

# Doping-Induced Immobile Charge Carriers in Polyazomethine: A Spectroscopic Study

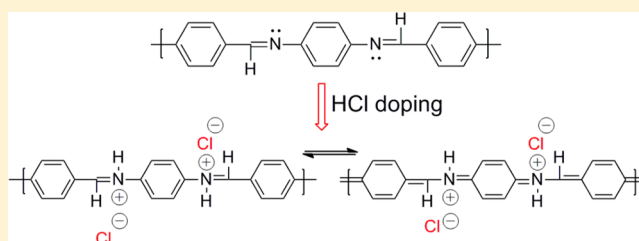
Jacek Gąsiorowski,<sup>\*,†</sup> Eric D. Głowacki,<sup>†</sup> Barbara Hajduk,<sup>‡</sup> Mariola Siwy,<sup>‡</sup>  
Małgorzata Chwastek-Ogierman,<sup>‡</sup> Jan Weszka,<sup>‡</sup> Helmut Neugebauer,<sup>†</sup> and Niyazi S. Sariciftci<sup>†</sup>

<sup>†</sup>Linz Institute for Organic Solar Cells (LIOS), Physical Chemistry, Johannes Kepler University, Altenberger Str. 69, 4040 Linz, Austria

<sup>‡</sup>Centre of Polymer and Carbon Materials of the Polish Academy of Sciences, ul. M. Curie-Skłodowskiej 34, 41-819 Zabrze, Poland

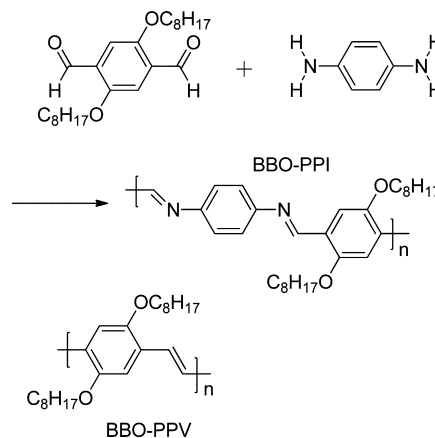
## S Supporting Information

**ABSTRACT:** Herein, we report the effect of protonation on the electronic properties and the conductivity of a soluble derivative of polyazomethine, poly(1,4-(2,5-bis(octyloxy)phenylenemethyldynenitrilo)-1,4-phenylenenitrilomethylidyne), BOO-PPI. Following protonation, a marked change in electronic structure occurs, as evidenced by a bathochromic shift in visible absorption and the appearance of a broad absorption in the infrared coupled with new infrared active vibrational modes, signaling the appearance of a new electronic state. In other conjugated polymers, such features usually evidence the formation of mobile polarons on the polymer chain, leading to an increase in electrical conductivity. Surprisingly, BOO-PPI protonation does not lead to such an increase. Protonation also does not result in an electron spin resonance signal. We propose a model for protonation inducing a charged state on the polymer chain with strongly limited delocalization accounting for the lack of the electron spin resonance signal and the missing conductivity. To our knowledge, this is the first time that spectral features usually corresponding to mobile charges in organic materials do not correspond to an actual change in conductivity.



## INTRODUCTION

Polyazomethines, or poly(1,4-phenylenemethyldynenitrilo-1,4-phenylenenitrilomethylidyne) (PPI), have been widely explored as potential nonlinear optical materials, with derivatives prepared via polycondensation of diamine and dialdehyde monomers in solution or by chemical vapor deposition.<sup>1–3</sup> Recently, soluble polyazomethines have been shown to work in bulk heterojunction organic solar cells.<sup>4</sup> The facile low-temperature polycondensation reaction to form PPI and its derivatives makes it attractive relative to other polymers in organic electronics by virtue of its simplicity and lack of side reactions. PPI is structurally related to poly(phenylene vinylene) (PPV) and possesses a protonable amine function like polyaniline (PANI). The unique protonation “doping” induced conductivity in PANI suggests that PPI may also show similar behavior. The conducting forms of doped PANI and PPV have been extensively studied;<sup>5</sup> however, the effect of chemical doping (i.e., in iodine vapor or by protonation) of polyazomethines has not been explored. To easily afford thin films of otherwise insoluble polyazomethine, we prepared a soluble derivative (BBO-PPI, structure shown in Figure 1) via polycondensation of 2,5-bis(*n*-octyloxy)terephthalaldehyde with *p*-phenylenediamine. For comparison, poly(2,5-bis(octyloxy)phenylene vinylene) (BOO-PPV, Figure 1), a well-characterized PPV derivative,<sup>6</sup> was used in parallel with BOO-PPI in our study.



