To provide a viable alternative for counter electrodes used in dye sensitized solar cells, polypyrrole (PPy) based films have been synthesized via electrochemical deposition in the presence of the ionic liquid 1-butyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) imidate (NTf2) and incorporated with gold nanoparticles (AuAu nanoparticles). The films were analyzed by SEM, UV-Vis-NIR, Raman, Electrochemical impedance spectroscopy, Cyclic voltammetry and Conductivity measurements. The presence of the ionic liquid is found to result in a more conductive film, to improve catalytic reduction of I3− and the electrochemical reversibility of the electrode. In addition to increase conductivity, impedance spectroscopy has shown that incorporating Au nanoparticles in the PPy/NTf2 film helps improving the interfacial charge transportation, the electrocatalytic properties and solar energy conversion efficiency. DSSCs assembled with PPy based CE presented nearly the same J-V characteristic parameters as observed from conventional Pt based device.

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Synthesis of gold nanoparticles.—Au nanoparticles were prepared according to Turkevich method. 1 mmol L\(^{-1}\) of HAuCl\(_4\) aqueous solution (100 mL) was refluxed at 120 °C under vigorous stirring, in a silicone bath. 10 mmol L\(^{-1}\) C\(_6\)H\(_{12}\)NaO\(_2\) (2.5 mL) was quickly added to the reaction vessel. A sudden color change from pale yellow to red indicated the synthesis of the Au nanoparticles.

Preparation of PPy/ LiClO\(_4\), PPy/ NTf\(_2\) and PPy/ NTf\(_2\)/Au nanop counter electrodes.—The electropolymerization of the films (electrodes) was carried out at room temperature in a galvanostat/potentiostat Autolab 302N, using a conventional three-electrode cell. Fluorine doped tin oxide substrates (FTO-glass, Solaronix, 152 mm\(^2\)) were used as working electrode, platinum plate (1 cm\(^2\)) was used as counter electrode, and Ag/AgCl was used as reference electrode. For the synthesis, the cyclic voltammetry method was performed from −0.3 to +1.3 V at a scan rate of 30 mV s\(^{-1}\). Electrodereposition solution was prepared by dissolving 0.1 mol L\(^{-1}\) of PPy in 10 mL of BMI/NTf\(_2\), obtained (PPy/NTf\(_2\)) electrodes. PPy/NTf\(_2\)/Au nanop electrodes were obtained by dipping PPy/NTf\(_2\) in concentrated Au nanoparticles colloidal solution during 24 hours. For comparison, LiClO\(_4\) doped PPy (PPy/LiClO\(_4\)) electrodes were synthesized using the same parameters.

DSSC assembling.—TiO\(_2\) pastes were screen-printed on FTO previously soaked in 40 mmol L\(^{-1}\) TiCl\(_4\) aqueous solution at 80 °C for 30 min. The substrate was heated on a hot plate at 125 °C for 20 min and at 450 °C for 30 min in a tubular oven. The mesoporous TiO\(_2\) electrode was immersed in 0.5 mmol L\(^{-1}\) cis-cis(isothiocyanato) bis(2,2′-bipyridyl-4,4′-dicarboxylato)-ruthenium(II) N-719 solution of acetone/tertbutyl alcohol (1:1 v/v) and kept at room temperature for 24 h. Two kinds of counter-electrodes were tested: i) standard platinum based counter-electrodes prepared by coating the FTO surface and ii) PPy-based counter electrodes (PPy/ LiClO\(_4\), PPy/ NTf\(_2\) and PPy/NTf\(_2\)/Au nanop). The mediator responsible for dye regeneration was placed between the dye sensitized photoanode and the counter electrode. The electrolyte was 0.6 mol L\(^{-1}\) BMIII, 0.03 mol L\(^{-1}\) I\(_2\), 0.10 mol L\(^{-1}\) guanidinium thiocyanate, and 0.5 mol L\(^{-1}\) 4-ter-butylpyridine in a mixture of acetonitrile and valeronitrile. The device was sealed using a low melting temperature polymeric film (Meltonix).

