ChemComm

Dual p- and n-type doping in an acid sensitive alternating bi(ethylenedioxythiophene) and pyridine polymer

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Received (in Columbia, MO, USA) 7th June 1999, Accepted 9th August 1999

Poly[2,5-bis(3,4-ethylenedioxy-2-thienyl)pyridine] exhibits multi-color electrochromism *via* easily accesible p- and n-type doping, and can be switched between a pale blue reduced state, a red neutral state, and a blue–purple oxidized state.

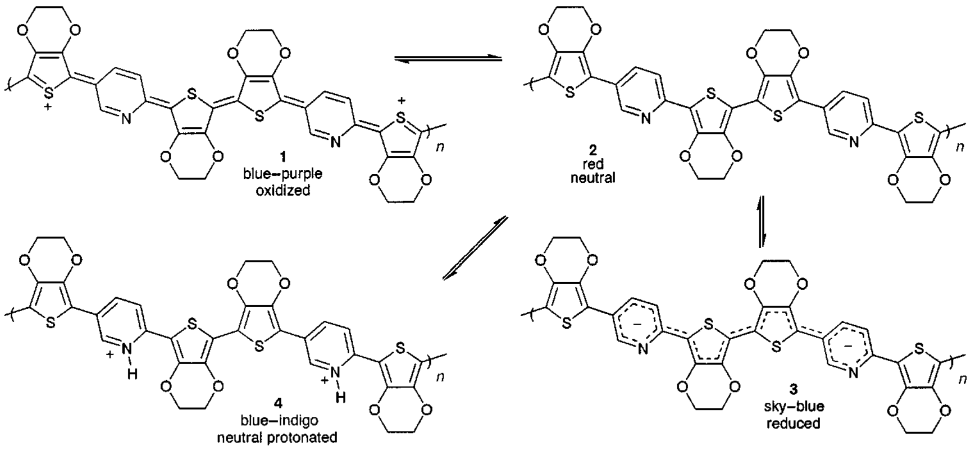
The ability to easily access both p- and n-type redox states in conducting and electroactive polymers may lead to useful materials.[1] While it is well-known that conjugated hydrocarbon polymers can be both p- and n-type doped, only recently has this been made possible in an electrochemically deposited film.[2] It has been shown by de Leeuw[3] that nitrogen-containing poly(heterocycles) induce stability in n-doped systems. One such example is poly(pyridine), which has a reduction potential of −2.1 V.† Other examples include poly(quinoline-2,6-diyl) which reversibly n-dopes at −1.8 V, along with poly(1,5-naphthyridine)[3] and poly(4,4′-dialkyl-2,2′-bithiazole-5,5′-diyl)s.[4] Relatively electron rich polyheterocycles are typically used in oxidative electropolymerization due to their propensity to form highly electroactive materials. While their p-doping characteristics are well-documented and can be outstanding, few systems show useful n-doping.[5–9] In many instances where a reduction is observed, the process is either irreversible and leads to rapid degradation of electroactivity, or leads to pinned anions and not true n-doping.[6]

We have undertaken a study of polyheterocycles containing alternating electron donor (D) and acceptor (A) units prepared *via* efficiently oxidatively polymerizable D–A–D monomers. Judicious choice of D and A units allows control of the energies of the π-system's effective HOMO and LUMO levels, which determine the polymer's oxidative (p-doping) and reductive (n-doping) properties, respectively. Thus, it has been shown that the electronic band gap of the polymer can be reduced significantly.[10] In addition, by using repeat units that are sensitive to the chemical environment, polymers that can provide an optical or electrical response upon exposure to species in electrolyte solutions can be used as sensor materials.

