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Dithiafulvenyl Unit as a New Donor for High-Efficiency Dye-Sensitized Solar Cells: Synthesis and Demonstration of a Family of Metal-Free Organic Sensitizers

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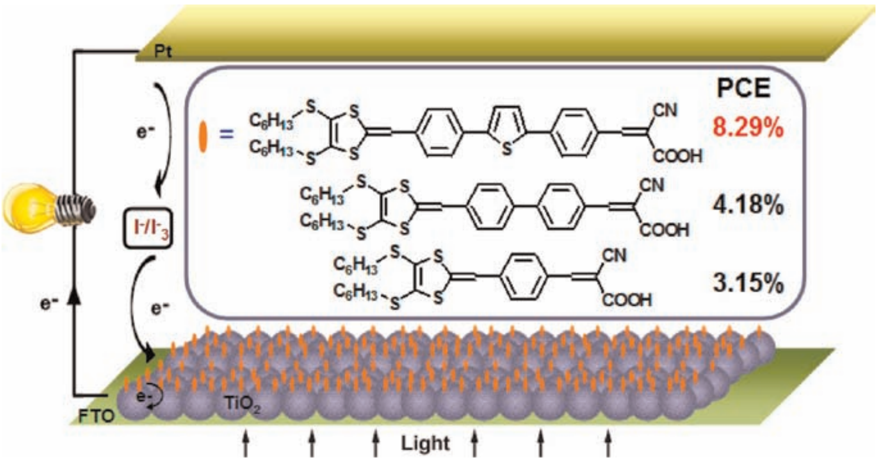
ABSTRACT



This work identifies the dithiafulvenyl unit as an excellent electron donor for constructing D−π−A-type metal-free organic sensitizers of dye-sensitized solar cells (DSCs). Synthesized and tested are three sensitizers all with this donor and a cyanoacrylic acid acceptor but differing in the phenyl (DTF-C1), biphenyl (DTF-C2), and phenyl−thiopheneyl−phenyl π-bridges (DTF-C3). Devices based on these dyes exhibit a dramatically improved performance with the increasing π-bridge length, culminating with DTF-C3 in η = 8.29% under standard global AM 1.5 illumination.

Dye-sensitized solar cells (DSCs) have shown the potential to achieve high power conversion efficiency (η).[1] One of the crucial components in DSCs is the sensitizer, which is responsible for harvesting sunlight to excite electrons and subsequently inject them into the conduction band of a transparent semiconductor network for collection. Ru(II)−polypyridyl complex photosensitizers have registered η exceeding 11% owing to their broad absorption from visible to near-infrared through the metal-to-ligand charge transfer (MLCT) transition and their long excited-state lifetimes.[2,3] From the viewpoint of practical application, however, the scarcity and high cost of the Ru source warrant minimizing and avoiding its use in DSCs. Most recently, a major advance in DSCs has been the

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development of a zinc porphyrin sensitizer reaping a η over 12%.[4] However, this was achieved by the cosensitization of the zinc porphyrin sensitizer and a triphenylamine sensitizer as well as the judicious usage of a Co$^{(II/III)}$ tris(bipyridyl)-based redox electrolyte. In parallel, there has been keen interest in developing donor–π-bridge–acceptor (D–π–A)-type metal-free organic sensitizers. Among the various organic donors, e.g., triphenylamine,[5] coumarin,[6] and indoline,[7] that have been explored in DSCs, triphenylamine has yielded η of $\sim$10%.[5c] Squaraine dyes have also been designed to enhance the light-harvesting property in the near-IR region.[8] Succeeding developments of such metal-free organic sensitizers need to address significant issues such as further η boost, cost reduction, and synthesis simplicity.

Tetrathiafulvene (**TTF**) is a well-known electron-donating group, and the preparation of its derivatives has primarily been motivated for applications as optoelectronic materials.[9] Recently, Grätzel et al. investigated the use of ex**TTF** (with extended π-conjugation) sensitizers in DSCs and obtained a moderate η.[10] By comparison, dithiafulvene (**DTF**)[11] can be regarded as a smaller version of the fulvene family characterized by a terminal electron-donating group, which could permit more concise synthesis, compact dye adsorption, and effective charge separation.

To our knowledge, however, the potential of the dithiafulvenyl group as a donor for DSCs has not been explored. Here, we report the facile synthesis and DSC performance of a series of organic D–π–A-type sensitizers based on the dithiafulvene derivative donor and a cyanoacrylic acid acceptor with different bridge lengths. This initial work has demonstrated a performance of the metal–free organic **DTF-C** sensitizers comparable to that of Ru-based dye N719 typically used in DSCs as a point of reference.

