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# Strategies towards Enhancing the Efficiency of BODIPY Dyes in Dye Sensitized Solar Cells

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#### **Graphical Abstract**



#### HIGHLIGHTS

- New BODIPY dyes with catechol anchoring and electron donating moieties for DSSCs
- Correlation between structural modification and excited state dynamics
- Correlation between excited state dynamics and power conversion efficiency
- Enhancing light harvesting capability by laser ablation of anode electrode

#### Abstract

The goal of this study is to reveal the effect of electron donating and anchoring group of the dye on the electron injection dynamics and photovoltaic performance of BODIPY dye sensitized solar cells. The effect of electron donating properties was studied by choosing methoxyphenyl and triphenylamine (TPA) as electron donor moieties. Therefore, four new BODIPY derivatives were designed and sensitized to achieve these goals. In addition, attachment of the dye to TiO<sub>2</sub> was studied by altering the surface morphology of TiO<sub>2</sub> with fs laser ablation.

The steady state absorption and emission spectra, femtosecond transient absorption spectra, incident photon-to-current conversion efficiency (IPCE) and I-V measurements of the studied dyes were investigated, systematically. It was found that methoxyphenyl moiety gives better performance than TPA moiety. BODIPY dye with methoxyphenyl moiety and one anchoring group demonstrated the best photovoltaic performance due to greater excited state lifetime in spite of the lower light harvesting ability, as compared to other studied dyes. Increasing the number of anchoring groups did not increase the photovoltaic performance of BODIPY dye with methoxyphenyl moiety, and electron injection rate to TiO<sub>2</sub> were enhanced by femtosecond laser ablation treatment of TiO<sub>2</sub> surface. Experimental results proved that power conversion efficiency was increased 47% when photoanode was laser ablation treated.

**Key words:** Borondipyrromethene, Catechol-BODIPY, Ultrafast charge injection, DSSC, Laser ablation

#### 1. Introduction

Dye sensitized solar cells (DSSCs) have drawn a great interest because of their increasing efficiency and low-cost fabrication, since it was invented by Grätzel and O'Regan, in 1991[1]. This technology enables an alternative option to conventional semiconductor based photovoltaic structures [2]. DSSCs are generally composed of molecular dyes to harvest sunlight, semiconductor oxide materials such as TiO<sub>2</sub> [3], ZnO [4], SnO<sub>2</sub> [5], a redox couple to regenerate oxidized dye [6], and a metal coated counter electrode such as Pt [7]. Light harvesting capability, localization of HUMO and LUMO energy levels of dye molecules and electron transfer dynamics between dye and TiO<sub>2</sub> layer play a key role to determine photovoltaic conversion efficiency of the cell [8-14]. Up to date, many organic dyes, such as porphyrin [15-18], phtalocyanine [19], and ruthenium complexes with long lived excited state lifetimes [20] including widely used carboxylic acid as an anchoring group have been investigated for their photophysical properties and employed in DSSC applications. New organic dyes optimized specifically for DSSC applications and their photovoltaic performance characterizations are needed to increase photovoltaic performance of DSSCs.

Boron dipyrromethene (BODIPY) dyes derived from 4,4-difluoro-4-bora-3a,4a-diaza-sindacene, have strong absorption and fluorescence properties in the visible and near infrared spectral regions, great molar absorption coefficients and photostability [21-23]. Diverse modification on the core of BODIPY structure at all positions and with any desired functionality, allows tuning their photophysical properties as well as electron transfer mechanisms. In the past nine years, a variety of BODIPY derivatives have been designed and sensitized for various applications. Unfortunately, their use in solar cell applications has been limited [24-26]. There are only a few works studying structural modification of BODIPY dyes for DSSC applications [27-30]. Our aim is to relate photovoltaic performance with the excited state lifetimes and electron injection dynamics. These relationships are crucial to develop strategies towards enhancing the efficiency of BODIPY dyes. Therefore, more systematic studies are needed in this field. However, there are only a few works investigating the relationship between structural modification and electron injection dynamics of BODIPY dyes as well as their effect on the performance of DSSCs [24, 31] .BODIPY fluorophores in the literature generally use cyanoacedic acid and carboxylic acid that act as an anchoring moiety localized at C2, C6 and C8 positions of BODIPY core [24, 28, 29]. Catechol moiety can also be used as an anchoring group for BODIPY dyes in DSSC application.

In this work, we plan to add electron donation functionality to the BODIPY dye with catechol anchoring group and investigate the electron injection dynamics as well as photovoltaic performance. Therefore, novel BODIPY derivatives with one or two catechol anchoring groups and having different electron donating properties were designed and sensitized in order to increase excited state lifetime in solution, systematically. Triphenylamine and methoxyphenyl moieties were chosen as electron donor moieties that were directly linked at C8 position. The catechol anchoring moiety was attach to C3 position only as well as C3 and C5 positions of the BODIPY core to see the effect of the symmetry. These positions were chosen because, C3 and C5 positions are susceptible to intramolecular electron transfer; hence influence the electron transfer mechanism and DSSC performance. Electron injection dynamics were investigated by ultrafast pump-probe spectroscopy technique to reveal photo physical mechanism behind the performance differences in DSSC. Power conversion efficiencies of DSSCs with the sensitized dyes were investigated by incident photon-to-current conversion efficiency (IPCE) and I-V measurements.

As well as molecular engineering, structural engineering of the DSSC cells are needed to improve the photovoltaic performance as well. Enhancing light harvesting capability of photoanode material has been a research topic for DSSC applications. Until now, several light trapping mechanism such as photonic crystals [32], plasmonic effects[33] and various micro/nanostructuring fabrication processes [34] were improved. Patterning on the semiconductor oxide surface can enable dye to harvest more light [34, 35]. In an attempt to investigate the effect of anchoring capability on the photovoltaic performance TiO<sub>2</sub> surface morphology was modified by femtosecond laser ablation technique and dye with highest photovoltaic performance was coated on to this modified TiO<sub>2</sub> surface to form anode electrode. The effect of micro ablation patterning of TiO<sub>2</sub> surface on the excited state lifetime of the dye molecule and charge transfer dynamics between dye and TiO<sub>2</sub> layer were investigated with ultrafast pump probe experimental technique.

