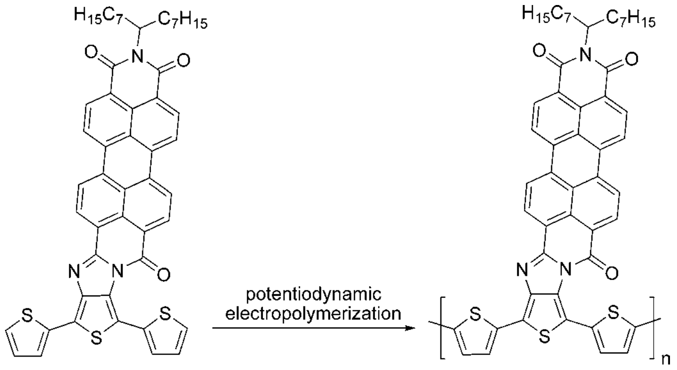
ABSTRACT



A peryleneamidine monoimide-fused terthiophene with a band gap of 1.4 eV has been synthesized. The donor–acceptor system can be electropolymerized to generate a functionalized polythiophene with a band gap of 0.9 eV and with ambipolar characteristics showing high electroactivity in both the p- and the n-doping process. This is the first example of a p-type conjugated polymer in direct conjugation with n-type perylenemonoimide moieties.

Organic narrow band gap polymers are currently the subject of an intense research effort due to their application as materials for organic photovoltaic devices, for deep red and near-IR emitting devices, for ambipolar organic field effect transistors, and for electrochromic devices mainly due to their potential multicolored states.[1] For these device applications it is important to control the electronic band structure of the polymer to achieve (a) a band gap of the desired magnitude and (b) HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) with appropriate energies.[2] The most general approach choice to achieve electropolymerizable polymers with band gaps as low as 0.3−0.5 V[3] involves the synthesis of polymers with alternation of electron-donating and electron-accepting moieties, showing that the mixing of monomer segments with higher HOMO and lower LUMO is effective to reduce the band

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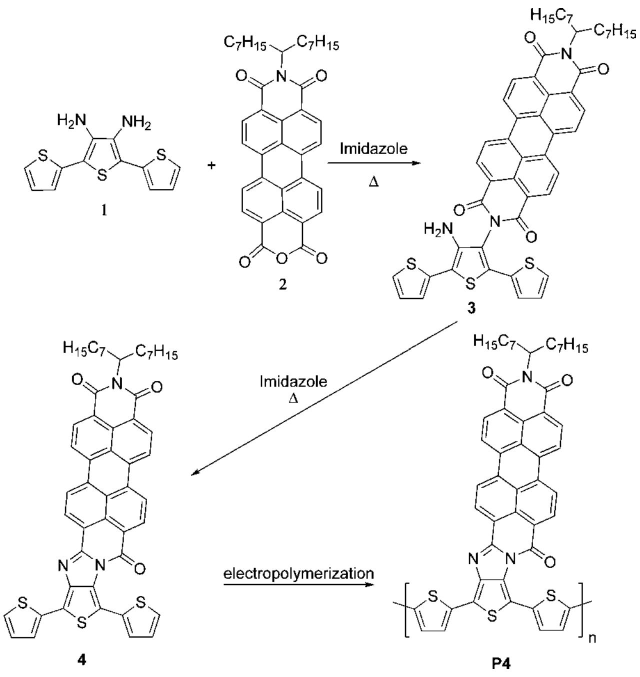
gap due to the intrachain charge transfer.[4] Thus, a number of trimeric thiophene derivatives have been synthesized in which the middle thiophene unit is fused with pyrazine or thiadiazole moieties which can subsequently be electropolymerized to the corresponding low band gap polymers.[4] These polymers are attractive to be used as donor polymers in combination with fullerene acceptors in organic photovoltaics. For this purpose, it is desired that a polymer be air stable (i.e., resistant to oxidation) to allow ease of handling and processing by having a fairly low-lying HOMO (~5.2 eV or lower[5]). On the other hand, a LUMO of 3.8 eV or above would be required to allow efficient photoinduced electron transfer from the donor polymer to the fullerene derivative acceptor.[2]

In an attempt to further control the band gap as well as the HOMO and LUMO energies in this kind of polymers, we extend this strategy to the synthesis and electrochemical polymerization of a peryleneamidine-imide derivative fused with a terthiophene moiety through an imidazole unit (**4**, Scheme 1).

