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Green to Blue BODIPY Dyes for Fluorescent Applications in the Solution and the Solid State

Roza Al-Aqar

Chemistry Department, College of Science, Basrah University, Basrah, Iraq

Email: rozachemistry@yahoo.co.uk

الخلاصة

تم في هذه الدراسة تم توضيح الخواص الفيزيائية لاصباغ البودبي مع ملاحظته ظاهرتي الامتصاص والتفلور في المنطقة الخضراء من الطول الموجي بين (500-565) نانوميتر، درست بامتزاز صبغه البودبي في الحالة الصلبة على مركب البولي داي مثيل سيلوكسين وتقع اعلى قمه امتصاص في 500 نانوميتر و اشاره صبغه البودبي في مركب البولي داي مثيل سيلوكسين يدل على وجود صبغه ممتزة في التراكيز العالية من صبغه البودبي. تم قياس ظاهرة التفلور في مذيب الكلوروفورم للصبغة، وتظهر اعلى قمه تفلور في 512 نانوميتر في التراكيز المختلفة. تقع اعلى قمه امتصاص لصبغه البودبي مع صبغه البودبي الخضراء في 517 نانوميتر، بينما تظهر اعلى قمه امتصاص لمركب أي أج 236 اف 1 في 511 نانوميتر، بينما تظهر اعلى قمه امتصاص لصبغة البودبي مع صبغه البودبي الزرقاء في 517 نانوميتر.

Abstract

The present study demonstrates the physical properties of BODIPY dye with efficient absorption and fluorescence phenomena in the green region of wavelength between (500-565) nm, the BODIPY dye adsorption over the solid state on polydimethyl siloxane PDMS, was studied. For this dye maximum absorption was at 500 nm and a BODIPY dye signal in the polydimethyl siloxane compound PDMS indicates the presence of adsorbed dye in the higher concentration of BODIPY dye. The fluorescence of this dye in chloroform was measured, this dye exhibited a maximum fluorescence at λ_{em} at 512 nm at different concentrations. The maximum absorption of BODIPY dye with green BODIPY dye, was located at 517 nm, while the maximum absorption of 5,5-difluoro-1,3,7,9-tetramethyl-10-(3,4,5-tris(dodecyloxy)phenyl)-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine eh236f1 compound was located at 511 nm. On the other hand, the maximum absorption of BODIPY dye with blue BODIPY dye, was located at 517 nm.

Keywords: Bathochromic shift, Blue dyes, Bodipy dyes, Fluorescence, and Solid state.

1. Introduction

In this paper the photophysical properties have been studied, for example fluorescence and absorption of derivative of borodipyromethene BODIPY molecule. The BODIPY is 4,4-Difluoro-4-bora-3a,4a-diaza-s-indacene which is described as BODIPY. The basic structure of this compound is shown in Fig. 1. The studies are focused on the 4,4' positions of BODIPY, Treibs and Kreuzer are studied the fluorinated and non-fluorinated BODIPY dyes in 1968. There are excellent properties for the BODIPY dyes, for example, high quantum yield, photochemical and thermal stabilities, high absorption, chemical robustness and also the high popularity [1]

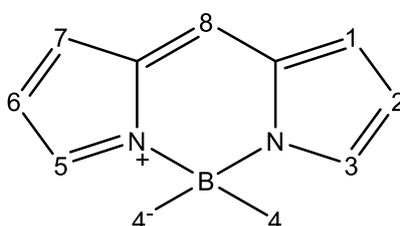


Figure 1 The structure of the BODIPY and numbered.

