ABSTRACT
Photoelectrochemistry is emerging as a promising technology for harvesting and utilizing solar energy in a wide range of applications. However, electrode materials still need to be improved to achieve optimal performance. Conductive polymers emerge as particularly promising organic compounds for this purpose due to their highly versatile properties. In this study, the galvanostatic synthesis of polypyrrole films co-doped with tetrakis(4-carboxyphenyl) porphyrin (PPy/TCPP) on fluorine doped tin oxide (FTO)-coated glass substrates was performed for the first time. In addition, an evaluation of these films as photoelectrodes was performed, focusing on key properties.
porphyrin into the polymer matrix was confirmed by UV-Vis and IR characterization. SEM micrographs showed the morphological changes induced by the codopant. Cyclovoltammetry was used to evaluate the conductivity of the film, its electroactivity, electroactive area and HOMO energy level. The chopped chronoamperometry confirmed the photoactivity of the material and its stability for 3000 s. The electrical and optical properties of the polymer were characterized by EIS and light absorption measurements to propose its energy level diagram. The PPy/TCPP coatings were obtained with high homogeneity on FTO, good conductivity, quasi-reversible electrochemical activity to ferrocene probe and stable photoactivity. Electrical characterization indicates high charge flow under illumination. An indirect bandgap of 2.51 eV and a HOMO level value of -4.59 eV were obtained for PPy/TCPP.

**Keywords:** polypyrrole films, codopant, photoelectrodes, stable photoactivity.

**RESUMO**
A fotoeletroquímica está surgindo como uma tecnologia promissora para coleta e utilização da energia solar em uma ampla gama de aplicações. No entanto, os materiais dos eletrodos ainda precisam ser melhorados para atingir um desempenho ideal. Os polímeros condutores surgem como compostos orgânicos particularmente promissores para essa finalidade devido as suas propriedades altamente versáteis. Neste estudo, foi realizada pela primeira vez a síntese galvanostática de filmes de polipirrol co-dopados com tetraquis(4-carboxifenil)porfirina (PPy/TCPP) em substratos de vidro revestidos com óxido de estanho dopado com flúor (FTO). Adicionalmente, foram realizadas avaliações desses filmes como fotoeletrodos, com foco nas principais propriedades. A incorporação da porfirina na matriz do polímero foi confirmada pela caracterização de UV-Vis e IR. As micrografias de SEM mostraram as alterações morfológicas induzidas pelo codopante. A ciclovoltametria foi usada para avaliar a condutividade do filme, sua eletroatividade, área eletroativa e nível de energia HOMO. A chronoamperometria picada confirmou a fotoatividade do material e sua estabilidade por 3000 s. As propriedades elétricas e ópticas do polímero foram caracterizadas por EIS e medições de absorção de luz para propor seu diagrama de nível de energia. Os revestimentos de PPy/TCPP foram obtidos com alta homogeneidade no FTO, boa condutividade, atividade eletroquímica quase reversível para a sonda de ferroceno e fotoatividade estável. A caracterização elétrica indica alto fluxo de carga sob iluminação. Um bandgap indireto de 2,51 eV e um valor de nível HOMO de -4,59 eV foram obtidos para PPy/TCPP.

**Palavras-chave:** filmes de polipirrol, codopante, fotoeletrodos, fotoatividade estável.

**RESUMEN**
La fotoelectroquímica está surgiendo como una tecnología prometedora para recolectar y utilizar energía solar en una amplia gama de aplicaciones. Sin embargo, aún es necesario mejorar los materiales de los electrodos para lograr un rendimiento óptimo. Los polímeros conductores se presentan como compuestos orgánicos especialmente prometedores para este fin debido a sus propiedades muy versátiles. En este estudio, se realizó por primera vez la síntesis galvanostática de películas de polipirrol co-dopadas con tetraquis(4-carboxifenil)porfirina (PPy/TCPP) sobre sustratos de vidrio recubiertos con óxido de estano (FTO) dopados con flúor. Además, se realizó una evaluación de estas películas como fotoelectrodos, centrándose en propiedades clave. La incorporación de porfirina a la matriz polimérica se confirmó mediante caracterización UV-Vis e IR. Las micrografías SEM mostraron los cambios morfológicos inducidos por el codopante. Se utilizó
ciclovoltametría para evaluar la conductividad de la película, su electroactividad, área electroactiva y nivel de energía HOMO. La cronoamperometría picada confirmó la fotoactividad del material y su estabilidad durante 3000 s. Las propiedades eléctricas y ópticas del polímero se caracterizaron mediante EIS y mediciones de absorción de luz para proponer su diagrama de niveles de energía. Los recubrimientos de PPy/TCPP se obtuvieron con alta homogeneidad en FTO, buena conductividad, actividad electroquímica casi reversible con sonda de ferroceno y fotoactividad estable. La caracterización eléctrica indica un alto flujo de carga bajo iluminación. Se obtuvo una banda prohibida indirecta de 2,51 eV y un valor de nivel HOMO de -4,59 eV para PPy/TCPP.

