Synthesis and Characterization of Multifunctional Symmetrical Squaraine Dyes for Molecular Photovoltaics by Terminal Alkyl Chain Modifications

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Abstract: Novel far-red sensitive symmetric squaraine (SQ) dyes with terminal alkyl chain modifications were designed, synthesized, and characterized, aiming towards imparting multifunctionalities such as photosensitization, dye aggregation prevention, and source of electrolyte components. The dye sensitizer SQ-80 with alkyl chain terminal modifications consisting of 1-methylimidazolium iodide was designed and synthesized as a new dye sensitizer for DSSCs based on symmetric SQ-4 without any terminal modification used as reference. Upon adsorption on the mesoporous TiO₂ surface, SQ-80 demonstrated reduced dye aggregation and stronger binding to the TiO₂ surface, leading to enhanced durability of DSSCs. Apart from the most common photosensitization behavior, the newly designed dye demonstrated multifunctionalities such as aggregation prevention and electrolyte functionality, utilizing iodine-based redox electrolytes in the presence and absence of I₂ and LiI additives. In the absence of LiI and I₂, a mixture of SQ-77 with alkyl chain terminal modifications consisting of iodide and SQ-80 demonstrated a photoconversion efficiency of 1.54% under simulated solar irradiation, which was about six times higher compared with the reference dye SQ-4 (0.24%) (having no alkyl chain terminal modification).

Keywords: dye-sensitized solar cells; squaraine dye; electrolyte effect; terminal modification; multifunctional; dye sensitizer

1. Introduction

The adoption of renewable energy resources is receiving enhanced global attention for solving future energy issues due to increasing energy demands owing to increasing population growth and standard of life, aiming towards the development of a sustainable society. This attempt is demonstrated by the fact that the share of electricity generated from renewable energy sources in power generation increased from 21.3% in 2012 to 29.9% in 2022. The installation of photovoltaic cells, a type of solar energy harvesting system, is being actively promoted, which increased the amount of electricity generated in 2022 by 25% compared with the previous year, and is almost equal to hydroelectric power generation [1]. However, there are some problems regarding installation locations due to the size and weight of the modules and how to treat them when they reach the end of their useful life [2]. On the other hand, the research and development of next-generation solar cells, such as organic thin film/polymer solar cells, perovskite solar cells, and dye-sensitized solar cells (DSSCs), has also gained momentum worldwide, aimed towards the realization of low-cost solar energy harvesting [3–5]. DSSCs have attracted much attention since their invention by O’Regan and Gratzel [6]. DSSCs have high potential due to their environmental friendliness, flexibility, simple manufacturing process, and efficient power generation capabilities under low-intensity indoor light [7–11]. Common DSSCs are composed of a working electrode of nanocrystalline TiO₂ adsorbed with a sensitizing dye sensitizer, a counter electrode having electrocatalytic, and an electrolyte...
that fills the gap of both working and counter electrodes. Its photovoltaic conversion efficiency (PCE) is calculated by the multiplication of the short-circuit current density (Jsc), the open-circuit voltage (Voc), and the fill factor (FF). Since Jsc in DSSCs is determined by the optical absorption of sensitizing dyes, various efforts have been attempted by many researchers. The dyes used in DSSCs include inorganic and organic dyes, both of which currently exhibit conversion efficiencies of over 11% [12–16]. Various efforts have also been directed toward other objectives in addition to improving PCE. These include further cost reductions by removing the use of precious metal catalysts, improving bi-facility and visibility by utilizing high transparency, and developing completely transparent DSSCs that absorb light at 800 nm and above [17–25]. These efforts are expected to further improve the efficiency of energy use not only by installing solar cells on windows and walls where existing solar cells have been difficult to use but also by applying them to greenhouses, etc. [26–28].

