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Design of NIR-Absorbing Simple Asymmetric Squaraine Dyes Carrying Indoline Moieties for Use in Dye-Sensitized Solar Cells with Pt-Free Electrodes

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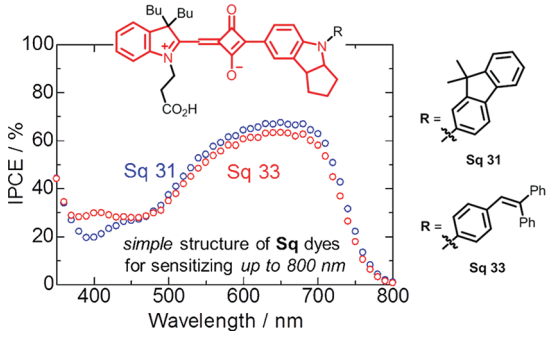
ABSTRACT



Novel near-infrared (NIR)-sensitizing (up to 800 nm) *simple* asymmetric squaraine dyes (Sq 31 and Sq 33) carrying indoline moieties *that did not require the introduction of any linker groups* were developed. DSSCs fabricated with Sq 33 exhibited remarkable characteristics in the long-wavelength visible and NIR region (up to 800 nm), such as a conversion efficiency of 3.75% (AM 1.5G) with an incident photon-to-current conversion efficiency of 63% (650 nm), a short-circuit photocurrent density of 13.64 mA, an open-circuit photovoltage of 0.48, and a fill factor of 0.57.

Dye-sensitized solar cells (DSSCs) that use metal-free organic dyes continue to attract interest as promising alternatives for practical photovoltaic devices because of their potential low manufacturing cost, ease of purification, high molar extinction, and structural diversity in the field of photovoltaic energy conversion.[1] Various types of metal-free organic dyes have been developed, and some have achieved power conversion efficiencies of greater

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(1) For a recent review, see: Hagfelt, A.; Boschloo, G.; Sun, L.; Kloo, L.; Petterson, H. *Chem. Rev.* **2010**, *110*, 6595.
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than 12% in standard AM 1.5G sunlight.[2] However, the main drawback of these dyes is a lack of absorption in the near-infrared (NIR) region.

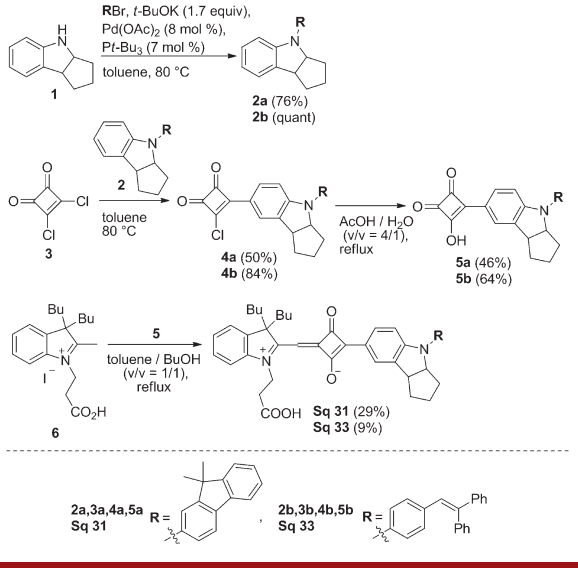
Recently, squaraines (**Sq**) have attracted attention because of their strong absorption and sensitizing abilities in the long-wavelength visible region of solar light. Consequently, the longest edge of incident photon-to-current conversion efficiencies (IPCEs) in DSSCs with **Sq** dyes that have been reported to date are *ca.* 750 nm.[3] By analogy to the molecular design of visible light-absorbing organic dyes, the introduction of not only linker groups, such as phenyl, alkenyl, thienyl, and pyrrole groups, between donor and acceptor groups in **Sq** dyes, but also another **Sq** moiety has been shown to lead to a red shift in the absorption maximum and sensitization in the NIR region (up to *ca.* 900 nm).[3b−d]

