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Synthesis of new julolidine dyes having bithiophene derivatives for solar cell

Hyunbong Choi,[a] Jae Kwan Lee,[a] Kyu Ho Song,[a] Kihyung Song,[b] Sang Ook Kang[a,*] and Jaejung Ko[a,*]

[a]*Department of Chemistry, Korea University, Jochiwon, Chungnam 339-700, Republic of Korea*
[b]*Department of Chemistry, Korea National University of Education, Cheongwon, Chungbuk 363-791, Republic of Korea*

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Abstract—Three novel organic dyes containing julolidine and bithiophene derivatives were synthesized. Nanocrystalline TiO_2 dye-sensitized solar cells were fabricated using these dyes. A solar-to-electric conversion efficiency of 2.95% is achieved with **JK-14**. We found that the power conversion efficiency was shown to be quite sensitive to the structural variations of bridging bithiophene moiety.

1. Introduction

Dye-sensitized solar cells are attracting widespread interest for a new renewable energy source because of the low cost and high efficiency.[1] Several Ru(II) polypyridyl complexes have achieved power conversion efficiencies over 11.1% in standard global air mass 1.5 and good stability.[2] Some metal free organic dyes are shown to be promising sensitizers for nanocrystalline solar cells in view of their properties such as high absorption efficiency, chemical stability of the redox reactions, and intramolecular charge-transfer(CT)-type absorption.[3] Recently impressive photovoltaic performance has been obtained with some organic coumarin,[4] indoline,[5] merocyanine,[6] and hemicyanine dyes[7] having efficiencies in the range of 5–9%. All the organic dyes should contain a structure with donor-to-acceptor moieties bridged by a π-conjugation unit. In most dyes, the amine derivatives act as the electron donor while a 2-cyanoacrylic acid or rhodanine moiety acts as the electron acceptor. These two parts are connected by π-conjugated systems such as the methine unit or thiophene chain. Changes in the electron-donating nature and structural variations of amine unit can result in a variation of electronic properties. For example, the absorption spectrum of **NKX-2510**, whose coumarin framework bears a diethylamino group, is blue-shifted relative to the spectrum of **NKX-2311** with a ring structure amino group.[8] Absorption spectrum and redox potentials were also found to be controllable by expansion of π-conjugated length. Extension of methine unit or the introduction of thiophene chain and aromatic unit extends the π-conjugation system, leading to red shift of dye absorption.[9] The length of the conjugated system may affect the redox potentials of the ground and excited states of the dyes. As part of our efforts to investigate the structural modifications that can enhance the efficiency and stability, small molecules containing julolidine structural motifs[10] instead of coumarin unit have been synthesized for DSSCs. The bridging thiophene units are used to increase the molar extinction coefficient of the dye as well as to increase the stability. The power conversion efficiency is quite sensitive to the structural modifications of the bridging bithiophene moiety due to the twisted nonplanar geometry. In this article, we report three new organic dyes containing julolidine as electron donor and cyanoacrylic acid as electron acceptor bridged by a bithiophenyl, 3,3′-dimethyl-2,2′-bithiophen-5-yl or 2,2′-bis(3,4-ethylenedioxythiophen)-5-yl unit (Fig. 1). We also investigated the effect of bridged structural modifications on the power conversion efficiency.

2. Results and discussion

The novel organic dyes **JK-13**, **JK-14**, and **JK-21** were prepared by the stepwise synthetic protocol illustrated in Scheme 1. New dyes are conveniently synthesized in four steps from the *cis*,*cis*-1,7-diethoxy-3-isopropyljulolidine.[10] The bromojulolidine **1** was synthesized by bromination with NBS in $CHCl_3$. The Suzuki coupling of **1** with 1.2 equiv of 2-(2,2′-bithiophen-5-yl)-1,3,2-dioxaborolane **2a**–**2c**[11] yielded **3a**–**3c**. Compounds **4a**–**4c** was prepared from **3a**–**3c** by a lithiation with 1.2 equiv *n*-butyllithium and subsequent quenching with DMF. The aldehyde **4a**–**4c**, on

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* Corresponding authors. Tel.: +82 41 860 1337; fax: +82 41 867 5396; e-mail: jko@korea.ac.kr

