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Study on Highly Efficient Organic Sensitizers for Dye-Sensitized Solar Cells Using Novel Squarylium Dyes

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July 2013

Doctoral Thesis at Osaka Prefecture University
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Chapter 1

General Introduction

1.1 Principle of DSSCs

Most of electric power is depend on the resources like oil, natural gas, coal, nuclear power and so on. The fossil fuel resources of oil, natural gas, and coal are non-renewable energy and greenhouse gas emissions come from burning these fossil fuels. The accident of nuclear power plant caused the anxiety against the safety for the operation and radioactivity release. To address a problem like as the carbon resources depletion, the clean energy, especially solar energy has attracted much attention, because it directly converts solar energy into electrical power leaving no environment load.

Nowaday various photovoltaic devices for electricity generation using organic or inorganic raw materials are widely investigated as shown Fig.1. Although silicon- and other semiconductor-based solar cells have dominated the solar cell market for decades, they have a definitive problem of the high module cost. The developments of the organic solar cells are expected to overcome the demerit of conventionally silicon-based crystalline solar cells because of the organic materials having the low productivity cost. In addition, organic materials for photovoltaic devices have been easily designed and synthesized because of the potential of organic materials, such as the facile structural modification. Among all organic solar cells, dye-sensitized solar cells (DSSCs) have attracted considerable interest ever since the breakthrough was made by Grätzel and co-workers.

![Fig. 1. Type of solar cells](image-url)
The general principle of DSSCs is illustrated in Fig.2. The photoactive component in DSSC is a dye adsorbed chemically onto the surface of semiconductor. When sun light hits this surface, the dye absorbs a photon and becomes an excited state; in this state it transfers an electron into the conduction band of TiO$_2$ semiconductor. Electron transport to the anode occurs \textit{via} diffusion of electrons through the disordered network of TiO$_2$ nanoparticles to the glass electrode. The positively charged dye then interacts with iodide ions in the redox mediator iodide/triiodide couple in the bulk electrolyte and is regenerated. The oxidized redox mediator I$_3^-$ is attracted to the counter-cathode where it is reduced back to iodide by electron transfer, and the circuit completed \textit{via} electron migration through the external load. The typical DSSC is constructed as a sandwich of two conducting glass electrodes filled with a redox electrolyte. One of the electrodes, covered with a transparent conducting layer of fluorine-doped tin dioxide, is coated by screen printing a colloidal preparation of mono-dispersed TiO$_2$ particles. The layer is heat treated to reduce resistivity and then soaked in a solution of dye until a dispersion of the dye on the TiO$_2$ is obtained [1].

The performance of DSSCs generally depends on the relative energy levels of the sensitizers and the kinetics of the electron-transfer processes at the interface between the dye bound to the semiconductor surface and the hole-transporting material. In DSSCs, the effective charge separation and an electron transfer after absorption of light are very important. To obtain the highly efficient organic sensitizers for DSSCs, the following five points of view for sensitizers must be considered [2].

I. Absorption range

The sensitizer should absorb over a wide range of the visible region into the
near-infrared (NIR) region. Molar extinction coefficients of sensitizers must be as high as possible to harvest efficient light.

II. Lowest unoccupied molecular orbital (LUMO)
For efficient electron injection into the anode, the LUMO of the sensitized dye should be localized near the anchoring group like as carboxylic group and above the conduction band edge of the semiconductor electrode.

III. Highest occupied molecular orbital (HOMO)
The HOMO of the sensitized dye should be sufficiently low to accept electron donation from an electrolyte or a hole conductive material.

IV. Charge recombination
To minimize charge recombination between the injected electrons and the resulting oxidized dye, the positive charge resulting after electron injection should be localized on the donor part, which is further away from the TiO$_2$ surface.

V. Minimization for aggregation of sensitized dyes
The sensitized dye should not aggregate on the surface to avoid non-radiative decay of the excited state to the ground state, which often occurs with thicker films.

Besides molecular design of sensitized dyes, the addition of deoxycholic acid (DCA) as a coadsorbent and 4-tert-butylpyridine (TBP) as an additive to the electrolyte has been developed to enhance the performance of DSSCs.

1.2 Typical sensitizers for DSSCs
A first paper published in 1991 by Grätzel et al. was the key to turning the DSSCs into a practical reality, and hence they are often called Grätzel cells [3]. Regarding to dyes for DSSCs, there are two categories of metal complex dyes and organic dyes as metal-free dyes. To date the dyes which have proved to be the best performace are all based upon the original bipyridyl ruthenium complex dye known as N3 or N719 or terpyridyl ruthenium complex dye such as the so-called “black-dye” N749 [1]. Though ruthenium complex dyes have provided a relatively high efficiency, there are several drawbacks like as the high cost and the limited amounts of noble metals.

To date organic dyes as alternative metal free sensitizers are also developed and exhibited such many advantages as molecular structural diversity, tunable absorption,
electrochemical properties through suitable molecular design, and high molar extinction coefficients. The development of effective dyes absorbing more wide range of solar radiation from the visible region to the NIR region as shown in Fig.3 is most important to obtain the highest photo-electricity conversion efficiency. For examples, cyanines, merocyanines, hemicyanines, anthocyanines, phthalocyanines, indolines, coumarins, xanthenes, perylenes, triarylamines, and quinolines offer tunable absorption and much higher extinction coefficients in the visible region. Although most of these dyes show modest conversion efficiencies, 8-9% conversion efficiency has been obtained with these organic dyes. Many of sensitizing dyes, including Ru complexes currently being developed, enabling the photoelectric conversion of only the visible light region of 700 nm or less, mainly. In that situation, the proportion of 55% of the solar energy only are used. Therefore, to improve the conversion efficiency of the DSSC, it is necessary to develop a sensitizing dye can be in the near infrared light region of 700 nm-1200 nm that are not yet fully utilized.

Fig. 3. Solar energy distribution
1.2.1 Ruthenium complex dyes

The typical ruthenium complex dyes are shown in Fig. 4. The ruthenium complex dyes are all based upon the bipyridyl ruthenium complex or terpyridyl ruthenium complex [3,4].

The black-dye N749 which has three thiocyanato and one terpyridyl ligands showed the panchromatic sensitization extending to the NIR region up to 920 nm and a 10.4% conversion efficiency under AM 1.5, 100 mW cm$^{-2}$ irradiation [4].

Improving the performance of ruthenium complex dyes entails several approaches [5]. One is to enhance the charge separation in the complex dyes so that charge recombination is minimized, for example, by attaching triphenylamine electron donors onto the bipyridyl rings as in N845. Second is different ways of attaching the complex dye to the TiO$_2$ using acid groups other than carboxylate, such as phosphonates, or by increasing the hydrophobicity of the dye by adding long alkyl groups to the bipyridyl moieties. The latter is coupled with extended conjugation to improve the light-gathering ability of the dyes such as Z991 and C101.

Though the C101 sensitizer maintains stability at efficiency levels over 9% under light soaking at 60 °C for more than 1000 h [6], the thiocyanate groups in N719-type dyes are a source of instability and replacing these by a cyclometalated group, namely 2-phenylpyridine, is said to give dyes with much enhanced stability [1, 7].

![Fig. 4. Ruthenium complex dyes](image-url)
1.2.2 Coumarin dyes

The typical coumarin dyes are shown in Fig. 5. In 2003, the coumarin dyes consisting with a cyanoacrylic unit conjugated by vinylene and thienyl were developed. This type of dyes shows the strong electron-withdrawing ability of cyano and carboxyl group. Though there are some problems of complicated synthesis process and isomerization in the vinylene unit based dye 1, it showed 6.0% efficiency under AM 1.5 G [8]. The thienyl unit based dye 2 exhibited ultrafast electron injection within 100 fs and showed 6.1 – 8.1% overall efficiency under AM 1.5G [9].

![Fig. 5. Coumarin dyes](image)

1.2.3 Indoline dyes

The typical indoline dyes are shown in Fig. 6. Indoline dyes 3 and 4 which introduced an additional rhodanine framework showed 8 - 9.0% conversion efficiency [10, 11]. Suppression of the π-stacked aggregation of the dyes on TiO₂ surface lead to 9.5% conversion efficiency[12].

![Fig. 6. Indoline dyes](image)

1.2.4 Triarylamine dyes

Yanagida and co-workers first synthesized the dyes 6 and 7 as sensitizers for DSSCs [13] as shown in Fig. 7. This type of dyes has been widely investigated and most of them have shown good power efficiencies in DSSCs.

Dimethylfluorenylamino-based organic dye 8 has developed and can ensure greater
resistance to degradation under explosion of light and high temperature. The fluorine-based DSSCs through introducing the alkyl chains into fluorene or \(\pi\)-bridge yielded an overall conversion efficiency of 8.6\% [14].

\[\text{Fig. 7. Triarylamine dyes}\]

\subsection{1.2.5 Carbazole dyes}
Koumur a et al. investigated systematically the effect of a \(\pi\)-conjugated system of 3-hexyl substituted oligothiophenes on DSSCs performance. A DSSCs based on carbazole dye 9 (Fig. 8) consisting of \(n\)-hexyl-substituted quarter-thiophene showed 8.3\% efficiency under simulated AM 1.5 G [15-16].

Optimization of a series of carbazole dyes, especially benzofuro[2,3-c] oxazolo[4,5-a]carbazole-type, revealed that a good electron injection yield is achieved in dye 10, and a carboxyl group plays a role as the electron acceptor but only as the anchoring group for attachment of the dye on the semiconductor surface. This provides a new strategy for the molecular design and synthesis of donor-acceptor \(\pi\)-conjugated dyes for DSSCs [17].

\[\text{Fig. 8. Carbazole dyes}\]

\subsection{1.2.6 N,N-Dialkylaniline dyes}
Organic dyes consisting with $N,N$-dialkylaniline unit as electron donor, methine or thielen as $\pi$-bridge, and cyanoacrylic acid or rhodanine acetic acid as electron acceptor have been developed by Hara and co-workers and an overall power conversion efficiency of 6.8% under AM 1.5 G with a DSSCs was obtained with the $N,N$-dialkylaniline dye 11 (Fig. 9) [18].

1.2.7 Hemicyanine and merocyanine dyes

Hemicyanine dyes consist of basic $p$-dialkylaniline groups as electron donor and cationic moieties as strong electron acceptor linked by methine $\pi$-bridge. The DSSCs fabricated on hemicyanine dyes have been investigated in 2000’s.

Kamat and Arakawa reported the effect of aggregation of merocyaine dyes 12 and 13 (Fig. 10) on DSSC performance and showed the strategy of the molecular design to suppress the dye H-aggregation on the semiconductor surface and improve the photovoltaic properties for DSSCs [19-20].

In benzothiazole merocyanine dyes, there are the relationship of alkyl chains lengths with formation of J-aggregates on TiO$_2$ surfaces, and the relationship of methylene chain lengths between the carboxy unit and the electron donor with H-aggregation. The increase of alkyl length is more facile to form the J-aggregates and thus improves the photovoltaic properties.

Other organic dye including tetrahydroquinoline dye, heteroanthracene dyes and
perylene dyes showed no higher efficiencies on DSSCs

1.3 Squarylium dyes as a sensitizer

1.3.1 Several Applications of squarylium dyes

Squarylium dyes, which consist of an electron-deficient central cyclobutene unit and two electron-donating aromatic / heterocyclic components, are well known for its especial photo-chemical properties, such as intense and sharp light absorption bands in the visible as well as NIR region (Fig. 11). 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 (Fig. 12). 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 unsymmetrical squarylium dyes have been prepared and used in a wide range of applications. Squarylium dyes are more widely recognized for their use in not only organic solar cells but also xerographic application, copy devices, photoconductors, optical recording media[21-24], organic light-emitting diodes [25], protein labels [26], chemosensors [27], noncovalent fluorescent probes for bioanalysis [28], supramolecular architectures [29] and metal probes [30-31] due to electrochromic, electroluminescent and electrophotographic properties.

Fig.11. Features of Squarylium dyes
1.3.2 Squarylium dyes for DSSCs

Squarylium dyes have attracted special interest in recent years for use in solar cells. On the benefits of squarylium dyes, the presence of the rigid squaric ring in the methine chain afforded the dyes with high stability towards cis–trans photoisomerization and resulted in intense absorption in the red/near-infrared region to affect the photo energy conversion. To improve the overall photoelectric conversion efficiency of DSSCs, it is important to use the whole range of the spectrum of sunlight including the visible and the NIR light.

DSSCs with the unsymmetrical dye produced a higher photocurrent, thus resulting in a higher efficiency of the unsymmetrical dye compared to that of symmetrical dye [32]. This effect was ascribed to the unidirectional flow of electrons, which resulted in favorable charge separation and electron injection into the TiO$_2$.

On the deficiency of squarylium dye, the aggregation due to the planar structure of the dye can cause lowering conversion efficiency. The DSSCs fabricated on the indole analogue 14 in Fig 10 showed a higher efficiency of 3.7% in the presence of chenodeoxycholic acid (CDCA) to prevent aggregation of the dye on the surface and a higher VOC value was obtained with tert-butylpyridine in the electrolyte [33].

More recently, the unsymmetric squaraine dye 15 was synthesized in which the carboxylic acid group is directly attached to the chromophore [34]. In an optimized cell with CDCA used as a coadsorbant, a high IPCE of 85% and a JSC value of 10.5 mAcm$^2$ was obtained, which yielded an overall efficiency of 4.5%—the highest for squarylium sensitizers (Fig.13).
The high overall performance was attributed to three factors, which are the basic strategy for the development of the squarylium dye for DSSCs. Firstly, the direct attachment of the carboxylic acid group to the conjugated \( \pi \)-system provides strong electronic coupling to the conduction band of TiO\(_2\) in such a way that electrons unidirectionally flow from the light-harvesting components of the sensitizer to the semiconductor surface. Secondly, the unsymmetry created by the molecular design of dyes prevents surface aggregation and minimizes self-quenching of the excited state. Finally, in order to enable efficient light harvesting with thinner TiO\(_2\) layers, the absorption of all incident light below the near-infrared wavelength of approximately 920nm and high molar extinction coefficient need. 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.

\[ \text{Fig.13. Squarylium dyes} \]

1.3.3 Synthetic strategy

Since the first synthesis of squaraine dyes was reported by Treibs and Jacob in 1965 [35], a lot of squaraine dyes have been developed as a novel class of organic dyes.

Squarylium dyes can be classified into two types depending upon the nature of the 1,3-substituents of cyclobutene core. If the substituents are identical, the dyes are classified as symmetrical squarylium dyes whereas if the substituents are different, the dyes are unsymmetrical squarylium dyes.

Synthesis of squarylium dyes involves double nucleophilic attack over squaric acid. Semisquaraines as intermediates are involved in this preparation. The condensation of semisquaraines with a heterocyclic quaternary salt under typical conditions for squarylium synthesis was expected to afford the basic structure of symmetrical or
unsymmetrical dyes.

Symmetrical squarylium dyes are normally synthesized by condensation of squaric acid and electron rich aromatic or heteroaromatic compounds with activated methyl group in one-step (Scheme 1) [36-37]. Unsymmetrical squarylium dyes are synthesized by a two-step route (Scheme 2) via semisquaraines as an intermediate in which the two pendant aromatic groups are attached in separate reactions[38]. The latter type of squarylium dyes were needed as the sensitizer for DSSCs having the more effective electron injection from carboxyl anchor to the conduction band on TiO$_2$ surface.

To develop the linear $\pi$-extended squarylium, the extension of the squarylium array needs to be accomplished by the introduction of a squaric acid moiety on the iodinated site of the indole ring in the squarylium as a precursor.

According to the Liebeskind’s method [39], the iodinated squarylium was reacted with the tributylstannylsquarate under Pd-catalyzed conditions to afford a squarate-attached squarylium. As the result, the linear $\pi$-extended squarylium was obtained hydrolysis to the corresponding squaric acid derivative and the typical condensation of the derivative with a heterocyclic quaternary salt [40].

![Scheme 1. Synthetic route of Symmetrical squarylium dyes](image1)

![Scheme 2. Synthetic route of Unsymmetrical squarylium dyes](image2)

With respect to the more structural modification of this type dyes, it can be achieved under mild and neutral reaction conditions, which is advantageous for the synthesis of novel squarylium dyes because the influence of the side reaction leading to decomposition of the dye is expected. The mild reaction conditions or an alternative route to escape the decomposition of the dye were reported [41-45].
1.4 Contents of this thesis

With the background mentioned above, it is important to develop new sensitizers for the high power conversion efficiency and the absorption efficiency of the whole range of solar radiation including NIR light of DSSCs by using the novel functionally squarylium dyes. This thesis is aimed at molecular design and synthesis of novel squarylium dye by new synthetic approaches using \( \pi \)-system conjugation. The contents of this thesis are described below.

In Chapter 2, the author shows the synthesis of novel squarylium dyes bearing terminally connected tetracyanoquinodimethane (TCQ), or tetracyanoanthraquinodimethane (TCAQ) as strong electron acceptors and their application as sensitizers for TiO\(_2\)-based DSSCs. Aiming to improve the open-circuit voltage of the DSSC based on squarylium sensitizing dye, by having a strong electron acceptor such as TCAQ to dye molecules end, and selecting the non-\( \pi \)-conjugated linker and a hydroxyl group as the anchor, the author conducted molecular design of squarylium-based diads exhibiting the injection of electrons generated in the donor into titanium oxide efficiently as shown Fig.14. The photovoltaic performance of DSSCs indicates that two chromophores, strong electron acceptors and squarylium components, make independent contributions to photosensitization of nanocrystalline TiO\(_2\). 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\(_2\). 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\(_2\) surface.

![Fig. 14. Molecular design of squaraine dyes bearing terminally connected strong electron-acceptor components](image-url)
Aiming for photoelectric conversion in the NIR region, the author conducted molecular design of π-extended squarylium sensitizing dyes with dicyanovinylene substitution and carboxylic acid as the anchor group introduced into the benzene ring of indolenine (Fig. 15), and examined the effect of dicyanovinylene substitution of sensitizers on performance of DSSC. These results were summarized in Chapter 3 and Chapter 6.

In Chapter 3, the author designed and synthesized near-infrared-absorbing π-extended squarylium-based dyes with dicyanovinylene substitution for dye-sensitized solar cell applications (Fig. 16). Novel π-extended squarylium dyes with dicyanovinylene substitution were synthesized through the Stille-type Pd-catalyzed cross-coupling reaction of a precursory iodinated squarylium dye with tributylstannyl squarate. The DSSCs based on the squarylium dyes displayed remarkable performances in a wide wavelength range from the visible to the near-infrared region around 800 nm. The power conversion efficiencies of the DSSCs based on In-CN-In-S-OH and In-CN-In-S-In-COOH reached 3.5% and 2.1%, respectively.
In Chapter 4, aiming for squarylium sensitizing dye with the extension of the π-conjugated system by introducing linearly squarylium chromophore (Fig. 17), the author designed squarylium dyes with linearly π-extended structures involving three cyclobutene cores and four heterocyclic components as metal-free sensitizing dyes that can enhance spectral responses in the range over 800 nm and successfully synthesized them through the combination of Pd-catalyzed cross-coupling using stannylcyclobutenediones and condensation reactions. The dyes exhibited intense absorption in the NIR region with maxima at around 850 nm and onsets at around 950 nm. Although the HOMO levels remained at the same levels as the corresponding standard squaraine dye, the LUMO levels of the dyes were at lower energies owing to the lowering of the bandgaps of the dyes. The DSSCs based on these dyes exhibiting significantly wide spectral response including the NIR region showed enhanced short-circuit current density. Co-sensitization of the NIR-absorbing dyes with a standard far-red absorbing squaraine dye produced a complementary effect in spectral response, resulting in the increase in short-circuit current density.

![Molecular design of linearly π-extended squaraine sensitizers with responses in the NIR region by the introduction of indolenine semi-squaraine moieties on both ends of the squarylium dye skeleton](image)

In Chapter 5, the author designed and synthesized unsymmetrical squaraine dyes bearing pyrylium and thiopyrylium components (Fig. 18). These dyes exhibited intense absorption in the far-red and near-infrared region in solution and on the TiO₂ surface. Pyrylium dyes SQP4 and SQP12 showed modest conversion efficiencies in DSSCs. A higher open-circuit voltage and short-circuit current density are obtained with pyrylium dye SQP12 having a dodecyl group. The thiopyrylium dye SQTP12 enhanced spectral responses in the range over 700 nm in DSSC. A DFT calculation for SQTP12 revealed that the lowest transition at the NIR region is mainly characterized by HOMO-LUMO excitation.
In Chapter 6, the author synthesized a symmetrical squaraine dye altered to possess dicyanovinylene functionality on a carbonyl group of the cyclobutene core (SQM1a) to elucidate the effects of the conformationally locked-in cis-like form ensured by the steric repulsion of dicyanovinylenes on the performance of dye-sensitized solar cells (DSSCs) through a comparison with an unsymmetrical analogue bearing one carboxy group (SQM1b) and a standard squaraine dye (MSQ) (Fig. 19). The FT-IR spectrum of the TiO$_2$ thin film immersed in the dye solution suggested that the linkages between the dye and TiO$_2$ were formed by both carboxy groups symmetrically incorporated on the pi-conjugation of dyes. The symmetrical and conformationally locked structure of SQM1a brought about a decrease in the non-radiative decay rate, which may have been induced by suppression of the possible photoisomerization of squaraines. In accordance with the finding of non-radiative decay, a DSSC fabricated with SQM1a exhibited a significantly enhanced short-circuit current density, which revealed an efficient electron injection derived from the double-anchored and conformationally locked structure of SQM1a. Consequently, the performance of DSSCs fabricated with SQM1a was higher than the performance of those fabricated with SQM1b and MSQ. This indicates that substantial advantages can be derived by restricting the conformation of symmetrical squaraine dyes.
1.5 References


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Chapter 2

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

2.1 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\(_2\), 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 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 chapter, the author reports the synthesis of novel squarylium dyes bearing terminally connected strong electron-acceptor components and their application as sensitizers for 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 dying conditions.
2.2 Experimental

2.2.1 General

The NMR spectra were obtained using a JEOL JNM LA-400 spectrometer operating at 400 MHz for $^1$H-NMR and 100 MHz for $^{13}$C-NMR. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in 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 mV s$^{-1}$, equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a Ag/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 squarilide 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-3H-indolium iodide (8), were prepared according to the conventional synthesis [48,49]. 7,7,8,8-Tetracyano-p-quinodimethanepropionic acid (4) [50], 3-[2'-(11,11,12,12-tetracyano-9,10-anthraquinodimethane)methoxicarbonyl]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.

2.2.2 Preparation of SQ1-TCQ

2.2.2.1 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; CH$_2$Cl$_2$/MeOH, 20/1, v/v), followed by washing with CH$_2$Cl$_2$ to afford squarylium 2 as a green solid (4.3 g, 49%). Mp 188-190 °C (lit.[53] mp 188–190 °C). $^1$H-NMR (CDCl$_3$): $\delta$ 0.99 (t, $J = 7.2$ Hz, 6H, –CH$_3$), 1.40 (m, 4H, –CH$_2$–), 1.63–1.65 (m, 4H, –CH$_2$–), 3.17 (s, 3H, NCH$_3$), 3.26 (br s, 1H, OH), 3.44 (t, $J = 7.8$ Hz, 4H, NCH$_2$–), 3.68 (t, $J = 5.6$ Hz, 2H, NCH$_2$–), 3.92 (m, 2H, –CH$_2$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). $^{13}$C-NMR (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 cm$^{-1}$. MALDI-TOF MS: m/z 434.19 ([M]$^+$).
2.2.2.2 Compound SQ1-TCQ

7,7,8,8-Tetracyano-p-quinodimethane propanoic 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 CH₂Cl₂ (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; CH₂Cl₂/MeOH, 95/5, v/v), followed by recrystallization, where the crystal was grown by slow diffusion from CHCl₃ solution to acetonitrile. The resulting material was further purified by recrystallization from CHCl₃ to afford SQ1-TCQ as brown crystals (48 mg, 13%). Mp 217 ºC (decomp).

1H-NMR (CDCl₃): δ 1.00 (t, J = 9.0 Hz, 6H, –CH₃), 1.38–1.42 (m, 4H, –CH₂–), 1.63–1.67 (m, 4H, –CH₂–), 2.58 (t, J = 6.0 Hz, 2H, –CH₂–), 3.16 (s, 3H, NCH₃), 3.17 (t, J = 6.0 Hz, 2H, –CH₂–), 3.46 (t, J = 6.0 Hz, 4H, NCH₂–), 3.81 (t, J = 6.0 Hz, 2H, NCH₂–), 4.41 (t, J = 6.0 Hz, 2H, OCH₂–), 6.75 (d, J = 9.0 Hz, 2H, ArH), 6.80 (d, J = 9.0 Hz, 2H, ArH), 7.19 (s, 1H, ArH), 7.32 (d, J = 9.0 Hz, 1H, ArH), 7.51 (d, J = 9.0 Hz, 1H, ArH), 8.28 (d, J = 9.0 Hz, 2H, ArH), 8.38 (d, J = 9.0 Hz, 2H, ArH). IR (KBr): 2216, 2180, 1726, 1610, 1585 cm⁻¹. MALDI-TOF MS: m/z 693.14 ([M+H]+). Anal. Calcd for C₄₂H₄₀N₆O₄•0.5H₂O: C, 71.88; H, 5.89; N, 11.97. Found: C, 71.65; H, 5.84; N, 11.90%.