**Figure 1.** Chemical structures of BOO-PPI and its analogous material BOO-PPV. BOO-PPI is prepared via polycondensation of 2,5-bis(*n*-octyloxy)terephthalaldehyde with *p*-phenylenediamine.

In this work, we investigate the electronic properties of both BOO-PPI and BOO-PPV using different electrochemical and spectroscopic techniques. First, we measure the possibility of oxidation and reduction reactions of polymer films via cyclic

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voltammetry. The reversibility of electrochemical oxidation or reduction is investigated to check whether stable doping by an oxidant or reductant, respectively, could be possible. Next, we obtain Fourier-transform infrared spectra (FT-IR) of thin films before and after exposure to possible dopants, such as iodine vapor and acids. With this technique, we study in situ vibrational changes and low-energy electronic excitations during reaction with dopants. In general, broad low-energy electronic absorptions in the near-infrared region along with new infrared active vibrations (IRAV bands) are connected with doping-induced formation of new electronic states, such as solitons, polarons, and bipolarons.<sup>6,7</sup> Similarly, we measure in situ changes of UV-vis absorptions during doping. In addition, we tried to characterize the new electronic states using electron-spin resonance (ESR) spectroscopy. However, no spin formation was observed in ESR studies. Finally, we prepared films of BOO-PPI and measured lateral electrical conductivity using a four-probe method before and after protonation as well as under conditions of illumination. In contrast to expectations based on the spectroscopic results, no conductivity increase of doped PPI was found.

## EXPERIMENTAL DETAILS

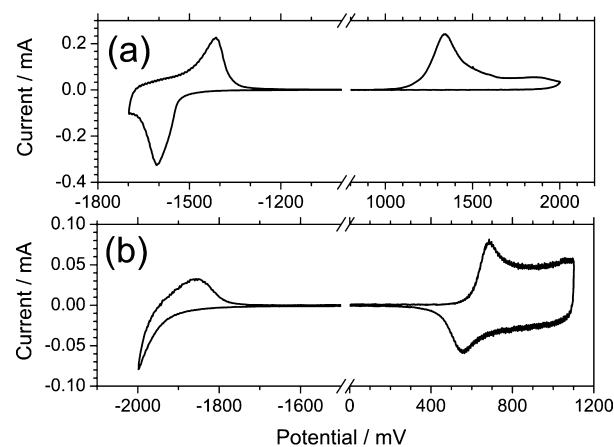
**Polymer Synthesis.** 1,4-Phenylene diamine (0.551 mmol, 0.0595 g) was dissolved in anhydrous toluene (9.05 mL), and lithium chloride (5.488 mmol, 0.2326 g) was added. The mixture was warmed to 100 °C to dissolve the diamine, and then the 2,5-bis(octyloxy)terephthalaldehyde (0.5 mmol, 0.1953 g) dissolved in anhydrous toluene (6 mL) was added to the solution at room temperature. The mixture was then refluxed under a nitrogen atmosphere for 48 h. An excess of the diamine (0.2714 mmol, 0.0293 g) was added, and the mixture was refluxed for one additional hour. The polymer was isolated by precipitation into methanol (75 mL) and purified by Soxhlet extraction with methanol for 1 week. The chemical reaction is presented in Figure 1. Polymer was dissolved in chloroform (20 mL) and filtered, and methanol (90 mL) was added dropwise (162 mg, 70%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, d, ppm): 9.02 (s, N=CH, 2H), 7.79 (s, H), 7.34 (d, 2H), 7.19 (d, 2H), 6.73 (s, H), 4.15 (m, CH<sub>2</sub>O, 4H), 1.86 (m, CH<sub>2</sub>, 4H), 1.5 (m, CH<sub>2</sub>, 4H), 1.31 (m, CH<sub>2</sub>, 16H), 0.88 (t, CH<sub>3</sub>, 6H). Anal. for C<sub>30</sub>H<sub>41</sub>N<sub>2</sub>O<sub>2</sub> (%) Found/Calcd: C = 78.19/78.04, N = 6.29/6.06, H = 9.24/8.95. T<sub>g</sub> = 283.44 °C.

