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Research Article

Synthesis and Photophysical Properties of Pyrene-BODIPY Functionalized Subphthalocyanine Dyad

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Abstract - The treatment of boron (III) subphthalocyanine chloride (SubPcCl) with borondipyrromethene (BODIPY) derivative consisting of one pyrene group in toluene gave the corresponding axially substituted boron (III) subphthalocyanine dyad (SubPcBodiPy). Novel compound has been fully characterized by FTIR, mass, NMR (^{1}H and ^{13}C) spectroscopy and elemental analysis. Photophysical properties of SubPcBodiPy was investigated and compared with its precursors by fluorescence and absorption spectroscopy in tetrahydrofuran (THF). Accordingly, fluorescence lifetimes were measured directly by single exponential calculation.

Keywords: Subphthalocynanine, BODIPY, pyrene, photophysical properties

1. Introduction

Supramolecular systems with two or more chromophores are scientifically important for highly important applications ranging between optoelectronic devices, light harvesting and sensors. [1-2]. It is important to examine the photophysical properties of these compounds in detail. This indicates their dependence on functional dye systems [3]. BODIPY dyes are a very important material unit fluorophore family that has been widely studied due to its important specifications such as long excited state lifetimes, high fluorescent quantum yields, high absorption coefficients and generally good solubility in organic solvents. [4]. In addition, boron (III) subphthalocyanine (SubPc) derivatives are of great interest to the scientific world due to their specific and dish-like structures and physicochemical features like strong fluorescence and nonlinear optical features resulting from the aromatic conjugation system with delocalized 14π electrons. [5]. SubPc derivatives are used as functional materials in different applications such as chemical sensors, organic thin-film transistors (OTFTs), organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), and supramolecular building blocks for molecular can be used [6-9]. The integration of BODIPY and SubPc on one molecule is expected to produce new photoactive materials. There are a few study on combination of SubPc-BODIPY derivatives reported in the literature. To the best of our knowledge, the first reported SubPc BODIPY derivatives exhibited highly efficient energy transfer [10] and then two axially substituted SubPc-BODIPY derivatives which have potentials to use in photodynamic therapy (PDT) applications have reported from our research group [11]. In recent years a series of SubPc-BODIPY compounds containing carbazole moieties which have energy transfer potential in efficient light-harvesting systems were reported by Ecik et al. [12]. In another study SubPc-BODIPY conjugates based photodevices have reported as photodiodes in solar tracking systems [13] and a series of BODIPY-SubPc dyads as photosensitizers for PDT [14].

In this study, synthesis and characterization of SubPcBodiPy were reported (Scheme 1). The photophysical properties of this novel compound were examined by UV-visible absorption and fluorescence spectral studies in THF. This novel compound retain the unique photophysical properties of its precursor BODIPY that showing its promise as photosensitizer.

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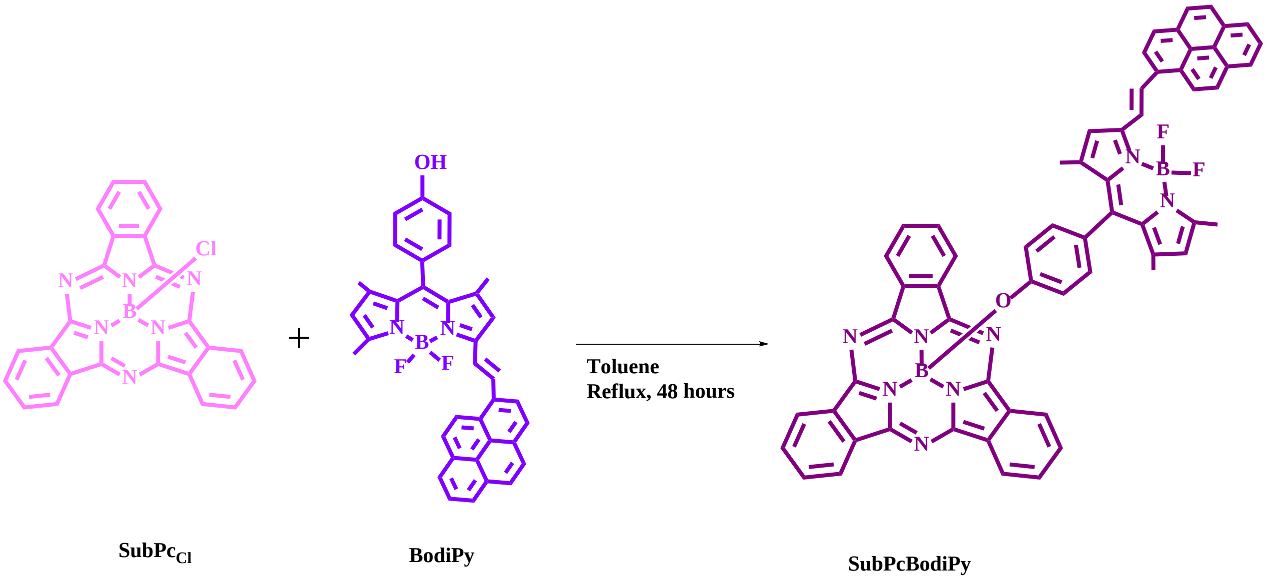

