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Regulation of energy levels and kinetics in dye-sensitized solar cells: Synergistic effect of *N*,*N*-bis(9,9-dimethyl-fluoren-2-yl)-aniline and 3,4-ethylenedioxythiophene

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HIGHLIGHTS

- The 3,4-ethylenedioxythiophene effectively improves short-circuit current density.
- The N,N-bis(9,9-dimethyl-fluoren-2-yl)-aniline can enhance open-circuit voltage.
- EIS and current-voltage analysis reveal light-intensity-dependent recombination.
- The cobalt electrolyte has relatively low light-intensity-dependent recombination.
- The cobalt electrolyte has the low free energy loss for dye regeneration process.

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ABSTRACT

Three D-π-A type organic dyes are used to demonstrate synergistic effect of 3,4-ethylenedioxythiophene (EDOT) and *N*,*N*-bis(9,9-dimethyl-fluoren-2-yl)-aniline (DFA) on performance of device in iodine and cobalt electrolytes. The integrative analysis of the incident photon-to-collected electron conversion efficiency (IPCE), the time-correlated single-photon counting (TCSPC) and transient absorption spectra disclose that the rich-electron EDOT effectively improves short-circuit current densities by achieving a broad spectra response from a molecular engineering viewpoint. Electrical impedance and current-voltage simulation reveal that DFA as an interface engineering block is able to enhance open-circuit voltage mainly by simultaneous decreasing the thermodynamics and kinetics loss. The quantitative analysis of energy loss shows that the cobalt electrolyte is suitable for highly efficient cell because of their relatively low free energy loss of regeneration process and low energy loss caused by light-intensity-dependent recombination.

1. Introduction

Dye-sensitized solar cells (DSCs) have received lots of attention over the last two decades as one of the most promising alternatives to conventional crystalline Si-based photovoltaic for widespread solar energy utilization [1]. They have relatively narrow spectra range to the solar spectrum meaning the low short-circuit current densities will be the one bottleneck of the efficiency of DSCs, compared to crystalline Si-based or inorganic thin film solar cells. Development of broad spectra sensitizers is therefore important for improving the efficiency of DSCs. Ruthenium sensitizers as a typical broad spectra dye have achieved remarkable efficiencies over 11% under standard air mass 1.5 sunlight with their onset spectra absorption range from 800 to 900 nm and the about 90% external quantum efficiency [2–6]. Development of broad spectra metal-free organic push-pull dyes are under intense investigations for dye-sensitized solar cells on account of their superior availability of raw materials compared to the conventional ruthenium dyes [7]. General organic sensitizers own D-π-A, where amine derivatives act as the electron donor, a 2-cyanoacrylic acid act as the electron acceptor, which are bridged by π-conjugation unit. The π-conjugation systems such as bithiophene [8], phenylenevinylene [9], dithienosilole [10], benzothiadizole [11], squaraine [12], dithieno [3,2-b; 2,3-d]thiophene [13] and 3,4-ethylenedioxythiophene (EDOT) [14] were used to develop the broad spectra dye to obtain the high short-circuit current density, but always brought the low open-circuit voltage in iodine electrolyte [14,15]. In order to simultaneously achieve high short-circuit current and open-circuit voltage, the DFA as an interface engineering block was chosen to regulate the interface energy level and

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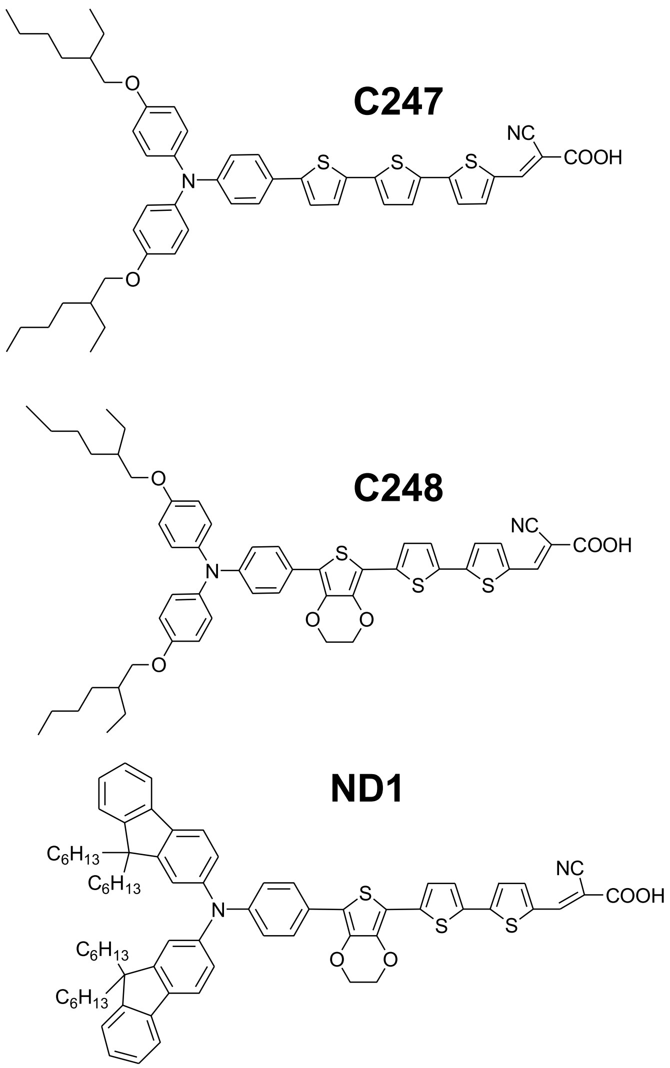

Fig. 1. The molecular structures of C247, C248 and ND1.

recombination. Considering the interaction between electrolyte and dye, the three dyes [16] (Fig. 1) were meticulously selected to understand the synergistic effect of DFA and EDOT on the efficiency of cell in iodine and cobalt electrolytes.

