

# Influence of the electrodeposition conditions on the energetics of polypyrrole thin films

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The influence of the solvent used for the electrodeposition and that of the dopant anion on the energetics of electrochemically grown polypyrrole were studied by means of a non-destructive optical technique: Photocurrent Spectroscopy. Polypyrrole films doped with the same anion and grown in different solvents, both aqueous and non-aqueous, show the same HOMO-LUMO gap and the same Fermi level location in respect to HOMO. Polypyrrole films doped with different anions in aqueous solutions, present different values of indirect band gap and flat band potential, indicating that dopant anion influences both the defects band and the Fermi level locations.

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## 1. Introduction

The possibility to replace the “conventional” inorganic semiconductors with organic materials was the driving force for numerous studies about the electrical and electronic properties of these compounds.

Conducting polymers are versatile materials which can behave like metals or insulators (or semiconductors) according to their oxidation state [1]; consequently, a modification of their electrochemical, optical and electronic properties occurs. In addition, conducting polymers are chemically inert, resistant against corrosion, low cost, light weight, etc. They are also easy to prepare and, by electrochemical polymerization, it is possible to control: morphology, thickness and doping level [2]. Already several investigations have been performed in order to study the physical properties of conducting polymers like photophysical and electrical behaviours [3-5]. Conducting polymers such as polythiophene and derivatives, polypyrrole, polycarbazole, etc. have already been applied in several electronic devices, in laboratory scale [1,2,6]. They were employed in rectifying junctions like Schottky diodes or p-n heterojunctions such as p-type Si [7] or n-type Si [8] / conducting polymer. They were also used in organic field effect transistors, for modulating the drain current [9] and in light emitting diodes because of their good optical properties.

In particular, polypyrrole and its substituted are good candidates for electrochromic displays, sensors, solar cells and high power supercapacitors [10].

In this work, we studied the dependence of electronic properties of polypyrrole, on the electrodeposition conditions by means of a non-destructive optical technique: Photocurrent Spectroscopy.

## 2. Experimental part

Anodic electropolymerization of pyrrole was carried out using a gold rod ( $S = 0.125 \text{ cm}^2$ ) as working electrode. Before the electropolymerization, the gold rod was mechanically treated using alumina suspension (1  $\mu\text{m}$  grain size) and after it was ultrasonicated in distilled water for 7 min.. The electrodeposition of the polymeric layers was performed potentiostatically, applying a potential of 0.8 V between working and counter electrodes. The charge circulated during each experiment was 103  $\text{mC}\cdot\text{cm}^{-2}$ . A multichannel potentiostat (VMP2 Princeton Applied Research) was used for applying the constant tension and for recording current vs time plots. The mechanism of electropolymerization typical of the heterocyclic compounds consists of the repetition of the following steps: oxidation, coupling and deprotonation [11-12]. Contemporaneously to the increasing of the chain length, the polymeric matrix is oxidized, so it includes anions from the solution in order to maintain electroneutrality. This process corresponds to the doping of the polymeric film [12].

As polypyrrole is soluble both in organic and inorganic solvents, the electrodeposition was carried out in acetonitrile (ACN) (HPL grade 99% anhydrous, Aldrich), propylene carbonate (PC) (99.8%, Aldrich) and distilled water. In order to investigate on the role of the electrodeposition solvent on the energetics of polypyrrole thin films, we used the same dopant anion in the three solvents mentioned above. The supporting electrolyte used for both giving electrical conductivity to the solution and furnishing the dopant anion was 0.1 M lithium perchlorate (99.9%, Aldrich).

For studying the role of the dopant anion on the electronic properties of polypyrrole, the polymeric films were electrodeposited in the following aqueous solutions: 1M KCl (99-100%, Aldrich), 0.5 M  $\text{H}_2\text{SO}_4$  (95-98%,

Aldrich), 0.1 M HNO<sub>3</sub> (65%, Aldrich), 0.1 M LiClO<sub>4</sub> (99.9%, Aldrich). Each electrolytic solution has a pH=1.7. pH was regulated adding HClO<sub>4</sub> (70%, Aldrich), HCl (37%, Aldrich) and NaOH (98 %, Aldrich) in the LiClO<sub>4</sub>, KCl, H<sub>2</sub>SO<sub>4</sub> and HNO<sub>3</sub> solutions respectively.

