BODIPY conjugated organic dyes with arylamine variety for efficient dye-sensitized solar cells

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Abstract. Three new D–π–A structured organic sensitizers (Dye1-3), with various arylamine as donor connected to a 2-phenyl cyanoacrylate BODIPY module, were designed and synthesized for application in dye-sensitized solar cells (DSSCs). The photophysical and electrochemical properties were systematically studied and their performances as sensitizers in DSSCs were comparatively investigated. The structure–property relationship suggests that the rotation freedom of benzene rings in arylamine has a significant influence on the electron-donating abilities, thus effect on the sensitizer’s optoelectronic and photovoltaic properties. The DSSCs based on Dye 1 presents the best photovoltaic performance with a $J_{sc}$ of 8.21 mA cm$^{-2}$, a $V_{oc}$ of 595 mV, and FF of 0.74, corresponding to an $\eta$ of 3.61% under AM 1.5 irradiation (100 mW cm$^{-2}$).

1. Introduction

With the continuous development of global energy consumption, the development of renewable energy resources has attracted significant attention of researchers. As a renewable resource of energy, dye-sensitized solar cells (DSSCs) became one of the most promising low-cost alternatives to conventional inorganic silicon-based solar cells [1-2]. DSSCs based on zinc-polypyridyl complexes photosensitizers have achieved remarkable light-to-power conversion efficiency above 12% [3-4]. As well, metal-free organic dyes, featuring high extinction coefficients, easier structural modification, simple synthesis process, lower cost and environmentally friendliness in comparison to Ru (II) complexes, are also under investigation [5]. Various organic dyes based on donor–π-acceptor system, including porphyrin [6], triarylamine [7], cyanine [8], coumarins [9], indoline [10] and phenothiazine [11] have been investigated as sensitizers for DSSCs.

Boron dipyrromethene (BODIPY) dyes, have been attracted numerous exploration in many potential applications owing to their strong absorption coefficient in the visible and near-IR ranges, high fluorescence quantum yield, long excited state lifetime and good solubility in organic solvents. Despite this, BODIPY based dyes have not been used as effective photosensitizers in DSSCs applications [12-13]. Usually, BODIPY dyes with strong donor groups at 3 and 5 positions, and acceptors at 8-position have been widely investigated [12]. However, energy transfer through the BODIPY bridges tends to be less efficiency in this type of molecules, because the acceptor at 8-
position shows poor conjugation with BODIPY, and typically exhibits poor electron flow from donor unit to the anchor group \(^\text{[13]}\). As far as donor parts are concerned, the triphenylamine derivatives are considered to be good photoelectric materials. It has strong absorption properties of spectrum, high hole-transport capacity and wide band gap, have a wide range of applications in the field of photoelectric materials \(^\text{[14-15]}\). As a result, the combination of BODIPY and arylamine derivatives to construct novel compounds and used in dye-sensitized cells caused our research interest.

Base on the above consideration, we designed and synthesized three novel BODIPY dyes \((\text{Dye1-3})\) with arylamine derivatives as the electron donor and phenyl cyanoacetic acid as electron acceptor respectively, show in Chart 1. The photophysical, electrochemical and photovoltaic properties of the DSSCs based on the three dyes were systematically investigated. The impact of arylamine structures on the donor's electron-donating ability and further on their electronic and photovoltaic properties were also comparatively studied. We expect to illuminate the structure–property relationships of these sensitizers and to develop an excellent photoelectric material.