#### 2. Experimental section

#### 2.1 General

Reagents were obtained from Merck and used as received without further purification. 4-(diphenylamino) benzaldehyde was prepared according to the procedure in the literature [36]. Reactions were monitored by thin layer chromatography using Silica gel plates (Merck, Kieselgel 60, 0.25 mm thickness) with  $F_{254}$  indicator. Column chromatography was carried out on silica (230-400 mesh). Melting points were determined on a Barnstead Electrothermal IA 9100 platform. Mass spectral analyses were performed on an Agilent 6224 TOF LC/MS spectrometer. <sup>1</sup>H-NMR spectra were recorded on a VARIAN Mercury 400 MHz spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or DMSO-d<sub>6</sub>, chemical shifts ( $\delta$ ) were given in ppm relative to solvent peaks (chloroform <sup>1</sup>H:  $\delta$  7.26; <sup>13</sup>C:  $\delta$  77.3 and DMSO <sup>1</sup>H:  $\delta$  2.50; <sup>13</sup>C:  $\delta$  39.51) with TMS as internal reference.

#### 2.2 Synthesis

# 2.2.1 4,4-Difluoro-8-(4-methoxyphenyl)-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (8met)

4-methoxybenzaldehyde (0.98 mL, 8.2 mmol) and 2,4-dimethylpyrrole (1.86 mL, 18.2 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (200 mL). One drop of trifluoroacetic acid (TFA) was added to the reaction mixture, and the resulting mixture was stirred in the dark for 12 h under argon atmosphere at room temperature. After the complete consumption of aldehyde, *p*-Chloranil (tetrachloro-1,4-benzoquinone) (3.0 g, 12.4 mmol) was added to the reaction mixture. When the mixture was stirred for further 12 h, DIPEA (N,N-Diisopropylethylamine) (10.0 mL, 57.4 mmol) and then BF<sub>3</sub>·OEt<sub>2</sub> (11.4 mL, 90.2 mmol) were added to the mixture. The stirring was continued overnight. The resulting solution was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by column chromatography (elution: chloroform-hexane, 70:30 v/v) to obtain orange-red crystal solid **8met**. (0.58 g, yield 20%). <sup>1</sup>H-NMR (400 MHz, CDCl3):  $\delta$  1.43 (s, 6H), 2.55 (s, 6H), 3.87 (s, 3H), 5.97 (s, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H). HRMS (TOF-ESI) (m/z) Calculated as 354.17151, found: 335.17452 [M-F]<sup>+</sup>.

# 2.2.2 4,4-Difluoro-8-[4-(diphenylamino)phenyl)]-1,3,5,7-tetramethyl-4-bora-3a,4a-diaza-s-indacene (8TPA)

4-(diphenylamino)benzaldehyde (1.45 g, 5.5 mmol) and 2,4-dimethylpyrrole (1.20 mL, 11.7 mmol) were dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (250 mL). One drop of trifluoroacetic acid (TFA) was

added to the reaction mixture as catalyst, and the resulting mixture was stirred in the dark for 12 h under argon atmosphere at room temperature. After the complete consumption of aldehyde, *p*-Chloranil (tetrachloro-1,4-benzoquinone) (1.96 g, 7.9 mmol) was added to the reaction mixture. When the mixture was stirred for further 12 h, DIPEA (N,N-Diisopropylethylamine) (6.50 mL, 37.0 mmol) and then BF<sub>3</sub>·OEt<sub>2</sub> (7.47 mL, 60.5 mmol) were added to the mixture. The stirring was continued overnight. The resulting solution was washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (elution: chloroform-hexane, 80:20 v/v) to obtain orange-red crystal solid **8TPA**. (0.66 g, yield 24%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  1.61 (s, 6H), 2.58 (s, 6H), 6.02 (s, 2H), 7.03-7.00 (m, 6H), 7.13-7.09 (m, 4H), 7.27-7.23 (m, 4H). HRMS (TOF-ESI) (m/z) Calculated as 491.23443, found: 492.24221 [M+H]<sup>+</sup>.

# 2.2.3 4,4-Difluoro-8-(4-methoxyphenyl)-1,5,7-trimethyl-3-[(1E)-3,4-dihydroxyphenyl]-4-bora-3a,4a-diaza-s-indacene (1) and 4,4-Difluoro-8-(4-methoxyphenyl)-1,7-dimethyl-3,5-bis-[(1E)-3,4-dihydroxyphenyl]-4-bora-3a,4a-diaza-s-indacene (3)

Compound **8met** (484 mg, 1.37 mmol) and 3,4-dihydroxybenzaldehyde (568 mg, 4.11 mmol) were refluxed in a mixture of toluene (50 ml), glacial acetic acid (2.2 mL) and piperidine (2.7 mL), the mixture was stirred at 120 °C for 6 h. Any water formed during the reaction, was removed azeotropically by heating overnight in a Dean-Stark apparatus. After the reaction was quenched with water at room temperature, the mixture was diluted with EtOAc and washed with water. The organic layer was collected from separating funnel and solvent was evaporated under reduced vacuum. The crude solid was dried in a vacuum oven, then purified by silica gel column chromatography by using mobile phase (elution: first chloroform, then chloroform-methanol, 70:30 v/v) to obtain monostyryl BODIPY dye 1 (105 mg, yield 16%) as red-purple powder (the purple colored fraction) and distyryl BODIPY dye 3 (202 mg, yield 25%) as green powder (green colored fraction). The monostyryl BODIPY dye 1, <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>): δ 1.38 (s, 3H), 1.43 (s, 3H), 2.45 (s, 3H), 3.81 (s, 3H), 6.14 (s, 1H), 6.63 (s, 1H), 6.77 (d, j = 8.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 8.8 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 6.89-6.87 (m, 2H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 1H), 7.09 (d, j = 10.0 Hz, 2H), 7.23 (d, j = 10.0 Hz, 7.23 (d, j = 10.0 Hz, 7.23 (d, j = 10.0 Hz, 16.4 Hz, 1H), 7.27 (d, j = 8.8 Hz, 2H), 7.38 (d, j = 16.4 Hz, 1H). HRMS (TOF-ESI) (m/z) Calculated as 474.19265, found: 473.18782 [M-H]<sup>-</sup>. Distyryl BODIPY dye **3**, <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  1.43 (s, 6H), 3.82 (s, 3H), 6.79 (d, j= 8.0 Hz, 2H), 6.90-6.87 (m, 4H), 7.07 (s, 2H), 7.09 (d, *j*= 8.8 Hz, 2H), 7.25 (d, *j*= 16.0 Hz, 2H), 7.29 (d, *j*= 8.8 Hz, 2H), 7.37 (d, j = 16.0 Hz, 2H). <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>)  $\delta$ : 160.2, 152.5, 148.1, 146.3, 141.6,

