

**FINAL PROJECT REPORT FOR EUROPEAN SCIENCE
FOUNDATION PROGRAMME (ORGANISOLAR)**

**Sensitization of TiO₂ electrode using Boradiazaindacenes
(BODIPYs),
Investigation of Solid State Solar Cell Performances**

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AIM of VISIT

Boradiazaindacene dyes have been tested for the first time in solid state dye sensitized solar cells. Also optimization studies for solar cells have been carried out. For this purpose, extensive studies has been conducted on the construction solid state dye sensitized solar cell systems by the use of BODIPY dyes. BODIPY dyes were supplied from Bilkent University. Molecular Structures which used to fabricate solid state dye sensitized solar cell and the detailed analysis figures are shown below. Publication planned with these results.

1. Introduction

Recent developments in the field of personal diagnostics and in the area of organic electroluminescent devices have boosted interest in the development of next-generation emissive dyes. Countless classes of highly fluorescent organic compounds are now known, but the difluoro-boraindacene family (4,4-difluoro-4-borata-3a-azonia-4a-aza-s-indacene, abbreviated hereafter as F-Bodipy) has gained recognition as being one of the more versatile fluorophores and this dye has steadily increased in popularity over the past two decades. Boradiazaindacenes, commonly known as BODIPY dyes, have been recognized [1] as useful fluorescent labels for biomolecules for some time. Within the past decade, there is much renewed interest [2, 3] in these dyes, due to the development of new avenues for derivatization and novel applications in a highly diverse field, including chemosensors [4], logic gates [5], light harvesters [6], energy transfer cassettes [7, 8], and photodynamic therapy [9] It is known that photostability of the BODIPY dyes is significantly better [10] than many sensitizers proposed. The first member of this class of compound was reported by Treibs and Kreuzer in 1968 [11], although relatively little attention was given to the discovery until the end of the 1980s [12]. Then, the potential use of this dye for biological labeling was recognized [13]. As a consequence, Bodipy came to be known to the biochemist and biologist as a photostable substitute for fluorescein, and the number of papers and patents started to escalate in the mid 1990s.

Among the metal-free organic dyes, triphenylamines as donor units have displayed promising properties in the development of photovoltaic devices [14-18]. There are several basic

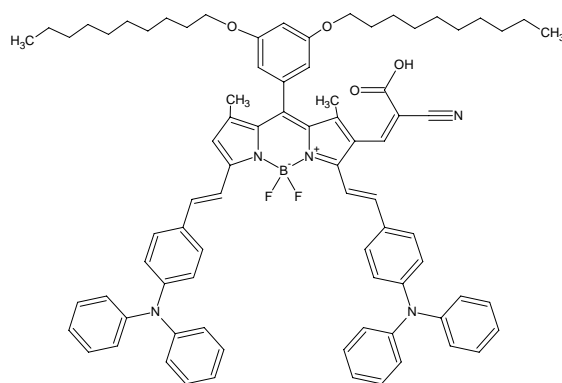
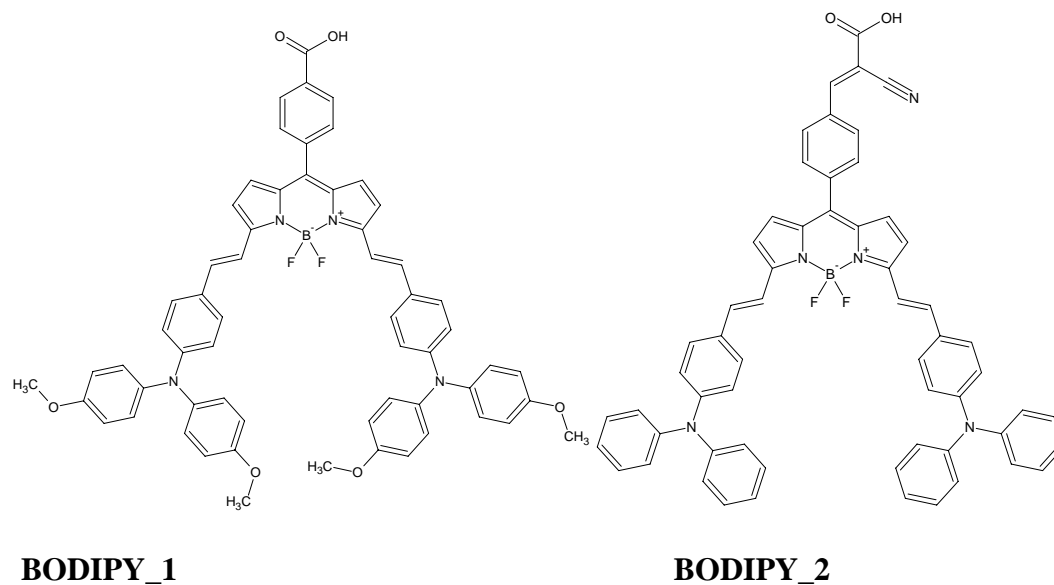
requirements guiding the molecular engineering of an efficient sensitizer. The excited-state redox potential should match the energy of the conduction band edge of the oxide. Light excitation should be associated with vectorial electron flow from the light-harvesting moiety of the dye toward the surface of the semiconductor surface providing efficient electron transfer from the excited dye to the TiO₂ conduction band. Finally, a strong conjugation across the donor and anchoring groups and good electronic coupling between the lowest unoccupied orbital (LUMO) of the dye and the TiO₂ conduction band should exist, to ensure high electron-transfer rates [19].

For this consideration, I wanted to test BODIPY in solid state dye sensitised solar cells. To the best of our knowledge, this is the first application in solid state dye sensitized solar cells for Bodipy dyes. BODIPY dyes have certain unique features that could make them highly advantageous compared to most other organic dyes, and thus, they are highly promising in this regard. (i) BODIPY dyes have high extinction coefficients (70 000-80 000 M⁻¹ cm⁻¹) and can easily be modified with any desired functionalities. (ii) Absorption peak can be moved to longer wavelengths through simple modifications, keeping strong absorption cross sections.

2. Results and Discussion

In this work, three different Bodipy dyes have been used to fabricate solid state dye sensitised solar cell. Molecular structures of used materials are below (Bodipy_1, Bodipy_2 and Bodipy_3) in Figure 1. Also absorption spectra of bodipy dyes were presented in Figure 2. Firstly, Bodipy_1 was tested in SDSCs. Dyesol TiO₂ paste without any dilution was used to fabricate solar cell. We have found that V_{oc} = 595 mV, J_{sc} = 0.26 mA/cm², FF= 40.40 %, η = 0.06 % for Bodipy_1 dye. Afterwards, Dyesol paste was diluted with terpineol (1:1 ratio). This diluted Dyesol TiO₂ paste was used to fabricate SDSC for Bodipy_1 dye. After dilution, we have improved the current and efficiency of solar cell. After testing solar cell with diluted TiO₂ paste, J_{sc} and efficiency were found that 0.60 mA/cm², 0.10 %, respectively. Results are shown below.

BODIPY DYES



BODIPY_3

Figure 1. Molecular structures of Bodipy Dyes

We select 3 different Boradiazaindacene dyes to compare the efficiencies to understand which Bodipy dye will give best efficiency in solid state dye sensitized solar cells. Only, boradiazaindacene which consists of cyanoacrilic acid group (Bodipy_2) has been tested in

dye sensitized solar cell with the cell performances of $V_{oc}= 562$ mV, $J_{sc}= 4.03$ mA/cm², FF= 0.735, $\eta= 1.66\%$ in literature [3]. We wanted to test Bodipy_2 also in solid state dye sensitized solar cell. Carboxylic acid group or cyanoacrylic group directly attached to boradiazaindacene core have not been tested both in dye sensitized solar cell with electrolyte system or solid state dye sensitized solar cells. Bodipy_3 dye also consists of long side chain (decyl group) attached to phenyl ring. For this purpose, this study is the novel application to see the efficiencies of boradiazaindacenes in solid state dye sensitized solar cells. All Bodipy dyes absorb in the visible region. Maximum absorption wavelength for Bodipy_2 and Bodipy_3 is approximately 700 nm. Maximum absorption wavelength for Bodipy_1 is 746 nm in Figure2.

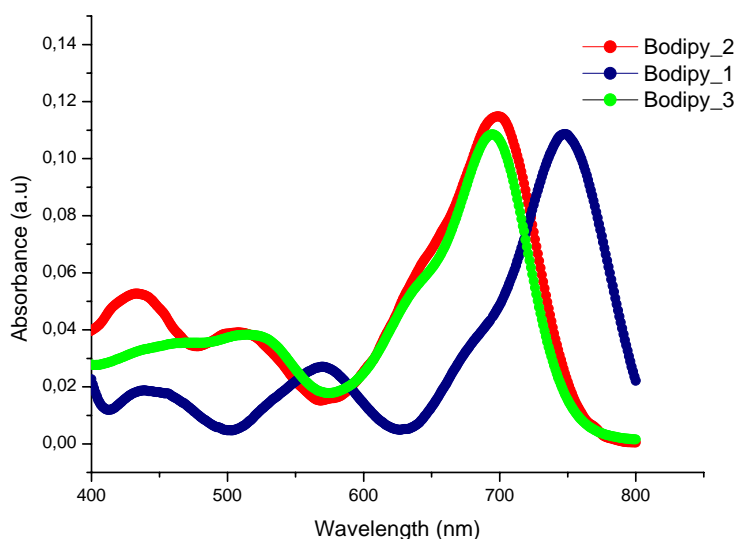


Figure 2. Absorption spectra of Bodipy dyes in CDCl₃ solution, $\epsilon= 47862$ $\lambda=746$ nm for **Bodipy_1**, $\epsilon= 69500$ $\lambda=700$ nm for **Bodipy_2**, $\epsilon= 79000$ $\lambda=695$ nm for **Bodipy_3**, $[c]=5.10^{-6}$ M

Solar Cell preparation was carried out according to literature [20]. After preparation of blocking and porous TiO₂ layer, electrodes were immersed into the 0.5 mM dye solutions which prepared in acetonitrile:tertbutanol (1:1 ratio).

2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-pirobifluorene (spiro-OMeTAD) was used as an organic hole-transporting material (HTM). Afterwards, 50 nm gold electrode was evaporated on top of device.

Solar cells were characterized by current-voltage ($I - V$) measurement. All current-voltage ($I - V$) measurements were done under 100 mW/cm² light intensity and AM 1.5 conditions. 450 W Xenon light source was used to give an irradiance of various intensities.

$I - V$ data collection was made by using Keithley 2400 Source-Meter and LabView data acquisition software. $I - V$ characteristics of dye sensitized solar cell in dark and under illumination is shown in Figures 3-5.

The entire energy conversion efficiency, η , is calculated by means of the following equations;

$$\eta = V_{oc} I_{sc} FF / P_{light}$$

Here, V_{oc} is open circuit voltage (V), I_{sc} is short circuit current (mA/cm^2), FF is fill factor.

