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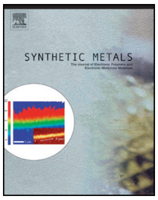

Synthesis of conducting azopolymers by electrochemical grafting of a diazonium salt at polypyrrole electrodes

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ABSTRACT

In this paper we report a new strategy for obtaining conducting azopolymers having pendant azobenzene moieties via functionalization of polypyrrole by electrochemical reduction of 4-[(4′-nitrophenyl)azo]benzenediazonium tetrafluoroborate ($NABDBF_4^-$). The functionalization of polypyrrole films with 4′-nitroazobenzene (NAB) groups has been evaluated by cyclic voltammetry and by spectroscopic techniques such as XPS, Raman and UV–vis spectroscopy. Moreover, the third-order nonlinear optical response of NAB-functionalized polypyrrole has been investigated using the optical third-harmonic generation technique. All these investigations confirmed the presence at the polymeric films surface of the functional groups introduced by the electrochemical reduction of diazonium salt. The versatility of this methodology allows not only the functionalization of polypyrrole-type materials with chromophore groups, but can also be successfully applied to other conjugated polymer systems in order to create various photoresponsive materials.

1. Introduction

The electrochemical synthesis of conductive polymers such as polypyrrole, polyaniline, and polythiophene represents a widely employed method for elaborating modified electrodes for applications in energy conversion and storage, electrochromism, electrocatalysis, and electrochemical sensors [1–5]. The chemical functionalization of conductive polymers offers the attractive possibility of developing materials that, in addition to their intrinsic electrical conductivity, incorporate specific properties of the functional group introduced [6]. Basically, the role of such functionality is to selectively respond to a chemical or a physical stimulus delivered by the external environment to the π-conjugated framework which is capable of transporting the electrical information from the sensing group to an external circuit, for signal processing purposes [7]. The electropolymerization of precursors derivatized with covalently attached functional groups represents the most straightforward method for the synthesis of such functional, conjugated polymers [8,9]. However, despite their apparent simplicity, the direct homo- and copolymerization of functional monomers have some limitations including the side reactions of functional groups during the polymerization or a decrease in the polymerizability of the functional monomer due to steric hindrance and/or incompatibility with the solvents used, or the polymerization process itself.

Post-polymerization functionalization of conducting polymers could therefore be a helpful tool in order to overcome such

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limitations. Our previous attempts in this direction involved the direct modification of unsubstituted polymers, such as polypyrrole [10].

Among photoresponsive materials, azobenzene and related compounds represent one of the most widely studied systems, due to their ease of synthesis and facile detection of photoisomerization [11–13]. The reversible *trans*–*cis* photoisomerization of azobenzene yields a *cis* state that is metastable and will thermally reconvert to the *trans* state [14]. The two isomers exhibit different chemical and physical properties and reversibly switch between two spectroscopically distinct forms by use of light. Polymers containing azobenzene moieties often display remarkable photo- and thermo-regulated behaviour when subjected to changes in incident light or heat [12]. In recent years, azobenzene-containing polymers have received much attention owing to their potential application in optical data storage, nonlinear optical (NLO) materials, holographic memories and waveguide switches [15–17]. The incorporation of chromophores into polymeric systems can be achieved in various ways, either by covalently linking the chromophores to the polymer chain, doping them in a polymer matrix or attaching them via supramolecular interactions with the polymer [14]. However, the photochromic properties of azobenzene groups are sometimes diminished in films because the closely packed film structure cannot provide enough free volume to allow the *trans* to *cis* photoisomerization which is accompanied by an increase in molecular size [18]. This makes, in particular, azobenzene-attached side-chain-type polymers promising materials to exhibit the desired optical properties [19].

The post-polymerization strategy allows the introduction of chromophore molecules into reactive precursor polymers without exposing them to aggressive polymerization conditions [20]. Another advantage of this strategy is the possibility to tune the chromophore loading level. Various post-polymerization reactions were reported in the literature, the most common being the esterification of carboxylic groups attached to polymer chains with hydroxy groups of the chromophores [21,22] and the azo coupling reactions between polymers and diazonium salts [23,24].

The reduction of arenediazonium salts represents a very convenient method for the covalent immobilization of various moieties onto electrode surfaces. Diazonium salt grafting is generally accepted to occur via a radical mechanism [25–29]. One electron transfer to the diazonium salt results in release of N_2 and the generation of aryl radicals, which react with the surface to form covalent bonds. Arenediazonium salts can be grafted by chemical and electrochemical reduction [29] or even spontaneously [27]. The electrochemical method is faster, and more controllable; thus homogeneous monolayers or two distinct overlaid layers can be prepared [28]. In the electrochemical method, the generation of phenyl radicals is localized at the electrode and the loss of diazonium salt by competing reactions in the bulk solution is minimal. This degree of control over the interfacial chemistry of conducting polymers will greatly impact the ability to tailor conducting polymeric materials for specific tasks.

