Novel D–A–π–A-Type Organic Dyes Containing a Ladderlike Dithienocyclopentacarbazole Donor for Effective Dye-Sensitized Solar Cells

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**Supporting Information

ABSTRACT: A novel ladderlike fused-ring donor, dithienocyclopentacarbazole (DTCC) derivative, is used to design and synthesize three novel donor–acceptor–π–acceptor-type organic dyes (C1–C3) via facile direct arylation reactions, in which the DTCC derivative substituted by four p-octyloxyphenyl groups is served as the electron donor and the carboxylic acid group is used as the electron acceptor or anchoring group. To fine-tune the optical, electrochemical, and photovoltaic properties of the three dyes, various auxiliary acceptors, including benzo[2,1,3]thiadiazole (BT), 5,6-difluorobenzo[2,1,3]-thiadiazole (DFBT), and pyridal[2,1,3]thiadiazole (PT), are incorporated into the dye backbones. The results indicate that all of the three dyes exhibit strong light-capturing ability in the visible region and obtain relatively high molar extinction coefficients (>31 000 M$^{-1}$ cm$^{-1}$) due to their strong charge transfer (CT) from donor to acceptor. Moreover, theoretical model calculations demonstrate fully separated highest occupied molecular orbital and lowest unoccupied molecular orbital energy levels for the three dyes, which is helpful for efficient charge separation and electron injection. Using the three dyes as sensitizers, conventional dye-sensitized solar cells (DSSCs) based on liquid iodide/triiodide redox electrolytes are fabricated. Our results indicate that the BT-containing dye C1 affords the highest power conversion efficiency of up to 6.75%, much higher than that of the DFBT-containing dye C2 (5.40%) and the PT-containing dye C3 (1.85%). To our knowledge, this is the first example reported in the literature where the DTCC unit has been used to develop novel organic dyes for DSSC applications. Our work unambiguously demonstrates that the ladderlike DTCC derivatives are the superb electron-donating blocks for the development of high-performance organic dyes.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) as a kind of clear-energy device have attracted worldwide attention due to their great potential in low-cost fabrication of highly flexible, large-scale energy conversion devices.$^{1−7}$ Thanks to great efforts in innovative materials design and device engineering, DSSCs have exhibited much enhanced power conversion efficiency (PCE) recently.$^{1−7}$ As the key part of DSSCs, sensitizers play a crucial role in light capture, charge separation/recombination, and photovoltaic properties of the devices.$^{8−12}$ Generally, the sensitizers can be divided into two main categories: metal organic complexes and metal-free organic dyes. Although metal organic complexes, especially for zinc porphyrin$^{13−18}$ and ruthenium polypyridine$^{19−21}$ have achieved superior photovoltaic performance relative to metal-free dyes, their intrinsic drawbacks, such as heavy metal toxicity, high cost, and difficulty in synthesis and purification,$^{9}$ would limit the further development. Recently, great interest has arisen to develop metal-free organic dyes owing to their tremendous advantages, including low production cost, tunable structure, and facile synthetic procedure.$^{22−24}$ So far, some metal-free sensitizers have obtained encouraging PCEs of above 12%,$^{25−27}$ which can be comparable to metal complex dyes. Undoubtedly, the development of novel sensitizers is one of the most promising approaches for further advances in photovoltaic performance as...
well as understanding the relationship between materials structure and performance.

As far as molecular design is concerned, current mainstream strategy for metal-free organic dyes is to construct donor−π−acceptor (D−π−A) or donor−acceptor−π−acceptor (D−A−π−A) configuration to ensure efficient light capture and strong intramolecular charge transfer.\(^28\)−\(^32\) Compared to D−π−A dyes, the properties of D−A−π−A-type organic dyes can be readily adjusted by inserting an auxiliary acceptor between the D and π units, which thereby endows them with more flexible photoelectric properties. Moreover, this delicate molecular modification can not only fine-tune energy-level structure and light response region but also facilitate electron transportation from D unit to anchor group.\(^24\) On the basis of this strategy, current research interest for ideal D−A−π−A-type organic dyes mainly focuses on the modulation of π-conjugated aromatic donors,\(^33\)−\(^37\) π-bridges,\(^38\)−\(^40\) anchoring groups,\(^41\) auxiliary acceptors,\(^42\)\(^43\) as well as solubilizing side chains.\(^44\)−\(^46\) Among them, the exploitation of novel π-conjugated aromatic donors is considered to be the most versatile approach to develop large numbers of high-performance organic dyes. Hence, further development of novel aromatic donors for high-performance D−A−π−A-type organic dyes is worthy of being studied.

