# Hybrid Co-Sensitization Using Natural and Synthetic Boron-Based Dyes for Enhanced Dye-Sensitized Solar Cells

Arcano Matheus Bragança Leite

Thesis submitted to the Graduate Program in Instrumentation and Applied Optics (PPGIO), jointly offered by the Federal Center for Technological Education Celso Suckow da Fonseca (CEFET/RJ) and Fluminense Federal University (UFF), in partial fulfillment of the requirements for the degree of Doctor of Electrical Engineering.

Adviser:

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# EPÍGRAFE

*“Transportai um punhado de terra todos os dias e fareis uma montanha”*

(Confúcio)

# RESUMO

## Co-sensibilização Híbrida Utilizando Corantes Naturais e Sintéticos à Base de Boro para Células Solares Sensibilizadas por Corante Aprimoradas

Arcano Matheus Bragança Leite

Orientadora: Profa. Dra. Ana Lucia Ferreira de Barros, D.Sc.

Este trabalho investiga a aplicação da técnica de cossensibilização para melhorar o desempenho fotovoltaico de células solares sensibilizadas por corante (DSSCs). Corantes fluorescentes baseados em complexos de boro, do tipo Boranil e Bodipy, foram sintetizados e utilizados como sensibilizadores, tanto de forma individual quanto em diferentes proporções volumétricas, conforme indicado pela Tabela 1. O desempenho desses sistemas foi comparado com o de corantes naturais extraídos de flores de *Chrysanthemum*. Na matriz de corantes naturais, o extrato de *Chrysanthemum* Violeta (CV) demonstrou o melhor desempenho individual, registrando uma eficiência de conversão energética (PCE) de 1.35%, suportada por uma densidade de corrente de curto-circuito ($J_{SC}$) de 0.85 mA/cm², tensão de circuito aberto ($V_{OC}$) de 0.58 V e fator de preenchimento (FF) de 0.44. Na avaliação dos compostos sintéticos em regime individual, a classe Bodipy exibiu superioridade frente ao Boranil, com a síntese ATH1005 (Bodipy D) alcançando um PCE de 2.26%. A mistura dos corantes Bodipy D e G, dispostos na proporção volumétrica de 1:3 (25%:75%), promoveu o maior aproveitamento do espectro eletromagnético na região visível do estudo. Esta configuração acarretou um rendimento (η) de 3.45%, acompanhado de um FF de 0.39, $V_{OC}$ de 0.59 V e $J_{SC}$ de 2.41 mA/cm² nas mesmas condições.

A caracterização óptica dos corantes foi realizada por espectroscopia UV-Vis e infravermelho por transformada de Fourier (FTIR), permitindo analisar o comportamento de absorção e a estrutura molecular dos sensibilizadores. A morfologia e a rugosidade superficial dos eletrodos foram investigadas por microscopia eletrônica de varredura (MEV) e microscopia de força atômica (AFM), evidenciando diferenças na uniformidade dos filmes e na interação com os corantes. O desempenho fotovoltaico das DSSCs foi avaliado por curvas densidade de corrente versus potencial (J–V) e potência versus potencial (P–V), complementadas por espectroscopia de impedância eletroquímica (EIS), permitindo analisar os processos de transporte de carga e recombinação.

Os resultados indicam que a cossensibilização com corantes à base de boro é uma estratégia eficaz para ampliar a captação de luz e melhorar o desempenho de dispositivos DSSCs, quando comparada ao uso de corantes individuais.

Palavras-chave: Células Orgânicas; Energia Solar; Cossensibilização, Energia Renovável.

# ABSTRACT

## Hybrid Co-Sensitization Using Natural and Synthetic Boron-Based Dyes for Enhanced Dye-Sensitized Solar Cells

Arcano Matheus Bragança Leite

Advisor: Profª. Drª. Ana Lucia Ferreira de Barros, D.Sc.

This work investigates the application of the co-sensitization technique to improve the photovoltaic performance of dye-sensitized solar cells (DSSCs). Boron-based fluorescent dyes, such as Boranil and Bodipy, were synthesized and used as sensitizers, both individually and in different volumetric proportions. The performance of these systems was compared with that of natural dyes extracted from Chrysanthemum flowers. In the natural dye matrix, the Chrysanthemum Violeta (CV) extract demonstrated the best individual performance, registering a power conversion efficiency (PCE) of 1.35%, supported by a short-circuit current density ($J_{SC}$) of 0.85 mA/cm², open-circuit voltage ($V_{OC}$) of 0.58 V, and fill factor (FF) of 0.44. In the evaluation of the synthetic compounds under individual conditions, the Bodipy class showed superiority over Boranil, with the ATH1005 synthesis (Bodipy D) achieving a PCE of 2.26%. The mixture of Bodipy D and G dyes, arranged in a volumetric ratio of 1:3 (25%:75%), promoted the greatest utilization of the electromagnetic spectrum in the visible region of the study. This configuration resulted in a yield (η) of 3.45%, accompanied by an FF of 0.39, $V_{OC}$ of 0.59 V and $J_{SC}$ of 2.41 mA/cm² under the same conditions.

The optical characterization of the dyes was performed by UV-Vis and Fourier transform infrared spectroscopy (FTIR), allowing the analysis of the absorption behavior and molecular structure of the sensitizers. The morphology and surface roughness of the electrodes were investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM), revealing differences in film uniformity and interaction with dyes. The photovoltaic performance of the DSSCs was evaluated by current density versus potential (J–V) and power versus potential (P–V) curves, complemented by electrochemical impedance spectroscopy (EIS), allowing the analysis of charge transport and recombination processes.

The results indicate that co-sensitization with boron-based dyes is an effective strategy to enhance light capture and improve the performance of DSSC devices when compared to the use of individual dyes.

Keywords: Organic cells; Solar energy; Co-sensitization, Renewable Energy.

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## List of Abbreviations

AFM Atomic Force Microscope.....13, 33, 42, 54, 62, 80

CEFET/RJ Centro Federal de Educação Tecnológica Celso Suckow da Fonseca.....13, 17, 34

CIGS Disseleneto de Cobre, Índio E Galio.....13, 18, 19, 20, 83

DSSC Dye Sensitized Solar Cell…….3, 19, 23, 24, 40, 48, 49, 60, 67, 70

EIS Electrochemical Impedance Spectroscopy……13, 33, 36, 48, 51, 58, 59, 77, 78

FF Fill Factor……..13, 48, 49, 50, 60, 76, 79, 80

FTIR Fourier Transform Infrared Spectroscopy……...13, 33, 36, 46, 54, 55, 66, 67, 68, 94

FTO Fluorine-doped Tin Oxide……..13, 23, 33, 37, 38, 51, 53, 54, 59, 60

HOMO Highest Occupied Molecular Orbital……..13, 24, 29, 47, 69

KI Iodeto de Potássio.....13, 39, 79

LaFEA Laboratório de Física Experimental Aplicada.....13, 34, 46, 47

LUMO Lowest Unoccupied Molecular Orbital……...13, 24, 29, 47, 69

MEV Microscópio Eletrônico de Varredura.....13, 33, 42, 43, 52, 59, 60, 80

MULTI Multi-potentiostat.....13, 33, 48, 57, 76

NANOFAB Laboratório Multiusuário de Nanofabricação e Caracterização de Nanomateriais. 13, 45, 53

NREL National Renewable Energy Laboratory……...13, 20

PEG Polietilenoglicol……13, 38

PCA Photocatalytic Activity…….13, 46, 60

PCE Power Conversion Efficiency……13, 15, 20, 26, 60, 77, 80

MSR Mean Squared Roughness……..13, 43

RPM Revolutions Per Minute……13, 38

TCO Transparent Conductive Oxide.....13, 23

UERJ Universidade do Estado do Rio de Janeiro.....13, 35, 36, 45, 53

UV-VIS UV Visible Spectrophotometer ..... ...13, 33, 46, 47, 56, 68, 80

## List of Symbols

$TiO_2$ Titanium dioxide

$P_{máx}$ Maximum power

$J_{sc}$ Short-circuit current

$V_{oc}$ Open Circuit Voltage

$I_{máx}$ Maximum current

$V_{máx}$ Maximum voltage

$\eta$ Performance

Pt Platinum

Si Silicon

SnO Tin Oxide

$I^-$ Iodide

$I_3^-$ Triodet

# Chapter 1 – Introduction

This work addresses the co-sensitization method in the fabrication of solar cells, aiming to increase power conversion efficiency (PCE) compared to cells manufactured using individual sensitization methods with Chrysanthemum flowers. It is worth highlighting the use of a novel combination, not previously described in the literature, of boron-derived sensitizers from the Bodipy class, specifically the dyes ATH1005, ATH1006, and ATH032, classified as (D), (E), and (G), respectively. The work is divided into five chapters. The first chapter provides a background on the chronological evolution of solar cells, contextualizing the state of the art of this technology and its importance in the field of renewable energies. The second chapter describes the entire experimental procedure for obtaining the cells, as well as a more detailed description of the procedures performed in this thesis. Chapter Three comprises the results and discussions of the analyses performed throughout the work, meaning both optical, structural, morphological, and electrochemical analyses, as well as a comparison with the literature. Chapter Four contains the conclusions obtained from the work and its future projections, while Chapter Five addresses all scientific production generated from the studies on solar cells.

## 1.1 - Motivation

Currently, the vast majority of technological developments are directly or indirectly linked to the production of electricity. Coupled with this, with population growth, the demand for electricity tends to increase over the years. For a promising future, we must therefore consider conscious development, to produce energy without causing significant environmental impacts. As a result of the aforementioned facts, we know that the demand for electricity will always be growing; we must therefore be concerned with how we can generate energy sustainably and meet this demand [1-4]. Therefore, one of the main challenges for society is replacing methods of generating electricity that degrade the environment, such as fossil fuels, for example [5,6]. In this sense, dye-sensitized solar cells, or DSSCs, are a good alternative because they produce electrical energy from a natural and abundant source: the sun. Dyes of natural origin are considered a viable option for sensitization in DSSCs because they have a low manufacturing cost compared to conventional silicon (Si) cells and are also readily available. [7].

## 1.2– Solar Cell Generations

Several technological advances have occurred that have led to the level of cell development we have today. Below, in Figure 1, a chronological summary of the main events in this area is presented.




**Figure 1.1** Chronology of the historical evolution of solar cells

### 1.2.1 - First Generation cells

The first cells to emerge comprise the first-generation cells, a photovoltaic technology based on thick crystalline films of Si, which can be monocrystalline or polycrystalline. They were first discovered in 1954, when Bell Laboratories announced the invention of silicon solar cells with an efficiency of 8%, which were considered the most efficient solar cells of the time. [8]. Approximately 90% of the photovoltaic market in 2016 consisted of crystalline silicon, making it the most common material used in the construction of solar panels [9].

An example of this type of technology are the panels present at CEFET/RJ, in Maracanã. Figure 1.2 shows an arrangement of panels installed at the institution; this set of panels is formed by crystalline silicon cells, delivering a power of 6 kilowatts-peak (kWp).

Its widespread use is due to its cost-effectiveness, with an efficiency of around 25% and an average lifespan of 20 years. Another key factor supporting the use of silicon is its elemental abundance, as it is the second most common element in the Earth's crust after oxygen [10, 11]. This widespread availability ensures a secure supply chain and benefits from substantial economies of scale as manufacturing expands. Furthermore, silicon exhibits excellent chemical and structural stability under standard operational conditions, which mitigates environmental degradation and ensures the long-term reliability of the devices. Therefore, we can conclude that first-generation solar cells are cells that have been introduced to the market for years, but from the point of view of increasing their efficiency, they have stagnated [12].



**Figure 1.2** First-Generation Panels Installed at CEFET/RJ

### 1.2.2 - Second Generation Cells

Second-generation cells are characterized by their use of thin-film technology in their production, aiming to manufacture cheaper cells than first-generation cells by using fewer materials and depositing them on glass composite substrates, which are equally abundant and inexpensive. Basically, second-generation cells have a structure composed of several ultra-thin layers of various semiconductors. An example is Copper Indium Gallium Diselenide (CIGS) thin-film cells [13]. Second-generation solar cells differ from first-generation cells mainly in the diversification of semiconductor materials. While first-generation cells, based on silicon, predominate in the market, second-generation cells explore a variety of materials, such as thin films of organic semiconductors, perovskites, and composite materials. This diversity allows for the optimization of specific properties, such as light absorption, charge mobility, and production cost. Second-generation solar cells generally operate on more advanced principles, such as absorbing photons to generate electron-hole pairs followed by the efficient separation of these charge carriers. Materials such as perovskites have gained prominence due to their unique crystalline structure, which facilitates the absorption of a wide range of wavelengths of sunlight.

Second-generation cells have important properties that make their application possible in various locations. A notable property is their flexibility, which is greater than that of first-generation cells, allowing for varied applications due to this characteristic, such as in portable devices, electronic clothing, and even solar devices in the civil construction and/or space sectors. An example of this purpose can be seen in Figure 1.3, which shows the extent of CIGS cells.

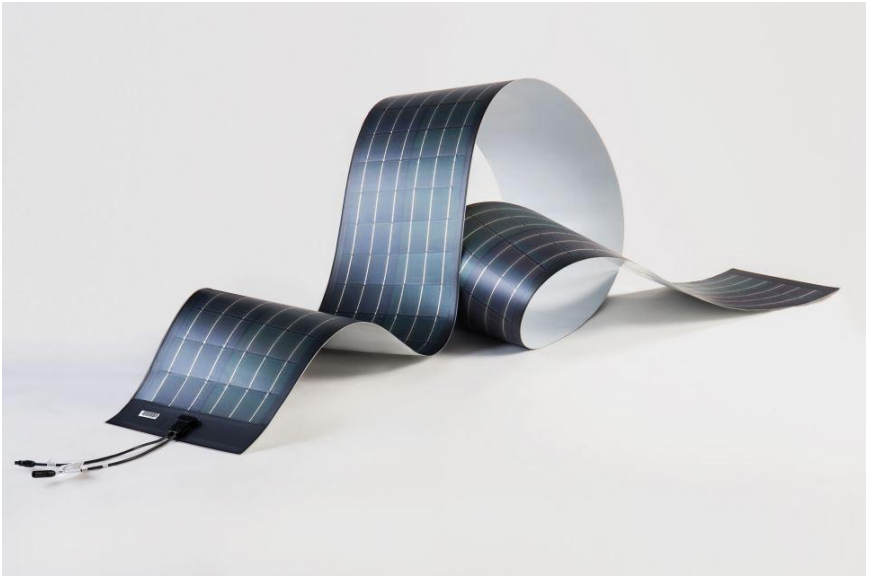


**Figure 1.3** Second-generation CIGS cell. [13]

However, second-generation cells have a lower yield level, the best efficiency achieved in the laboratory is 20.3%, as seen in CIGS [14]. Another point is that, depending on the manufacturing method of these cells, there may be limited availability of materials for construction, which leads to a long-term resource shortage.

### 1.2.3 – Third-Generation Cells and DSSC

Third-generation cells emerge as a way to optimize cells produced in the second generation, to research deposition techniques using thin film layers, employed in the second generation, but now on substrates with different shapes and new materials [14]. Third-generation solar cells aim to overcome the limitations of previous generations, seeking to improve overall efficiency and explore new energy conversion mechanisms. Unlike first- and second-generation cells, the third generation often incorporates concepts such as multiple photon absorption, quantum charge transfer, and the broader use of solar spectra. These innovations seek to maximize the efficiency in generating electricity from sunlight. Materials play a crucial role in the efficiency and functionality of third-generation solar cells. Nanomaterials, such as quantum dots and nanowires, have been widely explored due to their unique properties, such as the ability to tune light absorption across various ranges of the solar spectrum. In addition, conjugated organic materials continue to be the focus of intensive research, aiming to improve the stability and efficiency of these cells.

These types of third-generation cells are also known as emerging cells, as they are a recent technology with great potential. Among the cell types contained in third-generation cells, those shown in Figure 1.4 below stand out:

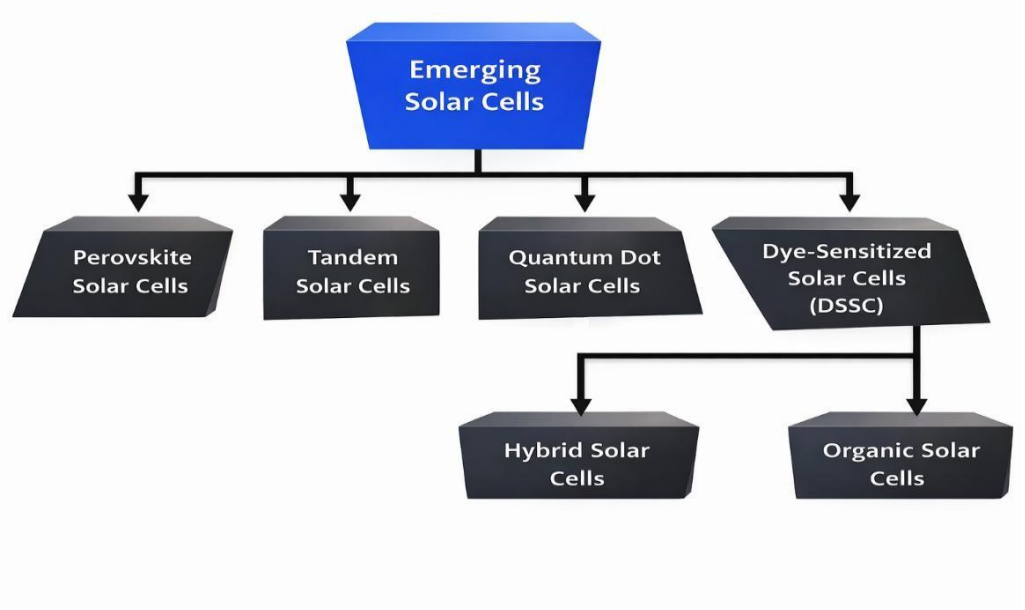



**Figure 1.4** Flowchart of the main third-generation cells.

Cells manufactured with Perovskite technology are cells built based on minerals with this particular structure. Perovskite has the property of superconductivity in converting solar radiation into electricity. A negative point in the large-scale production of this type of technology is that even with an efficiency of up to 20%, the production process of these cells shows some of the components with some degree of toxicity, such as lead, in addition to having a high deterioration compared to other technologies present in emerging cells [15]. Tandem technology is characterized by the combination of two subcells, usually of different materials, to increase PCE, while quantum dot technology uses quantum dots as photovoltaic absorption material. It attempts to replace materials such as silicon (Si), in bulk, and even second-generation CIGS.

Obtaining more efficient solar cells is fundamental to improving the cost/benefit of DSSCs, and with this, in recent decades all the integral parts of a solar cell have been studied, as well as its components, by various researchers around the world. Figure 1.5, created by the North American laboratory - National Renewable Energy Laboratory (NREL), projects the evolution from the point of view of energy efficiency of the types of solar cells made by various companies, from 1975 to the present day [16].

Based on the graph, it is possible to identify the categories of solar cells, divided into four main segments: multi-junction cells, silicon (Si) cells, thin-film cells, and emerging cells, with DSSCs falling into the last segment.

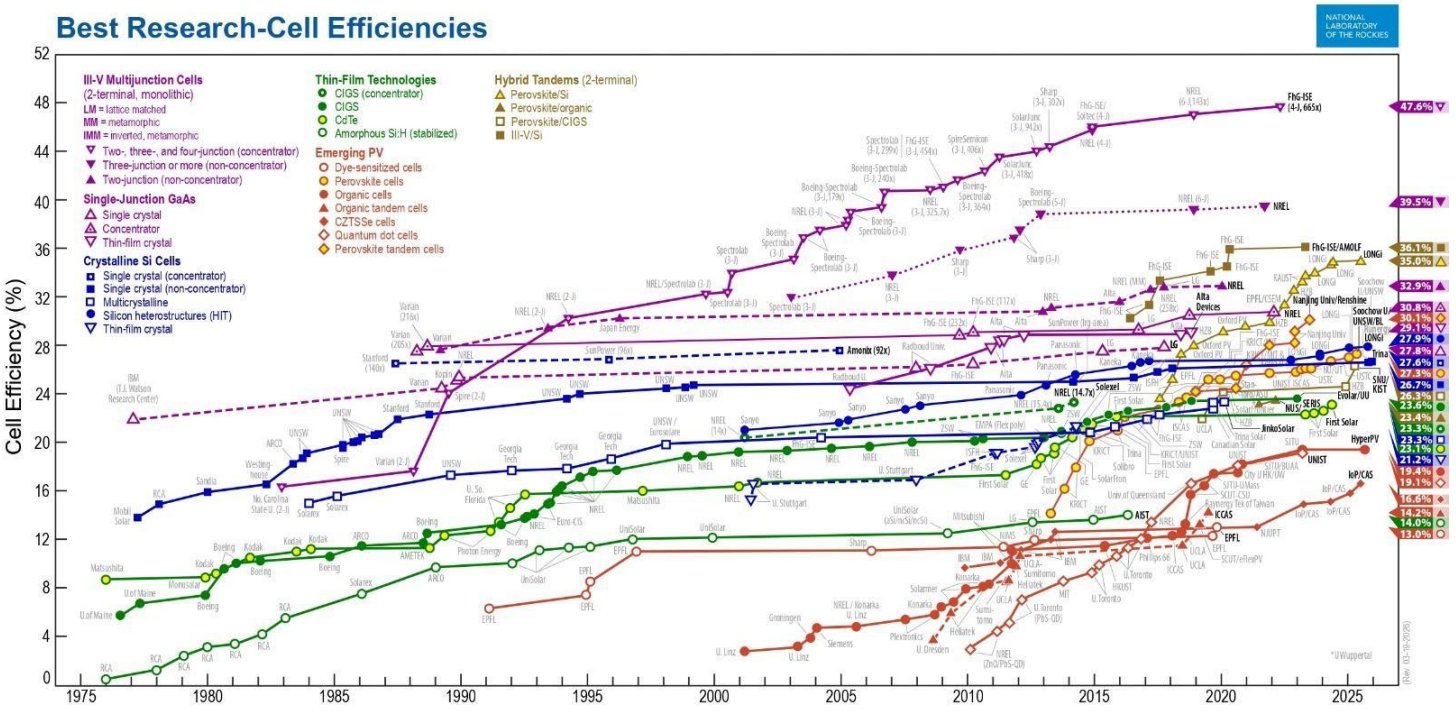



**Figure 1.5** Improved solar cell efficiencies over the years [16].

Although first- and second-generation solar cells dominate the commercial market due to their high stability and standard efficiencies (20–25%), their high manufacturing costs and rigorous processing requirements have driven the development of third-generation photovoltaic technologies. This emerging generation comprises two distinct strategies: high-efficiency multi-junction cells, which exceed 40% efficiency but are limited to niche aerospace applications due to extremely high production costs and low-cost alternative technologies. Among the latter, dye-sensitized solar cells (DSSCs) stand out as a highly promising alternative; despite offering lower energy conversion efficiencies, they can be manufactured via simple chemical routes and at a fraction of the cost, using abundant, non-toxic materials.

### 1.2.4 – Cells Developed in This Work

In this study, in order to investigate the impacts of using different sensitizers, a two-pronged approach was employed: the first was to analyze and understand the effects of individual natural sensitizers, more precisely sensitizers derived from the *Chrysanthemum* plant, where dyes were extracted from different Chrysanthemum species, namely violet, blue, and green, labeled as “C.V. (*Chrysanthemum Violet*)”, “C.B. (*Chrysanthemum Blue*)”, and “C.G. (*Chrysanthemum Green*)”, respectively. Chrysanthemums are one of the most popular garden flowers in autumn. Most chrysanthemums are easy to grow, needing only full sun, rich soil, good drainage, and good air circulation. Hundreds of varieties are available in various shapes and sizes, which can bloom from late summer to autumn. One of the advantages of working with natural sensitizers is the presence of various active groups for sensitization found in a wide variety of fruits, flowers, and plants in nature. Among them, we have chlorophyll, flavonoids, anthocyanins, cyanins, tannins, cyanidins, among others, as an accessible, fast, and sustainable option for application in DSSCs [17]. With these sensitizers, 3 complete cells were manufactured, composed of six electrodes, with 3 anodic electrodes coated with titanium dioxide ($TiO_2$) and 3 cathodic electrodes coated with platinum (Pt).

The second front of the research, after analyzing the behavior of cells manufactured with individual dyes, focused on studying the characteristics and properties of cells manufactured with a method not yet performed in the laboratory: hybrid sensitization or co-sensitization. From this, synthesized organic dyes were used, where prior knowledge of the excitation region in the electromagnetic spectrum was already available. These dyes, derived from boron (B) complexes, are called "Boranil" and "Bodipy". To compare the behavior of these individual dyes with the co-sensitized dyes, 7 complete cells were fabricated with single dyes: 3 derived from Boranil and 4 from Bodipy, totaling 14 electrodes for construction, 7 anodic ($TiO_2$) and 7 cathodic (Pt). In addition, 6 cells were fabricated with mixed dyes, requiring 12 electrodes for construction: 6 anodic ($TiO_2$) and 6 cathodic (Pt).

# Chapter 2 – Experimental Procedure

## 2.1 – Dye-Sensitized Solar Cells (DSSCs)

Dye-sensitized solar cells are also known as Gratzel cells, having been created in 1991 by Michael Gratzel and O'Regan [18]. Dye-sensitized solar cells or DSSCs are devices that have the ability to convert light energy, from photons, into electrical energy. This is done through semiconductor oxides that have a reasonably wide band, such as $TiO_2$, used in this study [19, 20]. There are DSSCs whose sensitization occurs through dyes with heavy metal complexes in their composition, as is the case with ruthenium-derived complexes, which, despite being the most efficient dyes registered within the class of emerging cells, with an energy conversion efficiency reaching up to 12%, using nanoporous electrodes [21], have a disadvantage in terms of environmental impact, since these heavy metal complexes, such as ruthenium polypyridyl, have low long-term availability [21]. In addition, they have a high cost, which makes the large-scale production of solar cells unfeasible. Thus, as an alternative, sensitizers or natural dyes can be used for the same purpose [22].

On the other hand, lately this research area has been focusing on sensitizers that are easily accessible and highly available in nature. This means dyes extracted from organic sources as photosensitizers. It is known that pigments containing anthocyanins and carotenoids denote an overall solar energy conversion efficiency of around 1%. These pigments are present in different parts of fruits and plants. It is also known that anthocyanins are part of a class of natural dyes that are responsible for various colors in the red-blue range, which can be easily found in nature. The anthocyanin molecule has some organic groups in its composition, two of which, the carbonyl and the hydroxyl, are able to bind to nanoporous surfaces.

Among the advantages of DSSCs, one of their main characteristics is the ability to work in cloudy or low-light conditions, thus having little impact on cell efficiency, whereas this is not possible with other cells, as they would fail under illumination below a certain threshold [23]. Another important factor is that, compared to traditional semiconductor cells, dye-sensitized solar cells have a low manufacturing and material cost. By controlling the deposition process, this cost is considerably reduced, as one of the main factors for the increased cost of manufacturing solar cells is the outsourcing of processes.

As it is a renewable energy generation process, environmental degradation is practically zero, and the conversion process is excited by a natural and abundant source, which is solar radiation.

### 2.1.1 - Components of a DSSC

Basically, a DSSC consists of layers, namely: a dye, a nanoporous semiconductor oxide anode, an electrolyte, a catalyst counter electrode, and two glass substrates coated with a conductive and transparent layer in the visible light spectrum in a TCO (Transparent Conductive Oxide) film, as shown in Figure 2.1.

When illuminated, titanium dioxide alone cannot absorb most of the solar spectrum, therefore it is necessary to apply the active layer or dye, which will be the layer responsible for sensitizing the thin film, absorbing photons and producing electrons, through an oxidation process. Subsequently, the electrons are injected into the semiconductor oxide, also called photoelectrode or photoanode. This oxide consists of a glass substrate coated with a transparent conductive oxide; in our case, this coating was made with fluorine-doped tin oxide (FTO). A thin film of nanoparticles of a specific semiconductor oxide is then deposited on its surface, in this study, it was $TiO_2$.

The cathode or counter-electrode is an element of the DSSC that regenerates the ions contained in the electrolyte. Therefore, attention must be paid to good components capable of adequately performing this catalytic effect, such as carbon, conductive polymers, among others [24]. In this work, platinum (Pt) was used, a material widely used in the literature for this function, and, similarly to the photoanode, the cathodic solution must be applied to the surface of a transparent conductive oxide, usually FTO.

The electrolyte consists of a liquid solvent containing a dissolved redox couple, which generates the positive and negative ions essential for charge transport within the DSSC. Once injected between the electrodes, this component bridges the chemical circuit of the cell. Specifically, the redox couple undergoes an oxidation process at the photoanode to regenerate the oxidized dye, and a subsequent reduction process at the counter electrode (photocathode), thereby closing the electrical circuit.

The compound ions in the electrolyte regenerate the oxidized dye and transport the electrons, through ionic transport, to the cathode, where they are regenerated [25, 26]. This cycle is illustrated in Figure 2.1:

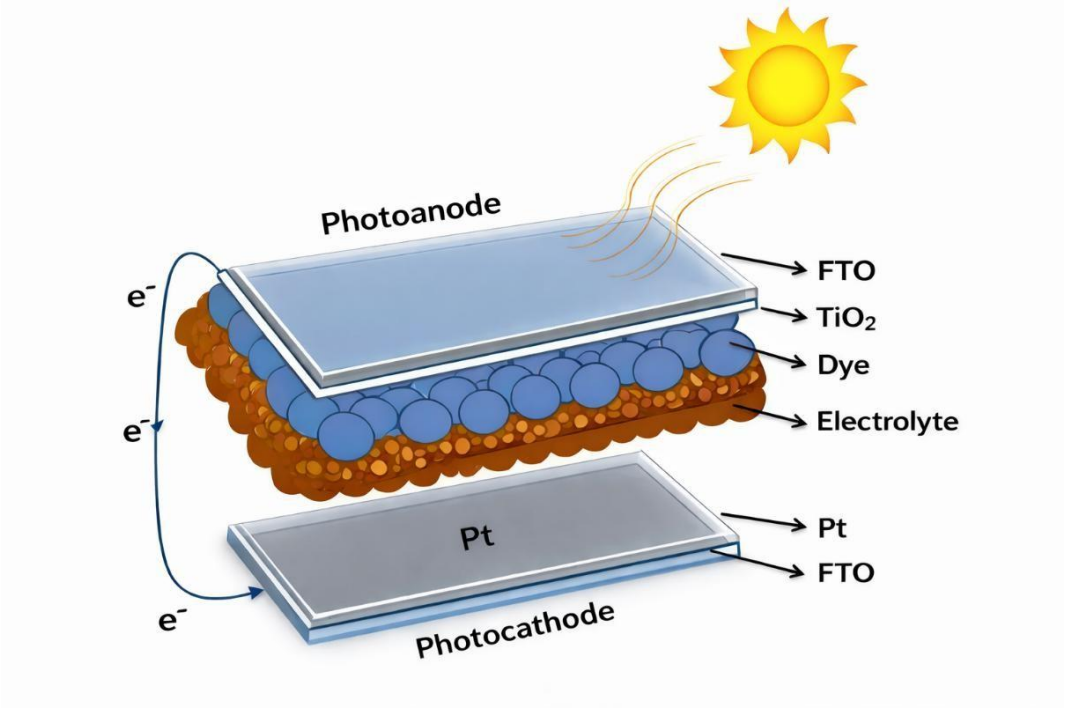



**Figure 2.1** Configuration scheme for the operation of a DSSC [28].

### 2.1.2 – Functioning of Developed Cells

It can be observed that initially the dye molecules are in their ground state, corresponding to the highest occupied molecular orbital (HOMO). When the solar radiation spectrum falls on the cell, the dye absorbs the photon and is excited from the HOMO to the lowest unoccupied molecular orbital (LUMO) [27]. In this excited state, the dye electron has enough energy to be injected into the conduction band of the semiconductor ($TiO_2$), which acts as an electronic transport medium. After the electron injection, the oxidized dye is regenerated by the redox electrolyte, ensuring the continuity of the photovoltaic process, as seen in Equations (1), (2), (3) and (4):

$$S \xrightarrow{\text{light}} S^* \quad (1)$$

Excited dye molecules (S*) are oxidized, according to Equation (2), and electrons are injected into the conduction band of the semiconductor. In this way, electrons can move freely, since the semiconductor is conductive at this energy level, as seen in step 2 of Figure 2.2.

$$S^* \rightarrow S^+ + e^- \quad (2)$$

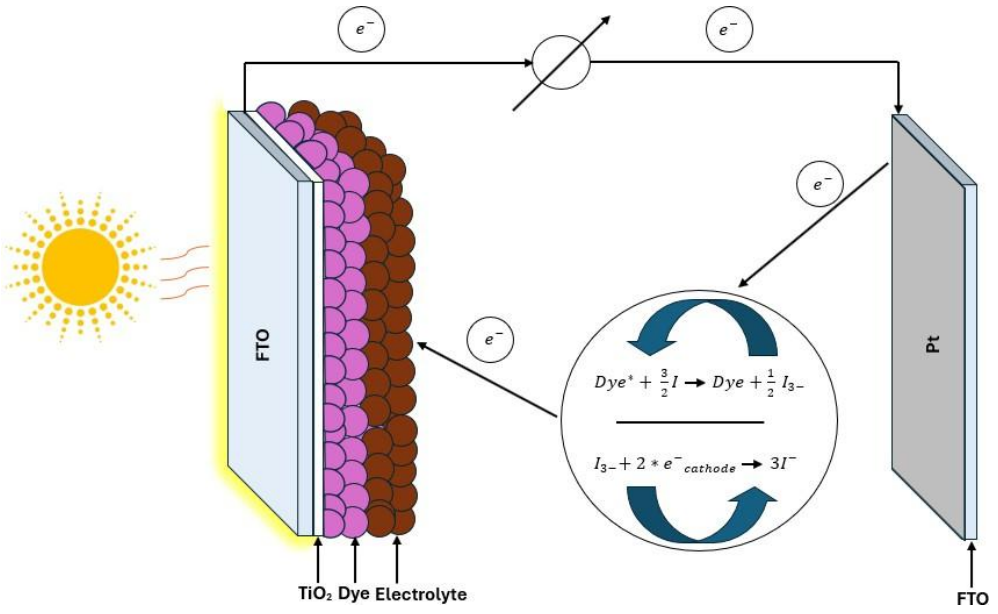



**Figure 2.2** Scheme of the operating principle of DSSCs [96].

Electrons are then transported to the anode current collector via diffusion processes. An electrical load can be supplied if connected. The oxidized dye (S+) is regenerated again by electron donation from the iodide in the electrolyte, as seen in step 3, according to Equation (3):

$$S^+ + \frac{3}{2}I^- \rightarrow S + \frac{1}{2}I_3 \quad (3)$$

In return, iodide is regenerated by the reduction of triiodide at the cathode, as seen in Equation (4) below:

$$\frac{1}{2}I_3^- + e^- \rightarrow \frac{3}{2}I^- \quad (4)$$

Electrons are then injected into the semiconductor oxide, and a redox pair enclosed in the electrolyte generates a decrease in the oxidized dye, which is regenerated at the cathode, as seen in the fourth step of Figure 2.2.

### 2.1.3 – Principle of Co-sensitization

Co-sensitization performed by two or more dyes with complementary optical absorption characteristics is an effective technique to increase the spectral response in DSSCs. Attention must be paid to the size and complementary optical absorption, because if they are not adequate in the sensitizers, the PCE may decrease instead of increasing, since in this case, desorption of the active material (dye) occurred during the co-sensitization process [29]. One of the advantages of working with natural sensitizers is the presence of several active groups for co-sensitization present in the most varied types of fruits and plants in nature. Among them, we have chlorophyll, flavonoids, anthocyanin, cyanin, tannins, cyanidins, among others as an accessible, fast and sustainable option for application in DSSCs [30-32]. This sensitization performed by the dye is essential because it plays a fundamental role in the absorption of the UV spectrum, in addition to the conversion of the photons present in this absorbed spectrum into actual electrical energy [33].

Simple dyes of Boron complexes, Boranil (ATH017, ATH019 and ATH024) and Bodipy (ATH1005, ATH1006, ATH031 and ATH032) were Labeled as A, B, C, D, E, F and G, respectively. As shown in the Figure 2.3.

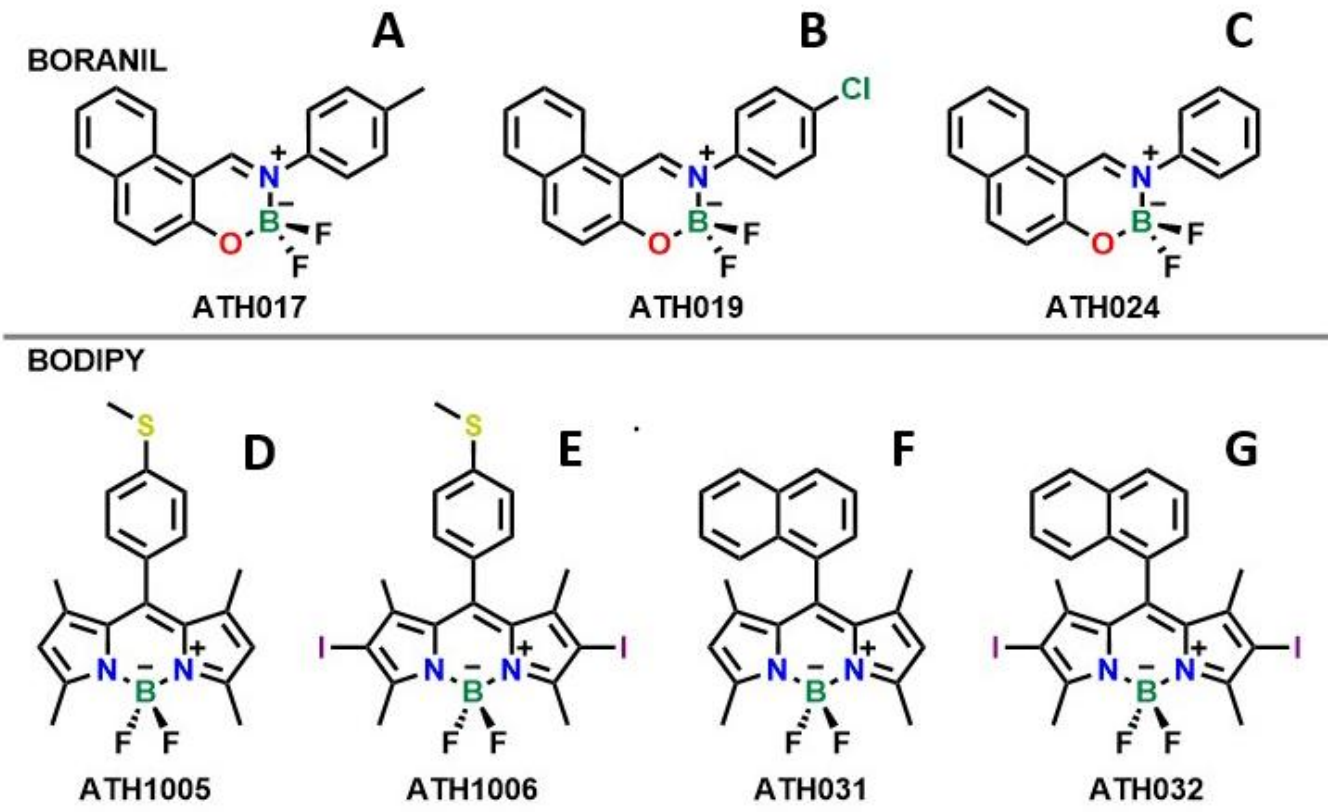



**Figure 2.3** Structures of the synthesized dyes.

Mixed dyes were classified as DG and EG (all prepared hybrid dyes were mixed in the volume percentage ratio of 75%:25%, 50%:50% and 25%:75%) and were used as co-sensitizers of the DSSCs present in this study. The description of the work shows that all PCEs of the fabricated cells increased when compared with a simple dye as a sensitizer. This denotes the fact that co-sensitization managed to cause an increase in the absorption spectrum and, thus, more photons were absorbed and converted into electricity. It is worth noting that in this study, the volume ratios whose spectral absorption increased were all 25%:75%. In other volume combinations, the mixtures reduced the photoactivity of the cell, not reaching the desired levels of efficiency. This work uses simple and mixed sensitizers for solar cells, extracted from different types of plants and synthetic dyes. The effect of the proportion of these mixtures after dye extraction is analyzed via optical, electrochemical, and photovoltaic properties.

