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Benzothiazole-cyclopentadithiophene Bridged D-A-π-A Organic Sensitizer with Enhanced Light Absorption for High Efficiency Dye-sensitized Solar Cells

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We demonstrate an efficient D−A−π−A sensitizer with a benzothiazole-cyclopentadithiophene moiety as the spacer into the triphenylamine organic dye for dye-sensitized solar cells. The dye has broad visible light absorption up to 800 nm. A power conversion efficiency > 9% has been achieved with $[Co(bpy)_3]^{2+/3+}$–based electrolyte.

Dye-sensitized solar cells (DSCs) have been considered to be a promising photovoltaic technology to address the ever increasing energy and environmental challenges since the pioneering work of O'Regan and Grätzel.[1] To date, power conversion efficiencies (PCE) greater than 11% have been achieved with the ruthenium (Ru)-based dyes.[2] However, the relatively high cost and environmental concerns associated with the use of Ru dyes have prompted strenuous efforts to develop organic dyes as an alternative choice of photosensitizers.[3,4] In addition, high molar extinction coefficients of organic dyes allow for the use of thinner TiO_2 film, which is beneficial for enhancing charge collection and photovoltage.[5,6] Moreover, organic dyes have versatile functional groups for tuning the electronic and optical properties. As such, many metal-free organic dyes, especially those based on the donor-*π spacer*-acceptor (D–π–A) systems, have been developed and exhibit relatively high performances.[6,7]

Recently, the performance of DSCs based on organic dyes has been further remarkably improved in conjunction with $Co^{III/II}$ polypyridyl complexes as redox mediator, and a record PCE more than 12% has been achieved,[8] which further corroborates organic dyes as a superior option for highly efficient DSCs. To promote the performance of DSCs to a new phase, it is however highly desirable to further enhance the light harvesting and at the same time retain the high efficiencies of charge separation and collection. Thus, the development of new photosensitizers concomitantly possessing absorption spectra extending into near infrared (NIR) region and high molar extinction coefficients, as well as matched energy levels with TiO_2 and redox electrolyte is highly demanded.

Additional acceptor chromophores have recently been introduced in D–π–A dyes between the donor and the π-spacer, leading to a D–A–π–A architecture that facilitates intramolecular charge transfer and tailors the bandgap energy for harvesting more NIR light.[4a,9] 2-cyano-3-{6-{4-[N,N-bis(4-hexyloxyphenyl)amino]phenyl}-4,4-dihexyl-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2-yl}acrylic acid (**D1**) has recently been reported, which contains a cyclopenta-
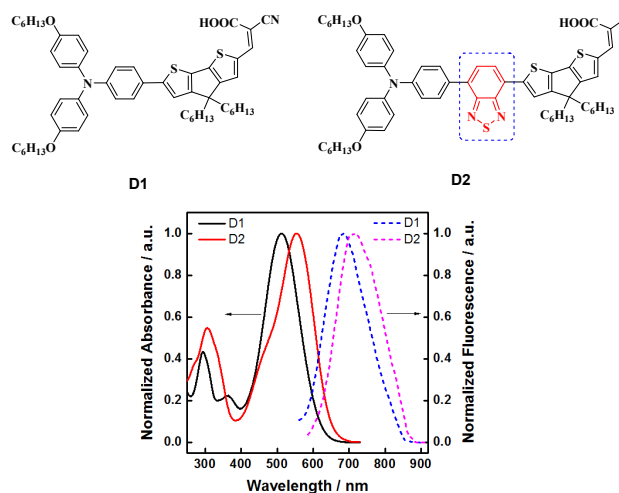

Fig. 1 Chemical structures of **D1** and **D2** and their absorption and emission spectra measured in CH_2Cl_2.