In this study we discuss a new strategy for obtaining conducting azopolymers having pendant azobenzene moieties via functionalization of polypyrrole by electrochemical reduction of a diazonium salt. Based on our knowledge, the electrochemical reduction of aryl diazonium salts modification technique was employed for the first time as a method for covalently linking the chromophores to a conducting polymer chain.

2. Experimental

2.1. Chemicals and reagents

Pyrrole was purchased from Aldrich and fractionally distilled before use. Anhydrous acetonitrile (99.8%, noted MeCN), tetra-n-butylammonium tetrafluoroborate (99%, noted $TBABF_4^-$) were obtained from Aldrich and were used as received. Other reagents were obtained from Aldrich or Merck and used as received.

Because 4-amino-4′-nitroazobenzene cannot be synthesized by direct coupling of diazotised 4-nitroaniline with aniline, the amino group of the latter was first protected via the *N*-(sulfonylmethyl) derivative. The protected amine was then coupled with 4-nitrobenzenediazonium chloride and 4-amino-4′-nitroazobenzene was finally obtained following a deprotection step in dilute NaOH solution (Scheme 1).

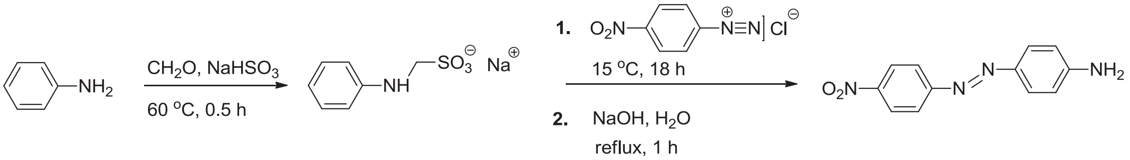
The 4-[(4′-nitrophenyl)azo]benzenediazonium tetrafluoroborate ($NABDBF_4^-$) was prepared by diazotisation of 4-amino-4′-nitroazobenzene with sodium nitrite in 40% fluoroboric acid solution as described in our previous studies [3,4].

2.2. 4-Amino-4′-nitroazobenzene

2.2 g (50 mmol) aniline was mixed with 16.15 g of 40% sodium bisulphite solution and 4.74 g of 37% aqueous formaldehyde. The resulting mixture was stirred at room temperature for 2 h, after which 90 mL of water were added and the mixture heated to 60 °C until a clear solution was obtained. 8.5 g of sodium bicarbonate were added next, the mixture cooled to 15 °C and then 110 mL of 4-nitrobenzenediazonium chloride solution prepared by diazotising 6.9 g of 4-nitroaniline was poured slowly, under stirring, during 6 h. The reaction mixture was further stirred for 12 h at room temperature and then filtered. The precipitate was refluxed for 1 h in 225 mL water containing 5.2 g NaOH, the solution cooled to room temperature and diluted with 500 mL of water. The crude 4-amino-4′-nitroazobenzene was filtered, dryed and purified by recrystallization from toluene (*yield* = 8.6 g, 71%). ^1H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.33 (d, 2H, *J* = 9.2 Hz), 7.94 (d, 2H, *J* = 9.2 Hz), 7.86 (d, 2H, *J* = 8.8 Hz), 6.75 (d, 2H, *J* = 8.8 Hz), 2.30 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm) δ: 156.7, 151.2, 148.0, 145.7, 126.4, 124.9, 123.0, 114.8.

2.3. 4-[(4′-Nitrophenyl)azo]benzenediazonium tetrafluoroborate

^1H NMR (400 MHz, CD_3CN, ppm) δ: 8.73 (d, 2H, *J* = 8.8 Hz), 8.43 (d, 2H, *J* = 9.2 Hz), 8.29 (d, 2H, *J* = 9.2 Hz), 8.17 (d, 2H, *J* = 8.8 Hz). ^{13}C NMR (400 MHz, CD_3CN, ppm) δ: 158.9, 155.6, 138.5, 135.1, 125.9, 125.7, 118.2, 116.5.



Scheme 1. The synthesis of 4-amino-4′-nitroazobenzene.

2.4. Instrumentation

The electrochemical experiments were performed under an argon atmosphere at room temperature and were controlled by an Autolab 128N potentiostat/galvanostat (Eco-Chemie). A three-electrode configuration consisting of bare or modified platinum (Pt), glassy carbon (GC) or gold (Au) (Metrohm, disks, diameter 2 mm) as working electrodes, Ag/10 mM $AgNO_3$, 0.1 M $TBABF_4^-$ as reference electrodes and a Pt wire as counter electrode were used.

NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer.

X-ray photoelectron spectra were acquired on a K-Alpha spectrometer (Thermo Electron) using monochromatic Al Kα X-rays (1486.6 eV). Electrostatic charging of the sample surface was compensated with a flood gun. Binding energies were calibrated by setting the C1s peak at 284.8 eV as internal standard. The XPS spectra were fitted using a combination of Gaussian (70%) and Lorentzian (30%) distributions after performing a Shirley-type background subtraction.

Raman spectra were recorded in the range 3400–50 cm^{-1} using a dispersive Raman microscope DXR (Thermo Fisher Scientific) employing a 532 m laser with a power of 10 mW. The ratio between S/N was 100.

