

# Very Stable Low Band Gap Polymer for Charge Storage Purposes and Near-Infrared Applications

Gursel Sonmez, Hong Meng, and Fred Wudl\*

Department of Chemistry and Biochemistry and Exotic Materials Institute, University of California, Los Angeles, California 90095-1569

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A new low band gap polymer, poly(1,3-bis(2'-[3',4'-ethylenedioxy]thienyl)-benzo[c]thiophene-N-2''-ethylhexyl-4,5-dicarboximide) P(DEDOT-ITNIm), was synthesized. Electrochemically prepared polymer films were very stable to overoxidation upon p-doping and stable upon n-doping. The low band gap of the polymer films, 1.10 eV, was determined from electrochemistry and spectroelectrochemistry. Thin polymer films on ITO-coated glass slides showed exceptional optical properties upon both p- and n-doping, these were small changes in the transparency and color of the polymer in the visible region but more dramatic changes in the near-infrared region. The charge storage capacity of P(DEDOT-ITNIm) films is very high when compared to other members of the conducting polymers family, making this polymer a good candidate for charge storage purposes; e.g., as supercapacitors.

## Introduction

The discoveries in the last two decades of the 20th century brought conjugated polymers to full commercialization with applications in electrochromic rearview mirrors,<sup>1–3</sup> windows,<sup>4–6</sup> thin-film transistors,<sup>7</sup> displays,<sup>8,9</sup> sensors,<sup>10,11</sup> polymer light-emitting diodes,<sup>12</sup> photovoltaics,<sup>13</sup> and electrochromic devices.<sup>14–17</sup> As the new century commences, the science of conducting polymers remains vibrant, with development of new molecules, phenomena, experimental techniques, and technologies. Recently, because of their cost-effectiveness, lightweight nature, and flexibility,<sup>18</sup> polymeric

materials that switch in the near-infrared (NIR) region have received considerable attention for a number of possible applications. Among these are variable optical attenuators,<sup>19</sup> camouflage materials,<sup>20,21</sup> and thermal emission detectors.<sup>22</sup> The most studied materials are poly(3,4-ethylenedioxythiophene) (PEDOT) and its derivatives because they exhibit fast switching times,<sup>23–25</sup> outstanding stability, and high contrast ratio in the visible and NIR regions.

A low band gap is desirable for additional applications of conducting polymers. Because the reduction of the band gap will enhance the probability of thermal population of the conduction band and thus increase the number of intrinsic charge carriers, oxidative or reductive doping would not be required to obtain intrinsic electrical conductivity. Lowering the band gap also moves the  $\pi-\pi^*$  transition of a neutral polymer outside the visible region, resulting in a transparent polymer in both neutral and oxidized states. There are several parameters that can help to control the band gap of conducting polymers, including the manipulation of bond length alternation, inter-ring torsion angle, inter-chain and substituent effects, and resonance energy. Among them, electron releasing or withdrawing sub-

\* To whom correspondence should be addressed. Tel: (310) 206-0941. Fax: (310) 825-0767. E-mail: wudl@chem.ucla.edu.

- (1) Byker, H. J. Gentex Corporation, U.S. Patent 4902108.
- (2) Mortimer, R. G. *Chem. Soc. Rev.* **1997**, *26*, 147.
- (3) Granqvist, C. G.; Azens, A.; Isidorsson, J.; Kharrazi, M.; Kullman, L.; Lindstroem, T.; Niklasson, G. A.; Ribbing, C.-G.; Roennow, D.; Stromme Mattsson, M.; Veszelei, M. *J. Non-Cryst. Solids* **1997**, *218*, 273.
- (4) Granqvist, C. G.; Azens, A.; Hjelm, A.; Kullman, L.; Niklasson, G. A.; Ribbing, C.-G.; Roennow, D.; Stromme Mattsson, M.; Veszelei, M.; Vaivars, G. *Solar Energy* **1998**, *63*, 199.
- (5) Rauh, R. D. *Electrochem. Acta* **1999**, *44*, 3165.
- (6) Pennisi, A.; Simone, F.; Barletta, G.; Di Marco, G.; Lanza, L. *Electrochem. Acta* **1999**, *44*, 3237.
- (7) Halls, J. J. M.; Walsh, C. A.; Greenham, N. C.; Marseglia, E. A.; Friend, R. H.; Moratti, S. C.; Holmes, A. B. *Nature* **1995**, *376*, 498.
- (8) Monk, P. M. S. *J. Electroanal. Chem.* **1997**, *432*, 175.
- (9) Bange, K. *Solar Energy Mater. Solar Cells* **1999**, *58*, 1.
- (10) Albert, K. J.; Lewis, N. S.; Schauer, C. L.; Sotzing, G. A.; Stitzel, S. E.; Vaid, T. P.; Walt, D. R. *Chem. Rev.* **2000**, *100*, 2595.
- (11) McQuade, D. T.; Pullen, A. E.; Swager, T. M. *Chem. Rev.* **2000**, *100*, 2537.
- (12) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402.
- (13) Brabec, C. J.; Sariciftci, N. S.; Hummelen, J. C. *Adv. Func. Mater.* **2001**, *11*, 15.
- (14) Rauh, R. D.; Wang, F.; Reynolds, J. R.; Meeker, D. L. *Electrochem. Acta* **2001**, *46*, 2023.
- (15) Schwendeman, I.; Hickman, R.; Sonmez, G.; Schottland, P.; Zong, K.; Welsh, D.; Reynolds, J. R. *Chem. Mater.* **2002**, *14*, 3118.
- (16) Sonmez, G.; Meng, H.; Zhang, Q.; Wudl, F. *Adv. Func. Mater.* **2003**, *13*, 726.
- (17) Sonmez, G.; Meng, H.; Wudl, F. *Chem. Mater.* **2003**, accepted for publication.

(18) Skotheim, T. A.; Elsenbaumer, R. L.; Reynolds, J. R. *Handbook of Conducting Polymers*, 2nd ed.; Marcel Dekker: New York, 1998.