**Palabras clave:** películas de polipirrol, codopante, fotoelectrodos, fotoactividad estable.

1 INTRODUCTION

Currently, the world is facing a climate change crisis that has generated an increase in the global average temperature and multiple environmental effects. Therefore, the research on clean energy sources and their implementation to limit the CO₂ emissions caused by the burning of fossil fuels is a necessity to achieve a sustainable future. Solar energy is one of the most favorable alternatives to replace fossil fuels because it is abundant, clean, and virtually free. However, one of the challenges of solar energy is the development of efficient methods to harvest and store the energy received. Here, photoelectrochemistry is a promising technology to transform solar energy into energy-rich chemical fuels such as hydrogen (H₂), hydrogen peroxide (H₂O₂), or methanol, and it is estimated that only 1 % Earth’s surface covered with photoelectrochemical cells (PECs) with efficiencies of 10 % could meet the projected 2050 global annual energy consumption of 36 TW.¹²

In essence, photoelectrochemistry is characterized by using semiconductor light-absorbing photoelectrodes, which transform absorbed solar photons into excited charge carriers (electrons and holes). Due to an electrical potential (applied or induced), electrons are separated from holes and subsequently the redox reaction can be carried out at the semiconductor/liquid interface, the oxidation half-reaction on the anode surface and the reduction half-reaction on the surface of the cathode. The heart of the photoelectrochemical process is the light-absorbing semiconductor photoelectrode. Hence, the search for low-cost, efficient, and highly durable photoelectrodes is essential to continue developing photoelectrochemical technology.¹⁻³

Photoelectrodes are divided into two categories: photoanodes and photocathodes.
Both have been extensively investigated using inorganic semiconductors. Generally, photoanodes utilize -n- type semiconductors, such as binary and ternary oxides (TiO$_2$, WO$_3$, ZnO, metal ferrites and tungstates). In contrast, photocathodes are based on -p- type semiconductors, and due to the limited materials availability; they have been researched in less proportion than photoanodes. Among the most commonly used materials as photocathodes are oxides, such as Cu and Fe oxides, which are interesting because of their abundance, good conductivity, and low toxicity. However, the use of inorganic materials for photovoltaic cells (PEC) has some disadvantages, including their instability in acidic or alkaline aqueous solutions, limited light absorption range, and low flexibility for bandgap engineering. As a result, inorganic semiconductors require the assistance of sacrificial reagents or significant bias.

As an alternative to inorganic semiconductors in photoelectrochemical cells, organic semiconductors based on conducting polymers have emerged as promising materials, including polyaniline (PANI), polythiophene (PTH), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT). In their pristine state, conducting polymers have certain electrical and optical proprieties, (low conductivity and limited radiation absorption), nevertheless, through a doping process these proprieties can be adjusted, simulating those of inorganic semiconductors. Besides, they maintain the characteristics of polymers such as their flexibility and low molecular weight. Additionally, conducting polymers show other advantages including high charge mobility, components are derived from abundant renewable sources, their fabrication cost is low, and through molecular design, the band gap of conducting polymers can be tuned. One of the most studied applications of photoelectrochemical technology: Photo(electro)catalytic water-reduction to produce hydrogen evolution reaction. Conducting polymers present interesting advantages for instance: an appropriate lowest molecular orbital (LUMO) to HER and visible-light absorption with a high absorption coefficient.