In addition, co-sensitization was performed between the *Musa* fruit (Banana) and the *Gerbera* plant, under the same conditions of distribution of the percentage volume proportions of the synthesized dyes. However, here, the dyes do not have electrochemical compatibility, which denotes desorption of the active material, reinforcing the need for molecular organic confluence between the sensitizers.

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## 2.2 – Solutions for Sensitizing Dyes

### 2.2.1 – *Chrysanthemum* Sensitizers




**Figure 2.4** – Individual Dyes from *Chrysanthemum* Flowers

The individual chrysanthemum dyes used in this work were commercially acquired and extracted from the petals of the *Chrysanthemum* flower. Single dyes were denoted as CV (*Chrysanthemum Violet*), CB (*Chrysanthemum Blue*), and CG (*Chrysanthemum Green*), respectively, as shown in Figure 2.4. These individual dyes were previously washed and sterilized in an oven. The preparation method involved separating 10 g of powdered flower petals, measured with a SHIMADZU ATY224 balance, and crushing them with a mortar and pestle. The powder samples were then dispersed in 100 mL of ethanolic solution. Ethanol was used as a solvent because it has a hydroxyl group capable of dissolving pigments [34]. The flower dye dispersion was filtered using filter paper. After that, the solutions were stored in sterilized test tubes and placed in the refrigerator, as shown below in Figure 2.5:

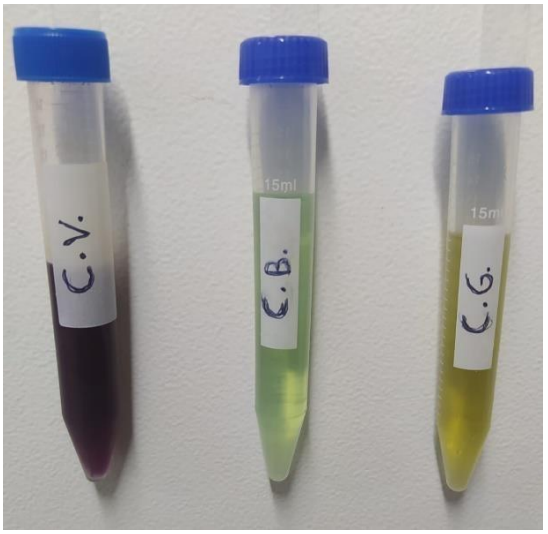



**Figure 2.5** – Individual Dyes from Stored *Chrysanthemum* Flowers

### 2.2.2 – Boranil and Bodipy Sensitizers

Currently, organic fluorescent dyes are considered potential materials due to their multidisciplinary applications in different fields, including bioimaging [35], organic light-emitting diodes (OLEDs), [36] dye-sensitized solar cells (DSSCs) [37], chemosensors [38], medicine and pharmaceutical applications, such as saccharide detection and explosive detection [39]. Boron difluoride complexes are known to have fluorescent optical properties. The study of different organic boron difluoride compounds has been the subject of much research interest [40,41]. In this context, researchers are focusing on developing new materials with desired properties through simple and low-cost synthetic procedures. This study makes use of two sensitizers derived from boron complexes, namely: Boranil and Bodipy.

The donor-acceptor (D-A) molecular system has gained considerable attention from the scientific community due to its applications in optoelectronic devices. Borodipyrromethene (Bodipy) dyes are known for their unique properties, such as strong absorption in the visible region, thermal and photochemical stability, and ease of synthetic functionalization [42, 43]. The growing interest in Bodipy-based complexes is mainly due to their spectroscopic properties, such as those mentioned above. In addition to these characteristics, many Bodipy derivatives exhibit a sharp absorption band (full width of half the maximum ~25 nm) around 500 nm and have long lifetimes in the excited state (about 5 ns for borodipyrrin dyes) [44]. The molecular structure of this sensitizer allows for the extension of the π-conjugated system and thus reduces the HOMO–LUMO energy gap. In some derivatives, the introduction of oxyethylene chains further contributes to chemical stability, good solubility, and film-forming properties, but these chains are not universal characteristics of the class. Thus, Bodipy derivatives form an important family of fluorescent dyes that have attracted considerable interest in recent years due to the combination of easy synthesis, stability and outstanding photosensitizing properties [45, 46].

The synthesized dyes from boron complexes were obtained in partnership with the Chemistry Department of the Institute of Exact Sciences (ICEx) of the Federal Fluminense University (UFF) - Volta Redonda Campus. The synthesized sensitizers were chosen considering the degree of excitation in the visible region of the electromagnetic spectrum, a region that favors the conversion of photons into DSSCs, in addition to the cataloging in the literature of the mixing of this class of dyes. Thus, the dyes from Boranil, more precisely the syntheses ATH017, ATH019 and ATH024 were classified as A, B and C, as indicated in Figure 2.6:

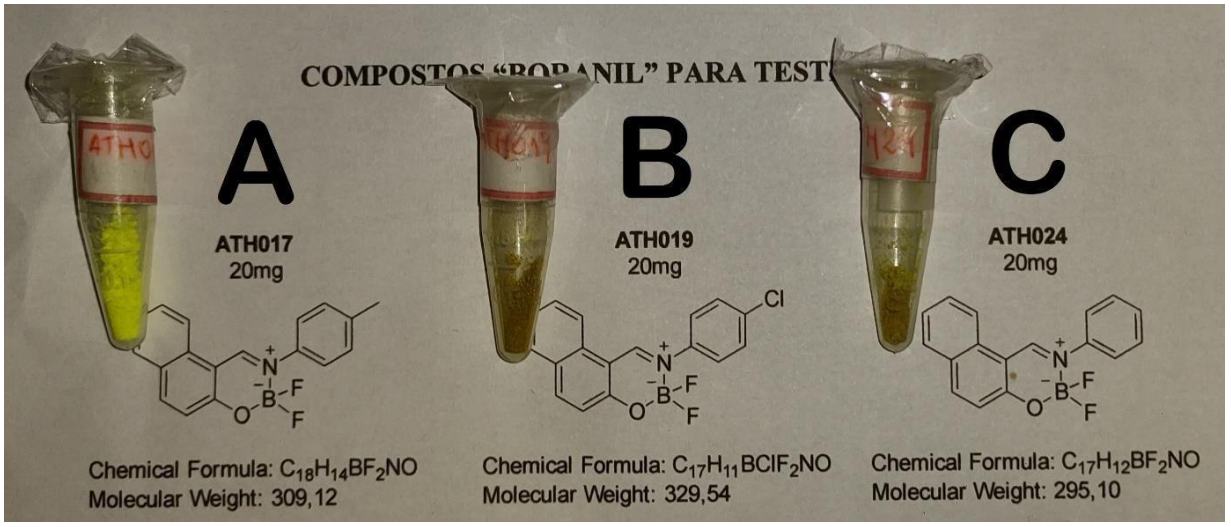



**Figure 2.6** – Boranil Individual Dyes

The Bodipy class dyes, also derived from boron complexes, specifically the syntheses ATH1005, ATH1006, ATH031, and ATH032, were similarly classified as D, E, F, and G, respectively, as described below in Figure 2.7:

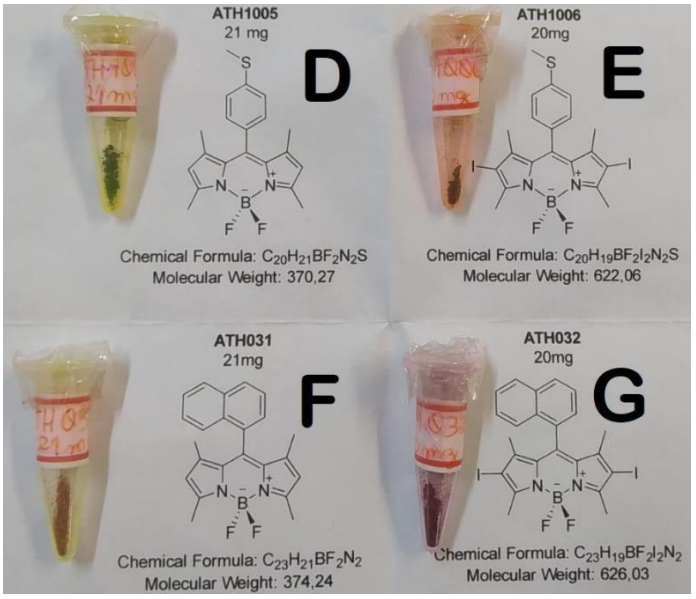



**Figure 2.7** – Bodipy Individual Dyes

Both classes of synthetic dyes were diluted in the same proportions as the *Chrysanthemum* dyes and similarly placed in tubes and stored for later refrigeration. Figure 2.8 shows the storage of the individual Boranil and Bodipy dyes.

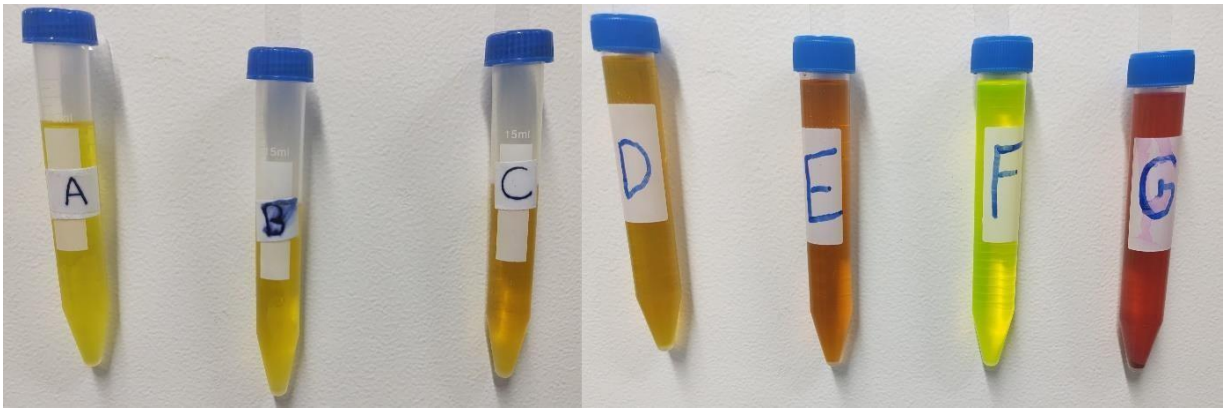



**Figure 2.8** – Individual dyes Boranil (A, B and C) and Bodipy (D, E, F and G)

Based on optical analyses performed on synthetic dyes, with the aim of obtaining the greatest coverage in the visible region of the electromagnetic spectrum, co-sensitization was carried out between dyes of the Bodipy class only, considering a better absorbance response under the same test conditions compared to synthesizers of the Boranil class.

### 2.2.2.1 – Co-sensitizers Dyes

To validate the co-sensitization method through mixing between Bodipy dyes, a third mix was made between banana fruit (*Musa*) and orange gerbera flower, both from previous studies [28, 48] with the intention of demonstrating the need for convergence between the sensitizers. The dyes used for this test are indicated in Figure 2.9.

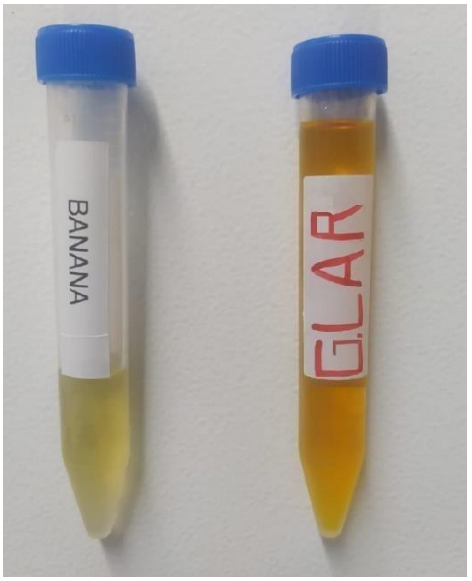



**Figure 2.9** Colorants extracted and filtered from Banana (B) and Orange Gerbera (L).

The volume ratio for each mixture was determined by taking 4 ml of a single dye as 100%. Therefore, for each mixture, the percentage volume division is directly based on 1 ml of a given dye, representing 25% of that dye. Since dyes from the Boranil class were disregarded for the sensitization process, Banana was classified as "B" and Gerbera Orange as "L". Thus, the distribution of sensitizers is shown in the table below.

**Table 1** Distribution of the sensitizers present in this study.

| Dyes | Concentration | Volume |
|---|---|---|
| ATH1005:ATH032 | (DG 3:1) | 75% D and 25% G |
| | (DG 1:1) | 50% D and 50% G |
| | (DG 1:3) | 25% D and 75% G |
| ATH1006:ATH032 | (EG 3:1) | 75% E and 25% G |
| | (EG 1:1) | 50% E and 50% G |
| | (EG 1:3) | 25% E and 75% G |
| Banana:G. Orange | (BL 3:1) | 75% B and 25% L |
| | (BL 1:1) | 50% B and 50% L |
| | (BL 1:3) | 25% B and 75% L |

After preparing simple dye solutions, nine mixed dye solutions were prepared as follows, as described in Table 1: ATH1005:ATH032 labeled as (DG 3:1) 75% D and 25% G, (DG 1:1) 50% D and 50% G, (DG 1:3) 25% D and 75% G, ATH1006:ATH032, labeled as (EG 3:1) 75% E and 25% G, (EG 1:1) 50% E and 50% G, (EG 1:3) 25% E and 75% G and Banana:G.Orange, labeled as (BL 3:1) 75% B and 25% L, (BL 1:1) 50% B and 50% L, (BL 1:3) 25% B and 75% L. After this, the solutions were placed in sterilized containers specifically for storage and refrigerated for use at any time. The dispersions of the synthesized, already sensitized dyes are shown in Figure 2.10.




**Figure 2.10** Mixed dyes of: ATH1005 (D), ATH1006 (E) and ATH032 (G)

Figure 2.10 shows the results of the dyes extracted from syntheses ATH1005, ATH1006, and ATH032. It is worth noting that the names on the bottles were merely classifications for the respective names of the syntheses carried out in partnership with UFF.

The mixture resulting from the blending of a fruit (*Musa*) and a flower (*Orange Gerbera*) is described in Figure 2.11.

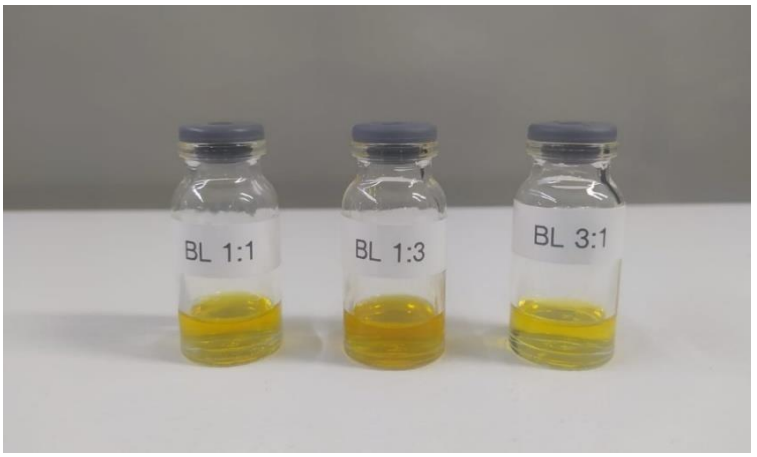



**Figure 2.11** Mixed dyes of: Banana (B) and Gerbera Orange (L)

## 2.3 – Reagents and Instruments

Photoanodes and photocathodes were fabricated on conductive glass substrates coated with fluorine-doped tin oxide (FTO), acquired from Sigma Aldrich and cut to dimensions of 2.5 cm × 2.5 cm. Other materials were also acquired from Sigma Aldrich, such as $TiO_2$ nanoparticles (size ~ 21 nm), polyethylene glycol, potassium iodide, iodine salts, and hexachloroplatinic acid. TEKBOND instant adhesive was used to fix the electrodes during assembly. FTIR spectroscopy analysis of the dyes extracted from chrysanthemum flowers and the dyes derived from boron complex was performed using an Agilent Cary 630 FTIR spectrometer. Analysis of the UV absorption spectra of the dyes extracted for this work was performed with a SHIMADZU UV-2600i UV-Vis spectrophotometer. The $TiO_2$ photoanodes were coated using a spin coating technique, i.e., by rotation, in a custom-made instrument, and hexachloroplatinic acid was deposited by dripping onto the photocathodes and calcined in a QUIMIS muffle furnace (model Q318S25T, Brazil). The analysis of the structural properties of the fabricated DSSCs, such as surface morphology, roughness, topography, among others, was performed using an atomic force microscope (AFM) model NANOSURF EasyScan2, a scanning electron microscope SEM-FEG model JEOL R JSM-7100F, and in addition a VARIAN 500 MHz NMR spectrometer, $^{1}H$: 499.84 MHz and $^{19}F$: 470.56 MHz, using tetramethylsilane (TMS) as an internal standard for the $^{1}H$ core and trifluoroacetic acid (TFA) as an external standard for the $^{19}F$ core. The analysis of the photovoltaic properties of the cells, such as photocurrent-voltage (JV), power-voltage (PV), and electrochemical impedance spectroscopy (EIS), was performed under the illumination of a solar simulator (Ivisun® IVIUM Technologies) with an lighting power of 16 mW/cm², using an IVIUM Compactstat multipotentiostat. All equipment used during the cell construction processes, whether for deposition, measurement, characterization, and others, is listed below:




**Figure 2.12** Experimental infrastructure and instrumentation used throughout this work. (a) Glassware and chemical preparation setup; (b) laboratory oven for thermal treatments; (c) analytical balance; (d) chemical fume hood; (e) water purification system; (f) thermostatic water bath; (g) sample preparation during dye extraction; (h) ultrasonic bath; (i) muffle furnace for calcination processes; (j) spin-coating system for thin film deposition; (k) portable spectroscopic/colorimetric analysis system; (l) UV–Vis spectrophotometer; (m) electrochemical workstation (potentiostat/galvanostat); and (n) impedance analyzer for electrochemical characterization.

The Laboratory of Experimental and Applied Physics (LaFEA), located at the Celso Suckow da Fonseca Federal Center for Technological Education (CEFET/RJ) in the city of Rio de Janeiro, has various equipment for constructing and characterizing dye-sensitized solar cells, in addition to some machinery intended for other lines of research. This section will present some of the equipment used to finalize the DSSCs present in this study.

For handling chemicals, reagents, and other substances involved in the study, the laboratory has various glassware, such as: Petri dishes, beakers, pipettes, among others, arranged and organized in a cabinet specifically for these items, as shown in Figure 2.12-a. To ensure that there is no contamination from dust or any other element present on the glassware, sterilization must be carried out in a drying oven with this function before handling, as shown in Figure 2.12-b. Furthermore, all measurements must have near-ideal accuracy; for this purpose, the Shimadzu ATY 224 balance is used, as shown in Figure 2.12-c. It is worth noting that acids and chemicals with high acidity levels should always be handled under a fume hood, as shown in Figure 2.12-d, to minimize the risk of an accident with this type of reagent. Another point is that the laboratory has a distiller, as shown in Figure 2.12-e, for removing unwanted minerals present in the water, which is of paramount importance for the preparation of some solutions, such as the anodic solution, for example. The storage of this water after the distillation process is done in a dedicated container, as shown in Figure 2.12-f. At various points in the study, it was necessary to mix materials homogeneously. For this purpose, an ultrasonic bath was used, as described in 2.12-h, in which the ultrasound waves will cause a molecular-scale vibration in the water present in the bath, the ultrasonic bath promotes cavitation, assisting in the dispersion, homogenization, and deagglomeration of particles in the solution.

The synthesis of the photoanodes and photocathodes took place in a muffle furnace, as shown in Figure 2.12-i. The electrodes were coated using the spin coating technique, with a portable rotary applicator, which distributes the solution homogeneously (Figure 2.12-g). Surface topography measurements of the electrodes were made using an Atomic Force Microscope, as shown in Figure 2.12-j.

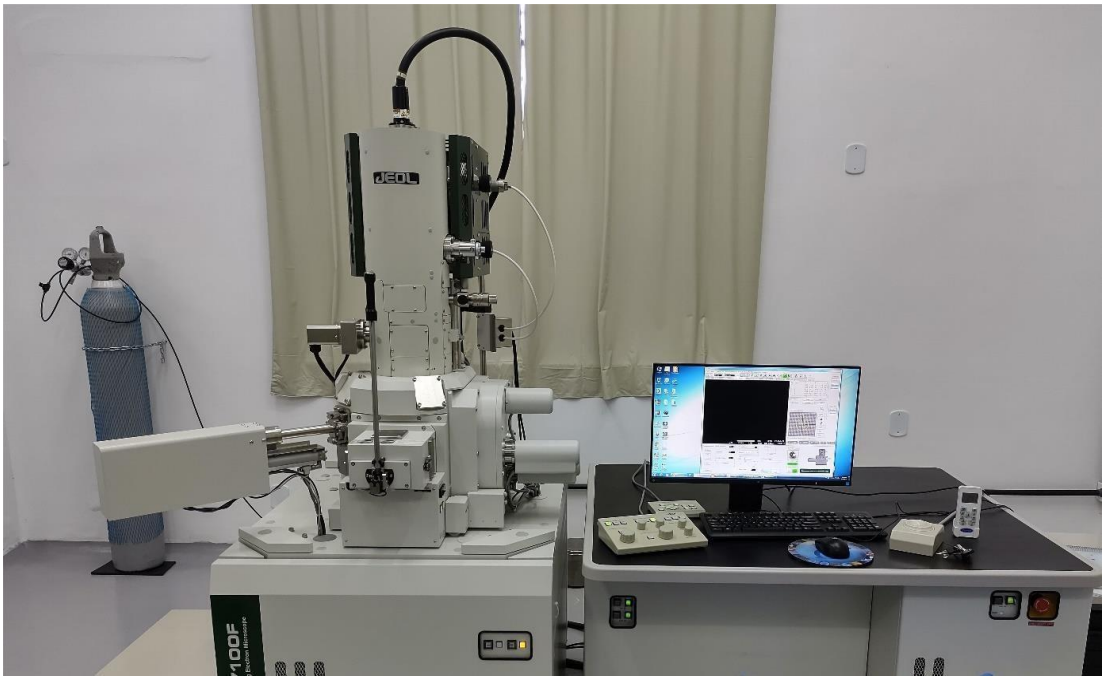



**Figure 2.13** Fotografia do Microscópio de Varredura Eletrônica utilizado na UERJ.

Optical transmittance properties were analyzed using an FTIR spectrometer, as shown in Figure 2.12-k, while absorbance spectra were characterized using a UV-Vis spectrophotometer, as shown in Figure 2.12-l. The photovoltaic properties of the cells—such as current density-voltage (J-V) and power-voltage (P-V) curves and electrochemical impedance spectroscopy (EIS) spectra—as well as the characteristics of the fabricated devices, were examined under illumination from a standard AM 1.5 solar simulator (IVISUN modulated light source). An illumination power of 16 mW/cm² was adopted for this study and used in all tests; measurements were performed using an IVIUM Compactstat multipotentiostat, as shown in Figures 2.12-m and 2.12-n. In addition to this equipment, other characterizations were carried out collaboratively using instruments such as the Scanning Electron Microscope (SEM) at UERJ, shown in Figure 2.13, and the Nuclear Magnetic Resonance (NMR) spectrometer at UFF (Volta Redonda campus), shown in Figure 2.14.




**Figure 2.14** 500 MHz Nuclear Magnetic Resonance Spectrometer – Varian VNMR500 used at UFF

## 2.4 - Preparation of the Counter-Electrode

In this study, platinum cathodes were manufactured to serve as counter electrodes. This choice was based on the observation of the superior results obtained, as mentioned in [47, 49] when compared to other conventional techniques for manufacturing the cathodic solution. The proper preparation of this electrode is extremely important, since it is in the cathode that the cell is driven by applying negative polarity. This is due to the basis of the process of electrical energy transmission in DSSCs, which is carried out by the interaction of a

semiconductor material, such as an anode and a dye, playing the role of photosensitizer, in addition to a redox electrolyte and, finally, a conductive counter electrode that acts as a cathode, as highlighted in [50].

The preparation of the photocathode was carried out using a glass substrate coated with fluorine-doped tin oxide (SnO) (FTO thin film). This substrate was previously cleaned in a solution of distilled water, ethanol, and isopropyl alcohol, using a USC-1400 MERSE ultrasonic bath (Figure 2.12-h) for 20 minutes. Drying was performed in a SX 1.1 STERILIFER oven at 80°C for 10 minutes (Figure 2.12-b).

After drying, the substrate's conductivity was measured using a multimeter, recording resistance values in the range of 10.3Ω to 12.5Ω. The solution for photocathode fabrication was prepared using 5mM hexachloroplatinic acid in an ethanolic solution. The solution was applied to the electrode using the drop casting technique on the conductive glass (FTO), followed by annealing in a muffle furnace at 350°C for 30 minutes. After this interval, the furnace was programmed to gradually reduce the temperature until it reached ambient temperature. Figure 2.15 shows these finished electrodes.

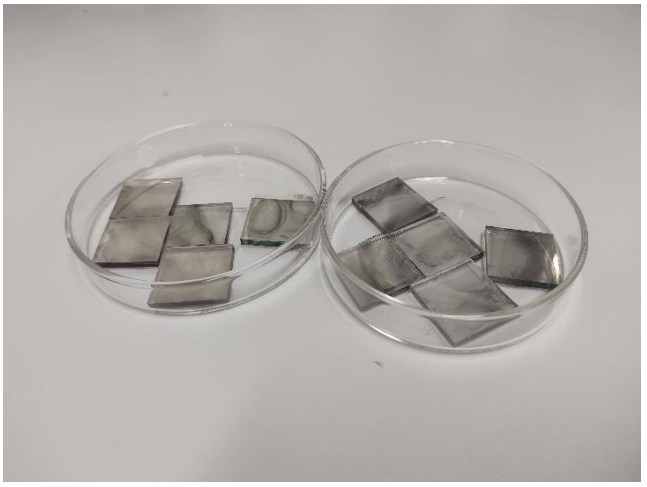


**Figure 2.15** FTO substrates coated with hexachloroplatinic acid.

## 2.5 – Preparation of Semiconductor Oxide

Similarly to the preparation of the photocathode, for the photoanodes, the substrates were cleaned in a solution of distilled water, ethanol, and isopropyl alcohol, using an ultrasonic bath for 20 minutes. Then, drying took place in an oven at 80°C for 10 minutes. After this step, the conductivity of the substrate was measured using a multimeter.

The photoanodes developed for this study were based on $TiO_2$, a window layer semiconductor material widely recognized in the literature for its specific optical properties. These properties include absorption in the UV region of the electromagnetic spectrum, with virtually no absorption in the visible region [51]. Shift absorption in the UV region occurs at 390 nm, equivalent to a wide band gap of 3.2 eV, as reported in the literature on the energy gap of

$TiO_2$ [52]. The anode solution was prepared using a mixture of 1g of P25 $TiO_2$ (Degussa-P25) nanopowder and 300mg of polyethylene glycol (PEG), combined with the same volume of glacial acetic acid and double-distilled water (v/v = 1/1), totaling 6ml in both [53]. This solution was subjected to an ultrasonic bath for three hours. The solution deposition technique on the FTO substrate was performed using Spin Coating, using a self-built device, as can be seen in Figure 2.12-g. This process aims to ensure a homogeneous distribution on the surface of the FTO semiconductor glass, with a rotation of 1000 RPM for 10 seconds. After applying the first layer, the technique was repeated to achieve an even more uniform distribution on the substrate surface [53]. Finally, the photoanode was subjected to an annealing process in a muffle furnace, reaching a temperature of 450 °C for a period of 30 minutes, as shown in Figure 2.12. The furnace programming was adjusted so that, at the end of this interval, there would be a gradual reduction in temperature until reaching ambient temperature, thus ensuring complete adhesion to the surface. The essential purpose of the annealing process is to promote the transformation of the $TiO_2$ thin film structure to the anatase phase. This alteration aims to ensure improved absorption of photons by the semiconductor material, in addition to promoting a reduction in the cell's internal resistance and improving electron transport along the semiconductor film [54]. These modifications contribute significantly to optimizing the performance of the photovoltaic cell. Next, with the photoanodes completed, the dyes extracted from the sensitizers studied were deposited, in addition to the mixtures made between dyes, so that the anode surface could homogeneously adsorb these dyes onto the surface of the $TiO_2$ thin film at room temperature. The completed electrodes are shown in Figure 2.16.

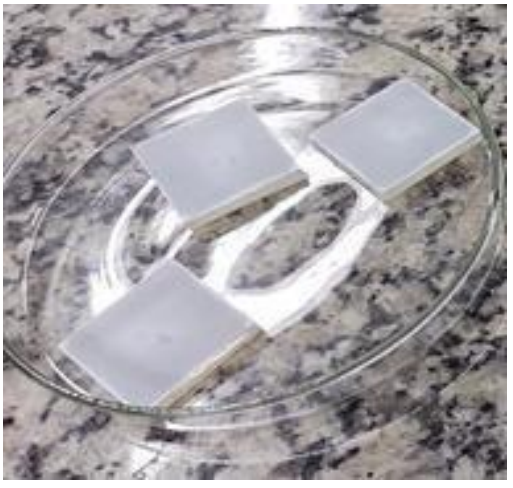


**Figure 2.16** FTO with a thin film layer of $TiO_2$.

In detail, Figure 2.17 shows the deposition of the synthesized dyes on the prepared anodic electrodes, as described previously. The deposition is carried out at room temperature, and drying also occurs at room temperature.




**Figure 2.17** Anodic electrodes with individual dyes Boranil (A, B and C) and Bodipy (D, E, F and G).

As reported in the experimental procedure, after the optical analysis of these same dyes, other anode electrodes were made for the best mixtures observed during the characterization processes from synthesizers based on boron complexes. Figure 2.18 shows the result of the deposition of the mixtures described above on the already completed electrodes.

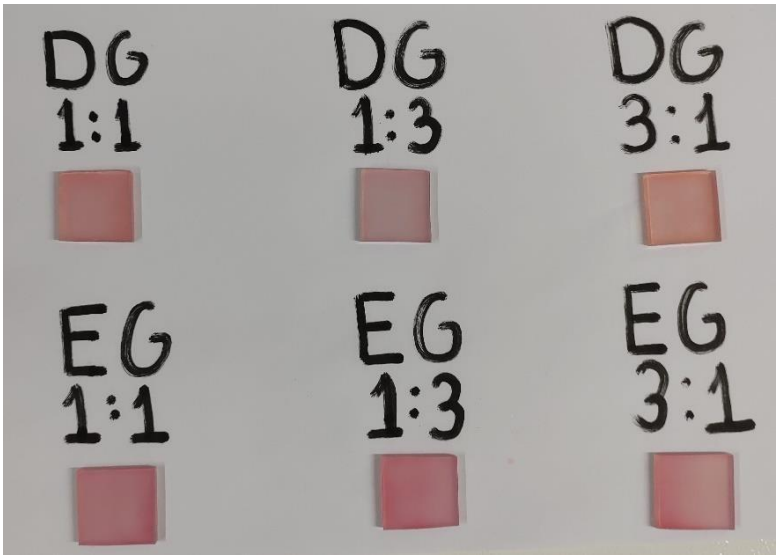



**Figure 2.18** Co-sensitized electrodes of Bodipy (D, E and G).

## 2.6 – Electrolyte Preparation

In the context of this study, the redox electrolyte used in the solar cell performance analysis was meticulously prepared, following the specific composition of 2.075 g of potassium iodide (KI) and 0.12 g of iodine (I2), which were dissolved in 5 ml of acetonitrile. Additionally, 0.02 g of polyethylene glycol was incorporated into the solution to optimize its properties [55, 56].

After the electrolyte solution was prepared, it was stored in an opaque container, preventing light from passing through to avoid oxidation of the acetonitrile [57]. The solution was then subjected to a 30-minute ultrasound treatment and subsequently stored at room temperature. Figure 2.19 illustrates the storage of the solution in the laboratory environment, highlighting the care taken to preserve its properties over time. These measures are crucial to ensure the stability and reliability of the electrolyte during experiments conducted in the laboratory.




**Figure 2.19** Electrolyte solution stored in a container

## 2.7 – Cell Assembly

For cell fabrication, the photoanode needs to be coated with the sensitizer or dye, and this drying must occur naturally. In this work, the dye drying after deposition on the $TiO_2$ thin film took 1 day. The second step is to coat the edges of the cathodic electrode with a generic spacer. In practice, Tek Bond glue was applied to three of the four sides of the cell, leaving a space on one side so that, after the cell was closed, that is, after the union of both electrodes (anode and cathode), there would be a side where the electrolytic solution could be injected to activate the DSSC.

In the present work, individual chrysanthemum cells were made to study the behavior of this type of sensitizer. From this type of plant, 3 complete cells were generated, containing 6 electrodes in total, 3 anodes and 3 cathodes. The same procedure was followed with the synthesized dyes derived from Boron (B) complex, with samples labeled A to G, resulting in 7 complete cells, totaling 14 electrodes, 7 anodes and 7 cathodes. After UV-Visible absorption spectroscopy analyses, it was possible to observe the best excitation conditions in the electromagnetic spectrum for the Bodipy class D, E, and G. Therefore, 6 different solar cells were constructed, each containing 12 distinct electrodes, 6 cathodes and 6 anodes. These constructed cells were manufactured using the co-sensitization method in different percentage volume ratios: 1:3, 1:1, and 3:1. Thus, we have DG 1:3 and EG 1:3 as the cells that showed the best results compared to other types of sensitization performed. It is worth highlighting that the co-sensitization performed is unprecedented in literature with respect to DSSCs, as well as the class of individual dyes derived from Boron (B) Boranil and

Bodipy complexes.

Full cells were labeled with their respective initials and kept at room temperature on a glass substrate, stored in a desiccator. Figure 2.20 illustrates the processes for making all the cells included in this work.

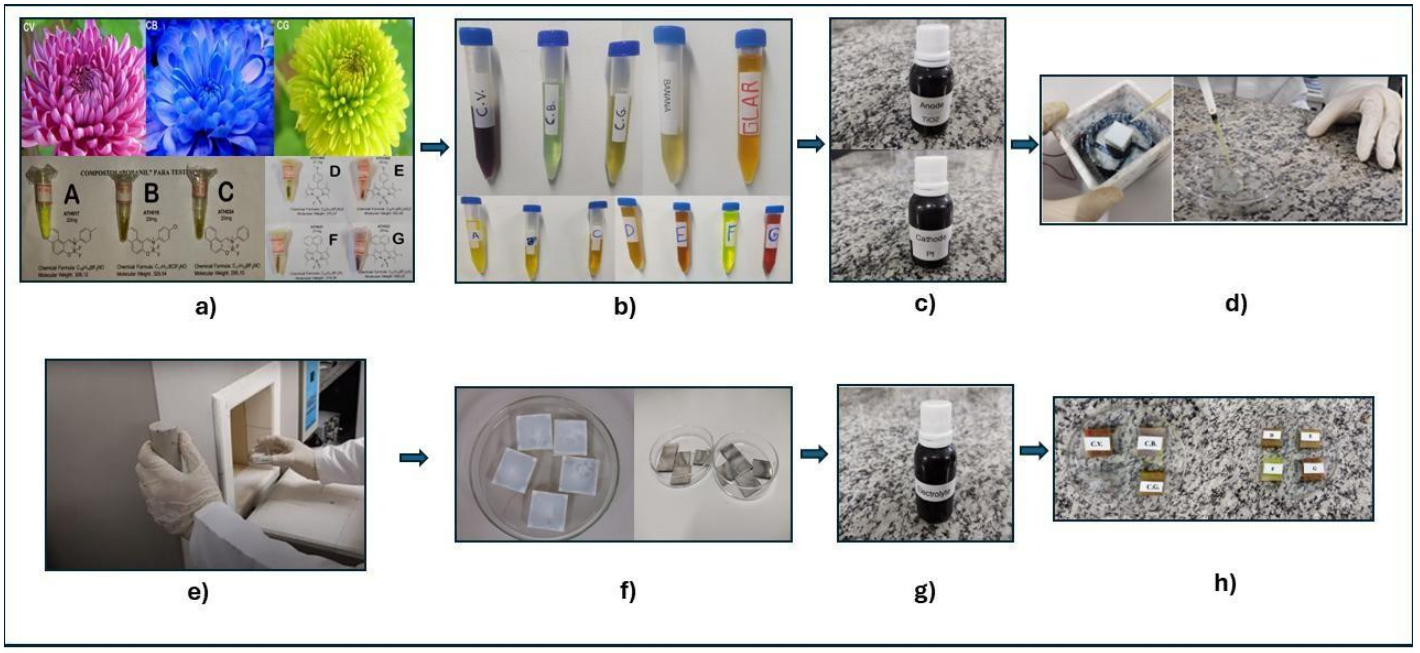



**Figure 2.20** Schematic representation of the dye extraction and device fabrication workflow.

Figure 2.20 provides an overview of the procedures performed chronologically, as described in the sequence listed below:

a) Separation of the sensitizers used in the study;

b) Identification of the dyes after filtration and/or preparation;

c) Preparation of the Anode and Cathode solutions for deposition;

d) Spin Coating and Drop Casting depositions of the anodic/cathodic solutions;

e) Annealing of the substrates;

f) Anode with titanium dioxide deposition and cathode with platinum deposition completed;

g) Preparation of the electrolyte for application;

h) Assembly and completion of the cells.

## 2.8 – Characterizations

A flowchart was developed to describe the procedures performed in relation to cell characterization, as shown in Figure 2.21. This section describes the functioning of the morphological characterization, optical characterization, and electrochemical characterization performed.

