



Cyclic thiourea functionalized dyes with binary π -linkers: Influence of different π -conjugation segments on the performance of dye-sensitized solar cells



Shengbo Zhu^a, Zhongwei An^{a,b,*}, Xinbing Chen^a, Pei Chen^a, Qianfeng Liu^c

^a Key Laboratory of Applied Surface and Colloid Chemistry, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, China

^b Xi'an Modern Chemistry Research Institute, Xi'an 710065, China

^c Xi'an Ruilian Modern Electronic Chemicals Co. Ltd., Xi'an 710077, China

ARTICLE INFO

Article history:

Received 24 October 2014

Received in revised form

24 December 2014

Accepted 23 January 2015

Available online 4 February 2015

Keywords:

Cyclic thiourea

Dye-sensitized solar cells

Binary π -linker

Thiophene

Thienothiophene

3,4-Ethylenedioxythiophene

ABSTRACT

A series of cyclic thiourea functionalized dyes containing binary π -linkers were synthesized and applied in the dye-sensitized solar cells. The only difference of these dyes is that one segment of the binary π -linkers is thiophene, *n*-hexylthiophene, thienothiophene, 3,4-ethylenedioxythiophene, and benzene, respectively. Among them, the dyes incorporating electron-rich thienothiophene or 3,4-ethylenedioxythiophene exhibit the broader absorption bands and higher molar extinction coefficients in the visible region, which can not only enhance the light-harvesting ability but also improve the short-circuit current density; on the other hand, the dyes bearing bulky *n*-hexylthiophene or 3,4-ethylenedioxythiophene can effectively suppress the intermolecular π - π aggregation and electron recombination owing to larger steric hindrance, which is beneficial to increase the open-circuit voltage.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

With the development of global economy, energy consumption is being in the high growth period, hence the shortage of energy sources will be a serious problem that humanity has to face. Once a technological breakthrough is achieved, solar energy will provide us with inexhaustible energy. Among various light-harvesting devices, dye-sensitized solar cells (DSSCs) have attracted increasing attention due to the features of low carbon, friendly to environment and easy fabrication [1–3]. As a key component of DSSC, the sensitizer affects the power conversion efficiency (PCE) because of its critical function in light harvesting and electron injection. To date, sensitizers based on ruthenium complexes have achieved the PCE of almost 12% [4–6]. However, the large scale application of ruthenium complexes has become a critical problem because of resource limitation and cumbersome purification [7]. To resolve these

issues, metal-free organic dyes have been developed as alternative sensitizers, because they exhibit advantages such as low material cost, high molar extinction coefficients, facile modification and ease of purification [8]. In past decade, there is a consecutive performance advancement of organic dyes as a result of systematic molecular engineering [9]. To the best of our knowledge, DSSCs based on single organic sensitizer has reached the PCE of 10.65% [10–13].

Most organic dyes tend to be designed with a dipolar D- π -A architecture, where the donor (D) pushes electron into the metal oxide via the π -conjugated linker and acceptor (A) [14–16]. Therefore, enormous efforts have been devoted toward the design and synthesis of the three parts. So far, acceptors have been dominated by 2-cyanoacrylic acid, but various donors and linkers have been exploited. For example, hydrazone [17–19], carbazole [20–23], coumarin [24,25], indoline [26,27], phenothiazine [28,29], phenoxazine [30], tetrahydroquinoline [31], and triphenylamine [12,23,32–34] are widely adopted as donors. The main advantages of such compounds containing electron-rich nitrogen, oxygen, and sulfur heteroatoms are good electron-donating ability and rapid charge-transporting ability [17,29,33,35]. To further improve device performance, a suitable π -conjugated linker is required between the donor and the acceptor based on the following consideration:

* Corresponding author. Key Laboratory of Applied Surface and Colloid Chemistry, School of Materials Science and Engineering, Shaanxi Normal University, Xi'an 710062, China.

E-mail address: gmeacz@163.com (Z. An).

(1) electron is easily transferred from the donor to the acceptor [16,29]; (2) the absorption band could be broadened by the increase of the conjugation length [15,36]; (3) the intermolecular aggregation can be suppressed by the steric hindrance of π -linkers [36–38]. Therefore, many kinds of electron-rich units have been introduced into the π -linkers, such as thiophene [20,39–41], thienothiophene (TT) [12,42,43], and 3,4-ethylenedioxythiophene (EDOT) [8,12].

In our previous studies [44,45], the cyclic thiourea functionalized triphenylamine containing more nitrogen and sulfur heteroatoms was employed as an electron donor to construct dye molecules. Compared with triphenylamine-based dyes, such dyes exhibited better photophysical and photovoltaic performances. Moreover, the hexyl chains attached at the N-atom sites of cyclic thiourea groups contribute to suppress intermolecular aggregation and increase the solubility of dyes [22,30]. Especially, the combination of cyclic thiourea functionalized triphenylamine as the donor and bithiophene (AZ6) or 3-hexyl-2,2'-bithiophene (AZ261) as the π -linkers showed broader spectral ranges and reduced intermolecular aggregation. Our results demonstrate that the increased conjugation of π -linkers is beneficial to improve the photocurrent density due to the broad absorption band. Therefore, a further optimization is carried out by increase of the linker conjugation via the insertion of an electron-rich fusing ring TT or an EDOT with a small torsion angle [12]. Three new organic dyes with different binary π -linkers were synthesized, which coded as AZ362 with TT, AZ463 with EDOT, and AZ564 with benzene (Fig. 1). Through density functional theory (DFT) calculations, we estimated these dyes have relatively small HOMO–LUMO energy gaps (E_g), which is suitable for a wide spectral response [8]. Here, various π_1 segments are inserted into the π -linkers, with a clear motivation to further investigate the impact of π -conjugation, geometry and electron-rich segment on photophysical, electrochemical and photovoltaic properties.