2. Result and discussion

2.1 Synthesis of \(\text{Dye1-3}\)

The synthesis strategy employed to access the target \(\text{Dye1-3}\) is shown in Scheme 1. For the construction of these molecules, we utilized the Pd-catalyzed Suzuki reaction to connect the arylamine donor units and BODIPY acceptor units, where \(\beta\)-iodinated BODIPY 7 and various arylamine donor moieties should be prerequisite for the synthesis. Firstly, iodination of BODIPY 3 with 1.3 equiv of ICl in the mixture solvent of methanol and dichloromethane readily afford the \(\beta\)-iodinated BODIPY 4 with a moderate yield. Then, a Suzuki coupling reaction between 4 and 5 gives the compound 6. Followed by another iodization, the desired key mediate 7 was successfully obtained. Secondly, construction of arylamine 10, 14 and 17 according to the literature procedures, followed by a Suzuki-Miyaura coupling reaction with B\(_2\)Pin\(_2\) in the presence of Pd(dppf)Cl\(_2\) catalyst smoothly afford the desired arylamine borates 11, 15 and 18. Thirdly, the Suzuki coupling reaction between the donor boron ester and BODIPY 7 was performed in the presence of Pd(PPh\(_3\))\(_4\) to procedure the corresponding aldehydes 19, 20 and 21 in excellent yields. Finally, the target dyes \(\text{Dye1-3}\) were obtained from Knoevenagel condensation of aldehydes 19-21 with cyanoacetic acid in the presence of a catalytic amount of piperidine. These newly synthesized target molecules were sufficiently soluble in THF, CH\(_3\)OH, to permit their characterization in solution as well as their application in DSSCs. The structure assignments of these novel molecules were confirmed by NMR spectroscopy and MALDI-TOF-MS.
2.2. Photophysical properties

As shown in Fig. 1, Dye1-3 exhibit absorption maxima in two distinct regions. The absorption of these BODIPY dyes in CH$_2$Cl$_2$ display intense absorption in 300-450 nm and 500-800 nm. The high-lying region is originated from the localized π–π* transition of the conjugated backbones, whereas the low-lying region is assigned to the S$_0$-S$_1$ transition along with the ICT interaction between the donor moieties and the BODIPYacceptor moieties. The spectrum of Dye 1 shows broader and more intense absorption bands than Dye 2 and Dye 3, and in the order of Dye 1>Dye 2>Dye 3. It indicated that the donor groups have significant effect on the absorption properties. Triphenylamine with three single phenyl exhibits stronger electron-donating ability than the arylamine with 5H-dibenzo[b,f]azepine and carbazole segments contained, which may due to the fact that the bonds between two phenyl in the
Scheme 1. Synthetic route of the BODIPY dyes Dye1-3.

arylamine prevents the free rotation of phenyl groups. In the other hand, Dye1-3 all exhibit broad absorption spectra with the absorption threshold up to 700-800 nm with moderate molar extinction coefficients $\varepsilon$ ($5.9 \times 10^4 - 1.1 \times 10^5$ M$^{-1}$ cm$^{-1}$), which suggests that these dyes can not only absorb energy in the visible region, but also absorb energy in the near infrared region, thus increasing the efficiency of light-harvesting.

Normalized absorption spectra of Dye1-3 adsorbed on TiO$_2$ films were obtained from the same TiO$_2$ film for solar cells are shown in Fig. 2. In comparison with the absorption spectra in CH$_2$Cl$_2$ solution, the solid-state absorption maxima have a slightly red-shifted. This effect is attributed to a $J$-type aggregation of the dyes on the TiO$_2$ surface and/or the dye-TiO$_2$ interactions might lead to the red shift. [16] The absorption peaks of these compounds are distinctly broadened in the region of 500–800 nm, which is desirable for harvesting solar light. The absorption maximum of Dye 2 has a more obvious red-shift compared to those of Dye 1 and Dye 3, this anticipated that Dye 2 is of higher degree of aggregation.

Fig. 1. Absorption spectra of Dye1-3 in CH$_2$Cl$_2$ solution.
Fig. 2. Normalized absorption spectra of Dye1-3 adsorbed on TiO2 films.