138.0, 137.7, 133.2, 130.2, 128.3, 126.7, 121.2, 118.3, 116.5, 115.4, 114.9, 113.4, 55.7, 14.8. HRMS (TOF-ESI) (m/z) Calculated as 594.21379, found: 593.21207 [M-H]<sup>-</sup>.

#### 2.2.4 4,4-Difluoro-8-[4-(diphenylamino)phenyl)]-1,5,7-trimethyl-3-[(1E)-3,4dihydroxyphenyl]-4-bora-3a,4a-diaza-s-indacene (2) and 4,4-Difluoro-8-[4-(diphenylamino)phenyl)]-1,7-dimethyl-3,5-bis-[(1E)-3,4-dihydroxyphenyl]-4-bora-3a,4adiaza-s-indacene (4)

Compound 8TPA (514 mg, 1.04 mmol) and 3,4-dihydroxybenzaldehyde (430 mg, 3.12 mmol) were refluxed in a mixture of toluene (40 ml), glacial acetic acid (1.7 mL) and piperidine (2.1 mL), the mixture was stirred at 120 °C for 6 h. Any water formed during the reaction, was removed azeotropically by heating overnight in a Dean-Stark apparatus. After the reaction was guenched with water at room temperature, the mixture was diluted with EtOAc and washed with water. The organic layer was collected from separating funnel and solvent was evaporated under reduced vacuum. The crude solid was dried in a vacuum oven, then purified by silica gel column chromatography by using mobile phase (elution: first chloroform, then chloroform-methanol, 60:40 v/v) to obtain monostyryl BODIPY dye 2 (90 mg, yield 14%) as red-purple powder (the purple colored fraction) and distyryl BODIPY dye 4 (130 mg, yield 18%) as green powder (green colored fraction). Monostyryl BODIPY dye 2, <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  1.55 (s, 3H), 1.60 (s, 3H), 2.47 (s, 3H), 6.17 (s, 1H), 6.79 (d, j = 8.0 Hz, 1H), 6.88 (d, j = 8.0 Hz, 1H), 6.93 (s, 1H), 7.12-7.06 (m, 10H), 7.23 (s, 1H), 7.26 (d, j = 16.4 Hz, 1H), 7.38-7.34 (m, 4H), 7.41 (d, j = 16.4 Hz, 1H). <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 160.0, 158.6, 153.4, 152.9, 148.0, 147.8, 146.8, 145.8, 142.4, 139.7, 139.2, 139.1, 138.0, 129.7, 129.3, 127.7, 127.5, 124.4, 123.6, 122.7, 121.0, 118.1, 116.0, 114.4, 112.7, 24.0, 14.5, 14.1. HRMS (TOF-ESI) (m/z) Calculated as 611.25557, found: 610.25491  $[M-H]^{-}$ .Distyryl BODIPY dye 4, <sup>1</sup>H-NMR (400 MHz, DMSO-d<sub>6</sub>):  $\delta$  1.60 (s, 6H), 6.79 (d, j= 8.4 Hz, 2H), 6.92-6.90 (m, 4H), 7.21-7.07 (m, 10H), 7.25 (s, 2H), 7.28 (d, j= 8.4 Hz, 2H), 7.41-7,34 (m, 6H). <sup>13</sup>C-NMR (100 MHz, DMSO-d<sub>6</sub>) δ: 159.7, 152.0, 147.6, 145.8, 141.1, 137.5, 137.2, 136.6, 132.7, 129.7, 128.8, 127.8, 126.2, 124.4, 120.7, 120.1, 117.8, 116.0, 114.9, 114.4, 112.9, 14.3. HRMS (TOF-ESI) (m/z) Calculated as 731.27671, found: 730.27704 [M-H]<sup>-</sup>.

#### 2.3 Optical measurements

The UV-Vis absorption spectra of the BODIPY sensitizers were recorded using a Shimadzu UV-1800 scanning spectrophotometer. Fluorescence spectra of the studied dyes were measured on Perkin Elmer LS55 spectrophotometer. Ultrafast transient absorption

spectroscopy measurements were carried out in femtosecond timescale by using a Ti: Sapphire laser amplifier and an optical parametric amplifier system with 52 fs pulse duration and 1 kHz repetition rate (Spectra Physics, Spitfire Pro XP, TOPAS). A commercial pump probe experimental setup (Spectra Physics, Helios) with a white light continuum probe was used to examine charge injection dynamics of studied dyes in solution and on the film of anode electrode. The pump wavelength for ultrafast pump probe spectroscopy experiments was chosen based on the maximum absorption wavelength. The excited state dynamics were measured between 0.1 ps to 3.2 ns timescale. Experimental data was analyzed by using Surface Xplorer software that is provided by Ultrafast Systems.

#### 2.4 Preparation of BODIPY sensitized solar cells

Fluorine doped tin oxide (FTO) ( $12 \text{ cm}^{-2}\Omega$ ) coated glasses were purchased from (Sigma Aldrich) and used in both photoelectrodes. The semiconductor oxide paste (TiO<sub>2</sub>-DSL 18 NR-T, Dyesol) was coated on conductive side of the glass substrates by doctor blade method. TiO<sub>2</sub> coated electrode was dried at 125 <sup>o</sup>C and sintered at 500 <sup>o</sup>C for 30 minutes, and it was immersed into the  $3x10^{-4}$  M solution of the **1**, **2**, **3** and **4** dyes in THF for 18 hours. In order to remove unlinked dyes from the surface, the films were washed with THF solvent and then dried on hot plate. Pt-coated glass (Solaronix) was used as a counter electrode and I<sub>3</sub><sup>-</sup> /I<sup>-</sup> (EL-HPE, Dyesol) solution was used as a redox couple to integrate cell components.