Due to their highly electron-donating nature and tunable modular structure, dithienocyclopentacarbazole (DTCC) derivatives have been widely utilized as the donor unit to develop a set of organic/polymeric semiconductors for organic solar cells (OSCs) and organic field-effect transistors (OFETs).\(^47\)−\(^50\) Since the first report on DTCC-based polymeric semiconductor by Hsu et al.,\(^47\) a series of DTCC-like aromatic fused rings and their organic/polymeric semiconductors have sprung up subsequently.\(^50\) Traditionally, they have been used as p-type semiconductors in OFETs and fullerene-based OSCs, which afford 0.001−0.14 cm\(^2\) V\(^{−1}\) s\(^{−1}\) hole mobilities and 3.7−4.6% PCE values.\(^37\)\(^38\) Our recent work reveals that, by

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**Figure 1.** Molecular structures of carbazole, DTCC, and DTCC-based organic dyes.

**Scheme 1.** Synthetic Routes to the Three Dyes C1−C3\(^44\)

Reagents and conditions: (a) Pd(PPh\(_3\))\(_2\)Cl\(_2\), K\(_2\)CO\(_3\), toluene/H\(_2\)O, 90 °C; (b) 1-bromo-4-(octyloxy)benzene, tetrahydrofuran (THF), n-BuLi, −78 °C for 2 h and then 70 °C for 24 h; acetic acid/H\(_2\)SO\(_4\), 85 °C, 4 h; (c) Pd(OAc)\(_2\), Cs\(_2\)CO\(_3\), PivOH, toluene, 110 °C, 4 h; (d) KOH, THF/H\(_2\)O (v/v, 3/1), 80 °C, 12 h.
embedding two strongly electron-deficient 3-(dicyanomethylene)indan-1-one terminal groups, the thiadiazole (PT). Investigation of the performance of DSSCs have demonstrated that the DSSC devices fabricated from the DTCC-IC has achieved an encouraging PCE of 6.0% and a high electron mobility of 2.17×10⁻³ cm² V⁻¹ s⁻¹. Over, its unique 3D spatial structure (see Figure 1) caused by embedding two strongly electron-withdrawing units as the auxiliary acceptors in the three dyes, including benzo[2,1,3]thiadiazole (BT), 5,6-difluorobenz[2,1,3]thiadiazole (DFBT), and pyridal[2,1,3]-thiadiazole (PT). Investigation of the performance of DSSCs has demonstrated that the DSSC devices fabricated from the BT-containing dye C1 achieves the highest PCE value of up to 6.75%, which is much higher than that of the DFBT-containing dye C2 (5.40%) and the PT-containing dye C3 (1.85%).

