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Electrosynthesis and Optical Characterization of Poly(*p*-phenylene), Polypyrrole and Poly(*p*-phenylene)-polypyrrole Films

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Poly(*p*-phenylene) (PPP), polypyrrole (PPY), and poly(*p*-phenylene-pyrrole) (PPP-PPY) films were electrochemically synthesized in acetonitrile by cyclic voltammetry. For comparison purposes, the films were characterized by cyclic voltammetry in a monomer-free solution, and their optical responses were also obtained in the UV-VIS range of energy after varying the applied potentials. The absorbance spectra of the PPP-PPY film exhibited bands typically seen in the spectra of the homopolymers, PPP and PPY films, but better defined, intense, and related to reversible color transitions. Although it was not possible to confirm by using infrared and Raman spectroscopy that a copolymer was in fact obtained, the presence of both monomers, pyrrole and biphenyl, in the polymerization medium turned easier the process of film formation, yielding darker, more uniform, and rougher films as it was verified by photographic images and AFM (atomic force microscopy) images.

Keywords: polyphenylene, polypyrrole, conducting polymers

1. Introduction

Over the last decades, conducting polymers have been studied aiming towards application in electrochromic displays, light-emitting devices, batteries, and sensors¹⁻⁴. The use of electrochemical methods of synthesis for the preparation of polyaniline, poly(*p*-phenylene), polythiophene, polypyrrole, and derivatives allows one to obtain a variety of conjugated polymers, including copolymers and bi-layers, with improved mechanical, optical, and electrical properties⁵.

Poly(*p*-phenylene) (PPP) has been studied as active layer in light emitting devices in the blue spectral range^{6,7}; PPP can be prepared by chemical oxidation of benzene in acidic medium, and exhibits thermal and chemical stabilities, relatively high conductivity ranging from 10⁻¹² to 10² S cm⁻¹ after chemical doping, and relatively high mechanical strength⁸. However, PPP when obtained in powder form has a limited use because of its low solubility in common organic solvents, making it difficult to prepare films. Therefore, PPP can be also electrochemically prepared yielding adherent and mechanically tough films, which allows one to control parameters such as final potential, potential range, and solvent–salt (electrolyte) combination⁹.

Thin PPP films have been frequently prepared by cyclic voltammetry at relatively high oxidation potentials

in strong acidic media (super acids) after oxidizing benzene or biphenyl^{9,10}. Only a few authors have briefly described the use of a mild solution, acetonitrile and tetrabutylammonium perchlorate, in order to obtain PPP films¹¹. The electrosynthesis of PPP films and poly(*p*-phenylene-pyrrole) (PPP-PPY) films has been previously studied in our group by using milder conditions (acetonitrile and low oxidation potentials)¹². From these results, we verified how synthesis parameters such as oxidation potentials had an influence on the electrochemical properties of the PPP-PPY films. Polypyrrole (PPY) films have been most often related to interesting properties such as high conductivity and stability in air¹³⁻¹⁵ when prepared in both aqueous and nonaqueous media, and at relatively low oxidation potentials^{16,17}. Here, we verified that the electropolymerization of biphenyl and pyrrole allows one to decrease the oxidation potential necessary to obtain PPP-PPY films in acetonitrile. These films were characterized by cyclic voltammetry, spectroelectrochemistry, and AFM (atomic force microscopy).

2. Experimental

Biphenyl and tetrabutylammonium perchlorate (TBAP) were dried under vacuum for 2 h. Pyrrole was purified by

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vacuum distillation. The amount of water in acetonitrile (ACN) was 0.0032 vol % (32 ppm, labeled value) before adding molecular sieves (4 Å) treated at 300–400 °C for 24 h.

All electrochemical experiments were carried out using a conventional three-electrode glass cell and a 283 EG&PAR potentiostat/galvanostat. Pt plates were used as the counter-electrodes after mechanical polishing with alumina powder. Commercial fluorine-tin-oxide coated glass (FTO) plates were used as the working electrodes. All potentials were measured vs a Ag-wire pseudo-reference electrode (Ag-QRE) immersed in a glass tube containing the electrolyte salt (TBAP) in acetonitrile (ACN). Since the potential of Ag-QRE was measured vs a standard calomel electrode (SCE), and showed to be stable during the electrochemical experiments, this electrode was considered to be suitable for using in acetonitrile. The potential of Ag-QRE in 0.01 mol L⁻¹ TBAP in ACN was measured as -128 ± 2 mV vs SCE.

