Custom-designed metal-free quinoxaline sensitizer for dye-sensitized solar cells based on cobalt redox shuttle

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ABSTRACT

Cobalt redox shuttles, as a single electron transfer system, have been attracted widely attention in the area of dye-sensitized solar cells (DSSCs) over the past years. Herein, by means of the expansion of the conjugate system and graft of long alkyl antenna group in organic sensitizer, the intramolecular charge transfer rate and electron recombination inhibition capability are evidently improved. Compared with the iodine electrolyte, the structural modification of the sensitizer is more significant for the cobalt electrolyte, especially the open circuit voltage. As a result, for **IQ4** and **IQ22**, the J_{sc} and V_{oc} increased from 13.30 mA cm^{-2} and 810 mV to 15.32 mA cm^{-2} and 840 mV, respectively. For iodine electrolyte, its open circuit voltage remained essentially unchanged. It proves to be a profitable groundwork for the photovoltaic relationship between cobalt redox couple and the structure of organic sensitizers.

1. Introduction

Dye-sensitized solar cell (DSSC), as a typical photovoltaic device of 3rd generation solar cell, its operating process is similar to plant's photosynthesis reaction (Amornpitoksuk and Leesakul, 2003). The dye as a sensitizer is available for harvesting photons and transfer electrons to nanocrystalline metal oxide semiconductor. It is the only solar cell with separated light absorption, charge separation and carrier transport process. Owing to its high-energy conversion efficiency, low-cost and simple fabrication, especially high stability, DSSC has received a lot of attention over the last decade as an economical alternative to conventional silicon-based photovoltaic devices (Agresti et al., 2015; Chou et al., 2011; Edvinsson et al., 2007; Hagfeldt et al., 2010; Han et al., 2012; Haque et al., 2004; Heo et al., 2013; Kinoshita et al., 2013; Koh et al., 2011; Koo et al., 2008; Lee et al., 2015; Li et al., 2011, 2017; Mathew et al., 2014; Numata et al., 2012; O'Regan and Grätzel, 1991; Qu et al., 2012; Ren et al., 2015; S et al., 2014; Sheng et al., 2017; Tian et al., 2007; Urbani et al., 2014; Wang et al., 2015; Yao et al., 2015; Yella et al., 2011; Zeng et al., 2013).

In the past years, some studies focused on the replacement of the I_3^-/I^- redox system by cobalt polypyridine complexes have achieved significant attention due to their low visible light absorption, the higher redox potential and the reduced corrosiveness towards counter electrode (Mathew et al., 2014; Nusbaumer et al., 2003; Sapp et al., 2002; Yum et al., 2012). In general, a higher device open-circuit photovoltage

(V_{oc}) can be achieved with cobalt-based redox electrolytes due to their lower energy level relative to iodine redox couple (Yang et al., 2014; Yum et al., 2012). However, under full sunlight, the PCE obtained with cobalt electrolytes was inferior relative to the I_3^-/I^- couple, especially for the dyes with small size donor units (Yang et al., 2014). Some factors such as slow mass transport (Nusbaumer et al., 2001), faster recombination of conduction band electrons with the oxidized redox species (common for one-electron systems) (Wang et al., 2010) and the slow regeneration of the Co(II) species at the counter electrode (CE) have effect on their photovoltaic performance (Cameron et al., 2004).

Not only the performance of the electrolyte, but also the light response of the sensitizer strongly influences the light-harvesting efficiency (LHE) of DSSCs (Hagfeldt et al., 2010; Heo et al., 2013; Kinoshita et al., 2013; Lee et al., 2015; Mathew et al., 2014; O'Regan and Grätzel, 1991; S et al., 2014; Yella et al., 2011). The quinoxaline unit shows great potential in recent organic photovoltaics due to its impressive performance both as polymer acceptors for bulk heterojuction (BHJ) solar cells (Chen et al., 2012; Duan et al., 2012; Kim et al., 2013) or as π-bridge in molecular sensitizers for DSSCs (Chang et al., 2011; Feng et al., 2013; Pei et al., 2013, 2014, 2012). For the DSSCs based on quinoxaline sensitizer **IQ4**, the optimum photoelectric conversion efficient (PCE) of 9.24% was got with liquid iodine electrolyte (Pei et al., 2013).

Due to the molecular structures influencing the self-assembly of sensitizers in the adsorption process, the kinetic processes of electron

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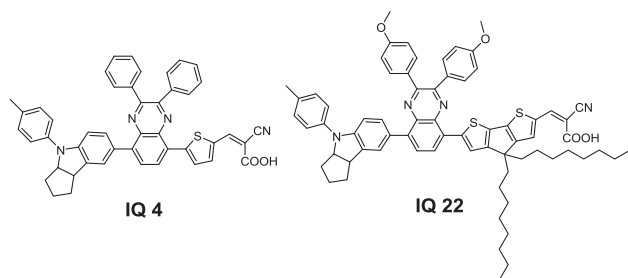
Scheme 1. Molecular structure of the D-A-π-A structure sensitizers **IQ22** and **IQ4**.

transport and the photovoltaic performances of the DSSCs, expanding the conjugation system between donor and acceptor not only can broaden the light capture region of the sensitizers to the infrared region, but also lower the electronic coupling rate improving the intramolecular charge separation property (Agresti et al., 2015; Chou et al., 2011; Han et al., 2012; Urbani et al., 2014; Wang et al., 2015; Yao et al., 2015). Thus, structural modification of sensitizer is an effective means to fit the transport properties of electrolyte and improve their photovoltaic performances. Compared with **IQ4**, cyclopentadithiophene (CPDT), octane and methoxy groups were introduced into the molecule of **IQ22** in our previous work (Scheme 1) (Wang et al., 2016). As a tentative study using cobalt electrolyte, a high photoelectric conversion efficiency 10.09% was got under low light intensity (30 mW cm^{-2}) with **IQ22** due to the matching energy levels and appropriate ion diffusion rate. In contrast, for the optimum devices with **IQ22** and **IQ4** as sensitizers, we have achieved high conversion efficiencies of 8.48% and 6.83% under 100 mW cm^{-2} illumination, respectively. Especially, the V_{oc} increases by 92 mV for **IQ22** compared with iodine electrolyte. It is a significant headway for the photovoltaic and stable performance of metal-free organic dyes sensitized solar cells.

