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Effect of different acceptors in di-anchoring triphenylamine dyes on the performance of dye-sensitized solar cells

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ABSTRACT

Three di-anchoring triphenylamine dyes, which were coded as **TPAC1**, **TPAR2** and **TPACR2**, were designed and synthesized for dye-sensitized solar cell application. The structural modification effect of different anchoring groups on photophysical, electrochemical and photovoltaic properties of the related DSSCs was extensively investigated. With the variation from cyanoacetic acid via rhodanine-3-acetic acid to co-rhodanine units, the molar extinction coefficients of the maximum absorption wavelength for the three dyes gradually increase due to the extension of π system. In comparison with that for **TPAC1** and **TPAR2**, DSSC based on dye **TPACR2** with double co-rhodanine groups shows the best overall conversion efficiency of 4.64% with simultaneous enhancement of photocurrent and photovoltage, which is attributed to the higher molar extinction coefficient ($6.5 \times 10^4\ M^{-1}\ cm^{-1}$), broader absorption spectra, broader IPCE spectra and longer electron lifetime.

1. Introduction

As a crucial component in dye-sensitized solar cells (DSSCs), the metal-free organic dyes have always attracted increased attention in the past decades by virtue of their ease of inexpensive synthesis, generally high molar extinction coefficients and tunable absorption spectral response. In the last decade, numerous investigations organic dyes, such as indoline [1–3], coumarin [4,5], cyanine [6–8], perylene [9,10], triphenylamine [11–14], carbazole [15–17], tetrahydroquinoline [18,19], phenothiazine [20–23], phenoxazine [24,25] and fluorene dyes [26,27], have been investigated. So far, organic sensitizers have gained promising overall conversion efficiencies [1,11] (η), which is comparable to ruthenium-based complexes.

By far, most typical metal-free organic dye sensitizers contain a structure of “Donor (D)–conjugated bridge (π)–Acceptor (A)”. In order to utilize the sun light as much as possible, two common structural strategies, incorporating more donor segments or enlarging π-conjugated linker into the D–π–A configuration to form the D–D–π–A or D–π–π–A structure, have been considered [28–32]. However, the complexity in the process of synthesis is the major problem. Different from donor and conjugated bridge segments, the electron acceptor (A) carries a polar carboxylic acid as anchoring group to TiO_2 surface. Varying the numbers of anchor groups via protonation state to tune the interfacial electron transfer or photovoltaic properties is very important for Ru-sensitizers. Especially, di-anchoring N719 dye gives higher cell efficiency than the protonated N3 dye with quadri-anchoring groups, which is attributed to the effect of the bound dye on the energy of the TiO_2 conducting band [33]. Similar to Ru-sensitizers, the notion of incorporating double electron acceptor units into the organic donor framework to form di-anchoring dye has been proposed to further enhance the binding strength of dyes on the TiO_2. Several di-anchoring organic dyes, which have been

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designed and synthesized for use in DSSCs, have demonstrated better cell performance than mono-anchoring D–π–A sensitizers with an improved photocurrent due to the extension of the π-conjugated system and the enhanced molar extinction coefficient [34–40]. Because the electrons from the photoexcitation of the dye molecules are injected to conduction band of the semiconductor through the electron acceptor parts, changes in the electron acceptor of the dye sensitizers can result in a significant variation of electronic and photovoltaic properties. As regards acceptor parts, cyanoacetic acid and rhodanine-3-acetic acid generally carried anchoring group to TiO_2 surface in the single D–π–A sensitizers which were discussed in previous work [41–43]. In addition, due to the strong electron withdrawing ability and the extension of the π-conjugation framework, co-rhodanine unit have also been successfully utilized for the application of DSSCs [1,3]. However, the contributions of different electron acceptors in di-anchoring dyes on the electronic and photovoltaic properties have not been well explored. Recently, we present three di-anchoring dyes comprised a triphenylamine group as an electron donor, which are coded as **TPAC1**, **TPAR2** and **TPACR2**. The three di-anchoring dyes were designed to have double electron acceptors (cyanoacetic acid, rhodanine-3-acetic acid, co-rhodanine unit), which are shown in Fig. 1. With the variation from cyanoacetic acid via rhodanine-3-acetic acid to co-rhodanine units, a π-conjugated extension of electron acceptor in di-anchoring organic sensitizers was observed for expanding the possibility of enhancing the optical and photovoltaic properties of the sensitizers. In our study, in comparison with cyanoacetic acid or rhodanine-3-acetic acid, the sensitizer with double co-rhodanine units as the anchor group exhibited the best overall conversion efficiency with simultaneous enhancement of photocurrent and photovoltage.

2. Experimental section

2.1. Materials

Tetrabutylammonium perchlorate (TBAP), 4-tert-butylpyridine (TBP), lithium iodide (LiI) and iodine (I_2) were purchased from Aldrich and used as received. The starting materials triphenylamine and (Z)-2-(2-(3-octyl-4-oxo-2-thioxothiazolidin-5-ylidene)-4-oxothiazolidin-3-yl) acetic acid was purchased from chemsolarism company. All the other solvents and the chemicals are puriss grade and used without further purification.