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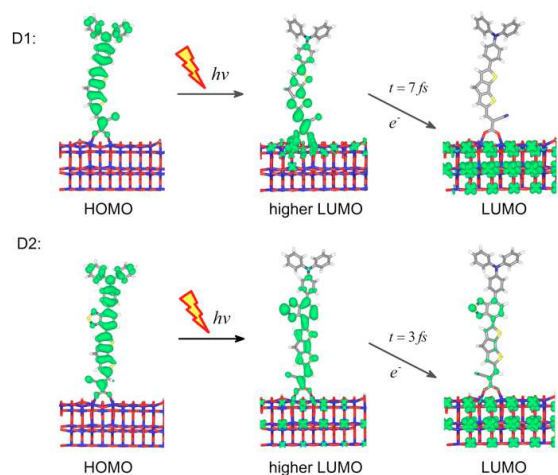
Fig. 2 Illustration of the photoinduced electron injection for dye **D1** on TiO$_2$ (101) (top panel) and for dye **D2** on TiO$_2$(101) (bottom panel). The crystal orbital analyses were carried out at the Γ-point of the Brillouin zone. The electron density of selected orbital are plotted at the isosurface of 8×10^{-4} a.u. The calculated electron injection times are also presented.

dithiophene segment as a conjugated spacer to construct a high absorption coefficient organic chromophore for DSCs.[10] However, the absorption of **D1** only covers the short wavelength region of visible light. Here we introduce benzothiazole-cyclopentadithiophene (**BT–CDT**) moiety as a spacer into the above dye to develop a novel D–A–π–A photosensitizer **D2** (Fig.1) with much enhanced long wavelength light absorption. The photophysical, electrochemical properties and photovoltaic characteristics of the D–A–π–A dye are extensively investigated.

As illustrated in Scheme S1(ESI†), **D2** was synthesized through Suzuki coupling reaction between boronic acid substituted triarylamine and aldehyde precursor **2** using Pd(PPh$_3$)$_4$ as a catalyst, followed by treatment with cyanoacetic acid in the presence of piperidine as a catalyst in acetonitrile. The synthesis of **D1** followed the reported procedures.[10] Their chemical structures were fully characterized by ^{1}H NMR, ^{13}C NMR, and MALDI-TOF MS (ESI†), and were found to be consistent with the proposed structures.

The UV–Vis absorption and emission spectra of **D1** and **D2** in CH$_2$Cl$_2$ are shown in Fig.1, and the corresponding data are summarized in Table S1 (ESI†). Both dyes exhibit two major absorption bands at 290–390 nm and 400–700nm. The absorption at 290–390 nm is ascribed to the localized aromatic π–π* transitions, while that at 400–700 nm is originated from the intramolecular charge transitions. The maximum absorption wavelengths (λ$_{max}$) for **D1** and **D2** appear at 512 and 556 nm, and the corresponding maximum extinction coefficients are 4.3×10^4 and 5.6×10^4 M^{-1} cm^{-1}, respectively, which are much higher than that of the ruthenium dye N719 (~ 10^4 M^{-1} cm^{-1}).[11] The λ$_{max}$ of **D2** is red-shifted by 44 nm as compared to **D1**, due to a better delocalization of electrons over the π–conjugated molecules when BT–CDT moiety is used as the linker. Moreover, when the two dyes are adsorbed onto 2.5 μm thick TiO$_2$ films, as a result of deprotonation and presumably H-aggregate formation[12] the absorption peaks of **D1** and **D2** are blue-shifted to 461 and 536 nm (Table S1 and Fig S1. ESI†), respectively. Apparently, **D1** reveals a sharp hypsochromic shift by 51 nm in the absorption spectrum, while it is only 20 nm for **D2** (Fig. S1).