The most well-known sensitizing dyes are those based on ruthenium complexes, with attractive features such as high stability. However, metal-based inorganic sensitizers have problems such as the use of precious metals and low molar absorption coefficients, and organic sensitizers are being actively investigated to address these problems. Inorganic and organic dyes, which show high conversion efficiencies exceeding 10%, have a relatively higher molar absorption coefficient absorbing light in the 300 nm to 700 nm wavelength region. The solution to this problem is to combine multiple dyes and extend the absorption region by co-sensitization [29–31]. Therefore, the development of dyes in the long wavelength (especially in the near-infrared (NIR) wavelength region) is inevitable for further enhancement of PCE. Various classes of dyes such as polymethine, cyanine, phthalocyanine, porphyrin, and squaraine have been used recently to try and circumvent this issue [32–35]. The NIR dyes achieve long wavelength absorption by increasing π-conjugation, but their planar structure promotes dye aggregation and hampers the device performance of DSSCs [36,37]. Therefore, it is necessary to co-adsorb other materials with dye molecules on TiO$_2$ to prevent dye aggregation, but this leads to hampered dye loading, especially in the case of non-absorbing aggregation-preventing agents like the most commonly used chenodeoxycholic acid. One of the well-adopted measures is to prevent aggregation by adding long alkyl chains to the dye [38,39]. Therefore, designing and developing novel sensitizing dyes with additional properties like aggregation prevention, surface passivation, and assisting electrolyte functionality is necessary. Cobalt or copper complex-based electrolytes are used to achieve higher Voc. Their redox potentials are deeper than a typical iodine-based redox couple, and higher values can be expected in Voc, which is determined by the gap between the conduction band (CB) of TiO$_2$ and the redox potential of the electrolyte. However, unlike iodine-based redox couples, it is well known that cobalt- and copper-complexed redox couples, which are composed of cations, frequently suffer from the back electron transfer/charge carrier recombination, needing strict surface passivation and utilization of relatively thinner TiO$_2$ layer.

Therefore, the realization of high PCE by using these redox couples has been reported only with limited dyes. These dye molecules require alkyl chains as anti-dye-aggregation and special structures to prevent this reverse electron transfer. Despite these previous researches, very few studies have investigated the substitution of alkyl chain ends. So far, our research group has been actively involved in the design of the development of NIR dyes belonging to the squaraine family of dye sensitizers [40–43]. Squaraine dyes are advantageous due to versatile synthesis, easy tuning of energetics, optical absorption window, and intense color, leading to their utilization for a wide range of applications, including photodynamic therapy, organic photovoltaics, ion sensors, fluorescent labels, and probes [44–48]. Regarding DSSCs, improving conversion efficiency and durability, ensuring safety, and reducing costs are unavoidable issues for their practical application. We have recently proposed multifunctional NIR dyes, which demonstrated their suitability as sensitizers of DSSCs [49]. This was accomplished by substituting the long alkyl chain terminals of the dye main framework with iodine or imidazole, to impart multifunctionality
such as prevention of dye aggregation and function as I$_2$ in iodine-based electrolytes. In the present study, we synthesized and characterized a novel multifunctional dye with 1-methyl imidazolium iodide substituted at the alkyl chain terminal (SQ-77) and SQ-80 and previous dyes were used as sensitizers for DSSCs to investigate their photophysical characteristics.

2. Materials and Methods

2.1. Materials

Lithium iodide (LiI) and iodine (I$_2$) were procured from Wako, Japan. Platinum catalyst precursor (Platisol T) and TiO$_2$ paste (Ti-nanoxide D/SP and T/SP) were procured from Solaronix. 4-tert-butylpyridine (t-BP) was procured from Sigma-Aldrich (Meguro-ku, Tokyo, Japan). 1,2-dimethyl-3-propyl-imidazoliumdide, squaric acid, 1-methylimidazole, and other materials needed for the synthesis were procured from Tokyo Chemical Industry Co., Ltd. (Chuo-ku, Tokyo, Japan). TB3017B resin, which is UV light-curable, was procured from ThreeBond Holdings Co., Ltd. (Shibuya-ku, Tokyo, Japan).

2.2. Intermediate and Dye Synthesis

The synthesis started utilizing an aromatic ring carboxy functionalized indole derivative 2,3,3-trimethyl-3H-indole-5-carboxylic acid, following the procedure described by Pham et al. [50]. The synthesis and characterization of symmetrical squaraine dyes SQ-4 and SQ-77 have been reported previously [49,51]. The newly proposed dye SQ-80 and the corresponding intermediate were synthesized as per the scheme shown in Figure 1.

