



π – π and p– π conjugation, which is more efficient for intermolecular charge transfer in starburst triarylamine donors of platinum acetylide sensitizers?



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ABSTRACT

Two novel starburst donors based platinum acetylide sensitizers with π – π conjugated span group (2-vinylthiophene) were synthesized and applied in dye-sensitized solar cells (DSSCs). The photovoltaic performances of sensitizers were investigated by photophysical, photovoltaic, electrochemical, and a theoretical approach. Compared with similar triphenylamine based platinum acetylide sensitizers which do not contain a 2-vinylthiophene group, it was found that the introduction of 2-vinylthiophene as a span group increased the donating ability of donor and the coplanar property between the donor and π -bridge, which are in favour of the intramolecular charge transfer. Moreover, the new DSSCs based sensitizers displayed a power conversion efficiency of 2.80% and 2.95%, which is significantly improved over that determined for the non-vinylthiophene containing analogues.

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1. Introduction

Replacing traditional fossil fuel-based energy by renewable resources is generally regarded as the most prospective methodology to solve the energy crisis of the world. Solar energy is regarded as one of the perfect renewable energy resources, owing to its huge reserves, inexhaustibility and pollution-free characteristic. Among the various processes to utilize solar energy, dye-sensitized solar cells (DSSCs) based on highly porous nanocrystalline films of titanium dioxide (TiO₂) have received considerable attention due to their demonstrated high power conversion efficiency, low cost, and high semiconductor stability [1].

As the key component of DSSCs, sensitizers, which are anchored to the surface of semiconducting TiO₂ nanocrystals, play a vital role in the device performance because of the function of absorbing incoming light and injecting electrons into the conduction band of

TiO₂ films. With the aim to improve the power conversion efficiency (PCE), a variety of sensitizers, including pure organic (i.e. metal-free) [2] and organometallic (i.e. metal-containing) [3] dyes, have been designed and prepared during the past few decades. The typical sensitizers usually consist of three parts: electron donors, conjugated π -bridges, and acceptors. The conventional electron donors are some electron-rich groups, such as coumarin [4a], triarylamine [4b], indoline [4c], phenoxazine [4d], carbazole [4e]. The π -bridges are often constructed by conjugated cyclic groups such as thiophene and benzene. The charge mobility of the π -bridge is a major factor which influence the intramolecular charge transfer (ICT) properties of the sensitizers. The most frequently used acceptor is carboxyl or cyanoacetic acid group except for some specific structures [5]. Notably, metal-containing sensitizers have attracted considerable attention due to their inherent advantages, such as wide absorption range, large molar extinction coefficient, and luminescent properties, when applied in DSSCs. Therefore, a wide variety of organometallic dyes have been investigated which exhibited excellent photovoltaic performance, for examples complexes of Ru [6], Fe [7], Os [8], Cu [9], and Re [10]. Many Ru(II)-complex based DSSCs are known to attain efficiencies of greater than 10% [6b–e].

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As an important functional linker, platinum acetylide unit has been extensively explored in the area of supramolecular self-assembly and functional materials science during the past few decades [11]. Owing to the unique π -conjugated character, some platinum acetylide complexes have exhibited interesting properties, such as luminescence [12a], energy transfer [12b], nonlinear absorption [12c], and electrical conductivity [12d]. Consequently the platinum acetylide moiety has been extensively explored in the areas of organometallic gels [13], molecular wires [14], polymer solar cells [15], functional oligomers [16] and functional metallocycles [17]. For instance, because of the special photophysics characteristics of platinum acetylide complexes, Schanze and co-workers reported the interesting delocalization in the singlet and triplet excited states of platinum acetylide oligomers [18]. Moreover, the use of platinum acetylide linkers as “spacer” groups for photoinduced charge separation has been also well investigated by Schanze’s group [19]. Recently, a series of novel platinum acetylide complexes, which exhibited potential applications as luminescent organometallic gels, have been successfully prepared by Yang’s group [20].

In order to enrich the library of organometallic sensitizers and expand the application of platinum acetylide complex, we have realized the design and synthesis of D- π -M- π -A structured platinum acetylide sensitizer Pts and successfully used them in dye-sensitized solar cells [21a]. For further improving the device performance, we unremittingly change and optimize the molecular structures of platinum acetylide sensitizers, and obtained the highest power conversion efficiency (PCE) of 4.21% (Scheme 1) [21b]. However, we found DSSCs based starburst triarylamine sensitizers **WY3–4** [21c] showing low power conversion efficiency of 1.71% and 2.28%, respectively. Generally, the donating ability of electron donors, the electron transport properties of π bridges, and the electron withdrawing ability of acceptors are three major factors in the design of sensitizers for DSSCs. However, in the structure of starburst triarylamine donors, the choice of the span atoms or span groups which are responsible for the collection and transfer of photo-exciting electrons have often been ignored. Herein, with the aim to improve the power conversion efficiency (PCE) of starburst triarylamine platinum acetylide sensitizers, two novel sensitizers **L1–2** (Scheme 2) with starburst triarylamine donors were prepared through the replacement of p- π (aniline in **WY3** and **WY4**) [21c] conjugated group with π - π (2-vinylthiophene in **L1** and **L2**) span

