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Dithieno[2,3-d;2',3'-d']benzo[1,2-b;4,5-b']dithiophene Based Organic Sensitizers for Dye-Sensitized Solar Cells

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We report two novel D-π-A type organic dyes with a coplanar dithieno[2,3-*d*;2',3'-*d*']benzo[1,2-*b*;4,5-*b*']dithiophene (DTBDT) as π-spacer for dye-sensitized solar cells. A best device performance with a power conversion efficiency of 6.32% is achieved, making DTBDT unit a promising building block for design of organic sensitizers.

Dye-sensitized solar cells (DSSCs), as one of the most promising photovoltaic technologies, have attracted sustained attention over the past decades because of their potential in low-cost solar-to-electricity conversion.[1-2] Sensitizers play a critical role in light harvesting and electron injection and thereby affect the power conversion efficiency (PCE) of the DSSCs.[3] Compared to expensive ruthenium complexes, metal-free organic dye sensitizers promise modest fabrication costs and grand flexibility in molecular tailoring.[4]

A donor-π spacer-acceptor (D-π-A) structure has been commonly exploited to lower the band gap and tune the molecular absorption for attaining panchromatic light-harvesting, relying on efficient intramolecular charge transfer (ICT).[5] Upon manipulating the three components of this chromophore one can optimize the performance of the DSSCs.[6] To date, a strong electron-poor unit such as cyanoacrylic acid bearing an anchoring group toward the TiO_2 surface is widely applied as the acceptor moiety,[7] while electron-rich units such as aromatic amines,[8-9] carbazoles,[10] and coumarins[11] are mostly adopted as donors. In addition to these, it is equally significant to judiciously modify the π spacer for modulating properties of the organic dyes. Many conjugated building blocks have been introduced as bridges between donor and acceptor units, for instance, oligoene,[12] oligothiophene,[13-14] thieno[3,2-*b*]thiophene,[15] cyclopentadithiophenes,[16-17] dithieno[3,2-*b*:2′,3′-*d*]silole,[8] dithieno[3,2-*b*:2′,3′-*d*]pyrrole,[18] benzo[1,2-*b*:4,5-*b*′]dithiophene,[19] indacenodithiophene,[20-21] and ladder-type pentaphenylene.[22] Among these linkers, fused heteroacenes (see examples in Fig. S1) possess good π-conjugation, increased coplanarity, and strong rigidification. It has proven that these features facilitate bathochromic and hyperchromic absorptions of organic dyes, leading to improved PCEs as compared to unplanar counterparts. The dyes containing coplanar spacers composed of three fused rings have been reported providing PCEs exceeding 9%.[18b] Coplanar building blocks with longer fused rings for DSSC dyes are relatively rare.[20-22] Therefore, from the view of material development it still keeps interesting to prepare new organic sensitizers containing coplanar π-spacers with large-conjugation-length for DSSC application.

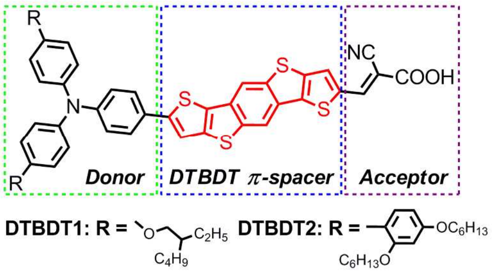
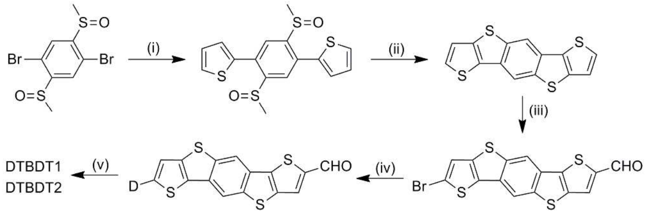


Fig. 1 Chemical structures of the two **DTBDT**-bridged organic sensitizers.