To evaluate the energetics of the two dye molecules, cyclic voltammetry was performed to measure the oxidation potentials ($E_{D/D+}$), which correspond to the HOMO level potentials of the dyes. As summarized in Table S1, the half-wave potentials of **D1** and **D2** are 1.02 and 1.09 V (vs. NHE), respectively, indicating the HOMO levels of both dyes are significantly more positive than that of the [Co(bpy)$_3$]$^{2+/3+}$ (0.57 V vs. NHE),[7c] and ensuring fast regeneration of the dyes. The excited state potential ($E_{D*/D+}$) reflecting the LUMO level of the dye, can be derived from the ground-state oxidation potential and the zero-zero excitation energy (E_{0-0}) determined from the intersection of the normalized absorption and emission spectra.[13] The $E_{D*/D+}$ of **D1** and **D2**, determined to be -1.01 and -0.86 V vs. NHE, respectively, is more negative than the conduction band of TiO$_2$ at approximately -0.50 V vs. NHE, indicating the driving force is sufficiently large for effective electron injection from the two dyes.[14]

The density functional theory (DFT) calculations were carried out to provide more insight of the electronic properties of the dyes. The electron distributions in HOMO and LUMO levels of the two dyes are shown in Fig. S2 (ESI†). The HOMOs of both D1 and D2 are fairly delocalized over the TPA-donor and spacer moieties and the LUMOs are extended over the cyanoacetic unit and part of the spacer. Such a spatially well-separated orbital distribution is highly desirable for efficient intramolecular charge separation upon photoexcitation. The photoinduced electron injection mechanism analyzed by the Γ-point crystalline orbital calculation is summarized in Fig. 2. The result is in line with the commonly accepted mechanism of DSC that the electron is transferred from the dye to the substrate through a photo-excitation process and followed by an electron injection process. The electron injection rate estimated by the Newns-Anderson approach is ~7 and 3 fs for **D1** and **D2**, respectively, suggesting it is not significantly affected by the presence of benzothiazole moiety in **D2**. The values are also in close accordance with other computational results for the D-π-A dyes,[15] suggesting electron injection for both dyes is fast enough to ensure efficient electron injection.

The j–V characteristics of DSCs sensitized with **D1** and **D2** on 7.0 μm TiO$_2$ films (without scattering layer) employing [Co(bpy)$_3$]$^{2+/3+}$ based electrolyte are shown in Fig. S3 and Table S2 (ESI†). The **D1** cells exhibited a maximum PCE of 6.53 % (j_{sc} = 11.8 mA cm^{-2}, V_{oc} = 768 mV, FF = 0.72). Under the same condition, the cells sensitized with **D2** had a PCE of 7.99 % (j_{sc} = 15.2 mA cm^{-2}, V_{oc} = 786 mV, FF = 0.67). The superior PCE of
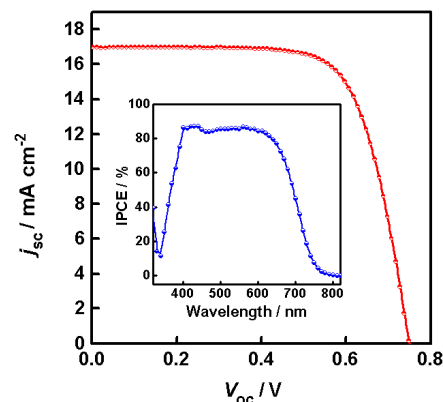
Fig. 3 j - V characteristics of a DSC sensitized with **D2**. The inset shows the IPCE spectrum of the cell. Light intensity for the j - V measurement is AM1.5G 100 mW/cm^2.

D2 is attributed to the relatively high j_{sc} stemming from its broader absorption and enhanced molar extinction coefficient in the visible region. The drastic enhancement of j_{sc} for **D2** over **D1** was also consistently seen in the incident photon-to-electron conversion efficiency (IPCE) spectra (Fig. S2).

In order to further improve the performance of **D2**, TiO$_2$ electrodes consisting of mesoporous TiO$_2$ layer and scattering particles (4.8 μm transparent + 2 μm scattering layers) were employed. The optimized PCE of **D2** reaches 9.01% with a J_{sc} of 17.0 mA cm^{-2} and V_{oc} of 749 mV. The IPCE spectrum of the cell is shown in Fig. 3, with onset wavelength extending to 780 nm and external quantum efficiency generally above 80% in the range of 400-650 nm. This matches well with its broader absorption spectrum and enhanced molar extinction coefficient. Interestingly, the PCE of **D2** cell was even raised to 9.31% (j_{sc} = 17.2 mA cm^{-2}, V_{oc} = 752 mV, FF = 0.72) after aging at room temperature for 20 days (Table S3).