2.2.1. Synthesis of 5-Carboxy-2,3,3-trimethyl-1-(12-1-methylimidazoledodecyl)-3H-indolium Iodide

Amounts of 1.2 g (2.3 mmol) of 5-Carboxy-2,3,3-trimethyl-1-(12-iodododecyl)-3H-indolium iodide and 360 mg (4.6 mmol) of 1-methylimidazole were dissolved in 30 mL of acetonitrile taken in 100 mL of a round-bottomed flask fitted with a condenser. For 12 h, the reaction mixture was refluxed. After cooling the reaction mixture and evaporating the solvent, 1.42 g of red crude product was obtained and purified by re-crystallization.
2.2.2. Synthesis of Symmetrical Squaraine Dye SQ-80

Amounts of 800 mg (1.8 mmol) of 5-Carboxy-2,3,3-trimethyl-1-(12-1-methyl-imidazole dodecyl)-3H-indolium iodide and 100 mg (0.88 mmol) of squaric acid were dissolved in 30 mL of toluene/pentanol (1:1) mixture taken in 100 mL of a round-bottomed flask fitted with a condenser. For 12 h, the reaction mixture was refluxed. After cooling the reaction mixture and evaporating the solvent, the product was purified using silica gel column chromatography with an eluting solvent of acetone, water, and acetic acid, yielding 167 mg of dark blue solid in a 19% yield. FAB-MS (for C60H81N6O6, measured m/z: 981.63 [M]+; calculated m/z: 981.35;) and 1H NMR (500 MHz, CD3OD): δ / ppm = 7.93 (d, 2H, Ar-H); 7.91(s, 2H, Ar-H); 7.53(d, 2H, Ar-H); 7.46(s, 2H, Ar-H); 7.13(d, 2H, Ar-H); 5.91(s, 2H, CH); 4.07(t, 4H, CH2); 4.06(t, 4H, CH2); 4.04(t, 4H, CH2); 3.83(s, 2H, CH); 1.72(d, 4H, CH2); 1.65(s, 12H, CH3); 1.32(m, 4H, CH2); 1.26(m, 4H, CH2); 1.14(m, 24H, CH2); 13C NMR (CD3OD) 184.40 (C1), 177.31 (C4), 173.66 (C29), 145.68 (C2), 142.69 (C11), 138.03 (C6), 137.77 (C26), 134.30 (C8), 131.19 (C7), 124.91 (C9), 124.42 (C27), 123.63 (C28), 110.61 (C10), 88.03 (C3), 50.81 (C5), 50.31 (C14), 44.78 (C25), 36.46 (C30), 31.16 (C24), 30.46 (C18-21), 30.30 (C17, 22), 28.06 (C15), 27.58 (C16), 27.38 (C23) 27.27 (C12,13) confirmed the structural identity of dye. The NMR (13C and 1H) charts are shown in Supplementary Materials in Figures S1 and S2.

2.2.3. Characterizations of Synthesized SQ-80

The synthesized intermediate dye and the final dye were characterized by fast ion bombardment (FAB) mass spectrometry in the positive ion monitoring mode to confirm structural identity. Synthesized dyes were dissolved in deuterated methanol to record nuclear magnetic resonance (NMR) spectra using an NMR spectrometer (JEOL, 500 MHz) to confirm the final structure. The electronic absorption spectra were measured in the solution and on the TiO2 film using a UV-vis-NIR spectrophotometer (JASCO V-550). Using cyclic voltammetry (CV), the dye’s highest occupied molecular orbital (HOMO) energy level was ascertained. The CV measurements were performed using an auto-polarization system (HSV-100, Hakuto Denko, Japan). The ferrocene (Fc) and 1 mM of each synthesized dye in dimethylformamide (DMF) were used for the CV measurement. An amount of 100 mM tetrabutylammonium hexafluorophosphate was also added as the electrolyte. The difference in the oxidation potential of the reference Fc+/Fc redox pair and the synthesized dye estimated the HOMO energy levels of the synthesized dye. The energies associated with the synthesized dye’s optical band edge (Eg) were estimated using the absorption spectra of dye-adsorbed TiO2 thin films. The lowest unoccupied molecular orbital (LUMO) energies were calculated from these values. An amount of 40 mM NaOH in a mixed solvent consisting of acetonitrile, t-butanol, ethanol, and water (1:1:1:1, v/v/v) was used to remove the dye adsorbed on TiO2 and the presence of the dye was measured by a spectrophotometer, comparing it to the dye when dissolved in the same solution to estimate the number of dye molecules adsorbed on the TiO2 layer.

