Fine-tuning the Electronic Structure of Organic Dyes for Dye-Sensitized Solar Cells

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ABSTRACT

A series of metal-free organic dyes exploiting different combinations of (hetero)cyclic linkers (benzene, thiophene, and thiazole) and bridges (4H-cyclopenta[1,2-b:3,4-b']thiophene (CPDT) and benzodithiophene (BDT)) as the central π-spacers were synthesized and characterized. Among them, the sensitizer containing the thiophene and CPDT showed most the broad incident photon-to-current conversion efficiency spectra, resulting in a solar energy conversion efficiency (η) of 6.6%.

In recent decades, increasing attention has been paid to the development of dye-sensitized solar cells (DSCs) as a source of renewable energy,1 mainly due to their potentially low-cost fabrication, possibility of transparency, and color selectivity, which can be integrated into building and automobile applications.2 In order to increase power conversion efficiency and decrease the fabrication cost, extensive research has been focused on the development of new metal-free organic dye sensitizers.3 In particular, donor-π-acceptor (D-π-A) dyes are seen as one of the most promising organic dyes, owing to their efficient intramolecular charge transfer (ICT) characteristics. Moreover most organic sensitizers are easy to synthesize and generally possess high molar extinction coefficients.4 Heterocyclic compounds such as thiophene and thiazole are widely used as building blocks in organic optoelectronics.5 To date, the molecular architecture of most donor fragments of the dyes is triphenylamine (TPA) in which a benzene ring typically serves as the linker. However, thiophene, which is a relatively more electron-rich heterocycle, and thiozole, which in contrast is relatively electron-deficient, are seldom employed to connect the nitrogen of the diarylamine with other π-bridges.6 Regarded as a fused-ring analogue of 3-alkylthiophene and a structural analogue of fluorene, CPDT has attracted considerable research interest.7 Organic dyes using the

alkyl-functionalized CPDT as the conjugated bridge showed an extremely high molar absorption coefficient and a high power conversion efficiency of 8.95% in liquid cell and 6% in a solid-state DSC. BDT, the dithiophene analog of phenanthrene, has several isomers, of which benzo[1,2-b:4,5-b’]-dithiophene and benzo[2,1-b:3,4-b’]-dithiophene have already been widely utilized in the construction of conjugated copolymers and D-π-A dyes for photovoltaic applications. Another isomer of BDT, benzo[1,2-b:4,3-b’]-dithiophene, however, to the best of our knowledge, has hardly been investigated in the DSC field.

Judiciously varying the conjugating π-spacer between the donor and acceptor fragments has been the most popular approach to structural modification for modulating the frontier orbital energy levels and for generating dyes with broad and intense absorption. Therefore, this work elaborates on the use of various (hetero)cyclic linkers (benzene, thiophene, and thiazole) combined with different conjugated π-bridges (CPDT and BDT) to evaluate the impact on the overall efficiency while maintaining the smallest band gap. This result clearly indicates that the electronic density on CPDT is richer than that of BDT and the absorption bands can be ascribed to the π−π* transition and intramolecular charge transfer (ICT) transitions of the D-π-A conjugated backbone. Apparently, in either case of the bridges (CPDT or BDT), the absorption maxima of ICT bands can be ascribed to the π−π* transition and intramolecular charge transfer (ICT) transitions of the D-π-A conjugated backbone. Apparently, in either case of the bridges (CPDT or BDT), the absorption maxima of ICT transitions are generally red-shifting in the sequence thiazole < phenyl < thiophene. The phenomenon is in line with the electronic richness of the relative (hetero)cycles, and due to the fortifed quinoidal character of thiophene, the adoption of the thiophene linker endows the corresponding dye with the smallest band gap. This result clearly indicates that modulation of the electron density of D-π-A dyes can be achieved by altering the electronic nature of the π-bridges.

Cyclic voltammetry (CV) is employed to estimate the first oxidation potential \( E_{ox} \), which corresponds to the HOMO levels of the dyes (Table 1, SI Figure S1). Normally, two oxidation waves are observed on the voltammograms. The first oxidation waves at lower oxidation potentials are generally from the contribution of triarylmethine, whereas the second ones, with higher oxidation potentials are depicted in Figure 2. Their absorption, electrochemical properties, and frontier orbital energy levels are summarized in Table 1. The electronic absorption spectra reveal two major characteristics depending on the substituted π-bridges. Specifically, the four dyes (G54, G104, and C220) containing CPDT as a bridge exhibit a single prominent band with the absorption maxima at ca. 530−570 nm, while the others (G55, G107, and G108) with BDT as the bridge have two absorption bands at ca. 370−410 nm and at ca. 450−510 nm. Such absorption characteristics indicate that the electron density on CPDT is richer than that of BDT and the absorption bands can be ascribed to the π−π* transition and intramolecular charge transfer (ICT) transitions of the D-π-A conjugated backbone. Apparently, in either case of the bridges (CPDT or BDT), the absorption maxima of ICT transitions are generally red-shifting in the sequence thiazole < phenyl < thiophene. The phenomenon is in line with the electronic richness of the relative (hetero)cycles, and due to the fortified quinoidal character of thiophene, the adoption of the thiophene linker endows the corresponding dye with the smallest band gap. This result clearly indicates that modulation of the electron density of D-π-A dyes can be achieved by altering the electronic nature of the π-bridges.