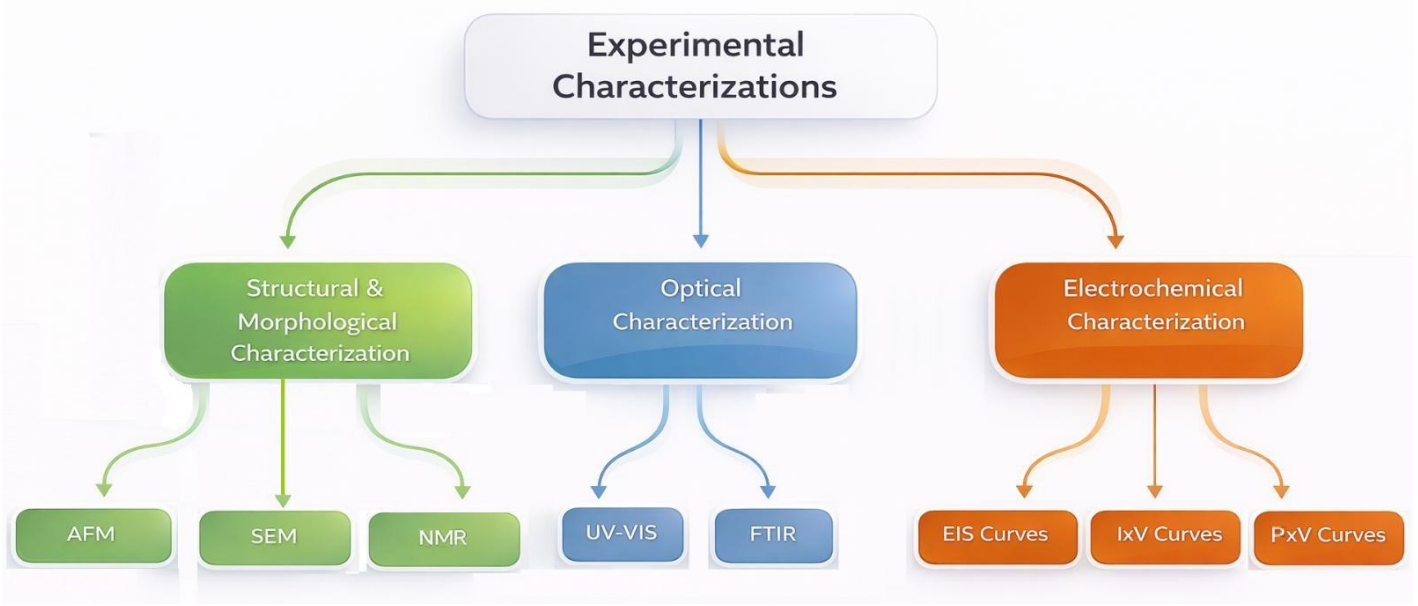



**Figure 2.21** Flowchart detailing the experimental characterizations performed in this work

### 2.8.1 – Structural Characterization

#### 2.8.1.1 – Atomic Force Microscope (AFM)

The particularities related to the surface morphology of the multilayer photoanode thin films and the platinum cathode were thoroughly examined using an Atomic Force Microscope (AFM), with the aid of the Nanosurf EasyScan 2 software, as exemplified in Figure 2.12-j.

In contrast to other types of microscopes, the AFM scans the sample surface with a cantilever with a sharp tip. When the tip is brought close to a point on the sample surface, the physical forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law [58]. Achieving maximum efficiency demands a meticulous approach at each stage of construction, optimizing fundamental tasks. Thus, if an AFM tip scans an elevated surface feature, the resulting deflection (and the subsequent change in the direction of the reflected beam) is recorded by the PSPD, as illustrated in Figure 2.22.

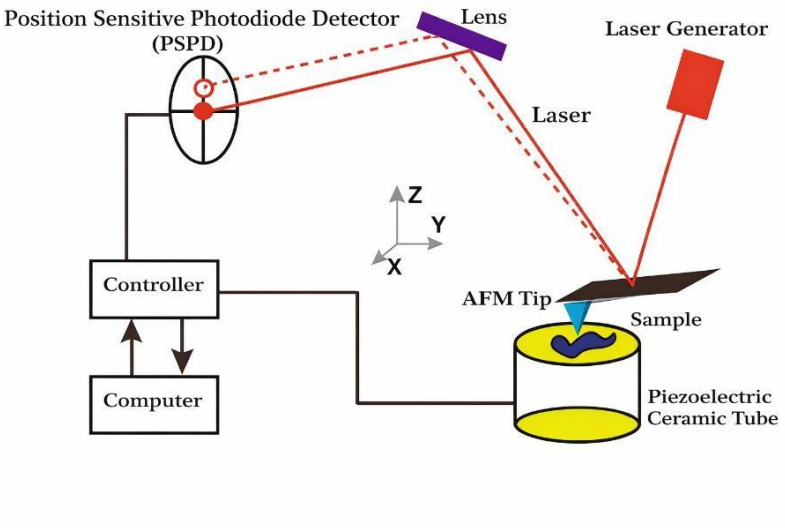



**Figure 2.22** How the Atomic Force Microscope Works. This figure was improved using IA from reference [59].

This study incorporated the analysis of mean squared roughness (MSR) for two layers, an approach supported by the literature due to its enhanced potential in photocatalytic performance [52]. Detailed evaluation of the electrode surface proves fundamental for the characterization of $TiO_2$ thin-film-based substrates, since parameters crucial for functional performance, such as the effectiveness of the semiconductor film and counter electrodes, are directly influenced by surface roughness.

An effective coating is identified by the adequate adsorption of the active layer (or dye). To achieve this characteristic, it is necessary that cavities or pores exist in the nanostructure of the thin film, ensuring homogeneous and mesoporous coatings throughout the substrate, without excessive elevations or craters in the anodic film [60, 61]. This configuration, forming nanoclusters, is particularly beneficial for applications in DSSCs [62, 63]. Ideally, generated images should be uniform, as homogeneity counteracts possible recombinatory processes along the anodic substrate. However, several factors, such as the deposition method (spincoater in this case), the similarity of the grains during the preparation of the $TiO_2$ solution, and the possible contamination of the sample during handling, can contribute to variations in the uniformity of the film [64].

### 2.8.1.2 – Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) plays a crucial role in providing images of the structural composition of samples, being an essential tool in the structural characterization of cells due to its high resolution in nanostructural analyses, especially in thin films of $TiO_2$ and Platinum.

Figure 2.23 offers a detailed view of the internal operating process of the Scanning Electron Microscopy (SEM) equipment. It can be observed that the SEM uses a high-energy electron beam, forming an electron gun, in addition to employing magnetic lenses to scan the

surface of the specimen. Unlike the characterizations performed by the optical microscope, it is important to emphasize that under no circumstances is it possible to obtain a real image of the sample from electrons [59].

This phenomenon occurs because of the beam illuminating the sample point by point, creating a rectangular scanning pattern. The intensity of the signal formed at each point reflects the differences in the sample. To generate an image, a scanning system that builds line by line and point by point is essential. The scanning system comprises two pairs of condenser lenses and electromagnetic deflection coils, capable of shifting the beam along a line and subsequently moving the position of the line to form the rectangular scan in the sample [58, 65].

The deflection coil is responsible for diverting the beam off the optical axis of the microscope, while the second pair return the beam to the axis, allowing focusing on the point of interest. Therefore, it is necessary to measure point by point on the sample surface to determine the contrast in the image, based on the intensity of the signal resulting from the interaction of the beam with the sample. After the generation of these signals, the data are collected by an electron detector, converted into photons by means of a scintillator, and then amplified in a photomultiplier. Finally, the signals are converted into electrical signals to modulate the intensity of the image generated on the monitor [66]. This detailed process highlights the complexity and precision involved in obtaining high-resolution images using SEM.

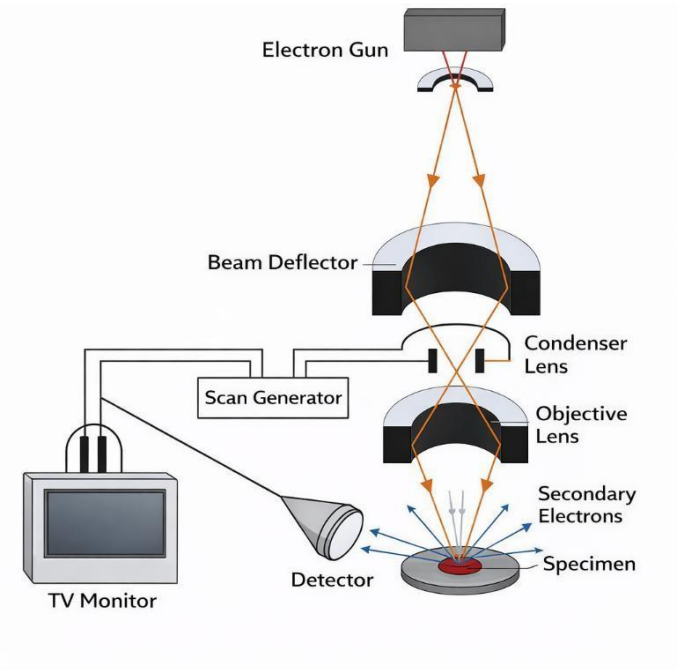



**Figure 2.23** How a Scanning Electron Microscope Works.
This figure was improved using IA from reference [66]

The equipment, a JEOL R JSM-7100F SEM-FEG model, operates using a focused beam of high-energy electrons, allowing the generation of a variety of signals on the surface of the samples. After data collection, a two-dimensional image is generated that reveals the spatial forms present in the samples, offering a deeper understanding of their structure.

It is worth highlighting that the FEG-SEM is an integral part of the instrumentation available at the Multi-User Laboratory for Nanofabrication and Characterization of Nanomaterials (NANOFAB) at the State University of Rio de Janeiro (UERJ), as shown in Figure 2.12, reinforcing its importance in the research and development of nanostructured materials.

### 2.8.1.3 – Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most powerful and versatile analytical tools for the structural elucidation of organic and organometallic compounds and advanced functional systems, including organic dyes used in photovoltaic and optoelectronic applications. Figure 2.24 illustrates its operating principle.

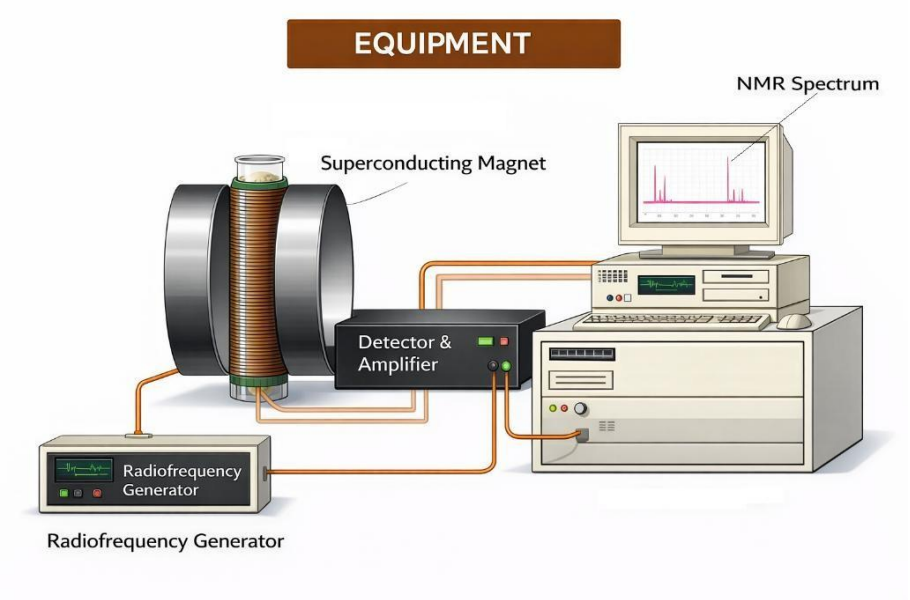



**Figure 2.24** How Nuclear Magnetic Resonance Spectroscopy (NMR) Works
This figure was improved using IA from reference [67]

Based on the interaction between nuclear magnetic moments and an intense external magnetic field, the technique allows for detailed investigation of the local electronic environment of atomic nuclei, providing direct information on molecular connectivity, structural symmetry, conjugation effects, and electron density distribution. These measurements were carried out in collaboration with the Chemistry Department of the Institute of Exact Sciences (ICEx) at the Federal Fluminense University (UFF) - Volta Redonda Campus and, therefore, were only performed on the compounds Boranil and Bodipy.

### 2.8.2 – Optical Characterization

The optical properties of the infrared spectra of the studied dyes were analyzed using an Agilent Cary 630 FTIR spectrometer. The absorption spectra of the dyes extracted for this study were analyzed using a Perkin (λ 650) UV-VIS spectrophotometer. These optical characterizations allowed us to determine if the solubility tests and sample preparation were performed adequately to better verify the substances and excitation characteristics contained in each sample.

#### 2.8.2.1 – Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy was used to obtain the functional groups present in the dye molecules in this laboratory [68], consisting of an optical characterization method that identifies the chemical elements of the sample. Figure 2.12-k shows the AGILENT CARY 630 model spectrometer at LaFEA used to measure the transmittance of the dyes used in this study.

With FTIR analysis, it is possible to observe several functional groups in the flower leaf extracts that prove the existence of the anthocyanin molecule (Figure 2.25), which may demonstrate better efficiency as a dye [69], and should be conducted for the sensitization of photoanode thin films.

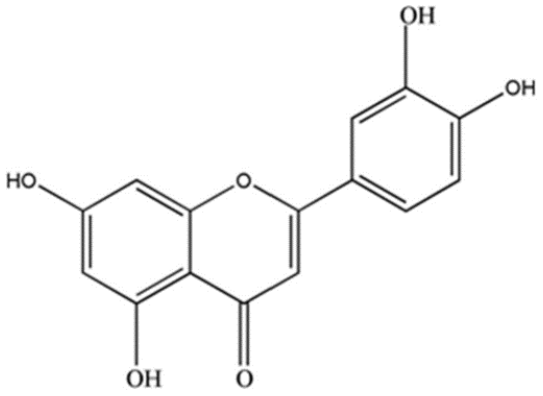



**Figure 2.25** Molecular structure of the anthocyanin base [69].

These pigments are notable for their rapid absorption in semiconductor oxides, especially in the $TiO_2$ oxide used in this study, due to its high photocatalytic activity (PCA) and chemical stability [70].

In this context, FTIR was used to identify bonds that can be attributed to the dye nuclei (flavonoids) contained in the extracts of *Chrysanthemum*, Boranil and Bodipy. Anthocyanins, which belong to the flavonoid group, are the main component of some natural dyes and are frequently found in fruits, flowers and leaves of plants [71].

### 2.8.2.2 – Ultraviolet-Visible Absorption Spectrophotometry (UV-Vis)

UV-Vis absorption spectra provide crucial information about absorption transitions between the ground and excited states of dye molecules, as well as about the range of solar energy absorbed by these molecules. This data is extremely important, especially considering the study's focus on photosensitization. In general, anthocyanins and their derivatives exhibit a broad absorption band in the visible light range, attributed to charge transfer transitions from HOMO to LUMO, representing electronic excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [72].

Anthocyanins are commonly responsible for the vibrant and attractive colors of various fruits, with absorption peaks around 520 nm [73]. Anthocyanins found in different plants exhibit diverse photosensitization performances [74]. Among the most common anthocyanins are cyanidins (orange), pelargonidins (orange), petunidins (blue-red), delphinidins (blue-red) and malvidins (blue-red) [75].

Figure 2.12-I illustrates the UV-2600I model spectrophotometer used in the Laboratory of Experimental and Applied Physics (LaFEA) for Ultraviolet/Visible absorption analyses. This equipment plays a fundamental role in characterizing the spectral properties of dyes, contributing to the understanding of the light absorption processes that occur during co-sensitization. Absorption spectrophotometry is defined by the analysis of the molecular characteristics of the substance under study, including the equipment used and the frequency range of the electromagnetic energy employed in the assay, covering the ultraviolet, visible or infrared regions [76]. Due to the presence of functional groups such as carbonyl and hydroxyl in the dye molecule, it can be easily anchored to the surface of the $TiO_2$ photoanode semiconductor, making it promising for application as a photosensitizer.

The specific type of spectrometry performed is determined by the frequency of electromagnetic radiation propagating in a specific wavelength range. These wavelengths are detailed in Table 2, providing valuable information about the spectral properties of the dye and aiding in understanding its interaction with the semiconductor substrate.

**Table 2** Types of spectrophotometry and their respective wavelengths.

| Wavelength Range | Spectrophotometry Class |
|---|---|
| 100 – 200 nm | Far Ultraviolet |
| 200 – 380 nm | Near Ultraviolet |
| 380 – 780 nm | Visible |
| 780 – 3000 nm | Infrared (near) |

Collimators play a fundamental role in guiding and focusing radiation beams in visible spectrophotometers. They generally consist of prisms designed to direct and reduce a specific wavelength range, allowing a particular beam of light to pass through a solution sample contained in a cuvette. During this process, some of the light is transmitted through the

sample, while another part is absorbed by it [77].

The reduction in light intensity is measured by a detector, which records the variation in the output electrical signal depending on the intensity of the incident light. The substance present in the cuvette generates an electrical signal in the form of absorbance. Figure 2.26 provides a visual representation of the basic structure of spectrophotometers, highlighting the essential components involved in the absorbance measurement process.

This illustration facilitates understanding of the operation of the spectrophotometer and the principles underlying the absorption spectrophotometry technique.

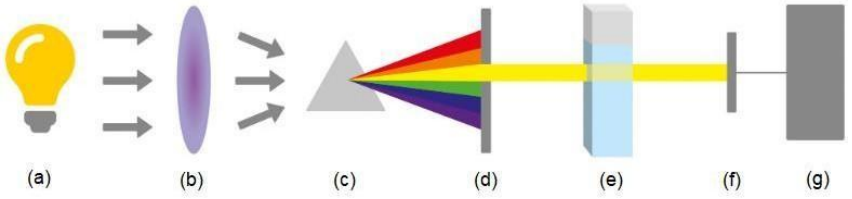



**Figure 2.26** Operation of the spectrophotometer: (a) Light source; (b) Collimator; c) Prism; d) Selector slit; (e) Cuvette containing solution; (f) Detector; (g) Reader [78]

### 2.8.3 – Electrochemical Characterization

Experimental electrochemical characterization tests are essential for evaluating and understanding the electrical and electrochemical properties of functional materials. These tests employ specific techniques that allow for the investigation of material behavior when subjected to electrical currents and potential under different operating conditions. In this context, electrochemical tests were conducted to determine the photovoltaic parameters of dye-sensitized solar cells (DSSCs) in this study. To this end, parameters associated with Electrochemical Impedance Spectroscopy (EIS) techniques, current density-voltage (J–V) characteristic curves, and power-voltage (P–V) curves were obtained. The EIS technique is based on the analysis of the system's response to small potential perturbations in alternating current, providing relevant information about the electrical resistance and capacitive effects of the material over a wide frequency range. This approach allows for a detailed investigation of the charge transfer and ionic transport mechanisms in the device. J–V and P–V curves were recorded after approximately five minutes of continuous illumination of each cell, allowing the evaluation of the electrical performance of the DSSCs. In order to analyze the photovoltaic and electrochemical characteristics of the organic dye-sensitized solar cells constructed, tests were carried out to determine specific factors, such as: short-circuit current density ($J_{sc}$), open-circuit voltage (Voc), fill factor (FF), maximum current density ($J_{max}$), maximum voltage ($V_{max}$), maximum power ($P_{max}$), impedance (EIS) and efficiency ($\eta$) [79].

Short-circuit current and open-circuit voltage are the two main factors that correspond to the efficiency of the DSSC. The open-circuit voltage is the difference between the Fermi level of the $TiO_2$ photoanode and the potential of a redox electrolyte, which depends mainly on the recombination rate and type of adsorption of the photosensitizer [80]. The performance of

the electrochemical parameters was performed using a multi-potentiostat (IVIUM Compactstat) coupled with a solar simulator AM 1.5G standard (Ivisun® IVIUM Technologies), with an lighting power of 16 mW/cm$^2$ as shown in Figure 2.12-m:

The multi-potentiostat is responsible for establishing the electrochemical scan of the completed cell, and in parallel, it reads the current from the reaction (Figure 2.12-n). It can be used in other applications, such as battery testing, corrosion measurements, and electrochemical research. It has a wide current analysis range, varying from ± 1 A to 1 pA on a full scale. Attached to the potentiostat, a device called a solar simulator was used to produce artificial light to excite the cells and the data were processed using LabVIEW® software. The electrochemical assay performed on the finished cells is described below in Figure 2.27.



**Figure 2.27** Testing a DSSC using a multi-potentiostat in conjunction with a solar simulator.

With these characterizations, it was possible to measure the response of the equivalent circuits of each cell, verifying if they are in accordance with the entire experimental procedure. Linked to this equivalent circuit measurement is its margin of error. Using this same technique, the J-V and P-V curves were obtained.

#### 2.8.3.1 – Current versus Voltage Curves (I x V)

Current-voltage (I × V) characteristic curves, also presented as current density (J) as a function of voltage (V), constitute the main tool for evaluating the photovoltaic performance of dye-sensitized solar cells (DSSC). From these curves, the essential electrical parameters were determined: short-circuit current density ($J_{SC}$), open-circuit voltage ($V_{OC}$), fill factor (FF), and energy conversion efficiency (η) [81]. Given the parameters mentioned above, the fill factor (FF) can be calculated, which is the variable that shows how much the maximum power (result of the product between $I_{max}$ and $V_{max}$) approaches the product between $J_{sc}$ and $V_{oc}$, in order to generate a parallelogram of right angles, meaning how much the smaller rectangle

approaches the larger one [82]. The closer the ratio is to 1, the more efficient the photovoltaic cell tends to be, since cell efficiency is linked to the FF as described in Equation 5. The behavior of an ideal I x V curve is described by Figure 2.28:

$$FF = \frac{V_{max} \cdot I_{max}}{V_{oc} J_{sc}} \quad (5)$$

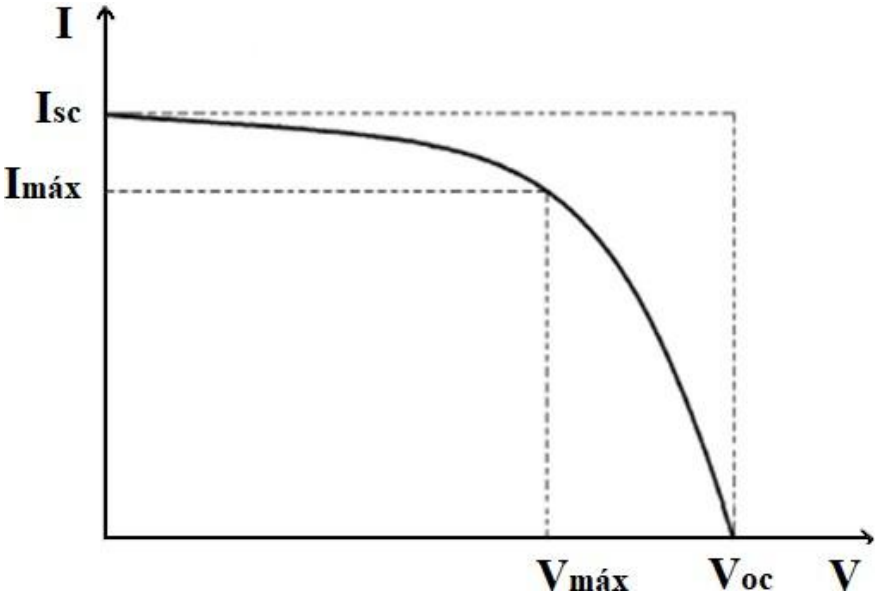



**Figure 2.28** Representation of an ideal I-V curve [83,84].

Equation 6 represents the rate of conversion of solar energy into electrical energy that a device can deliver; this phenomenon is called efficiency, which is calculated by the ratio between the maximum power and the power of monochromatic light incident on the cell in mW/cm², and A is equivalent to the active area of the solar cell.

$$\eta = \frac{I_{SC} \, V_{OC} \, FF}{P_{in}} \; x \; 100 \quad (6)$$

### 2.8.3.2 – Power versus Voltage Curves (P x V)

The maximum output power ($P_{max}$) is obtained by choosing an experimentally determined point on the (J-V) curve corresponding to which the product of the current ($J_{max}$) and potential ($V_{max}$) gives the maximum value. And this operating point depends on the impedance of the external circuit connected to the cell [83, 84], seen in Figure 2.29.

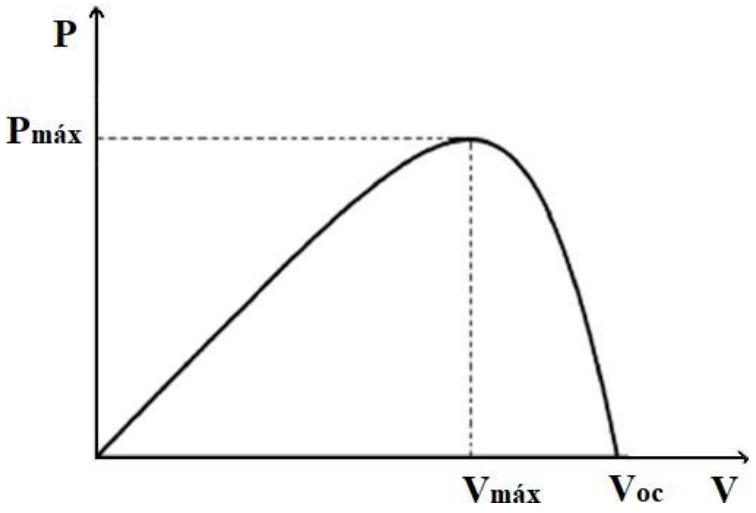



**Figure 2.29** Ideal maximum power generated in the cell as a function of its voltage [83, 84].

### 2.8.3.3 – Electrochemical Impedance Spectroscopy (EIS)

EIS analysis was conducted to evaluate the charge transfer dynamics at the dye/$TiO_2$/counter electrode interface. The Nyquist diagram obtained for the different dye compositions revealed two main semicircular arcs: the first, associated with the charge transfer resistance at the $TiO_2$/dye interface, and the second, related to the diffusion process in the redox electrolyte. Figure 2.30 shows the equivalent circuit of the internal impedances associated with fabricated cells. Each cell was modeled using the IVIUM solar simulator software to achieve the smallest possible error between the experimental and fitted results. Three Nyquist circuits were generated to model the behavior of the ideal equivalent circuit for the charge resistance between the counter electrode and the electrolyte, which represents the value (R1) of the circuit. Electron transport at the semiconductor oxide/dye/electrolyte interface corresponds to the mid-frequency regions, representing the resistance (R2) in the circuit. The $I^-$ / $I_3$ diffusion process in the electrolyte corresponds to the low frequency region, being constituted by the Warburg component. (R3) is attributed to diffusion in the electrolyte, while the ohmic resistance ($R_s$) is correlated with the electrolyte and the FTO electrode.

The fabricated cells showed discrepancies that allowed the three-loop circuit to be modeled; the cells that did not behave as desired with the three-loop circuit were modeled with the circuit that best suited that context.

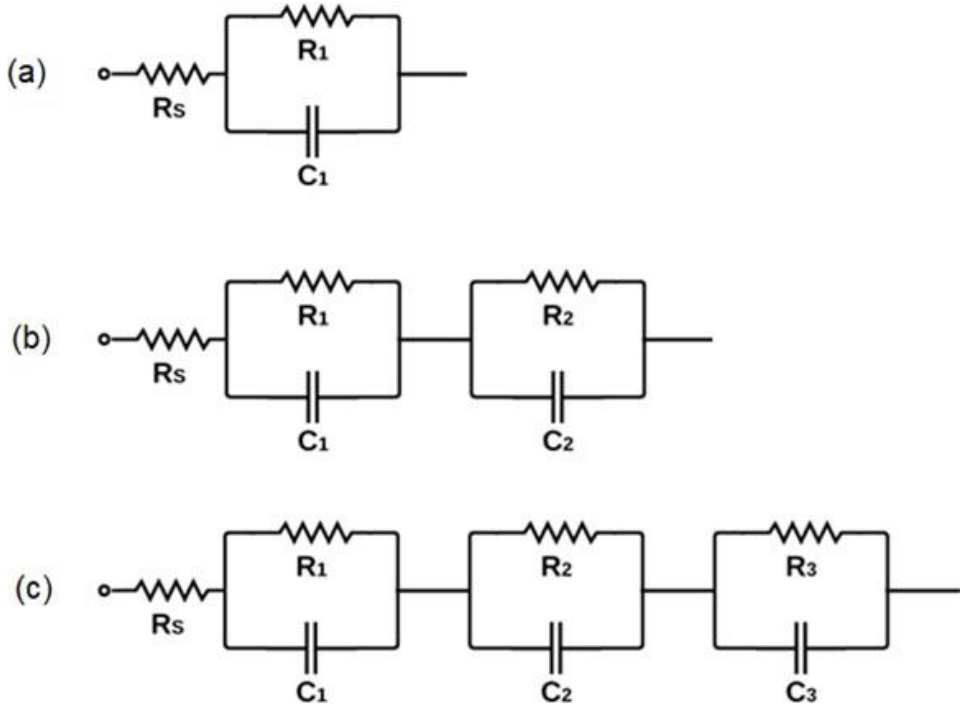



**Figure 2.30** Equivalent circuit corresponding to the manufactured DSSCs.

# Chapter 3 – Results and Discussion

## 3.1 – Analysis of DSSCs Manufactured with *Chrysanthemum* Sensitizers

### 3.1.1 – Structural Analysis

For a more in-depth analysis of the molecular structure, photoanodes composed of $TiO_2$ thin films, spin-coated with multiple layers, and platinum cathodes were subjected to Scanning Electron Microscopy (SEM) analysis. This procedure was conducted in collaboration with the Multi-User Laboratory for Nanofabrication and Characterization of Nanomaterials (NANOFAB), located at UERJ. The use of SEM allowed the observation of parameters such as grain size, thickness, uniformity, and porosity of the thin film. Nanostructural characterizations provided valuable insights into the effectiveness of the deposition performed by the spin coating technique.

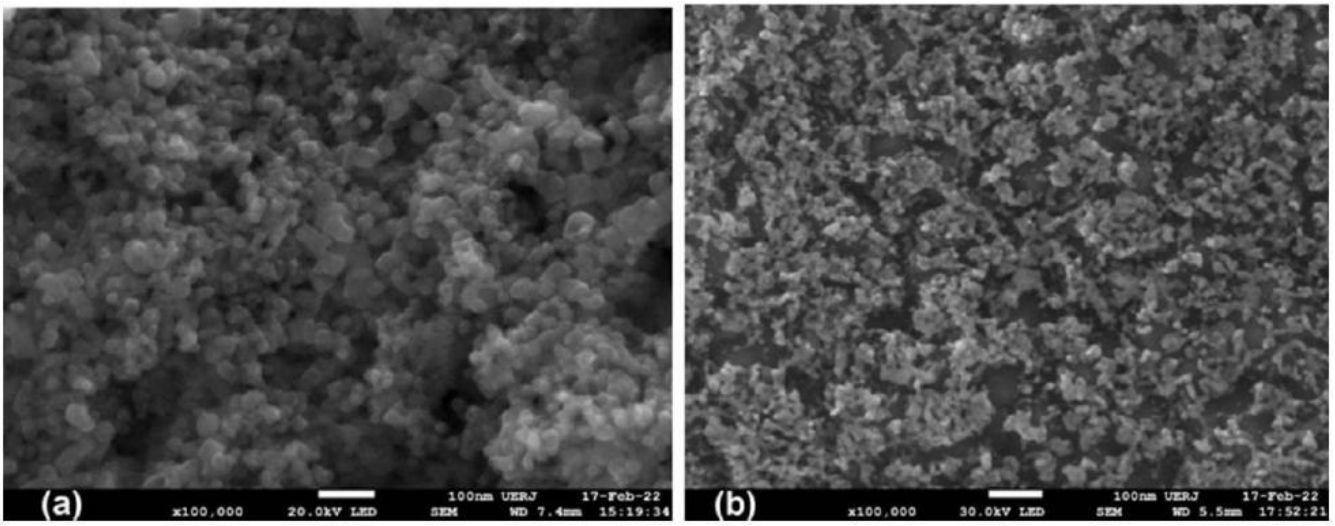



**Figure 3.1** (a) FESEM of the $TiO_2$ thin-film electrode and (b) FESEM of the platinum counter electrode.

Figure 3.1-a shows SEM images of nanostructured $TiO_2$, whose grain sizes range from 20 to 25 nm and appear well connected to each other, with adequate mesoporosity to allow the formation of an extensive electrode-electrolyte interface. Furthermore, the observation indicates that the morphology of the samples is very rough and may be beneficial for increasing dye adsorption due to its high surface roughness and high surface area. It is possible to observe that the granules are well connected to each other, with relevant mesoporosity to ensure the formation of an extensive electrode-electrolyte interface, favoring adsorption on the film surface [85]. Similarly, the morphology of the Pt-coated FTO photocathode was characterized by SEM. The cathode presented a hierarchical morphology when synthesized at 350 °C, showing pores of different dimensions, as shown in Figure 3.1-b. The image shows that the Pt coating occurred homogeneously on the outer face of the electrode, with a nanometric structure. Grain sizes range between 20 and 30 nm. The homogeneous coverage of the FTO substrate leads to increased light interactions and reflections in the device, which can enhance the photocatalytic activity of the device.

Furthermore, the images allowed for the analysis of the surface distribution of each material deposited on the electrodes, enabling an assessment of homogeneity in relation to these substrates. This comprehensive approach provides a more complete understanding of the structural characteristics of the components used, contributing to the optimization of the overall system performance.

Atomic force microscopy was used to generate 3D images with microscopic resolution, allowing the study of the surface morphology of $TiO_2$ and platinum thin films. Platinum cathodes were also subjected to evaluation with AFM, as shown in Figure 3.2-b. Platinum nanoparticles were uniformly distributed on the surface of the FTO electrode, forming a densely distributed film.

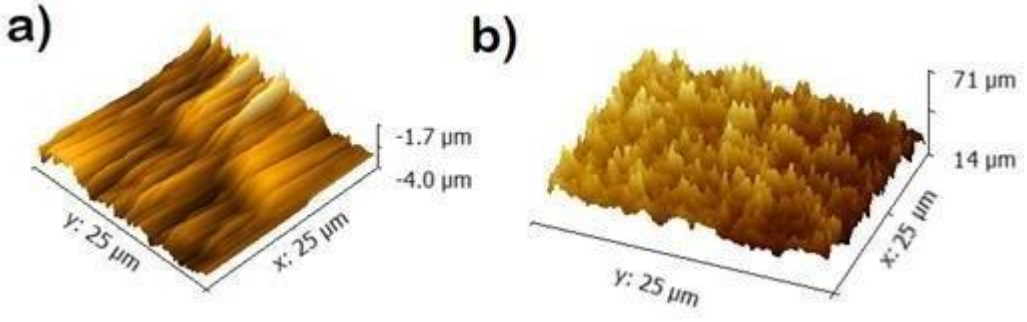



**Figure 3.2** Results of AFM analyses of (a) $TiO_2$ and (b) Platinum.

Comparative analysis reveals distinct topographic profiles with respect to the electronic kinetics of the device. In Figure 3.2-a, the $TiO_2$ film exhibits a vertical variation (peak-to-valley) of approximately 2.3 µm (ranging from -4.0 µm to -1.7 µm). This roughness amplitude, distributed over an area of 625 µm², confirms the formation of a complex three-dimensional network. This micrometric roughness is functionally desirable for the photoactive electrode, as it expands the effective surface area by orders of magnitude relative to the planar geometric area, allowing for a higher dye adsorption density and, consequently, a higher photocurrent. In contrast, the platinum film (Figure 3.2-b) exhibits a substantially higher height scale, with a gradient reaching 71 µm. The more pronounced roughness profile in platinum compared to the $TiO_2$ scale expands the active sites available for electrolyte reduction, decreasing the overvoltage of the charge transfer reaction [86].

### 3.1.2 – Optical Analysis

Fourier transform infrared (FTIR) spectroscopy was used to obtain the functional groups present in the dye molecules in this laboratory [88], consisting of an optical characterization method that FTIR spectroscopy provides information about molecular vibrations, chemical bonds, and functional groups present in the samples.

Figure 3.3 shows the comparison between the transmittance curves in the IR spectrum plotted for each dye, *Chrysanthemum Violet* (a), *Chrysanthemum Green* (b) and *Chrysanthemum Blue* (c), respectively.

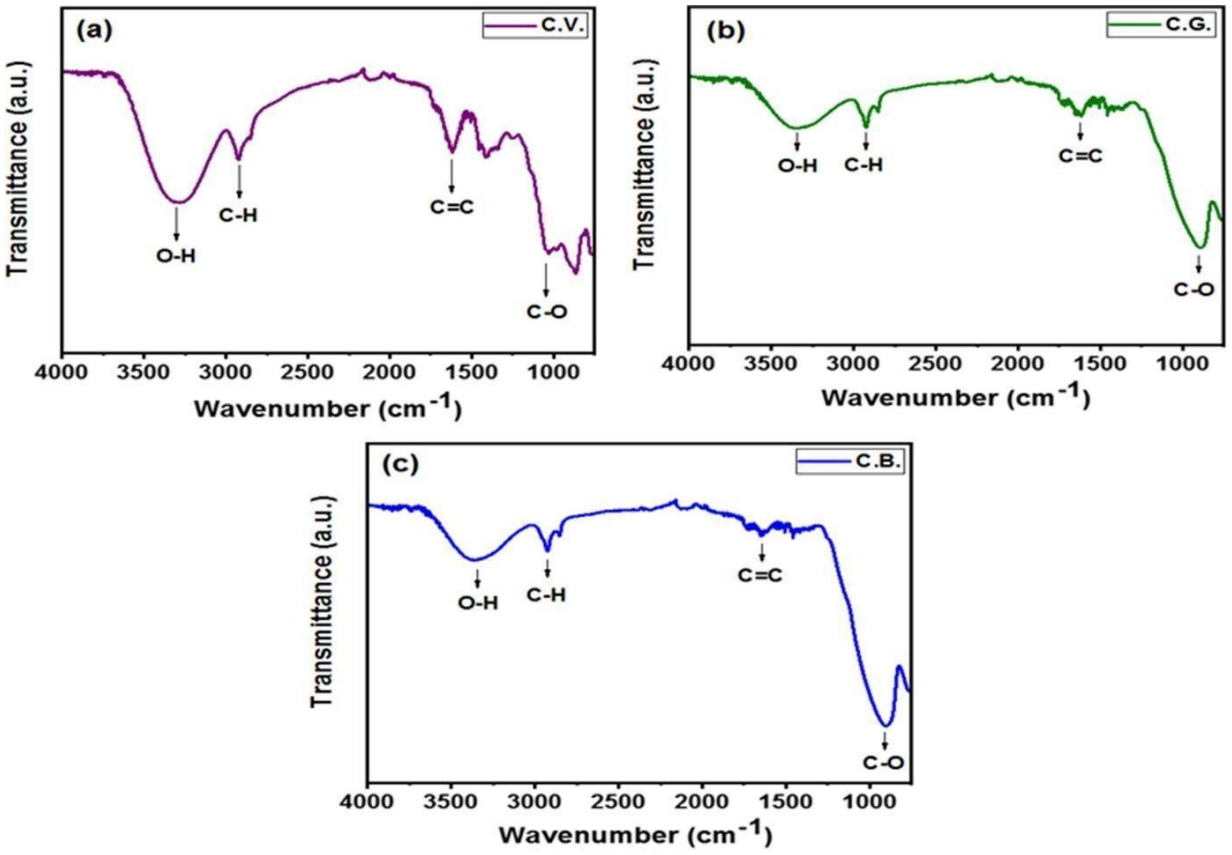



**Figure 3.3** FTIR spectra for different dyes: (a) *Chrysanthemum Violet* (b) *Chrysanthemum Green* and (c) *Chrysanthemum Blue*.

It was possible to analyze that the intense band obtained in the spectral region between 3100 and 3500 was due to the existence of vibrations of the hydroxyl group (OH) present in the dye molecules [87]. The peaks located between 3000 $cm^{-1}$ and 2850 $cm^{-1}$ are attributed to the symmetric and asymmetric stretching vibration modes of the CH group [88]. The peaks between 1750 and 1650 $cm^{-1}$ are attributed to the C=C stretching vibrations of the benzene and alkene rings, while the peak at ~ 1720 $cm^{-1}$ can be correlated to the stretching vibration mode of the carbonyl group (CO) [89]. The carbonyl group present in the dyes is capable of binding to semiconductor oxides, which facilitates the injection of electrons from the dye into the $TiO_2$ layer. With FTIR analysis, it is possible to observe that certain extracts containing a high concentration of anthocyanin molecules may demonstrate better efficiency as a dye [85] and should be used for the sensitization of photoanode thin films.