The polymer films were electrochemically prepared by cyclic voltammetry on FTO electrodes (1.0 cm²) at 50 mV s⁻¹ and 0.1 mol L⁻¹ of each monomer (pyrrole or biphenyl). Before starting the electrodeposition, the electrodes were ultrasonically cleaned in ethanolamine (20% v/v) for 30 min, aqua regia solution for 10 min, and then, isopropanol at 80 °C for 15 min; after that, they were dried with dry nitrogen gas. The potentials were cycled from 0.0 V to 2.0 V for biphenyl (0.1 mol L⁻¹), 0.0 to 1.0 V for pyrrole (0.1 mol L⁻¹), and -0.3 V to 1.1 V for the mixture of biphenyl (0.1 mol L⁻¹) and pyrrole (0.01 mol L⁻¹) (10:1 molar proportion). These values of concentrations were chosen once yielded films with better uniformity. Besides, the concentration of pyrrole was chosen to be ten times lower than that of biphenyl, following a previously established protocol, which has been successfully used for simultaneous polymerization of pyrrole and thiophene¹⁸.

The UV-VIS spectra were recorded *in situ* by sweeping potential with a Hitachi U-2001 spectrophotometer. These measurements were obtained for a film placed in a quartz cuvette containing 0.01 mol L⁻¹ TBAP/ACN solution; this cuvette had a cap which was connected to the three-electrode setup, resulting in a low-cost spectroelectrochemical cell.

A contact mode atomic force microscope (AFM) from Nanoscope IIIa (Digital Instruments) was used in tapping mode with a silicon nitride triangular shaped cantilever tip (0.06 N m⁻¹ spring constant). The analysis by FTIR (Fourier Transform Infrared Spectroscopy) were carried using a MB-102 Bomem (Hartmann & Braun) equipment.

3. Results and Discussion

Figure 1A (curves a and b) shows a series of cyclic voltammograms recorded for the FTO electrodes in 0.1 mol L⁻¹ biphenyl (a) or 0.1 mol L⁻¹ pyrrole (b) in acetonitrile (ACN). As it can be noticed from these curves, the current density increases gradually with the number of cycles, thus evidencing that the film thickness increases with time, in particular for pyrrole. In Figure 1A(a), the current density increases rapidly into the positive direction after +1.5 V, which clearly defines a relatively high oxidation potential for biphenyl. In this case, the current density decreases with the number of cycles after +1.5 V (see arrow in Figure 1A(a)). Upon successive cycling, coupling reactions yield

dimeric and oligomeric species, and then, after reaching 10 complete cycles, a polymer (PPP) film was deposited on the electrode surface (find an image for this film in Figure 1B (c)). Figure 1A (a) also shows a well-defined redox process within a potential ranging from +1.0 V to +0.7 V, with a color transition varying from brownish, at 0.0 V (neutral state), to blue, at +1.8 V (oxidized state). Once the current density increases more effectively for pyrrole, when compared to biphenyl, this type of response can be related to a continuous process of film deposition rather than a surface blocking effect, which will be discussed in more detail later. Besides, for pyrrole, the current density starts to increase at a relatively lower oxidation potential, +0.6 V, and then, increases continuously with time. The electrode surface upon successive cycling start to show a reversible color transition from gray, at -0.1 V (neutral state), to blue, at +1.0 V (oxidized state). An image of the PPY film is shown in Figure 1B(d), where it is evident that this film shows a quite good uniformity when compared to the PPP film.

The films prepared according to Figures 1A (a) and (b) were characterized by cyclic voltammetry in a monomer-free solution (Figure 1B (curves c and d)). Meanwhile the PPP film shows a well-defined redox process from +0.9 V to +0.7 V, in Figure 1B (c), the PPY film exhibits not well defined redox response, Figure 1B (d).