Characterization and measurements.— Morphology was studied by scanning electron microscopy (SEM) using an EVO50 Carl Zeiss microscope at 15 kV. Optical measurements were performed in a Perkin Elmer Lambda 25 spectrophotometer. Structural measurements were performed by Raman spectroscopy using an Olympus microscope, a single-pass monochromator and a charged-coupled device (CCD) detector, cooled with liquid nitrogen. Excitation was provided by 632.8 nm radiation from a 10 mW polarized He–Ne laser focused in a spot ∼2 μm in diameter. Electrochemical measurements were performed in a galvanostat/potentiostat Autolab 302N. The electrocatalytic activity of I\(^{-}/I^+\) was evaluated by cyclic voltammetry within a potential range from −0.6 to +1.3 V at different scan rates (20, 50, 100, 150, and 200 mV s\(^{-1}\)) and 10.0 mmol L\(^{-1}\) NaI, 1.0 mmol L\(^{-1}\) I\(_2\), and 0.1 mmol L\(^{-1}\) of LiClO\(_4\) in acetonitrile were used as electrolyte solution. The resistivities were measured directly from the films by the four-point technique using a JANDEL Universal probe. The distance between the points was fixed at 1.0 mm. DSSCs based on PPy/LiClO\(_4\), PPy/NTf\(_2\) and PPy/NTf\(_2\)/Au nanop counter electrodes were characterized by current versus potential curves and electrochemical impedance spectroscopy (EIS). Profile studies were performed using a Veeco Dektak 150 equipment.

Results and Discussion

The optical properties of the PPy based electrodes were investigated by UV-Vis-NIR spectrophotometry (Figure 1). The spectra present the characteristic absorptions of oxidized PPy. The bands at ca. 163 1550 nm and between 620 and 1240 nm are related to the transition from the bonding to the antibonding polaron state. The band at ca. 460 nm corresponds to the transition from the valence band to the antibonding bipolaron state, and the band at ca. 375 nm is related to the π→π* interband transitions. Among the films, polypyrrole is found in the higher oxidized state in PPy/LiClO\(_4\), which is characterized by the absence of the band at 1550 nm, followed by the weakening of 890 nm and the shift of the interband transition to higher energy. As one can observe, the presence of Au nanoparticles does not change significantly the electronic structure of polypyrrole. The band at 520 nm is attributed to the presence of Au nanoparticles.

The Raman spectra of the PPy films, acquired within the range of 800–1800 cm\(^{-1}\) are shown in Figure 2. PPy/LiClO\(_4\) and PPy/NTF\(_2\) present the vibrational bands characteristic of the oxidized state at ca. 1610 cm\(^{-1}\), related to a mixed vC=C and inter-ring vC-C vibration, ca. 1050, 1240, 1350, and at 930 cm\(^{-1}\), assigned to C-H out of the plane deformation. However, the vibration mode assigned to reduced form of the pyrrole ring, benzoid form, at ca. 980 cm\(^{-1}\), assigned to a ring deformation mode (δ_ar)\(^{10,17–19}\) is more intense for PPy/LiClO\(_4\) hence displaying high oxidation level, as earlier observed by optical measurements (Fig. 1). The spectra intensity ratio of the bands at ca. 1050 and at ca. 1080 cm\(^{-1}\), A\(_{1050}/A_{1080}\) increased from 0.80 in PPy/LiClO\(_4\) to 0.85 in PPy/NTF\(_2\) while the ratio A\(_{1560}/A_{1610}\) increased from 0.68 to 0.78, showing a less oxidized PPy in the NTF\(_2\) medium. An interesting result is the shift of the vibration mode of

![Figure 1. UV-Vis-NIR absorption spectra of the PPy based films.](image1)

![Figure 2. Raman spectra of the PPy based films.](image2)
The increase in relative intensity of the vibration modes are related to a significant reduction of the polymer chain, to a more polaronic state. The lattice deformation results in the loss of planarity of the chain. This geometrical distortion, although localized, leads to changes in bond strengths and torsion angles that affects the ability of PPy/NTf2. This result is related to the larger surface area resulting from the homogeneous morphology and porosity, and improved conductivity of the films synthesized in ionic liquid media. These results suggest that faster electron transfer kinetics is obtained for PPy/NTf2/Atunanop (e and f).

