



Influence of donor and bridge structure in D–A– π –A indoline dyes on the photovoltaic properties of dye-sensitized solar cells employing iodine/cobalt electrolyte



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ABSTRACT

D–A– π –A indoline dyes have exhibited an especially excellent performance and are regarded as one of the most promising classes of arylamine organic sensitizers. Two new D–A– π –A indoline dyes (XS45 and XS46) with different additional donor as well as a reference D– π –A indoline dye (XS47) have been synthesized to investigate the influence of donor and bridge structure in indoline dyes on the photovoltaic properties of dye-sensitized solar cells employing iodine/cobalt electrolyte. The incorporation of bulky dipropylfluorene unit in the donor part significantly increases the light harvesting ability and notably retards the charge recombination at the titania/electrolyte interface. On the other hand, the introduction of benzothiadiazole (BTD) in spacer not only evokes a large responsive range of wavelengths into NIR region, but also decreases the molar absorption coefficients of indoline dyes. DSCs incorporating Co(II/III)tris(1,10-phenanthroline)-based redox electrolyte/iodine electrolyte and three synthesized organic dyes as photosensitizers are described. The results confirm that using D–A– π –A indoline dyes as sensitizers for cobalt cells is feasible.

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1. Introduction

Dye-sensitized solar cells (DSCs), as a new type of photovoltaic technology, have been considered to be a credible alternative to conventional inorganic silicon-based solar cells because of their ease of fabrication, high efficiency and cost-effectiveness since the report by O'Regan and Grätzel [1]. To achieve high solar power conversion efficiency, great research efforts are focused on designing and synthesizing new photosensitizers [2,3] as well as deep understanding of essential interface processes [4–6] in DSCs. Amongst these emerging photosensitizers, arylamine organic sensitizers with robust availability, ease of structural tuning and generally high molar extinction coefficients, have recently received great attention [3,7–20].

Indoline dyes are promising arylamine organic sensitizers for DSCs based on TiO₂ films because of their good photoresponse in

the visible region and high efficiency [5,21–24]. In particular, Tian, Zhu, Wang and coworkers developed a series of D–A– π –A indoline dyes with long-term stability, displaying PCEs of 3–9.04% [25–30]. In comparison to the traditional D– π –A indoline dyes, an obvious advantage of the D–A– π –A indoline dyes is their significant improved spectral response region, contributing to high photocurrent of this type of dyes. For instance, a high *J*_{sc} of 18.00 mA cm⁻² was achieved by WS-9 following coadsorption with 20 mM CDCA [25]. Nevertheless, it is interesting to note that most of the D–A– π –A indoline dyes-related works were carried out only in the iodine electrolyte system, in which indoline dyes show generally low open-circuit voltage.

Recent works have revealed some disadvantages of the iodide/triiodide redox couple that limiting the performance of DSCs, such as (i) its relatively high overpotential for dye regeneration has led to a noticeable potential loss [31]; (ii) the halogen bonding between iodine and some electron-rich segments of dye molecules could cause a larger charge recombination rate at the titania/electrolyte interface [32–34]; (iii) competitive light absorption by the triiodide has led to a light harvesting loss [35,36]; (iv) the large-scale

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manufacturing of DSCs remains a challenge due to the corrosiveness of the iodide/triiodide redox couple toward most metals and sealing materials [37]. To avoid the problems mentioned above, research efforts to find alternate redox electrolytes has been focused on developing transition metal complexes and organic redox couples as well as solid-state hole conductors [38].

Amongst all iodine-free liquid electrolytes, so far only the cobalt redox couples have shown impressively high efficiencies comparable to iodide/triiodide electrolyte by using organic dyes [3]. For instance, by employing an organic dye JF419 in conjunction with tris(2,2'-bipyridine)cobalt(II/III) redox couple, Yella et al. obtained a 10.3%-efficiency DSC [39]. An advantage of the cobalt electrolyte over the iodide/triiodide redox couple is that very high open-circuit voltages can be realized, providing an opportunity for further improving the efficiency of organic dyes. However, this does not mean high efficient DSCs could be obtained by simply replacing the iodide/triiodide couple by cobalt redox couples. As a matter of fact, the same organic dye may exhibit quite different structure–property relationship in conjunction with different electrolyte [40,41]. In this regard, it is quite interesting to compare the structure–property relationship of D–A– π –A indoline dyes in iodine and cobalt electrolyte. Nevertheless, to the best of our knowledge, there have been few investigations on this issue. Herein, we reported the synthesis, characterization, and photovoltaic properties of two new D–A– π –A indoline dyes (XS45 and XS46, Fig. 1). For a comparison, XS47 featuring D– π –A was prepared as a reference. The influence of donor and bridge structure on the photovoltaic properties of D–A– π –A indoline dyes on the photovoltaic properties of DSCs employing iodine/cobalt electrolyte was investigated. To further reveal the structure–property relationship of D–A– π –A indoline dyes, the dependence of the cell performance on the thickness of TiO₂ film are also scrutinized in terms of incident photon-to-electron conversion efficiency (IPCE), interfacial kinetic parameters as well as their joint contribution to photovoltaic performance. Our study provides an important new insight into the structure–property relationship of D–A– π –A indoline dyes.

