

Electrochemical polymerization of EDOT modified Phthalocyanines and their applications as electrochromic materials with green coloration, and strong absorption in the Near-IR



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ABSTRACT

Electropolymerization by cyclic voltammetry of both Cu and Zn EDOT modified phthalocyanines is described. Polymeric films were successfully formed on Pt, ITO, and Pt containing a previously deposited layer of PEDOT. Based on electrochemical and spectroelectrochemical studies, a possible polymerization mechanism and a polymer structure are proposed. The films showed a green coloration in the reduced state and a grey coloration and also a very broad band that extends to the NIR zone in the fully oxidized state. Optical contrast ratios of 24% at 650 nm, and of 60% at 1050 nm were achieved, with very fast switching times. A window-type device was also constructed, demonstrating the possible applications of these electrochromic materials in smart windows, which could help in the control of light in the visible and in the control of heat flux because of their strong absorption in the NIR range.

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1. Introduction

The interest in the research and development of organic macromolecules and polymeric compounds for application in the construction of electronic and optoelectronic devices has continuously grown in the last years [1–4]. The reason for this is the potential advantages that organic materials have over conventional semiconductor constituents [5,6]. In fact, organic chemistry, through molecular engineering [7–9], makes possible the access to a nearly infinite number of functional materials, with adequate physical properties for uses as components in electronic devices [10,11]. In this context, it is expected that the development and application of organic conducting polymers with both optical and electronic adequate properties, will introduce an important advance in the construction of optoelectronic devices such as solar cells [12–15], lighting systems [16], and electrochromic windows [2,3].

Phthalocyanines and related tetrapyrrolic compounds are one of the most studied organic chromophores for the application in the development of electronic and optoelectronic devices, due to their unique structural and physicochemical properties [17–19]. A large

number of articles have been reported about the uses of several phthalocyanines derivatives as photoelectroactive material with applications in bulk heterojunction solar cells [20–24], dye sensitized solar cells [25–28], electrochromic devices [29,30] and organic field-effect transistors (OFET) [31,32]. Furthermore, phthalocyanines form stable polymers with vast application fields [33], in particular solution processed organic solar cells are an elegant example [34]. In this frame, electrochemically synthesized polymeric structures of specially designed phthalocyanines [35–37] have been used in modified electrodes as sensors [38–40] and electrochromic devices [41,42]. The generation of active polymers by electrochemical procedures is an attractive way to obtain modified electrode surfaces with utility in the construction of applied devices [43,44]. The use of electrochemical methodologies allows the generation of polymers and films in one-step, controlling their thickness and morphology [45–47]. In tetrapyrrolic derivatives electropolymerization typically occurs via different peripheral substituents, instead than by involving carbon atoms belonging to the macrocyclic ring [45,46]. Accordingly, metal-free and metallophthalocyanines electropolymers have been synthesized from tetrapyrrolic rings bearing diethyl aniline [48], thiophene [49,50], amino [51] and quinolin moieties [52], and used as components of optoelectronic devices. However, in the case of 3,4-ethylenedioxythiophene (EDOT) substituted mononuclear metallophthalocyanines electropolymerization in the

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thiophene rings was not satisfactorily obtained, possibly because of the limitations imposed by the solvent-supporting electrolyte system used [50]. Due to the fact that polyethylenedioxythiophene (PEDOT) is one of the most highly conductive and versatile polymers, with a huge number of applications in device constructions [53], the generation of electroconductive films holding both PEDOT and metallophthalocyanines, is a promising way to obtain a multipurpose material. In this sense there are reports about the electrochromic performance of mononuclear phthalocyanines involving redox-active metal centers [54], a Double decker lanthanide phthalocyanine holding EDOT residues, and other electropolymerizable metallophthalocyanines [49,52,53]. However, there are not reports about the electrochromic properties of polymer formed by electropolymerization of Zn and/or Cu phthalocyanines holding EDOT residues. The electrochromic performance of these electropolymers in both solution and solid state devices showed to be comparable or superior to those already reported for phthalocyanine containing systems.

In this work, we show the successful formation of two new EDOT modified phthalocyanines electropolymers by cyclic voltammetry, using Zn and Cu phthalocyanine monomers (Fig. 1). The obtained films are homogeneous and very stable, with excellent adherence to the electrode surface. Upon oxidation, EDOT moieties in the monomers undergo the well-known radical coupling, which conducts to phthalocyanine electropolymers formation. Moreover, we found adequate conditions for the growth of conductive polymers not only over Pt electrodes, but also over semitransparent indium tin oxide (ITO) and over previously electrochemical generated PEDOT surfaces. Upon oxidation-reduction steps, the films show green and dark grey colorations, and also absorptions in the NIR. The spectroelectrochemical characterization here outlined clearly demonstrates the possible applications of these electrochromic materials in smart windows, which could help not only in the control of light but also in the heat flux.

2. Experimental section

2.1. Monomer synthesis

Phthalocyanine macrocycle was synthesized from the corresponding phthalonitrile. This approach produced a mixture of the corresponding regioisomers [55] 4-((2,3-Dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy) phthalonitrile (EDOT-PN). A solution

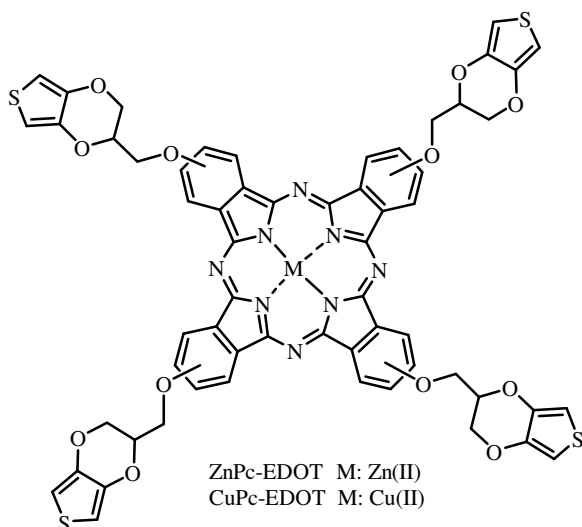


Fig. 1. Chemical structure of the monomers.

of 4-nitrophthalonitrile (200 mg, 1.15 mmol) and hydroxymethyl-EDOT (250 mg, 1.45 mmol) in 7.5 mL of DMF was stirred for 15 min under an argon atmosphere. After that, dry potassium carbonate (600 mg, 4.34 mmol) was added and the mixture was heated at 80 °C for 12 h. The solution was treated with water (50 mL) and extracted with dichloromethane/methanol (5%) (two portions of 50 mL each). The organic phase was separated and the solvent was removed under reduced pressure. The product purified by flash chromatography column (silica gel, dichloromethane) yielded 274 mg (80%) of the pure EDOT-PN. Spectroscopic data of EDOT-PN agree with those previously reported [50].

Zinc(II)2,9(10),16(17),23(24)-tetrakis((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy) phthalocyanine (ZnPc-EDOT). A solution of EDOT-PN (98 mg, 0.33 mmol) and zinc (II) acetate dihydrate (30 mg, 0.14 mmol) in 5 mL of *n*-pentanol was stirred for 10 min under an argon atmosphere. Then, 86 μ L of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 0.57 mmol) was added and the mixture was refluxed for 24 h. The reaction was cooled to room temperature. The mixture was treated with water (50 mL) and extracted with dichloromethane (three portions of 25 mL each). The organic solvent was evaporated under reduced pressure and precipitated with 50 mL of *n*-heptane. The solid was washed with *n*-heptane. This procedure yielded 42 mg (41%) of ZnPc-EDOT. Spectroscopic characterization of ZnPc-EDOT was consistent with those previously reported [50].