(19) McDonagh, A. M.; Bayly, S. R.; Riley, D. J.; Ward, M. D.; McCleverty, J. A.; Cowin, M. A.; Morgan, C. N.; Varrazza, R.; Pentyl, R. V.; White, I. H. *Chem. Mater.* **2000**, *12*, 2523.

(20) Kuhn, H. H.; Child A. D. In *Handbook of Conducting Polymers*, 2nd ed.; Skotheim, T. A., Elsenbaumer, R. L., Reynolds, J. R., Eds.; Marcel Dekker: New York, 1998.

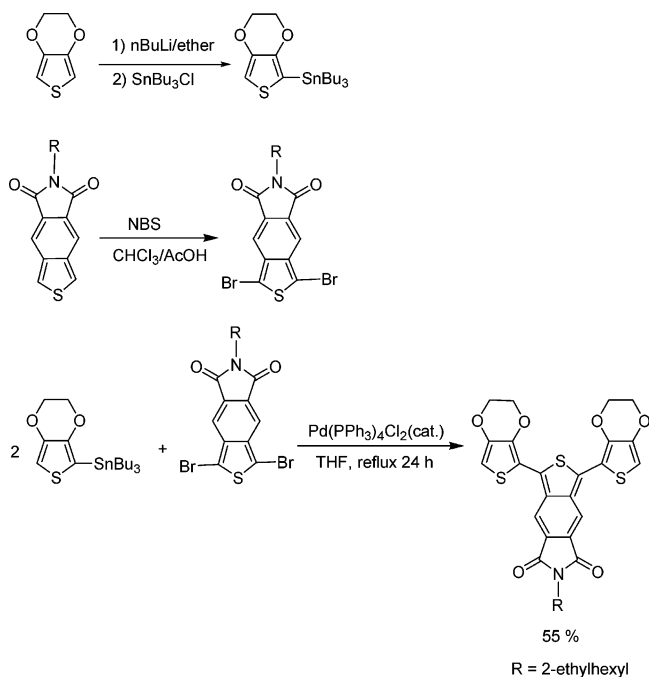
(21) Sonmez, G.; Schottland, P.; Zong, K.; Reynolds, J. R. *J. Mater. Chem.* **2001**, *11*, 289.

(22) Chandrasekhar, P.; Birur, G. C.; Stevens, P.; Rawel, S.; Pierson, E. A.; Miller, K. L. *Synth. Met.* **2001**, *119*, 293.

(23) Groenendaal, L. B.; Jonas, F.; Freitag, D.; Pielartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.

(24) Schwendeman, I.; Hwang, J.; Welsh, D. M.; Tanner, D. B.; Reynolds, J. R. *Adv. Mater.* **2001**, *13*, 634.

(25) Meng, H.; Tucker, D.; Chaffins, S.; Chen, Y.; Helgeson, R.; Dunn, B.; Wudl, F. *Adv. Mater.* **2003**, *15*, 146



**Figure 1.** Synthesis of 1,3-bis(2'-[3',4'-ethylenedioxy]thienyl)-benzo[c]thiophene-*N*-2''-ethylhexyl-4,5-dicarboximide.

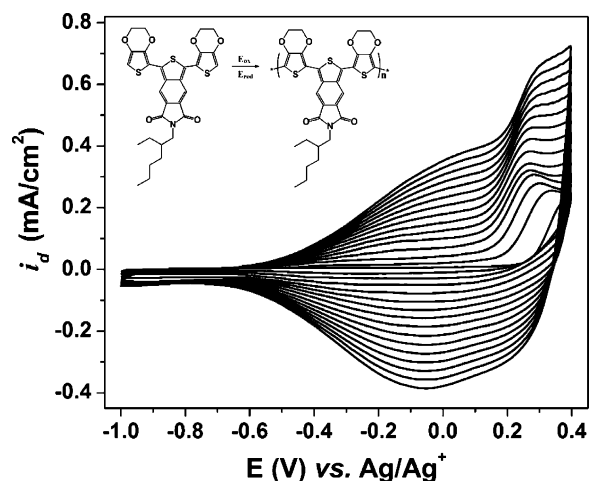
stituents have been widely used for tuning the band gap by modification of HOMO and LUMO levels of a conjugated polymer.<sup>26–29</sup>

In this study, we report the synthesis, and electrochemical and optical properties of a very stable, p- and n-dopable, low band gap polymer.

## Results and Discussion

**Monomer Synthesis.** Figure 1 shows the strategy for synthesis of the monomer 1,3-bis(2'-[3',4'-ethylenedioxy]thienyl)-benzo[c]thiophene-*N*-2''-ethylhexyl-4,5-dicarboximide (DEDOT-ITNIm). 2-Tributylstannyl-3,4-ethylenedioxythiophene<sup>16</sup> and 2,5-dibromo-benzo[c]thiophene-*N*-2''-ethylhexyl-4,5-dicarboximide<sup>25</sup> were prepared as described in our previous studies. The monomer DEDOT-ITNIm was prepared by Stille coupling of 2-tributylstannyl-3,4-ethylenedioxythiophene and 2,5-dibromo-benzo[c]thiophene-*N*-2''-ethylhexyl-4,5-dicarboximide as depicted in Figure 1. The yield was 55%. The presence of an acceptor unit, the benzo[c]thiophene-*N*-2''-ethylhexyl-4,5-dicarboximide (ITNIm), between two 3,4-ethylenedioxythiophene (EDOT) donor units was intended to decrease the LUMO and increase the HOMO energy levels, resulting in a low band gap. The imide group present in ITNIm was designed to stabilize the n-doped polymer.<sup>30</sup>

**Electropolymerization.** The first 15 scans of oxidative electropolymerization of 0.01 M DEDOT-ITNIm in 0.1 M LiClO<sub>4</sub>/propylene carbonate (PC) on a Pt button electrode (area = 0.02 cm<sup>2</sup>) at a scan rate of 50 mV/s are presented in Figure 2. An irreversible oxidation of