Scheme 1



It has been found that the introduction of arylimidazole to extend the conjugation in perylenetetracarboxylic acid diimide (PTCDI) derivatives is an efficient strategy to obtain materials which absorb radiation in the NIR region.[6] Conjugated polymers bearing PTCDI moieties have been recently reported to exhibit photoinduced electron transfer,[7] while oligothiophene derivatives covalently linked to PTCDI moieties have shown promising results as an active layer in organic photovoltaic devices.[8]

Despite previous reports of conjugated polymers covalently linked to PTCDI moieties,[9] **P4** represents the first example of a semiconducting polymer having perylenemonoimide moieties directly fused and conjugated to the polymer backbone.

The synthesis of PTCDI derivatives in which the conjugation is extended by the introduction of arylimidazole units can be carried out by reaction of *o*-phenylenediamines with anhydrides derived from perylenedicarboxylic acid.[10] By following this strategy we synthesized peryleneamidine-monoimide-terthiophene **4** as depicted in Scheme 1.

Thus, 3′,4′-diamino-2,2′:5′,2″-terthiophene **1**[4a] was treated with *N*-(10-nonadecyl)-3,4,9,10-perylenetetracarboxylic acid 3,4-anhydride-9,10-imide[11] (**2**) in imidazole in the presence of zinc acetate to afford the perylenebisimide-terthiophene dyad **3** as a red solid in 67% yield. **3** was again heated in imidazole in the presence of zinc acetate to give the peryleneamidine monoimide-fused terthiophene **4** as a deep violet solid (20% yield).[12] The isolation of intermediate **3** is in contrast with previous reports on the synthesis of peryleneamidine-imide derivatives[10] probably due to the lower solubility of our derivative **3**. However, the swallowtail alkyl group at the perylene unit provides sufficient solubility to target perylenemonoimide-fused terthiophene **4** to allow full spectroscopic and electrochemical characterization.

Cyclic voltammetry (CV) of **4** reveals an amphoteric redox behavior (Figure 1). Thus, characteristic reversible reduction waves of the perylenebisimide moiety involving two successive one-electron transfers are found at $E°_{\mathrm{red1}} = -1.07$

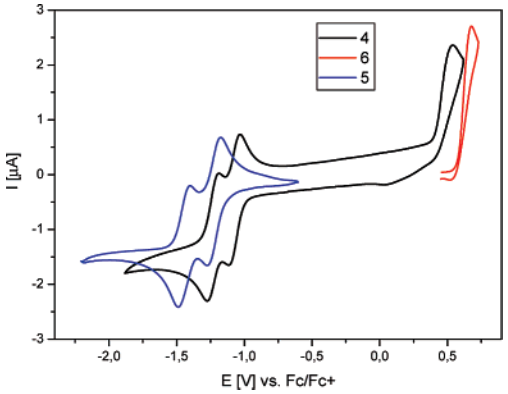


Figure 1. Cyclic voltammogram of perylenemonoimide-fused terthiophene **4** (black line) and of references **5** (blue line) and **6** (red line) in dichloromethane/tetrabutylammonium hexafluorophosphate (TBAHPF) (0.1 M) at 20 °C, concentration 5 × 10^{-3} M, scan rate of 100 mV/s, Pt disk working electrode, and potentials vs Fc/Fc$^+$.

