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Performance of new single rhodanine indoline dyes in zinc oxide dye-sensitized solar cell

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ABSTRACT

A new single rhodanine indoline dye **GU112** having both cyanoacrylic and rhodanine acetic acid groups in an anchor moiety showed the best stability among **GU110**, **GU111**, and **GU112** in zinc oxide dye-sensitized solar cell.

1. Introduction

In 2003, an indoline dye, **D149**, was reported to show high conversion efficiency of 6.1% on titanium oxide [1]. Since then, much effort has been put to improve the performance of indoline dyes [2–13]. Meanwhile, from the viewpoint of the practical use of dye-sensitized solar cells (DSSCs), it is also of importance to improve the stability of the solar cell. Long-term stability tests of DSSCs under outdoor and indoor circumstances have been reported [14–18]. Humidity [19], semiconductors [20–22], and electrolytes [23–30] could affect the stability. However, few papers are reported for the stability of sensitizers from the viewpoint of their molecular design. Oligothiophene-containing dyes have been reported to show high stability due to the location of holes produced upon irradiation on the oligothiophene moieties [31,32]. Tanaka et al. have reported the desorption of **D131** from titanium oxide coming from the decarboxylation of cyanoacrylic acid group [33]. We consider that when two anchor groups are introduced into the sensitizers, stability is improved. Porphyrin and squarylium dyes having two or four anchor carboxyl groups have been reported [34–38]. As indoline dyes having an anchor carboxyl group at the push moiety display a low conversion efficiency, an anchor group should be introduced into the pull moiety [39]. Meanwhile, the preparation of highly porous zinc oxide film by electrodeposition method was reported in 2004 [40]. The good point of this method is its low temperature preparation (70 °C). We report herein the molecular design, synthesis, performance, and stability of single rhodanine indoline dye having different kinds of carboxylic acid groups in zinc oxide DSSCs.

2. Results and discussion

2.1. Synthesis

A known single rhodanine acceptor **4a** was prepared as described in our previous paper [6]. Novel single rhodanine acceptors **4b** and **4c** and indoline dyes **GU110-GU112** are synthesized as shown in Scheme 1. *tert*-Butyl cyanoacetate (**1**) was allowed to react with octyl isothiocyanate (**2**) and ethyl bromoacetate (**3**) in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give an ester **4b'**, whose ester group was deprotected with triethylsilane to provide a carboxylic acid **4b**. An ester **4c'**, prepared as described in our previous paper [6], was hydrolyzed under severe conditions to afford a dicarboxylic acid derivative **4c**.

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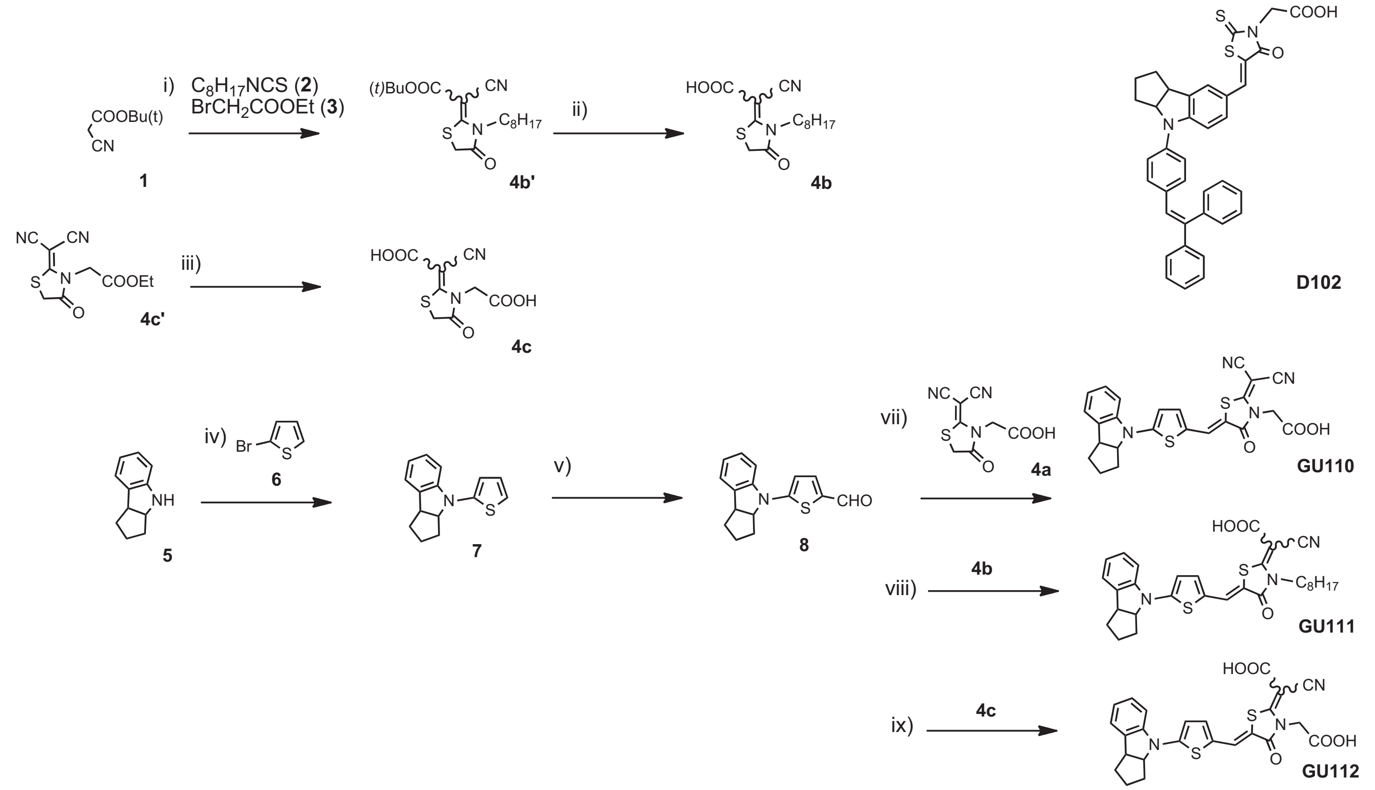