During the development of long-wavelength visible light- and NIR-absorbing organic dyes, such as asymmetric **Sq**[4] and heptamethincyanine (**KFH**)[5] dyes for use in DSSCs, we synthesized for the first time (1) two novel NIR-sensitizing *simple* asymmetric **Sq** dyes by changing a di-*n*-octylaminophenyl group to an indoline moiety. Furthermore, (2) the absorption maxima (λ_{max}) of these **Sq** dyes showed a red shift of 11 nm compared with that of dialkylaminophenylated **Sq**. Finally, (3) the *simple* asymmetric **Sq** dyes *that do not require the introduction of linker groups, such as phenyl, thienyl, or pyrrole groups,* are quite efficiently sensitized on titanium oxide (TiO_2) with the long-wavelength visible and NIR region (*up to 800 nm*) of the spectrum and show a remarkable conversion efficiency (η) of 3.75% (AM 1.5G) with an IPCE of 63% (650 nm), a short-circuit photocurrent density (J_{sc}) of 13.64 mA, an open-circuit photovoltage (V_{oc}) of 0.48, and a fill factor (*ff*) of 0.57.

We report here the details of the synthesis of novel NIR-absorbing simple asymmetric **Sq** dyes carrying indoline moieties for use in DSSCs with nanocrystalline TiO_2.

Sq 31 and **33** were synthesized as shown in Scheme 1. Indoles **2** were prepared in 76% to quantitative yields *via* the Buchwald−Hartwig cross-coupling reaction of 1,2,3,3a,4,8b-hexahydrocyclopenta[*b*]indole (**1**) with the corresponding bromoaromatics, such as 2-bromo-9,9-dimethyl-9*H*-fluorene and (2-(4-bromophenyl)ethene-1,1-diyl)dibenzene, in the presence of palladium acetate (8 mol %), tri-*tert*-butylphosphine (7 mol %), and potassium *tert*-butoxide (1.7 equiv) in toluene at 80 °C. The reaction of the indoles **2** with 3,4-dichlorocyclobut-3-ene-1,2-dione (**3**) in toluene at 80 °C gave 3-substituted 3-chlorocyclobut-3-ene-1,2-diones **4** in yields of 50−84%, and subsequent hydrolysis in a mixed solvent composed of acetic acid and water (v/v = 4/1) at reflux temperature for 4−29 h gave 3-substituted 4-hydroxycyclobut-3-ene-1,2-diones **5** in yields of 46−64%.

Scheme 1. Synthesis of **Sq 31** and **Sq 33**



Finally, 1-carboxyethyl-3,3-dibutyl-2-methylindolenium iodide (**6**)[5a] reacted with 4-hydroxybut-3-ene-1,2-diones **5** in a mixed solvent of toluene and butanol (v/v = 1/1) at reflux temperature for 5−24 h to produce **Sq 31** and **33** in yields of 9−29%.

The UV−vis absorption in DMSO solution and on nanoporous TiO_2, along with the emission and photochemical properties of **Sq 31** and **Sq 33**, are listed in Table 1 and shown in Figure 1. The absorption spectra of **Sq 31** and **Sq 33** show peaks in the long-wavelength visible region in DMSO solution, and the λ_{max} values of **Sq 31** and **Sq 33** are the same (643 nm). These values are red-shifted (by 11 nm) compared to that of **Sq 3** (λ_{max} = 632 nm, ε = 125 000 M^{-1} cm^{-1}), which has a di-*n*-octylaminophenyl group instead of an indoline group,[4] due to the potent electron-donating properties of the indoline moiety. The molar extinction coefficients (ε) of **Sq 31** and **Sq 33** were

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determined to be 139 000 and 86 200 M^{-1} cm^{-1} at the respective absorption maxima. The absorption spectra of **Sq 31** and **Sq 33** are broadened on a TiO_2 electrode.

Table 1. Absorption, Emission, and Electrochemical Properties of **Sq 31** and **33**

Dyes	$\lambda_{max}{}^a$ (nm)	ε^a (M^{-1} cm^{-1})	$F_{max}{}^a$ (nm)	E_{ox} (V)[b]	E_{0-0} (V)	E_{red} (V)[c]
Sq 31	643	139 000	731	0.72	1.82	−1.10
Sq 33	643	86 200	738	0.76	1.81	−1.05

[a] Measured in DMSO at a concentration of 5×10^{-6} M. [b] Determined by cyclic voltammetry. [c] Calculated on the basis of E_{ox} and λ_{int}.

