



Varied alkyl chain functionalized organic dyes for efficient dye-sensitized solar cells: Influence of alkyl substituent type on photovoltaic properties



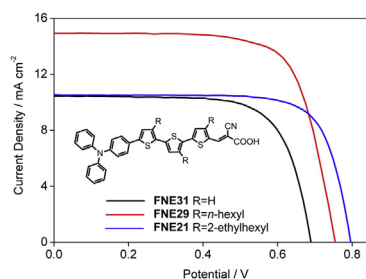
Quanyou Feng, Gang Zhou*, Zhong-Sheng Wang*

Department of Chemistry & Laboratory of Advanced Materials, Fudan University, 2205 Songhu Road, Shanghai 200438, PR China

HIGHLIGHTS

- Branched alkyl chains are superior in suppression of charge recombination in DSSC.
- Linear alkyl chains are better than branched alkyl chains in photocurrent generation.
- A power conversion efficiency of 8.12% was achieved for the DSSC based on **FNE29**.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 29 October 2012

Received in revised form

25 February 2013

Accepted 11 March 2013

Available online 29 March 2013

Keywords:

Organic dye

Dye-sensitized solar cell

Charge recombination

Alkyl chain

Open-circuit photovoltage

ABSTRACT

Suppression of dye aggregation and interfacial charge recombination by appropriate structural modification of the sensitizers is crucial to improve the performance of dye-sensitized solar cells (DSSCs). In this article, linear alkyl chains, i.e., hexyl groups, and branched alkyl chains, i.e., 2-ethylhexyl groups, are introduced into a sensitizer with a terthiophene unit as conjugated bridge. The effects of the linear and branched alkyl chains on the photophysical, electrochemical properties and photovoltaic properties are investigated. By comparison, branched alkyl chains are superior to linear alkyl chains in suppression of intermolecular interactions and the electron recombination between the injected electrons and the electron acceptors in the electrolyte. Consequently, a more significant improvement of the open-circuit photovoltage can be achieved by the introduction of branched alkyl chains to the π -conjugated bridge of the organic dye in comparison to the incorporation of linear alkyl chains. Conversely, linear alkyl chains are better than branched alkyl chains in broadening photoresponse and hence photocurrent generation. As a result, a power conversion efficiency of 8.12% was achieved for the DSSC based on **FNE29** with linear alkyl chains.

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1. Introduction

Dye-sensitized solar cells (DSSCs) have been extensively studied as potential photovoltaic devices due to their high power conversion efficiency (η) and relatively low cost [1]. Up to now, such cells

* Corresponding authors. Tel./fax: +86 21 5163 0345.

E-mail addresses: zhougang@fudan.edu.cn (G. Zhou), zs.wang@fudan.edu.cn (Z.-S. Wang).

employing mostly ruthenium polypyridyl complexes as sensitizers have achieved power conversion efficiencies above 11% under illumination of standard global air mass 1.5 (AM1.5G) simulated solar light [2]. However, the high cost of ruthenium, the difficulty of purification treatments and the low molar extinction coefficients may limit the large-scale application of this type sensitizer. As a result, metal-free organic dyes have attracted considerable attention for practical applications owing to their lower cost of production and better flexibility in terms of molecular tailoring [3].

Generally, organic sensitizers used for efficient DSSC devices are composed of three units which consist of a donor and acceptor connected by a π -conjugation bridge (D– π –A). In the last decade, many kinds of organic dyes with such configuration have been explored for DSSCs, including sensitizers based on thiophene [4], furan [5], selenophene [6], and pyrrole [7] derivatives, and impressive efficiency over 8% has been achieved in liquid electrolyte systems [4e,4h,8]. Recently, DSSC devices showing 12.3% efficiency have recently been achieved with zinc-porphyrin dye YD2–o–C8 cosensitized with an organic dye Y123 using cobalt-based electrolyte [9].

Despite the promising results obtained so far, many metal-free organic dyes have suffered from the dye aggregation problem [10], leading to molecules residing in the system not functionally attached to the TiO₂ surface and thus acting as light filters, which could have an adverse effect on the overall device efficiency [4e,11]. Another major hurdle in attaining higher solar-to-electric power conversion efficiency is the interfacial charge recombination losses [12]. Such interfacial charge carrier recombination may cause an open-circuit voltage (V_{oc}) reduction, hence decreasing the photoelectric conversion efficiency [13]. To control the π -stacked aggregation of organic dye molecules and those charge recombination processes, several kinds of additives, such as deoxycholic acid (DCA), have been introduced to coadsorb onto the semiconductor surface to prevent the intermolecular aggregation and improve the photovoltaic performance of DSSCs. We have clarified what intrinsic factors are responsible for the performance improvement and how they contribute to the enhancement quantitatively upon the coadsorption of DCA or its sodium salt [14]. In addition to the physical coadsorption on the TiO₂ surface, “chemical coadsorption” into the organic dye molecules was recently reported [4a,4i,15]. Linear alkyl chains were introduced into the dye skeleton, which not only prevented dye aggregation but also diminished the charge recombination between electrons and dye cations or acceptors in the electrolyte. However, the linear alkyl chain can significantly reduce the π – π interactions between adjacent molecules when the molecules are arranged in the direction coplanar to the π -conjugation plane, but cannot efficiently suppress the intermolecular π – π interactions when the molecules are arranged in the direction vertical to the π -conjugation plane. Therefore, when branched alkyl chains are incorporated into the π -bridge of dye molecules, the intermolecular π – π interactions can be reduced from two directions, and therefore higher V_{oc} is anticipated with the assistance of branched alkyl chains.

