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Near-infrared Absorbing Squarylium Dyes with Linearly Extended π-Conjugated Structure for Dye-sensitized Solar Cell Applications

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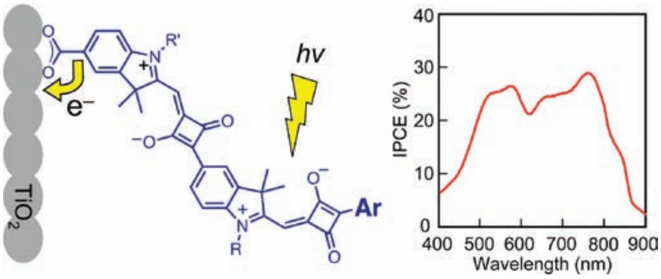
ABSTRACT



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 stannylcyclobutenediones, has been developed for dye-sensitized solar cells. The cells based on these dyes exhibited a significant spectral response in the near-infrared region over 750 nm in addition to the visible region.

Dye-sensitized solar cells (DSSCs) have attracted much attention because they have potential for the substantial development of highly efficient and cost-effective photovoltaic devices.[1,2] For the improvement of the overall photoelectric conversion efficiency of DSSCs, it is quite important to use the whole range of solar irradiation including visible and near-infrared (NIR) light. DSSCs sensitized with a trithiocyanate-ruthenium complex with a terpyridyl ligand, so-called “Black dye”, which shows broader absorption from the visible to the NIR region, achieved a high overall efficiency due to the efficient panchromatic photosensitization of nanocrystalline TiO_2.[3] 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.[4] Although the photovoltaic performances of DSSCs based on these dyes have been greatly improved to date, the spectral response of the cells in the NIR region is still insufficient.

Squarylium dyes have received much attention as photosensitizers due to their extremely high absorption coefficients in the visible to NIR region and their flexibility for synthetic manipulation.[5−7] Nazeerudin et al. reported far-red absorbing indole-based squarylium dye bearing carboxylic groups directly attached to the indole components

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and achieved high conversion efficiency (η = 4.5%) originating from the unidirectional flow of electrons from the light-harvesting components of the sensitizer to the semiconductor surface.[7g] For the synthesis of NIR-absorbing squarylium dyes, one of the most common methods is the extension of conjugation through the condensation of π-extended aromatics with squaric acid.[8] Oligomerization via the condensation of homoditopic heterocycles with squaric acid is also known as a design method for π-extended squarylium dyes. These methods utilize the condensation reaction based on squaric acid.[9] Liebeskind focused on the reactivity of 3-stannylcyclobutenediones as nucleophilic cyclobutenedione equivalents, which can react with various kinds of arylhalides under the Stille cross-coupling condition to afford novel semisquarates.[10] The approach using organometallic C–C coupling is beneficial to the synthesis of novel NIR-absorbing squarylium dyes due not only to the choice and availability of arylhalides but also due to the mild and neutral reaction conditions, which lessen the chances of side reactions leading to the decomposition of dyes.[11] Here, we report the synthesis of a novel class of NIR-absorbing squarylium sensitizers with linearly extended π-conjugated structures achieved by the Pd-catalyzed cross-coupling of tributylstannylsquarate and terminally iodinated squarylium dyes (Figure 1). Three dyes, in which indole, benzothiazol, and aniline moieties were adopted as terminal aromatic components, were designed to improve the light absorption capability and the photon-to-current conversion efficiency of DSSCs in the NIR region (Scheme 1).