The SEM images of the synthesized polypyrrole films are shown in Figure 3. The surface of PPy/LiClO4 consists of large granules up to 10 μm, resulting in a rough surface (1158 ± 178 nm) (Figures 3a and 3b). This morphology might be related to a high oxidation degree of PPy in PPy/LiClO4, resulting from an increased number of defects in the PPy chain. PPy oxidation results in electrons removal from the chain, which leads to lattice deformation, followed by the stabilization of the cation by nearby anionic species diffused into the polymer matrix. The lattice deformation results in the loss of planarity of the chain. This geometrical distortion, although localized, leads to changes in bond strengths and torsion angles that affects the ring deformation mode that consequently results in the formation of rough and irregular surface. Once the ionic liquid is added to the electrolyte this granular rough texture changes to a much smoother surface (39 ± 20 nm) for PPy/NTf2 film (Figs. 3c and 3d).

The surface of PPy/NTf2/Aunanop, confirmed by EDS (not shown), makes the PPy/NTf2 film rougher (82 ± 56 nm) (Figs. 3e and 3f). The thicknesses of the films were determined by profilometry as 3624 ± 340 nm, 373 ± 31, 192 ± 17 nm, for PPy/LiClO4, PPy/NTf2, and PPy/NTf2/Atunanop respectively. The decreasing thickness of PPy/NTf2/Atunanop can be related to the reduction of the PPy chain, as observed by Raman (Figure 2), resulting in the contraction and shrinkage of the chains.

The resistivity values obtained in this work (Figure 4a) are consistent with other works in the literature for electrochemically synthesized PPy films.26–28 As earlier shown in this work, the polypyrrole in PPy/LiClO4 present a higher oxidation level, hence we suggest that the lower electrical resistivity of PPy/NTf2 is related to a possible synergistic effect between PPy and the ionic liquid, improving structural ordering of the polypyrrole chains and facilitated delocalization of the charge carriers.22 As expected the lower resistivity is obtained from PPy/NTf2/Atunanop.

Dye regeneration rate in DSSCs is controlled by the counter-electrode (CE), therefore the CE shall provide a high reduction activity for the redox pair.29,30 Figure 4b shows the electrochemical catalytic activity, tested for I−/I3− using PPy electrodes (b). In this work, the analysis was focused on the I−/I3− couple.31,32 Table I shows the values of Ep−1 using PPy electrodes (b) and Ep of LiI, 1.0 mmol L−1 LiI, 1.0 mmol L−1 I2, and 0.1 mmol L−1 of LiClO4 in acetonitrile. Two pairs of redox peaks were observed for all electrodes, characteristic of I−/I3− couple (a/a’) and I3−/I2 (b/b’). The potential difference between two peaks (∆Ep) for electrodes of PPy/LiClO4, PPy/NTf2 and PPy/NTf2/Atunanop were found to be 630 mV, 436 mV and 401 mV respectively.

By comparing ∆Ep and values of current peaks from PPy/LiClO4 and PPy/NTf2 one can observe the better electrochemical catalytic ability of PPy/NTf2. This result is related to the larger surface area that results from the homogeneous morphology and porosity, and improved conductivity of the films synthesized in ionic liquid media. These results suggest that faster electron transfer kinetics is obtained.

| Table I. Electrochemical parameters obtained from the voltammograms presented in Figure 4b. |
|---------------------------------------------------|
| Electrode | Ep−1 (mV) | Ep (mV) | Jpa (mA. cm−2) | Jpc (mA. cm−2) |
|------------|------------|------------|----------------|----------------|
| PPy/LiClO4 | 530 | -100 | 0.55 | -0.31 |
| PPy/NTf2 | 430 | -6 | 0.70 | -0.63 |
| PPy/NTf2/Atunanop | 361 | -40 | 0.60 | -0.52 |

Figure 3. SEM images of PPy/LiClO4 (a and b), PPy/NTf2 (c and d) and PPy/NTf2/Atunanop (e and f).

