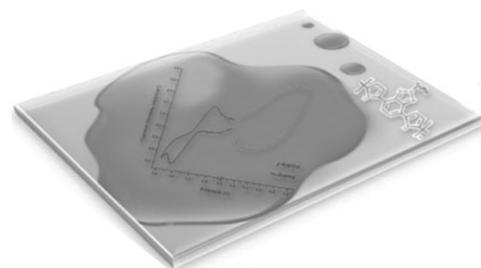


# Spectroelectrochemical and Photovoltaic Characterization of a Solution-Processable n-and-p Type Dopable Pyrrole-Bearing Conjugated Polymer<sup>a</sup>

Derya Baran, Abidin Balan, Beatriz-Meana Esteban, Helmut Neugebauer, Niyazi Serdar Sariciftci, Levent Toppare\*

D-A-D-type polymers are of high interest in the field of photovoltaics and electrochromism. In this study we report the synthesis and electrochemical properties of PPyBT along with its photophysical properties and photovoltaic performance. PPyBT is soluble in common organic solvents and both n- and p-type dopable, which is a desired property for conjugated polymers. During electrochemistry studies, the onset potentials of the polymer were determined as +0.2 V for oxidation and -1.4 V for reduction. Using these values, HOMO and LUMO energy levels were calculated. The photovoltaic properties of PPyBT were also studied. PL studies showed that there is a charge transfer between PPyBT (donor) and PCBM (acceptor).



D. Baran, A. Balan, L. Toppare  
Department of Chemistry, and Solar Energy Research and  
Development Center (GÜNAM), Middle East Technical University,  
06531 Ankara, Turkey

Fax: +90 312 210 3200; E-mail: toppare@metu.edu.tr

B. M. Esteban

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry,  
Johannes Kepler University of Linz, Austria, and Process Chemistry  
Centre, c/o Laboratory of Analytical Chemistry, Åbo Akademi  
University, FIN-20500 Åbo-Turku, Finland

H. Neugebauer, N. S. Sariciftci

Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry,  
Johannes Kepler University of Linz, Austria

<sup>a</sup> Supporting information for this article is available at the bottom of the article's abstract page, which can be accessed from the journal's homepage at <http://www.mcp-journal.de>, or from the author.

## Introduction

Conjugated polymers are currently the subject of intense research to produce low cost, lightweight and flexible optoelectronic devices.<sup>[1]</sup> Their optical and electronic properties such as strong optical absorption coefficients in the visible region make them great candidates for device applications.<sup>[2]</sup> Especially, solubility in common organic solvents and stability in both p- and n-doped states are attractive and desired features to manufacture organic optoelectronic devices.<sup>[3]</sup>

As an alternative source of cheap and clean energy, conversion of solar energy into electricity is becoming a very important issue. Conjugated polymers and their use in polymer photovoltaics offer a great potential for the next generation thin-film photovoltaic devices.<sup>[4]</sup> Low band gap polymers are a relatively hot topic of research for better photon harvesting in organic solar cells.<sup>[5]</sup> One way to

synthesize low band gap polymers is the donor/acceptor (push/pull) approach which allows having a high energy level for the highest occupied molecular orbital (HOMO) of the donor and a low energy level for the lowest unoccupied molecular orbital (LUMO) moieties incorporated into the monomer.<sup>[6]</sup> The low bandgap often causes polymers to be transparent in the doped state (p- or n-type). This makes them also useful in electrochromic smart windows where the transparency can be exploited. Additionally, low-bandgap polymers have a low-lying LUMO, which means that the LUMO is generally more accessible to n-type doping.<sup>[7]</sup>

Up to date, conjugated polymer based photovoltaics were constructed to yield efficiencies as high as 6.0–7.0%.<sup>[8]</sup> Promising results were achieved with bulk heterojunction devices based on dialkoxy poly(*p*-phenylenevinylene)s [PPVs, e.g. poly[2-methoxy-5-(2'-ethylhexyloxy)-*p*-phenylene vinylene] (MEH-PPV) or poly[2-methoxy-5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV)] or poly-(alkylthiophenes) (P3AT) as donors in combination with a soluble fullerene derivative such as 1-(3-methoxycarbonyl)propyl-1,1-phenyl-(6,6)C<sub>61</sub> (PCBM).<sup>[9]</sup> Via optimizations on film morphology, choice of electrodes and ratio of donor and acceptor moieties in the bulk, efficiency can be increased. Although the peak of photon flux from the sun occurs at around 1.5 eV, P3AT and MDMO-PPV type polymers do not have an appreciable absorbance in this wavelength range. Thus, their relatively high band gaps become the major limitation for operating PPV- or P3AT-based photovoltaic devices. In order to increase the number of photons absorbed, synthesis of new, narrow band gap polymers are required.<sup>[10]</sup>

Diaz et al.<sup>[11]</sup> reported polypyrrole in electrochemical applications due to the ease of its polymerization both chemically and electrochemically. Thin films of the parent polypyrrole are yellow/green ( $E_g = 2.7$  eV) in the undoped insulating state and blue/violet in the doped conductive state.<sup>[12]</sup> Although there are large numbers of pyrrole derivatives used in electrochromism, solar cells which have pyrrole derivatives as active layer are very rare.<sup>[13]</sup>

Pyrrole was recently used as a donor group against quinoxaline acceptor derivatives to give green to transmissive electrochromic polymers.<sup>[14]</sup> Insertion of pyrrole into the D-A-D type polymers with new acceptor units are significantly important since they can combine the ability of both p and n doping with the transparent regime property of such low band gap polymers.

