Dyes and Pigments 94 (2012) 150–155

Contents lists available at SciVerse ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Effects of different acceptors in phenothiazine-triphenylamine dyes on the optical, electrochemical, and photovoltaic properties

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ARTICLE INFO

Article history:
Received 27 August 2011
Received in revised form
25 November 2011
Accepted 23 December 2011
Available online 29 December 2011

Keywords:
Phenothiazine
Acceptor
Cyanoacetic acid
Rhodanine-3-acetic acid
Dye-sensitized solar cells
Photovoltaic property

ABSTRACT

In dye-sensitized solar cells (DSSCs), as the excited electrons from dye molecules are injected to the conduction band of semiconductor film through the acceptor moieties, the acceptor groups have significant influences on the photovoltaic properties of the dyes. In this paper, the effects of different acceptor groups (cyanoacetic acid and rhodanine-3-acetic acid) in two phenothiazine-triphenylamine dyes (**PTZ-1** and **PTZ-2**) on the optical, electrochemical properties and photovoltaic performances were studied. In comparison with **PTZ-2**, the photovoltaic performance of **PTZ-1** is significantly improved by replacing rhodanine-3-acetic acid to cyanoacetic acid. The conversion efficiency of solar cell based on the **PTZ-1** is increased about 110%. The lower efficiency of solar cell based on **PTZ-2** is mainly because the delocalization of the excited state is broken between the 4-oxo-2-thioxothiazolidine ring and the acetic acid, which affects the electron injection from **PTZ-2** to the conduction band of TiO_2.

1. Introduction

In dye-sensitized solar cells (DSSCs), the dye is one of the most important components influencing solar cell performance, because the choice of dye determines the photoresponse of the DSSCs and initiates the primary steps of photon absorption and the subsequent electron transfer process. DSSCs based on the Ruthenium sensitizers have shown very impressive solar-to-electric power conversion efficiencies, reaching 11% under standard AM 1.5G sunlight [1]. However, the large-scale application of ruthenium dyes is limited because of costs and environmental issues. More and more efforts have been dedicated to the development of metal-free organic dyes which exhibit not only higher molar extinction coefficients, but also simple preparation and purification procedures at lower cost.

Generally, metal-free organic dyes possess the evident molecular structure of the donor part and the acceptor part bridged by the conjugated chain. Coumarin [2], merocyanine [3], indoline [4], polyene [5], hemicyanine [6], triphenylamine [7], fluorene [8], carbazole [9] and phenothiazine [10] based-organic dyes have been developed. In metal-free organic dyes, the electron acceptor parts have significant influences on the photovoltaic properties due to the excited electrons from the dye molecules are injected to the semiconductor film through the acceptor parts, and typical acceptor groups are cyanoacetic acid and rhodanine-3-acetic acid. For example, Kim et al. employed cyanoacetic acid as the acceptor on triphenylamine-based dye **TA-St-CA** and attained the overall conversion efficiency of 9.1% [11]. Next, the **TA-DM-CA** dye was obtained by structural modification based on **TA-St-CA**, and attained the overall conversion efficiency of 9.67%, which was the highest value among the metal-free organic dyes so far [7]. Ito et al. used rhodanine-3-acetic acid as the acceptor on indoline-based dye **D149** and attained the overall conversion efficiency of 9.03% [12]. A new indoline dye **D205** was designed by introducing an n-octyl substitute onto the rhodanine ring of **D149** and exhibiting an η value of 9.52%, which is the highest efficiency obtained so far among DSSCs based on indoline-based dye [13].

Based on these studies, we can know that the different acceptors have significant influences on the photovoltaic properties of solar cells based on the dyes. Two phenothiazine-triphenylamine dyes (**PTZ-1** [14] and **PTZ-2** [15]), in which the cyanoacetic acid and rhodanine-3-acetic acid as the different acceptor groups were applied in DSSCs (Scheme 1). Here, we focus on the effects of

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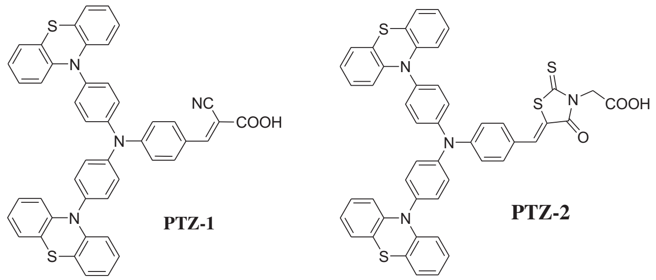
doi:10.1016/j.dyepig.2011.12.009



Scheme 1. Molecular structures of **PTZ-1** and **PTZ-2**.

Table 1
UV–vis, emission and electronchemical data.

Dye	λ_{max}[a]/nm (ε[b]/M^{-1} cm^{-1})	λ_{ex}[a]/nm	E_{ox}[c]/V (vsNHE)	E_{0-0}[d]/eV	E_{ox^*}[e]/V (vsNHE)
PTZ-1	433 (51,500)	530	0.636	2.626	−1.990
PTZ-2	468 (25,250)	543	0.410	2.476	−2.066

[a] Absorption and emission spectra were measured in CH_2Cl_2 solutions (2.5×10^{-5} M) at room temperature.

[b] The molar extinction coefficient at λ_{max} of the absorption spectra.

[c] The first oxidation potential of the dye was measured in DMF with 0.1 M n-Bu_4NPF_6 as electrolyte (scanning rate: 100 mV s^{-1}, working electrode and counter electrode: Pt wires, and reference electrode: Ag/AgCl), potentials measured vs Ag/AgCl were converted to normal hydrogen electrode (NHE) by addition of +0.2 V.