Figure 4. Four-point electrical resistivity of films (a). Voltammograms of I−/I3− at a scan rate of 20 mV s−1 using PPy electrodes (b).
Figure 5. Voltammograms of $I^-/I_3^-$ redox reaction at different scan rates using PPy electrodes.

when Au_{nanop} are incorporated in the film, which is related to higher catalytic activity, attributed to the active catalytic sites and increase in the conductivity of the electrode compared to PPy/NTf$_2$ electrode. The relationship between ion diffusivity, reaction kinetics and electrochemical catalytic activities were evaluated in $I^-/I_3^-$. Figure 5 shows the voltammograms of $I^-/I_3^-$, obtained using PPy/LiClO$_4$, PPy/NTf$_2$ and PPy/NTf$_2$/Au_{nanop}. In all electrodes, as scan rate is increased the anodic peak shifts to more positive potentials while the cathodic peak shifts toward the more negative direction. The electrodes synthesized in ionic liquid exhibit a pair of well-defined peaks for $I^-/I_3^-$ indicating a good reversibility and catalytic activity. Meanwhile, as scan rate is increased the PPy/LiClO$_4$ electrode loses reversibility, presenting less-defined peaks and the redox reaction for $I_3^-/I_2$ couples nearly disappear. This behavior is related to an easier oxidation of iodide than a reduction of iodine on the surface of PPy electrodes. The dependence of anodic and cathodic peaks of $I^-/I_3^-$ on the scan rate was evaluated for all electrodes by plotting the logarithm of the peak current (mA cm$^{-2}$) versus the logarithm of scan rate (mV s$^{-1}$). As described by the Randles-Sevcik equation, the electrochemical behavior of the studied PPy electrodes is governed by diffusion of iodide species inside the PPy chain. As one can observe in Figure 5, the slope of the anodic curve slightly varies from 0.50 to 0.53, which indicates that the synthesized PPy based electrodes possess nearly the same electroactive surface area. Figure 6 shows the $J_{pa}$ and $J_{pc}$ correspondence of $I^-/I_3^-$ and $I_3^-/I_2$ redox couples for different PPy electrodes during 30 consecutive cycles. These analyses exhibit linearity showing that these parameters are nearly steady after the cycles, suggesting a good electrochemical stability for $I^-/I_3^-$ based electrolyte reaction. However, the PPy/NTf$_2$ electrode exhibit very well-defined peaks when compared to PPy/LiClO$_4$.

Figure 7 displays the J-V curves of the DSSCs assembled with PPy counter electrodes (CEs) and for comparison a Pt based device is also evaluated (Table II). The highest fill factor (FF), open circuit potential...
Figure 6. Consecutive cyclic voltammograms (30 cycles) of I^-/I_3^- redox reaction at a scan rate of 20 mV s^{-1} using PPy electrodes. The relationship between consecutive 10 cycle times of I^-/I_3^- redox reaction peak currents for PPy electrodes.

(V_{oc}) value and efficiency (n \%) are obtained from Pt based device. In terms of FF the PPy films follow the order: PPy/NTf_2/Au_{nanop} > PPy/NTf_2 > PPy/LiClO_4. PPy/NTf_2/Au_{nanop} presents DSSC performance that is comparable to Pt and other PPy based CE reported in the literature.\cite{36,37,38} Hence, doping PPy with IL and embedding Au_{nanop} in the film is a potential methodology to obtain PPy based counter electrodes applied in DSSC.