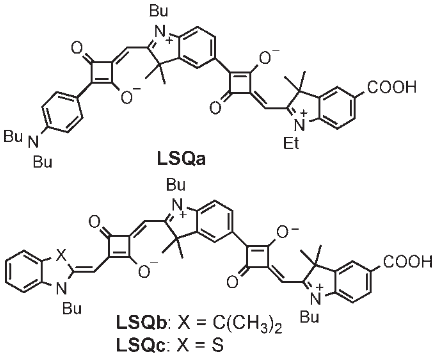
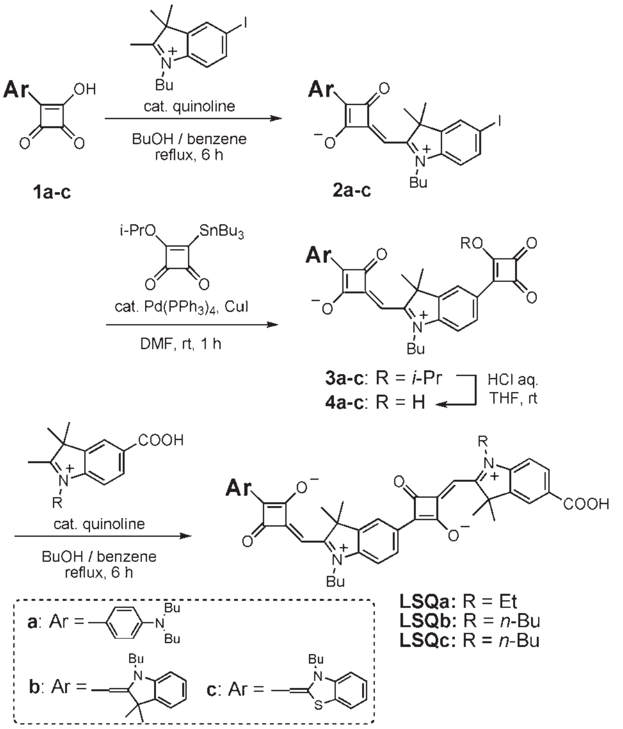


Figure 1. Molecular structures of squarylium sensitizers with linearly extended π-conjugated systems.

Scheme 1. Synthesis of **LSQa–c**



The carboxyl group was introduced to the 5-position of the terminal indole component to enable adsorption on the TiO_2-based photoelectrode and the efficient electron injection from dyes to conduction bands of TiO_2. These dyes were obtained in a three-step procedure. In the first step, an iodinated indolenium iodide was attached to the aniline-, indole-, and thiazol-based semisquaryliums (**1a–c**) by condensation in an azeotropic condition. In the next step, iodinated squarylium dyes (**2a–c**) were reacted with tributylstannylsquarate under the modified Stille condition and the resulting 2-propyl esters were hydrolyzed to obtain the corresponding squarylim dyes bearing the semisquaric acid group (**4a–c**).[10] Subsequently, condensation of the semisquaric acids with indolium salt having a carboxylic acid group produced linearly π-extended unsymmetrical squarylium sensitizers (**LSQa–c**).

Normalized absorption spectra of **LSQa–c** and their squarylium precursors (**2a–c**) in $CHCl_3$ are shown in Figure 2A, and the characteristic data are summarized in Table 1. Absorption maxima of **LSQ**s were bathochromically shifted (up to 138 nm for **LSQb**) in comparison with absorptions of **2a–c** and reached the near-infrared region. This indicated that the breaking of π-conjugation stemming from distortions between π-conjugated components

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was inhibited and therefore π-electrons were delocalized into the whole of the dye molecules including the additional semisquarylium components. The molar absorption coefficients at absorption maxima were found to be 1.89×10^5 for **LSQa**, 1.74×10^5 $M^{-1} cm^{-1}$ for **LSQb**, 1.89×10^5 for **LSQc**: much higher than those of Ru(II) polypyridyl complexes (ca. 1×10^4 $M^{-1} cm^{-1}$). Additional absorption peaks with moderate intensity were found in the visible region (475−700 nm), promising panchromatic performance for **LSQ**s. In the absorption spectra of **LSQ**s attached to TiO_2 films under the coadsorbent-free condition, blue-shifted absorptions were observed for the dyes indicating the formation of H-aggregates that usually impede the efficient electron injection into the conduction band of TiO_2 (Figure 2B).[12] In the presence of chenodeoxycholic acid (CDCA), the absorptions in the blue-shifted region were greatly weakened and the sharp absorptions in the NIR region were observed. Thus, the coadsorption of CDCA with dyes was effective in suppressing the aggregation of **LSQ**s on TiO_2 . The oxidation potentials E_{ox} corresponding to HOMO levels of **LSQ**s were measured by cyclic voltammetry (Table 1, Figure 1S, Supporting Information). All dyes exhibited reversible oxidation waves. The oxidation potentials were all sufficiently more positive than the I^-/I_3^- redox potential value (0.5 V vs normal hydrogen electrode, NHE), indicating that the oxidized dyes could thermodynamically accept electrons from the I^- ions.[13] The potential levels of $E_{ox} - E_{0-0}$, where E_{0-0} is the 0−0 energy of the dyes estimated from the absorption spectra, corresponding to the LUMO levels of **LSQ**s, 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.