**Spectroscopic and Electrochemical Measurements.** BOO-PPI and BOO-PPV were dissolved in chloroform (reagent Ph. Eur. stabilized with 0.6% ethanol, Prolabo Co.) at a concentration of 6 g L<sup>-1</sup>. Electrochemical properties of both polymers were determined by cyclic voltammetry in anhydrous acetonitrile (99.8%, Aldrich) containing 0.1 M Bu<sub>4</sub>NPF<sub>6</sub> (≥99%, Fluka Analytical). In the setup, conducting indium-doped tin oxide (ITO)-coated glass (15 Ω/□, Kintec Co.) was used as working electrode (WE), a Pt foil as counter electrode (CE), and Ag/AgCl as quasi-reference electrode (QRE). The QRE was calibrated using the ferrocene redox couple. The half-potential of Fc/Fc<sup>+</sup> vs QRE was measured at 0.38 V. Infrared spectra were recorded with an FTIR spectrometer (Bruker IFS66S) at room temperature in attenuated total reflection mode (ATR), using a mercury-cadmium telluride (MCT) detector cooled with liquid nitrogen prior to the measurements. ZnSe crystals were used as the ATR element for iodine-doping experiments and germanium (Ge) crystals in the case of doping with acid vapors. Both crystal types were pre-cleaned by polishing with diamond paste (1 and

0.25 μm) and rinsing in a reflux system with acetone prior to measurement. Polymer films were then spin-cast directly onto the ATR crystals. During exposure to iodine or acid vapors, ATR-FTIR spectra were recorded consecutively. By defining the first undoped spectrum as reference (T<sub>ref</sub>), and relating the subsequent doped spectra (T<sub>sample</sub>) to this reference spectrum, specific spectral changes during the chemical oxidation (in iodine vapors) or protonation (in HCl vapors) process were recorded. The difference spectra are calculated as  $(-\Delta T/T_{ref})$ , where  $\Delta T = T_{sample} - T_{ref}$ . The UV-vis absorption spectra were recorded with an Ocean Optics HR4000+ UV-vis spectrophotometer on films spin-cast on glass substrates. Conductivity measurements were done using platinum contacts sputtered onto cleaned glass slides. A thin film of polymer was then spin-cast from solution, and conductivity changes were measured using a Keithley 280 source meter under conditions of protonation, exposure to iodide, and irradiation with light using a white light xenon source. Evaporated platinum contacts below the polymer film were chosen as to minimize effects of electrical measurements in the presence of acid vapors. To avoid a false-positive measurement of increased conductivity due to the efficient ionic transport in an acid layer condensing on top of the polymer film, we did not use top contacts. ESR was measured on a Bruker X-band EMX setup using valved ESR tubes, allowing introduction of acid or iodine vapors.

## RESULTS AND DISCUSSION

**Cyclic Voltammetry.** Cyclic voltammograms were obtained for thin films of polymer cast on conducting indium-doped tin oxide (ITO)/glass functioning as the working electrode. Redox properties of the BOO-PPI are presented in Figure 2a. Films of polyazomethines were found to have an

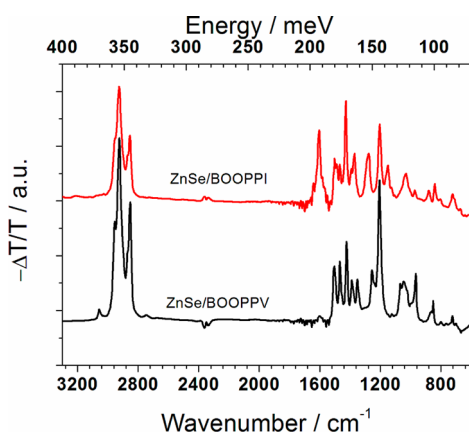


**Figure 2.** Cyclic voltammetry scans of BOO-PPI (a) and BOO-PPV (b). Like typical PPV derivatives, BOO-PPV can be reversibly oxidized. BOO-PPI shows the opposite behavior, with reversible reduction present, but lack of reversible oxidation.

