



A new gold electrode modified with azido-terminal BODIPY derivative: synthesis, characterization and electrochemical property

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Abstract

This paper was aimed to modify gold electrode surface with a BODIPY derivative and to examine its electrochemical behavior on the modified surface. Firstly, a BODIPY derivative including azido terminal was synthesized and characterized with several techniques such as NMR, FT-IR, element analysis and melting point. For the electrochemical studies, a triple electrode system was applied, with Gold electrode, Ag/AgCl (in aqueous medium) or Ag/Ag⁺ (in non-aqueous medium) and a Pt wire. The modified surface has been characterized using different electrochemical techniques. Then, the morphologies of the bare and modified electrode surfaces were evaluated with Scanning Electron Microscopy and Atomic Force Microscope. The metal adsorption property of the modified surface was investigated by using a copper solution.

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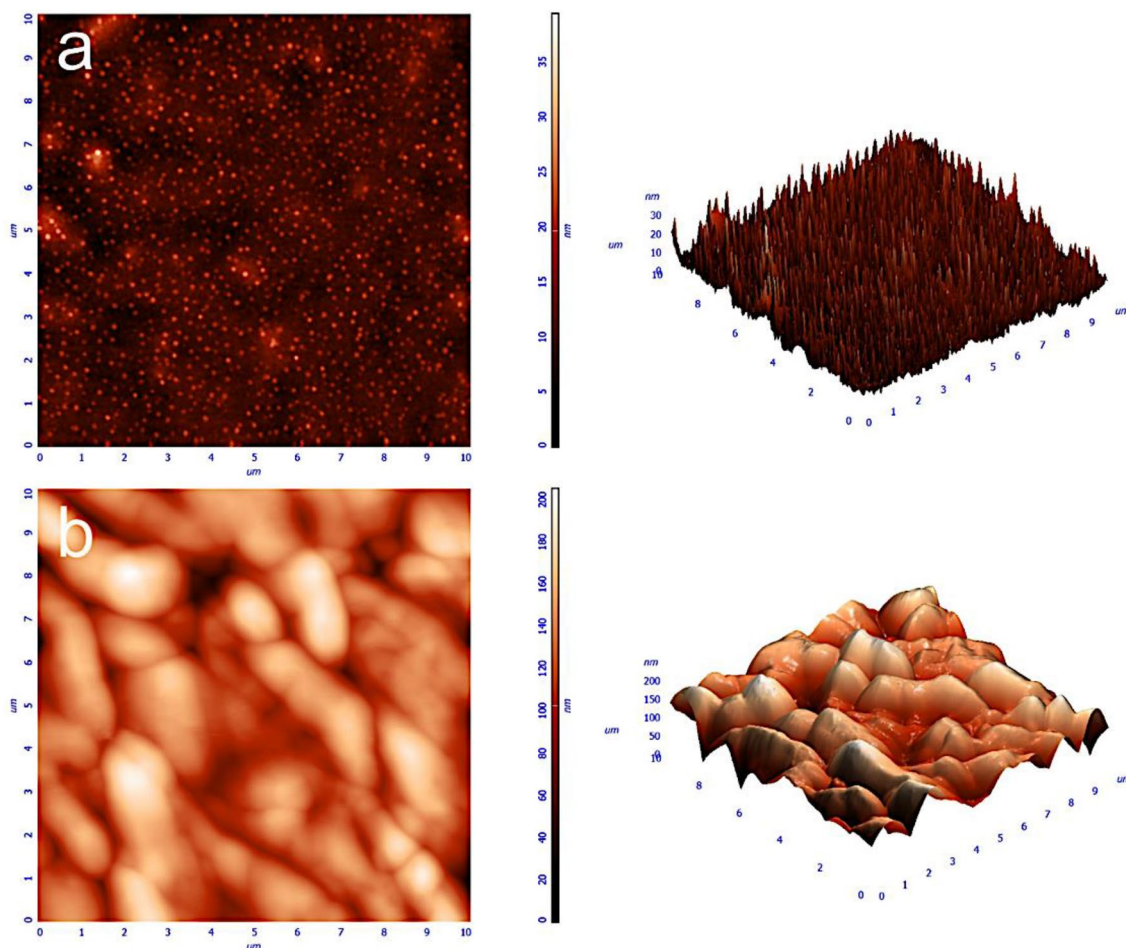
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Graphical abstract