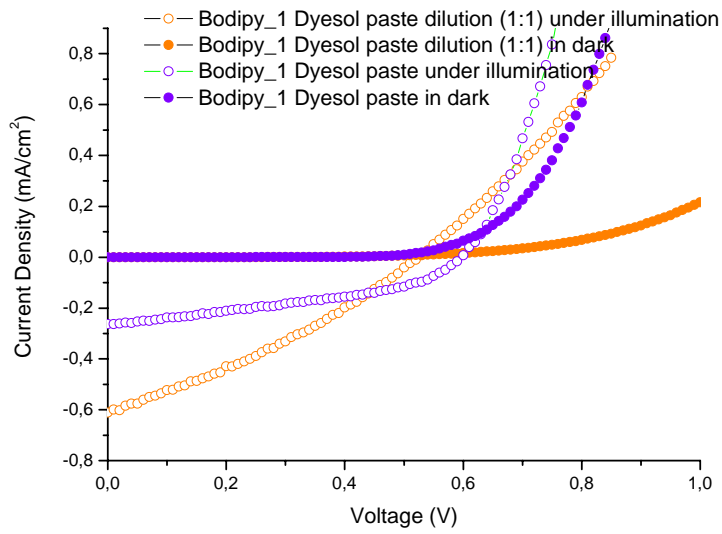
$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}}$$

where, V_{max} and I_{max} are voltage and current at the point of maximum power output of cell.

Firstly, Bodipy_1 dye which comprise carboxylic group tested in solid state dye sensitized solar cell. Dyesol paste was used to fabricate solar cell without any dilution. When I use dyesol paste, we obtained the cell performance with an efficiency of 0.06, a short-circuit photocurrent density (I_{sc}) of $0.26 \text{ mA}/\text{cm}^2$, an open-circuit voltage (V_{oc}) of 595 mV and a fill factor (FF) of 40.40 % in Figure 3 and Table 1. After dilution of the dyesol paste, solar cells have been improved. Dyesol paste was diluted 1:1 ratio. After fabricating solar cell using diluted dyesol paste, the cell performance has been obtained with an efficiency of 0.1, a short-circuit photocurrent density (I_{sc}) of $0.60 \text{ mA}/\text{cm}^2$, an open-circuit voltage (V_{oc}) of 525 mV and a fill factor (FF) of 31.19 % in Figure 3 and Table 1. Also IPCE curves are presented in Figure 3. IPCE curve shows better efficiency with diluted dyesol paste.

After we obtained the best results with diluted dyesol paste, Bodipy_2 dye was tested in solid state dye sensitized solar cell using diluted dyesol paste in Table 2. The cell performance has been obtained with an efficiency of 0.30, a short-circuit photocurrent density (I_{sc}) of $1.22 \text{ mA}/\text{cm}^2$, an open-circuit voltage (V_{oc}) of 635 mV and a fill factor (FF) of 39.30 % in Table 2.

a)



b)

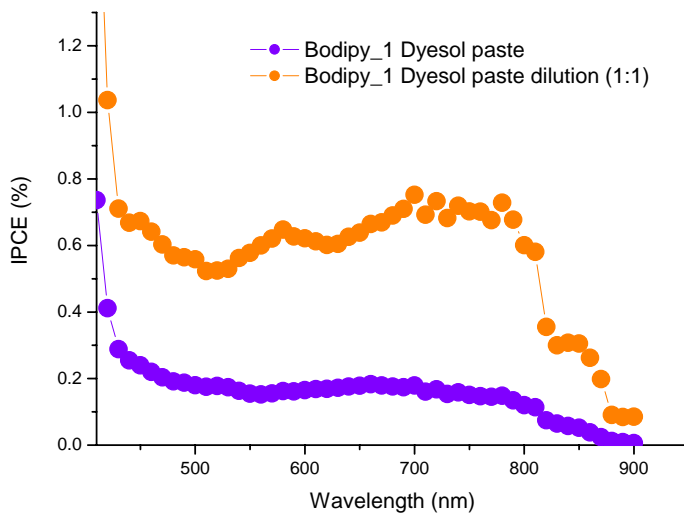


Figure 3. I-V (a) and IPCE (b) spectrum for Bodipy_1 using Dyesol paste with and without dilution

Table 1. V_{oc} , I_{sc} , FF and efficiency values for Bodipy_1 with and without dilution of Dyesol Paste

		V_{oc} (mV)	I_{sc} (mA/cm ²)	FF	Efficiency
Dyesol paste	Bodipy_1	595	0.26	40.40	0.06
Dyesol paste (diluted 1:1 ratio)	Bodipy_1	525	0.60	31.19	0.10

Table 2. V_{oc} , I_{sc} , FF and efficiency values for Bodipy_2 with dilution of Dyesol Paste

		V_{oc} (mV)	I_{sc} (mA/cm ²)	FF	Efficiency
Dyesol paste (diluted 1:1 ratio)	Bodipy_2	635	1.22	39.3	0.30

Afterwards, solaronix paste was used to fabricate solar cell. Figure 6 and Figure 7 show the SEM picture of cells using dyesol paste and solaronix paste. Film thickness of solaronix paste is 2.130 μm . This thickness is suitable for construction solid state dye sensitized solar cell without any dilution. First trial was done by using Bodipy_2. Bodipy_2 dye was solved in chlorobenzene for solid state dye sensitized solar cell fabrication. Voltage, current and efficiency values were increased when we used solaronix paste without any dilution. The cell performance has been obtained with an efficiency of 0.4, a short-circuit photocurrent density (I_{sc}) of 1.81 mA/cm², an open-circuit voltage (V_{oc}) of 715 mV and a fill factor (FF) of 31.20 %. Results are shown below in Table 3.

Table 3. Solid state dye sensitized solar cell efficiency for Bodipy_2 using diluted dyesol paste and solaronix paste without any dilution

		V_{oc} (mV)	I_{sc} (mA/cm ²)	FF	Efficiency
Dyesol paste (diluted 1:1 ratio)	Bodipy_2	635	1.22	39.3	0.30
Solaronix paste without any dilution	Bodipy_2	715	1.81	31.2	0.4

As a result, solaronix paste without any dilution showed good results with Bodipy-2 dye. We have improved the solar cell efficiency using solaronix paste. Therefore we fabricated the solid state solar cells with each of the Bodipy dyes using Solaronix TiO₂ paste. I-V and IPCE curves are shown below. Also, absorption spectrum on TiO₂ film for Bodipy dyes is in Figure 4.

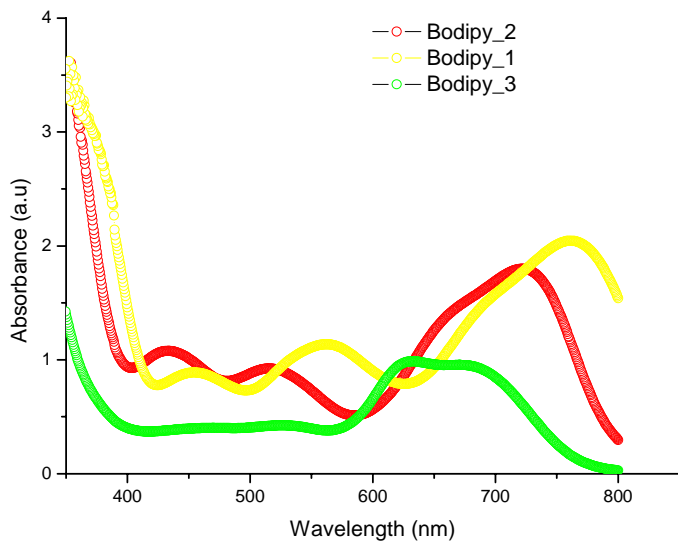
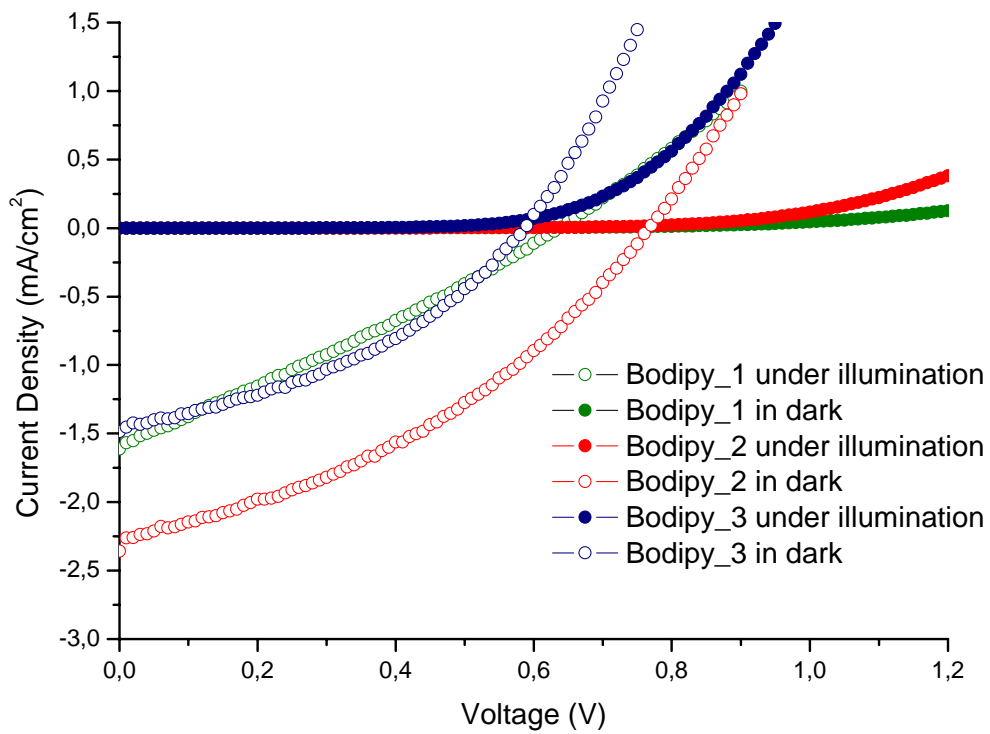


Figure 4. Absorption spectra of Bodipy dyes on TiO₂ films

a)



b)