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization. Synthetic routes to the three DTCC-based organic dyes are illustrated in Scheme 1. Detailed synthetic procedures and characterization data are provided in Supporting Information. Compound 3 was prepared via a Suzuki coupling reaction of 9-octyl-2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazole (1) and ethyl 2-bromothiophene-3-carboxylate (2) in high yields (75%). Subsequently, a double nucleophilic addition reaction of freshly prepared 4-(octyloxy)phenyllithium and compound 3 was performed to obtain an aromatic alcohol, which was then directly converted to the ladderlike dithienocyclopentacarbazole (DTCC) derivative via a Friedel–Crafts reaction. Additionally, a series of key intermediates (aryl halides, 9–11) were prepared via Suzuki coupling reactions of ethyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (5) and compounds 6–8. After that, the DTCC donor was translated to the D–A–π–A-type intermediates (12–14) via direct arylation reactions (DARs) in moderate yields of ca. 40%. It should be mentioned that this versatile DAR approach makes our synthetic procedures more environmentally friendly and facile, which enables direct coupling reaction between the DTCC donors and the aryl halides (9–11). Finally, the target organic dyes C1–C3 were obtained in high yields (>73%) by the hydrolysis of compounds 12–14. All of the dyes were purified by column chromatography on silica gel and then recrystallized from acetone. The chemical structures of all of the novel compounds were confirmed by
1H NMR, 13C NMR, and matrix-assisted laser desorption ionization time-of-flight (Figures S4–S34). Furthermore, the structural regioregularity of compound 11 was confirmed by 1H−1H nuclear Overhauser effect spectroscopy (Figure S22). The results reveal that no cross-correlation peaks can be observed between the PT (H1) and phenyl group (H2 and H3) protons (Figure S22), which thereby provides an evidence for the regioselective cross-coupling between compounds 8 and 5. We thus assume that the PT-containing dye C3 has a well-defined structural regioregularity.

2.2. Optical Properties. The UV−vis absorption spectra of the three dyes C1−C3 in diluted CHCl3 solutions (10−5 M) are presented in Figure 2a, and the relevant data are summarized in Table 1. As shown in Figure 2a, three dyes exhibit a similar absorption feature with two typical absorption bands in the ranges of 350−420 and 450−680 nm, respectively. The former bands can be attributed to a localized aromatic π−π* transitions, whereas the latter ones can be assigned to a charge transfer (CT) between DTCC donor and electron acceptor. The CT peaks and the corresponding molar extinction coefficients (ε) are observed at 516 nm ($\varepsilon = 3.46 \times 10^4$ M−1 cm−1) for C1, 509 nm ($\varepsilon = 3.89 \times 10^4$ M−1 cm−1) for C2, and 568 nm ($\varepsilon = 3.14 \times 10^4$ M−1 cm−1) for C3 (Figure S1). The results indicate that the incorporation of DTCC donor into the dye backbone can achieve high ε values (>3.14 × 104 M−1 cm−1). Therefore, these dyes are expected to efficiently capture light and enable high photocurrents in their DSSCs. Although DFBT unit has much stronger electron affinity as compared to BT unit, the CT peak of the DFBT-containing dye C2 still displays a slight blue shift by ca. 7 nm. This blue-shifted feature can be ascribed to the disruption of molecular planarity due to the introduction of two large fluoro substituents into C2, thereby resulting in larger dihedral angle (−38.2°) relative to C1 (−35.1°), which is demonstrated in theoretical model calculations in Figure 3. Moreover, a significant red shift of about 52 nm is observed for the PT-containing dye C3, as a result of the strong CT transfer and the enhanced molecular planarity among the three dyes (Figure 3). The normalized absorption spectra on TiO2 films are depicted in Figure 2b. Once anchored on TiO2 films, the CT peaks of C1, C2, and C3 are determined to be 512, 498, and 551 nm, respectively. In comparison to their solution spectra, all of the dyes show ca. 4−17 nm blue shift because of the deprotonation effect of the acid groups binding with TiO2.11