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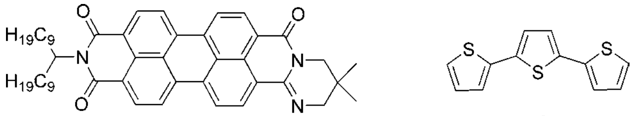
V and $E°_{red2} = -1.23$ V vs Fc/Fc$^+$, indicating the formation of stable radical anions and dianions. These values are shifted positive relative to peryleneamidine-imide reference **5**[10] (Figure 2, $\Delta E°_{red1} = -0.15$ V, $\Delta E°_{red2} = -0.21$ V), to perylenebisimide-terthiophene dyad **3** ($\Delta E°_{red1} = -0.08$ V, $\Delta E°_{red2} = -0.14$ V) or to recently reported terthiophene-derivatized PTCDI.[13]



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6

Figure 2. Peryleneamidine-imide dye (**5**) and α-terthiophene (**6**) references.

In the positive potential regime, the typical irreversible oxidation of the terthiophene moiety was determined at $E^p_{ox1} = 0.54$ V, which is negatively shifted compared to unsubstituted reference α-terthiophene **6** (Figure 2, $\Delta E^p_{ox1} = 0.13$ V). The anodic shift of the reduction as well as the cathodic shift of the oxidation in comparison with references **5** and **6** stems from the direct conjugation of both electroactive moieties. From the onset of reduction and oxidation processes we determine a relatively low band gap of 1.40 eV for **4**. For comparison purposes, the irreversible oxidation of the terthiophene moiety was determined at $E^p_{ox1} = 0.26$ V for the amino-substituted dyad **3**. In this case, the negative shift observed for the oxidation potential is due to the presence of the electron-donating amino group in the terthiophene moiety.

Oxidative polymerization of **4** was carried out by potentiodynamic cycling in the potential range of −0.6 to 0.6 V (Figure 3, black lines). The growth of a conducting polymer is reflected by gradually increasing currents in subsequent potential cycles whose thickness regularly increases with the number of cycles. The polymers obtained exhibited homogeneous morphologies and were strongly adhering to the working electrode. The peryleneamidine imide-fused polythiophene **P4** was electrochemically characterized in an electrolyte free of monomer (Figure 3, blue line). The CV clearly exhibits the characteristic broad redox wave of a polythiophene backbone ($E_{pa} = 0.52$ V), which is 0.12 V more negative compared to poly(terthiophene) **P6** synthesized from **6** under analogous conditions. This behavior stems again from the direct conjugation of both electroactive moieties.

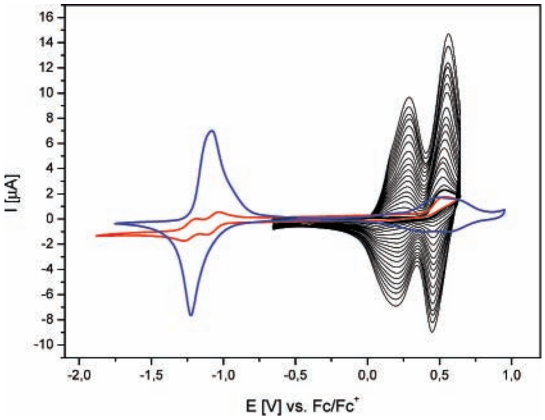

Figure 3. Electrochemical polymerization of terthiophene **4** (black lines) in dichloromethane/TBAHPF (0.1 M) and characterization of polymer **P4** (blue line) in acetonitrile/TBAHPF (0.1 M) in comparison to perylenemonoimide-fused terthiophene **4** (red line) in dichloromethane/TBAHPF (0.1 M). All the measurements were carried out at 20 °C, scan rate of 100 mV/s, Pt disk working electrode, and potentials vs Fc/Fc$^+$.

In the negative potential regime one nonsymmetrical reduction wave with peak potentials at $E_{pc} = -1.23$ V and $E_{pa} = -1.08$ V is visible including the transfer of two electrons as can be estimated from the peak current in comparison to that of the polythiophene backbone. The peak currents vary linearly with scan rate (Figure S1, Supporting Information), indicating that the redox-active polymer is anchored to the electrode surface. During repeated scanning no substantial decrease in electroactivity was observed pointing at a considerable stability of the film. The novel polymer exhibits amphoteric p- and n-doping behavior. Polymer HOMO (5.1 eV) and LUMO (4.2 eV) energies were estimated from the onsets of oxidation and reduction (Figure 3), and a very low band gap of $E_g \approx 0.9$ eV has been calculated.[14] The relatively low-lying LUMO of **P4** is close to the value of 5.2 eV desired for a polymer to be air stable.