#### 2.5 Dye adsorption measurements

In order to obtain the amounts of dye molecule adsorbed on  $TiO_2$  surface, transparent  $TiO_2$  films of surface area 1 cm<sup>2</sup> were dipped into a 6 mL of  $3x10^{-4}$  M dye solution for 18 hours. Then dye coated anode electrode washed with 2 ml THF to get rid of unbound dye molecules in the same beaker. The initial concentration and the concentration volume were known, so dye mass can be calculated from these values. After adsorption and washing process absorption spectra of the solution was measured and the concentration was determined by utilizing absorption coefficient of dye. The mass of the dye not adsorbed on  $TiO_2$  can be calculated from the concentration value and volume of the final solution. This mass value is subtracted from the initial mass value and the mass of dye adsorbed on  $TiO_2$  is obtained.

#### 2.6 Characterization of BODIPY dyes sensitized solar cells

The photocurrent density versus photovoltage of the solar cells were measured by recording J-V curves using Keithley 2400 source meter under illumination of AM 1.5 G simulated solar light (Newport with 300 W Xe lamp and AM 1.5 G filter). The incident light intensity was adjusted to 100 mW/cm<sup>2</sup> on the detector active area. The incident photon-to-current conversion efficiency (IPCE) spectra of the cells were measured with a commercial setup (Newport, Oriel). All device performance was carried out in ambient atmosphere, unless specified otherwise.

#### 2.7 Micro patterning fabrication

TiO<sub>2</sub> coated film onto FTO glass was ablated by femtosecond pulse laser. The vertical polarized laser with a wavelength of 400 nm, pulse duration of 52 fs and repetition rate of 1 kHz (Spectra Physics, Spitfire Pro XP, TOPAS) was used. Laser beam was passed through a number of natural density filters to adjust power and sent a convex lens to focus the beam on the surface of the sample. The laser energy per pulse was measures as 5.6  $\mu$ J. The film-coated glass was mounted on a motorized *xyz* stage (Newport). The stage speed on one direction (*x*) was adjusted to 20 mm s<sup>-1</sup> to be able to have one pulse reaching to one spot of the sample, which is placed at the focus and perpendicular to the laser beam. The film surfaces were ablated periodically line by line, by moving stage along *z* direction. The ablated film morphology was characterized by scanning electron microscopy (SEM, ZEISS EVO 40).

#### 3. Results and Discussion

#### **3.1 Steady state absorption and emission properties of BODIPY dyes and BODIPY**sensitized TiO<sub>2</sub> electrodes

Investigated dye molecules consist of an electron donor moiety and one or two anchoring group(s) (Scheme 1). Here, electron donating moieties which are triphenylamine and methoxyphenyl bound to meso (C8) position, while the catechol moiety which is the anchoring group attached to both C3 and C3-C5 positions of the BODIPY core via Knoevenagel condensation reaction. In order to evaluate the ground state interaction, linear absorption spectra of the sensitizers were measured both in THF solution and on TiO<sub>2</sub> surface.

Linear absorption properties of studied dyes (in THF) are given in **Fig. 1**. All studied dyes demonstrate high molar extinction coefficients at their absorption maxima (**Table 1**).

Dye **1** has methoxyphenyl moiety at meso (C8) position and 2-(3,4-dihydroxyphenyl) ethenyl moiety at C3 position of the BODIPY core and its absorption maximum wavelength is around 574 nm. Similarly, dye **2** which has triphenylamine (TPA) moiety at meso position, gives an absorption maximum at 576 nm. This slight red-shifting is due to the orthogonal alignment between meso substituent and the BODIPY core. An efficient way to red-shift the absorption and emission maxima is to extend the conjugation of the 3 and 5 positions of the BODIPY core [37]. Therefore, 2-(3,4-dihydroxyphenyl) ethenyl moieties bind to C3 and C5 positions of the BODIPY core and molecule became symmetrical structure (dyes **3** and **4**). When the molecule becomes symmetric, the color of the dye solution changes from bright pink to bluish and the absorption peaks are significantly red-shifted (about 75 nm) as compared to that of unsymmetrical dyes (dye **1** and dye **2**). The strong absorption band of studied BODIPY dyes at longer wavelengths around 575 nm and 650 nm are correspond to S<sub>0</sub>→S<sub>1</sub> transition, while the absorption band at shorter wavelengths region correspond to S<sub>0</sub>→S<sub>2</sub> transitions[38].

The sensitized BODIPY dyes show strong fluorescence spectra in THF solution, as illustrated in Fig. 2. It is obviously seen from the figure that the fluorescence intensity depends on the molecular symmetry. The fluorescence peaks are around 610 nm for dyes 1-2 and around 675 nm for dyes 3-4, respectively. The fluorescence intensity of dye 2 is lower than that of dye 1, due to electron donating properties of the TPA group. The TPA is a well-known electron donor moiety and affects the fluorescence intensity of the dye molecule. Furthermore, TPA moiety has a stronger electron donating ability than the methoxyphenyl moiety. Therefore, fluorescence intensity decreases in dyes containing TPA moiety due to the increasing intramolecular charge transfer [39]. When molecule becomes symmetrical (dyes 3 and 4), the fluorescence signals get considerably smaller as compared to that of unsymmetrical dyes (dyes 1 and 2). This may be due to the formation of a charge transfer state (CTS) lower than the excited singlet state and efficient intramolecular electron transitions to the formed CTS. The small fluorescence signals appearing about 740 nm, may be another indication of the formation CTS around this wavelength for dyes 3 and 4. In order to examine solvent effect on CTS, we did steady state absorption and emission measurements both in polar (EtOH) and nonpolar (Toluene) solution environments. The linear absorption spectra of the dyes in both solutions are given Fig. S16. All studied dyes showed similar absorption characteristic behaviors in both solutions. In the fluorescence spectra, there are significant differences

depending on the solvent polarity as shown in **Fig. S17**. Although all studied dyes demonstrated similar emission behavior in polar solutions (THF and EtOH), the fluorescence intensity decreases more in EtOH as compared to THF. That is because; intramolecular charge transfer increases in polar environment and therefore, fluorescence intensity decreases. In nonpolar solvent (Toluene), it is clearly seen that the fluorescence signal maxima shows a blue-shifting due to less polarity. On the other hand, the fluorescence signal has a shoulder that corresponds to emission from CTS in the lower energy side of the spectrum. These experimental measurements showed that CTS clearly depends on the solvent polarity.

