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A Novel Amine-Free Dianchoring Organic Dye for Efficient Dye-Sensitized Solar Cells

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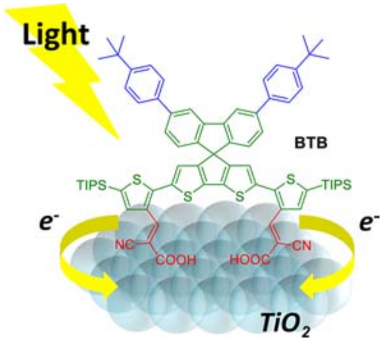
ABSTRACT



An amine-free oligothiophene-based dye (BTB) featuring a tailor-made dianchoring function, a spiro-configured central unit, and bulky end-capping TIPS groups to diminish intermolecular interactions and to suppress aggregation-induced self-quenching was synthesized to achieve efficient dye-sensitized solar cells with a high power conversion efficiency of 6.52%.

Since Grätzel's pioneering work in 1991, dye-sensitized solar cells (DSSCs) have evolved to be a potential candidate for a next-generation photovoltaic device.[1] Over the past two decades, tremendous research has been focused toward the search for efficient photosensitizers with desired physical properties, such as low band gap, high molar extinction coefficient, well-aligned energy levels, and suppressed aggregation behavior. To date, DSSCs with a remarkable power conversion efficiency (PCE) exceeding 11% have been realized using Ru-based sensitizers.[2] Very recently, DSSCs sensitized with complementary porphyrin-based and organic dyes have achieved a PCE as high as 12.3%,[3] making contemporay DSSCs highly competitive with other thin-film photovoltaic technologies. As such, metal-free organic dyes have attracted significant attention due to their various advantages such as great flexibility in structural tuning, low cost, resource availability, and generally large molar extinction coefficients.[4]

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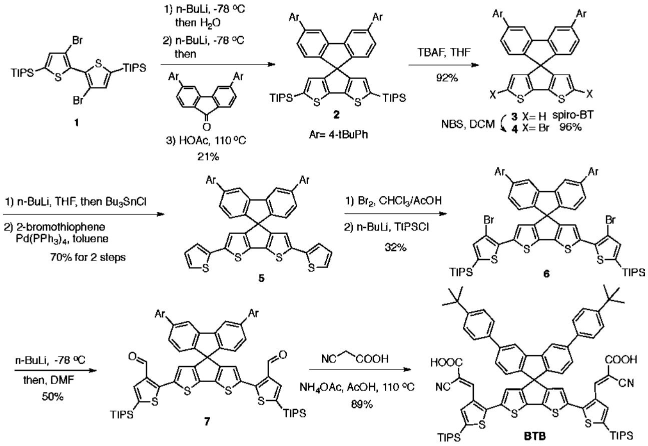
In the designs of metal-free organic dye sensitizers, the dipolar donor−(π-conjugated spacer)−acceptor (D−π−A) system is the most widely adopted molecular architecture, in which various arylamines such as triarylamine, carbazole, phenothiazine, and indoline are generally utilized as electron-donating moieties. The incorporation of these strong electron-donating groups in organic dyes facilitates effective photoinduced intramolecular charge transfer (ICT) and is, thus, beneficial in improving their light-harvesting abilities. Despite the wide adoption of such conventional arylamine-based donor structures, there were few reports of amine-free organic sensitizers.[5] The replacement of arylamines with an electron-rich moiety bearing a relatively compact spatial volume as the donor group enables the sensitizers to have higher dye densities on TiO_2 surfaces, rendering feasible the fabrication of cocktail cells for panchromatic photon harvesting.[6] In addition to the core skeletons, tailoring the structure and number of anchoring groups is also a research focus for developing efficient organic sensitizers.[7] For Ru-based sensitizers, the number of anchoring groups (carboxylic acid) can be fine-tuned from one to four to control interfacial charge transfer.[8] Recently, several organic sensitizers composed of two anchoring groups have also been introduced,[9] and these dianchoring organic sensitizers were found to possess several advantages such as extended π-conjugation, increased electron extraction channels, multibinding abilities, higher photocurrent, and enhanced stability over their monoanchoring counterparts.[10] As remarkable examples, the DSSCs sensitized with benzothiadiazole- and phenothiazine-based multianchoring dyes had demonstrated PCEs exceeding 6%.[11]