Natural pigments exhibit a high affinity for the $TiO_2$ surface, adsorbing rapidly through the interaction between their oxygenated functional groups—such as phenolic hydroxyls and carbonyls and the hydroxyl groups present on the semiconductor surface. This interaction promotes efficient anchoring of the dye molecules, facilitating photoinduced electron transfer from the excited state of the sensitizer to the $TiO_2$ conduction band. Furthermore, $TiO_2$ stands out as a photoanode due to its high chemical stability, resistance to photocorrosion, large surface area, and photocatalytic properties—characteristics that contribute to enhancing both the sensitization efficiency and the operational stability of dye-sensitized solar cells (DSSCs) [85].

UV-Vis absorption spectra provide essential information about the absorption transition between the ground state of the dye molecule, the excited state, and the solar energy range absorbed by the active layer molecule.

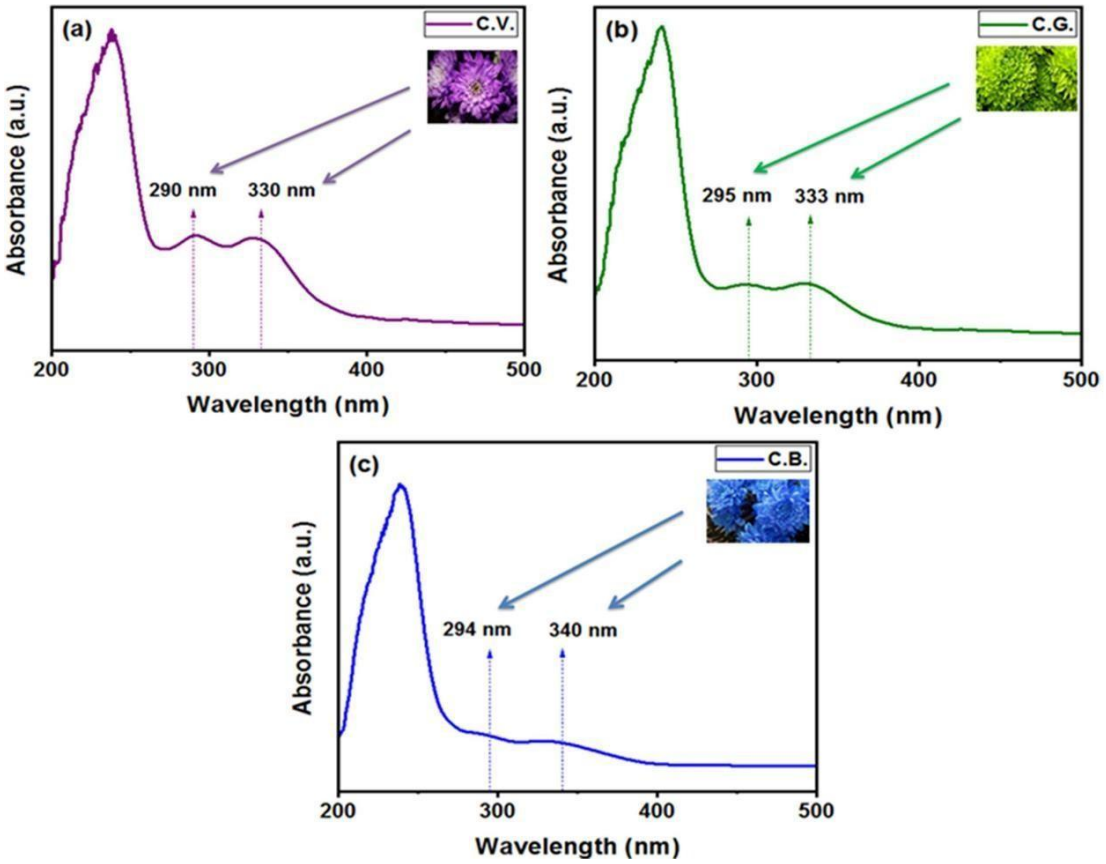



**Figure 3.4** UV absorption of the dyes of: (a) Chrysanthemum Violet (b) Chrysanthemum Green and (c) Chrysanthemum Blue.

The UV-Vis spectra shown in Figure 3.4 indicate that the optical response of the three Chrysanthemum extracts is predominantly concentrated in the ultraviolet region, with the most intense absorption occurring between 200 and 380 nm. This behavior is mainly associated with π→π electronic transitions of aromatic rings and conjugated phenolic structures present in anthocyanins, flavonoids and other polyphenolic compounds extracted from the flower petals. Although anthocyanins are generally expected to exhibit absorption bands extending into the visible region (typically between 500 and 550 nm), the intensity and position of these bands strongly depend on factors such as pigment concentration, extraction solvent, pH, molecular degradation, pigmentation effects and the relative abundance of different anthocyanin derivatives. Under the extraction conditions adopted in this work, these effects resulted in weak or poorly defined absorption features in the visible range, while the ultraviolet absorption remained dominant. Consequently, the natural extracts exhibited a limited capability for harvesting visible solar radiation, which explains the relatively low photovoltaic performance obtained for the individual Chrysanthemum-sensitized DSSCs. This limitation motivated the use of boron-based synthetic dyes, whose molecular structures were specifically designed to present intense and well-defined absorption bands in the visible region, thereby broadening the spectral response and improving the light-harvesting capability of the photoanodes.

### 3.1.3 – Electrochemical Analysis

To measure the current density (J) as a function of voltage (V) and obtain the characteristic curve, a multipotentiostat and a solarimeter were used to excite the photoanode and induce the photoelectric effect in the analyzed cells. The J × V curves obtained are shown in Figure 3.5:

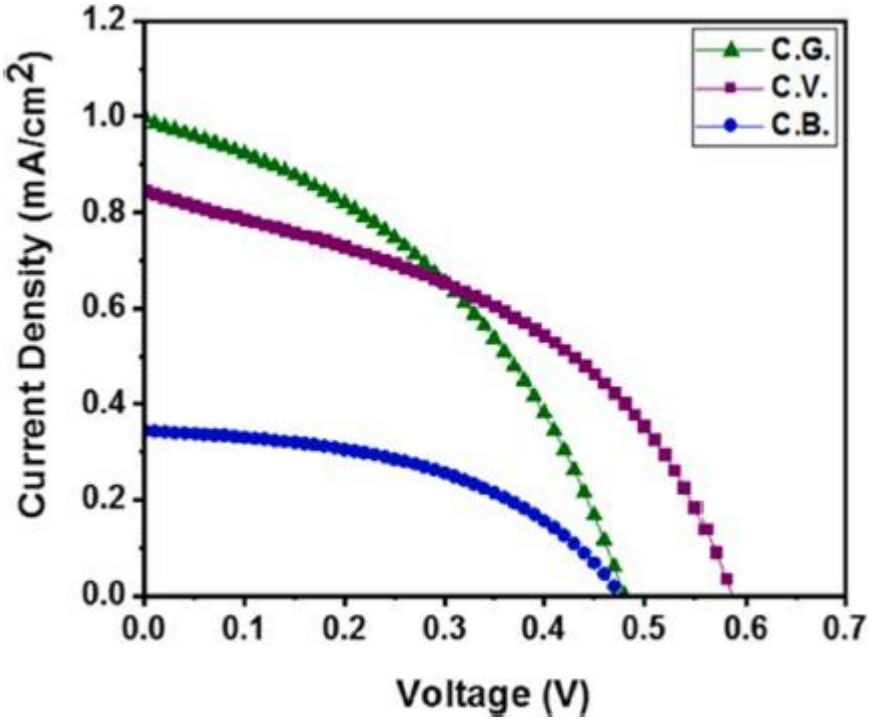



**Figure 3.5** Current density versus Voltage curves (*J-V*) of *Chrysanthemum* DSSCs.

Analyzing the curves in Figure 3.5, it is possible to observe that CB presents short-circuit current (Jsc) values of 0.344 mA/cm², similar to those of CV and CG, which have 0.845 mA/cm² and 0.999 mA/cm², respectively. For the open-circuit voltage (Voc) of CG and CB, very similar values were obtained, 0.48 V and 0.47 V, respectively. In the case of CV, this value was 0.58 V. The maximum power (PV) curves were obtained from the experimental J x V points, corresponding to the product of the current (Imax) and the electric potential (Vmax), reaching the maximum power values. It can be observed, through the P x V curves, that the cells sensitized with the *Chrysanthemum Violet* dye (CV) obtained the best parameters for the development of DSSCs. The behavior of the power curves of the cells constructed in this work is shown in Figure 3.6.

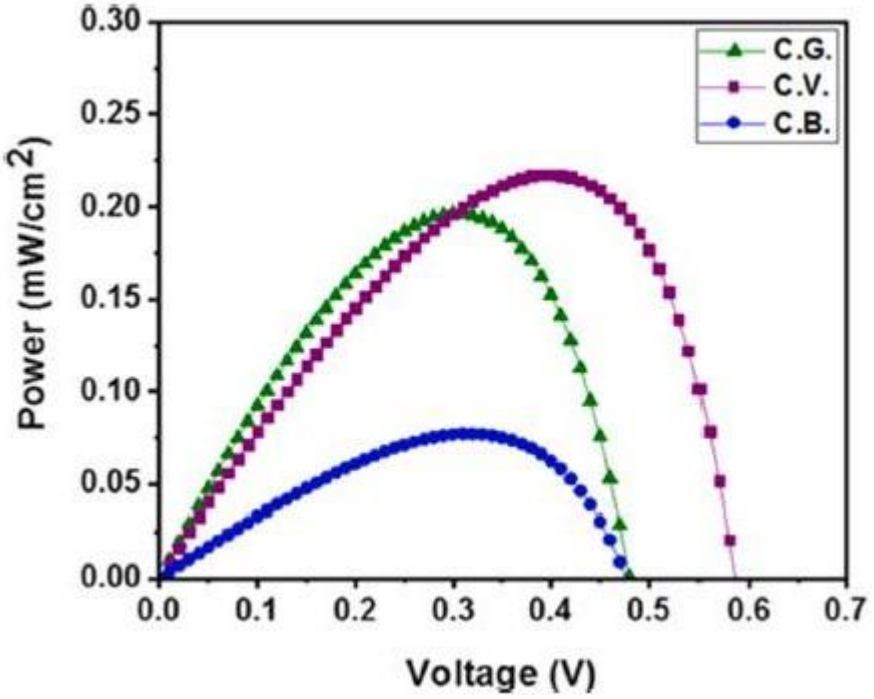



**Figure 3.6** Power versus Voltage curves (P-V) of *Chrysanthemum* DSSCs.

Figure 3.6 shows the comparison of Power (P) x Voltage (V) performance parameters between the sensitizations performed, comparing the different single dyes previously used. The analysis showed better behavior of the CV cell, following the behavior already indicated in Figure 3.5. To analyze the frequency response of a system, two impedance curves were generated, one representing the behavior of the cell defined as "Fitted", and the other representing the frequency response generated as an experimental result at the cell output defined as "Experimental". The result obtained after the electrochemical impedance spectroscopy characterization was in accordance with what was conjectured in Figure 3.7.

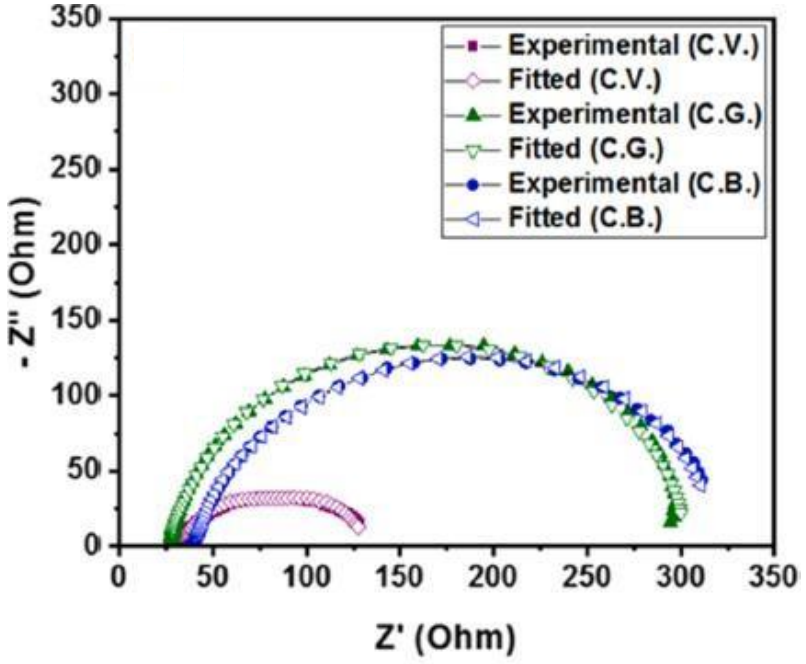



**Figure 3.7** EIS spectra of *Chrysanthemum* DSSCs

The analysis showed that the CV and CG sensitizers presented lower series resistance (Rs) than the CB device under identical operating conditions, indicating a more favorable charge transport through the photoanode/electrolyte system. Electrochemical impedance spectroscopy (EIS) measurements were performed under standard solar illumination (AM 1.5G, 16 mW $cm^{-2}$), using a small-amplitude AC perturbation superimposed on the open-circuit voltage (OCV). Under these conditions, the impedance response reflects the electrochemical processes occurring during the normal operation of the DSSCs, allowing the evaluation of charge transport, interfacial charge transfer and electron recombination mechanisms. For each device, the experimental impedance spectrum was fitted using an equivalent electrical circuit, generating the theoretical ("Fitted") response, which was compared with the experimentally acquired data ("Experimental"). The fitting quality demonstrates that the proposed equivalent circuit adequately reproduces the electrochemical behavior of the fabricated cells over the investigated frequency range. A simple RC equivalent circuit was not sufficient to accurately describe the impedance spectra obtained from the DSSCs, since the electrochemical response results from multiple interfacial phenomena occurring simultaneously. Consequently, a multi-element equivalent circuit was adopted, allowing the individual contribution of each physical process to be distinguished. The series resistance (Rs) represents the ohmic contribution of the FTO substrate, electrical contacts and electrolyte. The high-frequency time constant (R1) is associated with the rapid charge-transfer process occurring at the Pt/electrolyte interface, whereas the intermediate-frequency resistance (R2), together with its capacitive element, describes the electron transfer and recombination processes at the $TiO_2$/dye/electrolyte interface. Finally, the low-frequency resistance (R3) is related to ionic diffusion within the electrolyte and mass transport limitations, becoming more pronounced at longer relaxation times. The equivalent circuit parameters were obtained using the IviumSoft fitting routine through nonlinear least-squares optimization, minimizing the deviation between the experimental spectra and the theoretical model. The excellent agreement between the fitted and experimental curves confirms that the adopted equivalent circuit provides a reliable representation of the electrochemical behavior of the fabricated DSSCs, whereas a single RC model would not adequately reproduce the multiple time constants and interfacial processes observed experimentally. The fitted electrical parameters extracted from the impedance spectra are summarized in Table 3

**Table 3** Values of each element of the equivalent circuit with their associated errors.

| Dye | $R_S$ (Ω) | $R_1$ (Ω) | $R_2$ (Ω) | R3 (Ω) | $C_1$ (μF) | $C_2$ (μF) | $C_3$ (μF) |
|---|---|---|---|---|---|---|---|
| CV | 31.51 ± 0.35 | 47.85 ± 3.04 | 43.65 ± 3.15 | 7.09 ±7.24 | 81.2 ± 7.14 | 142.5 ± 3.02 | 92.42 ± 5.44 |
| CG | 27.76 ± 0.33 | 265.9 ± 0.46 | 8.058 ±8.54 | 8.098 ±8.23 | 49.66 ± 0.95 | 146.3 ±5.12 | 85.45 ±3.34 |
| CB | 40.12 ± 0.21 | 230.4 ± 1.41 | 42.61 ± 7.88 | 4.146 ±6.83 | 119.3 ± 2.91 | 164.6 ± 3.28 | 120.3 ± 6.86 |

Table 4 shows the conversion efficiency and photovoltaic performance of various cells using natural dyes reported in the literature. The highest energy conversion efficiency obtained in this study was achieved with the cell sensitized with the CV (Chrysanthemum Violet) dye, 1.35% PCE. The natural dyes studied, adsorbed on the $TiO_2$ surface, absorb visible light and promote electron transfer through the dye/semiconductor interface. The results obtained for the CV and CG dyes reached efficiency levels higher than those of some simple dyes present in the literature, such as dyes based on *Indigofera tinctoria* [93], Ixora Coccinea pigments [94] and others.

**Table 4** Photovoltaic performance of *Chrysanthemum* DSSCs with various natural dyes.

| Dye | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | η(%) | Ref. |
|---|---|---|---|---|---|
| *Leucanthemum* | 0.42 | 0.52 | 0.27 | 0.88 | [34] |
| *Thunbergia erecta* | 0.27 | 0.55 | 0.40 | 0.37 | [53] |
| Inthanin bok | 0.082 | 0.76 | 0.53 | 0.95 | [91] |
| Jabuticaba | 0.38 | 0.41 | 0.29 | 0.13 | [49] |
| Strobilanthescusia | 0.003 | 0.28 | 0.25 | 0.01 | [92] |
| *Indigofera tinctoria* | 0.37 | 0.49 | 0.63 | 0.11 | [93] |
| *Ixora Coccinea* | 0.40 | 0.53 | 0.76 | 0.16 | [94] |
| *Rubia tinctorum* | 0.14 | 0.58 | 0.48 | 0.13 | [95] |
| *Chrysanthemum Violet* | 0.85 | 0.58 | 0.44 | 1.35 | this work |
| *Chrysanthemum Green* | 0.99 | 0.48 | 0.41 | 1.23 | this work |
| *Chrysanthemum Blue* | 0.34 | 0.47 | 0.48 | 0.485 | this work |

## 3.2 – Analysis of DSSCs Manufactured with Boranil and Bodipy Sensitizers

### 3.2.1 – Structural Analysis

Figure 3.8 shows SEM images obtained from nanostructured $TiO_2$ thin-film photoanodes, in such a way that it can be seen that they appear to have good connections between them, with mesopority relevant to grant the formation of an extended electrode-electrolyte interface. Another important point in morphology is the roughness present in the material, which leads to a benefit in the adsorption of the dye due to its high surface roughness and also high surface area [96].

Likewise, the topography of the Pt-coated FTO glass was characterized with SEM. The cathode demonstrated hierarchical morphology after being synthesized at 350 °C, as it has pores in different dimensions, as shown in Figure 3.9. The image portrays that the Pt coating occurred homogeneously on the outer face of the nanostructured electrode. This class of hierarchical nanostructures increases the electrocatalytic activity or PCA and the electron transfer conductivity in the J x V performance in DSSC [96]. The darker parts within the formed uniform nanostructured network can be attributed to a lower particle deposition; in this section,

an annealing failure process may have occurred, considering that there was no change in the substrate structure in these regions, as reported below in Figure 3.9.

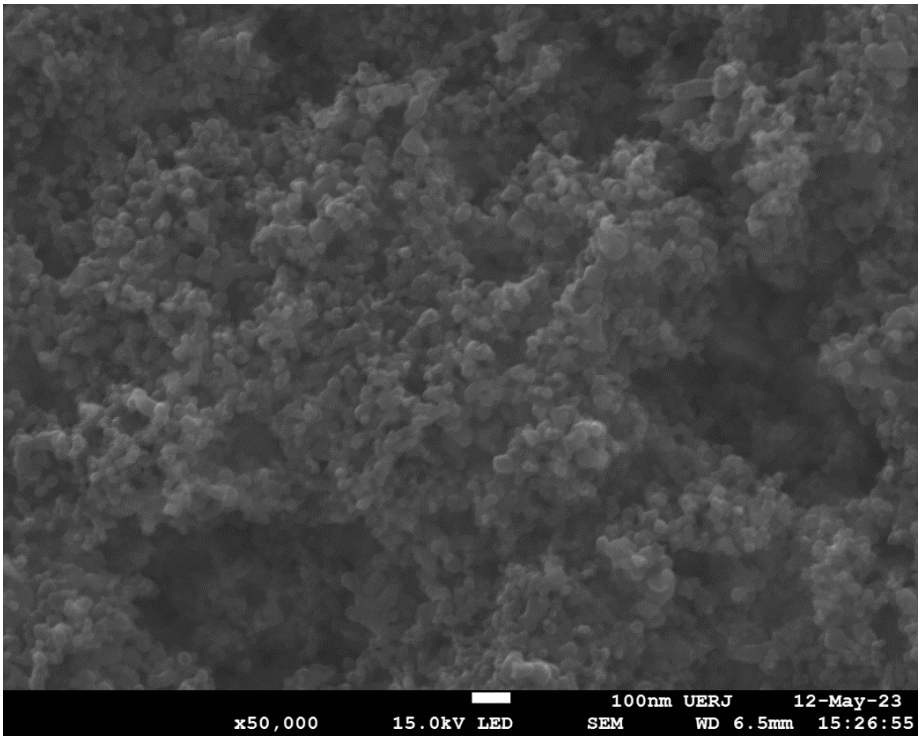



**Figure 3.8** SEM generated image of a $TiO_2$ film.

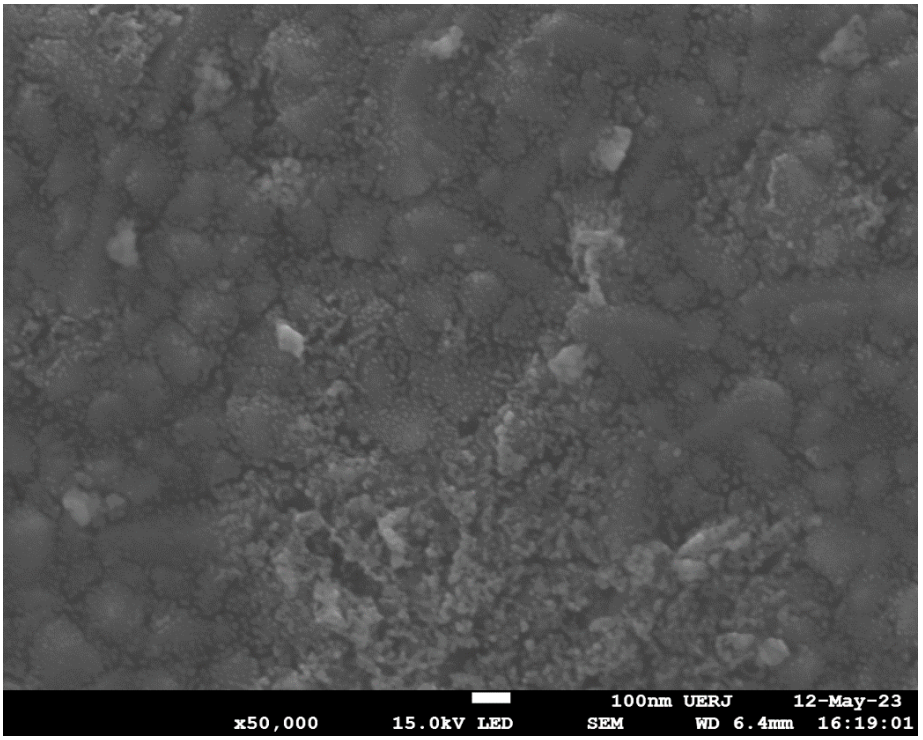



**Figure 3.9** Image obtained from SEM measurements of a platinum film.

In addition to analyzing the topographic roughness of the base electrodes, the surface morphology of the $TiO_2$ thin films with the synthesized dyes deposited on the substrate was

also analyzed. The results obtained can be seen in Figures 3.10-a and b.

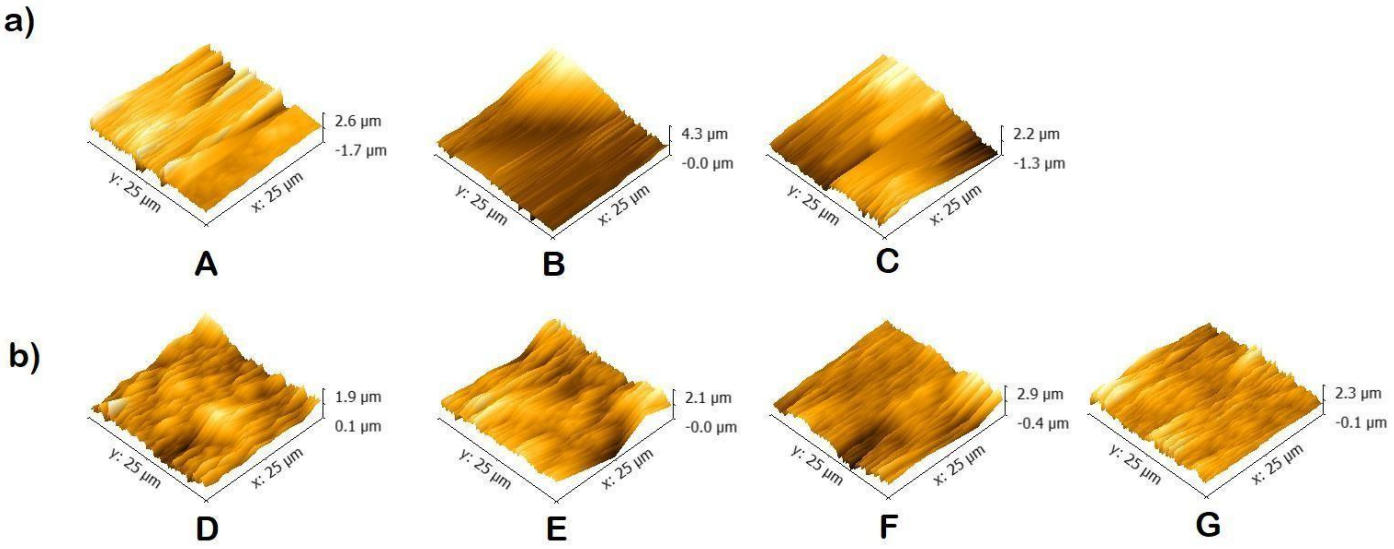



**Figure 3.10** Results of AFM analyses of (a) Boranil e (b) Bodipy.

Figure 3.10 shows the better topographic distribution of the films produced from Bodipy class dyes. When we analyze the electrodes manufactured with Boranil class dyes (Figure 3.10-a), we see that they have a more flattened distribution compared to the electrodes manufactured with Bodipy dyes (Figure 3.10-b). These have more pronounced peaks and valleys, but in a uniform manner, which favors the absorption of the active layer by the semiconductor electrode.

To obtain information relevant to the nuclear electronic environment of the dyes, characterization was performed using the aforementioned technique. Below are the results of the characterizations performed for the Boranil dyes:

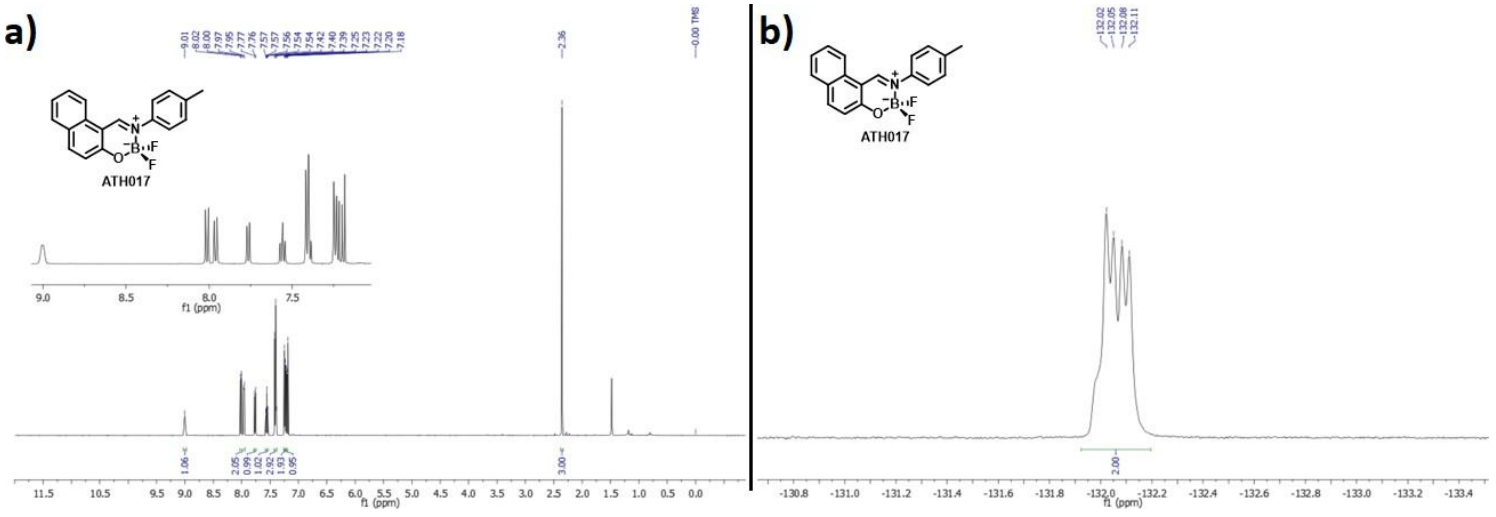



**Figure 3.11** – NMR spectrum of Boranil sample ATH017 (a) $^{1}H$ NMR e (b) $^{19}F$ NMR.

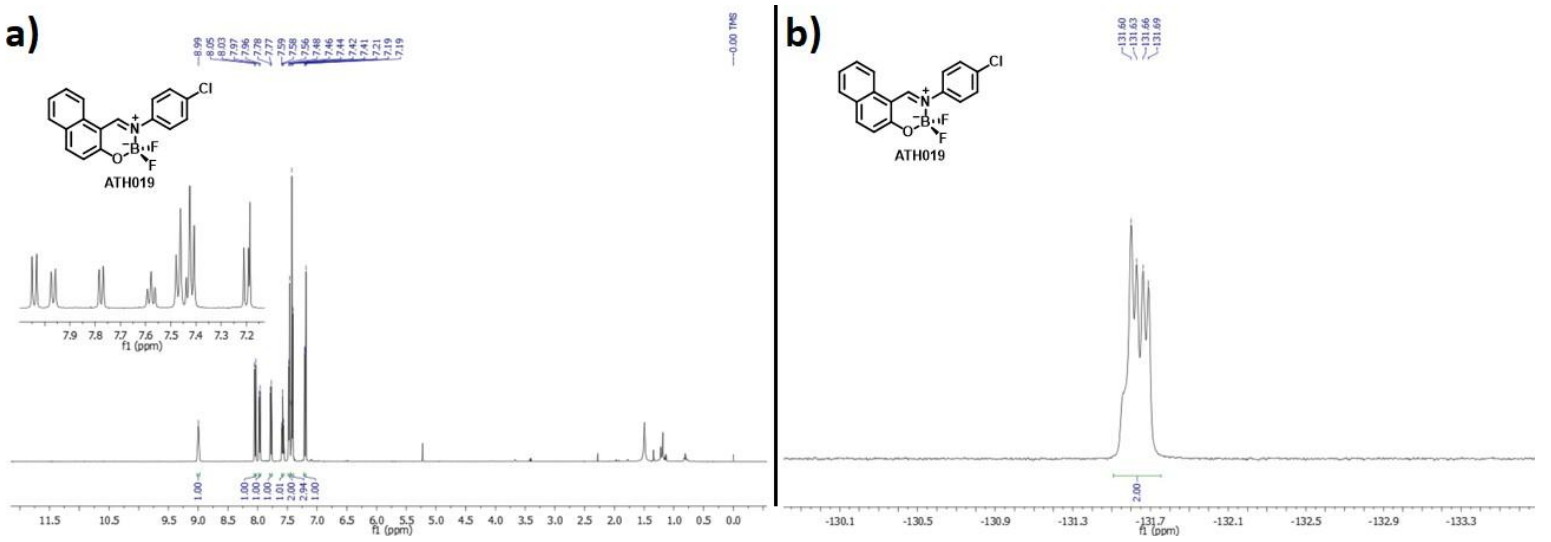



**Figure 3.12** – NMR spectrum of Boranil sample ATH019 (a) $^{1}H$ NMR e (b) $^{19}F$ NMR.

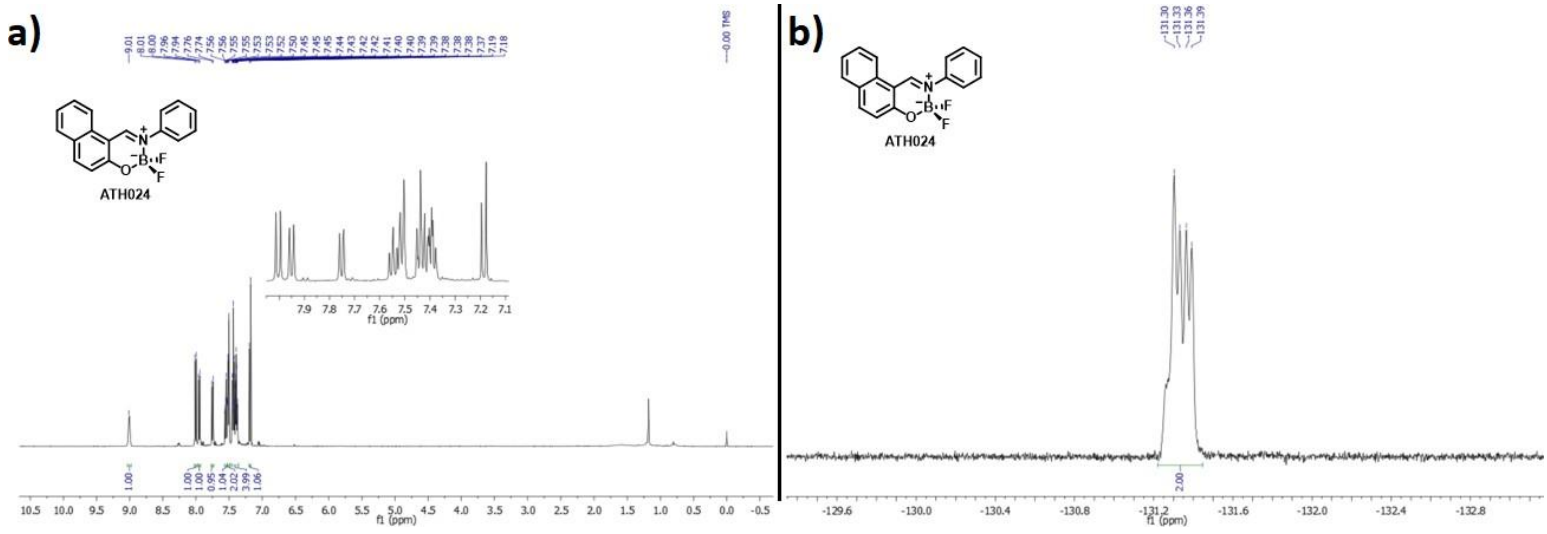



**Figure 3.13** – NMR spectrum of Boranil sample ATH024 (a) $^{1}H$ NMR e (b) $^{19}F$ NMR.

The $^{1}H$ NMR spectrum of the Boranil compounds ATH017, ATH019, and ATH024 generally showed similar and characteristic resonance signals of 6 hydrogens from the naphthyl ring in the range of 7.1 to 8.1 ppm and of the hydrogens from the phenyl group close to 7.4 and 7.2 ppm. The iminic hydrogen was observed close to 8.9 ppm in the form of a singlet, and for the compound ATH017, we can observe a singlet at 4.70 ppm referring to the methyl hydrogens that only this compound possesses.

To verify the complexation with BF3, an analysis was performed by $^{19}F$ NMR spectroscopy where a signal in the form of a quartet close to -131 ppm (J = 13.1Hz) was observed, referring to the two fluorine atoms of BORANIL that are equivalent. This multiplicity, as previously explained, is due to coupling with $^{11}B$.

