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Yakın-Kızılötesinde Absorplayan, Karboksilik Asit ile Fonksiyonlandırılmış Tiyofen Kaynaşık BODIPY Bileşiklerinin Sentezi ve Özellikleri

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ÖZET

Bor dipirrometen boyaları, kimyasal indikatörler, biyolojik etiketleme, fotodinamik terapi ve güneş pilleri gibi çeşitli alanlarda en önemli bileşik türlerinden biridir. Bu boyaların önemli türevlerinden biri de tiyofen ile kaynaşmış BODIPY yapılarıdır. Bu yapılar, yakın IR absorpsiyonu, ağır atomsuz ışığa duyarlılık ve kompakt yapı gibi özel özellikler kazandırır. Oldukça önemli özellikler barındırmalarına rağmen, bu boyar madde türevleri düşük sentetik verimlere sahip olabilmektedirler. Birkaç on yıl içinde, kaynaşmış BODIPY yapılarının çeşitli türevleri yayınlandı. Bununla birlikte, daha fazla özellikten yararlanmak ve sentetik verimi artırmak için bu boyaların sayısını artırmak için daha fazla çalışmaya ihtiyaç vardır. Bu çalışmada, CTFBOD1-2 olarak adlandırılan iki adet yakın kızılötesi bölgeden absorplama yapabilen tiyofen ile kaynaşmış Bodipy bileşikleri tasarlanmış, sentezlenmiş ve çeşitli teknikler kullanılarak karakterize edilmiştir. Her iki bileşik de mezo-4-karboksifenil birimleri ile türevlendirilmiştir, çünkü boya duyarlı güneş pili yapıları için potansiyel bileşik olma durumları vardır. Ve elektron verici yapıları olarak, bir donör-alıcı yapı oluşturmak için 4-metoksifenil ve hegziltiyofen birimleri de ayrıca sübstitüe edilmiştir. Fotofiziksel ve döngüsel voltametri karakterizasyonları da gerçekleştirilmiştir. Hegzil-tiyofen bağlı yapıda (CTFBOD2), muhtemelen tiyofen biriminin daha güçlü elektron itme kabiliyetine bağlı olarak hem absorpsiyon hem de emisyonda daha fazla batokromik kayma gözlemlenmiştir. Bu yapı ile 775 nm'ye kadar absorplama gözlenebilmekte ve güneş hasadı için kompakt yapılarla bu pencereye ulaşmak son derece önemlidir. Bileşiklerin, ışığa duyarlılaştırıcı olarak boya duyarlı güneş pili konsepti gibi çeşitli alanlarda yapı taşları olarak kullanılabileceği gözlemlenmiştir.

Synthesis and Properties of Carboxylic Acid Functionalized Near IR Absorbing Thiophene Fused BODIPY Compounds

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ABSTRACT

Boron dipyrromethene dyes are one of the most important types of compounds in various fields such as chemical indicators, biological labelling, photodynamic therapy, and solar cells. One of the important derivatives of these dyes are the thiophene-fused BODIPY structures. These structures impart special features such as near IR absorption, heavy atom free photosensitization and compact structure. Although having important aspects, these derivatives of dyes suffer from low synthetic yields. In a few decades various derivatives of fused BODIPY structures were published. However, still more studies are needed to increase the number of these dyes in order to exploit more features and increase the synthetic yields. In the current work, two near-infrared absorbing thiophene fused Bodipy compounds, named CTFBOD1-2, were designed, synthesized and characterized using various techniques. Both compounds were substituted with *meso*-4-carboxyphenyl units since we have investigated their potential for dye-sensitized solar cell structures. And as electron donor structures, 4-methoxyphenyl and hexylthiophene units were attached to form a donor-acceptor structure. Photophysical and cyclic voltammetry characterizations were also accomplished. In the hexyl-thiophene attached structure (CTFBOD2) we have observed more bathochromic shift in both absorption and emission probably due to the stronger electron pull ability of the thiophene unit. With this structure up to 775 nm absorption is observed, and it is highly important to reach this window with compact structures for solar harvesting. We have observed that the compounds could have been investigated as building blocks in various fields such as dye-sensitized solar cell concept as a photosensitizer.

