



# Phenoxazine-based panchromatic organic sensitizers for dye-sensitized solar cells



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## ABSTRACT

A series of metal-free organic dyes **LJJ101–LJJ103** composed of phenoxazine unit and indolinium carboxyl acid derivative have been synthesized for dye-sensitized solar cells. A systematic investigation has been conducted for the photology and electrochemistry properties of dyes **LJJ101–LJJ103**. Panchromatic spectra responses for all the three dyes have been obtained and extended to about 800 nm in near-infrared region. Compared to **LJJ101**, the introduction of thiophene and squaraine unit causes a red-shift absorption response for **LJJ102** and **LJJ103**, respectively. When applied in dye-sensitized solar cells under AM 1.5 illumination, the device sensitized by **LJJ103** yields the best conversion efficiency of 5.1% with a short-circuit photocurrent density of 13.7 mA/cm<sup>2</sup>, an open-circuit photovoltage of 502 mV and a fill factor of 74.0%.

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## 1. Introduction

As a kind of prospective photovoltaic (PV) devices, dye-sensitized solar cells (DSSCs) have attracted great attention because of the low fabrication cost and high conversion efficiency [1–3]. The performance of DSSCs lies in many aspects, the primal demand of the devices, however, is to be able to make as much use of the illumination as possible. Therefore, panchromatic photosensitizers with sufficient broad spectrum response are quite attractive for the researchers [4]. When applied into DSSCs under AM 1.5 illumination, the devices based on panchromatic dyes such as Ru-complexes and Zn porphyrin photosensitizers have gained extremely high conversion efficiencies up to 11% [5] and 13% [2], respectively. In spite of this, both two kinds of sensitizers have obvious disadvantages in cost or productivity which will limit their applications in DSSCs of large-scale. Thus, many researchers turn their attention to panchromatic metal-free organic dyes with simple synthesis processes and low costs. However, it is not easy to obtain panchromatic metal-free organic dyes for the strict demand of energy level, which should match the conduction band (CB) of nanoporous TiO<sub>2</sub> and redox potential of electrolyte in the meantime. Up to now, only few reports of panchromatic metal-free organic photosensitizers such as squaraine [6–10], bodipy [11,12]

and perylene [13,14] dyes and so on [15–17], have been successfully applied in DSSCs. Typically, indolinium carboxyl acid derivative is widely employed to build squaraine photosensitizers in near-infrared region. A feasible approach to get panchromatic response is to employ electron-rich unit [7]. As is known to us, phenoxazine and its derivatives own commendable electron donating abilities and have been successfully applied in DSSCs [18–22], which can be expected to be applied together with indolinium carboxyl acid derivative to achieve photosensitizers with good light-harvesting abilities.

In this work, a series of panchromatic metal-free organic dyes **LJJ101–LJJ103** (seen in Fig. 1) based on phenoxazine unit and 5-carboxy-1-butyl-2,3,3-trimethyl-3H-indolinium unit have been synthesized and applied in DSSCs. A thiophene unit has been employed into **LJJ102** to broaden absorption region of dyes on the basis of **LJJ101**. As for **LJJ103**, squaraine unit has been embedded next to anchoring group for increasing the electron-withdrawing ability. The photovoltaic properties of DSSCs sensitized by the three dyes have been investigated systematically.

## 2. Experimental section

### 2.1. Materials

F-doped tin oxide (FTO) conducting glass was purchased from Pilkington. The counter electrodes (Pt-coated FTO conducting

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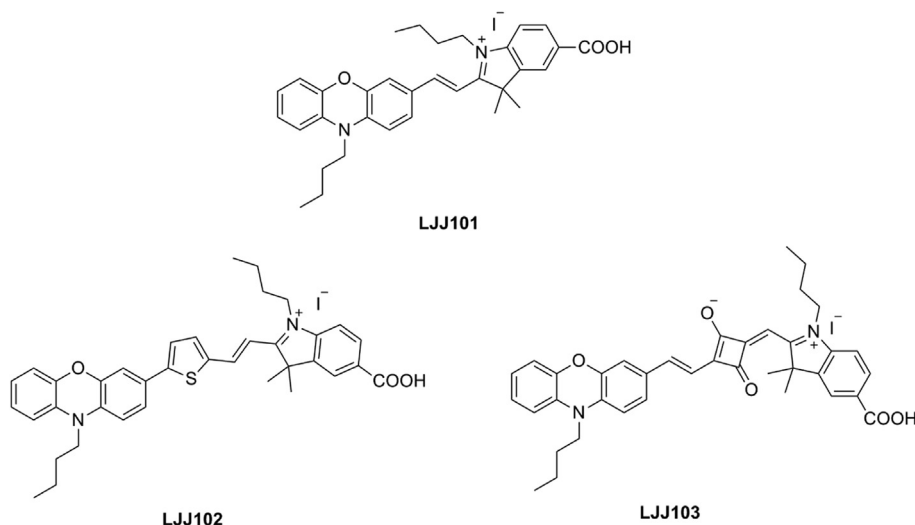


Fig. 1. The structures of LJJ101–LJJ103.

glass) and two kinds of TiO<sub>2</sub> pastes were achieved from Heptachroma. The Surlyn films were bought from Dupont. Other chemicals and reagents used in this work were obtained from Sigma–Aldrich. The purifications of the organic solvent were taken using standard process.