Similarly, NMR characterization of the Bodipy compounds was performed, obtaining the following results:

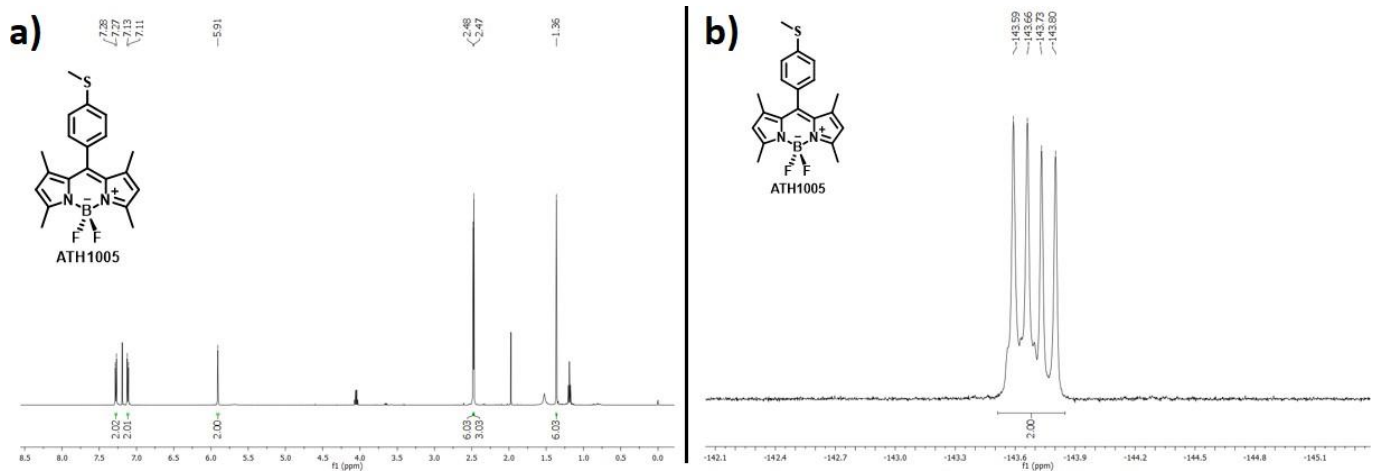



**Figure 3.14** – NMR spectrum of Bodipy sample ATH1005 (a) $^{1}H$ NMR e (b) $^{19}F$ NMR.

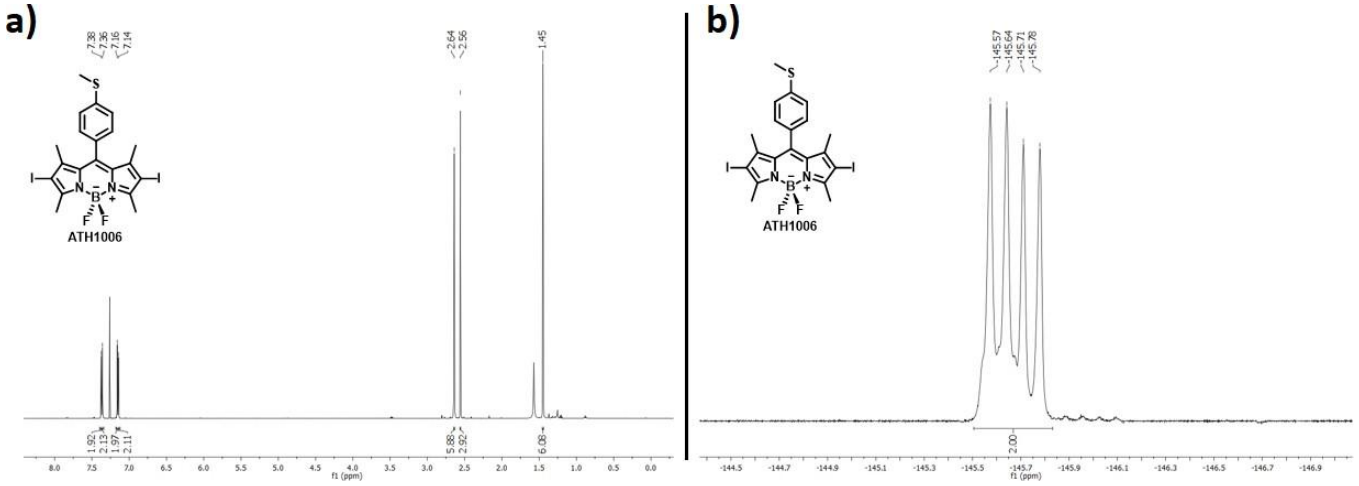



**Figure 3.15** – NMR spectrum of Bodipy sample ATH1006 (a) $^{1}H$ NMR e (b) $^{19}F$ NMR.

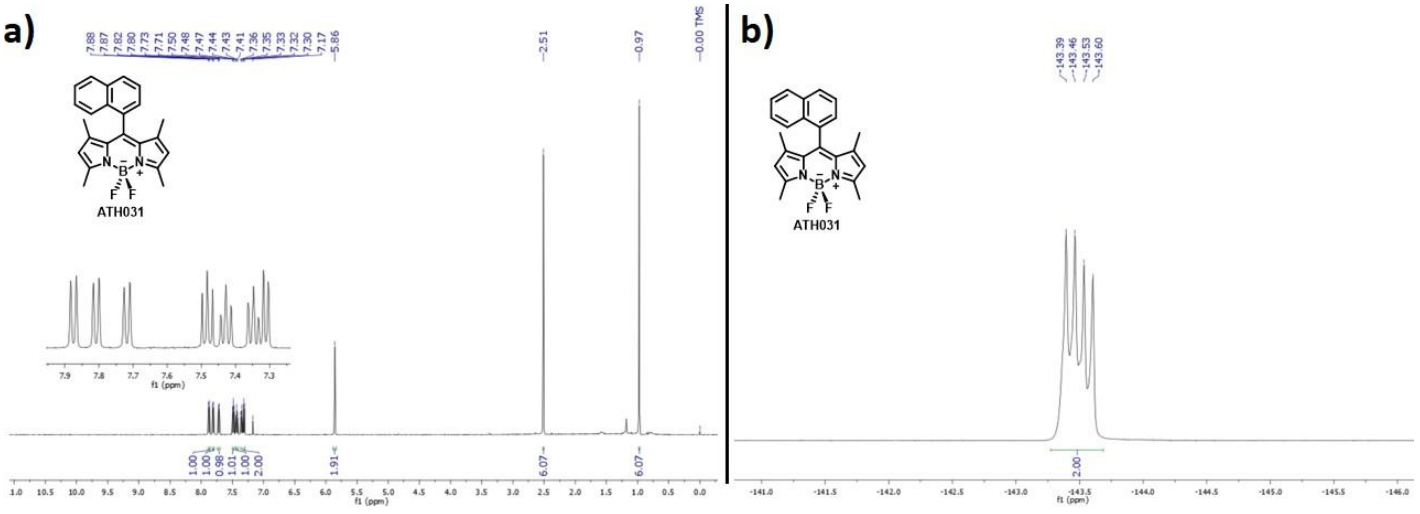



**Figure 3.16** – NMR spectrum of Bodipy sample ATH031 (a) $^{1}H$ NMR e (b) $^{19}F$ NMR.

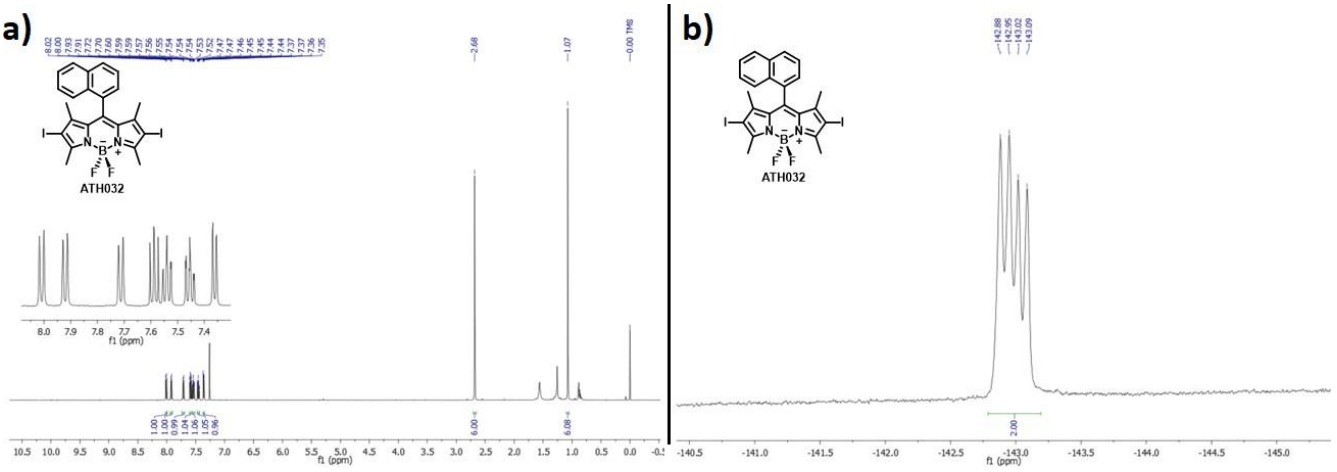



**Figure 3.17** – NMR spectrum of Bodipy sample ATH032 (a) $^{1}$H NMR e (b) $^{19}$F NMR.

Due to the high conjugation of the π electronic system in the Bodipy compounds (ATH1005, ATH031), they exhibit quite characteristic $^{1}$H NMR spectra. Signals characteristic of a highly symmetrical structure was observed. In general, one signal was observed near 5.9 ppm, a chemical shift characteristic of the resonance of aromatic peripheral hydrogens, referring to the two β-pyrrolic hydrogens. Two other simplets showed shifts near 2.5 ppm and 1.0 ppm, referring to the methyl hydrogens of the Bodipy nucleus, with integration to six hydrogens each. The signals observed in the region between 7.8 and 7.1 ppm correspond to the signals of the aromatic hydrogens present in the meso substituent of the Bodipy nucleus. For Bodipy ATH1005, the simplet with a shift of 2.5 ppm and integration to three hydrogens referring to the methyl group of the thiomethyl group was observed. To verify the complexation with BF3, a $^{19}$F NMR spectroscopy analysis was performed. $^{19}$F has an isotopic abundance of 100% and a spin of ½. In the 19F NMR spectrum, a signal in the form of a quartet near -143 ppm (J = 32 Hz) was observed for the Bodipys ATH1005 and ATH031, referring to the two equivalent fluorine atoms of the Bodipy. This multiplicity is due to coupling with 11B. The element boron has two isotopes, $^{11}$B (I=3/2) with a relative abundance of 80.1% and 10B (I = 3) with a relative abundance of 19.9%, both magnetically active. $^{11}$B has a spin of 3/2, meaning it can exist in the states m = 3/2, 1/2, -3/2, and -1/2. Therefore, there is an equal probability that the $^{19}$F nucleus will couple to $^{11}$B in each of its four spin states, generating a splitting into four lines of equal intensity (1:1:1:1), correctly referenced as a non-binomial quartet. However, the existence of another isotope, $^{10}$B, causes a change in the shape of this quartet. For the Bodipys ATH1006 and ATH032, characteristic signals of a highly symmetrical structure were observed, as well as in the non-iodinated precursor Bodipys (ATH1005 and ATH031). The absence of the previously observed signal near 5.9 ppm, referring to the two β-pyrrolic hydrogens, confirms the obtaining of the di-iodinated product. The other two simplets showed shifts at 2.5 ppm and 1.3 ppm corresponding to the 12 methyl hydrogens, as well as the hydrogens of the aromatic ring, and were well characterized in each case, showing no alteration in relation to the $^{1}$H NMR spectra of the non-iodinated Bodipys analogues.

In the $^{19}F$ NMR spectrum, a quartet close to -145 ppm (J = 32 Hz) was observed for all synthesized compounds, corresponding to the 2 fluorine atoms bonded to boron, without major alterations when compared to the non-iodinated Bodipys analogues ATH1005 and ATH031.

### 3.2.2 – Optical Analysis

Below are the results of the functional groups present in the synthesizers derived from the boron complex, shown in Figures 3.18 (Boranil) and 3.19 (Bodipy).

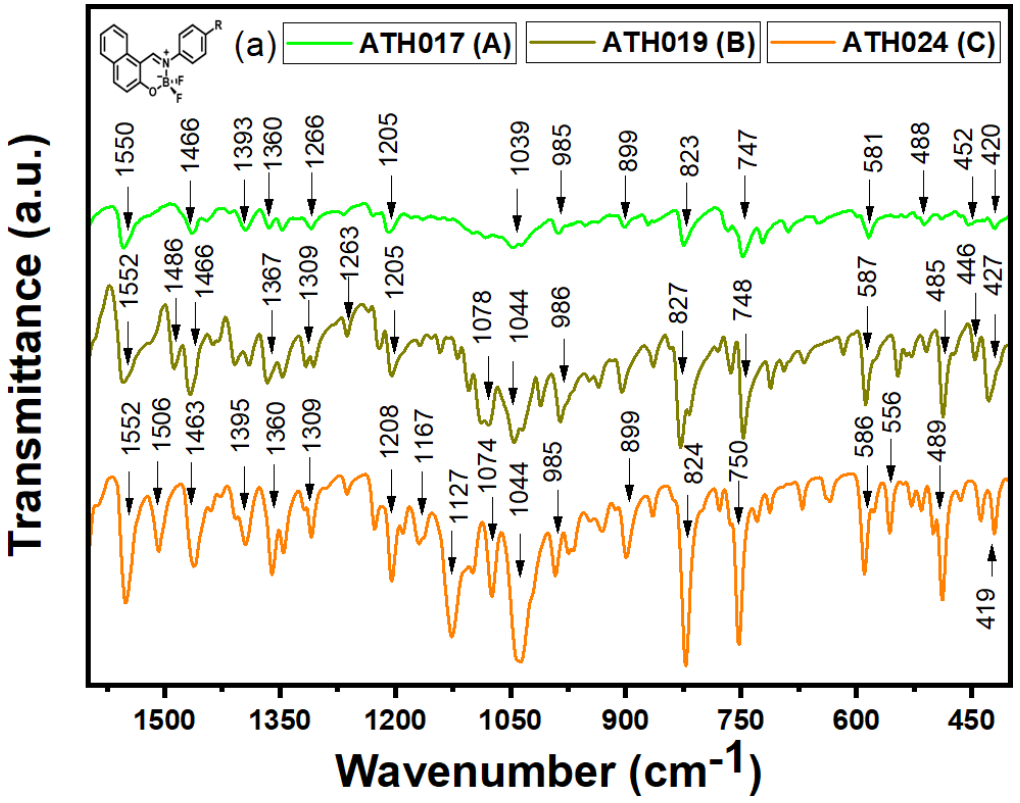



**Figure 3.18** FTIR spectra for different Boranil dyes: (a) ATH017 (b) ATH019 e (c) ATH024.

A literature review reveals that the FTIR spectrum curve has proven useful in confirming the proposed structure of Boranils and similar organic compounds [97]. The compounds studied were characterized by infrared spectroscopy where they exhibit several typical peaks with appropriate changes resulting from band formation. Depending on their molecular structure, the compounds studied exhibit C-H and C=C stretching and bending vibrations. These vibrations are extremely informative and very convenient for characterization purposes [98]. The FTIR-ATR spectra of the Boranil derivatives ATH017, ATH019 and ATH024 (Figure 3.18) exhibit several characteristic absorption bands that confirm the successful formation of the boron-coordinated fluorophore and provide important information regarding its molecular structure. The absorption band located near 1625 $cm^{-1}$ is assigned to the stretching vibration of the azomethine (C=N) bond belonging to the Schiff-base framework. Additional bands observed between approximately 1600 and 1500 $cm^{-1}$ are attributed to

aromatic C=C stretching vibrations of the naphthalene and phenyl rings, confirming the presence of an extended π-conjugated system responsible for the electronic delocalization of the dyes. The absorption region between 1450 and 1350 $cm^{-1}$ comprises contributions from C–N stretching vibrations together with the B–O coordination bond formed after complexation with boron. Characteristic bands at approximately 1309, 1208 and 1046 $cm^{-1}$ correspond to asymmetric and symmetric B–F stretching modes of the $BF_2$ chelate, while weaker absorptions below 900 $cm^{-1}$ are assigned to out-of-plane C–H deformation modes of substituted aromatic rings. Altogether, these absorption bands confirm the structural integrity of the synthesized Boranil derivatives. From the viewpoint of DSSC operation, these functional groups also play an important role in the adsorption of the sensitizer onto the $TiO_2$ surface. Unlike conventional ruthenium complexes or organic dyes containing carboxylic anchoring groups, the Boranil derivatives investigated in this work are adsorbed mainly through Lewis acid–base interactions established between surface $Ti^{4+}$ sites of $TiO_2$ and the electron-rich phenoxide oxygen incorporated in the N–B–O chelate. The rigid $BF_2$ coordination maintains the molecular planarity and extends the π-conjugation, favoring electronic coupling between the adsorbed dye and the semiconductor. This interfacial interaction enables efficient photoinduced electron injection from the excited Boranil molecule into the $TiO_2$ conduction band while preserving the photochemical stability provided by the boron coordination. Therefore, the FTIR results not only confirm the successful synthesis of the dyes but also demonstrate the presence of structural features that are directly associated with their adsorption mechanism and their applicability as sensitizers in dye-sensitized solar cells. In [97], we have a table with the respective vibration modes associated with their wavenumber.

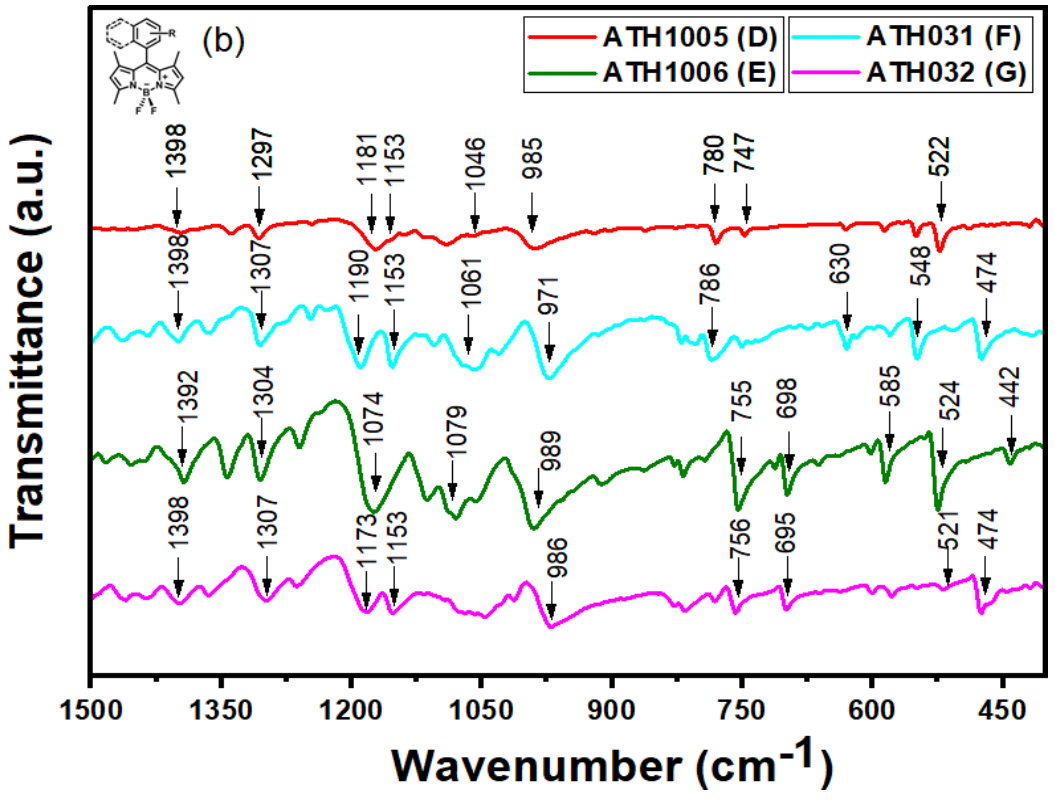



**Figure 3.19** FTIR spectra for different Bodipy dyes: (a) ATH1005- D (b) ATH1006 - E (c) ATH031 – F and (d) ATH032 - G.

Infrared (FTIR-ATR) analysis of Bodipys ATH1005 and ATH031 yielded spectra showing characteristic absorption bands related to the axial deformation of the C=N bond near 1606 $cm^{-1}$ and absorption bands near 1306 $cm^{-1}$, 1190 $cm^{-1}$, and 1061 $cm^{-1}$ characteristic of the stretching of the B-F bond of Bodipys. Despite the similarity to the spectra of Bodipys ATH1005 and ATH031, the infrared (FTIR-ATR) analysis of Bodipys ATH1006 and ATH032 highlights the observation of the characteristic absorption band of the C-I bond stretching near 524 $cm^{-1}$, confirming the successful insertion of iodine into the β-pyrrolic position. All peaks confirmed that the designed nanoparticles were successfully prepared. The synthesized dyes, derived from boron complexes, were subjected to characterization using a UV-Vis spectrophotometer. Samples derived from the Boranil class ATH017, ATH019, and ATH024 were designated A, B, and C, respectively. Samples from the Bodipy class ATH1005, ATH1006, ATH031, and ATH032 were designated D, E, F, and G, respectively.

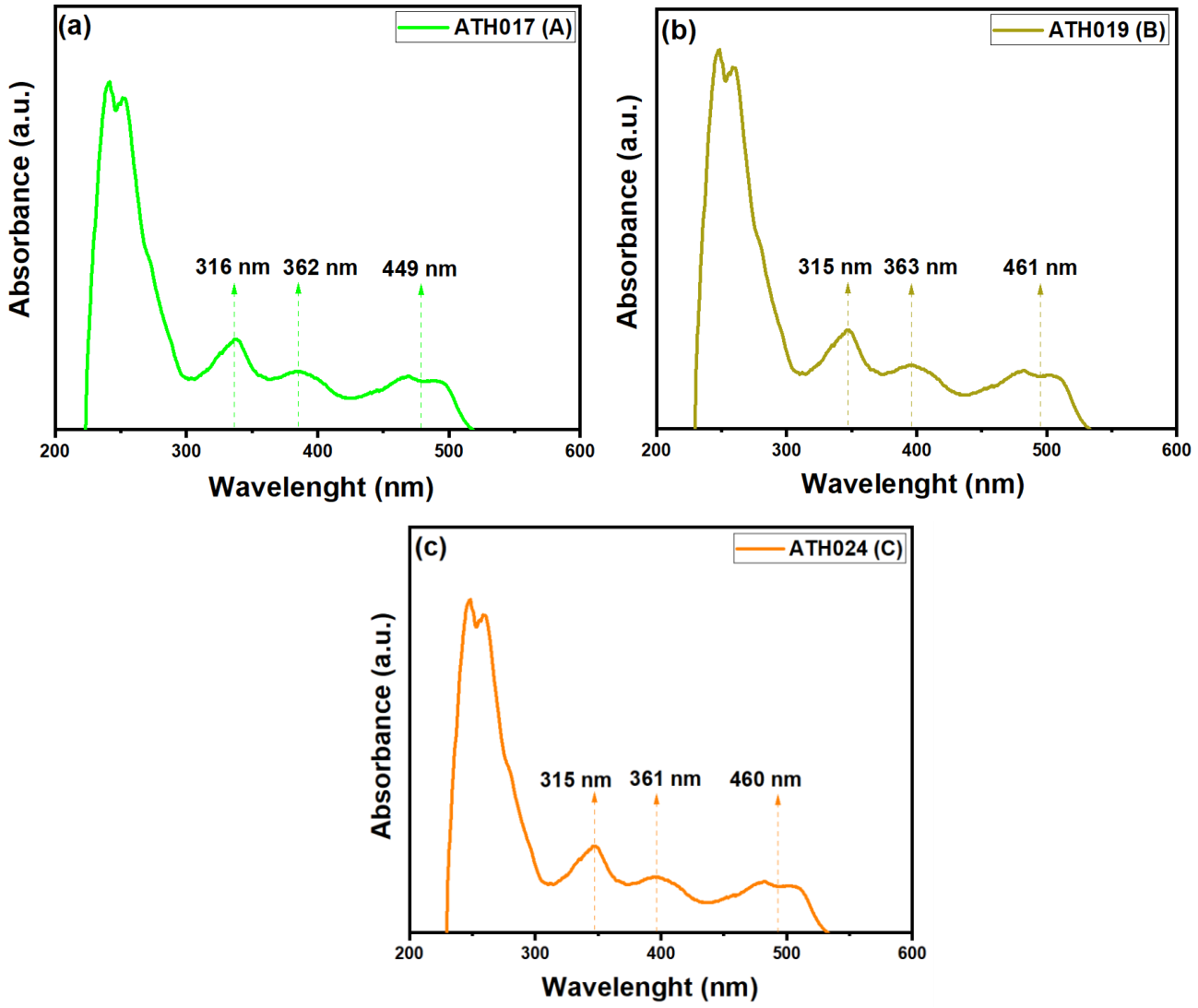



**Figure 3.20** UV absorption of Boranil dyes: (a) ATH017- A (b) ATH019 - B e (c) ATH024 - C.

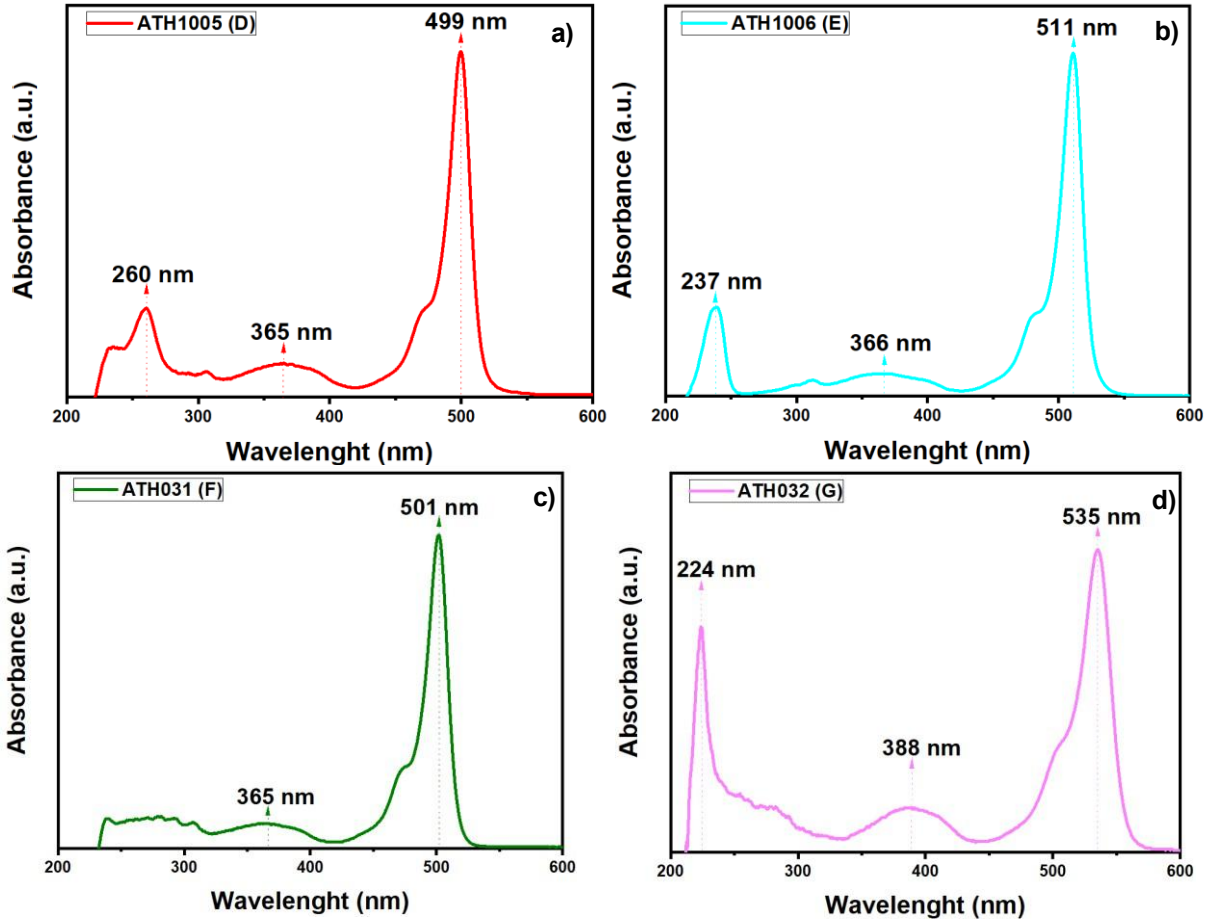



**Figure 3.21** UV absorption of Bodipy dyes: (a) ATH1005- D (b) ATH1006 - E (c) ATH031 – F e (d) ATH032 - G.

In Figure 3.20, the Boranil samples exhibit absorption peaks in the 315~363 nm range, which comprises the near ultraviolet region, in addition to these, there are peaks in the ultraviolet visible region 449~460 nm, but with little intensity.

The Bodipy samples show absorption peaks in the 365~388 nm and 499~535 nm range, covering a wavelength range with greater intensity than the Boranil dyes in the ultraviolet visible region. The peaks of the absorption spectra of the samples align with the HOMO-LUMO energy difference characteristic of the class of Boron-derived dyes [99], as can be seen in Figure 3.21:

For a more objective comparison, Figure 3.22 establishes the characteristics of each class of dyes in a single plot, respectively:

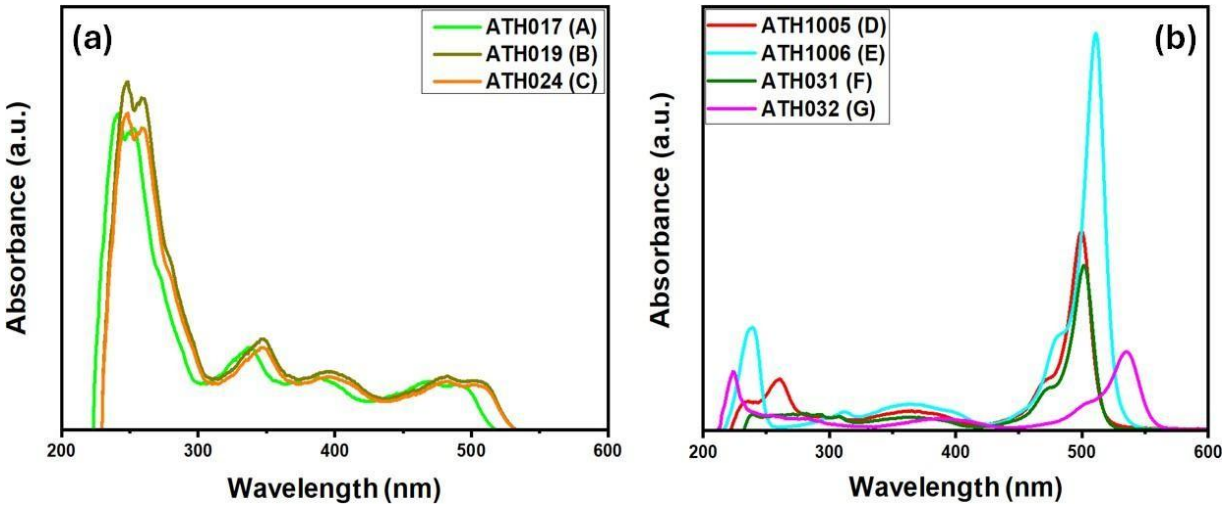



**Figure 3.22** UV-Vis spectra of synthesized dyes: (a) Boranil's and (b) Bodipy's.

The overall photoelectric performance of DSSC depends on the ability of the active materials (dye) to absorb light and the diffusivity of the electrons ejected through the window material [100]. An analysis of light absorption in the dyes was performed to evaluate their ability to capture photons in the ultraviolet region of the electromagnetic spectrum (200 to 800 nm). The optical absorption spectra of the individual dyes, as well as their mixed counterparts, are shown in Figures 3.21, 3.22, 3.23 and 3.24. It is evident that each dye contains pigments with varying capacities to absorb energy in specific wavelength ranges.

By observing the individual curves of the synthesized samples derived from Boron complexes, it can be concluded that the dyes of the Bodipy class exhibit better absorbance behavior, as they are excited in a wider region of the spectrum and have greater vibrational intensity compared to the dyes of the Boranil class. Therefore, to apply the co-sensitization technique to the synthesized dyes, the hypothesis of using Boranil was discarded in favor of comparing the data obtained with the Bodipy class. Analyzing the results obtained from the absorbance spectra characterizations of the Bodipy class dyes, sample F or ATH031 was discarded for the method, considering the vibrational properties presented by the dyes. Thus, the dyes whose co-sensitization window encompassed the largest differential range among the observed wavelengths were arbitrarily selected.

Consequently, this large difference is seen between dyes D and G, or ATH1005 and ATH032, respectively. It can be observed that in sample G, the first peak obtained in the near-ultraviolet region is presented at 224 nm, while in sample D, the peak is at 260 nm. Furthermore, in the visible region of the spectrum, sample D has the peak at the shortest wavelength value among the samples, located at 499 nm, while sample G has the longest value, at 535 nm. Therefore, it is expected that the co-sensitization between these will have the most satisfactory result. Sample E or ATH1006 was also included in the co-sensitization method for comparison and validation of the results. The results obtained with the mixing of dyes D, E, and G are shown below in Figures 3.23 and 3.24.

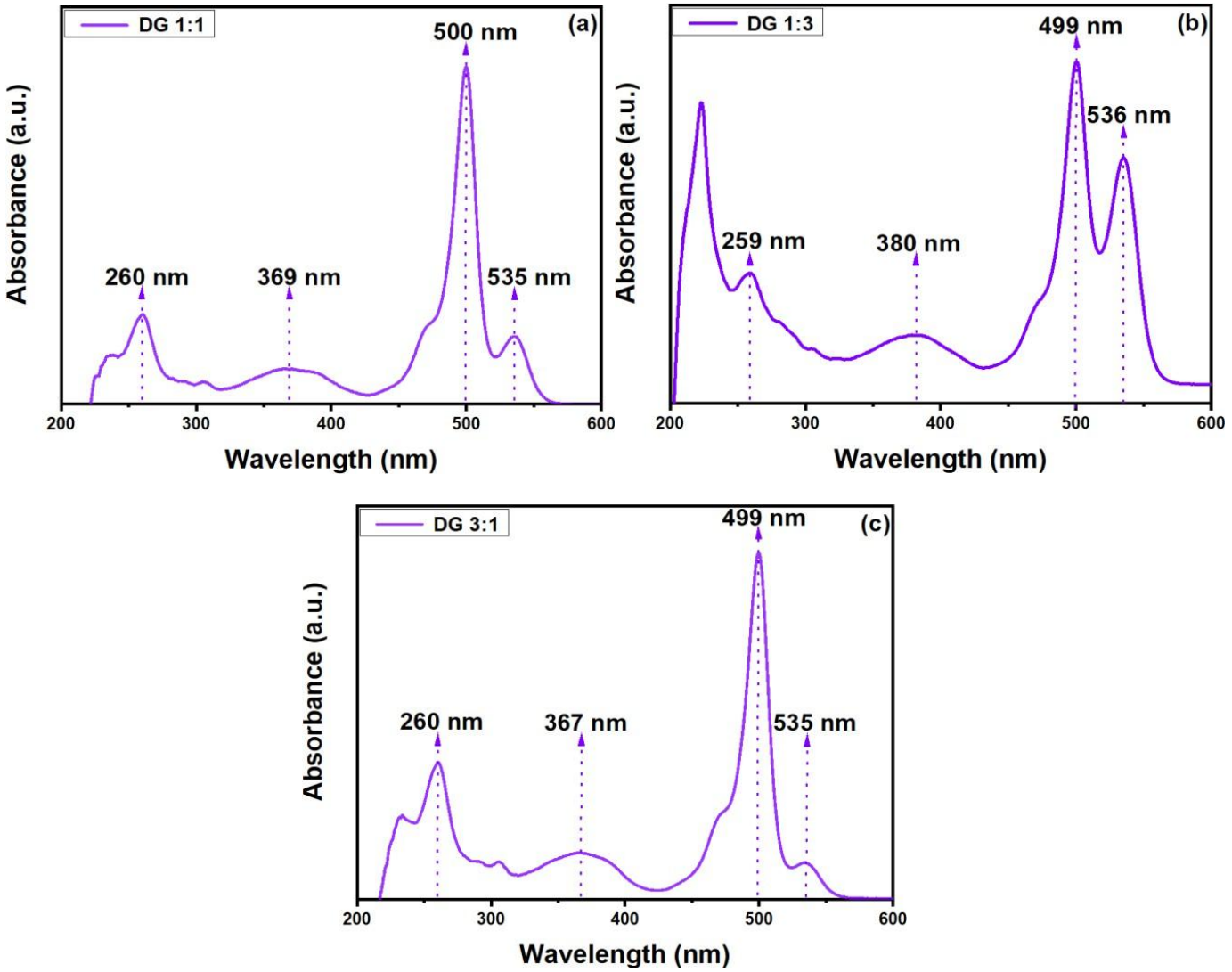



**Figure 3.23** UV absorption of Bodipy co-sensitizers: (a) DG 1:1 (b) DG 1:3 e (c) DG 3:1.

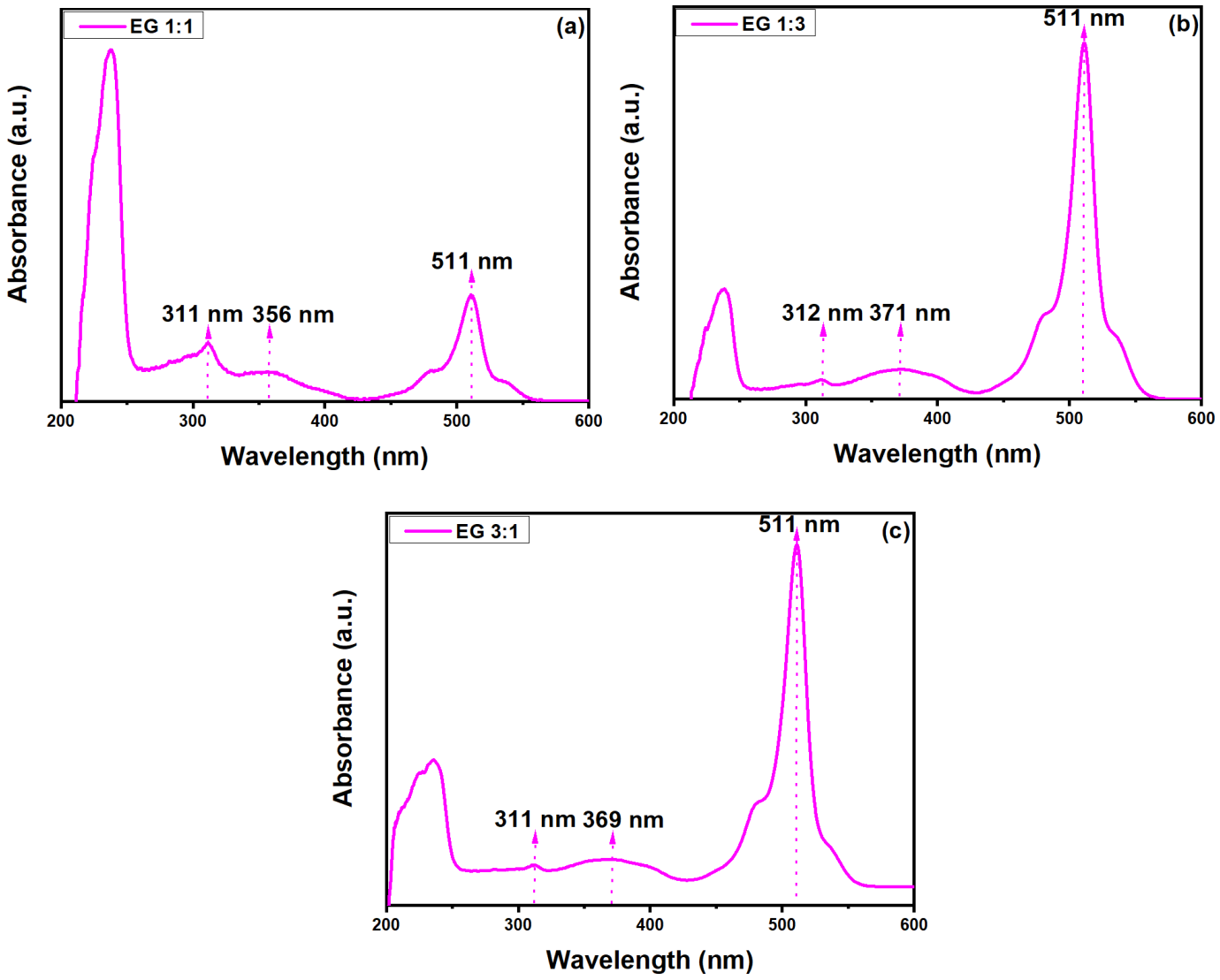



**Figure 3.24** UV absorption of Bodipy co-sensitizers: (a) EG 1:1 (b) EG 1:3 e (c) EG 3:1.

Figure 3.23 shows the absorption spectra of three mixed dyes labeled DG 1:1, DG 1:3, and DG 3:1. The main objective of combining these dyes is to broaden the absorption spectrum of solar radiation. Frequently, mixtures of various dyes with varying absorption spectrum are prepared to achieve maximum absorption in the near-visible, visible, and infrared regions. In the context of DSSC applications, these mixtures co-sensitize the device, improving overall absorption by utilizing the widest possible wavelength range and thus maximizing efficiency [101]. From Figure 3.23-b, the DG sample in a volume ratio of 1:3 exhibits an increased absorption spectrum. Peaks are observed at 259 nm, 380 nm, 499 nm, and 536 nm, with particularly high absorbance in the visible wavelength range. When the volume ratio is adjusted to 1:1, the absorption peak remains within the same wavelength range, but with reduced absorbance. On the other hand, the sample at a 3:1 ratio shows an even lower absorption peak within the same wavelength range. Notably, the 1:3 volume ratio represents the optimized configuration for the DG sample, exhibiting the widest absorption spectrum. It is worth highlighting that all DG samples share the same absorption peaks, but with varying intensities. Figure 3.24 shows the hybrid spectra between samples E and G, labeled EG, performed at the same ratio and volumetric concentrations as the previous assay.

