Novel and Stable D–A–π–A Dyes for Efficient Solid-State Dye-Sensitized Solar Cells

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ABSTRACT: Two novel organic donor–acceptor–π–acceptor sensitizers, W7 and W8, have been applied in efficient solid-state dye-sensitized solar cells (ssDSSCs). Using 2,2′,7,7′-tetakis(N,N-di-p-methoxyphenylamine) 9,9′-spirobifluorene (Spiro-OMeTAD) as hole-transport material (HTM), an excellent power conversion efficiency of 6.9% was recorded for W7, together with an excellent photocurrent of 10.51 mA cm⁻² and a high open-circuit voltage of 880 mV under standard AM 1.5 G illumination (100 mW cm⁻²). The solid-state solar cells based on W8 showed an efficiency of 5.2%, with a good photocurrent of 9.55 mA cm⁻² and an open-circuit voltage of 870 mV. Compared to that of the well-known WS2 sensitizer, the results show that the performance of the ssDSSC devices can be significantly improved by introducing triphenylamine moiety into their structure. In addition, results of photoinduced absorption spectroscopy show efficient dye regeneration for W7- and W8-based devices. A higher hole conductivity of the W7/HTM and W8/HTM layers compared to that of the WS2/HTM layer was observed, indicating an efficient charge transfer at the interfaces. The results obtained offer insights into the design of reliable and highly efficient ssDSSCs for large-scale applications.

1. INTRODUCTION

Dye-sensitized solar cells (DSSCs) have been widely investigated because of their low cost, environment friendliness, and high power conversion efficiency (PCE), as reported by O’Regan and Grätzel in 1991. Nowadays, over 14% of DSSC efficiency has been achieved on the basis of different liquid electrolytes. The device structures of DSSCs are based on various functional components, such as the light absorber, the charge-transport medium, and the electrodes. Among them, the light absorber (known as the sensitizer) has been the most crucial component for the design of highly efficient DSSCs. In the early stage, ruthenium-based dyes were widely investigated. However, because of the high cost of Ru and the potentially environmentally harmful impact, metal-free sensitizers have attracted an increasing attention. In 2006, the pioneering work by the Sun and Hagfeldt group highlighted the organic D5 dye (known as a D–π–A-type dye) in DSSCs. This type of molecule consists of three main components: a donor part (D), a conjugated linker (π), and an acceptor group (A). Subsequently, a large number of organic dyes have been synthesized and applied in DSSCs.

Because of potential leakage and corrosion problems of liquid DSSC electrolytes, recent research has instead focused on solid-state DSSC electrolytes (ssDSSCs). In addition, a lower driving force is required for effective dye regeneration in ssDSSCs in contrast to the liquid congener, which opens for higher open-circuit voltages. Until now, the best ssDSSCs have displayed just over 7% conversion efficiencies, utilizing low-cost organic dyes. In particular, Zhang and co-workers synthesized conducting polymers through a photoelectrochemical polymerization (PEP) method as hole-transport material (HTM), rendering devices with, for ssDSSCs, high efficiencies of up to 7.1%. Xu and co-workers synthesized a series of organic semiconductors for highly efficient ssDSSCs (efficiency of up to 7.7%). Also, it is reported that the modification of the p-type dopant for the HTMs used can successfully improve the performance of the devices through enhancement of the HTM conductivities and charge mobilities.

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In spite of the extensive use of D−π−A dyes in ssDSSCs, there is still scope for improvement in new generations of efficient and stable organic dyes. Recently, the D−A−π−A-type dyes have drawn much attention in the academic field. The use of an auxiliary electron-withdrawing unit incorporated into the conjugated linker, the intramolecular electron transfer, is expected to be facilitated from the donor to the acceptor. In addition, the additional electron-deficient unit may modulate the absorption ability and minimize the typical blue shift upon dye anchoring on the TiO₂ surface. Recently, the Tian group has synthesized a series of D−A−π−A dyes applied in liquid-type DSSCs. Their studies indicated that the WS51 dye combined excellent light-harvesting ability and rapid dye-adsorption capability via rational molecular engineering. Cui et al. showed that the long alkyl group in the benzotriazole moiety significantly enhances the open-circuit photovoltage. Kang et al. have studied the correlation between the structures of D−A−π−A dyes and the photovoltaic performance of solar cells. Pei et al. investigated the effects of co-sensitization of D−A−π−A dyes and pushed the efficiencies to over 10% in liquid-electrolyte-based devices. However, studies on the application of D−A−π−A dyes in ssDSSCs are quite few.