Dithieno[2,3-*d*;2',3'-*d*']benzo[1,2-*b*;4,5-*b*']dithiophene (**DTBDT**) is an analogue of pentacene with four benzene rings replaced by thiophenes, showing excellent coplanarity and π-conjugation as well as electron-rich characteristics. In recent years, it has been applied in high-mobility organic field-effect transistors (OFETs),[23-24] highly sensitive ammonia sensors,[25] and also been used as building block of semiconducting polymers.[26-27] These works inspired us to exploit it as a π-spacer to yield new organic dyes for DSSCs. Herein, we report two new D-π-A type organic sensitizers (Fig. 1) using coplanar **DTBDT** as the π-spacer, together with cyanoacrylic acid and triphenylamine derivative as acceptor and donor, respectively. Both sensitizers provide remarkable PCEs with a best value of 6.32% obtained from **DTBDT2**-based DSSC devices, indicating potential of the **DTBDT**-based compounds as DSSC dyes since further improvements of device efficiency could be achieved by modifying the **DTBDT** core. These two new dyes are prepared according to Scheme 1 and the detailed synthesis is described in the ESI.



Scheme 1 Synthetic route for sensitizers **DTBDT1** and **DTBDT2**. *Reagents and conditions*: (i) 2-tributyltinthiophene, $Pd(PPh_3)_2Cl_2$, DMF, 100 °C; (ii) 1) Eaton's reagent, r.t., 48 h; 2) H_2O, 60 °C, 30 min; (iii) 1) NBS, $CHCl_3$/AcOH, r.t., 12 h; 2) $POCl_3$, DMF, 1,2-dichloroethane, 80 °C, 12 h; (iv) pinacol ester of D (D=N,N-bis(4-(2-ethylhexyloxy)phenyl)aniline for **DTBDT1**, D=N,N-bis(2',4'-dihexyloxybiphenyl-4-yl)aniline for **DTBDT2**), $Pd(PPh_3)_4$, aq. K_2CO_3 (2 M), Aliquat 336, toluene, 90 °C, 12 h; (v) cyanoacetic acid, piperidine, $CHCl_3$, reflux, 12 h.

Fig. 2 depicts the UV-vis absorption and photoluminescence spectra of the dyes in chloroform solution (10^{-5} M). Both dyes display broad absorption bands ranging from 250 to 600 nm with high molar extinction coefficients (ε) of 3.67×10^4 M^{-1} cm^{-1} for **DTBDT1** and 3.48×10^4 M^{-1} cm^{-1} for **DTBDT2**. The absorption band in the high-energy region corresponds to the π-π* transition of the whole D-π-A conjugated backbone while the one between 400 and 600 nm can be attributed to the ICT from the donor to the acceptor. Compared to **DTBDT1** exhibiting an absorption maximum (λ_{max}) at 472 nm, **DTBDT2** reveals a red-shifted λ_{max} at 485 nm, which can be explained by the stronger electron-donating ability of the donor unit leading to a stronger photoinduced ICT. This feature is also reflected in the fluorescence spectra by a slight red-shift of the charge transfer emission maximum. In addition, a shoulder around 575 nm shows up for both dyes, which can be traced back to the emission from the locally excited state, with higher intensity for the **DTBDT1**.[21]

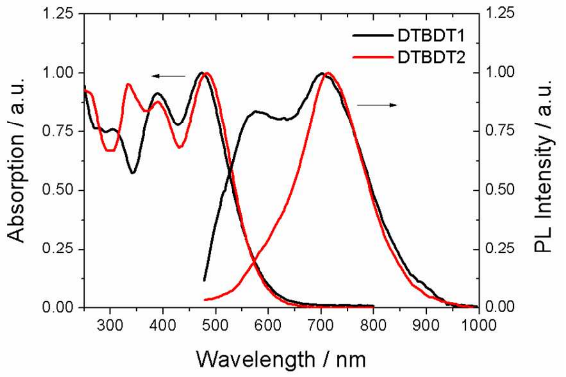


Fig. 2 UV-vis absorption and photoluminescence spectra of organic dyes **DTBDT1** and **DTBDT2** in chloroform.