In 1981 appeared the first report of photocathodes based on conducting polymers and the number of reports has risen in the last decades being polyaniline and polypyrrole the most utilized. Polypyrrole is a widely known conducting polymer due to its high stability, enhanced conductivity, and its easy synthesis. Furthermore, polypyrrole exhibits a facile film-forming process through electrochemical synthesis (oxidation) with the incorporation of anionic species (dopants). The electrosynthesis of polypyrrole involves the oxidation of the monomer by applying positive potential or current at the anode. When the polymer chain is generated, it can be oxidized removing π electrons from the valence
band, which creates radical cations called polarons. Further oxidation results in the formation of dications or bipolarons. Anionic species also called dopants are incorporated to the bipolaron structure enhancing the conductivity of the conducting polymer.\(^{11,12}\)

In photocatalytic applications, PPy composites have been investigated, especially in organic-inorganic semiconductors because PPy is often used to support inorganic catalysts and improve their performance\(^{13,14}\). Regarding photoelectrochemical devices, the use of polypyrrole in photoelectrodes is relatively scarce. Lattach \textit{et al} developed polypyrrole-Ru(2,2’bipyridine)\(^{2+}/\)Mo\(_{x}\) composite film as photocathode for HER.\(^{15}\) On the other hand, Da Hye Won \textit{et al} developed a new photocathode depositing PPy on the p-ZnTe electrode improving the photoelectrochemical CO\(_2\) reduction activity.\(^{16}\) The use of conducting polymers without inorganic co-catalysts has not been deeply explored. In 2021, Xiaoqing Gu \textit{et al} reported the photoassisted electrocatalyst for overall water splitting using polyaniline/carbon dots\(^{17}\) and in 2023, Gonzalez-Cruz \textit{et al} employed polyvinyl alcohol (PVA) films coated with polyaniline to study the Hg\(^{2+}\) electrosorption in them.\(^{18}\) Additionally, some reports that compare the performance of conducting polymers such as PANI, PPy, and PEDOT in photoelectrochemical CO\(_2\) reduction.\(^{19}\)

As previously stated, the chemical nature of the dopant significantly impacts the microstructure, conductivity, and optical properties of conducting polymers. Porphyrins are particularly attractive due to their ability to coordinate with a diverse range of transition metals, and possess various functional groups outside of the main ring. Porphyrins also exhibit high absorption coefficients over a wide range of wavelengths.\(^{20,21}\) However, porphyrins have been slightly explored in photoelectrochemical applications. Most studies involve heterojunction with inorganic or organic semiconductors, leaving little knowledge about the contribution of porphyrin to the optoelectronic and electrochemical properties in a photoelectrode\(^{20-22}\).\(^{22-24}\)

Taking advantage of the properties of PPy and porphyrins, our aim is to explore the use of an anionic porphyrin as a dopant in the electropolymerization of PPy on FTO substrates, and to evaluate its performance as a photocathode. The compound 4-[10,15,20-tris(4-carboxyphenyl)-21,23-dihydroporphyrin-5-yl]benzoic acid commonly named Tetrakis (4-carboxyphenyl) porphyrin (TCPP) is soluble in water over a wide pH range (7 to 13), making it suitable for electropolymerization in aqueous solutions. The carboxyl groups in porphyrins have been found to enhance their electroactivity\(^{20}\).

The reports of PPy doped with TCPP are few. Peshoira and Narula reported the synthesis of TCPP/PPy hybrid and its application as electrochemical sensor for the
detection of Cd$^{2+}$. Wang et al developed a N-doped porous carbons (NPC) from supramolecular crosslinked polypyrrole hydrogel (PPy-gel) with TCPP as a dopant and cross-linker to nanomolar level acetaminophen sensor. The PPy/metal-TCPP hybrid material was obtained through conventional organic synthesis. The electrocatalysis of the 2,6-diterbutylphenol reaction was evaluated using TCPP-doped PPy films.

Herein, in this study, we report for the first time the electrochemical synthesis of PPy films doped with anionic TCPP on FTO substrates and their performance as photocathode in a photoelectrochemical cells. This is justified since it is a novel, metal-free, and not investigated application of this system that could be contrasted with traditional inorganic materials employed as photocathodes. Finally, PPy films doped with TCPP were characterized physically and electrochemically to determine their photoelectrochemical proprieties and behavior.

