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Synthesis and dye sensitized solar cell applications of Bodipy derivatives with bis-dimethylfluorenyl amine donor groups†

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Three Bodipy dyes with strong absorptivities in the visible and near infrared regions were designed, synthesized and their potential as photosensitizers for liquid electrolyte-based dye sensitized solar cells have been evaluated. For the first time Bodipy derivatives with bis-dimethylfluorenyl amine donor groups which were known for their bulky structures as donor groups have been used together. We altered our mostly used triphenylamine group with these and investigated the dye-sensitized solar cell efficiencies of this new class of Bodipy dyes.

Introduction

The dye-sensitized solar cell (DSSC) concept is thought of as an important alternative to the traditional semiconductor based solar cells because of the limits and problems of these widely used constructs.¹ An important part of this emerging field is the choice of sensitizer.² Bodipy dyes which we use in our studies have a strong reputation as fluorophores³ and in recent years a number of DSSCs have been studied using these compounds. The first rationally designed example of a Bodipy-based sensitizer was reported a few years ago,⁴ followed by a few more recent articles including both liquid electrolyte and solid state based DSSCs.⁵ A few years ago, we have achieved an overall efficiency of 2.46 using a long wavelength-absorbing derivative.⁶ Lately, more efficient liquid electrolyte-based DSSCs based on Bodipy structures have been achieved with record values of overall power-to-current conversion efficiency of 4.89% and 5.31% by Zhang's group⁸ and 6.06% by Kubo's group.⁹ It is clear that the optimal solar cell performance of a photosensitizer is dependent on a large number of parameters; however, the absorption range, anchoring groups and the direction of electronic reorganization upon excitation should be among the most important ones.⁷ Recent developments in Bodipy chemistry allow diverse modifications on the core structure.^{3,8} Through these modifications, many

characteristics of the parent chromophore can be altered in the desired direction, for example, it is possible to shift the absorption wavelength through the red end of the electromagnetic spectrum by just simple chemical transformations.^{8b,9} In addition to these, solubility and aggregation characteristics of these dyes can also be modulated as needed.³

Thiophene is known to be used frequently in DSSCs because of its electron transfer ability.¹⁰ Since electron delocalization through the π -system is an important factor in DSSCs, we have appended the thiophene unit to the Bodipy structure. The thiophene carboxylic acid unit has been attached to the *meso* (8-) position of the Bodipy core, since this position was calculated to be more feasible for electron injection.^{5a,6} Direct attachment of the thiophene unit to the core was also thought to enhance the efficiency of electron transfer. As an anchoring group, the carboxylic acid was used due to the synthetic problems we faced while trying to attach the cyanoacetic acid moiety, which is also known to bind efficiently to the TiO₂ surface and increases the electron withdrawing ability of the electron-injecting unit. The electron donor part is also an important parameter in DSSC design and efficient usage of the donor groups has a substantial role in increased cell efficiencies. In this study, we altered our mostly used triphenylamine group with the bis-dimethylfluorenyl amine group. This group has been successfully utilized in some literature reports¹¹ and due to its bulky structure it has been widely proposed as a donor group. It has also been suggested that using bulky structures increases the stability of oxidized dye molecules. Hence, in Bodipy dyes we have designed and synthesized bis-dimethylfluorenyl amine donor groups for DSSC application for the first time to our knowledge. Fig. 1 shows the synthesized photosensitizers for DSSC application.

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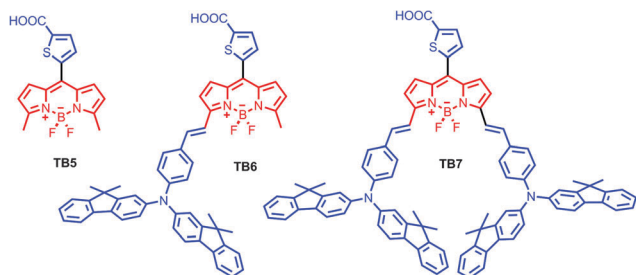


Fig. 1 Synthesized photosensitizers **TB5**, **TB6**, and **TB7**.