**Figure 2.** Electrodeposition of 1,3-bis(2'-[3',4'-ethylenedioxy]thienyl)-benzo[c]thiophene-*N*-2''-ethylhexyl-4,5-dicarboximide (DEDOT-ITNIm) by potential scanning from a 0.01 M solution of monomer in 0.1 M LiClO<sub>4</sub>/PC at 50 mV/s on a Pt button electrode.

the monomer appears in the first cycle at +0.38 V vs Ag/Ag<sup>+</sup>. Compared to EDOT and other bis-EDOT monomers,<sup>31,32</sup> this anodic process occurs at very low voltage (the oxidation potential of EDOT under the same conditions is 1.15 V vs Ag/Ag<sup>+</sup>). The modification by insertion of ITNIm between two EDOT monomers increases the conjugation in the monomer thus leading to a factor of ca. 3 lower monomer oxidation potential for DEDOT-ITNIm. Note that the alternation of electron donor and acceptor groups in the monomer may also be a factor. In subsequent cycles, the monomer oxidation happens at a slightly lower potential of about +0.28 V vs Ag/Ag<sup>+</sup>, likely due to modification of the electrode surface after the first cycle and formation of soluble oligomers in solution. The observed fast deposition rate yields a very broad redox system that grows rapidly at potentials lower than the monomer oxidation. Note that the broadness of the redox process corresponding to the polymer growth may stem from the large polydispersity of the product.

**Polymer Characterization.** The P(DEDOT-ITNIm) films were deposited potentiodynamically on a Pt button electrode under the same conditions mentioned above. After the films were rinsed in the electrolyte solution, they were characterized in monomer-free electrolyte solution at the following scan rates: 50, 100, 150, 200, 250, and 300 mV/s (Figure 3). The film's reversible oxidation process occurs at about -0.4 V vs Ag/Ag<sup>+</sup> (half wave,  $E_{1/2}$ ). The anodic and cathodic peak currents are linear in scan rate dependence up to 1000 mV/s. This demonstrates that the electrochemical processes are not diffusion-limited and are reversible, even at high scan rates. The fast, reversible switching in a nondiffusion-limited process at scan rates as high as 1000 mV/s is rather unusual and may be due to relatively thin films (ca. 40 nm).

Conducting polymers are known to be highly sensitive to over-oxidation<sup>33</sup> due to the degradation of the con-

(26) Karikomi, M.; Kitamura, C.; Tanaka, S.; Yamashita, Y. *J. Am. Chem. Soc.* **1995**, *117*, 6791.

(27) Van Mullekom, H. A. M.; Vakemans, J. A. J. M.; Havinga, E. E.; Meijer, E. W. *Mater. Sci. Eng.* **2001**, *32*, 1.

(28) Kitamura, C.; Tanaka, S.; Yamashita, Y. *Chem. Mater.* **1996**, *8*, 570.

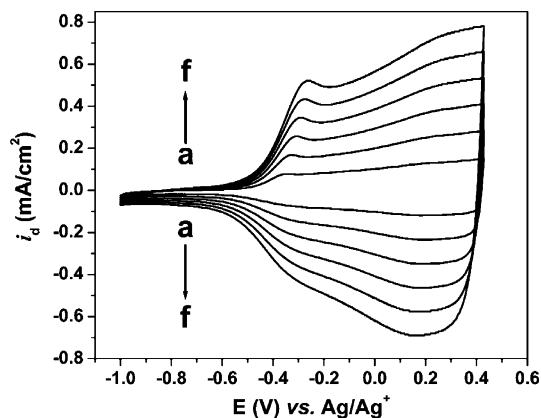
(29) DuBois, C. J.; Reynolds, J. R. *Adv. Mater.* **2002**, *14*, 1844.

(30) Meng, H.; Chen, Y.; Wudl, F. *Macromolecules* **2001**, *34*, 1810.

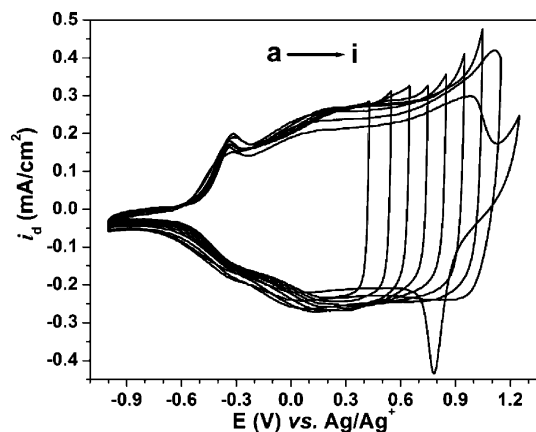
(31) Irvin, J. A.; Reynolds, J. R. *Polymer* **1998**, *39*, 2339.

(32) Irvin, J. A.; Schwendeman, I.; Lee, Y.; Abboud, K. A.; Reynolds, J. R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 2164.

(33) Chen, X. B.; Issi, J. P.; Devaux, J.; Billaud, D. *J. Mater. Sci.* **1997**, *32*, 1515.