Absorption peaks are evident in all EG sample mixtures (Figure 3.24-a, b, and c). In the 1:3 volume mixture, absorption peaks are observed at 312 nm, 371 nm, and 511 nm. The 1:1 mixture exhibits an absorbance peak at a wavelength with a smaller coverage zone, characterized by less absorption. On the other hand, the 3:1 volume ratio mixture shows an increased absorption peak compared to the 1:1 analysis, within the same wavelength range. Based on the results obtained, it can be concluded that the behavior of the sensitizers was as expected, considering that the highest degree of absorbance was achieved with a mixture of dyes D and G. For a visualization of the comparison between the materials, see Figure 3.25:

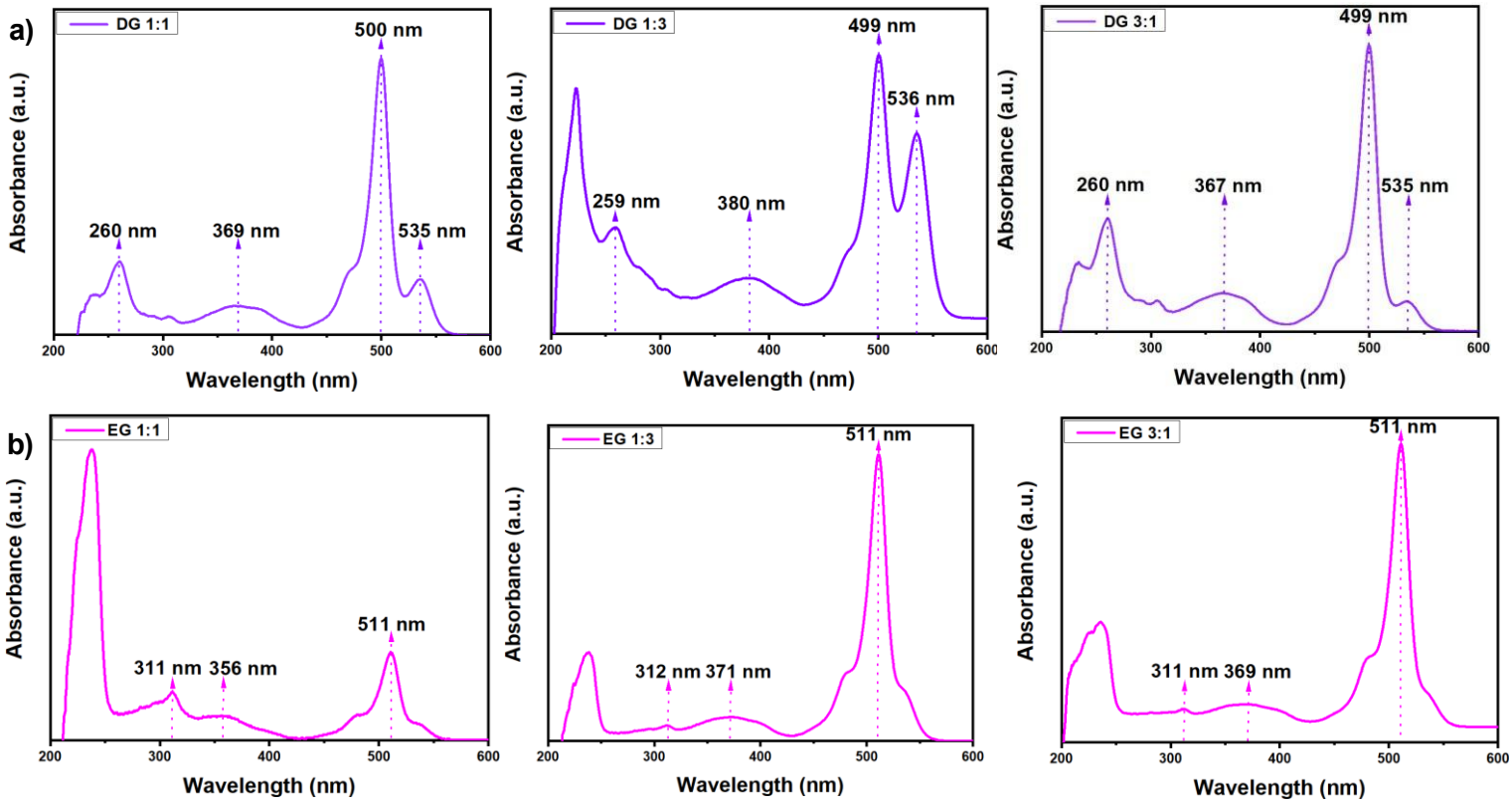



**Figure 3.25** UV-Vis spectra of hybrid dyes: (a) DGs and (b) EGs [96].

With intention to validate the co-sensitization method, a third mixing of dyes from previous studies was performed [28, 48]. As is known, the dye mixing method aims to increase the absorbance range of the samples; thus, it can be assumed that we simply take a dye with a degree of absorption in a smaller wavelength range and combine it with another dye whose absorption range in the ultraviolet is larger. Therefore, co-sensitization was performed between a fruit (Banana) and a flower (*Orange Gerbera*), labeled as BL, with different known absorbance peaks, to increase the overall absorption. The absorbance analyses of the dye mixture are shown in Figure 3.26. It is worth noting that the tests were performed in the same percentage volume proportions as the hybrid synthesizers used previously.

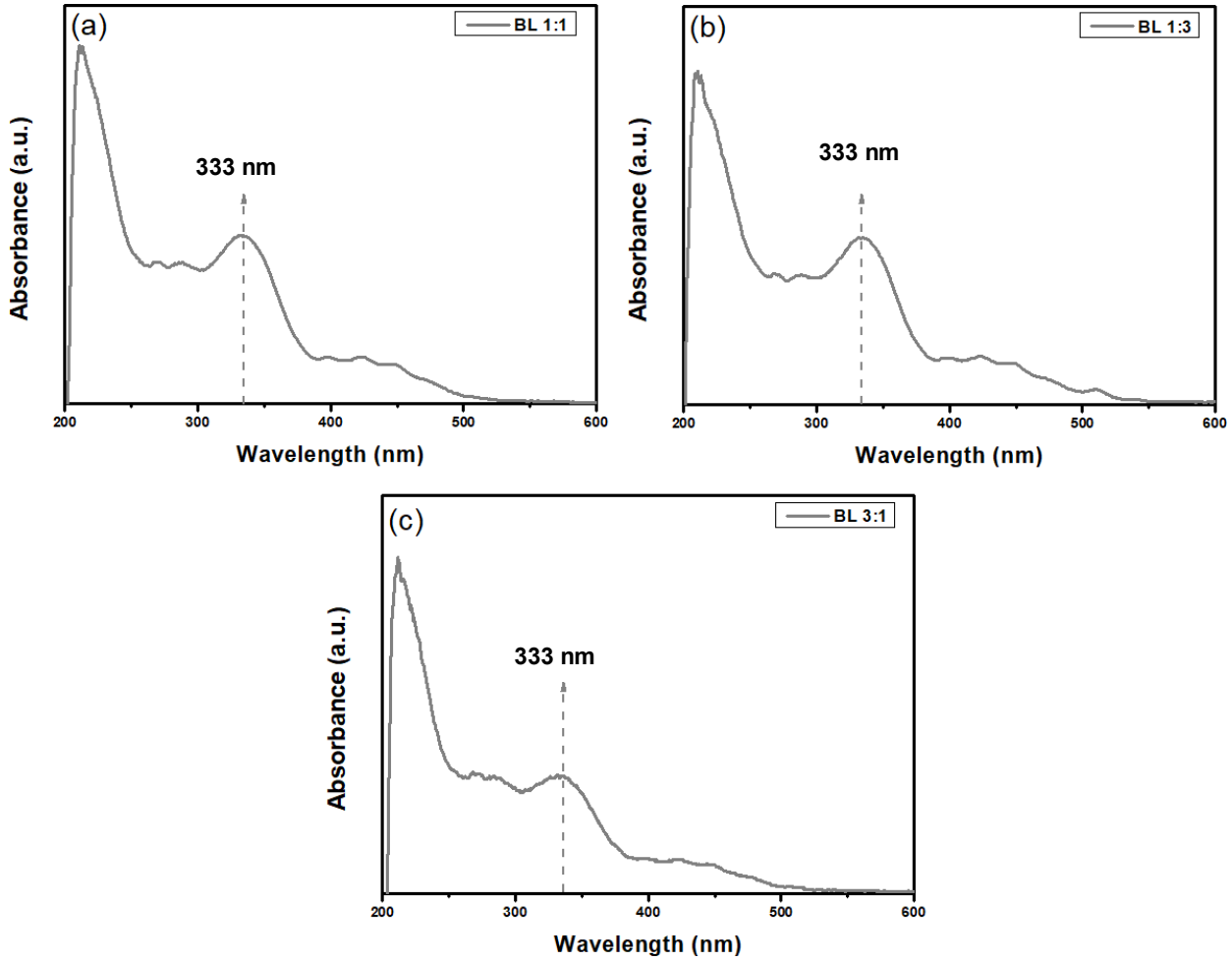



**Figure 3.26** UV absorption of banana and orange gerbera sensitizers: (a) BL 1:1 (b) BL 1:3 e (c) BL 3:1.

Figure 3.26 clearly demonstrates the need for congruence between the compounds responsible for cell sensitization. When mixing a fruit (Banana), whose compound class is characterized by beta-carotene, and a flower (Orange Gerbera), whose compound class is characterized by flavonoids, what was intended to increase overall efficiency actually decreased. From the region of interest, in this case the visible region of the electromagnetic spectrum ~380 nm, a decay is observed instead of an increase in the absorbance range. This is due to the fact that in this context there was desorption of the active material, resulting from the incompatibility between the groups that make up the structures of both co-sensitizers. This analysis shows us that the production method of hybrid photosensitizers must be carefully studied to prevent this desorption process from occurring, especially in the co-sensitization method, which, through the mixing of compatible dyes, aims to increase the absorption range of the solar radiation spectrum, increasing photon absorption and directly increasing the overall efficiency of DSSC.

### 3.2.3 Electrochemical analysis

To perform the J x V tests and consequently obtain the characteristic curves, a multipotentiostat coupled to a solar simulator was used. This experimental setup allowed for the controlled excitation of the $TiO_2$ photoanode, sensitized with different proportions of Bodipy and Boranil dyes, promoting the photoelectric effect responsible for generating current in the cell.

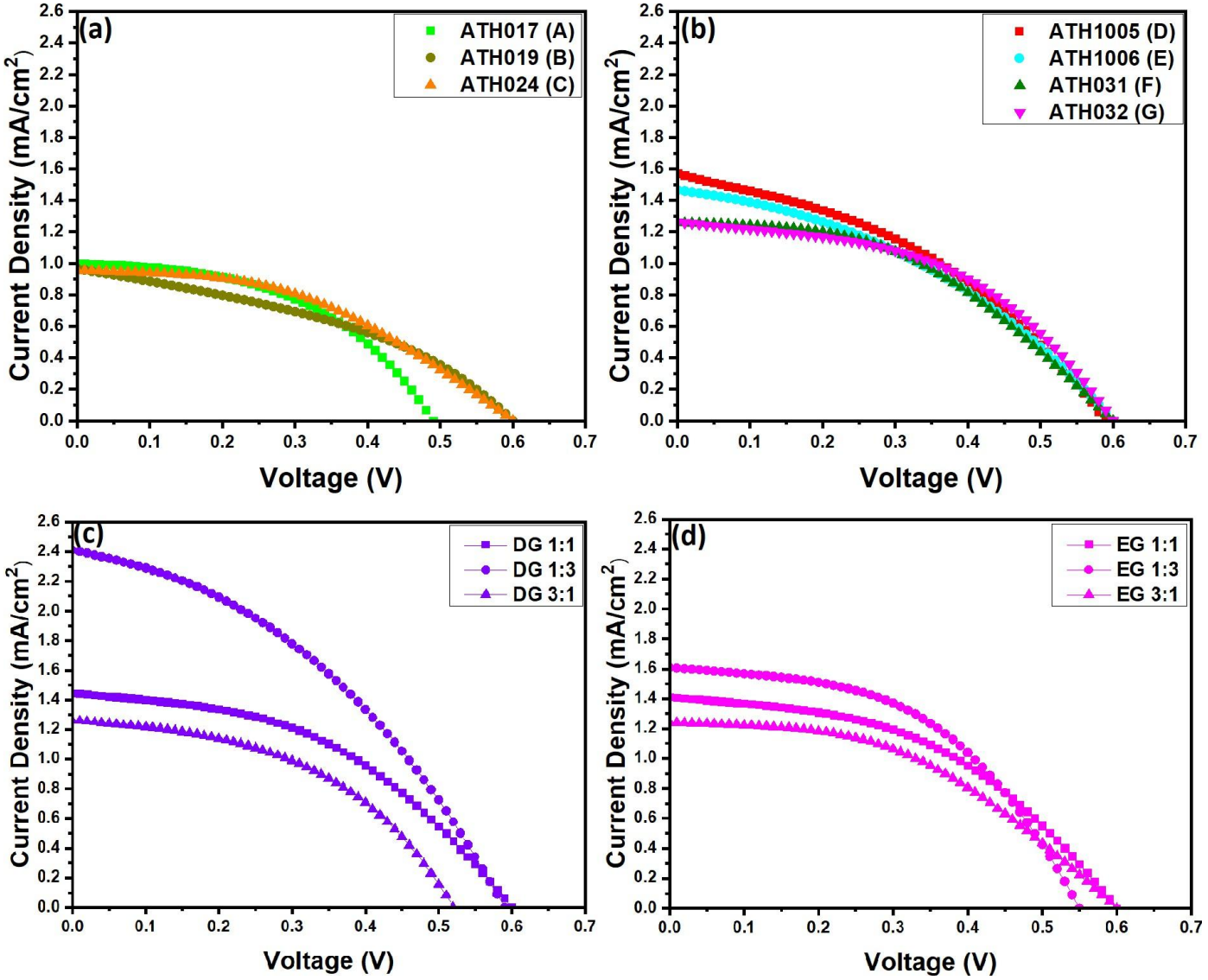



**Figure 3.27** Current density versus Voltage curves (J-V) of Boranil and Bodipy dyes.

Based on the analysis of the curves presented in Figure 3.27, it can be observed that the co-sensitized cells exhibited superior photovoltaic behavior compared to the cells sensitized by a single dye. In particular, the DG 1:3 cell demonstrated the best electrical response, approaching the ideal shape of the I×V characteristic curve, with the highest short-circuit current (JSC) and highest maximum power (Pmax) among the samples tested. This trend reflects the direct influence of the spectral synergy between the dyes, which, when used together, broaden the absorption range of the active layer and favor the injection of electrons into the $TiO_2$ conduction band.

In general, the cells with individual dyes presented less expressive I×V curves,

characterized by lower current densities. The cells sensitized only with Boranil dyes (A, B, and C) exhibited $J_{SC}$ of 0.99, 0.96, and 0.95 mA/cm², respectively. $V_{OC}$ values of 0.49 V, 0.60 V, and 0.60 V showed the lowest conversion efficiencies in the study. Cells with Bodipy dyes (D, E, F, and G) showed improvement in these parameters, reaching $J_{SC}$ values of 1.57, 1.46, 1.25, and 1.26 mA/cm², respectively. This superiority of the Bodipy group compared to Boranil stems from its more extensive π-conjugated structure, which favors light absorption up to the green region and facilitates electron transfer to the $TiO_2$ conduction band.

Analysis of the P × V curves provides a clear view of the maximum power point (Pmax) reached by each cell, directly related to the form factor (FF) and the overall efficiency of the device.

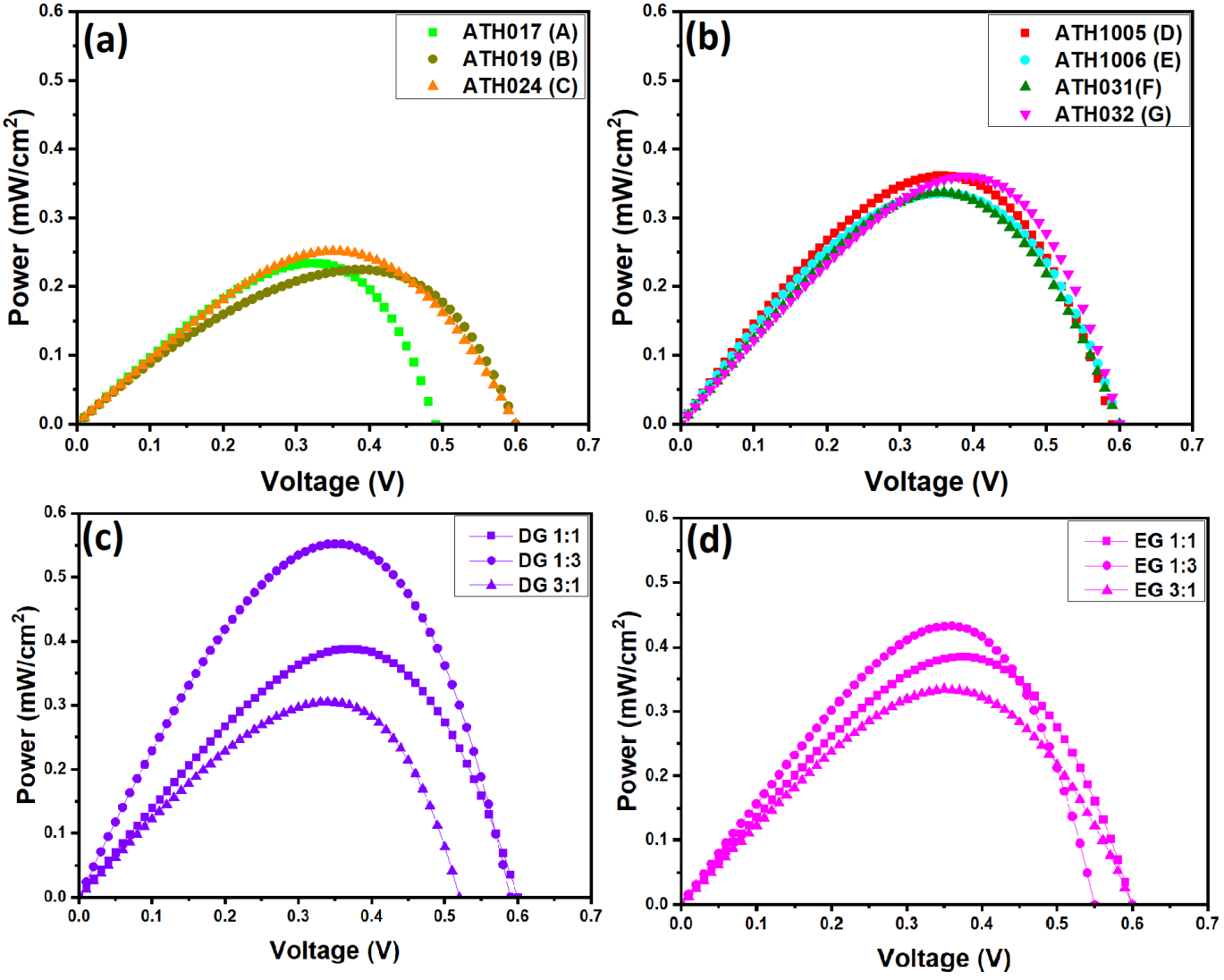



**Figure 3.28** Power versus Voltage curves (P-V) of Boranil and Bodipy dyes.

Through Figure 3.28, we can see that the devices containing Bodipy demonstrated superior performance to those based exclusively on Boranil, reaching higher maximum power values. The co-sensitized system (D:G = 25:75) obtained the highest Pmax, reflecting a conversion efficiency higher than the best device with individual sensitization. When compared to the results reported in [96], it is observed that, although the absolute PCE values are higher for the synthetic sensitizers (up to 3.45%), the relative trend of gain by co-sensitization is maintained. This demonstrates the robustness of the technique, regardless of

the nature of the dye used.

To evaluate the intrinsic resistance of each photosensitizer and understand the impact of dye mixing on solar cell performance, electrochemical impedance analyses were performed. The results, presented in Nyquist diagrams (Figure 3.29), reveal that solar cells with mixed photosensitizers exhibit a significantly smaller resistive semicircle compared to cells fabricated with individual dyes (Figure 3.29-c, d). For a more detailed analysis, the equivalent electrical circuit of the experimental and target photosensitizers is presented in Figure 3.29:

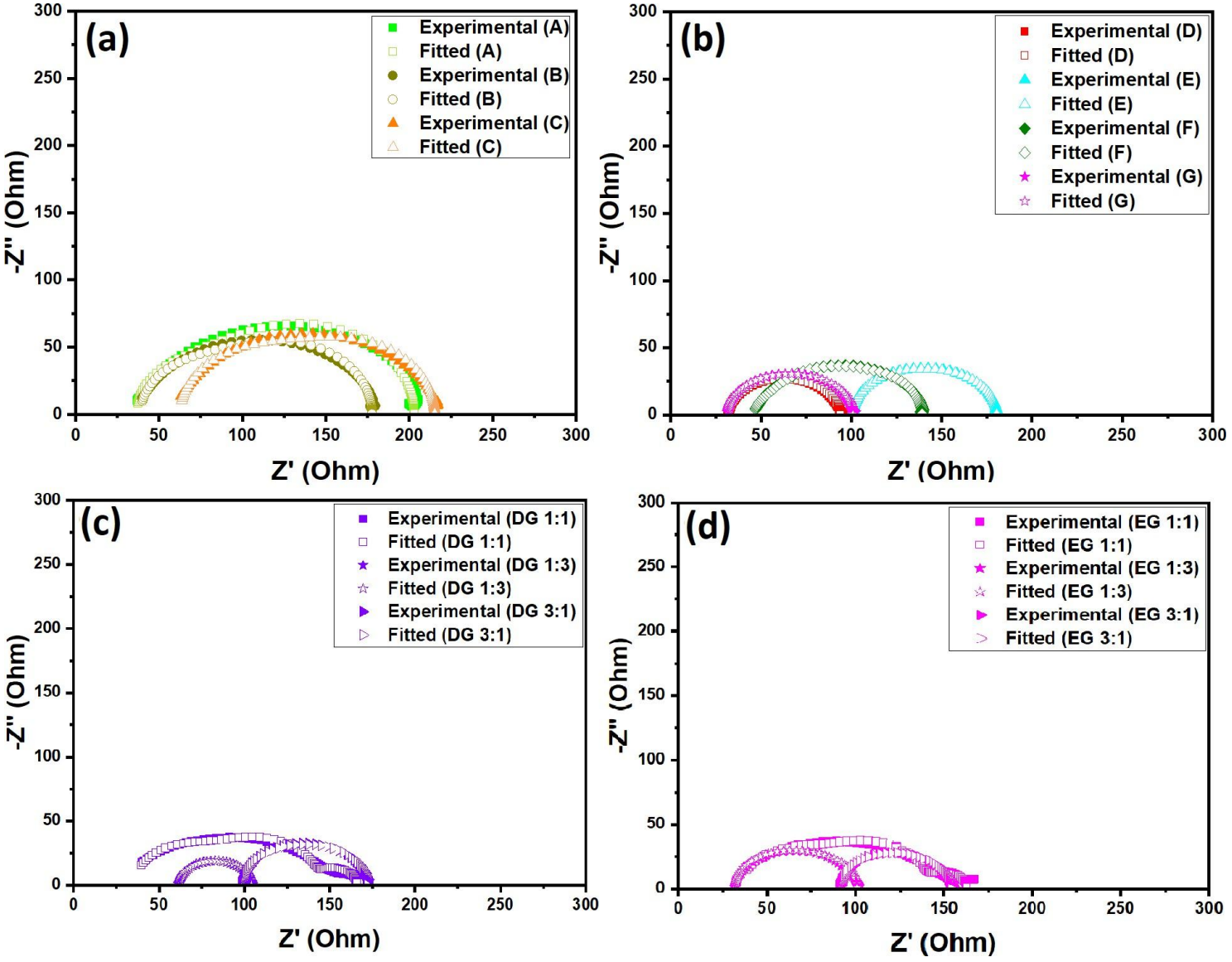



**Figure 3.29** EIS Specters of (a) Boranils, (b) Bodipys, (c) DGs and (d) EGs.

The values of the electronic components in this circuit, which represent physical elements of the solar cell (such as load resistances, Helmholtz layer capacitances), are summarized in Table 5. Comparing these values allows for a more in-depth interpretation of the impedance results, providing information about the charge transfer processes and the limitations of each photosensitizer.

**Table 5** Values found for the parameters obtained in the EIS analysis.

| Dyes | $R_S$ (Ω) | $R_1$ (Ω) | $R_2$ (Ω) | $R_3$ (Ω) | $C_1$ (μF) | $C_2$ (μF) | $C_3$ (μF) |
|---|---|---|---|---|---|---|---|
| Boranil (A) ATH017 | 36.39 ± 1.22 | 119.0 ± 2.44 | 46.88 ± 6.57 | 38.94 ±3.02 | 6.32 ± 6.14 | 2.65 ± 3.19 | 7.14 ± 2.17 |
| Boranil (B) ATH019 | 38.87 ± 1.14 | 89.91 ± 3.75 | 48.84 ±6.79 | 40.07 ±4.71 | 5.98 ± 8.03 | 2.14 ±3.03 | 6.55 ±3.81 |
| Boranil (C) ATH024 | 62.70 ± 0.92 | 86.28 ± 4.94 | 66.25 ± 6.33 | 49.52 ±3.72 | 7.44 ± 10.39 | 1.90 ± 2.91 | 6.49 ± 3.02 |
| Bodipy (D) ATH1005 | 32.02 ± 0.30 | 27.23 ± 14.6 | 34.31 ±11.6 | 34.14 ±2.78 | 82.49 ± 23.71 | 3.62 ±1.01 | 6.94 ±2.88 |
| Bodipy (E) ATH1006 | 100.1 ± 0.14 | 38.63 ± 8.01 | 40.98 ± 7.58 | 35.93 ±4.80 | 43.33 ± 13.3 | 13.35 ± 3.49 | 7.13 ± 4.55 |
| Bodipy (F) ATH031 | 46.61 ± 0.31 | 35.48 ± 7.57 | 48.56 ±4.62 | 8.62 ±8.98 | 39.54 ± 12.7 | 8.38 ±2.90 | 8.19 ±4.40 |
| Bodipy (G) ATH032 | 31.77 ± 0.30 | 33.46 ± 10.9 | 35.70 ± 10.3 | 40.29 ±8.16 | 43.64 ± 17.9 | 14.52 ± 5.35 | 7.78 ± 4.42 |
| DG 1:1 | 35.23 ± 1.75 | 22.93 ± 5.77 | 60.28 ±3.13 | 47.36 ±3.75 | 54.96 ± 13.6 | 6.27 ±7.57 | 1.10 ±3.18 |
| DG 1:3 | 62.05 ± 0.13 | 18.27 ± 1.73 | 23.97 ± 1.85 | 42.34 ±2.26 | 97.70 ± 3.63 | 8.21 ± 5.15 | 2.54 ± 3.23 |
| DG 3:1 | 98.93 ± 0.16 | 39.43 ± 9.48 | 33.68 ±11.1 | 45.91 ±3.77 | 33.08 ± 15.4 | 13.33 ±5.30 | 3.93 ±4.01 |
| EG 1:1 | 34.75 ± 1.69 | 22.06 ± 5.82 | 59.95 ± 3.10 | 84.67 ±3.82 | 52.61 ± 13.9 | 6.27 ± 7.49 | 1.14 ± 3.10 |
| EG 1:3 | 32.23 ± 0.35 | 26.56 ± 14.3 | 42.40 ±9.05 | 41.02 ±2.95 | 10.17 ± 24.4 | 20.65 ±4.39 | 4.14 ±2.27 |
| EG 3:1 | 91.55 ± 0.15 | 18.50 ± 13.3 | 44.46 ± 5.55 | 39.22 ±3.43 | 61.80 ± 22.3 | 8.18 ± 2.48 | 7.23 ± 5.73 |

In literature [102], a resistive component (R1) is associated with the charge transfer resistance at the counter electrode/electrolyte interface. The mid-frequency region in the Nyquist diagrams is attributed to electron transport at the semiconductor/dye/electrolyte interface and is represented by resistance R2 in the equivalent circuit. Resistance R3, in turn, is related to the internal diffusion process of the electrolyte, while the series ohmic resistance (RS) is attributed to the intrinsic resistance of the electrolyte [103]. Figure 3.29 represents a comparative analysis of the electrical parameters obtained from the photovoltaic tests and impedance modeling for each photosensitizer. This analysis allows establishing correlations between the resistance values (R1, R2, R3 and RS) and the overall performance of the solar cells, providing valuable information on the limiting mechanisms of each device.

Table 6 presents the solar conversion efficiency obtained for the sensitizers used in this work, compared with previous studies.

**Table 6** Photovoltaic performance of DSSCs sensitized with Boranil, Bodipy, and related synthetic dyes reported in the literature.

| Dyes | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | *FF* | $\eta$ (%) | Ref. |
|---|---|---|---|---|---|
| BODIPY | 1.42 | 0.43 | 0.55 | 0.34 | [104] |
| BODIPY 1 | 0.73 | 0.26 | 0.55 | 0.11 | [105] |
| BODIPY 2 | 3.10 | 0.37 | 0.54 | 0.63 | [105] |
| BODIPY 3 | 1.66 | 0.49 | 0.52 | 0.42 | [106] |
| BODIPY 9 | 1.32 | 0.18 | 0.51 | 0.49 | [107] |
| BODIPY 1/KI/I2 | 3.40 | 0.67 | 0.51 | 1.70 | [108] |
| BODIPY 2/KI/I2 | 4.00 | 0.69 | 0.52 | 2.10 | [108] |
| BODIPY 3/KI/I2 | 4.70 | 0.72 | 0.52 | 2.50 | [108] |
| H-T-BO:PC71BM 1:2 | 6.80 | 0.67 | 0.34 | 1.56 | [109] |
| Br-T-BO:PC71BM 1:2.5 | 7.62 | 0.72 | 0.35 | 1.96 | [109] |
| H-T-BO:PC71BM 1:2.5 | 11.3 | 0.74 | 0.35 | 3.13 | [109] |
| ATH017 (A) | 0.99 | 0.49 | 0.48 | 1.46 | this work |
| ATH019 (B) | 0.96 | 0.60 | 0.39 | 1.40 | this work |
| ATH024 (C) | 0.95 | 0.60 | 0.44 | 1.57 | this work |
| ATH1005 (D) | 1.57 | 0.59 | 0.39 | 2.26 | this work |
| ATH1006 (E) | 1.46 | 0.60 | 0.38 | 2.09 | this work |
| ATH031 (F) | 1.25 | 0.60 | 0.45 | 2.10 | this work |
| ATH032 (G) | 1.26 | 0.60 | 0.48 | 2.25 | this work |
| DG 1:1 | 1.44 | 0.60 | 0.45 | 2.43 | this work |
| DG 1:3 | 2.41 | 0.59 | 0.39 | 3.45 | this work |
| DG 3:1 | 1.26 | 0.52 | 0.46 | 1.90 | this work |
| EG 1:1 | 1.41 | 0.60 | 0.45 | 2.41 | this work |
| EG 1:3 | 1.60 | 0.55 | 0.49 | 2.71 | this work |
| EG 3:1 | 1.24 | 0.60 | 0.45 | 2.08 | this work |

# Chapter 4 – Conclusion and Future Work

This thesis systematically investigated the co-sensitization strategy as an effective approach to enhance the energy conversion efficiency of Dye-Sensitized Solar Cells (DSSCs). By integrating the synthesis of novel sensitizers with comprehensive structural, morphological, optical, and photovoltaic characterization, it was possible to validate the central hypothesis that combining dyes with complementary absorption profiles mitigates the intrinsic limitations associated with single-sensitizer systems.

Morphological analyses conducted by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM) confirmed that the spin-coating technique is a reliable and reproducible method for fabricating homogeneous $TiO_2$ photoanodes. The peak-to-valley height variation of approximately 2.3 μm proved advantageous, as it increases the effective surface area and promotes dye incorporation, directly contributing to improved photocurrent generation.

From a photovoltaic standpoint, clear performance distinctions were observed among the different sensitization strategies. Natural dyes extracted from *Chrysanthemum* flowers demonstrated modest efficiencies, with the Chrysanthemum Violet (CV) dye reaching a maximum power conversion efficiency (PCE) of 1.35%, alongside a short-circuit current density (JSC) of 0.44 mA/cm² and a fill factor (FF) of 0.39. Although these results surpass several natural sensitizers reported in the literature, they remain inherently limited due to restricted absorption ranges and less efficient charge transfer dynamics.

In contrast, synthetic dyes based on boron complexes, particularly the BODIPY class, exhibited significantly superior optical and electronic properties. These dyes showed strong and well-defined absorption bands in the visible region (499–535 nm), resulting in enhanced light-harvesting capability. Among them, the Bodipy D dye achieved the best individual performance, with a PCE of 2.26%, outperforming comparable systems reported in the literature.

The most significant advancement of this work was achieved through the implementation of co-sensitization. The optimized mixture of Bodipy D and Bodipy G dyes (1:3 ratio) resulted in a device efficiency of 3.45%, with a $V_{OC}$ of 0.59 V and a $J_{SC}$ of 2.41 mA/cm². This represents a substantial improvement of approximately 155% compared to natural dye-based devices and 52% relative to the best-performing individual synthetic dye. These findings confirm that proper tuning of dye proportions is critical for maximizing spectral complementarity, enhancing photon harvesting, and suppressing charge recombination processes.

Additionally, this study highlights that successful co-sensitization depends not only on optical complementarity but also on chemical and electrochemical compatibility between sensitizers. The unsuccessful combination of natural dyes from *Musa* (banana) and *Gerbera* species, which led to dye desorption and loss of photoactivity, underscores the importance of molecular affinity and interfacial stability in multi-dye systems.

The results demonstrate the strong potential of boron-based dyes, particularly Bodipy derivatives, as high-performance sensitizers for DSSCs. The co-sensitization approach, when carefully optimized, emerges as a powerful strategy to advance the efficiency of organic photovoltaic devices.

**Future Work**

Future research should focus on further optimizing both materials and device architecture. Key directions include:

- The development of advanced thin-film deposition techniques, such as High Vacuum Vaporization (HHV) and sputtering, to improve film uniformity, adhesion, and reproducibility;
- The exploration of ternary or multi-component co-sensitization systems to further broaden the absorption spectrum and enhance charge separation;
- The design and synthesis of new boron-based dyes with tailored energy levels and anchoring groups to improve interfacial electron injection and stability;
- Detailed investigations into the long-term thermal, chemical, and photochemical stability of sensitizers under real operating conditions;
- Integration of DSSCs into scalable and flexible device architectures, aiming at practical and commercial applications.

These perspectives provide a clear pathway toward improving device efficiency, stability, and scalability, contributing to the advancement of next-generation sustainable photovoltaic technologies.

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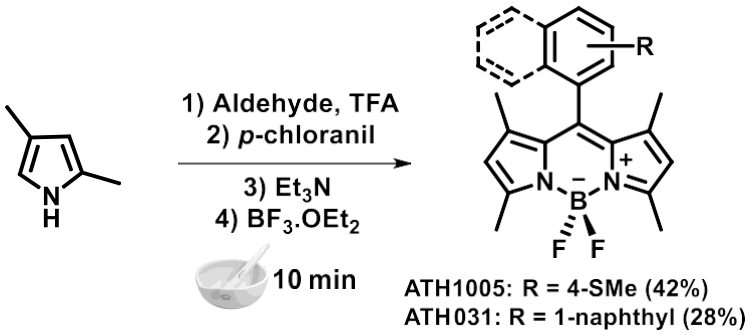
# APPENDIX – SUPPORTING INFORMATION

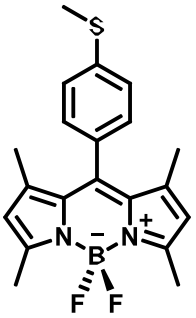
This appendix presents the supplementary information related to the synthesis and characterization of Boranil and BODIPY dyes employed in this work. This part of the study was carried out at the Universidade Federal Fluminense (UFF), Campus Volta Redonda, under the supervision of Prof. Dr. Leandro Ferreira Pedrosa, with the collaboration of his student Paula Romanhi. The experimental procedures, materials, and characterization techniques described herein were conducted at the Graduate Program in Chemistry and the Department of Chemistry of UFF, as detailed below. This section aims to provide comprehensive methodological support for the reproducibility and validation of the results discussed in the main text.

## A-1Materials and Methods

Starting materials obtained from commercial suppliers were used as received unless otherwise stated. The solvents and reagents used in this work were previously purified according to methods described in the literature. The reactions were monitored for thin layer chromatography, using silica gel chromatoplates supported on aluminium, Merck brand, with a layer thickness of 0.2 mm. Flash chromatography was carried on 35–70 mesh Merck silica gel. Melting points were obtained on PF1500 FARMA (Gehaka, Brazil) and are uncorrected. NMR spectra were obtained using a VARIAN NMR Spectrometer 500MHz, $^{1}H$: 499.84 and $^{19}F$: 470.56 MHz, using tetramethylsilane (TMS) as an internal standard for the $^{1}H$ core and Trifluoroacetic acid (TFA) as an external standard for the $^{19}F$ core. Chemical shifts (δ) were reported in parts per million (ppm) and coupling constants (*J*) in Hertz (Hz). The multiplicity of signs was marked as: s, simplets; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet; dd, double doublet; dt, double triplet. Attenuated Total Reflection spectra were collected using a Bruker ALPHA FT-IR spectrometer (Bruker Optics GmbH, USA) equipped with a single-reflection diamond ATR. Spectra were collected in the mid-IR range, 400-4000 $cm^{-1}$, with an optical resolution of 4 $cm^{-1}$; the registered spectrum is the mean of 64 scans, executed in 3 min.

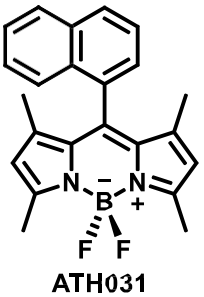
**A-2General procedure for the synthesis of BODIPYs ATH1005 and ATH031:**[1] 2,4-dimethyl-1*H*-pyrrole (0.9990 g, 10.5 mmol) and the corresponding aryl aldehyde (5.0 mmol) were mixed with a pestle and mortar. Trifluoroacetic acid (TFA) (5 drops) was added via a pipette, while the mixture was ground with the pestle for about 2 min. To the resulting paste, $CHCl_3$ (2.0 mL) was added, followed immediately by the addition of *p*-chloranil (1.81 g, 7.4 mmol). The purple paste was ground for 2 min, after which triethylamine (TEA) (6.0 mL, 43.0 mmol) was added via a syringe. The resulting dark brown paste was ground with the pestle for 3 min. Subsequently, boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) (6.0 mL, 47.4 mmol) was added slowly, dropwise, via a syringe and the mixture was ground for 3 min until a thick dark red paste was formed. The reaction mixture was dissolved in $CHCl_3$, transferred to a separation funnel, and washed with saturated $Na_2CO_3$ followed by brine. The solvent was evaporated under reduced pressure and the crude solid was purified by chromatographic column using hexane-chloroform gradient as eluent to give the desired product.




**8-(4-methylthiophenyl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene**

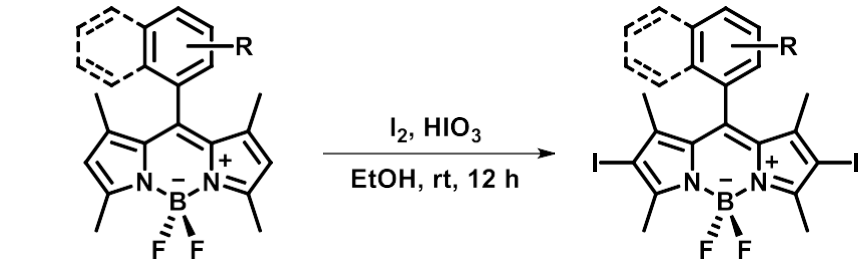
Purification by column chromatography on silica gel (*n*-hexane/$CHCl_3$ 7:3) yielded (777.6 mg, 42%) as a pink solid. **UV-Vis** (EtOH) λ/nm 498. **m.p. (°C)** = 186-187. **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 7.28 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 5.91 (s, 2H), 2.48 (s, 6H), 2.47 (s, 3H), 1.36 (s, 6H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -143.7 (q, *J* = 32.8, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 2969, 2918, 1595, 1535, 1398, 1297, 1181, 1153, 1046, 970, 816, 757, 699, 578, 474.




**8-(naphthalen-1-yl)-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene**

Purification by column chromatography on silica gel (*n*-hexane/$CHCl_3$ 8:2) yielded (523.9 mg, 28%) as an orange solid. **UV-Vis** (EtOH) λ/nm 501. **m.p. (°C)** = 223-225. **$^1$H NMR** (300 MHz, $CDCl_3$) δ: 7.87 (d, *J* = 8.3 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.30 (m, 2H), 5.86 (s, 2H), 2.51 (s, 6H), 0.97 (s, 6H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -143.50 (q, J = 31.7 Hz, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 3055, 2963, 2919, 1606, 1541, 1504, 1399, 1306, 1190, 1153, 1061, 971, 786, 630, 548, 474.