2 MATERIALS AND METHODS

2.1 MATERIALS

Sodium sulfate (Sigma sulfate, > 99%, India), 4-[10,15,20-tris(4-carboxyphenyl)-21,23-dihydroporphyrin-5-yl]benzoic acid (Sigma Aldrich, Dye content 75%, USA), tetrabutylammonium hexafluorophosphate, TBAPF$_6$, (Sigma Aldrich, 98%, Switzerland), ferrocene powder (Alfa Aesar, 99%, Germany), sulfuric acid (Merck, 96%, Darmstadt, Germany), acetonitrile (Sigma Aldrich, gradient grade for LC, Darmstadt, Germany), Pyrrole (Sigma Aldrich, 98%, Steinhein am Albuch, Germany) was distilled and stored under inert atmosphere. FTO glasses with an area of 2,5 cm x 1,25 cm (Ossila, TEC 8, Shefflled, UK) were cleaned in 10% w/w NaOH (Carlo Erba > 97%, Val de Reuli, France) for 3 minutes at 55°C. Afterwards, the substrates were sonicated twice in ultrapure water for 10 min.

2.2 ELECTROCHEMICAL SYNTHESIS OF PPy DOPED WITH TCPP (PPy/TCPP)

Electro-polymerizations of PPy films doped with TCPP were carried out in a conventional three-electrode cell. Using an Ag/AgCl electrode as reference electrode
(RE), a platinum foil as counter-electrode (CE), and FTO substrates were employed as working electrodes (WE).

The synthesis solution contained 1.26 mM TCPP, 100 mM pyrrole and 100 mmol Na₂SO₄ in deionized water. The pH was adjusted to 10 by adding 3M NaOH. TCPP-free PPy films were synthesized in the TCPP-free solution. Electropolymerization was performed by applying a galvanostatic signal of 0.05 mA/cm² until a charge of 42 mC/cm² was reached. Prior to synthesis, the solution was degassed by N₂ bubbling for 10 minutes.

2.3 PHYSICAL CHARACTERIZATION

The film’s morphology was evaluated using scanning electron microscopy (SEM) on TESCAN LYRA3 equipment (Brno–Kohoutovice, Czech Republic) at an accelerating voltage of 5.0 kV. UV-Vis spectra were obtained with an Analytik Jena SPECORD 50 PLUS spectrophotometer (Jena, Germany) and IR spectra were measured using an IRTracer-100 FTIR Shimadzu spectrophotometer (Kyoto, Japan).

2.4 PHOTOELECTROCHEMICAL AND ELECTROCHEMICAL CHARACTERIZATIONS

Cyclic voltammetry measurements were conducted in a 2.7 mM solution of ferrocene with 100 mM TBAPF₆ in acetonitrile to determine the electrochemical area of PPy films and estimate of the HOMO level of the polymer. The cell consisted of three electrodes: an Ag/AgCl electrode as the reference electrode (RE), a platinum foil as the counter electrode (CE), and PPy and PPy/TCPP films on FTO as the working electrodes.

Photoelectrochemical characterizations such as cyclic voltammetry and time-depend on photocurrent responses (chronoamperometry) under dark and illumination were accomplished in 100 mM Na₂SO₄ 4 pH with air presence using a solar simulator ABET technologies 10500 (Milford, CT, USA) with an illumination potency of 100 mW/cm² at room temperature.

Electrochemical impedance spectroscopy (EIS) was carried out at the same electrolyte conditions of photoelectrochemical characterization. EIS was measured in the 0.1 Hz – 100 MHz frequency range by applying a bias equal to –0.5 V vs Ag/AgCl.
3 RESULTS

3.1 SYNTHESIS OF FILMS, PHYSICAL AND MORPHOLOGICAL CHARACTERIZATION

The PPy/TCPP and PPy films were electrodeposited on FTO under galvanostatic conditions, as in both cases the synthesis potential was low enough to avoid overoxidation of the polypyrrole (Figure 1). The electropolymerization time was set to reach an electric charge of 42 mC/cm², which corresponds to a similar thickness for both films. At the beginning of the galvanostatic synthesis, there is a strong increase in potential associated with the charging of the double layer and the nucleation and growth stage of the polymer on the FTO surface.

As the electrode coverage increases, the restriction to mass transport from the solution increases and changes in surface polarization occur, which decreases the polymerization rate and thus the potential. After the potential drop, the potential remains stable at around 0.54 V until the end of the electropolymerisation. The faster potential drop during PPy/TCPP synthesis suggests faster nucleation and growth of PPy in the presence of TCPP.