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INTRODUCTION

The research on BODIPY (boron dipyrromethene) compounds and similar dye structures continue its popularity for a few decades and steadily find more space in literature over the years. Valuable properties of this kind of dye include high molar absorptivity, high fluorescence quantum yield, stability, and moderately easily modifiable structure [1]. A variety of different reactions could be performed on the BODIPY core either post- or pre-modification routes [2]. There have been various efforts to obtain near IR absorbing or fluorescing dyes/fluorophores [3-7]. Xanthene, rhodamine, and fluorescein are some of the important classes of compounds and their derivatives are also made available to work in this region. The dyes working in near IR region have found utilization in organic or bulk heterojunction solar cells [4, 8-10], photodynamic cancer therapy[11-13], or biological labelling [14, 15]. The reason for the utilization of near IR dyes in solar cells is due to a large amount of the solar radiation in this region. Traditional [16] (e.g. silicon-based solar cells) or new generation [17] (e.g. dye-sensitized solar cells) renewable energy sources play important roles to meet the high energy demand in today's world. Also, fluorescence detection methods have been frequently used in various fields such as the authentication of extra virgin olive oils [18].

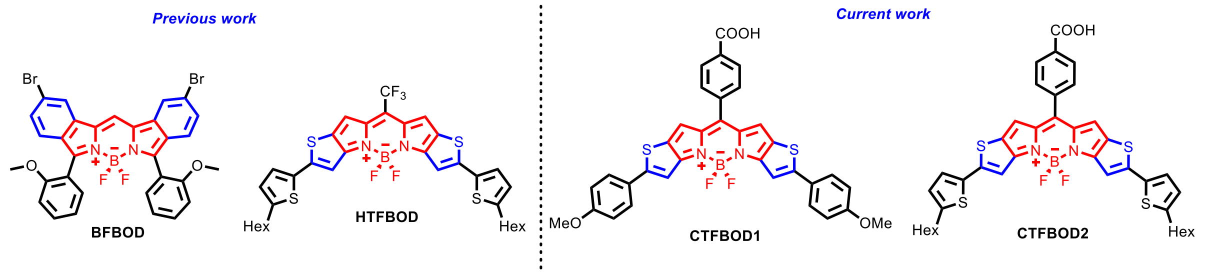

Figure 1

Fused BODIPY structures that were studied by our group previously (left) and in this current work (right). Nomenclature of BODIPY was also shown on BFBOD

BODIPY compounds could be post-modified for their utilization in the near-infrared regions including Knoevenagel condensation to obtain π electron extension from the methyl units, direct substitution with ethynyl units and C=N bond substitution [2]. Pre-modification includes synthesizing benzofused, thiophene-fused or furan-fused pyrroles and then the formation of the BODIPY core using these building blocks has been accomplished [3, 19, 20]. However, there are not many publications regarding the synthesis and applications of these fused structures, although they induce rich properties in the dye core. These properties include a rigid structure, high molar absorptivity and high fluorescence quantum yield. One drawback of these types of structures is their low synthetic yields.

In this work, two new thiophene fused BODIPY structures have been designed and synthesized (Figure 1-right). The structures of our previous efforts on fused BODIPY structures were also shown as a comparison (Figure 1-left) [3, 5]. These compounds have been synthesized with benzocarboxylic acid units arranged to the *meso* position of the BODIPY core for their potential utilization in dye sensitized solar cells concept. Different synthetic pathways have been investigated and the optimum synthetic path was considered to obtain the final compounds. The synthesized structures CTFBOD1 and CTFBOD2 both absorb around 700 nm making them available to be used in applications that necessitate near infrared region absorption or fluorescence. It has also been observed that carboxylic acid unit has an adverse effect on synthetic yields.

MATERIALS AND METHODS

Cyclic Voltammetry Measurements

Cyclic voltammetry was recorded on a Gamry Interface 1010E instrument in a single-component cell under a nitrogen atmosphere. 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile was used as an electrolyte was purged with nitrogen gas. Ag wire as reference electrode, Pt wire as auxiliary electrode and glassy carbon electrode as working electrode were used. Scanning range was between -1700 mV and +1700 mV and the scanning rate of 200 mV/s was adjusted. BODIPY compounds were dissolved in $CHCl_3$ (1 mg/mL) and they were added to the glassy carbon electrode surface and dried with nitrogen gas. As internal standard ferrocene was used and added to the electrolyte solution. For the calculations of optical bandgap, the equation of $E_g = 1243/\lambda$ (λ = start of the maximum absorbance) was used [21]. For the calculation of the HOMO-LUMO following equations were used [21]:

$$E_{LUMO} = -e.[E_{red}^{onset} + 4.4] \; ; \; E_{HOMO} = -e.[E_{ox}^{onset} + 4.4]$$