Herein, two types of alkyl substituents, i.e., linear alkyl chains (hexyl groups in **FNE29**) and branched alkyl chains (2-ethylhexyl groups in **FNE21**), are introduced into the terthiophene bridge of sensitizer **FNE31** (Fig. 1) to suppress the formation of dye aggregates and obstruct charge recombination in DSSCs. The influence of the branched 2-ethylhexyl chains and *n*-hexyl chains is

characterized by UV–vis absorption spectroscopy, photoluminescence (PL) spectroscopy, cyclic voltammetry (CV) and intensity-modulated photovoltage spectroscopy (IMVS). Moreover, effects of the branched alkyl chains and linear chains on photovoltaic performance and charge recombination dynamics in DSSCs were fully investigated.

2. Results and discussion

2.1. Synthesis and structural characterization

The synthetic approach to sensitizers **FNE21** and **FNE29** starting from the corresponding alkyl-functionalized terthiophene is depicted in Scheme 1. The compound **1b** was synthesized in a similar way as the preparation of **1a** [16]. After refluxing with a Vilsmeier reagent [17], the corresponding monoaldehyde-substituted derivatives **2a** and **2b** were obtained. Electron donor, triarylamine, was attached via C–H bond activation [18] and provided the precursors **3a** and **3b**. In the last step, the obtained precursors were converted to the corresponding sensitizers **FNE21** and **FNE29**, respectively, by Knoevenagel condensation [19] with cyanoacetic acid through refluxing acetonitrile in the presence of piperidine. It should be noted that a recently developed C–H bond activation was utilized to synthesize the precursor in moderate yield, which shortened the synthetic procedure by two steps. For comparison, **FNE31** is also synthesized according to reported method [4d]. The target compounds were characterized by ¹H NMR spectroscopy, ¹³C NMR spectroscopy, and mass spectroscopy, and were found to be consistent with the proposed structures. The obtained dyes are dark brown in the solid state and freely dissolve in dichloromethane (DCM) and tetrahydrofuran (THF) to produce a red solution.

2.2. Optical properties

The electronic absorption spectra of the three dyes in THF solutions are shown in Fig. 2. All of the dyes exhibit their major electronic absorption in the range of 400–600 nm in the visible region in THF solutions at room temperature, which can apparently be attributed to the intramolecular charge transfer (ICT) from the donor to the acceptor. The spectrum of **FNE31** displays a strong visible band at 478 nm ($\epsilon = 3.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$). Moreover, when the concentration of **FNE31** increases from $5 \times 10^{-7} \text{ M}$ to 10^{-5} M , a bathochromic shift of 11 nm for the maximum absorption wavelength can be observed, which is obviously due to the strong aggregation tendency of the organic dye molecules, even at extremely low concentration condition. This is a well-known behavior for none substituted oligothiophene derivatives [4h,20]. Compared with **FNE31**, **FNE29** exhibits a hypochromically shifted absorption maximum at 456 nm ($\epsilon = 3.4 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) with an intensity

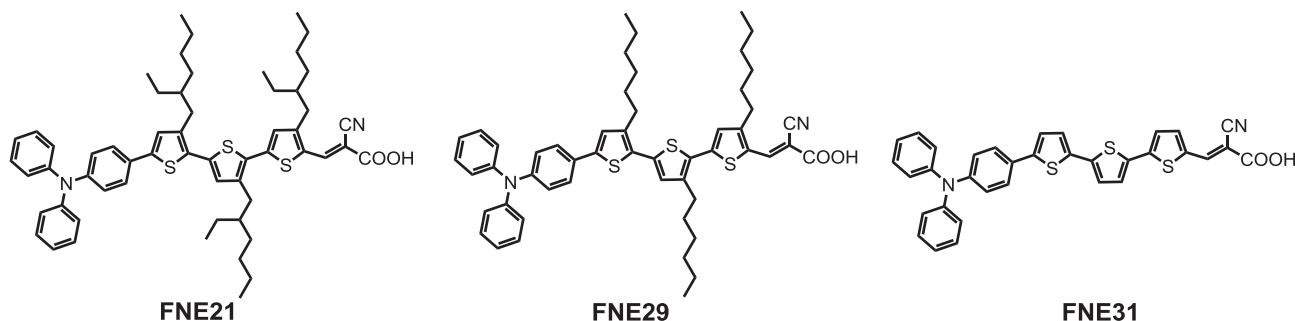


Fig. 1. Chemical structures of the dye molecules.

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