



# Molecular Engineering of Efficient Organic Sensitizers Containing Diyne-Bridge for Dye-Sensitized Solar Cells



Jing-Kun Fang<sup>a,\*</sup>, Xiangyu Hu<sup>a</sup>, Mengchen Xu<sup>a</sup>, Haobin Wang<sup>a</sup>, Yingjun Zhang<sup>b</sup>, Chuanfei Jin<sup>b</sup>, Xue Zhong<sup>b</sup>

<sup>a</sup> Department of Chemistry, School of Chemical Engineering, Nanjing University of Science and Technology, Xiaolingwei Street No. 200, Nanjing 210094, China

<sup>b</sup> State Key Laboratory of Anti-Infective Drug Development (No. 2015DQ780357), Sunshine Lake Pharma Co., Ltd, Dongguan 523871, China

## ARTICLE INFO

### Article history:

Received 26 April 2017

Received in revised form 10 September 2017

Accepted 17 September 2017

Available online 19 September 2017

### Keywords:

Dye-sensitized solar cells

Organic dyes

Diyne

Anthracene

Molecular engineering

## ABSTRACT

Diyne unit containing organic dyes coded as **FSD105** and **FSD106** were designed and synthesized to investigate their light harvesting capabilities and the DSSC performances. Through tuning the geometrical structures of dye molecules by introducing an extra ethynylene, **FSD105** and **FSD106** showed an obviously improved coplanar geometry, and thus the significantly bathochromic shifted absorption spectra, IPCE spectra and larger  $\Gamma$  values, leading to the enhancement of  $J_{sc}$  which guaranteed the highest  $\eta$  (3.82%) for **FSD106**-based DSSC. In order to avoid the dye aggregation,  $\text{CHCl}_3/\text{EtOH}$  was adopted as the sensitizing solvents instead of  $\text{CHCl}_3$  only or CDCA as coadsorbent was added to reduce the  $\Gamma$  value of **FSD106**-based DSSC. As a result, the  $J_{sc}$  and the  $\eta$  value increased significantly. Finally, **FSD106**/CDCA-based DSSC showed the highest  $\eta$  value (4.76%), which is 1.53-fold as the previous reported **FSD101**-based DSSC (3.12%) by introducing an extra ethynylene to improve the molecular coplanarity.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Dye-sensitized solar cells (DSSCs) have been well developed since it was firstly reported in 1991 [1]. Instead of conventional Ru-complex sensitizers [2–4], organic dyes have already been widely investigated for DSSCs due to their less pollution and lower cost [5–8]. For achieving higher power conversion efficiencies, a useful way is adopting various functional units into one dye molecule to realize the purpose of improving different performances parameters of the DSSCs [9–11]. Both single bonds and multiple bonds are widely applied to bridge the different functional groups [12–14]. Single-bond-bridge always leads to a non-coplanar feature of the connecting parts, which could suppress the dye aggregation and thus improve the device performance [15,16]. Nevertheless, the non-coplanar feature will also limit the absorption spectra range, which will restrict the utilization of the solar light [17]. Multiple-bond-bridge (double bond or triple bond) can make the connecting two parts coplanar resulting in an extended conjugation range and hence enlarge the absorption spectra range [18,19]. The carbon atoms in  $\text{C}\equiv\text{C}$  are  $sp$ -hybridized with a higher electronegativity, which could regulate the molecular electronic distribution and other properties efficiently. So ethynylenes are frequently adopted

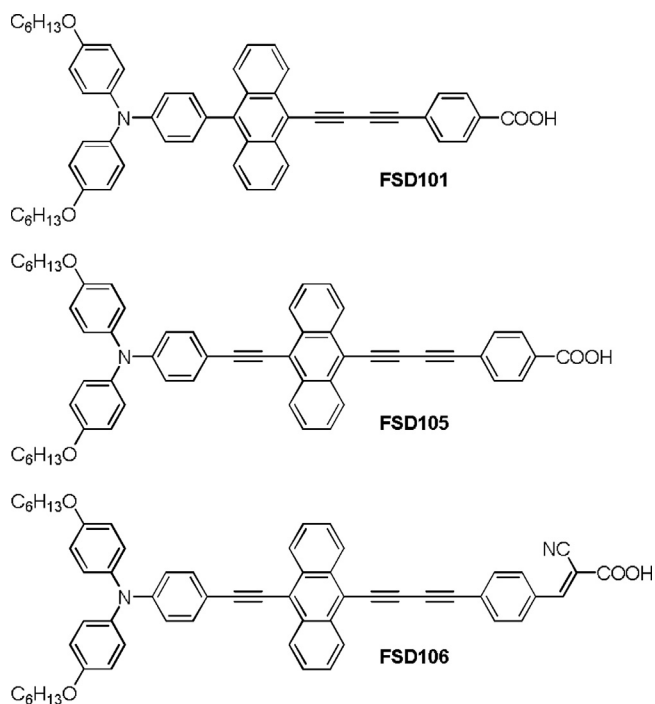
located near to the anchor motifs in dye molecules to regulate dyes' performance [20–22].