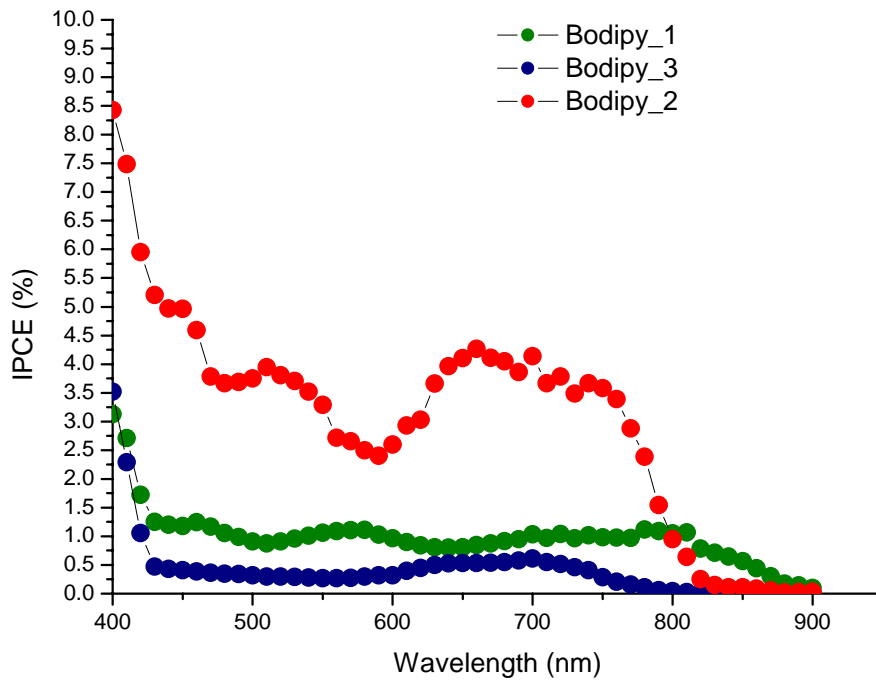


Figure 5. I-V and IPCE spectra for Bodipy dyes using Solaronix TiO₂ paste

As seen in Figure 5 and Table 4, the current densities improve significantly from the dye Bodipy₃ to Bodipy₁ and Bodipy₂, as 1.49 mA/cm², 1.61 mA/cm² and 2.27 mA/cm², respectively. Also V_{oc} values improve significantly from the dye Bodipy₃ to Bodipy₁ and Bodipy₂, as 585mV, 635 mV and 795 mV, respectively. Thus the solar cell with Bodipy₂ sensitizer gives the highest efficiency of 0,68% as compared to the Bodipy₁ and Bodipy₃ sensitizers. This demonstrates the beneficial influence of cyanoacrylic acid side chain attached to phenyl group on the solar cell performance. IPCE curves are presented in Fig. 5. Bodipy₂ gives 4.5 % efficiency in IPCE spectrum using solaronix paste.

In line with these statements, we now report the good efficiency under standard conditions obtained for a Bodipy₂ dye using Solaronix paste without any dilution that performs 795 mV open circuit voltage, 2.27 mA/cm² short-circuit current, 37.43 % fill factor and 0.68 % overall conversion efficiency.

Table 4. Solid state dye sensitized solar cell results for Bodipy dyes using Solaronix TiO₂ paste

TiO ₂ paste	Dye	V _{oc} (mV)	I _{sc} (mA/cm ²)	FF	Efficiency
Solaronix	Bodipy_1	635	1.61	27.56	0.28
Solaronix	Bodipy_2	795	2.27	37.43	0.68
Solaronix	Bodipy_3	585	1.49	37.90	0.33

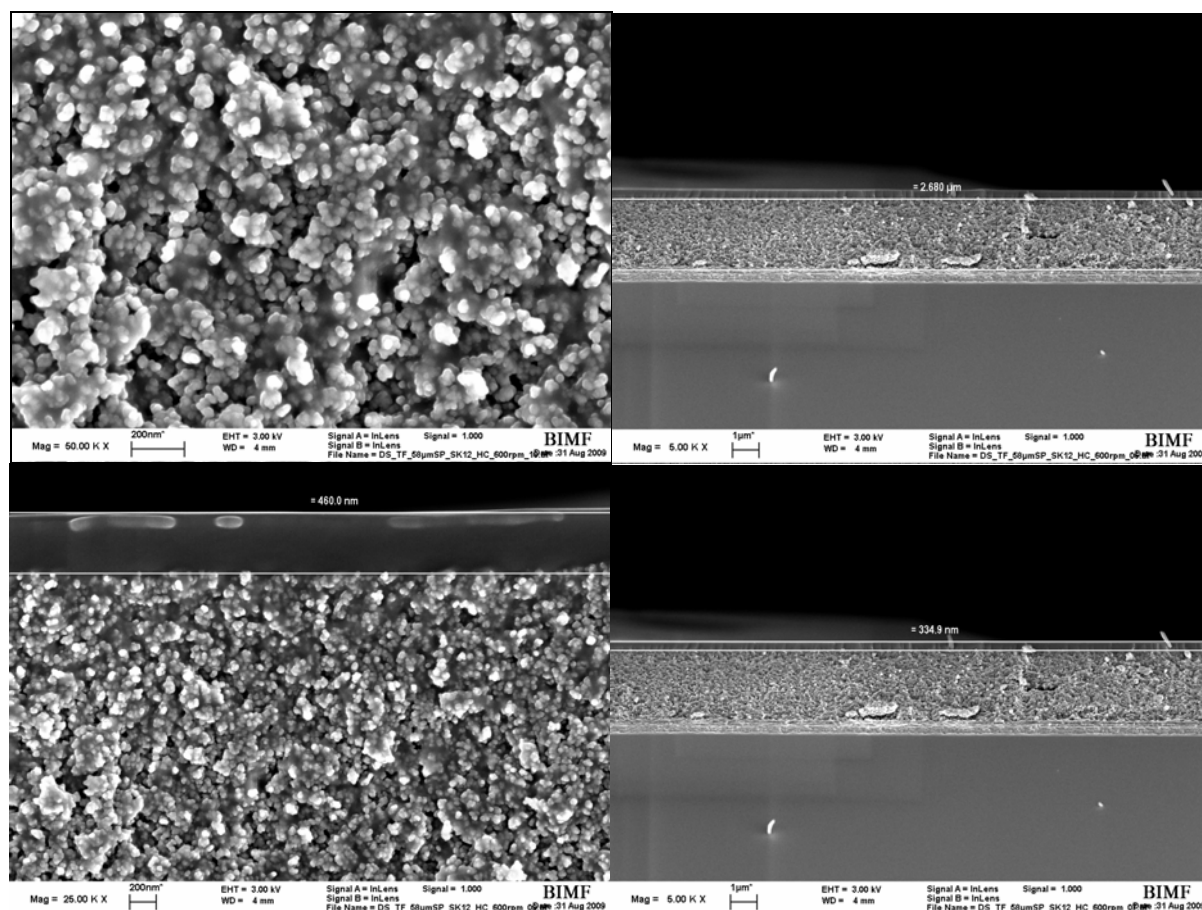


Figure 6. SEM pictures of thin films prepared by the Dyesol TiO₂

Figure 6 shows SEM images of Bodipy_1 using dyesol paste without dilution. The thickness of TiO₂ film is 2.680 μm. Also the thickness of HTM 460 nm. To obtain better efficiency in

solid state dye sensitized solar cells, both the thickness of TiO_2 and hole transport material (HTM) must be prepared thinner. Because of that reason we have diluted the Dyesol paste with the ratio of 1:1. Efficiency of the cells were improved in Figure 3.

When we fabricated the solar cell using Solaronix paste, we have obtained better results than dyesol paste. The SEM images of Bodipy_2 was shown below (Figure 7). The thickness of TiO_2 film is $2.130 \mu\text{m}$. This thickness is suitable for fabrication solid state dye sensitised solar cell without any dilution. The thickness of HTM is 250 nm . Efficiencies of solar cell using solaronix paste were increased in Figure 5 and Table 3.

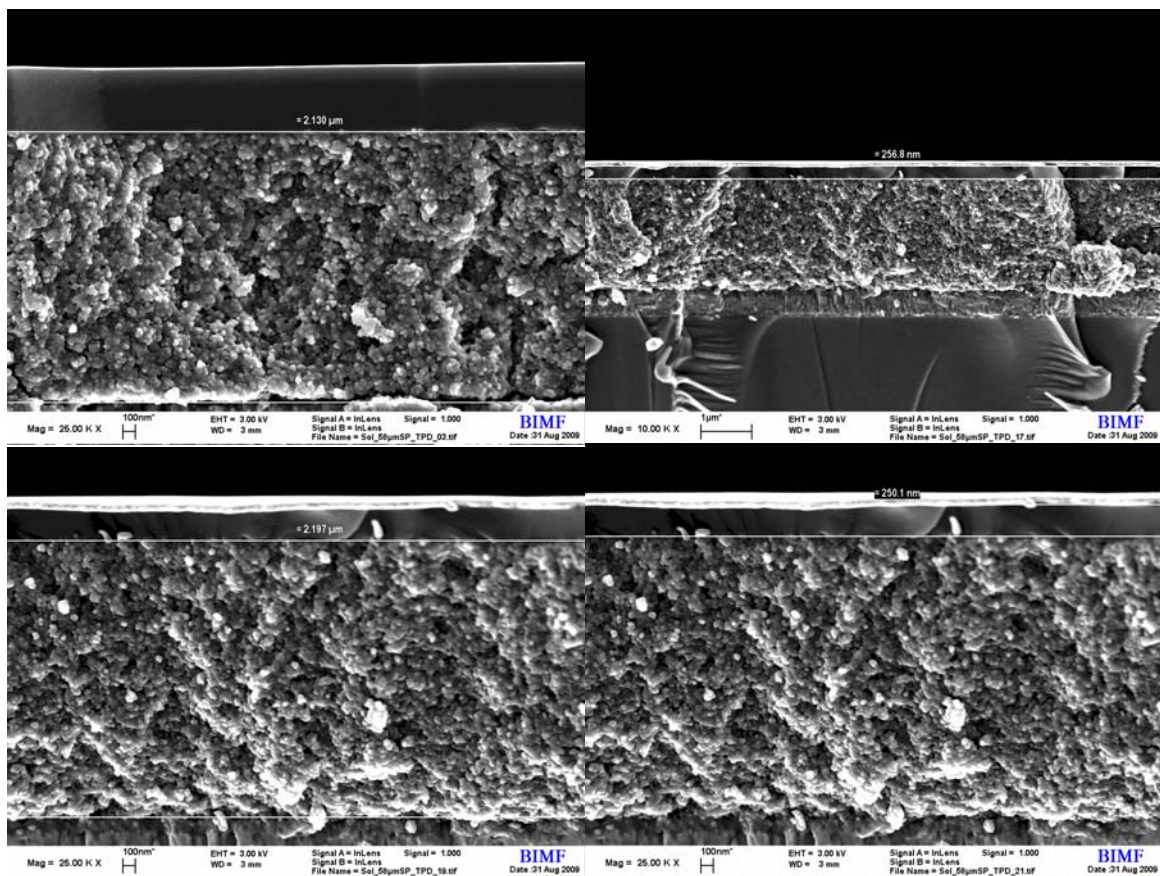


Figure 7. SEM pictures of thin films prepared by the Solaronix TiO_2 .