Here, we report a new amine-free dianchoring organic sensitizer, **BTB** (Scheme 1). This novel molecule was designed with the following structural characteristics: (i) it adopts oligothiophene as an electron-donating backbone to endow the dye with visible light absorption and a large molar extinction coefficient; (ii) the anchoring groups (cyanoacrylic acid) are introduced at γ-positions of the terminal thiophene rings to match the distance between the neighboring adsorption sites of the anatase TiO_2 surface and to ensure dianchoring adsorption (*vide infra*), which is critical for efficient electron transfer and better stability for dyes; (iii) it incorporates a spiro-configured central unit as a steric bulky group to diminish intermolecular interactions and to suppress aggregation-induced self-quenching that is usually encountered in organic dyes;[12] (iv) introduced bulky end-capping TIPS groups together with the central spiro-configured aryl group can form a hydrophobic shell to block the electrolyte diffusion and to reduce dark currents.

Scheme 1. Synthesis of Amine-Free Dianchoring Dye **BTB**



Scheme 1 depicts the synthesis of **BTB**. We established a modified approach for synthesizing spiro-bridged bithiophene, which avoids the use of reported cyclopenta[2,1-*b*:3′,4′-*b*′]dithiophen-4-one[13] as the essential intermediate. Our synthesis started from the selective lithium-bromo exchange reaction of 3,3′,5,5′-tetrabromo-2,2′-bithiophene[14] with *n*-BuLi, followed by quenching with chlorotriisopropylsilane (TIPS-Cl) to give TIPS-capped bithiophene **1** (46%).[15] For the subsequent cyclization reaction, the introduction of TIPS groups on the reactive α-position of thiophene is essential for preventing possible intermolecular

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reactions. The crucial intermediate **2** was obtained via a three-step process: (1) **1** was treated with *n*-BuLi and subsequent protonation with water; (2) the resulting monobromo intermediate was further treated with *n*-BuLi, followed by addition of a fluorenone, which was prepared by a Suzuki–Miyaura coupling reaction of 3,6-dibromo-9*H*-fluoren-9-one[16] and 4-*tert*-butylphenylboronic acid;[17] (3) the corresponding alcohol intermediate was subjected to acid-mediated intramolecular Friedel–Crafts cyclization in acetic acid to give **2** (21%, three steps). Protodesilylation of **2** with tetrabutylammonium fluoride yielded *spiro*-**BT** (**3**), which was then reacted with *N*-bromosuccinimide to give dibromo-**BT** (**4**) in 96% yield. Compound **4** was *in situ* transformed into a distannyl intermediate with *n*-BuLi, followed by quenching with Bu_3SnCl and then reaction with 2-bromothiophene to give tetrathiophene **5** (70%). The brominations at α- and γ-positions of the terminal thiophenes of **5** were successfully achieved by treating with bromine to give the tetrabromo intermediate, which was reacted with *n*-BuLi followed by the treatment with TIPS-Cl to produce **6** (32%, two steps). The bromo groups of **6** were converted to their corresponding carbaldehydes (**7**) by lithiation with *n*-BuLi and subsequently quenching with *N*,*N*-dimethylformamide. Finally, the dialdehyde **7** was condensed with cyanoacetic acid in the presence of ammonium acetate to afford the target dye **BTB** in 89% yield via a Knöevenagel reaction.

The electronic absorption spectrum of **BTB** in solution (10^{-5} M in THF) is shown in Figure 1a. The absorption spectrum of **BTB** shows two major absorption bands at λ_{max} = 317 (ε, 30 800 M^{-1} cm^{-1}) and 490 nm (ε, 30 000 M^{-1} cm^{-1}), respectively. The shorter wavelength band can be attributed to the π–π* transition of the local spiro-configured 3,6-disubstituted fluorenyl group,[16] whereas the longer one can be assigned to the π–π* transition of the tetrathiophene-based chromophore. The absorption spectrum of **BTB** anchoring on a 7 μm porous TiO_2 nanoparticle film (Figure 1b) shows an absorption maximum of 506 nm, which is red-shifted by 16 nm as compared to that in THF solution. The red shift is possibly due to the interaction between the TiO_2 surface and dyes that increases the delocalization of the π*-orbital of the entire conjugated configuration and thus lowers the energy level of the π*-orbital.[18] The observed broad and red-shifted absorption of **BTB** on the TiO_2 nanoparticle film will be beneficial to improve the light-harvesting capability, resulting in the higher photocurrent density and better PCEs.[19]