Figure 1A (e) shows the voltammetric response of the FTO electrode in a solution containing the co-monomers, biphenyl (0.1 mol L⁻¹) and pyrrole (0.01 mol L⁻¹), *i.e.*, at a 10:1 molar proportion. In this case, it is evident that the current density increases faster, and at more positive potentials, when compared to pyrrole. The current density increases slowly with the number of cycles up to reach the third cycle, and then, begins to increase faster up to reach the tenth cycle, indicating a preferential oxidation of pyrrole in detriment to biphenyl, even at a concentration of pyrrole ten times smaller than that of biphenyl. Therefore, Figure 1A (e) is close to Figure 1A (b), defining a typical response of an electrode in medium of pyrrole, with a redox response seen from +0.3 V to +0.3 V, and a current density which increases gradually with the number of cycles. An image of this film is shown in Figure 1B (f), where it is evident that uniform, darker films can be produced after oxidizing both biphenyl and pyrrole.

The PPP-PPY film obtained according to Figure 1A (e) was also analyzed by cyclic voltammetry, where a large, not well-defined response was obtained, Figure 1B (f). This film exhibited a stable, reversible color transition from gray at -0.8 V (neutral state) to blue at +0.9 V (conductive state).

In order to evaluate the process of film deposition on the electrode surface, the total charge was obtained per each cycle for PPP, PPY and PPP-PPY (Figure 2). During the preparation of the PPP films, it was noticed that the charge decreases with the number of cycles, indicating a block effect of the active area of the electrode in the presence of biphenyl. When pyrrole is the monomer, this passivation effect is not evident, and the charge increases with time, as related to an increase of the film thickness with the number of cycles, *i.e.* polymerization time. When both monomers are added together, the polymerization yields values of charge