The steady state linear absorption spectra of the sensitizers anchored on the transparent TiO<sub>2</sub> films are shown in Fig. 3. It is clearly seen from the figure that absorption of the dyes adsorbed on TiO<sub>2</sub> becomes significantly broadened compared to that of dyes in THF. Broadening effect could be due to aggregation on the surface of  $TiO_2$  or bound formation between the dye molecules and semiconductor TiO<sub>2</sub> layer [24, 28, 40, 41]. In order to explain the aggregation effect, we also performed fluorescence experiments and fluence dependence ultrafast pump probe experiments for BODIPY chromophores adsorbed on TiO<sub>2</sub>. In an attempt to understand the aggregation effect on emission characteristics, we recorded the fluorescence measurements for all studied dyes in THF solution as well as adsorbed on TiO2 layer. It is observed that the fluorescence signals of the anode electrodes are quenched significantly, while the dyes have strong fluorescence intensity in THF solution. The quenching mechanism can be ascribed to aggregation effect since BODIPY compounds have planar indacene skeletons and enable the form H or J type aggregates [40, 41]. Thus, broadened absorption bands of the dyes on TiO<sub>2</sub> might be a sign of intermolecular interactions of the molecules that are aggregated on the TiO<sub>2</sub> surfaces. On the other hand, in order to examine the aggregation effect, ultrafast pump probe spectroscopy experiments were performed with two pump beam fluences (about 8  $J/m^2$  and 4  $J/m^2$ ). The experimental results showed that the excited state lifetime of the dye adsorbed on TiO<sub>2</sub> decreases with increasing pump beam fluence as given in Fig. S18. That is because, in an aggregation environment, the excited singlet state of chromophores can act as a quenching system for singlet excitation of the other molecules. This phenomena causes decreasing excited state lifetimes for higher excitation intensities as well as fluorescence intensity [42]. The decreasing of the excited state lifetime at higher excitation fluence indicated that the dye molecules aggregate on TiO<sub>2</sub> layer.

The sensitizer dye molecule with catechol anchoring group have been known to bind to the  $TiO_2$  surface through a bidentate mononuclear chelating or a bidantate dinuclear bridging

linkages [43, 44]. The solar cell that is fabricated with sensitizer including catechol group is classified as type-II DSSC. The type-II DSSCs show a direct electron transition from dye to conduction band of TiO<sub>2</sub> via dye-to-TiO<sub>2</sub> charge transfer (DTCT) bands. For this mechanism, the dyes including anchoring catechol moieties show a strong absorption band in the lower energy side of the spectrum upon binding on TiO<sub>2</sub> layer. In **Fig. 3**, the dyes bounded on TiO<sub>2</sub> layer show a dominant absorption peak around 580 nm and 660 nm wavelengths which correspond to steady state absorption from HOMO to LUMO level of the dyes in solution. In addition, these bands have a tail around near infrared region as compared to that of in THF. Therefore, this weak absorption signals may be attributed to direct transition from dye to conduction band of TiO<sub>2</sub>. In this study, transitions occur from HOMO level to LUMO level of the dye then from LUMO level to conduction band of TiO<sub>2</sub> (indirect transition). Therefore, the indirect transition is dominant for the studied dye adsorbed on TiO<sub>2</sub> surface.

In an attempt to understand the number of anchoring groups adsorbed on TiO<sub>2</sub> we performed absorption measurements for symmetrical and unsymmetrical dye molecules in THF and on TiO<sub>2</sub> surface. Anchoring groups in BODIPY dyes especially on position of 3 and 5 are affected electron transfer from oxygen anion to BODIPY core in basic environment. Therefore bathochromic shift is observed on the absorption spectra in basic environment. If anchoring groups are covalently bounded to TiO<sub>2</sub>, oxygen anion does not form and therefore bathochromic shift is not observed in the absorption spectra of the anode electrode. In order to understand whether the mono or di-anchoring groups are bound to the TiO<sub>2</sub>, we conducted absorption measurements of dye 2 in THF solution and on TiO<sub>2</sub> surface of the anode electrode with and without KOH. Firstly, the absorption spectrum of dye 2 solution with KOH solution (in THF) was recorded and compared with dye 2 in THF (Fig. S19). It was seen that the spectrum was broadened and red shifted significantly, as expected. After the anode electrode with dye 2 was immersed in KOH solution, absorption spectrum was recorded and compared with anode electrode with dye 2. If there was unbounded anchoring group side on TiO<sub>2</sub>, we expect to see bathochromic shift in the absorption spectra. We did not see any shift in wavelength on the absorption spectra as seen in Fig. S20. The same process was performed for symmetrical dye 4 to see whether the di-anchoring groups are bound on TiO<sub>2</sub>. We did not observe any spectral shift in the absorption spectra of anode electrode with KOH for dye 4 as well (Fig. S21 and S22). We believe these results are the evidence that both mono and dianchoring groups are bounded to TiO<sub>2</sub> surface for dye 2 and 4, respectively.

#### 3.2 Ultrafast transient absorption spectroscopy measurements

In an attempt to investigate charge transfer dynamics and decay kinetics of the sensitizers, ultrafast pump probe spectroscopy experiments were performed for dyes both in solution and on TiO<sub>2</sub> film. **Fig. 4a-d** indicates the transient absorption spectra at different time delays upon pulsed laser excitation in THF for dyes **1-4**, respectively. The wavelength dependent transient absorption spectra are similar for dyes **1** and **2**. There is a negative absorption signal consisting of nested two bands, between 555 nm and 670 nm wavelengths. The negative signals around 585 nm and around 630 nm, can be ascribed to ground state and charge transfer state (CTS) bleaching, respectively. In addition, there are positive signals localized below 555 nm and above 670 nm, which can be attributed to excited state absorption (ESA). On the other hand, there is a negative signal (535 nm) buried in the ESA signal, causing to ESA signal decrease. Even if this signal seems to be positive, it is negative and competes with the positive ESA signals. This signal corresponds to shoulder of the main absorption peak in the linear absorption spectra.