Our previous work demonstrated that molecules with diyne unit could significantly raise the life time ( $\tau$ ) and reduce the sum of the radiative and nonradiative rates ( $k_r$  and  $k_{nr}$ ), and these two characters are beneficial to the power conversion efficiency of DSSCs [23,24]. Based on these results, we have reported two novel organic dyes (**FSD101** and **FSD102**) containing a diyne unit and the results indicated that the power conversion efficiency of the device could be significantly improved by introducing a diyne unit in the dye molecules [25]. However, the absorption maxima for **FSD101** and **FSD102** are only 448 and 461 nm, respectively. It means that these two dyes missed the utilization of a large fraction of the solar spectrum.

In order to extend the absorption spectra and enhance the light harvesting capabilities, two novel organic dyes (**FSD105** and **FSD106**) are reported in this paper by replacing the single-bond-bridge between triphenylamine and anthracene motifs in **FSD101** with triple-bond-bridge to obtain an extended conjugation system. The structures of **FSD101**, **FSD105** and **FSD106** are shown in Scheme 1. The novel dyes were fully characterized by  $^1\text{H}$  NMR (Nuclear Magnetic Resonance),  $^{13}\text{C}$  NMR and HRMS (High Resolution Mass Spectrometry), etc. The photophysical and electrochemical properties and photovoltaic parameters of DSSCs sensitized by these two dyes were well investigated.

\* Corresponding author.

E-mail address: [fjk@njust.edu.cn](mailto:fjk@njust.edu.cn) (J.-K. Fang).



Scheme 1. Molecular structures of dyes **FSD101**, **FSD105** and **FSD106**.

## 2. Results and discussion

### 2.1. Design and synthesis of the dyes

Scheme 2 depicts the synthetic routes for **FSD105** and **FSD106**. Intermediate **1** was prepared by a Sonogashira reaction between 9-bromo-10-iodoanthracene and prop-2-yn-1-ol. Sonogashira reaction between intermediate **1** and 4-ethynyl-*N,N*-bis(4-(hexyloxy)phenyl)aniline would obtain the intermediate **2**. Oxidation of **2** by manganese dioxide would afford the intermediate **3**. Intermediate **4** was synthesized by a double elimination protocol between **3** and 2-(4-((phenylsulfonyl)methyl)phenyl)-1,3-dioxolane. Carboxylic acid groups were formed by deprotection and oxidation of aldehyde group to give **FSD105** and cyanoacrylic acid group was introduced by a Knoevenagel reaction to give **FSD106** [25]. Each steps gave the desired products in a moderate to high yields. **FSD105** and **FSD106** were fully characterized with  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS, etc.

### 2.2. UV–VIS absorption spectra

We have discussed the significant mutual relationships between the light harvesting capabilities and absorption spectra of dyes. Thus, an extra ethynylene was adopted in **FSD105** and **FSD106** to enlarge their absorption spectra. The UV–vis absorption spectra of **FSD101**, **FSD105** and **FSD106** in dichloromethane (DCM) solutions ( $1.5 \times 10^{-5}$  M) and adsorbed on  $2 \mu\text{m}$   $\text{TiO}_2$  transparent films are depicted in Fig. 1. The corresponding data are listed in Table 1.

