



## Far-red absorbing squarylium dyes with terminally connected electron-accepting units for organic dye-sensitized solar cells

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### ABSTRACT

Novel squarylium dyes with either terminally placed tetracyanoquinodimethane or tetracyanoanthraquinodimethane moieties as strong electron acceptors were designed and synthesized for use as sensitizers for TiO<sub>2</sub>-based dye-sensitized solar cells (DSSCs). The photovoltaic performance of DSSCs indicates that two chromophores, strong electron acceptors and squarylium components, make independent contributions to photosensitization of nanocrystalline TiO<sub>2</sub>. DSSCs fabricated from squarylium-based diads as sensitizers and chenodeoxycholic acid as the coadsorbent exhibited a high open-circuit voltage (up to 0.66 V), suggesting that the electron-accepting components showed some effect on electron injection from the squarylium chromophore to the conduction band of TiO<sub>2</sub>. Under the coadsorbent-free conditions, the short-circuit photocurrent and overall solar-to-electrical energy conversion efficiency of the photovoltaic cells was improved by the contribution of photosensitizing effect in the wavelength range derived from the electron-acceptor components rather than the squarylium component. This phenomenon implies the possibility that the electron-accepting group acts as an anchoring unit to the TiO<sub>2</sub> surface.

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### 1. Introduction

Dye-sensitized solar cells (DSSCs) have attracted significant attention as high-efficiency and cost-effective photovoltaic cells for the conversion of solar energy, along with bulk heterojunction solar cells consisting of conjugated polymer-fullerene blends [1–3]. The utilization of nanocrystalline TiO<sub>2</sub>, which affords a vast surface area, and the development of Ru(II)–polypyridyl-complexes such as N3 [4], N719 [5], and black dye [6] has made it possible to obtain high solar energy-to-electricity conversion efficiency ( $\eta$ ) of up to 11% under solar simulation (AM 1.5 G) irradiation [7]. As an alternative to Ru complexes, metal-free organic dyes have also been utilized as sensitizers of DSSCs because they have advantages such as a high molar absorption coefficient, facile modification of dye structures, tunable absorption properties through molecular design, and cost-effectiveness [8]. Efforts are underway to improve the molecular design of metal-free sensitizing dyes to obtain a higher conversion efficiency comparable to that of Ru complex-based DSSCs. Recently,

numerous organic sensitizers, such as coumarin [9,10], indoline [11–14], cyanine [15–17], and others [18–22], have been identified, and photovoltaic performances of DSSCs based on these dyes have been gradually improved, resulting in a maximum conversion efficiency of 9.5% [12]. These results indicate that increasing the flexibility of the dye design expands the potential for modifying the cell performance.

Squarylium dyes are well known for their unique optical properties, such as intense and sharp light absorption in the visible to NIR region [23]. The optical band gap of these dyes can be tuned through the choice of electron-rich aromatic/heterocyclic components and the linear extension of the cyclobutene core. In addition, the electron distribution of the HOMO and LUMO of squarylium dyes are influenced by the molecular symmetry and functionality on the aromatic/heterocyclic components. Various types of symmetrical and nonsymmetrical squarylium dyes have been prepared and used in a wide range of applications, such as chemosensors [24–29], noncovalent fluorescent probes for bioanalysis [30–33], organic light-emitting diodes [34–36], supramolecular architectures [37,38] and bulk heterojunction solar cells [39,40]. One of the applications that has attracted the most attention is the use of squarylium dyes as metal-free sensitizers for DSSCs [41–46]. Various types of squaryliums have been used as sensitizers for wide

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band gap semiconductors, and some features associated with molecular design have been elucidated. Nazeerudin et al. achieved high conversion efficiency ( $\eta = 4.5\%$ ) by the use of an unsymmetrical indole-based squarylium dye bearing carboxylic groups directly attached to the indole components [47]. The squarylium was designed in such a way that electrons unidirectionally flowed from the light-harvesting components of the sensitizer to the semiconductor surface. For further improvement of the performance of cells based on squaryliums, the appropriate design of dye molecules, in order to enable efficient electron injection into the conduction band, will be needed along with control of the adsorption properties of dyes.

