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Synthesis and Characterization of Fluorenone Based Small Molecule and Investigation of Its Photophysical Properties

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Abstract

A fluorenone-based small molecule consisting of central 2,7-bis(ethynyl)-9-fluorenone core and BODIPY units at both sides (3) has been developed through the palladium/copper-catalyzed Sonogashira coupling reactions. The newly synthesized molecule was characterized by Fourier transform infrared (FT-IR), proton/carbon nuclear magnetic resonance ($^{1}H/^{13}C$ NMR), mass (MALDI-TOF), and elemental analysis. The photophysical properties of the new compound and its precursor were investigated by ultraviolet-visible (UV-Vis) and fluorescence spectroscopy techniques.

Keywords: fluorenone, BODIPY, photophysical properties, small molecule

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) consisting of two or more fused aromatic ring compounds, such as naphthalene, anthracene, pyrene, fluorene, and so on, have been significant attention in the scientific research field due to their wide diversity physical, chemical, and biological properties [1,2]. Fluorenone is a polycyclic aromatic ketone obtained from the oxidation of the 9-position of fluorene, a member of the PAH family. The presence of strong electron withdrawing carbonyl group at 9-position in the fluorenones makes them molecules of interest in organic electronic devices [3]. Detailed analysis of the electronic and fluorescent structure of fluorenone derivatives is crucial for their applications as organic semiconductors or fluorescent dyes [4]. The photophysical properties of fluorenones are easy tunable with respect to easy functionalized 2,7-position of fluorenone derivatives [5]. Therefore, they are commonly used as a building block for the development of materials with good absorption and photoluminescence properties [6].

On the other hand, BODIPY (boron dipyrromethene) dyes have also unique photophysical and optoelectronic properties, such as good photochemical stability, high fluorescence quantum yields, large absorption coefficient etc. Besides this, BODIPY dyes could easily be functionalized at all possible positions (*α, β, meso-)* of the BODIPY core through chemical modification [7-9]. Thanks to these excellent properties, BODIPY dyes have been widely used in many application areas such as sensors, biological labeling, optoelectronic and photovoltaic devices, as photosensitizers for photodynamic therapy [10-14]. The photophysical properties of these compounds can be adjusted by a modification to the BODIPY core, allowing absorption and emission regions to shift to longer wavelengths such as the red/NIR region of the electromagnetic spectrum. Many researchers focused on obtaining the bathochromic shift and some of these strategies are substituting pi-extended molecules into BODIPY dye, replacing 8-carbon atom with a nitrogen atom (forming aza-BODIPY), fusing some aromatic rings to the pyrrole core, and adding halogens to the structure [15-20].

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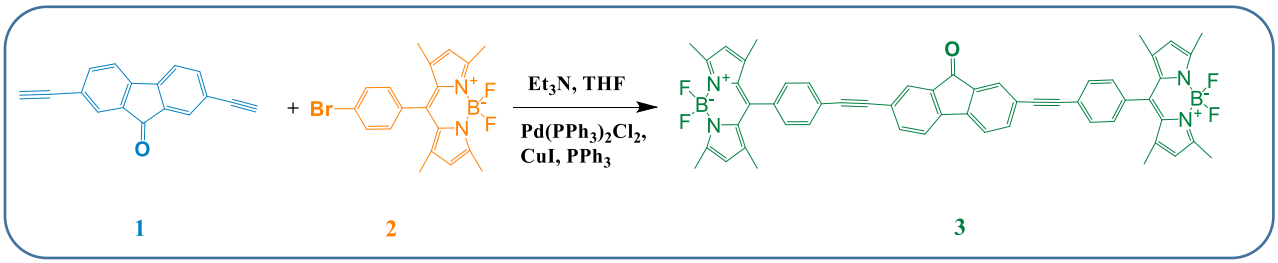
This thought encouraged us, we were able to design a small molecule with good photophysical properties using BODIPY dyes and fluorenone on the same platform. Herein, the newly compound and its precursor have been easily synthesized and fully characterized with standard spectroscopic techniques. Their photophysical properties were examined with absorption and fluorescence emission spectroscopy in dichloromethane.