Synthesis

Compound 1: This reaction is performed according to the previous report [19]. 5-bromo-2-thiophencarboxaldehyde (1.88 g, 9.86 mmol, 1 eq.) was dissolved in methanol (10 mL) and cooled to 0°C. Methylazidoacetate (3.82 g, 29.6 mmol, 3 eq.) was then added to the flask. Sodium methoxide (1.6 g, 29.6 mmol, 3 eq.) suspension was prepared in methanol (30 mL) and added dropwise to the reaction flask over 20 minutes while keeping the temperature low. It was stirred for another 30 minutes, and brought to room temperature, then stirred for 3 h in this way. Then, the saturated NH_4Cl solution was added dropwise to form the precipitate, and the precipitate was filtered, washed with water, and dried. This substance was dissolved in 30 mL of toluene and refluxed for 1.5 hours. The substance was obtained pure by the removal of the solvent (22% yield). ^1H NMR 400 MHz, $CDCl_3$, ppm: (d) 9.25 (br s, 1H), 7.1-6.9 (m, 2H), 3.90 (s, 3H).

Compound 2: This reaction is performed according to the previous report [19]. 4-(Methoxy)phenylboronic acid (0.180 g, 1.18 mmol, 1.1 eq.), compound **1** (0.280 g, 1.08 mmol, 1 eq.) were dissolved in degassed toluene (10 mL) and ethanol (2.5 mL) under inert atmosphere to an oven-dried two-neck flask fitted with a condenser. Tetrakis(triphenylphosphine)-palladium (0.016 g, 0.022 mmol, 0.02 eq) and Na_2CO_3 solution (0.045 g in 2.5 mL H_2O) were added. The mixture was refluxed for 6 hours at 80°C, and then cooled, extracted with diethyl ether, dried over magnesium sulfate and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, DCM) to afford **2** (80 mg, 26 %) as a yellow solid. ^1H NMR 400 MHz, $CDCl_3$, ppm: (d) 9.14 (br s, 1H), 7.54 (d, J= 8.6 Hz, 2H), 7.12 (s, 1H), 7.06 (s, 1H), 6.93 (d, J= 8.6 Hz, 2H), 4.36 (q, J= 7.2 Hz, 2H), 3.85 (s, 3H), 1.40 (t, J= 7.1 Hz, 3H).

Compound 3: This reaction is performed by modification of the previous report [22]. **2** (0.380 g, 1.32 mmol, 1 eq.) is dissolved in 22.5 mL of EtOH. Then, NaOH (1.11 g, 21 eq., 27.8 mmol) was dissolved in 11.3 mL of H_2O and added to the flask. The reaction was refluxed and the proceeding of the reaction was monitored using TLC for 1-2 hours. The flask was then cooled to room temperature and the pH was adjusted to 3 through addition of 6 M HCl. Then, the precipitates were filtered and substance **3** was obtained pure (0.336 g, 1.32 mmol, quantitative). ^1H NMR 400 MHz, DMSO-d_6, ppm: (d) 12.55 (br s, 1H), 11.97 (br s, 1H), 7.60 (m, 2H), 7.25 (s, 1H), 6.99 (m, 3H), 3.76 (s, 3H).

Compound 4: This reaction is performed by modification of the previous report [22]. Compound **3** (0.336 g, 1.23 mmol) was dissolved in TFA (7 mL, degassed with N_2) under N_2 gas. The reaction was heated to 40°C. After 10 minutes, the reaction was checked with TLC and neutralized with saturated sodium bicarbonate. Then, chloroform was added (10 mL) and the organic phase was washed with water

(3x10 mL). The organic phase was dried, and the solvent was removed. Column chromatography is performed with DCM, resulting in 51.4 mg of pure substance (18% yield). ^{1}H NMR 400 MHz, $CDCl_3$, ppm: (d) 8.25 (br s, 1H), 7.55 (d, J= 8.7 Hz, 2H), 7.1 (s, 1H), 6.97 (m, 1H), 6.92 (d, J=8.7 Hz, 2H), 6.46 (m, 1H), 3.83 (s, 3H). HRMS)$^+$; (M)$^+$ $C_{13}H_{12}NOS^+$ calculated for 230.0634, found 230.0658.