irreversible oxidation with an onset of 1.2 V vs Ag/AgCl QRE, allowing an estimation of HOMO energy of around  $-6.2$  eV. The values of the Fc/Fc<sup>+</sup> vs NHE and NHE vs vacuum level used in this work were 0.64 and  $-4.75$  V, respectively.<sup>8–10</sup> However, upon cyclic oxidation, it was found that the polymer was not stable and degraded with consecutive scans. It can be concluded that electrochemical generation of a stable cationic species on the polymer is not possible. This conclusion is consistent with the fact that the imine form of nitrogen is

already the more oxidized state of nitrogen, relative to a secondary or primary amine. On the other hand, electrochemical reduction was found to be highly reversible; from the onset of reduction at  $-1.5$  V, we estimate a LUMO energy of approximately  $-3.5$  eV. Thus, from the electrochemical point of view, BOO-PPI can accommodate negative charges. The electrochemistry of BOO-PPI is different than that of poly(phenylene vinylene) (Figure 2b), which supports a reversible oxidation. The inability of forming positive species on the PPI chain suggests that, unlike PPVs, it is unlikely to work as a hole-transporting polymer, but rather an electron-transporting one. However, all our attempts to measure n-type conductivity in field-effect transistor geometry as well as lateral conductivity under electrochemical reduction conditions failed to show any transport, suggesting that the mobility of such negative charges, maybe due to extensive charge trapping, is insufficient to support conduction.

**FT-IR Measurements.** Figure 3 shows FTIR spectra of BOO-PPI (top/red) and BOO-PPV (bottom/black). For

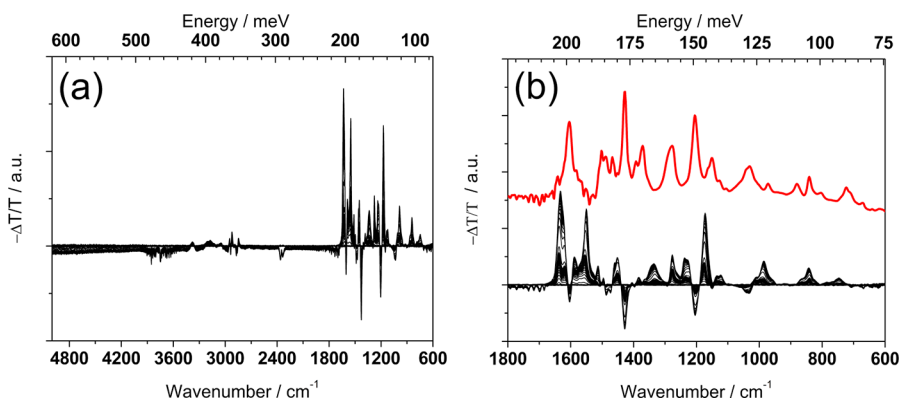


**Figure 3.** ATR-FTIR spectra of pristine BOO-PPI (top/red) and BOO-PPV (bottom/black) materials. ZnSe acts as the ATR element in both cases.

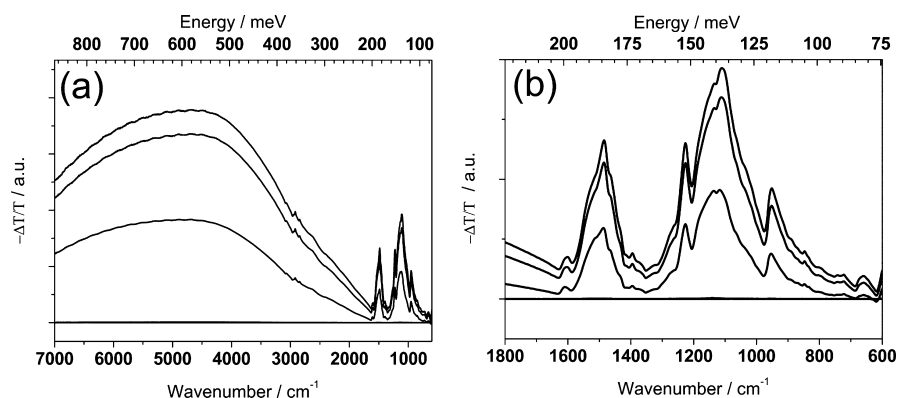
polyazomethine, characteristic vibrations associated with molecule vibrations were measured at 2928, 2854, 1604, 1503, 1468, 1427, 1370, 1278, 1204, 1151, 1030, 971, 880, 841, and  $722$   $\text{cm}^{-1}$ . For poly(phenylene vinylene), characteristic vibrations were detected at 2928, 2854, 1503, 1468, 1423, 1388, 1351, 1256, 1204, 1068, 1046, 965, 851, and  $722$   $\text{cm}^{-1}$ . The