2. Experimental

The BODIPY compound (**1**) was synthesized according to our previous work [21]. The compound (**2**) was synthesized and characterized according to literatures [22,23].

2.1. Synthesis of 2,7-bis((4-(5,5-difluoro-1,3,7,9-tetramethyl-5H-4l4,5l4-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-10-yl)phenyl)ethynyl)-9H-fluoren-9-one (3)

Compound **2** (0.097 g, 0.24 mmol) was suspended in triethylamine (Et_3N) (6 mL) and tetrahydrofuran (THF) (2 mL). Bis(triphenylphosphine)palladium(II) dichloride ($Pd(PPh_3)_2Cl_2$) (8 mg, 0.01 mmol), copper(I) iodide (4 mg, 0.02 mmol), and triphenylphosphine (PPh_3) (6 mg, 0.02 mmol) were added into the reaction mixture and stirred under argon atmosphere. The reaction mixture was heated to 60°C, and compound **1** (0.025 g, 0.11 mmol) was added. After stirring for 15 min at this temperature, the reaction was heated to 80°C and stirred overnight under argon atmosphere. When the reaction was completed, the mixture was cooled down to rt and extracted with dichloromethane and distilled water. The organic phase was dried over sodium sulphate, and concentrated. The crude product was purified through column chromatography on silica gel using hexane/CH_2Cl_2 (1/3, v/v) as the eluent to afford the target product as an orange solid (0.019 g, 20%). Elemental Analysis: (Found: C 75.38, H 4.95, N 6.48%, $C_{55}H_{42}B_2F_4N_4O$ (872.58) requires C 75.71, H 4.85, N 6.42%). MALDI-MS: m/z calc. 872.58; found: 872.33 $[M]^+$ and 853.13 $[M-F]^+$. FT-IR (cm^{-1}): 2957.9, 2918.4, 2849.9 (Aliphatic-CH), 1725.2 (-C=O), 1505.3, 1537.8 (B-N), 1368.7 (B-F), 1195.5 (-C-N-). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) 7. 86 (s, 2H), 7.71 (d, J = 7.7 Hz, 2H), 7.69 (d, J = 8.1 Hz, 4H), 7.58 (d, J = 7.7 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 6.00 (s, 4H), 2.56 (s, 12H), 1.44 (s, 12H). ^{13}C NMR (500 MHz, $CDCl_3$): δ (ppm) 195.16, 154.84, 142.46, 141.95,139,58,139.15,136.86,134.38, 133.53, 131.38,130.16, 127.39, 126.56, 123.17, 122.55, 120.40, 119.75, 89.64, 88.78, 13.97, 13.60, 13.04.



Scheme 1. Synthetic route of compound **3**.

3. Results and Discussion

The newly synthesized compound (**3**) was depicted in Scheme 1. Compounds (**1** and **2**) were synthesized and purified according to corresponding literatures. The target compound (**3**) was synthesized by palladium/copper catalyzed Sonogashira coupling reaction. The structures of the molecules were characterized through commonly used spectroscopic techniques and the results were consistent with expected structures. In Figure 1, the molecular ion peak of the new compound **3** was seen at m/z 872, and the peak at m/z 853 is belongs to removal of one fluorine unit of the BODIPY compound [10]. When compared FT-IR spectra of compounds, the acetylene C-H band of fluorenone (**1**) was disappeared and aliphatic C-H bands were observed which belong to BODIPY methyl groups (Figure 2). The ^1H NMR spectra of **3** is shown in Figure 3. The fluorene phenyl protons were located at 7.86, 7.71 and 7.58 ppm, and the proton signals of the phenyl groups which substituted at the BODIPY *meso*-position are located at 7.69 and 7.32 ppm. The proton signals of CH-groups and methyl groups on the pyrrole ring were located at 6.00 and 2.56, 1.44 ppm, respectively. ^{13}C NMR data was consistent with the structure due to carbonyl carbon which located at 195.16 ppm and the methyl carbons that located at 13.97-13.04 ppm (Figure 4) [24-25].