2.2.3 Preparation of SQ1-TCAQ

3-[2’-(11,11,12,12-Tetracyano-9,10-anthraquinodimethane)methoxicarbonyl]propanic acid (5) (87 mg, 0.20 mmol), EDC-HCl (38 mg, 0.20 mmol), and DMAP (24 mg, 0.20 mmol) were dissolved in CH₂Cl₂ (4 mL). The mixture was stirred for 30 min at room temperature, then squarylium 2 (87 mg, 0.20 mmol) was added and stirred for 1 h at room temperature. The reaction mixture was directly purified by silica gel column chromatography (eluent; CH₂Cl₂/MeOH, 94/6, v/v), followed by recrystallization, where the crystal was grown by slow diffusion from CHCl₃ solution to acetonitrile to afford SQ1-TCAQ as dark green crystals (110 mg, 65%). Mp 217–220 ºC (decomp). 1H-NMR (CDCl₃): δ 0.92 (t, J = 6.0 Hz, 6H, –CH₃), 1.29–1.37 (m, 4H, –CH₂–), 1.50–1.59 (m, 4H, –CH₂–), 2.53 (t, J = 6.0 Hz, 2H, –CH₂–), 2.61 (t, J = 6.0 Hz, 2H, –CH₂–), 3.11 (s, 3H, NCH₃), 3.50 (t, J = 9.0 Hz, 4H, NCH₂–), 3.80 (t, J = 6.0 Hz, 2H, NCH₂–), 4.25 (t, J = 6.0 Hz, 2H, OCH₂), 5.24 (s, 2H, OCH₂), 6.92 (d, J = 6.0 Hz, 2H, ArH), 6.95 (d, J = 6.0 Hz, 2H, ArH), 7.76 (d, J = 9.0 Hz, 1H, ArH), 7.83 (d, J = 6.0 Hz, 1H, ArH), 7.84 (d, J = 6.0 Hz, 1H, ArH), 8.05–8.09 (m, 4H, ArH), 8.15–8.18 (m, 2H, ArH), 8.21–8.25 (m, 2H, ArH). 13C-NMR (DMSO-d₆): δ 13.72, 19.48, 28.41, 28.55, 28.83, 29.21, 38.75, 49.87, 50.20, 50.43, 61.52, 64.26, 82.94, 83.26, 110.67, 112.96, 113.20, 113.90, 113.98, 118.35, 119.10, 125.52, 127.32, 127.40, 127.45, 129.40, 130.01, 130.05, 130.33, 130.60,
131.13, 132.08, 132.16, 140.92, 153.74, 153.90, 159.58, 159.61, 171.54, 171.75, 181.62, 184.84, 186.93. IR (KBr): 3458, 2957, 2927, 2221, 1733, 1610, 1586, 1394, 1356, 1175, 783 cm$^{-1}$. MALDI-TOF MS: m/z 850.28 ([M]$^+$). Anal. Calcd for C$_{52}$H$_{46}$N$_6$O$_6$•0.5H$_2$O: C, 72.63; H, 5.51; N, 9.77. Found: C, 72.67; H, 5.57; N, 9.68%.

Scheme 1.

### 2.2.4 Preparation of SQ1-TCAQH

#### 2.2.4.1 Compound 6

To the solution of squarylium 2 (0.44 g, 1.0 mmol) in CH$_2$Cl$_2$ (50 mL) was added succinic anhydride (0.80 g, 8.0 mmol), DMAP (1.0 g, 8.0 mmol), and pyridine (0.80 g, 10 mmol). The reaction mixture was stirred at room temperature for 3 h, and quenched with ice water and extracted with CHCl$_3$. The organic layer was washed with H$_2$O, dried over MgSO$_4$, and evaporated under reduced pressure. The crude product was purified by silica gel column chromatography (eluent: CH$_2$Cl$_2$/MeOH, 95/5, v/v), followed by recrystallization from CHCl$_3$-acetonitrile to afford 6 as dark green crystals (0.18 g, 33%). Mp 211–213 °C. $^1$H-NMR (DMSO-d$_6$): δ 0.93 (t, J = 6.0 Hz, 6H, –CH$_3$), 1.32–1.40 (m, 4H, –CH$_2$–), 1.53–1.61 (m, 4H, –CH$_2$–), 2.40–2.48 (m, 4H, –CH$_2$–), 3.16 (s, 3H, NCH$_3$), 3.52 (t, J = 6.0 Hz, 4H, NCH$_2$–), 3.83 (t, J = 6.0 Hz, 2H, NCH$_2$–), 4.27 (t, J = 6.0 Hz, 2H, NCH$_2$–), 6.96-6.99 (m, 4H, ArH), 8.12 (d, J = 9.0 Hz, 2H, ArH), 8.14 (d, J = 9.0 Hz, 2H, ArH), 12.2 (br s, 1H, OH). $^{13}$C-NMR (DMSO-d$_6$): δ 13.72, 19.48, 28.51, 28.67, 29.21, 38.91, 50.31, 50.42, 61.41, 112.98, 113.24, 118.38, 119.11, 131.15, 132.10, 153.76, 153.87, 172.03, 173.28, 181.63, 184.93, 187.02. IR (KBr): 3451, 2956, 2927, 1733, 1593, 1388, 1360, 1187, 786 cm$^{-1}$. MALDI-TOF MS: m/z 534.30 ([M]$^+$). Anal. Calcd for C$_{31}$H$_{38}$N$_2$O$_6$•0.5H$_2$O: C, 68.49; H, 6.96; N, 5.05%. Found: C, 68.81; H, 7.23; N, 5.15.
2.2.4.2 **Compound SQ1-TCAQH**

Compound 3 (53 mg, 0.10 mmol), EDC-HCl (19 mg, 0.10 mmol), and DMAP (12 mg, 0.10 mmol) were dissolved in THF (4 mL). The mixture was stirred for 20 min, and then added 2,6-dihydroxy-11,11,12,12-tetracyanoanthraquinodimethane (7) (34 mg, 0.10 mmol). After stirring for 15 h at room temperature, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CH$_2$Cl$_2$/MeOH, 98/2, v/v), followed by recrystallization from acetonitrile to afford **SQ1-TCAQH** as blue crystals (46 mg, 53%). Mp 235 ºC (decomp).

$^1$H-NMR (DMSO-$d_6$): δ 0.93 (t, $J = 6.0$ Hz, 6H, –CH$_3$), 1.30–1.41 (m, 4H, –CH$_2$–), 1.52–1.63 (m, 4H, –CH$_2$–), 2.65 (t, $J = 6.0$ Hz, 2H, –CH$_2$–), 2.87 (t, $J = 6.0$ Hz, 2H, –CH$_2$–), 3.15 (s, 3H, NCH$_3$), 3.52 (t, $J = 6.0$ Hz, 4H, NCH$_2$), 3.86 (t, $J = 6.0$ Hz, 2H, NCH$_2$), 4.28–4.35 (m, 2H, OCH$_2$–), 6.96 (d, $J = 6.0$ Hz, 2H, ArH), 6.99 (d, $J = 6.0$ Hz, 2H, ArH), 7.18–7.23 (m, 1H, ArH), 7.56 (dd, $J = 3.0$, 9.0 Hz, 1H, ArH), 7.59–7.65 (m, 1H, ArH), 7.92 (d, $J = 3.0$ Hz, 1H), 8.10 (d, $J = 9.0$ Hz, 1H, ArH), 8.08–8.12 (m, 1H, ArH), 8.13 (d, $J = 6.0$ Hz, 2H, ArH), 8.24 (d, $J = 6.0$ Hz, 2H, ArH), 11.3 (br s, 1H, –OH).

$^{13}$C-NMR (DMSO-$d_6$): 13.73, 19.49, 28.60, 28.73, 28.92, 29.22, 50.25, 50.44, 61.68, 80.53, 83.03, 113.00, 113.25, 113.85, 114.09, 114.22, 114.42, 118.37, 118.84, 119.11, 120.36, 120.46, 125.09, 127.67, 129.17, 129.96, 131.12, 132.13, 132.34, 132.38, 152.27, 153.79, 155.79, 158.85, 159.26, 160.98, 170.38, 171.63, 181.62, 184.84, 187.06. IR (KBr): 3435, 2958, 2928, 2224, 1587, 1384, 1361, 1179, 785 cm$^{-1}$. MALDI-TOF MS: $m/z$ 852.50 ([M]$^+$).

Anal. Calcd for C$_{51}$H$_{44}$N$_6$O$_7$ ·H$_2$O: C, 70.33; H, 5.32; N, 9.65. Found: C, 70.53; H, 5.19; N, 9.42%.

![Scheme 2](image-url)
2.2.5 Preparation of SQ2-TCAQH

2.2.5.1 Compound 9

Compound 1 (0.25 g, 0.83 mmol) and 1-(2-hydroxyethyl)-2,3,3-trimethyl-3H-indolium bromide (8) (0.23 g, 0.82 mmol) were dissolved in a mixture of 1-butanol (24 mL) and benzene (6 mL) under Ar atmosphere. Then a few drops of quinoline were added and the solution was heated at 100 ºC for 4 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/MeOH, 10/1, v/v), and dried to afford 9 as a green crystal (0.10 g, 25%). Mp 225 ºC.

1H NMR (CDCl₃): $\delta$ 0.98 (t, $J = 6.0$ Hz, 6H, –CH₃), 1.33–1.42 (m, 4H, –CH₂–), 1.56–1.65 (m, 4H, –CH₂–), 1.70 (s, 6H, –CH₃), 3.38 (t, $J = 6.0$ Hz, 4H, NCH₂–), 4.09 (t, $J = 6.0$ Hz, 2H, NCH₂–), 4.48 (t, $J = 6.0$ Hz, 2H, OCH₂–), 4.72 (s, 1H, OH), 6.12 (s, 1H, =CH–), 6.67 (d, $J = 9.0$ Hz, 2H, ArH), 7.21–7.26 (m, 2H, ArH), 7.34–7.39 (m, 2H, ArH), 7.52–7.60 (m, 1H, ArH), 7.60–7.66 (m, 1H, ArH), 8.03 (d, $J = 9.0$ Hz, 2H, ArH), 12.08 (s, 1H, –OH).

2.2.5.2 Compound 10

This compound was synthesized by a similar procedure to the preparation of 6. The crude product was purified by silica gel column chromatography (eluent; CH₂Cl₂/MeOH, 95/5, v/v), and the resulting product was used in next step without further purification. Yield 65%. 1H-NMR (DMSO-d₆): $\delta$ 0.93 (t, $J = 6.0$ Hz, 6H, –CH₃), 1.35 (m, 4H, –CH₂–), 1.55 (m, 4H, –CH₂–), 1.72 (s, 6H, CH₃), 2.29 (m, 4H, –CH₂–), 3.40 (m, 4H, NCH₂–), 4.50 (m, 2H, NCH₂–), 4.60 (m, 2H, OCH₂–), 6.13 (s, 1H, =CH–), 6.81 (d, $J = 9.0$ Hz, 2H, ArH), 7.29–7.35 (m, 1H, ArH), 7.41–7.48 (m, 1H, ArH), 7.52–7.60 (m, 1H, ArH), 7.60–7.66 (m, 1H, ArH), 8.03 (d, $J = 9.0$ Hz, 2H, ArH), 12.08 (s, 1H, –OH).

Scheme 3.
2.2.5.3 **SQ2-TCAQH**

This compound was obtained by a similar procedure for the preparation of **SQ1-TCAQH**. Yield 13%. Mp 230 °C (decomp). $^1$H-NMR (DMSO-$d_6$): $\delta$ 0.98 (t, $J = 6.0$ Hz, 6H, –CH$_3$), 1.31–1.44 (m, 4H, –CH$_2$–), 1.52–1.65 (m, 4H, –CH$_2$–), 1.84 (s, 6H, –CH$_3$), 2.57–2.70 (m, 2H, –CH$_2$–), 2.75–2.90 (m, 2H, –CH$_2$–), 3.41 (t, $J = 6.0$ Hz, 4H, NCH$_2$), 4.40–4.68 (m, 4H, –NCH$_2$CH$_2$O–), 6.28 (s, 1H, =CH–), 6.74 (d, $J = 9.0$ Hz, 2H, ArH), 7.06 (dd, $J = 9.0$, 3.0 Hz, 1H, ArH), 7.17–7.22 (m, 1H, ArH), 7.28–7.33 (m, 1H, ArH), 7.35-7.45 (m, 3H, ArH), 7.68 (s, 1H, ArH), 7.85 (d, $J = 9.0$ Hz, 1H, ArH), 8.05-8.08 (m, 2H, ArH), 8.27 (d, $J = 9.0$ Hz, 2H, ArH), 12.92 (br s, 1H, OH). IR (KBr): 2953, 2926, 2226, 1605, 1558, 1522, 1420, 1312, 1178 cm$^{-1}$. MALDI-TOF MS: $m/z$ 904.36 ([M]+). HRMS (FAB): calc for C$_{55}$H$_{49}$N$_6$O$_7$ (**SQ1-TCAQH** + H$^+$) $m/z$ 905.3663; found $m/z$ 905.3668.

![Scheme 4](image)

2.2.6 **General procedure for fabrication of the nanocrystalline TiO$_2$ solar cells**

Transparent TiO$_2$ photoelectrodes (~12 μm thick, 5 mm × 5 mm) were fabricated by screen-printing. Nanocrystalline TiO$_2$ paste [PST-18NR (particle size; ca. 20 nm), JGC Catalysts and Chemicals Ltd, Japan] was printed twice on the F-doped SnO$_2$ substrate (Nippon Sheet Glass, 4 mm thick). After drying 125 °C for 10 min, TiO$_2$ paste consisting of large TiO$_2$ particle (ca. 400 nm, JGC Catalysts and Chemicals Ltd, Japan) was coated on it as a scattering center. The resulting substrate was gradually heated and sintered at 500 °C for 15 min. After cooling, the sintered TiO$_2$ films with an area of 0.25 cm$^2$ were impregnated in a 40 mM TiCl$_4$ aqueous solution at 70 °C for 30 min and then washed with distilled water and methanol. After drying under reduced
pressure, treated TiO$_2$ films were sintered again at 500 ºC for 30 min. The resulting TiO$_2$ photoelectrodes were immersed in a solution of dyes (0.12 mM) and chenodeoxycholic acid (CDCA, 6 mM) in $t$-BuOH/acetonitrile and then kept at ambient temperature overnight, followed by washing with acetonitrile to remove non-adsorbed dye. In case of CDCA-free condition, TiO$_2$ photoelectrodes were dyed at 80 ºC for 1 h. The dye-adsorbed TiO$_2$ film and a Pt-coated ITO grass substrate were separated by Teflon spacer (25 µm thick), which had tiny two cuts for injection of the electrolyte and then clipped. The electrolyte consisting of 0.24 M 1,2-dimethyl-3-$n$-propylimidazolium iodide (DMPI$_3$ImI), 0.07 M LiI, and 0.018 M I$_2$ in CHCl$_3$/acetonitrile (1/1, v/v) was introduced into the interspace between the TiO$_2$ photoelectrode and the Pt counter electrode to obtain the sandwich cell.

2.2.7 Photovoltaic measurements of the solar cells

The photovoltaic performance of the DSSC was measured by using AM 1.5 solar simulator (CEP-2000, Bunko-Keiki, Japan) equipped with a source meter (Keithley 2400). The incident light intensity was calibrated with a standard Si solar cell. To prevent an over estimation of the energy conversion efficiency, a black mask was used. The incident photon-to-current conversion efficiency (IPCE) was measured using an action spectrum measurement system connected to a solar simulator (CEP-2000, Bunko-Keiki, Japan).

2.3 Results and discussion

2.3.1 Synthesis of squarylium-based diads

The $N,N$-dialkylanilino-squaraine bearing a hydroxyl group 2 was prepared by condensation of aniline derivative 3 with a monocondensation product of squaric acid and $N,N$-dibutylaniline 1 (Scheme 1). Then, squarylium 2 was reacted with a TCQ derivative bearing a carboxylic acid 4 to obtain the squarylium-TCQ diad (SQ1-TCQ). The squarylium-TCAQ diad (SQ1-TCAQ) was also prepared from squarylium 2 and a TCAQ derivative with a carboxyl group 5 (Scheme 2). The squarylium-TCAQ diad having a hydroxyl group (SQ1-TCAQH) was prepared by the condensation of a precursor dye 6 prepared from 2 and succinic anhydride with 2,6-dihydroxy-11,11,12,12-tetracyanoanthraquinodimethane 7 (Scheme 3). In order to examine the effect of the dye structure on photosensitization of TiO$_2$, a squarylium dye consisting of $N,N$-dibutylaniline and 1-(2-hydroxyethyl)-2,3,3-trimethylindolium was used as a dye component for the squarylium-TCAQ diad (Scheme 4). The condensation reaction of the semisquarylium 1 with the corresponding indolium salt under azeotropic
conditions in the presence of quinoline afforded the desired squarylium dye with a hydroxyl group 9. Squarylim 9 was converted to the carboxy precursor 10. Then, the nonsymmetrical squarylium-TCAQ diad with a phenolic hydroxyl group (SQ2-TCAQH) was successfully synthesized by the condensation of 10 with TCAQ derivative 7.

2.3.2 Light-absorbance, fluorescent emission, and electrochemical properties of squarylium-based diads

The absorption spectra of the obtained dyes in CHCl₃ (5.0 μM) at 298 K are displayed in Fig. 2a, and the detailed absorption properties are summarized in Table 1. Diads consisting of anilino-squarylium (SQ1-TCQ, SQ1-TCAQ, and SQ1-TCAQH) exhibited almost the same absorption properties, except for the absorption band for electron-accepting components. These dyes have absorption maxima at 632-633 nm with a molar absorption coefficient (ε_{abs}) of 3.3-3.5 × 10⁵ M⁻¹ cm⁻¹. SQ2-TCAQH exhibited the absorption maximum at a slightly longer wavelength and its molar absorption coefficient (ε_{abs}) was 2.7 × 10⁵ M⁻¹ cm⁻¹. In addition to sharp absorption of the corresponding squarylium component, absorptions corresponding to the TCQ and TCAQ moieties were also observed. Squarylium dyes having the TCAQ moiety showed a broad absorption at less than 500 nm.

Thus, all dyes exhibited an intense and sharp absorption in the far-red region. The fluorescence emission spectra of the obtained dyes are shown in Fig. 2b. These dyes exhibited fluorescence emissions at almost the same wavelength with a small Stokes’ shifts.
Fig. 2. Electronic absorption (a) and fluorescence emission spectra (b) of SQ1-TCQ (gray), SQ1-TCAQ (dotted), SQ1-TCAQH (plain), and SQ2-TCAQH (bold) in CHCl₃ at 298 K. Dye concentrations were adjusted to 5.0 μM.

To get an efficient charge separation, the LUMO of the dye should be more negative than the conduction band edge of TiO₂ (Eₑcb), and the HOMO of the dye should be more positive than the redox potential of I⁻/I₃⁻. Based on the cyclic voltammetry measurement, the first oxidation potential (Eₒx) corresponding to the HOMO level of SQ2-TCAQH (0.69 V vs NHE) was sufficiently more positive than the I⁻/I₃⁻ redox potential. In addition, the LUMO level estimated by the HOMO level and the 0-0 transition energy calculated from the wavelength where the normalized absorption and fluorescence spectra intersect (–1.18 V vs NHE) was also sufficiently more negative than the Eₑcb (–0.5 V vs NHE) [54].
Table 1. Electronic absorption data of squarylium derivatives (5 × 10^6 M in CHCl₃, 298 K)

<table>
<thead>
<tr>
<th>Dye</th>
<th>( \lambda_{\text{abs}} / \text{nm} )</th>
<th>( \lambda_{\text{em}} / \text{nm} )</th>
<th>( \varepsilon_{\text{abs}} / \text{M}^{-1} \text{cm}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ1-TCQ</td>
<td>633</td>
<td>656</td>
<td>350000</td>
</tr>
<tr>
<td>SQ1-TCAQ</td>
<td>632</td>
<td>656</td>
<td>340000</td>
</tr>
<tr>
<td>SQ1-TCAQH</td>
<td>633</td>
<td>655</td>
<td>329000</td>
</tr>
<tr>
<td>SQ2-TCAQH</td>
<td>637</td>
<td>665</td>
<td>271000</td>
</tr>
</tbody>
</table>

2.3.3 Photovoltaic performance of DSSCs sensitized with squarylium-based diads

To investigate the photovoltaic properties, DSSCs sensitized with squarylium-based diads were prepared using nanocrystalline TiO₂ photoelectrodes. The open-circuit photovoltage \((V_{\text{oc}})\), short-circuit photocurrent density \((J_{\text{sc}})\), fill factor \((\text{ff})\), and solar-to-electrical energy conversion efficiencies \((\eta)\) of DSSCs are summarized in Table 2.

Table 2. Photovoltaic performance of DSSCs conducted using squarylium-based dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>( J_{\text{sc}} / \text{mA cm}^{-2} )</th>
<th>( V_{\text{oc}} / \text{V} )</th>
<th>Fill factor</th>
<th>( \eta / % )</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ1-TCQ</td>
<td>0.81</td>
<td>0.53</td>
<td>0.65</td>
<td>0.28</td>
</tr>
<tr>
<td>SQ1-TCAQ</td>
<td>0.39</td>
<td>0.46</td>
<td>0.64</td>
<td>0.11</td>
</tr>
<tr>
<td>SQ1-TCAQH</td>
<td>1.26</td>
<td>0.55</td>
<td>0.66</td>
<td>0.46</td>
</tr>
<tr>
<td>SQ2-TCAQH</td>
<td>2.36</td>
<td>0.66</td>
<td>0.71</td>
<td>1.10</td>
</tr>
</tbody>
</table>

*Conditions: irradiated light, AM 1.5 (100 mW cm⁻²); dying condition, 120 \( \mu \text{M} \) dyes and 6 mM CDCA in acetonitrile/t-BuOH at room temperature.

The photon-to-current conversion efficiencies (IPCE) and the current density-voltage \((J-V)\) curves are shown in Fig. 3a and 3b, respectively. Action spectra of IPCEs for SQ1-TCQ and SQ1-TCAQ exhibited quite low values, indicating that squarylium dyes without hydroxyl groups were ineffective for sensitization of TiO₂. In contrast, SQ1-TCAQH and SQ2-TCAQH, which have hydroxyl groups on TCAQ components, gave higher IPCE values in the range from 500 to 700 nm than the dyes without hydroxyl groups. Therefore, the hydroxyl groups of SQ1-TCAQH and SQ2-TCAQH play an important role as the anchoring groups for the TiO₂ surface. The similarity between the IPCE spectra and the absorption spectra of SQ1-TCAQH and SQ2-TCAQH indicated that the photocurrent was attributable to the photosensitizing effect of squarylium-based diads. The photovoltaic performance for DSSCs based on the nonsymmetrical squarylium-based diad SQ2-TCAQH was superior to that of the symmetrical squarylium-based diad SQ1-TCAQH.
Fig. 3. Spectra of incident photon-to-current conversion efficiency (IPCE) (a) and $J-V$ curves (b) of DSSCs prepared with SQ1-TCQ (gray), SQ1-TCAQ (dotted), SQ1-TCAQH (plain), and SQ2-TCAQH (bold).

Das et al. pointed out the importance of the nonsymmetrical structure of squaryliums for the efficient electron injection originating from unidirectional electron flow from dyes to the TiO$_2$ conduction band [42]. In the nonsymmetrical squarylium dyes consisting of $N,N$-dialkylaniline and heterocyclic components linked through the methylene spacer, it is noted that the HOMO-LUMO excitation moved the electron distribution from the $N,N$-dialkylaniline moiety to the heterocycle with the methylene spacer. In the case of SQ2-TCAQH, these effects based on the nonsymmetrical structure of squaryliums should contribute to the photovoltaic performance. Although the $\eta$ value and $J_{sc}$ value of the DSSC based on SQ2-TCAQ were still low, a $V_{oc}$ value
of 0.66 V was achieved, which was the highest $V_{oc}$ value obtained so far among squarylium dye-based DSSCs. This might imply that the diad structure comprised of the strong electron-accepting component and the light-harvesting squarylium component contributed to the unidirectional flow of electrons from the light-harvesting components of the sensitizer to the semiconductor surface and thereby minimized the charge recombination of injected electrons with dye cations and $I_3^-$.  

2.3.4 Dying conditions for DSSCs sensitized with squarylium-based diads  

In general, acids such carboxylic acid or phosphoric acid are used as the anchoring units for adsorption of dyes onto the TiO$_2$ surface. In the case of squarylium-based diads, the hydroxyl group on the TCAQ component should work as an anchoring unit for adsorption of the squarylium-based diad SQ2-TCAQH onto the TiO$_2$ surface. DSSCs based on SQ2-TCAQH were prepared by dying with CDCA as a coadsorbent to prevent dye aggregation on the surface. However, this method would be ineffective for adequate absorption of the dye due to low loading of the dye and preferential adsorption of CDCA stemming from the lower acidity of the hydroxyl group relative to that of the carboxylic acid of CDCA. To improve the dye adsorption on the TiO$_2$ surface, DSSCs were prepared by dying at 80ºC without CDCA and their photovoltaic performances were evaluated (Table 3).

