

Photoelectroactive Corrole Monomer Functionalized with a Triphenylamine–Chalcone Derivative: Synthesis, Electropolymerization, and Electrochromic Applications [†]

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Abstract

In this work, we report the divergent synthesis of a novel corrole macrocycle with a T-shaped geometry, functionalized with triphenylamine (TPA) units. The synthetic route involved a green preparation of 5-(pentafluorophenyl)dipyrromethane, condensation with pentafluorobenzaldehyde, and DDQ oxidation to afford the target corrole. In parallel, a TPA-based chalcone derivative was obtained and introduced via regioselective nucleophilic aromatic substitution. The resulting photoactive corrole–TPA conjugate exhibited efficient electropolymerization, retaining the corrole chromophore while forming conductive TPB-linked films (TPB, tetraphenylbenzidine). Spectroelectrochemical studies confirmed reversible redox activity, color switching, and electrochromic behavior, highlighting its potential as a building block for photo- and electroactive devices.

Keywords: corrole; electropolymer; photoelectroactive

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1. Introduction

Corroles are tetrapyrrolic macrocycles closely related to porphyrins, but they differ by having a contracted ring due to the absence of one carbon atom. This structural variation gives them distinctive physicochemical behavior compared with porphyrins. Their extended π -conjugation and the presence of three inner nitrogen atoms provide intense light absorption, remarkable redox versatility, and the capacity to stabilize unusual oxidation states of metal ions. Because of these properties, corroles have attracted considerable attention for use in catalysis, sensors, and energy conversion [1]. Importantly, they also display enhanced chemical robustness and tunable electronic features, making them promising platforms for designing functional organic materials.

A particularly powerful approach for expanding the utility of corroles is to introduce electropolymerizable groups at their periphery. Substituents such as triphenylamine, carbazole, or thiophene derivatives can undergo anodic oxidation to generate radical cations

that subsequently couple, producing extended polymer networks. When these groups are anchored to a corrole framework, the resulting electropolymerization gives rise to stable films that combine the optical and electrochemical signatures of the corrole with the processability and conductivity of the polymer matrix. This method offers a straightforward route to obtain strongly adherent functional coatings on conductive or semiconductive electrodes, while retaining the intrinsic photophysical properties of the macrocycle.

In this study, a novel corrole derivative bearing TPA-chalcone units was synthesized via a divergent route in a total of four steps, achieving a high overall yield. The monomer was purified by column chromatography and subsequently characterized by NMR as well as spectroscopic and electrochemical methods. Additionally, polymers were synthesized by electrochemical techniques and characterized through electrochemical and spectroelectrochemical analyses, revealing properties of great interest for potential applications in optoelectronic devices. It is important to highlight that the literature contains only a few reports on the electrosynthesis of this class of macrocycles, and even fewer on the application of the resulting electropolymers in optoelectronic systems.

2. Materials and Methods

2.1. Materials

Chemicals were obtained from Sigma-Aldrich (Milwaukee, WI, USA). They were used without further purification. Organic solvents (GR grade) from Merck (Darmstadt, Germany) were distilled and maintained on molecular sieves. Chemicals for electrochemical experiments: Anhydrous 1,2-dichloroethane (DCE) and Tetrabutylammonium hexafluorophosphate (TBAPF₆) were obtained from Sigma-Aldrich and used as received.

2.2. Synthesis

5,10,15-Tris(pentafluorophenyl)corrole (**Co**) was synthesized in two steps following previously reported procedures from our group [2]. (*E*)-3-(4-(diphenylamino)phenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one (**TPA-Ch-OH**) was prepared following previously published methods [3,4].

A solution containing **Co** (1 eq) and **TPA-Ch-OH** (3.5 eq) was prepared in dry *N,N*-dimethylformamide (DMF), and K₂CO₃ (30 eq) was then added. The suspension was stirred at 90 °C for 3 h. The mixture was subsequently cooled and diluted with DCM. The organic phase was washed with water and dried over Na₂SO₄. The solvent was evaporated, and the residue was purified by column chromatography, affording **Co-TPA**.

2.3. Spectroscopic Studies

The UV-visible absorption spectra of **Co-TPA** were obtained in a diluted dichloroethane (DCE) solution and a thin film electrodeposited on indium tin oxide (ITO), respectively. The spectrum of **Co-TPA** was recorded and compared with that of **Co** (without TPA groups) at room temperature using a quartz cuvette with a 10 mm path. The absorption spectrum corresponding to **P-Co-TPA** on ITO was acquired by placing the electrode in the spectrometer cell holder. For background correction, a bare ITO electrode was utilized.