UV–vis transmission spectra of polymers on ITO-coated glass plates were measured with a double beam V-660 spectrometer (Jasco) in the 300–800 nm range, a clean ITO-coated glass plate being placed in the reference beam path.

Third harmonic generation measurements were performed using the experimental setup described in ref. [30] which employs a Q-switched Nd:YAG laser operating at a wavelength of 1064.2 nm with 6 ns pulse duration and 10 Hz repetition frequency.

2.5. Preparation of the modified electrodes

Prior to modification, the electrode surface was polished in 0.05 μm alumina slurry on a microcloth pad. After polishing the electrodes were thoroughly rinsed with water and sonicated for 5 min. in water and then rinsed again with water followed by MeCN. The PPY electrodes used for functionalization consisted of different thickness (30 nm, 60 nm, 90 nm and 120 nm) PPY films doped with BF_4^- anion, deposited galvanostatically (j = 0.4 mA/cm^2) on 2 mm diameter Pt disks. For every measurement a freshly obtained PPY film that was first cycled in a solution of 0.1 M $TBABF_4^-$ supporting electrolyte in MeCN.

The functionalization of the PPY electrodes was carried out in MeCN solutions containing 1 mM of diazonium salt and 0.1 M $TBABF_4^-$ supporting electrolyte by potential cycling at a scan rate of 0.1 V s^{-1}. For comparison the electrochemical grafting was performed at GC, Pt and Au electrodes. The modified electrode was then removed from the grafting solution and rinsed with large volumes of MeCN.

Polypyrrole films (90 and 120 nm thick, approx. area 2 cm^2) deposited on indium tin oxide coated glass (ITO) transparent electrodes were functionalized as described above and further characterized by Raman, XPS and optical methods.

Doped polypyrrole functionalized with 4′-nitroazobenzene groups was denoted NAB-PPY corresponding to the reactions with $NABDBF_4^-$ diazonium salt.

3. Results and discussion

3.1. Electrochemical reduction of 4-[(4′-nitrophenyl)azo] benzenediazonium tetrafluoroborate at polypyrrole electrodes

The electrochemical reduction of the $NABDBF_4^-$ diazonium salt at PPY/BF_4^- films and common substrates as GC, Pt and Au electrodes was comparatively studied by CV. The obtained cyclic voltammograms for a potential range of 0.4 V to −1.0 V at a scan rate of 0.1 V s^{-1} are presented in Fig. 1.

As reported in our previous study concerning several *para*-substituted arenediazonium salts [10], also in the case of $NABDBF_4^-$ the reduction at the polypyrrole electrode occurs more easily (E_p approx. +0.1 V) than at the other electrodes (E_p approx. −0.1 V), although the reduction peak is almost completely masked by the capacitive current that accompanies the polymer reduction.

It can be seen that following the first scan the modified GC, Pt and Au electrodes present a blocking effect toward the reduction of diazonium in solution because, in this potential range, no electroactive relay continues to exist for the grafted molecules [26]. Performing several scans leads to a more difficult electron transfer induced by thicker layers deposited on the electrode surface. In the case of the doped PPY film, the first voltammetric cycle shows a less intense reduction peak (at +0.1 V) corresponding to the reduction of the diazonium salt, but also the large peaks associated with the reduction and oxidation of the polymer (at −0.3 V and −0.1 V) can be observed. In the subsequent cycles only the reduction and oxidation peaks of the polymer appear. The $NABDBF_4^-$ reduction at PPY electrode is better illustrated in Fig. 2(a).

3.2. Electrochemical characterisation of NAB-functionalized PPY electrodes

The functionalized NAB-PPY electrode was characterized by recording the CVs in 0.1 M $TBABF_4^-$ in acetonitrile, in the potential range of 0.4 V to −1.0 V. The recorded voltammograms for the polymer electrode before and after functionalization are shown in Fig. 2(b), where one can see only a slight decrease of peak current density for the polymer reduction and oxidation respectively, without a significant shift of the peak potentials.

In Fig. 3(a) are presented the CVs recorded in pure electrolyte solution for NAB-PPY films in a larger potential range of +0.4 V to −2.0 V, at several scan rates. When the potential scanning is extended further in the cathodic direction, besides the reduction and oxidation peaks of the polymer, two supplementary redox systems can be observed having formal redox potential values of −1.135 V (ΔE_P = 30 mV) and −1.395 V (ΔE_P = 50 mV), respectively. These redox peaks can be attributed to a two-stage reduction of NAB (the first step corresponds to the formation of the radical anion and the second one to a further reduction to dianion) followed by oxidation of the generated species during the reverse scan [31]. These quasi-reversible peaks (ΔE_P less than 60 mV) are characteristic for redox species immobilized on the electrode surface and this proves that NAB groups are grafted on the polypyrrole electrode. Evidence for NAB grafting is given also by the influence of potential scan rate on both cathodic and anodic peak currents (Fig. 3(b)). Using potential scan rates from 0.04 to 0.1 V s^{-1}, the linear variation of peak current density with the scan rate observed for the redox couple at E = −1.135 V suggests that the electroactive species involved did not diffuse from the bulk solution but instead were grafted onto the electrode surface.