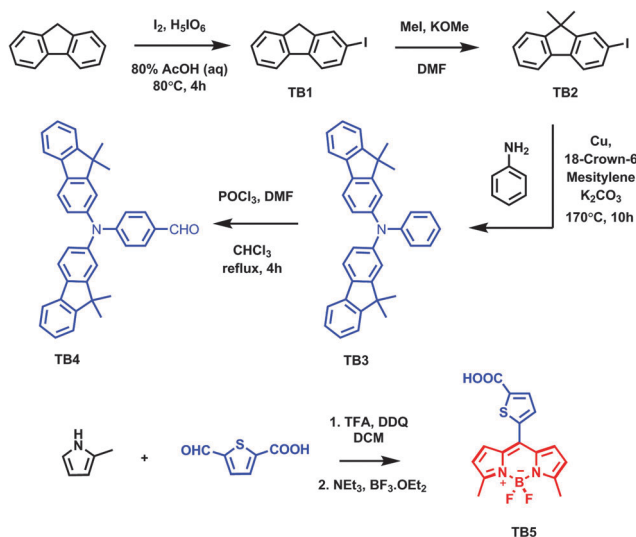


Fig. 2 Synthesis scheme of the precursor molecules.

In the synthesis part (Fig. 2), initially **TB1**–**TB4** have been synthesized.¹² We first iodinated the fluorene molecule to yield **TB1** in 90% yield. In the second reaction dimethylation reaction was accomplished by using a modified procedure from literature with MeI and KOMe in DMF. Then, in the third step we synthesized *N,N*-bis(9,9-dimethylfluoren-2-yl)aniline under the Ullman reaction conditions by using aniline and coupling reagents at high temperatures. Then, in order to synthesize **TB4**, which was needed for the Knoevenagel reaction, a typical Vilsmeier formylation reaction in CHCl_3 was carried out. After synthesis of the donor part, we moved to the synthesis of the Bodipy dye core. 5-Formyl-2-thiophenecarboxylic acid was obtained from suppliers and reacted with 2-methylpyrrole to get **TB5** and upon reaction with the synthesized aldehyde **TB4**, we obtained both **TB6** and **TB7** which were tested as photosensitizers in DSSCs (Fig. 3).

Experimental section

Materials

All chemicals and solvents obtained from suppliers were used without further purification. Reactions were monitored using thin layer chromatography over Merck TLC Silica gel 60 F_{254} .

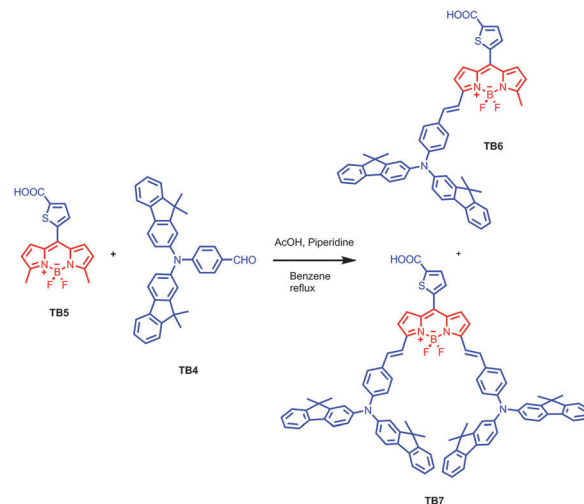


Fig. 3 Synthesis of the final PSs **TB6** and **TB7**.

Chromatography was performed over Merck Silica gel 60 (particle size: 0.040–0.063 mm, 230–400 mesh ASTM).

Characterization

^1H NMR and ^{13}C NMR spectra were recorded at room temperature on Bruker DPX-400 (operating at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR) in $\text{MeOD-}d_4$ and $\text{DMSO-}d_6$. Coupling constants (J values) are given in Hz and chemical shifts are reported in parts per million (ppm). Splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and p (pentet). Absorption spectra were acquired using a Varian Cary-100 spectrophotometer. Mass spectra were recorded on Agilent Technologies 6530 Accurate-Mass Q-TOF LC/MS. Spectrophotometric grade solvents were used for spectroscopy experiments.