To understand the interfacial charge transportation in the devices electrochemical impedance spectroscopy (EIS) was performed. In J-V curves, PPy/LiClO_4 has shown lowest FF; therefore, we did not perform EIS measurements for this device. For all other devices these measurements were performed in 0.1 mol.L^{-1} LiClO_4 in dark (Figure 8a) and under illumination (Figure 8b). The value of the V_{oc} under illumination was chosen as the applied bias for both conditions. The starting point of the Nyquist plot is the series resistance (R_s) caused by the substrates, connecting wires, etc.; followed by a small first semicircle observed at higher frequencies with resistance R_1 which is referred to the charge transfer resistance at the CE/electrolyte interface and a larger second semicircle corresponding to the charge transfer resistance (R_2) at the electrodes/dye/electrolyte interface.\cite{39,40} At first glance, in both experiments the real part of impedance is highest for PPy/NTf_2 and lowest for Pt based device. The data were fit to an equivalent circuit containing a combination of resistance components and constant phase elements (CPEs) as shown in the inset of Figure 8a and are presented in Table III.\cite{41} As one can observe R_s presents a clear dependence on the counter electrode following the same trend as observed for their resistivity values (Figure 4a), in addition, it remained nearly unaffected in dark and under illumination. At V_{oc} under illu-
Figure 7. J-V curves of DSSCs using on PPy films and Pt CEs and measurements were made after 24 hours of the assembled devices.

Table II. Electrical parameters obtained from the J x V curves of the DSSCs.

| CE                  | J_sc (mA cm⁻²) | V_oc (mV) | FF (%) | η (%) |
|---------------------|----------------|-----------|--------|-------|
| Pt                  | 13.3           | 0.61      | 65     | 5.3   |
| PPy/LiClO₄          | 13.7           | 0.60      | 59     | 4.7   |
| PPy/NTf₂             | 13.2           | 0.61      | 60     | 4.7   |
| PPy/NTf₂/Aunanop     | 13.7           | 0.60      | 61     | 5.0   |

Figure 8. Nyquist plots of the assembled DSSCs: (a) in dark and (b) under 1 Sun illumination. The inset displays the equivalent circuit used to fit the EIS data.

Conclusions

In summary, we have demonstrated that electrochemical polymerization of PPy in ionic liquid can drive the oxidation state of the polypyrrole chains. The PPy based electrodes have presented a promising electrochemical and chemical reversibility for I⁻/I₃⁻. The electron transport within metals and at metal liquid interfaces do not differ substantially which is contrary to what is usually observed in conducting polymers.

Table III. The values of the circuit elements obtained from the equivalent circuit fitting of EIS data.

| Sample                | Condition     | R_s (Ω) | Q₁(μF) | n₁ | R₁ (Ω) | Q₂(μF) | n₂ | R₂ (Ω) | R_T (Ω) |
|-----------------------|---------------|---------|--------|-----|--------|--------|-----|--------|---------|
| Pt                    | Dark          | 28.1    | 74.4   | 0.74| 6.1    | 424.7  | 0.74| 54.3   | 88.5    |
| PPy/NTf₂              |               | 45.9    | 15.5   | 0.76| 56.3   | 169.2  | 0.76| 633    | 735.2   |
| PPy/NTf₂/Aunanop      |               | 39.6    | 25.0   | 0.74| 11.7   | 151    | 0.74| 311    | 362.3   |
| Pt                    | 1 Sun Illum.  | 26.9    | 30.1   | 0.90| 2.1    | 547    | 0.90| 18.6   | 47.6    |
| PPy/NTf₂              |               | 43.2    | 9.6    | 0.84| 23.6   | 897    | 0.85| 384    | 450.8   |
| PPy/NTf₂/Aunanop      |               | 38.8    | 22.2   | 0.79| 6.3    | 53.7   | 0.79| 147    | 192.1   |
performance of the DSSCs using PPy-based counter electrodes was governed by the morphology, conductivity and electrocatalytic properties of the PPy films, while these properties were ultimately controlled by the presence of the ionic liquid. PPy/NTf2/Aunanop films are porous in nature, environment friendly, present low vapor pressure, low cost and high electrocatalytic activity for iodide/triiodide. All these characteristics make this material very interesting for application as counter electrodes for DSSC. However, the PPy based electrodes present low catalytic stability and new efforts are required to further improve their electrochemical properties in comparison to Pt.

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