Recently, benzotriazole containing donor/acceptor-type polymers synthesized in our group showed tremendous electrochromic properties and became great candidates to be used in display technologies.<sup>[7,15]</sup>

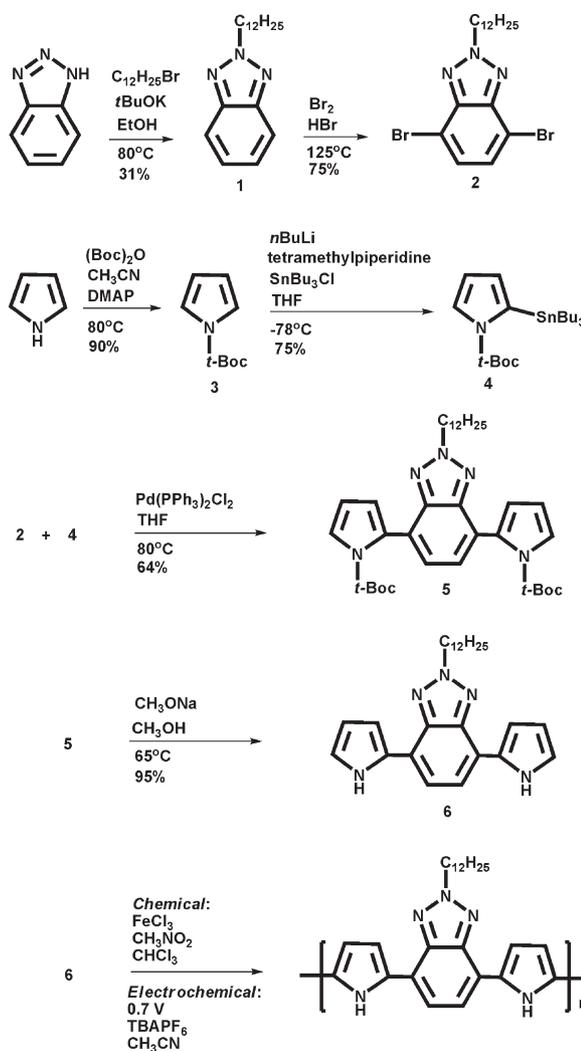
Here we report a novel polypyrrole derivative with 2-dodecyl benzotriazole in the main chain which was shown to be both p- and n-dopable by cyclic voltammetry (CV) and spectroelectrochemical experiments. The blue

(reduced) and highly transmissive (oxidized) colors of the different redox states, optical contrast, rapid switching, and solubility in different organic solvents make this polymer a nice candidate in electrochromic display technologies.

## Results and Discussion

### Synthesis

The synthetic route to the monomer and the polymer is revealed in Scheme 1. In order to achieve *N*-(*tert*-butoxycarbonyl)-2-(tributylstannyl)pyrrole,<sup>[16]</sup> pyrrole was *N*-protected using di-*tert*-butyl dicarbonate, (Boc)<sub>2</sub>O, and reacted with tributylstannyl chloride after lithiation at the 2 position. Alkylation of benzotriazole provided solubility for the final polymer.<sup>[17]</sup> In order to obtain large scale processable polymer, chemical polymerization was performed in the presence of FeCl<sub>3</sub>. The purity of monomer was proved by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and MS analyses.



■ Scheme 1. Synthetic route to monomer PyBT and the PPyBT.

## Electropolymerization

In order to work out the redox behavior of 2-dodecyl-4,7-di(1H-pyrrol-2-yl)-2H-benzo[1,2,3]triazole (PyBT) in detail, CV studies were carried through in a 0.1 M tetrabutylammonium hexafluorophosphate/acetonitrile (TBAPF<sub>6</sub>/ACN) solution. As described in Figure 1, PyBT shows a monomer oxidation peak at 0.7 V accompanied by a reversible redox couple for polymer at 0.2 and 0.4 V versus Ag/AgCl. During repetitive cycles, increase in current densities confirmed the formation of an electroactive polymer film on the ITO coated glass. Using the cyclic voltammogram of poly(2-dodecyl-4,7-di(1H-pyrrol-2-yl)-2H-benzo[1,2,3]triazole) (PPyBT), oxidation-to-reduction peak ratios are found to be very close to 1.0, which is a prominent indication for superior reversibility of the redox process. PyBT showed a significant decrease in monomer oxidation potential compared to other benzotriazole containing donor/acceptor-type molecules.<sup>[7,15b]</sup>

The redox behavior of the polymer film was investigated in a monomer free solution, using TBAPF<sub>6</sub>/ACN solvent/electrolyte system. A linear relationship between peak height and scan rate indicated a non-diffusion controlled redox process and a well adhered electroactive polymer film (see Supporting Information).