Scheme 1: Synthesis pathway of SubPcBodiPy

2. Materials and Methods

2.1. Materials

All chemical reactions were performed under inert argon atmosphere. Silica gel plates (Kieselgel 60, 0.25mm thickness) with F254 indicator were purchased from Merck for performed to thin layer chromatography (TLC). For purification of compounds, silica gel (Merck, Kieselgel 60, 230–400 mesh) was used for stationary phase on column chromatography with the appropriate eluents. 4-hydroxybenzaldehyde, boron trifluoride diethyl ether complex (BF_3OEt_2), piperidine, dichloromethane, tetrahydrofuran, chloroform-d ($CDCl_3$), ethylacetate (EtOAc), n-hexane, triethylamine (TEA) and toluene were obtained from Merck. Trifluoroaceticacid (TFA), para-toluenesulfonic acid (p-TsOH), 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) and 2,4-dimethyl-1H-pyrrole were purchased from Sigma-Aldrich. 1,8,9-antracenetriol which was used for mass analyses was obtained from Fluka. Boron (III) subphthalocyanine chloride and pyrene-1-carboxaldehyde were obtained from Alfa-Aesar.

2.2. Equipment

Elemental analyses were performed using a Thermo Finnigan Flash 1112 Instrument. Infrared spectra were measured on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer. Mass spectra were measured using a MALDI-MS (Bruker microflex LT MALDI-TOF MS). A Shimadzu 2001 UV spectrophotometer and a Varian Eclipse spectrofluorometer were used for UV–Vis and fluorescence experiments. Fluorescence emission spectra were taken at room temperature by a using 1 cm pathlength cuvettes. NMR spectra (^1H, ^{13}C) were obtained in $CDCl_3$ by a Varian 500 MHz spectrometer. Fluoro Hub-B Single Photon Counting Controller equipped Horiba-Jobin-Yvon-SPEX Fluorolog 3-2iHR was used for fluorescence lifetime measurements**.**

2.3. Synthesis

The starting BODIPY(BodiPy) compound was synthesized and purified according to literature procedures [11].

Phenol containing Bodipy compund (200 mg; 0.6 mmol, 1 eq) [10], pyrene-1-carboxaldehyde (135 mg, 0.6 mmol, 1 eq), p-TsOH (168 mg; 0.8 mmol, 1.3 eq) and piperidine (0.1 mL) were heated at boiling point of toluene (50 mL). The formed water throughout the reaction was moved away azeotropically by heating all night long in a Dean-Stark apparatus. The reaction mixture was concentrated by using vacuum and then chromatographed on silica gel using EtOAc: n-hexane (1:2) solvent system as eluent. BodiPy was collected as purple solid in (183 mg, 54% yield) [10]. The Analysis of Elemental: Founded: C 77.25, H 4.90, N 4.02%, $C_{36}H_{27}BF_2N_2O$ (553.3) needs C 78.27, H 4.93, N 5.07%. FTIR (ATR, cm^{-1}): 3309 (-OH), 3039 (Ar-CH), 2959–2890 (-CH), 1637 (-C=N-), 1367 (B-N str), 1322 (B-F). MALDI MS: m/z calc. 553.3; found: 553.0 $[M]^+$ and 553.0 $[M\text{-}F]^+$ ^1H NMR (in DMSO-d_6, δ, ppm) 10.02 (s, 1H, -OH), 8.94–7.98 (m, 9H, pyrene-H), 7.10 (d, 1H, J=16.2, H-C=C-H), 6.90 (d, 1H, J=16.2, H-C=C-H), 6.32 (d, 2H, J=7.2, Ar-H), 6.10 (d, 2H, J=7.2, Ar-H), 5.22 (s, 2H, pyrrole-H), 1.67 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.48 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm) 166.3, 153.2, 131.8, 131.7, 130.3, 128.6, 127.2, 123.3, 126.0, 125.9, 125.4, 125.3, 125.0, 124.9, 124.2, 124.1, 121.2, 120.5, 109.2, 94.5, 68.9, 17.0, 15.6, 15.4.

