

Electrochemical Generation of Aza-BODIPY Polymers as NIR-Absorbing Electrochromic Materials [†]

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Abstract

A novel aza-BODIPY derivative functionalized with triphenylamine (TPA) substituents was synthesized through a multi-step route involving Claisen–Schmidt condensation, Michael addition, cyclization, and subsequent complexation. The presence of TPA units was introduced to enable electropolymerization, which was successfully achieved on Pt and ITO electrodes via cyclic voltammetry (CV). The progressive growth of the polymer films was evidenced by increasing redox currents, while their formation and properties were determined by CV, UV–Vis, and spectroelectrochemical analyses. The resulting polymer exhibited reversible absorption changes spanning the visible and near-infrared regions, highlighting its potential as a promising material for advanced electrochromic applications. Notably, the absorption in the NIR region makes this polymer particularly useful for optoelectronic technologies.

Keywords: aza-BODIPY; triphenylamine; electropolymerization; electrochromism

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1. Introduction

Electrochromism refers to the ability of a material to reversibly change its color upon the application of an external voltage. This phenomenon has attracted growing interest within the scientific community because of its potential to enable energy-saving technologies [1]. One of the most prominent examples is **smart windows**, which operate by dynamically controlling the transmission of light and heat through selective modulation of the visible and near-infrared regions of the electromagnetic spectrum [2]. In this context, among the organic chromophores explored, the boron aza-dipyrromethenes (aza-BODIPYs) represent a particularly appealing class of compounds, not only by their high absorption coefficient in the red/NIR region, but also by the capacity and versatility with which their redox properties can be modified [3]. In this work, we report the high-yield, gram-scale synthesis of a novel aza-BODIPY derivative substituted at its periphery with triphenylamine (TPA) units. These substituents were introduced to enable radical

coupling reactions under electrochemical conditions. The monomer was electropolymerized, and the resulting films were subsequently evaluated as electrochromic materials. Notably, the electrochemical polymerization approach provides a one-step route for film formation, offering precise and convenient control over film thickness [4]. 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. Monomer Synthesis

The first step involved a Claisen–Schmidt condensation between 6'-methoxy-2'-acetophenone and 4-(diphenylamino)benzaldehyde, affording the corresponding chalcone derivative. This α,β -unsaturated ketone was then subjected to a Michael addition in the presence of CH_3NO_2 , yielding diaryl-4-nitrobutan-1-ones. Subsequent treatment with ammonium acetate (NH_4OAc) afforded the corresponding tetraarylazadipyrromethene intermediate. Finally, complexation with boron trifluoride diethyl etherate ($\text{BF}_3\cdot\text{OEt}_2$) and *N,N*-diisopropylethylamine (DIPEA) in dry 1,2-dichloroethane (DCE) led to the target aza-BODIPY bearing two TPA moieties (**aza-BODIPY-TPA**).

2.2. Instrumentation and Methods

The redox properties of the **aza-BODIPY-TPA** monomer were studied by differential pulse voltammetry (DPV) and cyclic voltammetry (CV) in a cell equipped with Pt or ITO working electrodes, a large area Pt wire as a counter electrode, and a silver quasi-reference electrode, using DCE and 0.10 M tetrabutylammonium hexafluorophosphate (TBAPF_6) as solvent and electrolyte, respectively.

Absorption spectra were recorded at room temperature using 1 cm path length quartz cells on a diode array spectrophotometer (Agilent Hewlett Packard, HP 8452A).

Spectroelectrochemical experiments were performed in a custom-built cell constructed from a UV-Visible cuvette containing a semitransparent working electrode (ITO), a Pt counter electrode, and an Ag wire as a quasi-reference. The cell was placed in the optical path of the sample light beam. Background correction was obtained by taking a spectrum from an electrochemical cell with a naked ITO, under conditions identical to those of the experiment with the polymer film.