The ultrafast transient absorption spectroscopy experiments of symmetrical dyes (**3** and **4**) were performed at 650 nm pump wavelength. In transient absorption spectra, there are two distinct negative absorption signals that are localized around 660 nm and 730 nm. The former can be attributed to ground state bleach signal and the latter can be ascribed to saturation of the CTS. In addition, a broad ESA signal centered around 485 nm and a negative signal around 600 nm buried in this broad ESA signal appear in the nonlinear absorption spectra for both dyes **3** and **4**. As mentioned above, this buried negative signal corresponds to shoulder of the main absorption peak in the linear absorption spectra.

The singlet excited state lifetimes of the dyes in THF solutions decay with several processes, which are transitions to lower vibrational states, charge transfer to the CTS, and decay to ground state. Therefore, decay kinetics of the excited state of the dyes in THF (**Fig. 5**) was fitted with three exponential decay functions to extract transient dynamics of the studied compounds and given in **Table 2**. Among the dyes studied dye **1** has the longest excited state lifetime (about 4 ns) in THF.

In an attempt to understand the charge injection dynamics between dye molecule and  $TiO_2$ , femtosecond transient absorption spectroscopy experiments were carried out for all the photoelectrodes (dyes adsorbed on  $TiO_2$  film on FTO glass). The results are given in **Fig. 6a-d**. There is a single negative signal ranged from 520 nm to 650 nm and ESA bands below 520

nm and above 650 nm for dyes 1 and 2. Similarly, in transient absorption spectra for dyes 3 and 4, there is a single negative signal localized at 650 nm and ESA bands below 600 nm and above 720 nm. It is clear that the charge transfer states seen for dyes in THF, disappear for adsorbed dyes due to binding of catechol moiety to  $TiO_2$  and fast electron transferring to the conduction band of  $TiO_2$ . The decay traces of the bleach signals (**Fig. 7**) were fitted to three exponential signals for all studied compounds and their time components are given in **Table 2**, as well. Note that middle component correspond to electron transfer from LUMO level of the dyes to conduction band of  $TiO_2$  for dyes on  $TiO_2$ . It is obviously seen that time components of dyes adsorbed on the  $TiO_2$  layer decrease as compared to that of dyes in THF, due to faster electron transfers from LUMO level of dye to the conduction band of  $TiO_2$ . **Table 2** shows that dye 1 shows fastest electron injection to  $TiO_2$ .

The time and wavelength dependent transient absorption spectra of the dyes adsorbed on TiO2 are shown in **Fig. S23** and **S24**. It is clearly seen from the figure that dye **1** has longer excited state lifetimes in solution and faster electron transfer to  $TiO_2$  and therefore, we expect dye **1** to have better photovoltaic performance in DSSC.

#### 3.3 Photovoltaic performance

BODIPY sensitized solar cells were fabricated in order to evaluate the photovoltaic performances by using dye coated  $TiO_2$  as a photoanode, Iodide/Triiodide redox couple as an electrolyte mediator and platinized FTO glass as a counter electrode. All device performance was carried out in ambient atmosphere, unless specified otherwise.

Monochromatic IPCE spectra, measured as a function of wavelength ranging from 300 nm to 1100 nm are given in **Fig. 8**. Unsymmetrical dyes (**1** and **2**) with different electron donors show external quantum efficiency between 500 nm and 750 nm. Among the unsymmetrical BODIPY dyes, the cell based on methoxyphenyl moiety (dye **1**) indicates greater IPCE spectrum, with a peak value of 7.5% at 610 nm, than that of TPA moiety (dye **2**) with a peak value of 5% at 610 nm. That is because dye **1** with methoxyphenyl moiety has longer excited state lifetime in solution and faster electron injection on photo anode film as compared to dye **2** with TPA moiety. This finding support our expectations based on ultrafast spectroscopy data. Despite the fact that sensitizer with TPA moiety has greater molar absorption coefficient and further light harvesting capability, it's IPCE value is lower. Enhancement in IPCE value could be attributed to differences on the electron donating properties of investigating dyes.

IPCE spectra of symmetrical dyes (3 and 4) showed similar characteristic behaviors to each other between 580 nm and 830 nm wavelengths as seen in Fig. 8. Surprisingly, IPCE values of dyes 3 and 4 are almost the same, despite the fact that they have different electron donating moieties as contrary to dyes 1 and 2. Note that dyes 3 and 4 have two catechol moieties as contrary to dyes 1 and 2, which have only one catechol moiety. Comparing investigated dyes with the same TPA electron donating properties and different number of catechol moieties (i.e. dyes 2 and 4), one could see that although both dyes show the same absorption intensity (as seen in Fig. 3), dye 4 showed lower photo conversion efficiency. That is because, although the anode electrodes with dye 2 and dye 4 have the same absorption value, the cell fabricated with dye 2 showed better photovoltaic performance due to the faster electron injection from excited state of the dye 2 to conduction band of the  $TiO_2$  than that of dye 4. The cell with dye 1 demonstrated better photovoltaic performance because its longer excited state lifetime in solution and faster electron injection to the conduction band of the TiO2. These results showed that the excited state lifetime is a very effective parameter to determine photovoltaic performance. The amount of the dye adsorbed on TiO<sub>2</sub> surface affect the photovoltaic performance of DSSCs. The dyes with methoxyphenyl moiety were more adsorbed on TiO<sub>2</sub> surface than those with TPA moiety. That is because the dyes with TPA moiety have more bulky structure as compared to methoxyphenyl moiety. Therefore, the electron donating property as well as number of anchoring group is a parameter that determines the amount of dye adsorbed on TiO<sub>2</sub>.