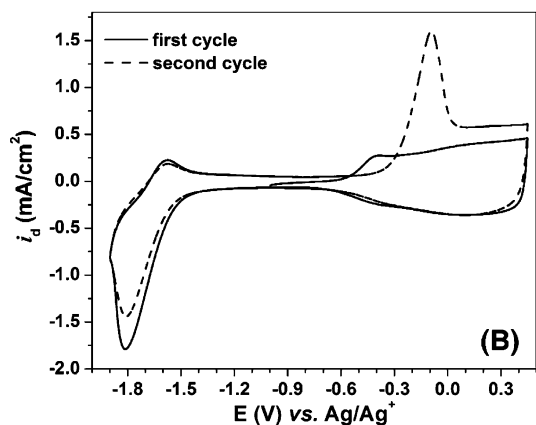
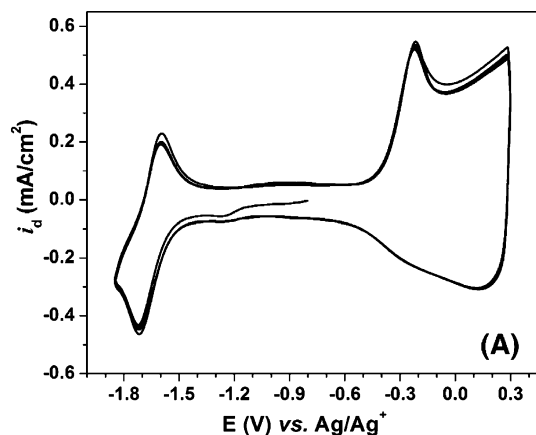
**Figure 3.** Scan rate dependence of P(DEDOT-ITNIm) film in monomer-free solution of 0.1 M LiClO<sub>4</sub>/PC at a scan rates of (a) 50, (b) 100, (c) 150, (d) 200, (e) 250, and (f) 300 mV/s.



**Figure 4.** Stability test of P(DEDOT-ITNIm) films to overoxidation by cycling the same polymer from  $-1.0$  V to (a) 0.43, (b) 0.55, (c) 0.65, (d) 0.75, (e) 0.85, (f) 0.95, (g) 1.05, (h) 1.15, and (i) 1.25 V vs Ag/Ag<sup>+</sup>. The polymer film was cycled 5 times at a scan rate of 100 mV/s in each potential window, and the last cycles are presented.

ducting polymer's backbone at high potentials. PEDOT and its derivatives are the most stable polymers reported to date.<sup>16,23</sup> A P(DEDOT-ITNIm) film has been exposed to a series of potentials above the  $E_{1/2,p}$  by multiple cycling between its neutral ( $-1.0$  V) and oxidized forms at different upper potential limits (from  $+0.4$  to  $+1.2$  V). After cycling 5 times in each potential window, the last cyclic voltammogram was recorded. The results, presented in Figure 4, show the stability of P(DEDOT-ITNIm) to overoxidation without any electroactivity loss up to  $+1.15$  V vs Ag/Ag<sup>+</sup>. This result demonstrates that the P(DEDOT-ITNIm) film can be switched between its neutral and oxidized states, in a potential window of 2.15 V (from  $-1.0$  V to 1.15 V), without any significant change in the anodic and cathodic currents up to 1.5 V above the  $E_{1/2}$  of the polymer. Moreover, the polymer films have very large capacitive currents at potentials above  $E_{1/2}$ . It should be noted that these capacitive currents are very stable and can be an advantage for this polymer's application in charge storage devices.

The charge involved during the electrochemical process was calculated from the CV of the polymer film between  $-1.00$  and  $+1.15$  V vs Ag/Ag<sup>+</sup> by integration of the current (Figure 4). The charge stored by the electrode covered with a ca. 50-nm thick film was



**Figure 5.** p- and n-Doping of P(DEDOT-ITNIm) film in monomer-free electrolyte solution of (A) 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/PC (10 cycles), and (B) 0.1 M LiClO<sub>4</sub>/PC (first and second cycles), at a scan rate of 200 mV/s.

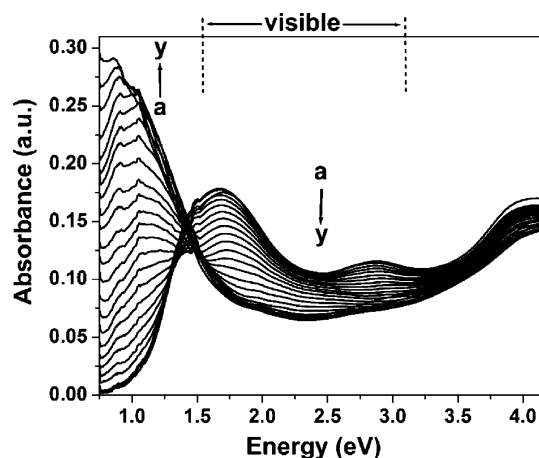
$7.75 \times 10^{-5}$  C. If we assume a density for the P(DEDOT-ITNIm) film as  $1.4$  g/cm<sup>3</sup> (usual densities of conducting polymers are between  $1.2$  and  $1.6$  g/cm<sup>3</sup>) and a volume of ca.  $1.0 \times 10^{-7}$  cm<sup>3</sup> (electrode area  $0.02$  cm<sup>2</sup>, thickness 50 nm), the mass of the polymer responsible to store this much charge should be  $1.4 \times 10^{-7}$  g. This means that the P(DEDOT-ITNIm) films store a charge of ca. 550 C per gram of the polymer when positively doped. With the addition of the charge stored at the negative side (n-doping), this number will increase to give a very desirable value for charge storage applications. For example, ca.  $1.1 \times 10^{-7}$  g of the polymer on a Pt button electrode was cycled between  $-1.85$  and  $+0.3$  V vs Ag/Ag<sup>+</sup> to examine p- and n-doping and stability of the polymer (see Figure 5A). The charge stored per gram of the polymer is about 325 C in this case. The reason for the decrease in the charge stored by polymer is the shorter cycle limited to  $+0.3$  V, instead of scanning up to 1.15 V. Note that the polymer film stores  $4.2 \times 10^{-5}$  C (ca. 300 C/g) of charge between  $+0.3$  and  $+1.15$  V. Examination of Figure 4 reveals that the area between ca.  $-0.7$  and ca.  $-0.3$  V is due to redox (Faradaic) and the area between ca.  $-0.3$  and  $+1.15$  V is due to non-Faradaic processes. Hence, only a fraction of the charge stored is due to oxidation of the polymer (less than 1 electron per monomer unit).<sup>34</sup> The values that we report here are high compared to those of other conducting

(34) Personal communication with Prof. Bruce S. Dunn at University of California, Los Angeles.

polymers,<sup>35–38</sup> and demand further investigation, which will be reported in due course.

