



Application of indoline dyes attached with strongly electron-withdrawing carboxylated indan-1,3-dione analogues linked with a hexylthiophene ring to dye-sensitized solar cells

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ABSTRACT

An indoline dye attached with a carboxylated indan-1,3-dione moiety linked with a hexylthiophene ring exhibited the highest conversion efficiency among six analogues and **D205**. This result comes from the bathochromic UV–vis absorption band, suitable energy levels, good stability for redox process, and sufficiently long excited-state lifetime.

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1. Introduction

Indoline dyes are one of the most efficient organic sensitizers in dye-sensitized solar cells (DSSCs).¹ Therefore, much effort has been devoted to obtain bathochromic indoline dyes by changing the pull moiety. Indoline dyes attached with cyanoacrylic acid,² single,³ double,⁴ and triple rhodanine acetic acid⁵ pull moiety have been prepared and evaluated as the sensitizers. The first absorption maximum (λ_{\max}) of triple rhodanine indoline dye was observed at 572 nm in chloroform.⁵ Those of double rhodanine indoline dyes linked with mono-, di-, and trithienyl spacers were observed at 568, 564, and 550 nm, respectively.⁶ Thus, these indoline dyes are not bathochromic as expected. In 2012, carboxylated indan-1,3-dione was used as an electron acceptor anchor moiety in DSSCs.⁷ Recently, an indoline dye attached with a 5-carboxyindan-1,3-dione pull anchor moiety linked with a thienyl ring has been reported to exhibit the λ_{\max} at around 600 nm in chloroform and to show higher conversion efficiency than **D205**.⁸ We consider that

the indoline dyes having more electron-withdrawing pull moiety can show more bathochromic absorption bands to exhibit higher conversion efficiency. We report here the synthesis and photoelectrochemical properties of novel indoline dyes with a carboxylated benzo[*b*]thiophene-3(2*H*)one, benzo[*b*]thiophene-3(2*H*)one 1,1-dioxide, benzo[*b*]thiophene-3(2*H*)dicyanovinilidene 1,1-dioxide, indan-1,3-dione, indan-1-dicyanovinilidene-3-one, and indan-1,3-bis(dicyanovinilidene) anchor pull moiety linked with a hexylthiophene ring in DSSCs.

