Significant Influence of a Single Atom Change in Auxiliary Acceptor on Photovoltaic Properties of Porphyrin-Based Dye-Sensitized Solar Cells

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Abstract: The rational design of porphyrin sensitizers is always crucial for dye-sensitized solar cells (DSSCs), since the change of only a single atom can have a significant influence on the photovoltaic performance. We incorporated the pyridothiadiazole group, as a stronger electron-withdrawing group, into the commonly well-established skeleton of D-porphyrin-triple bond-acceptor sensitizers by a single atom change for a well-known strong electron-withdrawing benzothiadiazole (BTD) unit as an auxiliary acceptor. The impact of the pyridothiadiazole group on the optical; electrochemical; and photovoltaic properties of D–π-A porphyrin sensitizers was investigated with comparison for a benzothiadiazole-substituted SGT-020 porphyrin. The pyridothiadiazole-substituted SGT-024 porphyrin dye was red-shifted so that the absorption range might be expected to achieve higher light harvest efficiency (LHE) than the SGT-020 porphyrin. However, all the devices were fabricated by utilizing SGT-020 and SGT-024, evaluated and found to achieve a cell efficiency of 10.3% for SGT-020-based DSSC but 4.2% for SGT-024-based DSSC under standard global AM 1.5G solar light conditions. The main reason is the lower charge collection efficiency of SGT-024-based DSSC than SGT-020-based DSSC, which can be attributed to the tilted dye adsorption mode on the TiO₂ photoanode. This may allow for faster charge recombination, which eventually leads to lower $J_{SC}$, $V_{OC}$ and power conversion efficiency (PCE).

Keywords: D–π–A structural porphyrin; acceptor units; dye-sensitized solar cells; charge recombination; charge collection efficiency

1. Introduction

A huge amount of work has recently concentrated on third-generation solar cell technology development with low cost as emerging photovoltaics, such as dye-sensitized solar cells (DSSCs) [1,2], organic photovoltaics (OPVs) [3–5], perovskite solar cells (PSCs) [6–8], etc. Among the various solar technologies, DSSCs have garnered considerable attention due to the simple fabrication process, low cost, low toxicity, and high PCE under ambient lighting conditions [9,10]. In 1991 Grätzel and O’Regan first introduced mesoporous TiO₂ nanocrystal layers into the DSSC system [11]. This led to a substantial improvement in photoelectric transformation efficiency. Since then, over the past 28 years, DSSCs have continued to show improved PCE [12–14]. Until now, state-of-the-art DSSCs have achieved PCEs approaching >11.9% for ruthenium complexes [15], >14% for metal-free D–π–A structural organic sensitzers [16], and 14.64% for D–π–A structural organic sensitizer-based tandem DSSCs under standard (1.5) illumination [13]. In comparison with ruthenium sensitizers [17,18] and metal-free sensitizers [19,20], D–π–A structural porphyrin sensitizers [21–23] have been attractive...
due to their extremely high molar extinction coefficient, exceptional ability to harvest light, and high photostability. To date, porphyrin-based DSSCs have achieved PCE by more than 13% under standard (1.5) illumination [24,25].

However, there are also some drawbacks due to the nature of porphyrins, such as the weak absorption in the range of 500–600 nm, the lack of absorption in the near-infrared region (NIR), and the dye aggregation caused by the extended π-conjugation structure [26–30]. It is apparent that these problems could be overcome by rational structural optimization. For example, long and well-adjusted alkoxy chains were introduced to porphyrin molecules, which significantly diminished the dye aggregation and reduced the interface back electron transfer rate [31]. The introduction of a benzothiadiazole (BTD) unit in the acceptor part to the well-established platform of D-porphyrin-triple bond-acceptor sensitizers was also a promising approach for elevating light-harvesting properties, as well as the photovoltaic performance. Up to now, the BTD unit was one of the most commonly used auxiliary electron acceptors in the well-known skeleton of D-porphyrin-triple bond-BTD-acceptor sensitizers for DSSCs [32–34].