In the present study, two different D−A−π−A dyes have been applied in ssDSSCs. The WS2 dye was also investigated as a reference. The structures of the materials studied here are presented in Figure 1.

2. RESULTS AND DISCUSSION

2.1. UV−Vis Absorption and Electrochemistry. The schemes of the ssDSSC device configuration and energy alignment are shown in Figure 2a,b, respectively. Initially, the sensitizers are excited via illumination, followed by the injection of photogenerated electrons into the conduction band of TiO₂. Then, the remaining holes are transferred by the hole conductors to the counter electrode to complete the internal circuit. From an energetic point of view, the HOMO level of the sensitizers should be higher than the conduction band of TiO₂. The HOMO was obtained from the redox potentials calibrated vs the normal hydrogen electrode (NHE) by the addition of ferrocene (E(Fc/Fc⁺) = 630 mV vs NHE) as reference. Eₜₐₐ was determined by the intersection between the absorption and emission spectra. E_LUMO = E_HOMO + E_0 was estimated from cyclic voltammetry results.

Table 1. Light-Absorption and Electrochemical Data of W7 and W8

| dye | λₑₓ,ₘₐₓ (nm) | HOMOa (V vs NHE) | E₀b (eV) | E_LUMOc (V vs NHE) |
|-----|--------------|------------------|----------|-------------------|
| W7  | 534 (25 240) | 0.96             | 1.98     | −1.02             |
|     | 423 (22 630) |                  |          |                   |
|     | 330 (61 380) |                  |          |                   |
| W8  | 532 (21 800) | 0.92             | 1.98     | −1.06             |
|     | 419 (29 530) |                  |          |                   |
|     | 329 (46 150) |                  |          |                   |

aThe HOMO was obtained from the redox potentials calibrated vs the normal hydrogen electrode (NHE) by the addition of ferrocene (E(Fc/Fc⁺) = 630 mV vs NHE) as reference. bE₀ was determined by the intersection between the absorption and emission spectra. cE_LUMO = E_HOMO + E_0 was estimated from cyclic voltammetry results.
be more positive than that of the hole conductors (on the NHE scale) to provide a sufficient driving force for the necessary charge-transfer process of dye reduction. Figure 2b shows the energy levels of the sensitizers as determined by electrochemistry. More details can be found in the Supporting Information. All electrochemical data are summarized in Table 1. The HOMO levels of W7 and W8 are 0.96 and 0.92 V versus the NHE, respectively, which are higher than the HOMO level of Spiro-OMeTAD (0.64 V) for both. Therefore, the charge transfer between the dyes and the hole conductors is energetically favorable for both W7 and W8 sensitizers.

Figure 3. (a) Absorption and emission spectra of W7 and W8 in CH2Cl2. (b) Absorption spectra of W7 and W8 on the titania film with and without additives (LiTFSI).

Figure 4. Frontier orbitals from the DFT calculations (isosurface value = 0.02).

Figure 5. J–V curves of ssDSSCs based on different sensitizers (a) and the corresponding IPCE spectra (b).
The light-absorption properties of W7 and W8 are studied. Figure 3a shows the light absorption and emission of W7 and W8 in solution. The related data are summarized in Table 1. The absorption peaks for both dyes are similar and located at 534 nm (W7) and 532 nm (W8), respectively. The thiophene unit as the linker part would increase the extinction coefficient similarly to the furan unit. The emission peaks are found at 720 and 716 nm for W7 and W8, respectively. Figure 3b shows the absorption spectra of W7 and W8 adsorbed onto TiO2 substrates. In the absence of additives, the absorption peaks are slightly blue-shifted compared to those in Figure 3a. This blue shift is most likely caused by the deprotonation of the terminal carboxylic group upon adsorption. In the presence of additives, the absorption peaks are less blue-shifted for both W7 and W8 sensitizers. Most likely, this effect can be attributed to the polarizing effect of the Li-ion salts.