2.4. Electrochemistry and Electrodeposition

Electrochemical studies were performed in a deaerated (with high purity argon) monomer solution containing 0.1 M of the supporting electrolyte or only with electrolyte. The last solution was used for the electrochemical responses of the electropolymerized films. A three-electrode system composed of a Platinum (Pt) or ITO coated glass working electrode, a platinum mesh counter electrode, and a silver wire quasi-reference electrode

were utilized for electrochemistry experiments. The ITO electrode substrates were cleaned sequentially in an ultrasonic bath with acetone, ethanol, and deionized water and dried before use.

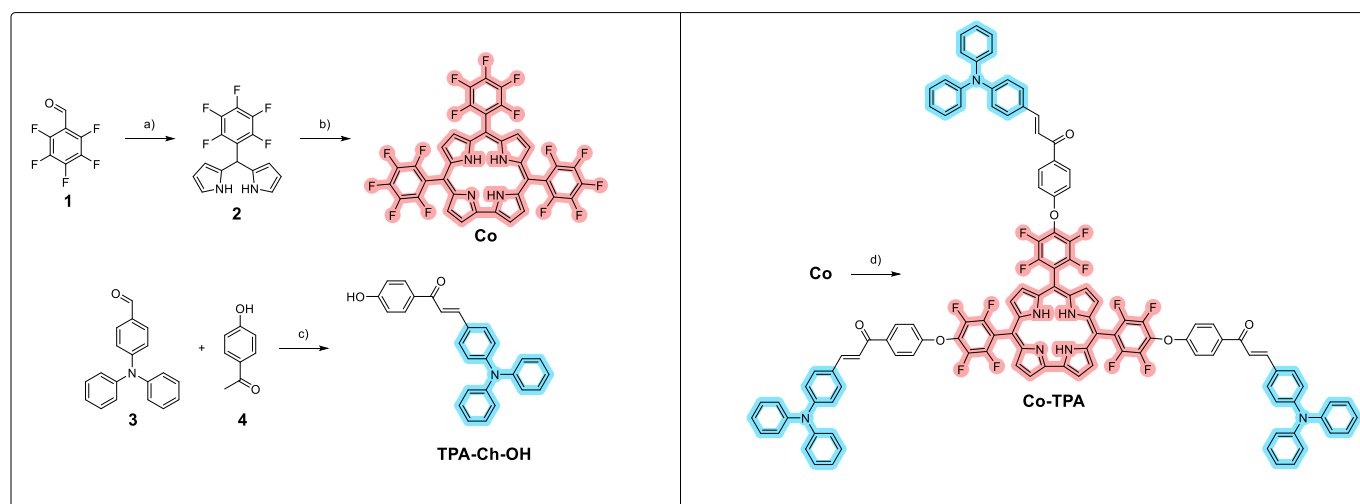
2.5. Spectroelectrochemistry

In situ UV-visible spectroelectrochemical measurements under potentiostatic control were obtained using a Hewlett Packard UV-vis diode array spectrophotometer at kinetic measurement mode by utilizing a three-electrode configuration of an ITO modified with polymeric film. A naked ITO electrode was used as a blank for absorption background correction.

3. Results and Discussion

3.1. Design, Synthesis, and Characterization of Co-TPA monomer

The divergent synthesis of the novel corrole macrocycle, featuring a T-shaped geometry and peripheral functionalization with TPA units, is shown in Scheme 1. The synthesis began with 5-(pentafluorophenyl)dipyrrromethane **2**, prepared via a green protocol by Dehaen [5]. This aryl dipyrrromethane **2** was condensed with pentafluorobenzaldehyde **1** in a MeOH/HCl aqueous mixture to yield a bilane intermediate, which was subsequently oxidized with DDQ to afford the target corrole **Co** bearing three pentafluorophenyl groups at the *meso* positions [5]. In parallel, a TPA-based chalcone derivative (**TPA-Ch-OH**) was synthesized through a Claisen–Schmidt condensation from 4-(diphenylamino)benzaldehyde (**3**) and 4'-hydroxyacetophenone (**4**) in a mixture of EtOH and 50% aqueous KOH solution [3,4]. The mixture was stirred at 50 °C for 3 h, cooled to room temperature, and left overnight. The resulting chalcone salts were poured into water and neutralized to pH 7 with 1 M HCl. The precipitate, crystallized from EtOH, was subsequently filtered, washed with EtOH, and dried to give **TPA-Ch-OH**. Finally, a regioselective nucleophilic aromatic substitution between **TPA-Ch-OH** and **Co** in dry DMF using K₂CO₃ as the base displaced the para-fluorine atoms, affording the functionalized monomer **Co-TPA** in high yield [2].