structural similarity of both polymers results in many of the same vibrational peaks. At  $2928$  and  $2854$   $\text{cm}^{-1}$ , characteristic aliphatic C–H vibrations appear. It can be noticed that the intensity of those peaks is proportionally higher in the case of BOO-PPV since this polymer has twice as many octyloxy side chains, compared with BOO-PPI. We can observe the same situation in the case of vibration at  $1204$   $\text{cm}^{-1}$ , which belongs to C–O stretching. The vibration peak related to C–C ring stretching is found at  $1503$   $\text{cm}^{-1}$ . Characteristic peaks at  $1468$  and  $1370$   $\text{cm}^{-1}$  describe C–H bending. C–C ring stretching is represented by vibration at  $1423$   $\text{cm}^{-1}$ . All of those peaks can be found in both spectra. However, a peak at  $1604$   $\text{cm}^{-1}$  exists only in PPI and is thus attributed to C=N stretching.<sup>11</sup>

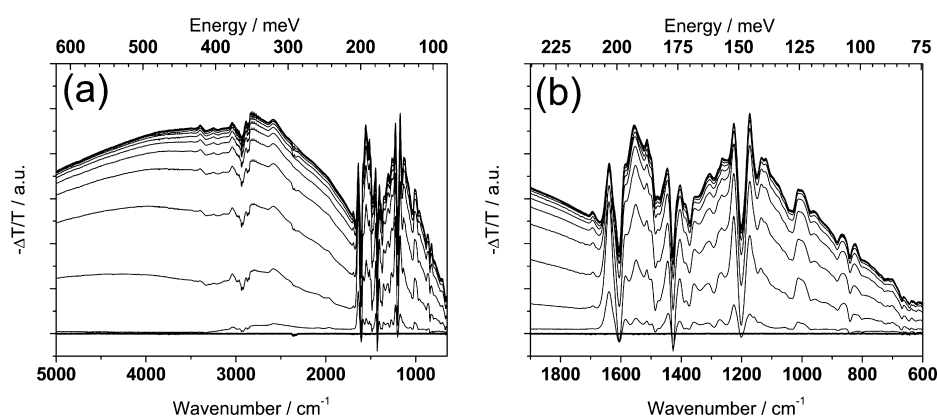
**Chemical Doping —  $\text{I}_2$  and Protonation.** Since conjugated polymers in their undoped state are semiconducting or insulating, a way to increase their conductivity is to dope them by introducing mobile charges, resulting in a distortion in the molecular structure. One method to introduce charges is by chemical doping. In this method, a layer of organic material is exposed to vapors of an oxidizing or reducing reagent. To achieve doping with positive charges (holes), a popular oxidant is  $\text{I}_2$ . In the case of chemical doping, the FTIR spectrum should exhibit a broad band connected with polaron formation and new infrared active vibrations (IRAVs), which can be described using the Girlando–Painelli–Soos (GPS) model.<sup>12–15</sup> In this theory, doping induces new charged states in the form of paramagnetic radicals, also known as polarons. The creation of polarons is associated with new electronic levels within the gap of the pristine materials, appearing as a broad low-energy absorption in the infrared region. The changes in symmetry in the polaron relative to the pristine material also induce new infrared active bands. The high intensity of IRAV mode absorption in this theory is correlated to the electron–phonon coupling in the system. Figure 4a shows the results of exposing polyazomethine film to iodine vapor. In the case of BOO-PPI, FTIR spectra show no evidence of doping upon iodine exposure. The region above  $1800$   $\text{cm}^{-1}$  is flat, suggesting no polaron formation. Although new positive or negative bands appear in the “fingerprint” region, based on their weak oscillator strength and overlap with the vibrations of the pristine material (Figure 4b), they cannot be described as IRAV bands, as discussed in the GPS model. They rather represent vibrational changes of the molecule during a degradative chemical reaction with iodine vapor and not a doping process.