Keywords BODIPY · Cyclic voltammetry · Gold electrode · Modification · Surface analysis

1 Introduction

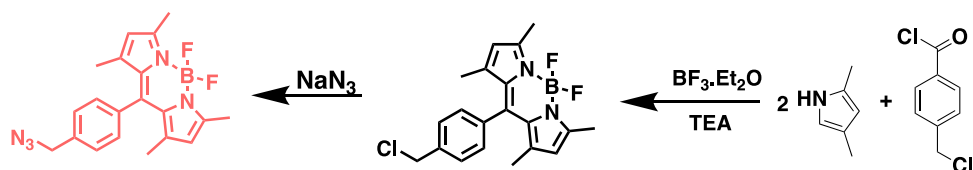
Numerous BODIPY syntheses have been published over the years of the first BODIPY complex of Dipyromethenes, reported by Treibs and Kreuzer in 1968. BODIPY dyes have many excellent optical properties such as great absorption coefficients, excellent chemical and photochemical stability, great fluorescence quantum yields, long excited-state lifetimes as well as high solubility in organic solvents [1, 2].

Because of their wonderful properties, BODIPY dyes are used in medical expertise such as bio labeling, bio-imaging, PDT, photodynamic therapy of cancer, etc. and different application areas such as solar energy conversion, chemical sensing, optoelectronic devices, laser dyes [3–11]. BODIPY dyes are unique materials with electrochemical properties comparable to those of aromatic hydrocarbons. Electrochemical studies to understand the redox properties of these complexes are beneficial [12,

13]. Most of the BODIPY research that has been done is on their properties, and there is less work on their electrochemical properties [14, 15]. But recently, electro-polymerization of BODIPY dyes containing electroactive groups has been investigated to produce low band gap polymers, electrochromic materials [16–19]. It has been observed that BODIPY dyes show good redox properties and exhibit both reduction and oxidation waves due to the addition or removal of electrons from the π -system [20, 21].

In this study, the electrochemical behavior of 8-{4-(azidomethyl)phenyl}-4,4-difluoro-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (BODIPY-I) (Fig. 1), which is a derivative of BODIPY synthesized for the first time by Kursunlu and his research group [22–28] was investigated by spectroscopic and electrochemical techniques on the gold electrode surface. Metal adsorbing property of the prepared BODIPY-I /Au surface in Cu^{2+} solution was investigated.

Fig. 1 Synthesis of 8-[4-(azidomethyl) phenyl]-4,4-difluoro-1,3,5,7-tetra methyl-4-bora-3a,4a-diaza-s-indacene (BODIPY-I)



2 Experimental

2.1 Materials

Acetic acid (100%) and potassium chloride (99.0%) were purchased from Riedel-de Haen. Acetonitrile (CH_3CN , ACN, 99.9%) was purchased from J.T.Baker. Copper (II) chloride (98.0%), boric acid (99.8%), *o*-phosphoric acid (85.0%), sodium hydroxide (97.0%), hydrochloric acid (37%) and sulfuric acid (95.0%) were purchased from Merck. Potassium ferricyanide (98.0%) and Potassium ferrocyanide (98.0%) were purchased from Alfa Aesar. Ruthenium hexamine (III) chloride (98.0%), sodium acetate trihydrate (99.0%) and tetrabutylammonium tetrafluoroborate (TBATFB, 99.0%) were purchased from Sigma-Aldrich. BODIPY-I was prepared a known synthesis procedure.