Cyclic voltammetry (CV) was carried out to investigate the electrochemical properties of the dyes. As shown in Fig. S2, both dyes exhibit one reversible oxidation wave at low potential ascribed to the removal of an electron from the triphenylamine moiety and additional quasi-reversible oxidation waves at higher potential attributed to the contribution from the **DTBDT** π-spacer. The first oxidation potential (E_{ox}) of the **DTBDT1** is lower than that of **DTBDT2**. This is due to the more delocalized π-conjugation caused by the introduction of two additional benzenes in **DTBDT2**.[19] The HOMO levels of both dyes estimated from the onset of the E_{ox} are more positive than that of $Co(II/III)(bpy)_3$ redox couples (0.56 V vs NHE), which is necessary to ensure that the neutral dye is effectively regenerated after being oxidized.[22] The LUMO levels are calculated from the HOMO levels and the zero-zero excitation energy ($E_{0\text{–}0}$=2.14 eV for both dyes) determined from the onset of the absorption spectra to be –2.84 eV for **DTBDT1** and –3.02 eV for **DTBDT2**. The values are sufficiently more negative than the conduction band edge of TiO_2 (–0.5 V vs NHE), in favor of efficient electron injection from the excited dye onto the TiO_2 electrode.[17]

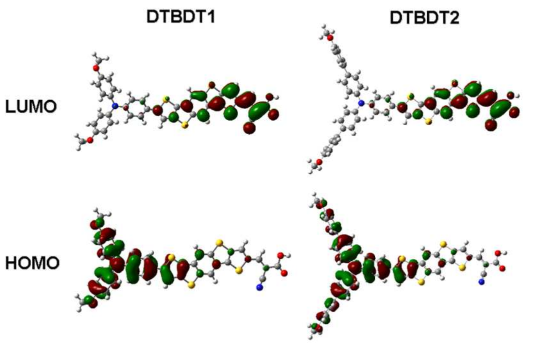


Fig. 3 Calculated frontier molecular orbitals of organic dyes **DTBDT1** and **DTBDT2** at B3LYP/6-31G* level.

Density functional theory (DFT) was employed to optimize the geometries and calculate the frontier molecular orbitals of the two dyes. The calculation reveals the coplanar structure of the **DTBDT** bridge and the electron distributions in the HOMO and LUMO levels of the dyes as illustrated in Fig. 3. HOMOs extend from the triphenylamine donor to the **DTBDT** π-spacer, while LUMOs are mainly localized from the cyanoacetic acid acceptor to its adjacent π-spacer. Such an electronic distribution will facilitate electron injection from the excited dye to the TiO_2 electrode.

Table 1 DSSC performances of the dyes measured at 100 mW cm^{-2} AM 1.5G. PCE shown in maximum value with deviation of 0.5%.

Dye	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
DTBDT1	0.65	8.90	0.70	4.05
DTBDT2	0.73	12.73	0.68	6.32

Both **DTBDT1** and **DTBDT2** were applied in DSSCs as photosensitizers in conjunction with the $Co(II/III)(bpy)_3$ redox couple as a TFSI salt. The cobalt complex redox shuttle was chosen since it yielded the highest open circuit potential (V_{OC}) hence the best DSSC efficiency so far.[28-30] The solar cell performances are summarized in Table 1 and the corresponding

J-V curves are shown in Fig. 4a as measured at 100 mW cm^{-2} AM 1.5G. Clearly, **DTBDT2** yields better PCE as compared to **DTBDT1**, owing to the higher V_{OC} and particularly to the more superior short circuit current density (J_{SC}). The significantly enhanced J_{SC} of about 4 mA cm^{-2} for the **DTBDT2** cell most probably originates from the amplified incident photon to current conversion efficiency IPCE, as illustrated in Fig. 4b. This phenomenon is in agreement with the observed red shift of the **DTBDT2** absorption relative to **DTBDT1**, as triggered by the stronger donor group in the former dye.