***Compound CTFBOD1*:** Dichloromethane (25 mL) was degassed with N_2 gas for 15 minutes. Then, 4 drops of trifluoroacetic acid (TFA) are added. Compound **4** (0.050 g, 0.22 mmol) and 4-formylbenzoic acid (0.017 g, 0.11 mmol) were added to the flask and left to stir overnight at room temperature. DDQ (0.025 g, 0.11 mmol) was then added to the solution. After stirring for 2 hours at room temperature, 0.3 mL of triethylamine and 0.3 mL of boron trifluoride diethyl ether were added, and the formation of green colour was observed. The reaction was added DCM (20 mL) and washed with water (3x20 mL). The organic layer is collected, dried and evaporated to dryness under reduced pressure. The purification of compound **CTFBOD1** was accomplished using silica gel flash column chromatography (5% MeOH/DCM) and the product was obtained pure in 31% yield (22 mg, dark green color). ^{1}H NMR 400 MHz, $CDCl_3$, ppm: (d) 8.25 (d, J= 6.6 Hz, 2H), 7.8-7.6 (m, 6H), 7.40 (s, 2H), 6.97 (d, J= 8.4 Hz, 4H), 6.76 (s, 2H), 3.87 (s, 6H). HRMS$^{;}$ (M)$^-$ 635. 1088 calculated for $C_{34}H_{22}BF_2N_2O_4S_2^-$, found 635.10540.

Compound 5: This reaction is performed according to the previous report [8]. 2,2'-bitiophene (2.0 g, 12.03 mmol, 1 eq.) was dissolved in 10 mL of benzene and cooled to 0°C. Hexanoyl chloride (1.7 mL, 12.51 mmol, 1.04 eq.) and $SnCl_4$ (1.4 mL; 12.87 mmol; 1.07 eq.) were added to the reaction mixture and stirred at 0°C under N_2 atmosphere for 15 min. Then the reaction was added ice and extracted with DCM. The organic phase was then extracted with $NaHCO_3$. Afterwards, the organic layer was collected, dried with Na_2SO_4, and the solvent was removed under reduced pressure. In the second part of the process 2.74 g (6 eq.; 72.18 mmol) of $LiAlH_4$ and 2.4 g (1.5 eq.; 18.05 mmol) of $AlCl_3$ in Et_2O (30 mL) were dissolved. The dried substance from the first part was dissolved in 12 mL of toluene and two solutions were combined. Then the flask was stirred at RT for 1 hour. Then, 10 mL of EtOAc and 20 mL of 6 M HCl were added to the flask. The organic phase was extracted with Et_2O, collected, dried with Na_2SO_4 and removed under reduced pressure. Compound **5** was used in the next step without any further purification (75% yield) ^{1}H NMR 400 MHz, $CDCl_3$, ppm: d 7.15 (dd, J = 1.1 Hz; 5.1 Hz, 1H), 7.08 (dd, J=1.1 Hz; 3.7 Hz, 1H), 6.95-7.00 (m, 2H), 6.65 (m, 1H), 2.78 (m, 2H), 1.66 (m, 2H), 1.2-1.5 (m, 6H), 0.88 (m, 3H).

Compound 6: This reaction is performed according to the previous report [8]. 1.02 mL (1.2 eq.; 10.89 mmol) of $POCl_3$ was added to 7 mL of DMF at 0 °C. The mixture was stirred for 1 h until it reached to RT. 2.27 g (1 eq.; 9.08 mmol) of 5-Hexyl-2,2'-bitiophene **5** was added to the reaction mixture and stirred overnight at 60°C. Then, 150 mL of ice-water was added to the reaction mixture and the pH value of the reaction was adjusted to around 7 using NaOH solution. Et_2O (30 mL) was added, and the organic layer was washed 3 times with deionized water. Then it was dried with Na_2SO_4, and the solvent was removed under reduced pressure. The crude mixture was then purified using silica gel column chromatography (Petroleum ether: EtOAc, 6/1), and the yield was calculated as 77%. ^{1}H NMR 400 MHz, $CDCl_3$, ppm: δ 9.83 (m, 1H), 7.65 (m, 1H), 7.17 (m, 2H), 6.75 (m, 1H), 2.81 (m, 2H), 1.68 (m, 2H), 1.1-1.5 (m, 6H), 0.88 (t, J= 5.0 Hz, 3H).

Compound 7: 5'-Hexyl-[2,2'-bitiophene]-5-carbaldehyde **6** (1.0 g, 3.58 mmol, 1 eq.) was dissolved in anhydrous ethanol (30 mL, molecular sieve dried) at RT. Ethylazidoacetate (1.85 g, 14.3 mmol, 4 eq.) was added and stirred at 0°C under N_2 atmosphere for 20 min. 0.774 g (4 eq.; 14.3 mmol) of NaOMe (dissolved in 6 mL dry ethanol) was added dropwise at 0°C for 20 min. The reaction mixture was stirred at this temperature for 30 minutes and stirring was continued at RT for 2 hours. The progress of the reaction was monitored using TLC, and 10 mL of saturated NH_4Cl solution was added to the reaction medium as soon as the starting material did not appear in TLC. The solid substance formed was then filtered and dissolved in 30 mL of toluene and refluxed for 1.5 hours. After evaporating the solvent, the mixture was submitted to silica gel column chromatography (Pet. Ether: EtOAC, 6/1). Compound **7** was then obtained in 56% yield. ^{1}H NMR 400 MHz, $CDCl_3$, ppm: (δ) 9.02 (br s, 1H), 7.07 (m, 1H), 7.03 (m, 1H), 6.96 (m, 1H), 6.70 (m, 1H), 3.90 (s, 3H), 2.81 (m, 2H), 1.67 (m, 2H), 1.1-1.5 (m, 6H), 0.90 (m, 3H).