The unique acceptor capacity of benzotriazole with pyrrole enables PPyBT to be n-type dopable. In literature, it is assumed that due to the high sensitivity in the reduced form, pyrrole containing polymers usually cannot be n-type doped.<sup>[6]</sup> We have overruled this bias using benzotriazole in D-A-D systems. Figure 2 exhibits a single-scan cyclic voltammogram of the polymer film under open air atmosphere in a 0.1 M TBAPF<sub>6</sub>/ACN solution. During the reduction of the polymer, a reversible redox couple at  $-1.67$

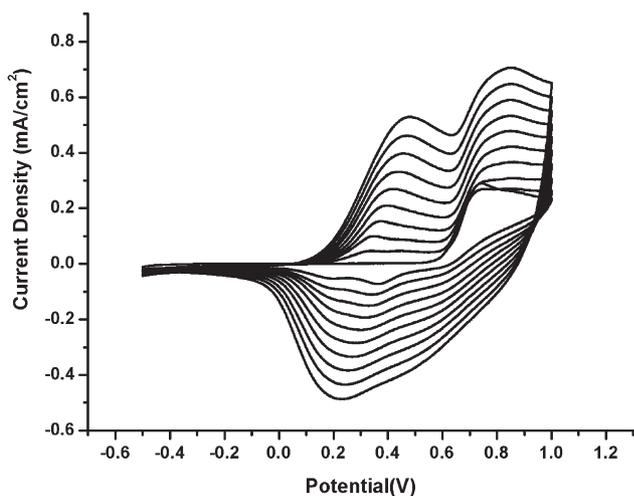


Figure 1. Electropolymerization of PyBT on ITO in 0.1 M TBAPF<sub>6</sub>/ACN electrolyte/solvent couple at a scan rate of 100 mV · s<sup>-1</sup>.

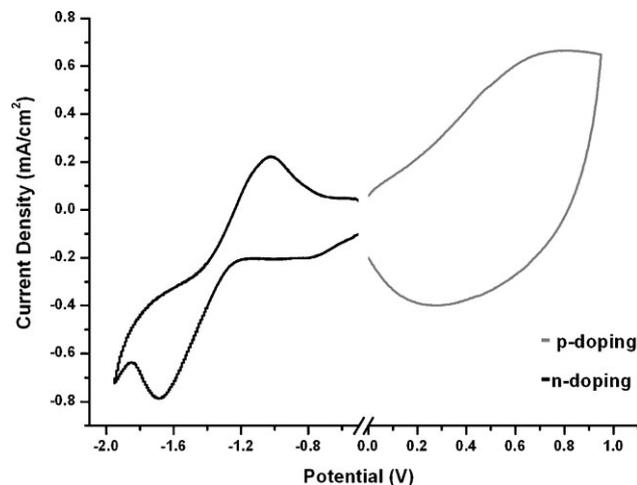


Figure 2. Single scan cyclic voltammogram of pristine polymer film of PPyBT for both p- and n-type doping under open air atmosphere.

and  $-1.05$  V of the polymer film was observed confirming the n-doping process.

Oxidation/reduction onset values of PPyBT were determined from CV. Hence, HOMO/LUMO values for the polymer were estimated from electrochemical data (Table 1). From CV experiments, the HOMO and LUMO levels of PPyBT were estimated as  $-4.95$  and  $-3.40$  eV, respectively, taking the value of the standard hydrogen electrode (NHE) as  $-4.75$  eV.<sup>[18]</sup>

## Spectroelectrochemistry

### In situ UV-Vis/NIR

To investigate the spectral changes upon doping and dedoping processes, PPyBT was characterized in a monomer-free solution of TBAPF<sub>6</sub>/ACN electrolyte, using UV-Vis/NIR spectrophotometry. Figure 3a demonstrates the change in the electronic absorption spectra of PPyBT upon increasing the applied potentials from 0 to +1.0 V. In the neutral form, the polymer shows two well-defined absorption maxima at 332 and 577 nm with a deep blue color (Y:32.2x:0.25y:0.24). These two maxima are the  $\pi$ - $\pi^*$  transitions due to the donor/acceptor nature of the polymer backbone.<sup>[19]</sup>

At low doping levels, the absorption bands at 332 and 577 nm decreased simultaneously and two new absorption maxima in the visible and near infrared (NIR) regions at 700 and 1230 nm intensified as a result of the polaronic/bipolaronic absorption bands.<sup>[20]</sup> Upon further oxidation of the polymer film, the bands in the UV-Vis regions reach a minimum value and the band at 700 nm starts to decrease probably due to the conversion of radical cations (polarons) to bipolarons on the polymer backbone which leads to a

Table 1. CV results for PPyBT.