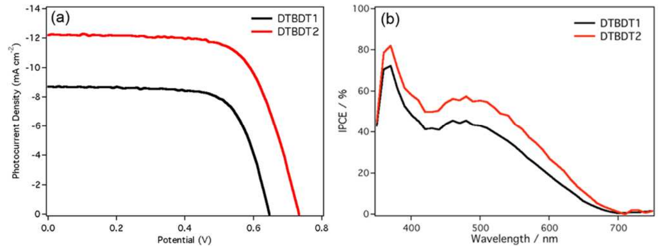


Fig. 4 (a) *J-V* curves and (b) IPCE spectra for DSSCs based on studied dyes.

In addition, the V_{OC} of the **DTBDT2**-based device is 80 mV higher than that based on **DTBDT1**. In order to explain this observation, photovoltage and photocurrent transient measurements were performed with the aim to investigate the differences in electron lifetimes within the TiO_2 photoanode and possible conduction band shifts in the TiO_2 layer of the DSSCs. As Fig. 5a highlights, electron lifetimes of the **DTBDT2** cells are superior in that comparison, thus accounting for the higher V_{OC}. Another source of V_{OC} alterations can stem from changes in the TiO_2 conduction bands. As Fig. 5b reveals, the changes in V_{OC} with the TiO_2 film capacitances are almost identical, implying that the conduction bands within the DSSCs of both sensitizers are very similar. Therefore, the measured variation in V_{OC} must result from a more suppressed charge recombination with $Co(III)(bpy)_3$ when utilizing the **DTBDT2** dye. This can be explained by the more bulky donor of **DTBDT2**, in this way more effectively blocking the $Co(III)(bpy)_3$ to approach the TiO_2 surface at which recombination takes place.[31] The efficiency we obtained from the **DTBDT2** is comparable with those of indacenodithiophene-bridged dyes with PCEs of 6−7%.[21] Both **DTBDT** and indacenodithiophene are composed of five fused rings. These dyes have slightly lower PCEs than those containing shorter fused spacers[15, 18] but higher ones than dyes with longer fused spacers.[22] All these spacer units possess coplanar structures and same backbone curvatures. It may thus imply that the conjugated length of coplanar π-spacers takes effect on the device efficiency, although different processing conditions cannot be excluded. This is worthy of further investigations.

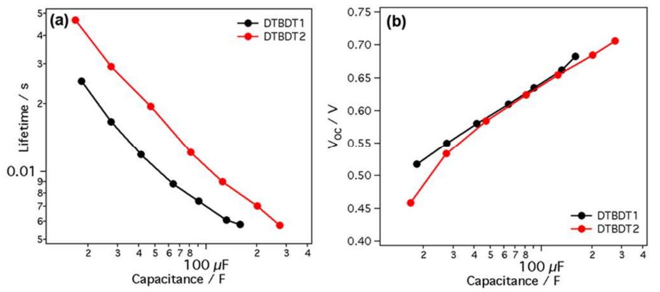


Fig. 5 (a) Electron lifetimes within the TiO_2 film and (b) shifts in V_{OC} in dependence of TiO_2 layer capacitance of the two **DTBDT** dyes.

In summary, we present two **DTBDT**-bridged organic sensitizers for DSSCs. The coplanar and electron-rich nature of the **DTBDT** spacer favors efficient ICT from donor to acceptor, which can shift the absorption to long wavelength and improve PCE of the dyes. The two title chromophores show broad absorption bands between 250 and 600 nm with a more red-shifted absorption from **DTBDT2** than **DTBDT1**. When applied in DSSCs with the cobalt complex redox electrolyte, the dye **DTBDT2** provides a better PCE of 6.32% than the **DTBDT1** thanks to higher V_{OC} and J_{SC} of the former. It should be noted that the rigid central **DTBDT** core is not substituted by any groups, which can cause undesirable aggregation between dye molecules. Thus, there is still room to further improve the performance of the **DTBDT**-based DSSCs by introducing substitutions either at the central benzene or at the outer thiophenes of the **DTBDT** unit. This work thus points toward the **DTBDT** unit as a promising π-spacer for new organic DSSC sensitizers.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Synthesis, characterization, NMR and HRMS spectra of the **DTBDT** dyes, and fabrication details of the DSSC devices. See DOI: 10.1039/c000000x/

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