BODIPY is an excellent molecule which is described as strong absorption coefficient in ranges of visible and near IR spectra and is soluble in organic solvents and the excited state lifetime is long. There are many potential applications of BODIPY dyes, for example, emission imaging and biomolecule labelling. These dyes can be used as photosensitizers in DSSCs (dye-sensitized solar cells) [2]. The small Stokes Shift is shown in these dyes, and in the visible region these dyes are absorbed. The energy of the fluorescence and the intensity are altered through the presence of electron donor/ or acceptor substituents. The absorption and emission spectra are affected through the presence of electron donating substituents in the positions 2 and 6 and the spectra shift to lower energy wavelengths, while the opposite effect is observed in electron-withdrawing groups. The quantum yield and redox properties are changed through the change of BODIPY substitution [3]. Because of the chemical and optical properties of BODIPY dyes, these dyes are utilized in many fields, for example, chemical sensors, fluorescent devices, biological labelling and photovoltaic devices. The bathochromic shift is gained through the synthesis of aza-BODIPY dyes and generation a push-pull motif, with the functionalization at meso position [4]. BODIPY dyes appear a bright green fluorescence. The electronic distribution outcomes from BODIPY chromophore excitation, which the electron transfers to nanocrystalline from the S_1 state [5]. The benefit of NIR absorption, near-infrared and NIR emission dyes synthesis are significant, the modification structure of the dyes is necessary for the promotion of a BODIPY dye to NIR and far-red regions [6]. The BODIPY dyes are shown a high

extinction coefficients (i.e. 70000- 80000 $M^{-1}.cm^{-1}$), therefore the absorption is shifted to longer wavelengths through the modifications [7]. The donor D-Acceptor A-substituted BODIPY dye sensitizers are utilized in DSSCs, that the electron donor is triphenyl amine at the 6-position while the electron acceptor is cyanoacrylic acid at the 2-position [8]. There are many fluorescent probes, emitting in the NIR region, for example, BODIPY dyes, cyanines, and Rhodamine [9].

Polydimethylsiloxane (PDMS) is utilized in microfluidic applications, and the polymer is a transparent elastomeric polymer, the transparency of the polymer is utilized in many cell-based applications. The polymer can be used instead of traditional materials, for example, glass, polystyrene, or silicon. PDMS can be bonded to glass in the irreversible process, then exposure to oxygen plasma [10]. In medical devices, the polymer is utilized in these devices and the BODIPY is coupled to the polymer [11].

The aim of this work, would be investigated of the photophysical properties of the BODIPY dye, 5,5-difluoro-1,3,7,9-tetramethyl-10-(3,4,5-tris(dodecyloxy)phenyl)-5H-4 λ^4 ,5 λ^4 -dipyrrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine, (eh236f1), i.e. absorption and fluorescence. Also it would involve study the dye adsorption in the solid state over polydimethyl siloxane PDMS, the dye consist of ($C_{12}H_{25}O$) group, Fig. 2 shows the structure of the compound of eh236f1.

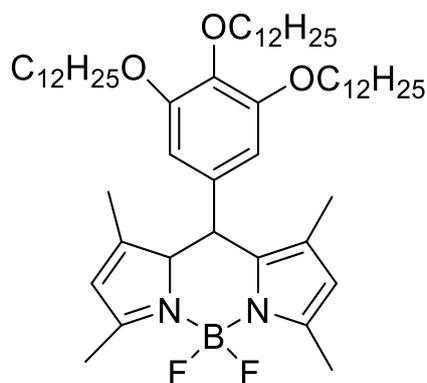


Figure 2 The structure of the (eh236f1) compound [12]

1. Photophysical properties of the compound eh236f1

2.1. The absorption

The absorption of the compound in concentration range (0.0156-0.25 M) chloroform $CHCl_3$ are shown in Figs. 3,4. The dye shows a strong absorption

band at 511 nm in chloroform solvent, which is assigned to the transition ($S_0 \rightarrow S_1$) [8]. In general, the BODIPY dyes show the absorption maximum in two regions which are separated, therefore the absorption spectra in $CHCl_3$ show intense absorption in two regions bands 300- 420 nm and 420-550 nm [2]. BODIPY derivatives display a highly coloured and have narrow absorption bands, and the maximum of the wavelength is greater than 500 nm. In Fig. 3, the absorption values are increased by the concentrations, with the λ_{abs} is located at 511 nm, while Fig. 4 shows the absorption spectrum of this dye, in chloroform in different concentrations (0.4-0.5 M), the λ_{abs} is located at 511 nm at 0.00408-0.025 M, the wavelength maximum is shifted to 523 nm (bathochromic shift) at 0.064 M, and λ_{abs} is located at 503 nm at higher concentrations (i.e. 0.4 M). The aggregation is formed at highly conjugated π - π systems in a nonpolar solvent by the interactions of π - π [6].