Table 3. The effect of dying concentration upon photovoltaic performance of SQ2-TCAQH-based DSSCs

<table>
<thead>
<tr>
<th>Dye conc. (μM)</th>
<th>$J_{sc}$/mA cm$^{-2}$</th>
<th>$V_{oc}$/V</th>
<th>Fill factor</th>
<th>$\eta$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>2.51</td>
<td>0.40</td>
<td>0.55</td>
<td>0.55</td>
</tr>
<tr>
<td>60</td>
<td>2.78</td>
<td>0.41</td>
<td>0.62</td>
<td>0.71</td>
</tr>
<tr>
<td>30</td>
<td>2.89</td>
<td>0.43</td>
<td>0.63</td>
<td>0.78</td>
</tr>
<tr>
<td>15</td>
<td>4.33</td>
<td>0.47</td>
<td>0.65</td>
<td>1.31</td>
</tr>
<tr>
<td>10</td>
<td>3.48</td>
<td>0.45</td>
<td>0.62</td>
<td>0.97</td>
</tr>
</tbody>
</table>

$^a$ Conditions: irradiated light, AM 1.5 (100 mW cm$^{-2}$); dying condition, in acetonitrile/ $t$-BuOH at 80 °C without CDCA.

First, we examined the influence of the concentration of SQ2-TCAQH on the efficiency of the DSSC. The $\eta$ value increased with decreasing concentration of the dye and reached a peak at 15 μM. Fig. 4 shows the absorption spectra of SQ2-TCAQH in CHCl$_3$ and on TiO$_2$ films prepared from 15 and 30 μM solutions of SQ2-TCAQH. The absorption spectra of SQ2-TCAQH on TiO$_2$ were broadened compared to those of the solution state, indicating strong interactions between the dyes and the TiO$_2$ surface. In a
TiO$_2$ film dying at 30 μM, a seriously broadened and blue-shifted strong absorption was clearly observed. This absorption would be attributable to H-type aggregation of dyes on the TiO$_2$ surface, which would allow the quenching process between the aggregated dyes [55].

Thus, the decrease of the $\eta$ value of DSSCs dyed at concentrations of 30 μM or higher was due to the aggregation effect. Interestingly, the broad peak around 475 nm was newly observed in the action spectra of IPCE as a result of the change in dying conditions (Fig. 5).

![Absorption spectra of SQ2-TCAQH adsorbed on a TiO$_2$ film at various dyeing concentrations: 15 μM (solid) and 30 μM (gray).](image1)

**Fig. 4.** Absorption spectra of SQ2-TCAQH adsorbed on a TiO$_2$ film at various dyeing concentrations: 15 μM (solid) and 30 μM (gray).

![IPCE for SQ2-TCAQH-based DSSCs dyed in various dye concentration without CDCA as a coadsorbent.](image2)

**Fig. 5.** IPCE for SQ2-TCAQH-based DSSCs dyed in various dye concentration without CDCA as a coadsorbent.
Segawa et al. reported a DSSC based on the charge-transfer complex of tetracyanoquinodimethane derivatives with TiO$_2$ [56]. They pointed out that the charge-transfer complex was formed by the nucleophilic addition of hydroxyl groups on TiO$_2$ to TCQ moieties. In addition, Houlding and Grätzel reported that 8-hydroxyquinoline was chemically absorbed onto anatase TiO$_2$ to give a broad absorption spectrum in the visible region [57]. The peak at around 475 nm in the IPCE spectrum of SQ2-TCAQH-based DSSC might originate from these chemical species on TiO$_2$ derived from the TCAQ component. The $J_{sc}$ value was significantly improved as a result of the photosensitizing effect at the TCAQ component. The conversion efficiency $\eta$ was improved in response to an increase in the $J_{sc}$ value, although $V_{oc}$ was somewhat reduced by the change in dyeing conditions. Furthermore, SQ2-TCAQH-based DSSC prepared by pretreating the TiO$_2$ photoelectrode with triethylamine and then thoroughly rinsing the triethylamine away exhibited the highest $J_{sc}$ and $\eta$ values (Fig. 6, Table 4).

![Image](image_url)

**Fig. 6.** IPCE spectra (a) and $J$-$V$ curves (b) obtained with DSSCs based on SQ2-TCAQH (solid), SQ1-TCQ (dotted), and SQ1-TCAQ (broken) with the pretreated TiO$_2$ photoelectrode
Table 4. Photovoltaic performance of squarylium-based DSSCs prepared in CDCA-free condition\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Dyes</th>
<th>Dye conc. ((\mu)M)</th>
<th>(J_{sc}/\text{mA cm}^{-2})</th>
<th>(V_{oc}/\text{V})</th>
<th>Fill factor</th>
<th>(\eta/%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ2-TCAQH</td>
<td>15</td>
<td>7.77</td>
<td>0.50</td>
<td>0.59</td>
<td>2.29</td>
</tr>
<tr>
<td>SQ1-TCQ</td>
<td>15</td>
<td>3.51</td>
<td>0.47</td>
<td>0.63</td>
<td>1.03</td>
</tr>
<tr>
<td>SQ1-TCAQ</td>
<td>60</td>
<td>3.18</td>
<td>0.48</td>
<td>0.63</td>
<td>0.95</td>
</tr>
<tr>
<td>SQ1-TCAQ</td>
<td>15</td>
<td>2.12</td>
<td>0.43</td>
<td>0.60</td>
<td>0.55</td>
</tr>
<tr>
<td>SQ1-TCAQ</td>
<td>60</td>
<td>2.81</td>
<td>0.37</td>
<td>0.64</td>
<td>0.67</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Conditions: irradiated light, AM 1.5 (100 mW cm\(^{-2}\)). \textsuperscript{b} Using a TiO\(_2\) photoelectrode pretreated with triethylamine; dying condition, in acetonitrile/t-BuOH at 80 °C without CDCA.

In the action spectra, the IPCEs of 600 to 700 nm originating from the squarylium components were enhanced significantly. Thus, the photovoltaic performance of the DSSC with SQ2-TCAQH showed two independent contributions from the TCAQ chromophore and squarylium chromophore. DSSCs prepared with SQ1-TCQ and SQ1-TCAQ as sensitizers and CDCA as coadsorbent exhibited low performance due to quite low loading of dyes on TiO\(_2\) caused by the lack of hydroxyl groups. In the CDCA-free condition, however, these dyes can moderately adsorb on TiO\(_2\) surface. Absorption of squarylium components increased with increasing the dyeing concentration, although TiO\(_2\) films treated with the 15 \(\mu\)M solution of SQ1-TCQ or SQ1-TCAQ exhibited little absorption in the far-red region (Fig. 7). Unlike the results of SQ2-TCAQH, which showed absorption arising from the aggregation on TiO\(_2\) in the 30 \(\mu\)M condition as shown in Fig. 4, absorption indicating the aggregation of SQ1-TCQ and SQ1-TCAQ was slightly observed in the 60 \(\mu\)M condition. The photovoltaic performances of cells dyed with SQ1-TCQ and SQ1-TCAQ in the CDCA-free condition were improved compared with DSSCs containing CDCA with increase in the adsorbed amount (Table 4, Fig. 6). The efficiencies of SQ1-TCQ and SQ1-TCAQ increased up to 1.03 % and 0.67 %, respectively. In their IPCE spectra, peaks originated from the contribution of the TCQ or TCAQ chromophore were observed in addition to the squarylium chromophore. However, IPCE values in far-red region were relatively low compared to those at ca. 475 nm. These results indicated that TCQ and TCAQ components are involved in adsorption of dyes on the TiO\(_2\) surface and independently contribute to photoelectric conversion. Meanwhile, the DSSC prepared with SQ2-TCAQH in the CDCA-free condition have IPCE maximum at the absorption region of the squarylium component. This result indicates that two chemical species on the TiO\(_2\) surface such as the dye anchored by the hydroxyl group and anchored through the interaction of TCAQ component with TiO\(_2\) independently contribute the
photoelectric conversion.

![Absorption spectra of TiO$_2$ films treated with solutions of SQ1-TCQ and SQ1-TCAQ.](image)

**Fig. 7.** Absorption spectra of TiO$_2$ films treated with solutions of SQ1-TCQ and SQ1-TCAQ.

### 2.4 Conclusions

The author has demonstrated the design and synthesis of novel squarylium dyes bearing strong electron acceptors as photosensitizers for application to DSSCs. Tetracyanoquinodimethane and tetracyanoanthraquinodimethane moieties with/without hydroxyl groups were used as acceptor components and were incorporated into three squarylium dyes with $N_N$-dialkylanilines at the 1,3-position of the cyclobutene core. A nonsymmetrical squarylium dye, having a $N_N$-dialkylaniline and an indolinium moiety on the cyclobutene ring with an ester linking group was also obtained resulting in a total of four squarylium-based diads. The squarylium-based diads exhibited intense absorption bands in the far-red region together with weak absorption bands attributed to acceptor components. The squarylium-based diads having a hydroxyl group were successfully adsorbed on nanocrystalline TiO$_2$, and DSSCs fabricated from them exhibited a high $V_{oc}$ value (0.66 V), whereas the $J_{sc}$ and $\eta$ values were still low. These results strongly suggest that the electron-accepting components had effects on the electron injection from the light-harvesting squarylium components to the conduction band of the TiO$_2$. In the case of the DSSCs prepared without the incorporation of the CDCA, the $J_{sc}$ and $\eta$ values of photovoltaic cells were improved by the contribution of the photosensitizing effect in the range of wavelength derived from the TCQ and TCAQ chromophore, rather than the squarylium chromophore. This peculiar property implies
that TCAQ moieties may act as anchoring units for the TiO$_2$ surface. Our results suggest that photovoltaic cells using squarylium-based diads showed two independent contributions from the TCAQ chromophore and squarylium chromophore under optimized conditions.
2.5 References


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Chapter 3
Near-infrared-absorbing π-extended squarylium-based dyes with dicyanovinylene substitution for dye-sensitized solar cell applications

3.1 Introduction

Dye-sensitized solar cells (DSSCs) are attracting much attention as high-efficiency, cost-effective, and substantial photovoltaic cells [1, 2]. In these cells, the most successful charge-transfer sensitizers to date are ruthenium polypyridyl complexes, yielding 9-11% efficiencies under AM 1.5 G irradiation [3]. The early ruthenium polypyridyl complexes exhibited absorptions in a narrow range in the visible region around 535 nm, leading to limited spectral responses of the DSSCs based on them [4]. For an increase in the power conversion efficiency of the DSSCs, it is important to use the whole range of solar radiation, including visible and near-infrared (NIR) light. DSSCs sensitized with “Black dye” having a terpyridyl ligand showed a broader absorption range from the visible to the NIR region, and a high overall efficiency due to the efficient panchromatic photosensitization of nanocrystalline TiO$_2$ [5]. Therefore, the development of novel sensitizing dyes exhibiting spectral responses in the NIR region is required for the improvement of the photovoltaic performances of DSSCs. Metal-free organic dyes as alternative sensitizers to Ru complexes have certain advantages, including high molar absorption coefficients, flexibility of molecular design, and tunable absorption properties, which make them more cost-effective [6, 7].

Squarylium dyes are well known for their intense absorption in the red / NIR regions and their flexibility for synthetic manipulation [8-10]. Nazeeruddin et al. achieved a high conversion efficiency (η = 4.5%) through the use of an unsymmetrical indole-based squarylium dye bearing carboxylic groups attached directly to the indole components [11]. Squarylium sensitizers possessing absorption properties in the NIR region were synthesized through the incorporation of π-extended heterocyclic components with the cyclobutene core [12-14]. We previously reported NIR-absorbing squarylium sensitizers with linearly extended π-conjugation prepared by the Pd-catalyzed cross-coupling of tributylstannyl squarate and terminally iodinated squarylium dyes followed by condensation with an electron-rich heterocycle with activated methyl groups [15]. The organometallic C-C coupling can be achieved under mild and neutral reaction conditions, which is advantageous for the synthesis of novel NIR-absorbing squarylium dyes because the influence of the side reaction leading to decomposition of the dyes is expected to be reduced [16]. The substitution of one carbonyl group in the cyclobutene core with a dicyanovinylene group exhibiting
attractive electron-accepting character promises a red shift in the absorption. Therefore, dicyanovinylene substitution can be used as an auxiliary method for obtaining NIR-absorbing squarylium sensitizers [17-19].

In this present chapter, the author reports the synthesis, absorption, and electronic properties of novel π-extended squarylium-based sensitizers with dicyanovinylene substitution and their application as sensitizers for DSCCs.

3.2 Experimental

3.2.1 Materials and General

The NMR spectra were recorded on a JEOL ECX-400P spectrometer (1H, 400 MHz and 13C, 100 MHz). Chemical shifts of 1H NMR and 13C NMR signals reported δ ppm referenced to the solvent or an internal tetramethylsilane. MALDI-TOF MS spectra were recorded on a Shimadzu AXIMA spectrometer. The electron spray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer. The elemental analyses were performed on a Yanako CHN CORDER JM-10 analyzer. Melting points were measured on Rigaku Thermo Plus EVO. 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 JASCO FP-6600 spectrofluorometer. The oxidation potential of the dye was measured on Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of 100 mVs⁻¹, equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a nonaqueous Ag/AgNO₃ reference electrode. The measurement was performed in a CH₂Cl₂ solution including 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. The system was internally calibrated with ferrocene / ferrocenium (Fc / Fc⁺). All solvents and reagents were of reagent grade quality, purchased commercially from Tokyo Chemical Industry co., Ltd. and Wako Pure Chemical Industries, Ltd., and used without further purification. The reagent, tetrakis(triphenylphosphine)palladium(0), was purchased from Tokyo Chemical Industry co., Ltd. Triethylammonium 2-[(1-butyl-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene)methyl]-3-(dicyanomethylidene)-4-oxocyclobut-1-en-1-olate 1 was prepared according to the reference [20]. 3-Isopropyloxy-4-(tributylstannyl)-3-cyclo butene-1,2-dione 3 was synthesized by the previously reported method [21]. The butyl quaternary salts, 5-iodo-1-butyl-2,3,3-trimethylindolium iodide and 1-butyl-5-carboxy-2,3,3-trimethylindolium iodide, were obtained by N-alkylation of 5-iodo-1-butyl-2,3,3-trimethylindolenine and 1-butyl-5-carboxy-2,3,3-trimethylindolenine as their precursors [22, 23].
3.2.2 Preparation of In-CN-In-S-OH

3.2.2.1 Compound 2

1 (3.00 g, 6.51 mmol) and 5-iodo-1-butyl-2,3,3-trimethylindolium iodide (3.06 g, 6.51 mmol) were dissolved in a mixture of 1-butanol (100 mL) and toluene (100 mL) under an argon atmosphere and the solution was heated under reflux for 20 h. After cooling, the solvent was evaporated under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: CH$_2$Cl$_2$/MeOH = 100/1, v/v), followed by washing with isopropyl ether (IPE) to afford compound 2 as a green solid (3.40 g, 76%). Mp: 208 °C.

$^1$H NMR (DMSO-$d_6$, 400 MHz): δ 0.91 (t, $J = 6.0$ Hz, 3H), 0.92 (t, $J = 6.0$ Hz, 3H), 1.40 (m, 4H), 1.68 (s, 6H), 1.68 (s, 6H), 1.68 (m, 4H), 3.98 (t, $J = 6.0$ Hz, 2H), 4.07 (t, $J = 6.0$ Hz, 2H), 6.27 (s, 1H), 6.37 (s, 1H), 7.24 (d, $J = 6.0$ Hz, 1H), 7.29 (t, $J = 6.0$ Hz, 1H), 7.42 (t, $J = 6.0$ Hz, 1H), 7.48 (d, $J = 6.0$ Hz, 1H), 7.57 (d, $J = 6.0$ Hz, 1H), 7.72 (d, $J = 6.0$ Hz, 1H), 7.93 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 100 MHz): δ 173.0, 172.8, 169.9, 167.8, 167.7, 165.8, 165.0, 164.5, 144.5, 142.6, 142.0, 141.8, 136.8, 131.3, 128.0, 124.9, 122.3, 118.9, 118.9, 111.6, 110.4, 89.7, 89.0, 87.1, 77.2, 49.6, 49.0, 44.4, 44.1, 40.9, 29.5, 29.2, 26.7, 26.4, 20.1, 13.9. IR (KBr, cm$^{-1}$): 2190, 1720, 1618, 1492, 1454, 1290, 1108. ESI-MS: m/z 682.31 ([M(C$_{37}$H$_{39}$IN$_4$O)]$^+$ = 682.21). Anal. Calcd. for C$_{37}$H$_{39}$IN$_4$O: C, 65.10; H, 5.76; N, 8.21. Found: C, 65.29; H, 5.89; N, 8.08%.

3.2.2.2 Compound 4

A mixture of 2 (1.10 g, 16.1 mmol), 3-isopropoxy-4-(tributylstannyl)-3-cyclobutene-1,2-dione 3 (0.69 g, 16.1 mmol), Pd(PPh$_3$)$_4$ (0.18 g, 1.61 mmol) and CuI (61.4 mg, 3.22 mmol) in toluene (50 mL) was stirred at 100 °C for 6 h. After cooling, the solvent was removed under the reduced pressure, and the residue was purified three times by silica gel column chromatography (eluent: CHCl$_3$/MeOH = 100/2, v/v), followed by washing with IPE to afford compound 4 as a red copper-colored solid (0.78 g, 75%). Mp: 256 °C (decomp.). $^1$H NMR (DMSO-$d_6$, 400 MHz): δ 0.92 (t, $J = 6.0$ Hz, 6H), 1.41 (septet, $J = 6.0$ Hz, 4H), 1.52 (d, $J = 3.0$ Hz, 6H), 1.72 (s, 3H), 1.72 (m, 4H), 3.36 (br s, 2H), 3.51 (br s, 2H), 4.01 (t, $J = 6.0$ Hz, 2H), 4.14 (t, $J = 6.0$ Hz, 2H), 5.51 (quartet, $J = 3.0$ Hz, 1H), 6.33 (s, 1H), 6.48 (s, 1H), 7.35 (t, $J = 6.0$ Hz, 1H), 7.46 (t, $J = 6.0$ Hz, 1H), 7.57 (d, $J = 6.0$ Hz, 2H), 7.65 (d, $J = 6.0$ Hz, 1H), 7.93 (d, $J = 6.0$ Hz, 1H), 7.92 (s, 1H). $^{13}$C NMR (DMSO-$d_6$, 100 MHz): δ 193.0, 192.5, 190.9, 173.7, 172.2, 170.5, 168.2, 166.7, 166.4, 162.1, 145.2, 142.4, 142.1, 141.1, 128.2, 127.8, 125.7, 122.8, 122.3, 119.8, 118.1, 112.0, 111.1, 89.6, 88.6, 79.8, 69.6, 49.7, 47.9, 44.2, 43.3, 39.0, 29.1, 28.6, 26.3, 25.3, 22.4, 19.3, 13.6, 13.6. IR (KBr, cm$^{-1}$): 2194, 1780,
1739, 1456, 1278, 1190, 1108. HRMS (ESI): m/z calcd for [M(C44H46N4O4)]+, 694.3519; found 694.3515. MALDI-TOF MS: m/z 694.81 ([M(C44H46N4O4)]+).

3.2.2.3 In-CN-In-S-OH

To a solution of 4 (300 mg, 0.46 mmol) in THF (30 mL) was added 18 wt% HCl aq (3 mL), and the mixture was heated at reflux for 1.5 h. After cooling, the solvent was removed by evaporation, and the residue was purified by silica gel column chromatography (eluent; CH2Cl2/MeOH = 10/2, v/v), followed by washing with IPE and heptane to afford in-CN-In-S-OH as a green solid (250 mg, 89%). Mp: 261 °C (decomp.). 1H NMR (DMSO- d6, 400 MHz): δ 0.92 (t, J = 6.0 Hz, 6H), 1.42 (sextet, J = 6.0 Hz, 4H), 1.71 (s, 6H), 1.71 (s, 6H), 1.71 (m, 4H), 4.06 (br, 4H), 6.34 (s, 1H), 6.36 (s, 1H), 7.27 (t, J = 6.0 Hz, 1H), 7.41 (t, J = 6.0 Hz, 1H), 7.45 (d, J = 6.0 Hz, 1H), 7.49 (d, J = 6.0 Hz, 1H), 7.58 (d, J = 6.0 Hz, 1H), 8.06 (s, 1H), 8.09 (d, J = 6.0 Hz, 1H). 13C NMR (DMSO- d6, 100 MHz): δ 214.8, 196.8, 174.4, 172.4, 171.5, 170.2, 166.3, 164.5, 163.6, 142.0, 141.5, 141.3, 129.1, 128.1, 124.8, 123.7, 122.3, 118.4, 116.7, 111.3, 111.2, 88.3, 88.2, 69.7, 49.1, 48.8, 43.7, 38.6, 28.9, 26.1, 25.8, 19.4, 13.7. IR (KBr, cm-1): 2196, 1762, 1573, 1492, 1276, 1191, 1107. HRMS (ESI): m/z calcd for [M(C41H39N4O4)-H]-, 651.2971; found 651.2947. MALDI-TOF MS: m/z 651.37 ([M(C41H39N4O4)-H]- = 651.30).

3.2.3 Preparation of In-CN-In-S-In-COOH

A mixture of In-CN-In-S-OH (45.0 mg, 0.074 mmol) and 1-butyl-5-carboxy-2,3,3-Trimethylindolium iodide (34.6 mg, 0.089 mmol) in a 1-butanol / toluene mixture (1/1, v/v, 3 mL) was stirred at 100°C for 30 min in the presence of quinoline (0.3 mL). After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CH2Cl2/MeOH=10/1, v/v), followed by washing with IPE and heptane to afford in-CN-In-S-In-COOH as a black solid (40.0 mg, 60%). Mp: 270 °C (decomp.). 1H NMR (DMSO-d6, 400 MHz): δ 0.94(m, 9H), 1.43 (sextet, J = 6.0 Hz, 6H), 1.72 (s, 6H), 1.73 (s, 6H), 1.81 (s, 6H), 1.72(m, 6H), 4.04 (m, 2H), 4.12 (m, 2H), 4.45 (m, 2H), 6.33 (s, 1H), 6.35 (s, 1H), 6.45 (s, 1H), 7.32 (t, J = 6.0 Hz, 1H), 7.44 (t, J = 6.0 Hz, 1H), 7.53 (d, J = 6.0 Hz, 2H), 7.62 (d, J = 6.0 Hz, 1H), 7.85 (d, J = 6.0 Hz, 1H), 8.10 (d, J = 9.0 Hz, 1H), 8.14 (s, 1H), 8.17 (d, J = 6.0 Hz, 1H), 8.27 (s, 1H). 13C NMR (DMSO-d6, 100 MHz): δ 192.3, 182.5, 179.1, 178.8, 172.9, 172.3, 168.5, 167.2, 166.7, 166.5, 165.8, 162.3, 144.5, 143.6, 143.2, 142.3, 142.3, 141.3, 130.2, 129.3, 128.2, 127.3, 127.2, 125.5, 123.6, 122.4, 119.1, 118.2, 113.4, 111.8, 111.6, 91.9, 89.2, 88.9, 69.7, 67.2, 51.1, 49.5,
48.1, 44.9, 44.1, 43.6, 29.5, 29.1, 28.9, 26.3, 25.5, 24.9, 22.7, 19.4, 19.4, 13.7, 13.7, 13.6. IR (KBr, cm\(^{-1}\)): 2196, 1716, 1608, 1554, 1492, 1274, 1178, 1099. ESI-MS: m/z 892.30 ([M(C\(_{57}H_{58}N_{5}O_{5}\)-H]- = 892.44). Anal. Calcd for C\(_{57}H_{58}N_{5}O_{5}\): C, 76.57; H, 6.65; N, 7.83. Found: C, 76.31; H, 6.74; N, 7.69%.