In this paper, we report the synthesis of novel squarylium dyes bearing terminally connected strong electron-acceptor components and their application as sensitizers for  $\text{TiO}_2$ -based DSSCs (Fig. 1). Tetracyanoquinodimethane (TCQ), tetracyanoanthraquinodimethane (TCAQ), and TCAQ with a hydroxyl group as an anchoring group (TCAQH) were chosen as electron-accepting units, and were incorporated in a *N,N*-dialkylanilino-squaraine and a squaraine consisting of indolenine and *N,N*-dialkylaniline components through ester linkages. Then, the effect of the incorporation of strong electron acceptors on the photovoltaic performance is discussed together with the effect of various dyeing conditions.

## 2. Experimental

### 2.1. General

The NMR spectra were obtained using a JEOL JNM LA-400 spectrometer operating at 400 MHz for  $^1\text{H}$  NMR and 100 MHz for  $^{13}\text{C}$

NMR. Chemical shifts are reported in parts per million ( $\delta$ ) downfield from tetramethylsilane (TMS) as an internal standard in  $\text{CDCl}_3$ . MALDI-TOF MS spectra were recorded on a Shimadzu AXIMA spectrometer. The elemental analyses were performed on a Yanako CHN CORDER JM-10 analyzer. The IR spectra were recorded using a Shimadzu FT-IR 8400S spectrophotometer. The absorption spectra and fluorescence emission spectra were measured in a 1.0 cm quartz cell on a Shimadzu UV-3100 spectrophotometer and a Shimadzu RF-5000 spectrofluorometer. The oxidation potential of the dye was measured with a Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of  $100 \text{ mV s}^{-1}$ , equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a  $\text{Ag}/\text{Ag}^+$  reference electrode. The measurement was performed in an acetonitrile solution including 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. 3-[4-(Dibutylamono)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione was prepared from *N,N*-dibutylaniline and squaryl chloride obtained by a reaction of squaric acid with thionyl chloride according to the conventional method [48]. 2-(*N*-methylphenylamino)ethanol (**3**), 1-(2-hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium iodide (**8**), were prepared according to the conventional synthesis [48,49]. 7,7,8,8-Tetracyano-*p*-quinodimethanepropanoic acid (**4**) [50], 3-[2'-(11,11,12,12-tetracyano-9,10-anthraquinodimethane)methoxycarbonyl]propionic acid (**5**) [51], and 2,6-dihydroxy-11,11,12,12-tetracyanoanthraquinodimethane (**7**) [52] were synthesized by the previously reported methods. Dicyclohexylcarbodiimide (DCC), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl), 4-(dimethylamino)pyridine (DMAP), succinic anhydride, pyridine, and quinoline were purchased from Tokyo Chemical Industry and Wako Pure Chemical and used as received. Organic solvents for the preparation of the compounds were purchased as anhydrous reagent grade and used as received.