The photocurrent density-photo voltage (J-V) curves of the BODIPY sensitized solar cells are seen in **Fig. 9** and the results are summarized in **Table 3**. J-V results show that unsymmetrical dye with methoxyphenyl moiety has more efficient electron injection process than that of TPA moiety. Note that power conversion efficiency found for dye 1 (0.44%) and dye 3 (0.11%) with methoxyphenyl are comparable with the BODIPY dyes including trimethoxyphenyl (0.13%) in the literature [24]. Similarly, power conversion efficiency of dye 2 (0.35%) and dye 4 (0.09%) with TPA moiety are also comparable with BODIPY dyes with TPA moieties in the literature [26, 28]. Among the unsymmetrical dyes, dye 1 with methoxyphenyl moiety has a longer excited state lifetime in THF solution, and demonstrates efficient electron transfer to anode electrode. J-V measurements of the investigated dyes are in line with the IPCE measurements explained above.

The fabricated cells with symmetrical dyes (3 and 4) showed lower photovoltaic performance as compared to that of asymmetrical dyes (1 and 2). It is clearly seen from the photocurrent

action spectra that both short-circuit photocurrent density  $(J_{sc})$  and open circuit voltage  $(V_{oc})$ are lower for symmetrical BODIPY dyes. The lower photocurrent efficiencies frequently originate from inefficient electron injection from dye to TiO<sub>2</sub> [10, 45]. The symmetrical dyes have linear absorption appearing near infrared (NIR) region of the absorption spectrum of anode electrode as compared to asymmetrical dyes. These signals can be attributed to absorption from HOMO level to trap states of the TiO<sub>2</sub> due to the direct transition. This result leads to back electron transfer from trap states to the oxidized dye and decrease in the Jsc. On the other hand, the symmetrical dyes in THF showed shorter excited state lifetime and slow electron injection rate from LUMO of dye to conduction band of TiO<sub>2</sub> as compared to asymmetrical dyes. Similar studies revealed that the electron injection dynamics is much slower for the dyes demonstrating inefficient electron transfer [45, 46]. Additionally, since the absorption spectra of symmetrical dyes shift to longer wavelength region as compared to that of unsymmetrical dye, electron transfer from the excited state of the dye to the trap states of  $TiO_2$ , is possible as well. On the other hand, the decrement of  $V_{oc}$  is generally related to band edge shift of TiO<sub>2</sub> conduction band. Increasing the number of anchoring group leads more protons to transfer to TiO<sub>2</sub> upon dye molecules bounding to TiO<sub>2</sub>. Therefore, positively charged TiO<sub>2</sub> causes lowering the conduction band edges of TiO<sub>2</sub> and therefore lowering V<sub>oc</sub> [47, 48].

In an attempt to investigate the effect of anchoring capability on the photovoltaic performance we modified the surface roughness of TiO<sub>2</sub> film by using fs laser ablation technique. Four anode electrodes were produced with dye **1** by using the same procedure. The anode electrodes were placed perpendicular to the focused laser beam and scanned with a motorized xyz stage such that each laser pulse hit one spot on the sample. The surface of the films scanned line by line. While the first electrode had no scanning, the others were scanned with about 20  $\mu$ m, 40  $\mu$ m, and 60  $\mu$ m line separations as seen from the SEM images in **Figure 8ad**, respectively. The absorption properties of the scanned anode electrodes (given in **Fig. 9**) show that anode electrode with 20  $\mu$ m scanned line separation show higher absorption properties. This may be the indication that the more the surface roughness, the better the adsorption of the dye on anode electrode. Ultrafast pump probe experiments performed on bare anode electrode and scanned with 20  $\mu$ m line separation given in **Fig. 10** revealed that the scanned anode show shorter lifetime i.e. faster electron injection to the conduction band of TiO<sub>2</sub>. IPCE and J-V measurements proved that scanning the anode electrode gives better photovoltaic performance (**Fig. 11, Fig. 12**, and **Table 4**). Power conversion efficiency

improved 47% compared to the same cell without laser ablation. There might be two explanations for these findings. One of them is the fact that scanning increases the surface area of the material and therefore, increases anchoring capability of dye as seen in the literature (13.5%) [34]. The other explanation could be that fs pulses may break the bonds between Ti and oxygene atoms and produce  $Ti^+$  ions, which could be used by catechol moiety to form covalent bonding. We leave this point open to discussion.

#### 4. Conclusion

The goal of this study is to reveal the parameters affecting the photo conversion efficiencies of BODIPY dye sensitized solar cells. Therefore, the effects of electron donating moieties as well as molecular symmetry, on electron injection dynamics and photovoltaic performance were studied. Attachment of the dye to  $TiO_2$  was studied by altering the surface morphology of TiO<sub>2</sub> with fs laser ablation. Four new BODIPY derivatives were designed and sensitized to achieve these goals. Among the sensitized dyes, dye with methoxyphenyl electron donor group and unsymmetrical structure (i.e. one anchoring group at C3 position) showed the best photovoltaic performance despite of the lowest absorption spectra on TiO<sub>2</sub> layer, comparing to the other sensitizers. This dye showed the longer excited state lifetime in solution and faster electron injection dynamics to TiO<sub>2</sub> as compared to the other sensitizers. Therefore, while designing new chromophores for DSSC applications one should consider not only the light harvesting capability but also the longer excited state lifetime in solution and shorter electron transfer time to TiO<sub>2</sub> on the film of anode electrode. In addition, we show that increasing the number of the anchoring group on the studied dye molecules may not result better photovoltaic performance. On the other hand, fs laser ablation treatment of the TiO<sub>2</sub> surface enhances the anchoring capability, shortens the electron injection time to TiO<sub>2</sub> conduction band, and therefore, increases the DSSC performance by about 47%. We believe that our results are useful while designing new BODIPY chromophores for DSSC applications.

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#### **Figure Captions**

Figure 1.Linear absorption spectra of BODIPY dyes, *c*=5x10-5 M in THF

Figure 2.Fluorescence spectra of BODIPY dyes 1, 2, 3 and 4, *c*=5x10-5 M in THF

Figure 3.Linear absorption spectra of the BODIPY sensitizers adsorbed on TiO<sub>2</sub> layer

Figure 4. Transient absorption spectra of the a) 1, b) 2, c) 3 and d) 4 BODIPY dyes in THF.