2.2 Instruments

While Gamry Reference 600 and Series G 750 potentiostat/galvanostat/ZRA instruments were used for electrochemical studies, applications of electrochemical impedance spectroscopy (EIS) technique were made with EIS 300. Gamry Framework, Echem Analyst, PHE 200, PV 220 and EIS 300 software in the computer system connected to the main unit were used to automatically perform the applied voltametric techniques and EIS technique and to evaluate the data obtained from these computer-controlled electrochemical measurement systems. A three-electrode Bioanalytical system (BAS) C3 cell system was used for electrochemical studies in which working, reference and counter electrodes were used together.

BAS Model MF-2013 gold (Au) electrode was used as working electrode. The reference electrode was used as: (i) a Ag/AgCl in saturated KCl (Ag/AgCl/(sat.KCl)), which was used in aqueous media; or (ii) a Ag/Ag⁺ (in 10 mM AgNO₃), which was used in non-aqueous media [to prepare a Ag/Ag⁺ reference electrode, 10 mM AgNO₃ was dissolved in acetonitrile (CH_3CN) with 100mM tetrabutylammoniumtetrafluoroborate (TBATFB)]. Pt wire was used as counter electrode.

2.3 Preparation and modification of gold electrode

The slightest contamination on the electrode surface can cause adverse effects such as the decrease in the peak current

in voltammograms and negative or positive shifts in the peak potential. Before starting the electrochemical experiments, the surfaces of the working electrodes to be used in the experiment must be clean. The purpose of electrode surface cleaning processes can be explained as the removal of substances adsorbed to the surface that interferes with electron transfer [29]. For this purpose, the gold (Au) electrode was first electrochemically cleaned in 0.1 M H₂SO₄ solution for 10 cycles in the potential range of $-0.2/+1.8$ V. Then, suspended alumina powder was placed on the velvet surface, and this electrode was cleaned with alumina powder in circular movements in equal numbers. After cleaning with alumina, the electrode surface was washed with pure water to remove any alumina dust that might remain on the surface. Then, the electrode was sonicated in pure water and acetonitrile for three minutes each.

The gold electrode surface was modified by the drop dry method [21, 30]. 20 μL of BODIPY-I solution (1.0×10^{-3} M) prepared in ACN medium containing 0.1 M tetrabutylammonium tetrafluoroborate as the supporting electrolyte was dropped to the cleaned gold (Au) electrode surface, and then the electrode surface was waited to dry at room temperature. The surface prepared after this step was defined as BODIPY-I/Au electrode.

3 Results and discussions

3.1 Characterization of the modified electrode

Since the BODIPY dye includes a near planar π -system and the two pyrrole rings being held co-planar by the tetrahedral geometry of the boron atom, there is scope for adsorption onto the electrode through π - π stacking similarly to what has been defined before with phthalocyanines [31, 32]. The modified electrodes were prepared and characterized several times.

3.2 Electrochemical characterization of bare Au and BODIPY-I/Au surfaces by cyclic voltammetry

The electron transfer behavior of the bare and modified BODIPY-I/Au electrode was examined using the cyclic voltammetry (CV) technique in 1mM Fe(CN)₆³⁻ solution prepared in Britton–Robinson (BR) buffer solution (pH 2.0) (Fig. 2). The varying peak potentials are the result of different