Compound 8: Compound **7** (0.333 g, 0.958 mmol, 1 eq.) was dissolved in ethanol (16 mL). In another flask NaOH (0.804 g, 20.1 mmol, 21 eq.) was dissolved in 8 mL of water and added to the reaction dropwise, and it was refluxed for 1 hour. After cooling the reaction a few mL of 6 M HCl was added. Resulting solids were filtered and compound **8** was obtained quantitatively. ^{1}H NMR 400 MHz, DMSO-d_6, ppm: (d) 11.6 (br s, 1H), 7.07 (m, 1H), 6.97 (s, 1H), 6.75 (m, 2H), 2.75 (m, 2H), 1.60 (m, 2H), 1.4-1.1 (m, 6H), 0.85 (m, 3H).

Compound 9: Compound **8** (0.250 g, 0.72 mmol) was dissolved in TFA (7 mL) under N_2 atmosphere. Then the reaction was heated to 40 °C and stirred for 10 minutes. The reaction was completed by the addition of saturated $NaHCO_3$ solution (20 mL). Then, ethyl acetate (30 mL) was added, and the organic phase was extracted with water (3x20 mL), filtered, dried, and evaporated under reduced pressure to obtain compound **9** (75% yield). ^{1}H NMR 400 MHz, $CDCl_3$, ppm: (d) 8.2 (br s, 1H), 6.9-7.1 (m, 3H), 6.65 (m, 1H), 6.42 (m, 1H), 2.80 (m, 2H), 1.68 (m, 2H), 1.2-1.5 (m, 6H), 0.90 (m, 3H). HRMS) $^+$; (M)$^+$ $C_{16}H_2ONS_2^+$ calculated for 290.1032, found 290.1060.

Compound CTFBOD2: 25 ml of dichloromethane was degassed with nitrogen gas for 15 minutes and 0.05 g of substance **9** (0.17 mmol) and 0.0125 g of 4-formylbenzoic acid (0.08 mmol) were dissolved in this solvent. Then, 4 drops of trifluoroacetic acid (TFA) were added and left to stir overnight. Subsequently, DDQ (0.019 g, 0.08 mmol, 1 eq.) was added to the solution. After stirring at room temperature for 1 h, 0.25 ml of triethylamine and 0.25 ml of boron trifluoride diethyl ether were added. After 1 h, deionized water (25 mL) was added. The organic phase was washed 3 times with deionized water (3x25 mL) and then dried with Na_2SO_4 and the solvent was removed under reduced pressure. Silica gel column chromatography was performed (MeOH in DCM, 5%) and product **CTFBOD2** was obtained in 44% yield with a dark green colour (0.028 g). ^{1}H NMR 400 MHz, $CDCl_3$, ppm: (d) 8.25 (m, 2H), 7.68 (m, 2H), 7.25 (m, 4H), 6.77 (m, 2H), 6.63 (m, 2H), 2.85 (m, 4H), 1.72 (m, 4H), 1.1-1.5 (m, 12H), 0.92 (m, 3H). HRMS)$^-$; (M)$^-$ $C_{40}H_{38}BF_2N_2O_2S_4$- calculated for 755.1883, found 755.19975.

RESULTS AND DISCUSSION

Synthesis

Compound CTFBOD1 was synthesized in five steps (Figure 2). First, 5-bromo-2-carboxaldehyde was submitted to Hemetsberger-Knittel indolization reaction using ethyl azidoacetate, and sodium methoxide in methanol. Afterwards, a second heating step was applied in toluene and compound 1 was obtained in 22% yield. In the second step, 1 and 4-methoxyphenylboronic acid were reacted according to the Suzuki coupling reaction protocol and 2 was obtained in 13% yield. Later, the methyl ester unit of 2 was hydrolysed in the basic medium in a quantitative yield. Then, thiophene fused pyrrole derivative was reacted with TFA and decarboxylation was achieved to obtain the compound 4. In the final step, compound CTFBOD1 was obtained by utilizing the BODIPY formation procedure, using pyrrole derivative 4 and 4-carboxybenzaldehyde in 31% yield.