Figure 5 displays the CV of P(DEDOT-ITNIm) films between  $-1.85$  and  $+0.30$  V vs  $\text{Ag}/\text{Ag}^+$  in a monomer-free electrolyte solution of  $0.1$  M  $\text{Bu}_4\text{NPF}_6/\text{PC}$  (Figure 5A) and  $0.1$  M  $\text{LiClO}_4/\text{PC}$  (Figure 5B). The polymer films show different characteristics in different electrolyte solutions during the oxidation (hole injection) and the reduction (electron injection) of the neutral polymer. P(DEDOT-ITNIm) films demonstrated reversible oxidation and reduction waves and reasonable stability in n-doping, as well as very high stability in p-doping processes during 10 cycles with  $\text{Bu}_4\text{NPF}_6$  as the electrolyte (Figure 5A). This stability is relatively high and uncommon compared to that of other n-dopable conjugated polymers that have been previously reported.<sup>39,40</sup> Generally n-dopable polymer films lose their electroactivity after several cycles because of the high reactivity of the radical polyanions and anions formed upon reduction to ambient exposure. Note that the 10 cycles were recorded after equilibrating the polymer by cycling 3 times in the same potential window, and experiments were conducted in an open laboratory by purging argon during the cycling. The polymer films showed slightly higher currents in the first cycle of n-doping, then stabilized starting from second cycle. The band gap calculated from the onset potentials of the oxidation and reduction is about  $1.10$  eV. This value was expected from the design considerations. The control experiments for n-doping were conducted using the ITNIm monomer itself in the same electrolyte solution; no electron addition was observed when scanned to  $-1.90$  V vs  $\text{Ag}/\text{Ag}^+$ .

Contrary to the above observations, when  $\text{LiClO}_4$  was the electrolyte, irreversible waves were observed (Figure 5B). As the CV was initiated from  $-1.0$  V and scanned in the positive direction, preoxidation of the polymer at  $-0.38$  V with an onset of  $-0.60$  V vs  $\text{Ag}/\text{Ag}^+$  followed by capacitive behavior was observed. Upon potential reversal at  $+0.45$  V, reduction of the oxidized polymer occurs at almost the same potential as that observed for oxidation. Upon further scanning in the cathodic direction, a reductive process at  $-1.80$  V with an onset at  $-1.50$  V vs  $\text{Ag}/\text{Ag}^+$  was observed. Upon changing polarity and scanning to the anodic side, the  $\text{LiClO}_4$  starts to show its presence compared to  $\text{Bu}_4\text{NPF}_6$ . A reverse of the reduction peak appears at  $-1.57$  V for the n-doped polymer, but all of the negative charges created during n-doping cannot be removed. This may stem from the strong interaction of lithium ion present in the electrolyte solution with the polymer backbone as explained by Zotti et al.<sup>41</sup> A very strong oxidation peak observed at  $-0.10$  V in the second cycle upon the oxidation of the polymer might correspond to releasing



**Figure 6.** Spectroelectrochemistry of thin P(DEDOT-ITNIm) film (ca. 80 nm) in  $0.1$  M  $\text{LiClO}_4/\text{PC}$  at applied potentials of (a)  $-1.00$ , (b)  $-0.90$ , (c)  $-0.80$ , (d)  $-0.70$ , (e)  $-0.60$ , (f)  $-0.55$ , (g)  $-0.50$ , (h)  $-0.45$ , (i)  $-0.40$ , (j)  $-0.35$ , (k)  $-0.30$ , (l)  $-0.25$ , (m)  $-0.20$ , (n)  $-0.15$ , (o)  $-0.10$ , (p)  $-0.05$ , (q)  $0.00$ , (r)  $+0.05$ , (s)  $+0.10$ , (t)  $+0.15$ , (u)  $+0.20$ , (v)  $+0.25$ , (w)  $+0.30$ , (x)  $+0.35$ , and (y)  $+0.40$  V vs  $\text{Ag}/\text{Ag}^+$ .

the charge trapped during the n-doping. In the second cycle, an increase was observed in the capacitive currents after the oxidation of the polymer. Reduction of the oxidized polymer follows the same pathway without considerable change in the first cycle currents at the anodic side. The peak currents drop gradually in each cycle starting from this point, and the polymer film loses its electroactivity after several cycles. From these data we conclude that the interaction of lithium with the n-doped polymer backbone destroys its electroactivity.

**Spectroelectrochemistry and Colorimetry.** Figure 6 depicts the spectroelectrochemistry of P(DEDOT-ITNIm) films electrochemically deposited on an ITO-coated glass slide. The  $\pi-\pi^*$  transition of the neutral polymer (at  $-1.0$  V vs  $\text{Ag}/\text{Ag}^+$ ) is located at the edge of the visible region at  $\lambda_{\text{max}} = 780$  nm ( $1.59$  eV) and is accompanied by a “secondary” absorption at  $\lambda_{\text{max}} = 440$  nm ( $2.82$  eV). This “secondary” peak at  $440$  nm may stem from the two carbonyl groups of the imide group. Note that monomer solutions have a reddish-brown color and absorb at  $475$  nm. The electronic band gap calculated from the onset of the  $\pi-\pi^*$  transition is about  $1.10$  eV. The values determined from electrochemistry and spectroelectrochemistry are in excellent agreement. Upon electrochemical oxidation, the  $\pi-\pi^*$  transition and the  $440$  nm band are depleted at the expense of an intense absorption band centered in the NIR, corresponding to the low energy charge carriers. Spectroelectrochemistry studies of conducting polymers (including PEDOT) usually show similar transmittance changes ( $\% \Delta T$ ) upon oxidation at the wavelengths where the absorption of the neutral and oxidized polymers are located. The P(DEDOT-ITNIm) films show an unusual spectroelectrochemistry compared to that of other conducting polymers with  $\% \Delta T$  of 8, 15, and 49% at  $440$  ( $2.82$  eV),  $780$  ( $1.59$  eV), and  $1700$  ( $0.70$  eV) nm, respectively. Clearly, for unknown reasons, the  $\% \Delta T$  in the NIR is more than 3 times that in the visible region.