Argon gas was first applied to the 20 mL reaction flask and then toluene (15 mL) was added to the flask. SubPcCl (78 mg, 0.18 mmol, 2 eq) was placed in the flask and then BodiPy (50 mg, 0.09 mmol, 1 eq) was added. The reaction mixture was stirred under reflux for 48 hours. By checking the reaction mixture by thin layer chromatography (TLC), the reaction was complete when BodiPy was finished. The mixture was then cooled to room temperature and filtered. Toluene was returned to evaporate. The residue was chromatographed on a column of silica gel using n-hexane as the eluent until the pink band containing unreacted compound appeared. Then the solvent system was changed to n-hexane-ethyl acetate (2:1) to take the pink-purple band which is refer to the new compound. It was collected and evaporated in vacuo to remove the solvent. The Analysis of Elemental: Founded: C 75.20, H 3.95, N 12.08%, $C_{60}H_{38}B_2F_2N_8O$ (946.64) needs C 76.13, H 4.05, N 11.84%. FTIR (ATR, cm^{-1}): 2924.5, 2850.6 (Al-CH), 1730.5 (-N=C-), 1650.4 (-C=C-), 1592.5, 1536.3 (Ar-CH), 1508.7 (B-N), 1383.4 (B-F), 1303.5 (-N-CH_3), 1242.2 (-N-C-), 1115.5 (-C-O-), 1067.9 (-C-C-), 1017.8 (B-O) (Figure 1). MALDI MS: m/z calc. 946.64; found: 946.77 $[M]^+$ and 926.43 $[M\text{-}F]^+$ (Figure 2). ^1H NMR (500 MHz, $CDCl_3$) ὸ: 9.08-8.96 (m, 6H, SubPc-Hα), 8.33-7.99 (m, 9H, Py-H), 8.08 (d, J =16.2 Hz, 1H, -HC=CH-), 7.39-7.18 (m, 2H, ArH), 7.09-6.86 (m, 6H, SubPc-Hβ), 7.09-6.84 (m, 2H, ArH), 6.83 (d, J = 16.2 Hz, 1H, -HC=CH-), 6.49 (s, 1H, pyrrole-H), 5.97 (s, 1H, pyrrole-H), 2.39 (s, 3H, CH3), 2.33 (s, 3H, CH3), 2.18 (s, 3H, CH3) (Figure 3). ^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm) 169.8, 165.2, 162.9, 161.3, 158.8, 151.3, 144.4, 143.3, 141.0, 139.3, 138.2, 136.0, 135.7, 133.8, 132.2, 130.0, 129.3, 128.4,126.9,125.8,122.9,121.8,120.4,119.3,118.8,115.8,114.3,112.7, 110.3, 104.4, 40.1, 21.2, 17.0, 15.1 (Figure 4).