2. Experimental section

2.1. Materials and reagents

Thienothiophene (TT), 3,4-ethylenedioxythiophene (EDOT), 5-formyl-2-thiopheneboronic acid, N-bromosuccinimide (NBS), and Pd(PPh₃)₄ were purchased from Aladdin-reagent Co. All chromatographic separations were carried out on silica gel (200–300 mesh). Transparent FTO conducting glass (fluorine

doped SnO₂, sheet resistance 15 Ω /square, transmission > 90% in the visible region) was obtained from Nippon Sheet Co., Ltd. All the chemicals and solvents used in this work were of analytical grade and used without further purification unless otherwise stated.

2.2. Characterizations

2.2.1. Structure confirmation

¹H NMR and ¹³C NMR spectra were recorded on Bruker AV-300 MHz or Bruker AV-400 MHz instruments with tetramethylsilane (TMS) as the internal standard. Gas chromatography mass spectra (GC-MS) were acquired in the electron ionization mode (EI) on Thermo DSQII. High resolution mass spectra (HRMS) were measured with a Bruker maXis mass spectrometer. Elemental analysis (C H N) was carried out on a VARIO-EL-III elemental analyzer.

2.2.2. Photophysical measurements

UV–Vis absorption spectra of the dyes in MeCN-DCM (1:1, v/v, where MeCN is acetonitrile, and DCM is dichloromethane; 1×10^{-5} M) solutions and on the adsorbed TiO₂ films (6.5 μ m) were measured with a Shimadzu UV-3600 spectrophotometer.

2.2.3. Electrochemical measurements

Cyclic voltammograms (CV) were conducted on a CHI 660D Electrochemical Workstation at a scan rate 100 mV s⁻¹, measured in a MeCN-DCM (3:1, v/v) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) as a supporting electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: non-aqueous Ag/Ag⁺ electrode) under argon atmosphere. The redox potentials were calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as the internal reference.

Electrical impedance spectra (EIS) under dark with bias –0.7 V were also measured with CHI 660D Electrochemical Workstation at frequencies of 0.05–1,00,000 Hz. The magnitude of the alternative signal was 10 mV. Charge-transfer resistances were determined by fitting the impedance spectra using Z-view software.

2.3. Theoretical calculations

The electronic configuration and geometry structure of the dyes were optimized by density functional theory (DFT) calculations with the Gaussian 03 program package at the B3LYP/6-311G(d, p) level.

2.4. Fabrication and characterization of DSSCs

TiO₂ films were prepared with a screen printing method according to the published method [45]. Then the films were immersed into a 0.4 mM dye bath in DCM solution under dark for 24 h at room temperature. The active area of the TiO₂ photoanode film was approximately 0.25 cm². All other fabrication processes of DSSCs were also performed according to the published method [45].

Photocurrent–voltage (J – V) characteristics of the DSSCs were measured under illumination with AM 1.5 G solar light from a 300 W xenon lamp solar simulator (94022A, Newport Co., USA). The incident light intensity was calibrated to 100 mW cm⁻² with a standard silicon solar cell. J – V characteristics were recorded with a digital source meter (Keithley 2400) controlled by a computer. The action spectra of monochromatic incident photon-to-current conversion efficiency (IPCE) for solar cells were tested on a commercial setup (QTest Station 2000 IPCE Measurement System, CrownTech, USA).

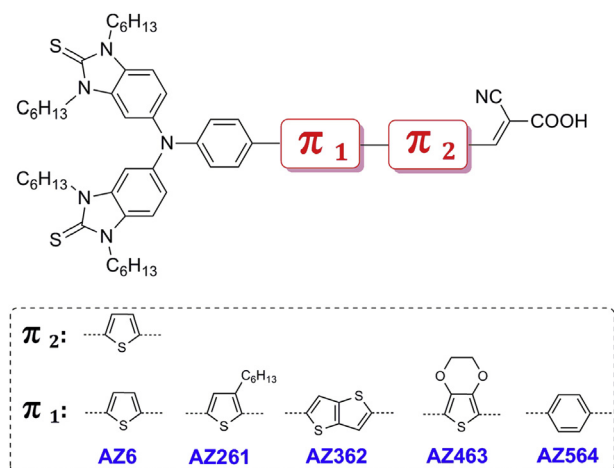


Fig. 1. Chemical structures of the dyes. Herein C₆H₁₃ denotes *n*-hexyl.

Download English Version:

<https://daneshyari.com/en/article/175871>

Download Persian Version:

<https://daneshyari.com/article/175871>

[Daneshyari.com](https://daneshyari.com)