The UV–vis absorption spectra of the dyes in CH₂Cl₂ solutions are depicted in Figure 2. Their absorption, electrochemical properties, and frontier orbital energy levels are summarized in Table 1. The electronic absorption spectra reveal two major characteristics depending on the substituted π-bridges. Specifically, the four dyes (G54, G104, and C220) containing CPDT as a bridge exhibit a single prominent band with the absorption maxima at ca. 530−570 nm, while the others (G55, G107, and G108) with BDT as the bridge have two absorption bands at ca. 370−410 nm and at ca. 450−510 nm. Such absorption characteristics indicate that the electron density on CPDT is richer than that of BDT and the absorption bands can be ascribed to the π−π* transition and intramolecular charge transfer (ICT) transitions of the D-π-A conjugated backbone. Apparently, in either case of the bridges (CPDT or BDT), the absorption maxima of ICT transitions are generally red-shifting in the sequence thiazole < phenyl < thiophene. The phenomenon is in line with the electronic richness of the relative (hetero)cycles, and due to the fortified quinoidal character of thiophene, the adoption of the thiophene linker endows the corresponding dye with the smallest band gap. This result clearly indicates that modulation of the electron density of D-π-A dyes can be achieved by altering the electronic nature of the π-bridges.

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123 butions though the cyanoacrylate and its adjacent
122 delocalized from the diarylamino donor to the heterocyclic
117 calculations at the B3LYP.6-31G(d) level. SI Figure S2
116 the dyes are optimized by density functional theory (DFT)
115 frontier molecular orbitals of these dyes, the geometries of
114 efficient dye regeneration.
113 triiodide redox couple (0.4 V vs NHE) guaranteeing
112 all the dyes exhibit more positive HOMO levels than that of the iodide/
110 (13) B
109 (Fc/Fc ) as an internal reference and converted to NHE by addition of
108 values are much more negative than the Fermi level of TiO2
107 levels of these dyes (see Table 1). The thus obtained LUMO
106 the HOMO level energy, is used to calculate the LUMO
105 onset wavelength of the absorption spectra together with
102 whereas the thiophene linked molecules exhibit the lowest
101 first oxidation potential than that of the BDT based dyes,
100 CPDT and BDT potentials and quasi-reversible behavior, are from the
97 Estimated from onset wavelength in absorption spectra.
96 NHE vs the vacuum level is set to 4.5 V.13
95 potentials and quasi-reversible behavior, are from the
94 CPDT and BDT π-bridge. It is obvious that the Eox varies
93 in accord with the electron density of the conjugated
92 π-bridges. Generally, the CPDT based dyes have a lower
91 first oxidation potential than that of the BDT based dyes,
90 whereas the thiophene linked molecules exhibit the lowest
89 oxidation potential among the three kinds of (hetero)cyclic
88 linkers. The zero—zero energy (E0−0), estimated from the
87 onset wavelength of the absorption spectra together with
86 the HOMO level energy, is used to calculate the LUMO
85 levels of these dyes (see Table 1). The thus obtained LUMO
84 values are much more negative than the Fermi level of TiO2
83 (−0.5 V vs NHE), allowing efficient electron injection
82 from the excited dyes into the TiO2 electrode. All the dyes
81 exhibit more positive HOMO levels than that of the iodide/
80 triiodide redox couple (0.4 V vs NHE) guaranteeing
79 efficient dye regeneration.
78 To gain further insight into the molecular structure and
77 frontier molecular orbitals of these dyes, the geometries of
76 the dyes are optimized by density functional theory (DFT)
75 calculations at the B3LYP.6-31G(d) level. SI Figure S2
74 displays the relative energies and electron distributions of
73 the HOMO and LUMO of the dyes. HOMOs are mainly
72 delocalized from the diarylamino donor to the heterocyclic
71 π-spacer, whereas LUMOs show localized electron distributions
70 though the cyanoacrylic acid and its adjacent
71 π-spacer. This separation of electrons will ensure efficient
70 electron injection from the dye to the TiO2 film.