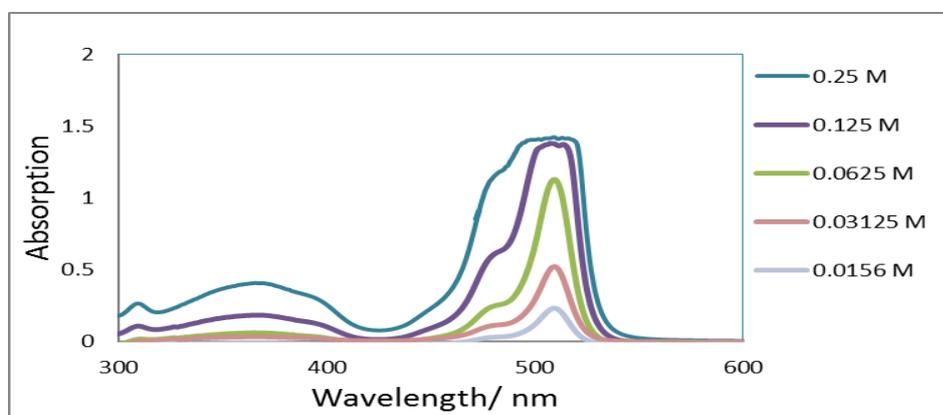


Figure 3 The absorption spectrum of the compound (eh236f1) in chloroform, the concentrations from 0.25 M to 0.0156 M.

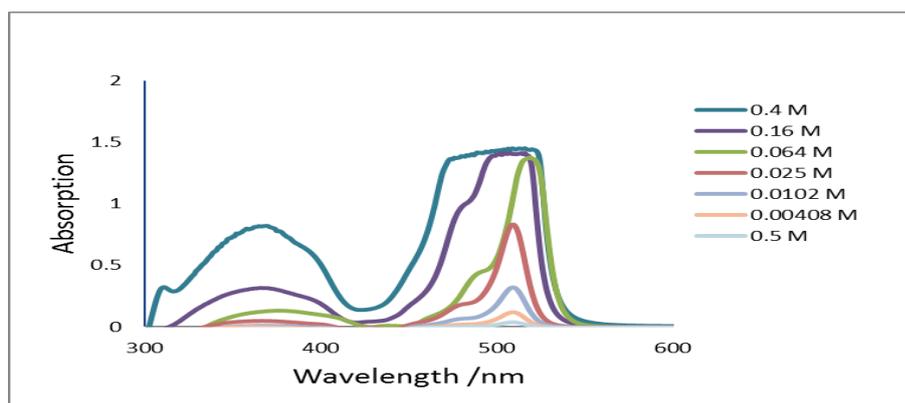


Figure 4 The absorption spectrum of the compound (eh236f1) in chloroform, at different concentrations .

The BODIPY dye adsorption over the solid state on polydimethyl siloxane PDMS was studied, the BODIPY adsorption and desorption on the polymer were studied [10]. The maximum absorption was located at 500 nm, Fig. 5, that shows the absorption spectrum of the compound (eh236f1) with drops of PDMS, and BODIPY dye signal in the PDMS indicates the presence of

adsorbed dye, i.e. the higher concentration of BODIPY, therefore higher emission signals on PDMS and the higher concentration of the dye indicate the BODIPY dyes could be absorbed deeper into the PDMS bulk because of its porous nature. The PDMS-BODIPY showed the absorption similar to the dye without PDMS, but with a slight red shift of the bands because of the solid state nature and microenvironment [11].

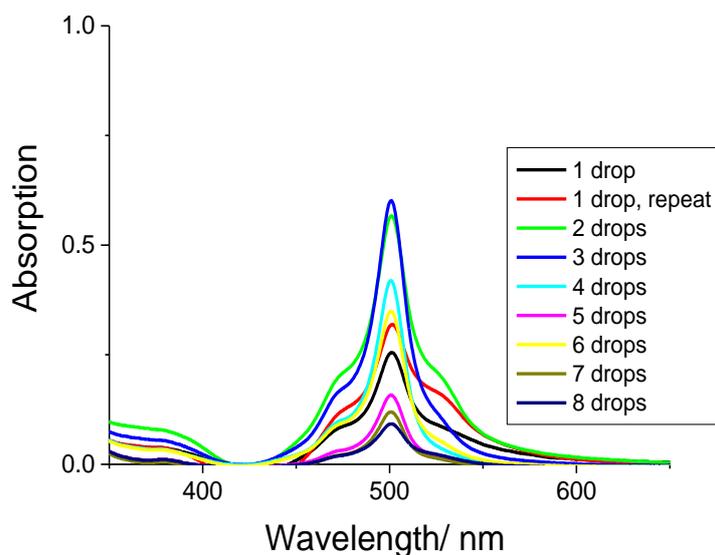


Figure 5 The absorption spectrum of the compound (eh236f1) with drops of PDMS.