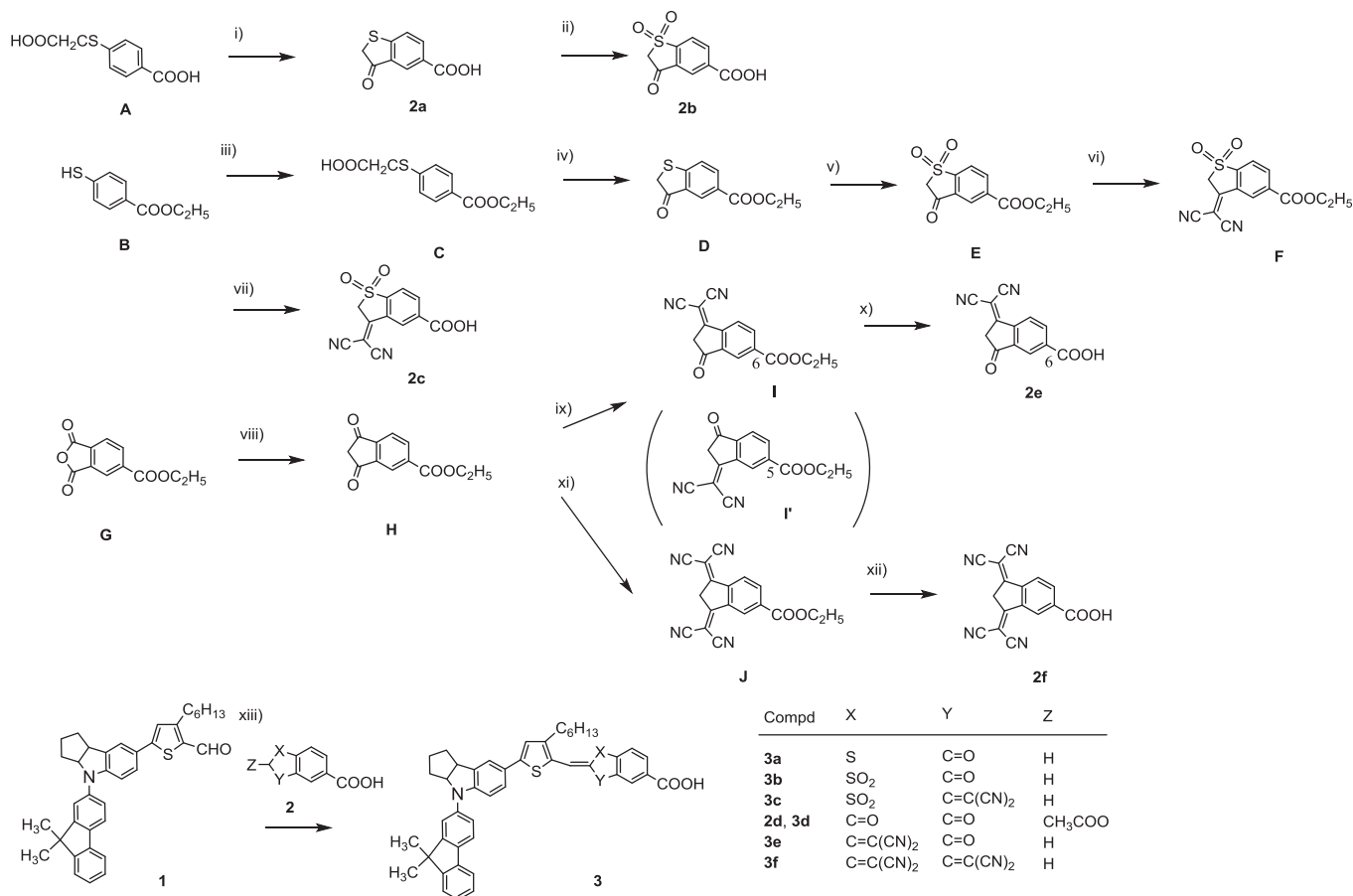
2. Results and discussion

2.1. Synthesis

Novel indoline dyes **3a**, **3b**, **3c**, **3d**, **3e** and **3f** were synthesized as shown in Scheme 1. Compound **2a** was obtained by the intramolecular Friedel–Crafts alkanoyl reaction of **A**.⁹ Compound **2b** was provided by the oxidation of **2a**. Compound **B**, prepared by the reaction of 4-mercaptobenzoic acid with ethanol in the presence of concentrated sulfuric acid, was allowed to react with chloroacetic acid to afford a carboxymethylthio derivative **C**, followed by the

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Scheme 1. Reagents and conditions: i) **A** (1.0 M amount), SOCl₂ (excess), AlCl₃ (4.0 M amounts), CH₂ClCH₂Cl, 0 °C, 20 min then rt, 18 h, ii) **2a** (1.0 M amount), oxone (2.0 M amounts), 1,4-dioxane-water (5/1), rt, 3 h, iii) CH₂ClCOOH (1.5 M amounts), K₂CO₃ (2.0 M amounts), MeCN, rt, 3 h, then **B** (1.0 M amount), 60 °C, 3 h, iv) **C** (1.0 M amount), SOCl₂ (5 M amounts), reflux, 30 min, then, AlCl₃ (4.0 M amounts), CH₂ClCH₂Cl, 0 °C, 30 min, then rt, 21 h, v) **D** (1.0 M amount), oxone (2.0 M amounts), 1,4-dioxane-water (5/1), rt, 23 h, vi) **E** (1.0 M amount), CH₂(CN)₂ (2.5 M amounts), AcONa (1.0 M amount), EtOH, reflux, 17 h, vii) **F** (1.0 M amount), Me₃SiOK (1.0 M amount), THF, rt, 21 h, then 10% HCl, viii) **G** (1.0 M amount), AcCH₂COOEt (1.0 M amount), Et₃N, (6.0 M amounts), Ac₂O, 70 °C, 30 min, ix) **H** (1.0 M amount), CH₂(CN)₂ (3.0 M amounts), AcONa (1.0 M amount), EtOH, reflux, 1 h, x) **I** (1.0 M amount), Me₃SiOK (3.0 M amounts), rt, 24 h, xi) **H** (1.0 M amount), CH₂(CN)₂ (4.0 M amounts), AcONa (1.0 M amount), EtOH, reflux, 17 h, xii) **J** (1.0 M amount), H₂O (excess), LiOH (7.0 M amounts), THF, rt, 24 h, xiii) **1** (1.0 M amount), **2a**, **2b**, **2c** (1.3 M amounts), AcOH, AcONH₄ (cat.), 120 °C, 2–4 h, or **1** (1.0 M amount), **2d**, **2e**, **2f** (1.0 M amount), AcOH, 55–100 °C, 3–4 h.