2. Experimental section

2.1. Materials and instruments

The synthetic routes for dyes XS45, XS46 and XS47 are shown in Scheme 1. *n*-butyllithium, Pd(PPh₃)₄, 7-dibromobenzo [1,2,5] thiazole and cyanocetic acid were purchased from Energy Chemical (China). 4-tertpyridine (TBP) and 0.1 M Lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) were purchased from Aldrich. *N,N*-Dimethylformamide was dried over and distilled from CaH₂ under an atmosphere of nitrogen. Phosphorus oxychloride was freshly distilled before use. Dichloromethane was distilled from calcium hydride under nitrogen atmosphere. All other

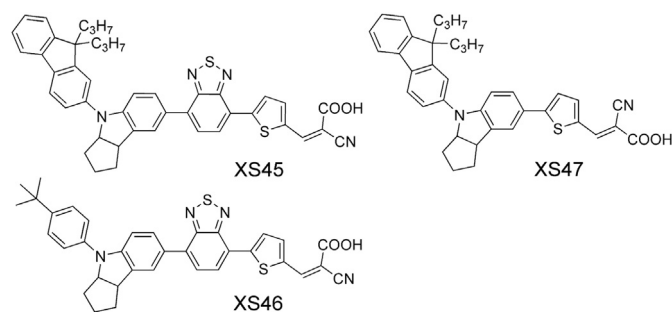


Fig. 1. Molecular structures of dyes.

solvents and chemicals used in this work were analytical grade and used without further purification.

¹H NMR and ¹³C NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer. The reported chemical shifts were against TMS. High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer. The melting point was taken on a RY-1 thermometer and temperatures were uncorrected.

2.2. Optical and electrochemical measurements

The absorption spectra of dyes and sensitized films were measured by SHIMADZU UV-2600 spectrophotometer. Fluorescence measurements were carried out with a HITACHI F-4500 fluorescence spectrophotometer.

Cyclic voltammetry (CV) measurements for sensitized films were performed on a Zennium electrochemical workstation (ZAHNER, Germany), with sensitized electrodes as the working electrode, Pt-wires as the counter electrode, and an Ag/AgCl electrode as the reference electrode at a scan rate of 50 mV s⁻¹. Tetrabutylammonium perchlorate (TBAP, 0.1 M) and MeCN were used as supporting electrolyte and solvent, respectively. The results were calibrated using ferrocene as standard. CV measurements for dyes were performed according to the same procedure of sensitized films, except that Pt-wires were used as working electrode and counter electrode.

Charge densities at open circuit and intensity modulated photovoltage spectroscopy (IMVS) were performed on a Zennium electrochemical workstation (ZAHNER, Germany), which includes a green light emitting diode (LED, 532 nm) and the corresponding control system. The intensity-modulated spectra were measured at room temperature with light intensity ranging from 5 to 75 W m⁻², in modulation frequency ranging from 0.1 Hz to 10 kHz, and with modulation amplitude less than 5% of the light intensity.

2.3. Fabrication and characterization of DSCs

The TiO₂ paste (particle size, 20 nm) was printed on a conducting glass (Nippon Sheet Glass, Hyogo, Japan, fluorine-doped SnO₂ over layer, sheet resistance of 10 Ω /sq) using a screen printing technique. The film was dried in air at 120 °C for 30 min and calcined at 500 °C for 30 min under flowing oxygen before cooling to room temperature. The heated electrodes were impregnated with a 0.05 M titanium tetrachloride solution in a water-saturated desiccator at 70 °C for 30 min and fired again to give a ca. 3 μ m thick mesoscopic TiO₂ film. The TiO₂ electrode was stained by immersing it into a 0.3 mM dye solution in a mixture of DCM/EtOH (v/v, 2:3) and kept at room temperature for 12 h. The sensitized electrodes were then rinsed with dry ethanol and dried by a dry air flow. Pt catalyst was deposited on the FTO glass by coating with a drop of H₂PtCl₆ solution (40 mM in ethanol) with the heat treatment at 395 °C for 15 min to give photoanode. The sensitized electrode and Pt-counter electrode were assembled into a sandwich type cell by a 25 μ m-thick Surlyn (DuPont) hot-melt gasket and sealed up by heating. The iodine electrolyte, E1, is composed of 0.25 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPII), 0.1 M LiTFSI, 0.05 M I₂, and 0.5 M TBP in acetonitrile. For comparison, a cobalt electrolyte consisting of 0.25 M [Co(II)(phen)₃](PF₆)₂, 0.05 M [Co(III)(phen)₃](PF₆)₃, 0.5 M 4-tertpyridine (TBP) and 0.1 M LiTFSI in acetonitrile, namely E2 was formulated.

The photocurrent–voltage (*J*–*V*) characteristics of the solar cells were carried out using a Keithley 2400 digital source meter controlled by a computer and a standard AM 1.5 solar simulator—Oriel 91160–1000 (300 W) SOLAR SIMULATOR 2 x 2 BEAM. The light intensity was calibrated by an Oriel reference solar cell. A

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