

## Effect of nature of anchoring groups on photosensitization behavior in unsymmetrical squaraine dyes



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### ABSTRACT

A series of indole based unsymmetrical squaraine dyes bearing various anchoring groups such as carboxylate (SQ-A), cyanoacrylate (SQ-B) and thiophene-bridged cyanoacrylate (SQ-C) were synthesized and evaluated for their performance in dye sensitized solar cells (DSSCs) under similar experimental conditions. Electronic absorption spectral investigation on thin films of these dyes adsorbed on nanoporous TiO<sub>2</sub> reveals relatively enhanced spectral broadening upon the incorporation of cyanoacrylate functionality as anchoring group. Incorporation of thiophene  $\pi$ -bridge between the main chromophore and anchoring group (SQ-C) although resulted in to bathochromic shift in the far-red region but hampered photon harvesting due to relatively enhanced dye aggregation. Unsymmetrical squaraine dye (SQ-B) bearing cyanoacrylate anchoring group directly substituted and in conjugation with aromatic chromophore exhibited the best photovoltaic performance giving photoconversion efficiency of 5.03% under simulated solar irradiation.

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### 1. Introduction

Ruthenium based dye sensitized solar cells (DSSCs) [1–3] with the conversion efficiency over 10% had provided a new hope for the realization of relatively low cost solar cells. Relatively high cost, rarity of Ru metal and photon harvesting mainly in the visible region limits the use of ruthenium complexes as a single sensitizer to fabricate high efficiency DSSCs. To further enhance the efficiency there is a critical need for design and synthesis of suitable sensitizers having good photon harvesting in near infrared (NIR) to IR wavelength region, so that such metal free organic sensitizers can be utilized with potential visible photon harvesting sensitizers through dye bilayer architecture in hybrid or tandem solar cells [4,5]. Squaraine dyes showing intense and sharp absorption in the NIR region and high molar extension co-efficient have recently been used as potential NIR sensitizers for DSSCs [6–8]. Report of 4.5% photoconversion efficiency by Yum et al. [9] on unsymmetrical squaraine dye bearing carboxylic acid anchoring group directly attached to its indole chromophore opened up the new idea that dyes bearing carboxylic group directly linked to aromatic chromophore are superior in performance as compared to that of their alkyl side chain carboxyl substituted dye counterparts

[10]. Afterward, several research groups followed the same idea and reported many squaraine dyes bearing carboxylic acid anchoring group attached to various heterocyclic and aromatic donors as potential NIR sensitizers for DSSCs [11–15].

It is well known that anchoring group plays an important role in attaching the dye on the surface of titania nanoparticles and also electron injection from excited dye molecule to conduction band (CB) of TiO<sub>2</sub> [15]. Carboxylic acid, cyanoacrylic acid and rhodanine-3-acetic acid are well known electron acceptors and have been widely employed as anchoring groups for the attachment of the visible wavelength absorbing D- $\pi$ -A dyes on TiO<sub>2</sub> surface [16,17]. Amongst them cyanoacrylic acid as an anchoring group was preferred exhibiting pronounced spectral broadening and enhancement in the photoconversion efficiency as compared to its carboxylic acid [18] and rhodanine-3-acetic acid [19] counterparts. Since development of NIR sensitizer is crucial to attain the panchromatic photon harvesting, it is also necessary to investigate the role of such anchoring groups on their photon harvesting behavior. In this context, efforts have been directed to study the influence of anchoring groups like carboxylic acid and cyanoacrylic acid for porphyrin [20] as well as phthalocyanine [21] class of NIR dyes, where introduction of cyanoacrylate anchoring group was reported to have the hampered photon harvesting as compared to its carboxylate anchoring group counterparts. To further investigate the effect of anchoring groups on the photophysical behavior in solution as well as after their attachment on the thin nanoporous TiO<sub>2</sub>

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films, three indole based unsymmetrical squaraine dyes (Fig. 1) with varying anchoring groups like carboxylate (**SQ-A**), cyanoacrylate (**SQ-B**) and thiophene bridged cyanoacrylate (**SQ-C**) were synthesized and their photovoltaic characteristics as well as photon harvesting behavior were investigated under similar experimental conditions.

## 2. Experimental

### 2.1. Materials, instruments and methods

All the chemicals for synthesis or solvents are of analytical or spectroscopic grade and used as received without further purification. Flash chromatography was performed using silica gel 60 (230–400 mesh) eluting with solvents as indicated. Purity of all compounds including intermediates and final products were confirmed by high performance liquid chromatography (JASCO). Mass of the intermediates as well as final dyes was confirmed by MALDI-TOF mass (Applied Biosystems) or fast ion bombardment mass (FAB-MS) and high resolution mass (HR-MS) spectra on a JEOL JMS-SX 102A instrument. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM A (500 MHz) spectrometer in CDCl<sub>3</sub> or DMSO-d<sub>6</sub> solvents with reference to tetramethyl silane (TMS) for structural elucidation. All proton NMR signal shifts are given in parts per millions (*s* = singlet; *d* = doublet; *t* = triplet; *m* = multiplet). Electronic absorption spectroscopic investigations in solution and thin film adsorbed on TiO<sub>2</sub> surface were conducted using UV-visible spectrophotometer (JASCO model V550). The highest occupied molecular orbital (HOMO) energy level was measured using photoelectron spectroscopy in air (Riken, model AC3). The lowest unoccupied molecular orbital (LUMO) energy level was determined from the edge of optical absorption considering it as optical band gap (*E<sub>g</sub>*) using the relation LUMO = HOMO + *E<sub>g</sub>*.