2. Experimental

2.1. Materials

Acetonitrile and chlorobenzene were distilled before use. All other solvents and reagents, unless otherwise stated, were of analytical grade and used as received. Iodine, lithium iodide (LiI), 4-*tert*-butylpyridine (TBP), lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), nitrosonium tetrafluoroborate ($NOBF_4$) guanidinium thiocyanate (GNCS), 3α,7α-dihydroxy-5β-cholic acid (cheno), piperidine and 2-cyanoacetic acid were purchased from Sigma-Aldrich. C247, C248, 1,3-Dimethylimidazolium iodide (DMII) [17], tris(1,10-phenanthroline) cobalt di[bis(trifluoromethanesulfonyl)imide] ($Co(phen)_3$ $[TFSI]_2$) [18] and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide [17] were synthesized according to literature methods. The synthetic route of ND1 and preparation details of its intermediates is presented in ESI.†

2.2. Cell fabrication

The negative electrode of a DSC was fabricated with a bilayer titania film screen-printed onto a pre-cleaned fluorine-doped tin oxide (FTO) conducting glass electrode (NSG, Solar, 4 mm thick), which consists of An 2.7-μm-thick transparent titania layer consisting of 23-nm-sized TiO_2 particles and a 3-μm-thick second layer of scattering titania particles (WER2-O, Dyesol). The preparation procedures of TiO_2 nanocrystals paste for screen-printing and nanostructured TiO_2 film were reported in a previous paper [19]. A bench-top Ambios XP-1 stylus profilometer was used to measure the film thickness. A circular TiO_2 electrode (~0.28 cm^2) was stained by immersing it into a chlorobenzene solution of 150 μM dye and 300 μM cheno for 5 h. After rinsing with acetonitrile and drying by air flow, the dye-coated titania electrode was assembled with a thermally platinized FTO positive electrode possessing an electrolyte-perfusion hole, which was beforehand produced with a sand-blasting drill. The two electrodes were separated by a 30-μm-thick Bynel (DuPont) hot-melt gasket. A liquid electrolyte was perfused to the internal space with a vacuum back filling system. Ultimately, a Bynel sheet and a thin glass cover were able to hermetically close the hole on the positive electrode by heating. Two kinds of electrolytes, E1: 1.0 M DMII, 0.05 M LiI, 0.02 M iodine, 1.0 M TBP and 0.1 M GNCS in acetonitrile; E2: 0.3 M $Co(phen)_3$ $[TFSI]_2$, 0.075 M $NOBF_4$, 0.5 M TBP and 0.1 M LiTFSI in acetonitrile.

2.3. Electronic absorption and voltammetric measurements

A UNICO spectrometer was used to record electronic absorption spectra. Square-wave voltammetric measurements were carried out on a CHI660C electrochemical workstation, with a three-electrode electrochemical cell equipped with platinum gauze as counter electrode and a Ag/AgCl (sat. KCl) as auxiliary electrode. The dye-coated titania on fluorine-doped tin oxide (FTO) was used as working electrode. The ferrocene was used as the internal reference (−5.14 eV versus vacuum) to calibrate the redox potentials in this paper.

2.4. Photovoltaic characterizations

Incident photon-to-collected electron conversion efficiency (IPCE) measurements were carried out with a homemade setup, consisting of a Zolix Omni-λ300 monochromator, a 500 W xenon lamp, and a Keithley 2400 source meter, with a wavelength sampling interval of 10 nm and a current sampling time of 2 s under the full computer control. A Hamamatsu S1337-1010BQ silicon diode used for IPCE measurements was calibrated in National Institute of Metrology, China. A model LS1000-4S-AM1.5G-1000W solar simulator (Solar Light Company, USA) in combination with a metal mesh was employed to give an irradiance of 100 mW cm^{-2}. The light intensity was tested with a PMA2144 pyranometer and a calibrated PMA 2100 dose control system. Current-voltage ($J-V$) characteristics were measured automatically with home-built Labview software equipped with a Keithley 2602 source meter to apply the bias potential and measure the cell current. An antireflection film ($\lambda < 380$ nm, ARKTOP, ASAHI Glass) was adhered to the DSC photoanode covered a metal mask with an aperture area of 0.158 cm^2 during all measurements.

2.5. Transient absorption and emission measurements

Transient absorption measurements were carried out on a LP920 laser flash spectrometer with a nanosecond tunable OPOLett-355II laser to supply a pump light. The sample was kept at a 45 angle with respect to the excitation beam. The probe light from a xenon arc lamp was passed through various optical elements, a testing sample, and a monochromator before been detected by a fast photomultiplier tube and recorded with a TDS3012C digital signal analyzer. Emission spectrum and time-correlated single photon counting (TCSPC)