**Figure 4.** ATR-FTIR difference spectra during exposure of BOO-PPI in iodine vapors. Full range shown in (a) demonstrates lack of broad absorption characteristic of the appearance of in-the-gap states. (b) Difference spectra in the fingerprint region (black) are compared with the original FT-IR spectrum of the pristine material (red).



**Figure 5.** ATR-FTIR difference spectra during chemical oxidation of BOO-PPV in iodine vapors. The absorption features rise over time of exposure. The appearance of a broad absorption coupled with IRAV modes is indicative of the formation of a delocalized electronic state within the band gap of the pristine material.



**Figure 6.** ATR-FTIR difference spectra during protonation of BOO-PPI in HCl vapors. The appearance of a broad absorption coupled with IRAV modes is indicative of the formation of a delocalized electronic state within the band gap of the pristine material, much like in the case of iodation of BOO-PPV.

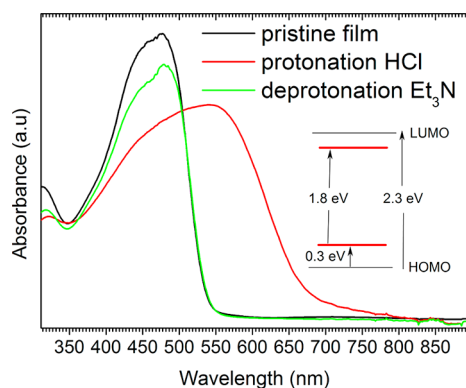
This is consistent with the lack of observed reversible oxidation in cyclic voltammetry. Iodine exposure also failed to yield an ESR signal, confirming that polaron formation does not occur. In contrast, BOO-PPV upon doping with iodine shows a typical infrared spectrum of doped conducting polymers (Figure 5a). We observe a broad peak with a maximum at 580 meV originating from the creation of new in-gap states and associated IRAVs characteristic of polaronic distortion. These new bands are presented in detail in Figure 5b. Strong broadening and intensity of these IRAV bands suggest, according to the GPS model, good electron–phonon coupling.

Since BOO-PPI has protonatable imines in the polymer chain, we expected that, as in the case of polyaniline, protonation will have an effect on its electronic properties. Though iodation does not appear to dope BOO-PPI, we found that protonation with acid results in an infrared pattern characteristic for the generation of a delocalized electronic state. Since the Schiff base ( $-\text{C}=\text{N}-$ ) of polyazomethine readily lends itself to protonation, we hypothesized that it may support a protonation-induced insulator–metal transition much like structurally related polyaniline.<sup>16,17</sup> Upon protonation, the base form of the polyazomethine should change to the salt form. To test this hypothesis, the polymer film was exposed to HCl vapors during FTIR measurement. The differential FT-IR spectra are shown in Figure 6. Protonated polyazomethine exhibits formation of a broad peak very much like in iodated PPV. This new in-gap state is accompanied by the appearance

of IRAV bands. In the “fingerprint” region, new peaks arise at 1641, 1555, 1513, 1481, 1446, 1403, 1226, 1173, 1126, and 1004  $\text{cm}^{-1}$ . At the same time, three negative peaks (1603, 1423, and 1204  $\text{cm}^{-1}$ ) appear. These negative peaks are in the same position as the main vibrations of pristine polyazomethine. The sharpness of the new vibrational peaks suggests strong localization of the charge in the polymer.<sup>18</sup>