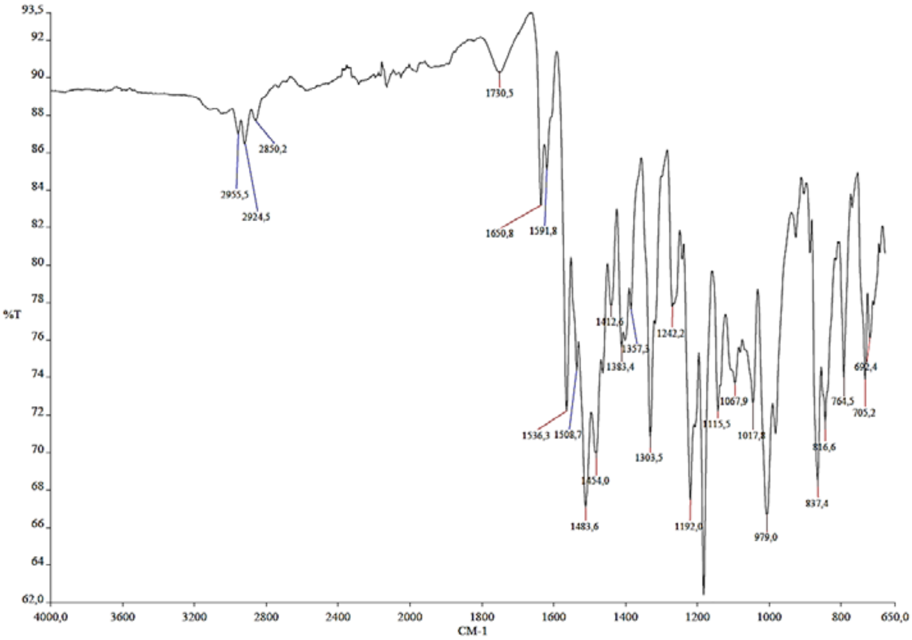

Figure 1. FTIR spectra of SubPcBodiPy

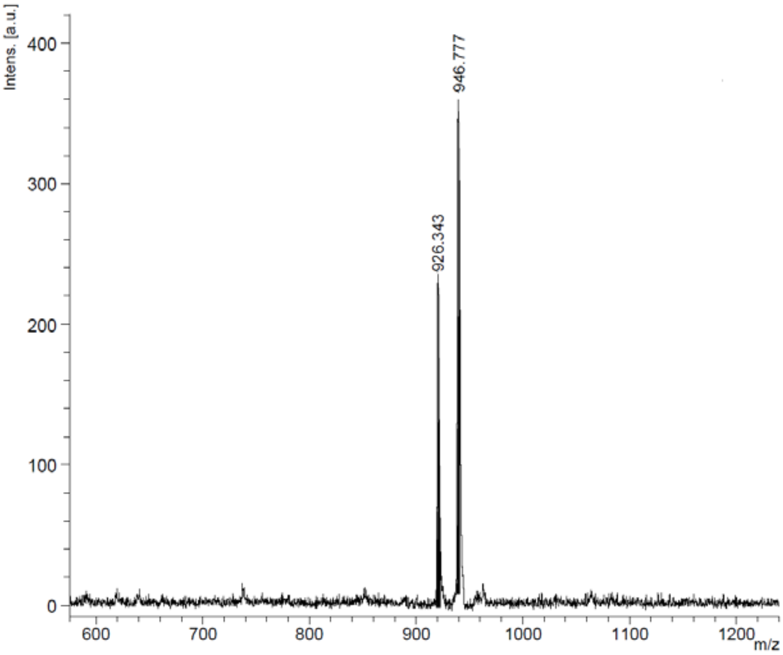

Figure 2. MALDI MS spectra of SubPcBodiPy

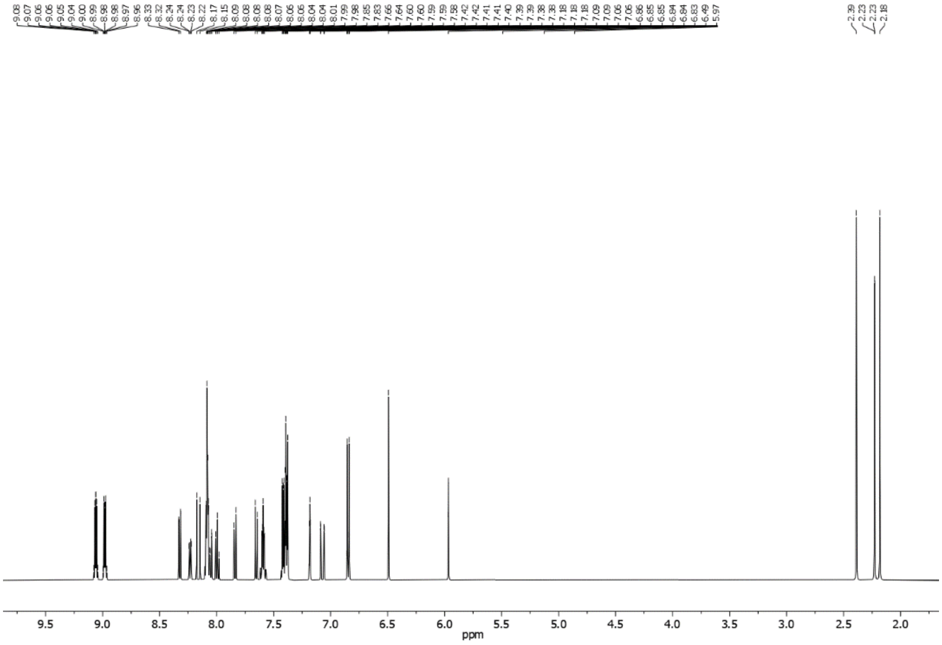

Figure 3. ^{1}H NMR spectra of SubPcBodiPy

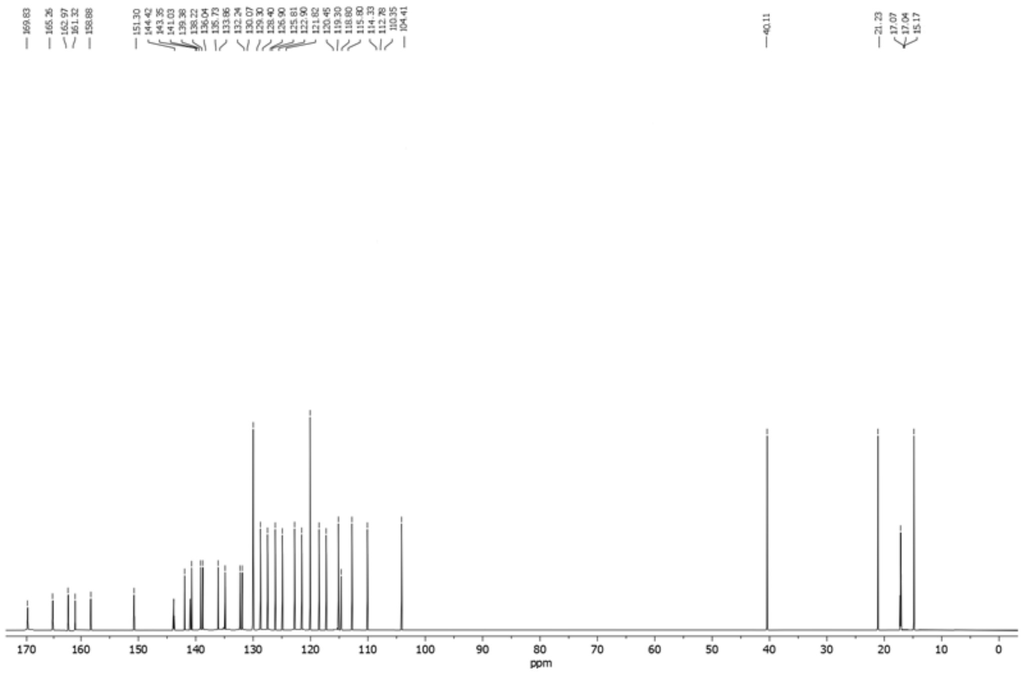

Figure 4. ^{13}C NMR spectra of SubPcBodiPy

3. Results and Discussions

All these spectroscopy experiments were performed using a micropipette in a quartz spectroscopic cuvette at 25 °C. The photophysical properties of SubPcBodiPy were investigated in THF solutions using fluorescent spectroscopy and UV-visible absorption techniques and compared with its precursors (BodiPy and SubPcCl) (Figure 5). According to Figure 5a, the absorption maximum of SubPcBodiPy was observed at 594 nm like its precursor BodiPy, and according to Figure 5b, the emission maximum of SubPcBodiPy was found at 609 nm. The fluorescence lifetimes of the compounds (Figure 6) were measured directly with a single exponential calculation and lifetime measurements were made for each compound separately: 3.0±0.006 (SubPc), 2.9±0.004 (BodiPy), 2.9±0.005 (SubPcBodiPy).