Relative luminance ( $\% Y$ ) is more informative than transmittance because, with only one value, it provides information about the perceived transparency of a

(35) Ferraris, J. P.; Eissa, M. M.; Brotherston, I. D.; Loveday, D. C. *Chem. Mater.* **1998**, *10*, 3528.

(36) Gofer, Y.; Sarker, H.; Killian, J. G.; Poehler, T. O.; Searson, P. C. *Appl. Phys. Lett.* **1997**, *71*, 1582.

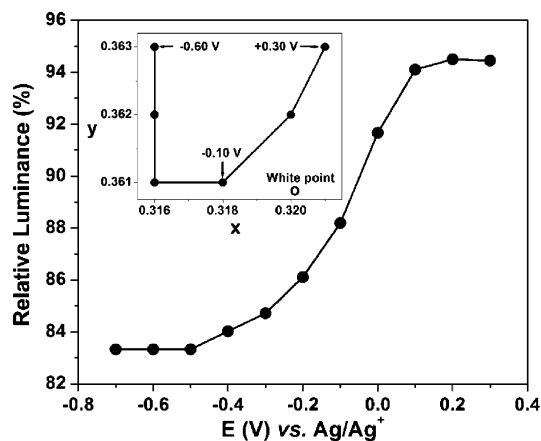
(37) Gottesfeld, S.; Ferraris, J. P.; Rudge, A.; Raistrick, I. *Electrochim. Acta* **1994**, *39*, 273.

(38) Stenger-Smith, J. D.; Webber, C. K.; Anderson, N.; Chafin, A. P.; Zong, K.; Reynolds, J. R. *J. Electrochem. Soc.* **2002**, *149*, A973.

(39) Roncali, J. *Chem. Rev.* **1997**, *97*, 173.

(40) Pomerantz, M.; Gu, X.; Zhang, S. X. *Macromolecules* **2001**, *34*, 1817.

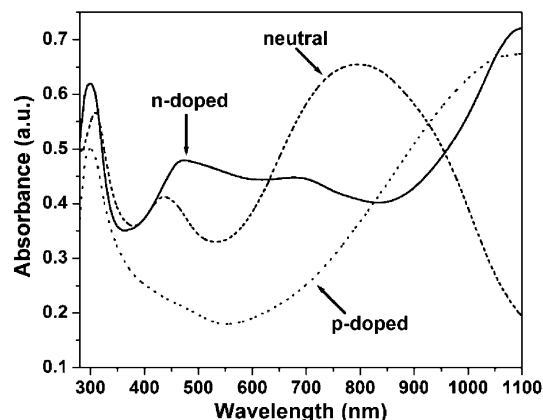
(41) Zotti, G.; Schiavon, G.; Zecchin, S. *Synth. Met.* **1995**, *72*, 275.



**Figure 7.** Relative luminance of P(DEDOT-ITNIm) film on ITO-coated glass slide as a function of the potential applied vs  $\text{Ag}/\text{Ag}^+$ ; colorimetry (x–y diagram) of the same film is given in the inset figure.

sample over the entire visible range of light.<sup>42</sup> %Y is different from %T (single wavelength) as it takes into account the full spectrum and the light sensitivity of the human eye, which is not constant over this range.<sup>43,44</sup> Because neutral P(DEDOT-ITNIm) films absorb over the whole visible region, %Y can be more informative to understanding the transparency of this polymer in this region. The change in %Y of P(DEDOT-ITNIm) films between reduced and oxidized states is about 11% (Figure 7). If we consider this value as an average value of the  $\% \Delta T$  in the visible region, the change in transmittance in the NIR becomes almost 5 times the change in the transmittance in the visible. The inset of Figure 7 depicts the color change of the polymer. The film's change in the x–y values upon oxidation is very small and close to the white point, meaning that it is very transmissive and almost no color change is observed. The human eye is relatively insensitive to such small variations in color and the P(DEDOT-ITNIm) films appeared rather transparent, much like a neutral density filter.

The anions formed upon reduction of n-dopable conducting polymers are very sensitive to the environment making it difficult to obtain spectroelectrochemical results. Hence, very few spectroelectrochemistry reports exist for all three states (neutral, and p- and n-doping) of a conducting polymer.<sup>45–47</sup> The spectroelectrochemistry of the neutral, p-doped, and n-doped forms of the same polymer on an ITO-coated glass slide are presented in Figure 8. It should be noted that the spectroelectrochemistry experiments for n-doping were conducted in an open atmosphere. Because the re-doped polymer is very sensitive to moisture, a Hewlett-Packard 8453 UV–Visible diode array spectrophotom-



**Figure 8.** Spectroelectrochemistry of P(DEDOT-ITNIm) film in 0.1 M  $\text{Bu}_4\text{NPF}_6/\text{PC}$  at three different oxidation levels: (a) neutral ( $-1.0$  V, dashed line), (b) n-doped ( $-1.90$  V, solid line), and (c) p-doped ( $+0.5$  V, dotted line), polymer.

eter was used instead of a Shimadzu UV 3101PC UV–Visible-NIR. The latter is a scanning instrument and too slow to intercept the negative polarons and bipolarons. As explained in previous sections, the neutral polymer has a strong absorption band at about 780 nm with an additional peak at 440 nm. Upon oxidation, the  $\pi$ – $\pi^*$  transition in the visible region is depleted at the expense of an absorption band in the NIR, corresponding to low energy charge carriers (see also Figure 9). In case of n-doping, negative charges are created on the polymer backbone, converting the polymer to its n-type conductive state. As the polymer film is n-doped at  $-1.90$  V vs  $\text{Ag}/\text{Ag}^+$  the  $\pi$ – $\pi^*$  transition in the visible region is depleted again at the expense of a strong absorption in the NIR. Interestingly, the absorption at 440 nm shifts to 470 nm with another peak at 690 nm. As a result, a flat spectrum was obtained in the entire visible region with a region transmitting about 35% of the light. This may stem from the possible resonance contributors of the n-doped polymer, proposed in Figure 9. On the other hand, the strong absorption of the n-doped polymer in the NIR, which is as high as that of the p-doped polymer, indicates that almost the same amount of charge can be created on the polymer backbone upon p- and n-doping. This should be considered further proof of n-doping.