During repeated cycling of the functionalized $NAB\text{-}PPY/BF_4^-$ films from +0.4 V to −2 V in 0.1 M $TBABF_4^-$/MeCN solution, the peak current densities of the redox couples located at −1.135 V and −1.395 V potentials decrease in intensity, the most important decrease being observed between the 1st and 2nd scan (Fig. 4a). The same behavior is found in the case of a glassy carbon electrode functionalized with NAB in a similar manner (Fig. 4b). However, in the latter case the differences between the 2nd and the 10th cycle are much smaller.

There are two possibilities to explain this behaviour: one is the removal of a part of the grafted layer during repeated cycling or the

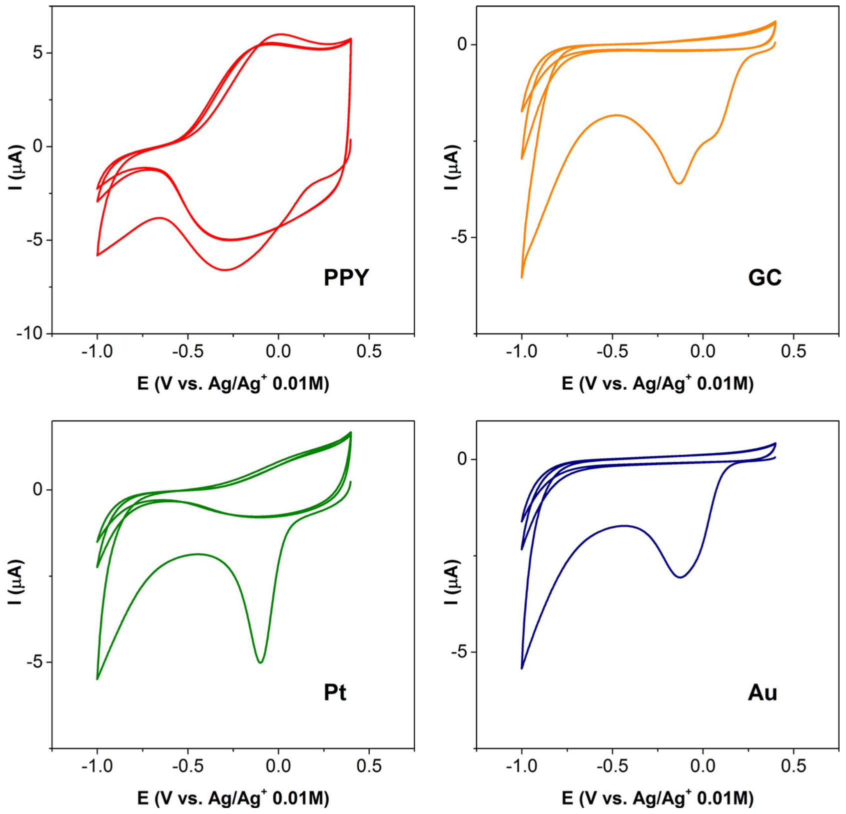


Fig. 1. The electrochemical reduction of $NABDBF_4^-$ (1 mM in 0.1 M $TBABF_4^-$/MeCN) at PPY/BF_4^-, 60 nm (a), GC (b), Pt (c) and Au (d) electrodes, by cycling in the potential range of +0.4 V to −1.0 V, at a scan rate of 0.1 V s^{-1}.

irreversible degradation of the 4′-nitroazobenzene due to traces of oxygen or water present in the electrolyte. The first hypothesis is supported by cyclic voltammograms recorded for a NAB-functionalized glassy carbon electrode subjected to ultrasonic treatment in acetonitrile – quite similar voltammograms after one cycle or 15 min of sonication were observed. This fact seems to indicate that NAB multilayers are deposited on the conductive polymer surface, and a part of the grafted groups are being removed on repeated cycling (Fig. 6).

3.3. X-ray photoelectron spectroscopy (XPS) of NAB-modified electrodes

In order to confirm the presence of 4′-nitroazobenzene groups, NAB-PPY/BF_4^- films were investigated using X-ray photoelectron spectroscopy (XPS).

In the N 1s core level spectrum of the functionalized PPY (Fig. 5) two peaks can be observed, the one at 406.1 eV being positively attributed to nitrogen atoms from the —NO_2 groups [32]. From the second peak, two secondary peaks resulted after deconvolution, which correspond both to nitrogen atoms from the polypyrrole backbone, as well as nitrogen atoms in the —N=N— group (Table 1). From the ratio of peak areas one can deduce a degree of functionalization of approximately 0.8 NAB groups for one pyrrole ring.