Synthetic details

TB1, **TB2**, **TB3** and **TB4** were synthesized according to the literature.¹²

Compound TB5. 400 mL of argon-degassed CH_2Cl_2 was added into 2-methyl pyrrole (11.5 mmol, 0.93 g) and 5-formyl-2-thiophenecarboxylic acid (5.46 mmol, 0.85 g). One drop of TFA was added and the solution was stirred under N_2 at room temperature for 1 day. After addition of *p*-chloranil (5.46 mmol, 1.34 g) 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 (3×100 mL) which was then extracted into the DCM (3×100 mL) and dried over anhydrous Na_2SO_4 . The solvent was evaporated and the residue was purified using silica gel column chromatography employing $\text{DCM}:\text{MeOH} = 80:20$ as an eluant. Red solid (0.75 g, 40%). ^1H NMR (400 MHz, $\text{MeOD-}d_4$): δ 7.79 (1H, d, $J = 3.8$ Hz, ArH), 7.50 (1H, d, $J = 3.9$ Hz, ArH), 7.12 (2H, d, $J = 4.1$ Hz, ArH), 6.44 (2H, d, $J = 4.4$ Hz, ArH), 2.62 (6H, s, CH_3). MS (TOF-ESI): m/z : calcd: 301.0788, found: 301.0798 $[\text{M}-\text{COOH}]^-$, $\Delta = 3.3$ ppm. $\epsilon_{\text{abs}} = 43\,700$ (in MeOH).

Compounds TB6 and TB7. TB5 (0.29 mmol, 0.10 g) and TB4 (0.38 mmol, 0.19 g) were added into a 100 mL round-bottomed flask containing 50 mL of 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 the reaction was monitored by TLC (DCM:MeOH = 80 : 20). When all the starting material had been consumed, the mixture is concentrated and directly added to a chromatographic column by using DCM:MeOH/80 : 20 and TB7 was separated as a pure product in green color in 52% yield (0.152 mmol, 0.2 g). To separate the mono Knoevenagel product TB6 a second column chromatography was done with DCM:MeOH/90 : 10 and TB6 was separated as a pure product in 15% yield in deep blue color (0.04 mmol, 0.035 g).

TB6: ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δH 7.80 (2H, d, J = 8.0 Hz, ArH), 7.77 (2H, d, J = 7.3 Hz, ArH), 7.72 (1H, d, J = 16.3 Hz, CH), 7.62 (1H, d, J = 3.8 Hz, ArH), 7.49–7.60 (5H, m, ArH), 7.43 (1H, d, J = 16.3 Hz, CH), 7.25–7.38 (9H, m, ArH), 7.05–7.15 (4H, m, ArH), 6.48 (2H, d, ArH), 2.56 (3H, s, ArCH_3), 1.38 (12H, s, CCH_3). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δC 163.6, 156.7, 155.4, 153.8, 149.4, 146.4, 139.1, 138.6, 135.2, 133.6, 133.0, 131.3, 129.8, 129.4, 127.6, 127.4, 124.4, 123.2, 122.4, 121.7, 120.2, 119.8, 118.5, 116.2, 47.0, 30.1, 27.1 ppm. MS (TOF-ESI): m/z : calcd: 833.3059, found: 833.2955 [M], Δ = 12.5 ppm. ϵ_{abs} = 38 800 (in DCM). **TB7:** ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δH 7.76 (4H, d, J = 8.0 Hz, ArH), 7.72 (4H, d, J = 6.8 Hz, ArH), 7.65 (2H, d, J = 16.6 Hz, CH), 7.40–7.50 (12H, m, ArH; CH), 7.20–7.35 (16H, m, ArH), 7.07 (8H, m, ArH), 1.34 (24H, s, CCH_3). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δC 163.4, 155.4, 154.8, 153.7, 149.2, 146.3, 138.5, 137.8, 135.3, 135.2, 132.6, 131.8, 130.0, 129.7, 129.2, 129.0, 127.5, 127.4, 124.3, 123.1, 122.3, 121.7, 120.1, 119.7, 117.9, 116.6, 46.9, 27.1 ppm. MS (TOF-ESI): m/z : calcd: 1320.5359, found: 1320.5085 [M], Δ = 20.7 ppm. ϵ_{abs} = 53 700 (in DCM).