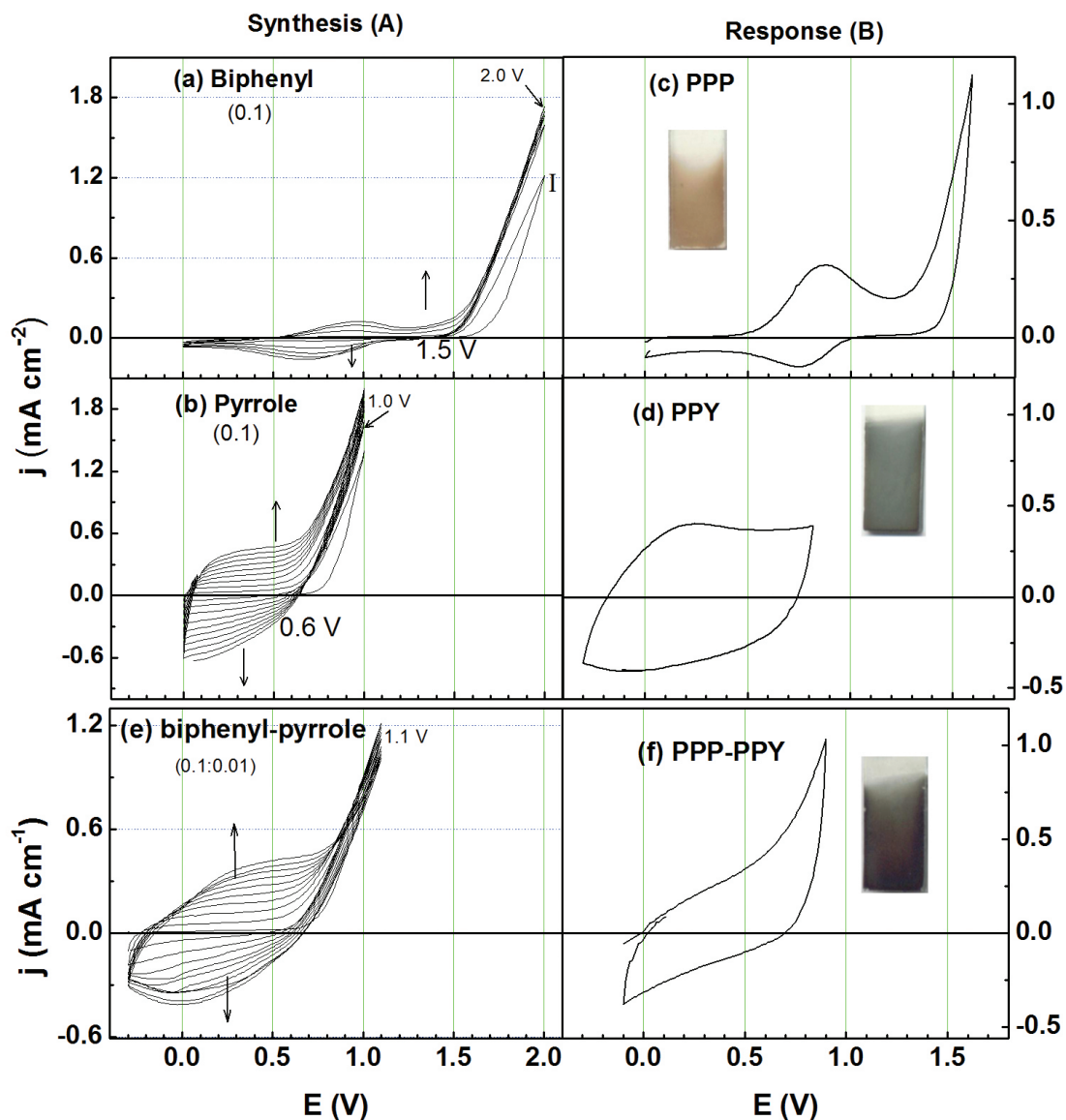


Figure 1. Cyclic voltammograms of the FTO electrodes (A) during the synthesis of (a) PPP, (b) PPY, and (e) PPP-PPY, and electrochemical response (B) of (c) PPP, (d) PPY, and (f) PPP-PPY films. Scan rate = 50 mV s⁻¹.

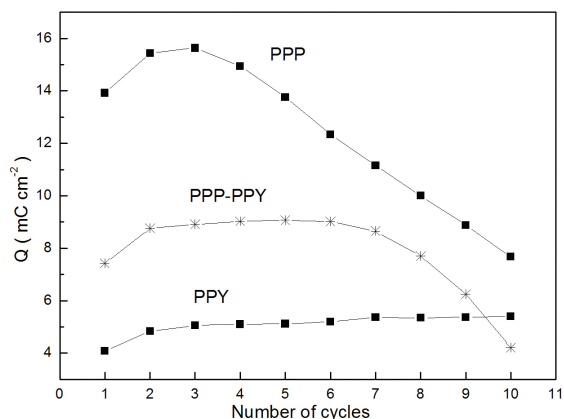


Figure 2. Values of total charge obtained per cycle during the electrochemical deposition of the PPP, PPY and PPP-PPY films.

that are intermediate than those obtained individually, with practically the same values from 2th up to 7th cycle, and decreasing at higher numbers of cycles. If one considers that for the preparation of the PPP-PPY films the molar proportion of biphenyl/pyrrole used was 10:1, one infers that the presence of pyrrole, even at low concentrations, turns easier the process of film formation.

The absorption spectra for the PPP, PPY and PPP-PPY films were taken *in situ* after varying the doping states, *i.e.*, under different applied potentials into the positive direction (Figure 3). For the PPP film (Figure 3a and 3b), the band at 325 nm can be assigned to the intraband transition in PPP, which also appears in the absorption spectra of PPP films, which were electrochemically prepared via oxidation of benzene¹⁹. Upon applying different potentials, this band decreases in intensity after applying -0.3 V to 1.6 V (see