3. Synthesis and Characterization of BODIPY dyes

3.1. Synthesis and Characterization of Bodipy_1

3.1.1. Synthesis of SK_04

To a 1 L round-bottomed flask containing 400 mL argon-degassed CH_2Cl_2 were added 2-methyl pyrrole (12.3 mmol, 1.0 g) and 4-carboxybenzaldehyde (6.0 mmol, 0.9 g). One drop of TFA was added and the solution was stirred under N_2 at room temperature for 1 day. After addition of a solution of DDQ (6.0 mmol, 1.36 g) in 100 mL of dichloromethane to the reaction mixture, stirring was continued for 30 min. 5 mL of Et_3N and 5 mL of $\text{BF}_3 \cdot \text{OEt}_2$ were successively added and after 30 min, the reaction mixture was washed three times with water (50 x 100 mL) which was then extracted into the CHCl_3 (3 x 100 mL) and dried over anhydrous Na_2SO_4 . The solvent was evaporated and the residue was purified by silica gel column chromatography using (CHCl_3 : MeOH 95:5) as the eluant. Red solid (1.25 g, 30%). ^1H NMR (400 MHz, CDCl_3): δ_{H} 8.25 (2H, d, $J = 7.6$ Hz, ArH), 7.65 (2H, d, $J = 7.7$ Hz, ArH), 6.70 (2H, s, ArH), 6.30 (2H, d, $J = 3.4$ Hz, ArH), 2.70 (6H, s, CH_3). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} 170.5, 158.5, 140.9, 139.4, 134.5, 130.6, 130.5, 130.2, 130.0, 119.9, 15.0 ppm;

3.1.2. Synthesis of Bodipy_1

SK-04 (0.88 mmol, 0.30 g) and *N,N*-di(4-methoxyphenyl)aminobenzaldehyde (3.53 mmol, 1.18 g) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC (CHCl_3 : MeOH 93:7): When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over Na_2SO_4 , evaporated and residue was purified by silica gel column chromatography using (CHCl_3 : MeOH 93:7) as the eluant. Black waxy solid (0.17 g, 20%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ_{H} 8.25 (1H, s, COOH), 8.05 (2H, d, $J = 8.3$ Hz, ArH), 7.64 (2H, d, $J = 8.2$ Hz, ArH), 7.52 (2H, d, $J = 17.2$ Hz, CH), 7.38 (4H, d, $J = 8.7$ Hz, ArH), 7.32 (2H, d, $J = 15.2$ Hz, CH), 7.15 (2H, d, $J = 4.6$ Hz, ArH), 7.10-7.05 (8H, m, ArH), 6.95-6.85 (12H, m, ArH), 6.78 (2H, d, $J = 4.6$ Hz, ArH), 6.72 (4H, d, $J = 8.5$ Hz, ArH). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ_{C} 167.5, 156.9, 154.9, 150.2, 139.5, 138.2, 137.8, 135.4, 132.6, 131.0, 129.9, 129.8, 129.6, 129.3, 129.1, 128.0, 127.7, 120.2, 118.4, 117.6, 115.5, 55.7 ppm;