## 2.2. Characterization and measurement

The measurements of <sup>1</sup>H-NMR and <sup>13</sup>C NMR spectra were conducted with Varian INOVA 400 MHz (USA) and <sup>1</sup>H-NMR measurements were obtained with TMS as comparison standard. Mass spectrometry (MS) data were recorded with GCT CA156 (UK), HP1100 LC/MSD (USA) and LC/Q–TOF MS (UK). UV–Vis absorption spectra of the dyes were measured with HP8453 (USA) both in CH<sub>2</sub>Cl<sub>2</sub> solution and on nanoporous TiO<sub>2</sub>. Cyclic voltammetry (CV) measurements were performed to get redox potentials of dyes and were recorded on BAS100B electrochemistry workstation (USA) using a three-electrode system with a glassy carbon working electrode, a Pt wire counter electrode and an Ag/Ag<sup>+</sup> reference electrode. In this system, tetra-butylammonium hexafluorophosphate (TBAPF<sub>6</sub>) in acetonitrile was used as the supporting electrolyte and ferrocenium/ferrocene (Fc/Fc<sup>+</sup>) redox couple was applied as comparison potential reference. Mott–Schottky measurements were performed on the electrochemical workstation (Zennium, Zahner, Germany) under dark conditions from –1 V to 0 V. The dye-adsorbed TiO<sub>2</sub> electrode used as working electrode, Pt wire as auxiliary electrode and Ag/Ag<sup>+</sup> as the reference electrode with I<sup>–</sup>/I<sup>3–</sup> electrolyte (0.6 M DMPII, 0.25 M LiI, 0.02 M I<sub>2</sub>, 0.1 M TBAI). The FTIR spectra of dye powder dye-anchored TiO<sub>2</sub> power were conducted by FTIR equipment (NEXUS, America) with KBr as a blank. The photocurrent density–voltage (*J*–*V*) characteristics of DSSCs were measured under standard AM 1.5 irradiation (16S–002, Solar Light Co. Ltd., USA) with simulated illumination intensity of 100 mW/cm<sup>2</sup>. A mask with a hole was used to keep the working area of 0.159 cm<sup>2</sup>. The *J*–*V* curves were obtained by linear sweep voltammetry (LSV) method using an electrochemical workstation (LK9805, Lanlike Co. Ltd., China). The incident photon-to-current conversion efficiency (IPCE) spectra were obtained by a Hypermono–light (SM–25, Jasco Co. Ltd., Japan). Electrochemical impedance spectroscopy (EIS) was measured with an impedance/gain–phase analyzer (PARSTAT 2273, USA) under dark condition.

## 2.3. Synthesis

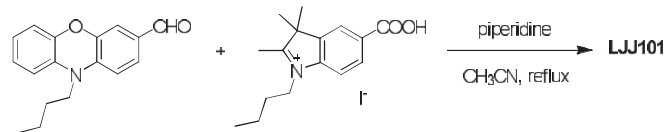
The synthetic routes for LJJ101–LJJ103 are displayed in Scheme 1, Scheme 2 and Scheme 3, respectively. 2,5-carboxy-1-butyl-2,3,3-trimethyl-3H-indolium, 10-butyl-10H-phenoxazine-3-carbaldehyde and 5-(10-butyl-10H-phenoxazin-3-yl)-thiophene-2-carbaldehyde were synthesized according to the literature [23,24].

### 2.3.1. (*E*)-1-Butyl-2-(2-(10-butyl-10H-phenoxazin-3-yl)vinyl)-5-carboxy-3,3-dimethyl-3H-indol-1-ium iodide (LJJ101)

To a solution of 10-butyl-10H-phenoxazine-3-carbaldehyde (267 mg, 1 mmol) and 5-carboxy-1-butyl-2,3,3-trimethyl-3H-indolium (464 mg, 1.2 mmol) in CH<sub>3</sub>CN (30 ml), piperidine was added as catalyst. The mixture was stirred and refluxed for 12 h. After the reaction finished, the solvent was removed by rotary evaporation. The residuum was purified by silica gel chromatography method with dichloromethane: methanol (15:1) as developing solvent to obtain LJJ101. Yield: 81%. <sup>1</sup>H-NMR (400 MHz, Acetone-*d*<sub>6</sub>, ppm) δ<sub>H</sub> 8.38 (1H, s), 8.15 (1H, d, *J* 8.3), 8.07 (1H, d, *J* 8.3), 7.27 (1H, dd, *J* 8.4, 2.2), 7.02 (1H, d, *J* 2.2), 6.91–6.85 (1H, m), 6.78–6.70 (2H, m), 6.70–6.64 (2H, m), 4.45 (2H, t, *J* 7.5), 3.69–3.61 (2H, m), 1.57 (6H, s), 1.45–1.10 (4H, m), 1.68 (2H, tt, *J* 7.9, 6.6), 1.51 (2H, dq, *J* 14.6, 7.3), 1.01 (3H, t, *J* 7.3), 0.83 (3H, t, *J* 5.5). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ = 175.4, 166.8, 153.5, 147.7, 144.9, 144.5, 138.2, 137.6, 132.6, 131.1, 129.6, 128.7, 127.7, 124.5, 124.4, 124.1, 123.9, 123.5, 115.3, 113.8, 113.6, 112.1, 67.5, 51.8, 46.3, 33.2, 30.7, 25.1, 25.1, 19.7, 19.5, 13.4, 13.4. GC/Q–TOF MS: Found *m/z* 509.2806, Calc. for C<sub>33</sub>H<sub>37</sub>N<sub>2</sub>O<sub>3</sub><sup>+</sup> 509.2799.

### 2.3.2. (*E*)-1-Butyl-2-(2-(5-(10-butyl-10H-phenoxazin-3-yl)thiophen-2-yl)vinyl)-5-carboxy-3,3-dimethyl-3H-indol-1-ium iodide (LJJ102)

To a solution of 5-(10-butyl-10H-phenoxazin-3-yl)-thiophene-2-carbaldehyde (349 mg, 1 mmol) and 5-carboxy-1-butyl-2,3,3-



Scheme 1. Synthetic route for LJJ101.

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