Oxidation potential		Reduction potential		Bandgap		Orbital levels	
V		V		eV		eV	
$E_{\text{ox}}$	$E_{\text{onset,ox}}$	$E_{\text{red}}$	$E_{\text{onset,red}}$	$E_{\text{g}}^{\text{ec}}$	$E_{\text{g}}^{\text{op}}$	HOMO	LUMO
0.4	0.2	-1.7	-1.4	1.6	1.6	-5.0	-3.4

highly transmissive film with a blue color (Y:67.6x:0.29y:0.32) in the visible region. The optical band gap of PPyBT was calculated (from the low energy transition) as 1.6 eV which can be regarded as a low band gap material among conjugated polymers.<sup>[13]</sup>

Table 2 summarizes various properties of pyrrole and 3,4-ethylenedioxythiophene (EDOT)-containing D-A-D systems synthesized previously.<sup>[7,14], [19b,c]</sup> When quinoxaline moiety was used with EDOT as the donor; the green color, was achieved in the neutral forms of the polymers. In a similar manner, pyrrole containing monomers with the same acceptor group revealed also green color in their reduced states. Poly 4,7-bis(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-2-dodecyl-2H benzo[1,2,3]triazole (PBEBT), which consists of benzotriazole and EDOT units, was blue in its neutral state as its homolog PPyBT. However, the chemically produced polymer of PBEBT was blue-shifted and did not result in blue color as was the chemically produced polymer of PPyBT. It is noteworthy to state that PPyBT is the only one which is soluble when polymerized both electrochemically and chemically.

n-dopable conducting polymers with stable negatively doped states are of high interest in solar cells, organic field-effect transistors (OFETs),<sup>[22]</sup> and organic light-emitting diodes (OLEDs).<sup>[23]</sup> To attain such significant property under

ambient conditions makes these polymers more attractive for such studies. As stated previously by DuBois and Reynolds, only a simple electrochemical reduction is not sufficient to prove that the process is n-type doping.<sup>[24]</sup> In addition to reversible peaks observed in CV, confirmation for mobile charge carrier formation upon reduction should also be studied. Figure 3b reveals the encouraging n-doping behavior of PPyBT upon applied negative potentials. PPyBT film was coated potentiostatically for 2 min until 5 mC charge was deposited on indium/tin oxide (ITO, 0.01 M monomer in 0.1 M TBAPF<sub>6</sub>/ACN solution). A drastic increase in absorption in the NIR region at negative potentials is a clear evidence for n-doping process. When reduced, polymer film showed a light blue color (Y:70.3x:0.30y:0.31). As shown in Table 2, none of the pyrrole-containing polymers is n-type dopable. It is important to state that the low-lying LUMO allows PPyBT to be n-dopable.

Coloration efficiency is the ratio of injected/ejected charge per unit area of the electrode to the change in optical density at a dominant wavelength.<sup>[25]</sup> The corresponding value at 577 nm was calculated for 256 cm<sup>2</sup> · C<sup>-1</sup> for PPyBT.

#### In situ Infrared Spectroscopy Characterization

The redox response of PPyBT film was studied by in situ Fourier-transform infrared attenuated total reflection

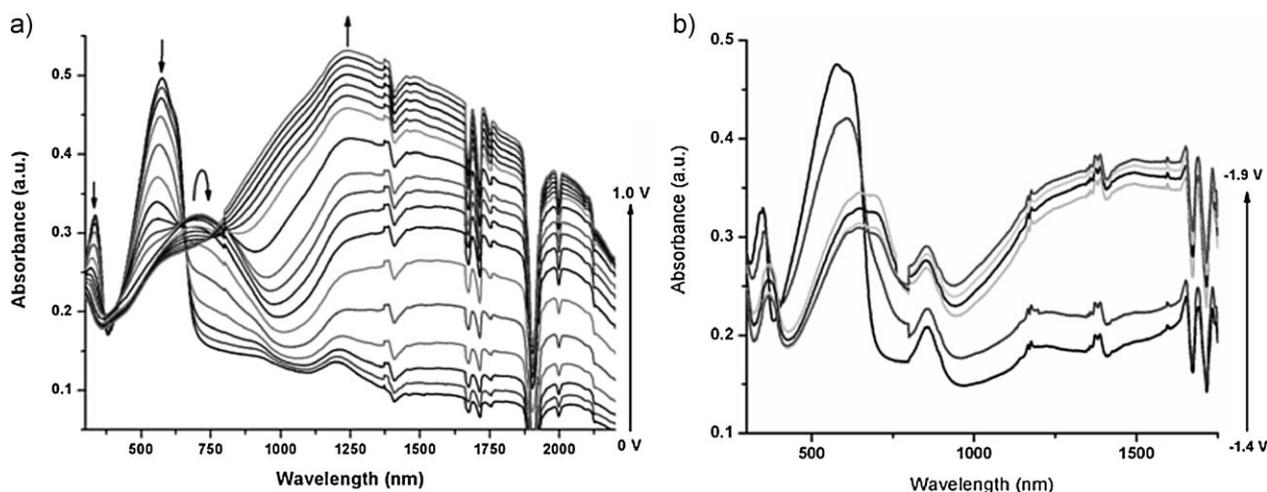
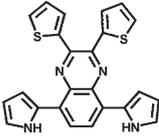
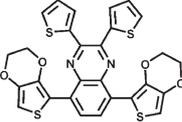
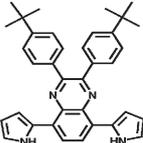
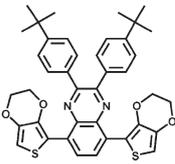
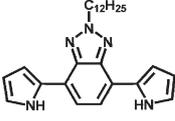
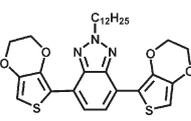


