



# Synthesis of new di-anchoring organic sensitizer based on quinoxaline acceptor for dye-sensitized solar cells

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## ABSTRACT

New quinoxaline-based organic sensitizer bearing di-anchoring group for dye-sensitized solar cells (DSSCs) was synthesized from diethyl 4,5-diaminophthalate, in which was prepared under mild condition by using Takehito's method. The synthesized sensitizer was compared with mono-anchoring sensitizer through absorption spectra, emission spectra, *J-V* curve, and IPCE spectra, indicating the di-anchoring group leads to a noticeable improvement of  $J_{sc}$  value owing to more efficient intramolecular charge transfer and channel number increment.

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## Introduction

Solar energy is the most sustainable energy source known to mankind. Over the past few decades, dye-sensitized solar cells (DSSCs) have attracted substantial attention owing to their low cost and high power-conversion efficiency [1]. Since O'Regan and Grätzel's pioneering work in 1991 [2], thousands of dye molecules, which play an important role as the sensitizers in DSSCs, have been developed to improve the power-conversion efficiency and makes these devices more practical [3–7]. Recently, Grätzel's group achieved an efficiency of 13% in the lab [8].

Dye molecules for DSSCs can be divided into two basic groups: metal organic sensitizers and metal-free organic sensitizers. Metal-free organic sensitizers have been widely investigated for practical applications owing to their high molar extinction coefficients, low production cost, good flexibility of molecular tuning, and eco-friendliness [9–12].

In general, metal-free dyes for DSSCs feature a push-pull structure, which facilitates effective intramolecular charge transfer (ICT) from an electron donor to an electron acceptor. When a dye absorbs light, electrons in the dye are excited and an electron-donating group pushes electrons to the electron-withdrawing group. The transported electrons are injected into the conduction band of a semiconductor through an anchoring group that is linked to the acceptor.

In recent years, studies have shown that the anchoring group determines the binding energy of the dye on  $\text{TiO}_2$  and the electron injection rate [13]. Thus, the number of anchoring groups can be tailored to the photocurrent and stability; multi-anchors serve as electron extraction channels and enhance the binding strength [14–21]. Some previous studies have reported that dyes with two anchors lead to better cell performance than those with a single anchor; these studies have used a variety of sensitizers, including triphenylamines, and phenothiazines [21–24].

Quinoxaline units have been investigated as electron acceptors in DSSCs, due to their strong electron withdrawing ability, which stems from the high electron affinity derived from two symmetric unsaturated nitrogen atoms in their heterocycle [25]. Despite many attempts to use quinoxaline units as electron acceptors in DSSCs, metal-free sensitizers based on quinoxalines bearing multi-anchoring groups are rare.

In our previous work, we investigated the photovoltaic properties of chromophores, that used phenothiazines as electron donors and quinoxaline groups as electron acceptors, and carboxylic acids as anchoring groups [26]. In this study, we present a novel synthetic route for introducing two anchors to an acceptor (e.g. quinoxaline derivatives) and report the design, synthesis, and characterization of a new di-anchoring sensitizer based on quinoxaline for DSSCs. **NQX4** was also used so we could compare mono-anchoring and di-anchoring sensitizers. (Fig. 1)

For introducing two anchors to the quinoxaline moiety, it is essential to prepare diethyl 4,5-diaminophthalate, which is a precursor of quinoxaline derivative. A synthetic method of

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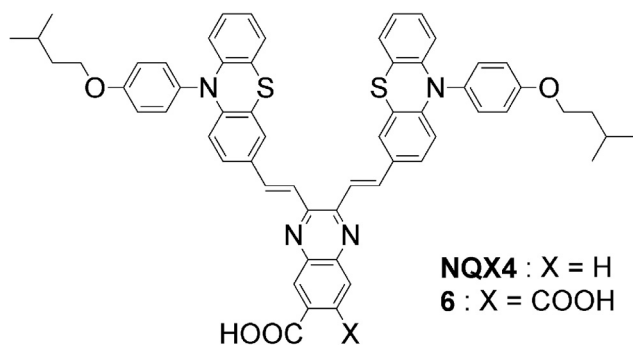


Fig. 1. Molecular structures of quinoxaline-based dyes.

fabricating dimethyl 4,5-diaminophthalate has already reported, but that synthesis requires a moisture-stable atmosphere and expensive reagent for reduction of diethyl 4-amino-5-nitrophthalate because it uses hydrogen gas and palladium on carbon as a catalyst [27]. Herein, for the first time, we confirmed the reduction of nitro group in diethyl 4-amino-5-nitrophthalate by using Takehito's method [28]. This method employs zinc metal-mediated chemoselective reduction of nitroarenes using an inexpensive reagent. The process was relatively easy to operate, and reduced the reaction time to only one hour with a high yield. As-prepared diethyl 4,5-diaminophthalate undergoes condensation with diketone derivative, resulting in quinoxaline derivative that have two ester groups.

The overall synthetic route of **6** is demonstrated in Scheme 1. 4-acetamido-5-nitrophthalic acid (**1**) [27] and 10-(4-(isopentyloxy)phenyl)-10*H*-phenothiazine-3-carbaldehyde [26], were prepared as starting materials via routes reported in the literature. Esterification of **1** with ethanol in the presence of H<sub>2</sub>SO<sub>4</sub> as a catalyst afforded compound **2** with a yield of 80%. Substantial reduction via Takehito's method gave diethyl 4,5-diaminophthalate (**3**) with a yield of 85%. Next, condensation with 1,4-dibromo-2,3-diketone afforded compound **4** with a yield of 88%. Compound **4** was converted into the corresponding Wittig reagent by reaction with triethylphosphite, and a substantial Wittig reaction with 10-(4-(isopentyloxy)phenyl)-10*H*-phenothiazine-3-carbaldehyde produced compound **5** with a yield of 80%. Finally, hydrolysis afforded target compound **6** with a yield of 94%. Details of the experimental procedures and identification data are described in the Supplementary Material.