Figure 5. Time evolution of the dyes 1, 2, 3 and 4 in THF at their bleach maxima

Figure 6. Transient absorption spectra of the a) 1, b) 2, c) 3 and d) 4 BODIPY dyes on TiO<sub>2</sub>

Figure 7. Time evolution of the dyes 1, 2, 3 and 4 on TiO<sub>2</sub> at their bleach maxima

**Figure 8.** Incident photon to current conversion efficiencies as a function of wavelength for BODIPY dyes sensitized solar cells

Figure 9. I-V curves of dyes 1, 2, 3 and 4 sensitized solar cells under A.M. 1.5 G illumination

Figure 10. SEM images of a) bare, b) 60  $\mu$ m, c) 40  $\mu$ m and d) 20  $\mu$ m line pattern on the laser ablated TiO<sub>2</sub> film.

Figure 11. Linear absorption spectra of dye 1 adsorbed on bare and scanning TiO<sub>2</sub> layers

Figure 12. Time evolution of the dye 1 on bare and 20  $\mu$ m line patterning TiO<sub>2</sub> at their bleach maxima

Figure 13. Incident photon to current conversion efficiencies as a function of wavelength for dye 1 sensitized solar cells using adsorbed on bare and scanning  $TiO_2$  layers

**Figure 14.** I-V curves of dye **1** sensitized solar cells using adsorbed on bare and scanning TiO<sub>2</sub> layers, under A.M. 1.5 G illumination

#### Figure 1







Figure 4



Figure 5









#### Figure 9











**Scheme 1.** Synthetic pathway of the BODIPY dyes; (i) cat. trifluoroacetic acid, rt, 12 h; (ii) tetrachloro-1,4-benzoquinone, rt, 12 h; (iii) (1) N,N-diisopropylethylamine; (2) BF<sub>3</sub>.Et<sub>2</sub>O, rt, 24 h; (iv) 3,4-dihdyroxybenzaldehyde, piperidine, acetic acid, reflux, 6 h.

| $\lambda_{max}(nm)$ in THF | $\epsilon \left( M^{-1} \text{ cm}^{-1} \right)$         | λ <sub>flu</sub> (nm)<br>in THF | $\lambda_{max}(nm)$<br>on TiO <sub>2</sub>  | Dye amount (10 <sup>-7</sup> mol<br>cm <sup>-2</sup> )  |
|----------------------------|--|---------------------------------|---|---|
| 574                        | 12580  | 603                             | 583   | 8,2   |
| 576                        | 17560  | 608                             | 585   | 5,9   |
| 650                        | 11480  | 670                             | 661   | 6,9   |
| 652                        | 22500  | 682                             | 665   | 6,8   |
|                            | λ <sub>max</sub> (nm) in THF<br>574<br>576<br>650<br>652 |                                 | $\begin{array}{c} \lambda_{max}(nm) \text{ in THF} & \epsilon \left( M^{-1} \text{ cm}^{-1} \right) & \begin{array}{c} \lambda_{flu} (nm) \\ \text{ in THF} \end{array} \\ \hline 574 & 12580 & 603 \\ 576 & 17560 & 608 \\ 650 & 11480 & 670 \\ 652 & 22500 & 682 \end{array}$ | $\begin{array}{c cccc} \lambda_{max}(nm) \text{ in THF} & \epsilon (M^{-1} \text{ cm}^{-1}) & & \lambda_{flu}(nm) & \lambda_{max}(nm) \\ \hline n \text{ THF} & \text{ on TiO}_2 \\ \hline 574 & 12580 & 603 & 583 \\ 576 & 17560 & 608 & 585 \\ 650 & 11480 & 670 & 661 \\ \hline 652 & 22500 & 682 & 665 \\ \hline \end{array}$ |

Table 1. Photophysical properties of sensitized dyes in THF and on TiO<sub>2</sub>

Table 2. Time components of the BODIPY dyes in THF and adsorbed on  $TiO_2$ 

|      | Dye |                     | $	au_1(\mathrm{ps})$ | $\tau_2(\mathrm{ps})$ | $	au_3(\mathrm{ps})$ |
|------|-----|---------------------|----------------------|-----------------------|----------------------|
|      | 1   |                     | 0.9±0.2              | 102.1 <u>+</u> 3.4    | 4128±182             |
|      | 2   | in THF              | 0.7±0.2              | 197.7±5.8             | 3820±206             |
|      | 3   |                     | $0.5 \pm 0.1$        | 466.1±21.2            | 2841±417             |
|      | 4   |                     | 0.4 <u>±</u> 0.1     | 21.8±1.2              | 2010±242             |
|      | 1   |                     | 0.1±0.05             | 1.1±0.2               | 365.8±126            |
|      | 2   | on TiO <sub>2</sub> | $0.4 \pm 0.05$       | 5.7±1.3               | 321.7±112            |
|      | 3   |                     | 1.7±0.2              | 44.36±8.1             | 243.4±48             |
|      | 4   |                     | 1.2±0.2              | 13.7±3.2              | 138±26               |
| PC C |     |                     |                      |                       |                      |

| Dye | J <sub>sc</sub> (mA cm <sup>-2</sup> ) | Voc (V) | FF   | η (%) |
|-----|--|---------|------|-------|
| 1   | 1,66                                   | 0,45    | 0,59 | 0,44  |
| 2   | 1,31                                   | 0,44    | 0,60 | 0,35  |
| 3   | 0,73                                   | 0,32    | 0,47 | 0,11  |
| 4   | 0,63                                   | 0,25    | 0,52 | 0,09  |

Table 3. Photovoltaic parameters in DSSCs based on studied BODIPY dyes

 Table 4. Photovoltaic parameters in DSSC based on dye 1

|       | J <sub>sc</sub> (mA cm <sup>-2</sup> ) | V <sub>oc</sub> (V) | FF   | η (%) |
|-------|--|---------------------|------|-------|
| Bare  | 1,86                                   | 0,44                | 0,47 | 0,44  |
| 60 µm | 1,88                                   | 0,46                | 0,48 | 0,46  |
| 40 µm | 2,16                                   | 0,48                | 0,44 | 0,52  |
| 20 µm | 2,58                                   | 0,47                | 0,47 | 0,65  |