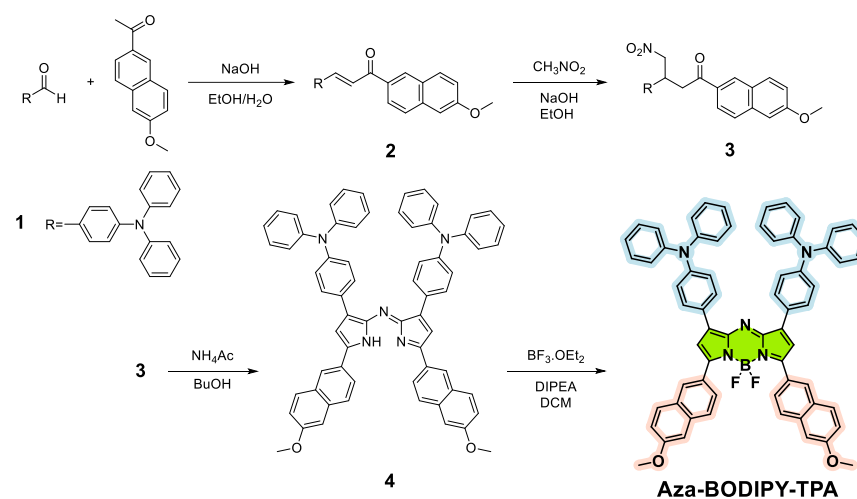
3. Results

3.1. Synthesis

The detailed synthetic route for the preparation of aza-4,4-difluoro-4-bora-3a,4a-diaza-s-indacenes (aza-BODIPYs) is shown in Scheme 1. Chalcone **2** was prepared in good yield by aldolic condensation of the commercially available 6'-Methoxy-2'-acetophenone and 4-(diphenylamino)benzaldehyde **1**. After the Claisen-Schmidt condensation, the α,β -unsaturated ketone **2** was subjected to a Michael addition in the presence of CH_3NO_2 and NaOH in ethanol at reflux, affording 72% of **3**. The next step to the conjugate addition reaction was the treatment of the diaryl-4-nitrobutan-1-ones **3** with NH_4OAc in refluxing butanol to give the tetraarylazadipyrromethene **4** in 34% yield. Finally, a complexation reaction with $\text{BF}_3\cdot\text{OEt}_2$ and DIPEA in dry DCE was carried out to uneventfully yield the target **aza-BODIPY-TPA**.

The synthetic design of this NIR absorber enabled the preparation of a monomer bearing two electropolymerizable, electron-donating TPA groups, suitable for the fabrication of surfaces by electrosynthesis in which the aza-BODIPY cores are embedded within

the polymeric matrix. Moreover, the presence of strongly electron-donating TPA moieties at the 1,7-positions, combined with the extended π -system provided by the naphthyl-fused groups at the 3,5-positions, affords an aza-BODIPY derivative with high absorption in the near-infrared region.



Scheme 1. Synthesis of **aza-BODIPY-TPA**.

3.2. Electrochemistry

CV and DPV were carried out to investigate the electrochemical properties of **aza-BODIPY-TPA** (Figure 1). Anodic scans over different potential ranges were explored to examine the processes associated with the electroactive groups, namely the TPA substituents and the aza-boron dipyrromethene core. The first two oxidation and the reduction peaks can be assigned to the aza-BODIPY center [5], while subsequent oxidation events correspond to the TPA moieties. DPV, known for its superior resolution of multi-electron processes, confirmed the CV observations, revealing two oxidation peaks and a broad feature at 1.2–1.7 V, likely arising from overlapping oxidation events. The oxidation of TPA groups is consistent with the well-known radical cation coupling mechanism, leading to the formation of TPA dimers (tetraphenylbenzidine, TPB) that can themselves undergo reversible redox processes. In the monomeric state, such coupling is expected to promote the generation of electroactive oligomeric or polymeric species [6,7].