Electrochemistry of Bodipy dyes

CV measurements were made by using CH-Instrument 660 B Model potentiostat equipment. Solution was prepared in chloroform (10^{-3} M). A three-electrode cell was used consisting of a glassy carbon working electrode, a Pt wire counter electrode and an Ag/AgCl reference electrode, all placed in a glass vessel. Tetrabutylammonium hexafluorophosphate (TBAPF_6), 0.1 M, was used as a supporting electrolyte. Ferrocene was used as an internal reference electrode. HOMO/LUMO values were calculated according to literature.⁶

Dye sensitized solar cell device characterization

The current density *versus* voltage (I - V) characteristics of the devices were measured using a Keithley 2400 source measurement unit. The device performance was characterized under AM 1.5 G conditions with an illumination intensity of 100 mW cm^{-2} using a solar simulator. A special mask was used to define the active area in the devices and measurements were carried out using this special mask. Reproducibility of measurements was checked several times for the accuracy and precision.

Results and discussion

Optical properties

After the synthesis of TB6 and TB7 along with the sole Bodipy TB5, we performed photophysical analysis, CV measurements, and theoretical studies in order to determine the suitability of these units for constructing a cell with TiO_2 and redox couple I^-/I_3^- . Absorbance spectra of these dyes in solution (Fig. 4) and on the TiO_2 (Fig. S5, ESI[†]) surface was investigated and it was found that TB5 exhibited a narrow absorption spectrum with a λ_{max} at 520 nm in solution, which is characteristic for Bodipy dyes and the molar absorptivity of this compound was 43 700 in MeOH at this wavelength. This compound was barely soluble in DCM or CHCl_3 . TB6 exhibited a broader absorption spectrum with an absorption maximum at 665 nm in DCM and fluorene moieties were also found to absorb strongly in the UV region of the spectrum at around 370 nm. The molar absorptivity of this compound was 38 800 at 665 nm. Since the fluorene moieties that inhibit π - π stacking of the compound increases the solubility; we were able to dissolve them in DCM. TB7 exhibited a strongly red-shifted absorbance maximum at 773 nm in DCM. This compound was found to be promising in this respect because absorption in the near IR end of the spectrum is highly desired due to strong sunlight illumination in this wavelength region. For example, one of our previously studied sensitizers, PS1, which had a record efficiency among the Bodipy dyes when published in DSSC applications, exhibited an absorption maximum at 724 nm.¹³ TB7 had a molar absorptivity of 53 700 and an absorption maximum at 773 nm. All the three compounds exhibited very weak emission, which was due to the charge transfer events because of the thiophene-carboxylic acid group, which is usual for these types of dyes.

Electrochemical properties

Cyclic voltammetry results of the synthesized compounds are shown in Fig. 5. The results obtained from these data are summarized in Table 1, showing explicitly the oxidation/reduction bands of these compounds and the HOMO-LUMO

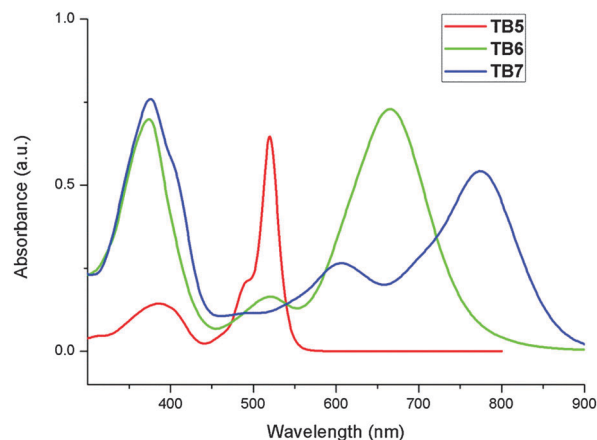


Fig. 4 Absorbance spectra of the compounds synthesized. TB5 in MeOH and TB6 and TB7 in DCM.