3.2.4 Fabrication and photovoltaic measurements of dye-sensitized solar cells

Transparent TiO\(_2\) photoelectrodes (12 \(\mu\)m thick, 5 mm \(\times\) 5 mm) were fabricated by screen-printing. Nanocrystalline TiO\(_2\) paste [PST-18NR (particle size; ca. 20 nm), JGC Catalysts and Chemicals Ltd, Japan] was printed two times on the grass substrate coated with transparent conduction oxide (F-doped SnO\(_2\)). After drying 125 \(^\circ\)C for 10 min, TiO\(_2\) paste consisting of large TiO\(_2\) particle (ca. 400 nm, JGC Catalysts and Chemicals Ltd, Japan) was coated on it as a scattering center. Resulting substrate was gradually heated and sintered at 500 \(^\circ\)C for 15 min. After cooling, the sintered TiO\(_2\) films were impregnated in a 40 mM TiCl\(_4\) aqueous solution at 70 \(^\circ\)C for 30 min and then washed with distilled water and methanol. After drying under reduced pressure, treated TiO\(_2\) films were sintered again at 500 \(^\circ\)C for 30 min. Resulting TiO\(_2\) photoelectrodes were immersed in a solution of dyes (0.12 mM) and chenodeoxycholic acid (6.0 mM) in \(t\)-BuOH/acetonitrile (1/1 (v/v)) and then kept at room temperature overnight, followed by washing with acetonitrile to remove non-adsorbed dye. The dye-adsorbed TiO\(_2\) film and a Pt-coated ITO grass substrate were separated by Teflon spacer (25 \(\mu\)m thick), which had tiny two cuts for injection of the electrolyte and then clipped. The electrolyte consisting of 0.5 M 1,2-dimethyl-3-\(n\)-propylimidazolium iodide (DMPImI), 0.2 M LiI, and 0.05 M I\(_2\) in CHCl\(_3\)/acetonitrile (1/1, v/v) was introduced into the interspace between the TiO\(_2\) photoelectrode and the Pt counter electrode to obtain the sandwich cell. The photovoltaic performance of the DSSC was measured using AM 1.5 solar simulator (CEP-2000, Bunko-Keiki, Japan) equipped with a source meter (Keithley 2400). The incident light intensity was calibrated with a standard Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured using an action spectrum measurement system connected to a solar simulator (CEP-2000, Bunko-Keiki, Japan).

3.2.5 Cyclic voltammogram of squarylium dyes

The cyclic voltammograms of In-CN-In-S-OH and In-CN-In-S-In-COOH showed reversible oxidation waves in the potential range from 0 V to 1 V. The reversibility was proven by estimating the ratio of each anodic and cathodic peak current which approached unity in all dyes.
3.2.6 Schematic diagram of the frontier molecular orbitals of squarylium dyes

Schematic diagram of the frontier molecular orbitals of In-CN-In-S-OH and In-CN-In-S-In-COOH calculated at the B3LYP/6-31G(d) level of theory [24]. The surfaces are generated with an isovalue at 0.02. The calculations were performed on the models in which methyl groups replaced alkyl substituents.

3.3 Results and discussion

3.3.1 Synthesis of squarylium-based diads

Two squarylium-based dyes, In-CN-In-S-OH and In-CN-In-S-In-COOH, were designed according to the combination of dicyanovinylene substitution and the linear extension of \( \pi \)-conjugation achieved by Pd-catalyzed cross coupling (Scheme 1). Terminally iodinated squarylium dye 2 with dicyanovinylene substitution was prepared by the condensation of 1 with a corresponding indolenium salt. In-CN-In-S-OH bearing the semisquaric acid group was synthesized through the reaction of 2 with tributylstannyl squarate under Stille cross-coupling conditions, followed by the hydrolysis of isopropyl ester. Subsequently, the condensation of In-CN-In-SOH with the corresponding indolenium salt afforded In-CN-In-S-In-COOH with a carboxylic acid group.

![Scheme 1. Synthesis of squarylium-based dyes.](image-url)
2.3.2 Absorption, fluorescent emission, and electrochemical properties of In-CN-In-S-OH and In-CN-In-S-In-COOH

The electronic absorption spectra of In-CN-In-S-OH and In-CN-In-S-In-COOH in CHCl₃ at 298 K are shown in Fig. 1. The absorption, emission, and electrochemical properties are summarized in Table 1.

![Absorption spectra](image)

**Fig. 1.** Electronic absorption spectra of In-CN-In-S-OH (bold) and In-CN-In-S-In-COOH (plain) in CHCl₃ (5.0 μM) at 298 K.

The absorption maximum of In-CN-In-S-In-COOH was shifted bathochromically compared to that of In-CN-In-S-OH in CHCl₃, and reached the NIR region over 810 nm. The absorptions in the extremely long wavelength region arise from the planarity between the central indolenine moiety and the semisquarylium component, achieving a highly delocalized π-conjugation system over the whole molecule including the dicyanovinylene units. The absorption of In-CN-In-S-In-COOH was found in the longer wavelength region compared to a corresponding unfunctionalized dye reported previously [15]. Thus, the dicyanovinylene substitution results in a red shift in the absorption of squarylium sensitizers, as indicated elsewhere [18].

These dyes exhibited intense absorptions in the NIR region (ε = 1.34 × 10⁵ M⁻¹ cm⁻¹ for In-CN-In-S-OH and 1.93 × 10⁵ M⁻¹ cm⁻¹ for In-CN-In-S-In-COOH), promising good light-harvesting properties in the DSSCs. In-CN-In-SOH exhibited fluorescence emission maxima in the NIR region, whereas the emission of In-CN-In-S-In-COOH was almost unobservable in the NIR region.
Table 1. Absorption, fluorescence emission and electrochemical properties of squarylium-based dyes.

<table>
<thead>
<tr>
<th>dye</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt; (nm)</th>
<th>λ&lt;sub&gt;em&lt;/sub&gt; (nm)</th>
<th>ε (M&lt;sup&gt;−1&lt;/sup&gt;cm&lt;sup&gt;−1&lt;/sup&gt;)</th>
<th>E&lt;sub&gt;ox&lt;/sub&gt;</th>
<th>E&lt;sub&gt;ox&lt;/sub&gt;–E&lt;sub&gt;0-0&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-CN-In-S-OH</td>
<td>711</td>
<td>732</td>
<td>1.34 × 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>0.89</td>
<td>−0.86</td>
</tr>
<tr>
<td>In-CN-In-S-In-COOH</td>
<td>812</td>
<td>–</td>
<td>1.93 × 10&lt;sup&gt;5&lt;/sup&gt;</td>
<td>0.89</td>
<td>−0.64</td>
</tr>
</tbody>
</table>

<sup>a</sup>Absorption and fluorescence emission spectra were measured on the concentration 5.0 μM in CHCl<sub>3</sub> at 298 K. <sup>b</sup>Oxidation potentials were measured by cyclic voltammetry. <sup>c</sup>E<sub>0-0</sub> values were estimated from onsets of the absorption spectra.

3.3.3 Cyclic voltammetry measurements of In-CN-In-S-OH and In-CN-In-S-In-COOH

For efficient electron injection to be achieved, the highest occupied molecular orbital (HOMO) of the dye must be more positive than the redox potential of I<sup>−</sup> / I<sub>3</sub><sup>−</sup> (0.5V vs. normal hydrogen electrode, NHE), and the lowest unoccupied molecular orbital (LUMO) of the dye must be more negative than the conduction band edge of TiO<sub>2</sub> (E<sub>cb</sub>). On the basis of cyclic voltammetry measurements, the first oxidation potentials (E<sub>ox</sub>) corresponding to the HOMO level of In-CN-In-S-OH (0.89V vs. NHE) and In-CN-In-S-In-COOH (0.89V vs. NHE) are sufficiently more positive than the I<sup>−</sup> / I<sub>3</sub><sup>−</sup> redox potential [25]. This shows the reproduction of the dyes through the reduction of the dyes after electron injection. In addition, the LUMO levels of the dyes estimated from the HOMO level and the 0-0 transition energy calculated from the onset of the absorption spectra are also sufficiently more negative than the E<sub>cb</sub> of TiO<sub>2</sub> (10.5V vs. NHE) (Table 1). These results indicate that the electron-injection processes of these dyes are thermodynamically favorable. Furthermore, the HOMO energy level of In-CN-In-S-In-COOH is stabilized in comparison with that of a corresponding unfunctionalized squarylium dye reported previously [15]. This suggests that the HOMO levels of squarylium sensitizers can be adjusted by dicyanovinylene substitution in such a way as to optimize the photoinduced redox cycle involving electron injection and the reduction of the oxidized dyes.

3.3.4 Photovoltaic performance of DSSCs based on In-CN-In-S-OH and In-CN-In-S-In-COOH

For investigation of the photovoltaic properties, DSSCs were fabricated with In-CN-In-S-OH or In-CN-In-S-In-COOH and nanocrystalline TiO<sub>2</sub> photoelectrodes [26]. These dyes were immobilized on TiO<sub>2</sub> photoelectrodes through the immersion of TiO<sub>2</sub> in a solution of the dye (0.12mM) and chenodeoxycholic acid (CDCA, 6.0mM) as
a coadsorbent, which prevents the surface aggregation of dyes on TiO$_2$ in acetonitrile/t-butyl alcohol [27]. The preliminary evaluations of the incident photon-to-current conversion efficiency (IPCE) and the $J$-$V$ curves for the devices are shown in Fig. 2 and 3, respectively, and their photovoltaic properties are summarized in Table 2. The IPCEs for the devices based on In-CN-In-S-OH and In-CN-In-S-In-COOH reached 29% at 718 nm and 15% maximum at 790 nm, respectively. In addition to their photovoltaic performances in the NIR region, the DSSCs exhibited panchromatic responses in the visible region.

![Fig. 2. Spectra of incident photon-to-current conversion efficiency (IPCE) of DSSCs prepared with In-CN-In-S-OH (bold) and In-CN-In-S-In-COOH (plain).](image)

**Table 2.** Photovoltaic performance of DSSCs based on In-CN-In-S-OH and In-CN-In-S-In-COOH.$^a$

<table>
<thead>
<tr>
<th>dye</th>
<th>$J_{sc}$ (mA cm$^{-2}$)</th>
<th>$V_{oc}$ (V)</th>
<th>$FF$</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-CN-In-S-OH</td>
<td>12.09</td>
<td>0.484</td>
<td>0.59</td>
<td>3.46</td>
</tr>
<tr>
<td>In-CN-In-S-In-COOH</td>
<td>10.18</td>
<td>0.400</td>
<td>0.52</td>
<td>2.10</td>
</tr>
</tbody>
</table>

$^a$Conditions: irradiated light, AM 1.5G (100 mW cm$^{-2}$)

The In-CN-In-SOH-based cell exhibited a higher conversion efficiency ($\eta = 3.46\%$), corresponding to a high short-circuit current density ($J_{sc} = 12.09$ mA cm$^{-2}$, $V_{oc} = 0.48$ V, $FF = 0.59$) under AM 1.5 G solar illumination (100 m W cm$^{-2}$), suggesting that the acidic hydroxy group of the cyclobutene component has a possibility as an anchor group (Figure 3).
Fig. 3. $J-V$ curves of DSSCs prepared with In-CN-In-S-OH and In-CN-In-S-In-COOH. Conditions: irradiated light, AM 1.5G (100 mW cm$^{-2}$); photo-electrode, TiO$_2$ (12 μm thickness and 0.5 cm × 0.5 cm working area); electrolyte, 0.05 M I$_2$, 0.2 M LiI, and 0.5 M DMPImI, in acetonitrile/chloroform (1/1, v/v); dye solution, acetonitrile / t-butanol (0.12 mM) with addition of CDCA (6.0 mM).

3.3.5 Density functional theory (DFT) calculations on In-CN-In-S-OH and In-CN-In-S-In-COOH

According to density functional theory (DFT) calculations on In-CN-In-S-OH, the LUMO is located on the hydroxy group of the terminal cyclobutene moiety as an anchor to the TiO$_2$ surface, whereas the HOMO is delocalized over the central cyclobutene (Fig. 4) [25]. This suggests that the directional electron transfer from the central cyclobutene core to a hydroxy anchor connected directly to the π-conjugation systems contributes to the high photovoltaic performance in the NIR region. The In-CN-In-S-In-COOH sensitized cell showed a $J_{SC}$ value of 10.18 mA cm$^{-2}$, a $V_{OC}$ value of 0.40V, and a fill factor of 0.52, corresponding to an overall conversion efficiency of 2.10%. The conversion efficiency of the DSSC based on In-CN-In-S-In-COOH was higher than that of the DSSC based on a squarylium analogue without dicyanovinylene substitution, owing to the enhancement of the broad spectral response from the visible to the NIR region [15]. Thus, dicyanovinylene substitution contributes to the enhancement of the broad spectral response from the NIR region over 900 nm, resulting in enhanced photovoltaic performances of the DSSCs.
3.4 Conclusions

In summary, novel \( \pi \)-extended squarylium-based dyes consisting of cyclobutene cores with dicyanovinylene substitution were designed and synthesized through the Pd-catalyzed cross-coupling reaction of an iodinated squarylium precursor with the tributylstannyl squarate derivative. The dyes exhibited intense absorption in the NIR region over 800 nm. Dicyanovinylene substitution gives rise to a good photovoltaic performance of the DSSCs, not only in the remarkably long wavelength region around 800 nm, but also in the broader range of the visible region. Considering the high performance of \textit{In-CN-In-S-OH} as a sensitizer, the acidic hydroxy groups on the cyclobutene core can work effectively as anchor units for TiO\(_2\). Metal-free sensitizers showing absorption in the NIR region over 800 nm are rare, despite the demand for such materials in DSSC research. The synthetic method presented here, in which the \( \pi \)-conjugation of dicyanovinylene-substituted squarylium is elongated by the fusion of additional squarylium moieties in a linear manner, may contribute to the development of NIR-absorbing sensitizers, although further effort toward structural modification is required for the improvement of device performance.
3.5 References


Chapter 4

Linearly $\pi$-extended squaraine dyes enable the spectral response of dye-sensitized solar cells in the NIR region over 800 nm

4.1 Introduction

Squaraine dyes consisting of an electron-deficient central cyclobutene unit and two electron-donating aromatic/heterocyclic components are being actively researched due to their intense absorption in the long-wavelength region and their molecular packing tendency in the solid state [1]. Valuable applications that can take advantage of these unique properties include use as chemosensors [2], noncovalent fluorescent probes for bioanalysis [3], nonlinear optics [4], organic light-emitting diodes [5], and organic thin-film solar cells [6]. One of the applications that has attracted the most attention is the use of squarylium dyes as metal-free sensitizers for dye-sensitized solar cells (DSSCs) [7]. To improve the overall photoelectric conversion efficiency of DSSCs, it is important to use the whole range of the spectrum of sunlight including visible and near-infrared (NIR) light. Squaraine dyes contribute to the enhancement of photovoltaic performance in the far-red and NIR regions, for which high-performance, metal-free sensitizers with a donor–$\pi$–acceptor array, as typified by triarylamine- and carbazole-based compounds having cyanoacrylic acids, show insufficient performance owing to the lack of light-harvesting ability [7, 8].

Far-red-absorbing indolenine-based squarylium dyes bearing carboxylic groups directly attached to the indole components and cyanoacryl groups incorporated by thiophene linkers achieved a high conversion efficiency, originating from the unidirectional flow of electrons from cyclobutene cores to the semiconductor surface [9]. Although a lot of squaraine dyes exhibiting absorptions mainly in the far-red region have been reported as efficient sensitizers of TiO$_2$ photoelectrodes, the photo-to-electric conversion efficiency of DSSCs based on these dyes in the NIR region above 800 nm is still insufficient [10]. The use of $\pi$-extended heterocycles as substituents on the 1,3-position of the cyclobutene instead of indolenines causes the shift of absorption wavelength from the far-red to NIR region[11]. Dyes with $\pi$-extended heterocycles have been utilized as sensitizers for DSSCs, and the cells have shown spectral response in the NIR region. The use of homoditopic heterocyclic components for squaraine synthesis, which allows condensation with two equivalents of semi-squarylium and thereby produces squaraines with two cyclobutenedione cores, is effective for the synthesis of NIR-absorbing squaraine dyes since the two cyclobutenedione cores lie in the same
plane, enhancing the extension of the π-conjugation [12]. However, the connection of squaraines through π-conjugated linkers may seem to contribute to a redshift of their absorptions in solutions, but have only limited effect in the absorption because intramolecular charge transfers between the squaraine dyes via π-conjugated linkers are inhibited by the distortion between the squaraines and linker components [6f, 13]. The polymers in which squaric acid residues and N-alkylated pyrroles were alternately connected by a condensation reaction exhibited intense absorption in the NIR region over 800 nm, suggesting that a direct connection between the squaraine chromophore and additional cyclobutene cores benefit the NIR absorption property [1c].

In the current work, the author proposed a novel class of near-infrared-absorbing squarylium sensitizers with linearly extended π-conjugated structures, which were obtained by Pd-catalyzed cross-coupling reactions with stannylcyclobutenedione used as a nucleophilic cyclobutenedione equivalent [14]. The absorption was bathochromically shifted up to 138 nm by the incorporation of an additional semi-squaraine to a squaraine chromophore. The DSSCs based on these dyes showed a significant spectral response in the region over 750 nm. According to the design method, further extension of the π-conjugation should be accomplished by the subsequent fusion of semi-squaraine components to the linearly π-extended squarylium dyes and lead to the development squaraine sensitizers for DSSCs with improved spectral responses in the NIR region.

![Fig. 1. Linearly π-extended squaraine dyes (TSQ) and a standard squaraine dye (MSQ).](image-url)
The author reports here the synthesis of squaraine dyes exhibiting absorption in the range over 800 nm by means of the linear π-extension method utilizing Pd-catalyzed cross-coupling reactions with stannylocyclobutenediones, and their application to DSSCs (Fig. 1). The spectral response of DSSCs based on these dyes in which three cyclobutene cores and four heterocyclic components were alternately connected was found from around 1000 nm to the visible region. Furthermore, DSSCs fabricated with a mixture of the newly synthesized dye and far-red-absorbing squaraine dyes exhibited enhancement of short-circuit current density due to the complementary effect in light harvesting, indicating the potential use of linearly π-extended squaraines as co-sensitizers.

4.2 Experimental

4.2.1 Materials and general procedures

All starting materials, catalysts, and dehydrated solvents were purchased from Tokyo Chemical Industry, Wako Pure Chemicals and Aldrich. Silica gel (SiO₂, spherically-shaped, neutral) for flash chromatography was purchased from Kanto chemical. 1-Heptyl-5-iodo-2,3,3-trimethyl-3H-indolium iodide, 1-butyl-2,3,3-trimethyl-3H-indolium iodide 5a, 3-butyl-2-methyl-1,3-benzothiazol-3-ium iodide 5b, and 1-butyl-5-carboxy-2,3,3-trimethyl-3H-indolium iodide (9) were prepared according to literatures [15]. 3-(1-Methyl)ethyloxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione 2 was synthesized by the reaction of 3,4-bis(1-methylethoxy)-3-cyclobutene-1,2-dione with (tri-n-butylstannyl)trimethylsilane [16]. The NMR spectra were obtained using a JEOL ECX-400 spectrometer operating at 400 MHz for ¹H-NMR and 100 MHz for ¹³C-NMR. Chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in CDCl₃ or DMSO-d₆. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed on a Shimadzu AXIMA-CFR plus spectrometer using dithranol as a matrix. 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 at a scanning rate of 100 mV s⁻¹ on a Hokuto Denko HZ-5000 electrochemical measurement system equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a nonaqueous Ag/AgNO₃ reference electrode. The measurement was performed in a CH₂Cl₂ solution including
0.1 M tetrabutylammonium perchlorate as a supporting electrolyte. The system was internally calibrated with ferrocene/ferrocenium (Fc/Fc⁺).

4.2.2 Preparation of compound TSQa
4.2.2.1 Compound 1
3,4-Dihydroxy-3-cyclobutene-1,2-dione (0.50 g, 4.4 mmol) and 1-heptyl-5-iodo-2,3,3-trimethyl-3H-indolium iodide (4.72 g, 9.23 mmol) were dissolved in a mixture of 1-butanol (4 mL) and benzene (1 mL). Then a catalytic amount of quinoline was added and the solution was heated under reflux for 6 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/hexane/EtOAc, 7/2/1, v/v/v). Compound 1 was precipitated from CHCl₃/hexane solution as a green crystal (3.0 g, 82%). ¹H NMR (CDCl₃, 400 MHz): δ 7.60–7.57 (m, 4H), 6.72 (d, J = 8.2 Hz, 2H), 5.92 (s, 2H), 3.98-3.81 (m, 4H), 1.74 (m, 16H), 1.37–1.24 (m, 16H), 0.85 (t, J = 6.9 Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C₄₀H₅₀I₂N₂O₂) + H]⁺, 845.20; found 845.46. IR (KBr, cm⁻¹): 2952, 2920, 1601, 1499, 1452, 1342, 1275, 1171, 1084, 1042. Anal.Calcd. for C₄₀H₅₀I₂N₂O₂; C, 56.88; H, 5.97; N, 3.32 %. Found: C, 56.86; H, 5.64; N, 3.18 %.

4.2.2.2 Compound 3
In a two-necked round-bottom flask equipped with a condenser, 1 (0.30 g, 0.36 mmol), Pd(PPh₃)₄ (12 mg, 0.010 mmol), and Cul (2.1 mg, 0.011 mmol) were dissolved in tetrahydrofuran (10 mL) under an N₂ atmosphere. To the solution was added 3-(1-methyl)ethyloxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione 2 (0.23 g, 0.53 mmol), and the mixture was stirred at 50 ºC for 27 h. After cooling, the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/EtOAc, 9/1, v/v). Compound 3 was precipitated from CHCl₃/hexane solution as a green crystal (0.12 g, 38%). ¹H NMR (CDCl₃, 400 MHz): δ 8.06 (d, J = 8.3 Hz, 1H), 7.97 (s, 1H), 7.66–7.63 (m, 2H), 7.04 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.1 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 6.03 (s, 2H) 5.66–5.60 (m, 1H), 4.15–3.88 (m, 4H), 1.82–1.79 (m, 16H), 1.58 (d, J = 6.2 Hz, 6H), 1.38–1.28 (m, 16H), 0.88 (t, J = 6.6 Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C₄₇H₅₇I₂N₂O₅)]⁺, 856.33; found 855.99. IR (KBr, cm⁻¹): 2953, 2918, 1782, 1738, 1601, 1504, 1391, 1344, 1273, 1171, 1082, 1042. Anal.Calcd. for C₄₇H₅₇I₂N₂O₅; C, 65.88; H, 6.70; N, 3.27 %. Found: C, 65.70; H, 6.52; N, 3.15 %.
4.2.2.3 Compound 4

Compound 3 (0.40 g, 0.46 mmol) was dissolved in a mixture of THF–3.6% HCl aq. (THF/HCl aq., 10/1(v/v), 37 mL) and then stirred for 20 h at 60 ºC. After removal of solvent, the residue was washed with water and a mixture of CHCl₃ and hexane (CHCl₃/hexane, 1/2, v/v), and dried in vacuo to give 4 as a purple solid (0.37 g, 97%), which was used in the next step without further purification.

1H NMR (DMSO-d₆, 400 MHz): δ 8.02–7.98 (m, 2H), 7.87 (s, 1H), 7.64 (d, J = 9.8 Hz, 1H), 7.40 (d, J = 8.4 Hz, 1H), 7.14 (d, J = 8.5 Hz, 1H), 5.81 (s, 1H), 5.78 (s, 1H), 4.07–4.02 (m, 4H), 1.66–1.64 (m, 16H), 1.32–1.26 (m, 16H), 0.81 (t, J = 6.8 Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C₄₄H₅₁IN₂O₅)]⁺, 814.28; found 814.98. IR (KBr, cm⁻¹): 2953, 2926, 1765, 1599, 1580, 1502, 1400, 1344, 1273, 1169, 1105, 1086, 1041.

4.2.2.4 Compound 6a

Compound 4 (0.13 g, 0.17 mmol) and 1-butyl-2,3,3-trimethyl-3H-indolium iodide 5a (68 mg, 0.20 mmol) were dissolved in a mixture of 1-butanol (6.0 mL) and benzene (1.5 mL). Then a catalytic amount of quinoline was added and the solution was heated at 65 ºC for 18 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/acetone, 4/1, v/v). Compound 6a was precipitated from CHCl₃/hexane solution as a dark purple crystal (0.13 g, 75%). 1H NMR (DMSO-d₆, 400 MHz): δ 8.13 (d, J = 8.8 Hz, 1H), 8.11 (s, 1H), 7.94 (s, 1H), 7.78–7.73 (m, 2H), 7.71 (d, J = 8.4 Hz, 1H), 7.53 (t, J = 7.8 Hz, 1H), 7.49–7.46 (m, 2H), 7.23 (d, J = 8.4 Hz, 1H), 6.30 (s, 1H), 5.86 (s, 2H), 4.51–4.40 (m, 2H), 4.18–4.01 (m, 4H), 1.79–1.68 (m, 24H), 1.45–1.25 (m, 18H), 0.95 (t, J = 7.3 Hz, 3H), 0.85 (t, J = 6.7 Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C₆₈H₇₀IN₃O₄)]⁺, 1011.44; found 1011.79. IR (KBr, cm⁻¹): 2953, 2926, 1742, 1612, 1558, 1493, 1394, 1342, 1319, 1265, 1167, 1082, 1038. Anal.Calcd. for C₆₈H₇₀IN₃O₄: C, 70.02; H, 6.97; N, 4.15 %. Found: C, 69.94; H, 7.01; N, 4.08 %.