3.4. Raman spectroscopy of NAB-modified electrodes

NAB-functionalized polypyrrole films were further characterised by Raman spectroscopy. Raman spectra of 120 nm-thick films of doped polypyrrole prepared by electrochemical polymerization onto transparent ITO electrodes were recorded before and after functionalization with NAB using a dispersive Raman microscope equipped with a laser emitting at 532 nm as excitation source. The spectra of PPY/BF_4^- presented in Fig. 7 agree with other published spectra collected using excitation sources of similar wavelength [34]. A summary of the band positions and their assignments is provided in Table 2. For NAB-functionalized polypyrrole two very weak bands appear at 1145 cm^{-1} and 1450 cm^{-1}, which can be associated with normal modes involving the azo group and attributed to the phenyl-N=N- and —N=N— stretches, respectively [35].

3.5. Optical properties of NAB-functionalized polypyrrole

The UV–vis absorption spectra for pristine and NAB-functionalized polypyrrole films (deposited on ITO coated glass plates) were recorded in the 300–800 nm range. The spectrum corresponding to a film of PPY/BF_4^- (90 nm), presented in Fig. 8A, shows a broad absorption band centered at 465 nm which can be assigned to the π–π^* transition (valence band to antibonding cation/dication level transition) [36].

For NAB-PPY/BF_4^- films (90 nm) the spectrum presented in Fig. 8B shows that the π–π^* transition for the doped polymer shifted from 465 to 450 nm and a new absorption band appeared at 370 nm. The latter band is characteristic for the chemisorbed 4′-nitroazobenzene molecule [37]. In the UV–vis absorption spectra of a thicker NAB-PPY/BF_4^- film (approx. 120 nm), the chromophore absorption is further shifted to 375 nm (Fig. 8C).

It is interesting to mention that in solution and for solid 4′-nitroazobenzene films this band appears at approx. 330 nm, but when this molecule is chemisorbed on sp^2 hybridized carbon surfaces (e.g. pyrolyzed photoresist films) the band is red-shifted above 355 nm. This proofs that significant electronic coupling

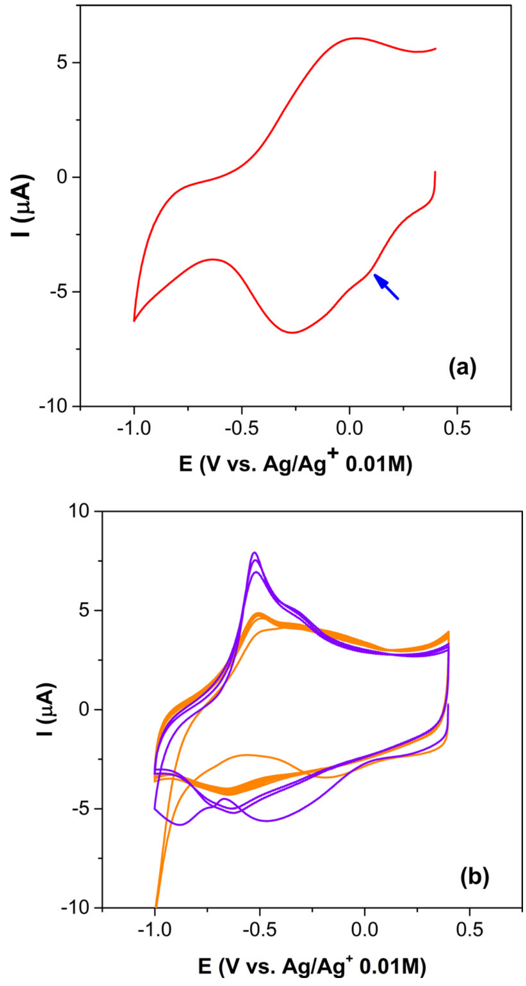


Fig. 2. Cyclic voltammograms for (a) PPY/BF_4^- (60 nm) films in NABDBF$_4^-$ solution (1 mM in 0.1 M TBABF$_4^-$/MeCN), 1st cycle; (b) PPY/BF_4^- (60 nm) films before (—) and after NAB functionalization (—) in 0.1 M TBABF$_4^-$/MeCN, scan rate 0.1 Vs^{-1}.