In designing an electroactive polymer that has three accessible charge states (oxidized, neutral, and reduced), while simultaneously being responsive to the pH of the bathing electrolyte solution, we prepared poly[2,5-bis(3,4-ethylenedioxy-2-thienyl)pyridine] [poly(BEDOT-Py)], which is efficiently synthesized *via* the corresponding D–A–D monomer. We have previously shown that 3,4-ethylenedioxythiophene is extremely effective as the oxidatively polymerizable moiety for the synthesis of poly(BEDOT-arylene)s that are highly electroactive and provide structurally controlled electrochromic properties.[11,12] It has been shown that while separate films of poly[2,5-bis(2-thienyl)pyridine] (PBTh-Py) can be p- or n-type doped, an electrochemical memory effect precludes both states from being accessed in a single film.[13] In addition to its propensity to stabilize reduced systems, the pyridine central unit is sufficiently basic to yield distinct spectroscopic shifts in an acidic medium and may be useful as a pH sensitive switching material.

BEDOT-Py was synthesized using a Negishi-type aryl cross coupling reaction (93% yield). Electropolymerization/film formation of poly(BEDOT-Py) was carried out using either repeated scan or constant potential methods from 10 mM BEDOT-Py and 0.1 M Bu_4NClO_4 in MeCN–CH_2Cl_2 (1 : 1) or 7.5 mM BEDOT-Py and 0.1 M Bu_4NClO_4 in MeCN. The monomer oxidizes at a bare Pt electrode with a peak ($E_{p,m}$) at 0.65 V. The redox processes for poly(BEDOT-Py) include broad oxidation and reduction (to the neutral form) peaks centered at 0.55 and 0.37 V, respectively, resulting in an $E_{1/2}$ of 0.49 V. While the monomer's $E_{p,m}$ is comparable to BEDOT-benzene (0.61 V), the resultant poly(BEDOT-Py) exhibits a higher $E_{1/2}$ by >250 mV when compared to poly(BEDOT-benzene).[11] This confirms the dominance of the terminal EDOT during polymerization, while the electron-accepting pyridine has a strong effect on the polymer's redox properties.

To study the optical properties and combined p- and n-doping electrochemistry, poly(BEDOT-Py) was deposited potentiostatically from a 7.5 mM MeCN solution since CH_2Cl_2 is not stable to the reduction potentials used during the experiment. Fig. 1 shows a combination of the separate and stable oxidative and reductive cyclic voltammetric scans for a film deposited onto a Pt button electrode. This method allowed isolation of the two processes while experiments conducted by repeatedly cycling



Scheme 1

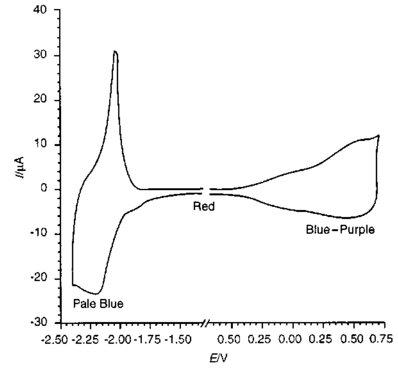


Fig. 1 Oxidative and reductive cyclic voltammetric scan of poly(BEDOT-Py) on a Pt button in 0.1 M TBAP in MeCN; scan rate = 100 mV s^{-1}.

between p- and n-doped states led to the formation of pre-peaks that increased in intensity with each subsequent scan. These pre-peaks, which may be due to trapped charge carriers,[6] can be misinterpreted as redox doping peaks if separate oxidation and reduction experiments are not performed.

The band gap of neutral poly(BEDOT-Py) is estimated to be 1.9 eV from the onset of the π–π^* transition, with λ_{max} = 478 nm. It was observed that, with increasing film thickness, the absorbance does not change significantly at energies below 1.9 eV, indicating a well-reduced polymer with little or no trapped charges.

The observance of reduction peaks in the cyclic voltammogram is not proof on n-doping. It has been shown that reduction of polybithiophene does not lead to n-doping, and this process has been attributed to the formation of pinned anionic states.[6] Our group has observed similar results in cyanovinylene-linked poly(biheterocycles).[14] To establish the definitive formation of charge carriers and the ability to access both the p- and n-type states in a single film, spectroelectrochemistry was carried out on poly(BEDOT-Py) through both the oxidative and reductive processes. It should be noted that the latter experiment requires rigorous exclusion of oxygen and water due to the reactivity of the reductively doped state. Fig. 2(*a*) shows the spectroelectrochemical series for p-doping from 0.0 to +1.0 V, while Fig. 2(*b*) shows the series for n-doping from 0.0 to −1.8 V. When the polymer is held between −1.5 and +0.2 V the neutral film is a deep red in color. This optical state is quite similar to polythiophene and its alkyl substituted analogs, and, as expected, the band gap lies between the values observed for poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyridine. Stepwise oxidation [Fig. 2(*a*)] leads to the typical evolution of the spectra for p-doping with peaks at *ca.* 1 and 1.75 eV as bipolaronic charge carriers are formed. The oxidized form is a deep blue–purple in color, again analogous to the polythiophene parent.