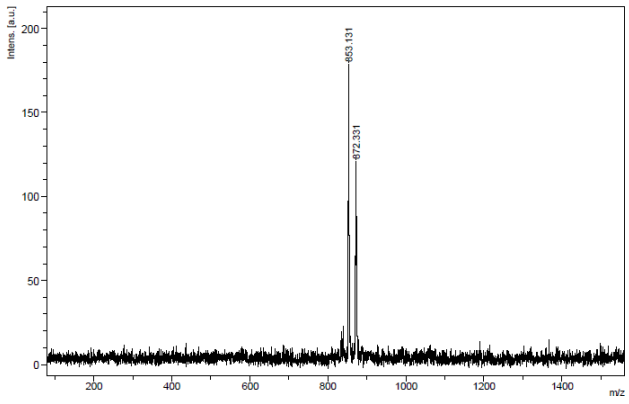


Figure 1. MALDI-TOF spectra of compound **3**.

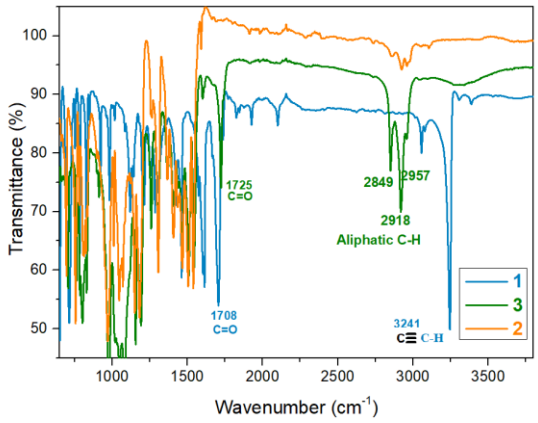


Figure 2. FT-IR spectra of compounds (**1**-**3**)

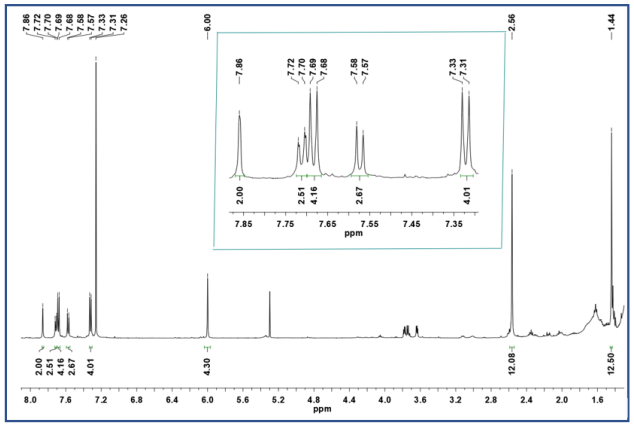


Figure 3. ^{1}H NMR spectra of compound **3**.

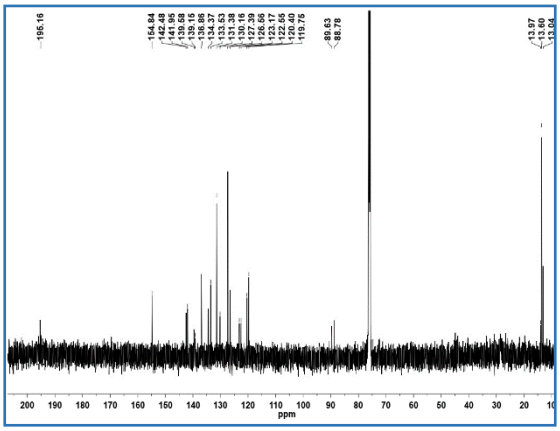


Figure 4. ^{13}C NMR spectra of compound **3**.