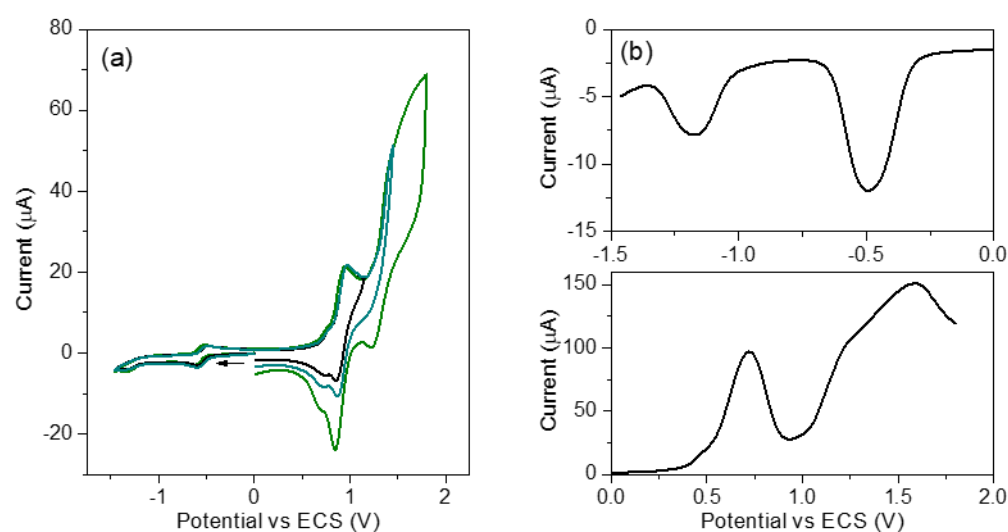


Figure 1. (a) CV sweeps at different applied potential programs (b) DPV cathodic and anodic of **aza-BODIPY-TPA** monomer. Pt working electrode, scan rate 100 mV/s. DCE/0.10 M, TBAPF₆.

Figure 2a shows that continuous cycling through the higher oxidation potentials produces a progressive increase in both oxidation and reduction currents, along with the appearance of new redox systems, indicating the growth of electroactive films on the electrode surface. As established in the literature, oxidized TPA units generate highly reactive radical cations that couple to form TPB, which are more easily oxidized than the parent monomers [6]. To confirm film formation, electrochemical responses were recorded in a monomer-free solution (Figure 2b). The resulting films displayed two main reversible redox processes, with bell-shaped voltammograms characteristic of adsorbed reversible couples [6]. Moreover, the linear dependence of peak current on scan rate supports this assignment. These processes can be attributed to the redox activity of both the aza-BODIPY core and the TPB units [5–7].