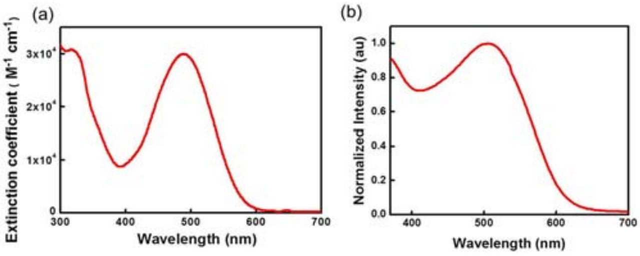

Figure 1. (a) Absorption (measured in THF solution 10^{-5} M) of **BTB**. (b) Absorption spectra of **BTB** anchoring on the 7 μm porous TiO_2 nanoparticle film.

The interactions between carboxylic groups of **BTB** and TiO_2 were probed by FTIR. Figure 2 shows the FTIR spectra of pristine **BTB** and **BTB** adsorbed on the TiO_2 surface. Obviously, the cyano group absorption band (2215 cm^{-1}) remained unchanged before and after interacting with TiO_2, indicating cyano groups were not involved in anchoring functions. For **BTB** adsorbed on the TiO_2 film, the IR absorption band at 1700 cm^{-1} corresponding to the free carboxylic acid groups disappeared, while the absorption band at 1620 cm^{-1} (overlapped with aromatic C=C stretching) appeared, which was identified as asymmetric stretching of carboxylate adsorbed on TiO_2. The absence of free carboxylic groups as indicated by the FTIR is a good indication of the dianchoring adsorption of **BTB** on the TiO_2 surface, agreeing with the previously reported behavior of dianchoring dyes.[20]

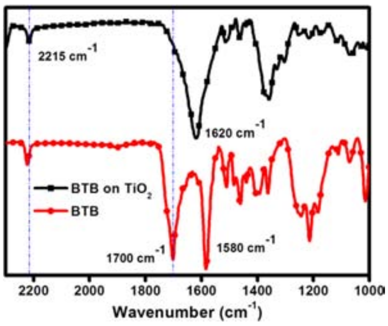

Figure 2. FTIR spectra of **BTB** measured as solid powders (●) and as stained onto the 7 μm porous TiO_2 nanoparticle film (■).

To gain more insight into the structural and electronic features of **BTB**, DFT (density function theory) calculations were performed. The distance between two anchoring carboxylic acid groups of **BTB** was calculated to be *ca.* 10.72 Å (Figure S1), which nicely matches the distance between two neighboring adsorption sites (10.23 Å) on the anatase TiO_2 surface.[21] This result confirms **BTB** possesses a suitable molecular configuration for dianchoring adsorption on the TiO_2 surface. This dianchoring feature is believed to benefit efficient surface adherence and

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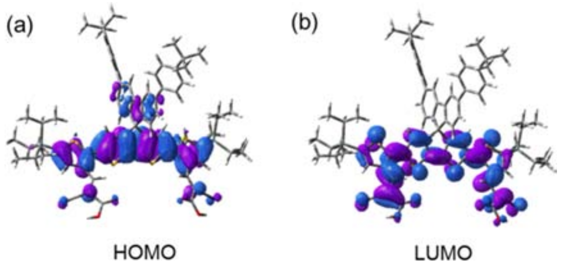

Figure 3. DFT HOMO and LUMO of **BTB** calculated at the B3LYP/6-31G(d) level.