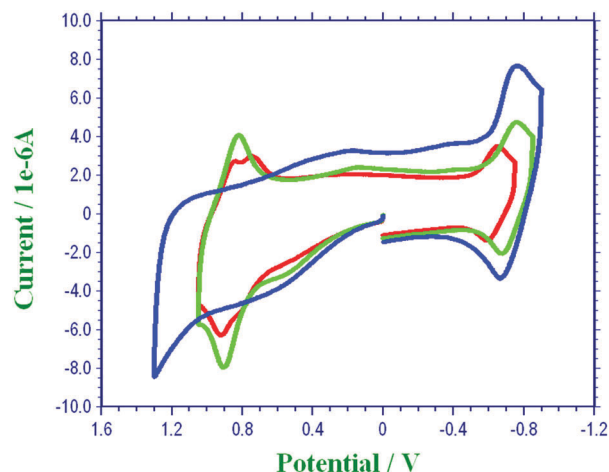


Fig. 5 Cyclic voltammetry measurements of **TB5** (blue), **TB6** (green) and **TB7** (red).

Table 1 Redox potentials and E_{HOMO} and E_{LUMO} levels of Bodipy derivatives

	E_{ox}^a (Volt)	E_{red}^b (Volt)	E_{fer}^c (Volt)	E_{HOMO}^d (eV)	E_{LUMO}^e (eV)	$E_{\text{Band gap}}^f$
TB5	0.54	−0.70	0.58	4.84	3.52	1.32
TB6	0.87	−0.72	0.57	5.10	3.51	1.59
TB7	0.83	−0.63	0.61	5.02	3.56	1.46

^a Oxidation potential of Bodipy derivatives. ^b Reduction potential of Bodipy derivatives. ^c Potential of ferrocene, the internal reference electrode. ^d HOMO energy level of Bodipy derivatives. ^e LUMO energy level of Bodipy derivatives. ^f Energy band gap of Bodipy derivatives.

band levels and band gaps. Energy levels of the HOMO and the LUMO are highly important in the DSSC concept. To summarize, upon photoexcitation of the dye molecules, electrons are excited from the HOMO to the LUMO of the dye and then electron injection from the LUMO to the conduction band of TiO_2 takes place. Hence, the LUMO energy level should be higher in energy than that of the conduction band of TiO_2 .

The energy level of the conduction band was estimated to be 4.2 eV.^{2a} In all three Bodipy dyes; **TB5**, **TB6**, and **TB7**, their LUMO levels were convenient for electron injection with 3.51–3.56 eV values which were higher in energy, as shown in Fig. 6. HOMO levels of the Bodipy dyes should also be considered since their energy level should be lower than the redox couple energy level (I^-/I_3^-), which was also calculated to be 4.9 eV. In Table 1, we can observe that only **TB5** was not convenient for reducing the Bodipy dye by the redox couple. On the other hand, **TB6** and **TB7** had the desired energy levels of 5.10 and 5.02 eV, respectively. However, it was emphasized in a recent review by Ooyama and Harima that, the energy difference between these levels should be at least 0.2–0.3 eV for an efficient electron regeneration.¹³ In our molecules, these were 0.2 and 0.12 eV for **TB6** and **TB7**, respectively. Although, these values seem to be appropriate, a larger gap would be better suited.

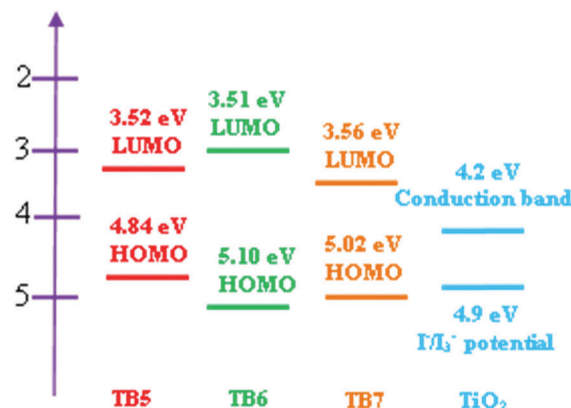


Fig. 6 Energy level diagrams of **TB5**, **TB6** and **TB7** from the electrochemical data summarized in Table 1.