The second compound CTFBOD2 was synthesized in six steps (Figure 3). First, 2,2'-bithiophene was alkylated in two steps using tin(IV) chloride and hexanoyl chloride in benzene. Then, the carbonyl group was reduced using $LiAlH_4$ to achieve the compound 5. Then, formylation reaction was applied according to the Vilsmeier-Haack reaction procedure to obtain the compound 6. Later, 6 was submitted to the Hemetsberger-Knittel indolization reaction to obtain the compound 7 and with this critical reaction thiophene fused pyrrole was obtained. By employing similar steps as compound CTFBOD2, compounds 8, 9 and the final structure CTFBOD2 were obtained. The final three reactions were accomplished with a total yield of 33%.

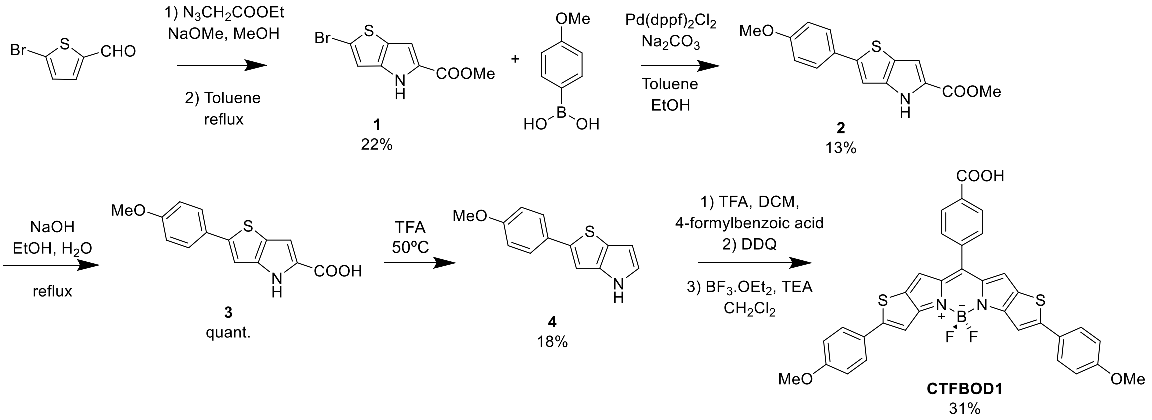

Figure 2
Synthesis scheme for the CTFBOD1 thiophene fused BODIPY structure

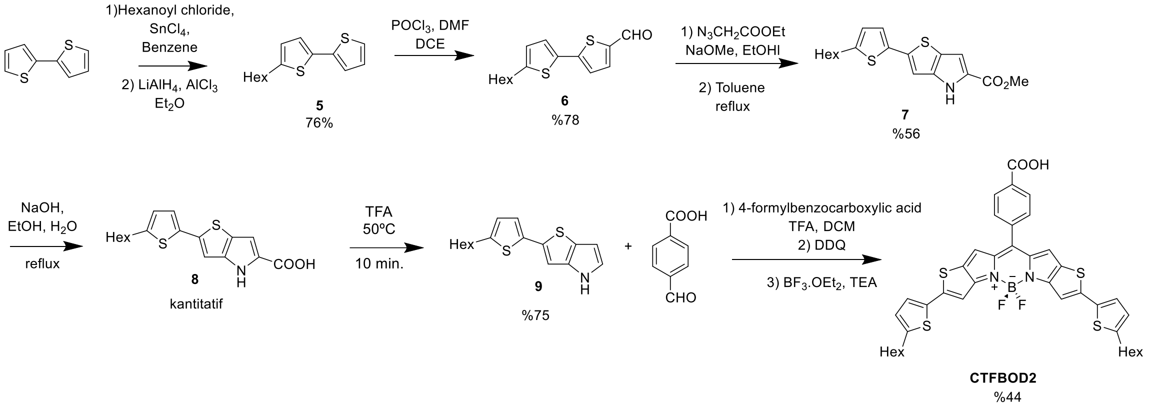

Figure 3
Synthesis scheme for the CTFBOD2 thiophene fused BODIPY structure

Photophysical Characterization and Cyclic Voltammetry Measurements

After synthesis of the compounds, absorption, and fluorescence emission of the compounds in chloroform were obtained (Figure 4). 4-methoxyphenyl substituted structure CTFBOD1 has absorbance and fluorescence maxima at 681 nm and 714 nm, respectively (Table 1). The regular tetramethyl-Bodipy core has absorbance maximum of around 500 nm and a huge shift to the red end of the electromagnetic spectrum of around 200 nm was observed with this thiophene fused structure. For the second structure, CTFBOD2, even more redshift was observed in both spectra. The absorbance maximum was observed at 707 nm and the fluorescence maximum was observed at 735 nm. More, the range of absorption is up to 800 nm, and for the fluorescence it is 850 nm. The difference between absorbance maxima of CTFBOD1 and CTFBOD2 is around 30 nm and this difference can be attributed to the stronger electron donating effect of the additional thiophene unit upon comparison with the methoxyphenyl unit of compound CTFBOD1. Both compounds have 4-carboxyphenyl moiety in the *meso* position