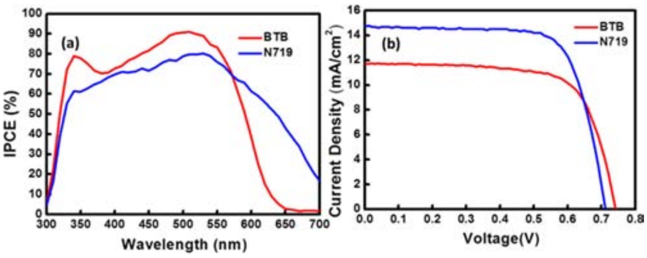

Figure 4. (a) IPCE spectra of DSSCs based on **BTB** (red) and **N719** (blue). (b) Current–voltage curves for DSSCs incorporating **BTB** (red) and **N719** (blue) under AM 1.5 G simulated sunlight.

subsequent electron transfer. In addition, DFT calculations suggest that the HOMO of **BTB** is mainly localized on the spirofluorene-bridged oligothiophene, whereas the LUMO is populated through the oligothiophene-conjugated backbone and cyanoacrylic acid fragments (Figure 3). This spatially separated arrangement of HOMO/LUMO ensures not only effective intramolecular charge transfer between donor and acceptor moieties but also efficient photoinduced electron injection from **BTB** to the TiO_2 electrode.

The electrochemical properties of **BTB** were investigated by cyclic voltammetry. As shown in Figure S2, **BTB** exhibits two reversible oxidation waves. The first oxidation potential (E_{ox}, 1.25 V vs normal hydrogen electrode, NHE) is more positive than the iodide/triiodide (I^-/I_3^-) redox couple (0.4 V vs NHE), indicating oxidized **BTB** is able to accept electrons from I^- thermodynamically for effective dye regeneration. The zero–zero excitation energy (E_{0-0}, 2.31 eV) estimated from the intersection of the absorption and emission spectra was combined with the ground-state oxidation potential (E_{ox}) to calculate the excited-state oxidation potential ($E_{ox}^* = E_{ox} - E_{0-0}$). The more negative E_{ox}^* (−1.06 V vs NHE) of **BTB** relative to the conduction band edge of TiO_2 (−0.5 V vs NHE)[22] reveals the electron injection from excited **BTB** to TiO_2 should be energetically favorable.

The photovoltaic characteristics of **BTB** as a sensitizer for DSSCs were evaluated with a sandwich DSSC cell using 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.05 M LiI, 0.03 M I_2, 0.5 M 4-*tert*-butylpyridine, and 0.1 M guanidinium thiocyanate in a mixture of acetonitrile–valeronitrile (85: 15, v/v) as the redox electrolyte (details of the device preparation and characterization are described in the Supporting Information (SI)). The incident monochromatic photon-to-current conversion efficiency (IPCE) spectrum of the DSSC is shown in Figure 4a. The DSSC based on **BTB** shows an IPCE of > 70% from 330 to 570 nm and reaches an IPCE maximum of 91% around 500 nm, indicating highly efficient DSSC performance. Figure 4b shows the current density–voltage (*J*–*V*) curve of the DSSC under standard global AM 1.5G solar irradiation. The short-circuit photocurrent density (J_{SC}), open-circuit voltage (V_{OC}), and fill factor (FF) of the DSSC based on **BTB** are 12.51 mA/cm^2, 0.74 V, and 0.70, respectively, yielding an overall PCE of 6.52%. For a fair comparison, the **N719**-sensitized DSSC was also fabricated and tested under similar conditions (see SI). The efficiency of the **BTB** cell reaches ~85% of the **N719** cell efficiency.

In summary, a new tailor-made amine-free, dianchoring DSSC sensitizer (**BTB**) featuring a tetrathiophene as the donor skeleton and elaborately equipped with cyanoacrylic acid anchoring groups at the γ-positions of terminal thiophene rings has been synthesized and characterized. The DFT calculation showed the distance (10.72 Å) between two carboxylic acid groups of **BTB** was close to the two neighboring adsorption sites on the anatase TiO_2 surface, rendering proper dianchoring adsorption, confirmed by the absence of free carboxylic acid in the FTIR spectra. A DSSC sensitized with **BTB** exhibited a high PCE of 6.52% with J_{SC} = 12.51 mA/cm^2, V_{OC} = 0.74 V, and FF = 0.70. Our study introduces a new approach to developing amine-free, dianchoring sensitizers for efficient and stable DSSCs.

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Supporting Information Available. Synthesis, characterization, copies of ^{1}H and ^{13}C NMR spectra, device fabrication, and optimization of solar cells. This material is available free of charge via the Internet at http://pubs.acs.org.

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The authors declare no competing financial interest.