Synthesis, Characterization and Dye-Sensitized Solar Cell Application of a Novel Symmetric Diphenylpyran Dye with Dual Rhodamine-3-acetic Acid Anchors

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Abstract. With simple three-step method, a new symmetrical metal free organic diphenylpyran dye containing dual rhodamine-3-acetic acid anchors was successfully synthesized, characterized and applied to dye-sensitized solar cells (DSSC). The dye has saturated methylene in its acceptor part, which makes the electron withdrawing group and the anchor group cannot be conjugated well. In addition, the exhibits lower molar extinction coefficients of the dye and its blue-shifted absorption spectrum also influenced the light capture ability. The resulting weaker intramolecular charge transfer and the electron coupling effect of the dye hindered the dye charge injection and shorten the electron lifetime, leading to an average power conversion efficiency of 0.65 % (Jsc = 2.32 mA cm⁻², Voc = 448 mV and FF = 0.63). Further design of an efficient dye molecule needs efficient conjugation between the electron-withdrawing group and anchoring group, as well as an effective light harvest capability.

1. Introduction

Industrial development and population growth have gradually increased global energy consumption. In the past three decades, many researchers have devoted themselves to explore pollution-free renewable energy sources through development of new materials and innovative technology, expecting significant improvement of power conversion efficiency (PCE) and device stability [1, 2]. In 1991, Grätzel and co-workers reported breakthrough work on the PCE of dye sensitized solar cells (DSSC) [3]. With its advantages of low cost, simple preparation process and high PCE, DSSC is expected to be a potential candidate device for alternating traditional inorganic solar cells [4]. As one of the basic components in DSSC, dye molecules should be designed under the consideration of the energy levels, electronic structure, light absorption, and dye-aggregation [5]. The common molecular engineering strategy is to design a donor-π-acceptor (D-π-A) structure [6], thereby the optical and electrical properties of the dye can be adjusted through variation of the D or A part [7, 8]. As a good electron-donating group, 2, 6-diphenyl-4H-pyranylidene (DP) has been successfully applied in organic field...
effect transistors [9] (hole carrier mobility up to 0.05 cm$^2$V$^{-1}$s$^{-1}$ and 0.1 cm$^2$V$^{-1}$s$^{-1}$) and n-type dye-sensitized solar cells (photovoltaic conversion up to 5.3 %) [10], due to their intensive light absorption in the visible region and good energy levels matchable with titanium dioxide and iodide/triiodide redox couples. Previously we reported DP dyes with multi-anchor group for improving the photovoltaic performance [11]. Changes in acceptor units mainly affect dye spectral response [12], and the dynamic driving forces between the lowest unoccupied molecular orbital (LUMO) energy of the dye and conduction bands of titanium dioxide photo anode [13, 14], furthermore, the kinetic parameters such as photocurrent density, open circuit voltage and electrochemical impedance of solar cells are affected [15, 16]. Cyan acetic acid is usually preferred as the acceptor group of DSSC dye due to its low cost and simple synthesis [17, 18]. Other acceptors such as rhodamine-3-acetic acid have also been used, compared to cyan acetic acid dye derivatives, some of their derivatives have a red shift and a wide absorption band [19, 20]. In this paper, a novel symmetrical dye WRh were synthesized using DP as donor moiety and dual rhodanine-3-acetic acid groups as acceptor parts, respectively. The photo physical and electrochemical properties of dyes as well as the photovoltaic properties of devices were investigated in detail compared with dual cyan acetic acid DP dye W2.

2. Experimental section

2.1. Materials and instruments

Solvents were purified from the associated reagents. All reagents were purchased from Shanghai Macklin Alfa, Aesar and Sigma-Aldrich. All reactions were carried out under an argon atmosphere. UV absorption spectrum was measured using a Perkin-Elmer Singapore Lambda 35 UV-visible spectrophotometer. Under argon protection, the redox potentials were measured by ZAHNER CIMPS photo-electrochemical workstation at a scan rate of 100 mV s$^{-1}$, with saturated calomel electrodes (SCE) as the reference electrode, glassy carbon electrode as the working electrode and Pt wire as the counter electrode, using supporting electrolyte of 0.1 M of tetrabutylammonium hexafluorophosphate. The fabrication of DSSC and the corresponding photovoltaic measurements as reported previously [21].