Copper (II) 2,9(10),16(17),23(24)-tetrakis((2,3-dihydrothieno[3,4-b][1,4]dioxin-2-yl)methoxy)phthalocyanine (CuPc-EDOT) was synthesized as described above for ZnPc-EDOT using copper (II) acetate dihydrate (28 mg, 0.14 mmol) to yield 45 mg (43%) of CuPc-EDOT. ¹HNMR (DMSO-*d*₆) δ [ppm] 4.30–4.74 (20H, –CH–, –CH₂–), 6.65–6.77 (8H, aromatic EDOT-H), 7.40–7.52 (4H, aromatic-H), 7.81–7.88 (4H, aromatic-H), 8.25–8.38 (4H, aromatic-H). ESI-MS [m/z] 1256.1023 (M+H) (1255.0945 calculated for C₆₀H₄₀N₈O₁₂S₄Cu).

2.2. Instrumentation and Measurements

Absorption spectra were recorded at 25.0 \pm 0.5 °C using 1 cm path length quartz cells on a Shimadzu UV-2401PC spectrometer. Proton nuclear magnetic resonance spectra were recorded on an FT-NMR Bruker Avance DPX400 spectrometer at 400 MHz. Mass Spectra were taken with a Bruker micrO-TOF-QII (Bruker Daltonics, MA, USA) equipment with an ESI source operated in positive/negative mode, using nitrogen as nebulizing.

The voltammetric characterization of the redox processes and electropolymerization of the phthalocyanine monomers was performed with a potentiostat-galvanostat Autolab (Electrochemical Instruments) using a Pt working and a Pt counter electrode in a conventional three-electrode cell. Indium tin oxide (ITO) electrodes (Delta Technologies) with a nominal resistance of 8–12 Ω /square were also used as working electrodes. When large area ITO electrodes were used, the counter electrode was isolated from the monomer solution by a glass frit in order to avoid interference with the redox reactions occurring at the working electrode. Electrochemical studies of phthalocyanines were carried out in 1,2-dichloromethane (DCM) deoxygenated solution (nitrogen bubbling), with 0.10 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. All the electrochemical responses of the electropolymerized films were carried out in (DCM) deoxygenated solution (nitrogen bubbling), with 0.10 M tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte. A silver wire quasi-reference electrode was used. The Pt working electrode was cleaned between experiments by polishing with 0.3 μ m alumina paste followed by solvent rinses. After each voltammetric experiment, ferrocene was added as an internal standard, and the potential axis was calibrated

against the formal potential for the Saturated Calomel Electrode (SCE).

Spectroelectrochemical experiments were carried out in a homemade cell built from a commercial UV–visible cuvette. The ITO-coated glass was used as working electrode; a Pt wire was used as counter electrode, and an Ag wire was used as the reference electrode. The cell was placed in the optical path of the sample light beam. The background correction was obtained by taking an UV–vis spectrum of a blank cell (an electrochemical cell with an ITO working electrode without the polymer film) with conditions and parameters identical to those of the polymer experiment.

The electrochromic device was constructed using the architecture ITO/ZnPc-film/electrolyte/ITO. A solid polymer electrolyte film was sandwiched between the ITO/ZnPc-film working electrode, and the ITO counter electrode. The solid polymer electrolyte was prepared by mixing polymethylmethacrylate (0.5 g, 30%, wt. %), propylene carbonate (1 ml), and TBAPF₆ (0.1 M) in 10 mL of acetonitrile. The mixture was stirred for 24 h. The solid polymer electrolyte was drop casted onto ITO glass at 45 °C for 2 h.

Examinations of phthalocyanine-film morphologies were performed on a Carl Zeiss EVO MA 10 SEM, with electron beam energy of 18 KeV.

Atomic force microscopy (AFM) experiments were performed with an Agilent 5500 SPM microscope (Agilent Technologies, Inc.)

working in acoustic AC mode. Commercial Si probes with stiffness of 42 N/m (MikroMasch, HQ:XSC11/Al BS) were used for the experiments. The obtained images were processed and analysed by using the Gwyddion 2.44 SPM image analysis software. The thicknesses of the generated polymers were measured by difference between the height of the ITO/polymer film and the bare layer of ITO. ITO layer was removed from the glass using Zn powder and HCl (2 M).

3. Results and discussion

3.1. Electrochemistry

Cyclic voltammetry experiments were carried out to obtain information about the electrochemical processes of the monomers, and the capacity of these to form electropolymers. Both, ZnPc-EDOT and CuPc-EDOT monomers present a reversible oxidation process at similar potentials (0.38, and 0.50 V, respectively, see inset Fig. 2a, and c), and a second irreversible wave at more anodic potentials, which shows a peak current much higher than the first oxidation process (Fig. 2a, and c, red lines). In the second anodic cycle an increase in the oxidation/reduction currents is detected, and the currents keep growing with the increasing number of cycles, indicating the deposition of an

