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Synthesis of conjugated organic dyes containing alkyl substituted thiophene for solar cell

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Abstract—Three organic dyes, **JK-41**, **JK-42**, and **JK-43** containing bis-dimethylfluoreneaniline and alkyl substituted thiophene unit are designed and synthesized. Under standard global AM 1.5 solar condition, the **JK-41** sensitized cell gave a short circuit photocurrent density (J_{sc}) of 15.23 mA cm^{-2}, open circuit voltage (V_{oc}) of 0.67 V, and a fill factor of 0.67, corresponding to an overall conversion efficiency η of 7.69%. Molecular-orbital calculations of the three dyes suggest that the electron distribution moves from the aniline derivative to the cyano-acrylic acid moiety. We found that the power conversion efficiency was shown to be quite sensitive to the structural variations of alkyl substituted thiophene moiety.

1. Introduction

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources in recent years.[1] The conversion of solar energy to electricity appears as one of the substitutes that can replace fossil fuels. Dye-sensitized nanocrystalline TiO_2 solar cells (DSSCs) based on Ru complex photosensitizers[2] have been intensively studied because of both their high performance as unconventional solar cells and the possibility for low-cost production of such devices. Organic dyes have been also utilized as photosensitizers in DSSCs. Recently, the solar cell performance of DSSCs based on organic dye photosensitizers has been remarkably improved and obtained efficiencies in the range of 6–9%.[3–8,13] However, organic dyes have several disadvantages as photosensitizers. First, organic sensitizers have relatively sharp absorption bands in the visible region. The absorption spectra of organic dyes must be broadened and red shifted for harvesting the entire solar spectrum. Second, the emission lifetimes of their excited states are generally shorter than those of metal complexes.[9] One of the approaches to extend the absorption region of dyes is to introduce the methine unit in order to increase the π-conjugation. Such an extended π-conjugation with a methine chain often results in instability of organic dyes due to the possibility of isomer formation. In the excited state the dye not only rotates but also undergoes trans–cis isomerization about the central methine bond (CH=CH).[10] Such trans–cis photoisomerization is one of the major nonradiative deactivations for the excited singlet.[11] Accordingly, a restriction on the excited state makes the photoisomerization less feasible.[12] One of the approaches for the rigid configuration of the excited state would be to introduce the long alkyl chain in order to prevent isomerization by the restriction of rotation around the methine chain.[13]

Recently, Sun and co-workers[15] reported an efficient polyene-diphenylaniline dye containing an extended π-conjugation with a methine chain. We envisioned that if the thiophene unit conjugated with a methine unit has a long alkyl group, we could make the photoisomerization less efficient by the restriction of rotation, resulting in increasing the power conversion efficiency η. In this article, we have designed and synthesized the novel unsymmetrical organic sensitizers **JK-41**, **JK-42**, and **JK-43** (Fig. 1) that consist of the bis-dimethylfluoreneaniline moiety acting as electron donor and cyanoacrylic acid moiety acting as acceptor, the two functions being connected by thiophene-ethylene unit. We also investigated the effect of bridged structural modifications on the power conversion efficiency.

2. Results and discussion

The unsymmetrical organic sensitizers **JK-41**, **JK-42**, and **JK-43** were synthesized by the stepwise synthetic protocol

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Keywords: Organic dye; Alkyl substituted thiophene; Solar cell.

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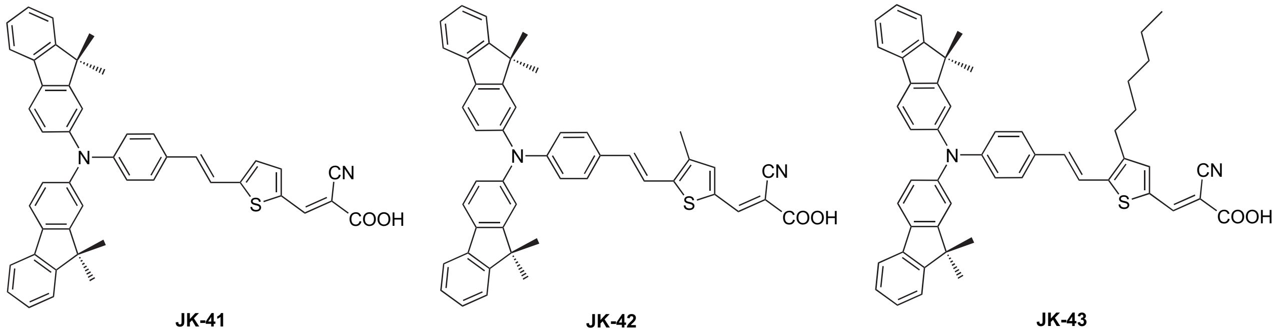

Figure 1. Structures of the dyes **JK-41**, **JK-42**, and **JK-43**.

illustrated in Scheme 1. Organic dye **JK-41** is readily prepared in four steps starting from the *N*,*N*-bis(9,9-dimethylfluoren-2-yl)-4-bromoaniline.[16]

