



## New sensitizers bearing quinoxaline moieties as an auxiliary acceptor for dye-sensitized solar cells



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### ABSTRACT

Two organic sensitizers (**LI-40** and **LI-41**) containing 6,7-bis(hexyloxy)-2,3-dimethylquinoxaline unit and thiophene or furan as conjugated bridge were synthesized and utilized for dye-sensitized solar cells (DSSCs). The incorporation of quinoxaline unit brought about impressive changes in absorption spectra and energy levels, thus, enhanced the light-harvesting for photovoltaic conversion and facilitated the electron transfer, resulting in a great improvement in the electron distribution of the whole molecule. The solar cell based on **LI-40** exhibited a broad incident photon-to-current conversion efficiency (IPCE) spectrum and high conversion efficiency ( $\eta = 6.75\%$ ). While under the same measuring conditions, the reference sensitizer **PSS**, which had similar structure to **LI-40** but without the quinoxaline unit in the conjugated bridge, only gave the  $\eta$  value of 4.50%, indicating that the sensitizers are promising candidates to improve the performance of DSSCs.

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### 1. Introduction

Metal-free organic sensitizers have attracted considerable attention in the academia for applications in dye-sensitized solar cells (DSSCs), owing to their high molar extinction coefficients, easy molecular tailoring of the electronic properties, facile synthesis, and low costs [1–3]. Up to now, the solar-cell performances of DSSCs based on metal-free organic sensitizers have been remarkably improved and achieved impressive efficiencies [4–19]. Most of organic sensitizers are designed based on D- $\pi$ -A system, in which the electron-donating (D) and accepting (A) moieties are linked by  $\pi$ -conjugated spacers. Generally, D- $\pi$ -A molecules with short  $\pi$ -conjugation length only absorb photons in short wavelengths, while long  $\pi$ -conjugated sensitizer molecules are apt to form unfavorable aggregation and unstable when irradiated with high-energy photons [20]. For remedying this deficit in solar light absorption of a dipolar compound, one of the strategies is to

incorporate a strong electron donating or accepting unit into the  $\pi$ -conjugated space to form a more effective bridge, which could enhance the charge transfer between donor and acceptor unit [21]. Recently, a series of organic sensitizers containing different electron-deficient segments, also termed as auxiliary acceptors, in conjugated bridge, have been investigated and gave good performance [22–24].

Quinoxaline and its derivatives have been widely used in polymer solar cells (PSCs) as electron-accepting materials because of their high electron affinity derived from the two symmetric unsaturated nitrogen atoms [25,26]. But few examples have been reported concerning the quinoxaline-based sensitizers in the literature [27,28]. In our researches of DSSCs, we noticed that a derivative of quinoxaline, 6,7-bis(hexyloxy)-2,3-dimethylquinoxaline, might be suitable for incorporating into the conjugated bridge as an auxiliary acceptor due to the following considerations: 1) an additional electron withdrawing group introduced to the D- $\pi$ -A system can make the energy gap between HOMO and LUMO smaller, directly leading to the long responsive wavelength; 2) the introduction of alkoxy chain to the spacer, can not only form a blocking layer to keep  $I_3^-$  ions away from the  $TiO_2$  electrode surface, also prevent the intermolecular  $\pi$ - $\pi$  stacking; 3) as a weak electron acceptor, this unit can ensure that the major LUMO orbital is delocalized over the acceptor units, giving an