Figure 3. (a) Change in the electronic absorption spectra of PPyBT at potentials between 0 and +1.0 V with 0.05 V potential increments and (b) the electronic absorption of PPyBT upon reduction between -1.4 and -1.9 V with 0.1 V potential intervals.

Table 2. The structures of pyrrole- and EDOT-based D-A-D-type monomers and properties of their polymers.

Monomer	$E_m^{ox}$ V	$\lambda_{max}$ nm	Optical bandgap eV	Solubility	n-Type character
	0.7	400, 815	1.0	no	no
	0.85	405, 780	1.2	no	yes
	0.54	408, 745	1.3	no	no
	0.9	452, 711	1.2	no	yes
	0.7	577	1.6	yes	yes
	0.97	618	1.6	yes <sup>a)</sup>	yes

<sup>a)</sup>Only soluble when produced chemically (as opposed to electrochemical synthesis).<sup>[21]</sup>

(FTIR-ATR) spectroscopy in 0.1 M TBAPF<sub>6</sub>/ACN solutions. Figure 4a shows the FTIR-ATR spectra during oxidation of the film between -0.5 and +0.6 V. The reference spectrum was chosen at a potential where the polymer was in its neutral form. Then, the subsequent spectra are related to this reference spectrum. In this way, structural and electronic changes in the material can be studied in this

potential range during the charging process (p-doping) of PPyBT. The CV is shown in the inset of Figure 4a. The arrows indicate where the difference spectra have been measured. Enlargement of the spectra in the wavenumber region 2000–600 cm<sup>-1</sup> is shown in Figure 4b. In Figure 4a the spectra are dominated by a broad absorption above 2000 cm<sup>-1</sup> extending into the NIR range. This electronic

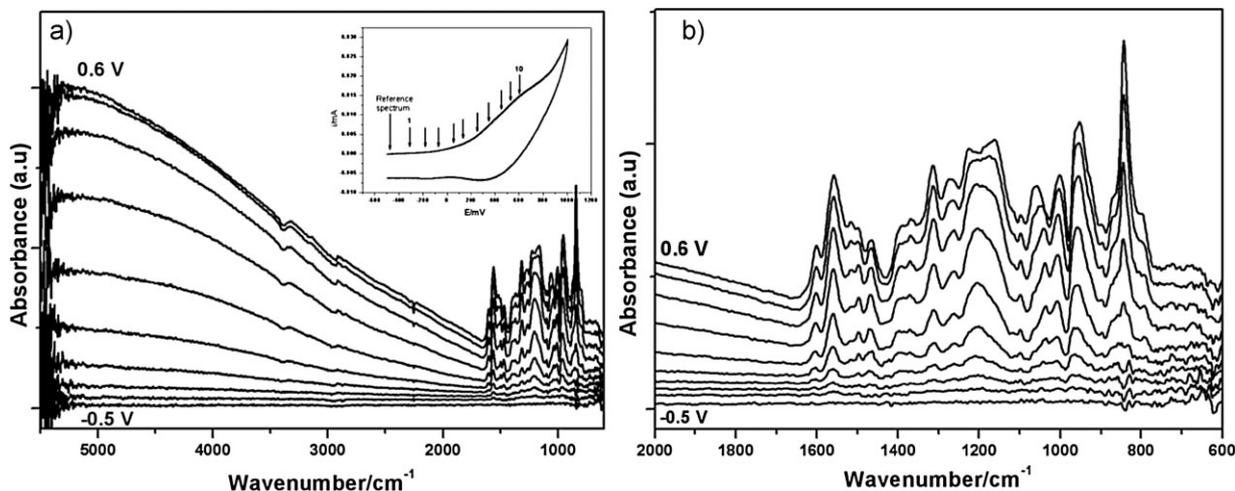


Figure 4. In situ FTIR-ATR spectra recorded during oxidation (p-doping) of a PPYBT film between  $-0.5$  and  $+0.6$  V (a) in the wavenumber region  $5500$ – $600$   $\text{cm}^{-1}$  (the numbers indicate the potential values where each spectrum was recorded and refer to the cyclic voltammogram in the inset and (b) in the wavenumber region  $2000$ – $600$   $\text{cm}^{-1}$ .