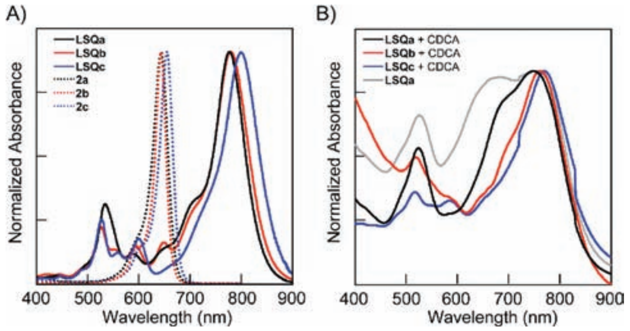

Figure 2. Absorption spectra of **LSQa−c** and **2a−c** (A) in $CHCl_3$ and (B) on TiO_2 thin films. Dye-loaded films were prepared by dipping in dye solution (1.2×10^{-4} M) and in *t*-butanol/acetonitrile (1/1 (v/v)) with/without addition of CDCA (6×10^{-2} M).

Table 1. Absorption and Electrochemical Properties of the Squarylium Dyes

dye	λ_{max} nm (ε, $M^{-1} cm^{-1}$)[a]	λ_{max} nm (on TiO_2)	E_{ox} (V vs NHE)[b]	$E_{ox} - E_{0-0}$ (V vs NHE)[c]
LSQa	777 (174 000)	750	0.85	−0.51
LSQb	779 (180 000)	761	0.77	−0.61
LSQc	800 (189 000)	769	0.72	−0.69

[a] Measured in $CHCl_3$ solutions (5×10^{-6} M). [b] Oxidation potential was measured on 0.1 M tetrabutylammonium perchlorate in CH_2Cl_2 (working electrode: Pt; reference electrode: nonaqueous $Ag/AgNO_3$ calibrated with ferrocene/ferrocenium (Fc/Fc^+); counter electrode: Pt). [c] E_{0-0} value was estimated from the onset of the absorption spectrum.

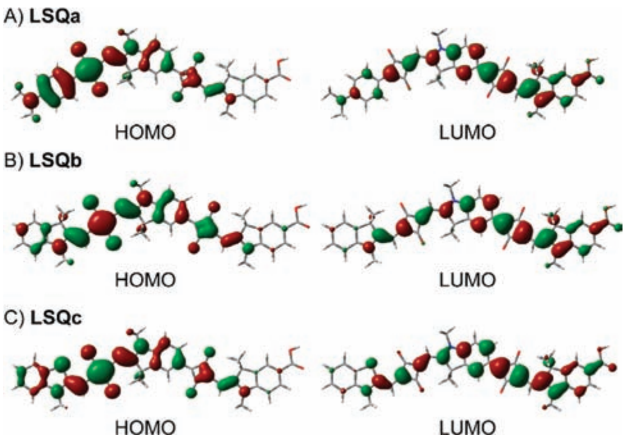

Figure 3. Schematic diagram of the frontier molecular orbitals of **LSQa−c** calculated at the B3LYP/6-31G(d) level of theory. The surfaces are generated with an isovalue at 0.02. The calculations were performed on the models in which methyl groups replaced alkyl substituents.

DFT calculations at the B3LYP/6-31G(d) level of the theory supported the directional charge transfer on excitation.[14] It is important for efficient electron injection from excited dyes to the conduction band of TiO_2 to situate the LUMO close to the anchoring groups because the orbital overlap with the titanium 3d orbitals is enhanced.[4] The electron density of HOMO is delocalized over the cyclobutenes, whereas the LUMO is primarily located on terminal indolium components bearing carboxylic acid as an anchoring site to the TiO_2 surface (Figure 3). This indicates a clear directional electron transfer from the π framework of the cyclobutene core to the terminal indolium with the anchoring group.

DSSCs were fabricated using **LSQ**s as the sensitizers with nanocrystalline anatase TiO_2 as the photoelectrode. The evaluation conditions for these dyes were determined to be 0.12 mM of dyes in acetonitrile/*t*-butanol as a dye bath, 48−60 mM chenodeoxycholic acid (CDCA) as a