Scheme 1. Synthesis of **Co-TPA**. Reaction conditions: (a) H₂O, HCl, 25 °C; (b) 1- MeOH/HCl, 25 °C, 2- DDQ, 25 °C; (c) 1- KOH, MeOH, 50 °C, 2- HCl (1 M), H₂O; (d) **TPA-Ch-OH**, K₂CO₃, DMF, 90 °C.

Co-TPA features a photoactive, electron-accepting corrole core covalently linked to the electron-donating and electropolymerizable TPA moiety, making it a promising material for photoactive and electroactive materials. The TPA groups were selected to promote electrochemical radical coupling upon anodic oxidation.

3.2. Electrochemical Characterization of Co-TPA and Electrochemical Synthesis and Deposition of P-Co-TPA Polymeric Film

Electrochemical studies were performed to evaluate the redox properties of the **Co-TPA** monomer and its ability to form polymeric films. Cyclic voltammetry experiments were conducted in DCE with 0.1 M TBAPF₆ at a scan rate of 100 mV·s⁻¹, using a Pt working electrode. Figure 1a shows the first anodic scan of the **Co-TPA** monomer, which displays an oxidation peak around 0.80 V. This process can be attributed to the formation of the TPA radical cation (TPA^{•+}) [6]. In subsequent scans (Figure 1b), a new redox couple appears at slightly lower potentials. This behavior is consistent with the generation of TPB species via an ECE mechanism, in which unstable TPA^{•+} radicals couple to form a more conjugated TPB dimer. Because of its extended π -system, TPB undergoes reversible one-electron redox processes more readily than TPA [7]. The peak observed at 1.1 V can be assigned to the formation of TPB²⁺. This observation can be explained by considering that the coupling reaction leading to TPB formation is sufficiently fast for TPA^{•+} to couple during the first cycle, generating TPB, which is subsequently oxidized [7]. As cycling proceeds, the progressive increase in both anodic and cathodic currents indicates the formation of a polymeric film strongly adsorbed on the electrode surface.

On the other hand, the voltammogram does not show a distinct peak corresponding to corrole oxidation. This can be rationalized by assuming that the corrole oxidation occurs at a potential close to that of TPA, making it difficult to resolve separately [8]. This hypothesis will be further corroborated by complementary spectroscopic and spectroelectrochemical studies

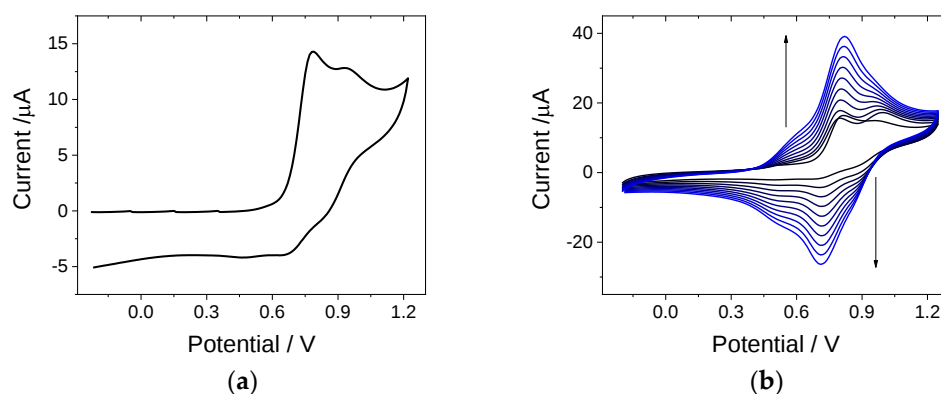


Figure 1. (a) First anodic scan of **Co-TPA** monomer. (b) Ten consecutive anodic scans. All measurements were conducted in DCE, TBAPF₆ (0.1 M) at 100 mV/s, using a Pt electrode.