Polymer films of different thicknesses were created and electrochemically investigated. In Figure 4 the CVs of **P4** films formed after 15, 25, and 30 scans are depicted. By integrating the charge flow of the reduction and the oxidation wave we find a ratio of 1.81 for the thinnest film (15 cycles),

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(12) Selected data for **4**: ^{1}H NMR (CDCl$_3$, 200 MHz). δ 8.12 (bs, 2H, *Pery*), 7.93 (d, $J = 8.0$ Hz, 1H, *Pery*), 7.82 (d, $J = 8.0$ Hz, 1H, *Pery*), 7.74 (d, $J = 8.2$ Hz, 1H, *Pery*), 7.71 (d, $J = 8.2$ Hz, 1 H, *Pery*), 7.63−7.56 (m, 2H, *Pery*), 7.38 (dd, $^3J = 5.2$ Hz, $^4J = 1.2$ Hz, 1H, *Th*), 7.08 (dd, $^3J = 3.6$ Hz, $^3J = 3.4$ Hz, 1H, *Th*), 6.80 (dd, $^3J = 3.6$ Hz, $^4J = 1.0$ Hz, 1H, *Th*), 6.74 (dd, $^3J = 3.6$ Hz, $^4J = 1.0$ Hz, 1H, *Th*), 6.46 (dd, $^3J = 4.0$ Hz, $^3J = 3.8$ Hz, 1H, *Th*), 6.33−6.31 (m, 1H, *Th*), 5.11 (m, 1H, −CH−N), 2.19 (m, 2H, $-CH_2-$), 1.91 (m, 2H, $-CH_2-$), 1.56 (s, 4H, $-CH_2-$), 1.36−1.25 (m, 16H, $-CH_2-$), 0.88 (t, 6H, $-CH_3$); ^{13}C-NMR (CDCl$_3$, 75 MHz), δ 155.96, 153.14, 144.67, 134.38, 132.88, 132.81, 132.63, 131.96, 129.90, 128.55, 126.98. 126.81, 125.47, 125.34, 124.76. 123.73, 122.39, 121.95, 121.95, 121.95, 121.61, 119.55, 110.80, 105.88, 54.35, 32.39, 31.88, 29.58, 29.31, 27.18, 22.67, 14.14; FT-IR (KBr). ν 2924, 2852, 1695, 1654, 1593, 1578, 1335, 1265 cm^{-1}; MS (FAB) (*m*/*z*): 845 (M$^+$), 634 ($M^+ - C_7H_{15}-CH-C_7H_{15}$); Anal. calcd. for $C_{51}H_{45}N_3O_3S_3$: C, 72.57; H, 5.37; N, 4.98. Found C, 72.33; H, 5.68; N, 4.86.

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(14) HOMO and LUMO energies are derived from the electrochemical data based on the assumption that the Fc/Fc$^+$ redox couple is 5.1 eV relative to vacuum.

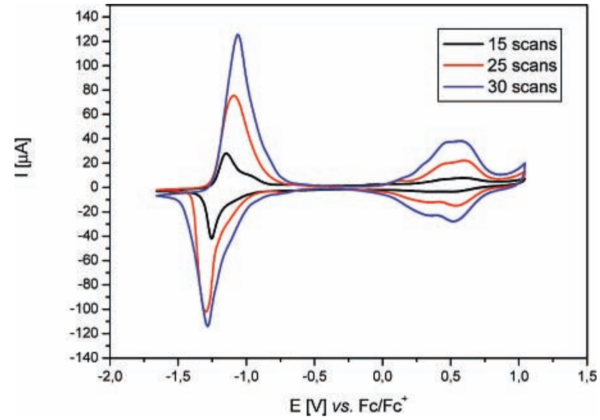

Figure 4. Electrochemical characterization films of polymer **P4** electropolymerized with a different number of scans (black line, film formed after 15 scans; red line, after 25 scans; blue line, after 30 scans) in acetonitrile/TBAHPF (0.1 M at 20 °C, scan rate of 100 mV/s, Pt disk working electrode, and potentials vs Fc/Fc$^+$).

