



# Triazatruxene-based organic dyes containing a rhodanine-3-acetic acid acceptor for dye-sensitized solar cells



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## ARTICLE INFO

### Article history:

Received 4 August 2014  
Received in revised form  
6 October 2014  
Accepted 7 October 2014  
Available online 25 October 2014

### Keywords:

Dye-sensitized solar cells  
Organic dyes  
Triazatruxene  
Rhodanine-3-acetic acid  
Conjugated spacers  
Efficient electron injection

## ABSTRACT

Two novel triazatruxene-based organic dyes with a rhodanine acceptor have been designed, synthesized, and applied as photosensitizers for dye-sensitized solar cells. The photophysical and electrochemical properties of the dyes were investigated using UV–vis absorption spectroscopy, electrochemistry, and density functional theory calculations. Dyes with  $\pi$ -conjugated spacers, thiophene and benzene, both showed broad IPCE responses even up to 800 nm which covers almost the whole visible light spectrum and offers great potential in DSSCs. An overall conversion efficiency of 3.60% under AM 1.5 illumination ( $100 \text{ mW cm}^{-2}$ ) was achieved with the benzene spaced dye.

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## 1. Introduction

Solar energy application has been considered as a powerful alternative to petroleum and coal and has attracted increasing attention because of the fossil fuel depleting. As a low-cost device for solar energy-to-electricity conversion, dye-sensitized solar cells (DSSCs) have been extensively explored [1,2]. In DSSCs, the sensitizer is the crucial component for better light harvesting and high conversion efficiency [3]. Recently, metal-free organic sensitizers have been widely investigated for their structural diversity, high molar extinction coefficient, facile synthesis, low cost, and environmentally friendly characteristics [4].

Most of the organic sensitizers for DSSCs are characterized by an electron donor, a  $\pi$ -conjugated bridge, and an electron acceptor (D- $\pi$ -A) [5]. Triazatruxene (TAT), owing to its unique discotic  $\pi$ -extended and electron-rich aromatic structure, has been used to produce various functional materials [6]. Benefiting from its strong intramolecular charge transfer characteristic, synthetic flexibility, and high stability, novel triazatruxene-based sensitizers were

recently designed and synthesized for dye-sensitized solar cells in our group [7].

Generally, organic dyes are required to possess broad and intense spectral absorption in the visible light region for achieving high conversion efficiency [8]. Electron acceptor units also have significant influence on the photo-electronic properties because the excited electrons from the dye molecules are injected to the semiconductor film through the acceptor units [9]. To induce intramolecular charge transfer (ICT) from donor to acceptor efficiently, an electron-deficient acceptor is essential [10]. Rhodanine-3-acetic acid, due to its strong electron-withdrawing ability, has been used as an efficient electron acceptor in a series of organic dyes. For example, indoline-based dye D149 (Fig. 1) with rhodanine-3-acetic acid as the acceptor gave power conversion efficiency (PCE) of 9.03% [11]. Another indoline dye D205 (Fig. 1) was designed by introducing a *n*-octyl group onto the rhodanine ring of D149, and exhibited a PCE value of 9.52%, using an anti-aggregation reagent (chenodeoxycholic acid), which is the highest efficiency obtained among DSSCs based on indoline-based dyes [12]. Based on these studies, we report here the synthesis, structural characterization, and investigation of the electrochemical, photophysical, and photovoltaic properties of two novel organic dyes based on triazatruxene (5,10,15-triethyl-10,15-

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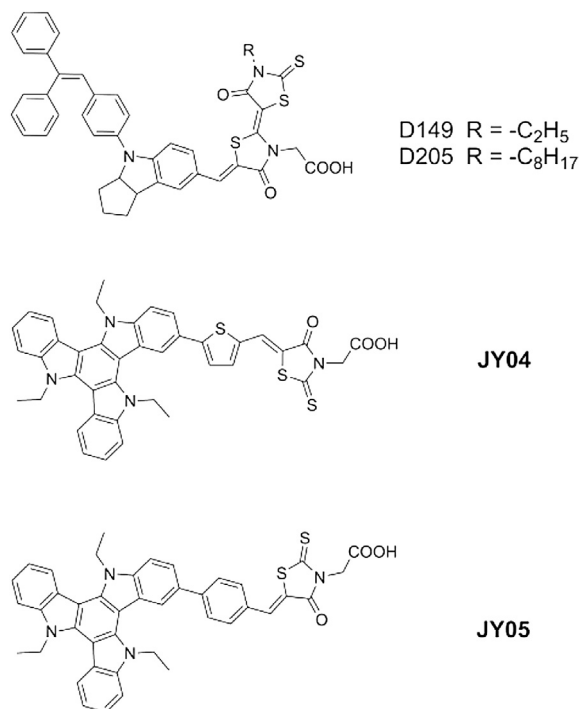


Fig. 1. Chemical structures of D149, D205, JY04, and JY05.

dihydro-5H-diindolo[3,2-a:3',2'-c]carbazole) framework containing a rhodanine-3-acetic acid. Thiophene and benzene were applied as the  $\pi$ -conjugated linkers, and the resultant molecular structures are shown in Fig. 1.