The concentration of the monomer (Pyrrole 98%, Aldrich) was 0.1 M and before each experiment, it was distilled at atmospheric pressure.

For the characterization of the energetics of polypyrrole films, prepared in different experimental conditions, photocurrent spectroscopy (PCS) studies were carried out. In Figure 1, the PCS set up is shown.

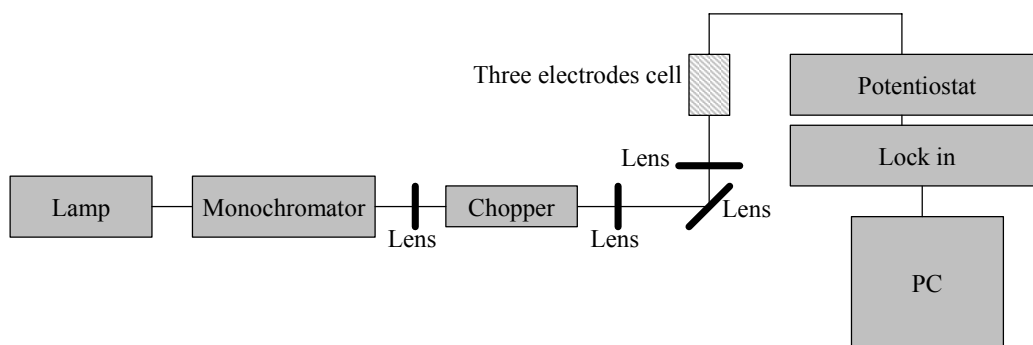


Fig. 1. Experimental set up for PCS studies.

Light is generated by a 450W UV-vis xenon lamp (Xenonlampenversorgung Typ SVX 1450, Müller) coupled with a monochromator (Kratos) that allows to select a specific wavelength ( $\lambda$ ) or to varying it with different scan rates. A series of lenses is used to focus the light ray on the sample. As photocurrent is the difference between the total current and the current in dark condition, a mechanical chopper (Model 650 Light Chopper Controller, EG&G Instruments) was used. It separates the current under dark conditions from the total current, with a frequency of 13 Hz. The photocurrent is detected by a two-phases lock in amplifier (Model 7260 DSP, EG&G Instruments) in connection with the mechanical chopper.

A three electrodes cell endowed with quartz windows was used in order to avoid the absorption of high energy photons ( $h\nu \geq 4$  eV). An Ag/AgCl electrode and a platinum foil were employed as reference and counter electrodes respectively.

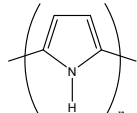
Both photocurrent spectra ( $I_{ph}$  vs  $\lambda$ ) and photocharacteristics ( $I_{ph}$  vs  $U_E$ ) were recorded. All the experiments were performed at 298 K.

### 3. Results and discussion

#### 3.1 Effect of the electropolymerization solvent

In order to study the effect of the solvent used for the electrodeposition, three different films were prepared and compared. They were doped with the same anion (0.1 M ClO<sub>4</sub><sup>-</sup>) and the charge circulated during the electropolymerization was 103 mC.cm<sup>-2</sup>. The solvents used for the preparation of the polymeric films were: ACN, PC and water. A summary of these polypyrrole films preparations is reported in table 1

Table 1. Summary of polypyrrole films preparations

Polymer	Dopant anion	Solvent	$Q_{\text{electrod.}}$ (mC.cm <sup>-2</sup> )
	ClO <sub>4</sub> <sup>-</sup>	ACN	103
		PC	
		Water	

The PCS tests were performed in the same solution of electrodeposition, monomer free.

All the samples are not photoactive in their oxidized state because no photocurrent was found at anodic potentials ( $U_E = 0.5$  V Ag/AgCl;  $U_E = 0.1$  V Ag/AgCl). Photocurrent spectra were recorded at  $U_E = -1.0$  V Ag/AgCl and  $U_E = -1.2$  V Ag/AgCl. The presence of photocurrent just at cathodic potentials suggests that, in their reduced state, polypyrrole films behave like p-type semiconductors. This is in agreement with the data reported in literature [13]. On the contrary, the absence of photocurrent at anodic potentials means that, in their oxidized state, they behave like metals or strongly degenerate semiconductors. Under cathodic polarization, a depletion layer is formed in the compact polymer film. Illumination produces electron-hole pairs which are separated by the electric field across the space charge region. Electrons move toward the polymer/electrolyte interface and reduce a redox couple in solution. Holes move toward the polymer bulk and give rise to a cathodic photocurrent. The raw photocurrent spectra at  $U_E = -1.0$  V Ag/AgCl for the films prepared in different solvents, are shown in Fig. 2.