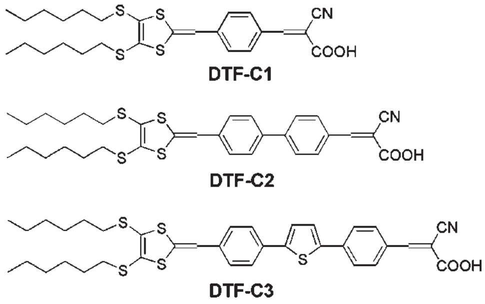

Figure 1. Molecular structures of **DTF-C1**, **DTF-C2**, and **DTF-C3**.

Illustrated in Figure 1 are chemical structures of the three D–π–A-type sensitizers we have synthesized, which are designated as **DTF-C1**, **DTF-C2**, and **DTF-C3** in the order of increasing π-bridge length. To prevent aggregation of these sensitizers as well as to retard charge recombination,[7b] two *n*-hexyl groups were symmetrically attached on the dithiafulvenyl donor unit. The synthesis of the sensitizers involved two major steps (Scheme S1, Supporting Information): (1) Horner–Wittig condensation of 4,5-bis(hexylthio)-1,3-dithiole-2-thione (**HDT**) as the donor moiety and aromatic dialdehydes **A1**–**A3** produced the key intermediate π-extended DTF-bearing aldehydes **B1**–**B3**; (2) Knoevenagel reaction of the resulting aldehydes and cyanoacetic acid in the presence of piperidine afforded the target sensitizer compounds **DTF-C**. As the starting reagents for the condensation in Scheme S1 (Supporting Information), **HDT** was prepared by the reaction of $[Et_4N]_2[Zn(DMIT)_2]$ with 1-bromohexane following a protocol from the literature (Scheme S2, Supporting Information),[12] and the aromatic dialdehydes were obtained commercially or by Suzuki couplings (Scheme S3, Supporting Information).

Figure 2 shows absorption spectra of the **DTF-C** sensitizers, and the corresponding spectroscopic parameters extracted are summarized in Table S1 (Supporting Information). All three of the sensitizers have a relatively strong absorption in the 400–500 nm region attributable to the π–π^* charge transfer transition in π-extended DTF chromophores. The absorption maximum (λ_{max}) was observed at 428 nm (molar extinction coefficient $\varepsilon = 1.87 \times 10^4\ M^{-1}\ cm^{-1}$) for **DTF-C1** and 406 nm ($\varepsilon = 2.75 \times 10^4\ M^{-1}\ cm^{-1}$) for **DTF-C2**. While the trend of extinction coefficient is plausible, such a blue-shift as a result of the lengthening the π-bridge is counter to our expectation. From Table S1 (Supporting Information), we find that the Stokes shift of **DTF-C2** is much larger than that of **DTF-C1** (7908 cm^{-1} vs 6270 cm^{-1}). This indicates a larger

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excitation-induced geometry change of **DTF-C2** than that of **DTF-C1**. To further improve the spectral response for DSCs, we opted to introduce a thiophene unit into the π-bridge on the premise that extension of the π-bridge would increase the ε value and insertion of electron-rich moiety would red shift and broaden the absorption spectrum. The resulting sensitizer is **DTF-C3**. As expected, one observes an increased ε and a broadened absorption band for **DTF-C3** (λ_{max} = 427 nm, ε = 3.83 × 10^4 M^{-1} cm^{-1}), and this improves the light-harvesting efficiency. From the UV−vis spectra of all three sensitizers adsorbed on transparent mesoporous TiO_2 films (~4 μm thick) (Figure S3, Supporting Information), red-shifted absorption onsets by ~100 nm are observed relatve to those of their solution spectra, indicating the possible formation of aggregates.

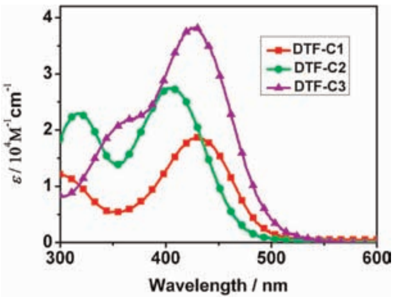

Figure 2. UV−vis absorption spectra of sensitizers **DTF-C1**, **DTF-C2**, and **DTF-C3** in THF.