2.3. Theoretical Model Calculations. To investigate the influence of various auxiliary acceptors on geometric configuration and electron distribution, we performed density functional theory (DFT) calculations at the B3LYP/6-31G* level. Herein, four octyloxy groups in the dyes C1−C3 were replaced by four methoxy groups to shorten calculation time. The optimized molecular structures, as depicted in Figure 3, reveal that the four aryl side groups locate outside of the main backbone, thereby forming a unique 3D backbone configuration. This 3D backbone feature is believed to suppress dye aggregation on TiO2 films and thus give high photovoltaic efficiency.11 For the three dyes, relatively small twisted dihedral angles (<3.4°) can be observed between the DTCC unit and the adjacent auxiliary acceptors. Compared to C1 (35.1°) and C3 (4.7°), the DFBT-containing C2 exhibits larger dihedral angles (38.2°) between the DFBT unit and phenyl group because the backbone coplanarity of C2 is sharply disrupted by introducing two large fluoro substitutes. However, due to the weak steric effect between adjacent groups, the PT-containing dye C3 exhibits excellent backbone coplanarity with the smallest twisted dihedral angles of 4.7°, which is much smaller than those of the BT-containing dye C1 (35.1°) and the DFBT-containing dye C2 (38.2°). Although a good backbone coplanarity will facilitate charge transfer, aggregation of dyes on TiO2 films caused by coplanar backbone is also enhanced. Thus, this feature generally leads to strong electron recombination on the TiO2/dye/electrolyte interface, which thereby gives partial explanation for the lowest PCE values of the C3-based DSSCs. Moreover, as shown in Figure 3, for the HOMO orbitals of the three dyes C1−C3, the electrons mainly distribute on the DTCC donors and also partly extend to the auxiliary acceptors, whereas the LUMO orbitals dominantly delocalize over the acceptor and the π-linker groups. This fully separated HOMO and LUMO orbitals distribution can guarantee the efficient charge separation and electron injection.11

Figure 3. Optimized molecular geometries and electron distributions of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the dyes C1−C3.
2.4. Electrochemical Properties. Cyclic voltammetry (CV) measurements were performed to study the electrochemical properties and energy-level structures of the dyes C1–C3. Typical CV curves and the corresponding energy-level diagram are provided in Figure 4. The relevant data are collected in Table 1. As shown in Figure 4a, three DTCC-based dyes exhibit one strong clear oxidation couple. We note that the first oxidation potentials \(E_{\text{ox}}\) of the dyes C1–C3, which correspond to the HOMO energy levels, are determined to be 1.10, 1.17, and 1.14 V (vs normal hydrogen electrode (NHE)), respectively; it should be mentioned that all of these \(E_{\text{ox}}\) values are externally calibrated by the ferrocenium/ferrocene (Fc+/Fc, see Figure S3) couple and addition of 0.63 V to the potential (vs Ag/AgCl).\(^{51}\) The observed results reveal that the \(E_{\text{ox}}\) values are much more positive than those of iodide/triiodide (I\(^{-}\)/I\(_3\)\(^{-}\)) redox couple (0.4 V vs NHE, Figure 4b), which provides enough driving forces for dye regeneration from excited-state dye to ground-state dye via capturing electron from I\(^{-}\)/I\(_3\)\(^{-}\) redox couple. On the other hand, the \(E_{\text{0-0}}\) energies of the dyes C1–C3, which were determined from the intersections of the normalized absorption and emission spectra, are calculated to be 2.14, 2.17, and 1.94 eV, respectively. According to the empirical equation of \(E_{\text{ox}} - E_{\text{0-0}}\), the reduction potentials \(E_{\text{red}}\) vs NHE are determined to be −1.04, −1.00, and −0.80 V, respectively. Thus, for the three dyes, more negative \(E_{\text{red}}\) values are observed as compared to the conductive band (CB) of TiO\(_2\) (−0.5 V vs NHE, Figure 4a); moreover, the calculated energy-level differences \(E_{\text{gap}}\) between \(E_{\text{red}}\) and CB of TiO\(_2\) are ca. 0.54, 0.50, and 0.30 eV, which are much larger than that of the theoretical requirement \(E_{\text{gap}} > 0.2\) eV.\(^{58}\) Therefore, we assume that three dye-based DSSCs would conduct an efficient electron injection from excited dye into TiO\(_2\) conductive band. However, the low-lying \(E_{\text{red}}\) value of C3 relative to C1 and C2 reveals that its driving force for electron injection may be less sufficient.

2.5. Photovoltaic Performance. To investigate the photovoltaic properties of the dyes C1–C3, conventional liquid DSSCs were fabricated and tested using I\(^{-}\)/I\(_3\)\(^{-}\) redox couple as the electrolyte. The detailed fabrication procedures are provided in Supporting Information. Figure 5a shows the typical photocurrent density–voltage \((J-V)\) curves of the dyes C1–C3 measured under global AM 1.5G sunlight with irradiance of 100 mW cm\(^{-2}\) at 298 K. All of the device parameters are summarized in Table 2. For the BT-containing dye C1, the optimized DSSCs achieved an excellent PCE of 6.20%.