Figure 1 also shows that the potential reached by the system is lower in the presence of TCPP, indicating that this ion stabilizes and facilitates the polymerization process more compared to the presence of SO₄²⁻ as the only dopant. This could also be the reason for the greater uniformity of the PPy/TCPP film, as parallel reactions are less likely to occur.
The polymers were characterised by UV-Vis and IR spectroscopy to confirm the presence of bands specific to the compounds. The UV absorption spectrum of a TCPP solution was also taken.

In Figure 2 the UV-Vis spectrum of the PPy film, the band at 431 nm corresponds to the $\pi \rightarrow \pi^*$ transition of conjugated and doped PPy chain. The band beyond 600 nm is due to the transition from the valence band to polaron/bipolaron structure. Regarding the PPy/TCPP film and TCPP in solution, one Soret Band ($S_0 \rightarrow S_2$) at 414 nm was observed, in PPy/TCPP this Soret band suffered a slight red shift. Moreover, a tiny band was observed at 518 nm for TCPP in solution which is attributed to one of the four Q bands ($S_0 \rightarrow S_1$) that TCPP possesses. In PPy/TCPP films, a similar slight red shift is observed for this Q band. In this sense, as reported in the literature, PPy/TCPP exhibits only the Soret band and small red shift, probably corresponding to $\pi \rightarrow \pi$ stacking interactions between the PPy chains and the porphyrin.
Figure 2. UV-Vis absorption spectra of PPy/TCPP and PPy films on FTO substrates, and TCPP in solution.

Figure 3 shows the IR spectra of PPy and PPy/TCPP films. The peaks at 3315 and 1560 cm\(^{-1}\) correspond to the N—H and C—C stretching bands of pyrrole, respectively, meanwhile the peak at 1470 cm\(^{-1}\) is attributed to C—N stretching band in conjugate chains. The broad band at 1202 cm\(^{-1}\) corresponds to the C—N stretching and the band at 1036 cm\(^{-1}\) is assigned to the C—H in-plane deformation vibration. Finally, the peaks at 912 and 745 cm\(^{-1}\) are associated with the C—C and C—N bands out of plane ring deformation, demonstrating the presence of polymerized polypyrrole.\(^{32-34}\) Regarding the PPy/TCPP film, there are six peaks associated with TCPP. Firstly, there is no defined peak at high wavenumber values due to the interaction between bipolaronic PPy chains and the conjugated base of TCPP. The small band in the IR spectra of the PPy/TCPP films at high wavenumber was associated to the N—H stretching band. The peak at 1680 cm\(^{-1}\) was assigned to C=O stretching band, and in the literature, the C=O stretching in TCPP is a huge peak at 1703 cm\(^{-1}\), nevertheless, when TCPP is utilized as a dopant, this band suffers an important decrease in its high and experiences a redshift to 1680 cm\(^{-1}\). This peak confirms the presence and role of -COO\(^{-}\) group in TCPP as dopant for the cationic structure of oxidized PPy. On the other hand, the peaks observed at 1422, 1341 and 1139 cm\(^{-1}\) are attributed to the C—O—H in plane bending, C—O stretching and C—N in plane deformation vibrations of TCPP respectively. Finally, the peak at 745 cm\(^{-1}\) corresponds to C—H out of plane bending vibration of the phenyl ring.\(^{25}\)
The morphology of the PPy and PPy/TCPP films was evaluated by SEM micrographs. Figure 4 shows the images of PPy and PPy/TCPP films electrodeposited on FTO glass at 40,000x magnification.

The PPy film has a globular morphology with moderately spherically packed aggregates, and coverage is not complete (Figure 4a). On the other hand, Figure 4b shows the PPy/TCPP films in which smaller aggregates and more irregular shapes are observed, appearing cauliflower-like, as has been reported when PPy is doped with bulky or surfactant-like molecules. Moreover, for PPy/TCPP, the coating on the FTO glass is more homogeneous and complete. Both films show porosity on their surface, which benefits their photocatalytic performance.
3.2 ELECTROCHEMICAL AND PHOTOELECTROCHEMICAL CHARACTERIZATION