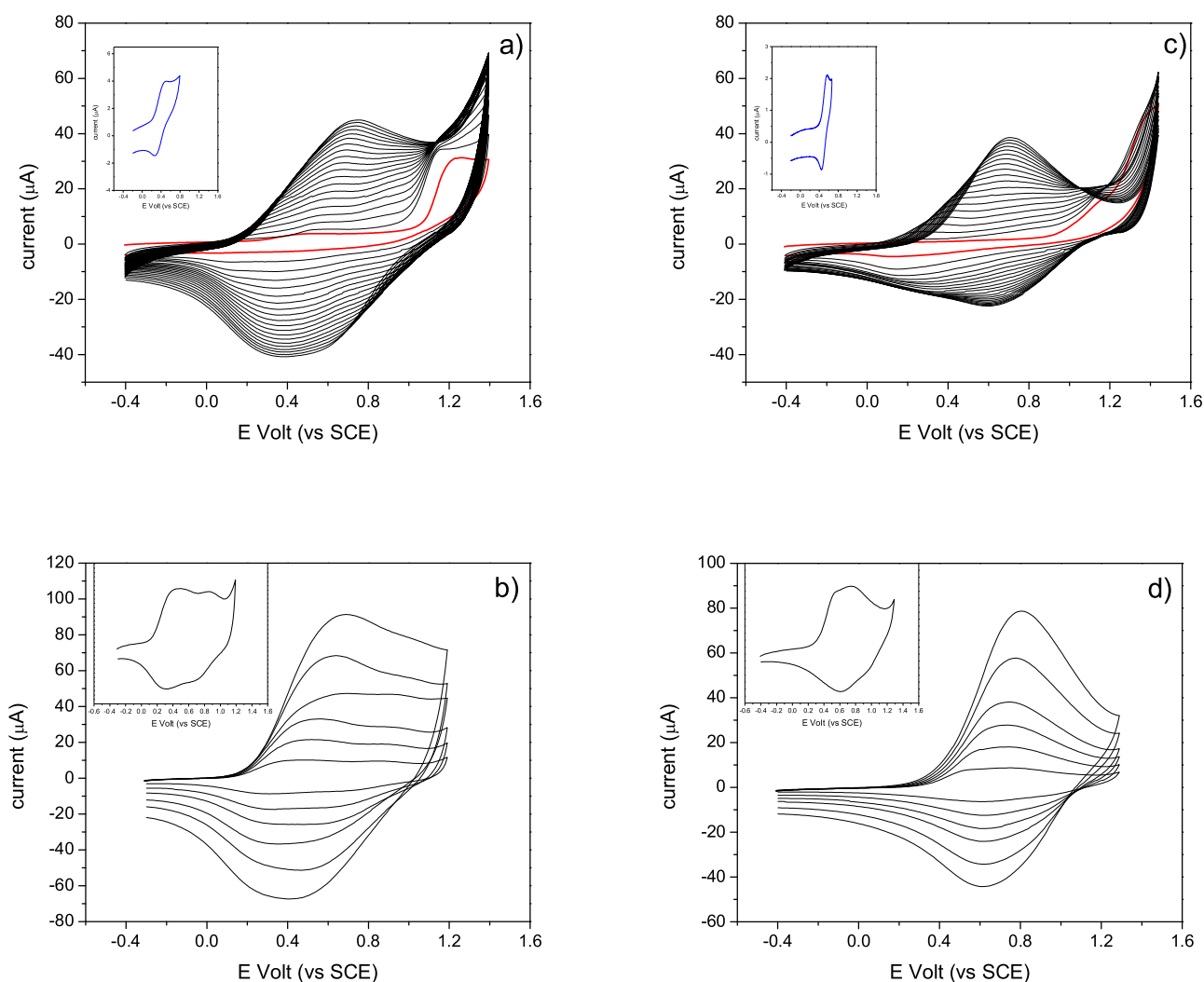


Fig. 2. First (red) and 2nd–20th (black) cyclic voltammograms of a) ZnPc-EDOT, and c) CuPc-EDOT. Scan rate: 100 mV s⁻¹. The measurements were done in DCM containing TBAPF₆ using a Pt working electrode. Electrochemical responses of electropolymerized films of b) ZnPc-EDOT, and d) CuPc-EDOT, in DCM containing only support electrolyte, at different scan rates (25, 50, 75, 100, 150, 200 mV s⁻¹). Inset shows the electrochemical response of the films at 25 mV s⁻¹.

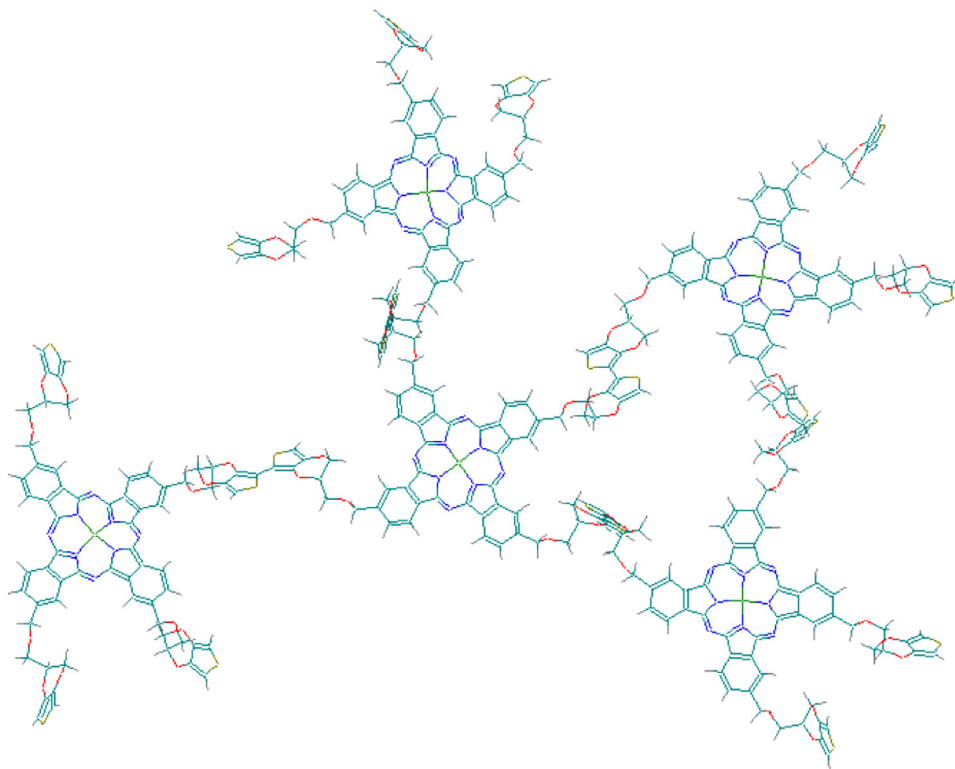


Fig. 3. Idealized structure of the polymers.

electroactive and conductive film on the electrode surface (Fig. 2a, and c). Also, the onset of the oxidation currents occurs at less anodic potentials than those observed in the first cycle, indicating that the formed product is easier to oxidize than the monomer. To confirm the deposition of a film on the electrodes, these were washed with DCE, and then the voltammetric responses were recorded in a solution containing only supporting electrolyte. It can be seen from Fig. 2b, and d that both films present broad oxidation and reduction peaks, and at low scan rate (25 mV s^{-1}) the responses seem to consist of at least two redox processes, very close one to the other (inset Fig. 2b, and d). Also, the peak currents of the electropolymeric films are proportional to the scan rate in the $25\text{--}200 \text{ mV s}^{-1}$ range. The proportionality between the peak currents and the scan rate, together with the presence of new redox systems, confirm that stable and electroactive films have been produced on the electrode surfaces from both, Zn and Cu Phthalocyanine monomers. It must be remarked that continuous cycling in the ranges of the first monomer oxidation peak (-0.4 to 0.8 V) does not produce any increase in the oxidation currents.

Regarding the polymerization mechanism, Zinc and Copper Phthalocyanines commonly present one reversible oxidation process, which is attributed to oxidation of the macrocycle [51,56]. The oxidation potentials of Zn, and Cu phthalocyanines have been reported to be 0.50 and 0.67 V vs SCE, similar to the values obtained for ZnPc-EDOT and CuPc-EDOT [50,56]. On the other hand, it is known that EDOT is oxidized at around 1.2 V vs SCE, showing an irreversible peak in the first anodic scan. In the successive cycles EDOT oxidation conducts to the apparition of a new redox system with an onset oxidation at about 0.0 V , which corresponds to the formation of polymer (PEDOT) on the electrode surface [57,58]. In the present case, both ZnPc-EDOT, and CuPc-EDOT monomers present a first reversible oxidation peak, which could be attributed to oxidation of the macrocycle. The second irreversible redox can be assigned to oxidation of the EDOT units bounded to the macrocycle, because, as it was already shown

above, the films are only formed when the second oxidation peak or the onset of this is reached. Therefore, the formation of the films on the electrodes could be attributed to the reaction of EDOT radical cations produced in the anodic cycling, generating EDOT dimers, whose oxidation and reduction processes are detected as a growing new redox couple. Thus, the voltammetric responses of the films depicted in Fig. 2b, and d, can be assigned to oxidation of both, EDOT dimers and Pc macrocycles. Based on the spectroelectrochemical evidence discussed below, the peak observed at low applied potentials is assigned to processes involving oxidation of coupled EDOT units (see inset Fig. 2b and d), and the second oxidation peak at more anodic potentials corresponds to oxidation of the Pc macrocycle. Fig. 3 shows a tridimensional idealized structure of the formed electropolymers, which presents phthalocyanine units connected by EDOT dimers. However, the formation of trimers, tetramers and/or EDOT oligomers cannot be ruled out. It is not unlikely that Pc-EDOT cations formed by electro-oxidation react with poly or oligo ethylenedioxythiophene to form more complex structures. We evaluated the possibility of phthalocyanine film formation on previously electrodeposited PEDOT layers.