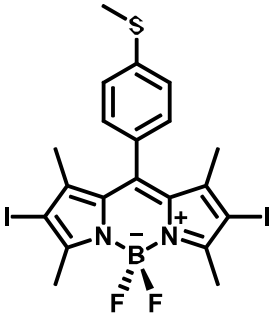
**A3-General procedure for the synthesis of the iodinated BODIPYs ATH1006 and ATH032:**[2] In round-bottomed flask, iodic acid ($HIO_3$) (0.276 mmol), iodine ($I_2$) (0.276 mmol), were add to a solution of 10 mL of ethanol and the corresponding BODIPY (0.138 mmol). The resulting solution was then stirred at room temperature for 12h. The mixture was poured in 40 mL of water and then, extracted with chloroform for three times. The organic layer was dried over $Na_2SO_4$ and the solvent was evaporated under vacuum. The resulting residue was purified by chromatographic column using hexane-chloroform gradient as eluent.




ATH1005: R = 4-SMe
ATH031: R = 1-naphthyl

ATH1006: R = 4-SMe (91%)
ATH032: R = 1-naphthyl (68%)

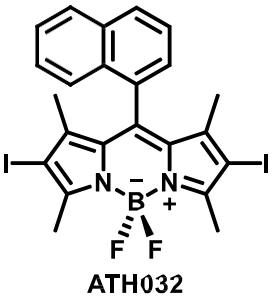
**8-(4-methylthiophenyl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene**



ATH1006

Purification by column chromatography on silica gel (*n*-hexane/$CHCl_3$ 3:1) yielded **2a** (78.1 mg, 91%) as a purple solid. **m.p. (°C)** = 204-206. **UV-Vis** (EtOH) λ/nm 532. **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 7.30 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.3 Hz, 2H), 2.57 (s, 6H), 2.49 (s, 3H), 1.38 (s, 6H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -145.7 (q, *J* = 32.0, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 2918, 1678, 1523, 1392, 1304, 1174, 1079, 980, 755, 698, 585, 524, 442.

**8-(naphthalen-1-yl)-2,6-diiodo-1,3,5,7-tetramethyl-4,4-difluoro-4-bora-3*a*,4*a*-diaza-*s*-indacene**

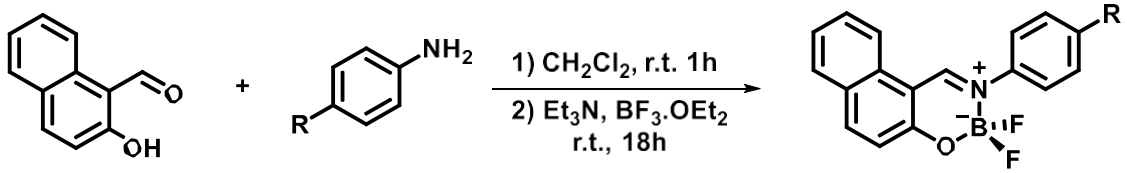


ATH032

Purification by column chromatography on silica gel (*n*-hexane/$CHCl_3$ 4:1) yielded (58.7 mg, 68%) as a purple solid. **UV-Vis** (EtOH) λ/nm 501. **m.p. (°C)** = 210-211. **$^1$H NMR** (500 MHz, $CDCl_3$) δ: 8.36 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1H), 8.14 (t, *J* = 1.8 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.60 (dt, *J* = 7.6, 1.4 Hz, 1H), 2.59 (s, 6H), 1.30 (s, 6H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -142.98 (q, *J* = 32.0, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 2970, 1521, 1398, 1307, 1173, 1090, 988, 780, 748, 630, 586, 522.

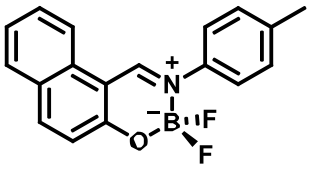
**A-5General procedure for the synthesis of BORANIL ATH017, ATH019 and ATH024:**[3]

In round-bottomed flask, 2-hydroxy-1-naphthaldehyde (361.6 mg, 2.1 mmol) were add to a solution of 50 mL of dichloromethane and the corresponding aryl amine (2.0 mmol). The resulting solution was then stirred at room temperature for 1h, monitored by thin layer chromatography. After a period of 1h, triethylamine (TEA) (2.8 mL, 20.0 mmol) was added via a syringe. Subsequently, boron trifluoride diethyl etherate ($BF_3{\cdot}OEt_2$) (5.1 mL, 40.0 mmol) was added slowly, dropwise, via a syringe. The resulting solution was then stirred at room temperature for 18h. The mixture was poured in 40 mL of water and then, extracted with dichloromethane for three times. The organic layer was dried over $Na_2SO_4$ and the solvent was evaporated under vacuum. The resulting residue was purified by chromatographic column using dichloromethane gradient as eluent.




ATH017: R = Me (78%)
ATH019: R = Cl (73%)
ATH024: R = H (73%)

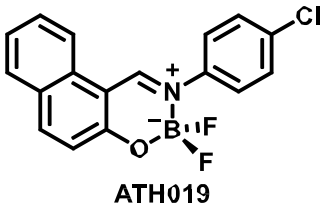
**3,3-difluoro-2-(*p*-tolyl)-3*H*-2a,3a-naphtho[1,2-*e*][1,3,2]oxazaborinine**



ATH017

Purification by column chromatography on silica gel (dichloromethane) yielded (482.2 mg, 78%) as a green solid. **UV-Vis** (EtOH) λ/nm 501. **m.p. (°C)** = 158-159. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ: 9.01 (s, 1H), 7.99 (dd, *J* = 26.3, 8.7 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 3H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.21 (d, *J* = 9.1 Hz, 1H), 2.36 (s, 3H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -132.07 (q, *J* = 13.3, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 1625, 1549, 1360, 1204, 1126, 1037, 899, 821, 752, 589, 488, 420.

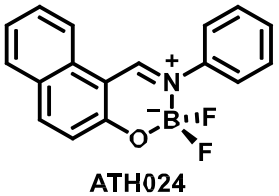
**3,3-difluoro-2-(4-chlorophenyl)-3*H*-2a,3a-naphtho[1,2-*e*][1,3,2]oxazaborinine**



ATH019

Purification by column chromatography on silica gel (dichloromethane) yielded (481.1 mg, 73%) as a green solid. **UV-Vis** (EtOH) λ/nm 501. **m.p. (°C)** = 162-164. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ: 9.00 (s, 1H), 8.04 (d, *J* = 9.1 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.3 Hz, 1H), 7.47 (d, *J* = 8.7 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 3H), 7.22 – 7.19 (m, 1H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -131.65 (q, *J* = 13.1, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 1625, 1552, 1466, 1367, 1204, 1078, 1045, 984, 828, 746, 587, 487, 427.

**3,3-difluoro-2-phenyl-3*H*-2a,3a-naphtho[1,2-*e*][1,3,2]oxazaborinine**



ATH024

Purification by column chromatography on silica gel (dichloromethane) yielded (430.8 mg, 73%) as a yellow solid. **UV-Vis** (EtOH) λ/nm 501. **m.p. (°C)** = 140-141. **$^{1}$H NMR** (500 MHz, $CDCl_3$) δ: 9.09 (d, *J* = 2.9 Hz, 1H), 8.08 (d, *J* = 9.1 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.54 – 7.44 (m, 4H), 7.29 – 7.25 (m, 1H). **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ: -131.34 (q, *J* = 13.0, 2F). **ATR-FTIR** ν ($cm^{-1}$) = 1606, 1552, 1463, 1395, 1309, 1208, 1046, 987, 824, 748, 583, 511, 419.