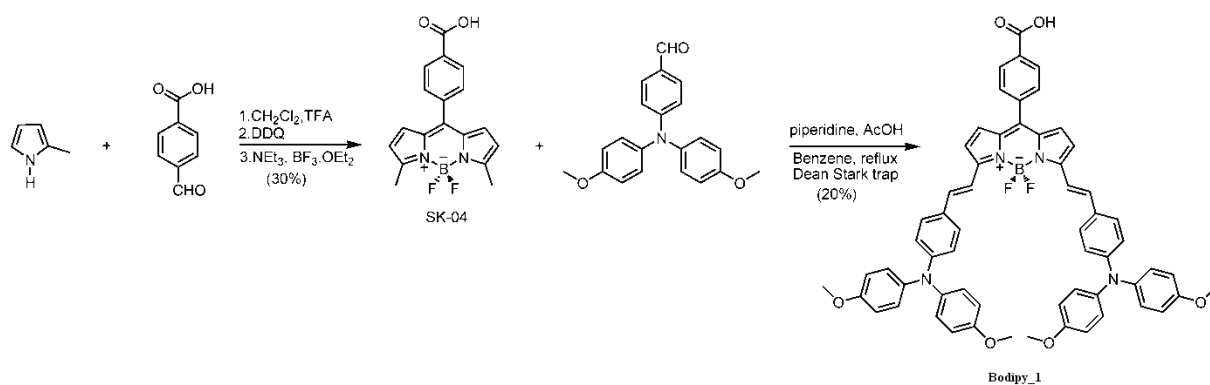


Figure 8. Synthetic route of the synthesis of Bodipy_1

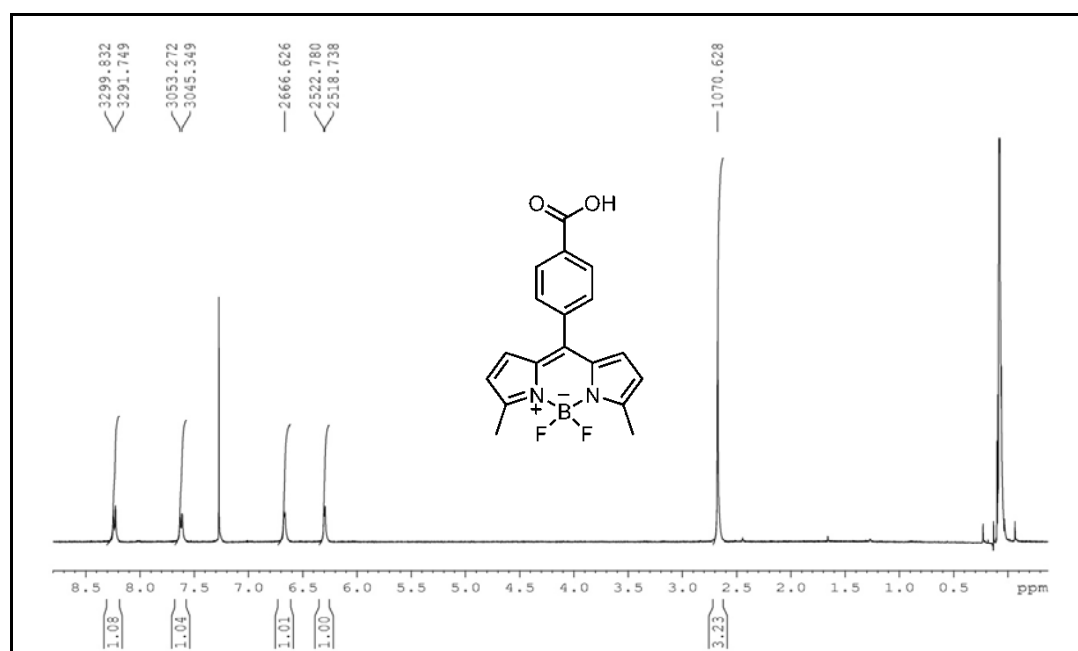


Figure 9. ^1H NMR spectrum of SK-04

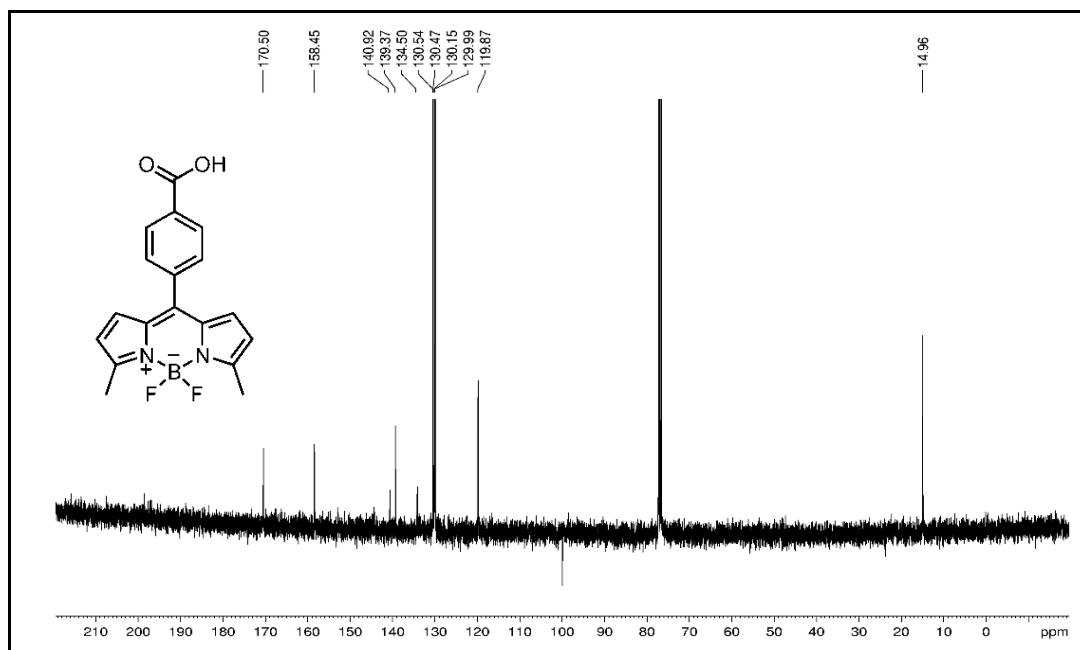


Figure 10. ^{13}C NMR spectrum of SK-04

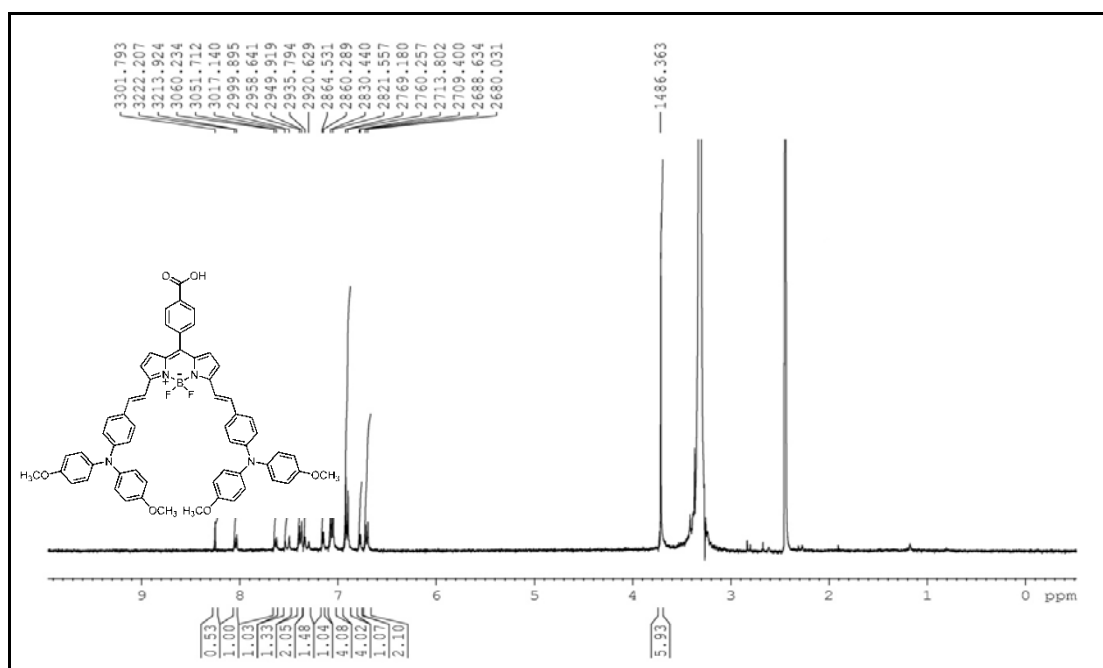


Figure 11. ^1H NMR spectrum of Bodipy_1

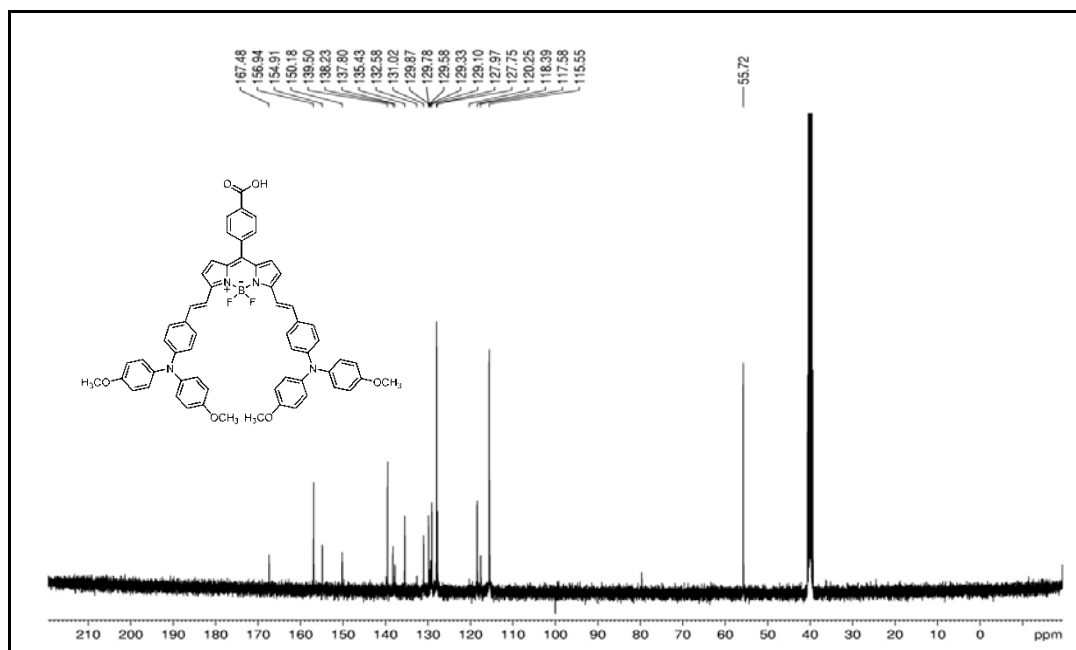


Figure 12. ¹³C NMR spectrum of Bodipy_1

3.2. Synthesis and Characterization of Bodipy_2

3.2.1. Synthesis of compound 4

2,4-dimethyl-3-ethylpyrrole (7.4 mmol, 0.912 g) and 4-dioxolanylbenzaldehyde (**S1**, 3.7 mmol, 0.66g) were dissolved in absolute CH₂Cl₂ (200 ml) (Argon gas was bubbled through CH₂Cl₂ for 30 min.) under Ar atmosphere. One drop of TFA was added and the solution was stirred at rt nearly 3-4 h. At this point, a solution of DDQ (3.7 mmol, 0.91 g) in 50 ml absolute CH₂Cl₂ was added, stirring was continued overnight followed by the addition of 3 ml of Et₃N and 3 ml of BF₃.OEt₂. After 30 min the reaction mixture was washed 3 times with water and dried over Na₂SO₄. The solvent was evaporated to dryness and the residue was purified by silica gel column chromatography (CHCl₃). Red solid (1.11 mmol, 0.5 g, 30%).

¹H NMR (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.95 Hz, 2H), 7.24 (d, *J* = 7.95 Hz, 2H), 5.79 (s, 1H), 4.11 (dd, *J* = 6.86 Hz, 1H), 4.09 (dd, *J* = 3.13 Hz, 1H), 4.01 (dd, *J* = 3.2 Hz, 1H), 3.99 (dd, *J* = 6.88 Hz, 1H), 2.45 (s, 6H), 2.22 (q, *J* = 7.58 Hz, 4H), 1.19 (s, 6H), 0.90 (t, *J* = 7.54 Hz, 6H).
¹³C NMR (100 MHz, CDCl₃) δ 153.8, 139.6, 138.6, 138.3, 136.7, 132.8, 130.7, 128.3, 127.2, 103.4, 65.3, 17.0, 14.5, 12.4, 11.8; FAB-HRMS calcd for 452.24, found 475.2343 (M+Na) Δ = 0.2 ppm

3.2.2. Synthesis of compound 6

Compound **4** (1.11 mmol, 0.5 g) and 4-(diphenylamino)benzaldehyde (**5**, 11.1 mmol, 3.0 g) were refluxed in a mixture of benzene (50 ml), glacial acetic acid (0.5 ml) and piperidine (0.6

ml). Any water formed during the reaction was removed azeotropically by heating for 2h in a dean-stark apparatus. Crude product was then concentrated under vacuum, and purified by silica gel column chromatography (CHCl₃). The green colored fraction was collected and the solvent was removed under reduced pressure to yield the green solid (0.654 mmol, 630 mg, 59%).

¹H NMR (400 MHz, CDCl₃) δ 7.60-7.50 (m, 4H), 7.40 (d, J= 8.56 Hz, 4H), 7.27 (d, J= 7.93 Hz, 2H), 7.20-7.15 (m, 8H), 7.10-7.05 (m, 9H), 7.00-6.95 (m, 9H), 5.81 (s, 1H), 4.13 (dd, J= 7.01 Hz, 1H), 4.11 (dd, J= 3.10 Hz, 1H), 4.03 (dd, J= 3.01 Hz, 1H), 4.00 (dd, J= 6.9 Hz, 1H), 2.52 (q, J= 7.49 Hz, 4H), 1.23 (s, 6H), 1.06 (t, J= 7.44 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 147.2, 146.3, 137.5, 134.2, 132.7, 131.9, 130.4, 128.3, 128.1, 127.8, 127.3, 126.2, 123.8, 123.1, 122.3, 122.0, 121.6, 117.3, 110.6, 102.4, 64.3, 17.3, 13.0, 10.6; FAB-HRMS calcd for 962.45, found 985.4423 (M+Na) Δ= 1.7 ppm

3.2.3.Synthesis of compound 7

Compound **6** (0.2 mmol, 200 mg) was dissolved in THF (100 ml) containing 50 ml of 5% HCl. After 20h at 25°C, the solvent was removed under reduced pressure and residue was purified by silica gel column chromatography (CHCl₃). Green solid (0.145 mmol, 133.6 mg, 70%). ¹H NMR (400 MHz, CDCl₃) δ 10.05 (s, 1H), 7.95 (d, J= 7.99 Hz, 2H), 7.59 (d, J= 16.64 Hz, 2H), 7.47 (d, J= 7.92 Hz, 2H), 7.40 (d, J= 8.30 Hz, 4H), 7.20-7.15 (m, 8H), 7.10-7.05 (m, 9H), 7.10-6.95 (m, 9H), 2.52 (q, J= 7.04 Hz, 4H), 1.21 (s, 6H), 1.07 (t, J= 7.42 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 191.5, 148.5, 147.2, 136.5, 131.2, 130.2, 129.3, 129.2, 128.4, 124.9, 124.1, 123.4, 122.8, 122.6, 118.1, 117.3, 114.9, 112.6, 18.3, 14.1, 11.6; FAB-HRMS calcd for 918.43, found 941.4180 (M+Na) Δ= 0.2 ppm

3.2.4.Synthesis of Bodipy_2

An acetonitrile solution of compound **7** (0.11 mmol, 100 mg) and cyanoacetic acid (0.11 mmol, 9.36 mg) was refluxed in the presence of catalytic amount of piperidine for 5h. Crushed ice was added to the cold reaction mixture, and the resulting solid was filtered and washed with water. The residue was purified by silica gel column chromatography (20% MeOH : CHCl₃). Dark green solid (0.0825 mmol, 81 mg, 75%).

¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, J= 8.18 Hz, 2H), 8.00 (s, 1H), 7.55-7.50 (m, 8H), 7.40-7.30 (m, 9H), 7.27 (d, J= 16.67 Hz, 1H), 7.15-7.05 (m, 12H), 6.99 (d, J= 8.64 Hz, 4H), 2.61 (q, J= 7.38 Hz, 4H), 1.24 (s, 6H), 1.10 (t, J= 7.40 Hz, 6H). FAB-HRMS calcd for C₆₅H₅₄BF₂N₅O₂+Na⁺ 1008.4236, found 1008.4236 (M+Na) Δ= 0.0 ppm. Elemental analysis calcd for C₆₅H₅₄BF₂N₅O₂ C: 79.18, H 5.52, N 7.10; found: C: 79.03, H 5.54, N 6.99.