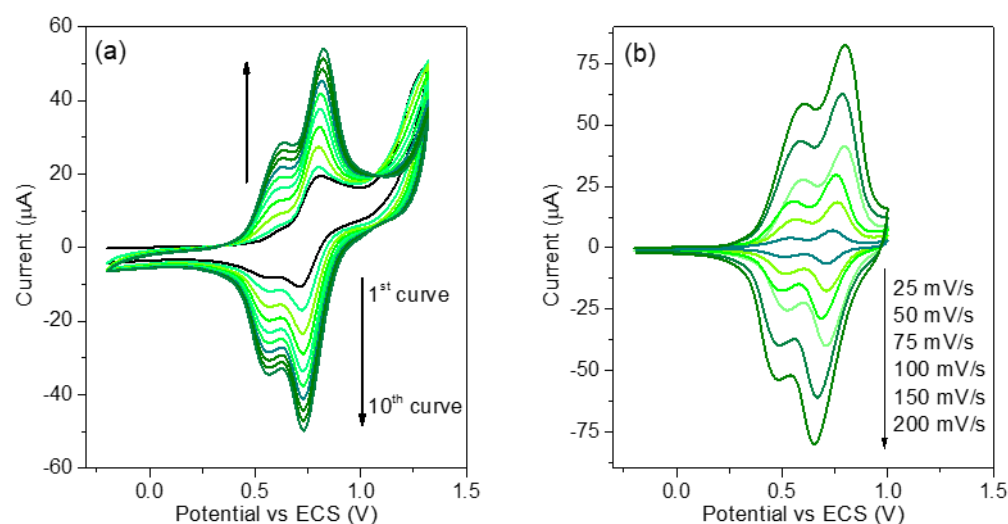


Figure 2. (a) CV of **aza-BODIPY-TPA** recorded over 10 successive anodic cycles in DCE/0.10 M TBAPF₆ on Pt electrode. (b) Electrochemical response of the polymeric film vs. scan rate using a monomer-free solution (DCE/0.10 M, TBAPF₆).

3.3. UV-Visible Absorption Properties of Monomers and Films

The absorption spectra of **aza-BODIPY-TPA** were recorded in DCE (Figure 3a). The compound displayed an absorption band with $\lambda_{\text{max}} \sim 800$ nm with a high molar absorption coefficient, together with an additional band with $\lambda_{\text{max}} \sim 540$ nm [5,8]. Both the monomer and the polymer (Figure 3a,b) exhibited similar spectral characteristics: a dominant absorption band in the visible and near-IR region. However, the absorption bands are broader and red-shifted in comparison with those of the monomer in solution. Comparable spectral patterns have been reported for other diphenylamino-substituted systems, including subphthalocyanines, phthalocyanines, and BODIPYs [9,10]. These facts indicate the presence of interaction between aza-BODIPY centers in the branched film structure [8]. Finally, spectroscopic analyses confirm that the **aza-BODIPY-TPA** chromophore remains intact within the polymer chain formed after the electropolymerization process.

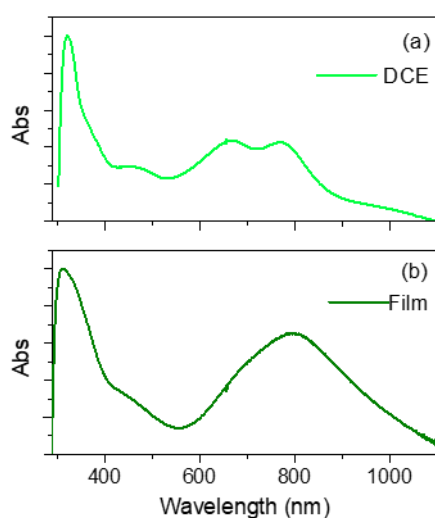


Figure 3. Absorption spectra of the **aza-BODIPY-TPA** monomer (a) in DCE solution; (b) polymer film.

3.4. Spectroelectrochemical Characterization of Film

To evaluate the electro-optical properties and reversibility of the redox processes, polymeric films were deposited on semitransparent ITO electrodes. As on Pt, the films remained electroactive and irreversibly adsorbed to the surface (Figure A1). In the neutral state, the spectra exhibited a band at 315–400 nm, assigned to π – π^* transitions of TPB units, together with the characteristic aza-BODIPY band near 450 nm and a broad absorption centered at ~800 nm [4,5]. When cycled to the highest oxidation potentials (Figure 4a), the TPB band at 315–400 nm progressively decreased, while new features appeared: a band at 470–500 nm, attributed to TPB radical cations, and a broad absorption between 600–1000 nm with a maximum at ~745 nm, assigned to TPB dications [5,6]. A weaker near-IR feature at ~1030 nm also developed during oxidation. Traces of absorption maxima versus potential (Figure 4b) enable to observe these spectral changes: the 340 nm band diminished as potential increased, while the 470 nm band initially grew but decreased as radical cations converted to dications, accompanied by the bleaching of the aza-BODIPY band [4,7]. The 745 nm band rose at the onset of the second oxidation and reached its maximum intensity at full oxidation. Importantly, all bands recovered their original intensity upon the reverse scan, demonstrating full reversibility of the electrochemical processes. These reversible spectral changes, spanning the visible and near-IR regions, underscore the potential of these films for electrochromic applications such as smart windows, combining light modulation with thermal control.