2. Experimental details

2.1. Device fabrication

All raw materials were purchased from commercial sources and used without further purification unless indicated elsewhere. Tertbutylpyridine (TBP), lithium iodide, and 1-methyl-3-propylimidazolium iodide (PMII) were obtained from Adamas. Tris(2,2-bipyridine) cobalt(II) di[bis-(trifluoromethanesulfonyl)imide] and tris(2,2′-bipyridine)cobalt(III) tris[bis(trifluoro-methanesulfonyl)imide] were prepared in the same manner reported previously (Aribia et al., 2013). Transparent (18 NRT) and active opaque (18NR-AO) TiO₂ paste were obtained from Dyesol Ltd (Australia). The transparent fluorine-doped tin oxide (FTO) conducting glass (fluorine-doped SnO₂, transmission > 90% in the visible range, sheet resistance 15 W/square) was from Yingkou OPV Tech New Energy Co., Ltd. It was washed with a detergent solution, deionized water, acetone and ethanol successively under ultrasonication for 20 min before use.

2.1.1. Working electrode

The working electrode was composed of an 8 μm thick TiO₂ film (active area 0.25 cm²), including a 4 μm transparent layer with 18 NRT and 4 μm scattering layer with 18NR-AO. The dye solutions were 0.3 mM in chloroform/ethanol (3/7) and the photoanodes underwent dipping for 12 h to complete the loading with sensitizers.

2.1.2. Counter electrode

The counter electrode was prepared by drop casting an H₂PtCl₆ solution (0.02 M in 2-propanol solution) onto FTO glass and sintered under 400 °C for 15 min.

2.1.3. Electrolyte preparation

The electrolytes used in this work include cobalt and iodine electrolytes. The cobalt electrolyte is composed of 0.25 M tris(2,2-bipyridine) cobalt(II) di[bis-(trifluoromethanesulfonyl)imide], 0.05 M tris (2,2′-bipyridine)cobalt(III) tris[bis(trifluoro-methanesulfonyl)imide], 0.5 M 4-tertbutylpyridine (TBP), and 0.1 M lithium bis-(trifluoromethanesulfonyl)imide (LiTFSI) in acetonitrile. The iodine electrolyte was a solution of 0.1 M LiI, 0.05 M I₂, 0.6 M 1-methyl-3-propylimidazolium iodide (PMII), and 0.5 M TBP in a mixture of acetonitrile and valeronitrile (volume ratio of 85:15).

2.1.4. Cell assembly

For the assemblage of DSSCs, the dye-covered TiO₂ electrode and Pt-counter electrode were assembled into a sandwich type cell and sealed with a hot-melt gasket of 25 μm thickness made of the ionomer Surlyn 1702 (DuPont). And then, a drop of the electrolyte was put on the hole in the back of the counter electrode. It was introduced into the cell via vacuum backfilling. The hole in the counter electrode was sealed by a film of Surlyn 1702 and a cover glass (0.1 mm thickness) using a hot iron bar. The size of the TiO₂ electrodes used was 0.25 cm² (i.e., 5 mm × 5 mm). Both conductivity and Tafel polarization curves were recorded by assembling symmetric dummy cells consisting of Pt CE|electrolyte|Pt CE.

2.2. Device characterization

2.2.1. J-V characterization

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No. 91160, Newport). The power of the simulated light was calibrated to 100 mW cm^{-2} using a Newport Oriel PV reference cell system (Model 91150V). J-V curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of photocurrent were 10 mV and 40 ms, respectively. Cell active area was tested with a mask of 0.158 cm².

2.2.2. IPCE measurement

Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640).

3. Results and discussion

3.1. The structural advantages of IQ22 for cobalt couple

As we all know, the high molecular extinction coefficients and long wavelength response are highly preferable with respect to metal-free organic sensitizers. Therefore, we focus on the improvement of absorption capability and light-harvesting region of pure organic dyes, given that the photoresponse range of sensitizers is prerequisite and foundation of short-circuit current density (J_{sc}) values. In our previous work, a promising dye, **IQ4**, based on quinoxaline unit was well studied (Pei et al., 2013). In this context, the almost same J_{sc} (17.58 mA cm^{-2}) with **IQ4** was got based on iodine electrolyte, reflecting its good reproducibility. As shown in Scheme 1, with high conjugation building block CPDT as the π bridge instead of the traditional thiophene unit for **IQ22**, it may be more suitable for the Co(II/III) redox shuttle system due to its high intermolecular charge transfer (ICT) process. On the other hand, n-Octyl chains, grafted on the CPDT, can inhibit oxidizing component (I₃⁻/Co³⁺) of electrolyte from diffusing into porous TiO₂ membrane, especially for Co(II/III) system. Other advantages for **IQ22** in DSSCs are its higher molecular extinction coefficients (up to 63200 M^{-1} cm^{-1}, 2.47-fold greater than that of the reference dye **IQ4**)