### 2.2. Preparation of SQ1-TCQ

#### 2.2.1. Compound **2**

3-[4-(Dibutylamono)phenyl]-4-hydroxycyclobut-3-ene-1,2-dione (**1**) (6.0 g, 20 mmol) and 2-(*N*-methylphenylamino)ethanol (**3**) (3.0 g, 20 mmol) were dissolved in a mixture of 2-propanol and triethoxymethane (20 mL, 5/1, v/v) under Ar atmosphere and the solution was heated under reflux for 13 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent;  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 20/1, v/v), followed by washing with  $\text{CH}_2\text{Cl}_2$  to afford squarylium **2** as a green solid (4.3 g, 49%). Mp 188–190 °C (lit. [53] mp 188–190 °C).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  0.99 (t,  $J = 7.2$  Hz, 6H,  $-\text{CH}_3$ ), 1.40 (m, 4H,  $-\text{CH}_2-$ ), 1.63–1.65 (m, 4H,  $-\text{CH}_2-$ ), 3.17 (s, 3H,  $\text{NCH}_3$ ), 3.26 (br s, 1H, OH), 3.44 (t,  $J = 7.8$  Hz, 4H,  $\text{NCH}_2-$ ), 3.68 (t,  $J = 5.6$  Hz, 2H,  $\text{NCH}_2-$ ), 3.92 (m, 2H,  $-\text{CH}_2\text{O}$ ), 6.73 (d,  $J = 9.6$  Hz, 2H, ArH), 6.77 (d,  $J = 9.6$  Hz, 2H, ArH), 8.26 (d,  $J = 9.3$  Hz, 2H, ArH), 8.34 (d,  $J = 9.3$  Hz, 2H, ArH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  13.84, 20.21, 29.57, 39.61, 51.22, 55.01, 59.91, 112.39, 112.56, 119.26, 119.76, 133.05, 133.16, 153.48, 154.74, 183.53, 186.59. IR (KBr): 3418, 2949, 2922, 1589, 1414, 1194  $\text{cm}^{-1}$ . MALDI-TOF MS:  $m/z$  434.19 ( $[\text{M}]^+$ ).

#### 2.2.2. Compound SQ1-TCQ

7,7,8,8-Tetracyano-*p*-quinodimethanepropanoic acid (**4**) (0.14 g, 0.50 mmol), squarylium **2** (0.22 g, 0.5 mmol), DCC (0.10 g, 0.5 mmol), and DMAP (61 mg, 0.50 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (25 mL) and the mixture was stirred for 2 h at room temperature. The reaction mixture was directly purified by silica gel column chromatography (eluent;  $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 95/5, v/v), followed by recrystallization, where the crystal was grown by slow diffusion from  $\text{CHCl}_3$  solution to acetonitrile. The resulting material was further purified by recrystallization from  $\text{CHCl}_3$  to afford SQ1-TCQ

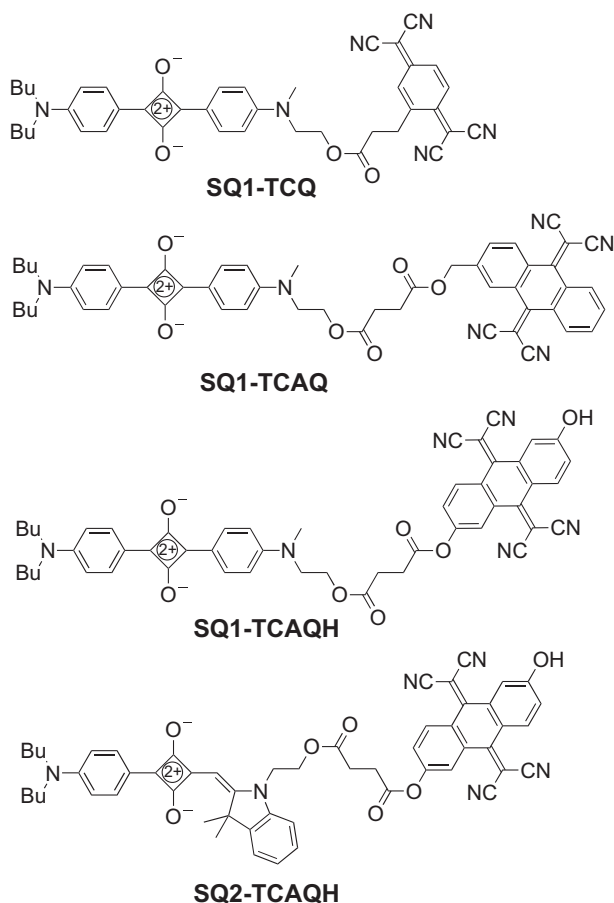


Fig. 1. Molecular structures of the squarylium-based diads.

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