intramolecular Friedel–Crafts alkanoyl reaction to yield a sulfide **D**. Compound **D** was oxidized to provide a sulfone **E**, which was allowed to react with malononitrile followed by the hydrolysis of the ester moiety to give a dicyanovinilidene derivative **2c**. Compound **G** was allowed to react with ethyl acetoacetate to give a compound **H**, which was reacted with 3.0 M amounts of malononitrile to provide both the mono(dicyanovinilidene) **I** and **I'** (51%) and bis(dicyanovinilidene) derivatives **J** (28%). The mono and bis derivatives were separated by column chromatography. For the mono derivative, both the 6- and 5-ethoxycarbonyl regio isomers **I** and **I'** were formed. These isomers were not separated by chromatography due to the same R_f value (SiO₂ TLC, R_f = 0.35, CHCl₃: MeOH = 3: 1). However, when the mixture was recrystallized from ethanol, only the 6-ethoxycarbonyl isomer **I** was obtained as a crystalline form in a 28% yield.

The heteronuclear multiple bond coherence (HMBC) spectrum of **I** is shown in Fig. 1. The spectrum indicates that the H⁵ peak correlates with the C⁷, C⁵, and COO peaks. The H⁷ peak correlates with the C⁵, C^{3a}, and COO peaks. The H⁴ peak correlates with the C⁶, C^{7a}, and C³ peaks. Thus, compound **I** was identified as ethyl indan-3-dicyanovinilidene-1-one-6-carboxylate. The hydrolysis of ester moiety of **I** afforded the carboxyl derivative **2e**. Compound **H** was allowed to react with 4.0 M amounts of malononitrile to give **J** in a

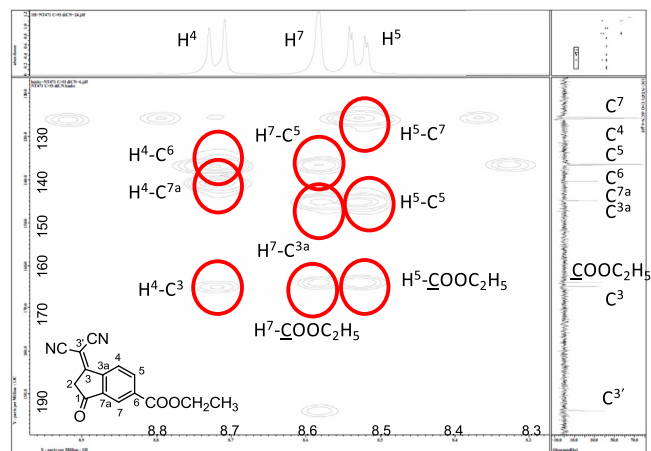


Fig. 1. HMBC spectrum of **I**.

78% yield. The hydrolysis of the ester moiety of **J** provided a carboxylic acid **2f**. Finally, an indoline carboxaldehyde **1** was allowed to react with **2a**, **2b**, **2c**, **2d**, **2e**, and **2f** to afford **3a**, **3b**, **3c**, **3d**, **3e**, and

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