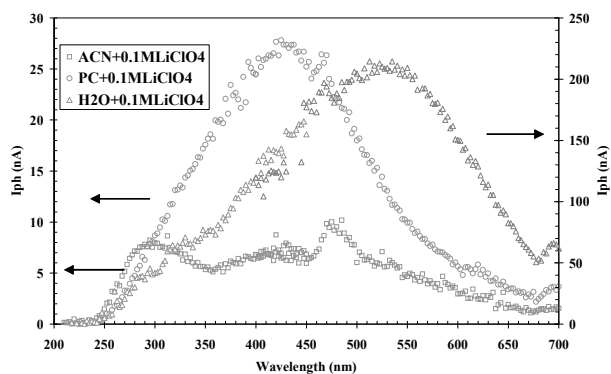


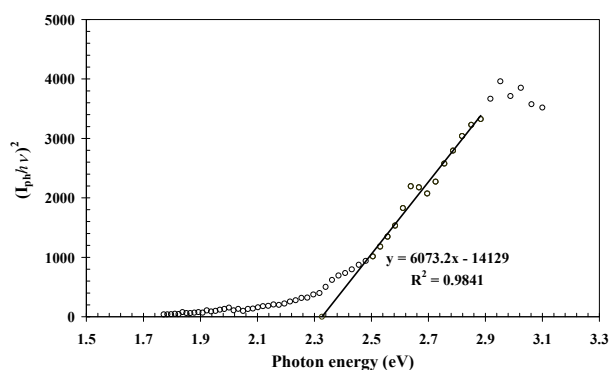
Fig. 2. Raw photocurrent spectra recorded at  $U_E = -1.0 V$  Ag/AgCl for polypyrrole films grown in different solvents.

All the samples are photoactive even at low energies (high wavelengths). The maximum value of photocurrent changes with the system polypyrrole/solvent. A maximum value of 20 nA at 315 nm is evident for polypyrrole electrodeposited in ACN; 28 nA at 425 nm is shown in the case of polypyrrole electrodeposited in PC and a value of 210 nA at 520 nm is evident for polypyrrole electrodeposited in water. The differences in the wavelength corresponding to the maximum value of photocurrent could be assigned to recombination processes occurring at different energies. Photocurrent intensity is one order of magnitude higher in aqueous solutions in respect to organic solvents. This is due to the different cathodic semi-reactions taking place in the different systems. In organic solvents, the cathodic semi-reaction is the reduction of the oxygen diffused in solution. In aqueous solutions, it is the reduction of  $H^+$  at  $H_2$ .

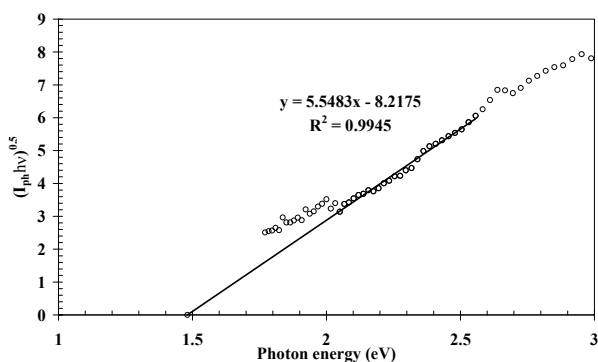
For the study of the optical transitions occurring in the polypyrrole semiconducting films, we used the following equation (Eq. 1):

$$\alpha(\nu) = \frac{A(h\nu - E_g)^n}{h\nu} \quad (1)$$

where  $\alpha(\nu)$  is the absorption coefficient, A is a constant,  $h$  is Planck's constant,  $\nu$  is the frequency of the incident light,  $E_g$  is the optical band gap value of the semiconductor and  $n$  is the power law coefficient.  $n$  assumes the values 0.5 and 2 for direct optical and indirect (or non-direct) optical transitions respectively. Eq. 1 represents a law of direct proportionality between the photocurrent corrected for the efficiency of the system lamp-monochromator and the absorption coefficient. In Figure 3, the corrected spectrum at  $U_E = -1.0 V$  Ag/AgCl and the extrapolations of Eq. 1 for  $n = 0.5$  and  $n = 2$  are shown, for the polypyrrole film electrodeposited in propylene carbonate.