## Conclusion

In summary, a new p- and n-dopable, highly stable, low band gap polymer was electrochemically synthesized. The band gap numbers (1.10 eV) obtained for P(DEDOT-ITNIm) films from electrochemistry and optical measurements are in excellent agreement. P(DEDOT-ITNIm) films were very stable to overoxidation upon p-doping and electrochemically relatively stable upon n-doping. Thin polymer films on ITO-coated glass slides showed exceptional optical properties upon both p- and n-doping, such as small changes in the transparency and color of the polymer in the visible but substantial changes in the NIR, which can be very useful for NIR devices. Charge storage capability of P(DEDOT-ITNIm) films is very high compared to that of the other conducting polymers, making this polymer a good candidate for charge storage purposes.

(42) Sonmez, G.; Schwendeman, I.; Schottland, P.; Zong, K.; Reynolds, J. R. *Macromolecules* **2003**, *36*, 639.

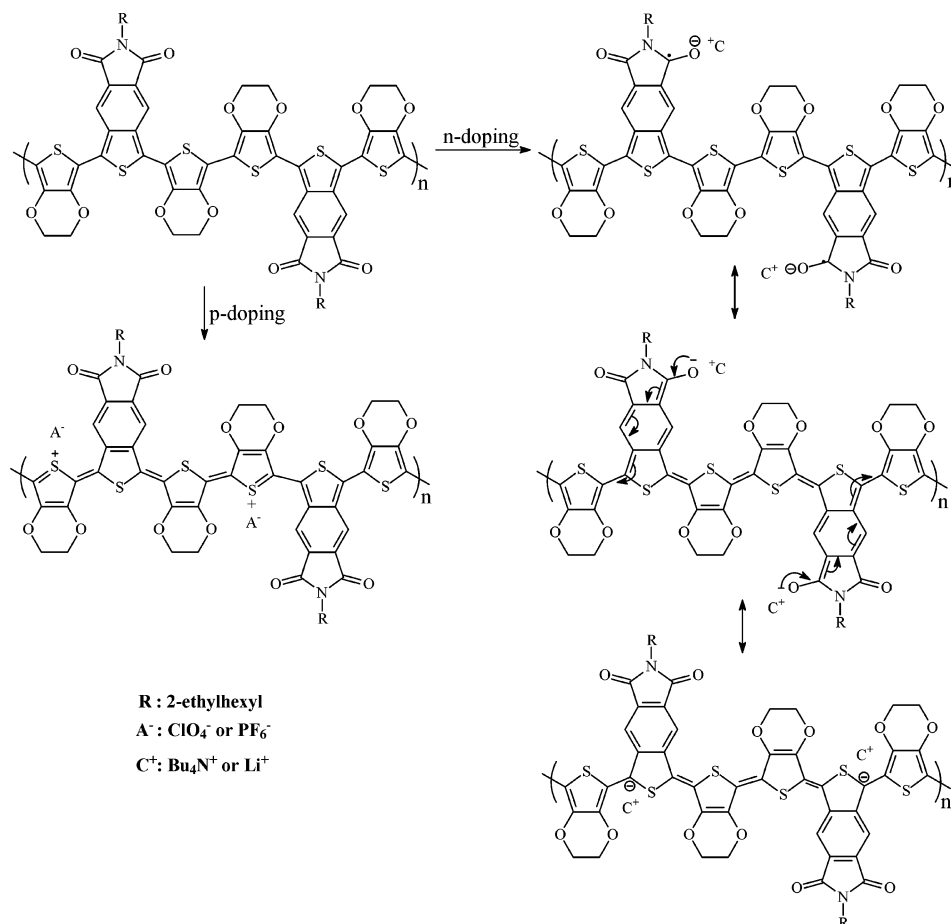
(43) Thompson, B. C.; Schottland, P.; Sonmez, G.; Reynolds, J. R. *Synth. Met.* **2001**, *119* (1–3), 333.

(44) Nassau, K. *Color for Science, Art and Technology*; Elsevier: Amsterdam, The Netherlands, 1998.

(45) Ahonen, H. H.; Lukkari, J.; Kankare, J. *Macromolecules* **2000**, *33*, 6787.

(46) Iraqi, A.; Crayston, J. A.; Walton, J. C. *J. Mater. Chem.* **1998**, *8*, 31.

(47) Ballarin, B.; Costanzo, F.; Mori, F.; Mucci, A.; Pigani, L.; Schenetti, L.; Seeber, R.; Tonelli, D.; Zanardi, C. *Electrochim. Acta* **2001**, *46*, 881.



**Figure 9.** Proposed mechanism for n- and p-doping of P(DEDOT-ITNIm).

### Experimental Section

All chemicals were purchased from Aldrich Chemical. Propylene carbonate (PC) (99.7%, anhydrous) was distilled over calcium hydride before use. All new compounds were characterized by <sup>1</sup>H, <sup>13</sup>C NMR, MS, and elemental analysis. NMR spectra were taken on a Bruker ARX 400 spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS). Melting points were measured using a capillary melting point apparatus (MelTemp from Laboratory Devices) and were uncorrected. Elemental analysis results were obtained from Desert Analytics Co.