Cyclic voltammetry (CV) at different scan rates was used to evaluate the electroactivity of the polymers and to roughly estimate an effect of TCPP on the electroactive area of PPy. For this purpose, measurements were performed in a 2.7 mM ferrocene solution with 100 mM TBAPF$_6$ in acetonitrile at rates between 50 and 250 mV/s in a potential window of -0.6 to 1.2 V vs. Ag/AgCl. The results (Figure 5 and Figure S1) show in both cases a pair of well-defined redox peaks corresponding to the redox activity of ferrocene. At a rate of 150 mV/s, the E$_{pa}$ was 584 mV for PPy/TCPP and 596 mV for PPy. The E$_{pc}$ was 304 mV for PPy/TCPP and 318 mV for PPy. This results in peak separations (ΔE$_{p}$) of 280 mV for PPy/TCPP and 278 mV for PPy. The ΔE$_{p}$ remains significantly unchanged by the incorporation of TCPP into the PPy matrix. However, the peak potentials become less positive in the presence of TCPP, suggesting a favorable thermodynamic effect for the reaction of the redox probe. The well-defined ferrocene redox peaks and their separation demonstrate the high conductivity of the two polymers and a quasi-reversible behavior of the probe on these surfaces (Figure 5 and Figure S1).

Furthermore, for both polymers the peak current (anodic and cathodic) was proportional to the square root of the scan rate (Figures S2 and S3), indicating a diffusion controlled electrochemical reaction. The ΔE$_{p}$ remains significantly unchanged by the incorporation of TCPP into the PPy matrix, so no change in the electroactivity of the polymer is detected by this technique.

Furthermore, both polymers obey the Randles-Sevcik relationship (Equation S1), as shown by the proportionality between the peak current (anodic and cathodic) and the square root of the scan rate (Figures S2 and S3). This behavior indicates a diffusion controlled electrochemical reaction of ferrocene on both surfaces. The slopes of the anodic straight lines were 1.81 x 10$^{-4}$ A s$^{1/2}$/mV$^{1/2}$ for PPy/TCPP and 1.65 X10$^{-4}$ A s$^{1/2}$/mV$^{1/2}$ for PPy, which can be related to a larger electroactive area for PPy/TCPP and is consistent with the microstructure observed in SEM images (Figure 4).
Figure 5. Cyclovoltammograms of 2.7 mM ferrocene in acetonitrile with 100 mM TBAPF$_6$ at different scan rates. Working electrode is a PPy/TCPP film on FTO substrate.

The photoelectrochemical activity of PPy and PPy/TCPP films was evaluated by CV at 20 mV/s in a potential window of $-0.7 \leq E \leq 0.3$ V vs. Ag/AgCl in 100 mM Na$_2$SO$_4$ at pH 4. Illumination conditions simulating 1 sun intensity (100 mW/cm$^2$) and darkness were used. The solutions were pre-pumped with air for 15 minutes. Figure 6 shows the cyclic voltammograms for both films and the FTO substrate.

Figure 6. Cyclovoltammograms in 100 mM Na$_2$SO$_4$(ac) at pH = 4 under illumination (1 sun) and darkness. The working electrode is a PPy or PPy/TCPP film on FTO substrate.
Both polymer films showed a cathodic peak due to electrochemical reduction of oxygen in the solution. \(^{37}\) The PPy/TCPP film at about -0.48 V and the PPy film at about -0.53 V. For both materials, there was an increase in the intensity of this signal under illumination conditions. The current intensities comparing dark and light for the two polymers were 14.3 µA/cm² and 22.3 µA/cm² (PPy/TCPP); 11.5 µA/cm² and 21.5 µA/cm² (PPy).

The photoelectrochemical performance of PPy and PPy/TCPP films was also evaluated by chronoamperometry measurements using chopped light (Figure 7). Chronoamperometries were performed at -0.4 V vs. Ag/AgCl in 100 mM Na₂SO₄ at pH 4, aerated for 15 min, with light and dark periods of 5 min each. Both films exhibited cathodic photoactivity. These photocurrents can be attributed to the oxygen reduction reaction, since in previous experiments negligible photocurrents were observed in a nitrogen atmosphere. \(^{38}\)

The photocurrents showed minimal changes during the measurements, indicating high stability of the films under the conditions used. The PPy/TCPP films had an average photocurrent density (\(J\)) of 13.9 µA/cm² and the PPy films 13.7 µA/cm². Therefore, the presence of TCPP in PPy did not significantly change the photocurrent density of the polymer. However, it should be noted that the incorporation of TCPP increases the stability of the polymer during the evaluation period. To further investigate the electrical properties, EIS measurements of the polymer films were performed in 100 mM Na₂SO₄ at pH 4.0 in the frequency range 0.1 Hz - 100 MHz using a DC potential of -0.5 V vs. Ag/AgCl.