Carbaldehyde **2** was prepared from **1** by lithiation with 1.2 equiv *n*-butyllithium and subsequent quenching with dimethylformamide. Coupling reaction of carbaldehyde **2** with diethyl [5-(5,5-dimethyl-1,3-dioxan-2-yl)thiophen-2-yl]methylphosphonate under Horner–Emmons–Wittig reaction[17] led to intermediate **3**. The thiophene derivative **3** was converted into its corresponding thiophene aldehyde **4** by dedioxanylation with trifluoroacetic acid (TFA). An acetonitrile solution of **4** and cyanoacetic acid were refluxed in the presence of piperidine for 6 h. Solvent removal followed by purification using chromatography yielded **JK-41**. We have also designed similar organic dyes to **JK-41** with alkyl substituted thiophene group. It is well established that introduction of alkyl chain of thiophene unit probably prevents photoisomerization by rather rigid configuration of the excited state, improving the solar cell efficiency.[13] The synthetic strategy for the alkyl substituted dyes **JK-42** and **JK-43** is quite different from that of **JK-41**. Coupling reaction of carbaldehyde **2** with [(3-alkylthiophen-2-yl)methyl]-triphenylphosphonium bromide under Horner–Emmons–Wittig coupling condition led to **5**/**6**. These were then converted to the aldehydes **7**/**8**, which yielded the dyes **JK-42** and **JK-43** on treatment with cyanoacetic acid.

Figure 2 shows the absorption and emission spectra of the **JK-41**, **JK-42**, and **JK-43** sensitizers measured in ethanol and the data are listed in Table 1. The absorption spectrum of **JK-41** displays two absorption maxima at 461 nm (ε=55,890 dm^3 mol^{-1} cm^{-1}) and 368 nm (ε=70,330 dm^3 mol^{-1} cm^{-1}), which are due to the π–π* transitions of the conjugated system. Under the same conditions the **JK-42** sensitizer that contains the methyl group on thiophene unit exhibits absorption peaks at 463 nm (ε=28,730 dm^3 mol^{-1} cm^{-1}) and 366 nm (ε=40,960 dm^3 mol^{-1} cm^{-1}) that are almost the same as the peaks of **JK-41**. On the other hand, the introduction of hexyl group on thiophene unit in **JK-41**, giving **JK-43**, caused a blue shift to 456 nm compared to the **JK-41** and **JK-42** sensitizers. A blue shift of **JK-43** can be readily understood from molecular modeling studies of the three dyes. The ground state structure of **JK-43** possesses an 8.15° twist between *N*,*N*-bis(9,9-dimethylfluoren-2-yl)aniline and the methine units (Fig. 3). The dihedral angle of the methine and thienyl units is 7.35°. For **JK-41**, the dihedral angles between the phenyl and the methine unit and methine-thienyl unit are 1.18° and 0.65°, respectively. Accordingly, a red shift of **JK-41** relative to **JK-43** derives from more delocalization over an entire conjugated system.

When the **JK-41**, **JK-42**, and **JK-43** sensitizers were adsorbed on TiO$_2$ electrode, a slight blue shift of 4–6 nm was found due to the H-aggregation (Fig. 2b).[12] The absorption spectra of the three dyes on TiO$_2$ are broadened. Such a broadening of the absorption spectra is due to an interaction between the dyes and TiO$_2$.[18] This broadening of the absorption spectrum is desirable for harvesting the solar spectrum and leads to a large photocurrent. When the **JK-41**, **JK-42**, and **JK-43** sensitizers are excited within their π–π* bands in an air-equilibrated solution and at 298 K, they exhibit strong luminescence maxima at 582, 589, 587 nm, respectively. No emission signal was observed for the three dyes on TiO$_2$ films, suggesting that the interaction of the excited electron from the excited dye to the TiO$_2$ electrodes is efficient.

The electrochemical data for the dyes **JK-41**, **JK-42**, and **JK-43** are listed in Table 1. The cyclic voltammogram of the three dyes on TiO$_2$ measured in CH$_3$CN solvent containing 0.1 M tetrabutylammonium tetrafluoroborate shows a quasi-reversible behavior. The oxidation potential of **JK-41** dye was measured to be 1.09 V versus NHE with a separation of 0.13 V between anodic to cathodic peaks. Under similar conditions the **JK-42** and **JK-43** dyes show the redox couple at 1.08 V and 1.07 V versus NHE, respectively. The reduction potentials of the three dyes calculated from the oxidation potentials and the $E_{0\text{–}0}$ determined from the intersection of absorption and emission spectra are listed in Table 1. The excited state oxidation potentials (E^*_{ox}) of the dyes (**JK-41**: -1.27 V vs NHE; **JK-42**: -1.27 V vs NHE; **JK-43**: -1.29 V vs NHE) are all higher than the energy level of TiO$_2$ conduction band edge (-0.5 V vs NHE), showing that the energy injection should be possible thermodynamically. A slight positive shift of the reduction potentials in **JK-41** and **JK-42** is due to more delocalization of the π-conjugation system, in keeping with the theoretical analysis presented above.

To gain insight into the geometrical and electronic properties of the **JK-41**, **JK-42**, and **JK-43** sensitizers, we performed DFT calculations on the three organic sensitizers using the Gaussian 03 program package. In particular we used B3LYP as exchange-correlation functional and 3-21G* as