groups. Interestingly, the DSSCs based on sensitizers **L1–2** yield higher power conversion efficiency (PCE) than that of **WY3–4**. In order to explain the increase of PCE, **L1–2** were investigated by photophysical, photovoltaic, electrochemical, and theoretical approach. It was found that the π - π conjugated span group is more effective for ICT in starburst triarylamine donors of platinum acetylide sensitizers than p- π conjugated span group in this study, which is in favour of improving the power conversion efficiency (PCE). These results not only expanded the choice of platinum acetylide sensitizers, but also demonstrated that the span groups in electron donors play a vital role in the design of sensitizers.

2. Experimental

2.1. Materials and general methods

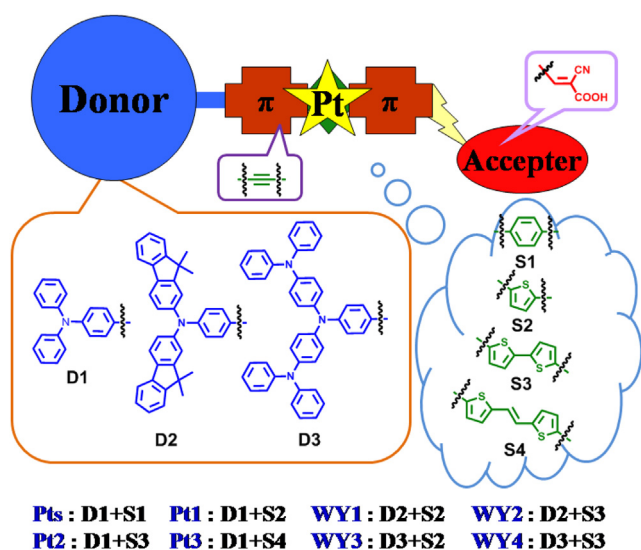
The FTO conducting glass (FTO glass, fluorine doped tin oxide over-layer, transmission >90% in the visible, sheet resistance $15 \Omega \text{ square}^{-1}$) was obtained from the OPV Tech. New Energy Co., Ltd. of China. Titania pastes of DSL 90T were purchased from Dyesol (Australia). Lithium iodide was from Fluka and iodine (99.999%) was from Alfa Aesar. The ionic liquid used in the electrolyte such as 1-butyl-3-methyl-imidazolium iodide (BMII) and 1,2-dimethyl-3-propylimidazolium iodide (DMPII) were from Jingge Science and Educational Co. Ltd. of China. Reagents were purchased and used without further purification. THF was distilled from sodium/benzophenone. DCM was distilled from calcium chloride. Et_2NH was dried from potassium hydroxide. Acetonitrile was dried from sodium sulphate. All of them were degassed under N_2 for 30 min before use. All reactions were performed in standard glassware under an inert N_2 atmosphere. The starting materials, 3-(5-bis(4(diphenylamino)styryl)thiophen-2-yl)-2-carb-aldehyde (**1**) [22], 5-ethynylthiophene-2-carbal-dehyde (**5a**) [23] and 5'-ethynyl-[2,2']bithiophene-5-carbaldehyde (**5b**) [23], were synthesized according to literature procedures, respectively.

^1H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Bruker 400 MHz Spectrometer at 298 K. The ^1H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ 0.0). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, br = broad. IR spectra were recorded on a Bruker Tensor 27 infrared spectrophotometer. The absorption spectra of sensitizer dyes in solution and adsorbed on TiO_2 films were measured with a Varian Cary 500 spectrophotometer. Cyclic voltammograms were recorded with a Zennium IM6 electrochemical workstation (Zahner, Germany) using a three-electrode cell in acetonitrile solvent with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, TiO_2 films stained with sensitizer as the working electrode, Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The SCE reference electrode was calibrated using the Fc/Fc^+ redox couple as an external standard.

2.2. Synthesis of sensitizers **L1–2**

2.2.1. Synthesis of compound **2**

A 200 mL Schlenk flask, charged with compound **1** (1.23 g, 1.97 mmol) and PPh_3 (1.29 g, 4.93 mmol), was degassed and back-filled with N_2 three times. After anhydrous CH_2Cl_2 (55 mL) was added under nitrogen, the mixture was stirred at 0°C (ice bath) for 5 min. Then the solution of CBr_4 (0.82 g, 2.46 mmol) in anhydrous CH_2Cl_2 (15 mL) was added. The reaction mixture was stirred under an inert atmosphere at room temperature for 2.5 h, then extracted with water (3×100 mL). The organic layer was separated and dried



Scheme 1. Three series of platinum acetylide sensitizers which our group previously reported [21].

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