The phthalocyanine films were also successfully formed on a previous electrodeposited layer of PEDOT. These PEDOT films were formed by cycling the Pt electrodes in an EDOT solution (DCM) containing TBAPF₆ as supporting electrolyte, in the same range where the phthalocyanines were electrodeposited. During continuous cycling increases in the oxidation/reduction currents appear, which indicate formation of the PEDOT layer (Fig. 4a) [59]. The voltammetric response of the PEDOT layer obtained in a solution containing only supporting electrolyte presents the typical shape of PEDOT, which is characterized by a very broad oxidation in the -0.4 to 1.25 V range (Fig. 4b) [60]. After formation of the PEDOT layer both, ZnPc-EDOT and CuPc-EDOT polymers were grown on top of this layer to form PEDOT/ZnPc-EDOT, and PEDOT/CuPc-EDOT, modified electrodes. The first voltammetric cycle of ZnPc-EDOT (Fig. 4c, red line) over the electrodeposited PEDOT layer

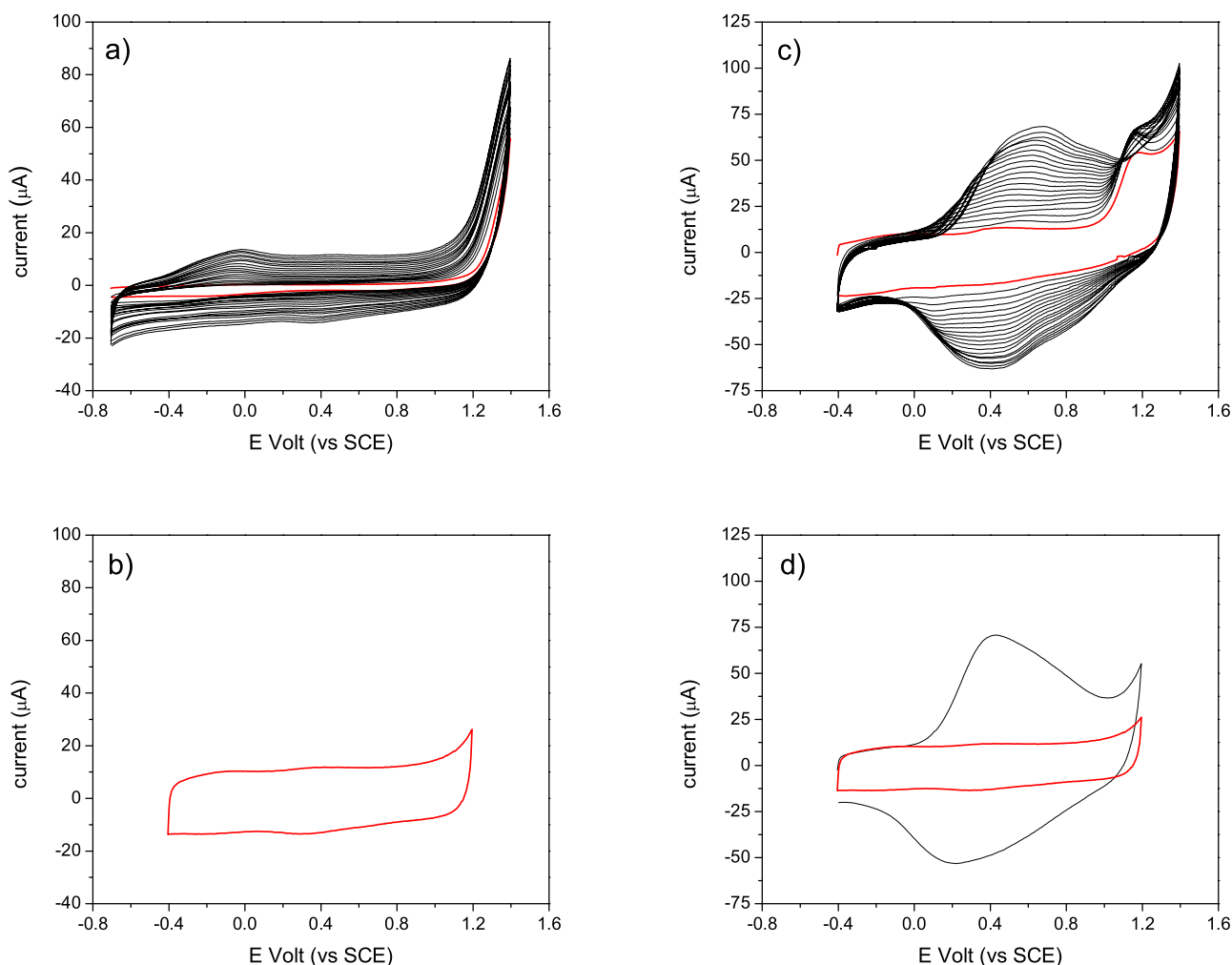


Fig. 4. First (red) and 2nd–20th (black) cyclic voltammograms of a) EDOT, and c) ZnPc-EDOT, on top of the PEDOT layer. Scan rate: 100 mV s^{-1} . The measurements were done in DCM containing TBAPF₆ using a Pt working electrode. Electrochemical responses of electropolymerized films of b) EDOT, and d) ZnPc-EDOT on top of the PEDOT layer, in DCM containing only support electrolyte.

presents the same redox processes than those observed in a naked Pt electrode (oxidation of the macrocycle and oxidation of the EDOT units, respectively), which are mounted on top of the PEDOT electrochemical response. In the successive cycles, increases in the oxidation/reduction currents are observed, indicating the formation of the phthalocyanine film adsorbed on the Pt/PEDOT surface. The response of the film in a solution containing only supporting electrolyte presents similar redox processes than those obtained in naked Pt, with the exception that the film shows now a bigger pseudocapacitive current, which is attributed to the PEDOT layer redox processes. In the same way CuPc-EDOT monomer was electropolymerized on top a PEDOT layer, presenting also a similar electrochemical response to that obtained in Pt electrode, but with a contribution in the current attributed to the PEDOT layer. This confirms that both, PEDOT and Phthalocyanine layers are electrochemically active, and demonstrate that bilayer heterojunctions can be formed by a simple electrochemical method [43].

In addition to the growing of the Phthalocyanines over Pt, and PEDOT, both monomers were also electropolymerized on semi-transparent ITO electrodes, to evaluate the possible application of the films in optoelectronic devices. Also, the electropolymerization on ITO electrodes permits the study of the spectroscopical, spectroelectrochemical, and morphological properties of the films. These studies also allow gaining more information about the electropolymerization mechanism. The films electropolymerized

on ITO electrodes presented voltammetric responses similar to those obtained on Pt electrodes.

3.2. UV-Visible Absorption properties of monomers and films

Absorption spectra of ZnPc-EDOT and CuPc-EDOT were measured in different solvents (Fig. 5). In toluene, both phthalocyanines showed an intense Q-band in the region of $\sim 678 \text{ nm}$, which is characteristic of these metallo phthalocyanine derivatives dissolved as monomeric molecules. On the other hand, ZnPc-EDOT and CuPc-EDOT were very poorly solubilized as monomer in more polar solvents, such as methanol. Aggregation was observed by the broadening and the low intensity of the Q-bands. The spectra of phthalocyanine derivatives in methanol showed two characteristic long wavelength peaks, the one at $\sim 630 \text{ nm}$ corresponds to absorption by the aggregate [61], while the other at $\sim 675 \text{ nm}$ is due to absorption by the monomeric molecule. Many phthalocyanines have a tendency to aggregate in polar solvents, especially when the macrocycle is substituted by lipophilic groups [61].