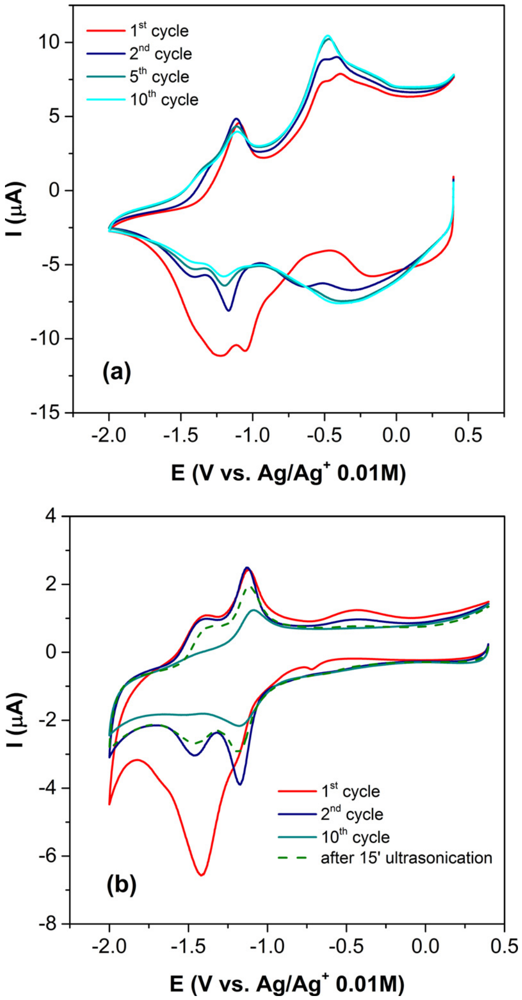


Fig. 4. Cyclic voltammograms for (a) NAB-PPY/BF_4^- (120 nm) films and (b) NAB-GC in 0.1 M TBABF$_4^-$/MeCN: (—) 1st cycle; (—) 2nd cycle; (—) 10th cycle, scan rate 0.1 V s^{-1}.

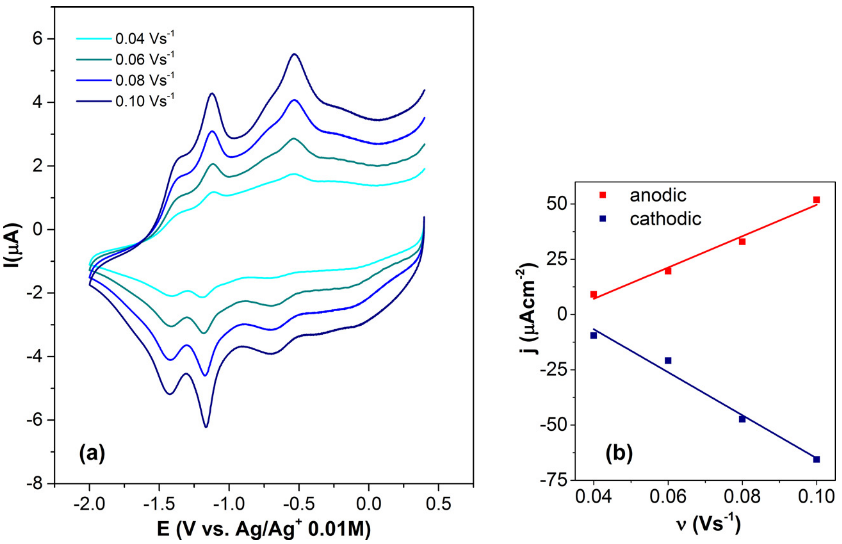


Fig. 3. (a) Cyclic voltammograms registered using scan rates between 0.04 and 0.1 V s^{-1} for NAB-PPY/BF_4^- (60 nm) films in 0.1 M TBABF$_4^-$/MeCN (functionalization performed by CV in the potential range of +0.4 V to −1.0 V, 0.1 V s^{-1}, 1 cycle); (b) The influence of the potential scan rate on both cathodic and anodic peak currents observed for the redox system $E^0 = -1.135$ V on the CV recorded in 0.1 M TBABF$_4^-$/MeCN solution for NAB-PPY/BF_4^- (60 nm) electrode.

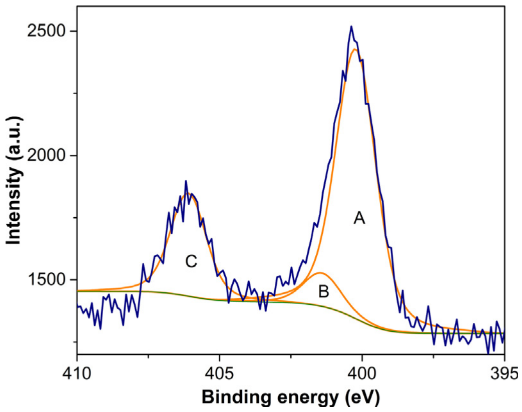


Fig. 5. XPS N 1s core level spectrum of NAB-PPY/BF_4^- films (60 nm, deposited on ITO substrates) obtained by $NABDBF_4^-$ (1 mM) electroreduction by CV for 5 cycles in the potential range of +0.4 V to −1.0 V, 0.1 V s^{-1}.

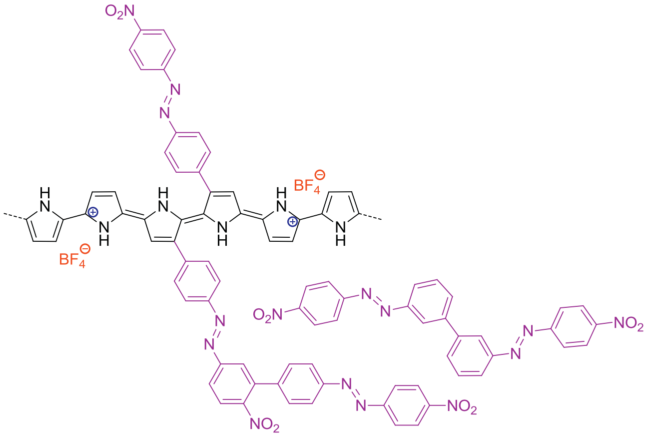


Fig. 6. Hypothesized structure for NAB-functionalized polypyrrole.

exists between the chemisorbed NAB molecules and the conducting substrate, as has been shown in ref. [37]. By analogy, the red-shift of the absorption band to 370 nm in the spectrum corresponding to NAB-functionalized polypyrrole is an indication of electronic coupling between NAB and the conducting polymer backbone, resulting in changes in orbital energies that lead to a decrease of the chromophore's HOMO–LUMO gap.