of the BODIPY core. Therefore, an effective electron push-pull has been expected from the edges to this carboxy unit. Compound CTFBOD2 has a stronger donor unit and, a more effective electron push-pull and a smaller HOMO-LUMO bandgap are expected. In our previous work, we have studied a similar dye, hexylbithiophene fused Bodipy structure, HTFBod (Figure 1) [3]. This structure has a stronger electron withdrawing trifluoromethyl unit in the *meso* position of the BODIPY core, then a smaller bandgap and more bathochromic shift were observed. The compound has absorbance and emission maxima at 764 and 788 nm, respectively and around 60 nm difference compared to CTFBOD2 was observed.

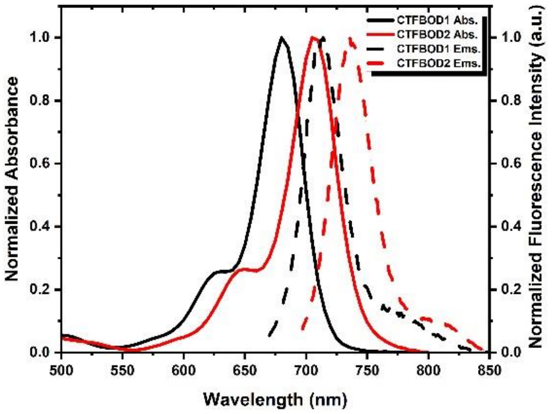

Figure 4
Absorptivity and Fluorescence Spectra of the compounds CTFBOD1 and CTFBOD2

Another fused structure that is similar to the synthesized compounds is the compound BFBOD, which was studied in our previous work (Figure 1) [5]. This compound has 2,3-benzo fused BODIPY structure, rather than the 1,2-thiophene fused structures of the current study. BFBOD has absorbance maxima at 622 nm which corresponds to around 60 nm hypsochromic shift compared to CTFBOD1. Therefore, it would be concluded that for more near IR absorption applications the design of 2,3-thiophene-fused structures is more convenient than 1,2-benzofused structures.

Table 1
Photophysical properties of compounds CTFBOD1 and CTFBOD2

Compounds	$\lambda_{abs,\ max}$ (nm)[1]	$\lambda_{ems,\ max}$ (nm)[1]	ε ($M^{-1}.cm^{-1}$)[1]
CTFBOD1	681	714	96000
CTFBOD2	707	735	92000

[1] In $CHCl_3$

Electrochemical Characterizations

Synthesized near-IR dyes CTFBOD1-2 were examined by cyclic voltammetry (CV) to obtain the oxidation and reduction potentials, the corresponding frontier orbital energy levels (HOMO and LUMO energy levels) and the bandgap (Figure 5a). In these calculations starting points of the first reduction and oxidation peaks were considered. For calculations of the electrochemical bandgap, potential difference between LUMO and HOMO were calculated.