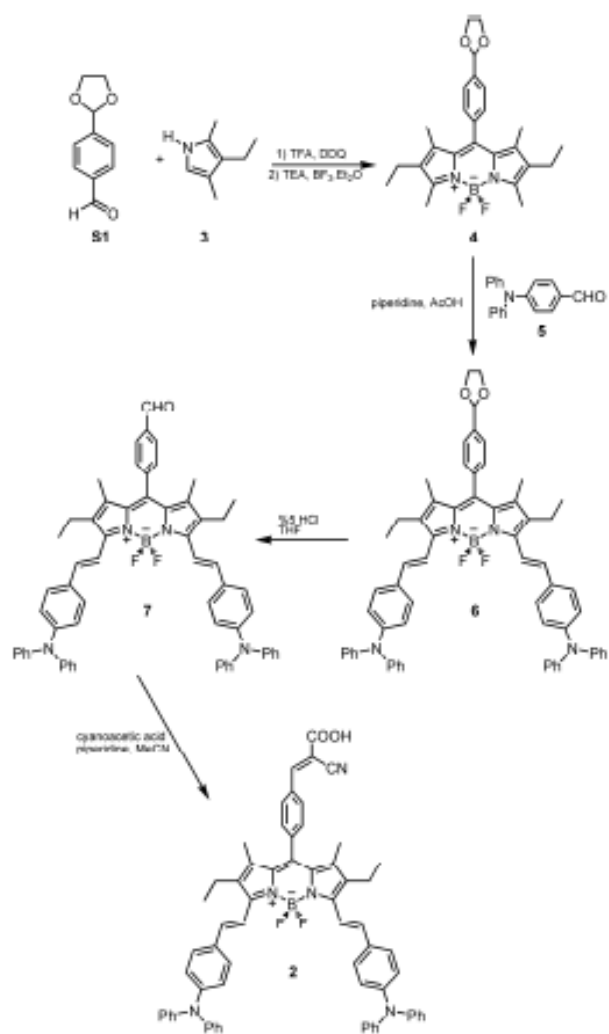


Figure 13. Synthetic route of synthesis of Bodipy_2

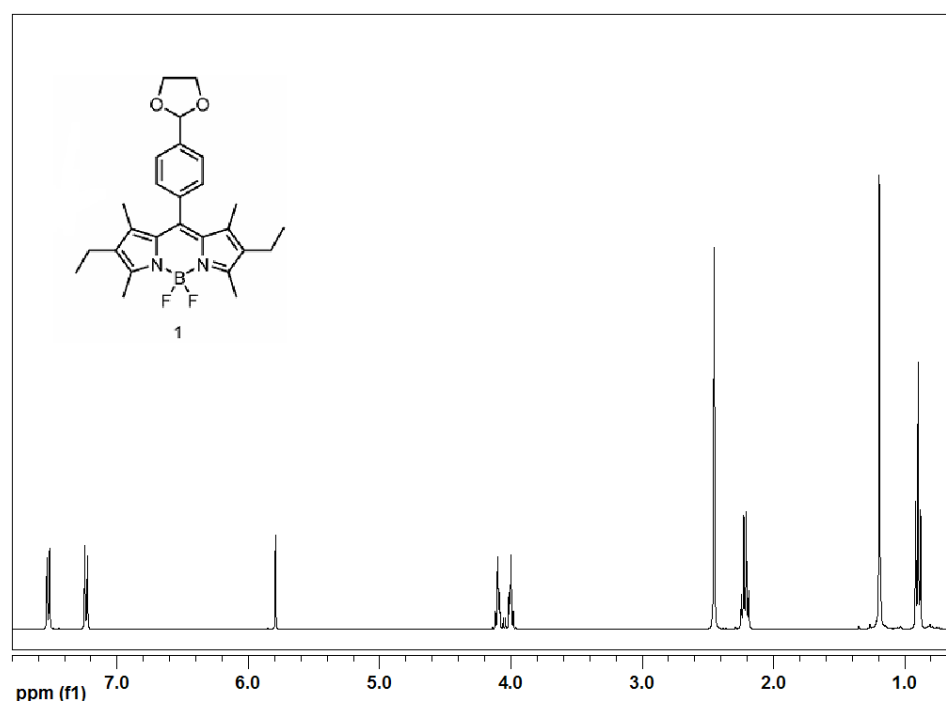


Figure 14. ^1H NMR Spectrum of compound 4

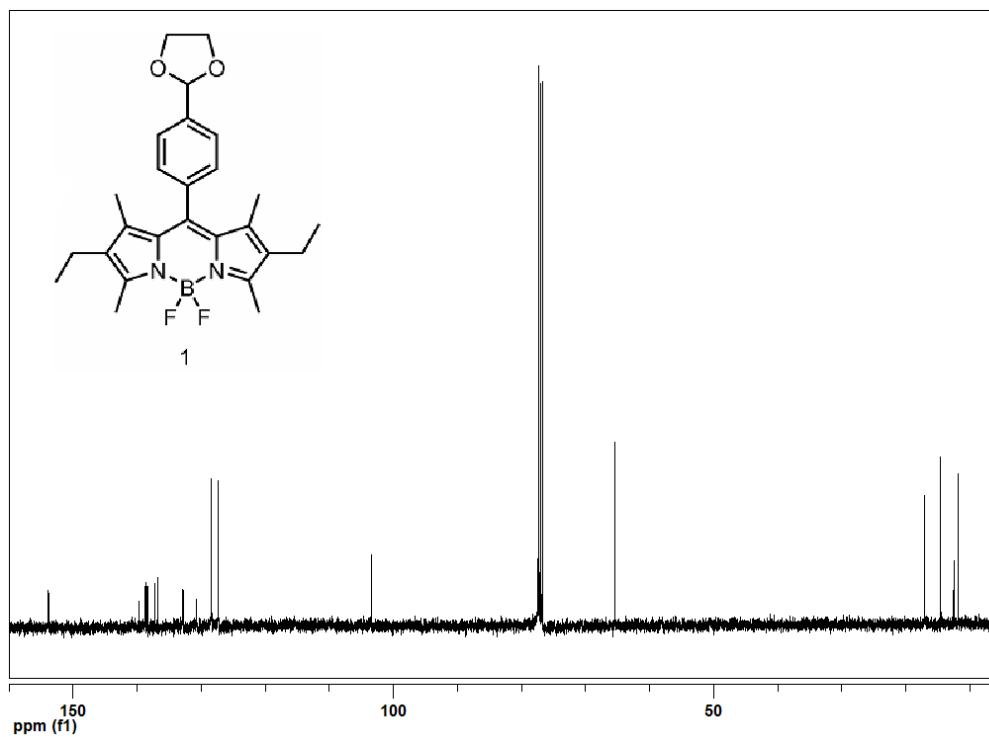


Figure 15. ^{13}C NMR Spectrum of compound 4

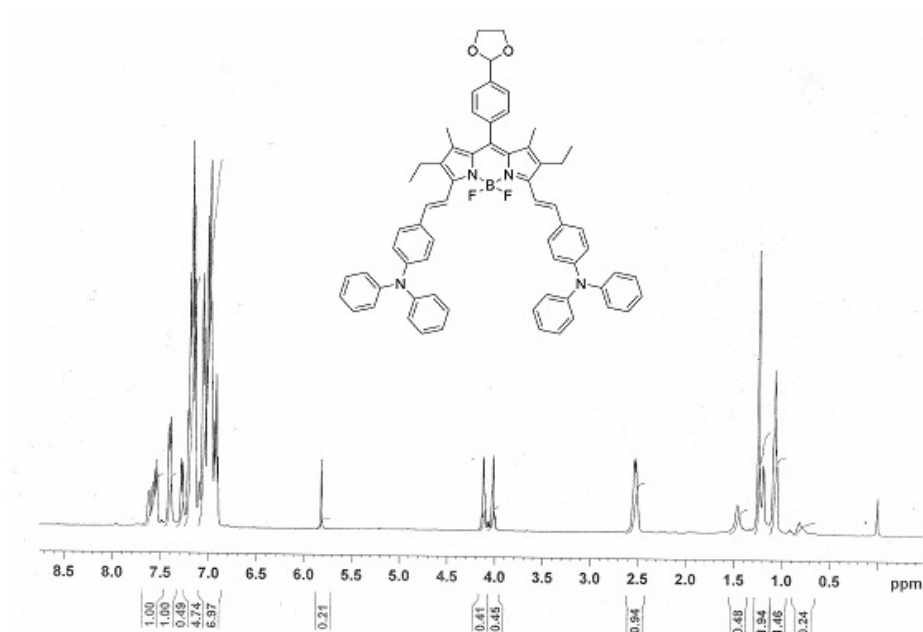


Figure 16. ^1H NMR Spectrum of compound 6

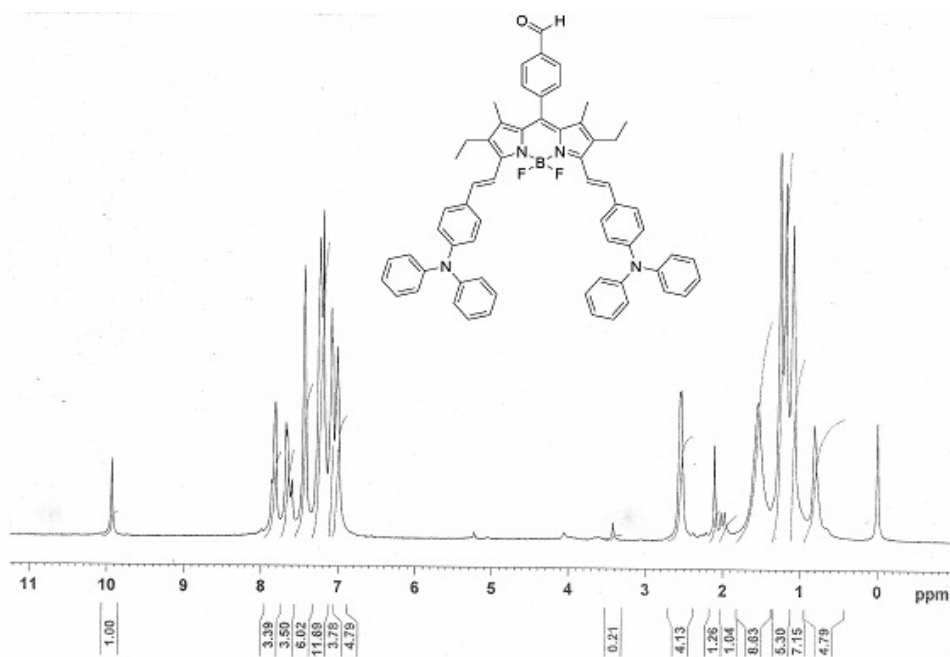


Figure 17. ¹H NMR Spectrum of compound 7

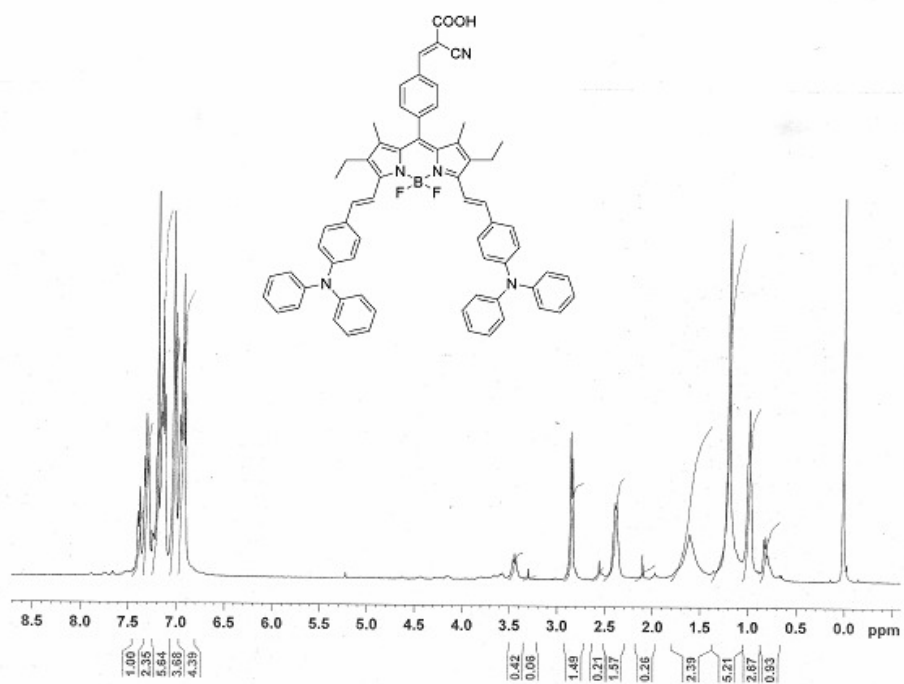


Figure 18. ¹H NMR Spectrum of Bodipy_2

3.3. Synthesis and Characterization of Bodipy_3

3.3.1. Synthesis of Formillated Bodipy derivative

A mixture of DMF (6 mL) and POCl₃ (6 mL) was stirred under argon for 5 min in the ice bath. After warming solution up to rt, it was stirred for additional 30 min. decylBOD (0.50 mmol, 158.0 mg) in 60 mL dichloroethane was added to the solution and temperature raised to 50^oC. After stirring for 2 h, the mixture was cooled to rt and then poured in to iced cooled saturated aqueous solution of NaHCO₃ (150 mL). Then reaction mixture was stirred for 30 min after warming solution to rt. After 30 min. the mixture was washed with H₂O (2x100 mL). The product was extracted into the dichloromethane. Organic phase dried over Na₂SO₄. Reddish-brown solid was obtained (157.0 mg, 89%). ¹H NMR (400 MHz, CDCl₃, 300K) : δ_H 10.02 (s, 1H, CHO), 6.58 (t, 1H, *J*=2.61 Hz, ArH), 6.41 (d, 2H, *J*=2.20 Hz, ArH), 6.15 (s, 1H, ArH), 3.92 (t, 4H, *J*=6.60 Hz, OCH₂), 2.81 (s, 3H, CH₃), 2.60 (s, 3H, CH₃), 1.85 (s, 3H, CH₃), 1.75 (m, 4H, CH₂), 1.42 (m, 4H, CH₂), 1.40-1.15 (m, 24H, CH₂), 0.85 (t, 6H, *J*=6.68 Hz, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ_C 185.8, 161.4, 156.4, 147.3, 143.5, 142.9, 135.5, 133.8, 130.8, 129.5, 128.8, 126.3, 123.8, 106.1, 102.5, 68.5, 31.9, 29.5, 29.3, 29.1, 26.0, 22.7, 15.0, 14.7, 14.1, 13.0, 11.5;