Fig. 2 shows the UV-visible absorption spectra and fluorescence spectra of **NQX4** and **6** in a THF solution. The corresponding numerical results are summarized in Table 1. The compounds have two absorption bands. The band located near 320 nm was caused

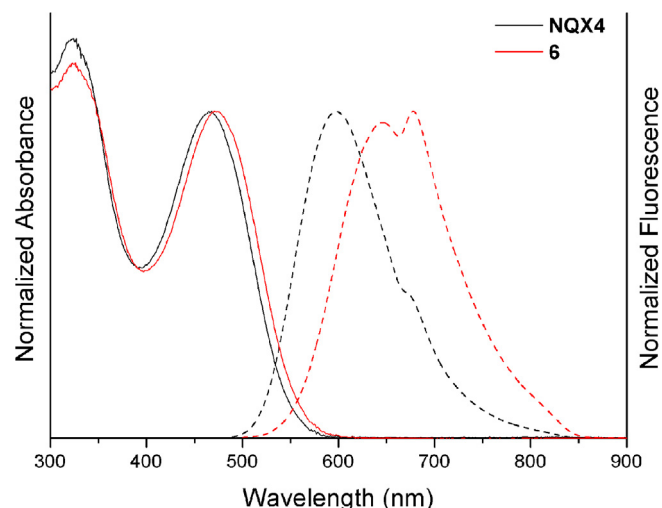


Fig. 2. Normalized absorption (line) and emission (dashed) spectra of **NQX4** and **6** in THF solution.

Table 1  
Photophysical and electrochemical properties of **NQX4** and **6**.

Dyes	<b>NQX4</b>	<b>6</b>
$\lambda_{\max}$ (nm) <sup>a</sup>	466	471
Log $\epsilon$ <sup>a</sup>	4.54	4.58
F <sub>max</sub> (nm) <sup>b</sup>	597	678
E <sub>g</sub> <sup>ec</sup> (eV) <sup>c</sup>	2.29	2.27
E <sub>g</sub> <sup>op</sup> (eV) <sup>d</sup>	2.25	2.21
HOMO (eV) <sup>e</sup>	-5.33	-5.46
LUMO (eV) <sup>e</sup>	-3.04	-3.19

<sup>a</sup> Measured in a THF solution ( $1.0 \times 10^{-5}$  M).

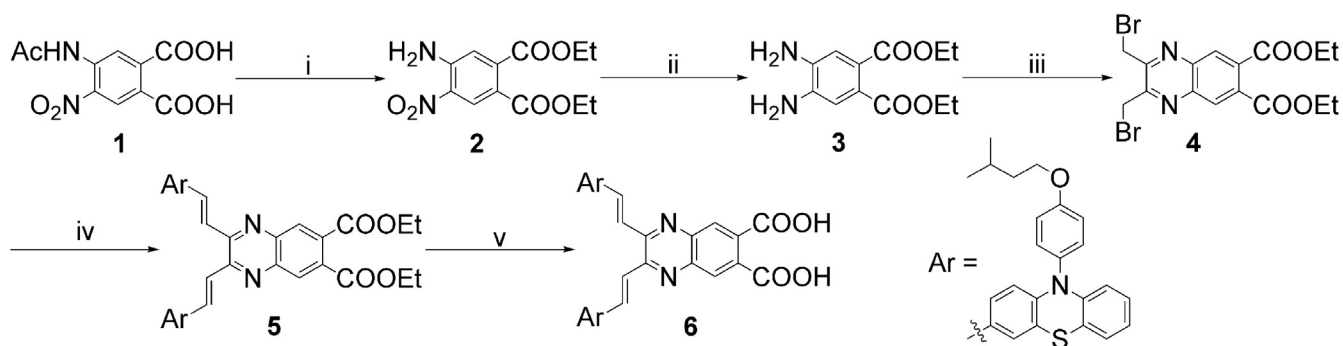
<sup>b</sup> Excited at their  $\lambda_{\max}$  values.

<sup>c</sup> Obtained from CV.

<sup>d</sup> Estimated from the onset wavelength in absorption spectra.

<sup>e</sup> Calculated from electrochemical results. The details are described in Supplementary data.

by two phenothiazine groups, which acted as electron donors, and an efficient  $\pi$ - $\pi^*$  transition [29]. The band near 470 nm resulted from intramolecular charge transfer (ICT) between the donor and acceptor groups [9]. The additional anchoring group led to a slight red shift of  $\lambda_{\max}$  and a slightly higher molecular absorption coefficient ( $\epsilon$ ) with an increase in the relative intensity of the ICT transition, which is result from extension of electron delocalization and increase of push-pull effect in the molecule [22,30,31]. Moreover, the emission band of **6** shows a bathochromic shift and a larger Stokes shift compared to **NQX4**. This could



Scheme 1. Synthetic route of **6**. (i) H<sub>2</sub>SO<sub>4</sub>, EtOH, reflux; (ii) Zn, NH<sub>4</sub>Cl, MeOH, reflux; (iii) 1,4-dibromo-2,3-butandione, *p*-TsOH, MeOH, reflux; (iv) triethylphosphite, reflux; 10-(4-(isopentyloxy)phenyl)-10*H*-phenothiazine-3-carbaldehyde, KOt-Bu, THF, r.t.; (v) NaOH, H<sub>2</sub>O, EtOH, THF, r.t.

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