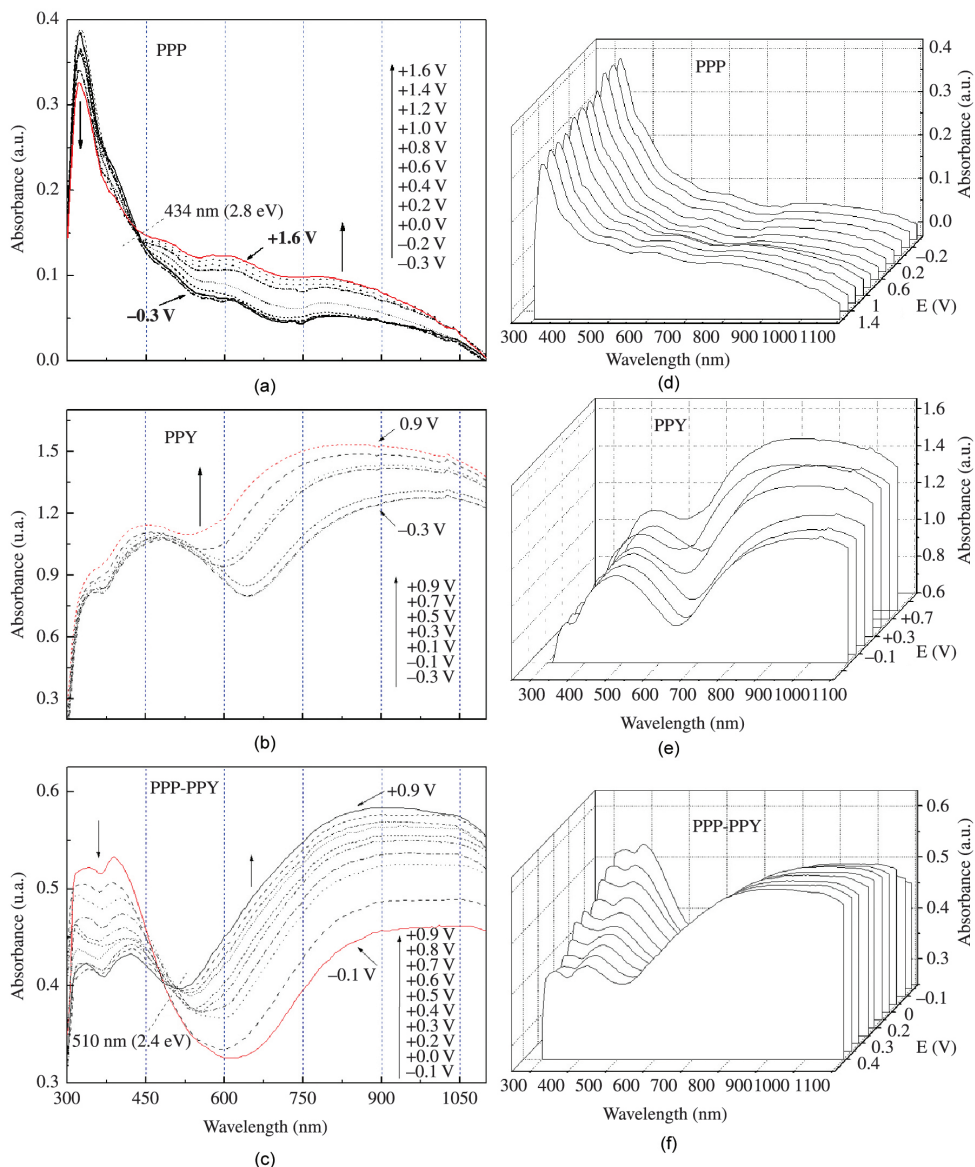


Figure 3. *In situ* UV-VIS spectra obtained for (a), (d) PPP, (b), (e) PPY and (c), (f) PPP-PPY films.

arrow in Figure 3a), and, at the same time, new bands become to be more defined at 470 nm, 580 nm, and 830 nm under applying positive potentials (*p*-doping).

Figure 3b and 3e shows the spectra of the PPY films, with a main large band centralized at 470 nm, and assigned to the electronic transitions of a neutral PPY structure. Upon increasing the applied potential, a broad band evolves after 600 nm, shifts to lower wavelengths, and centralizes at 900 nm at +0.9 V. This absorbance band can be assigned to the electronic transitions of doped PPY²⁰.

For the PPP-PPY film, the spectra show two absorption bands at 330 nm and 390 nm (Figure 3c and 3f), which decrease continuously in intensity upon increasing the applied potential, as can be also seen in the spectra of the PPP films. Besides, the band centralized at 825 nm increases in intensity and shifts to higher wavelengths upon applying positive potentials such as +0.9 V; this spectral profile is

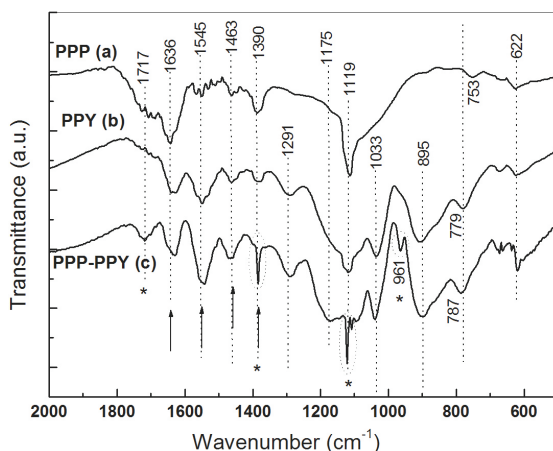


Figure 4. FTIR spectra for the PPP (a), PPY (b) and PPP-PPY (c) films obtained by cyclic voltammetry after 10 complete cycles.