absorption is related to the increase of conductivity of the film due to the formation of free charge carriers during the p-doping (oxidation). Figure 4b shows new infrared induced bands; the so-called infrared active vibration (IRAV) bands. These bands are Raman bands, activated and strongly enhanced in the infrared due to the strong e-/ph coupling of charges in conjugated polymers. IRAV bands that grow with increasing doping level can be found at  $\approx 1557$ ,  $1468$ ,  $1666$ ,  $1306$ ,  $1226$ ,  $1103$ ,  $1059$ , and  $955$   $\text{cm}^{-1}$ . Additionally, a band at  $842$   $\text{cm}^{-1}$  is seen which is due to the presence of  $\text{PF}_6^-$  anions that migrates into the film during oxidation. The pattern of the IRAV bands is very complicated; this makes the assignment of each vibrational band very difficult. However, some similarities have been found with the IRAV bands appearing during oxidation of polypyrrole,

electrochemically polymerized in acetonitrile solutions containing  $\text{LiClO}_4$  as the electrolyte.<sup>[26]</sup> IRAV bands of polypyrrole can be found at  $1446$ ,  $1288$ ,  $1217$ ,  $1038$ ,  $924$ , and  $782$   $\text{cm}^{-1}$ . Additionally spectral features were found in the spectra of polypyrrole at  $1452$  and  $1376$   $\text{cm}^{-1}$ .

Figure 5a shows the FTIR-ATR spectra taken between  $0.7$  and  $1.0$  V. The reference spectrum to which the rest of the spectra were normalized was chosen at  $-0.5$  V. In this way, only changes of the electronic and vibrational properties of the film during the second step of the p-doping are studied. The CV is shown in the inset of Figure 5a. The arrows indicate where the difference spectra have been measured. From Figure 5a, it is seen that the broad electronic absorption at higher wavenumbers decrease as the potential is swept to more positive values (higher doping

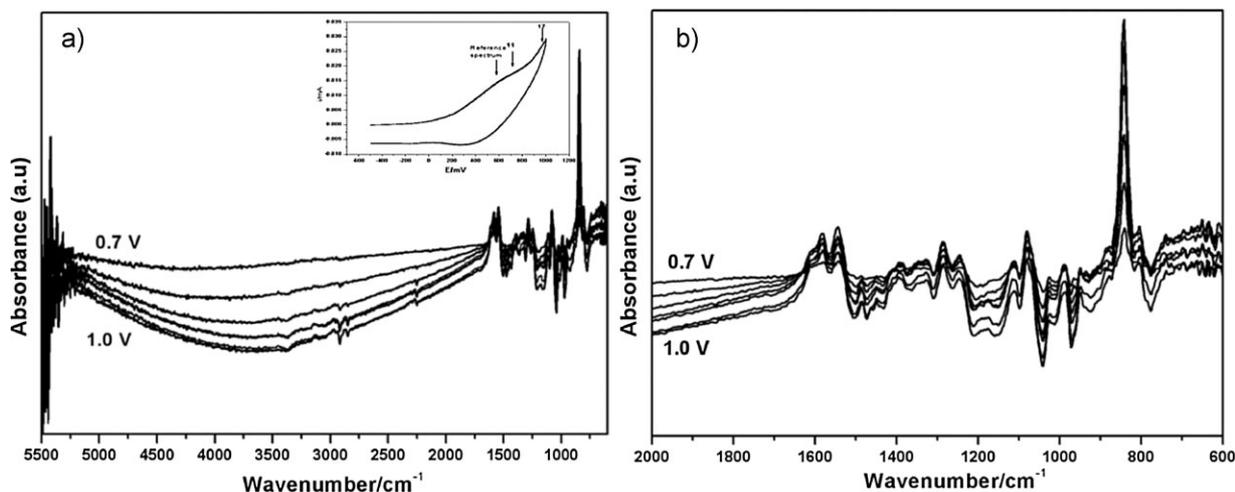


Figure 5. In situ FTIR-ATR difference spectra recorded during oxidation (p-doping) of a PPYBT film between  $0.7$  and  $1.0$  V (a) in the wavenumber region  $5500$ – $600$   $\text{cm}^{-1}$  and (b) in the wavenumber region  $2000$ – $600$   $\text{cm}^{-1}$ .

level). Figure 5b shows the vibrational part of the spectra where the IRAV bands can be found. Spectral features extending upwards show that new species appear and spectral features pointing downwards reveal the disappearance of species during the electrochemical process. The pattern of the IRAV bands is rather complicated since some bands are disappeared and new bands occur during the second step of the electrochemical process. This might be an indication that at higher doping levels different parts of the polymer are affected by the electrochemical doping. Furthermore, these changes are fully reversible upon reduction of the PPyBT film. The experimental results suggest that the charging reaction of PPyBT involves two different steps as shown by FTIR-ATR studies.