The molecular orbital energy levels of the sensitizers have been derived from cyclic voltammograms (CV) (Figure S1, Supporting Information) in combination with the excitation transition energies (E_{0-0}) determined by the intersection of absorption and PL spectra (Figure S2, Supporting Information) and are presented in Table S1 (Supporting Information). The first oxidation potentials (E_{ox}) are associated with the HOMO levels of our **DTF-C** sensitizers. The LUMO levels of **DTF-C1**, **DTF-C2**, and **DTF-C3**, calculated as $E_{ox}-E_{0-0}$, are sufficiently negative relative to the conduction-band edge of TiO_2 (−0.5 V vs NHE) and shift negatively upon increasing the π-bridge length due presumably to increasing charge separation, further building up the thermodynamic driving force for the electron injection. The HOMO levels are generally more positive than the iodine/iodide redox potential (0.4 V vs NHE), indicating a thermodynamically downhill regeneration of the photooxidized sensitizers by accepting electrons from the surrounding I^- ions.

Figure 3a shows the photocurrent−voltage characteristics for the **DTF-C-** and **N719**-sensitized solar cells under illumination of the standard AM 1.5 simulated sunlight (1 sun, 100 mW cm^{-2}). Relevant photovoltaic parameters including short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), fill factor (FF), and η were determined from those curves and are collected in Table 1. Several features are self-evident. First, the η of the DSCs increases as the π-bridge length of the sensitizers increases from **DTF-C1** (3.15%) to **DTF-C2** (4.18%), ending with **DTF-C3** soaring to the highest value of 8.29%. The η of this new metal-free organic sensitizer is remarkable and can almost stand comparison with that of the N719-sensitized cell (η = 8.76%) fabricated and tested under similar conditions. Second, while the FF values are similar, both J_{sc} and V_{oc} increase significantly with the π-bridge length in the order of **DTF-C1**, **DTF-C2**, and **DTF-C3**, and most dramatic is the last jump to **DTF-C3** achieving a high J_{sc} of 14.35 mA/cm^2 and a very impressive V_{oc} of 0.83 V.

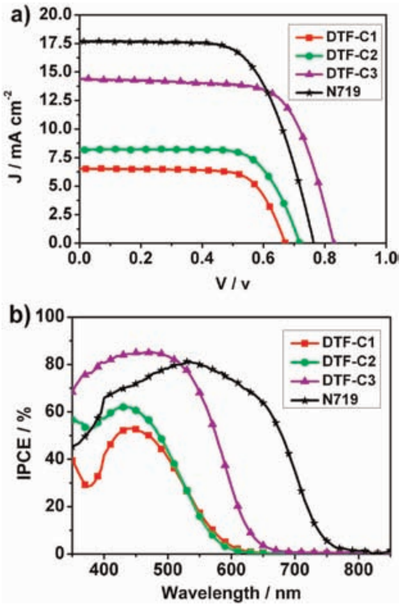

Figure 3. (a) Photocurrent−voltage curves of the DSCs based on **DTF-C1**, **DTF-C2**, **DTF-C3**, and **N719**. (b) Incident photon to current efficiency (IPCE) spectra of **DTF-C1**-, **DTF-C2**-, **DTF-C3**-, and **N719**-based DSCs.

The incident photon to current efficiency (IPCE) spectra shown in Figure 3b have confirmed the trend of J_{sc} variation in the order of **DTF-C3** > **DTF-C2** > **DTF-C1**. For **DTF-C1** and **DTF-C2**, relatively low IPCE values (< 65%) and narrow photoresponse bands were observed. In contrast, the IPCE curve of **DTF-C3** is both broad in width extending from 350 to 550 nm and high in magnitude with values over 70% and maxima at 85% (~475 nm).

To find out how the increase of π-bridge length impinges on the photoinduced charge separation, density functional theory (DFT) calculations were performed on electron-density distributions of the HOMOs and LUMOs of the three sensitizers. As shown in Figure S4 (Supporting Information), the HOMO electron density for the **DTF-C** sensitizers is mainly located at the electron-donor part and the adjacent aromatic rings and more and more shifted toward the donor unit in going from **DTF-C1** to **DTF-C2** and to **DTF-C3**. The LUMO electron density, on the other hand, is more and more shifted to the acceptor unit down this sensitizer series. Therefore, upon photoexcitation, the electron density is redistributed in the LUMO moving toward the acceptor unit anchored on TiO_2 and the increasing π-bridge length of our sensitizers appears to be desirable for the required charge separation in DSCs.