2.2. Theoretical Calculations. Quantum chemistry calculations have been performed to get insights into the electron structure of the sensitizers. The frontier orbitals of W7 and W8 are shown in Figure 4. The dye molecules typically exhibit push–pull electron effects, where the HOMO and the LUMO are mainly composed of donor and acceptor moieties, respectively. For both W7 and W8, we can note that the HOMO and HOMO − 1 are mainly localized on the triphenylamine (TPA) units (donors), and the LUMO and LUMO + 1 are to a large extent localized on the benzotriazole and carboxylic acid units (acceptors). Time-dependent density functional theory (TD-DFT) calculations have also been performed to give insights into the composition of the excited states of the sensitizers. These results are summarized in the Supporting Information. The HOMO → LUMO transition dominates the contribution to the maximum absorption band (Table S1). This is reasonable because there is a large spatial overlap between the HOMO and LUMO in both W7 and W8 molecules. The HOMO → LUMO transition also shows a mixing between long-range charge transfer and local excitation, and the resultant oscillator strength for the lowest excited state is significant.

2.3. Characterization of ssDSSC Devices. The J–V curves of the ssDSSCs based on different sensitizers studied at 1 sun illumination under standard global AM 1.5G conditions are shown in Figure 5, with the corresponding photovoltaic parameters summarized in Table 2. Also, the statistical data are included in the Supporting Information. As shown in Figure 5a, by employing Spiro-OMeTAD as HTMs, devices based on WS2 yield an open-circuit potential (Voc) of 672 mV and a short-circuit current (Jsc) of 7.04 mA/cm², yielding PCEs of 2.3%. The efficiency was limited by the low photocurrent. On the other side, W7 and W8 yield Voc and Jsc of 880 mV and 10.51 mA/cm², and 870 mV and 9.55 mA/cm², respectively, yielding PCEs of 6.9% and 5.2%, respectively.

| ms (mA cm⁻²) | Voc (mV) | FF | PCE (%) |
|--------------|----------|----|---------|
| WS2          | 7.04     | 672| 0.49    | 2.3    |
| W7           | 10.51    | 880| 0.74    | 6.9    |
| W8           | 9.55     | 870| 0.62    | 5.2    |

Table 2. Photovoltaic Parameters of Devices Studied at a Light Intensity of 100 mW cm⁻² (AM 1.5G)

All HTM solutions were doped with AgTFSI.
devices show a maximum monochromatic efficiency of 60% at 550 nm, compared to that of 40% (550 nm) for the devices based on the WS2 dye.

2.4. Electron Lifetimes. To study the recombination process in ssDSSCs, electron lifetime measurements were performed (Figure 6). The W7-based devices show the longest electron lifetimes, whereas the WS2-based devices showed the shortest lifetimes. These differences could be traced to the different donor groups in the sensitizers studied. The steric properties and size of the donor moiety in the sensitizers may have a serious impact on the recombination process at the photoelectrode interface in the ssDSSC devices. The introduction of a bulky donor into the framework of the sensitizers may significantly suppress the recombination of the electron–hole pairs and thus push the pseudo-Fermi level of the TiO2 substrate up, resulting in a higher $V_{oc}$.26

2.5. Photoinduced Absorption (PIA) and Conductivity. PIA measurements were performed to investigate the photo-electrode interface charge transfer in ssDSSCs. The general process can be described as follows: the sensitizers will be excited by incident light and inject energy-rich electrons into the conduction band of the TiO2 film, leaving holes in the oxidized sensitizers. The light absorption of the oxidized sensitizers can be studied using PIA measurements. In the presence of HTMs, the photogenerated holes can be transferred into the HTMs, and, if the transfer is efficient, the light absorption of the oxidized dye molecules will be reduced. In Figure 7a, in the absence of an HTM layer, the positive peaks between 700 and 900 nm can be assigned to the oxidized WS2 dye. After deposition of the HTM layer on top of the WS2 dye layer, we can note that the absorption from the oxidized WS2 is slightly reduced, indicating a poor regeneration process mediated by the HTM layer. On the contrary, the W7 and W8 dyes appear to be efficiently regenerated. In Figure 7b,c, referring to dyes W7 and W8, respectively, the presence of an HTM layer in contrast indicates an efficient charge transfer from the HTM to the dyes. These results may highlight the reason for the excellent photocurrents of W7- and W8-based devices noted in Figure 3.