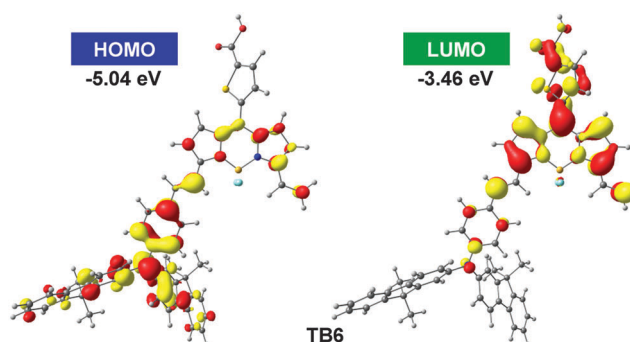


Fig. 7 Schematic representation of HOMOs and LUMOs of **TB6**. The UB3LYP/CEP-31G level of theory.

Theoretical studies

In order to understand the structure–performance relationship of the photosensitizers, we calculated the HOMO–LUMO diagrams (for calculation details, see the ESI†). The HOMO–LUMO of **TB6** are shown in Fig. 7, in which the HOMO molecular orbital electron density can be seen on the bis-dimethylfluorenyl group and the LUMO electron density on the Bodipy and the thiophene unit. It was apparent that upon photoexcitation, electrons moved from the bis-dimethylfluorenyl unit to the anchoring thiophene unit with $\pi-\pi^*$ type excitation. However, in the LUMO π -electron localization on the Bodipy core was not desired and this may be responsible for the low electron injection efficiency. In optimized geometry of the molecule, the angle between the Bodipy plane and the thiophene carboxylic acid unit plane was 46.6°, which seemed to be enough to achieve an effective conjugation between these two units. Although this angle seemed to be large, it was smaller when compared to that of the 8-aryl Bodipy molecules (almost 90°) synthesized from 2,4-dimethylpyrrole due to the steric effect of the extra methyl units and in this case, the π -electron conjugation was limited.

The electron localization of the HOMO–LUMO of **TB7** (Fig. 8) was similar to that of **TB6** according to the computational studies. The HOMO was localized mainly on the donor group,

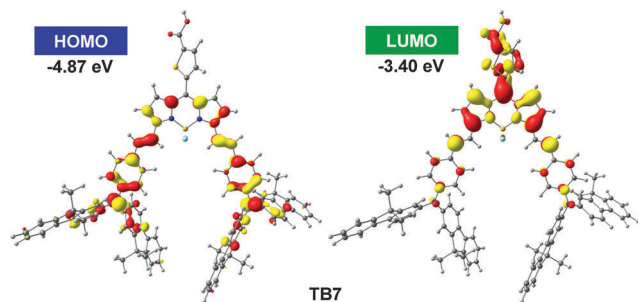


Fig. 8 Schematic representation of HOMOs and LUMOs of **TB7**. The UB3LYP/CEP-31G level of theory.

Table 2 TD-DFT transitions for **TB6** and **TB7**

Dye	$S_0 \rightarrow S_1$ Transition	Absorption (nm)	Oscillator strength	LHE (%)
TB6	HOMO \rightarrow LUMO	869	0.9619	89
TB7	HOMO \rightarrow LUMO	975	0.6896	79

while the LUMO on thiophene and Bodipy. The angle between the Bodipy plane and thiophene (49.1°) was slightly wider compared to that of **TB6**.

The light-harvesting efficiency (LHE)¹⁴ of the dyes were calculated using $LHE = 1 - 10^{-f}$, where f is the oscillator strength of the dyes. LHE values were 89% and 79% for **TB6** and **TB7**, respectively. TD-DFT results are summarized in Table 2. Besides an acceptable deviation of the computed absolute numerical values from the measurements, the TD-DFT results are in very good agreement with the prediction of the red shifting (106 nm computed) of the main $S_0 \rightarrow S_1$ transition and the LHE trend (in favor of **TB6**).