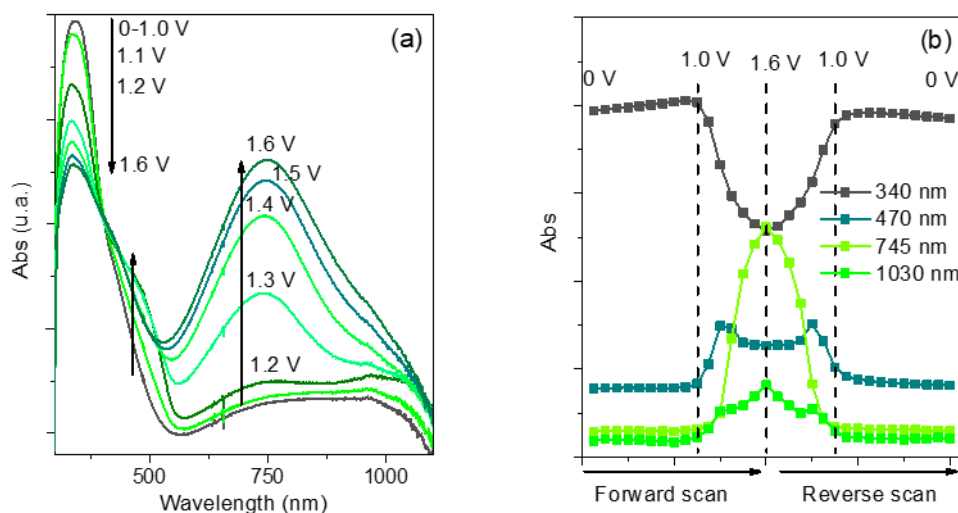


Figure 4. (a) Spectra of the film at different applied potentials according to CV. (b) Absorption traces of the film at selected wavelengths as a function of the advance in the forward and reverse scans of the CV in (a).

4. Conclusions

An aza-BODIPY monomer functionalized with TPA groups was successfully designed, synthesized, and electropolymerized onto Pt and ITO electrodes through repeated CV cycling. Electrochemical and spectroelectrochemical analyses confirmed the presence of TPB units in the resulting films, supporting an electropolymerization mechanism based on the coupling of radical cations generated during anodic scans. Furthermore, the films were evaluated as electrochromic materials, exhibiting distinct absorption changes in both the visible and near-infrared regions upon redox switching. These findings highlight the potential of this new aza-BODIPY-based polymer as a promising candidate for advanced electrochromic device applications.

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

Abbreviations

The following abbreviations are used in this manuscript:

Aza-BODIPY	Boron aza-dipyrromethene
CV	Cyclic voltammetry
DPV	Differential pulse voltammetry
TPA	Triphenylamine

Appendix A

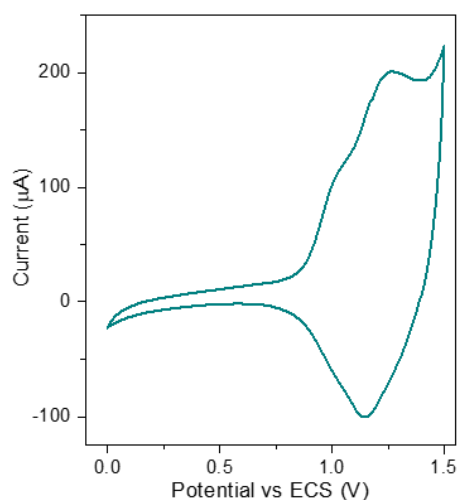


Figure A1. CV polymeric film on ITO electrode (DCE/0.10 M, TBAPF₆).

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