### 2.2. Synthesis of SQ-dyes and dye intermediates

Detailed synthesis of all the three unsymmetrical squaraine dyes under present investigation has been shown in the Schemes 1–3 respectively. The dyes **SQ-A** and **SQ-B** bearing carboxylate and cyanoacrylate functionality were synthesized following the methods developed in our earlier reports [10,23]. **SQ-C** bearing thiophene bridged cyanoacrylate has been synthesized by modifying the method developed by Shi et al. [22]. The intermediates 2,3,3-trimethyl-3H-indole-5-carboxylic acid (**4a**) and 3-(5-Bromo-1-butyl-3,3-dimethyl-2,3-dihydroindol-2-ylidenemethyl)-4-hydroxy cyclobut-3-ene-1,2-dione (**10**) were synthesized according to the reported procedures [9,24].

#### 2.2.1. Synthesis of 2,3,3-trimethyl-1-ethyl-3H-indolium iodide [2]

3.17 g (20 mmol) of 2,3,3-trimethyl-3H-indole (**1**) and 4.68 g (30 mmol) of 1-iodoethane were dissolved in 100 mL of dehydrated acetonitrile and reaction mixture was refluxed for 18 h. After completion of the reaction, solvent was evaporated and the crude product was washed with ample diethyl ether giving 5.7 g of titled compound as whitish powder in 91% yield having 99% purity as confirmed by HPLC. FAB-mass, observed [M–Iodine]<sup>+</sup> 188.0 for C<sub>13</sub>H<sub>18</sub>IN (calcd 315.04.13).

#### 2.2.2. Synthesis of 3-butoxy-4-[(1-ethyl-1,3-dihydro-3,3-dimethyl-2H-indole-2-ylidene)methyl]-3-cyclobutene-1,2-dione [3]

In a round bottom flask fitted with condenser, 1.26 g (4 mmol) of compound **2**, 900 mg (4 mmol) of 3,4-dibutoxy-3-cyclobutene-1,2-dione and 0.8 mL of triethylamine were dissolved in 6 mL butanol. Reaction mixture was heated at 70 °C for 1 h leading to green solution. Solvent was removed at rotary evaporator and product was purified by column chromatography (Silica gel) with ethyl acetate and hexane as eluent giving 920 mg of titled compound in 50% yield and 99% purity as confirmed by HPLC. Compound was confirmed by MALDI-TOF-mass, observed [M + H]<sup>+</sup> 340.60 for C<sub>21</sub>H<sub>25</sub>NO<sub>3</sub> (calcd 339.18).

#### 2.2.3. Synthesis of 5-carboxy-2,3,3-trimethyl-1-ethyl-3H-indolium iodide [4a]

820 mg (4 mmol) of 2,3,3-trimethyl-3H-indole-5-carboxylic acid and 3.21 g (20 mmol) of 1-iodoethane were dissolved in 60 mL of dehydrated acetonitrile and reaction mixture was refluxed for 18 h under nitrogen. After the completion of the reaction, solvent was evaporated and the crude product was washed with ample diethyl ether giving 1.14 g of titled compound as off white powder in 79% yield having 98% purity as confirmed by HPLC. FAB-mass, observed [M–Iodine]<sup>+</sup> 232.0 for C<sub>14</sub>H<sub>18</sub>INO<sub>2</sub> (calcd 359.0382).

#### 2.2.4. Synthesis of unsymmetrical squaraine dye SQ-A

Unsymmetrical squaraine dye **SQ-A** was synthesized using semi-squaraine ester (**3**) and compound (**4a**) as follows: In a round bottom flask fitted with condenser, 466 mg (1 mmol) of compound (**3**) was dissolved in 10 mL ethanol followed by 0.54 mL (1.5 mmol) of aqueous NaOH. Reaction mixture was refluxed for 30 min which was then cooled followed by addition of 1 N HCl (3.6 mL) giving compound **4**. Solvent was then removed at rotary evaporator followed by addition of 359 mg (1 mmol) of compound (**4a**) and 20 mL of 1-butanol:toluene mixture (1:1, v/v). Reaction mixture was refluxed for 18 h using Dean-Stark trap. Reaction mixture was cooled, solvent was evaporated and product was purified by silica gel column chromatography using chloroform: methanol as eluting solvent. 350 mg of final titled compound was obtained as blue

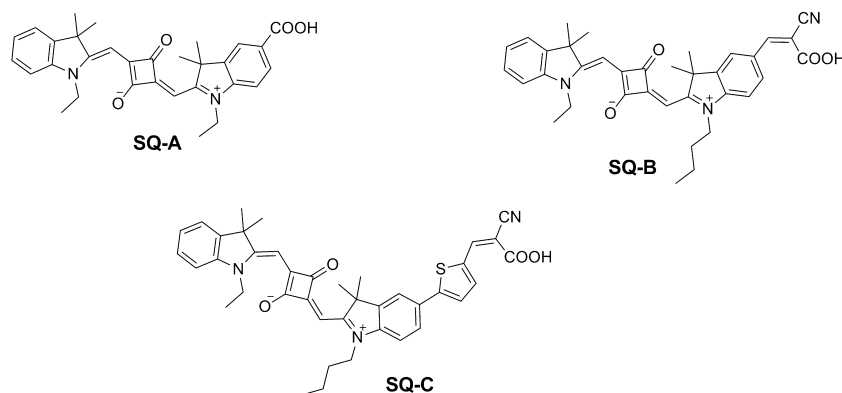


Fig. 1. Structure of unsymmetrical squaraine dyes.

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