In order to reduce the HOMO (highest occupied molecular orbital)–LUMO (lowest unoccupied molecular orbital) energy gap as well as extend the absorption range, a boosted electron-withdrawing pyridothiadiazole unit was introduced into the well-established platform of D-porphyrin-triple bond-BTD-acceptor sensitizers by a single atom change for the well-known strong electron-withdrawing benzothiadiazole (BTD) unit as an auxiliary acceptor. Although the pyridothiadiazole unit has been widely used in D–A polymers in OPVs [35,36] and metal-free organic sensitized solar cells [37,38], no application of the pyridothiadiazole unit has been explored in porphyrin-sensitized solar cells. Thus, based on our previously reported dye of SGT-020 [25], we expected that the pyridothiadiazole unit in D–π–A porphyrin sensitizers could improve the absorption ability in NIR as well as the light harvest efficiency. Thus, a novel D–π–A structural porphyrin sensitizer was designed and synthesized, named as SGT-024, as shown in Scheme 1. Meanwhile, the optical properties, electrochemical properties, and photovoltaic performances were systemically investigated.

![Molecular structures of SGT-020 and SGT-024 sensitizers.](image)

**Scheme 1.** Molecular structures of SGT-020 and SGT-024 sensitizers.

2. Synthetic Procedure

All reagents were purchased from Alfa Aesar (Haverhill, MA, USA), TCI (Tokyo, Japan), and Sigma–Aldrich (St. Louis, MO, USA) unless stated otherwise. The synthesis routes of SGT-024 were shown in Scheme 2, and compound 1 [37], compound 3 [25], and SGT-020 [25] were synthesized according to the respective literature procedures. Details on the synthetic procedure, instrumentation, DSSC fabrication, photovoltaic parameters, 1H-NMR, 13C-NMR, and MALDI-TOF data are given in the Supplementary Materials.
3. Results and Discussion

The UV-visible spectra of the dyes SGT-020 and SGT-024 in THF were collected and reported in Figure 1. It is obvious that SGT-020 and SGT-024 showed two intense absorption regions within the ranges of 400 to 500 nm (Soret band) and 600 to 800 nm (Q band). In Table 1, compared with the molar extinction coefficient ($\varepsilon$) of 143,040 M$^{-1}$ cm$^{-1}$ at the maximum absorption wavelength ($\lambda_{\text{max}} = 454$ nm) observed for SGT-020, the $\lambda_{\text{max}}$ of SGT-024 is 430 nm with a coefficient of 123,162 M$^{-1}$ cm$^{-1}$. It should be noted that the Soret band peaks of SGT-024 were blue-shifted but the Q bands were significantly red-shifted when a pyridothiadiazole unit was introduced into the platform of D-porphyrin-triple bond-acceptor sensitizers by a single atom change for the well-known strong electron-withdrawing benzothiadiazole (BTD) unit. Furthermore, the fluorescent emission spectra were also measured in THF, as shown in Figure 1. SGT-020 and SGT-024 exhibited major emission bands at 724 and 791 nm, respectively. Therefore, the optical properties of these two porphyrin sensitizers revealed that the light capture region could be expanded by introducing the stronger electron-withdrawing moiety of the pyridothiadiazole unit.

![Scheme 2. Synthesis routes of SGT-024.](image)

**Figure 1.** Absorption spectra and emission spectra of SGT-020 and SGT-024 in THF.
The electrochemical properties of SGT-020 and SGT-024 were evaluated in THF with 0.1 M TBAPF$_6$ as an electrolyte, using cyclic voltammetry (CV) (see Figure S2); the corresponding data are collected in Table 1. As shown in Figure 2, due to the fact that they have the same donor unit, their ground state oxidation potentials, which correspond to the HOMO energy levels of SGT-020 and SGT-024, are nearly the same. Meanwhile, from the HOMO–LUMO band gap and the oxidation potential, the reduction potentials of SGT-020 and SGT-024 were determined to be $-0.93$ and $-0.81$ eV, respectively. This difference in reduction potentials could be ascribed to the structural changes in the acceptor group. The results also revealed that the reduction potential values are much more negative than the conducting band (CB) of TiO$_2$ and the oxidation potential values are much more positive than the Co(bpy)$_{3}^{2+}/^{3+}$ (bpy = 2,2′-bipyridine) redox couple (0.56 V vs. NHE), indicating that all of the electron transfer processes for two porphyrin sensitizers should occur efficiently due to the sufficient driving force.