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effective electron transmission and reduce the degree of charge trapping at the electron deficient moiety; 4) considering that 4-*tert*-butylpyridine (TBP), imidazole, pyrimidine, and benzimidazole have been employed as additives in the electrolyte to increase open-circuit photovoltage ( $V_{oc}$ ), here the nitrogen-containing heterocyclic group of the quinoxaline unit might be expected to enlarge the open-circuit photovoltage ( $V_{oc}$ ). Therefore, the 6,7-bis(hexyloxy)-2,3-dimethylquinoxaline unit was incorporated into the conjugated bridge to further develop new D- $\pi$ -A- $\pi$ -A configuration sensitizers (**LI-40** and **LI-41**). In these two sensitizers, triphenylamine act as the donor, cyanoacetic acid as the acceptor, thiophene or furan was chosen as a  $\pi$  spacer linked together with the quinoxaline unit. In order to highlight the role of 6,7-bis(hexyloxy)-2,3-dimethylquinoxaline unit, we also synthesized a reported sensitizer with no electron withdrawing group in spacer (**PSS**) (Fig. 1) [29] for comparison. The photovoltaic performance of **LI-40**-sensitized solar cells exhibited an overall conversion efficiency of 6.75%, much higher than the contrastive sensitizer (**PSS**,  $\eta = 4.50\%$ ) under standard global AM 1.5 solar light condition. Herein, we report their syntheses, structural characterization, electrochemical properties, theoretical calculations, and photovoltaic performance.

## 2. Experimental

### 2.1. Materials

Tetrahydrofuran (THF) and toluene were dried over and distilled from K–Na alloy under an atmosphere of dry nitrogen. *N,N*-Dimethylformamide (DMF) was dried over and distilled from CaH<sub>2</sub> under an atmosphere of dry nitrogen. 1, 2-Dichloromethane was dried over and distilled from phosphorus pentoxide. Phosphorus oxychloride was freshly distilled before use. All reagents were purchased and used as received. 3,6-Dibromo-4,5-bis(hexyloxy)benzene-1,2-diamine (**1**) was prepared following the procedure reported in the literature [30].

### 2.2. Instrumentation

<sup>1</sup>H and <sup>13</sup>C NMR spectroscopy study was conducted with a Varian Mercury 300 spectrometer using tetramethylsilane (TMS;  $\delta = 0$  ppm) as internal standard. UV–visible spectra were obtained using a Shimadzu UV-2550 spectrometer. Cyclic voltammograms were carried out on a CHI 660 voltammetric analyzer at room temperature in nitrogen-purged anhydrous dichloromethane with tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>) as the supporting electrolyte at a scanning rate of 100 mV/s. A platinum disk and a Ag/AgCl electrode were used as the working electrode and

quasi-reference electrode, respectively. The ferrocene/ferrocenium redox couple was used for potential calibration. Elemental analyses were performed by a 73 CARLOERBA-1106 micro-elemental analyzer. EI-MS spectra were recorded with a Finnigan PRACE mass spectrometer.

#### 2.2.1. 5,8-Dibromo-6,7-bis(hexyloxy)-2,3-dimethylquinoxaline (**2**)

To the solution of **1** (2.30 g, 5.0 mmol) in ethanol (60 mL), diacetyl (0.65 g, 7.5 mmol) was added slowly and the resultant solution was stirred at 60 °C overnight. The mixture was transferred to a separatory funnel, extracted with chloroform and washed with water. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. Removal of the solvent gave a crude product, which was further purified by silica-gel column chromatography to yield **6** as a light yellow oil (1.91 g, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 4.18–4.14 (m, 4H, –CH<sub>2</sub>–), 2.78 (s, 6H, –CH<sub>3</sub>), 1.93–1.85 (m, 4H, –CH<sub>2</sub>–), 1.55 (br, 4H, –CH<sub>2</sub>–), 1.37 (br, 8H, –CH<sub>2</sub>–), 0.92 (br, 6H, –CH<sub>3</sub>).

#### 2.2.2. General synthesis of **3**

To a solution of 5,8-dibromo-6,7-bis(hexyloxy)-2,3-dimethylquinoxaline (1.01 g, 2.0 mmol) and tributyl(thiophen-2-yl)stannane or tributyl(furan-2-yl)stannane (5.0 mmol) in toluene (20 mL) was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.012 g, 0.01 mmol) under an atmosphere of nitrogen. After refluxing for 12 h, the mixture was cooled to room temperature and then poured into water, the organic layer was extracted by CH<sub>2</sub>Cl<sub>2</sub> and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The crude product was purified through a silica gel chromatography column to give **3**.