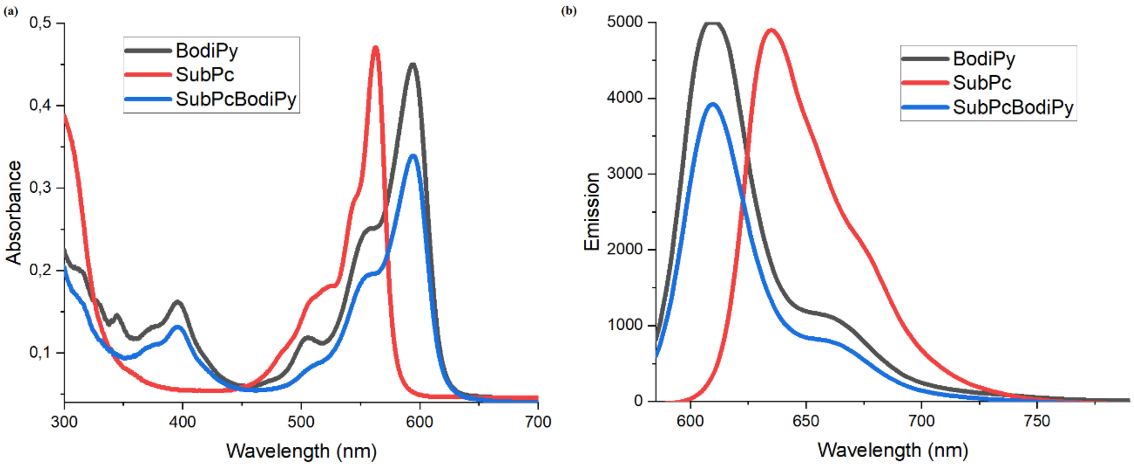

Figure 5. (a) Normalized absorption and (b) normalized emission spectra of compounds (Excitation wavelength: 510 nm)

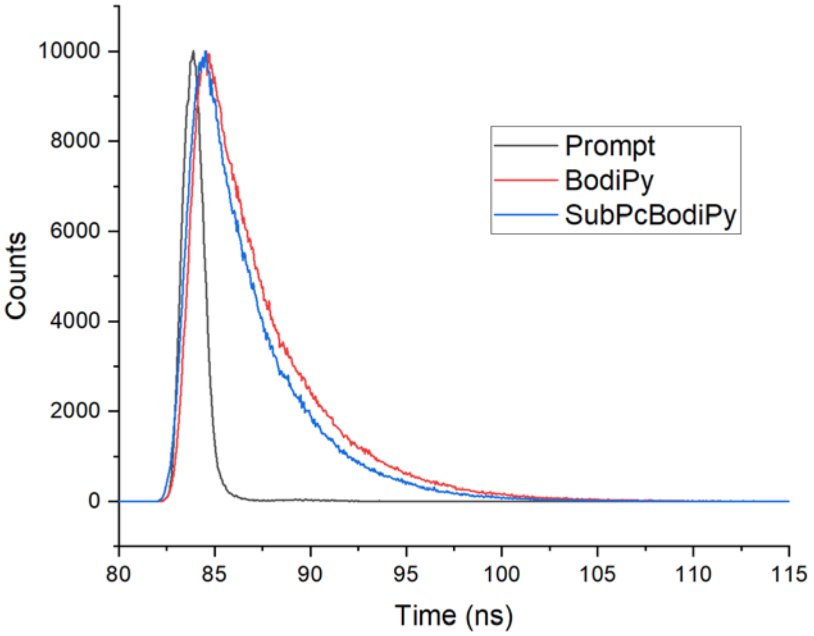

Figure 6. Fluorescence lifetime decay of BodiPy and SubPcBodiPy

Novel SubPcBodiPy derivative was prepared according to Scheme 1. The phenol containing Bodipy compound was first prepared by treating 2,4-dimethylpyrrole with 4-hydroxybenzaldehyde via sequential condensation, oxidation, and complexation reactions according to the literature [10]. In the following step this compound underwent Knoevenagel condensation reaction with pyrene-1-carboxaldehyde in the presence of piperidine to give the mono-styryl compound BodiPy. BodiPy was then treated with the commercially available boron (III) subphthalocyanine chloride in toluene to afford SubPcBodiPy compound. This novel compound was characterized by elemental analysis and FTIR, mass, ^{1}H and ^{13}C NMR spectrometry. All the results were consistent with the predicted structures as shown in the experimental section.

4. Conclusion and Future Work

In this study, a novel BODIPY-subphthalocyanine dyad (SubPcBodiPy) was synthesized and fully characterized by mass, FTIR, mass, NMR (^{1}H and ^{13}C) spectroscopy and elemental analysis. The photophysical characteristics of all compounds were examined by using UV-visible absorption and fluorescence spectroscopy in THF, and according to the obtained data, SubPcBodiPy retained the unique photophysical properties of its precursor BodiPy and a photosensitizer was obtained. Future studies will help determine the possibility of this compound for the photodynamic therapy of cancer and its ability to produce singlet oxygen will help.

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