## 2. Experimental

### 2.1. Materials and instruments

All NMR solvents were used as received. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on Bruker 400 MHz spectrometer using TMS as internal standard. Cyclic voltammetry experiments were carried out with a conventional three-electrode system employing glassy carbon electrode as working electrode, Ag/Ag<sup>+</sup> electrode as reference electrode, and Pt wire as counter electrode. The redox potentials were measured in dichloromethane, using 0.1 M *n*-Bu<sub>4</sub>NPF<sub>6</sub> as supporting electrolyte with a scan rate of 100 mV S<sup>-1</sup>. IR spectra were recorded from KBr disk on the Bruker Tensor 27. All other chemicals were used as received without further purification. All solvents were purified according to standard methods.

### 2.2. Fabrication and characterization of DSSCs

A TiO<sub>2</sub> film (thickness, ~10  $\mu$ m) was prepared according to the doctor-blade method by coating a commercial TiO<sub>2</sub> sol (particle size, 20 nm, China National Academy of Nanotechnology & Engineering) onto the pre-treated FTO glass (Nippon Sheet Glass, Japan, fluorine-doped SnO<sub>2</sub> over layer, sheet resistance of 15  $\Omega$ /sq). A scattering layer (thickness, ~4  $\mu$ m, particle size, 200 nm) was then applied over the transparent layer, and the film was calcined at 500 °C for 60 min in a Muffle furnace at air. The resulting TiO<sub>2</sub> electrodes were treated by 40 mM TiCl<sub>4</sub> solution for 1 h at 70 °C and sintered again at 500 °C for 60 min. The active area of cells is 0.16 cm<sup>2</sup>. The Pt electrode was obtained by thermal deposition a platinum layer on the surface of FTO at 450 °C for 30 min. The TiO<sub>2</sub> photoanodes were immersed in commercial N719 dye solution

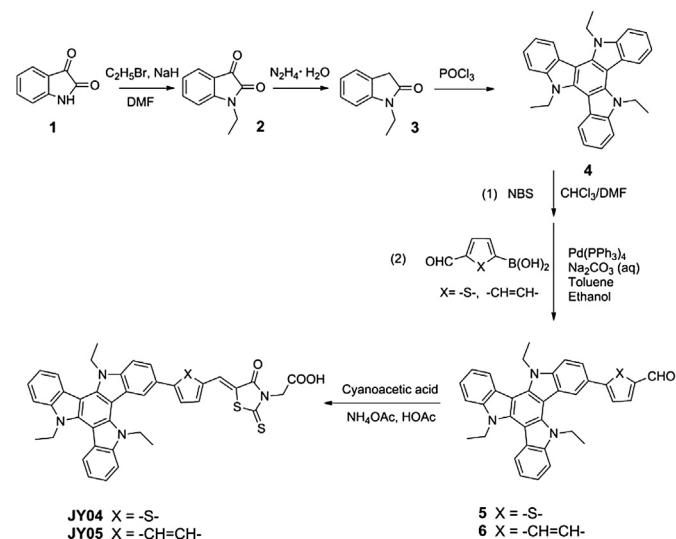
(0.3 mM in ethanol) for 24 h. The adsorption of the triazatruxene-based dyes on TiO<sub>2</sub> was carried out with 0.3 mM dye solution in tetrahydrofuran for 12 h. Chenodeoxycholic acid (CDCA) (10 mM) as a coadsorbent was added into the dye solution to prevent the aggregation of dye molecules on the surface of TiO<sub>2</sub>. The electrolyte was composed of 0.3 M DMPII, 0.1 M LiI, 0.05 M I<sub>2</sub>, and 0.5 M 4-*tert*-butylpyridine in acetonitrile. The DSSCs were illuminated by a solar simulator (Oriel® Sol2A, 94022A, Newport Corporation) under 100 mW/cm<sup>2</sup> irradiation, which was calibrated by a standard silicon solar cell (91150V, Newport Corporation). The measurement of the incident photon-to-current conversion efficiency (IPCE) was performed by using a commercial setup (QTest Station 2000 IPCE Measurement System, CROWNTech, USA). The photocurrent intensity-voltage (*J*-*V*) characteristic curves of the DSSC under simulated sunlight were recorded using an IM6ex electrochemical workstation (Zahner, Germany).

### 2.3. Dye synthesis

The synthetic routes of the sensitizers JY04 and JY05 are shown in Scheme 1. Target dyes were synthesized from isatin by five reaction steps. The intermediates 2, 3, and 4 were prepared according to literature procedures [13]. Bromination and subsequent Suzuki-coupling of compound 4 produced the  $\pi$ -extended triazatruxene bearing aldehydes 5 and 6. Knoevenagel reaction of the resulting aldehydes and cyanoacetic acid afforded the target sensitizers JY04 and JY05.

#### 2.3.1. Synthesis of compound 5

A solution of *N*-bromosuccinimide (NBS) (166 mg, 0.93 mmol) in DMF (5 mL) was added dropwise to the chloroform (30 mL) solution containing compound 4 (400 mg, 0.93 mmol) at 0 °C. Then the mixture was slowly warmed to room temperature and stirred for 1 h before it was poured into water. The organic phase was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated, the crude product was transferred into a two-neck round bottomed flask. 5-Formylthiophene-2-boronic acid (284 mg, 1.82 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (53 mg, 0.045 mmol), aqueous 2 M Na<sub>2</sub>CO<sub>3</sub> (7 mL), toluene (15 mL), and ethanol (5 mL) were successively added. The flask was charged with N<sub>2</sub>. The mixture was heated under reflux for 5 h before it was poured into water. Then,



Scheme 1. Synthetic procedures for triazatruxene-based dyes.

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