3.3.2. Synthesis of Bodipy derivative consisting of cyanoacrylic acid group

Formillated bodipy derivative (0.12 mmol, 83.0 mg) and cyanoacetic acid (0.49 mmol, 42.3 mg) were dissolved in toluene. One drop of piperidine and catalytic amount of acetic acid were added to the mixture under argon atmosphere. The reaction mixture was refluxed and stirred under argon for 3 h. Then mixture washed with water (2x50 mL). Organic phase dried over Na₂SO₄ and solvent was evaporated and the residue was purified by silica gel column chromatography using (CHCl₃ : MeOH 90:10) as the eluant. Red solid was obtained (50.0 mg, 57%). ¹H NMR (400 MHz, CDCl₃): δ_H 8.18 (1H, s, CH), 6.55 (1H, s, ArH), 6.41 (2H, d, *J* = 1.9 Hz, ArH), 6.08 (1H, s, ArH), 3.91 (4H, t, *J* = 6.5 Hz OCH₂), 2.57 (6H, s, CH₃), 1.80-1.68 (4H, m, CH₂), 1.63 (3H, s, CH₃), 1.59 (3H, s, CH₃), 1.48-1.37 (4H, m, CH₂), 1.45-1.18 (24H, m, CH₂), 0.86 (6H, t, *J* = 6.8 Hz CH₃). ¹³C NMR (100 MHz, CDCl₃): δ_C 161.4, 153.7, 142.8, 140.6, 135.6, 133.4, 130.8, 123.9, 123.3, 106.1, 102.6, 68.5, 31.9, 29.6, 29.4, 29.3, 29.1, 25.9, 14.6, 14.1 ppm;

3.3.3. Synthesis of Bodipy_3

Bodipy derivative consisting of cyanoacrylic acid group (0.12 mmol, 90.0 mg) and N,N-diphenylaminobenzaldehyde (0.37 mmol, 100.9 mg) were added to a 100 mL round-bottomed flask containing 50 mL benzene and to this solution was added piperidine (0.3 mL) and acetic

acid (0.3 mL). The mixture was heated under reflux by using a Dean Stark trap and reaction was monitored by TLC (CHCl₃ : MeOH 93:7). When all the starting material had been consumed, the mixture was cooled to room temperature and solvent was evaporated. Water (100 mL) added to the residue and the product was extracted into the chloroform (3 x 100 mL). Organic phase dried over Na₂SO₄, evaporated and residue was purified by silica gel column chromatography using (CHCl₃: MeOH 93:7) as the eluant. Green solid was obtained (52.2 mg, 35%). ¹H NMR (400 MHz, CDCl₃): δ_H 8.24 (1H, s, CH), 7.61-7.52 (1H, m, CH), 7.47 (2H, d, *J* = 8.0 Hz, ArH), 7.33-7.24 (6H, m, ArH), 7.21-7.08 (12H, m, ArH), 7.04-6.93 (8H, m, ArH), 6.90-6.69 (4H, m, ArH), 6.62 (1H, s, ArH), 6.46 (2H, s, ArH), 3.92-3.61 (4H, m, OCH₂), 1.89-1.54 (4H, m, CH₂), 1.52-1.49 (4H, m, CH₂), 1.48-1.12 (30H, m, CH₂, CH₃), 0.91-0.74 (6H, m, CH₃). ¹³C NMR (100 MHz, CDCl₃): δ_C 161.1, 148.5, 147.1, 147.0, 139.0, 136.4, 132.7, 129.4, 129.3, 128.9, 128.6, 125.4, 125.1, 124.8, 123.7, 123.3, 122.6, 122.3, 117.0, 106.8, 68.4, 31.9, 29.6, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.7, 14.5, 14.1 ppm;

