



# Near-infrared absorbing isoindigo sensitizers: Synthesis and performance for dye-sensitized solar cells



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## ABSTRACT

A series of isoindigo-based metal-free organic sensitizers have been synthesized and used in dye-sensitized solar cells (DSSCs). Measurement data indicated that the fine-tuning of the donor or linker moiety could conveniently adjust the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. All DSSCs sensitized by three new dyes displayed an efficient panchromatic spectra response with the improved light-harvesting capability in near-infrared region, in which a highest photovoltaic conversion efficiency of 5.56% was obtained by the DSSCs of benzene-bridge isoindigo-based sensitizer, with a short-circuit photocurrent density ( $J_{sc}$ ) of 13.16 mA/cm<sup>2</sup>, an open-circuit photovoltage ( $V_{oc}$ ) of 582 mV, and a fill factor ( $ff$ ) of 0.73.

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## 1. Introduction

In recent decades, as a promising candidate for renewable energy source, dye-sensitized solar cells (DSSCs) have attracted a great deal of interest. The sensitizer is imperative to the performance of a DSSC for harvesting sunlight and converting the solar energy into electric energy. Among all the different sensitizers, such as polypyridyl Ru complexes and porphyrin dyes, metal-free organic dyes have become increasingly attractive for the merits of high molar extinction coefficients, low cost, environment-friendly character and high flexibility of molecular design. Almost all of the metal-free organic dyes are constructed with donor- $\pi$  spacer-acceptor (D- $\pi$ -A) architecture for the benefit of intramolecular charge transfer (ICT). Among the reported D- $\pi$ -A metal-free organic sensitizers, the highest conversion efficiencies of DSSCs based on this kind of dyes is about 10% [1–4]. There is still room to enhance their conversion efficiencies since they haven't fully exploited the near/far-infrared light. In order to harvest sunlight as much as possible, it is essential to extend the absorption spectra and enhance the molar extinction coefficients of organic sensitizers. Several organic NIR dyes such as squaraine [5–8], cyanine [9,10] and related compounds containing tetrahydroquinoline [11], phenoxazine [12], perylene [13,14] units alike

have been reported. Nonetheless, their photovoltaic performance was not ideal, mainly due to the existence of aggregation and unmatched energy levels. LUMO energy level should be sufficiently high to promote electron injection while HOMO energy level should be sufficiently low to accelerate dye regeneration. Recently, a new type of dyes with an additional acceptors introduced between the donor and  $\pi$ -bridge have been designed and characterized as a D-A- $\pi$ -A [15] architecture, which facilitates intramolecular charge transfer and adjusts the band gap for harvesting more NIR light. As reported, the additional  $\pi$ -conjugated acceptor chromophore such as fused thiophenes [16,17], diketopyrrolopyrrole [18–21], benzothiadiazole [22–24], benzotriazole [25,26] and quinoxaline [27–30] are introduced into D-A- $\pi$ -A dyes.

Isoindigo has a strong electron-withdrawing property due to the two lactam rings. It has been widely used in the dye industry and can be obtained easily from various natural sources. In the past few years, the photovoltaic performance of isoindigo-based polymer solar cells [31–33] has been reported and the best power conversion efficiency of 6.3% has been reached. Small molecular dyes containing an isoindigo moiety for DSSCs have been explored in our previous paper [34]. According to it, the large  $\pi$ -conjugated system of isoindigo has the problem of strong  $\pi$ - $\pi$  stacked aggregation on TiO<sub>2</sub>, which may reduce the electron injection efficiency in DSSCs. Therefore, long alkyls were connected to isoindigo in **ID1** (Fig. 1) to restrain dye aggregation and charge recombination. However, there's still a certain degree of aggregation for this dye. Recently, it

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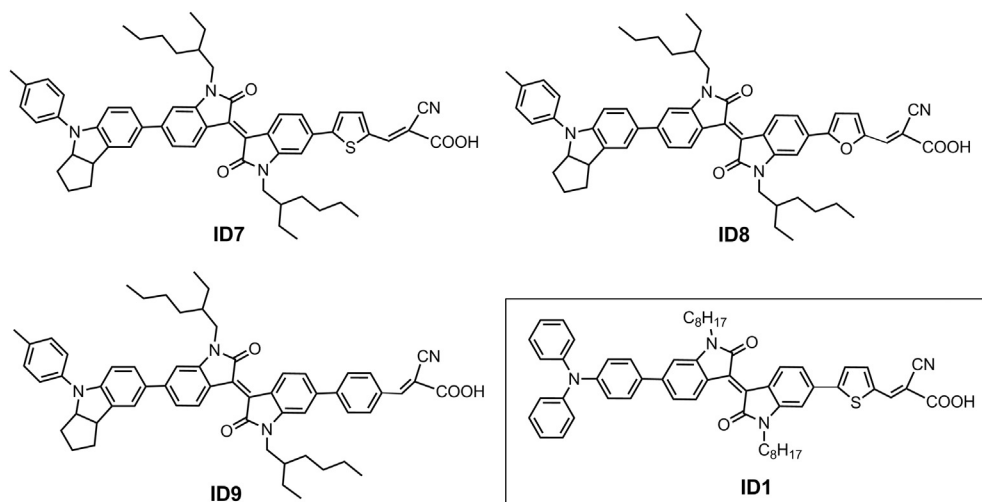


Fig. 1. Chemical structures of ID7–ID9 and reference dye ID1.

is found that attaching a bulky and branched alkyl chain to the middle part of the sensitizer is a more effective way to reduce  $\pi$ – $\pi$  stacking of molecules on the TiO<sub>2</sub> film [19]. In view of this, we attached 2-ethylhexyl alkyl instead of *n*-octyl in order to decrease aggregation more effectively. In addition, we replaced triphenylamine (TPA) unit with the stronger electron-donating indoline moiety [22,35] as the donor part to further broaden the absorption spectrum and improve the efficiency. Thus, three new isoindigo-based sensitizers (ID7–ID9) were designed and synthesized. Their chemical structures are presented in Fig. 1.