Table 1 Photophysical and electrochemical data of Dye1-3.

| Dyes | $\lambda_{\text{max}}$ (solution) (nm/ M$^{-1}$ cm$^{-1}$) | $\lambda_{\text{max}}$ (TiO2) (nm) | $E_{\text{ox}}$ vs NHE (V) | $E_{0,0}$ (eV) | $E^*_{\text{ox}}$ vs NHE (V) | $E_{\text{HOMO}}$ (eV) | $E_{\text{LUMO}}$ (eV) |
|------|-----------------------------------------------------|---------------------------------|--------------------------|--------------|--------------------------|------------------|------------------|
| Dye 1 | 627 (1.1 × 105) | 632 | 0.89 | 1.59 | -0.70 | -5.39 | -3.80 |
| Dye 2 | 605 (8.4 × 104) | 621 | 0.91 | 1.65 | -0.74 | -5.41 | -3.76 |
| Dye 3 | 590 (5.9 × 104) | 595 | 0.95 | 1.78 | -0.83 | -5.45 | -3.67 |

2.3. Electrochemical properties

To evaluate the feasibility of electron injection from the excited state molecule to conduction band of TiO2, the electrochemical behavior of Dye1-3 has been examined by cyclic voltammetry (CV) in CH2Cl2 containing 0.1 M n-Bu4NPF6 as supporting electrolyte and the CV curves were shown in Fig. 3, using ferrocene as a standard. The first oxidation potentials ($E_{\text{ox}}$) were obtained, and the excited-state oxidation potentials ($E^*_{\text{ox}}$) were estimated by subtracting the zero-zero transition energy values ($E_{0,0}$) from $E_{\text{ox}}$, and the data were listed in Table 1. The oxidation potentials ($E_{\text{ox}}$) of Dye1-3 ranging from 0.89 to 0.95 V vs NHE, are more positive than the iodide/tri-iodide redox couple (about 0.42 V vs NHE), indicating that the oxidized dye formed after electron injection into the conduction band of TiO2 can be regenerated from the reduced species in the electrolyte. The excited-state oxidation potentials ($E^*_{\text{ox}}$), ranging from -0.70 to -0.83 V vs NHE, are higher than the conduction band of TiO2 (about -0.5 V vs NHE), ensuring facile electron injection from the excited-state molecule to TiO2 conduction band. As a result, more sufficient electron flow from the excited dyes to the TiO2 surface. Among them, Dye 1 give lower oxidation potential and higher reduction potential than those for Dye 2 and Dye 3, resulting a lower bandgap, which is consistent with the absorption measurements. In addition, the trend of energetic potentials coincides with the results of spectrum analysis.
Fig. 3. Cyclic voltammograms of the Dye1-3 in CH₂Cl₂ solution.

Table 2. Optimized structures and electronic distributions in HOMO and LUMO levels of Dye1-3.

| Dyes | Optimized structure | HOMO | LUMO |
|------|---------------------|------|------|
| Dye 1 | ![Image](image1.png) | ![Image](image2.png) | ![Image](image3.png) |
| Dye 2 | ![Image](image4.png) | ![Image](image5.png) | ![Image](image6.png) |
| Dye 3 | ![Image](image7.png) | ![Image](image8.png) | ![Image](image9.png) |

2.4. Theoretical calculations
In order to further understand the possibility of charge transfer from donor to acceptor on electronic excitation and explain the structural properties of Dye1-3, the geometry optimized structures and frontier orbital energy levels of the dyes were calculated using the density functional theory (DFT) at the B3LYP/6-31G* level. The optimized structures with torsion angles and electron densities of HOMOs and LUMOs of the dyes are showed in Table 2.

In the optimized structures, the dihedral angels between arylamine connectivity ring and the BODIPY core and the dihedral angels between BODIPY and the terminal phenyl cyanoacrylic acceptor are computed to be 26.5° and 6.4° for Dye 1, 16.0° and 4.8° for Dye 2, and 13.6° and 1.4° for Dye 3, respectively. It showed that the tendency of torsion angels was in order of Dye 3< Dye 2< Dye 1, implying the lowest level of ICT transition in Dye 1, leading the minimum absorption threshold. Nevertheless, in terms of spectral absorption, these compounds exhibit exactly the opposite results, with the absorption thresholds in the order of Dye3< Dye 2< Dye 1. It suggests that the triphenylamine donor in Dye 1 exhibits the strongest electron-donating ability than the 5-phenyl-5H-dibenzo[b,f] azepine in Dye 2 and 9-phenyl-9H-carbazole in Dye 3 with the free rotation of benzene ring in which
restricted. In addition, the simulated HOMO-LUMO levels and trends in band gaps of the dyes molecules were in agreement with UV-vis absorption and CV measurements of these dyes.