1.90 for the medium thick film (25 cycles), and 1.74 for the thickest film (30 cycles). This behavior suggests that all the peryleneamidine monoimide units are electroactive in the film, which is in contrast to the behavior of other polythiophenes[9,13] in which peryleneimide moieties are linked via insulating side chains. In the so far known systems, the reduction of the acceptor unit and the n-doping process is suppressed and characterized by an electron hopping transport that can be identified by the decrease in peak current with increasing film thickness.[9] As a consequence of the structure, in our case, **P4** shows band-like conductivity and polaronic/bipolaronic delocalization as well for the p-doping and for the n-doping.

The UV−vis spectrum of **4** (Figure 5, blue line) covers the whole UV−visible region. The spectrum shows the fingerprints of the peryleneamidine-imide (**5**) at ca. 500 nm (red line) and terthiophene (**6**) at ca. 350 nm (not shown) and some new bands appearing at lower energies. The broad absorption band with a maximum at ca. 610 nm and extending until 800 nm has a large charge-transfer character as can be demonstrated by analyzing the electron density shift from the HOMO to the LUMO, which are the orbitals responsible for the transition (Figure S2, Supporting Information). In addition, ZINDO/S calculations show a very high state dipole for the low-energy band, clearly indicating a charge-transfer character. Furthermore, the characteristic fluorescence of **5**, which is a photostable fluorescent dye,[10] is quenched in the peryleneamidine-monoimide-terthiophene **4**.

UV−vis−NIR spectra of **P4** polymer films electrochemically deposited on a platinum working electrode were recorded in situ in a reflection mode by means of an optic fiber showing that the onset of the absorption of **P4** extends to the NIR (black line in Figure 5), which corresponds to a band gap of 0.9 eV.

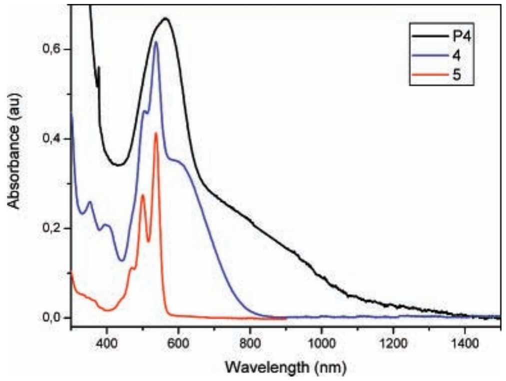

Figure 5. UV−vis spectra of terthiophene **4** (blue line) and peryleneamidine-imide **5** (red line) in dichloromethane solution and of polymer film **P4** (black line).

In conclusion, we have developed a synthetic route toward the preparation of a novel ambipolar perylenemonoimide-terthiophene **4**, which can be electropolymerized to corresponding functionalized polythiophenes **P4** exhibiting a narrow band gap of 0.9 eV. In comparison with previous examples of oligothiophene derivatives covalently linked to PTCDI moieties, the films obtained are highly electroactive in both the p- and the n-doping processes, as a consequence of the direct conjugation of the polythiophene and peryleneimide moieties. Work is in progress to prepare analogues of **4** with substituted perylene and terthiophene derivatives in order to further stabilize the HOMO level to obtain polymers more stable toward oxidation and with appropriate LUMO levels to allow efficient photoinduced electron transfer from the polymer to fullerene derivative acceptors.

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Supporting Information Available: Experimental details, the scan rate dependence of the electrochemical characterization of polymer **P4** and the optimized molecular geometry (AM1) and molecular orbital diagrams of the HOMO and LUMO levels of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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