The DSC performances of all the dyes are evaluated
71 under AM 1.5 G irradiation at 100 mW cm−2 (details of the
70 devices’ fabrication and testing are described in the Support-Ing. Information). Hereby, the focus is on the influence
69 of the two different bridging units CPDT and BDT, together
68 with the three varying linker groups, on the DSC characteristics. First, the effect of the BDT in comparison to CPDT is highlighted in terms of the changes in
67 VOC. When scrutinizing the dyes with the same linkers
66 (C220 vs G55 for the phenyl, G54 vs G107 for the thiophene,
65 and G104 vs G108 for the thiazole linkers), it is apparent that the VOC increases by more than 40 mV in the presence of BDT (Table 2 and Figure 3a). This observation is reflected by the corresponding VOC shifts toward higher
64 values when plotted against capacitance (Figure 4a). For instance, in comparing C220 with G55, the capacitance for the latter is shifted toward higher VOC (Figure 4a), indicating a higher TiO2 conduction band ultimately resulting in an elevated VOC for the G55 cell. The same trend is observed for G54 vs G107 and G104 vs G108 (Figure 4a), emphasizing the fact that the BDT unit triggers an upward shift of the TiO2 conduction band, which is beneficial for enhancing the VOC. Since the same TiO2 layers are employed for all cells and all dyes investigated, it is highly unlikely that changes in TiO2 trap states are the cause for the observed variations in conduction bands. In terms of VOC, the effect of the linker group is even more dramatic than replacing BDT with the CPDT acceptor. For the same π-bridge, the incorporation of thiophenes or thia-
63 zoles instead of the common phenyl as linkers severely
62 reduces the VOC more significantly than 100 mV (Table 2, Figure 3a) even though the difference between thiophene and thiazole is not as major. This behavior is also reflected by the shift in VOC in the dependence of capacitance as illustrated by the photovoltage decay measurements (Figure 4a). Overall, the combination of the BDT bridge and the phenyl linker poses a powerful system in achieving an outstanding VOC, surpassing 800 mV, one of the highest values reported for the I3−/I− redox couple.

<table>
<thead>
<tr>
<th>dye</th>
<th>combination</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C220</td>
<td>benzene-CPDT</td>
<td>15.4</td>
<td>756</td>
<td>0.76</td>
<td>8.8</td>
</tr>
<tr>
<td>G55</td>
<td>benzene-BDT</td>
<td>9.4</td>
<td>810</td>
<td>0.74</td>
<td>5.6</td>
</tr>
<tr>
<td>G54</td>
<td>thiophene-CPDT</td>
<td>14.9</td>
<td>622</td>
<td>0.71</td>
<td>6.6</td>
</tr>
<tr>
<td>G107</td>
<td>thiophene-BDT</td>
<td>10.1</td>
<td>671</td>
<td>0.70</td>
<td>4.8</td>
</tr>
<tr>
<td>G104</td>
<td>thiazole-CPDT</td>
<td>11.8</td>
<td>603</td>
<td>0.75</td>
<td>5.4</td>
</tr>
<tr>
<td>G108</td>
<td>thiazole-BDT</td>
<td>9.6</td>
<td>683</td>
<td>0.78</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Even though the BDT has the advantage of increasing the VOC, the absorption however is blue-shifted compared to the CPDT unit as already shown by the UV–vis absorption spectra. This phenomenon is mirrored in the incident photon-to-current conversion efficiency (IPCE) of the corresponding dyes (Figure 3b). Consequently, all