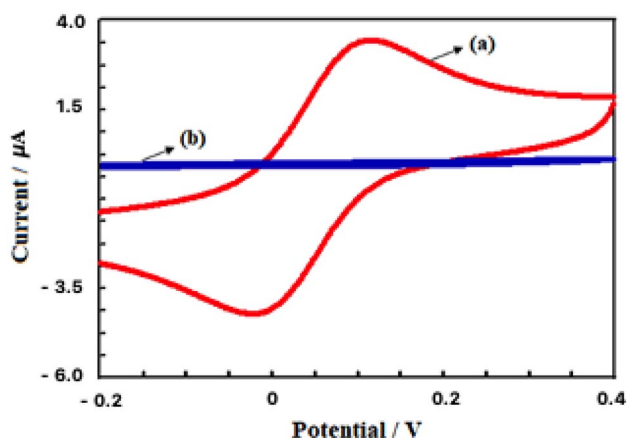


Fig. 2 Comparison of voltammograms of bare Au (a) and BODIPY-I/Au (b) electrode surfaces in 1 mM $\text{Fe}(\text{CN})_6^{3-}$ solution prepared in BR buffer solution (pH 2.0) (applied at 100 mV/s scan rate against Ag/AgCl reference electrode)

surfaces of the electrodes showing the different ability to electron transfer [33].

Bare electrode surface allowed electron transfer for $\text{Fe}(\text{CN})_6^{3-}$, while modified electrode surface coated with BODIPY-I did not allow electron transfer for $\text{Fe}(\text{CN})_6^{3-}$. Thus, it was determined as a result of the surface modification that a different surface was obtained from the bare electrode surface. It shows that the electrode surface is modified with BODIPY-I material since the currents and potentials of the $\text{Fe}(\text{CN})_6^{3-}$ peaks cannot be determined on the electrode surface. We can say that the azide unit in the BODIPY-I compound binds to the gold electrode surface, thus the compound is modified to the surface. However, this does not mean that the desired analytes cannot be determined [21, 34].

A scan rate study was performed to examine the reversibility or irreversibility of the reaction on the electrode surface modified with BODIPY-I and to determine whether the redox process of BODIPY-I material on the gold electrode surface is diffusion-controlled or adsorption-controlled. For this purpose, cyclic voltammograms were taken at different scan rates in 1.0×10^{-3} M BODIPY-I solution (Fig. 3A).

The slope value of $\log V - \log I_p$ graphs gives information about whether the redox processes are diffusion or adsorption controlled. In diffusion-controlled processes, 0.5 as the slope value is the theoretical value [35–37] (Fig. 3B). In Fig. 3B, it is observed that the reaction occurring on the surface is not diffusion-controlled because of the slope is not close to 0.5.

3.3 Characterization of bare Au and BODIPY-I/Au surfaces by EIS

Bare Au and BODIPY-I/Au electrode surfaces were spectroscopically characterized by the EIS technique and the results were compared (Fig. 4).

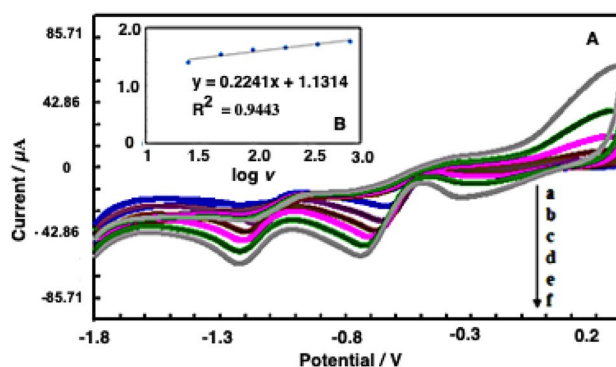


Fig. 3 A Cyclic voltammograms and B graph of $\log V$ versus $\log I$ of Au electrode surface in 1.0×10^{-3} M BODIPY-I solution in CH_3CN medium containing 0.1 M TBATFB at different scan rates [(a) 25 mV/s; (b) 50 mV/s; (c) 100 mV/s; (d) 200 mV/s; (e) 400 mV/s; (f) 800 mV/s]

When the data obtained as a result of the characterization with the EIS technique were evaluated, it was observed that the modified electrode surface showed more resistance to electron transfer in the $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ a solution containing the redox couple relative to the bare electrode surface. It shows that the BODIPY-I compound formed a film on the electrode surface and it was concluded that these data can be supported by the results obtained using the cyclic voltammetry technique.