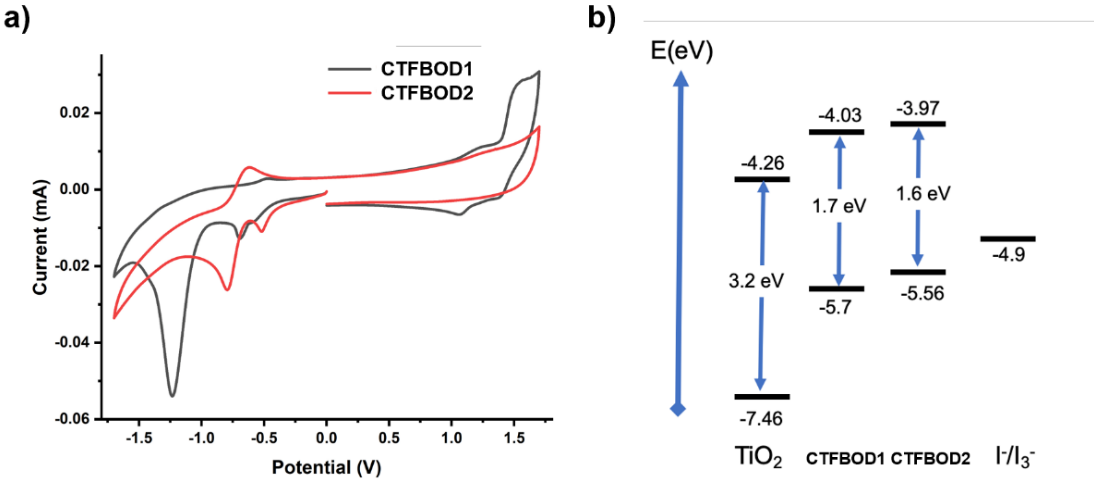

Figure 5
(a) Cyclic voltammograms of the compounds CTFBOD1 and CTFBOD2. (b) Energy levels of synthesized dyes, TiO_2 and iodide-triiodide electrolyte

Table 2
Electrochemical data of the CTFBOD1 and CTFBOD2 compounds based on the CV and spectroscopic measurements

Dye	E_{ox}^{onset} (V)[a]	HOMO (eV)[a]	HOMO (eV)[b]	E_{red}^{onset} (V)[a]	LUMO (eV)[a]	Eg (eV)[a]	Eg (eV)[b]
CTFBOD1	0.98	–5.38	**–5.7**	**–0.38**	**–4.03**	1.36	**1.67**
CTFBOD2	0.98	–5.38	**–5.56**	**–0.43**	**–3.97**	1.41	**1.59**

The results of the calculations are shown in Table 2. When determining the HOMO and LUMO energy levels of compounds CTFBOD1 and CTFBOD2, CV and optical measurements were used, and HOMO energy levels were calculated as –5.7 and –5.56 eV for CTFBOD1 and CTFBOD2, respectively. Corresponding LUMO levels are calculated as –4.03 and –3.97 eV, respectively. While calculating these reduction potentials, optical bandgaps were considered and written in bold in Table 2 since the oxidation peaks in CV were not clear. These calculated data, TiO_2 and iodide/triiodide energy levels were depicted in Figure 5b. According to these data, electron transfer from the LUMO energy levels of CTFBOD1 and CTFBOD2 to the TiO_2 conduction band of –4.26 eV seems probable. In the same way, electron transfer from the electrolyte solution to the HOMO energy levels of the dyes also seems possible.

CONCLUSIONS

In this study, synthesis, and characterization of two novel derivatives of [*b*]-thiophene fused BODIPY structures were investigated. Fused BODIPY structures are one of the fascinating derivatives of this type of dye and have largely been studied in recent decades [19, 22]. These types of structures could be used in applications such as organic photovoltaics, photodynamic therapy, bioimaging and chemosensors. In this current work, for the synthesis of thiophene-fused BODIPY structures, various synthetic routes have been considered, and optimum synthesis routes were accomplished. Hemetsberger-Knittel indolization reaction by using ethylazidoacetate or methylazidoacetate is the critical step where ultimate care is necessary to form the corresponding fused-pyrrole. At the end of the various efforts, we were able to synthesize the compounds CTFBOD1 and CTFBOD2 in moderate yields. During photophysical characterizations near IR absorption and fluorescence of the molecules were achieved. The *meso* position of the BODIPY core was substituted with carboxy-phenyl functionality, rendering them suitable for dye-sensitized solar cell applications. The HOMO-LUMO energy levels were also determined using cyclic voltammetry studies, and the suitability for electron injection/collection upon use in this type of solar cell was also confirmed. More, the carboxy groups in the molecules could also be investigated in biological studies since they facilitate solubility in aqueous medium. Near IR absorption up to 800 nm is highly desired for these types of applications. Therefore, the derivatives in this study are of great importance in various fields and could be adapted to the growing area of high technological products. Similar studies with these types of novel structures and their investigation in various fields are currently under study in our research group.

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Ethical Statement

This study is an original research article designed and developed by the author.

Author Contributions

Research Design (CRediT 1) Y.Ç. (%100)
Data Collection (CRediT 2) Y.Ç. (%100)
Research - Data Analysis - Validation (CRediT 3-4-6-11) Y.Ç. (%100)
Writing the Article (CRediT 12-13) Y.Ç. (%100)
Revision and Improvement of the Text (CRediT 14) Y.Ç. (%100)

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