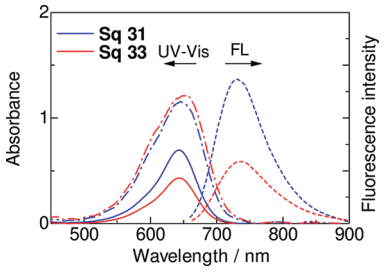

Figure 1. UV−vis absorption in DMSO (solid line) and adsorbed on TiO_2 (dash-dotted line) and fluorescence spectra (dotted line) of **Sq 31** and **Sq 33**.

To estimate the HOMO levels of **Sq 31** and **Sq 33**, cyclic voltammetry was performed using a three-electrode cell. The first oxidation potential (E_{ox}) was found to correspond to the HOMO level and was determined to be 0.72 V vs NHE for **Sq 31** and 0.76 V vs NHE for **Sq 33**. Since the E_{red} values of **Sq 31** and **Sq 33** were not observed, the LUMO levels of **Sq 31** and **Sq 33** could be obtained by $E_{ox} - E_{0-0}$. The values of E_{0-0} for **Sq 31** and **Sq 33** were obtained based on the intersection (683 nm for **Sq 31** and 684 nm for **Sq 33**) of the normalized absorption and fluorescence spectra, respectively. The energy levels of E_{ox} (HOMO) for **Sq 31** and **Sq 33** are more positive than the redox potential of the iodide/triiodide couple used as an electrolyte. The potential of E_{red} (LUMO) for **Sq 31** and **Sq 33** is sufficiently negative to inject electrons into the conduction band of TiO_2.

To determine the electronic and geometrical structures of **Sq 33**, a molecular orbital calculation was performed for **Sq 33** with the density functional theory (DFT) at the B3LYP/6-31G level with Gaussian 09, and the electron distributions for HOMO−2, HOMO−1, HOMO, LUMO, LUMO+1, and LUMO+2 are shown in Figure 2. HOMO is delocalized throughout the dye, and HOMO−2 is entirely localized within the squaraine core. On the other hand, while LUMO is delocalized throughout the dye, LUMO+2 is entirely localized in the indolenium moiety, including the carboxylic substituent.

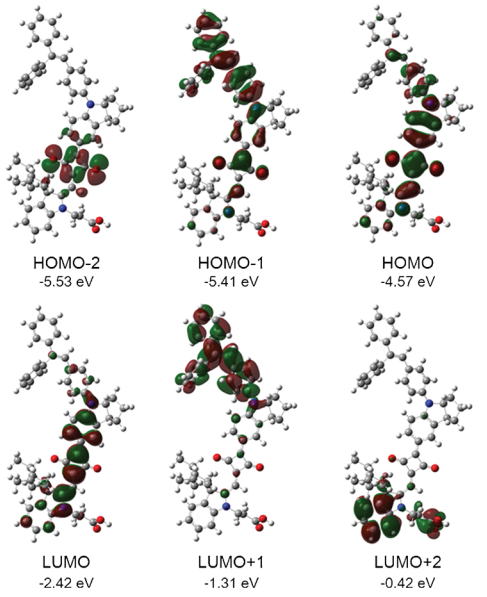

Figure 2. Graphic representation of the frontier orbital and the geometry of **Sq 33** (N blue, O red, C gray, H white) by B3LYP/6-31G (d,p).

Table 2 summarizes the photovoltaic properties of DSSCs fabricated with **Sq 31** and **Sq 33** on TiO_2 films with a liquid electrolyte consisting of 0.1 M iodine (I_2), 0.1 M lithium iodide (LiI), and 1.0 M 1,2-dimethyl-3-propylimidazolium iodide (DMPImI) in 3-methoxypropionitrile (3-MPN), together with the results for a DSSC with N719 as a standard. A TiO_2 film was prepared by the screen-printing method (a transparent layer of up to 9 μm using 18 nm particles + a scattering layer of up to 5 μm using 400 nm particles). The TiO_2 electrode was stained by immersion in a mixed solution of acetonitrile−*tert*-BuOH (v/v = 1/1) containing 0.1 mM **Sq** dyes and 0.5 mM deoxycholic acid (DCA) as a coadsorbent. A PEDOT-PTS coated film on FTO glass was used as a counter electrode. The cells have an effective area of 0.50 cm^2, and their performance was evaluated under AM 1.5G illumination (100 mW cm^{-2}). Consequently, the **Sq 33**-sensitized solar cell gave a slightly better η value of 3.75%, with a J_{sc} of 13.64 mA cm^{-2}, a V_{oc} of 0.48 V, and an *ff* of 0.57, compared to that (3.50%) of **Sq 31**. The use of electrolytes either without LiI or with both *N*-methylimidazole (NMBI) and guanidine thiocyanate (GuNCS) resulted in a significant reduction of J_{sc}.