Figure 7. Photocurrent responses as a function of time for PPy/TCPP and PPy at - 0.4 V in aerated 100 mM Na₂SO₄ solution at pH 4. b) Comparison of photocurrent changes in both films.

Source: Authors
Figure 8. Nyquist plots. B) Bode plots. From EIS measurements of PPy and PPy/TCPP (0.1 to 10^5 Hz at 0.4 V in aerated 100 mM Na_2SO_4 solution at pH 4.

Table 1. Electrical parameters of PPy and PPy/TCPP obtained from the equivalent circuit and the Bode plot in Figure 8 (R_s: solution resistance, R_{ct}: charge transfer resistance, f_{max}: maximum frequency, t_{eff}: electron lifetime).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>R_s (Ω)</th>
<th>R_{ct} (Ω)</th>
<th>f_{max} (Hz)</th>
<th>t_{eff} (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy/TCPP-light</td>
<td>34.3</td>
<td>159</td>
<td>112.7</td>
<td>1.4</td>
</tr>
<tr>
<td>PPy-light</td>
<td>23.0</td>
<td>114</td>
<td>98.8</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Figure 8 shows the impedance spectra for PPy and PPy/TCPP plotted as Nyquist (Figure 8a) and Bode (Figure 8b) plots in the presence of light and dark. Nyquist (Fig. 8a) plots the imaginary impedance (-Z'') versus the real impedance (Z'). If a semicircle appears on the Nyquist plot, it is due to a charge transfer resistance (R_{ct}) associated with an interfacial reaction. The shape and size of the semicircle indicate the characteristics of the charge transfer, including kinetics and double layer effects. The straight line at the end of the semicircle indicates a diffusion process limited by mass transport, which is well characterized by the Warburg impedance (W)^{39,40}. PPy/TCPP has a higher Warburg slope than PPy, indicating faster mass transport at this interface, which could be related to a more homogeneous morphology of this polymer.

In addition, it is convenient to take into account the high porosity and the presence of surface defects in the polymers, which are well represented by the constant phase elements (CPE) included in the equivalent circuit (Figure 8a). From the adjustments to the circuit, R_{ct} values under darkness and illumination of 203 Ω and 159 Ω (PPy/TCPP) were obtained. And in the case of PPy, values of 115 Ω and 114 Ω, respectively.

For PPy/TCPP, the R_{ct} decreases under illumination conditions, suggesting a higher flow of electrons that are activated by the absorption of photons compared to the
flow experienced by PPy.\textsuperscript{41,42} However, regardless of dark or light conditions, the Rct of PPy/TCPP was higher than that of PPy, indicating that the presence of TCPP in the polymer matrix hinders charge transport in the structure. This could be explained by the bulky size of TCPP, which can alter the orientation of the polymer chains, leading to greater disorder and segregation and therefore lower conductivity\textsuperscript{43}. This higher disorder in the microstructure compared to PPy is visible in the SEM micrograph (Figure 4).

Figure 8b shows the Bode plot, which illustrates the change in phase angle with frequency. The maximum angle occurred at approximately 100 Hz for both polymers, under both light and dark conditions. This suggests that the electron lifetime in the two materials is of the same order of magnitude, regardless of illumination (\(t_{\text{eff}} = (2f_{\text{max}})^{-1}\)) (Table 1). The maximum angle is slightly larger in the dark for both polymers, which is consistent with the higher Rct observed from Nyquist.

3.3 DETERMINATION OF BAND GAP

The Tauc plot is a common method for characterizing the optical properties of photoelectrodes, obtained from light absorption measurements. It involves calculating the transition energy using the energy equation of a photon (equation 1).

\[
E = h\nu \rightarrow E = \frac{1240}{\lambda} \text{eV} \quad \text{Eq 1.}
\]

\[
\alpha = 2,303 \frac{A}{l} \quad \text{Eq 2.}
\]

Where \(\lambda\) is the wavelength in nm, \(\alpha\) is the molar absorption coefficient of the material, \(A\) is its absorbance, and \(l\) is the optical path (equation 2). In this case, \(l\) is the thickness of the polymer film as determined by SEM. The Tauc equation relates the band gap of a semiconductor material to its absorption coefficient:

\[
(\alpha h\nu)^{1/\gamma} = B(h\nu - E_g) \quad \text{Eq 3.}
\]

\(h\) is Planck's constant, \(\nu\) is the photon frequency, \(E_g\) is the bandgap of the semiconductor, and \(\gamma\) is a factor that depends on the nature of the electronic transition.
For direct transitions $\gamma$ is 0.5 and for indirect transitions it is 2.\(^{44}\). For materials such as PPy, it is more common to consider the indirect transition,\(^{45}\) means that the energy required to excite an electron from the valence band to the conduction band involves a change in electron momentum, and this is associated with a lower absorption coefficient of the material.