In this report, we disclose not only the synthesis of three dyes, but also the research of photophysical properties, electrochemical properties and the corresponding performance of DSSCs.

## 2. Experimental section

### 2.1. Materials

All chemicals and reagents were used as purchased from suppliers without further purification. Tetrahydrofuran (THF) was dried using molecular sieves and distilled under argon with sodium benzophenoneketyl immediately prior to use. The starting materials 6, 6'-dibromoisindigo and indoline boronic acid were prepared according to the published procedures [34,36].

### 2.2. Characterization and instruments

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained with a Bruker AM 400 spectrometer. Mass spectra were measured with an HP 5989 mass spectrometer. The UV–Vis spectrum was measured with a Varian Cary 500 spectrophotometer. The IR spectrum was measured with a Nicolet 380 FT-IR spectrometer. Cyclic voltammograms (CV) were performed via a Versastat II electrochemical workstation (Princeton applied research) using a three-electrode system consisted of a Pt working electrode, a Pt wire counter electrode and a standard calomel reference electrode in saturated KCl solution. All CV measurements were performed under an argon atmosphere with supporting electrolyte of 0.1 M tetra-*n*-butylammoniumhexa-fluoro phosphate (TBAPF<sub>6</sub>) in dichloromethane at scan rate of 50 mV/s, in which ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) was used as an internal reference. The electrical impedance spectroscopy (EIS) experiments were performed in the dark by Zahner IM6e Impedance Analyzer, with a frequency range from 0.1 Hz to 100 kHz

and a potential modulation of 10 mV. The applied bias potential was kept at –0.7 V.

### 2.3. Synthesis

#### 2.3.1. Synthesis of (*E*)-6,6'-dibromo-1,1'-bis(2-ethylhexyl)-[3,3'-biindolinylidene]–2,2'-dione (**1**)

6,6'-dibromoisindigo (420 mg, 1.0 mmol) and potassium carbonate (824 mg, 6.0 mmol) were dissolved in DMF (20 mL) under argon. After the mixture was stirred for half an hour and heated to 60 °C, 2-ethylhexyl bromide (424 mg, 2.2 mmol) was added into this mixture by a syringe before it was heated at 100 °C for 18 h. After cooling down, the mixture was poured into water and extracted with CH<sub>2</sub>Cl<sub>2</sub>. Then the solvent was removed under reduced pressure. The residue was chromatographed on a silica gel column with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (1:2 by volume) as eluant to give a dark red solid (530 mg, 82% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.05 (d, *J* = 12.6 Hz, 2H), 7.17 (dd, *J*<sub>1</sub> = 4.6 Hz, *J*<sub>2</sub> = 8.4 Hz, 2H), 6.89 (d, *J* = 4.0 Hz, 2H), 3.65 (m, 4H), 1.83 (m, 2H), 1.37–1.30 (m, 16H), 0.95–0.89 (m, 12H).

#### 2.3.2. Synthesis of (*E*)-5-(6'-bromo-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)thiophene-2-carbaldehyde (**2a**)

A mixture of **1** (386 mg, 0.6 mmol), Pd<sub>2</sub>(dba)<sub>3</sub> (15 mg), P(*o*-tolyl)<sub>3</sub> (10 mg) and K<sub>3</sub>PO<sub>4</sub> (0.5 g, 0.6 mmol) in THF (15 mL) was stirred and heated to 50 °C under argon. A solution of 5-formyl-2-thiopheneboronic acid (78 mg, 0.5 mmol) in THF (10 mL) was added. Then the mixture was heated to 80 °C and refluxed for 12 h. After removing the solvent under reduced pressure, the residue was chromatographed on a silica gel column with CH<sub>2</sub>Cl<sub>2</sub>/PE (1:2 to 1:1 by volume) to give a black solid (135 mg, 40% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.92 (s, 1H), 9.22 (d, *J* = 8.0 Hz, 1H), 9.07 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 4.2 Hz, 1H), 7.49 (d, *J*<sub>1</sub> = 4.2 Hz, 1H), 7.37 (dd, *J*<sub>1</sub> = 4.8 Hz, *J*<sub>2</sub> = 8.2 Hz, 1H), 7.18 (dd, *J*<sub>1</sub> = 8.2 Hz, *J*<sub>2</sub> = 12.6 Hz, 1H), 7.03 (d, *J* = 4.6 Hz, 1H), 6.91 (s, 1H), 3.74–3.63 (m, 4H), 1.87–1.84 (m, 2H), 1.39–1.25 (m, 16H), 0.94–0.90 (m, 12H).

#### 2.3.3. Synthesis of (*E*)-5-(6'-bromo-1,1'-bis(2-ethylhexyl)-2,2'-dioxo-[3,3'-biindolinylidene]-6-yl)furan-2-carbaldehyde (**2b**)

The synthetic method was similar to **2a** and gave a black solid **2b** (147 mg, 55% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 9.71 (s, 1H), 9.22 (d, *J* = 8.0 Hz, 1H), 9.05 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.36 (d, *J*<sub>1</sub> = 4.2 Hz, 1H), 7.19 (d, *J*<sub>1</sub> = 4.2 Hz, 1H), 7.17 (dd, *J*<sub>1</sub> = 8.2 Hz,

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