Figure 3 shows the incident photon-to-current conversion efficiency (IPCE) spectra of DSSCs based on **Sq 31** and **Sq 33**, respectively. Despite not only the absence of thienyl and phenyl groups as linker groups in the dye structure but also the red shift of λ_{max} by only 11 nm compared to that of **Sq 3** carrying a di-*n*-octylaminophenyl group, they show broader IPCE spectra from 300 to 800 nm, with maximum values of 68% at 650 nm for **Sq 31** and 63% at 650 nm for **Sq 33**, respectively. However, the effect of the

Table 2. Performance Parameters of **Sq 31**- and **Sq 33**-Based DSSCs[a]

Dyes	J_{sc} (mA cm^{-2})	V_{oc} (V)	*ff*	η (%)
Sq 31	13.39	0.473	0.53	3.50
Sq 33	13.64	0.480	0.57	3.75
N719	16.77	0.488	0.57	4.30
Sq 33[b]	6.83	0.614	0.67	2.83
Sq 33[c]	4.01	0.644	0.76	1.96

[a] Irradiation light: 100 mW cm^{-2} simulated AM 1.5G solar light; working area: 0.5 cm^2; electrolytes 0.1 M I_2, 1.0 M DMPII, 0.1 M LiI in 3-MPN. [b] Without LiI. [c] With NMBI and GuNCS.

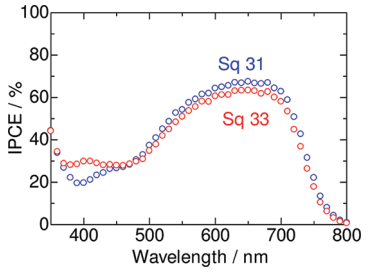

Figure 3. Action spectra of **Sq 31**- and **Sq 33**-based DSSCs.

indoline moieties for the broader IPCE spectra is not clear at the present time.

Figure 4 shows Nyquist plots of DSSC cells with **Sq 31**, **Sq 33**, and N719, measured under illuminated conditions (100 mW cm^{-2}, V_{oc} conditions). Two semicircles were observed in the Nyquist plots. The radii of the smaller semicircles on the right, which are attributed to the defusion of electrolytes, do not vary greatly among the three dyes. The radii of the larger semicircles on the left, which contain R_1 from charge transfer at the counter electrode and R_2 from electron transport at the TiO_2/dye/electrolyte interface, decreased in the order **Sq 31** $\approx$ **Sq 33** $>$ N719. This result indicates that the electron generation and transport in DSSCs based on **Sq 31** and **Sq 33** are similar, but slightly worse than those of N719.

In conclusion, two novel NIR-absorbing simple asymmetric squaraine dyes (**Sq 31** and **Sq 33**) carrying indoline moieties as potent electron-donating groups were synthesized for use in NIR-active DSSCs with porous TiO_2. Despite the absence of any linker groups in the dye, **Sq 33** was quite efficiently sensitized on TiO_2 with the long-wavelength visible and NIR region (up to 800 nm) of the spectrum and showed remarkable performance, such as an η of 3.75% (AM 1.5) with an IPCE of 63% (650 nm), a J_{sc} of 13.64 mA, a V_{oc} of 0.48, and an *ff* of 0.57.

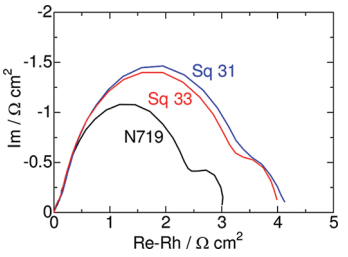

Figure 4. Nyquist plots for **Sq 31**-, **Sq 33**-, and N719-based DSSCs.

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Supporting Information Available. Detailed procedures and characterization of all of the new compounds, ^{1}H and ^{13}C NMR spectra for **2**, **4**, **5**, and **Sq** dyes. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.