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coadsorbent. Figure 4A shows the current density–voltage (J–V) characteristics measured under AM 1.5 G solar illumination (100 mW cm^{-2}). The **LSQa** sensitized cell gave a photocurrent density (J_{SC}) of 9.05 mA cm^{-2}, a open-circuit voltage (V_{OC}) of 0.46 V and a fill factor (ff) of 0.54, corresponding to an overall conversion efficiency (η) of 2.26% (Table 2). Under the same composition of electrolyte, a **LSQb**-based DSSC produced η of 0.78% (J_{SC} = 3.3 mA cm^{-2}, V_{OC} = 0.40 V, ff = 0.60), suggesting that photovoltaic performance was influenced by the structure of heterocyclic components. The lower η value compared to the **LSQa**-based cell might be attributable to the charge recombination of injected electrons with dye cations and I_3^- and the low electron-injection yield.[4,13] The J_{SC} and η value of a **LSQb** sensitized cell significantly increased to 9.01 mA and 2.01%, respectively, through the use of an electrolyte with high LiI concentration (1.0 M). The improvements of J_{SC} and η were assumed to be due to the enhanced efficiency of electron injection through the Li ion effect.[15] The cell consisting of **LSQc** sensitized TiO_2 electrode exhibited a η value of 1.82% (J_{SC} = 9.01 mA cm^{-2}, V_{OC} = 0.40 V, ff = 0.51). These results indicated that the structure of **LSQ**s was effective for the unidirectional flow of electrons, which enables efficient electron injection from excited dyes into the conduction band of TiO_2 as predicted by the DFT calculation. Action spectra of incident photon-to-current conversion efficiency (IPCE) of the devices are shown in Figure 4B. It is interesting to note that the IPCE for the devices based on **LSQa**–**c** reached a maximum at 750–775 nm and that the onset of the IPCE spectra was over 900 nm. Thus, **LSQ**s enabled the conversion of photons with energy lower than 1.65 eV, which are not sufficiently utilized so far, to electricity. In addition to the remarkable responses in the NIR region, the **LSQ**-based DSSCs exhibited a panchromatic response due to the existence of additional absorption peaks in 475–700 nm.

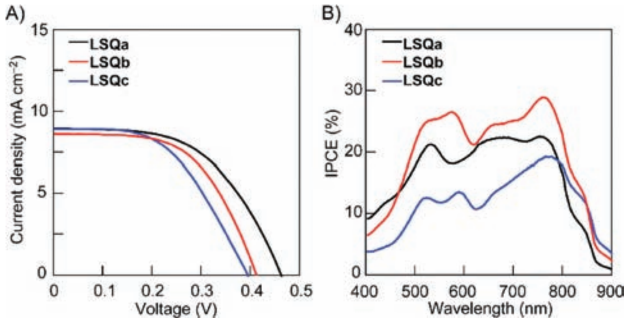

Figure 4. (A) Photocurrent density–voltage (J–V) curves and (B) IPCE spectra of DSSCs based on **LSQa**–**c**.

Table 2. Photovoltaic Performance of DSSCs based on the Squarylium Dyes with Linearly π-Extended Squarylium Dyes[a]

dye	V_{oc} (V)	J_{sc} (mA)	fill factor	η (%)
LSQa	0.46	9.05	0.54	2.26
LSQb[b]	0.41	8.64	0.57	2.01
LSQc[b]	0.40	9.01	0.51	1.82
N719	0.52	13.0	0.59	4.02

[a] Condition: irradiated light, AM1.5 G (100 mW/cm^2); photoelectrode, TiO_2 (12 μm thickness and 0.25 cm^2 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 (60 mM). [b] Electrolyte: 0.05 M I_2, 1.0 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 (48 mM).

In conclusion, we have synthesized three novel squarylium dyes (**LSQa**–**c**) with two cyclobutene cores for DSSC applications through the Pd-catalyzed coupling reaction of iodinated squarylium and tributylstannylsquarate followed by condensation with carboxy indolium. DSSCs based on **LSQa**–**c** displayed not only remarkable responses in the NIR region over 750 nm but also a panchromatic response. The power conversion efficiencies of DSSCs based on **LSQa**–**c** reached approximately 2%. This strategy for the design of NIR absorbing squarylium dyes for DSSC applications is very simple and has potential for the development of sensitizers harvesting long-wavelength light. However, the overall conversion efficiencies (η) of the devices comprised of **LSQ**s remain at modest value due to low V_{oc} attributed to back electron transfer from TiO_2 and severe charge recombination, and reduced J_{sc} values attributed to self-quenching in aggregated dyes.[7h,16] Further efforts for structural modification including an introduction of long alkyl chains and/or three-dimensional structures to prevent the charge recombination and dye aggregations are in progress.

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Supporting Information Available. Experimental details, cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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