



Application of indoline dyes having a carboxylated 1,3-indandione ring linked with thienyl or hexylthienyl ring to dye-sensitized solar cells

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ABSTRACT

The performance of a new indoline dye having a carboxylated 1,3-indandione unit linked with a hexylthienyl ring showed higher conversion efficiency than the analogous dye without the hexyl group.

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1. Introduction

Indoline dyes are one of the most efficient organic sensitizers in dye-sensitized solar cells (DSSCs). Until now, the anchor groups of indoline dyes were limited to α -cyanoacrylic acid (**D131**) [1–8], single rhodanine acetic acid (**D102**) [9–23], and double rhodanine acetic acid groups (**D149**, **D205**, **DN319**, **DN350**) [24–39]. Furthermore, thienyl [28,40], dithienyl [28,40], trithienyl [28], and 3-oxocyclobut-1-enolate rings [41] have been used as the linker moieties for indoline dyes.

Recently, an indoline dye having a carboxylated 1,3-indandione unit linked with a thienyl ring, **DN475**, has been reported to exhibit conversion efficiency of 5.76% on a plastic-substrate [40]. We report here more efficient indoline sensitizer than **DN475** having a 1,3-indandione anchor group.

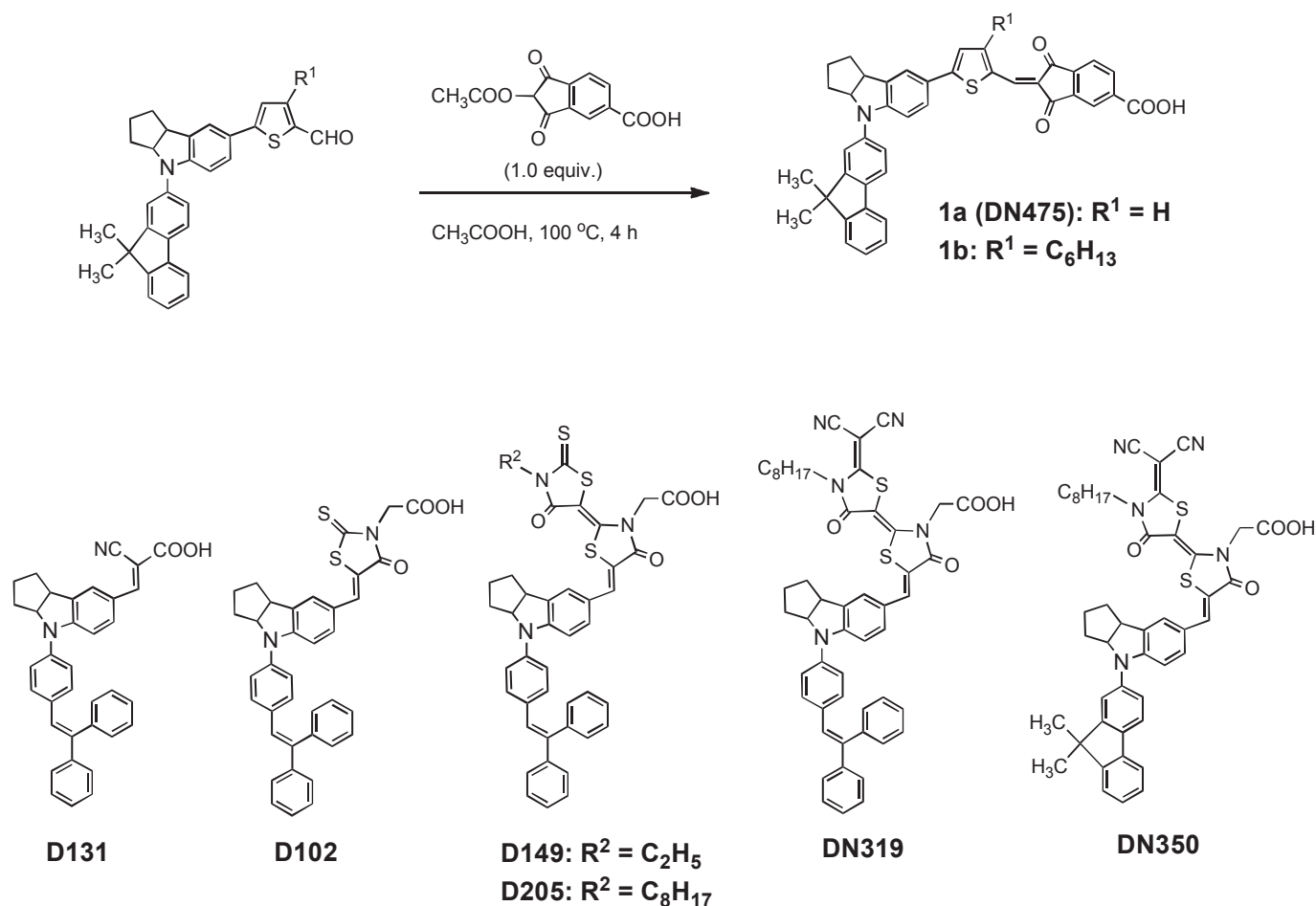
2. Experimental

2.1. Instruments

Melting points were measured with a Yanaco MP-S2 micro-melting-point apparatus. NMR spectra were taken with a JEOL 400 spectrometer. Mass spectra were taken on a JEOL HMS-700 MStation spectrometer. IR spectra were obtained by a Shimadzu IR Affinity-1 spectrophotometer. Elemental analysis was performed with a Yanaco MT-6 CHN analyser. UV-Vis absorption and fluorescence spectra were taken on Hitachi U-4100 and JASCO FP-8600 spectrophotometers, respectively. Electrochemical measurement was carried out using an EG&G Princeton Applied Research Potentiostat/Galvanostat (Model 263A) driven by the M270 software package.

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Scheme 1. Dyes.

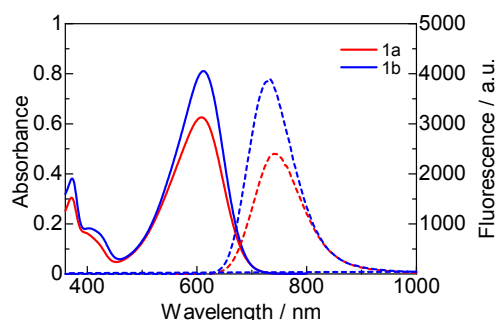