The electron distributions of Dye1-3 indicate that π-electrons in the HOMO are distributed along the arylamine units, while their LUMO orbitals are mainly localized on cyanoacrylic acid and its adjacent BODIPY motifs (Table 2). The result suggests that the HOMO→LUMO excitation by light would induce a transfer of the electron from the carbazole donor moiety to the acceptor moiety. These electron distributions allow sufficient charge separation within the dyes. Apparently, the electron transfer from the HOMO to the LUMO can easily result in electron redistribution from the arylamine unit to the cyanoacrylic acid moiety, which is highly significant in the electron injection from excited state dyes into the CB band of TiO2 semiconductor.

2.5. Photovoltaic performances of DSSCs

In order to investigate the photovoltaic performance of Dye1-3 and to understand the effect of different electron-donating units on their photovoltaic performance, a set of DSSCs were fabricated and tested under standard conditions (AM 1.5 G, 100 mW cm\(^{-2}\)). The photocurrent density (\(J_{sc}\)), fill factor (\(FF\)), and overall PCE (\(\eta\)) were measured and the corresponding data are summarized in Table 3. The photovoltaic performance of these dyes as sensitizers for DSSCs was tested using 0.5 M LiI 0.05 M I\(_2\), 0.1 M guanidinium thiocyanate, 0.6 M PMII and 0.5 M 4-tert-butylpyridine (TBP) in 3-methoxypropionitrile as the redox electrolyte. As well known, the thickness of the TiO\(_2\) film is one of the important factors to dominantly affect the performance of a cell. Generally, thicker TiO\(_2\) films can provide more dye molecules to adsorb on them. Meanwhile, the electron transporting path becomes longer with thicker TiO\(_2\) films, which may cause a higher probability of recombination. As a result, the open-circuit voltage (\(V_{oc}\)) for the pertinent DSSCs may decrease with further increase in the thickness of the TiO\(_2\) film. The optimized thickness of 200 nm particle sized TiO\(_2\) film for the referenced N719 dye in our work is about 3 \(\mu\)m. In order to make a comparison, the three DSSCs (Dye1-3) are also adopted the same thickness of the TiO\(_2\) film.