Many factors may affect the dye regeneration process. The steric effect of the donor part in the dye molecules could be vital. The aggregation tendency may be reduced by large bulky donor parts, resulting in a better interaction between the sensitizers and the HTM. Indoline-based donor parts may enhance the aggregation of the dye molecules and result in lower photocurrents.26

Previous studies have shown that the dye layer can act as a hole-transport layer in ssDSSCs.35,36 Therefore, the hole-hopping process between the dye molecules most likely affects the overall performance. From the calculation results, the reorganization energy of WS2 is noted to be lower than that for the other two materials, which would indicate better transport abilities (Table 3). The results from the conductivity measurements also support this hypothesis. From the data in Table 3, the hole conductivities of WS2, W7, and W8 are 2.91 × 10−7, 1.01 × 10−7, and 1.22 × 10−7 S cm−1, respectively. However, after the deposition of the HTM layer on top of the dye layer, the WS2/HTM film shows the lowest conductivity. This may indicate that the charge transfer at the interface of the WS2/HTM system can be inefficient, which is consistent with the results of the PIA measurement. Such low conductivity is expected to increase the charge-transport resistance in the ssDSSC devices and thus lower the FF and $J_{sc}$.12,26

Figure 8. SEM images for the cross section of ssDSSCs based on different sensitizers: (a) WS2-based devices, (b) W7-based devices, and (c) W8-based devices.

hand, the devices based on the W7 dye show $V_{oc}$, $J_{sc}$, and FF of 880 mV, 10.51 mA cm−2, and 0.74, respectively, yielding a higher PCE of 6.9%. Similarly, the ssDSSCs based on W8 dyes yielded an efficiency of 5.2%, with a photocurrent of 9.55 mA cm−2, a photovoltage of 870 mV, and a fill factor of 0.62. From the performance of the devices mentioned above based on different sensitizers, the TPA units seem to offer improved $V_{oc}$ and $J_{sc}$, resulting in the higher efficiencies recorded. In addition, the incident photon-to-current conversion efficiency (IPCE) data are in good agreement with the results shown in Table 2. In general, the light-absorption range of three different dyes is quite similar. However, the W7 dye shows the highest maximum monochromatic efficiency of 70% at 560 nm. The W8-based
2.6. Scanning Electron Microscopy (SEM). To investigate the morphology of the inner structure of ssDSSCs on the basis of different dyes, SEM has been employed. Figure 8b,c shows no obvious presence of a capping layer of HTM, indicating full penetration of the HTM into the TiO$_2$/dye layers. However, in the case of WS2-based ssDSSCs, a thin HTM layer can be distinguished under the Ag electrode layer. The inefficient pore filling could limit the charge transfer between the dye molecules and the hole conductor, thus suppressing the overall performance of the devices.

2.7. Aging Stability Study. The stability of solid-state photovoltaic devices is crucial for any future real-life application. Aging tests under ambient but dark conditions of the ssDSSCs based on different D−A−π−A dyes were therefore performed. All devices were stored in the dark at room temperature and in a relative humidity of around 25%. The resulting photovoltaic data are summarized in Figure 9. In general, all of the devices remain stable for 170 h. The short-circuit current of the WS2-based devices starts to drop after around 50 h of aging. The W7-based solar cells show better stability with only a small decline in the performance (about 6%) during the test period. After 170 h of aging, the W8-based solar cells retain around 5% overall conversion efficiency, which is quite close to its original performance.

3. CONCLUSIONS

Two novel organic dyes of D−A−π−A configuration, W7 and W8, have been studied for use in efficient ssDSSCs. The W7-based devices yielded an excellent PCE of 6.9%, with a photocurrent of 10.51 mA cm$^{-2}$, a high open-circuit voltage of 880 mV, and a good fill factor of 0.74 under standard AM 1.5 G illumination (100 mW cm$^{-2}$). The W8-based solid-state solar cells showed an efficiency of 5.2%, with a fill factor of 0.62, a photocurrent of 9.55 mA cm$^{-2}$, and an open-circuit voltage of 870 mV. Compared to that of the well-known WS2 sensitizer, the results show that the performance of the ssDSSC devices can be significantly improved by introducing an extra TPA moiety into the molecular structure of the dye. In addition, results of PIA spectroscopy show efficient dye regeneration for both W7- and W8-based devices. The conductivity measurements show a higher hole conductivity for the W7/HTM and W8/HTM layers compared to that of the WS2/HTM layer, indicating an efficient charge transfer at the interfaces of the two former systems. The results obtained offer insights into the design of reliable and highly efficient ssDSSCs with a potential for large-scale applications.