Widely absorption spectra range of dyes **FSD105** and **FSD106** were observed. It could be ascribed to the transitions from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) [26]. The absorption spectra of **FSD105** and **FSD106** showed absorption maxima ( $\lambda_{\text{max}}$ ) at 511 nm and 505 nm, respectively. Compared to **FSD101**, the absorption maxima of **FSD105** and **FSD106** were bathochromic shifted 63 nm and 57 nm, respectively. Obviously, the reason for

the bathochromic shifts should be fully attributed to the extra ethynylenes between triphenylamine and anthracene units. After introducing of an extra ethynylene, molecular coplanarity was efficiently improved (Figs. 4 and 5) resulting in a significant bathochromic shift.

Typically, hypsochromic shift would be observed for the absorption spectra after attaching dyes on  $\text{TiO}_2$  films, due to the deprotonation of the carboxylic acid group and *H*-aggregation state of the dyes on  $\text{TiO}_2$  [27]. The absorption maxima for **FSD105** and **FSD106** on  $2 \mu\text{m}$   $\text{TiO}_2$  transparent films were 476 and 478 nm, respectively. They showed a hypsochromic shift of 35 nm for **FSD105** and 27 nm for **FSD106** compared to their corresponding absorption spectra in DCM solution. The fewer hypsochromic shifts of **FSD106** might be the reason why it showed higher power conversion efficiency ( $\eta$ ) compared with **FSD105** (see below).

### 2.3. Electrochemical properties

The Cyclic voltammetry was performed to study the redox behavior of the dyes and also to evaluate the feasibilities of the electron injections and dye regenerations [28]. The cyclic voltammograms are showed in Fig. 2 and the corresponding data are listed in Table 1.

The oxidation potential ( $E_{\text{ox}}$ ) (refers to the HOMO level) was estimated by the two peak potentials ( $E_{\text{pa}}$  is the upper peak and  $E_{\text{pc}}$  is the lower peak in Fig. 2):  $E_{\text{ox}} = (E_{\text{pa}} + E_{\text{pc}})/2$ . The  $E_{\text{ox}}$  of dyes **FSD105** (0.90 V) and **FSD106** (0.94 V) were sufficiently more positive  $I_3^-/I^-$  than the redox potential value (0.4 V vs. NHE), providing the efficient dye regeneration of the oxidized dyes by the  $I^-/I_3^-$  electrolyte [29]. Fig. 3 shows the energy band diagrams of the dyes. The optic band gap energies ( $E_{0-0}$ ) [30] of **FSD105** (2.07 V) and **FSD106** (1.88 V) were lower than that of **FSD101** (2.28 V). It means broader adsorption spectra for **FSD105** and **FSD106**, which would improve the light harvesting capabilities.  $E_{\text{red}}$  (refers to the LUMO level) can be calculated from  $E_{\text{ox}} - E_{0-0}$ . The  $E_{\text{red}}$  of dyes **FSD105** (−1.17 V) and **FSD106** (−0.94 V) were more negative than the Fermi level of  $\text{TiO}_2$  (−0.5 V vs. NHE), which would ensure the thermodynamic feasibility of electron injection from the excited dyes into the  $\text{TiO}_2$  semiconductor's conduction band [29]. These results indicate that dyes **FSD105** and **FSD106** containing extra ethynylenes with lower band gap energy compared with **FSD101**, would be potentially excellent sensitizers applied in DSSCs.

### 2.4. Theoretical calculation

To investigate the effect of geometrical structures and electron distributions of the dyes on the performances of DSSCs, the geometries and energies of the dyes were optimized by density functional theory (DFT) calculations with the B3LYP exchange correlation functional under the 6-31G (d) basis set implemented in the Gaussian 09 program. The computed optimized structures and electron distributions in HOMO and LUMO levels of the dyes is shown in Fig. 4 (**FSD101** as a reference [25]), with the isodensity surface values fixed at 0.02.

According to the corresponding molecular orbital profiles, these dyes exhibited a typical D- $\pi$ -A architecture with the electrons of the HOMOs mainly distributed over the triphenylamine and anthracene moieties, while the LUMOs delocalized over the anthracene moieties and carboxylic or cyanoacrylic acid acceptors. As a result, the electrons can easily transfer from the donor part to the acceptor part and hence an efficient electron injection from the excited dyes into the acceptor group-connected  $\text{TiO}_2$ , less distributions over the anthracene moieties in **FSD106** indicated its more efficient electron transfer.

Download English Version:

<https://daneshyari.com/en/article/6470200>

Download Persian Version:

<https://daneshyari.com/article/6470200>

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