Scheme 1. Reagents and conditions: i) **1** (5.0 mmol), **2** (5.0 mmol), DBU (5.0 mmol), **3** (10.0 mmol), MeCN, rt to reflux, 3 h, MeCN, ii) **4b'** (3.26 mmol), TFA, Et_3SiH (8.12 mmol), CH_2Cl_2, rt, 2 h, iii) **4c'** (1.0 mmol), conc. HCl, AcOH, 100 °C, 13 h, iv) **5** (5.0 mmol), **6** (5.0 mmol), $Pd_2(dba)_3$ (3.0 mol%), XPhos (9.0 mol%), *t*-BuOK (12.5 mmol), toluene, reflux, 17 h, v) **7** (1.0 mmol), $POCl_3$ (2.0 mmol), DMF, rt, 17 h, vi-viii) **8** (0.37 mmol), **4** (0.4 mmol), piperidine, BuOH, 110 °C, 2 h.

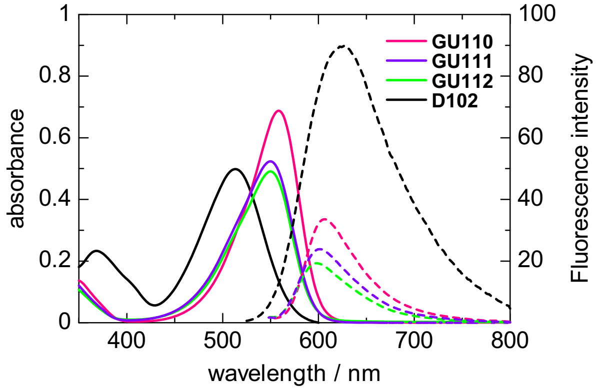

Fig. 1. UV absorption and fluorescence spectra of **GU110–GU112** and **D102** in chloroform measured on 1×10^{-5} mol dm^{-3} of compound at 25 °C.

Compound **5** was allowed to react with 2-bromothiophene (**6**) to give *N*-(2-thienyl) derivative **7**, followed by formylation to give **8**, which was allowed to react with single rhodanine acceptors **4a** – **4c** to provide **GU110** – **GU112**, respectively.

2.2. UV–vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of **GU110**–**GU112**, and **D102** are shown in Fig. 1. The results are also listed in Table 1. **GU110** – **GU112** showed the absorption maxima (λ_{max}) in the range of 550–558 nm. Their molar absorption coefficients (ε) were observed in the range of 49,100 – 68,800 dm^3 mol^{-1} cm^{-1}. **D102** showed the first and second λ_{max} at 513 and 368 nm with ε of 49,800 and 23,300 dm^3 mol^{-1} cm^{-1}, respectively. The fluorescence maxima (F_{max}) of **GU110** – **GU112** were observed at around 600 nm, being no significant difference compared with **D102**. However, the fluorescence quantum yield (Φ_f) of **GU110** (0.013), **GU111** (0.010), and **GU112** (0.007) was remarkably smaller than that of **D102** (0.110). The fluorescence lifetime (τ_f) in chloroform was determined as described in the Supporting information. The lifetime of **GU110**, **GU111**, **GU112**, and **D102** were observed to be 0.091, 0.080, 0.062, and 0.61 ns, respectively. On the basis of Φ_f and τ_f, their fluorescence rate constants (k_f) and non-radiation rate constants (k_{nr}) were calculated. The results are listed in Table 1.

2.3. DFT Calculations

The structures of **GU110**, **GU111**, and **GU112** were optimized by the B3LYP/3-21G level. The result is shown in Fig. 2 and Table 1.

In the case of **GU110**, a conformer **A**, in which the dihedral angle between the indoline ring and the thienyl moiety is 2.8°, is more stable than a conformer **B** whose dihedral angle is 14.6°. This could come from less steric repulsion between the hydrogen atom at the 5-position on the indoline ring and that at the 3-position on the thienyl ring in **A**. For the double bond between the thienyl ring and rhodanine moiety, the *Z*-isomer **A** is more stable than the *E*-isomer **C**. This may be attributed to either the affinity between the sulfur atoms at the thienyl ring and that at the rhodanine moiety or electronic repulsion between the sulfur atom at the thienyl ring and the carbonyl-oxygen in the rhodanine moiety. Thus, the structure **A** is calculated to be most stable for **GU110**.

For **GU111** and **GU112**, the isomers **D** and **F**, in which the double bond at the terminal cyanoacrylic moiety is *Z*-form, are more stable than the *E*-isomers **E** and **G**, respectively. This result could come from the absence of steric repulsion between the cyanoacrylic carboxyl group and the octyl group for **D** and that between the cyanoacrylic acid group and carboxylmethyl group for **F**, respectively.