Photovoltaic performances

After careful investigation of CV results, we constructed the cells by using typical methods as mentioned in the experimental section. Firstly, we measured the short-circuit photocurrent density (J_{sc}), the open-circuit photovoltage (V_{oc}), the photocurrent–voltage curve (J – V curve) (Fig. 9), the fill factor (ff)

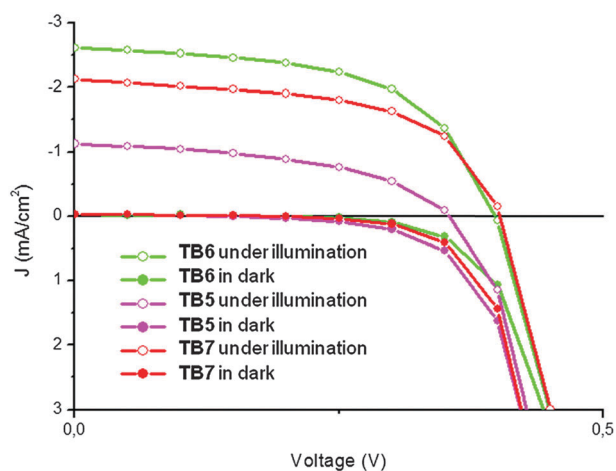


Fig. 9 Current vs. voltage graphs of the photosensitizers.

Table 3 Photovoltaic performance of TiO_2 -based dye-sensitized solar cells

	J_{sc} (mA cm^{-2})	V_{oc} (mV)	ff	η (%)	Adsorbed dye ($\times 10^{-7}$ mol cm^{-2})
TB5	1.12	370	0.48	0.19	1.7
TB6	2.61	400	0.57	0.59	3.9
TB7	2.12	400	0.58	0.49	3.0

and the incident photon-to-current conversion efficiency (IPCE) (Fig. S6, ESI†) and by the help of these parameters, we calculated the solar energy-to-electricity conversion yield (η). These values are tabulated in Table 3. **TB6** produced more photocurrent with 2.61 mA cm^{-2} under AM 1.5 simulated sunlight (100 mW cm^{-2}). The cell constructed from **TB6** had an open-circuit voltage of 400 mV and a fill factor of 0.57 and the calculated total sunlight-to-electricity conversion yield (η) was 0.59 (Table 3). This made this dye more efficient compared to **TB5** and **TB7** without using chenodeoxycholic acid as a coadsorbent. Herein, it is worth noting that the adsorbed amount of **TB6** on the TiO_2 surface was more (see Table 3) so this may also be a reason for this result. Also, the incident photon-to-current conversion efficiency (IPCE) spectrum gave us information about the response of the dye molecules upon illumination with the monochromatic light over a wide range of wavelengths. This spectrum resembles the absorbance of the dyes, interestingly large amounts of photocurrent were observed for **TB6** and **TB7** in the range 300–400 nm (Fig. S5 and S11, ESI†). However, the irradiation of sunlight in this range is not strong and its reflection to the solar-light photocurrent is limited. For **TB6** we observed effective photocurrent in the range 600–700 nm.

We also constructed the cell from **TB5** for comparison and we reached lower solar cell parameter values using this dye with $\eta = 0.19$. For **TB7**, we acquired similar but also lower values compared to **TB6**. The critical parameters for this dye exhibited a highly panchromatic nature of the IPCE spectrum (Fig. S5, ESI†). Although the photocurrent was low, it was generated in a wide spectrum, ranging 500–850 nm. The open-circuit voltage (V_{oc}) was 400 mV, the photocurrent density was 2.12 mA cm^{-2}