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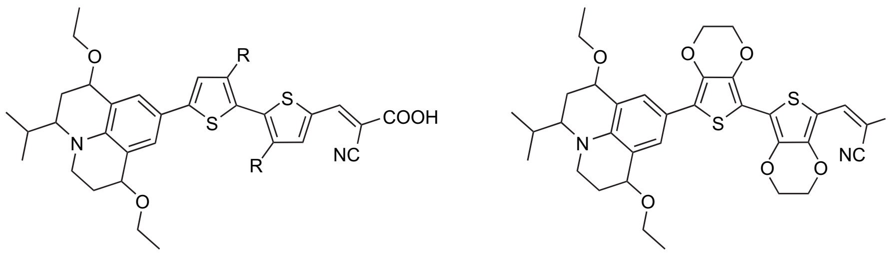
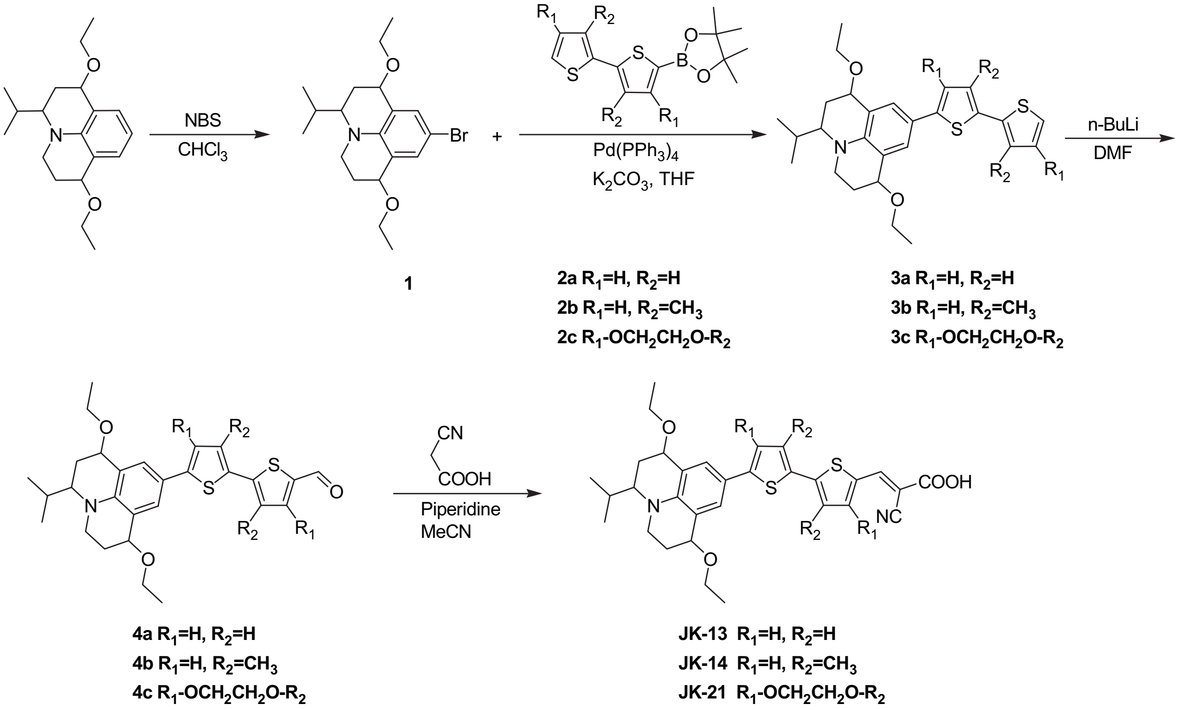


JK-13 : R = H
JK-14 : R = CH_3

JK-21

Figure 1. Structure of the dyes of **JK-13**, **JK-14**, and **JK-21**.



Scheme 1. Schematic diagram for the synthesis of organic dyes **JK-13**, **JK-14**, and **JK-21**.

reaction with cyanoacetic acid in the presence of piperidine in CH_3CN, produced the **JK-13**, **JK-14**, and **JK-21** dyes.

Figure 2 shows the absorption and emission spectra of **JK-13** in ethanol. The absorption spectrum of the **JK-13** sensitizer shows two absorption maxima at 462 (ε=17,400 $dm^3\,mol^{-1}\,cm^{-1}$) and 352 nm (ε= 10,100 $dm^3\,mol^{-1}\,cm^{-1}$), which are due to the π–π* transitions of the conjugated molecule. Under similar conditions the **JK-14** sensitizer exhibits absorption peaks at 422 (ε=12,000 $dm^3\,mol^{-1}\,cm^{-1}$) and 347 nm (ε= 20,000 $dm^3\,mol^{-1}\,cm^{-1}$) that are blue-shifted relative to the peaks of **JK-13**. On the other hand, introducing a bis-EDOT group to **JK-13**, giving **JK-21**, caused a further red shift to 506 nm. This can be understood from molecular modeling studies of the dyes. The ground state structure of **JK-13** possesses a 20.7° twist between the julolidine and the thienyl unit (Fig. 3). The dihedral angle of two thienyl units is 4.2°. For the 3,3′-dimethyl-2,2′-bithiophen-5-yl case, the dihedral angles between the julolidine and the thienyl unit and two thienyl units are 21.9 and 29.0°, respectively, giving more

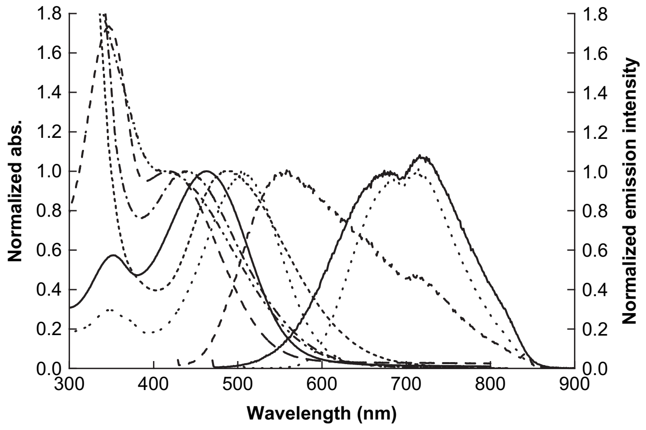


Figure 2. Absorption and emission spectra of **JK-13** (solid line), **JK-14** (dashed line), and **JK-21** (dotted line) in ethanol and absorption spectra of **JK-13** (dashed dot line), **JK-14** (dashed dot-dot line), and **JK-21** (short dashed line) absorbed on TiO_2 film. The emission spectra were obtained using the same solution by exciting at 450 nm for **JK-13**, 410 nm for **JK-14**, and 500 nm for **JK-21** at 298 K.