3.3. Electrochemical Characterization of P-Co-TPA

To confirm the formation of a film over the electrode, CVs were performed in a solution containing only supporting electrolyte at different scan rate. The electrochemical response of the film is formed by two oxidation/reduction couples which present a bell shape in the CV (Figure 2a), that are very close one to the other. As shown in the Figure 2b, the polymeric film of **Co-TPA**, (now **P-Co-TPA**) presents a linear relation between anodic and cathodic peak currents with the scan rate, indicating that a product is irreversibly adsorbed over the electrode surface.

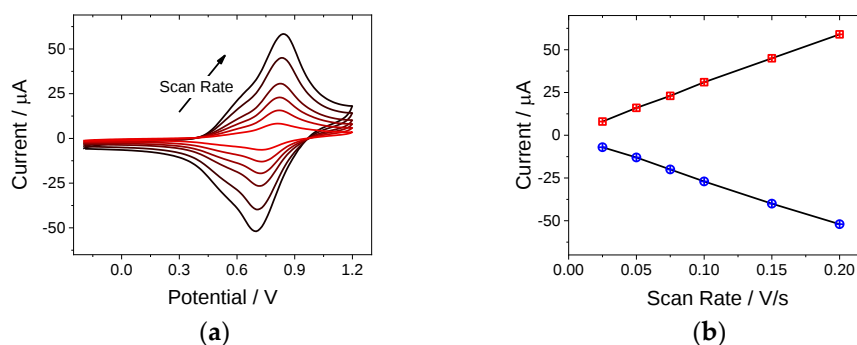


Figure 2. (a) Electrochemical responses after ten consecutive anodic scans, at different scan rates (0.025, 0.050, 0.075, 0.100, 0.150, 0.200, V/s) and (b) anodic and cathodic peak currents vs. scan rate for the polymeric film in a solution containing only supporting electrolyte, using a Pt electrode.

3.4. Spectroscopic Characterization of Co, Co-TPA and P-Co-TPA

Spectroscopic properties of the reference (**Co**), monomer (**Co-TPA**) and polymer (**P-Co-TPA**) were studied at room temperature using UV–visible spectroscopy. Figure 3a,b shows the absorption spectra of **Co** and **Co-TPA** in DCE diluted solutions. As can be observed, both spectra exhibit similar absorption profiles. In the blue region of the electromagnetic spectrum, the Soret band appears sharp and well-defined around $\lambda_{\text{max}} = 410$ nm for **Co** and $\lambda_{\text{max}} = 425$ nm for **Co-TPA**, with a molar absorptivity coefficient (ϵ) of $\sim 1 \times 10^5 \text{ M}^{-1}\text{cm}^{-1}$. In the visible region, Q bands are observed between 500 and 700 nm, exhibiting molar absorptivity values approximately one order of magnitude lower. These spectroscopic features are consistent with those previously reported for corrole derivatives [2]. Moreover, in the **Co-TPA** spectra we can observe the presence of an intense band (~ 300 nm) characteristic of compounds containing TPA. The absorption spectra of **P-Co-TPA** ($\lambda_{\text{max}} = 430$ nm) electropolymerized over ITO electrode (Figure 3c) is comparable to the absorption spectra of the monomer in solution, indicating that the whole tetrapyrrolic macrocycle conjugated system has not been altered during the polymerization process.

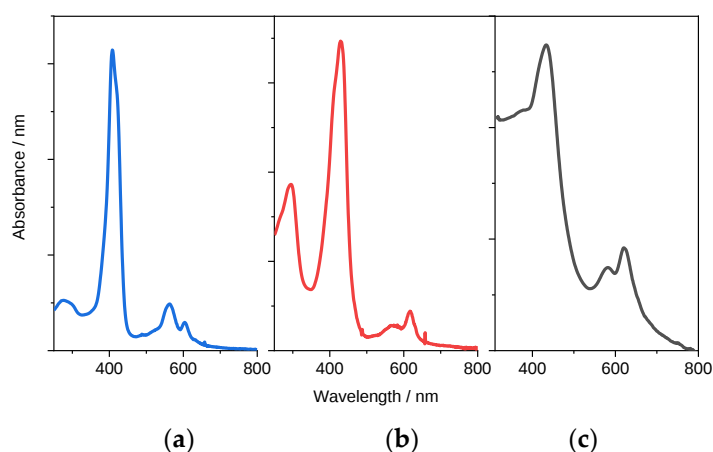


Figure 3. Normalized absorption spectra for of **Co** (blue line), **Co-TPA** (red line) and **P-Co-TPA** (black line), acquired in DCE or ITO.