2.3. Fabrication and Characterization of DSSCs

2.3.1. Device Fabrication

After 30 min UV/O3 treatment, detergent water, distilled water, acetone, and 2-propanol were used to ultrasonically clean fluorine-doped tin oxide (FTO) glass substrates (10 Ohm/sq). Before sintering in the muffle furnace (FO100, Yamato Scientific Co., Ltd., Chuo-ku, Tokyo, Japan) for 45 min at 450 °C, cleaned substrates were soaked in 40 mM TiCl4 aqueous for an hour at 70 °C (TiCl4 treatment). They were then rinsed with distilled water and ethanol. Treated FTO glasses were set by a screen printer with a 50 µm thickness metal mask. The clearance between the FTO glass and the metal mask was adjusted very little in order to make a thin film. To obtain a 12 µm TiO2 layer, Ti-nanoxide T/SP was
printed on substrates and sintered for 45 min at 500 °C using a muffle furnace. Then, Ti-nanoxide D/SP was printed and sintered on mesoporous TiO$_2$ at the same condition for Ti-nanoxide T/SP. The TiO$_2$-coated substrates were subjected to TiCl$_4$ treatment again. Then, the substrates were soaked for four hours in a solution containing synthesized dyes (0.2 mM) and CDCA (10 mM) in ethanol. After dye adsorption, they were rinsed with ethanol to remove any dye molecules that had not been chemically adsorbed on TiO$_2$. The same procedure as previously mentioned was used to clean pre-drilled FTO glass substrates. Platisol T was applied by spin-coating for 10 s at 1400 rpm and sintered for 30 min at 500 °C. The working and counter electrodes were sandwiched using a hot melt spacer (25 µm). Subsequently, the pre-drilled hole in the counter electrode was used to inject the iodine-based redox electrolyte ($I_3^-/I^-$), which was composed of LiI (100 mM), $I_2$ (50 mM), 1,2-dimethyl-3-propyl-imidazoliumdide (600 mM), and t-BP (500 mM) in acetonitrile. Finally, TB3017B resin was put in two holes in the DSSCs and solidified by UV laser to seal the DSSCs.

2.3.2. Device Characterization

The photocurrent density–voltage (J–V) curves were measured under 100 mW/cm$^2$ of simulated solar irradiation using a solar simulator (CEP-2000 Bunko Keiki Co. Ltd., Hachioji-shi, Tokyo, Japan) with a xenon lamp (Bunko Keiki BSO-X150LC). Additionally, 100 mW/cm$^2$ simulated solar irradiation was measured using a common calibration Si photodetector (BS-520 S/N 007, Bunko-Keiki Co. Ltd., Hachioji-shi, Tokyo, Japan). The active area of the DSSCs was controlled at 0.25 cm$^2$ using a black metal mask. The photocurrent at each wavelength was measured by monochromatic light irradiation using an action spectrum measurement system connected to a solar simulator (CEP-2000, Bunko Keiki Co. Ltd., Hachioji-shi, Tokyo, Japan). The amount of light in each wavelength range was calculated from the sensitivity of a calibration silicon solar cell (S1337, Bunko Keiki Co. Ltd., Hachioji-shi, Tokyo, Japan) and the measured photocurrent of S1337. Then, the photocurrent of the sample was measured at each wavelength and the incident photon-to-current conversion efficiency (IPCE) was calculated. The electrochemical impedance spectroscopic (EIS) measurement was performed using a frequency response analyzer (Solartron Analytical, 1255B, AMETEK, Inc., Berwyn, PA, USA) coupled to a potentiostat (Solartron Analytical, 1287, AMETEK, Inc., Berwyn, PA, USA) between 0.1 and 10$^5$ Hz with 10 mV AC amplified and 0 V DC potential (vs. Voc) under the same irradiation as the J–V curve measurements. EIS data were analyzed using Bode and Nyquist plots to examine each interfacial resistance.