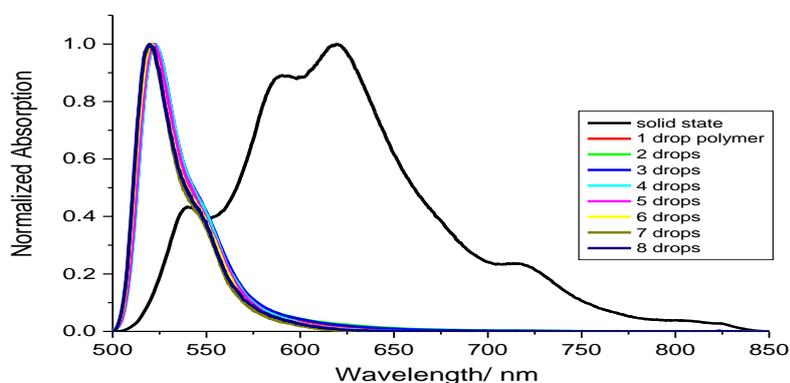


Figure 6 The normalized absorption spectrum of the compound (eh236f1) with PDMS.

Fig 6 shows the absorption of BODIPY dye in the solid state, and with PDMS, the green fluorescence signal (520 nm) and at higher concentration of the dye, there is a higher green fluorescence signal on PDMS, the red fluorescence (619 nm) refers higher concentration of BODIPY in the solid state [10].

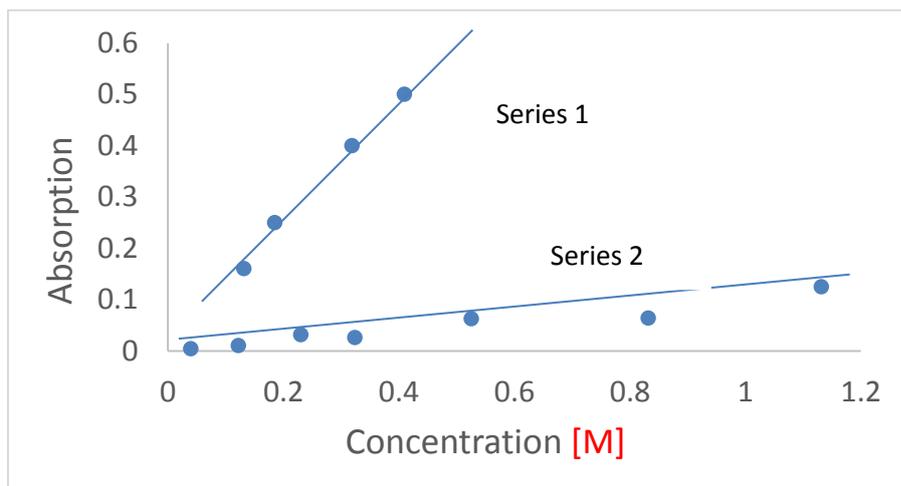


Figure 7 The Beer-Lambert of eh236f1 compound.

The compound shows a linear plot to the Beer-Lambert equation in chloroform solvent, Fig 7 which the concentrations from 0.004 M to 0.125 M.