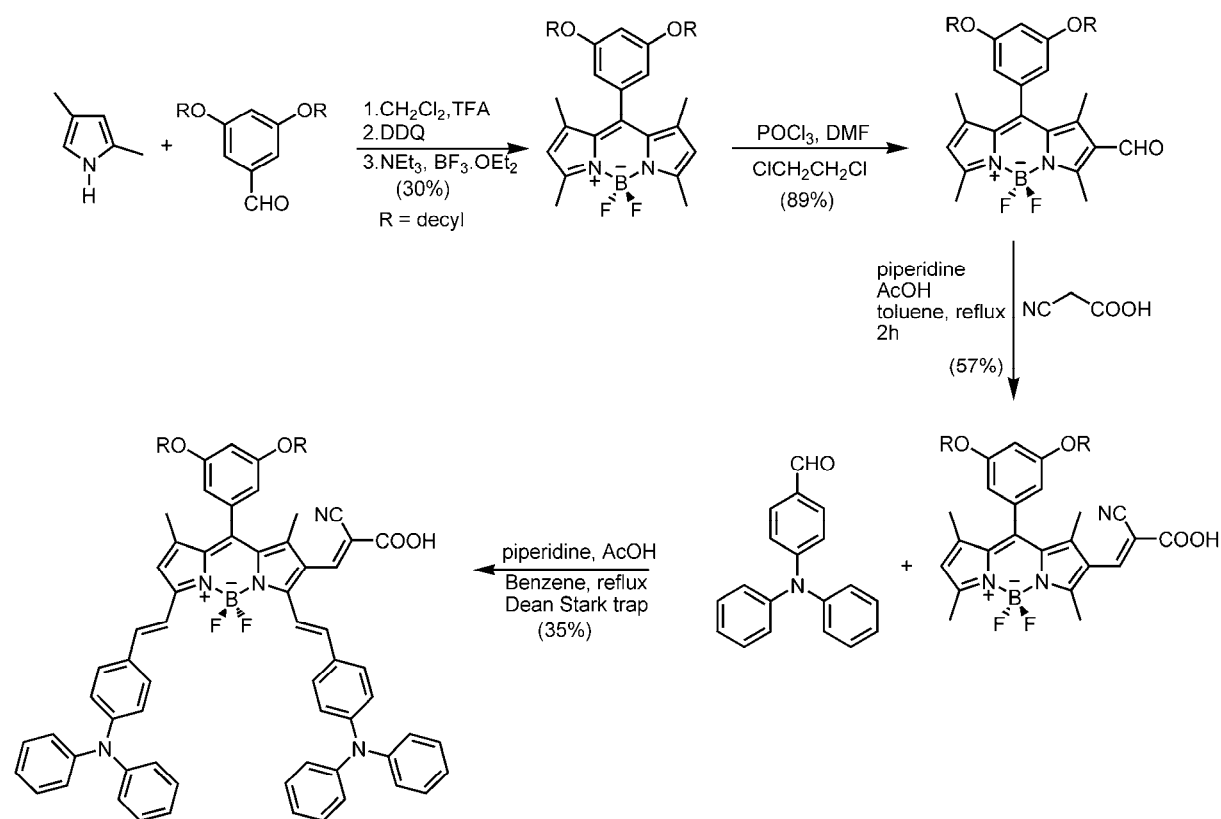


Figure 19. Synthetic route of the synthesis of Bodipy₃

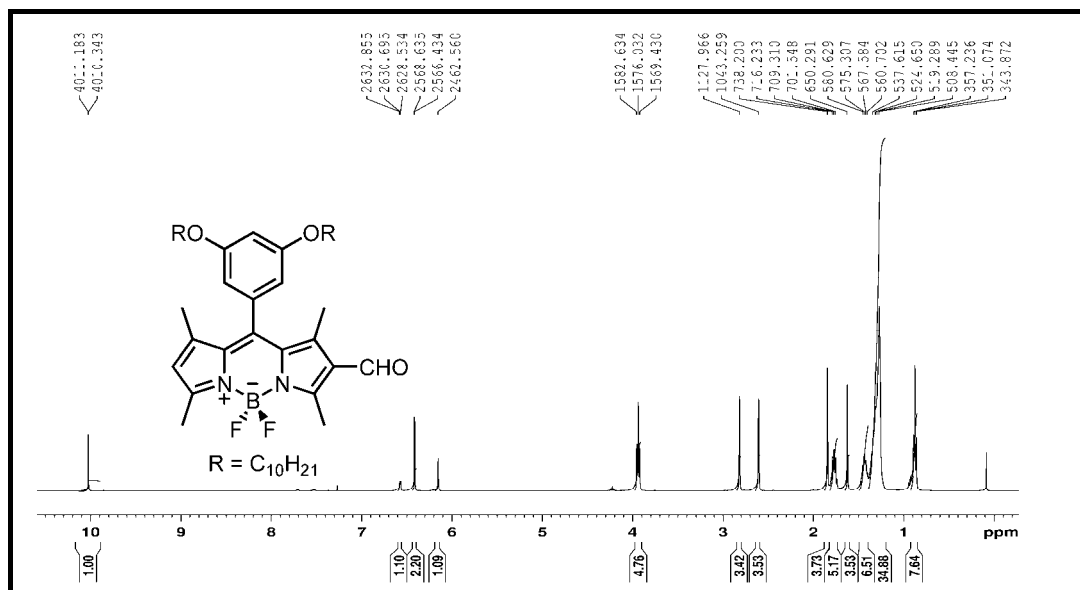


Figure 20. 1H NMR Spectrum of formillated bodipy

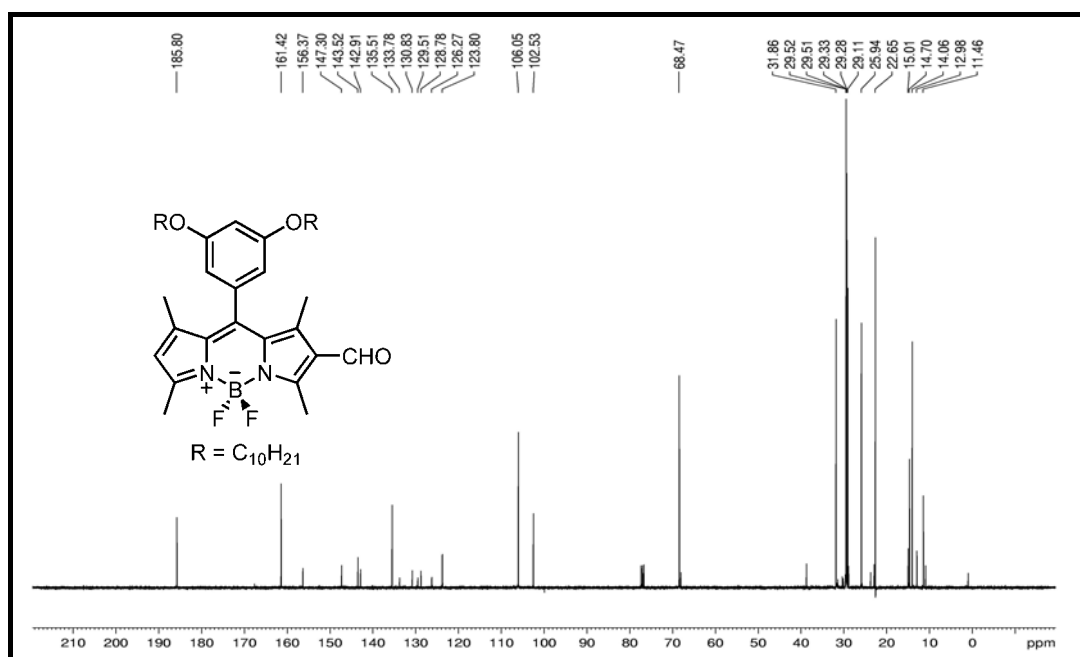


Figure 21. ^{13}C NMR Spectrum of formillated bodipy

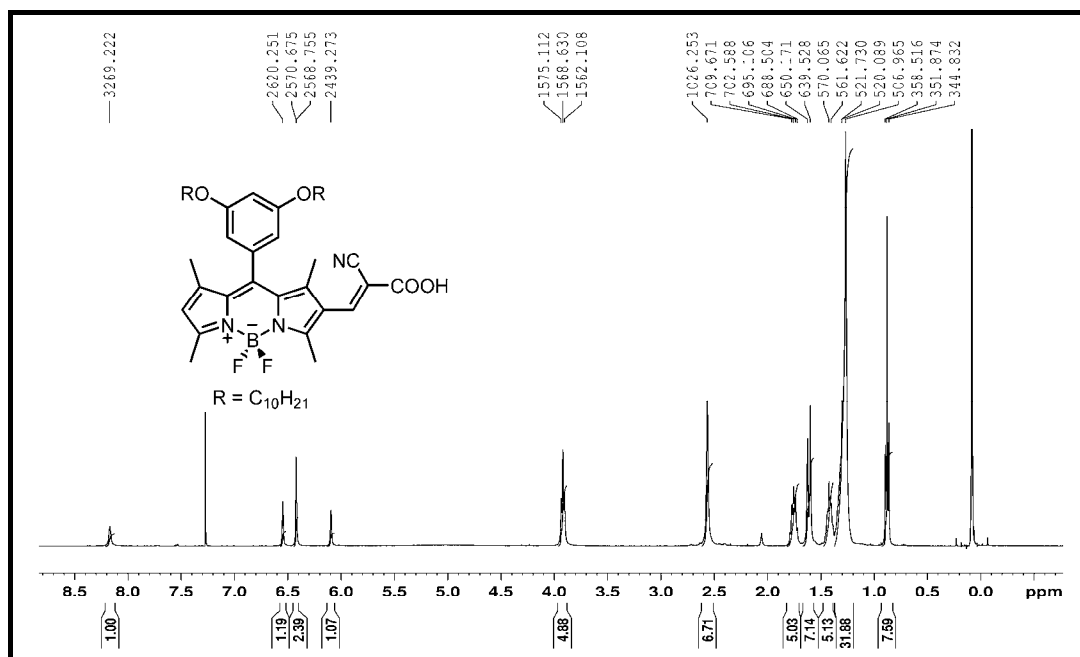


Figure 22. ¹H NMR Spectrum of Bodipy derivative consisting of cyanoacrylic acid group

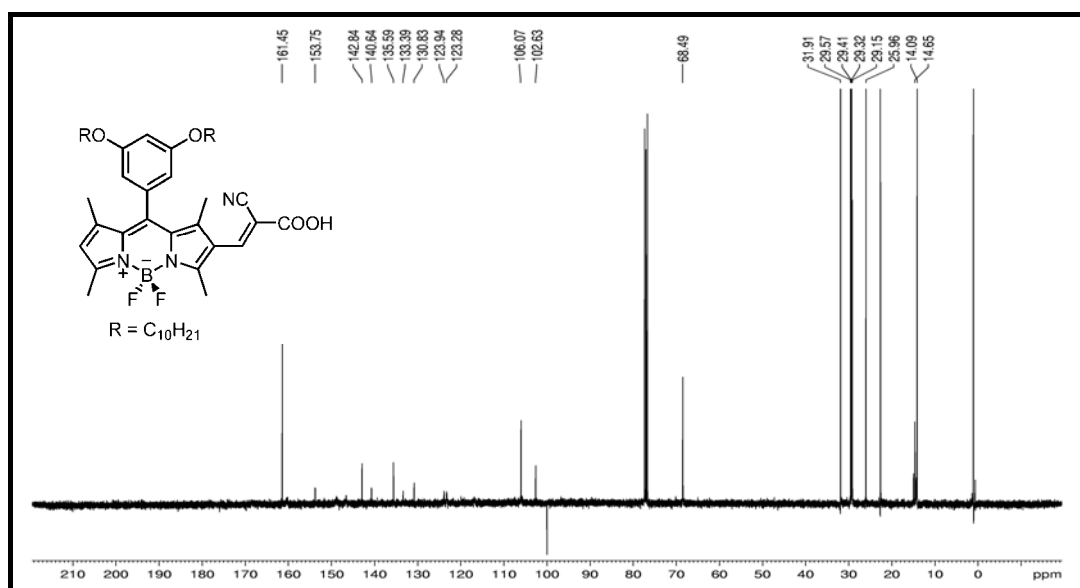


Figure 23. ¹³C NMR Spectrum of Bodipy derivative consisting of cyanoacrylic acid group

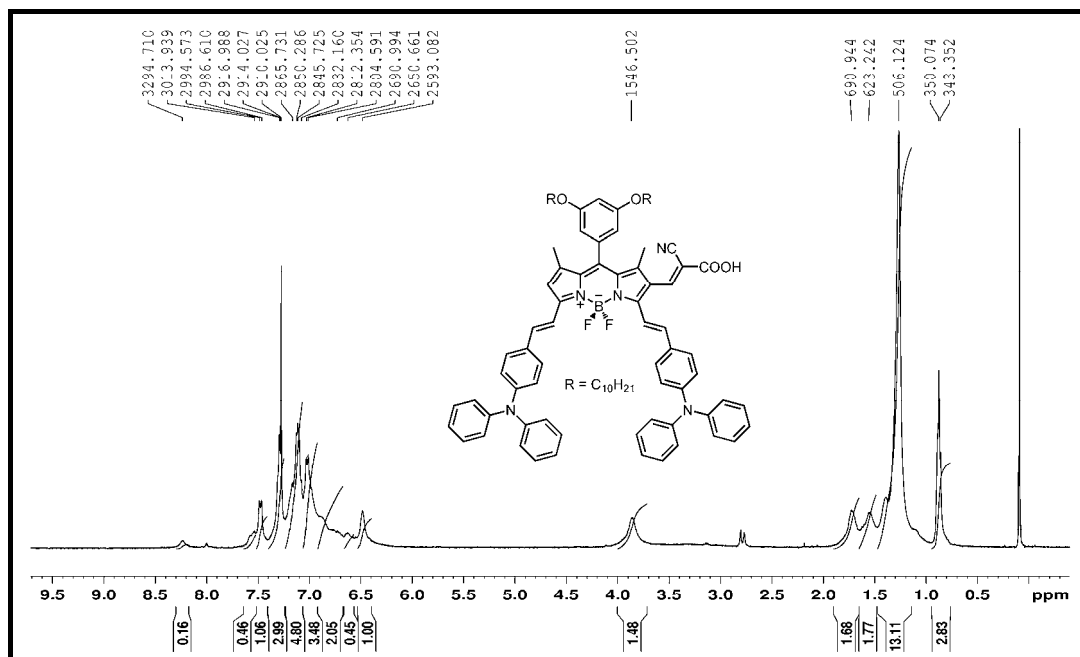


Figure 24. ¹H NMR Spectrum of Bodipy_3

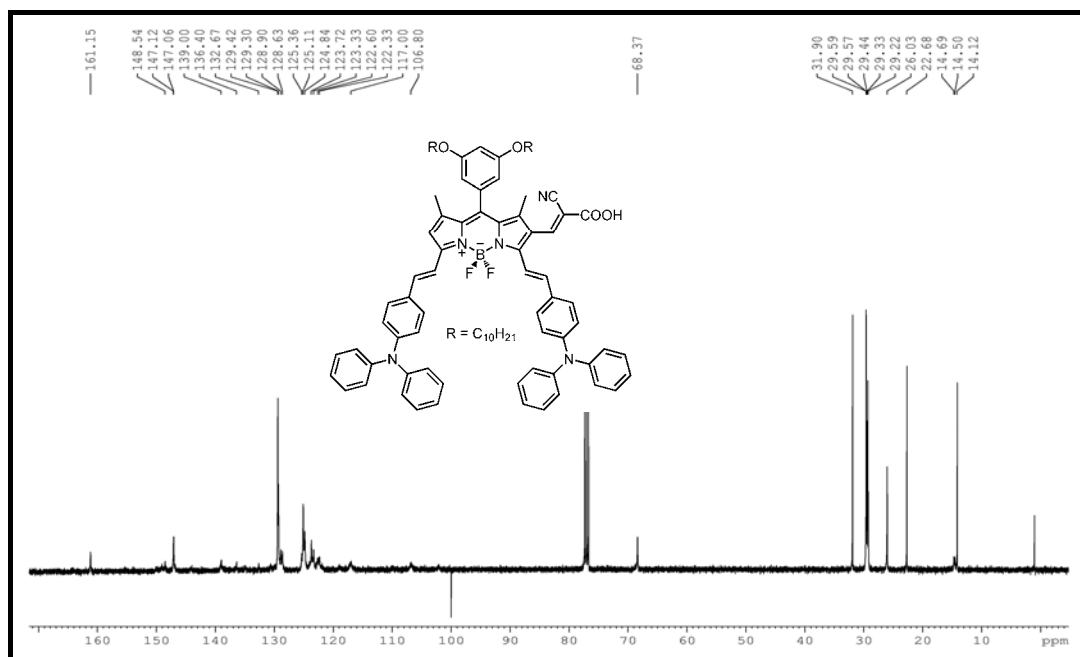


Figure 25. ¹³C NMR Spectrum of Bodipy_3

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