3. Results and Discussion

3.1. Electronic Absorption Spectra

Figure 2a shows the electronic absorption spectra of synthesized symmetric squaraine dyes (5 µM in ethanol). It shows that the dyes had highly narrow, strong, and sharp light absorption, primarily in the 550 nm to 700 nm wavelength region. Because the primary π-conjugated framework of all three dyes was the same, the absorption maximum ($\lambda_{\text{max}}$) was almost the same, appearing at 646 nm. These squaraine dyes also exhibited a shoulder in the solution state, a common feature of squaraine dyes, at a 550–650 nm wavelength. It was found that the molar extinction coefficient varied depending on the type of terminal substituents, even though the $\lambda_{\text{max}}$ was identical. Compared with the standard SQ-4, SQ-77, bearing the terminal with iodine, showed a dark colour. On the other hand, SQ-80, with a modified terminal consisting of 1-methylimidazole, showed a pale color compared with SQ-4. The analysis of dye adsorption behavior on mesoporous TiO$_2$ surfaces has provided important findings regarding dye aggregation that must be controlled to improve photon harvesting and maximize DSSC performance. Figure 2b shows the electronic absorption spectra of the synthesized dyes adsorbed on a transparent 4 µm TiO$_2$ and Table 1 shows summarized optical parameters from Figure 2.
The solid-state electronic absorption spectrum was broadened and redshifted compared with the absorption spectrum of squaraine dye in the ethanol solution shown in Figure 2a. This indicates dye aggregation and interaction between the TiO$_2$ surface and dye molecules [52]. The $\lambda_{\text{max}}$ values were the same for the alkyl terminal substitutions (H, I, 1-methylimidazole). However, the spectral broadening and optical absorption edge changed, indicating differences in the dye molecule aggregation on the TiO$_2$ surface. The vibronic shoulder seen in Figure 2b at 610 nm in the solution was more noticeable in the solid state than in the solution and was thought to be caused by the dye aggregate formation [53]. The ratio of the absorbance at 610 nm (aggregation) and 650 nm (monomeric dye) was utilized to estimate the relative extent of the dye aggregation [54]. It was clearly shown in the solid-state absorption spectrum that the 1-methylimidazole at the terminal of the alkyl chain in SQ-80 exhibited an aggregation index (monomeric dye absorbance/aggregation absorbance) of 0.67, which was smaller than SQ-4 (0.83) and SQ-77 (0.88). This suggests that the 1-methylimidazole group increased the intermolecular distance and decreased the electrostatic interaction among the dye molecules, hampering the dye aggregation. Since the alkyl chain length was the same, the hampered dye aggregation for SQ-80 indicates the role of imidazolium iodide terminal functionality in dye aggregation prevention.

### Table 1. Extracted optical parameters of symmetrical SQ dyes from Figure 2.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$\lambda_{\text{max}}$ (Solution)</th>
<th>$\varepsilon$ (Solution) (dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
<th>$\lambda_{\text{max}}$ (TiO$_2$)</th>
<th>Absorption Edge nm (eV)</th>
<th>Aggregation Index</th>
<th>Dye Loading (nmol/cm$^2$)</th>
<th>Dye Desorption Rate (nmol/cm$^2$/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-4</td>
<td>646 nm</td>
<td>2.96 $\times$ 10$^5$</td>
<td>650 nm</td>
<td>700 nm (1.77 eV)</td>
<td>0.83</td>
<td>29.3</td>
<td>5.86</td>
</tr>
<tr>
<td>SQ-77</td>
<td>646 nm</td>
<td>2.91 $\times$ 10$^5$</td>
<td>648 nm</td>
<td>700 nm (1.77 eV)</td>
<td>0.88</td>
<td>54.0</td>
<td>6.00</td>
</tr>
<tr>
<td>SQ-80</td>
<td>646 nm</td>
<td>3.28 $\times$ 10$^5$</td>
<td>646 nm</td>
<td>687 nm (1.80 eV)</td>
<td>0.67</td>
<td>35.6</td>
<td>2.09</td>
</tr>
</tbody>
</table>

3.2. Adsorption of Dye Molecules on TiO$_2$

Experiments of dye adsorption and desorption were conducted to measure the amount of dye adsorbed on TiO$_2$ and the strength of binding of dye molecules to the TiO$_2$ surface along with the summarization of results in Table 1. To determine the total loading of dye adsorbed on TiO$_2$, dye molecules were fully adsorbed on the TiO$_2$ surface and then completely desorbed using a mixed solution consisting of acetonitrile, tert-butanol,
water, and NaOH (1:1:1 v/v). Synthesized SQ dye sensitizers were adsorbed on TiO₂ to estimate dye stability. The quantity of dye desorbed within a designated time was calculated using spectrophotometry. Table 1 shows that, even under the same dye desorption circumstances (TiO₂ thickness and area and dipping time duration), the binding strength of each synthesized dye sensitizer onto mesoporous TiO₂ was not the same. Due to their comparatively quick dye desorption (5.86 and 6.00 nmol/cm²/min) for SQ-4 and SQ-77, respectively, SQ-80 exhibited nearly three times stronger binding to the TiO₂ surface (2.09 nmol/cm²/min).