### Kinetic Studies

Chronoamperometry studies were performed to monitor the changes in transmittance as a function of time while sweeping the potential between fully oxidized and reduced states to obtain the switching speed of the polymer film at its maximum absorption wavelengths. During the experiment, optical contrasts of the polymer film at corresponding wavelengths were recorded using a UV-Vis/NIR spectrophotometer while the potential was switched between 0.0 and +1.0 V in 5 s time interval. PPyBT revealed 30% optical contrast at 577 nm between its neutral and oxidized states with a short switching time of 0.5 s. In NIR region, polymer film showed 46% transmittance change within 1.2 s (see Supporting Information).

Relative luminance studies which measure the amount of transmitted light through the polymer film (film lightness or darkness) were performed on electrochemically polymerized PPyBT films. The values ranged from 33% i.e.,

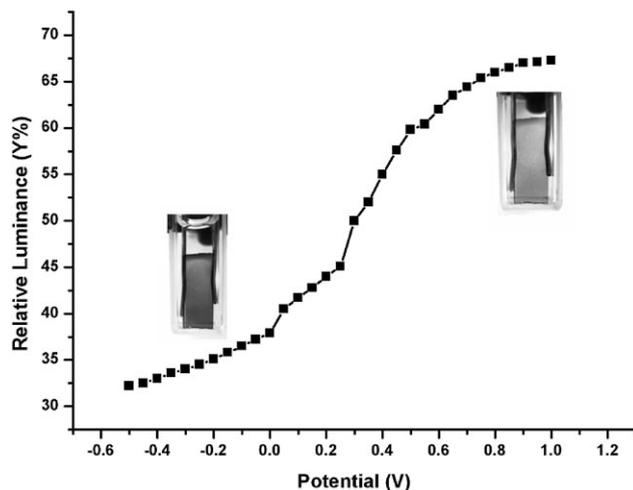


Figure 6. Relative luminance (Y%) values for PPyBT upon applied potential.

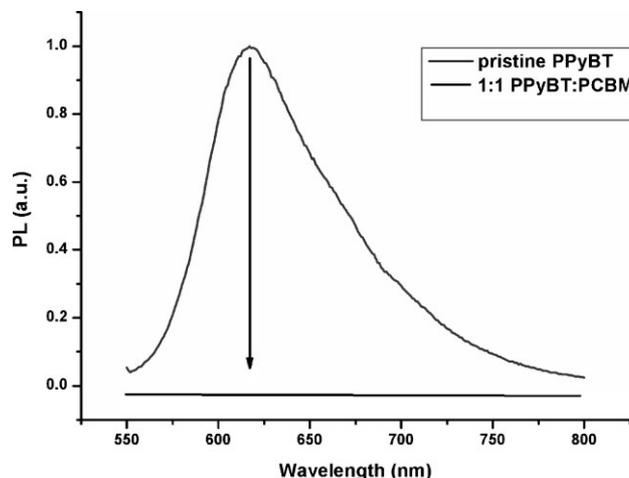


Figure 7. PL quenching of PPyBT when mixed with 50 wt.-% of PCBM.

neutral state, to 67% when the polymer film is light blue (Figure 6).

To determine the long term switching ability of the polymer film, PPyBT was deposited on ITO coated glass using CV in 0.01 M monomer and 0.1 M TBAPF<sub>6</sub>/ACN solution. Chronoamperometry was utilized to investigate the stability of PPyBT. Switching the polymer film between colored and bleached states resulted in less than 10% charge loss after 1 000 full switches for the polymer (see Supporting Information).

### Fabrication and Characterization of Solar Cells

In order to use PPyBT as a donor material in organic bulk heterojunction (BHJ) solar cells, it was chemically polymerized and mixed with PCBM as the acceptor.<sup>[9]</sup> The

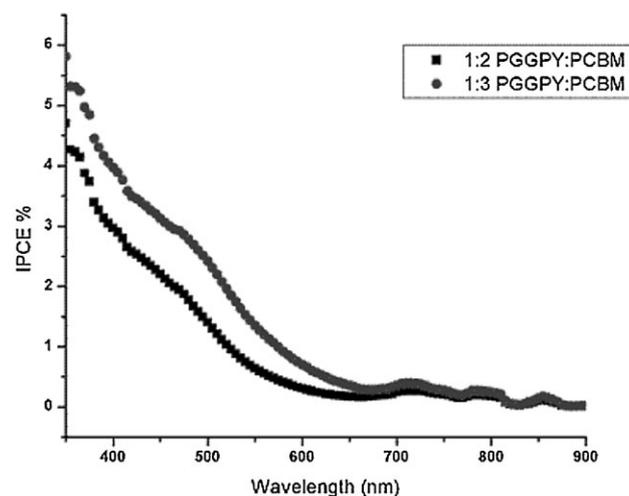


Figure 8. IPCE % plots of PPyBT:PCBM blends of 1:2 and 1:3 (w/w).