4. EXPERIMENTAL SECTION

4.1. Chemicals and Sensitizers. Most of chemicals were purchased from Sigma-Aldrich. In particular, dye WS2 was obtained from Dyenamo AB. Details on the route of synthesis...
could be found in the Supporting Information. $^3$H and $^{13}$C NMR spectra were recorded for the dyes.

4.2. Electrochemical Setup and UV–Vis Absorption Measurement. We used a Lambda 750 UV–Vis spectrophotometer for the UV–Vis measurement. The electrolytic solution for the electrochemical measurement is 0.1 M LiTFSI in dichloromethane. A stainless steel plate was used as the counter electrode, and Ag/AgCl/3 M NaCl was used as the reference electrode.

4.3. Device Fabrication and Characterization. The detailed process of fabrication can be found in our previous paper. $^{34}$ Briefly, fluorine-doped SnO$_2$ (FTO) glass substrates were dipped into a Zn-HCl solution (2 M) via the etch process. After this initial step, the substrates were cleaned using deionized water, acetone, and ethanol in an ultrasonic bath. The compact layer used the spray pyrolysis deposition technique. After sintering on a hot plate at 500 °C for 30 min, the substrate was post-treated in a solution of 0.2 M aqueous TiCl$_4$ at 70 °C for 30 min. Then, the substrates were rinsed with deionized water and ethanol and subsequently annealed on a hot plate at 500 °C for another 30 min. The dye bath solution in this study contained 0.2 mM of the dye in a mixed solvent of tert-butanol and acetonitrile (1:1). The time for dye bath is 5 h. After that, we used ethanol to rinse the electrodes. The surfaces of the dried substrates were then covered by a solution of the HTM, also containing additives, and spin-coated for 30 s at 2000 rpm. Finally, a 200 nm thick Ag layer was made as the counter electrode using the process of thermal evaporation in a vacuum chamber (Leica EM MED020).

The current–voltage curves of the ssDSSCs were recorded under 100 mW cm$^{-2}$ (AM 1.5) radiation using a Keithley Model 2400 SourceMeter. $^{34}$ The light source was also calibrated before use. We used a black mask with an aperture area of 0.126 cm$^2$ for the measurements. The electron lifetime data and the IPCE spectra were recorded according to our previous paper. $^{34}$

4.4. PIA Spectroscopy. The PIA spectra were recorded on a specially constructed setup. $^{35}$ A 20 W tungsten–halogen lamp was used to generate the white probe light. A square-wave modulated (on/off) blue light source (Thorlabs DC3100 LED system, 470 nm) was used for excitation. A light intensity of 6.1 mW cm$^{-2}$ and a modulation frequency of 9.33 Hz were used for the blue light light excitation.

4.5. Quantum Chemistry Calculations. The quantum calculations based on DFT were performed to generate the relaxed geometries of the molecules under study. Optimization and single-point energy calculations were performed using the B3LYP functional and 6-311G* basis sets for all atoms. All reported calculations were carried out using Gaussian 09. $^{39}$ The absorption spectra and excitation energies were estimated by TD-DFT using the MPW1K functional. $^{39}$ The solvent effects were taken into consideration using the polarizable continuum model. The equation for calculating the internal reorganization energy ($\lambda$) was based on the Nelson four-point method: $^{40}$ $\lambda = E_{r}^{*} - E_{r} + E_{e}^{*} - E_{e}$, where $E_{r}^{*}$ is the energy of the neutral molecule in the cation symmetry, $E_{e}^{*}$ is the total energy of the optimized cationic molecule, $E_{e}^{*}$ is the total energy of the cationic molecule in the neutral symmetry, and $E$ is the total energy of the optimized neutral molecule.
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