3.3. Cyclic Voltammetry

In DSSC studies, CV is used not only for electrochemical characterization of dye sensitizers but also to estimate the energetics of sensitizing dyes to judge their suitability as sensitizers. Figure 3 shows CV recordings of each synthesized SQ dye and Fc as the standard reference in DMF solution using similar electrochemical cell conditions such as electrodes, electrolytes, and scan rates.

![Cyclic voltammograms of Fc and symmetrical SQ dyes in I⁻/I⁻ redox electrolyte (scan rate was 50 mVs⁻¹).](image)

The energy of the HOMO of the dyes was calculated using the shift of the first oxidation peak of the dye relative to the Fc/Fc⁺ redox pair used as a reference. It is widely recognized that the redox potential of the Fc/Fc⁺ redox pair is 0.403 V with reference to a saturated calomel electrode, which is equivalent to −5.09 eV from the vacuum level [55]. The oxidation potentials of Fc, SQ-4, SQ-77, and SQ-80 were found to be 0.45 V, 0.42 V, 0.45 V, and 0.48 V, respectively. The results showed that the synthesized dyes shifted −0.03, +0.05, and +0.03, respectively, compared with the first oxidation potential of Fc. From the redox potential of −5.09 eV for Fc/Fc⁺, the estimated values of the HOMO energy were −5.06 eV, −5.14 eV, and −5.12 eV for SQ-4, SQ-77, and SQ-80, respectively. The CVs of individual SQ-dyes are shown in Figures S3–S5.

3.4. Energy Band Diagram

In addition to strong light absorption, the presence of a suitable anchoring group, and favourable electrochemical bonding with TiO₂, the dye sensitizer of DSSCs must demonstrate energetic matching for the electron transporting wide bandgap semiconductor
and redox electrolyte (TiO₂ and I⁻/I₃⁻ in the present case) for the facile electron injection and dye regeneration, respectively. Table 1 also summarizes the estimated values of the energy band gap (Eg) estimated from the onset of the optical absorption edge of Figures 2b and S6. The energy of the LUMO was estimated using the relation LUMO = HOMO + Eg. Based on earlier publications, the CB energy of TiO₂ and the redox energy level of the I⁻/I₃⁻ electrolyte were reported to be −4.00 eV and −4.90 eV, respectively, as shown in the energy band diagram depicted in Figure 4 [56]. The LUMO energies of all synthesized SQ dyes were higher than the TiO₂ CB, with a driving force of 0.6–0.7 eV that allowed easy electron injection from the LUMO of photoexcited dye molecules into the TiO₂. Compared with the standard SQ-4, the LUMO of SQ-77 and SQ-80 (terminal substitution) were decreased. Decreases in LUMO have been reported with terminal substitution of alkyl chains [49,57]. In addition, the HOMO energy levels of synthesized dye were lower than the iodide/triiodide redox potential, suggesting that dye regeneration may easily occur following the injection of electrons from the photoexcited dye molecules into TiO₂.

### Figure 4.
Energy band diagram of the symmetrical SQ dyes to justify their suitability as sensitizers with TiO₂ as electron acceptor and I⁻/I₃⁻ redox electrolyte.

#### 3.5. Photovoltaic Characterization

The current density–voltage (J-V) characteristics of DSSCs for evaluating their photovoltaic performances using different SQ dyes are shown in Figure 5a. These measurements were carried out under solar irradiation of 100 mW/cm². Based on the J-V characteristics, photovoltaic metrics such as PCE, FF, Voc, and Jsc were calculated and are presented in Table 2. DSSCs with the SQ-4 dye recorded the highest PCE of 4.2% among the three dyes with Jsc, Voc, and FF of 12.0 mA/cm², 0.62 V, and 0.57, respectively. Additionally, SQ-77 and SQ-80 showed a slightly lower PCE of 3.8 and 3.7%, respectively. Despite the higher dye loading in the case of SQ-80 (35.6 nmol/cm²) compared with that of SQ-77 (54 nmol/cm²), their photovoltaic performances were nearly similar. This could be explained by considering the compensation of reduced dye loading by decreased dye aggregation in the case of SQ-80 compared with that of SQ-77. It has been reported that monomeric dyes exhibit enhanced electron injection compared with that of dye aggregates, hampering Jsc and PCE of the DSSCs [58]. The IPCE spectrum provides information on the photon harvesting behaviour of dye molecules for each wavelength, so monochromatic light was used for this measurement. Figure 5b shows the IPCE spectra of DSSCs using SQ-4, SQ-77, and SQ-80. Since the peak at about 350 nm was due to TiO₂.
absorption, the values of the peaks were nearly identical, representing 50% of each dye. The results showed that the maxima were 68% at 658 nm for all three dyes. Photon harvesting was demonstrated in the actual fabricated DSSCs, although the synthesized SQ dyes did not demonstrate light absorption in the 400–500 nm range, as shown in Figure 2. SQ-77 demonstrated the largest photon harvesting in this range, while SQ-80 demonstrated the smallest. It was also the same trend for dye aggregation, as discussed in Section 3.1.