3.5. Spectroelectrochemical Characterization of P-Co-TPA

Like we saw, the monomer **Co-TPA** presents Soret and Q bands in the visible region and other band in the UV region at ~ 300 that indicates the presence of TPA unit. We can do a similar interpretation for the **P-Co-TPA**. For corroborate this explanation we realized

spectroelectrochemical experiments. The absorption spectra obtained during the spectroelectrochemical studies were plotted as ΔAbs (Figure 4a). To do this, the absorption spectrum obtained at 0.00 V was subtracted from the absorption spectra taken at the different applied potentials. Positive and negative absorptions are related to species that appear and species that are bleached, respectively. When the applied potential is lower than 0.60 V, **P-Co-TPA** is in the neutral state and no changes are detected. When the film is oxidized until the first oxidation peak the absorption at 350 nm disappears and two new bands, one in the visible region (505 nm) and a second one that starts around 690 nm appears (green light line in Figure 4a). At more anodic applied potentials, the band at 505 nm decreases and a new band centered at 785 nm starts to grow, until the film is fully oxidized. At 1.1 V the corrole band centered at 430 nm starts to decrease, demonstrating that at this potential the corrole nucleus is oxidized. The principal absorption traces of the polymeric films were also followed during the anodic scan and are depicted in Figure 4b. When the films are in the neutral state all traces maintain their initial values. When the films start to get oxidized the trace related to the TPB band decreases (350 nm) and the trace related to TPB $^{\bullet+}$ (505 nm) grows in intensity. At potential values close to the first oxidation peak, the 505 nm trace is maxima and at the same time the 690 nm trace begins to increase. In the second oxidation process, the trace at 785 nm (trace related to TPB $^{+2}$) reach their maxima value. During the reverse scan all traces present an opposite behavior until they recover their initial values at the end of the scan. The electrochemical and spectroelectrochemical data are in agreement with the presence of TPB units in the chemical structure of **P-Co-TPA**. When **P-Co-TPA** was oxidized, the absorption spectra of the semi and fully oxidized states showed bands characteristics of TPB radical cation and dication respectively [7,8].

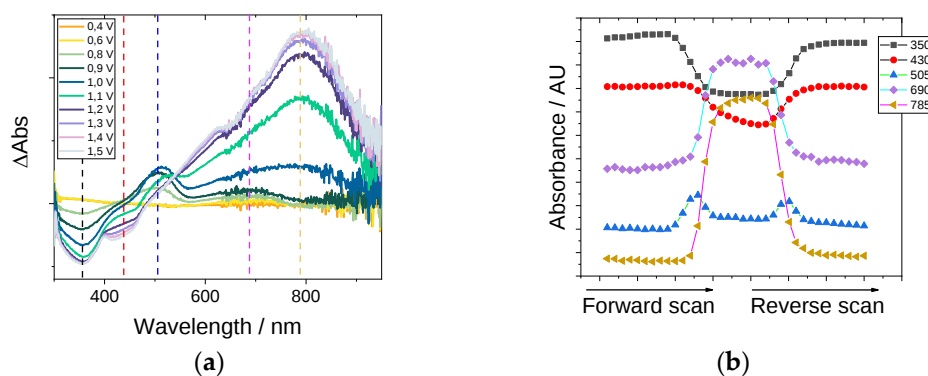


Figure 4. (a) Difference absorption spectra (ΔAbs) and (b) Changes in the principal absorption traces of P-Co-TPA deposited over ITO electrodes obtained during an anodic scan. All measurements were conducted in DCE (0.10 M TBAPF₆) at 20 mV/s.

4. Conclusions

In this work, we successfully designed and synthesized a corrole monomer functionalized with a TPA-chalcone derivative and demonstrated its ability to undergo efficient electropolymerization on conductive substrates. Electrochemical studies revealed the formation of stable polymeric films through radical cation coupling of TPA units, leading to covalently linked networks that preserve the corrole macrocyclic core. Spectroscopic and spectroelectrochemical analyses confirmed the retention of the characteristic Soret and Q bands, together with the emergence of additional absorptions associated with TPA/TPB species. The polymer films exhibited reversible electrochemical responses, enhanced redox activity, and an electrochromic behavior with reversible color changes. These results highlight the potential of the **Co-TPA** system as a versatile photo- and electroactive

building block for the development of advanced optoelectronic devices, particularly in electrochromic applications.

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Conflicts of Interest: The authors declare no conflicts of interest.

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