2.2. The fluorescence

The fluorescence of this compound in chloroform is shown in Fig. 8, the dye shows a fluorescence maximum λ_{em} occurs at 512 nm at different concentrations (i.e. 0.0039, 0.0156, 0.0625) M. The fluorescence shows emission from BODIPY unit, centred at 512 nm, the λ_{em} is shifted to 506 nm at high concentration 0.25 M. The dye showed a structured emission band displaying a slight red shift from 506 (0.25 M) to 512 (0.0039) M, upon decreasing the concentration ($\Delta\lambda_{max}^F = 6$ nm). The concentration decreases, the emission intensity shifts to a longer wavelength.[13]

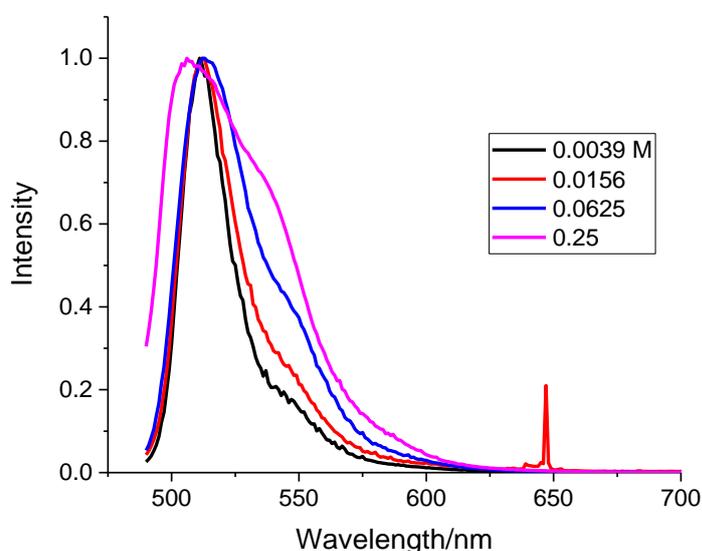


Figure 8 The fluorescence spectrum of the eh236f1 compound in chloroform.

The main obstacle of the BODIPY application, in the OLED is the small Stokes Shift (14 nm), Fig. 9.[14]

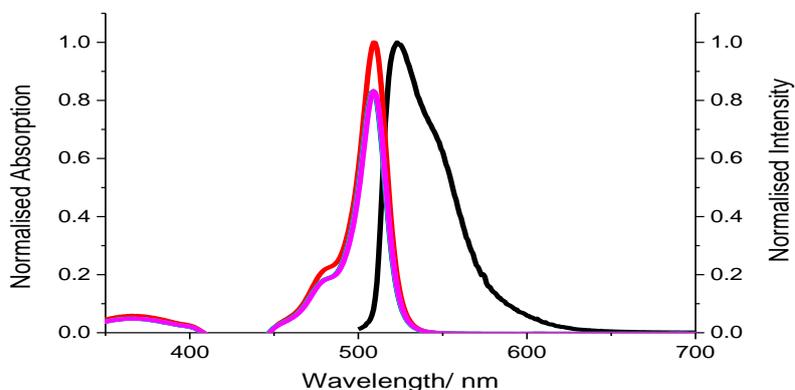


Figure 9 The absorption spectrum (red curve), fluorescence spectrum (black curve), excitation spectrum (pink curve) of eh236f1 compound.

2.3. The photophysical properties of BODIPY dye with blue and green BODIPY dyes

Fig. 10, shows the absorption of BODIPY dye with green BODIPY, maximum absorption at 517 nm, while the maximum absorption is located at 511 nm of eh236f1 Fig. 3, the high absorption at about 517 nm while the poor absorption at about 519 nm.

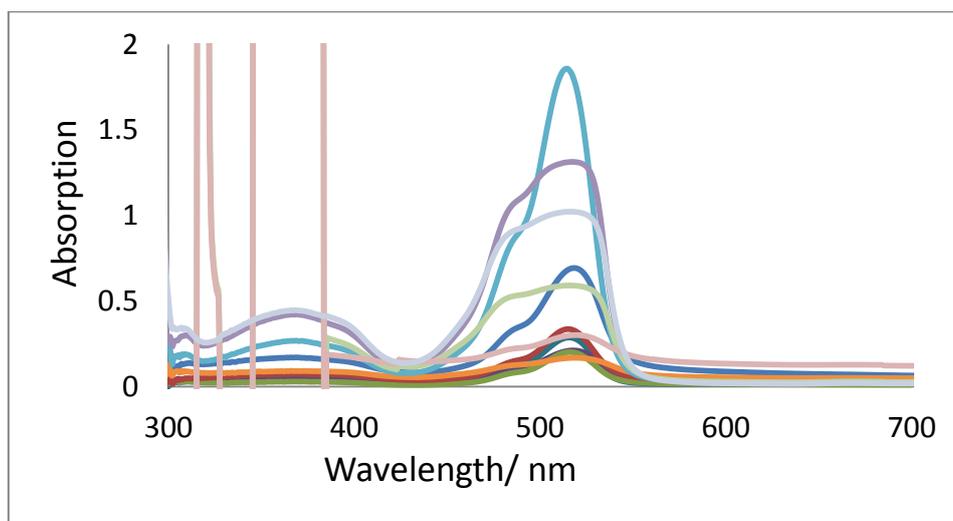


Figure 10 The absorption spectrum of eh236f1 compound with green BODIPY.