The absorption and fluorescence emission of compounds (**1**-**3**) was measured at rt in dichloromethane (Figure 5). The absorption maximas of fluorenone core are located at 269, 279, 311, 323, and 328 nm, corresponding to π-π* electronic transition of the fuorenone, and around 400 nm weak absorption band is attributed to symmetry forbidden n-π* transition of the carbonyl unit [26]. The absorption maximas of the target compound were seen at 305 and 356 nm which belongs to fluorenone core and at the maxima of 504 nm is attributed to BODIPY unit when compared to BODIPY precursor [21]. The target molecule (**3**) emission was located at 518 nm and seen nearly 3 nm red-shifted when compared with the BODIPY dye (**2**). To increase the red shift of the compound, it can be achieved with some modifications such as substitution of α-position with π-extended rings or adding heavy atom to β-position of BODIPY core. Furthermore, the polarity of the surrounding solvents can be affected on the fluorescence emission properties [27-28]. In general, increased solvent polarity causes the emission spectrum to shift (red shift) to longer wavelengths.

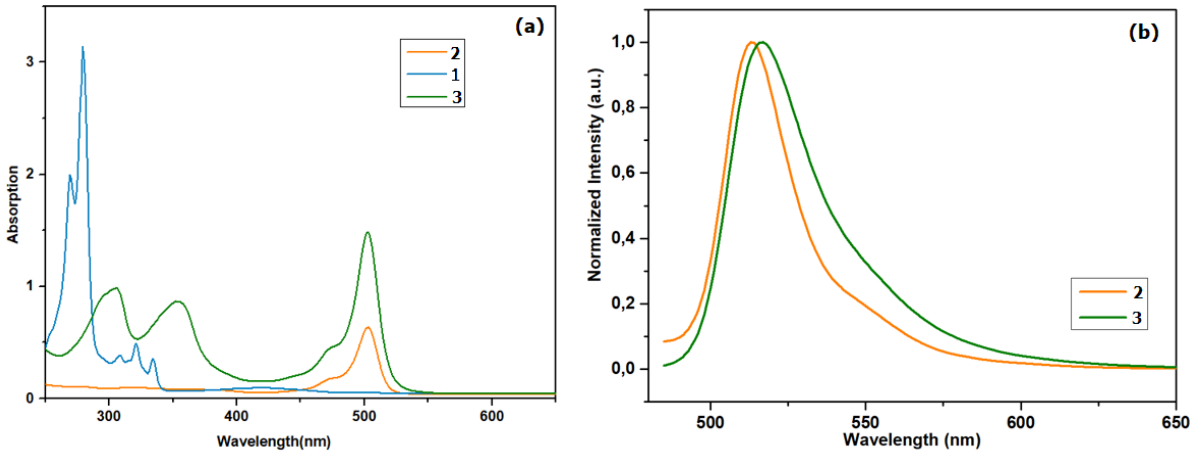


Figure 5. (a) Uv-Vis absorption spectra and (b) normalized fluorescence emission spectra of compound **3** in CH_2Cl_2.(Excitation: 470 nm)

4. Conclusion and Future Work

In summary, we have synthesized a novel conjugated small molecule with a central fluorenone core and BODIPY terminal units at both sides using a Sonogashira coupling reaction. The obtained molecule has been obviously characterized with common spectroscopic techniques in means of FT-IR, ^{1}H and ^{13}C NMR, mass spectroscopy, and elemental analysis. The optical/photophysical properties were investigated via absorption and emission spectroscopy methods and approximately 3 nm bathochromic shift were seen when compared with BODIPY terminal precursor. The bathochromic shift can be obatined via extension of conjugation. Therefore, some modification of the BODIPY compound will be done in future studies.

In addition, these investigations were led to us prior information to determine possible application in optoelectronic devices. Therefore, analyzing of the electronic properties of the compound will be included in future studies.

Acknowledgment

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