[d] 0–0 transition energy, estimated from the intercept between absorption and emission spectra in CH_2Cl_2.

[e] The estimated excited state oxidation potential of the dye was calculated from E_{ox}−E_{0-0}.

different acceptor groups in **PTZ-1** and **PTZ-2** on the optical, electrochemical properties and photovoltaic performances.

2. Experimental section

2.1. Materials

All solvents and other chemicals were reagent grade and used without further purification. 3-Hexyl-1-methylimidazolium Iodide (HMII) was prepared according to the literature [16]. Lithium iodide (LiI) was purchased from Acros. cyanoacetic acid, rhodanine-3-acetic acid, 4-tert-butylpyridine (TBP) and 3-Methoxypropionitrile (MPN) were purchased from Aldrich.

2.2. Photophysical and electrochemical measurements

Absorption spectra were measured with SHIMADZU (model UV1700) UV–vis spectrophotometer. Emission spectra were recorded with a Hitachi (model RF-5301) Spectrophotometer. Cyclic voltammetry experiments were performed on a CH Instruments 660C electrochemical workstation at a scan rate of 100 mV/s in dimethylformamide (DMF) (5×10^{-4} mol/L) containing 0.1 mol/L n-Bu_4NPF_6 as the supporting electrolyte, platinum as counter and working electrodes and Ag/AgCl as reference electrode.

2.3. Theoretical calculations

Gaussian 03 package was used for Density functional theory (DFT) calculations [17]. The geometries and energies of **PTZ-1** and **PTZ-2** were determined using the B3LYP method with the 6-31G(d,p) basis set. Importantly, none of the frequency calculations generated negative frequencies, being consistent with an energy minimum for the optimized geometry.

2.4. Fabrication of DSSCs

TiO_2 colloid was prepared according to the literature [18]. The FTO glass substrates were immersed in 4.0×10^{-2} mol/L $TiCl_4$ aq. at 70 °C for 30 min and washed with water and ethanol. The 12 μm thick mesoporous nano-TiO_2 films composed of 15–20 nm anatase TiO_2 particles were coated on the FTO glass plates by doctor blade. After drying the nanocrystalline TiO_2 layer at 125 °C, a 4 μm thick second layer of 300–500 nm sized light scattering anatase particles (Shanghai Cai Yu Nano Technology Co., Ltd, http://shkangyu.cn.gongchang.com) was deposited by doctor blade onto the first layer. The TiO_2 electrodes were heated at 450 °C for 30 min. After the sintering, when the temperature cooled to about 90 °C, the electrodes were immersed in a dye bath containing 2.0×10^{-4} mol/L **PTZ-1** and **PTZ-2** in acetonitrile and left overnight. The films were then rinsed in ethanol to remove excess dye. Solar cells were assembled, using a 25 μm thick thermoplastic Surlyn frame, with a platinized counter electrode. An electrolyte solution was then introduced through the hole predrilled in the counter electrode, and the cell was sealed with thermoplastic Surlyn covers and a glass coverslip. The electrolyte employed was a solution of 0.3 M HMII, 0.5 M LiI, 0.05 M I_2 and 0.5 M TBP in MPN.

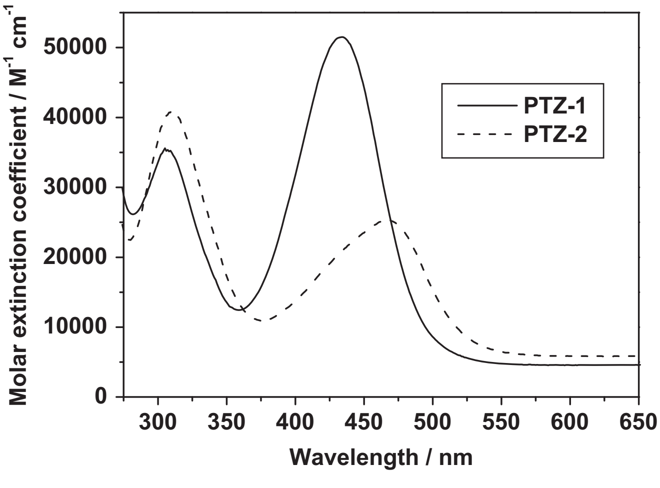


Fig. 1. Absorption spectra of **PTZ-1** and **PTZ-2** recorded in dichloromethane.

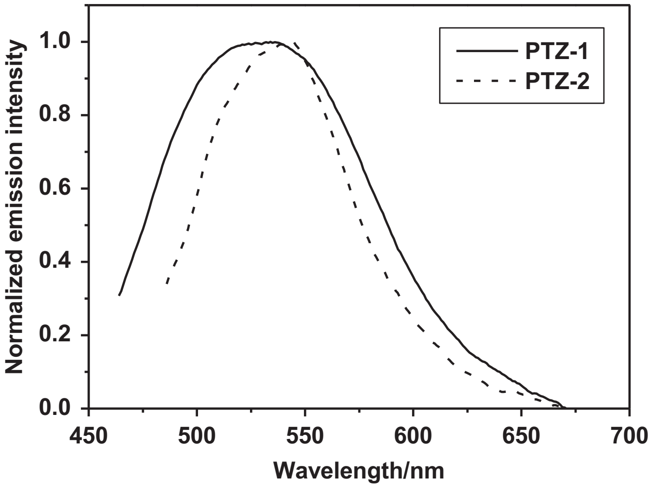


Fig. 2. Emission spectra of **PTZ-1** and **PTZ-2** in dichloromethane.