To rationalize the superior performance of **D2**, we further investigated the electron-dye recombination (EDR) and dye regeneration. Their respective time constants τ_{edr} and τ_{reg} can be quantified using transient absorption (TA) decay measurement (Fig. 4). The excitation wavelength was fixed close to the maximum absorbance of **D2**, to avoid interferences of the pump beam when probing at the maximum of the absorption peak. The absorption traces can be fitted to a stretched exponential decay function $\Delta A(t) \propto A_{0exp}[-(t/\tau_{WW})^\beta]$, where A_0 is the pre-exponential factor, τ_{WW} is the characteristic stretched exponential lifetime, and β is the stretch factor.[16] The characteristic stretched exponential lifetime of EDR and regeneration of oxidized dye were derived using cells containing an inert and a $[Co(bpy)_3]^{2+/3+}$ containing electrolyte, respectively. As direct comparison of τ_{WW} values could be meaningless if β varies, weighted average lifetime (τ_{obs}) was adopted to calculate the rate constants:

$$\tau_{obs} = \frac{1}{k_{obs}} = \frac{\tau_{WW}}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

where k_{obs} is the observed rate constant for the reduction of oxidized dye, and $\Gamma(\ )$ is the gamma function. The resultant reduction rate constant of oxidized dye is 2.4×10^5 s^{-1} in cells with $[Co(bpy)_3]^{2+/3+}$ which is the sum of regeneration and EDR rate constant ($k_{rg}' + k_{edr}'$), while that in redox inactive inert cells is 19.6 s^{-1} (k_{edr}'). Regeneration efficiency (η_{reg}) of **D2** is calculated to be more than 99.9% with $k_{rg}' / (k_{rg}' + k_{edr}')$.

In summary, we report a new D–A–π–A organic dye – **D2**. Due to the presence of a strong electron-withdrawing benzo-thiadiazole unit in the π-bridge, **D2** exhibits much enhanced absorption of long wavelength photons compared with the reference D–π–A dye. Computational and experimental studies reveal that **D2** has ultrafast charge injection in TiO$_2$ upon photoinduced excitation and almost unity regeneration efficiency in $[Co(bpy)_3]^{2+/3+}$–based electrolyte in DSCs. As a result, the cells have achieved a power conversion efficiency > 9% under AM1.5 1 sun illumination, which is much superior to the D–π–A dye under similar conditions. These results suggest that rational structural engineering of organic dyes in conjunction with a favorable redox mediator could concomitantly improve the j_{sc} and V_{oc} of DSCs and eventually lead to much enhanced power conversion efficiency.
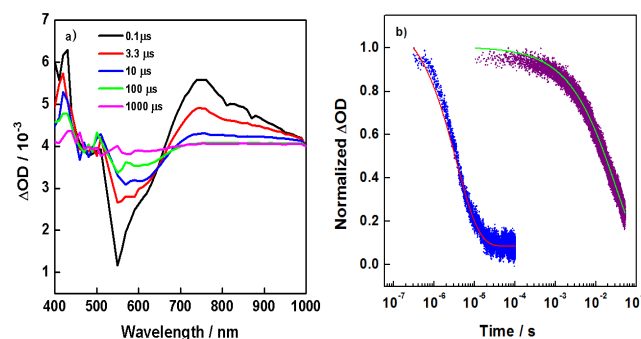
Fig. 4 (a) Transient absorption spectra for a cell sensitized with D2. (b) Transient absorption decay measured for D2 cells with inert (purple) and $[Co(bpy)_3]^{2+/3+}$-based (blue) electrolytes.

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