Table 1. Photovoltaic Performance of DSCs Based on **DTF-C1**, **DTF-C2**, **DTF-C3**, and **N719**

sensitizers	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	η (%)
DTF-C1	6.51	0.67	0.72	3.15
DTF-C2	8.20	0.73	0.70	4.18
DTF-C3	14.35	0.83	0.69	8.29
N719	17.63	0.76	0.65	8.76

Next, we measured the injected electron lifetimes in the conduction band of TiO_2 by intensity-modulated photovoltage spectroscopy (IMVS) to disscuss the possible orgins of the increasing V_{oc} from **DTF-C1** to **DTF-C2** and to **DTF-C3**, and the result is shown in Figure 4. Pursuant to common knowledge, the variation of V_{oc} can be attributed to the changing electron recombination time.[13] Gratifyingly, the electron lifetimes of the three sensitizers are positively correlated with their π-bridge lengths. In particular, **DTF-C3** has the longest π-bridge and hence holds the longest electron lifetime which is almost 10-fold higher than that of **DTF-C1**. This result shows that for the sensitizer series studied here the electron lifetime is mainly determined by the recombination with the contiguous electrolyte as commonly believed. Plausibly, with the increasing length of the π-bridge, it would become increasingly more difficult for the injected electron in the TiO_2 CB to recombine with the redox electrolyte due to the formation of a thicker dye block layer. Additionally, electron recombination with the photooxidized adsorbed sensitizers could also be decreased with increasing π-bridge length simply due to the ionized HOMO being more spatially removed from the TiO_2 substrate. This naturally explains the highest V_{oc} (0.83 V) for **DTF-C3**.

There are several contributing factors to IPCE and thus J_{sc} of a DSC in connection with the sensitizer. The first is the molar extinction coefficient.[1d] In general, the light absorption also follows the increasing order from **DTF-C1** to **DTF-C2** and to **DTF-C3**. Although the absorption maximum of **DTF-C2** (406 nm) is blue-shifted from that of **DTF-C1** (428 nm), the molar extinction coefficient of **DTF-C2** is about 1.47 times larger than that of **DTF-C1**. For **DTF-C3**, although the λ_{max} (427 nm) is close to that of **DTF-C1**, its absorption band is evidently broadened. More important, the ε of **DTF-C3** is more than double that of **DTF-C1**, which in effect is the largest of all the three sensitizers. Second, charge separation also appears to be enhanced from **DTF-C1** to **DTF-C2** and to **DTF-C3**. It is reasonable that a longer π-bridge be associated with a better charge separation owing to the more extended charge delocalization. Indeed, this has been confirmed by the DFT calculation result described above (Figure S4, Supporting Information). Taken together, the enhanced light absorption and charge separation arising from the $\pi-$bridge lengthening should boost respectively the light capture and charge injection, thus raising the IPCE and thus J_{sc}.

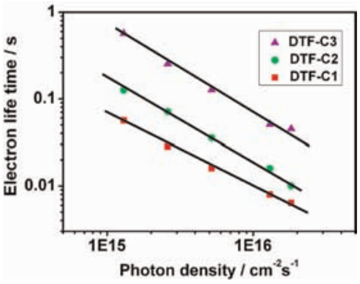

Figure 4. Variation of electron lifetime for the **DTF-C1**-, **DTF-C2**-, and **DTF-C3**-based DSCs with incident light intensity.

In conclusion, we have by facile synthesis developed a series of D$-\pi-$A-type, new metal-free organic sensitizers and thereby validated the dithiafulvenyl unit as an effective electron-donating group for high-performance DSCs.[14] The DSC performance increases with the π-bridge length. Even though the maximum absorption of **DTF-C3** is located in a relatively blue region at 427 nm, the η of the **DTF-C3**-sensitized solar cells has reached 8.29% under standard AM 1.5 solar conditions. This brings such metal-free organic sensitizers to the rank of the Ru-based N719 sensitizer prototype (η = 8.76%) in terms of the DSC performance. We have shown that increasing the π-bridge length not only enhances photon capture but also improves photoinduced charge separation and retards charge recombination, accounting for the trend of DSC performance variation for the sensitizers. Given the preliminary experiment, there is much room for improvement by, for example, further broadening the photoresponse of the sensitizers. Overall, this work has blazed a new path for developing high-performance organic dye-sensitized solar cells.

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Supporting Information Available. Synthesis procedures, characterization of all compounds, spectra data, cyclic voltammetric results, device fabrication, and DFT computation methods. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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(14) In response to a reviewer's comment, we have inserted a discussion in the Supporting Information comparing the results of our new donor-based sensitizers with those based on the triphenylamine donor.