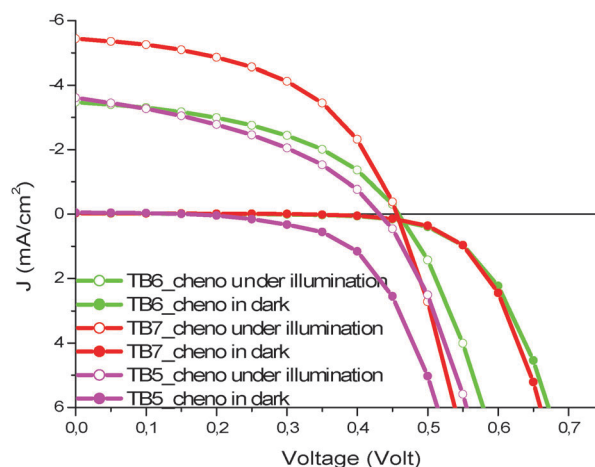
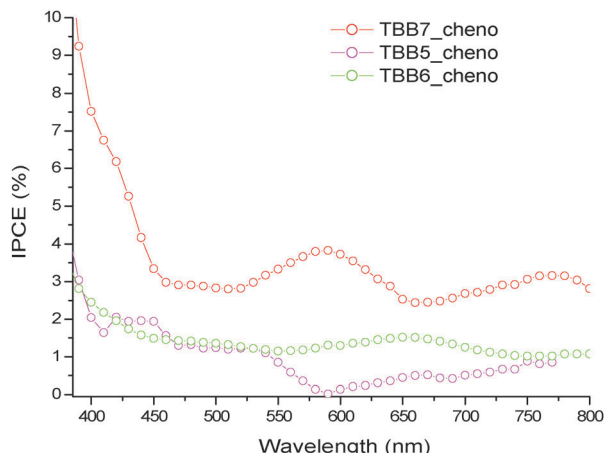


Fig. 10 Current vs. voltage graphs of the photosensitizers after adding Cheno (2 mM).

Table 4 Photovoltaic performance of TiO₂-based dye-sensitized solar cells after adding Cheno (2 mM)

	J_{sc} (mA cm ⁻²)	V_{oc} (mV)	ff	η (%)
TB5	3.60	450	0.38	0.61
TB6	3.47	450	0.47	0.73
TB7	5.32	450	0.52	1.25

**Fig. 11** Incident photon-to-current conversion efficiencies of the liquid electrolyte based-DSSCs as a function of wavelength after adding Cheno.

and the fill factor was 0.58. The overall sunlight energy-to-electricity conversion yield (η) was 0.49.

After these initial results, we constructed the DSSCs again but this time we used the coadsorbent chenodeoxycholic acid (2 mM) in order to inhibit the stacking of the dye molecules on the TiO₂ surface. The IPCE spectrum and the J - V curve are shown in Fig. 11 and 10, respectively. Table 4 shows the photovoltaic performances and this time we can observe an increase in the efficiency of all the photosensitizers. The major increase in the overall efficiency was observed in **TB7** from 0.49 to 1.25. The J_{sc} of this cell increased from 2.12 to 5.32 mA cm⁻². We observed a small increase with **TB6** in overall efficiency from 0.59 to 0.73. These results confirm that **TB7** was superior to **TB6** when a coadsorbent molecule was used.

Conclusion

The novelties of this study include a bulky donor group and a thiophene π -electron linker. As a donor group, we used the bis-dimethylfluorenyl amine group which was used for the first time with Bodipy dyes as far as we know and due to its sterically bulky structure it is expected to inhibit the aggregation of the dyes on the TiO₂ nanocrystalline surface. After constructing the cells using the Bodipy dyes that we have synthesized, the overall efficiency (η) was calculated to be 0.59 for **TB6** and 0.49 for **TB7**. By using chenodeoxycholic acid as a coadsorbent, we observed an increase in efficiency of all the photosensitizers tested. And the efficiency of **TB7** was observed to increase from 0.49 to 1.25. Although we used the bulky donor group, it seemed that using a

coadsorbent was still needed to inhibit the stacking of the dye molecules on TiO₂. The second parameter we used in these molecules was the π -electron linker unit, thiophene. This group has been widely used in various dye-sensitized solar cells due to its high π -electron localization ability and when we inspected the LUMOs we observed that the electron density moved successfully from the donor group to the acceptor unit. The main obstacle may be the fact that the electron density was not fully transferred to the acceptor and there was some residual density on the Bodipy core. This complication may be resolved by using the oligothiophene unit as a π -electron linker for a more efficient electron transfer. Further studies to solve the addressed problems and develop more efficient DSSCs suitable for near-IR sensitization are underway.

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