![Figure 5. (a) J-V curves and (b) IPCE spectra of DSSCs using SQ dye sensitizer with different terminal substitutions.](image)

Table 2. Photovoltaic parameters of DSSCs using different dye sensitizers.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-4</td>
<td>12.0</td>
<td>0.62</td>
<td>0.57</td>
<td>4.21</td>
</tr>
<tr>
<td>SQ-77</td>
<td>11.0</td>
<td>0.61</td>
<td>0.56</td>
<td>3.77</td>
</tr>
<tr>
<td>SQ-80</td>
<td>10.7</td>
<td>0.59</td>
<td>0.59</td>
<td>3.74</td>
</tr>
</tbody>
</table>

3.6. Electrochemical Impedance Spectra

When examining the charge transfer process occurring at various interfaces, DSSC research has extensively used the EIS technique. R in the Nyquist plot represents the almost identical sheet resistance of the FTO substrate. DSSCs are made up of three main impedance parts. The interface between the platinum used as the counter electrode and the electrolyte is represented by component 1 (R₁); the interface between the TiO₂ semiconductor used as the working electrode and dye and the electrolyte is represented by component 2 (R₂); and the impedance resulting from the behaviour of the electrons in the electrolyte near the electrode is represented by component 3 (R₃) [59,60]. The DSSCs fabricated using different SQ dyes under investigation were subjected to EIS measurement, and corresponding Bode and Nyquist plots are shown in Figure 6. The electrical parameters that were fitted using an equivalent circuit or calculated from the EIS measurement are shown in Table 3. The typical three half arcs were shown in the SQ-4 Nyquist plot. On the other hand, the shapes of Nyquist plots were not typical in SQ-77 and SQ-80. Moreover, R₂ was the interfacial resistance directly related to the dye in the research, reporting general dye development. However, R₂ among the three SQ dye sensitizers compared in this study was similar. Instead, R₁ of SQ-77 was larger, and the third arc of SQ-80 was smaller than that of the other dyes. Moreover, the connection between each arc in the Nyquist plot of SQ-80 was smooth, and each interface was difficult to identify compared with the other dyes. These reasons imply that SQ-77 and SQ-80 influenced R₁ and R₂, which should not involve dyes, because SQ-77 and SQ-80 not only absorbed light but also acted as electrolytes. The
relationship $\tau = 1/2\pi f_p$, where $f_p$ is the peak at a lower frequency in Bode plots, can be used to compute the electron lifetime ($\tau$). Since electron lifetime is proportional to peak frequency, it increases with decreasing peak frequency. SQ-80 ($\tau_e = 4.22$ ms) had a shorter electron lifetime than SQ-4 and SQ-77 ($\tau_e = 8.41, 5.31$ ms). The short electron lifetime indicated that a lot of recombination by reverse electron transfer was occurring. At the same time, the Voc and $R_2$ of SQ-80, which had the shortest electron lifetime, was the smallest among the three SQ dye sensitizers. It is well known that these decreases were caused by the aggregation of dye molecules. On the other hand, the aggregation index of SQ-80 was smaller than other dyes, which implies that it might be due to the end-modified 1-methyl imidazolium iodide.

![Figure 6](image_url)

**Figure 6.** (a) Nyquist plots and equivalent circuits for data fitting and (b) Bode plots of the DSSCs using symmetrical SQ dye sensitizers.