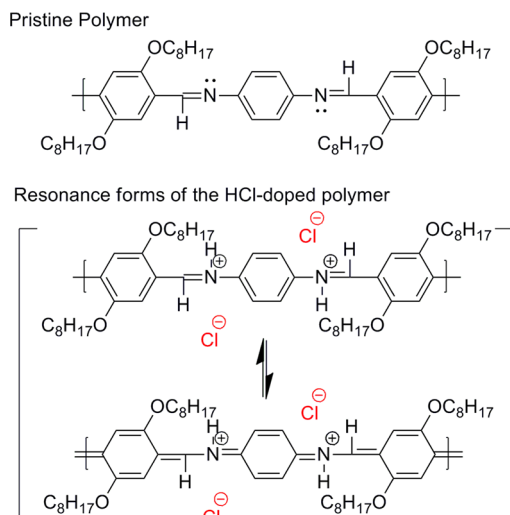
The appearance of a new electronic structure in protonated BOO-PPI is reflected also in the UV–vis absorption spectrum. The UV–vis of the polymer before and after protonation is presented in Figure 7. The maximum absorption for BOO-PPI polymer was found at 470 nm. The optical band gap estimated from onset is 2.3 eV. As is typical for most organic thin films, this value is lower than the estimate from electrochemistry (2.7 eV). Upon exposure to HCl vapors, a bathochromic shift of absorption onset of about 100 nm is observed, accompanied with broadening (Figure 7). Exposure of the sample to base vapors, such as triethylamine, deprotonates the material and reproduces the original spectrum.

Concluding from FT-IR and UV–vis spectra that protonation induces the formation of a new electronic structure in the polymer, we measured conductivity of films before and after protonation. Surprisingly, we found that both the unprotonated and the protonated forms of the polymer were excellent insulators, with resistivity in the  $>10 \text{ G}\Omega$  range. This indicates that the charges induced by protonation along the polymer chain are not mobile. Additionally, we found that irradiation



**Figure 7.** In-situ UV-vis of BOO-PPI during protonation with HCl vapors, and deprotonation with triethylamine. The electronic level diagram shown in the inset features the apparent lessening of the gap estimated from visible absorption shift upon protonation while the low-energy transition (0.5 eV) is estimated from the peak of the broad absorption measured in FT-IR (see Figure 6).

with light yielded no photoconductivity effect in both, unprotonated and protonated films. It was also found from in situ ESR measurements during protonation that no uncoupled spins are present in either form of the polymer. To explain the unexpected results, that is, the observations of a new electronic structure upon doping, but no unpaired spins and no electrical conductivity enhancement, we propose the molecular structures shown in Figure 8. Upon doping with HCl, the nitrogen lone-



**Figure 8.** The molecular structure of undoped PPI is shown on top, with the proposed extreme resonance forms of the protonated polymer shown below. It can be seen that the resonance of the double bonds along the chain does not result in mobile charge, which we attribute as the reason for the lack of conductivity increase upon doping.

pair bonds to hydrogen, generating a positive charge on the nitrogen atom stabilized by a chloride anion. The charged species has no unpaired electron, and therefore, no ESR signal occurs. Drawing resonance forms of the polymer, it can be seen that, unlike in polyaniline, a double-bond shift does not change the charge position when going from one to the other extreme resonance structures. The immobile charge is highly localized, resulting in the lack of conductivity and also in the lack of photoconductivity. These observations are unusual, as accord-

ing to the GPS model, the same spectral features indicate the presence of mobile charge carriers.

## CONCLUSIONS

Our interest in BOO-PPI was motivated by the ease of preparation of polyazomethines relative to typical organic electronic materials and their similarity to well-known conducting polymers, such as PPV and polyanilines. Despite being structurally related to PPV and PANI, polyazomethines have markedly different properties. From cyclic voltammetry studies, we found that BOO-PPI can be reversibly reduced, but not oxidized—the opposite behavior relative to PPV. Polyazomethine cannot be doped by the oxidant iodine, like in the case of PPV. However, it can be readily protonated like PANI to yield a new electronic structure with an optical signature that, for all conducting polymers, is associated with delocalized polaronic states; nevertheless, this electronic state does not translate to mobile charges, as evidenced by lack of electrical conductivity enhancement. This is the first report on polaronic spectroscopic features of doped/protonated conducting polymers that are present in BOO-PPI, but these do not correspond to an actual increase in conductivity.

## ASSOCIATED CONTENT

### Supporting Information

Figures of the oxidation of BOOPPI as a function of the maximum achievable potential and of the oxidation of BOOPPI as a function of the scan rate. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [jacek.gasiorowski@jku.at](mailto:jacek.gasiorowski@jku.at). Phone: +43 732 2468-8854. Fax: +43 732 2468-8770.

### Notes

The authors declare no competing financial interest.

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