![Energy-level diagram of SGT-020 and SGT-024.](image_url)

**Table 1.** Photophysical and electrochemical data for SGT-020 and SGT-024.

| Dye    | $\lambda_{\text{abs max}}$ a (nm) | $\varepsilon$ (M$^{-1}$ cm$^{-1}$) | $\lambda_{\text{em max}}$ a (nm) | $E_{0-0}$ b (eV) | $S^{+}/S^{0}$ c (eV) [V vs. NHE] | $S^{+}/S^{*}$ d (eV) [V vs. NHE] |
|--------|----------------------------------|-----------------------------------|----------------------------------|-----------------|---------------------------------|---------------------------------|
| SGT-020| 454                             | 143,040                           | 724                              | 1.73            | 0.83                            | $-0.93$                         |
| SGT-024| 430                             | 123,162                           | 791                              | 1.65            | 0.84                            | $-0.81$                         |

a Absorption and emission spectra were measured in THF. b $E_{0-0}$ was determined from the intersection of normalized absorption and emission spectra in THF. c Oxidation potentials of dyes were measured in THF with 0.1 M TBAPF$_6$, ferrocene/ferrocenium internal reference. d Excited-state oxidation potentials were calculated according to $(S^{+}/S^{0}) - E_{0-0}$. 

[Figure 1. Absorption spectra and emission spectra of SGT-020 and SGT-024 in THF.]

[Figure 2. Energy-level diagram of SGT-020 and SGT-024.]

Co(bpy)$_{3}^{2+}/^{3+}$
DFT calculations at the M06 [39]/6-31G [40] (LANL2DZ [41] for Zn atom) level were carried out to better understand the electron distribution and the molecular geometries. The optimized ground state molecular structures and dihedral angles (between BTD/pyridothiadiazole unit and benzoic acid) of two porphyrins are shown in Figure 3 and Table S1. The electron distribution of the HOMO energy levels was mainly delocalized at the diphenylamine donor unit and porphyrin core. However, as for the electron distribution of the LUMO energy levels, SGT-024 showed a more evident shift to the unit of benzoic acid than SGT-020. Thus, SGT-024 was expected to show enhanced intramolecular charge transfer (ICT) compared to that of SGT-020. Furthermore, in the optimized structures of SGT-020 and SGT-024, the dihedral angles between the adjacent auxiliary acceptor and benzoic acid are 35.02° and 16.06°, respectively. Therefore, owing to the significant reduction of the torsion angle, SGT-024 displayed more efficient π-conjugation and a better coplanar geometry in comparison with SGT-020, but this geometry would increase the possibility of dye aggregation.

| Dye    | Optimized structure | HOMO      | LUMO      |
|--------|---------------------|-----------|-----------|
| SGT-020| ![Optimized structure](image1) | 35.02°    |           |
| SGT-024| ![Optimized structure](image2) | 16.06°    |           |

Figure 3. Optimized molecular geometries and electron distributions of the HOMO and LUMO energy levels of SGT-020 and SGT-024.