![Figure 4](image4.png)

**Figure 4.** (a) CV curves recorded in CHCl\(_3\) solution. (b) Energy-level diagram of the dyes C1–C3.

![Figure 5](image5.png)

**Figure 5.** (a) \(J-V\) curves and (b) incident photon-to-electron conversion efficiency (IPCE) spectra of the dyes C1–C3.

### Table 2. Photovoltaic Performance of the Three Dyes with/without CDCA

| Dyes    | \(J_{sc}\) (mA cm\(^{-2}\)) | \(V_{oc}\) (mV) | \(\eta\) | PCE (%) |
|---------|----------------------------|----------------|--------|--------|
| C1      | 12.98                      | 671            | 0.71   | 6.20   |
| C2      | 10.44                      | 653            | 0.70   | 4.74   |
| C3      | 3.27                       | 562            | 0.77   | 1.42   |
| C1 + CDCA | 14.00                     | 685            | 0.70   | 6.75   |
| C2 + CDCA | 10.91                     | 685            | 0.72   | 5.40   |
| C3 + CDCA | 4.19                      | 580            | 0.76   | 1.85   |
6.2%, along with a short-circuit current density ($J_{sc}$) of 12.98 mA cm$^{-2}$, an open-circuit voltage ($V_{oc}$) of 671 mV, and a fill factor (ff) of 0.71. Compared to C1, the DFBT-containing dye C2 afforded relatively lower PCE of 4.74% and recorded a disappointing $J_{sc}$ of 10.44 mA cm$^{-2}$, a slightly dropped $V_{oc}$ of 653 mV, and a comparable ff of 0.70. We assume that the reduced PCE value for C2 mainly results from a 12.2% decrease in $J_{sc}$ value as compared to C1-based DSSCs. Although the PT-containing C3 obtained a broad absorption band relative to C1 and C2, the optimized C3-based DSSCs still gave quite low $J_{sc}$ and $V_{oc}$ values (3.27 mA cm$^{-2}$ and 562 mV, respectively), thereby leading to the lowest PCE of up to 1.42% among the three dyes. The reduced photovoltaic efficiency for C3 may partly result from its unexpected dye aggregation and electron recombination caused by its enhanced backbone coplanarity as demonstrated in the DFT calculation above. Another explanation presumably can be ascribed to its low-lying $E_{red}$ ($-0.80$ V) and too small $E_{gap}$ (0.30 eV) between $E_{red}$ and CB of TiO$_2$, which make the electron injection from excited dye to CB of TiO$_2$ much less efficient than those of C1 and C2. Upon coadsorbing with 5 mM chenodeoxycholic acid (CDCA), both $J_{sc}$ and $V_{oc}$ values of the C1–C3-based DSSCs were further improved due to the suppression of dye aggregation and charge recombination. Among the three dyes, C1-based DSSCs exhibited the highest PCE of up to 6.75%.

To further analyze $J_{sc}$ value, we measured the incident photon-to-electron conversion efficiency (IPCE) spectra of the C1–C3-based DSSCs. As shown in Figure 5b, both dyes C1 and C2 exhibited strong and broad absorption response in the visible region with the absorption onsets extended to ca. 700 nm, which enables both DSSC devices to obtain strong light-capturing ability and high $J_{sc}$ value. On the contrary, in the whole visible region, the C3-based DSSCs showed a quite weak absorption response with a maximum IPCE value of ca. 17%, thereby resulting in low $J_{sc}$ values. On the other hand, in comparison to C2, the C1-based cells displayed higher and broader IPCE values and achieved IPCE values over 60% at 400–630 nm. In general, the IPCE spectra have a positive effect on $J_{sc}$ and PCE of DSSCs; the highest IPCE values for C1 guarantee its highest $J_{sc}$ and PCE values among the three dyes.

After the addition of 5 mM CDCA, the IPCE values of the three dyes were slightly improved and hence leading to enhanced $J_{sc}$ and PCE values compared to those of the DSSCs without CDCA.