4.2.2.5 Compound 7a

In a Schlenck flask, 6a (0.16 g, 0.16 mmol), Pd(PPh₃)₄ (18 mg, 0.016 mmol), and Cul (2.9 mg, 0.015 mmol) was dissolved in DMF (4 mL) under an N₂ atmosphere. To the solution was added 3-(1-methyl)ethyloxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione 2 (0.10 g, 0.24 mmol), and the mixture was stirred at 50 ºC for 2 h. After cooling, the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/EtOAc/acetone, 5/3/2, v/v/v). Compound 7a was precipitated from the CHCl₃/hexane solution as a black solid (0.10 g, 68%). 1H
NMR (CDCl$_3$, 400 MHz): $\delta$ 8.36 (d, $J = 8.2$ Hz, 1H), 8.30 (s, 1H), 8.05 (d, $J = 8.4$ Hz, 1H), 7.94 (s, 1H), 7.50 (d, $J = 7.2$ Hz, 1H), 7.47–7.26 (m, 3H), 7.07 (d, $J = 8.6$ Hz, 1H), 7.02 (d, $J = 8.3$ Hz, 1H), 6.34 (s, 1H), 6.08 (s, 1H), 6.04 (s, 1H), 5.64–5.58 (m, 1H), 4.27 (t, $J = 7.5$ Hz, 2H), 4.15–3.88 (m, 4H), 1.86–1.80 (m, 24H), 1.57–1.55 (m, 10H (overlapping with peaks of H$_2$O)), 1.52–1.47 (m, 2H), 1.40–1.27 (m, 16H), 1.01 (t, $J = 7.3$ Hz, 3H), 0.87 (t, $J = 6.6$ Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C$_{66}$H$_{77}$N$_3$O$_7$) + H]$^+$, 1024.58; found 1024.88. IR (KBr, cm$^{-1}$): 2953, 2928, 1738, 1601, 1506, 1458, 1393, 1263, 1165, 1082, 1036. Anal. Calcd. for C$_{66}$H$_{77}$N$_3$O$_7$: C, 77.39; H, 7.58; N, 4.10 %. Found: C, 77.61; H, 7.82; N, 4.30 %.

4.2.2.6 Compound 8a

Compound 7a (0.11 g, 0.10 mmol) was dissolved in THF (7 mL), and 3.6% HCl aq. (0.7 mL) was added to the solution. Then it was stirred at 60 ºC for 20 h. After removal of the solvent, the residue was washed with water and a mixture of EtOAc and hexane (EtOAc/hexane, 1/1, v/v), and dried in vacuo to give 8a as a dark green solid (98 mg, 95%), which was used in the next step without further purification. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 8.14–8.02 (m, 4H), 7.74–7.71 (m, 2H), 7.53–7.50 (m, 1H), 7.46–7.39 (m, 3H), 6.28 (s, 1H), 5.91 (s, 1H), 5.87 (s, 1H), 4.43 (m, 2H), 4.14–4.10 (m, 4H), 1.78–1.71 (m, 24H), 1.45–1.25 (m, 18H), 0.95 (t, $J = 7.3$ Hz, 3H), 0.84 (t, $J = 6.5$ Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C$_{63}$H$_{71}$N$_3$O$_7$)–H]$^+$, 980.53; found 980.57. IR (KBr, cm$^{-1}$): 2953, 2918, 1757, 1603, 1560, 1493, 1396, 1344, 1267, 1167, 1088, 1038. Anal. Calcd. for C$_{63}$H$_{71}$N$_3$O$_7$: C, 77.03; H, 7.29; N, 4.28 %. Found: C, 77.28; H, 7.41; N, 4.27 %.

4.2.2.7 Compound TSQa

Compound 8a (81 mg, 0.082 mmol) and 1-butyl-5-carboxy-2,3,3-trimethyl-3H-indolium iodide 9 (38 mg, 0.098 mmol) were dissolved in a mixture of 1-butanol (1.1 mL) and benzene (0.3 mL). Then a catalytic amount of quinoline was added and the solution was heated at 60 ºC for 20 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl$_3$/EtOAc/CH$_3$OH, 7/2/1, v/v/v). Compound TSQa was precipitated from CHCl$_3$/CH$_2$OH/hexane solution as a dark purple crystal (0.46 g, 45%). $^1$H NMR [CDCl$_3$-CD$_2$OD (16/1(v/v)), 400 MHz]: $\delta$ 8.37–8.27 (m, 4H), 8.19–8.16 (m, 2H), 7.55–7.42 (m, 3H), 7.38–7.25 (m, 2H (overlapping with peaks of CHCl$_3$)), 7.12–7.06 (m, 2H), 6.47 (s, 1H), 6.46 (s, 1H), 6.11 (s, 1H), 6.09 (s, 1H), 4.36–4.25 (m, 4H), 4.18–3.99 (m, 4H), 1.83–1.72 (m, 32H), 1.52–1.23 (m, 20H), 0.98 (t, $J = 7.3$ Hz, 6H), 0.87 (t, $J = 6.6$ Hz, 6H), 0.84 (t, $J = 6.5$ Hz, 6H).
0.84 (t, J = 6.9 Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C79H90N4O8) + H]+, 1223.68; found 1223.19. IR (KBr, cm⁻¹): 3445, 2961, 2924, 1742, 1612, 1560, 1491, 1394, 1342, 1263, 1165, 1078, 1034. Anal. Calcd. for C79H90N4O8 • 2H2O: C, 75.33; H, 7.52; N, 4.45 %. Found: C, 75.43; H, 7.29; N, 4.41 %.

4.2.3 Preparation of compound TSQb

4.2.3.1 Compound 6b

Compound 4 (0.15 g, 0.18 mmol) and 3-butyl-2-methyl-1,3-benzothiazol-3-ium iodide 5b (74 mg, 0.22 mmol) were dissolved in a mixture of 1-butanol (3.7 mL) and benzene (0.9 mL). Then a catalytic amount of quinoline was added and the solution was heated at 90 °C for 4.5 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/EtOAc/CH₃OH, 40/10/1, v/v/v). Compound 6b was precipitated from CHCl₃/hexane solution as a dark purple crystal (90 mg, 49%). ¹H NMR (CDCl₃, 400 MHz): δ 8.25–8.20 (m, 2H), 7.83 (d, J = 8.3 Hz, 1H), 7.64–7.58 (m, 3H), 7.53–7.50 (m, 2H), 7.02 (d, J = 8.3 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 6.44 (s, 1H), 6.01 (s, 1H), 5.96 (s, 1H), 4.41 (t, J = 7.9 Hz, 2H), 4.08–3.85 (m, 4H), 1.92–1.88 (m, 2H), 1.82–1.77 (m, 16H), 1.56–1.51 (m, 2H), 1.40–1.25 (m, 16H), 1.04 (t, J = 7.3 Hz, 3H), 0.88 (t, J = 6.7 Hz, 6H). MALDI TOF-MS: m/z calcd for [M(C56H64N3O4S)⁺], 1001.37; found 1001.76. IR (KBr, cm⁻¹): 2953, 2926, 1738, 1601, 1493, 1393, 1340, 1265, 1167, 1081, 1038. Anal. Calcd. for C56H64N3O4S: C, 67.12; H, 6.44; N, 4.19 %. Found: C, 67.49; H, 6.77; N, 4.08 %.

4.2.3.2 Compound 7b

In a Schlenck flask, 6b (0.13 g, 0.13 mmol), Pd(PPh₃)₄ (15 mg, 0.013 mmol), and Cul (2.6 mg, 0.014 mmol) were dissolved in DMF (3.2 mL) under an N₂ atmosphere. To the solution was added 3-(1-methyl)ethyloxy-4-(tributylstannyl)cyclobut-3-ene-1,2-dione 2 (84 mg, 0.20 mmol), and the mixture was stirred at 50°C for 2 h. After cooling, the solvent was removed at reduced pressure, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/EtOAc/acetone, 20/5/1, v/v/v). Compound 7b was precipitated from CHCl₃/hexane solution as a black solid (73 mg, 55%). ¹H NMR (CDCl₃, 400 MHz): δ 8.27–8.23 (m, 2H), 8.06 (d, J = 8.4 Hz, 1H), 7.94 (s, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.63 (d, J = 8.7 Hz, 1H), 7.55–7.52 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.3 Hz, 1H), 6.46 (s, 1H), 6.09 (s, 1H), 6.03 (s, 1H), 5.65–5.59 (m, 1H), 4.42 (t, J = 8.0 Hz, 2H), 4.10–3.91 (m, 4H), 1.96–1.79 (m, 18H), 1.62–1.51 (m, 19H (overlapping with peaks of H₂O)), 1.40–1.24 (m, 18H), 1.04 (t, J = 7.4 Hz, 3H), 0.89 (t,
$J = 6.5 \text{ Hz, } 6H)$. MALDI TOF-MS: $m/z$ calcd for $[\text{M(C}_{63}\text{H}_{71}\text{N}_{3}\text{O}_{7}\text{S} + \text{H}]^+]$, 1014.50; found 1014.58. IR (KBr, cm$^{-1}$): 2957, 2922, 1740, 1603, 1391, 1344, 1267, 1169, 1080, 1040. Anal. Calcd. for $\text{C}_{63}\text{H}_{71}\text{N}_{3}\text{O}_{7}\text{S} \cdot \text{H}_2\text{O}$: C, 73.30; H, 7.13; N, 4.07 %. Found: C, 73.39; H, 7.21; N, 4.03 %.

4.2.3.3 Compound 8b

Compound 7b (61 mg, 0.060 mmol) was dissolved in THF (4 mL); then, 3.6% HCl aq. (0.4 mL) was added to the solution, and the mixture was stirred at 65 ºC for 18 h. After removal of solvent, the residue was washed with water and a mixture of CHCl$_3$ and hexane (CHCl$_3$/hexane, 1/2, v/v), and dried *in vacuo* to give 8b as a black solid (54 mg, 93%), which was used in the next step without further purification. $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 8.25 (d, $J = 7.4 \text{ Hz, } 1H), 8.05–7.97 (m, 5H), 7.71–7.67 (m, 1H), 7.60–7.57 (m, 1H), 7.41–7.34 (m, 2H), 6.55 (s, 1H), 5.84 (s, 2H), 4.72–4.61 (m, 2H), 4.18–4.00 (m, 4H), 1.78–1.67 (m, 18H), 1.42–1.22 (m, 18H), 0.90 (t, $J = 6.6 \text{ Hz, } 3H), 0.82–0.80 (m, 6H). MALDI TOF-MS: $m/z$ calcd for $[\text{M(C}_{60}\text{H}_{65}\text{N}_{3}\text{O}_{7}\text{S}]^+]$, 971.45; found 970.63. IR (KBr, cm$^{-1}$): 2953, 2928, 1757, 1599, 1578, 1491, 1439, 1394, 1344, 1267, 1167, 1094, 1040. Anal. Calcd. for $\text{C}_{60}\text{H}_{65}\text{N}_{3}\text{O}_{7}\text{S}$: C, 74.12; H, 6.74; N, 4.32 %. Found: C, 74.04; H, 6.36; N, 3.94 %.

4.2.3.4 Compound TSQb

Compounds 8b (46 mg, 0.047 mmol) and 9 (22 mg, 0.056 mmol) were dissolved in a mixture of 1-butanol (1.5 mL) and benzene (0.4 mL). Then a catalytic amount of quinoline was added and the solution was heated at 85 ºC for 2 h. After cooling, the solvent was removed to a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: CHCl$_3$/EtOAc/CH$_3$OH, 3/1/1, v/v/v). Compound TSQb was precipitated from CHCl$_3$/CH$_3$OH/hexane solution as a dark purple crystal (24 mg, 42%). $^1$H NMR [CDCl$_3$-CD$_2$OD (16/1(v/v)), 400 MHz]: $\delta$ 8.28 (d, $J = 8.2 \text{ Hz, } 1H), 8.23 (s, 1H), 8.16–8.11 (m, 4H), 7.87 (d, $J = 8.0 \text{ Hz, } 2H), 7.63–7.57 (m, 1H), 7.55–7.49 (m, 2H), 7.06–7.01 (m, 2H), 6.55 (s, 1H), 6.40 (s, 1H), 6.04 (s, 1H), 6.01 (s, 1H), 4.44 (t, $J = 7.7 \text{ Hz, } 2H), 4.25 (t, J = 7.7 \text{ Hz, } 2H), 4.06–3.92 (m, 4H), 1.86–1.77 (m, 26H), 1.53–1.25 (m, 20H), 1.02–0.96 (m, 6H), 0.84 (t, $J = 6.7 \text{ Hz, } 6H). MALDI TOF-MS: $m/z$ calcd for $[\text{M(C}_{76}\text{H}_{84}\text{N}_{4}\text{O}_{8}\text{S}]^+]$, 1212.60; found 1212.02. IR (KBr, cm$^{-1}$): 3445, 2928, 1736, 1601, 1558, 1506, 1491, 1394, 1340, 1261, 1165, 1078, 1034. Anal. Calcd. for $\text{C}_{76}\text{H}_{84}\text{N}_{4}\text{O}_{8}\text{S} \cdot \text{H}_2\text{O}$: C, 74.12; H, 7.04; N, 4.55 %. Found: C, 74.08; H, 7.05; N, 4.46 %.
4.2.4 General procedure for fabrication and photovoltaic measurements of dye-sensitized solar cells

Transparent TiO$_2$ photoelectrodes (~12 μm thick, 5 mm × 5 mm) were fabricated by screen-printing. Nanocrystalline TiO$_2$ paste [PST-18NR (particle size; ca. 20 nm), JGC Catalysts and Chemicals Ltd, Japan] was printed two times on the glass substrate coated with transparent conduction oxide (F-doped SnO$_2$). After drying at 125 ºC for 10 min, TiO$_2$ paste consisting of large TiO$_2$ particles (ca. 400 nm, JGC Catalysts and Chemicals Ltd, Japan) was coated on it as a scattering center. The resulting substrate was gradually heated and sintered at 500 ºC for 15 min. After cooling, the sintered TiO$_2$ films were impregnated in a 40 mM TiCl$_4$ aqueous solution at 70 ºC for 30 min and then washed with distilled water and methanol. After drying under reduced pressure, treated TiO$_2$ films were sintered again at 500 ºC for 30 min. The resulting TiO$_2$ photoelectrodes were immersed in a solution of dyes (0.12 mM) and chenodeoxycholic acid (CDCA, 6.0 mM) in $t$-BuOH/acetonitrile (1/1 (v/v)) and then kept at given temperature overnight, followed by washing with acetonitrile to remove the non-adsorbed dye. The dye-adsorbed TiO$_2$ film and a Pt-coated ITO glass substrate were separated by a Teflon spacer (25 μm thick) that had two tiny cuts for injection of the electrolyte and then clipped together. The electrolyte consisting of 0.6 M 1,2-dimethyl-3-$n$-propylimidazolium iodide (DMPImI), 0.1 M LiI, and 0.05 M I$_2$ in CHCl$_3$/acetonitrile (1/1, v/v) was introduced into the interspace between the TiO$_2$ photoelectrode and the Pt counter electrode to obtain a sandwich cell. The photovoltaic performance of the DSSC was measured using an AM 1.5 solar simulator (CEP-2000, Bunko-Keiki, Japan) equipped with a source meter (Keithley 2400). The incident light intensity was calibrated with a standard Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured using an action spectrum measurement system connected to a solar simulator (CEP-2000, Bunko-Keiki, Japan).

4.2.5 DFT calculations of TSQa-b

The ground-state geometries of TSQa-b were optimized in the gas phase by DFT calculations with the Gaussian 09 program [15]. The calculations were performed on the models in which alkyl substituents have been replaced by methyl groups with the B3LYP exchange-correlation functional under a 6-31G basis set.
4.3 Results and discussion

4.3.1 Synthesis of linearly π-extended squaraine dyes (TSQa-b)

For DSSC applications, anchoring groups on the dye were needed to ensure the adsorption on the TiO$_2$-based photoelectrode and efficient electron injection from the dyes to the conduction bands of TiO$_2$ [7]. We designed our unsymmetrical squaraine-based dyes with a carboxy group on the terminal indolenine components accordingly. A diiodinated indolenine-based squarylium dye was used as a starting material and reacted with stannylcyclobutenedione according to the previous method to afford a semi-squarate 3 in which an iodine substitution remained on one side (Scheme 1) [14]. The semi-squarate was hydrolyzed and the resulting semi-squarylium 4 was reacted with indolenine and benzothiazole derivatives under azeotropic conditions to afford bis-squaraine dyes with a iodine substitution 6a-b.

![Scheme 1. Synthesis of linearly π-extended squaraine dyes (TSQa-b).](image)

The mono-iodide derivatives were subsequently coupled with stannylcyclobutenedione, and the resulting semisquarates 7a-b were hydrolyzed to give precursory semi-squarylium 8a-b. Finally, condensation of the precursors with indolenium salt having a carboxy group gave linearly π-extended unsymmetrical, squarylium sensitizers possessing three cyclobutene cores and four heterocyclic components (TSQa-b).
2.3.2 Absorption and electrochemical properties of linearly \(\pi\)-extended squaraine dyes (TSQa-b).

The absorption spectra of TSQa, TSQb, and a standard squaraine dye (MSQ) in solution are shown in Fig. 2, and the characteristic data are summarized in Table 1. These dyes exhibited intense and sharp absorption in the NIR region. Maxima were found at 856 nm for TSQa and 848 nm for TSQb and their onsets of absorption reached approximately 950 nm. The absorption maxima of TSQ were bathochromically shifted ca. 200 nm compared to MSQ and ca. 70 nm compared to previously-reported squarylium sensitizers in which two cyclobutene cores and three heterocyclic components were alternately connected [14]. This indicated that \(\pi\)-electrons were delocalized into the whole of the dye molecules including the additional semisquarylium components without the breaking of \(\pi\)-conjugation stemming from distortions between \(\pi\)-conjugated components.

![Absorption spectra of TSQ in CHCl\(_3\) / CH\(_3\)OH (20/1, v/v, 0.3 \(\mu\)M, A) and immobilized on TiO\(_2\) thin films (B)](image)

**Fig. 2.** Absorption spectra of TSQ in CHCl\(_3\) / CH\(_3\)OH (20/1, v/v, 0.3 \(\mu\)M, A) and immobilized on TiO\(_2\) thin films (B)
Table 1. Absorption and electrochemical properties of linearly π-extended squaraine dyes (TSQa-b).

<table>
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<th>Dye</th>
<th>λ_{max}^a</th>
<th>ε^a</th>
<th>λ_{onset}^b</th>
<th>λ_{onset}^b</th>
<th>E_{0-0}^c</th>
<th>E_{0-0}^{d}</th>
<th>E_{0-0}</th>
<th>E_{0-0}^{d} vs. NHE</th>
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<tr>
<td>TSQa</td>
<td>856</td>
<td>3.36 × 10^5</td>
<td>763, 832</td>
<td>942</td>
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<tr>
<td>TSQb</td>
<td>848</td>
<td>3.47 × 10^5</td>
<td>759, 844</td>
<td>956</td>
<td>1.29</td>
<td>0.68</td>
<td>-0.61</td>
<td></td>
</tr>
<tr>
<td>MSQ</td>
<td>642</td>
<td>2.56 × 10^5</td>
<td>643</td>
<td>683</td>
<td>1.82</td>
<td>0.72</td>
<td>-1.10</td>
<td></td>
</tr>
</tbody>
</table>

^a Measured in CHCl₃ solutions (5 × 10⁻⁶ M). ^b Measured using titania thin film (10 μm-thickness) immobilized with a given dye. ^c Estimated from the onset of absorption spectra on TiO₂. ^d The oxidation potential was measured on 0.1 M tetrabutylammonium perchlorate in CH₂Cl₂ (working electrode: Pt; reference electrode: nonaqueous Ag/AgNO₃ calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 0.63 V; counter electrode: Pt).

TSQ exhibited absorption in the visible region from 700 to 450 nm with moderate intensity, promising panchromatic performance for TSQ. The molar absorption coefficients at absorption maxima were found to be 3.36 × 10⁵ for TSQa and 3.47 × 10⁵ M⁻¹cm⁻¹ for TSQb. These values were higher than that of standard MSQ (2.56 × 10⁵ M⁻¹cm⁻¹), indicating high light-harvesting properties in the NIR region. Absorption spectra of TSQ immobilized to TiO₂ films in the presence of chenodeoxycholic acid (CDCA) were broadened, implying an interaction between dyes immobilized on TiO₂ and electronic coupling between the dye and TiO₂ [11c, 18].
2.3.3 Photovoltaic performance and Oxidation potentials of DSSCs sensitized with linearly π-extended squaraine dyes (TSQa-b).

Fig. 3. Cyclic voltammograms of TSQa (A) and TSQb (B) in CH₂Cl₂ with 0.1 M tetrabutylammonium perchlorate as supporting electrolytes.

The cyclic voltammograms of TSQa and TSQb showed irreversible oxidation waves with two peaks in the potential range from −0.20 to 0.75 V, but showed reversible waves in the scan from −0.2 to 0.3 V (Fig. 3). These results indicate that TSQ exhibited electrochemical reversibility under the one-electron oxidation condition, while the electroactive species yielded in two-electron oxidation of TSQ showed no clear reversibility in the measurement condition. To obtain an efficient charge separation, the LUMO of the dye should be more negative than the conduction band edge of TiO₂ (E_{cb}), and the HOMO of the dye should be more positive than the redox potential of the redox
mediator as typified by $\Gamma/\Gamma^\cdot$. Therefore, the HOMO and LUMO energy levels of TSQ were estimated by the oxidation potentials measured by cyclic voltammograms and the optical bandgap determined by the onsets of absorption (Fig. 4).

![Figure 4. HOMO and LUMO energy levels of TSQa-b and MSQ.](image)

The oxidation potentials $E_{ox}$ corresponding to HOMO levels of TSQ were almost same as that of standard MSQ, although the $\pi$-conjugation was significantly expanded by the fusion of the additional two squaraine chromophores. The oxidation potentials were all sufficiently more positive than the $\Gamma/\Gamma^\cdot$ redox potential value (0.5 V vs NHE), indicating that the oxidized dyes could thermodynamically accept electrons from the $\Gamma$ ions. The bandgap of TSQ (1.32 eV for TSQa, 1.29 eV for TSQb) was much lower than those of previously reported squaraine dyes owing to the linear extension of $\pi$-conjugation. Therefore, $E_{ox} - E_{0-0}$ corresponding to the LUMO levels of TSQ were much higher than that of MSQ. However, the potential levels of $E_{ox} - E_{0-0}$ of TSQ were more negative than the potentials of the TiO$_2$ conduction band edge (−0.5 V vs NHE), which remained at high energy for thermodynamically favorable injection of electrons.

### 2.3.4 Schematic diagram of the frontier molecular orbitals of TSQa-b

To obtain insight into their molecular structures and electron distributions of TSQ, DFT calculations were carried out at the B3LYP/6-31G level (Fig. 5). The HOMOs for TSQ are $\pi$ orbitals delocalizing mainly on central cyclobutene cores and heterocyclic
components. The HOMO–1 orbitals are found on the cyclobutene cores located on either side of central squaraine chromophores. By contrast, the LUMOs are spread throughout the dye molecules. This suggests that the LUMOs are significantly affected by the fusion of additional squaraine components to central squaraine components while the HOMOs depend on the central squaraine components despite the expansion of the π-conjugations. It is important for efficient electron injection from excited dyes to the conduction band of TiO$_2$ to situate the LUMOs close to the anchoring groups because the orbital overlap with the titanium 3d orbitals is thereby enhanced [19]. In the LUMO of TSQ, the electron density was located on terminal indolenium components bearing carboxylic acid to the TiO$_2$ surface, indicating that the transitions from HOMO to LUMO could effectively convert the electron density to the anchoring group. Thus, a unidirectional electron transfer from the cyclobutene core to the terminal indolenine with the anchoring group could take place through a HOMO-LUMO transition in TSQ, promising efficient electron injection to TiO$_2$.

**Fig. 5.** Schematic diagram of the frontier molecular orbitals of TSQa-b calculated at the B3LYP/6-31G level of theory. The surfaces are generated with an isovalue at 0.02. The calculations were performed on the models in which methyl groups replaced alkyl substituents.

### 2.3.5 Photovoltaic performance of DSSCs based on the squaraine-based dyes(TSQa-b)

The photovoltaic properties of the solar cells fabricated with TiO$_2$ photoelectrodes sensitized with TSQa and TSQb and an iodine-based electrolyte are summarized in
Table 2, and the $J-V$ curves and incident photon-to-current conversion efficiency (IPCE) spectrum for the devices are illustrated in Fig. 6.