Table 1. Optical and Electrochemical Properties of the Dyes

<table>
<thead>
<tr>
<th>dye</th>
<th>λmax (nm)</th>
<th>ε (M−1 cm−1)</th>
<th>t (µM)</th>
<th>Eox (V) vs NHE</th>
<th>E0−0 (V) vs NHE</th>
<th>Eox−E0−0 (V)</th>
<th>HOMO/LUMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G45</td>
<td>565</td>
<td>454</td>
<td>0.635</td>
<td>1.79</td>
<td>−1.15</td>
<td>−5.14/</td>
<td></td>
</tr>
<tr>
<td>G55</td>
<td>375</td>
<td>386</td>
<td>0.86</td>
<td>2.18</td>
<td>−1.32</td>
<td>−5.36/</td>
<td></td>
</tr>
<tr>
<td>G104</td>
<td>539</td>
<td>505</td>
<td>0.96</td>
<td>1.97</td>
<td>−1.01</td>
<td>−5.46/</td>
<td></td>
</tr>
<tr>
<td>G107</td>
<td>406</td>
<td>416</td>
<td>0.75</td>
<td>1.95</td>
<td>−1.2</td>
<td>−5.25/</td>
<td></td>
</tr>
<tr>
<td>G108</td>
<td>381</td>
<td>424</td>
<td>1.08</td>
<td>2.15</td>
<td>−1.07</td>
<td>−5.58/</td>
<td></td>
</tr>
<tr>
<td>C220</td>
<td>502</td>
<td>212</td>
<td>1.08</td>
<td>2.15</td>
<td>−1.07</td>
<td>−5.43/</td>
<td></td>
</tr>
<tr>
<td></td>
<td>458</td>
<td>255</td>
<td>0.815</td>
<td>1.87</td>
<td>−1.05</td>
<td>−5.32/</td>
<td></td>
</tr>
</tbody>
</table>

* Measured in 2 × 10−6 M of CH2Cl2 solutions at room temperature.

† Slightly lower than the value measured in chloroform.3b as Measured in CH2Cl2 containing 0.1 M of tetraethylammonium tetrafluoroborate (TBABF4) electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: Pt; calibrated with ferrocene/ferrocenium (Fc/Fc+) as an internal reference and converted to NHE by addition of 630 mV). Estimated from onset wavelength in absorption spectra.

Table 2. Photovoltaic Performance Data of the Dyes
170 sensitizers containing BDT exhibit a \( J_{SC} \) of only \( \sim 10 \) mA cm\(^{-2}\), whereas all other compounds consisting of CPDT result in better cell performances with a much higher \( J_{SC} \) (Table 2), even though all of the BDT based dyes yield more enhanced electron lifetimes than the CPDT counterparts as evidenced by photocurrent decay measurements (Figure 4b).

Having elucidated the effect of the bridging units on the \( J_{SC} \), it is also crucial to understand which role the linkers play in this aspect. Taking into consideration the BDT dyes G55, G107, and G108, it is apparent that the \( J_{SC} \) increases with the linkers thiophene > thiazole > phenyl, even though those changes are not significant (Table 2). On the other hand, the sensitizers containing CPDT show a decline in \( J_{SC} \) according to the trend phenyl > thiophene > thiazole. Hereby, the linkers impinge a more dramatic impact on the \( J_{SC} \), particularly for the thiazole case where the \( J_{SC} \) is reduced by more than \( 3 \) mA cm\(^{-2}\) (Table 2). This behavior is simply the result of the corresponding blue shifts as indicated by the IPCE (Figure 3b). Based on these findings, the CPDT seems to be more prone to the nature of the linkers than the BDT bridge.

In addition, the linkers also have an effect on the electron lifetimes in the TiO\(_2\) film. As the photocurrent decay measurements indicate (Figure 4b), for both the BDT and CPDT bridges, the phenyl linker leads to the longest lifetimes, whereas the thiophene and thiazole units shorten the lifetimes. There are no notable differences in lifetimes between those two linkers themselves. Furthermore, as compared to the CPDT with the same linkers, the BDT sensitizer based TiO\(_2\) layers exhibit prolonged lifetimes as well. Overall, the BDT bridge is very appealing in terms of both the observed upper shift of the TiO\(_2\) conduction band desired for a high \( V_{OC} \) and the longer lifetimes of the electrons.

In summary, we have synthesized a series of metal-free organic sensitizers based on the D-\( \pi \)-A structure and studied the impact of various conjugated \( \pi \)-spacers on the device performance in DSCs. The power-conversion efficiency of DSCs is higher when CPDT and/or phenyl are used as the \( \pi \)-conjugated spacer. The introduction of CPDT instead of BDT contributed to improving the cell’s \( J_{SC} \) but deteriorating the \( V_{OC} \) while the use of phenyl rather than thiophene and thiazole mainly resulted in an increased \( V_{OC} \), respectively. Among the synthesized new dyes, G54 containing CPDT and thiophene yielded the best conversion efficiency of 6.6% due to the relatively highest \( J_{SC} \). On the other hand, although with much poorer absorption ability, BDT and phenyl bridged G55 showed the highest \( V_{OC} \) and longest electron lifetime, which thus dramatically improved the DSC performance (5.6%). These results strongly suggest that metal-free organic dyes could be tuned by appropriate control of the energy levels of \( \pi \)-conjugated spacers through systematic structure modification of the \( \pi \)-system, leading to further development of highly efficient organic dyes.

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**Supporting Information Available.** Experimental details, DSSCs fabrication, and characterization details for new compounds. The material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.