The photovoltaic characteristics of the SGT-020- and SGT-024-based devices were measured under standard AM 1.5 conditions. The porphyrin-based TiO$_2$ films were used as the photoanode in DSSCs, employing the Co(bpy)$_3$$^{2+}$/3$^+$ redox couple as electrolyte and CDCA (chenodeoxycholic acid) as co-adsorbent. The relevant photocurrent density-voltage (J-V) curves are shown in Figure 4a and the device parameters are summarized in Table 2. As compared to the reference dye SGT-020 ($J_{sc} = 14.8 \text{ mA cm}^{-2}$, $V_{oc} = 0.806 \text{ V}$, FF = 73.2% and PCE = 8.7%), the pyridothiadiazole-incorporated dye SGT-024 only showed a moderate PCE of only 1.7%. The $J_{sc}$ value of SGT-024 dramatically dropped to 3.3 mA cm$^{-2}$ and its $V_{oc}$ also decreased to 0.655 V. To further investigate the $J_{sc}$ value of each porphyrin sensitizer, the corresponding IPCE (incident photon-to-electron conversion efficiency) spectra of SGT-020 and SGT-024-based devices were measured under AM 1.5G solar light. As shown in Figure 4b, SGT-024 sensitizers exhibited a broader, weaker absorption response (the absorption onset extended to almost 900 nm) than SGT-020 (to ~850 nm), which displayed a similar tendency with the absorption spectra on TiO$_2$ film, as shown in Figure S1. On the contrary, the SGT-024-based DSSCs exhibited an extremely low IPCE value (no more than 20%) from 400 to 900 nm; thus, lower $J_{sc}$ values were observed.
Figure 4. (a) Current-voltage characteristics of the SGT-020 and SGT-024-based DSSCs and (b) the corresponding IPCE spectra under 100 mW cm\(^{-2}\) simulated AM 1.5G solar light.

Table 2. Photovoltaic parameters of the SGT-020 and SGT-024-based DSSCs under 100 mW cm\(^{-2}\) simulated AM 1.5G solar light.

| Dye     | Co-Adsorbent | Adsorption Amount (10\(^{-8}\) mol cm\(^{-2}\)) | \(I_{sc}\) (mA cm\(^{-2}\)) \(\pm\) | \(V_{oc}\) (mV) \(\pm\) | FF (%) | PCE a (%) |
|---------|--------------|---------------------------------|-----------------|-----------------|--------|-----------|
| SGT-020 | CDCA         | 2.13                            | 14.8 ± 0.53     | 806 ± 9.8       | 73.2 ± 2.4 | 8.7 ± 0.25 |
| SGT-024 | CDCA         | 1.95                            | 3.3 ± 0.25      | 655 ± 7.3       | 76.3 ± 1.7 | 1.7 ± 0.15 |
| SGT-020 | HC-A1        | 1.87                            | 16.9 ± 0.32     | 795 ± 8.5       | 76.8 ± 2.1 | 10.3 ± 0.12 |
| SGT-024 | HC-A1        | 1.79                            | 7.3 ± 0.12      | 724 ± 6.7       | 79.0 ± 1.8 | 4.2 ± 0.19 |

In order to further improve the photovoltaic performance of SGT-020 and SGT-024-based DSSCs, another co-adsorbent called HC-A1 was introduced in this study. HC-A1, a multi-functional co-adsorbent widely used in our previous research [13,42], and its structure are shown in Figure S3. As expected, because of the light harvesting in shorter wavelength regions and efficient charge recombination retardation [43–46], the PCE of SGT-020 and SGT-024-based solar cells was dramatically improved to 10.3% and 4.2%, respectively (see Figure 5). In addition, the dye loading amounts for SGT-020 and SGT-024 were found to be almost no different, implying that the effect of the dye loading amount on photovoltaic performance in this study is relatively small.
The results obtained above are consistent with the photovoltaic performance difference as well as the interfacial charge transfer in all DSSC devices. Nyquist plots and Bode plots are shown in Figure 6 (a) and (b), respectively, and the EIS data are collected in Table 3. As far as we know, the first, second, and third semicircles correspond to the charge transfer resistance at the counter electrode, the resistance of TiO$_2$/dye/electrolyte interface, and the diffusion resistance of Co(bpy)$_3^{2+}/3^+$ redox couple in the electrolyte, respectively. The second semicircle of SGT-024 ($R_{rec} = 6.12$) was found to be much smaller than SGT-020 ($R_{rec} = 16.8$), indicating that the electron recombination rate of SGT-024 is higher than that of SGT-020. On the other hand, according to the equation $\tau_r = C_{\mu} \cdot R_{rec}$, the electron lifetime was calculated to be 5.12 or 3.33 ms for SGT-020 and SGT-024, respectively. Meanwhile, the charge-collection efficiency $\eta_{cc}$, derived from $\eta_{cc} = (1 + R_{tr}/R_{rec})^{-1}$ [47], was confirmed to be 84% for SGT-020 and 68% for SGT-024. The results obtained above are consistent with the $V_{oc}$ values for the SGT-020-based device (0.795 V) and SGT-024-based device (0.724 V). Thus, when compared to SGT-020 and SGT-024, the higher charge recombination rate and the lower charge collection efficiency of the SGT-024-based device may be the main reasons for its disappointing lower photovoltaic performance.
Table 3. EIS data for the SGT-020- and SGT-024-based DSSCs.