(a)



(b)

Fig. 3. Extrapolations of Eq. 1 for the corrected photocurrent spectrum at low energies recorded at  $U_E = -1.0 V$  Ag/AgCl of polypyrrole film grown in PC. (a) for  $n = 0.5$ ; (b) for  $n = 2$ .

Both direct and non-direct or indirect transitions are possible. For  $n = 0.5$  we obtained a direct band gap of 2.41 eV, for  $n=2$  a non-direct band gap of 1.48 eV. For each polypyrrole film, the values of direct and indirect band gaps are shown in table 2.

Table 2. Direct and indirect band gap energies of polypyrrole films

Solvent	$E_g^{dir}$ (eV)	$E_g^{ind}$ (eV)
ACN	2.42	1.30
PC	2.41	1.48
Water	2.41	1.41

The value of the direct band gap does not change with the system polypyrrole/solvent of electrodeposition. The value 2.41 eV is in agreement with the data from literature that assign to polypyrrole a band gap ranging from 2.59 to 2.80 eV [13,14,16,17]. The optical transitions corresponding to 2.41 eV could be attributed to the promotion of the electron from the bonding ( $\pi$ ) to the antibonding ( $\pi^*$ ) orbitals. So it represents the HOMO-LUMO gap of the polymer. The values of the indirect band gap could be attributed to lower energy optical transitions. These occur from HOMO to some defects

bands located in the energy gap. These energy bands could be polaronic or bipolaronic but this discrimination is not possible with photocurrent spectroscopy. Photocurrent *vs* applied potential plots (photocharacteristics) were recorded irradiating the samples with light of constant wavelength. The scan rate of potential was  $10 \text{ mV}\cdot\text{s}^{-1}$  toward the anodic values.

As the system polypyrrole/water gave higher values of photocurrent, it was possible recorded photocharacteristics even at 300 and 700 nm. For the two systems polypyrrole/organic solvent, the photocurrent signal at 700 nm was too low and it was not possible to record photocharacteristics. Photocurrent *vs* applied potential plots, for polypyrrole grown in water and in ACN, show a shape that does not change with wavelength. On the contrary, the system polypyrrole/PC shows a photocurrent *vs* applied potential plots that change with wavelength. This phenomenon is due to recombination processes occurring inside the polymer film. In each case, there is no inversion of photocurrent, as we expected for semiconducting compounds. In Figure 4, the photocharacteristics at 400 nm are shown for the studied systems.

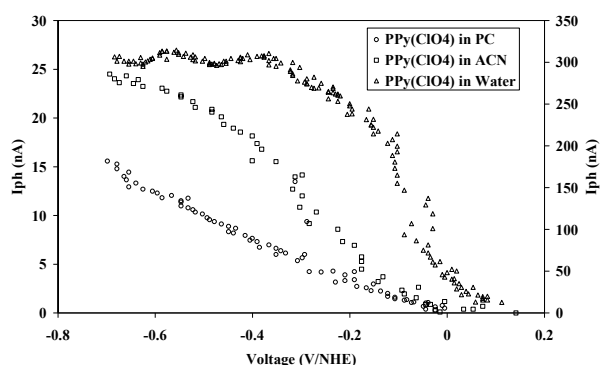


Fig. 4. Overlap of the photocharacteristics at 400 nm for the three studied systems.

The potential at which the value of the photocurrent is zero, is called flat band potential ( $V_{fb}$ ). From the estimation of  $V_{fb}$ , it is possible to locate the Fermi level, according to the following equation (Eq. 2):

$$E_F = -|e|V_{fb} \quad (2)$$

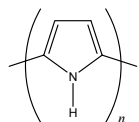
The polymeric films grown in organic solvents present a flat band potential at 0 V/NHE. A more anodic value of  $V_{fb}$  (0.1 V/NHE) was found for polypyrrole electrodeposited in water.

### 3.2 Effect of the dopant anion

In order to study the effect of the dopant anion, polypyrrole films were electrodeposited in aqueous

solution and were doped with different anions ( $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ). The charge circulated during the electropolymerization was  $103 \text{ mC}\cdot\text{cm}^{-2}$ . The experimental conditions used for the preparation of the samples are summarized in table 3.