Electropolymerization was carried out with a BAS 100B/W potentiostat, employing a platinum button (diameter 1.6 mm; area 0.02 cm<sup>2</sup>) or ITO-coated glass slides as working electrode, a platinum flag or wire as counter electrode, and a silver wire or 0.01 M Ag/AgNO<sub>3</sub> (Ag/Ag<sup>+</sup>) as reference. The electrolytes used were 0.1 M of LiClO<sub>4</sub>/PC and 0.1 M of tetrabutylammonium hexafluorophosphate (Bu<sub>4</sub>NPF<sub>6</sub>) in PC. The electrodeposition was performed from a 0.01 M solution of the monomer in the electrolyte potentiodynamically at a scan rate of 20 mV/s or potentiostatically at the potential of 0.40 V vs Ag/Ag<sup>+</sup>. Cyclic voltammetry was carried out using the same electrode setup using monomer-free electrolyte of 0.1 M LiClO<sub>4</sub>/PC or 0.1 M Bu<sub>4</sub>NPF<sub>6</sub>/PC.

Spectroelectrochemical data were recorded on a Shimadzu UV 3101PC UV-Visible-NIR or Hewlett-Packard 8453 UV-Visible spectrophotometer connected to a computer. A three-electrode cell assembly was used where the working electrode was an ITO-coated glass slide (7 × 50 × 0.6 mm, R<sub>s</sub> ≤ 10 Ω/□, Delta Technologies Inc.), the counter electrode was a platinum wire, and a Ag wire was used as a pseudo-reference electrode. The pseudo-reference was calibrated externally using a 5 mM solution of ferrocene (Fc/Fc<sup>+</sup>) in the electrolyte (E<sub>1/2</sub>(Fc/Fc<sup>+</sup>) = +0.140 V vs Ag wire and +0.075 V vs Ag/Ag<sup>+</sup> in 0.1 M LiClO<sub>4</sub>/PC). The potentials are reported versus Ag/Ag<sup>+</sup>. Polymer films

for spectroelectrochemistry were prepared by potentiostatic deposition on ITO-coated glass slides. ITO-supported films were grown at 0.40 V vs Ag/Ag<sup>+</sup> in 0.1 M LiClO<sub>4</sub>/PC containing 0.01 M of monomer.

Colorimetry measurements were obtained using a Minolta Chroma Meter CS-100A and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements.<sup>48</sup> As for spectroelectrochemistry, a three-electrode cell was employed. The potential was controlled by the same BAS 100B/W potentiostat. The sample was illuminated from behind by a D50 (5000 K) light source in a light booth (Minolta GTI ColorMatcher) specially designed to exclude external light and illumination from behind. The color coordinates are expressed in the CIE 1931 Yxy color space where the Y value is a measure of the luminance in Cd/m<sup>2</sup>. The relative luminance, expressed in %, was calculated by dividing the Y value measured on the sample by the Y<sub>0</sub> value corresponding to the background. Note that the relative luminance is frequently reported instead of the luminance because it gives a more meaningful value.<sup>49</sup>

**1,3-Bis(2'-[3',4'-ethylenedioxy]thienyl)-benzo[c]thiophene-N-2''-ethylhexyl-4,5-dicarboximide.** The monomers 2-tributylstannyl-3,4-ethylenedioxythiophene<sup>16</sup> and 2,5-dibromobenzo[c]thiophene-N-2'-ethylhexyl-4,5-dicarboximide<sup>25</sup> were synthesized as described by Swager et al.<sup>50</sup> and in our previous studies. Under argon atmosphere, 2-tributylstannyl-3,4-ethylenedioxythiophene (262 mg, 0.608 mmol) and 2,5-dibromobenzo[c]thiophene-N-2'-ethylhexyl-4,5-dicarboximide (115 mg, 0.243 mmol) were dissolved in 20 mL of THF. To this solution was added a catalytic amount of dichlorobis(triphenylphos-

(48) Markus, R. T. In *Color for Science, Art and Technology*; Nassau, K., Ed.; Elsevier: Amsterdam, The Netherlands, 1998; pp 31–96.

(49) Overheim, R. D.; Wagner, D. L. *Light and Color*; Wiley: New York, 1982; p 77.

(50) Zhu, S. S.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12568.

phine)palladium(II) [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (50 mg, 0.07 mmol), and the mixture was refluxed for 24 h. During the reaction, the color changed from yellow to black as Pd<sup>0</sup> was formed. After cooling, the reaction mixture was poured into saturated sodium chloride solution (100 mL). Ethyl acetate (60 mL) was added. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate (20 mL × 3). The combined organic layers were dried over anhydrous magnesium sulfate and filtered. After evaporation of the solvents, the residue was purified by chromatography with hexane/ethyl acetate (10:1) as the first eluent, hexane/ethyl acetate (10:3) as the second eluent on silica gel to remove the impurities, and then hexane/ethyl acetate (4:1) as the final eluent to get the orange-color fluorescent product. After removing the solvents, the light red-brown powders were collected (80 mg, 55%). Mp 152–153 °C. EI, MS *m/z* (%): 595 (100, M<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ 8.39 ppm (s, 2 H), 6.51 ppm (s, 2 H), 4.36 ppm (dd, 4H), 4.31 ppm (dd, 4H), 3.62 ppm (d, 2 H), 1.88 ppm (m, 1 H), 1.65 ppm

(m, 4 H), 1.34 ppm (m, 4 H), 0.89 ppm (m, 6 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 500 MHz): δ 168.1, 141.9, 138.9, 134.7, 130.2, 125.7, 119.7, 108.9, 100.7, 65.07, 64.44, 42.11, 38.11, 30.49, 28.47, 23.81, 22.89, 13.49, 10.36 ppm. Anal. Calcd. for C<sub>30</sub>H<sub>29</sub>NO<sub>6</sub>S<sub>3</sub>: C, 60.48; H, 4.91; N, 2.35; S, 16.15. Found: C, 59.09; H, 4.60; N, 2.32.

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