



Substituent effect of fluorine atom on benzothiadiazole bridging unit in dye sensitized solar cells



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ARTICLE INFO

Article history:

Received 25 July 2013

Received in revised form 11 November 2013

Accepted 14 November 2013

Available online 3 December 2013

Keywords:

Dye sensitized solar cells
Organic sensitizer
Fluorine substitution
Benzothiadiazole
Substituent effect

ABSTRACT

Dye sensitized solar cells performances using two organic dyes with fluorinated-benzothiadiazole spacer, 3-{5-[7-(5-{4-[Bis(9,9-dimethyl-9H-fluoren-2-yl)-amino]-5-fluoro-phenyl}thiophen-2-yl)benzo-[1,2,5]thiadiazol-4-yl]thiophen-2-yl}-2-cyano acrylic acid (**JK-311**) and 3-{5-[7-(5-{4-[Bis(9,9-dimethyl-9H-fluoren-2-yl)-amino]-5,6-difluorophenyl}thiophen-2-yl)benzo-[1,2,5]thiadiazol-4-yl]thiophen-2-yl}-2-cyano acrylic acid (**JK-312**), were systematically investigated by solar simulation equipment, stepped light-induced transient measurements of photocurrent and voltage, and electrochemical impedance spectroscopy. To investigate substituent effect of fluorine atom on benzothiadiazole, molecular orbital calculations of two dyes using a time dependent density functional theory model with B3LYP/3-31G* were also carried out. **JK-312** showed a unique electronic transition from HOMO-1 to LUMO. Short circuit current and open-circuit voltage in DSSCs performances were increased by the introduction of fluorine atom into spacer segment, compared to fluorine-free dyes.

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1. Introduction

Development of organic dyes for use in dye sensitized solar cells (DSSCs) has been considered as an interesting research area because of high photon to current efficiency, nearly over 10%, compared to that of ruthenium dye.¹ To achieve high efficiency in DSSCs, organic dyes are generally composed of three segments, donor, spacer, and acceptor/anchoring group. Although many organic dyes have similar molecular structure or architecture, the efficiency of DSSCs is strongly governed by substituents of dyes. For example, introduction of fluorine atom into molecular framework is the simplest way to move short wavelength region.² Fluorine atom as a substituent in organic dyes leads to an inverted charge density distribution with respect to the corresponding hydrocarbon due to its strong electron-withdrawing properties. In addition, fluorine atom has a strong influence on inter- and intra-molecular interaction via hydrogen bonding and also give a low-lying highest

occupied molecular orbital to polyconjugated organic dyes, resulting in high photon-to-current efficiency.^{3–5} In order to obtain high photovoltaic performance in dye sensitized solar cells, high short circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (ff) are logically required. The unique features of fluorine atom, therefore, can be made efficient dye sensitized solar cells by tuning J_{sc} and ff even V_{oc} . With the aim of increasing DSSC efficiency, several approaches on the development of organic dyes possessing fluorine substituents have been introduced. Chou et al.⁴ were reported *ortho*- and *meta*-fluorine substituted phenylene spacer with 4,4'-dihexylcyclopenta[2,1-*b*:3,4-*b'*]dithiophene unit for efficient solid state DSSCs. In addition, Chow et al.⁵ were also reported *ortho*-other functional group substituted phenylene spacer for tuning electron flow in DSSCs. Although such reports showed similar substituent effect, it is notable that the *ortho*-fluorinated phenylene spacer can act as an important role in improvement of photovoltaic performance especially open-circuit voltage issue.

Recently, we reported an efficient organic dye, 3-{5-[7-(5-{4-[Bis(9,9-dimethyl-9H-fluoren-2-yl)-amino]phenyl}thiophen-2-yl)benzo-[1,2,5]thiadiazol-4-yl]thiophen-2-yl}-2-cyano acrylic acid (**JK-68**) bearing benzothiadiazole spacer.⁶ The DSSC device based on **JK-68** with a polymer gel electrolyte showed a moderate

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photoconversion efficiency of 4.66% and long-term stability. However, further improvement of the photovoltaic performance using benzothiadiazole analogies is still needed. Therefore, we designed and synthesized new **JK-68** derivatives, **JK-311** and **JK-312**, with fluorinated-benzothiadiazole spacer, as shown in Fig. 1. Herein, we report the investigation of substitution effect of fluorine atom at 5- and/or 6-position of 2,1,3-benzothiadiazole bridging unit and photovoltaic performance using three synthesized dyes.