2.2. Synthesis

In order to investigate the structural modification of different electron acceptor groups upon the photophysical, electrochemical and photocurrent density–voltage characteristics of the DSSCs, double electron acceptor groups were applied into the three dyes with triphenylamine electron donor. The synthetic route of **TPAC1**, **TPAR2** and **TPACR2** dyes is shown in Fig. 1. **DFTPA** and **TPAR2** were synthesized according to the corresponding literature methods [44]. The final step was a Knoevenagel reaction between the carbaldehyde and two equivalent of different electron acceptors (cyanoacetic acid, rhodanine-3-acetic acid or (Z)-2-(2-(3-octyl-4-oxo-2-thioxothiazolidin-5-ylidene)-4-oxothiazolidin-3-yl) acetic acid) in the presence of ammonium acetate in acetic acid.

2.2.1. Synthesis of **TPAC1**

A 25 mL acetic acid solution of **DFTPA** (151 mg, 0.5 mmol), cyanoacetic acid (85 mg, 1.0 mmol) and ammonium acetate (20 mg, 0.26 mmol) was refluxed for 6 h under argon atmosphere. After cooling to room temperature, the precipitate was filtered and washed by distilled water. The crude product was purified by column chromatography (methylene chloride/methanol = 10/1) to obtain **TPAC1** (200 mg, 92%) as a red solid. ^1H NMR (500 MHz, $CDCl_3$): δ/ppm: 7.86 (s, 1H, CH), 7.84 (s, 1H, CH), 7.36 (t, 2H, $J = 7.5$ Hz, ArH), 7.23 (t, 1H, $J = 8.5$ Hz, ArH), 7.28 (d, 2H, $J = 8.5$ Hz, ArH), 7.15 (d, 4H, $J = 8.0$ Hz, ArH), 7.00 (d, 2H, $J = 8.0$ Hz, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm: 151.5, 145.7, 144.9, 133.8, 132.7, 129.5, 127.7, 126.2, 125.8, 125.4, 119.4, 116.5. MALDI-TOF-MS (m/z): calcd for $(M-2H)^-$ $C_{26}H_{15}O_4N_3$: 433.1063, found: 433.1093.

2.2.2. Synthesis of **TPACR2**

The same procedure as for **TPAC1** but with (Z)-2-(2-(3-octyl-4-oxo-2-thioxothiazolidin-5-ylidene)-4-oxothiazolidin-3-yl) acetic acid (160 mg, 0.4 mmol) were used. The crude product was purified by column chromatography (methylene chloride/methanol = 10/1) to obtain **TPACR2** (150 mg, 70%) as a red solid. ^1H NMR (500 MHz, $CDCl_3$): δ/ppm: 7.78 (s, 1H, CH), 7.76 (s, 1H, CH), 7.54 (d, 2H, $J = 8.5$ Hz, ArH), 7.40 (t, 2H, $J = 7.7$ Hz, ArH), 7.26 (t, 1H, $J = 7.5$ Hz, ArH), 7.18 (d, 8H, $J = 8.0$ Hz, ArH), 4.76 (s, 4H, CH_2), 4.06 (t, 4H,

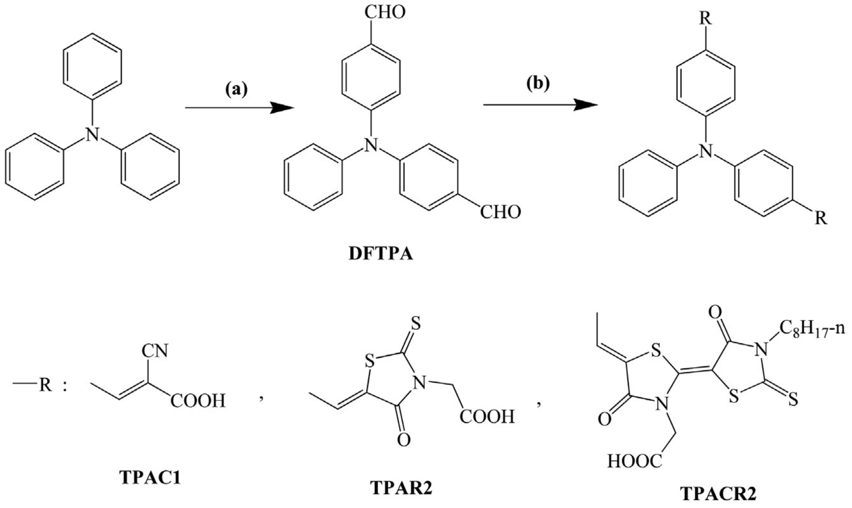

Fig. 1. The synthetic route of the three dyes (**TPAC1**, **TPAR2** and **TPACR2**). (a) $POCl_3$, DMF, reflux, 5 h; (b) cyanoacetic acid, rhodanine-3-acetic acid or (Z)-2-(2-(3-octyl-4-oxo-2-thioxothiazolidin-5-ylidene)-4-oxothiazolidin-3-yl) acetic acid, ammonium acetate, acetic acid, reflux, 6 h.