**Fig. 6.** IPCE spectra (A) and photocurrent density–voltage curves of DSSCs based on TSQ1a-b, MSQ, and DSSCs co-sensitized of TSQa and MSQ.
Table 2. Photovoltaic performance of DSSCs based on the squaraine-based dyes

<table>
<thead>
<tr>
<th>dye</th>
<th>$J_{sc}$ / mAcm$^{-2}$</th>
<th>$V_{oc}$ / V</th>
<th>FF</th>
<th>$\eta$ / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSQa</td>
<td>8.05</td>
<td>0.45</td>
<td>0.59</td>
<td>2.13</td>
</tr>
<tr>
<td>TSQb</td>
<td>8.89</td>
<td>0.45</td>
<td>0.61</td>
<td>2.43</td>
</tr>
<tr>
<td>TSQa +MSQ</td>
<td>11.57</td>
<td>0.44</td>
<td>0.56</td>
<td>2.82</td>
</tr>
<tr>
<td>TSQb</td>
<td>5.25</td>
<td>0.52</td>
<td>0.69</td>
<td>1.88</td>
</tr>
</tbody>
</table>

$^a$ Condition: irradiated light, AM1.5 G (100 mW/cm$^2$); photoelectrode, TiO$_2$ (15 μm-thickness and 0.25 cm$^2$ working area); electrolyte, 0.05 M I$_2$, 0.1 M LiI, and 0.6 M DMPImI, in acetonitrile/ chloroform (1/1(v/v)). $^b$ Dye bath, dye (0.12 mM) in acetonitrile/t-butanol (1/1 (v/v)) with addition of CDCA; $^c$ Electrolyte, 0.05 M I$_2$, 0.2 M LiI, and 0.6 M DMPImI, in acetonitrile/ chloroform (1/1(v/v)); Dye bath, TSQa (0.06 mM) and MSQ (0.06 mM) in acetonitrile/t-butanol (1/1 (v/v)) with addition of CDCA (6 mM).

DSSCs based on both dyes exhibited spectral responses in the remarkably long-wavelength region from ca. 1000 nm and local maxima around 850 nm. In addition, the IPCE values of DSSCs based on TSQ found in the visible region from 600 to 400 nm indicated the contribution of the additional absorption properties observed in their absorption spectra. The short-circuit current density ($J_{sc}$) values of the DSSCs with TSQ (8.05 mA/cm$^2$ for TSQ1a, 8.89 mA/cm$^2$ for TSQb) were greater than that with MSQ (5.25 mA/cm$^2$) fabricated under same conditions. The improvements of $J_{sc}$ should be attributed the expansion of the light-harvesting ability ensuring panchromatic response in addition to the NIR response. However, the open-circuit voltage ($V_{oc}$) of the TSQ-based cell was low (0.45 V), which had a significant influence on their overall conversion efficiency ($\eta$). This result would be attributed to the significant charge recombination between the cationic species and electrons injected into TiO$_2$. The use of two sensitizers in DSSCs, which are complementary in their light-harvesting properties, leads to enhancement of spectral responses [20]. To gain insight into the possibility of TSQ for co-sensitizers combined with visible-light-absorbing sensitizers, DSSCs with TSQa and far-red absorbing MSQ were preliminarily fabricated and characterized. The spectral response from 700 to 550 nm was improved by the sensitizing effect of MSQ. Reflecting the result, the $J_{sc}$ value of the cell was improved to 11.6 mA/cm$^2$ although the $V_{oc}$ remained at a low value. Thus, effort should be directed at the improvement of $V_{oc}$ including the modification of device structure and dye design, but TSQa was found to act as a co-sensitizer making up for deficiencies of the spectral response in the NIR region.
4.4 Conclusions

Novel squarylium dyes (TSQa-b), in which three cyclobutene cores and four heterocyclic components were alternately fused to linearly expand π conjugation, were successfully synthesized through the combination of the Pd-catalyzed coupling reaction of iodinated squarylium and tributylstannylsquarate and the condensation of the resulting semi-squarylium with heterocyclic moieties. The dyes showed absorption in the NIR region with maxima at around 850 nm. The cyclic voltammetry of TSQ indicated that HOMO levels of TSQ were comparable to those of a standard squaraine dye (MSQ). In contrast, the lowering of the band gap attributed to the extension of π-conjugation lowered the LUMO energy levels. Thus, the red shifts in the absorption spectra of the three dyes are attributed to a shift of the LUMO levels to higher energies rather than to a decrease in the energy of the HOMO levels. DSSCs based on TSQ displayed not only remarkable responses in the NIR region to 1000 nm but also a panchromatic response, leading to enhanced short-circuit current density in DSSCs. The power conversion efficiencies of DSSCs with TSQ reached up to 2.4%, although the open-circuit voltage remained low due to the severe charge recombination. Co-sensitization with NIR-absorbing TSQ and far-red absorbing MSQ showed a complementary effect in spectral response and resulted in enhanced short-circuit current density. Thus, TSQ contributed to the enhancement of spectral response of DSSCs in the range over 800 nm. At the same time, however, this work elucidated that further π-extension achieved by the synthetic method could result in a mismatch of the LUMO levels of obtained dyes and the conduction band of TiO₂ because the LUMO levels of dyes significantly lowered with the decrease of their band gaps. The utilization of other wide-band-gap semiconductors such as SnO₂ may be required to obtain further π-extended squaraine dyes by this method.
4.5 References


Chapter 5

Squaraine dyes with pyrylium and thiopyrylium components for harvest of near infrared light in dye-sensitized solar cells

5.1. Introduction

Utilization of near-infrared (NIR) light is clearly essential to improve the photovoltaic performance of organic solar cells because nearly 50% of solar energy falls in the NIR spectral region [1]. In the dye-sensitized solar cells (DSSCs), the sensitizer is one of the key components to harvest sunlight from visible to NIR regions, therefore a lot of sensitizers exhibiting various spectral responses were developed to achieve efficient solar energy conversion of DSSCs [2–4]. Recently, metal complex sensitizers exhibiting red-shifted absorption as represented by black dye [N749, triisothiocyanato-(2,2’:6’,2”-terpyridyl-4,4’,4”-tricarboxylato)Ru(II)tris(tetra-butylammonium)] have made it possible to achieve high conversion efficiency owing to the wide range of spectral response including NIR region [5–7]. Meanwhile, metal-free sensitizing dyes promoting photosensitizing effect of TiO$_2$ in NIR region are still under early stage of development in spite of their advantages such as a high molar absorption coefficient, facile modification of dye structures, tunable absorption properties through molecular design, cost-effectiveness [8].

Squarylium dyes have received much attention as a potential candidate for far-red/NIR sensitizers of DSSCs due to their extremely high absorptivity and flexibility for synthetic manipulation [9–13]. The conversion efficiency of DSSCs based on squarylium dyes reached over 6% through the optimization of dye structures involving donor components, anchoring units, and alkyl groups [14–24]. However, spectral response of DSSCs in the NIR region above 750 nm is still insufficient [25].

Recently, the author reported the synthetic methodology for the extension of π-conjugation in squarylium dyes utilizing the Pd-catalyzed cross-coupling of 3-stannylcyclobutenediones and aryl halide [26]. Squarylium-based dyes obtained according to the strategy showed absorption in NIR region and the DSSCs based on them exhibited spectral response in NIR region [27–29]. The author has also reported the NIR-absorbing squaraine dyes with π-extended heterocycles and their application to sensitizers in DSSCs [30]. Among these dyes, pyrylium-based sensitizers showed moderate photovoltaic performance in the long-wavelength region, therefore we intend to modify the dye structure with pyrylium components. Herein the author reports the novel NIR absorbing squarylium sensitizers with pyrylium and thiopyrylium...
components and their application to DSSCs.

5.2. Experimental

5.2.1 General

The NMR spectra were obtained using a JEOL ECX-400 and ECS-400 spectrometer operating at 400 MHz for $^1$H-NMR and 100 MHz for $^{13}$C-NMR. Chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in CDCl$_3$. The electron spray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer. The FT-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 Shimazu UV-3600 spectrophotometer and a Horiba Fluorolog-3 spectrofluorometer. Fluorescence lifetimes were measured using a Horiba Jobin Yvon FluoroCube spectroanalyzer with a 624 and 735 nm LED light sources for excitation. Colloidal silica suspension in water was used as scatterer to determine the instrumental response. Fluorescence quantum yields were measured in THF at 25 ºC using a Hamamatsu Photonics C9920 PL quantum yield measurement system. The oxidation potential of the dye was measured on Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of 100 mV s$^{-1}$, equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a nonaqueous Ag/AgNO$_3$ reference electrode. The measurement was performed in a dichloromethane solution including 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte.

All starting materials, catalysts, and dehydrated solvents were purchased from Tokyo Chemical Industry, Wako Pure Chemicals and Aldrich. Silica gel (SiO$_2$, spherically-shaped, neutral) for the flash chromatography was purchased from Kanto chemical. di-$n$-butylsquarate [31], 2,6-di-$n$-tert-butyl-4-methylthiopyrylium hexafluoro phosphate [32], 1-butyl-5-carboxy-2,3,3-trimethyl-3H-indolium iodide [33], 5-carboxy-1-dodecyl-2,3,3-trimethyl-3H-indolium iodide [34] were prepared according to the literature. Monocondensation products that 3-butoxy-4-((2,6-di-$n$-tert-butyl-4H-pyran-4-ylidene)methyl)cyclobut-3-ene-1,2-dione and 3-butoxy-4-((2,6-di-$n$-tert-butyl-4H-thiopyran-4-ylidene)methyl)cyclobut-3-ene-1,2-dione were prepared in a similar way according to the literature [35].

5.2.2. Preparation of squaraine dyes with pyrylium or thiopyrylium components

5.2.2.1. Compound SQP4

3-butoxy-4-((2,6-di-$n$-tert-butyl-4H-pyran-4-ylidene)methyl)cyclobut-3-ene-1,2-dione
(0.30 g, 0.83 mmol) and 1-butyl-5-carboxy-2,3,3-trimethyl-3H-indol-1-ium iodide (0.32 g, 0.83 mmol) were dissolved in a mixture of 1-butanol (9 mL) and benzene (2.4 mL). Then a drop of quinoline were added and the solution was heated under reflux for 8 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/AcOEt, 1/1, v/v), and the product was precipitated from CHCl₃/hexane solution to obtain SQP4 as a dark red solid (13 mg, 3.0%).

**1H NMR [CDCl₃, 400 MHz]**: δ 0.96 (t, J = 7.4 Hz, 3H), 1.31 (s, 9H), 1.38 (s, 9H), 1.39–1.48 (m, 2H), 1.71–1.85 (m, 8H), 3.89–4.10 (m, 2H), 5.94 (s, 1H), 6.00 (s, 1H), 6.34 (d, J = 1.7 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 8.08–8.12 (m, 1H), 8.76 (d, J = 1.7 Hz, 1H).

**13C NMR [CDCl₃, 100 MHz]**: δ 183.78, 181.97, 178.62, 172.60, 171.63, 170.02, 169.13, 151.43, 147.01, 142.27, 131.17, 124.13, 124.08, 109.69, 109.11, 108.62, 104.14, 88.89, 48.71, 43.52, 36.90, 36.57, 29.19, 28.11, 27.93, 27.19, 20.31, 13.89. IR (KBr): ν = 2964, 2930, 2870, 1709, 1645, 1599, 1566, 1556, 1493, 1485, 1447, 1402, 1391, 1358, 1315, 1269, 1230, 1215, 1184, 1124, 1097, 1086, 1068, 1034, 926 cm⁻¹. HRMS (ESI): m/z calcld for [M(C₄₂H₅₇NO₅) − H]⁻, 542.2907; found 542.2898.

5.2.2.2. **Compound SQP12**

3-butoxy-4-((2,6-di-tert-butyl-4H-pyran-4-ylidene)methyl)cyclobut-3-ene-1,2-dione (0.21 g, 0.59 mmol) and 5-carboxy-1-dodecyl-2,3,3-trimethyl-3H-indol-1-ium iodide (0.30 g, 0.59 mmol) were dissolved in a mixture of 1-butanol (16 mL) and benzene (4 mL). Then 3 drops of quinoline were added and the solution was heated under reflux for 20 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/AcOEt, 1/1, v/v), and the product was precipitated from CHCl₃/hexane solution to obtain SQP12 as a blue solid (72 mg, 32%).

**1H NMR [CDCl₃, 400 MHz]**: δ 0.87 (t, J = 6.6 Hz, 3H), 1.21-1.27 (m, 20H), 1.31 (s, 9H), 1.38 (s, 9H), 1.71–1.85 (m, 8H), 3.89–4.03 (m, 2H), 5.94 (s, 1H), 6.00 (s, 1H), 6.34 (d, J = 1.5 Hz, 1H), 6.97 (d, J = 8.4 Hz, 1H), 8.04 (s, 1H), 8.10 (d, J = 8.5 Hz, 1H), 8.76 (d, J = 1.4 Hz, 1H).

**13C NMR [CDCl₃, 100 MHz]**: δ 183.80, 183.53, 181.98, 178.47, 172.56, 171.58, 170.37, 169.12, 151.39, 146.97, 142.24, 131.17, 124.20, 124.07, 109.65, 109.09, 108.63, 104.09, 88.85, 48.69, 43.69, 36.88, 36.55, 31.91, 29.59, 29.52, 29.45, 29.37, 29.34, 28.09, 27.92, 27.15, 27.11, 26.98, 22.69, 14.14. IR (KBr): ν = 2964, 2924, 2853, 1703, 1647, 1603, 1566, 1485, 1447, 1400, 1356, 1315, 1271, 1186, 1124, 1099, 1086, 1067, 928 cm⁻¹. HRMS (ESI): m/z calcld for [M(C₄₂H₅₇NO₅) − H]⁻, 654.4159; found 654.4160.
5.2.2.3. Compound SQTP12

3-butoxy-4-((2,6-di-tert-butyl-4H-thiopyran-4-ylidene)methyl)cyclobut-3-ene-1,2-dione (70 mg, 0.19 mmol) and 5-carboxy-1-dodecyl-2,3,3-trimethyl-3H-indol-1-ium iodide (93 mg, 0.19 mmol) were dissolved in a mixture of 1-butanol (4 mL) and benzene (1 mL). Then a drop of quinoline were added and the solution was heated under reflux for 45 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl₃/AcOEt, 1/1, v/v), and the product was precipitated from CHCl₃/hexane solution to obtain SQTP12 as a green solid (14 mg, 11%).¹H NMR [CDCl₃, 400 MHz]: δ 0.87 (t, J = 6.7 Hz, 3H), 1.21-1.27 (m, 20H), 1.38 (s, 9H), 1.49 (s, 9H), 1.70–1.86 (m, 8H), 3.89–4.06 (m, 2H), 6.02 (s, 1H), 6.15 (s, 1H), 6.97 (d, J = 8.5 Hz, 1H), 7.06 (s, 1H), 8.04 (s, 1H), 8.08–8.13 (m, 1H), 9.36 (s, 1H).¹³C NMR [CDCl₃, 100 MHz]: δ 184.13, 180.91, 163.42, 162.84, 150.37, 145.19, 136.66, 131.59, 131.16, 125.57, 124.82, 124.06, 110.22, 48.72, 39.69, 38.86, 31.91, 30.87, 30.68, 29.70, 29.59, 29.52, 29.45, 29.38, 29.34, 27.13, 27.08, 26.96, 22.69, 14.13. IR (KBr): ν = 2959, 2924, 2853, 1730, 1703, 1605, 1566, 1485, 1472, 1396, 1356, 1294, 1244, 1227, 1182, 1090, 1070, 1057 cm⁻¹. HRMS (ESI): m/z calcd for [M(C₄₂H₅₇NO₄S) − H]⁺, 670.3930; found 670.3920.

5.2.3. General procedure for fabrication of the nanocrystalline TiO₂ solar cells

Transparent TiO₂ photoelectrodes (~15 μm thick, 5 mm × 5 mm) were fabricated by screen-printing. Nanocrystalline TiO₂ paste [PST-18NR (particle size; ca. 20 nm), JGC Catalysts and Chemicals Ltd, Japan] was printed two times on the grass substrate coated with transparent conduction oxide (F-doped SnO₂). After drying 125 ºC for 10 min, TiO₂ paste consisting of large TiO₂ particle (ca. 400 nm, JGC Catalysts and Chemicals Ltd, Japan) was coated on it as a scattering center. The resulting substrate was gradually heated and sintered at 500 ºC for 15 min. After cooling, the sintered TiO₂ films were impregnated in a 40 mM TiCl₄ aqueous solution at 70 ºC for 30 min and then washed with distilled water and methanol. After drying under reduced pressure, treated TiO₂ films were sintered again at 500 ºC for 30 min. The resulting TiO₂ photoelectrodes were immersed in a solution of dyes (0.12 mM) and chenodeoxycholic acid (12 or 24 mM) in EtOH and then kept at given temperature 4 hours, followed by washing with acetonitrile to remove non-adsorbed dye. The dye-adsorbed TiO₂ film and a Pt-coated FTO grass substrate were sealed with a hot-melt gasket of 50 μm thickness made of the ionomer HIMILAN 1652 (Mitsui-Dupont) spacer. The internal space was filled with a liquid electrolyte using capillary action. The electrolyte injecting one of two holes on the counter electrode glass substrate made with
a drill was sealed with HIMILAN 1652 and a thin glass cover by heating. The electrolyte consisting of 0.6 M 1,2-dimethyl-3-\textit{n}-propylimidazolium iodide (DMPImI), 0.05 M LiI, and 0.05 M I\textsubscript{2} in acetonitrile/valeronitrile (85/15, v/v) was introduced into the interspace between the TiO\textsubscript{2} photoelectrode and the Pt counter electrode. The photovoltaic performance of the DSSC was measured using AM 1.5 solar simulator (CEP-2000, Bunko-Keiki, Japan) equipped with a source meter (Keithley 2400). The incident light intensity was calibrated with a standard Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured using an action spectrum measurement system connected to a solar simulator (CEP-2000, Bunko-Keiki, Japan).

5.3. Results and discussion
5.3.1. Synthesis of unsymmetrical squarylium dyes with pyrylium and thiopyrylium components

Unsymmetrical squarylium dyes with pyrylium and thiopyrylium components were synthesized via a two-step procedure. Pyrylium-based 4 and thiopyrylium-based semisquarylium 5 prepared by the condensation of 3,4-dibutoxycyclobutene-1,2-dione with pyrylium 2 and thiopyrylium moiety 3, respectively (Scheme 1). The condensation of semisquarylium compounds and 5-carboxy-2,3,3-trimethyl-3H-indolium iodide with butyl and dodecyl group on the nitrogen atom afford pyrylium-based dyes SQP4 with butyl group, SQP12 with dodecyl group and thiopyrylium-based dyes SQTP4 with butyl group, SQTP12 with dodecyl group.

Scheme 1. Synthesis of unsymmetrical squaraine dyes with pyrylium and thiopyrylium components.
5.3.2. Light-absorbance, fluorescent emission, and electrochemical properties of SQP and SQTP

SQP with a pyrylium moiety have sharp and intense absorption peak at 688 nm with a molar absorption coefficient ($\varepsilon$) of $2.0 \times 10^5$ M$^{-1}$ cm$^{-1}$ in CHCl$_3$ (Figure 1, Table 1). Meanwhile absorption maximum of SQTP with a thiopyrylium moiety was observed at 745 nm ($\varepsilon = \text{ca. } 2.1 \times 10^5$), indicating that the sulfur atom affects on extension of $\pi$ conjugation of the dyes. These dyes exhibited fluorescence emission in 704 nm for SQP and 758 nm for SQTP.

![Absorption spectra of SQP and SQTP in CHCl$_3$ (A) and on TiO$_2$ thin films (B)](image)

**Fig. 1.** Absorption spectra of SQP and SQTP in CHCl$_3$ (A) and on TiO$_2$ thin films (B)
<table>
<thead>
<tr>
<th>dye</th>
<th>$\lambda_{\text{max}}^a$ /nm</th>
<th>$\varepsilon^a$ /M$^{-1}$cm$^{-1}$</th>
<th>$\lambda_{\text{max}}$ on TiO$_2^b$ /nm</th>
<th>$\lambda_{\text{onset}}^b$ /nm</th>
<th>$E_{0,0}^c$ V</th>
<th>$E_{\text{ox}}^d$ V vs. NHE</th>
<th>$E_{\text{ox}}-E_{0,0}$ V vs. NHE</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQP4</td>
<td>688</td>
<td>$2.0 \times 10^5$</td>
<td>1.65</td>
<td>0.61</td>
<td>–1.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SQP12</td>
<td>688</td>
<td>$2.0 \times 10^5$</td>
<td>1.65</td>
<td>0.61</td>
<td>–1.04</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SQTP4</td>
<td>745</td>
<td>$2.1 \times 10^5$</td>
<td>1.79</td>
<td>0.67</td>
<td>–1.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SQTP12</td>
<td>745</td>
<td>$2.1 \times 10^5$</td>
<td>1.79</td>
<td>0.67</td>
<td>–1.12</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Measured in CHCl$_3$ solutions ($5 \times 10^{-6}$ M). $^b$ Measured using titania thin film (10 $\mu$m-thickness) immobilized with a given dye. $^c$ Estimated from the cross section of absorption spectra and emission spectra. $^d$ The oxidation potential was measured on 0.1 M tetrabutylammonium perchlorate in CH$_2$Cl$_2$ (working electrode: Pt; reference electrode: nonaqueous Ag/AgNO$_3$ calibrated with ferrocene/ferrocenium (Fc/Fc$^+$) as an internal reference and converted to NHE by addition of 0.63 V; counter electrode: Pt).

5.3.3. Schematic diagram of the frontier molecular orbitals of SQP and SQTP

DFT calculations indicated that the extremely intense and long wavelength absorptions of these dyes were attributable to the intramolecular charge transfer characteristics of these dyes (Figure 2). Although the absorption maxima of these dyes immobilized on the TiO$_2$ surface were almost the same as those in solution, the absorption spectra were broadened compared to those in solution, indicating a strong interaction between the dyes. These spectral features make these dyes promising for light harvesting in the long-wavelength region.
Fig. 2. Schematic diagram of the frontier molecular orbitals of SQP and SQTP calculated at the B3LYP/6-31G(d) level of theory.

5.3.4. Cyclic voltammetry measurements of SQP and SQTP

To get an efficient charge separation in DSSCs, the LUMO of the dye should be more negative than the conduction band edge of TiO$_2$ ($E_{\text{cb}}$), and the HOMO of the dye should be more positive than the redox potential of I$^-$/I$_3^-$. Based on the cyclic voltammetry measurements, the first oxidation potentials ($E_{\text{ox}}$) corresponding to the HOMO level of SQP (0.67 V vs NHE), SQTP (0.61 V vs NHE) was sufficiently more positive than the I$^-$/I$_3^-$ redox potential (Figure 3). In addition, the LUMO level estimated by the HOMO level and the 0-0 transition energy calculated from the wavelength where the normalized absorption and fluorescence spectra intersect (–1.12 V for SQP, –1.04 for SQTP) was also sufficiently more negative than the $E_{\text{cb}}$ (–0.5 V vs NHE) [8].
Fig. 3. Cyclic voltamograms of SQP and SQTP (A) and schematic diagram of HOMO and LUMO energy levels (B).

5.3.5. Photovoltaic performance of DSSCs based on SQP and SQTP

DSSCs based on SQP4 with a butyl group and SQP12 with a dodecyl group in indolenine moiety were fabricated to conform the effect of alkyl chain length on their cell performance (Figure 4, Table 2).
Fig. 4. Photocurrent density-voltage ($J-V$) curves (A) and IPCE spectra (B) of DSSCs based on SQP4 and SQP12.

Table 2. Photovoltaic performance of DSSCs based on SQP12 and SQTP12

<table>
<thead>
<tr>
<th>Dye</th>
<th>Electrolyte$^b$</th>
<th>Adsorbent$^c$</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA)</th>
<th>Fill factor</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQP4$^d$</td>
<td>a</td>
<td>12</td>
<td>0.40</td>
<td>3.01</td>
<td>0.57</td>
<td>0.73</td>
</tr>
<tr>
<td>SQP12$^d$</td>
<td>a</td>
<td>12</td>
<td>0.44</td>
<td>4.60</td>
<td>0.59</td>
<td>1.21</td>
</tr>
<tr>
<td>SQP12</td>
<td>b</td>
<td>24</td>
<td>0.52</td>
<td>7.72</td>
<td>0.61</td>
<td>2.44</td>
</tr>
<tr>
<td>SQP12</td>
<td>b</td>
<td>12</td>
<td>0.51</td>
<td>6.03</td>
<td>0.65</td>
<td>2.03</td>
</tr>
<tr>
<td>SQTP12</td>
<td>b</td>
<td>24</td>
<td>0.38</td>
<td>3.90</td>
<td>0.67</td>
<td>1.00</td>
</tr>
<tr>
<td>SQTP12</td>
<td>b</td>
<td>12</td>
<td>0.37</td>
<td>2.19</td>
<td>0.68</td>
<td>0.55</td>
</tr>
</tbody>
</table>

$^a$ Condition: irradiated light, AM1.5 G (100 mW/cm$^2$); photoelectrode, TiO$_2$ (15 μm-thickness and 0.25 cm$^2$ working area). $^b$ Electrolyte a, 0.05 M I$_2$, 0.05 M LiI, and 0.6 M DMPImI in acetonitrile/valeronitrile (85/15(v/v)); electrolyte b, 0.03 M I$_2$, 0.05 M LiI, and 0.6 M DMPImI in acetonitrile. $^c$ Concentration of CDCA in dye bath, dye (0.12 mM) in acetonitrile/t-butanol (1/1 (v/v)) with addition of CDCA; $^d$ Dye bath, dye (0.12 mM) in ethanol with addition of CDCA (12 mM).
The DSSC based on **SQP12** showed a higher open-circuit voltage compared to that on **SQP4**. According to previous reports, the enhancement of the open-circuit voltage is attributed to the suppression of charge-recombination between cationic species such as I$_3^-$ and injected electrons [36]. In addition to the enhancement of open-circuit voltage, the photocurrent of **SQP12** also increased compared to **SQP4** in this condition. As a result, the cell performance of **SQP12** is higher than that of **SQP4**. The IPCE spectra of **SQP** display the spectral response from ca. 800 nm, in reflect with their absorption.