Table 3. Dopant anions and experimental conditions for polypyrrole films preparation

Polymer	Dopant anion	Solvent	$Q_{\text{electrodep.}}$ ( $\text{mC}\cdot\text{cm}^{-2}$ )
	$\text{Cl}^-$	Water	103
	$\text{ClO}_4^-$		
	$\text{SO}_4^{2-}$		
	$\text{NO}_3^-$		

The photocurrent spectroscopy studies were performed in 0.1 M  $\text{LiClO}_4$  in ACN. Both anodic and cathodic potentials were applied in order to record photocurrent spectra. Under anodic polarization, polypyrrole films are not photoactive. Photocurrent spectra were recorded just under cathodic polarization. This is the typical behaviour of p-type semiconducting materials.

The applied potentials were:  $U_E = -1.0 \text{ V Ag/AgCl}$  and  $U_E = -1.2 \text{ V Ag/AgCl}$ . In Figure 5, photocurrent spectra at  $U_E = -1.2 \text{ V Ag/AgCl}$  not corrected for the efficiency lamp-monochromator are reported, for polypyrrole films differently doped.

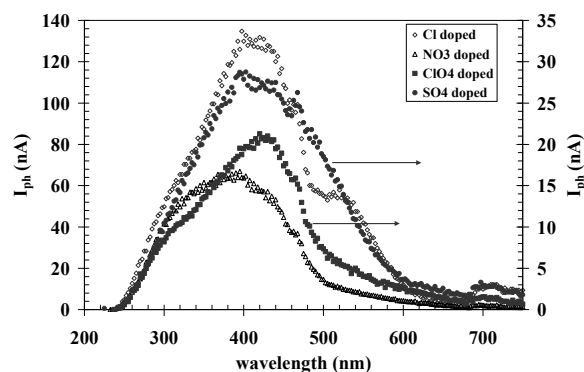


Fig. 5. Raw photocurrent spectra recorded at  $U_E = -1.2 \text{ V Ag/AgCl}$  for polypyrrole films doped with different anions.

The shapes of photocurrent spectra change with the dopant anion introduced in the polymeric matrix during the electrodeposition process. In fact the wavelengths corresponding to the maximum value of photocurrent differ, indicating that recombination processes occur at different energies. On comparing the  $I_{ph}$  *vs*  $\lambda$  plots of the different samples, Cl doped polypyrrole appears more photoactive than the other films. In Figure 6, the extrapolations of the spectrum at  $U_E = -1.0 \text{ V Ag/AgCl}$  with Eq. 1 are reported for the system  $\text{ClO}_4^-$  doped polypyrrole.

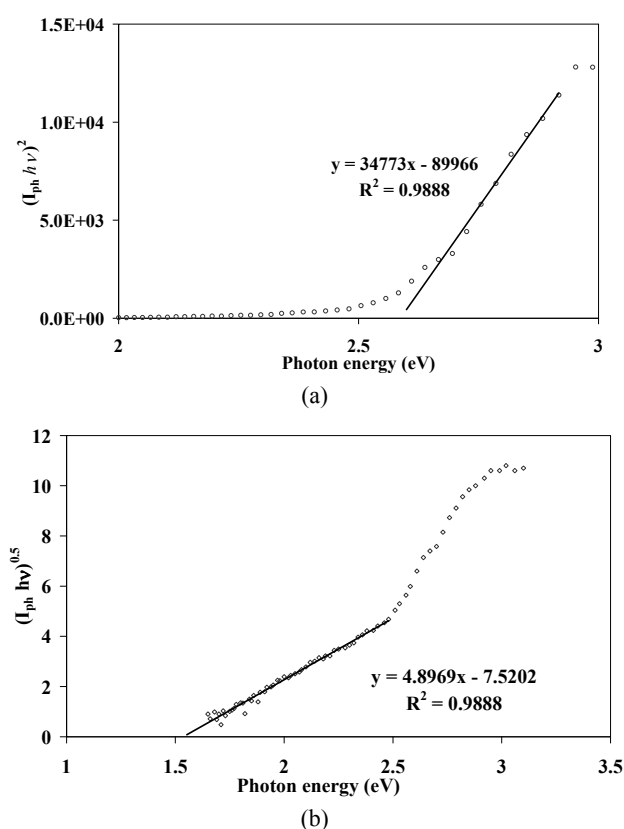


Fig. 6. Extrapolations of Eq. 1 for the corrected photocurrent spectrum at low energies recorded at  $U_E = -1.0$  V Ag/AgCl of polypyrrole film doped with  $\text{ClO}_4^-$ . (a) for  $n = 0.5$ ; (b) for  $n = 2$ .