3.6. Third-order nonlinear optical properties

It is well known that conjugated polymers posses large cubic nonlinearities due to the delocalisation of π electrons along the polymer chains [38], therefore a study of the non-linear optical (NLO) properties of NAB-functionalized polypyrrole was undertaken.

The third-order NLO response of doped polypyrrole and the corresponding NAB-functionalized polymer was investigated using the third-harmonic generation (THG) technique. Briefly, a pulsed laser beam (1064.2 nm fundamental wavelength, 6 ns pulse duration and 10 Hz repetition frequency) with well-defined polarization was focused on a thin polymer sample deposited on a substrate. The sample was rotated along an axis perpendicular to the beam propagation direction, the THG signal was separated from the fundamental beam using filters and its intensity measured with a photomultiplier tube as a function of the incidence angle. Fig. 9 shows the experimental dependence of THG intensity on the incidence angle for PPY/BF_4^- and NAB-PPY/BF_4^- films (90 nm) deposited on ITO coated glass substrates.

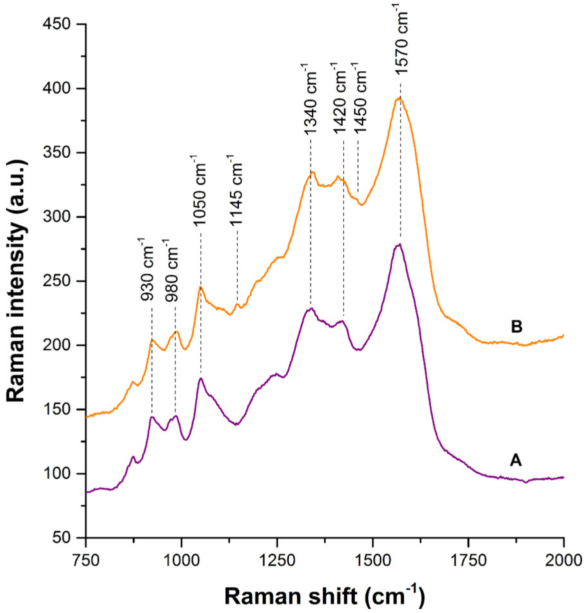


Fig. 7. Raman spectra (532 nm, 10 mW) of PPY/BF_4^- A before and B after functionalization with NAB by performing 5 CV cycles, in the potential range of +0.4 V to −1.0 V, 0.1 V s^{-1} in $NABDBF_4^-$ diazonium salt solution (1 mM in 0.1 M $TBABF_4^-$/MeCN).

Table 2
Raman band frequencies for PPY/BF_{4-} and NAB-PPY/BF_{4-} (excitation wavelength 532 nm).

Frequencies (cm^{-1}) PPY/BF_4^-	NAB-PPY/BF_4^-	Assignment [34,35]
1570	1570	C=C str.
–	1450	N=N str.
1420	1420	C—N str.
1340	1340	C—C str.
–	1145	phenyl-N=N str.
1050	1050	C—H def.
980	980	pyrrole ring def., sym.
930	930	pyrrole ring def., asymm.

The magnitude of the third-order susceptibility ($\chi^{(3)}$) was evaluated by fitting the experimental data following the detailed analysis of Kajzar et al. presented in ref. [39], which takes into

Table 1
Deconvolution of the N 1s high resolution spectrum for 4′-nitroazobenzene functionalized PPY/BF_4^- films.

Peak	Assignment [32,33]	Binding energy (eV)	Relative atomic percentage (%)
A	—**N**H— —**N**=**N**—	400.2	68.5
B	—**N**H^+— =**N**H^+—	401.4	8
C	—**N**O_2	406.1	23.5

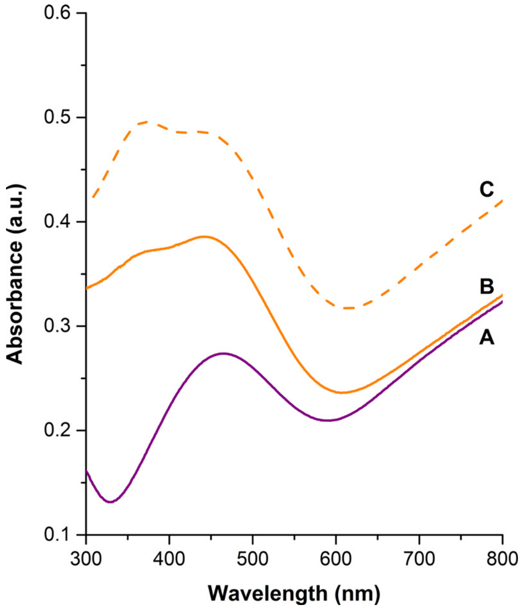


Fig. 8. UV–vis absorption spectra for A $\mathrm{PPY/BF_4^-}$ films (90 nm) before functionalization, B $\mathrm{NAB\text{-}PPY/BF_4^-}$ films (90 nm) and C $\mathrm{NAB\text{-}PPY/BF_4^-}$ films (120 nm) after functionalization by performing 5 CV cycles in the potential range of +0.4 V to −1.0 V, 0.1 V s^{-1} in $\mathrm{NABDBF_4^-}$ diazonium salt solution (1 mM in 0.1 M $\mathrm{TBABF_4^-}$/MeCN).