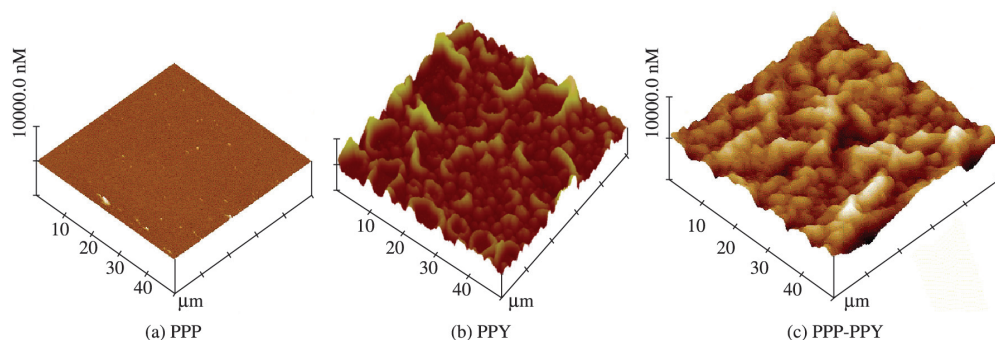


Figure 5. AFM images for the (a) PPP, (b) PPY and (c) PPP-PPY films obtained by cyclic voltammetry after 10 complete cycles.

also typical for the PPY films, as we have obtained here, and also, in the literature²⁰⁻²³.

From Figures 3a and c, it can be possible to estimate the optical bandgaps for the PPP and PPP-PPY films using the values of isosbestic point, which are defined in these figures as 2.8 eV (PPP) and 2.6-2.4 eV (PPP-PPY). Although it is not possible to completely eliminate error in this estimative, these values can be comparable to the those reported in the literature (PPP, 3.0 eV^[8] and PPY, 2.8 eV^[24]).

The FTIR spectra of the PPP, PPY and PPP-PPY films are shown in Figure 4. For the PPP-PPY film, there is a mixture of absorption bands when they are compared to those seen in the spectra of the homopolymers. However, since the spectrum of the PPP film exhibits only a few bands, and which can be attributed to a simple structure containing only phenylene moieties, one infers that the spectra of PPY and PPP-PPY are similar, but with some differences noticed in intensity and shape, as it was marked in the figure. Therefore, it can be assumed that the PPP-PPY film has unique characteristics, which are different from those seen for the homopolymers, PPY and PPP; on the other hand, it not possible to estimate the types of linkages formed via simultaneous polymerization of pyrrole and biphenyl.

Figure 5 shows the AFM images for the PPP, PPY and PPP-PPY films. The PPP film (Figure 5a) shows a denser, compact structure; for PPY, its morphology is globular, with holes distributed uniformly over the surface, Figure 5b.

The PPP-PPY film, Figure 5c, shows a more regular morphology, with large surface globules, which gives arise

from the coalescence of smaller globules. These images also have indicated that the electrochemical oxidation of pyrrole and biphenyl yields uniform films as an efficient process of film forming.

4. Conclusions

Our results have shown that it can be possible to obtain PPP-PPY films in acetonitrile under a narrow potential range, and with a response between those obtained for the homopolymers, PPP and PPY. The electrochemical preparation of the PPP-PPY films can be carried out in a potential range close to that used for the preparation of the PPY film. FTIR and *in-situ* UV-VIS spectra for the PPP-PPY films showed contributions from the bands of both materials, PPP and PPY. Therefore, the electrochromic response of the PPP-PPY film improved due to the presence of PPY incorporated within the film, thus indicating the formation of a novel material that can be applied in displays and devices. The electrochemical preparation of PPP-PPY film in a mild solution has proved to be useful to obtain a film with good adhesion, uniformity, and surface quality.

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