Fig. 11, shows the absorption of BODIPY dye with blue BODIPY, maximum absorption at 517 nm, the high absorption at about 517 nm while the poor absorption at about 522 nm, we can obtain the blue absorption which is used in the ratiometric fluorescence bioimaging applications of the BODIPY dye. [15]

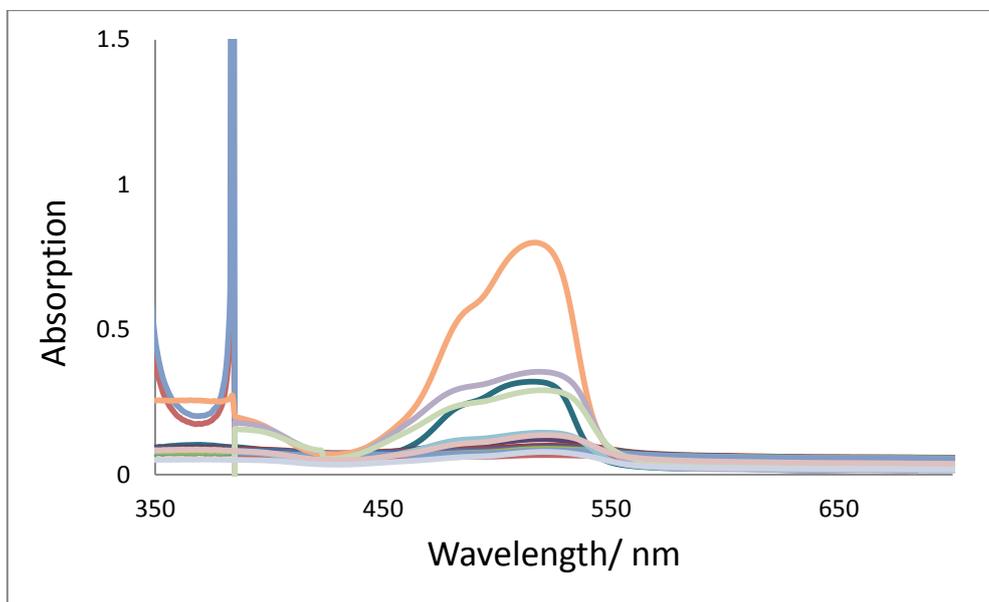


Figure 11 The absorption spectrum of eh236f1 compound with blue BODIPY.

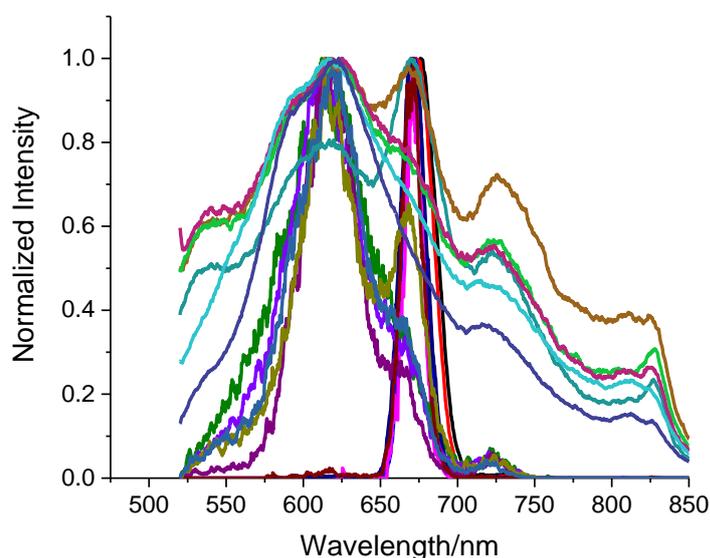


Figure 12 The fluorescence spectrum of eh236f1 compound with blue BODIPY.