3.4 The morphology of bare Au and BODIPY-I/Au surfaces by scanning electron microscope (SEM)

The Scanning Electron Microscopy technique was used to take surface images of the electrode surfaces, to have information about the surface morphology of the electrodes and

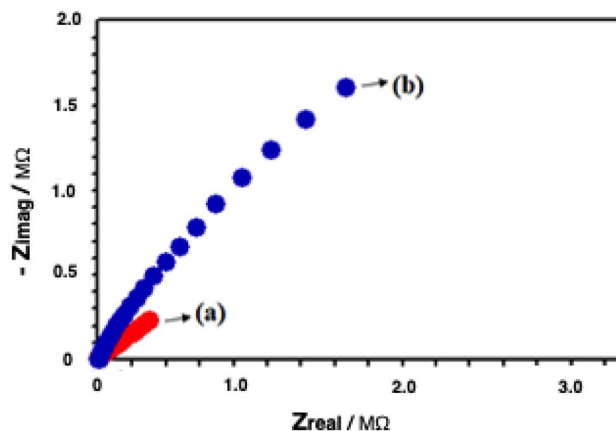


Fig. 4 Nyquist plots of 1.0mM $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ solution in 0.1 M of KCl of bare Au electrode (a) and BODIPY-I/Au electrode (b) (applied at 100mV/s scan rate against Ag/AgCl/KCl(sat.) reference electrode, Frequency range is from 0.03 to 100,000 Hz)

to observe the physical changes on the electrode surfaces (Fig. 5) [38].

The morphology of the BODIPY-I coated Au surface was characterized by SEM (ZEISS EVO LS 10). When the SEM images are examined, it is clearly seen that the empty gold surface (Fig. 5a) has a flat and smooth structure before the coating and that there are deposits of BODIPY-I on the gold surface after the coating (Fig. 5b). The BODIPY-I film layer formed on the surface after coating had been created pores on the surface. This increased the microscopic area of the electrode and facilitated the interlayer diffusion of analyte species [39].

As can be seen from the figures above, when the SEM image of the surface of the modified electrode was compared with the image of the bare electrode, it was seen that the

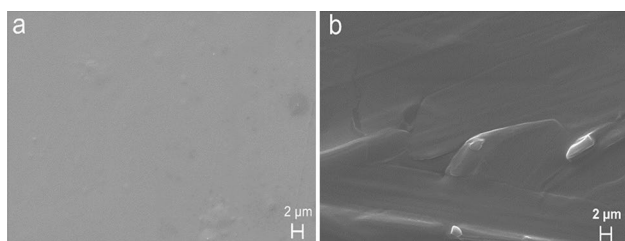
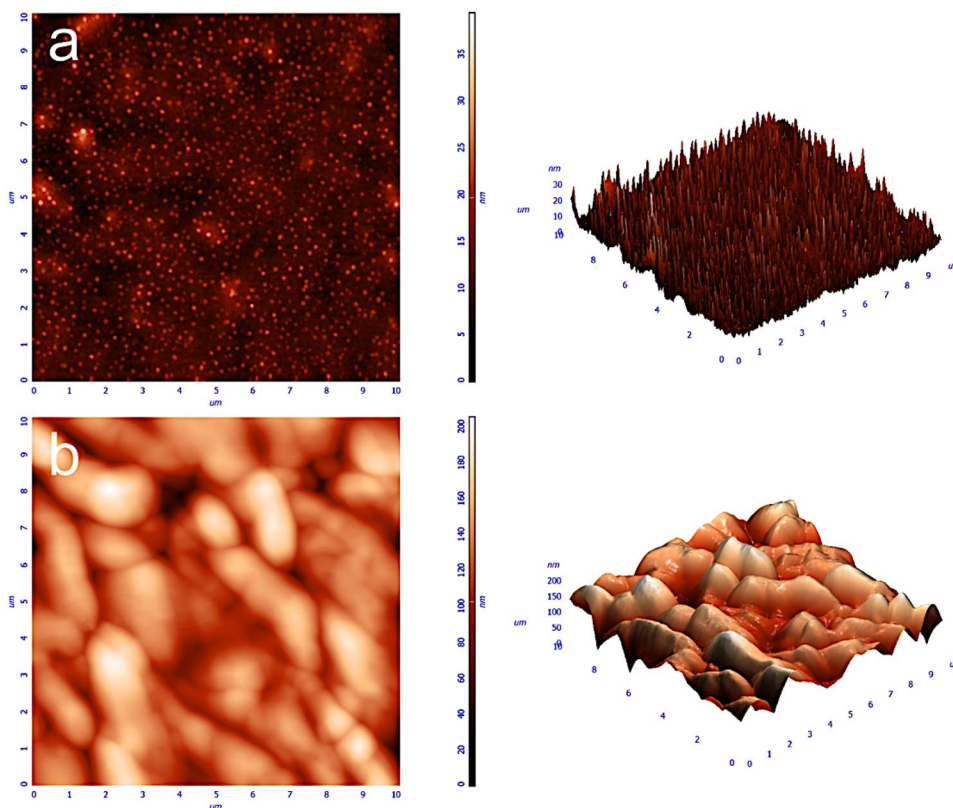