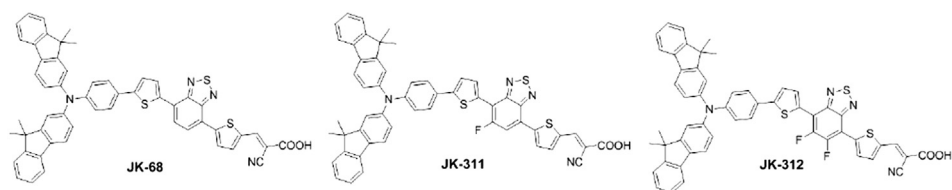
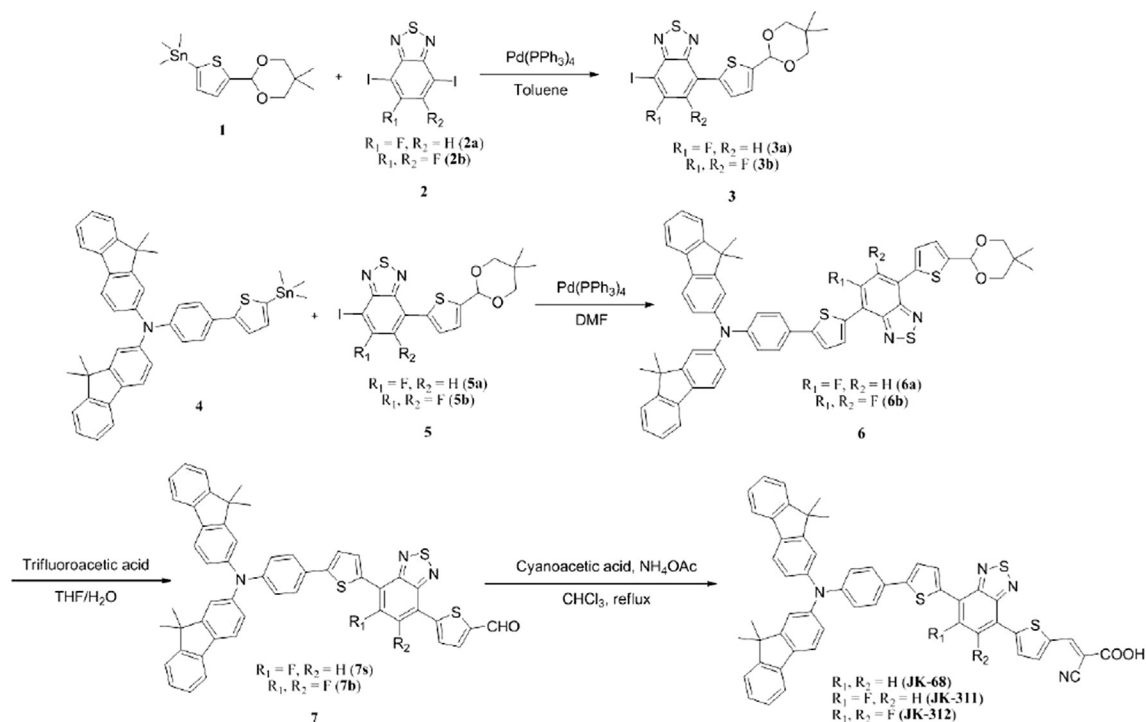


Fig. 1. Molecular structures of **JK-68**, **JK-311**, and **JK-312** in this study.

2. Result and discussion

The fluorinated organic sensitizers **JK-311** and **JK-312** were prepared by synthetic protocol in Scheme 1. Compound **3a** and **3b** were synthesized by Stille cross coupling reaction of fluorinated-benzothiadiazole compound (**2a** and **2b**)⁷ with compound **1**. Also, bis(9,9-dimethylfluorenyl)amine derivatives **6** were prepared by Stille reaction of stannyl compound **4** with acetal compound **5**. Deprotecting reaction of **6** with trifluoroacetic acid (TFA) in tetrahydrofuran (THF) and D.I. water yielded **7**. The aldehydes **7a** and **7b**, upon reaction with cyanoacetic acid in the presence of ammonium acetate in chloroform produced the sensitizers **JK-311** and **JK-312**. The sensitizer **JK-68** was prepared by previous references.⁶



Scheme 1. Synthesis of **JK-311** and **JK-312**.

Fig. 2 shows the absorption and emission spectra of sensitizers **JK-68**, **JK-311**, and **JK-312** measured in THF and the data are listed in Table 1. The absorption spectrum of **JK-311** displays two absorption maxima 537 nm and 328 nm, which are assigned as the $\pi-\pi^*$

transition of the conjugated system. Under the same conditions **JK-312** also exhibits two intense absorption maxima at 462 nm and 337 nm. The absorption maximum of **JK-311** is very similar to **JK-68**, while a remarkable blue-shifted absorption is observed in **JK-312**. We deduced blue-shift behavior is due to two fluorine substituents of spacer in **JK-312**. In general, the absorption bands in the sensitizers absorbed on TiO_2 electrode appeared at longer wavelength compared to those of their solution state. However, these obser-

ations were not observed in our all dyes. In our empirical experience for DSSC, this behavior is due to the fluorine atom with electron-withdrawing nature⁸ and amorphous amine moiety. In addition, the presence of fluorine atoms in spacer segment causes the suppression of intermolecular *J*-aggregation between sensitizers absorbed on TiO_2 surface. The absorption spectra of the three dyes on TiO_2 electrode are broaden and such a broadening of the absorption spectra is due to an interaction between the sensitizers and TiO_2 .⁹

To investigate the feasibility of electron transfer from the excited state of the dyes to the conduction band of TiO_2 electrode, we carried out cyclic voltammetry experiments in order to evaluate the redox potentials (Table 1). The redox potentials of all dyes were

measured in CH_3CN with 0.1 M tetrabutylammonium hexafluorophosphate. TiO_2 films coated with each dye were used as working electrodes. The **JK-311** and **JK-312** dyes were shown a reversible oxidation at 0.83 and 0.80 V (vs NHE), respectively. These

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