To improve the photovoltaic performance, the electrolyte condition was modified and the solvent for dying of TiO$_2$ photoelectrodes was changed to CH$_3$CN / t-butanol with 12 or 24 mM of CDCA as a coadsorbent (Figure 5). The cell performance of the **SQP12**-based DSSC fabricated with the condition of 24 mM CDCA was higher than that with 12 mM CDCA condition. This result was related to covering effect ensured by CDCA, which is attributed to the lifetime of injected electrons [37].

![Figure 5](image)

**Fig. 5.** Photocurrent density-voltage (**J-V**) curves (A) and IPCE spectra (B) of DSSCs based on **SQP12** and **SQTP12**.
DSSCs based on SQTP12 were fabricated with same electrolyte condition. Similar to the result in SQP12, the DSSC fabricated with the condition of 24 mM CDCA exhibited higher photovoltaic performance and their conversion efficiency reached to 1%. The SQTP12 exhibited spectral responses from 850 nm and their maxima reached over 750 nm. Thus, unsymmetrical squaraine sensitizers with pyrylium and thiopyrylium components have a potential to harvest the long-wavelength light.

5.4. Conclusions

Unsymmetrical squaraine dyes bearing pyrylium or thiopyrylium components were synthesized and their light-absorbing properties in the long-wavelength region were investigated. Condensations of 2,6-Di-tert-butyl-4-methylpyrylium and thiopyrylium salt with butyl squarate afford corresponding semi-squaryliums. The semi-squaryliums are reacted with indolenium with carboxyl group to give target unsymmetrical dyes. They exhibited intense absorption in the far-red and near-infrared region in solution and on the TiO₂ surface. Electrochemical measurements revealed that electron injection from the excited dyes to the TiO₂ conduction band was thermodynamically permitted. A molecular-orbital calculation indicated that the electron distribution moved from the cyclobutene core to not only the pyrylium / thiopyrylium components but also indolenine bearing carboxyl anchors, by photoexcitation. The photovoltaic performances of DSSCs based on unsymmetrical squarylium dyes achieved comparatively high performance in metal-free NIR sensitizers. These results suggest that pyrylium and thiopyrylium components strongly affect not only the physical properties of the dyes but also the photovoltaic performances of DSSCs based on these dyes.
5.5. References


Chapter 6
Conformational effect of symmetrical squaraine dyes on the performance of dye-sensitized solar cells

6.1 Introduction

Dye-sensitized solar cells (DSSCs) based on photoinduced redox cycles involving nanocrystalline oxide semiconductors sensitized with dyes, redox mediators, and metal cathodes have shown high photo-electric conversion efficiency due to the vast surface area of the oxide semiconductors, in which light-harvesting properties are enhanced through the photosensitizing effect coming from immobilized dyes [1]. Utilization of the whole range of solar irradiation, including visible and near-infrared (NIR) light, for the photo-to-electricity conversion leads to improved photovoltaic performance of DSSCs [2]. In addition, the unidirectional flow of electrons from sensitizing dyes to the semiconductor surface upon photoexcitation is required to enhance highly efficient electron injection [3].

Metal-free organic dyes have also been utilized as sensitizers alternative to Ru complexes, which are widely regarded as high-performance sensitizers, 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 [4]. With metal-free dyes, long-wavelength absorption is attributable to an intramolecular charge transfer from electron-donating components to electron-deficient components in the extended π-conjugation. However, the use of photoisomerizable bonds as typified by C-C double bonds to elongate π-conjugation systems may decrease the quantum efficiency of the organic dyes due to the energy loss from the unintended photoisomerization [5]. Therefore, to improve the conversion efficiency of DSSCs based on metal-free dyes, it is very important to suppress the photoisomerization. Squaraine dyes have been regarded as one of the most promising candidates for far-red/NIR sensitizers due to their extremely high absorption coefficients in the visible-to-NIR region and their flexibility for synthetic manipulation [6].

Squaraine dyes with polar functionality, which anchor the dye to the TiO₂ surface, have shown a high conversion efficiency in the long-wavelength region originating from the unidirectional flow of electrons from the dyes to the semiconductor surface [7]. Although existing squaraine dyes obtained by the condensation of squaric acid with heterocycles including activated methylene groups as typified by a
2,3,3-trimethyl-3\(H\)-indolenine moiety are widely used as sensitizers of DSSCs, they can in principle adopt cis-like conformation in addition to the thermodynamically stable trans-like conformation [8, 9]. The trans-like conformers can photoisomerize to cis-like conformers via the twisted intramolecular charge transfer state (TICT), a process which allows the non-radiative deactivation of excited squaraine dyes [10].

Therefore, the inhibition of photoisomerization would contribute to the advancement of the conversion efficiency of DSSCs as in the case of sensitizing dyes with a non-radiative path resulting from the trans/cis isomerization of C-C double bonds [11]. One of the strategies to suppress the photoisomerization leading to non-radiative decay of exited squaraine dyes is the insertion of substitutions providing an energy barrier for photoinduced twisting of sensitizing dyes. Barolo and coworkers have reported that the insertion of a carboxy group and a long alkyl chain to both indolenine moieties in an indoleine-based standard squaraine dye, thereby providing symmetrical squaraines, contributed to the depression of the non-radiative decay rate [12]. Introduction of a bulky electron-withdrawing substituent on the cyclobutene core has an impact on the conformation, absorption, and electrochemical properties of squaraine dyes [13]. Beverina and coworkers elucidated the effect of substitution on the cyclobutene core on the photovoltaic properties of DSSCs, focusing on the light-harvesting property of an unsymmetrical squaraine sensitizer possessing a diethylthiobarbiturate as a core substituent [14]. DSSCs with this dye exhibited a remarkable panchromatic response, achieving high photovoltaic performance. From the point of view of the structural effect of core substitution, the conformation of squaraine dyes is locked in a cis-like form by the cyclobutene core substitution owing to the steric effect. Therefore, the conformational change caused by core substitution should affect the suppression of the photoisomerization, leading to enhancement of the efficient electron injection from excited dyes to TiO\(_2\).

![Fig. 1.](image)

**Fig. 1.** (A) Molecular structures of squarylium dyes, (B) an ORTEP drawing of the X-ray structure of SQM1a.
In this chapter, symmetrical indolenine-based squaraine dye altered to possess dicyanovinylene functionality on carbonyl groups of the cyclobutene core (SQM1a) was designed and synthesized to elucidate the effects of conformational lock in a cis-like form on the performance of DSSCs through the comparison of an unsymmetrical analogue bearing one carboxy group (SQM1b) and a standard squaraine dye (MSQ) (Fig. 1). The symmetrical and conformationally locked structure of SQM1a brought about a decrease in the nonradiative decay rate. As a result, the short-circuit current density of DSSCs based on SQM1a was enhanced and the performance of DSSCs was improved compared with that of the other two dyes.

6.2 Experimental
6.2.1 Materials and general procedures

The NMR spectra were obtained using a JEOL ECX-400 and ECS-400 spectrometer operating at 400 MHz for $^1$H-NMR and 100 MHz for $^{13}$C-NMR. Chemical shifts were reported in parts per million (δ) downfield from tetramethylsilane (TMS) as an internal standard in CDCl$_3$, CD$_3$OD, DMSO-$d_6$. The electron spray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer. The elemental analyses were performed on a Yanako CHN CORDER JM-10 analyzer. The FT-IR spectra were recorded using a Shimadzu FT-IR 8400S spectrophotometer. For measurements of IR spectra of SQM1a-b immobilized on TiO$_2$, the TiO$_2$ thin films prepared on KCl plates using a titania paste (PST-18NR) were immersed in a solution of dyes (0.12 mM) in $t$-BuOH/acetonitrile (1/1 (v/v)) and then kept at ambient temperature overnight, followed by washing with acetonitrile to remove non-adsorbed dye. FT-IR spectra of the dye-adsorbed TiO$_2$ films were measured by transmission spectroscopy. The spectra of free SQM1a-b were measured using KBr method. The absorption spectra and fluorescence emission spectra were measured in a 1.0 cm quartz cell on a Shimazu UV-3100 spectrophotometer and a JASCO FP-6600 spectrofluorometer. Fluorescence lifetimes were measured using a Horiba Jobin Yvon FluoroCube spectroanalyzer with a 625 nm LED light source for excitation. Colloidal silica suspension in water was used as scatterer to determine the instrumental response. Fluorescence quantum yields were measured in CHCl$_3$ at 25 °C using a Hamamatsu Photonics C9920 PL quantum yield measurement system. The oxidation potential of the dye was measured on Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of 100 mV s$^{-1}$, equipped with a normal one-compartment cell with a Pt working electrode, a Pt counter electrode, and a nonaqueous Ag/AgNO$_3$ reference electrode. The measurement was performed in a dichloromethane solution including 0.1
M tetrabutylammonium perchlorate as a supporting electrolyte.

All starting materials, catalysts, and dehydrated solvents were purchased from Tokyo Chemical Industry, Wako Pure Chemicals and Aldrich. Silica gel (SiO$_2$, spherically-shaped, neutral) for the flash chromatography was purchased from Kanto chemical. Triethylamination 2-butoxy-3-dicyanomethylidene-4-oxocyclobut-1-en-1-olate 1 [15], 1-butyl-5-carboxy-2,3,3-trimethyl-3H-indolium iodide 2 [16], triethylamination 2-[(1-butyl-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene)methyl]-3-dicyanomethylidene-4-oxocyclobut-1-en-1-olate 3 [13b], and 3-[(1-butyl-3,3-dimethyl-1,3-dihydro-2H-indol-2-ylidene)methyl]-4-hydroxycyclobut-3-ene-1,2-dione 4 [17] were prepared according to the literature.

6.2.2 Preparation of symmetric dicyanovinylene-substituted squaraine dye (SQM1a)

1 (0.59 g, 1.9 mmol) and 2 (1.7 g, 4.4 mmol) were dissolved in a mixture of 1-butanol (20 mL) and pyridine (20 mL). Then 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: CHCl$_3$/MeOH (v/v = 5/1)), and the product was precipitated from CHCl$_3$/MeOH/hexane solution to obtain SQM1a as a green solid (0.18 g, 0.28 mmol, 15%). $^1$H NMR [CDCl$_3$-CD$_3$OD (16/1(v/v)), 400 MHz]: $\delta$ 8.13 (dd, $J$ = 8.4, 1.2 Hz, 2H), 8.08 (d, $J$ = 1.2 Hz, 2H), 7.12 (d, $J$ = 8.4 Hz, 2H), 6.63 (s, 2H), 4.07 (t, $J$ = 7.6 Hz, 4H), 1.86–1.78 (m, 16H), 1.57–1.44 (m, 4H), 1.00 (t, $J$ = 7.6 Hz, 6H). $^{13}$C NMR [CDCl$_3$-CD$_3$OD (16/1(v/v)), 100 MHz]: $\delta$ 172.91, 172.85, 168.35, 168.24, 168.07, 145.85, 142.49, 131.10, 128.43, 126.51, 124.05, 118.83, 109.86, 90.65, 44.64, 41.28, 29.54, 26.68, 20.18, 13.96. IR (KBr, cm$^{-1}$): 2957, 2928, 1601, 1556, 1520, 1410, 1342, 1286, 1178, 1111, 1065. TOF-MS (ESI): m/z calcd for [M(C$_{39}$H$_{40}$N$_4$O$_5$)]$^+$, 644.30; found 644.50. Anal. Calcd for C$_{39}$H$_{40}$N$_4$O$_5$: C, 72.65; H, 6.25; N, 8.69. Found: C, 72.81; H, 6.15; N, 8.49 %.

6.2.3 Preparation of unsymmetric dicyanovinylene-substituted squarylium dye (SQM1b)

3 (0.104 g, 0.225 mmol) and 2 (0.0870 g, 0.225 mmol) were dissolved in a mixture of 1-butanol (4.5 mL) and toluene (4.5 mL). Then the solution was heated under reflux for 5 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: CHCl$_3$/MeOH (v/v = 8/1)), and the product was precipitated from CHCl$_3$/hexane solution to obtain SQM1b as a green solid (0.0943 g, 0.157 mmol, 70%). $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 8.12 (d, $J$ = 8.6 Hz, 1H), 8.03 (s, 1H), 7.43–7.35 (m, 2H), 7.28 (d, $J$ = 7.4 Hz, 1H), 7.13 (d, $J$ = 7.9 Hz, 1H), 6.72 (s, 2H), 4.07 (t, $J$ = 7.6 Hz, 4H), 1.86–1.78 (m, 16H), 1.57–1.44 (m, 4H), 1.00 (t, $J$ = 7.6 Hz, 6H). $^{13}$C NMR [CDCl$_3$-CD$_3$OD (16/1(v/v)), 100 MHz]: $\delta$ 172.91, 172.85, 168.35, 168.24, 168.07, 145.85, 142.49, 131.10, 128.43, 126.51, 124.05, 118.83, 109.86, 90.65, 44.64, 41.28, 29.54, 26.68, 20.18, 13.96. IR (KBr, cm$^{-1}$): 2957, 2928, 1601, 1556, 1520, 1410, 1342, 1286, 1178, 1111, 1065. TOF-MS (ESI): m/z calcd for [M(C$_{39}$H$_{40}$N$_4$O$_5$)]$^+$, 644.30; found 644.50. Anal. Calcd for C$_{39}$H$_{40}$N$_4$O$_5$: C, 72.65; H, 6.25; N, 8.69. Found: C, 72.81; H, 6.15; N, 8.49 %.
Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 6.65 (s, 1H), 6.52 (s, 1H), 4.10 (t, J = 7.5 Hz, 2H), 4.00 (t, J = 7.2 Hz, 2H), 1.85–1.73 (m, 16H), 1.56–1.43 (m, 4H), 1.03–0.96 (m, 6H). $^{13}$C NMR [CDCl$_3$-CD$_2$OD (16/1(v/v)), 100 MHz]: $\delta$ 173.78, 173.00, 170.62, 168.31, 168.11, 167.84, 165.08, 145.94, 142.58, 141.87, 141.49, 130.79, 128.15, 125.75, 125.46, 123.62, 122.30, 110.02, 118.94, 110.78, 109.13, 89.84, 89.39, 49.91, 48.61, 44.55, 44.04, 40.20, 29.51, 29.19, 26.64, 26.14, 19.98, 13.73, 13.70. IR (KBr, cm$^{-1}$): 2957, 2928, 1601, 1556, 1520, 1410, 1342, 1286, 1178, 1111, 1065. TOF-MS (ESI): m/z calcd for [M(C$_{38}$H$_{40}$N$_4$O$_3$)]$^+$, 600.31; found 600.50. Anal. Calcd for C$_{38}$H$_{40}$N$_4$O$_3$: C, 75.97; H, 6.71; N, 9.33. Found: C, 75.91; H, 6.62; N, 9.30 %.

6.2.4 Preparation of unsymmetric squarylium dye (MSQ)

4 (80 mg, 0.26 mmol) and 2 (109 mg, 0.28 mmol) and catalytic amount of quinoline were dissolved in 1-butanol–toluene (4/4 (v/v)) (1.7 mL). Then the solution was heated at 70 ºC reflux for 5 h. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent; CHCl$_3$/MeOH (15/1, v/v), and the product was precipitated from CHCl$_3$/hexane solution to obtain MSQ as a dark brown solid (49 mg, 0.088 mmol, 34%).$^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 7.99 (d, J = 1.4 Hz, 1H), 7.95 (dd, J = 8.4, 1.4 Hz, 1H), 7.57 (d, J = 7.2 Hz, 1H), 7.45–7.37 (m, 2H), 7.34 (d, J = 8.4 Hz, 1H), 7.24 (dd, J = 7.2 Hz, 1H), 5.91 (s, 1H), 5.82 (s, 1H), 4.16 (t, J = 7.6 Hz, 2H), 4.10–4.00 (m, 2H), 1.75–1.66 (m, 16H), 1.47-1.36 (m, 4H), 0.98-0.92 (m, 6H). $^{13}$C NMR [CDCl$_3$-CD$_2$OD (24/1(v/v)), 100 MHz]: $\delta$ 181.31, 176.94, 172.39, 169.27, 168.79, 146.87, 142.61, 142.17, 142.03, 131.05, 128.01, 124.67, 124.64, 123.99, 122.49, 110.15, 108.50, 87.80, 87.54, 49.95, 48.59, 44.00, 43.62, 29.41, 29.15, 27.31, 26.89, 20.43, 13.97, 13.95. IR (KBr, cm$^{-1}$): 3475, 2964, 2920, 1749, 1599, 1558, 1506, 1277, 1180, 1097. TOF-MS (ESI): m/z calcd for [M(C$_{38}$H$_{40}$N$_4$O$_3$)]$^+$, 551.30; found 551.22. Anal. Calcd. for C$_{35}$H$_{40}$N$_2$O$_4$: C, 75.82; H, 7.49; N, 4.95. Found: C, 76.06; H, 7.29; N, 5.07 %.

6.2.5 Fabrication and Photovoltaic Measurements of DSSCs

Transparent TiO$_2$ photoelectrodes (15 μm thick, 5 mm × 5 mm) were fabricated by screen-printing. Nanocrystalline TiO$_2$ paste [PST-18NR (particle size; ca. 20 nm), JGC Catalysts and Chemicals Ltd, Japan] was printed two times on the grass substrate coated with transparent conduction oxide (F-doped SnO$_2$). After drying 125 ºC for 10 min, TiO$_2$ paste consisting of large TiO$_2$ particle (ca. 400 nm, JGC Catalysts and Chemicals Ltd, Japan) was coated on it as a scattering center. Resulting substrate was gradually heated and sintered at 500 ºC for 15 min. After cooling, the sintered TiO$_2$
films were impregnated in a 40 mM TiCl$_4$ aqueous solution at 70 ºC for 30 min and then washed with distilled water and methanol. After drying under reduced pressure, treated TiO$_2$ films were sintered again at 500 ºC for 30 min. Resulting TiO$_2$ photoelectrodes were immersed in a solution of dyes (0.12 mM) and chenodeoxycholic acid (6.0 mM) in t-BuOH/acetonitrile (1/1 (v/v)) and then kept at ambient temperature overnight, followed by washing with acetonitrile to remove non-adsorbed dye. The dye-covered TiO$_2$ electrode and Pt-coated ITO grass substrate were sealed with a hot-melt gasket of 50 μm thickness made of the ionomer HIMALAN 1652 (Mitsui-Dupont) spacer. The internal space was filled with a liquid electrolyte using a vacuum backfilling system. The electrolyte injecting hole on the counter electrode glass substrate made with a drill, was sealed with a HIMALAN 1652 and a thin glass cover by heating. The electrolyte consisting of 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide (DMPImI), 0.05 M guanidium thiocyanate, 0.05 M LiI, and 0.03 M I$_2$ in acetonitrile/valeronitrile (85/15, v/v) was introduced into the interspace between the TiO$_2$ photoelectrode and the Pt counter electrode. The photovoltaic performance of the DSSC was measured using AM 1.5 solar simulator (CEP-2000, Bunko-Keiki, Japan) equipped with a source meter (Keithley 2400). The incident light intensity was calibrated with a standard Si solar cell. The incident photon-to-current conversion efficiency (IPCE) was measured using an action spectrum measurement system connected to a solar simulator (CEP-2000, Bunko-Keiki, Japan). Absorption spectra of the dyes immobilized on TiO$_2$ were measured using TiO$_2$ thin films (5 μm-thickness) prepared from a nanocrystalline TiO$_2$ paste (PST-18NR). The electrochemical impedance spectroscopy (EIS) measurements for were carried out with a Hokuto Denko HZ-5000 electrochemical measurement system with an impedance module. These measurements were carried out under illumination of AM 1.5G simulated sunlight at a bias potential set at open-circuit. The measurements were performed in a frequency range of 0.1 to 10$^5$ Hz and the alternate current amplitude of 10 mV.

6.2.6 X-ray structure determination

Crystallographic data for SQM1a: C$_{39}$H$_{40}$N$_4$O$_6$, A black prism crystal having crystal dimensions of 0.15 × 0.10 × 0.08 mm$^3$, $M$ = 660.77, triclinic, $a$ = 10.684(8), $b$ = 13.943(9), $c$ = 15.095(11) Å, $α$ = 105.322(9)$^o$, $β$ = 110.321(6)$^o$, $γ$ = 93.504(11)$^o$, $V$ = 2004(2) Å$^3$, space group $P-1$, $Z$ = 2, $ρ$ = 1.095 g cm$^{-3}$, $μ$(Mo-K$α$) = 0.744 cm$^{-1}$, F(000) = 700.0. Reflection data (2θ < 62.1$^o$) were collected on a Rigaku Mercury CCD area detector at 296 K with a graphite monochromated Mo-K$α$ radiation ($λ$ = 0.71070 Å). Of the 18394 reflections that were collected, 10774 were unique ($R_{int}$ = 0.046);
equivalent reflections were merged. A numerical absorption correction was applied which resulted in transmission factors ranging from 0.989 to 0.994. Lorentz and polarization corrections were applied. The structure was solved by a direct methods using the SIR92 program [18], expanded using the DIRDIF99 program [19]. The final cycle of full-matrix least-squares refinement on $F$ was based on 3587 observed reflections ($I > 1.50\sigma(I)$) and 480 variable parameters and converged to $R_1 = 0.1127$, $wR_2 = 0.0980$ and $GOF = 1.202$. One oxygen atom (O6) was found from the Fourier synthesis and may correspond to a water molecule from the solvent or environment used in the preparation of single crystals. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using the riding model. All the calculations were performed using the Crystal Structure 3.8 software package of the Molecular Structure Corporation [20]. Full crystallographic details excluding structure factors have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC-901550 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6.2.7 DFT Calculations of SQM1a-b and MSQ
The ground-state geometries of SQM1a-b and MSQ were optimized in the gas phase by DFT calculations with the Gaussian 09 program [21]. The calculations were performed on the models in which the butyl substituents have been replaced by methyl groups with the B3LYP exchange-correlation functional under a 6-31G(d) basis set. The time-dependent DFT (TD-DFT) calculations were performed to calculate the compositions in terms of molecular orbital contributions based on their corresponding optimized geometries calculated at the B3LYP/6-31G(d) level. In TDDFT calculations, the lowest 4 singlet-singlet excitations were calculated. The calculation for MSQ showed only a transition with higher oscillator strength ($f = 1.5$) characterized to HOMO-LUMO excitation.

6.2.8 Absorption spectra of SQM1a-b immobilized on TiO$_{2}$
Absorption spectra of the dyes immobilized on TiO$_{2}$ were measured using TiO$_{2}$ thin films (5 μm-thickness) prepared from a nanocrystalline TiO$_{2}$ paste (PST-18NR). The TiO$_{2}$ films were immersed in the dye bath including dyes (0.12 mM) and chenodeoxycholic acid (6.0 mM) in t-BuOH/acetonitrile (1/1 (v/v)) and then kept for given time at room temperature. The resulting films were washed with acetonitrile to remove non-adsorbed dyes.
6.3 Results and discussion

6.3.1 Synthesis of symmetrical squaraine SQM1a and unsymmetrical squaraines SQM1b and MSQ

The symmetrical and dicyanovinylene-substituted squaraine SQM1a was synthesized by the condensation of the triethylammonium 2-butoxy-3-dicyanomethylene-4-oxo-1-cyclobuten-1-olate 1 with 5-carboxy-1-butyl-2,3,3-trimethyl-3H-indolium iodide 2 under azeotropic conditions (Scheme 1(A)). Unsymmetrical squaraines SQM1b and MSQ were prepared by the reaction of semisquaraines, which were derived from a corresponding squaric acid derivative and 1-butyl-2,3,3-trimethyl-3H-indolium iodide, with 2 (Scheme 1(B) and (C)).

![Scheme 1. Synthesis of squarylium dyes](image)

An X-ray crystal structure analysis of SQM1a indicated that indolenine components lie on the same side of the plane, resulting in cis-like conformation in order to reduce the steric repulsion between cyano groups and indolenine components, whereas the squaraine dyes such as MSQ possess trans-like arrangements (Fig. 1(B))
and 2) [22]. Thus, dicyanovinylene groups significantly affect the conformation of sensitizing dyes, as indicated in previous reports [13].

![An ORTEP drawing of SQM1a. Thermal ellipsoids are set at the 50% probability level.](image)

**Fig. 2.** An ORTEP drawing of SQM1a. Thermal ellipsoids are set at the 50% probability level.

### 6.3.2 FT-IR spectra of dye-adsorbed TiO2

The FT-IR spectra of SQM1a-b immobilized on TiO2 thin films prepared on KCl plates and free dyes were measured to characterize their adsorption on TiO2 (Fig. 3).