Fig. 12, shows the fluorescence of the eh236f1 with the blue BODIPY, the structure of this dye is seen in Figure 14 BODIPY, Fig (12) exhibits a series of transitions centred at about 619, 675, and 724 nm, while the dye eh236f1 exhibits a fluorescence maximum centred at 512 nm, therefore the BODIPY

core position according to the electronic density different allows to obtain the red shifted spectral bands [16], and the π -conjugation leads to the red-shifted emission [17].

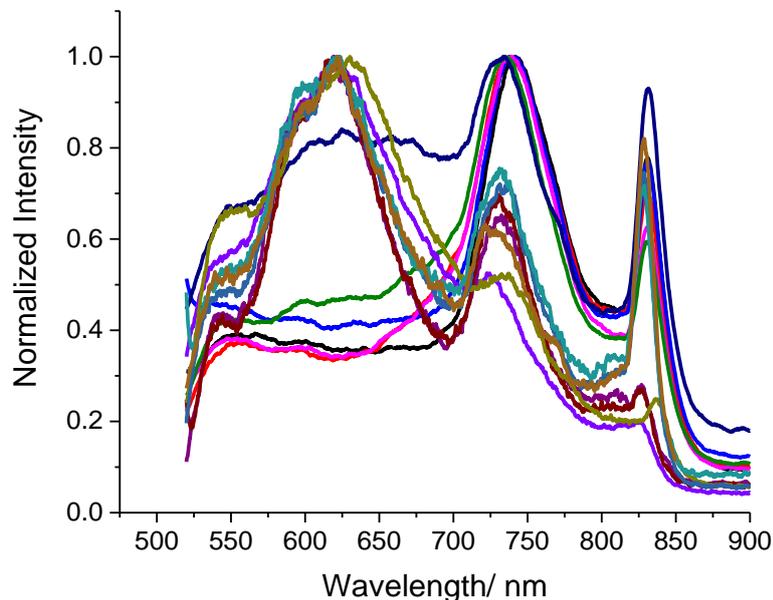


Figure 13 The fluorescence spectrum of eh236f1 compound with green BODIPY.

Fig.13, shows the fluorescence of the eh236f1 with the green BODIPY, the structure of this dye is seen in Fig 15, Fig (13) exhibits a series of transitions centred at about 621, 739, and 830 nm, while the dye eh236f1 exhibits a fluorescence maximum centred at 512 nm, the charge transfer character is obtained from the dimethylamino group, electron donating (green BODIPY) to the BODIPY core which is the more electron deficient [18]. There is a stronger displacement to the NIR for the green BODIPY, the presence of the electron donating such as dimethylamino results the push-pull structure and more spectral different through the process of the intramolecular for example charge transfer [17].

3. Conclusions

This study focused on investigation of the physical properties of BODIPY dye with efficient absorption and fluorescence in the green wavelength region (500-565) nm. The BODIPY dye adsorption over the solid state on polydimethyl siloxane PDMS, was studied. The absorption maximum is located at 500 nm and a BODIPY dye signal in the PDMS indicates the presence of adsorbed dye. The fluorescence of this compound in chloroform was measured. This dye exhibited a fluorescence maximum λ_{em} occurs at 512 nm at different concentrations. The absorption of BODIPY dye with green BODIPY, maximum absorption was located at 517 nm, while the maximum absorption was located at 511 nm of eh236f1 compound. On the other hand, the absorption of BODIPY dye with blue BODIPY, maximum absorption was located at 517 nm, the fluorescence of the eh236f1 with blue BODIPY, shows the structure of BODIPY dye. The dye exhibits a series of transitions centred at about 619, 675, and 724 nm, while the dye eh236f1 exhibits a fluorescence maximum centred at 512 nm. The fluorescence of the eh236f1 with the green BODIPY shows the structure of BODIPY dye. The dye exhibits a series of transitions centred at about 621, 739, and 830 nm, while the dye eh236f1 exhibits a fluorescence maximum centred at 512 nm. The charge transfer character is obtained from the dimethylamino group, electron donating (green BODIPY) to the BODIPY core which is more electron deficient.

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