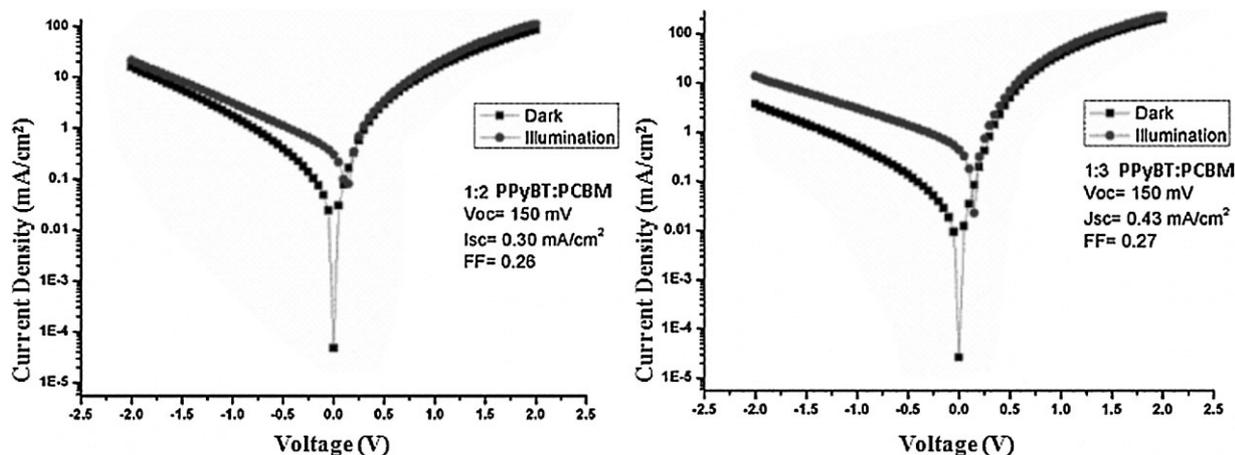


Figure 9. Current/voltage ( $I/V$ ) characteristics of the PPyBT/PCBM blends of 1:2 and 1:3 in the dark and under white light illumination (AM 1.5 conditions) shown in semilogarithmic plot.

molecular weight data of the chemically prepared polymer were found to be as  $\bar{M}_n$ : 11 900 and  $\bar{M}_w$ : 30 600. Determined from the CV measurements, PPyBT has an oxidation onset at 0.2 V and a reduction onset at  $-1.35$  V versus NHE referring to HOMO and LUMO levels of  $-4.95$  and  $-3.40$  eV. For PCBM,  $-6.1$  and  $-4.3$  eV were taken as the HOMO/LUMO levels.<sup>[27]</sup> BJJ solar cell devices were constructed according to these band energies. There is enough energy difference ( $\approx 0.3$ – $0.4$  eV) between the LUMO of the donor and the acceptor for a charge transfer taking place from photoexcited polymer to PCBM.<sup>[13]</sup>

Photovoltaic devices were prepared using PPyBT and PCBM (1:2 and 1:3 w/w; 5 mg PPyBT:10 mg PCBM for 1:2 ratio) blends in a solution of chlorobenzene (CB). The dodecyl group on the benzotriazole unit enables solubility in common organic solvents such as chloroform, THF, and CB. Onto poly(3,4 ethylenedioxythiophene) (PEDOT): poly(styrenesulfonate) (PSS) coated ITO glass slides, the active layer (PPyBT:PCBM blends) was spin-coated and aluminum (100 nm) was thermally evaporated as the top electrode to achieve the layered structure of BJJ solar cell (see Supporting Information).

Charge transfer was confirmed by a quenched photoluminescence (PL) emission upon adding 50 wt.-% PCBM (Figure 7). Such PL quenching can be the indication of photoinduced charge transfer from the PPyBT to PCBM.<sup>[28]</sup>

Photocurrent measurements showed that the PPyBT:PCBM blend can generate electrons almost over the whole range of the absorption spectrum of pristine polymer. The incident photon-to-current efficiency (IPCE) is used to acquire information on the number of photons of different energies that contributes the charge generation in the BJJ solar cell.<sup>[29]</sup> In Figure 8, the IPCE plot spans from 350 to 900 nm and shows slightly over 3% contribution at around 450 nm.

The  $I/V$  characteristics of the solar cells in dark and under illumination of PPyBT:PCBM are shown in Figure 9.

The BJJ devices under white light illumination ( $100 \text{ mW} \cdot \text{cm}^{-2}$ ) showed short circuit current densities ( $J_{sc}$ ) of 0.3 and  $0.43 \text{ mA} \cdot \text{cm}^{-2}$ , an open-circuit voltage ( $V_{oc}$ ) of 0.15 V and fill factors of 0.26 and 0.27, respectively. The low rectification ratios can be attributed to the rather poor film formation of the active layer.<sup>[30]</sup>

## Conclusion

A pyrrole-bearing donor/acceptor/donor-type monomer PyBT was synthesized and polymerized both electrochemically and chemically. The resultant polymer (PPyBT) was investigated using electrochemical and photovoltaic methods such as CV, UV-Vis/NIR, in situ FTIR, PL,  $I/V$ , and IPCE. PPyBT is soluble in common organic solvents and is both n- and p-type dopable. Benzotriazole subunits led PPyBT to be n-type dopable due to its outstanding acceptor properties. Preliminary results showed that PPyBT can be an interesting candidate for device applications.

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