![FT-IR spectra of SQM1a (A) and SQM1b (B) (solid line, KBr method) and on TiO2 thin films (bold line).](image)

**Fig. 3.** FT-IR spectra of SQM1a (A) and SQM1b (B) (solid line, KBr method) and on TiO2 thin films (bold line)
The IR spectra of free dyes showed absorptions attributable to C=O stretching bands of carboxy groups at 1682 cm$^{-1}$ for SQM1a and 1689 cm$^{-1}$ for SQM1b. In the spectra of dyes on TiO$_2$, the carbonyl stretching bands for carboxy groups completely disappeared, and an absorption around 1390 cm$^{-1}$ and shoulders of peaks at 1515 cm$^{-1}$ for SQM1a and 1510 cm$^{-1}$ for SQM1b were observed instead. These peaks can be assigned to O–C–O symmetric and asymmetric stretching in the carboxylate, suggesting that SQM1a-b are chemically adsorbed on TiO$_2$ with a carboxylate coordination after deprotonation [12,23]. Moreover, these spectral changes upon adsorption of SQM1a on TiO$_2$ indicate that SQM1a with a cis-like conformation is double-anchored by two carboxy groups.

6.3.3 Absorption and electrochemical properties

The absorption and fluorescence spectra of SQM1a-b and MSQ in CHCl$_3$ are shown in Fig. 3, and the characteristic data are summarized in Table 1.

These dyes exhibited intense and sharp absorptions in the far-red region. Substitution with a dicyanovinylene group resulted in a strong redshift of absorption relative to the absorption of MSQ. The shift of absorption maxima reached 63 nm (1392 cm$^{-1}$) for SQM1a and 50 nm (1125 cm$^{-1}$) for SQM1b. In comparison to SQM1b, the absorption of SQM1a was bathochromically shifted owing to two carboxy groups symmetrically placed in SQM1a, which act as acceptor units.

![Fig. 4. Absorption and fluorescence spectra of CHCl$_3$ solutions (A) and absorption spectra of dyes immobilized on TiO$_2$ films (B) (Inset: Plots of absorbance dye-loaded TiO$_2$ versus immersion time)](image-url)
Table 1. Photophysical and electrochemical properties of squaraine dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}^{a}/\text{nm}$</th>
<th>$\varepsilon^{a}/\text{M}^{-1}\text{cm}^{-1}$</th>
<th>$\lambda_{\text{em}}^{a}$/nm</th>
<th>$\lambda_{\text{max}}^{\text{on}}$/nm</th>
<th>TiO$_2$/nm</th>
<th>$E_{0,0}^{b}$/V</th>
<th>$E_{\text{ox}}^{c}$/V</th>
<th>$E_{\text{ox}}-E_{0,0}^{b}$/V</th>
<th>$\Phi_F^{a}$</th>
<th>$\tau^{a,d}$/ns</th>
<th>$k_{nr}^{e}$/ns$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQM1a</td>
<td>705</td>
<td>$1.58 \times 10^5$</td>
<td>712</td>
<td>730</td>
<td>1.73</td>
<td>0.94</td>
<td>–0.79</td>
<td>0.47</td>
<td>3.60</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>SQM1b</td>
<td>692</td>
<td>$1.88 \times 10^5$</td>
<td>685</td>
<td>718</td>
<td>1.76</td>
<td>0.91</td>
<td>–0.82</td>
<td>0.27</td>
<td>2.14</td>
<td>0.34</td>
<td></td>
</tr>
<tr>
<td>MSQ</td>
<td>642</td>
<td>$2.56 \times 10^5$</td>
<td>643</td>
<td>656</td>
<td>1.80</td>
<td>0.72</td>
<td>–1.08</td>
<td>0.18</td>
<td>1.14</td>
<td>0.72</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Measured in CHCl$_3$ solutions. $^b$ The zeroth-zeroth transition $E_{0,0}$ was estimated from the intersection of the absorption and emission spectra. $^c$ The oxidation potential was measured on 0.1 M TBACIO$_4$ in CH$_2$Cl$_2$ (working electrode: Pt; reference electrode: nonaqueous Ag/AgNO$_3$ calibrated with ferrocene/ferrocenium (Fc/Fc+); counter electrode: Pt). $^d$ Lifetimes were determined by fitting the decay curves with a single-exponential decay function. The quantities that express the mismatch between data and fitted function ($\chi^2$) are 1.07 for SQM1a, 1.07 for SQM1b, and 1.04 for MSQ. $^e$ The $k_{nr}$ values were obtained by following equation: $k_{nr} = \tau^{-1}(1-\Phi_F)$.

Consistent with the result in a previous report, SQM1a-b exhibit additional absorption with moderate intensity in the visible region below 500 nm [13]. The absorption spectra of SQM1a-b attached to TiO$_2$ films in the presence of chenodeoxycholic acid (CDCA) were broadened but still showed spectral features observed in solution, implying increased interaction between the dyes immobilized on TiO$_2$ and the electronic coupling between the dye and TiO$_2$ [7e]. The plots of absorbance of dye-loaded TiO$_2$ versus immersion time reveals that adsorptive capability and adsorption rate of SQM1a is higher than that of SQM1b owing to the double-anchoring of symmetrical SQM1a as evidenced by the IR measurement (Fig. 4B inset and 5).
Fig. 5. Absorption spectra of SQM1a (A) and SQM1b (B) immobilized on TiO$_2$ (5 μm-thickness) with the change of immersion time.

Fig. 6. Cyclic voltammograms of SQM1a (A), SQM1b and MSQ (B) in CH$_2$Cl$_2$ with 0.1 M tetrabutylammonium perchlorate as supporting electrolytes. A Pt working electrode, a Pt counter electrode, and a nonaqueous Ag/AgNO$_3$ reference electrode were used. The scan rate was 100 mV/s.

The oxidation potentials $E_{\text{ox}}$ corresponding to the HOMO levels of dyes were measured by cyclic voltammetry (Table 1, Fig. 6). The cyclic voltammograms of SQM1a and SQM1b showed two reversible oxidation waves in the potential range from −0.25 to 1.0 V, respectively. The potential of oxidation waves of SQM1a remains unchanged for a hundred scans, implying that SQM1a is electrochemically stable under the measurement condition. In case of MSQ, a reversible oxidation wave was not
observed in the potential range from –0.25 to 1.0 V, but observed from –0.1 to 0.3 V. These results indicate that MSQ exhibited electrochemical reversibility under the one-electron oxidation condition, although the electroactive species yielded in two-electron oxidation of MSQ showed no clear reversibility. SQM1a-b were shown to possess higher oxidation potential (E_{ox}) than MSQ due to the stabilization of HOMO enhanced by the delocalization of π electrons. The oxidation potentials were all sufficiently more positive than the I^{-}/I_{3}^{−} redox potential value (0.5 V vs NHE), indicating that the oxidized dyes could thermodynamically accept electrons from the I^{-} ions. The potential levels of E_{ox}−E_{0-0} corresponding to the LUMO levels of dyes were more negative than the potentials of the TiO_{2} conduction band edge (−0.5 V vs NHE), which are at sufficiently high energy for thermodynamically favorable injection of electrons.

6.3.4 Fluorescence quantum yield and lifetime

The fluorescence quantum yield (Φ_{F}) and lifetime (τ) of these dyes in CHCl_{3} are shown in Table 1. The lifetimes were determined by fitting the decay curves with a single-exponential decay function (Fig. 7).

![Fig. 7. Fluorescence decay of SQM1a, SQM1b, and MSQ in CHCl_{3}. Excitation wavelength λ_{ex} = 625 nm.](image)

In SQM1a-b, photoisomerization from the trans-like to cis-like conformation, which can occur in typical squaranines, is expected to be suppressed due to the steric
effect of dicyanovinylene groups [10]. In fact, the non-radiative decay rate \( k_{nr} \) of SQM1a-b estimated by fluorescence quantum yields and lifetimes is smaller than that of MSQ. In particular, the \( k_{nr} \) of the dicyanovinylene substitution is effective for the suppression of nonradiative decay, probably due to the inhibition of the photoisomerization pathway. Moreover, the incorporation of a carboxy group to both the indolenine moieties in a dicyanovinylene-substituted squaraine dye, providing symmetrical squaraines (SQM1a), contributed to the further depression of the non-radiative decay rate.

6.3.5 Molecular orbital calculations

![Schematic diagram of the frontier molecular orbitals of SQM1a-b and MSQ](image)

Fig. 8. Schematic diagram of the frontier molecular orbitals of SQM1a-b and MSQ calculated at the B3LYP/6-31G(d) level of theory. The surfaces are generated with an isovalue at 0.02. The calculations were performed on the models in which methyl groups replaced alkyl substituents.

To gain insight into the electronic structures of SQM1a-b, DFT/TDDFT calculations were carried out at the B3LYP/6-31G(d) level. In both dyes, the electron density of HOMO was delocalized over the dicyanovinylene groups in addition to the cyclobutenes, while HOMO–1 was delocalized over dicyanomethylene and indolenine units (Fig. 8). The LUMO is located on indolium components bearing carboxylic acid as an anchoring site to the TiO\(_2\) surface. TD-DFT calculations for SQM1a-b revealed that the lowest transition at 1.8 eV \( (f = 1.0) \) is mainly characterized by HOMO-LUMO excitation. The second-lowest transitions (2.8 eV) for SQM1a-b with high oscillator
strength were characterized as HOMO–1-LUMO excitations attributable to the absorption around 450 nm observed for CHCl$_3$ (Table 2). Thus, in SQM1a-b, a clear unidirectional electron transfer from the cyclobutene core to the terminal indolenine with the anchoring group can be achieved through HOMO-LUMO and HOMO–1-LUMO transition, promising panchromatic performance for SQM1a-b and efficient electron injection to TiO$_2$ [14].

<table>
<thead>
<tr>
<th>Dye</th>
<th>$E$ (eV)</th>
<th>$F$</th>
<th>Composition$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQM1a</td>
<td>1.83</td>
<td>0.56</td>
<td>H–1 → L (16%), H → L (69%)</td>
</tr>
<tr>
<td></td>
<td>2.79</td>
<td>1.06</td>
<td>H–1 → L (69%)</td>
</tr>
<tr>
<td>SQM1b</td>
<td>1.88</td>
<td>0.55</td>
<td>H–1 → L (17%), H → L (69%)</td>
</tr>
<tr>
<td></td>
<td>2.83</td>
<td>0.99</td>
<td>H–1 → L (68%)</td>
</tr>
<tr>
<td>MSQ</td>
<td>2.27</td>
<td>1.47</td>
<td>H → L (71%)</td>
</tr>
</tbody>
</table>

$^a$ $n$ is the ordering number of the calculated excited state. $^b$ H = HOMO, L = LUMO

### 6.3.6 Characterization of DSSCs

To evaluate the effect of dicyanovinylene groups in SQM1a-b on photovoltaic performance, preliminary dye-sensitized solar cells with an effective area of 0.25 cm$^2$ were fabricated with a liquid electrolyte system based on iodine (Fig. 9, Table 3).

![Fig. 9](image)

**Fig. 9.** IPCE spectra (A) and photocurrent density–voltage curves of DSSCs based on SQM1a-b and MSQ
Table 3. Photovoltaic performance of DSSCs based on SQM1a-b and MSQ \(^a\)

<table>
<thead>
<tr>
<th>dye</th>
<th>(J_{sc})/ mAcm(^2)</th>
<th>(V_{oc})/ V</th>
<th>(FF)</th>
<th>(\eta)/ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQM1a</td>
<td>14.2</td>
<td>0.50</td>
<td>0.51</td>
<td>3.6</td>
</tr>
<tr>
<td>SQM1b</td>
<td>10.3</td>
<td>0.53</td>
<td>0.53</td>
<td>2.9</td>
</tr>
<tr>
<td>MSQ</td>
<td>10.0</td>
<td>0.44</td>
<td>0.50</td>
<td>2.2</td>
</tr>
<tr>
<td>N719</td>
<td>15.5</td>
<td>0.77</td>
<td>0.49</td>
<td>5.8</td>
</tr>
</tbody>
</table>

\(^a\) Condition: irradiated light, AM1.5 G (100 mW/cm\(^2\)); photoelectrode, TiO\(_2\) (15 \(\mu\)m thickness and 0.25 cm\(^2\) working area); electrolyte, 0.03 M I\(_2\), 0.05 M LiI, and 0.6 M DMPImI, 0.05 M GuNCS in acetonitrile/valeronitrile (85/15, (v/v)); dye solution, acetonitrile/t-butanol (0.12 mM) with addition of CDCA (60 mM). \(^b\) Electrolyte, 0.03 M I\(_2\), 0.5 M BMImI, 0.1 M GuNCSm 0.5 M TBP in acetonitrile/valeronitrile (85/15, (v/v)).

SQM1a-b exhibited greater spectral response than MSQ in the longer wavelength region, between 800 nm and 530 nm. In addition to the long-wavelength responses, relatively high IPCE values at 500–400 nm were found in the spectra of DSSCs based on SQM1a-b, indicating that the additional light-harvesting properties were the result of the substitution with dicyanovinylene groups. The short-circuit current density \((J_{sc})\) values of the DSSCs sensitized with SQM1a (14.2 mA/cm\(^2\)) were greater than those with SQM1b (10.3 mA/cm\(^2\)) and MSQ (10.0 mA/cm\(^2\)). The \(J_{sc}\) value of symmetrical SQM1a was improved by 38% compared to that of unsymmetrical SQM1b although the light harvesting efficiency (LHE) estimated from absorption maxima of dye-loaded TiO\(_2\) electrodes was not much different between SQM1a (LHE = 0.98) and SQM1b (LHE = 0.99). This suggests that symmetrical SQM1a have a much higher probability of electron injection assuming that efficiency of dye regeneration and collecting injected charge are almost identical \([24]\). Thus, the improvements of \(J_{sc}\) found in the DSSC with SQM1a should be attributed not only to the panchromatic response but also to the efficient electron injection, which was probably due to the reduction in energy loss resulting from photoisomerization, as suggested by the results of fluorescence decay. As shown in the current-voltage curves of DSSCs, the open-circuit voltage of DSSCs based on SQM1a-b (0.50 V for SQM1a, 0.53 V for SQM1b) were also higher than that of MSQ (0.44 V). To understand the improvements of \(V_{oc}\) electrochemical impedance spectral (EIS) analyses of DSSCs based on SQM1a-b and MSQ were carried out (Fig. 10).
Fig. 10. (A) Nyquist and (B) Bode plots of DSSCs based on SQM1a-b and MSQ under AM 1.5G simulated light at the applied bias voltage set at the open-circuit voltage of the cells.

In Bode plots, the peaks at middle frequency are associated with charge-transfer resistances at the TiO$_2$/dye/electrolyte interface corresponding to the large semicircles in Nyquist plots. The electron lifetimes are correlated with the reciprocal of the peak frequency for middle-frequency peaks [25]. The peaks for SQM1a-b were left-shifted compared to MSQ, indicating that DSSCs based on SQM1a-b, in which the conformations are set into cis-like arrangement, exhibited longer electron lifetimes, thereby contributing the higher $V_{oc}$ of DSSC based on SQM1a-b. As a consequence of the improvements of $J_{sc}$ and $V_{oc}$, the overall conversion efficiency ($\eta$) values for SQM1a (3.6%) were higher than those for SQM1b (2.9%) and MSQ (2.2%), although their fill factors (FF) were comparable (0.51 for SQM1a, 0.53 for SQM1b, and 0.50 for MSQ). Considering the result for a DSSC with a benchmark dye (N719) fabricated with the same components, which continued to show low performance in spite of the use of an efficient electrolyte for N719, the conditions that affect the overall conversion efficiency can be further optimized. This study, however, reveals the great advantages that can be realized by restricting the conformation of symmetrical squaraine dyes.

6.4 Conclusions

Substitution of carbonyl groups in squaraine dye with dicyanovinylene groups causes changes in the conformation, absorption and fluorescence properties. Dicyanovinylene-substituted squaraine sensitizer adopt cis-like conformation in order to reduce the steric repulsion between cyano groups and indolenine components. Symmetrical SQM1a with dicyanovinylene-substitution can be adsorbed on TiO$_2$ by the interaction at two carboxy groups. By the double-anchoring, the adsorptive capability of
SQM1a on TiO₂ was better than unsymmetrical analogue bearing one carboxy group (SQM1b). The conformational lock of squaraine dyes in the cis-like form resulted in an increase of the fluorescence quantum yield (Φ_F) and expansion of the lifetime (τ), thereby reducing the non-radiative decay rates.

Furthermore, dicyanovinylene-substituted SQM1a with a symmetrical structure exhibited a further decline in the non-radiative decay rate. Thus, the conformational lock of symmetrical squaraine dyes was effective for the suppression of non-radiative decay. The short-circuit current density of DSSCs based on SQM1a was significantly enhanced in comparison with that of the unsymmetrical analogue bearing one carboxy group (SQM1b) and the standard squaraine dye (MSQ), suggesting that suppression of non-radiative decay brought about the efficient electron injection.

The electron lifetimes of DSSCs based on dicyanovinylene-substituted SQM1a-b were expanded in comparison to that of the standard MSQ, resulting in higher V_{oc} of cells. As a result, the DSSC photovoltaic property of symmetrical and dicyanovinylene-substituted SQM1a was improved significantly. Dicyanovinylene substitution is applicable to various kinds of squaraine dyes. These results present a new design strategy for developing high-efficiency and long-wavelength response squaraine sensitizers for application to DSSCs.
6.5 References


Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.


Chapter 7

General Conclusions

In this thesis, the author discussed the performance of DSSCs fabricated with new molecular-designed squarylium dyes. To investigate the effective dyes for DSSCs, five improvable points, which are absorption range, LUMO level, HOMO level, suppression of charge recombination and minimization for aggregation, must be considered. I especially showed the attractive design of squarylium dyes to attain the high photo-electric energy conversion efficiency on DSSCs by focus on the donor-π-bridge-acceptor (D-π-A) structure with a strong electron acceptor and the π-extended structure with / without dicyanovinylene–substituent, unsymmetrical structure bearing pyrylium or thiopyrylium components, the conformationally locked structure possessing dicyanovinylene–substituent. The results and findings are summarized as follows.

In Chapter 2, 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$_2$-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$_2$. 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$_2$. 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$_2$ surface.

In Chapter 3, novel π-extended squarylium dyes with dicyanovinylene substitution were synthesized through the Stille-type Pd-catalyzed cross-coupling reaction of precursory iodinated squarylium dye with tributylstannyl squarate. Dye-sensitized solar cells (DSSCs) based on the squarylium dyes displayed remarkable performance in a wide wavelength from the visible to the near-infrared region around 800 nm. The power
conversion efficiencies of the DSSCs based on In-CN-In-S-OH and In-CN-In-S-In-COOH reached 3.5% and 2.1%, respectively.

In Chapter 4, squarylium dyes with linearly π-extended structures involving three cyclobutene cores and four heterocyclic components were designed as metal-free sensitizing dyes that can enhance spectral responses in the range over 800 nm and successfully synthesized through the combination of Pd-catalyzed cross-coupling using stannylecyclobutenediones and condensation reactions. The dyes exhibited intense absorption in the NIR region with maxima at around 850 nm and onsets at around 950 nm. Although the HOMO levels remained at the same levels as the corresponding standard squaraine dye, the LUMO levels of the dyes were at lower energies owing to the lowering of the band gaps of the dyes. Dye-sensitized solar cells (DSSCs) based on these dyes exhibiting significantly wide spectral response including the NIR region showed enhanced short-circuit current density. Co-sensitization of the NIR-absorbing dyes with a standard far-red absorbing squaraine dye produced a complementary effect in spectral response, resulting in the increase of short-circuit current density.

In Chapter 5, Unsymmetrical squaraine dyes bearing pyrylium or thiopyrylium components were synthesized and their light-absorbing properties in the long-wavelength region were investigated. Condensations of 2,6-Di-tert-butyl-4-methyl pyrylium and thiopyrylium salt with butyl squarate afford corresponding semi-squaryliums. The semi-squaryliums are reacted with indolenium with carboxyl group to give target unsymmetrical dyes. They exhibited intense absorption in the far-red and near-infrared region in solution and on the TiO₂ surface. Electrochemical measurements revealed that electron injection from the excited dyes to the TiO₂ conduction band was thermodynamically permitted. A molecular-orbital calculation indicated that the electron distribution moved from the cyclobutene core to not only the pyrylium / thiopyrylium components but also indolenine bearing carboxyl anchors, by photoexcitation. The photovoltaic performances of DSSCs based on unsymmetrical squarylium dyes achieved comparatively high performance in metal-free NIR sensitizers. These results suggest that pyrylium and thiopyrylium components strongly affect not only the physical properties of the dyes but also the photovoltaic performances of DSSCs based on these dyes.

In Chapter 6, a symmetrical squaraine dye altered to possess dicyanovinylene functionality on a carbonyl group of the cyclobutene core (SQM1a) was synthesized to elucidate the effects of the conformationally locked-in cis-like form ensured by the steric repulsion of dicyanovinylenes on the performance of dye-sensitized solar cells (DSSCs) through a comparison with an unsymmetrical analogue bearing one carboxy
group (SQM1b) and a standard squaraine dye (MSQ). The FT-IR spectrum of the TiO$_2$ thin film immersed in the dye solution suggested that the linkages between the dye and TiO$_2$ were formed by both carboxy groups symmetrically incorporated on the π-conjugation of dyes. The symmetrical and conformationally locked structure of SQM1a brought about a decrease in the non-radiative decay rate, which may have been induced by suppression of the possible photoisomerization of squaraines. In accordance with the finding of non-radiative decay, a DSSC fabricated with SQM1a exhibited a significantly enhanced short-circuit current density, which revealed an efficient electron injection derived from the double-anchored and conformationally locked structure of SQM1a. Consequently, the performance of DSSCs fabricated with SQM1a was higher than the performance of those fabricated with SQM1b and MSQ. This indicates that substantial advantages can be derived by restricting the conformation of symmetrical squaraine dyes.

In conclusion, the author indicated that π-extended squarylium dyes have the adequate HOMO-LUMO level as the sensitizer for DSSCs and DSSCs based on π-extended squarylium dyes exhibited the power conversion efficiencies and spectral responses in the long-wavelength region. As our results, the π-conjugation strategy of squarylium dyes may contribute to the development of NIR-absorbing sensitizers, although further effort toward structural modification is required for the improvement of device performance. The development of the NIR absorbing Squarylium dye as the sensitizer of photo-to-electron conversion device has potential for not only the study of tandem-type cell by using each dyes light-harvesting at short and long wavelength, but also the synthetic strategy of π-extended squarylium dye. There is no doubt that the development of NIR absorbing dye will be one of the major target of future research. The author also indicated that dicyanovinylene functionality caused conformationally locked structure and a decrease in the non-radiative decay rate to enhance the performance of DSSCs fabricated with dicyanovinylene-substituted sqarylium dyes. The derivatization of dicyanovinylene-substituted showed one of the new possibility to apply a carbonyl group with no related to π-conjugation system in squarylium structure to another synthetic strategy and new functionality.

The author expects this thesis makes a great role to overcome problems of the development for DSSCs.
Acknowlegdement

The author would like to express my sincere gratitude to my supervisor, Professor Hiroyuki Nakazumi for providing me this precious study opportunity as a Ph.D student in his laboratory, helpful comments and valuable suggestions throughout this work. The author also wishes to express gratitude to Professor Akiya Ogawa and Professor Masaya Matsuoka for valuable comments and discussions. The author would also like to thank Dr. Shigeyuki Yagi and Dr. Takeshi Maeda for his elaborated guidance, considerable encouragement and invaluable discussion during this work.

The author is very grateful to president Takeru Kitashoji, Dr. Katsunori Shibata and NARD members of my company (NARD Institute, Ltd.) for their helpful supports and valuable suggestions, and all the members of Prof. Nakazumi’s laboratory for their cooperation in my experiments.

Finally, the author gratefully appreciates the financial support of the Kansai Bureau of Economy, Trade, and Industry (METI-KANSAI) that made it possible to complete my thesis.

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July, 2013
List of Publications

Chapter 2
T. Maeda, H. Nakao, H. Kito, H. Ichinose, S. Yagi, H. Nakazumi
“Far-red absorbing squarylium dyes with terminally connected electron-accepting units for organic dye-sensitized solar cells”

Chapter 3
H. Nakao, T. Maeda, H. Nakazumi
“Near-infrared-absorbing π-extended squarylium-based dyes with dicyanovinylene substitution for dye-sensitized solar cell applications”

Chapter 4
T. Maeda, S. Arikawa, H. Nakao, S. Yagi, H. Nakazumi
“Linearly π-extended squaraine dyes enable the spectral response of dye-sensitized solar cells in the NIR region over 800 nm”

Chapter 5
T. Maeda, S. Nitta, H. Nakao, S. Yagi, H. Nakazumi
“Squaraine dyes with pyrylium and thiopyrylium components for harvest of near infrared light in dye-sensitized solar cells”
*Dyes Pigm.*, submitted.

Chapter 6
“Conformational effect of symmetrical squaraine dyes on the performance of dye-sensitized solar cells”