The important parameters, short-circuit photocurrent density (\(J_{sc}\)), open-circuit photovoltage (\(V_{oc}\)), fill factor (\(FF\)), and overall PCE (\(\eta\)) were measured and the data are summarized in Table 3, and the \(J-V\) plots are shown in Fig. 4. The DSSC based on the dye N719 under the optimized conditions exhibits the \(\eta\) of 7.52% with a \(J_{sc}\) of 14.34 mA cm\(^{-2}\), a \(V_{oc}\) of 718 mV and an \(FF\) of 0.73. Under the same conditions, The DSSCs sensitized with Dye 1, bearing triphenylamine as the donor, showed a \(J_{sc}\) of 8.21 mA cm\(^{-2}\), a \(V_{oc}\) of 595 mV, and an \(FF\) value of 0.74, generating an overall conversion efficiency \(\eta\) of 3.61%, which reached 48% of the N719 cell efficiency. However, when two free rotating benzene rings in triphenylamine were replaced with a 5H-dibenzo[b,f]azepine group bearing restricted free rotation of benzene rings, the Dye 2 exhibited a \(J_{sc}\) of 7.35 mA cm\(^{-2}\), a \(V_{oc}\) of 590 mV, an \(FF\) of 0.75, and a \(\eta\) of 3.25%. It found that Dye 1 and Dye 2 show similar \(V_{oc}\) and \(FF\) values, while the \(J_{sc}\) value was about 0.86 mA cm\(^{-2}\) higher for Dye 1 with a triphenylamine donor than Dye 2 with a 5-phenyl-5H-dibenzo[b,f]azepine donor. It is due to the fact that the triphenylamine based Dye 1 exhibit an extensive absorption spectral range to a longer wavelength than that of 5-phenyl-5H-dibenzo[b,f]azepine based Dye 2, enable to absorb more photons and convert them into electrons in DSSC. Moreover, when two free rotating benzene rings in triphenylamine were replaced by a carbazole group and linked with the carbazole segment to the BODIPY bridge, Dye 3 displayed a \(J_{sc}\) of 5.77 mA cm\(^{-2}\), and a \(V_{oc}\) of 610 mV, and an \(\eta\) of 2.75%. It found that Dye 3 displayed lower \(J_{sc}\) than Dye 2, due to the fact that carbazole is a fragment with more rigid structure than 5H-dibenzo[b,f]azepine. The results clearly demonstrated that the rotation freedom of benzene rings in triphenylamine has a significant influence on the electron-donating abilities and steric configurations, and hence effect on the parameters of \(J_{sc}\) in their dyes sensitized DSSCs. Benefit for a strong electron-donating donor advantage, Dye 1 sensitized cell displayed the best photovoltaic performance among the three DSSCs. The excellent device performance is also originated in the effective electron injection from photo-excited Dye 1 to the conduction band of TiO\(_2\) film, leading to higher electron injection efficiency. It is worth noting that all these dyes sensitized cells exhibit high \(FF\) values,
indicating that the special spatial structure of these molecules effectively suppress excessive dye aggregation on the surface of TiO₂.

![Fig. 4. J-V curves for DSSCs with the dyes Dye1-3 under AM 1.5 simulated sunlight (100 mW cm⁻²) illumination.](image)

| Dye    | J_{sc} (mA·cm⁻²) | V_{oc} (mV) | FF  | PCE (%) |
|--------|------------------|-------------|-----|---------|
| Dye 1  | 8.21             | 595         | 0.74| 3.61    |
| Dye 2  | 7.35             | 590         | 0.75| 3.25    |
| Dye 3  | 5.77             | 610         | 0.78| 2.75    |
| N719   | 14.34            | 718         | 0.73| 7.52    |

3. Conclusions
In this study, we have designed and synthesized a series of D-π-A type organic dyes Dye1-3, featuring arylamine with structural variety as donor, BODIPY as central π-bridge, and phenyl cyanoacetic acid as terminal acceptor. The structure-property relationships demonstrated that the rotation freedom of benzene rings in arylamine has a significant influence on the electron-donating abilities, thus a remarkable effect on the sensitizer’s optoelectronic and photovoltaic properties. Triphenylamine shows stronger electron-donating ability than the 5-phenyl-5H-dibenzo[b,f]azepine and the 9-phenyl-9H-carbazole. Thus, Dye 1 exhibits the more intensive ICT, although it has a more distorted space configuration, resulting in narrower band gap and thus broader and more intensive absorption both in solution and on the surface of TiO₂ than Dye 2 and Dye 3. The photovoltaic performance of DSSCs based on Dye 1 is obviously superior to Dye 2 and Dye 3 not only in J_{sc}, but also in the overall conversion efficiency. The DSSCs based on Dye 1 presents the best photovoltaic performance with a J_{sc} of 8.21 mA cm⁻², a V_{oc} of 595 mV, and FF of 0.74, corresponding to an η of 3.61% under AM 1.5 irradiation (100 mW cm⁻²), which is a moderate device performance in DSSCs but a fairly good value in BODIPY based DSSCs. The results indicate that well designed arylamine-BODIPY conjugates are promising candidate for efficient DSSCs.

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