![Synthesis route of the dye WRh and structure of W2.](image)

**Figure 1.** Synthesis route of the dye WRh and structure of W2.

2.2. Synthesis

The synthesis route of dye WRh is shown in Figure 1. The procedure is followed by the previously reported method [21]. To a stirred solution of compound W2-1 (0.10 g, 0.16 mmol), rhodamine-3-
acetic acid (0.19 g, 1.00 mmol) and ammonium acetate (0.03 g, 0.39 mmol) in acetic acid (3 mL). The reaction mixture was refluxed under argon for 24 h. After the reaction, water was added to quench the reaction, followed by a filtration to obtain a solid. The product was purified by column chromatography on silica gel (dichloromethane / methanol, 10:1), and 0.14 g of dark reddish solid was obtained (yield: 89.0 %). $^1$H NMR (600 MHz, DMSO) $\delta$ 13.84 – 13.02 (m, 2H), 7.94 (s, 1H), 7.91 (d, $J = 11.0$ Hz, 2H), 7.89 (s, 3H), 7.80 – 7.69 (m, 8H), 7.63 (d, $J = 7.3$ Hz, 4H), 7.47 – 7.24 (m, 10H), 6.67 (s, 2H), 4.71 (s, 4H).

3. Results and discussion

3.1. Photo physical and electrochemical properties

The UV-visible spectra of W2 and WRh were recorded in ethanol (EtOH) as well as those adsorbed on TiO$_2$ films as shown in Figure 2(a) and 2(b). The corresponding spectroscopic parameters are summarized in Table 1. Both dyes have distinct absorption bands in solution but WRh exhibits lower molar extinction coefficients $\varepsilon$ than dye W2 over all. The first absorption peaks locating in the range of 260–350 nm are assigned to the aromatic $\pi$–$\pi^*$ electron transitions of the dye molecules. The secondary peaks at 389 nm for WRh and 404 nm for W2 owned $\varepsilon$ of 23800 and 34500 M$^{-1}$cm$^{-1}$, respectively, which resulted from the intramolecular charge transfer (ICT) between the diphenylpyran donor and Rhodamine acetic acid or cyan acetic acid acceptor group. The thioxo-thiazolidinone group has a better electron extraction ability relative to the carboxyl group, leading to a slight red shift in the absorption end of the WRh compared to W2. On the film, the WRh absorption peak has a shift of 29 nm towards short wavelength direction compared to that in solution, which is probably caused by the twisted structure of WRh. In addition, the absorption of WRh on the film has a blue shift of 57 nm relative to that of W2. In Figure 2(c), the electrochemical properties of W2 and WRh were measured with cyclic voltammetry and the data are listed in Table 1. The first oxidation potentials of WRh and W2 are 0.92 and 0.93 V (vs. NHE), respectively, which are lower than the redox energy level of I$^-$/I$_3^-$, ensuring available charge transfer during the dye regeneration process. The excited state potentials $E_{\text{ox}}^{*}$ of the dyes were estimated from the equation $E_{\text{ox}}^{*} = E_{\text{ox}} - E_{0-0}$, where $E_{0-0}$ represents the band gap estimated from the edge of the absorption spectra, resulting in $E_{\text{ox}}^{*}$ of –1.41 V for WRh and –1.43 V for W2.

| Dye | $\lambda_{\text{max}}^a$/nm (10$^4$/M$^{-1}$cm$^{-1}$) | $\lambda_{\text{max}}^b$/ nm | $E_{\text{ox}}^{\varepsilon}$/ V (vs.NHE) | $E_{0-0}^\delta$/ eV | $E_{\text{ox}}^{\varepsilon}$/ V (vs.NHE) |
|------|---------------------------------|----------------|-----------------|-----------------|-----------------|
| WRh  | 291 (1.55)                      | 418            | 0.92            | 2.33            | –1.41           |
|      | 389 (2.38)                      |                |                 |                 |                 |
| W2   | 322 (3.96)                      | 475            | 0.93            | 2.36            | –1.43           |
|      | 404 (3.45)                      |                |                 |                 |                 |
3.2. Theoretical studies

As in Figure 3, the optimized structures and electron distributions of the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of WRh were calculated using Gaussian 09 at the B3LYP/ 6-31G * level. Due to the saturated methylene of WRh, LUMO is not delocalized on the carboxylic anchor group, which probably weakens the ICT, thus hindering the electron injection from the dye into the conduction band of TiO$_2$. At the same time, a larger distance between the holes of the dye and the electrons of TiO$_2$ induced by the distortion structure of dye and the long distance between the donor and the acceptor, which could greatly reduce the electron recombination. The ground state delocalized electrons of WRh in HOMO are almost consistent with that of W2.
3.3. Photovoltaic performance