2.6. Electrochemical Impedance Spectroscopy (EIS).

Electrochemical impedance spectroscopy (EIS) is a powerful technique to study interfacial charge transfer in devices. To elucidate correlation of $V_{oc}$, we performed the Nyquist plots and Bode plots of the dye cells in complete darkness with a forward bias of $-0.70$ V and a frequency region at 0.01–100 kHz, respectively. As shown in Figure 6a,c, two semicircles from left to right in the Nyquist plot are visible; the larger semicircle in theory means the larger $R_{CT}$, generally providing the slower electron recombination rate. For the DSSCs without CDCA, the radius of the large semicircle increases in the order of C3 (20 Ω) < C2 (70 Ω) <
C1 (92 Ω) (Figure 6a,c), suggesting that the electron recombination rate increases in the order of C1 < C2 < C3, which is consistent well with the V_{oc} tendencies of C3 (562 mV) < C2 (653 mV) < C1 (671 mV). In comparison to the DSSCs without CDCA, the addition of CDCA has caused an increase of R_{CT} at the same forward bias for the C1–C3-based DSSCs, thereby leading to enhanced V_{oc} and PCE values.

The electron lifetime (τ) of the exited dyes can be associated with the peak frequency (f) at intermediate-frequency regions in Bode plots, which can be calculated from the equation of
\[ f = \frac{1}{2\pi \tau} . \]

The smaller the charge recombination rate, the longer the electron lifetime is, generally leading to improved V_{oc} and J_{sc} values. As shown in Bode plots (Figure 6b,d), the f values increase in the order of C1 (5.0 Hz) < C2 (5.8 Hz) < C3 (32 Hz). As a result, the τ values increase in the order of C3 (5.0 ms) < C2 (27.5 ms) < C1 (31.8 ms). On the basis of the results observed above, the best performance of the C1-based DSSCs mainly results from its strongest light-capturing ability and smallest charge recombination rate compared to the other two dyes. To further elucidate the effect of CDCA on photocatalyst performance, we also studied the Bode plots of the DSSCs with 5 mM CDCA. By comparison of the f values, we found that coabsorbing CDCA led to the reduced charge recombination rate due to the effective retard of dye aggregation, thereby providing higher photocatalyst performance that of the DSSCs without CDCA.

3. CONCLUSIONS

In summary, for the first time, a ladderlike fused-ring donor (dithienocyclopentacarbazole (DTCC) derivative) has been used to design and synthesize three novel D–A–π–A-type organic dyes (C1, C2, and C3) via facile direct arylation reactions. We have demonstrated that the use of auxiliary acceptors (BT, DFBT, and PT) can effectively manipulate the optical, electrochemical, and photocatalyst performances of the three dyes. Moreover, strong D–A interaction endows the three dyes with strong intramolecular charge transfer and high molar extinction coefficients of above 3,14 × 10^{4} M^{-1} cm^{-1}, thereby ensuring their strong light-capturing ability. Investigation of DFT calculations reveals that the well-separated HOMO and LUMO orbitals of the three dyes are observed, which is helpful for efficient charge separation and electron injection. Although the PT-containing C3 obtains a broad absorption band relative to C1 and C2, larger charge recombination rate caused by dye aggregation in TiO2 led to quite low J_{sc}, V_{oc}, and PCE values. Under AM 1.5G illumination, the BT-containing C1-based DSSCs afford the best photocatalyst performance with a V_{oc} of 671 mV, a J_{sc} of 12.98 mA cm^{-2}, an ff of 0.71, and a PCE value of 6.20%. Upon the addition of 5 mM CDCA, both the J_{sc} and V_{oc} values are further improved due to the enhanced electron life of the devices, which thereby provides an enhanced PCE of 6.75%. Our findings indicate that the ladderlike DTCC derivative donors have great potential to design broad novel organic dyes for high-performance DSSCs.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b01387.

Detailed experimental procedures, device fabrication, characterization data, and Figures S1–S34 (PDF)

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Notes

The authors declare no competing financial interest.

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