The absorption spectrum of ZnPc-EDOT polymeric film presents a broad band in the $600\text{--}740 \text{ nm}$ range, while CuPc-EDOT film shows two bands located at 620 and 675 nm (both films in the neutral state). Also, a band at around 330 nm , and a smaller one at 450 nm can be seen for both films. The absorption bands are broad and located at wavelength values comparable with those observed

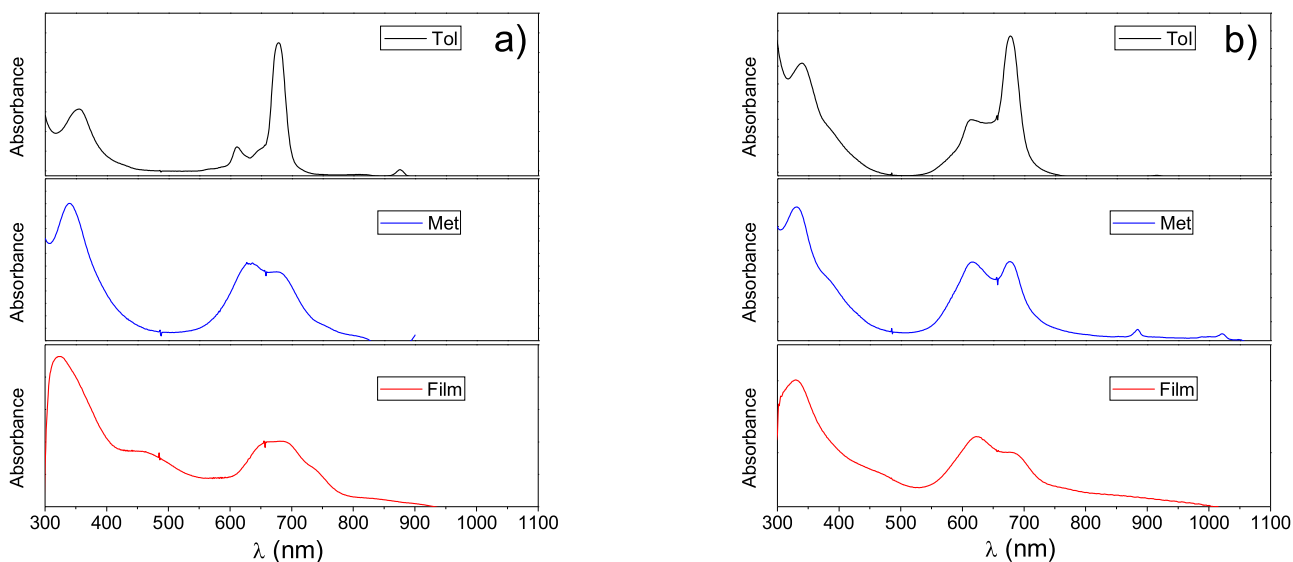


Fig. 5. Absorption spectra of a) ZnPc-EDOT, and b) CuPc-EDOT monomers in Toluene solution (black) and, Methanol solution (blue). Electropolymerized films of a) ZnPc-EDOT, and b) CuPc-EDOT (red), on ITO electrodes.

for ZnPc-EDOT and CuPc-EDOT in methanol solution. The Q bands in the films are similar in intensity (CuPc-EDOT), or present a broad absorption band (ZnPc-EDOT), indicating the presence of aggregates in the solid state. It has been reported that similar Phthalocyanines adsorbed on TiO_2 films also show a broadening of the Q bands [62]. The similarities between the absorption spectra of the films and those in solution indicate that the macrocycles have not been altered during the electrodeposition process.

3.3. Morphology

SEM and AFM techniques were used to investigate the surface morphology of the polymeric films on ITO electrodes. The SEM images of ZnPc-EDOT and CuPc-EDOT films show that the electropolymerization process produces a very flat and

homogeneous film without cracks or pinholes, free of agglomerations, and totally covers the ITO surface. Fig. 6 shows a typical SEM image obtained from the surface of a ZnPc-EDOT electropolymer film.

However, high resolution AFM allows observing nanoscale structural features that are not as visualized by SEM. Fig. 7a, and b, show that the electrochemical growth of the two monomers used in the study gives rise to materials with globular structures. Also AFM topography images reveal that both polymers, ZnPc-EDOT as well as CuPc-EDOT, cover the ITO electrode completely with a film presenting a smooth topography free of structural defects. Indeed, the ZnPc-EDOT and CuPc-EDOT surface showed a RMS roughness of 6.15 and 6.12 nm respectively for images of $1000 \text{ nm} \times 1000 \text{ nm}$ and 512×512 pixels. However, the polymer formed by electropolymerization of CuPc-EDOT presents smaller globular structures arranged in cluster globule formations that seem not to be

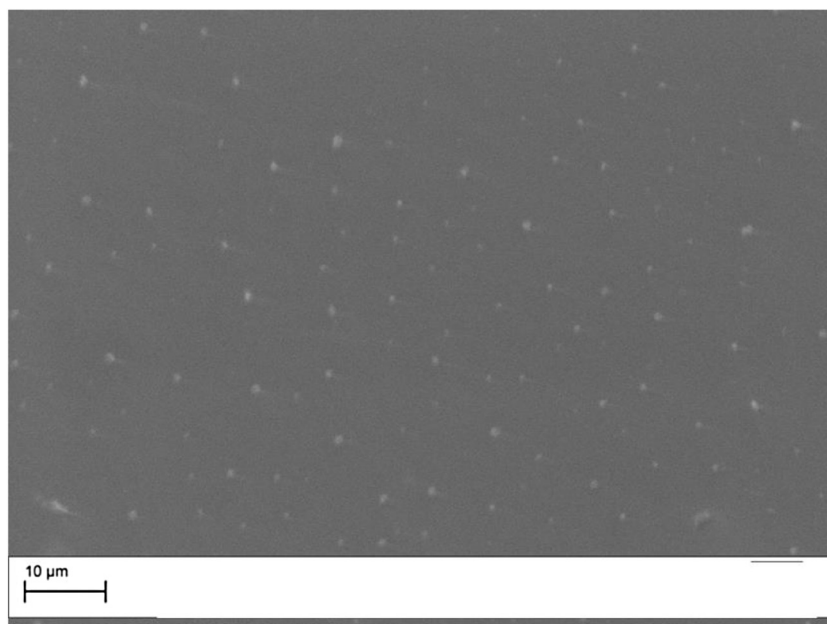


Fig. 6. SEM image of ZnPc-EDOT film on ITO.