#### 2.2.3. 6,7-Bis(hexyloxy)-2,3-dimethyl-5,8-di(thiophen-2-yl)quinoxaline (**3a**)

Yellow oil. 0.89 g. Yield: 86%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.93 (br, 2H, ArH), 7.52(d,  $J = 4.2$  Hz, 2H, ArH), 7.19 (br, 2H, ArH), 3.98 (t,  $J = 7.2$  Hz, 4H, –CH<sub>2</sub>–), 2.70 (s, 6H, –CH<sub>3</sub>), 1.85–1.72 (m, 4H, –CH<sub>2</sub>–), 1.36–1.29 (m, 12H, –CH<sub>2</sub>–), 0.89 (br, 6H, –CH<sub>3</sub>).

#### 2.2.4. 6,7-Bis(hexyloxy)-2,3-dimethyl-5,8-di(furan-2-yl)quinoxaline (**3b**)

Yellow oil. 0.81 g. Yield: 83%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 7.68 (br, 2H, ArH), 7.04 (br, 2H, ArH), 6.63 (br, 2H, ArH), 4.10 (br, 4H, –CH<sub>2</sub>–), 2.72 (s, 6H, –CH<sub>3</sub>), 1.95–1.85 (m, 4H, –CH<sub>2</sub>–), 1.48–1.36 (m, 12H, –CH<sub>2</sub>–), 0.90 (br, 6H, –CH<sub>3</sub>).

#### 2.2.5. General synthesis of **4**

DMF (0.50 g, 6.8 mmol) was added to freshly distilled POCl<sub>3</sub> (0.52 g, 3.4 mmol) under an atmosphere of dry nitrogen at 0 °C, and the resultant solution was stirred until its complete conversion into a glassy solid. After the addition of compound **3a** or **3b** (1.7 mmol) in 1, 2-dichloroethane (20 mL) dropwise, the mixture was stirred at room temperature overnight, then poured into an aqueous solution of sodium acetate (1 M, 200 mL), stirred for another 2 h. The mixture was extracted with chloroform for several times, the organic fractions were combined and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing the solvent under vacuum, the crude product was purified through a silica gel chromatography column to give **4**.

#### 2.2.6. 5-(6,7-Bis(hexyloxy)-2,3-dimethyl-8-(thiophen-2-yl)quinoxalin-5-yl)thiophene-2-carbaldehyde (**4a**)

Orange oil. 0.81 g. Yield: 82%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  (ppm): 10.01 (s, 1H, –CHO), 8.06 (br, 1H, ArH), 7.97 (br, 1H, ArH), 7.83 (d,  $J = 3.3$  Hz, 1H, ArH), 7.55 (br, 1H, ArH), 7.21 (br, 1H, ArH), 3.96 (br, 4H, –CH<sub>2</sub>–), 2.72 (s, 6H, –CH<sub>3</sub>), 2.03–1.83 (m, 4H, –CH<sub>2</sub>–), 1.37–1.29 (m, 12H, –CH<sub>2</sub>–), 0.89 (br, 6H, –CH<sub>3</sub>).

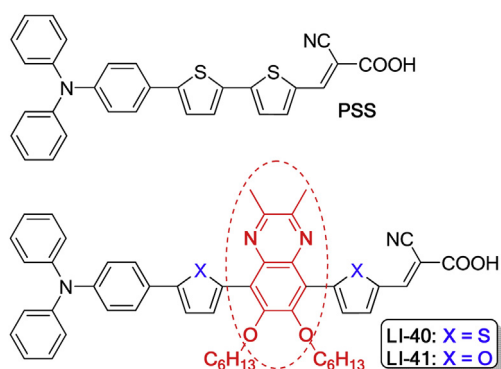


Fig. 1. Molecular structures of sensitizers.

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