Comparison of the results shown in Fig. 2(*a*) and 2(*b*) bring out the unique spectroscopic nature of this polymer upon reduction. The similarity of the results, loss of intensity of the interband transition with concurrent evolution of peaks at 1 and 1.75 eV, are proof of the facile n-doping of this polymer and the fact that both the p- and n-doped states can be attained in the same film. Interestingly, the relative intensity of these two peaks is different in the two forms. While they are similar in intensity in the p-doped form, the NIR peak is dominant in the n-doped form. This has a profound effect on the electrochromic properties as the n-doped form is sky-blue in color and more highly transmissive to visible light. Note the high degree of light transmission between 1.5 (825 nm) and 2.5 eV (500 nm) corresponding to a major fraction of the visible spectrum. This is similar to the optical properties observed for the p-doped PEDOT family of polymers.

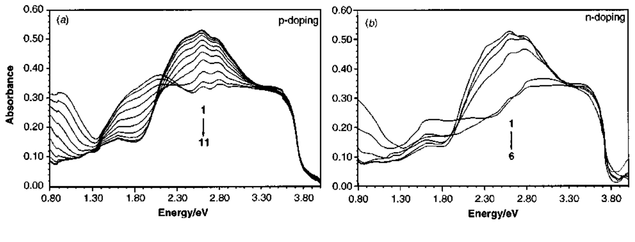


Fig. 2 Spectroelectrochemical series for p- and n-type doping of poly(BEDOT-Py): (*a*) p-doping at (1) 0.0, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4, (6) 0.5, (7) 0.6, (8) 0.7, (9) 0.8, (10) 0.9 and (11) 1.0 V; (*b*) n-doping at (1) 0.0, (2) −1.4, (3) −1.5, (4) −1.6, (5) −1.7 and (6) −1.8 V.

A unique property of poly(BEDOT-Py) is that it contains sites that can be quaternized. A series of UV–VIS–NIR spectra were obtained for the neutral film as a function of pH upon exposure to an aqueous citric acid buffer and 0.1 M HCl. There is little change in λ_{max} as the pH is reduced to 2, upon which there is a sharp 70 nm red-shift through pH 1 as the band gap is lowered to 1.5 eV. The neutral film changes from red to indigo–blue with exposure to acid, and the resulting band gap is close to that observed for the PEDOT family of polymers. It is interesting to note that protonation of the film occurs at a much higher acidity than for pyridine. This observation is supported in the literature in which a set of thiophene- and furan-substituted pyridines show a marked decrease in basicity relative to pyridine and can be attributed to an electron-withdrawing inductive effect of the 2-EDOT rings.[15] The films can be reversibly switched between the protonated and neutral state by exposure to 1 M HCl followed by rinsing with deionized water.

The unique chemical and electrochemical properties of poly(BEDOT-Py) are outlined in Scheme 1. The as-made blue–purple p-doped state **1** can be converted to the red neutral form **2** upon reduction. The neutral form can be reversibly reoxidized back to **1**, reduced to the sky-blue n-doped state **3**, or protonated to yield blue–indigo polycationic, electrochemically neutral state **4**. Studies are underway to further elucidate the redox properties of polycationic polymer **4** (both protonated and alkylated), and gain a deeper understanding of the n-doped form **3**.

This work was supported by grants from the AFOSR (F49620-96-1-0067), the NSF (CHE 96-29854), and the NAWC, China Lake CA. We appreciate the donation of EDOT from the AG Bayer corporation.

Notes and references

† All potentials given *vs.* Ag/Ag$^+$.

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Communication 9/04584H