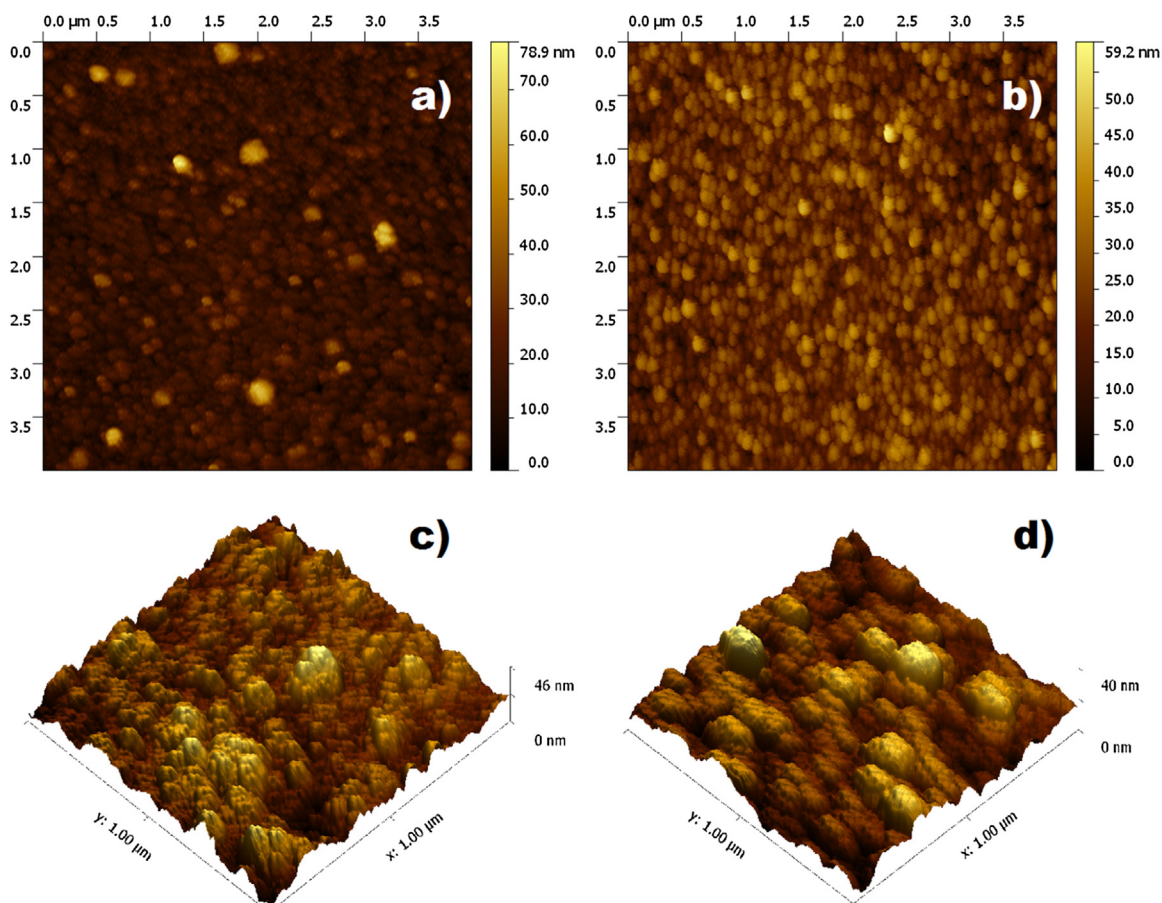


Fig. 7. AFM topography images of films electrochemically generated from a) ZnPc-EDOT and b) CuPc-EDOT. High-resolution 3D AFM topography images of films electrogenerated from c) ZnPc-EDOT and d) CuPc-EDOT on ITO.

observed in the ZnPc-EDOT (Fig. 7c, and d). The surface of the globular structure in the material grown from ZnPc-EDOT appears to be very smooth. Films with strong adhesion to the electrode and flat surfaces are desired in the production of bi or multilayer structures because they form well defined interfaces.

3.4. Spectroelectrochemistry and proposed polymerization mechanism

Spectroelectrochemistry of the films was conducted in order to gain more information about the possible polymerization mechanism, and the structure of the polymers. As it was mentioned above, in the neutral state (0.00 V black lines in Fig. 8a, and c) the films present a band at around 330 nm which is assigned to the phthalocyanine B band, and two more bands in the 550–760 nm range associated to the phthalocyanine Q bands. At more anodic potentials (0.60 V, red lines) there is an increase in the absorbance of the films from 600 to 900 nm (on top of the phthalocyanines bands), and another rise that starts at 900 nm and that extends to the IR region. At 0.80 V the absorption spectra present a new band at around 550 nm, a decrease in the Q bands, and also an increase in the broad band in the 800–1100 nm (Fig. 8a, and c, green lines). When the films are totally oxidized at 1.2 V the bands associated to the macrocycle completely disappear, and a very broad band that extends from about 500 nm to the IR region grows in intensity (blue lines).

Fig. 8b and d show the changes in the principal absorption wavelength traces plotted against the applied potential. As it can be seen the 740 (ZnPc-EDOT film), and 715 nm traces (CuPc-EDOT film) are increased at potentials where the films start to get

oxidized, and they decrease when the second redox process is reached. Also, the 650 and 630 nm traces (black lines), associated to the macrocycles, remain almost constant during the first oxidation process, and start to decrease at the potential of the second oxidation process. At the onset of the second oxidation peak the 1050 nm traces (blue lines) grow in intensity, and they are maxima when the films are totally oxidized. In the reverse scan all traces recover their initial values, indicating that the films are very stable.

The electrochemical and spectroelectrochemical experiments show that the films present two oxidation processes which could be attributed to oxidation of EDOT dimers, and phthalocyanine units, respectively. In the neutral state the absorption spectra of the films show bands that undoubtedly are assigned to the phthalocyanine centers (Q bands), and the band at 450 nm could be attributed to dimers of EDOT and/or longer chains of coupled EDOT residues [60]. At 0.60 V (Fig. 8a, and c, red lines) the bands assigned to the macrocycles are not altered, but new bands appear on top of the phthalocyanine Q bands, which indicates that the macrocycles have not been oxidized, and that the new absorption bands must be related to oxidation of the EDOT dimers. Also, the traces at 740 and 715 nm are increased at the first oxidation peak, supporting this assignment. At 0.80 V the bands associated to the phthalocyanine centers decreased, confirming that the macrocycles are oxidized and related to the second oxidation process of the films. A similar change in the absorption bands during oxidation was observed in related phthalocyanine polymers [63]. The band at around 550 nm could be assigned to the radical cation of the phthalocyanines [25,64]. When the films are totally oxidized, the band NIR zone could be attributed to the presence of delocalized

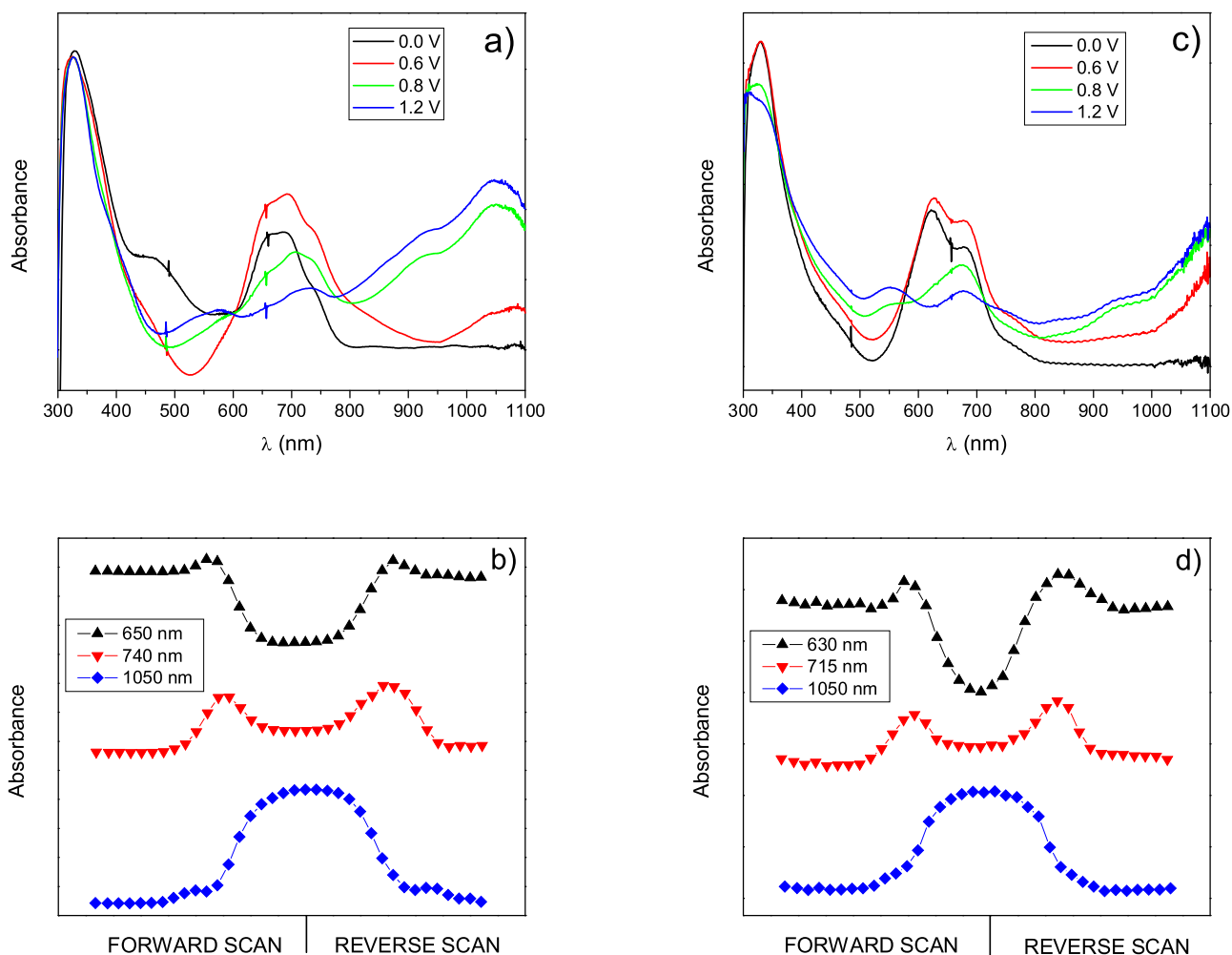


Fig. 8. Spectroelectrochemical measurements of a) ZnPc-EDOT film and, c) CuPc-EDOT film, at different applied potentials. Absorption traces of b) ZnPc-EDOT film and, d) CuPc-EDOT film at selected wavelengths as function of the advances in the forward and backward CV scans. Scan rate 20 mV s^{-1} .