Figure 9 shows the Tauc diagram for the PPy/TCPP film. The value of the band gap energy ($E_g$) of PPy/TCPP for an indirect transition is obtained by intersecting the linear region of the Tauc diagram with the X-axis. In this case it was 2.51 eV. This value is comparable to that reported for PPy doped with different ions, such as p-toluenesulfonate, in which case an $E_g$ of 2.05 eV was obtained\(^{46,47}\). In any case, it should be noted that the value of $E_g$ depends on several factors, such as the thickness of the polymer, its composition and its microstructure.

![Tauc plot of the indirect transition for a PPy/TCPP film on FTO substrate.](source: Authors)

Figure 9. Tauc plot of the indirect transition for a PPy/TCPP film on FTO substrate.

3.4 ENERGY LEVELS OF PPy/TCPP

Cyclic voltammetry allows a very rough estimation of the energy value of the HOMO level of organic semiconductors. This is done by measuring the formal potential of the ferrocene/ferrocinium pair as a vacuum reference ($E_{ox(ferrocene)}$) and also by measuring the oxidation potential ($E_{ox}$) of the polymer in a ferrocene solution\(^{48}\). The potentials are determined as $E_{onset}$ by cutting tangents (Figure S4, S5).
Cyclovoltammograms were performed in 2.7 mM ferrocene solution with 100 mM TBAPF$_6$ in acetonitrile:

$$\text{HOMO} = -(E_{\text{ox}} + 4.80 - E_{\text{ox(ferrocene)}}) \text{ eV} \quad \text{Eq.4}$$

From the cyclovoltammograms of Figures S4 and S5, $E_{\text{ox(ferrocene)}}$ is 0.36 V and $E_{\text{ox}}$ is 0.15 V. Substitution into equation 4 gives a HOMO of -4.59 eV. Using the $E_g$ determined by Tauc (2.51 eV), the energy of the lowest unoccupied molecular orbital (LUMO) of PPy/TCPP is -2.08 eV, this from:

$$\text{LUMO} = \text{HOMO} + E_g \quad \text{Eq 5.}$$

From these values for PPy/TCPP, Figure 10 shows a diagram of the polymer energy levels. The plot also shows the redox potentials of water$^{49}$, N$_2$$^{50}$ and CO$_2$$^{51}$ vs NHE (V). Based on the position of their energy levels, the polymer would be suitable for photoelectrochemical conversion of CO$_2$ to CO, HCO$_2$H, and H$_2$C$_2$O$_4$ at pH 0, as it meets the thermodynamic requirements for these CO$_2$ reduction reactions.$^{49,51}$

Figure 10. Diagram of the energy levels of PPy/TCPP with respect to the vacuum level and the NHE (V) at pH 0.

\[ \begin{array}{|c|c|}
\hline
\text{E vs Vacuum (eV)} & \text{E vs NHE (V)} \\
\hline
\text{ETO 4.4 eV} & \text{ETO 4.4 eV} \\
\text{PPy/TCPP} & \text{H}_2\text{O/H}_2 \\
\text{-2.08 eV} & \text{H}_2\text{O} \\
\text{-4.59 eV} & \text{O}_2/\text{H}_2\text{O} \\
\hline
\end{array} \]

Source: Authors
4 CONCLUSIONS

In this study, the electropolymerization of a PPy/TCPP film (polypyrrole codoped with tetrakis (4-carboxyphenyl) porphyrin) on transparent glass electrodes coated with FTO was conducted. The presence of TCPP facilitated galvanostatic polymerization by lowering the potential required for the initial synthesis stage, resulting in a deposit of good homogeneity and coverage on the electrode. Characterization of the polymer morphology revealed the presence of small aggregates with some cauliflower-like shapes. The PPy/TCPP films exhibited photoactivity and, according to the EIS results, experienced a higher charge flow than PPy. Additionally, the proposed energy level diagram of this polymer revealed that the positions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels are conducive to catalyzing reactions of interest.

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REFERENCES