The DSSC devices were fabricated and measured according to our previous report. The current-voltage (I–V) plots was shown in Figure 4 (a), and the photovoltaic results are compiled in Table 2. WRh showed an average power conversion efficiency of 0.65 % ($J_{sc} = 2.32$ mA cm$^{-2}$, $V_{oc} = 448$ mV and $FF = 0.63$). The decreased photocurrent was caused by the lower ε of WRh and its blue shifted absorption on film as compared with dye W2, which makes it to have a poor light capture ability. The incident photon-to-current conversion efficiency (IPCE) was further measured, as shown in Figure 4 (b). The maximum IPCE value of the DSSC based on WRh was 27.3% at 411 nm. The results show that the IPCE spectrum of the dye is consistent with their I-V curves.

| Dye | $J_{sc}$ / mA cm$^{-2}$ | $V_{oc}$ / mV | FF / % | PCE / % |
|-----|------------------------|--------------|--------|---------|
| WRh | 2.32                   | 448          | 62.95  | 0.65    |
| W2  | 11.61                  | 585          | 70.20  | 4.77    |

Illumination: 100 mW cm$^{-2}$ simulated AM 1.5 G solar light. Electrolyte solution comprising 0.6 M DMPImI, 0.1 M LiI, 0.2 M I$_2$, and 0.5 M TBP (in acetonitrile).

### Table 3. The electrochemical parameters of DSSC based WRh and W2.

|         | $R_s$ / Ω | $R_{pt}$ / Ω | $R_{ct}$ / Ω | $f_{max}$ / Hz | $\tau_e$ / ms |
|---------|------------|--------------|--------------|----------------|--------------|
| WRh     | 17.87      | 28.06        | 1388         | 35.9           | 4.44         |
| W2      | 14.63      | 6.18         | 108.6        | 3.00           | 53.08        |

Electrochemical impedance spectroscopy (EIS) measurement revealed the interfacial charge transfers and recombination processes. The corresponding Nyquist and Bode plots of EIS for the DSSC of the WRh and W2 dyes are shown in Figure 5 and the relevant parameters are shown in Table 3. The two semicircles on Nyquist plots represent two different charge transfer processes and their diameters represent the degree of charge recombination. The semicircle at higher frequency corresponds to the charge transfer resistance $R_{pt}$ at the platinum/electrolyte interface and the semicircle at intermediate frequency corresponds to the charge transfer resistance $R_{ct}$ at the TiO$_2$/dye/electrolyte interface. The electron lifetime ($\tau_e$) can be obtained from the bode plots using the equation of $\tau_e = 1/(2\pi f_{peak})$, where $f$ is the frequency of the mid-frequency peak. DSSC based on WRh shows significantly larger semicircle diameter of $R_{ct}$ than that of W2, which indicates that WRh has a higher recombination resistance, resulting from long distance of its LUMO site and the anchor group and thus a relatively weak electronic coupling. A much poor electron life time of WRh based DSSC than that of dye W2 DSSC was also displayed in Bode plot. Therefore, the effective injection of electrons is lower in WRh based DSSC, leading to much lower $J_{sc}$ and $V_{oc}$. 

![WRh: LUMO](image1.png)  
[WRh: HOMO](image2.png)  

**Figure 3.** Electron distribution on molecular orbital of dye WRh.
4. Conclusion

Taken together, we reported the synthesis of a new di-anchored dye WRh using DP group as donor, biphenyl rings as π-bridge, rhodamine-3-acetic acid as acceptor by a simple three-step method. The photo physical and electrochemical properties and DSSC performance were also investigated. Compared with W2 dye, DSSC based on WRh dye exhibited a low PCE of 0.6 %, due to the saturated methylene in its acceptor part, which makes the electron withdrawing group and the anchor group cannot be conjugated well. While compared with dye W2, the lower ε and the blue shifted absorption of WRh on TiO$_2$ film makes it to have an insufficient light-harvesting for improving the photocurrent. The resulting weaker ICT and the electron coupling effect of the dye hindered the charge injection and shorten the electron lifetime, which was demonstrated from the EIS experiments. Further molecule modification for enhancement of DSSC efficiency is in progress.

Acknowledgments

This work is supported by National Natural Science Foundation of China (Grant No. 21762033), the High Level Talents Scientific Foundation of Inner Mongolia Normal University (Grant No. 2015YJRC001). The corresponding authors are Altan Bolag and Wu Yun.