charge states in the EDOT dimers. On the other hand, it is known that PEDOT presents a broad band in the 450–700 nm range, which is not present in the absorption spectrum of the phthalocyanine films (even at potentials close to -0.40 V). Therefore, based on the spectroelectrochemical experiments, we propose a polymeric structure where the phthalocyanine units are mainly connected by EDOT dimers. However, the presence of a band at 450 nm in the reduced form of the films (see Figs. 5 and 8), could indicate the presence of EDOT trimers, tetramers and/or oligomers in the polymer structure. Also, the low on-set oxidation potential of the films could be another indication of the presence of EDOT

oligomers. However, the spectroelectrochemical evidence does not show the presence of long chain polymeric EDOT. Thus, it is proposed that the films are formed by a polymeric structure where the phthalocyanines are mainly connected by EDOT dimers, and with the presence of some EDOT trimer and/or tetramer units.

3.5. Electrochromic Properties

The spectral changes observed for both films at different applied potentials produce various colorations, which can be seen by the naked eye (Fig. 9). As it was mentioned above, the films

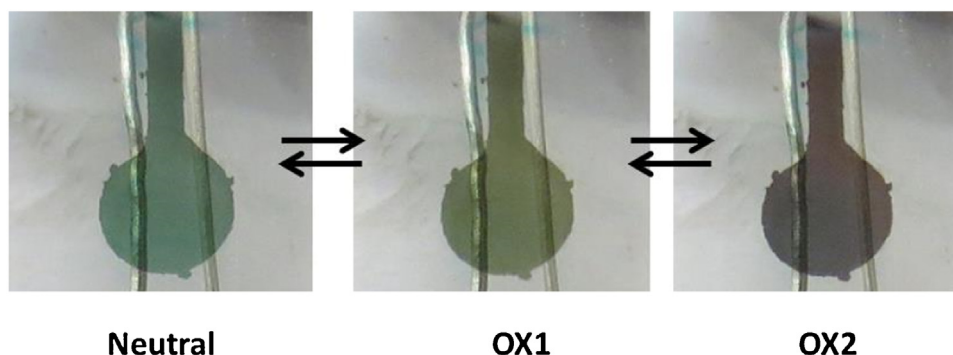


Fig. 9. Photograph images of ZnPc-EDOT film deposited on ITO, showing the different colorations.

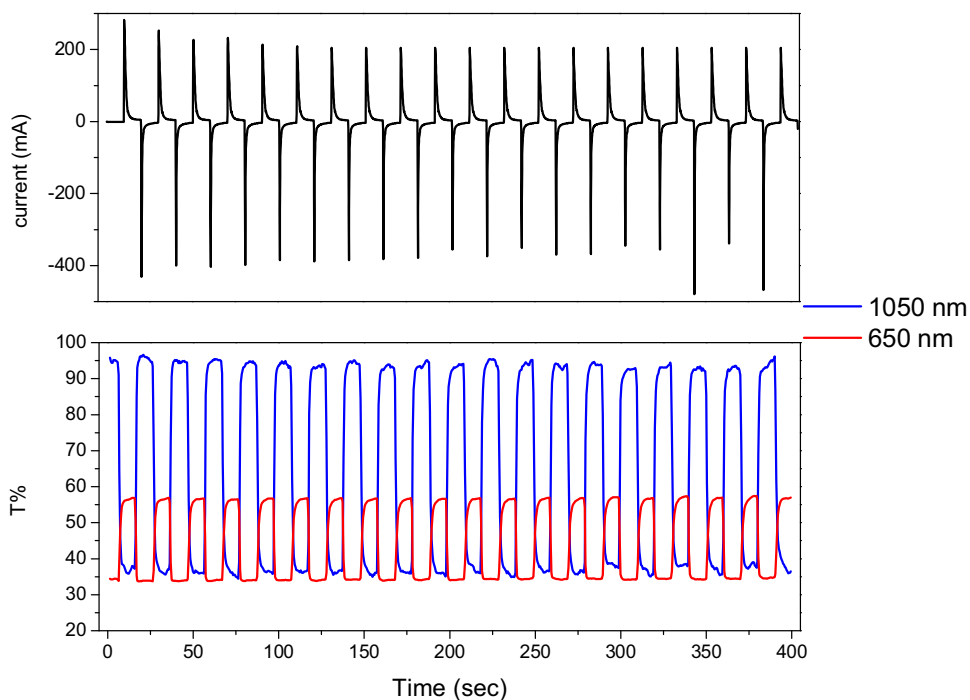


Fig. 10. Dynamic changes of the transmittance and current upon switching the potential between 0.00 and 1.20 V with a pulse width of 10 s applied to the electrodeposited ITO/film of ZnPc-EDOT in DCM containing 0.1 M TBAPF₆. A total of 40 pulses are shown. The absorptions were recorded at 650 and 1050 nm.

present three redox states being these neutral, semioxidized (first oxidation peak), and fully oxidized (second oxidation peak). In the neutral state the films present a light green color, in the semioxidized form a light green/grey coloration, and a dark grey color in the fully oxidized state. In order to study the electrochromic properties of the films square wave potential step absorptiometry was carried out. The applied potential was

switched from the neutral state (0.00 V) to the fully oxidized state (1.20 V) for 20 cycles at 10 second time intervals. As it can be seen from Fig. 10 the changes in T% at the different principal wavelengths are constant during the 20 cycle switches, indicating that the film is very stable. Also the ZnPc-EDOT film (120 nm thickness) produces a contrast ratio of ($\Delta T\%$) 60% at 1050 nm, and 24% at 650 nm. The time required for reach 90% of the full change in

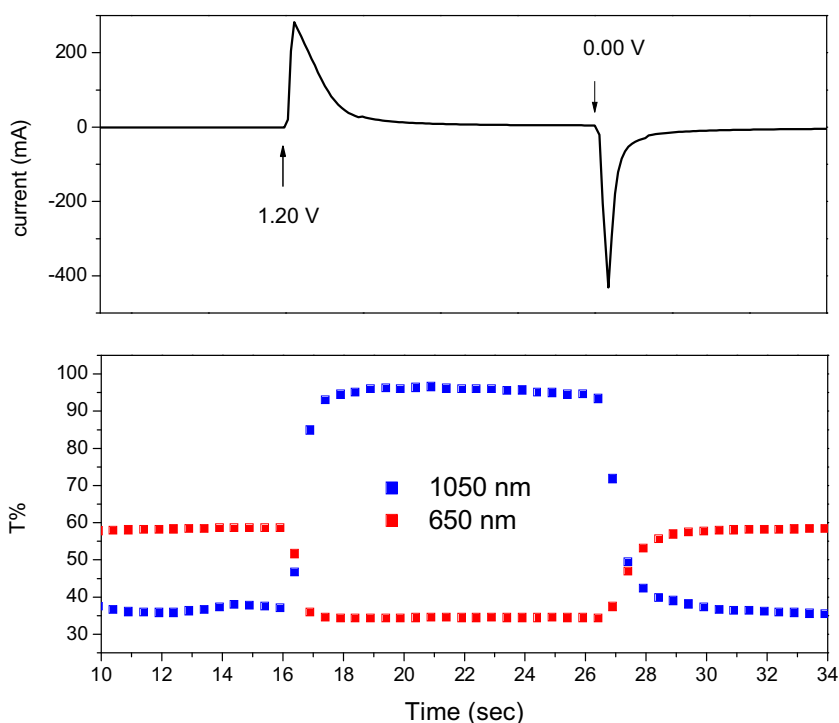


Fig. 11. Dynamic change of the transmittance and current upon switching the potential between 0.00 and 1.20 V with a pulse width of 10 s applied to the electrodeposited ITO/film of ZnPc-EDOT in DCM containing 0.1 M TBAPF₆. Only one oxidation-reduction cycle is shown. The absorptions were recorded at 650 and 1050 nm.