## NMR and ATR-FTIR spectra

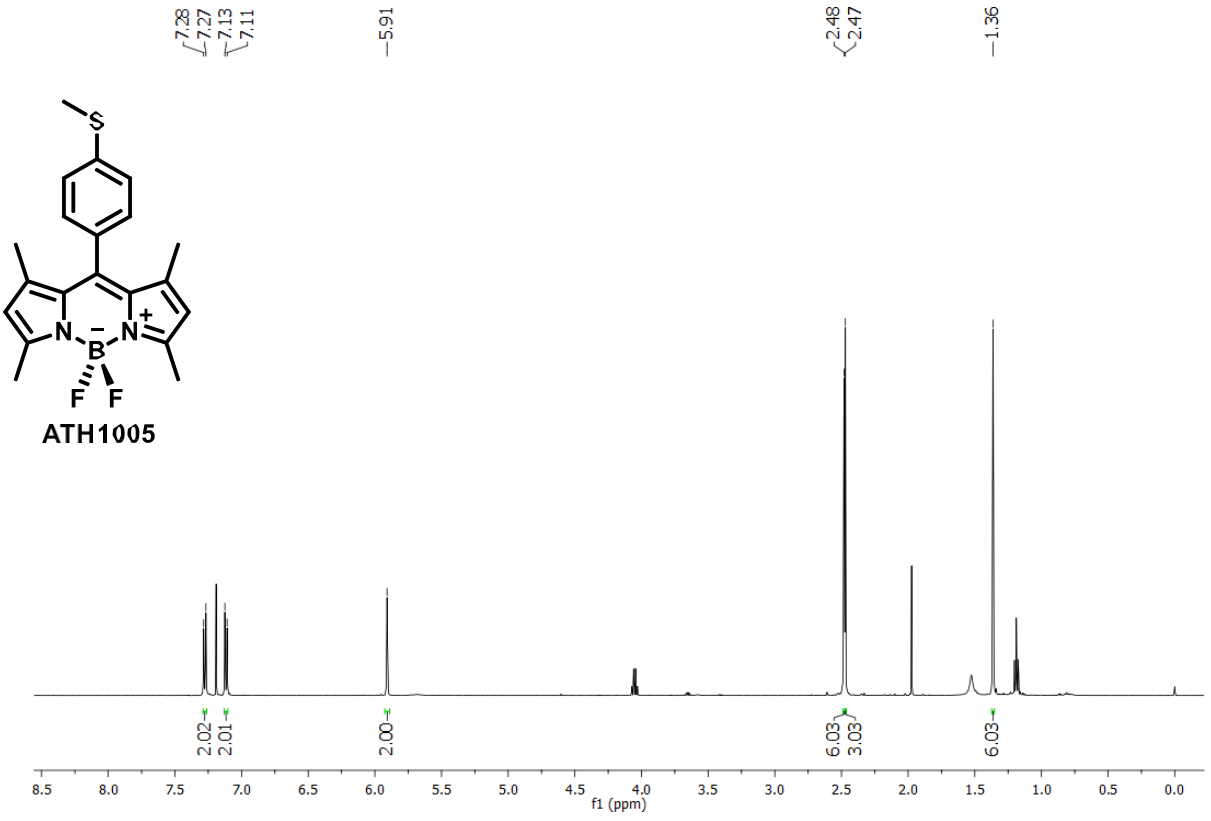



**Figure S1**: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH1005**.

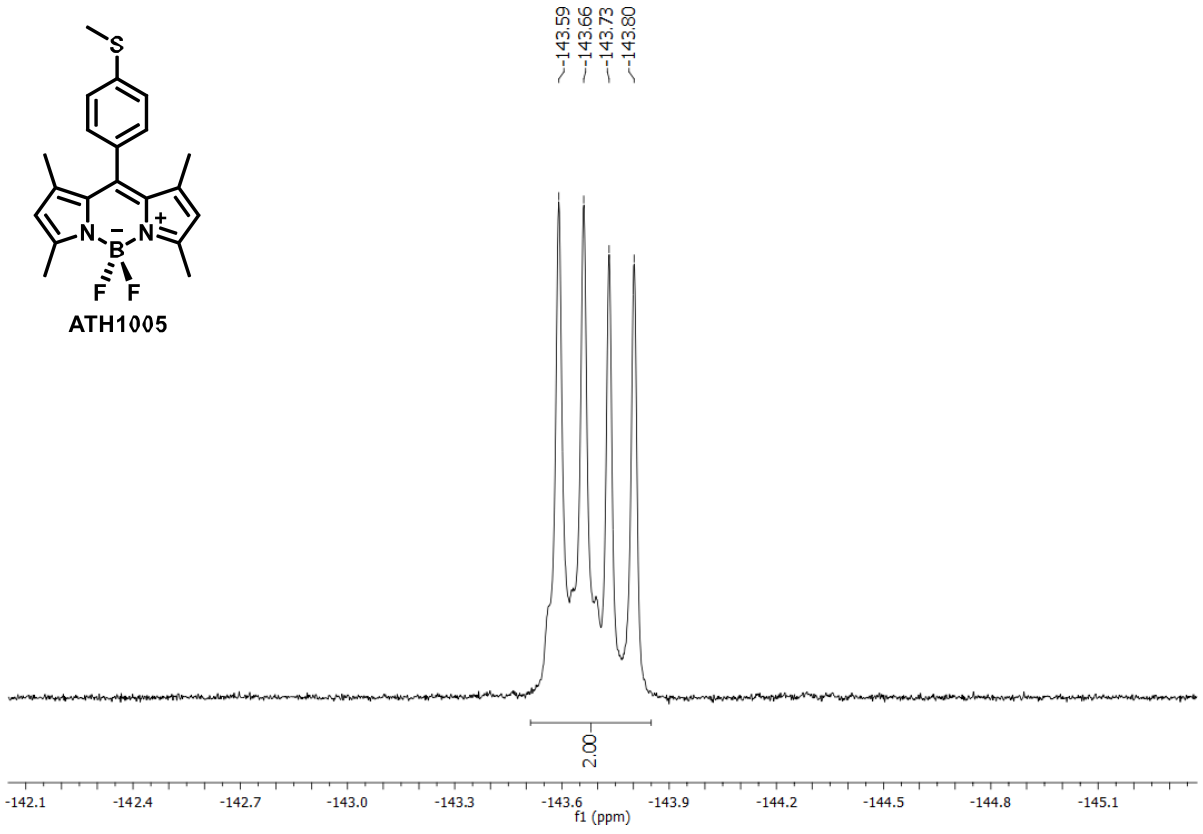



**Figure S2**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH1005.**

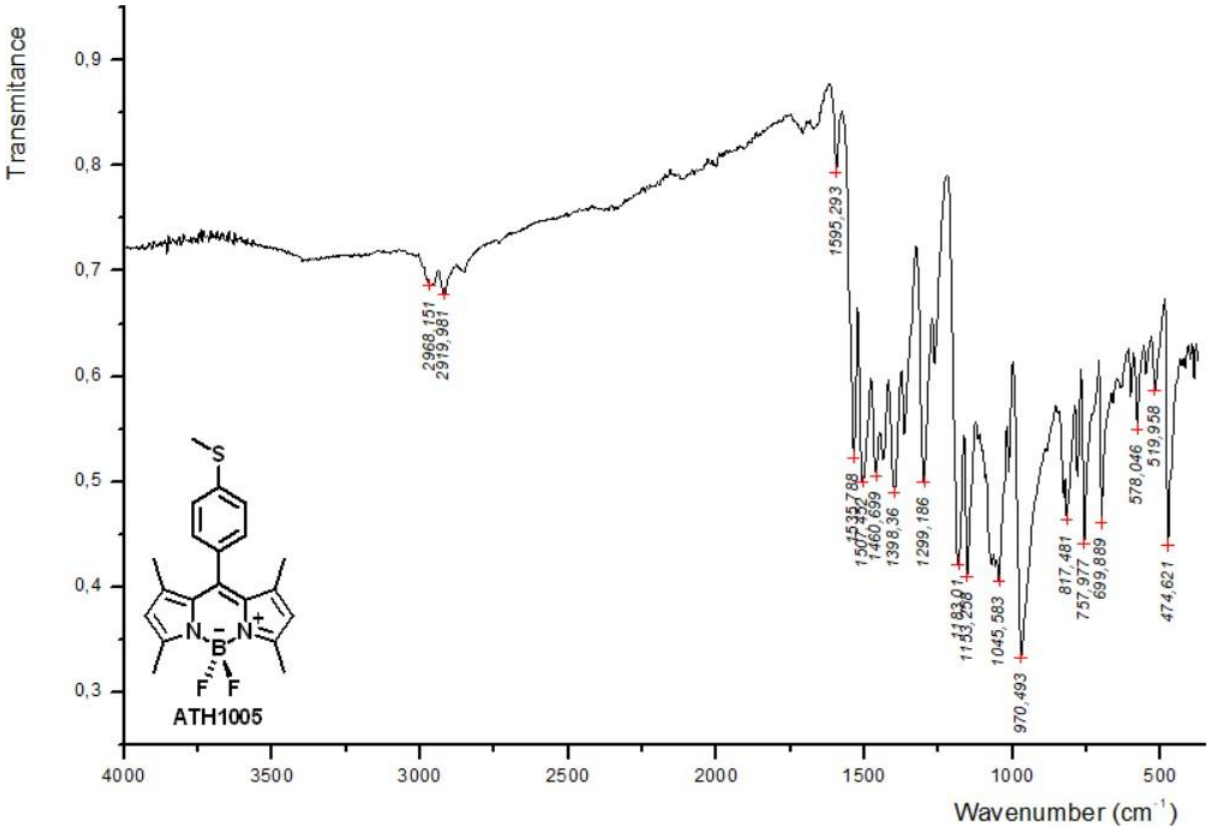



**Figure S3**: ATR–FTIR spectrum for compound **ATH1005.**

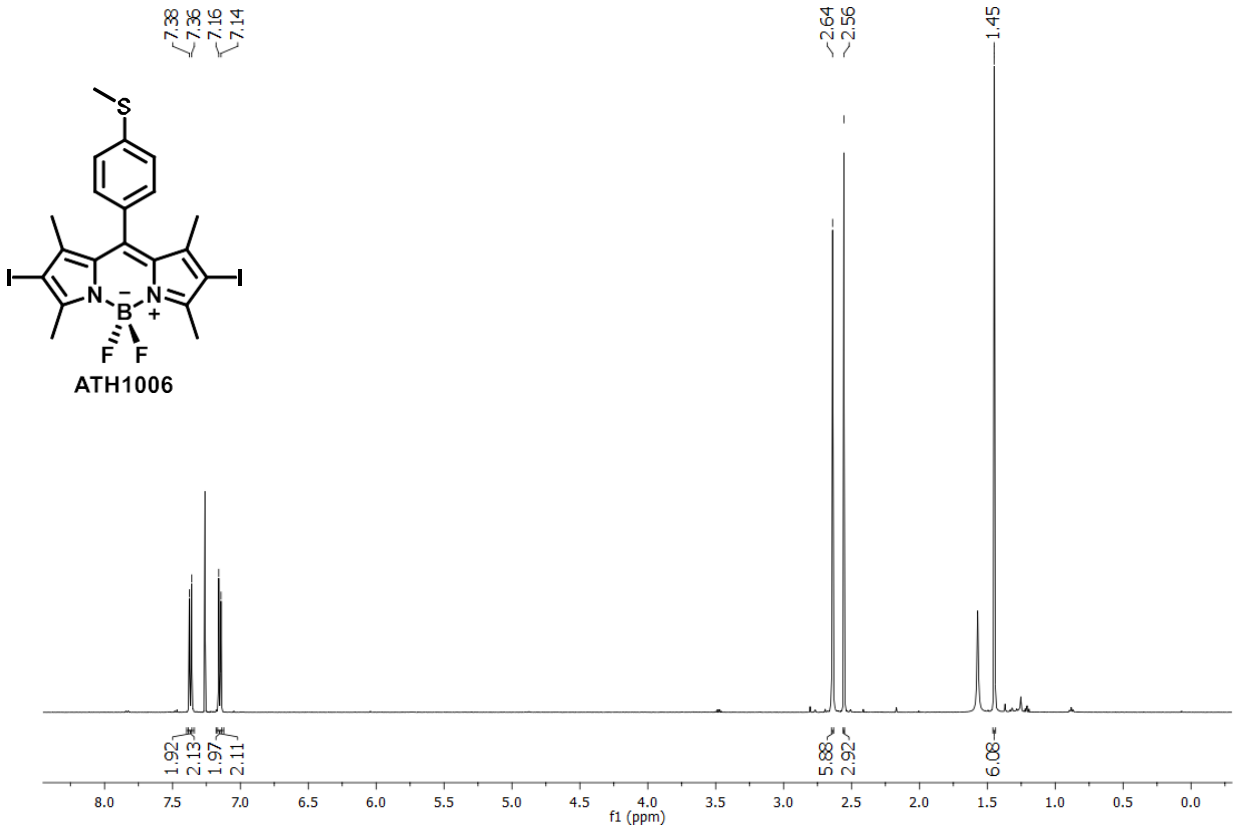



**Figure S4**: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH1006**.

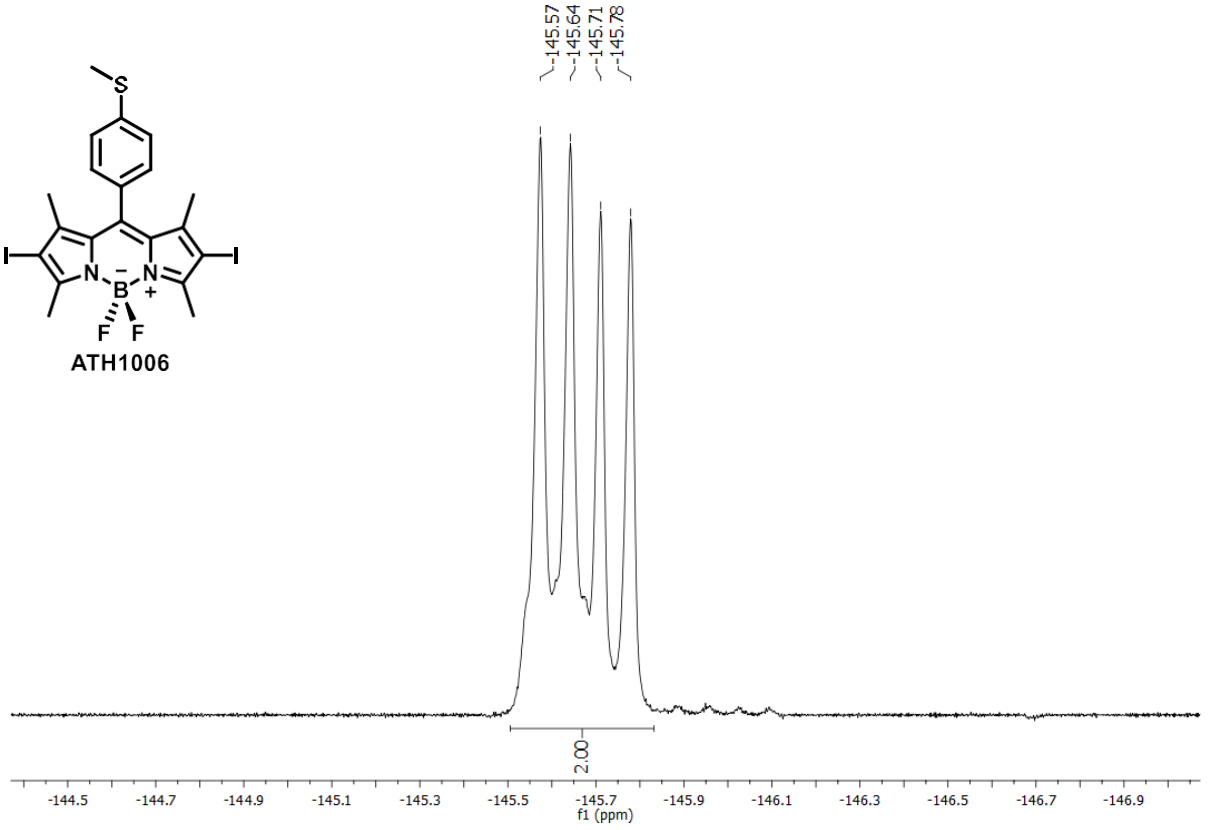



**Figure S5**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH1006.**

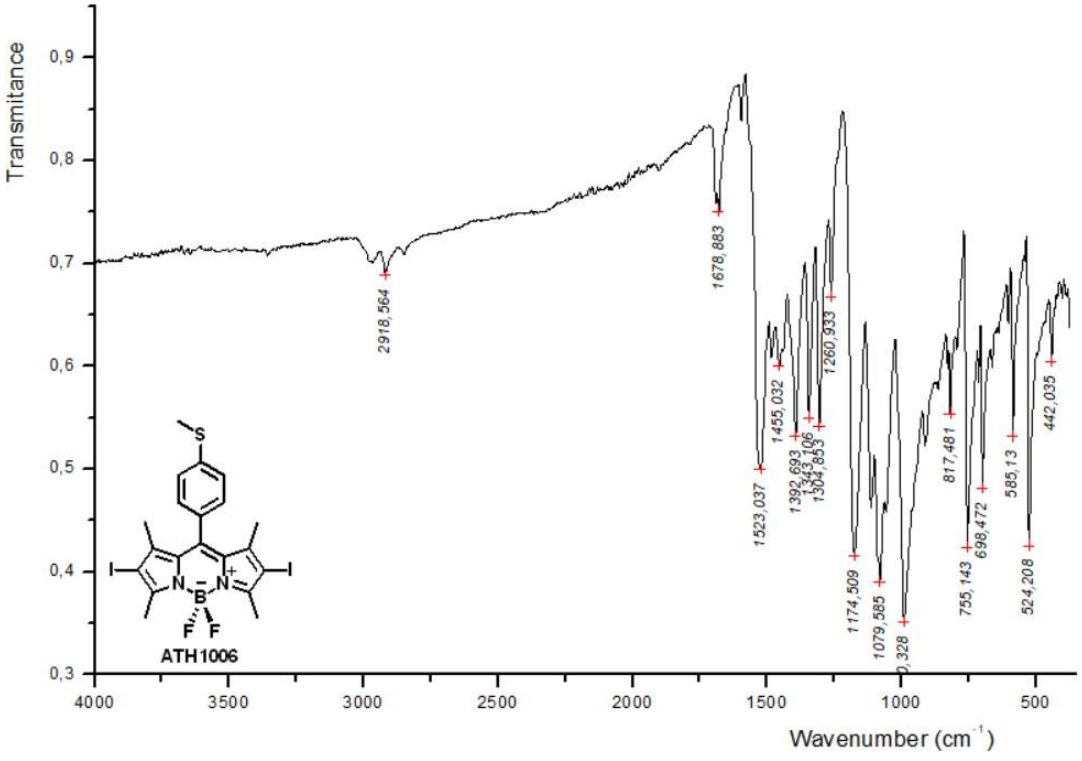



**Figure S6**: ATR–FTIR spectrum for compound **ATH1006.**

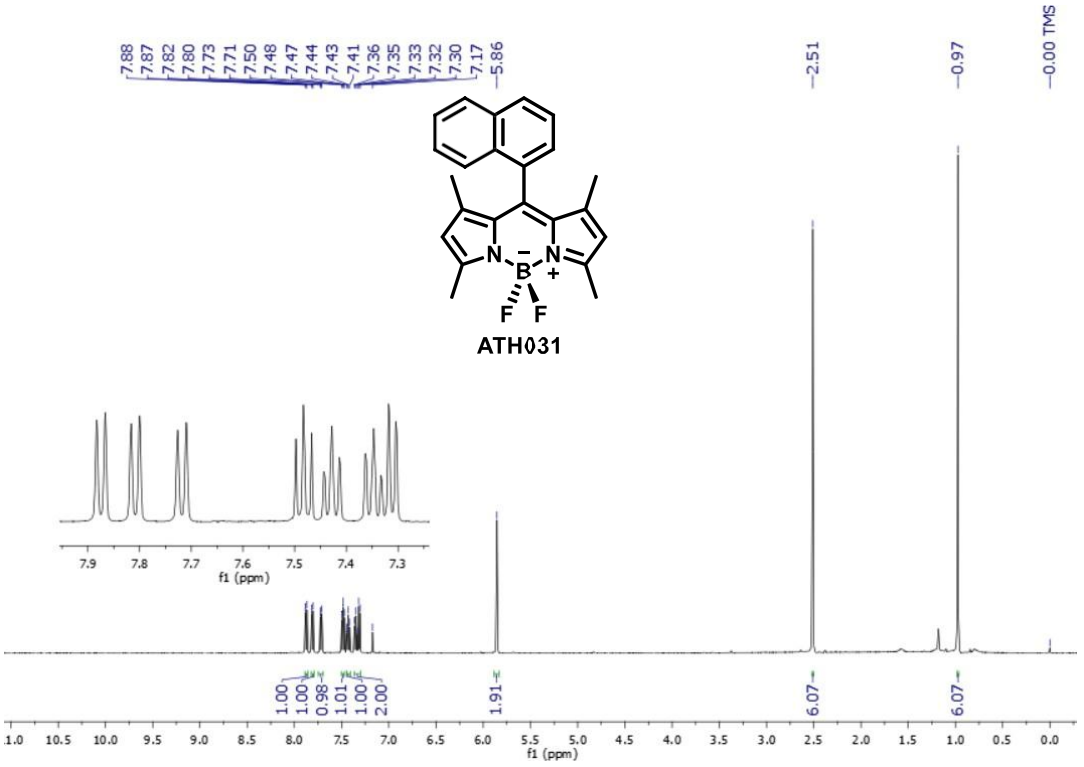



**Figure S7**: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH031**.

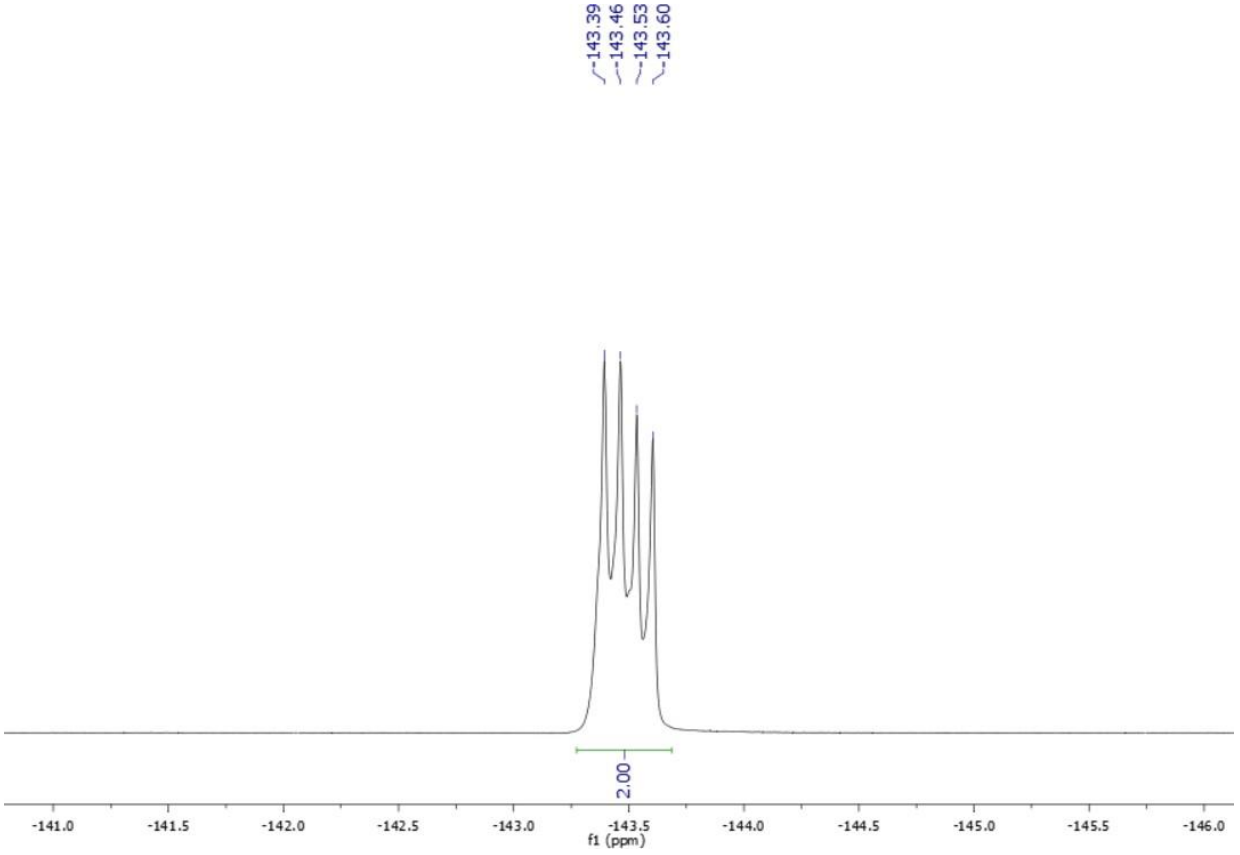



**Figure S8**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH031.**

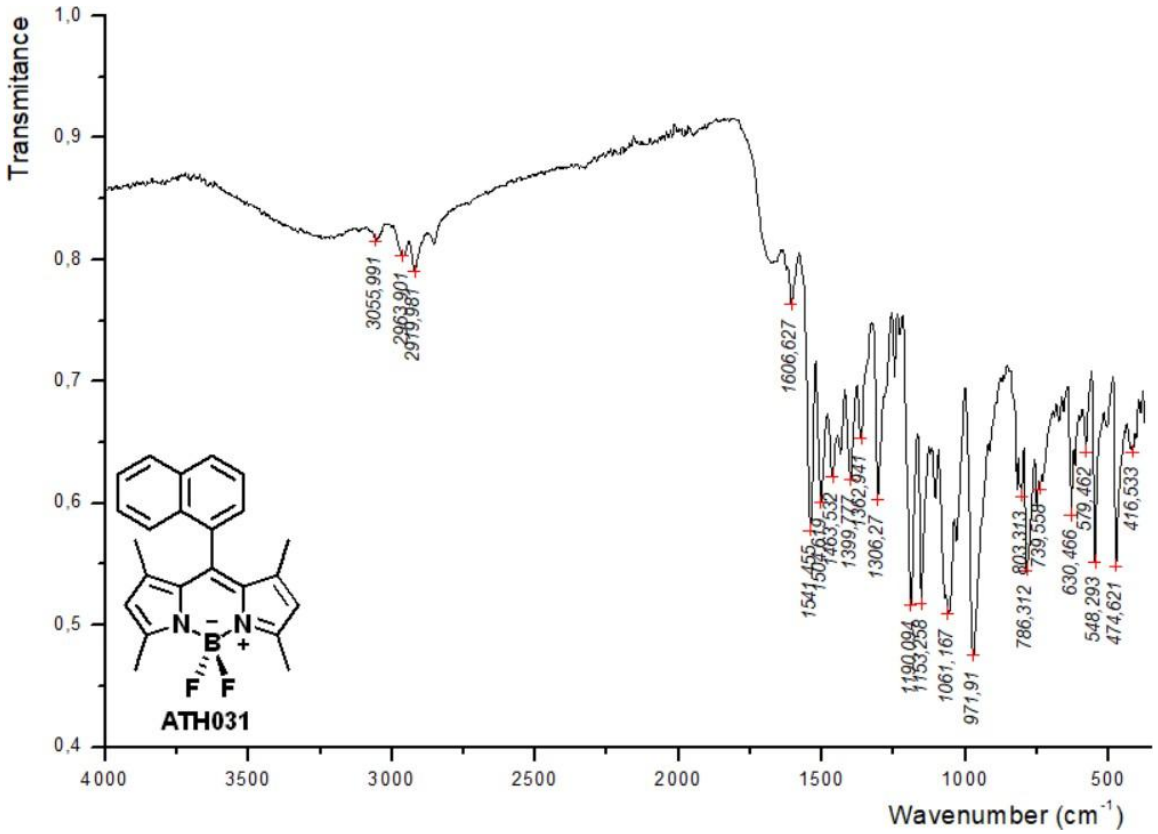



**Figure S9**: ATR–FTIR spectrum for compound **ATH031.**

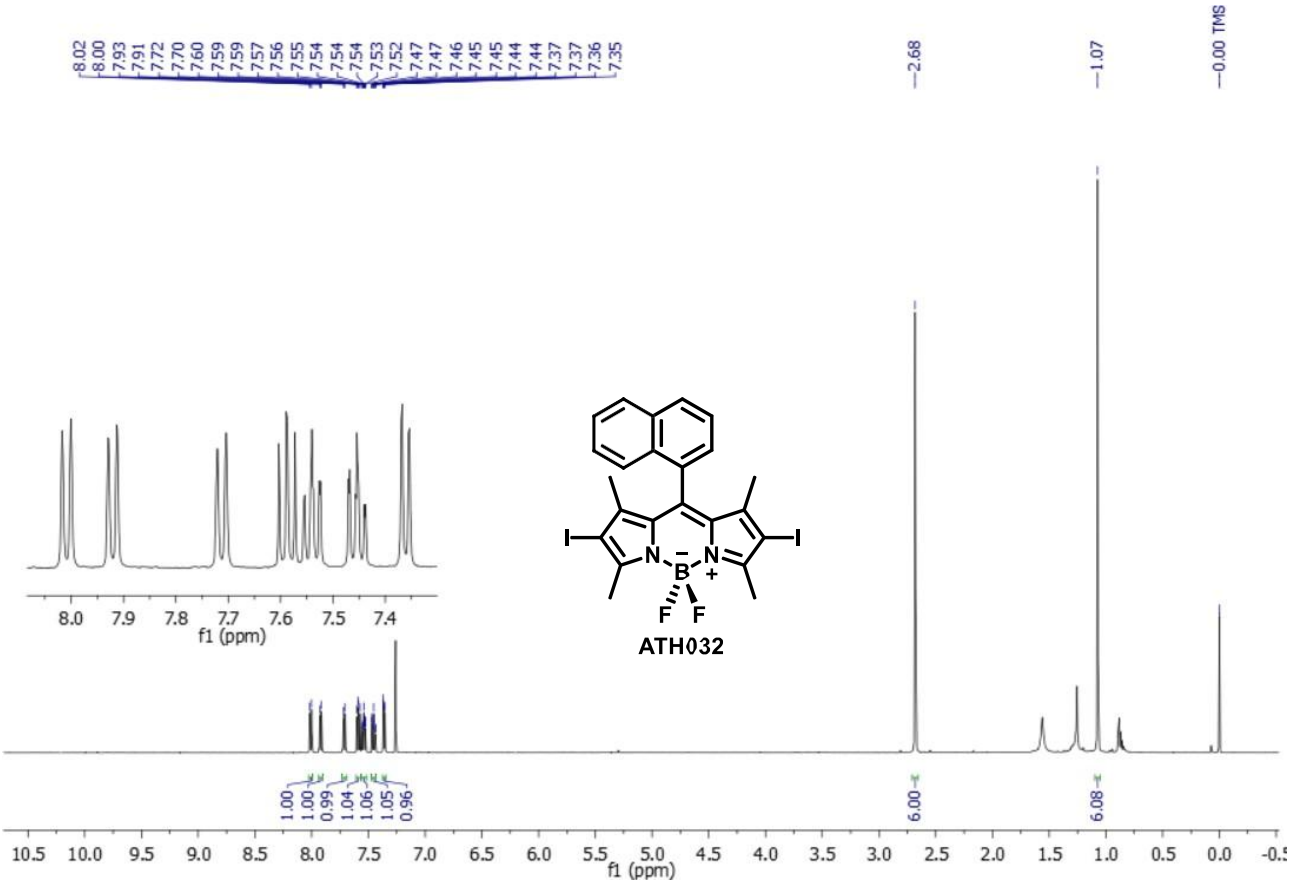



**Figure S10**: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH032**.

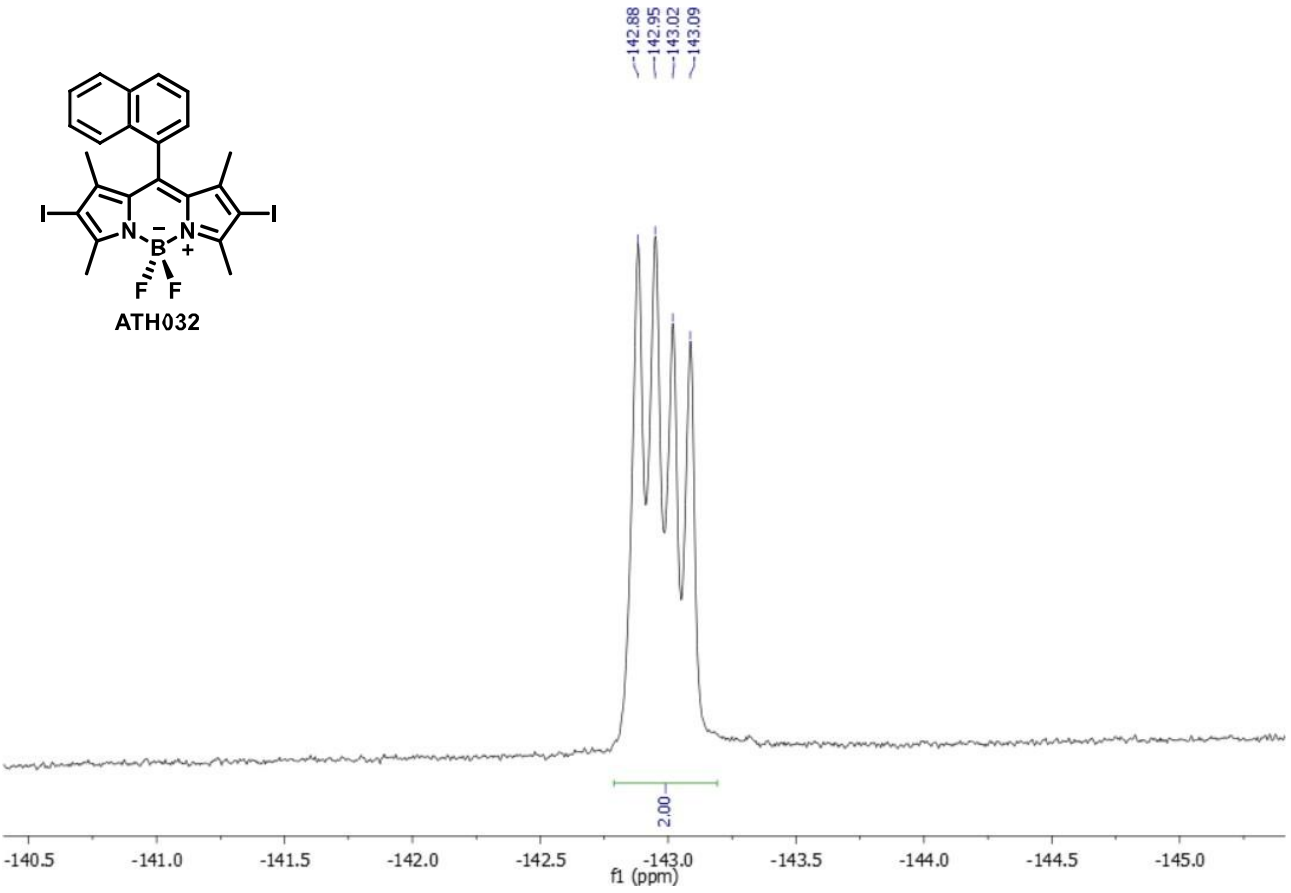



**Figure S11**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH032.**

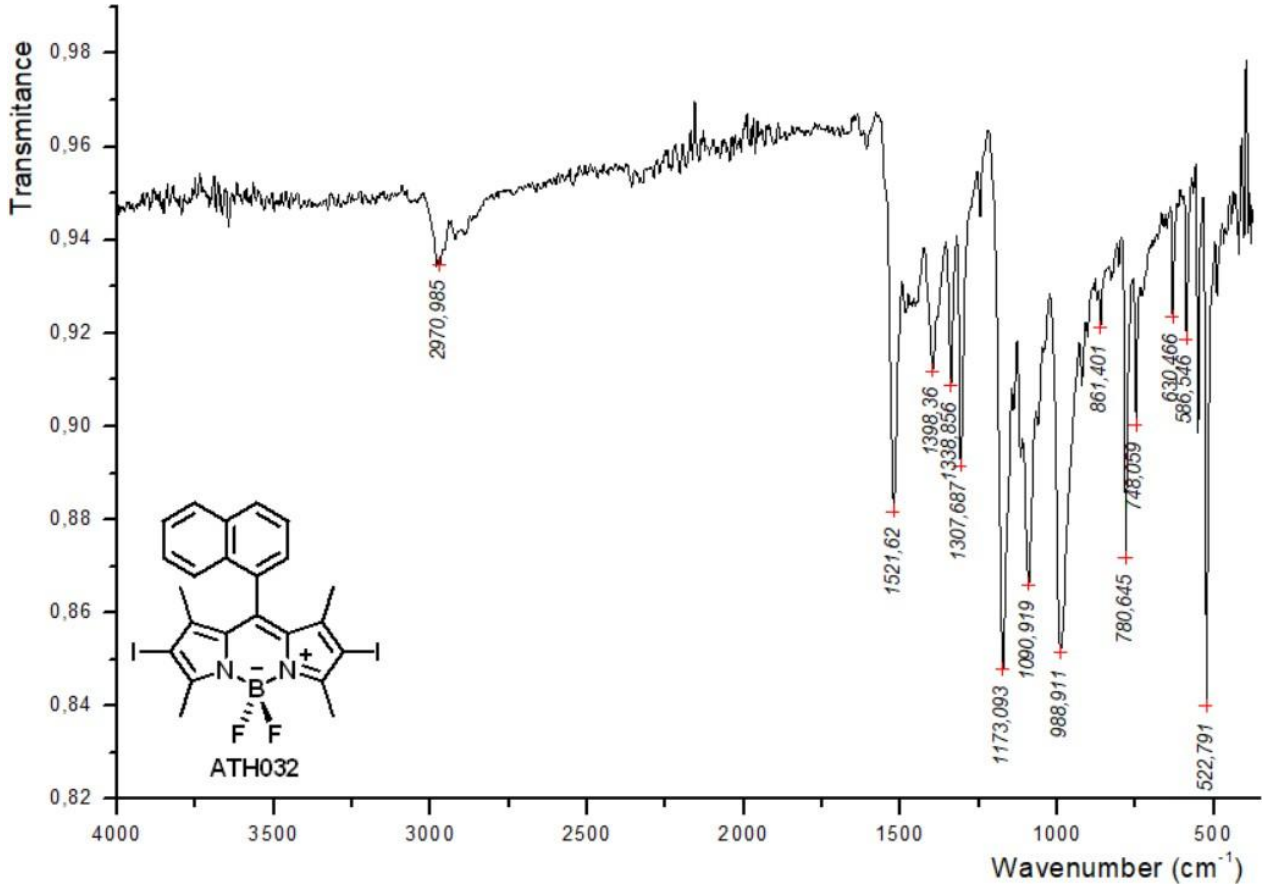



**Figure S12**: ATR–FTIR spectrum for compound **ATH032.**

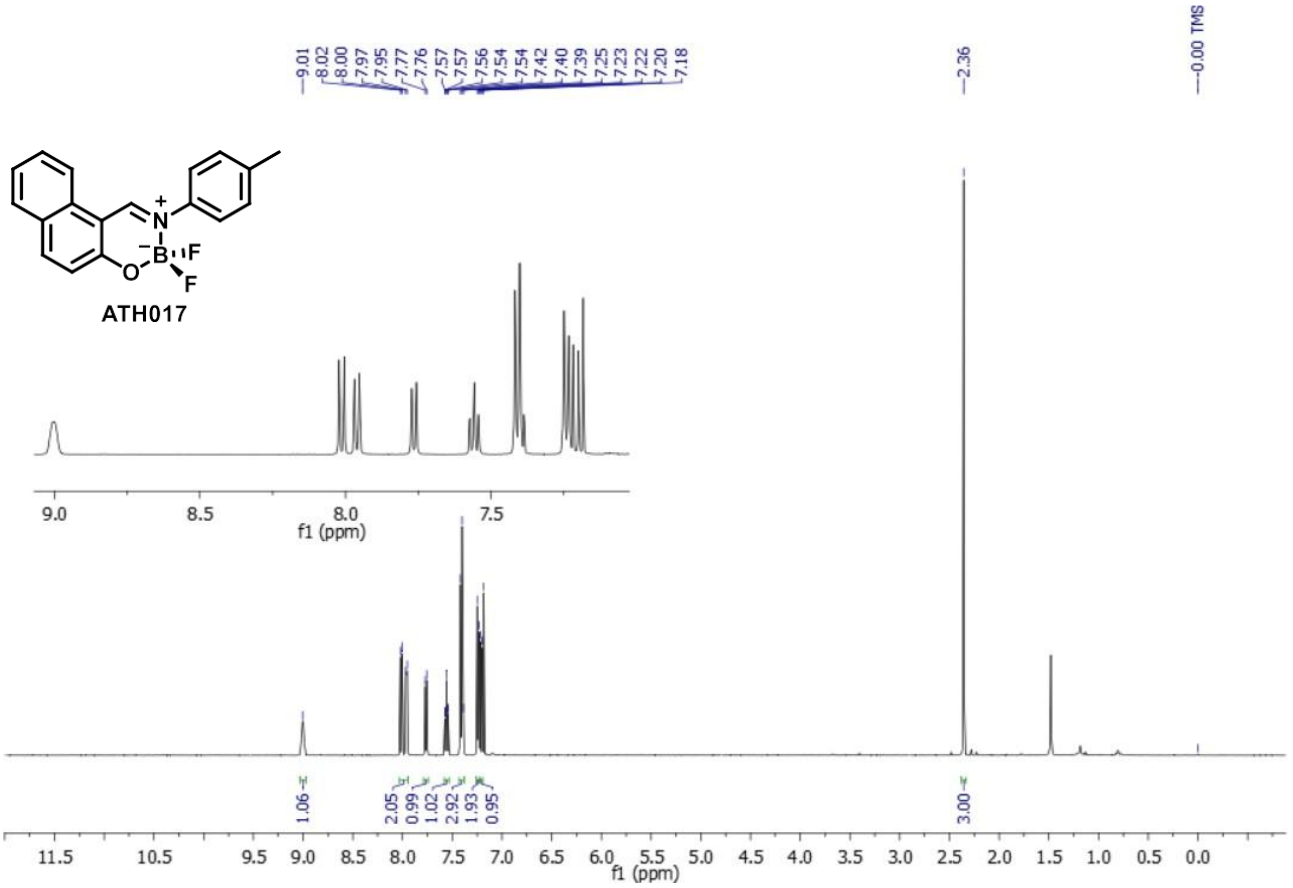



**Figure S13**: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH017**.

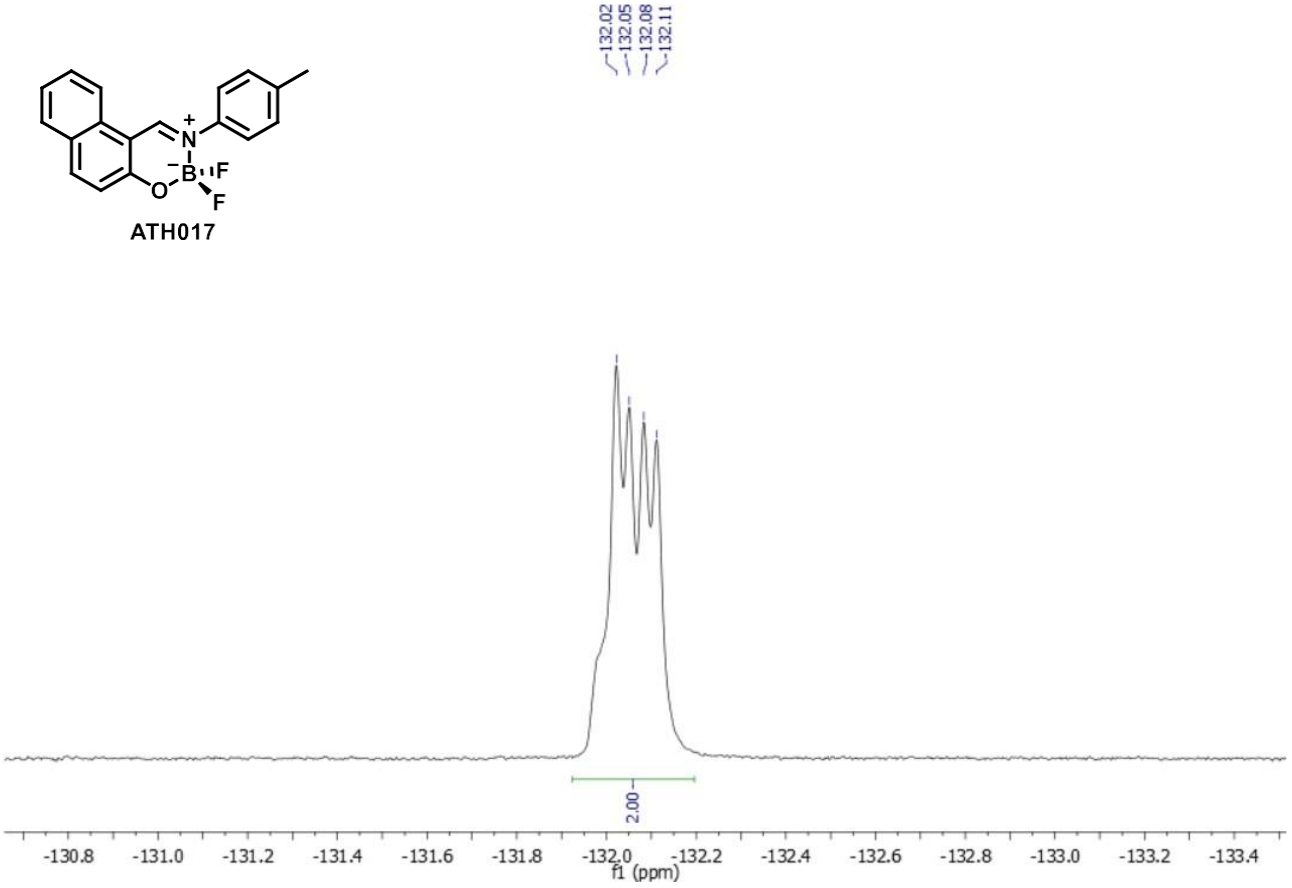



**Figure S14**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH017.**

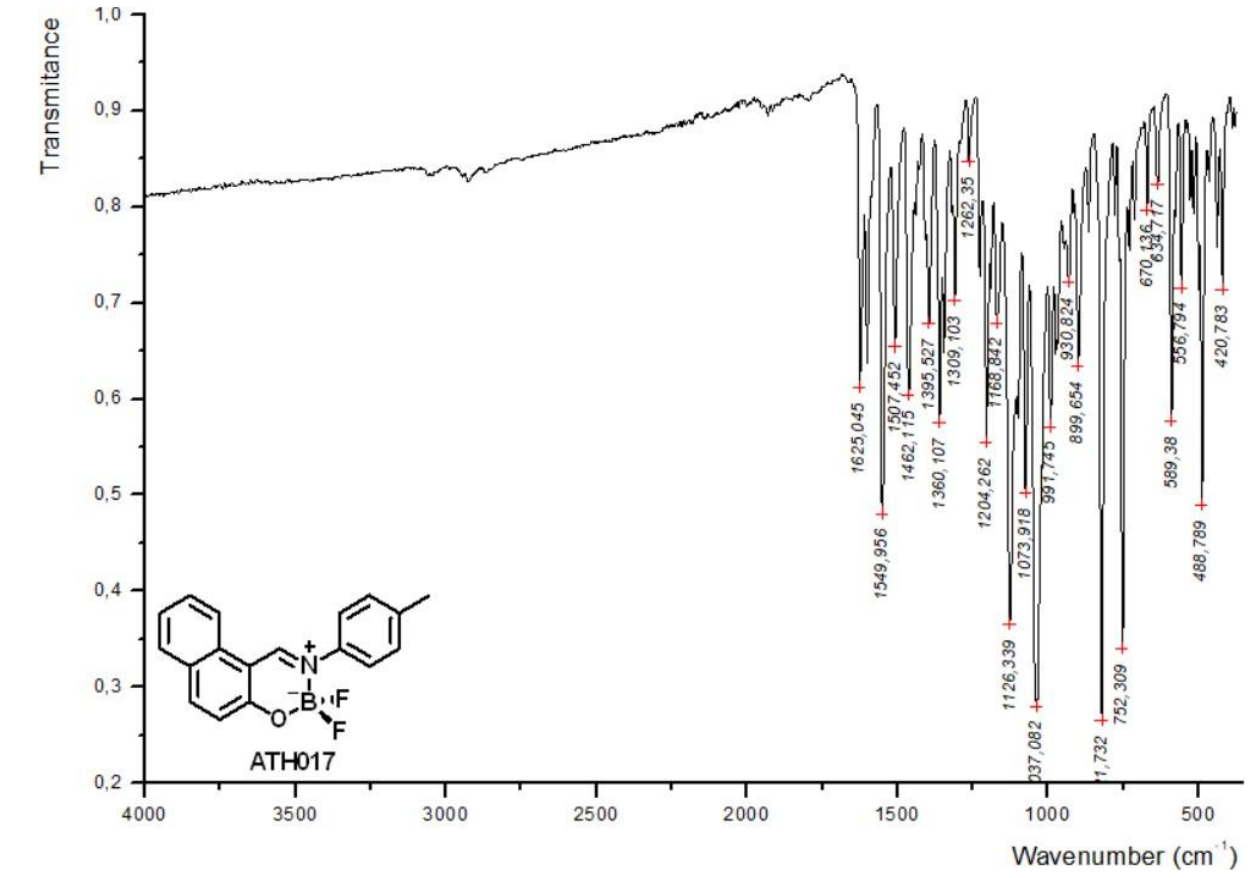



**Figure S15**: ATR–FTIR spectrum for compound **ATH017.**

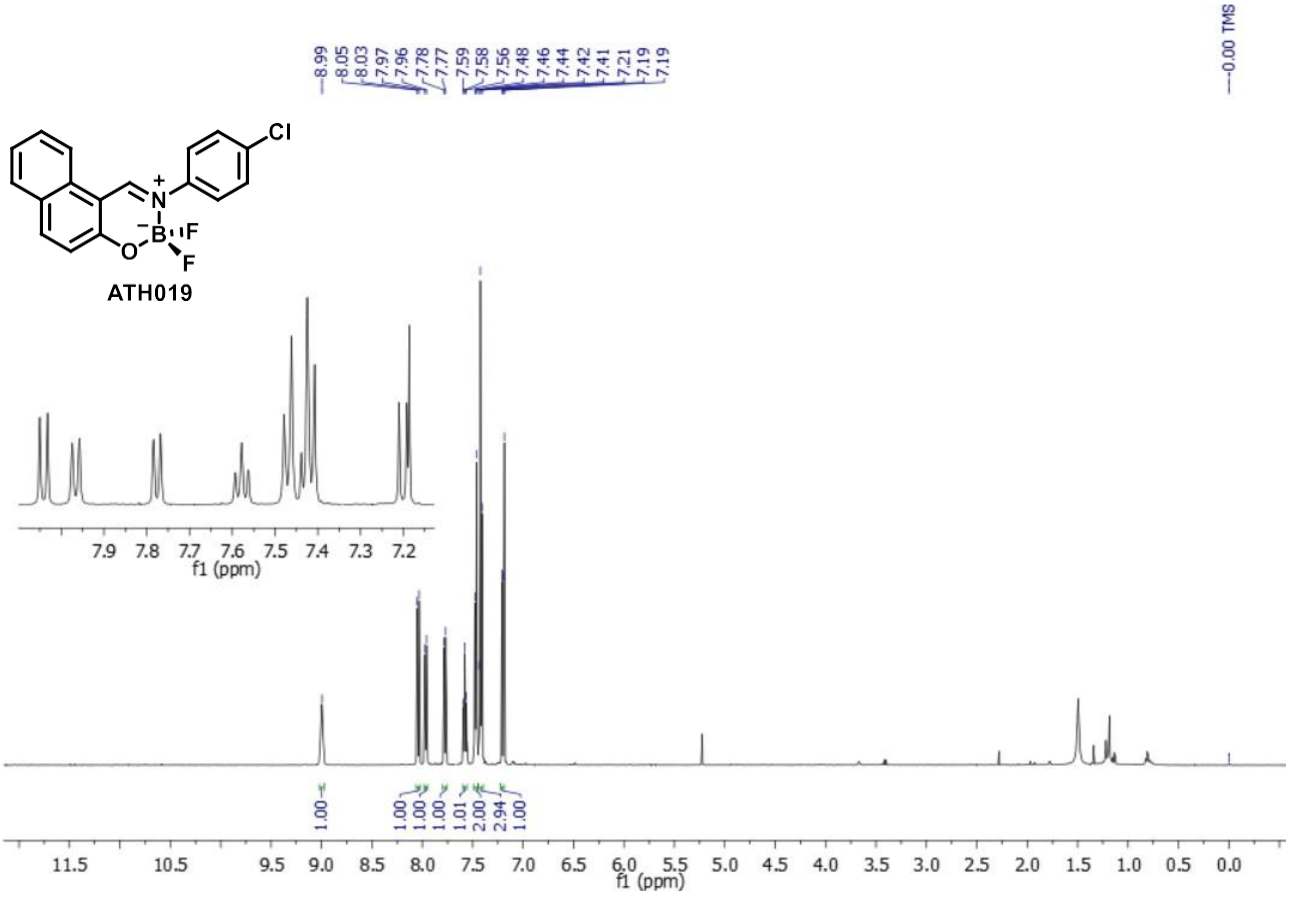



**Figure S16**: $^{1}$H NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH019**.

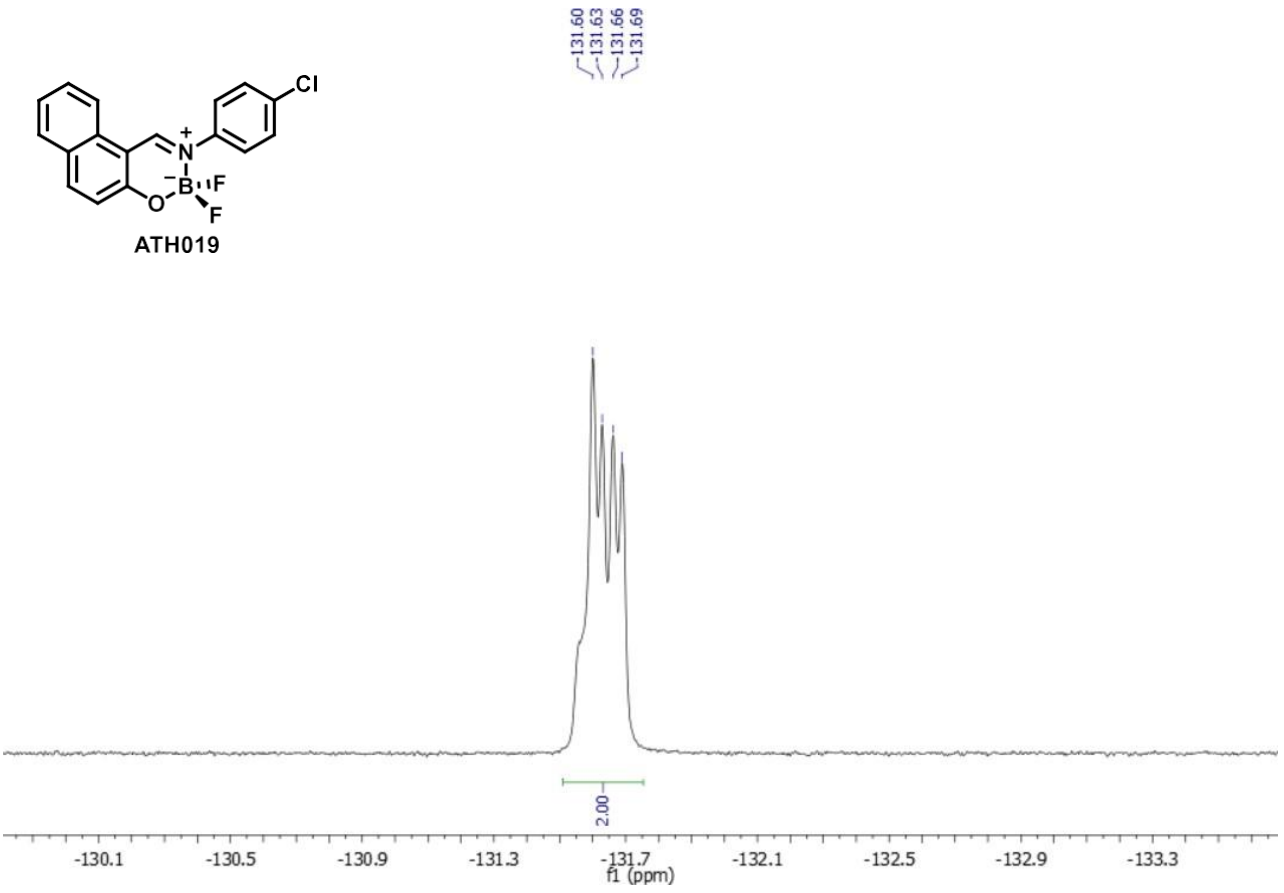



**Figure S17**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH019.**

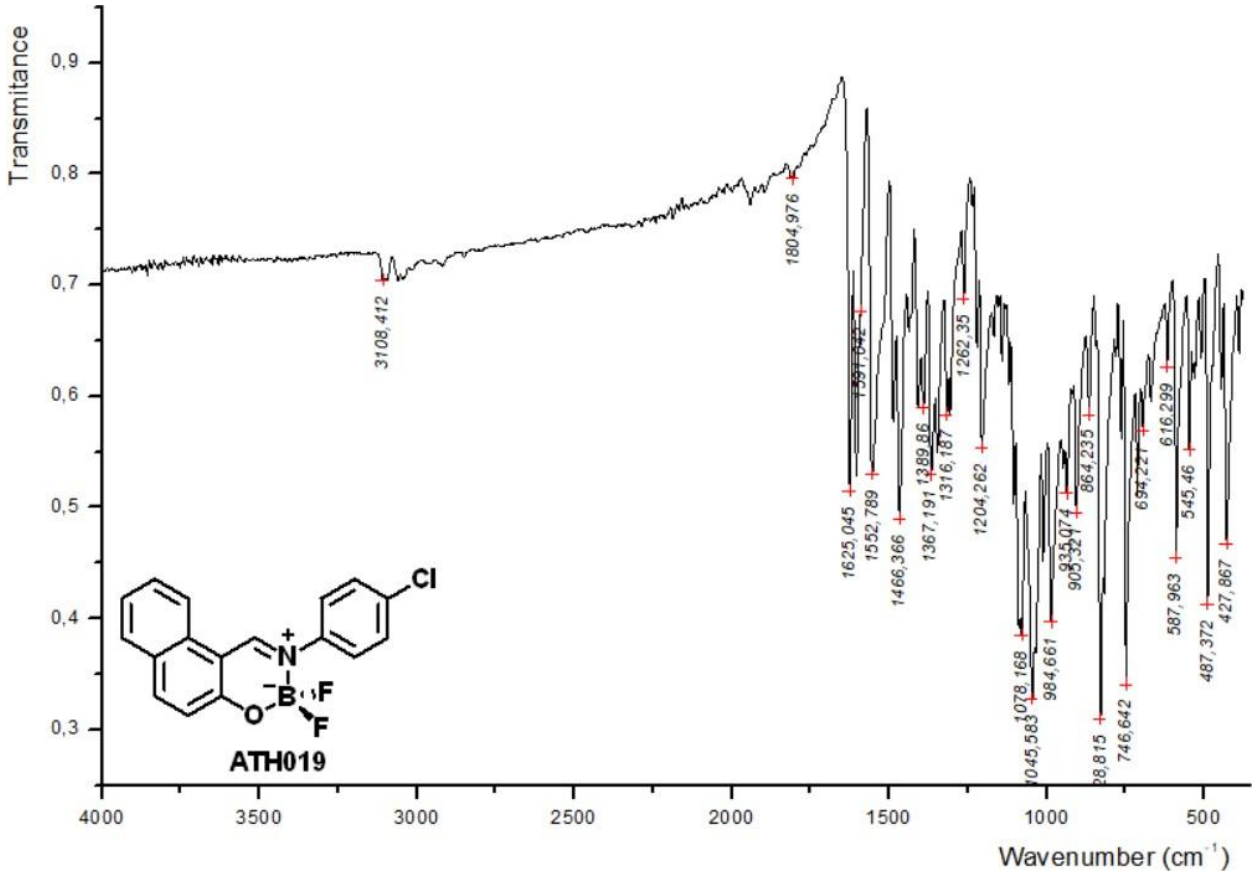



**Figure S18**: ATR–FTIR spectrum for compound **ATH019.**

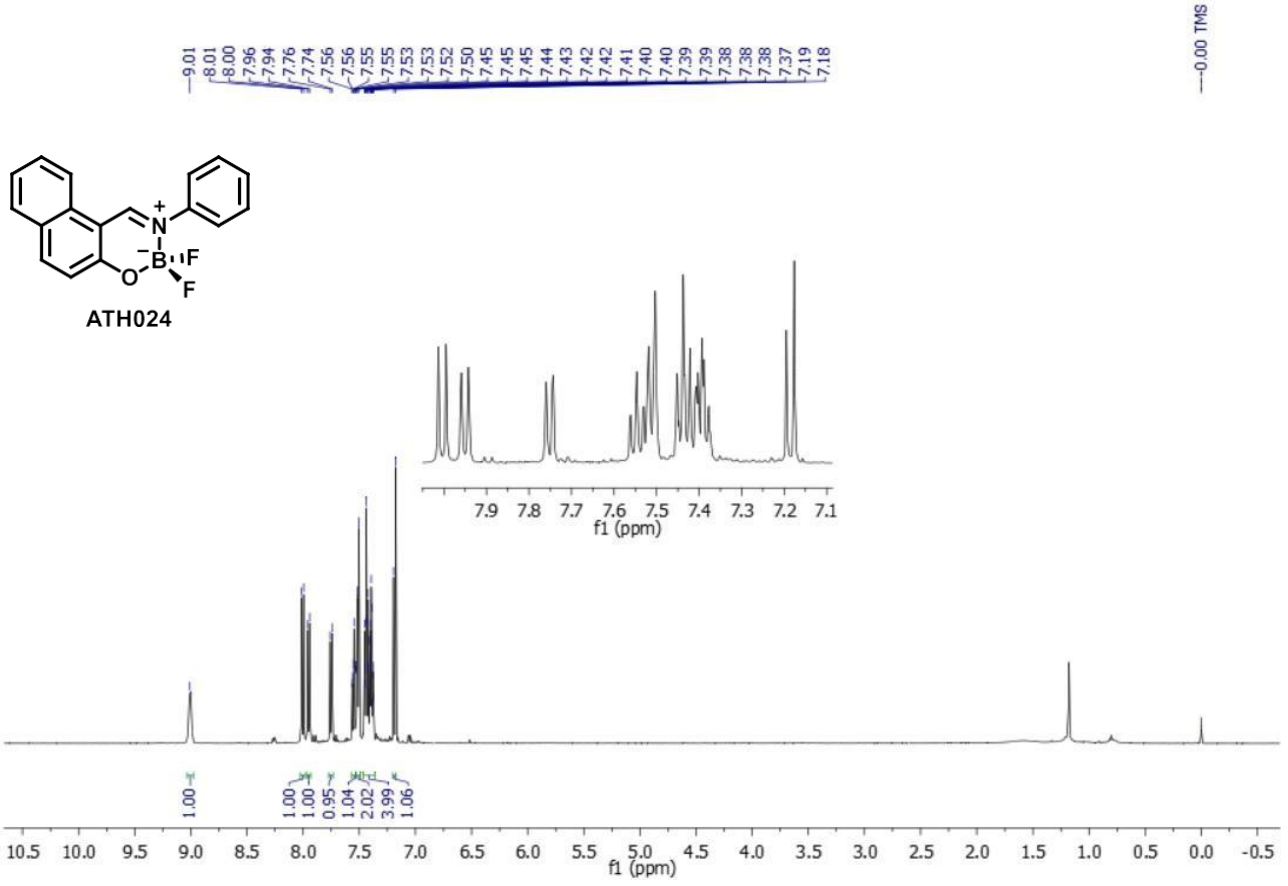



**Figure S19**: $^{1}H$ NMR spectrum (500 MHz, $CDCl_3$) of compound **ATH024**.

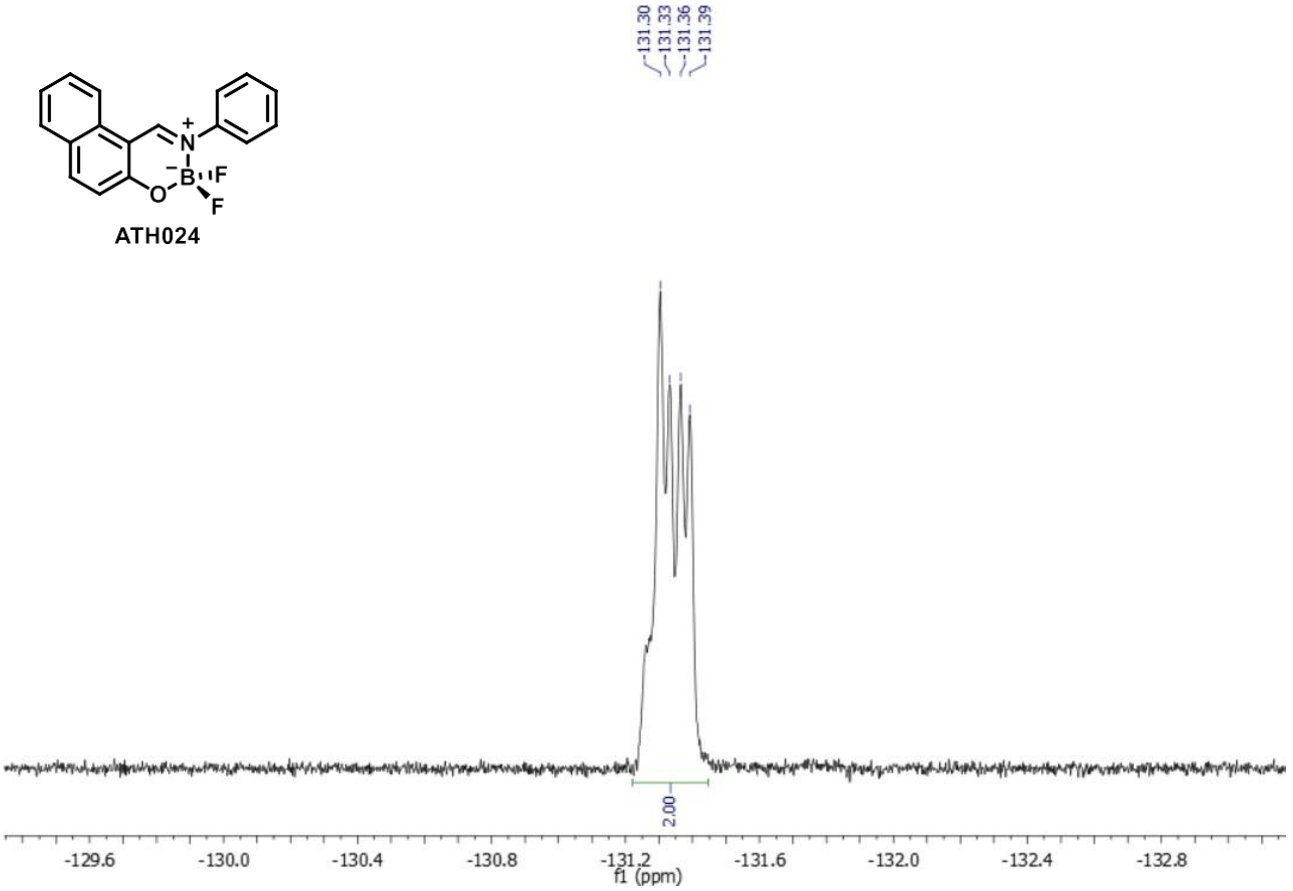



**Figure S20**: $^{19}F$ NMR spectrum (470 MHz, $CDCl_3$) for compound **ATH024.**

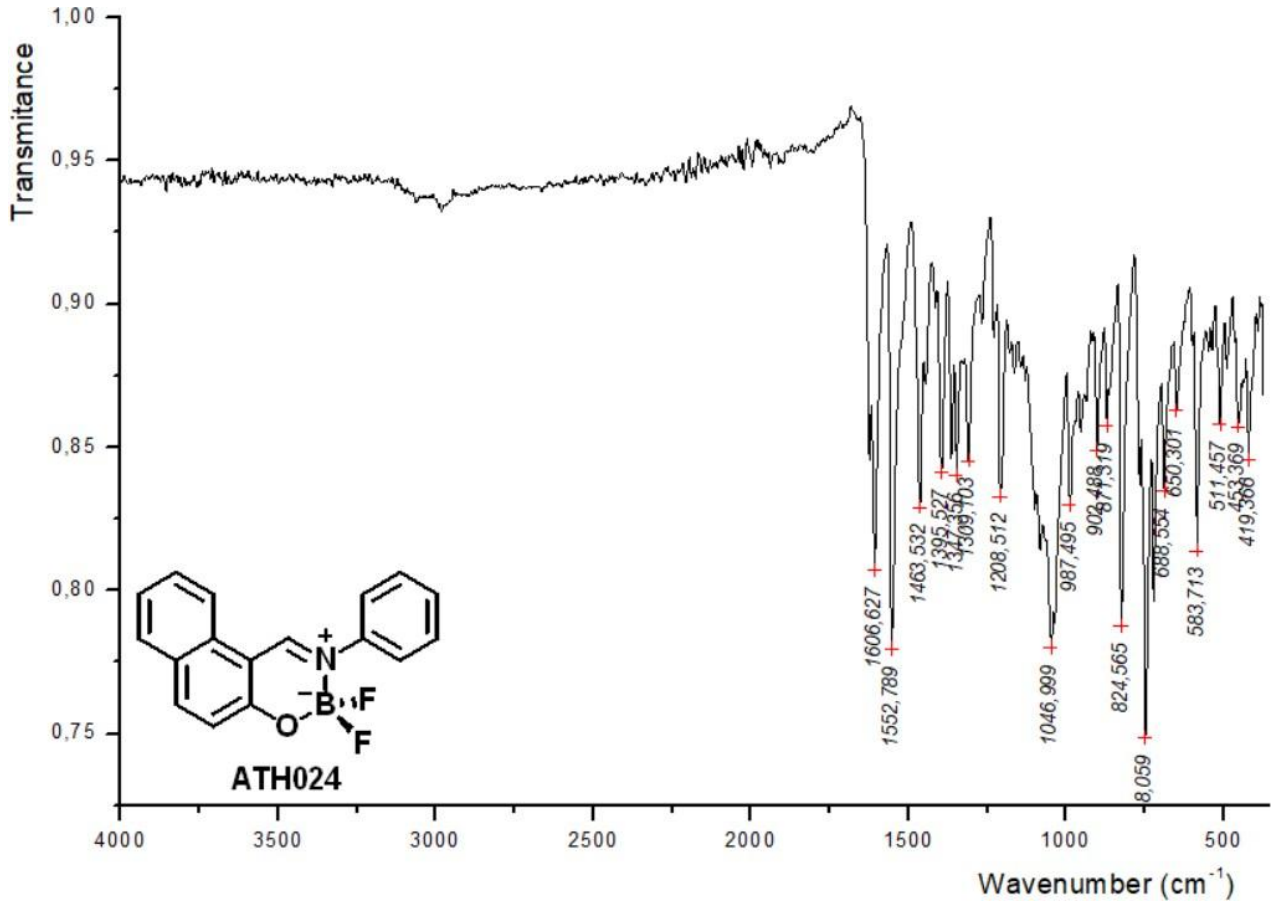



**Figure S21**: ATR–FTIR spectrum for compound **ATH024.**