Fig. 5 SEM images of **a** bare Au and **b** BODIPY-I/Au electrodes surfaces

Fig. 6 AFM images of **a** bare Au and **b** BODIPY-I/Au electrodes surfaces



surface images are different. These surface images prove that the electrodes have been modified with BODIPY-I.

3.5 Topography of bare Au and BODIPY-I/Au surfaces by atomic force microscopy (AFM)

The topography of the electrode surface modified with BODIPY-I was also investigated by AFM studies. The presence of BODIPY-I substance on the electrode surface was demonstrated from AFM images (Fig. 6).

The significant increase in the roughness of the gold surface after coating indicated that BODIPY-I molecules were bound. The average roughness values (root mean square, rms) were 3.81 nm for the bare gold surface (Fig. 6a) and increased to 28.40 nm after coating (Fig. 6b). The higher sensitivities in electrochemical measurements can be expected using this modified electrode [40].

3.6 Metal application

To find the application areas of the prepared BODIPY-I/Au electrode surface and to examine the metal retention of the BODIPY-I material modified to the surface, BODIPY-I/Au electrode was immersed in CuCl_2 solution (acetate buffer pH 5.0) and kept for different times (1; 2; 4; 12 h). It was reduced using the cyclic voltammetry technique ($-0.9/+0.9$ V), then the copper retained on the surfaces