account the sample absorption at the harmonic wavelength and the contribution of the substrate to the resulting THG intensities. The overall THG intensities of substrate + polymer film were calibrated by independent third-harmonic generation measurements on a fused silica plate performed under identical experimental conditions, for which the value of $\chi^{(3)}$ is known [30].

The calculated values of the third-order susceptibility were $\chi^{(3)} = (1.48 \pm 0.17) \times 10^{-12}$ esu for $\mathrm{PPY/BF_4^-}$ and $\chi^{(3)} = (1.24 \pm 0.12) \times 10^{-12}$ esu for $\mathrm{NAB\text{-}PPY/BF_4^-}$, respectively. The value of $\chi^{(3)}$ for $\mathrm{PPY/BF_4^-}$ is in accordance with the resonant third-order susceptibility of 3.5×10^{-12} esu for chemically prepared polypyrrole reported by Ghoshal [40].

It has been demonstrated that the cubic susceptibility $\chi^{(3)}$ has an inverse dependence on the sixth power of the optical bandgap [41,42]. The slightly smaller value of $\chi^{(3)}$ corresponding to the NAB-functionalized polypyrrole points to the fact that the functionalization reaction perturbs the delocalization of π electrons, the increase of the optical bandgap for polypyrrole being consistent with the blueshift of the π–π* transition band apparent in the UV–vis spectrum of $\mathrm{NAB\text{-}PPY/BF_4^-}$. This represents a confirmation of our previous results discussed in ref. [10] which concern the electrochemical functionalization of polypyrrole with *para*-substituted phenyl groups via diazonium chemistry.

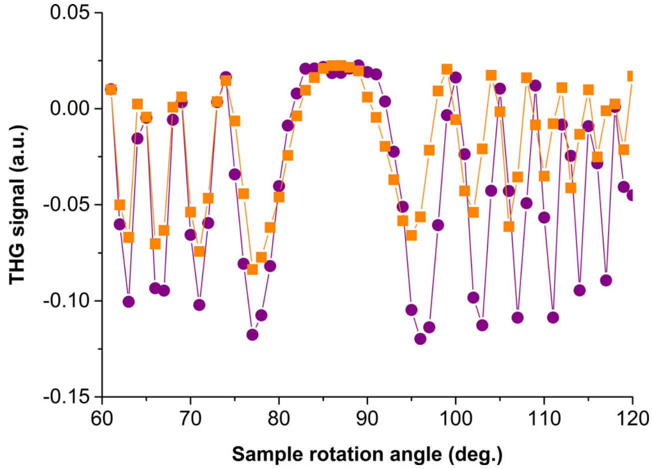


Fig. 9. Experimental (points) and calculated values (solid lines) of third-harmonic intensities as a function of the incidence angle for $\mathrm{PPY/BF_4^-}$ (●) and $\mathrm{NAB\text{-}PPY/BF_4^-}$ films (■) (90 nm).

4. Conclusions

In this work we demonstrate a new strategy for obtaining conducting azopolymers through a simple, versatile and cost-effective procedure. Based on our knowledge, the method of covalently attaching chromophores to a conducting polymer chain by the electrochemical reduction of aryl diazonium salts was employed for the first time.

The functionalization of doped polypyrrole films with 4′-nitroazobenzene (NAB) was evaluated by cyclic voltammetry, as well as by spectroscopic techniques such as XPS, Raman and UV–vis spectroscopy. The voltammetric characterization of the functionalized PPY films in a pure electrolyte solution showed a similar behavior with the pristine polymer. The redox signature of 4′-nitroazobenzene was evidenced in CV measurements, and a behaviour characteristic for redox species immobilized on the electrode surface proved that NAB groups are in fact grafted on the polypyrrole electrode. Evidence for the presence of azo groups was also given by XPS and Raman spectroscopy.

Moreover, the presence of the absorption band characteristic for the 4′-nitroazobenzene molecule which is red-shifted in the UV–vis spectrum corresponding to NAB-functionalized polypyrrole represents also an indication of electronic coupling between NAB and the conducting polymer backbone.

Furthermore, the third-order nonlinear optical response of NAB-functionalized polypyrrole was investigated using the optical third-harmonic generation technique. The measured magnitude of the third-order susceptibility for the NAB-modified polymer is comparable to that of polypyrrole.

The versatility of this methodology allows not only the functionalization of polypyrrole-type materials with chromophore groups, but can also be successfully applied to other conjugated polymer systems in order to create various photoresponsive materials.

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