Fig. 1. UV-Vis absorption and fluorescence spectra of **1a** and **1b** (1.0×10^{-5} mol dm $^{-3}$) in chloroform.

Table 1
Physical data of **1a** and **1b**.

Dye	$\lambda_{\max}(\epsilon)$	F_{\max}^a/nm	Φ_f	τ_f^b/ns	E_{ox}^b/V	E_{red}^b/V
1a	371 (30,000), 608 (62,000)	741	0.18	1.04	0.91	−0.69
1b	372 (38,000), 611 (81,000)	732	0.24	1.32	0.92	−0.70

2.2. Materials

Dye **1a** was prepared as described in literature [40]. 5-(4-(9,9-Dimethyl-9H-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-3-hexylthiophene-2-carbaldehyde and 2-(acetyloxy)-1H-indene-1,3-(2H)-dione were supplied from Chemica Inc.

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2.3. Synthesis of **1b**

To an acetic acid solution (3 mL) of 5-(4-(9,9-dimethyl-9H-fluoren-2-yl)-1,2,3,3a,4,8b-hexahydrocyclopenta[b]indol-7-yl)-3-hexylthiophene-2-carbaldehyde (110 mg, 0.2 mmol) was added 2-(acetyloxy)-1H-indene-1,3-(2H)-dione (50 mg, 0.2 mmol). The mixture was heated at 100 °C for 4 h. After the reaction was complete, the reaction mixture was poured into water (3 mL). The resulting precipitate was purified by column chromatography (SiO₂, CHCl₃: MeOH = 100: 1). Yield 55%; mp 152–154 °C; IR (KBr) $\nu = 3429, 1724$ cm $^{-1}$; ^1H NMR (DMSO-*d*₆) $\delta = 0.85$ (t, $J = 6.5$ Hz, 3H), 1.26–1.29 (m, 4H), 1.32–1.34 (m, 2H), 1.40–1.43 (m, 1H), 1.47 (s, 3H), 1.48 (s, 3H), 1.61–1.65 (m, 3H), 1.75–1.77 (m, 1H), 1.83–1.90 (m, 2H), 2.07–2.13 (m, 1H), 2.80 (t, $J = 7.2$ Hz, 2H), 3.82–3.85 (m, 1H), 5.00–5.02 (m, 1H), 6.93 (dd, $J = 8.2$ and 6.2 Hz, 1H), 7.26–7.29 (m, 2H), 7.32 (t, $J = 7.6$ Hz, 1H), 7.48 (s, 1H), 7.52–7.53 (m, 3H), 7.57 (s, 1H), 7.74 (d, $J = 6.8$ Hz, 1H), 7.78–7.80 (m, 2H), 7.84 (t, $J = 7.6$ Hz, 1H), 8.18 (d, $J = 5.5$ Hz, 1H), 8.27 (t, $J = 8.6$ Hz, 1H); ^{13}C NMR (DMSO-*d*₆) $\delta = 13.93, 22.05, 24.08, 26.83, 26.97, 28.61, 28.95, 30.60, 31.00, 32.97, 34.86, 44.33, 46.58, 68.88, 107.54, 114.58, 119.15, 119.51, 119.70, 120.94, 122.40, 122.65$ (2C), 122.83, 125.00, 126.62, 127.06, 128.59, 131.52, 132.27, 133.36, 135.48, 136.24, 138.40, 139.49, 140.63, 141.20, 142.13, 143.81, 149.02, 153.16, 154.78, 157.45, 160.51, 166.15,

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