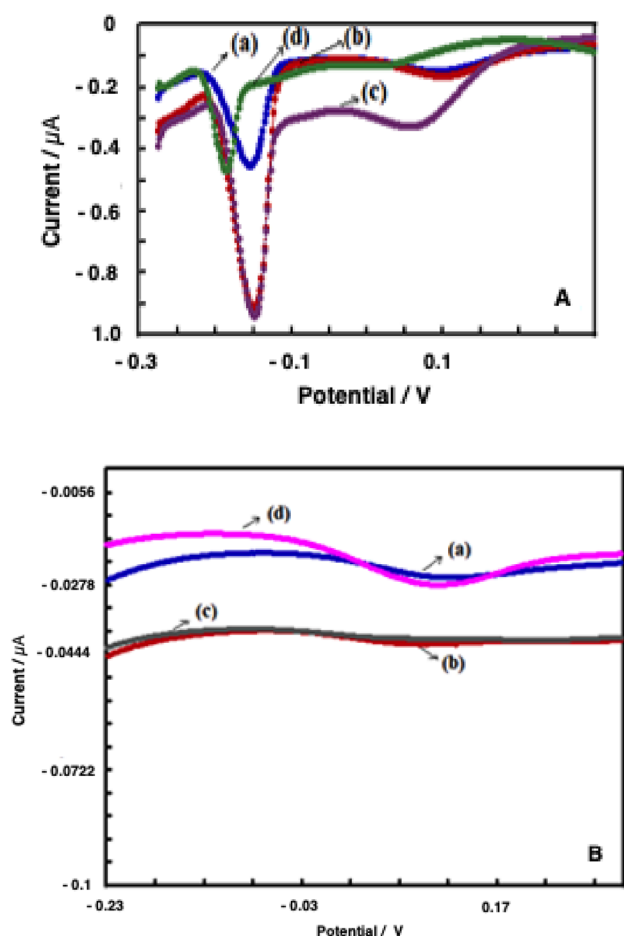


Fig. 7 DPV stripping voltammograms of BODIPY-I/Au electrode surfaces obtained after being kept in Cu^{2+} solution prepared in acetate buffer (pH 5.0) (A) and in acetate buffer (pH 5.0) (B) for different times [(a) 1 h; (b) 2 h; (c) 4 h; (d) 12 h]

was stripped by applying the differential pulse voltammetry technique ($-0.3/+0.3$ V). Then, the metal retention of the prepared electrodes was examined. It was determined as a result of the analysis that the copper was retained on the electrode surface. The variation with time of the bonding capacity of copper on the electrode surfaces was investigated from the peak current heights of the differential pulse voltammograms shown in Fig. 7A.

To understand whether copper or whether functional groups in the BODIPY-I compound of material were stripped from the surface, BODIPY-I/Au electrode surface was kept in pH 5.0 buffer solution for the same periods. The same procedures were applied to these electrodes with the techniques of cyclic voltammetry and differential pulse voltammetry, respectively. The resulting voltammograms were recorded (Fig. 7B). The obtained peak current heights were compared with the peak current heights obtained by copper stripping (Table 1).

Table 1 Difference of peak current heights obtained from DPV voltammograms of BODIPY-I/Au electrode surfaces kept in CuCl_2 prepared in acetate buffer (pH 5.0) and acetate buffer (pH 5.0) solution

Time (h)	Cu^{2+} solution in acetate buffer solution (pH 5.0) (Peak current height)	Acetate buffer solution (pH 5.0) (Peak current height)	Current difference
BODIPY-I/Au			
1	452.8	25.71	427.09
2	913.4	42.91	870.49
4	939.0	41.14	897.86
12	470.5	28.00	442.50

The results obtained from the BODIPY-I/Au electrode surface kept in Cu^{2+} and acetate buffer (pH 5.0) solutions are shown in Table 1.

According to the results obtained; It has been determined that the BODIPY-I/Au electrode surface is an active electrode in terms of metal retention. According to the test results in the copper solution medium, the gold electrode surface kept the copper for up to 4 h, after the 4th hour, no more copper could hold on the surface and the copper got off by oneself from the surface.

4 Conclusions

Due to the small number of electrochemical studies with BODIPY compound in the literature, the redox study of a BODIPY dyestuff was investigated in this study. The newly synthesized BODIPY-I compound was modified to the Au electrode surface by the drop-dry method. Our goal of surface modification with BODIPY-I dyestuff was successful. Successful results were obtained by examining the redox properties of BODIPY-I with electrochemical methods. In order to use the gold electrode as an electrochemical sensor, the change in the quality and conductivity of the electrode surface was investigated. The prepared electrode surface was successfully characterized and its usability in the field of metal applications was determined by voltametric methods. It is thought that this new electrode can be used successfully in studies to be carried out on the accumulation and removal of heavy metal copper.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10800-023-01963-3>.

Author contributions TG carried out the electrochemical applications. ZY carried out the some measurements. ANK synthesized compounds. EG wrote the main manuscript text.

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Data availability Not applicable.

Declarations

Competing interests The authors declare no competing interests.

Ethical approval Not applicable.

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