| Device   | $R_t$ (Ω) | $R_{rec}$ (Ω) | $C_µ$ (mF) | $τ_n$ (ms) | $τ_r$ (ms) | $η_{cc}$ (%) |
|----------|-----------|---------------|------------|------------|------------|--------------|
| SGT-020  | 3.27      | 16.8          | 0.30       | 0.99       | 5.12       | 84           |
| SGT-024  | 2.85      | 6.12          | 0.54       | 1.55       | 3.33       | 68           |

$a$ DSSCs were fabricated with HC-A1. $b$ forward bias of 0.85 V under dark conditions. $R_t$: transport resistance; $R_{rec}$: charge recombination resistance; $C_µ$: chemical capacitance; $τ_n$: transport time; $τ_r$: electron lifetime; $η_{cc}$: charge collection efficiency.

4. Conclusions

In this work, in order to investigate the structure-performance relationship between the photovoltaic performance and the structure of various acceptors, the pyridothiadiazole group, as a stronger electron-withdrawing group, was incorporated into the well-established skeleton of D-porphyrin-triple bond-acceptor sensitizers by a single atom change for the well-known strong electron-withdrawing benzothiadiazole (BTD) unit. The impact of the pyridothiadiazole group on the optical, electrochemical, and photovoltaic properties of D–π–A porphyrin sensitizers was investigated by comparing with a benzothiadiazole-substituted SGT-020 porphyrin. The porphyrin SGT-024 presents a red-shifted and broadened Q-band in comparison with SGT-020, which could be attributed to the stronger electron-withdrawing nature of pyridothiadiazole than the BTD unit. This revealed that the introduction of pyridothiadiazole would be an effective strategy for strengthening the absorption of the well-established skeleton of D-porphyrin-triple bond-acceptor sensitizers, although it shows a more moderate PCE of 4.2% than the DSSC based on SGT-020 (10.3%). The serious efficiency loss for the SGT-024-based device could be for two main reasons: the fast charge recombination rate caused by the strong electron-withdrawing acceptor, and thus lower charge collection efficiency observed; and the enhanced backbone co-planarity in SGT-024 leading to unexpected dye aggregation. However, the pyridothiadiazole unit is still a promising synthetic strategy to explore D–π–A structural porphyrins with extended absorption properties. Our study has underlined the importance of a suitable auxiliary acceptor between the dye and the anchoring group for a sensitizer. This should be seriously considered in the further rational design of dye-sensitized solar cells.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-4991/8/12/1030/s1. Informative details of material synthesis and characterization, DSSC fabrication, and photoelectrochemical measurements are available in the Supplementary Materials. Figure S1: UV spectra of the porphyrin sensitizers on a TiO$_2$ film (3 µm), Figure S2: Cyclic voltammograms of SGT-020 and SGT-024 in THF / TBAPF$_6$ and ferrocene external reference, Figure S3: Co-adsorbents used in the dye-sensitized solar cells, Figure S4: $^1$H-NMR spectrum (300 MHz, (CD$_3$)$_2$CO) of SGT-024, Figure S5: $^{13}$C-NMR spectrum (300 MHz, (CD$_3$)$_2$CO) of SGT-024, Figure S6: Maldi-TOF spectrum of SGT-024, Table S1: Photophysical and electrochemical properties of porphyrin sensitizers by DFT calculations.

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Conflicts of Interest: The authors declare no conflict of interest.

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