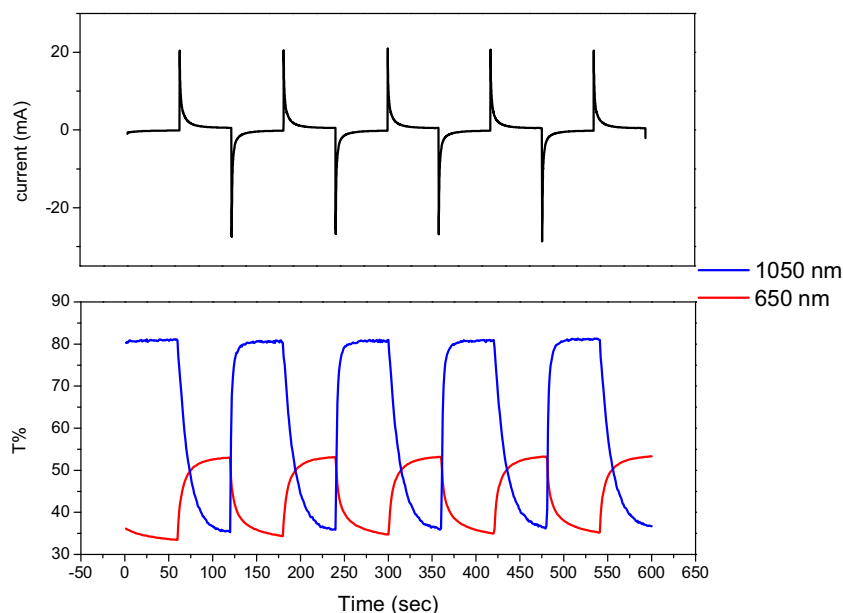


Fig. 12. Dynamic changes of the transmittance and current upon switching the potential between -0.80 and 1.80 V with a pulse width of 60 seconds applied to the device ITO/ZnPc-EDOT film/electrolyte/ITO. A total of 10 pulses are shown. The absorptions were recorded at 650 and 1050 nm.

absorbance after switching the potential between 0.00 to 1.2 V are 1.9 and 2.5 sec (Fig. 11). These fast switching times indicate that the films present rapid electron transfer kinetics. Similar $\Delta T\%$, and switching times values have been reported for an electropolymerized cobaltphthalocyanine–quinolone hybrid [52]. However, the here reported electrochromic properties are better than those informed for a similar electropolymerized double-decker lutetium (III) phthalocyanine [49], and for metallophthalocyanines [37].

In order to evaluate the possible applications of the electropolymers as electrochromic materials, a window-type device with the sandwich structure ITO/ZnPc-EDOT/electrolyte/ITO, was constructed. To do this, double potential-step chronoamperometry and chronoabsorptometry was used. The applied potential was varied between the reduced state (-0.4 V) and the oxidized state (1.80 V). Fig. 12 shows the changes in T% at principal wavelength as function of the time for a device using ZnPc-EDOT film. The electrochromic device presents a $\Delta T\%$ of 45 at 1050 nm, and 20% at 650 nm. The time required for reach 90% of the full change in T% after switching the potential between -0.80 to 1.8 V are about 29 and 15 seconds. Also the changes in T% are constant during the switching, showing the stability of the film. Fig. 13 shows photographic images of the non-optimized device in the two redox states. As it was mentioned above, the device presents a green color in the reduced state, and a grey coloration in the oxidized state. The spectral changes observed at the different applied potentials, demonstrate the possible applications of these electrochromic materials in smart windows, which could help in the control of light in the visible, and heat flux because of their strong absorption in the NIR range.

4. Conclusions

Two phthalocyanine monomers containing EDOT units were successfully electropolymerized on Pt, ITO, and Pt electrodes with a previously electropolymerized PEDOT layer. An electropolymerization mechanism was proposed, which involves the reaction between two EDOT radical cation units to form EDOT dimmers. A possible polymer structure in which the Phthalocyanine units are connected by EDOT dimmers was suggested. The

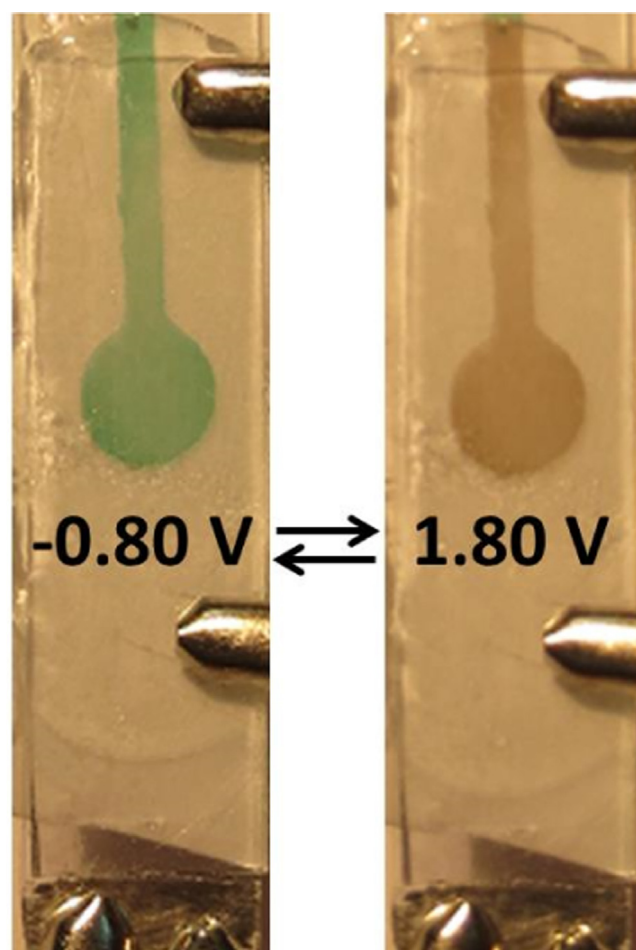


Fig. 13. Photograph images of the device ITO/ZnPc-EDOT film/electrolyte/ITO, showing the different colorations at -0.80 , and 1.80 V.

electropolymerized films showed absorptions in diverse ranges of the visible spectra and, also presented absorption bands in the IR zone in the different redox states. The films presented a green coloration in the reduced state, which is a challenging electrochromic color, and a grey color in the fully oxidized state. The switching times (in solution) between the reduced and oxidized forms were fast indicating rapid electron transfer kinetics. Also, a window-type device was constructed, showing the possible application of these polymers. These new materials could not only be useful in visible coloration changes for display application, but also for climate control. Also, due to the strong absorption in the NIR range they could be used in smart window constructions.

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