The direct band gap is the distance expressed in eV between the bonding ( $\pi$ ) and antibonding ( $\pi^*$ ) orbitals. So it represents the HOMO-LUMO gap. The lower energies band gaps are assigned to transitions from HOMO to defects levels [15] located in the band gap. The summary of direct and indirect (or non-direct) band gaps is reported in table 4.

Table 4. Direct and indirect band gap energies of doped polypyrrole film.

Polymer	Dopant anion	$E_g^{\text{dir}}$ (eV)	$E_g^{\text{ind}}$ (eV)	$V_{fb}$ (V/NHE)
	$\text{Cl}^-$	2.52	1.80	-0.08
	$\text{NO}_3^-$	2.55	1.33	-0.50
	$\text{ClO}_4^-$	2.52	1.17	0.17
	$\text{SO}_4^{2-}$	2.30	1.72	0.15

The values of the direct band gap are in agreement with the data reported in literature [13]. They do not change in the case of:  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  doped polypyrroles. A lower value of 2.3 eV was found for the system  $\text{SO}_4^{2-}$  doped polypyrrole. This can be assigned to different semiconducting properties of this doped polymer. This value can represent the HOMO-LUMO gap or a transition

from the HOMO to a polaronic or bipolaronic level [15] which is located 0.2 eV under the LUMO.

As regards the values of the indirect band gap (or non-direct), they are strongly influenced by the dopant anion introduced in the polymeric film.

The photoelectrochemical characterization was completed with the study of the dependence of the photocurrent on the applied electric field, at constant wavelengths ranging from 300 nm to 600 nm. The scan rate of potential was  $10 \text{ mV}\cdot\text{s}^{-1}$ . In Figure 7 are shown the photocharacteristics recorded at 400 nm for the different systems polypyrrole/dopant anion.

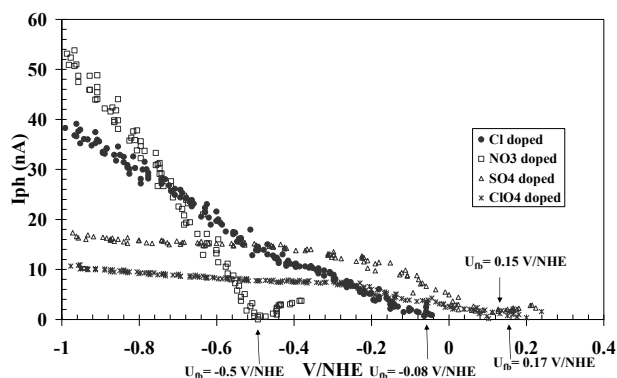


Fig. 7. Overlap of the photocharacteristics at 400 nm for the studied systems.

By comparing the studied systems, it is evident that the flat band potential strongly depends on the dopant agent. So the Fermi level location depends on the supporting electrolyte used during the film growth.

#### 4. Conclusions

A photoelectrochemical characterization on electrodeposited polypyrroles has been performed. Regardless of the conditions of electropolymerization, polypyrrole films behave like p-type semiconductors because they show just a cathodic photocurrent. From PCS measurements on differently doped polypyrroles, it is evident that the dopant anion influences the location of polaronic or bipolaronic levels in respect to HOMO. In fact these values vary from 1.1 to 1.8 eV. Direct band gap values do not change in the case of  $\text{Cl}^-$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$  doped polypyrroles and they can be assigned to HOMO-LUMO transitions. A lower value of direct band gap was found in the case of  $\text{SO}_4^{2-}$  doped polypyrrole. This value can be assigned to a transition from the HOMO to the higher polaronic or bipolaronic level. Moreover, dopant anion influences the location of Fermi level, because the values of flat band potential strongly vary with the system polypyrrole/dopant anion. It also influences the intensity of photocurrent, in fact, higher values of photocurrent were found in the case of  $\text{Cl}^-$  doped polypyrrole.

As regards the influence of the solvent used during electrodepositions on the energetics of polypyrrole, no variations of the direct band gap and of the Fermi level location were found. It seems instead that it influences the position of defects levels in the band gap.

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