References

[1] Mishra, A.; Fischer, M. K.; Bauerle, P., Metal-free organic dyes for dye-sensitized solar cells: from structure: property relationships to design rules. Angew. Chem., Int. Ed. 48 (2009) 2474 - 2499.
[2] Jadhav, M. M.; Chowdhury, T. H.; Bedja, I., Near IR emitting novel rhodanine-3-acetic acid
based two donor-π-acceptor sensitizers for DSSC: Synthesis and application. Dyes Pigm. 165 (2019) 1391 - 1399.

[3] O’regan, B.; Grätzel, M., A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO₂ films. Nature. 353 (1991) 737 - 740.

[4] Wang, H.; Bao, B.; Hu, X., Efficient Small Molecule Organic Dyes Containing Different Bridges in Donor Moieties for Dye-Sensitized Solar Cells. Electrochim. Acta 250 (2017) 278 - 284.

[5] Jiao, Y.; Mao, L.; Liu, S., W., Effects of meta or para connected organic dyes for dye-sensitized solar cell. Dyes Pigm. 158 (2018) 165 - 174.

[6] Haid, S.; Marszalek, M.; Mishra, A.; Grätzel, M.; Bäuerle, P., Significant Improvement of Dye-Sensitized Solar Cell Performance by Small Structural Modification in π-Conjugated Donor-Acceptor Dyes. Adv. Funct. Mater. 22 (2012) 1291 - 1302.

[7] Clifford, J. N.; Martinez-Ferrero, E.; Viterisi, A., Sensitizer molecular structure-device efficiency relationship in dye sensitized solar cells. Chem Soc Rev. 40 (2011), 1635 - 1646.

[8] Lu, J.; Liu, S.; Wang, M., Push-Pull Zinc Porphyrins as Light-Harvesters for Efficient Dye-Sensitized Solar Cells. Front Chem. 6 (2018) 541.

[9] Bolag, A.; Mamada, M.; Nishida, J.-i.; Yamashita, Y., Field-Effect Transistors Based on Tetraphenylpyrylindenes and the Sulfur Analogues. Chem. Mater. 21 (2009) 4350 - 4352.

[10] Bolag, A.; Nishida, J.-i.; Hará, K.; Yamashita, Y., Enhanced performance of dye-sensitized solar cells with novel 2,6-diphenyl-4H-pyrylindene dyes. Org. Electron. 13 (2012) 425-431.

[11] Zhang, X.; Bolag, A.; Yun, W.; Eerdun, C.; Du, Y.; Ning, J.; Alata, H., Dye Sensitized Solar Cells Based on Diphenylpyrylindene Sensitizers with Mono and Dual Cyanoacrylic Acid Anchoring Groups. Chem. Lett. 48 (2019) 204 - 207.

[12] El-Zohry, A. M., The origin of slow electron injection rates for indoline dyes used in dye-sensitized solar cells. Dyes Pigm. 160 (2019) 671 - 674.

[13] Liang, M.; Chen, J., Arylamine organic dyes for dye-sensitized solar cells. Chem Soc Rev. 42 (2013) 3453 - 3488.

[14] Grätzel, M., Dye-sensitized solar cells. J J. Photochem. Photobiol., C. 4 (2003) 145 - 153.

[15] Su, R.; El-Shafei, A.; Adhikari, A. V., New indole based co-sensitizers for dye sensitized solar cells exceeding 10% efficiency. RSC Adv. 6 (2016) 30205 - 30216.

[16] Elsherbiny, D.; Cheema, H.; El-Shafei, A., Highly efficient panchromatic dye-sensitized solar cells: Synergistic interaction of ruthenium sensitizer with novel co-sensitizers carrying different acceptor units. Dyes Pigm. 132 (2016) 316 - 328.

[17] De Angelis, F.; Fantacci, S.; Selloni, A.; Grätzel, M.; Nazeeruddin, M. K., Influence of the sensitizer adsorption mode on the open-circuit potential of dye-sensitized solar cells. Nano Lett. 7 (2007) 3189 - 3195.

[18] Huang, Z.-S.; Meier, H.; Cao, D., Phenothiazine-based dyes for efficient dye-sensitized solar cells. J. Mater. Chem. C. 4 (2016) 2404 - 2426.

[19] Wiberg, J.; Marinado, T.; Hagberg, D. P., Effect of anchoring group on electron injection and recombination dynamics in organic dye-sensitized solar cells. J. Mater. Chem. C. 4 (2016) 3881 - 3886.