<table>
<thead>
<tr>
<th>Dye</th>
<th>$R_s$ (Ω)</th>
<th>$R_1$ (Ω)</th>
<th>$R_2$ (Ω)</th>
<th>$R_3$ (Ω)</th>
<th>$f_p$ (Hz)</th>
<th>$\tau_e$ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-4</td>
<td>27.5</td>
<td>9.42</td>
<td>20.3</td>
<td>1.30</td>
<td>18.9</td>
<td>8.41</td>
</tr>
<tr>
<td>SQ-77</td>
<td>24.0</td>
<td>26.7</td>
<td>18.0</td>
<td>3.35</td>
<td>30.0</td>
<td>5.31</td>
</tr>
<tr>
<td>SQ-80</td>
<td>29.2</td>
<td>12.0</td>
<td>16.9</td>
<td>0.53</td>
<td>37.8</td>
<td>4.22</td>
</tr>
</tbody>
</table>

### 3.7. Relative Durability of DSSCs

In DSSCs, durability evaluation is an important factor for practical application. The durability includes volatilization of the electrolyte, degradation of Pt (the catalyst used for the counter electrode), and dye desorption [42,61,62]. After preparing DSSCs with four samples, each of SQ-4 and SQ-80, the DSSCs were stored in a desiccator in the dark and DSSC performance was measured after the storage time of 0, 100, 200, 300, and 450 h. Figure 7 shows the J-V curves and tracked PCE with time along with the summarization of photovoltaic parameters in Table 4. DSSCs with SQ-4 resulted in a 48% reduction in PCE at 450 h compared with 0 h. On the other hand, SQ-80 maintained 78% PCE after 450 h, indicating that SQ-80 was relatively more stable with higher durability. The decrease in PCE for these two dyes was mainly due to decreased Jsc for SQ-4, which was 60% maintaining 40% after 450 h. On the other hand, DSSCs based on SQ-80 retained 67% of Jsc after 450 h. This significant difference between SQ-4 and SQ-80 can be attributed to the intensity of dye desorption described in Section 3.2 and Table 1. Another factor was the degradation of electrolytes. If the $I^-/I_3^-$ redox couple was decreased due to the long-term measurement, the oxidized dye would not be regenerated and degraded. This led to the
deceiving of the PCE of the SQ-4 dye. On the other hand, 1-methylimidazolium iodide in the SQ-80 dye molecule assisted in the generation of redox couples in electrolytes and PCE was maintained.

![Figure 7.](image_url)

**Figure 7.** (a) Tracked PCE as a function of time and (b) photovoltaic characteristics (solid line: 0 h; dotted line: 450 h) of the DSSCs using symmetrical SQ dye sensitizers (SQ-4 and SQ-80).

**Table 4.** Summarized photovoltaic parameters deduced from the J-V characteristics in Figure 7b. (These parameters were calculated for standard deviations using four samples prepared with the same conditions.)

<table>
<thead>
<tr>
<th>Dye</th>
<th>Time (h)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SQ-4</td>
<td>0</td>
<td>8.26 (±0.90)</td>
<td>0.61 (±0.01)</td>
<td>0.60 (±0.02)</td>
<td>3.00 (±0.23)</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>3.31 (±0.18)</td>
<td>0.66 (±0.01)</td>
<td>0.72 (±0.002)</td>
<td>1.57 (±0.11)</td>
</tr>
<tr>
<td>SQ-80</td>
<td>0</td>
<td>7.17 (±0.32)</td>
<td>0.583 (±0.005)</td>
<td>0.618 (±0.02)</td>
<td>2.58 (±0.12)</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>4.81 (±0.46)</td>
<td>0.65 (±0.01)</td>
<td>0.67 (±0.031)</td>
<td>2.14 (±0.14)</td>
</tr>
</tbody>
</table>

### 3.8. Verification of Electrolyte Functionality by Mixture of SQ-77 and SQ-80 Dyes

We have already reported the electrolyte effect of the dye molecule itself, which demonstrated that DSSCs worked without I₂ in electrolytes using the terminal iodine modification of SQ-77. Interested by this observation, the SQ-80 dye was synthesized bearing 1-methylimidazole at the alkyl chain terminal, expecting this dye to play an important role as the electrolyte component in the iodine-based electrolyte. To demonstrate the electrolyte effect, the blended SQ-77 and SQ-80 dyes added to their terminal modification as a source of iodine and I⁻ for iodine-based redox electrolyte. The reference dye SQ-4 was used at different concentrations of I₂ and LiI in the electrolyte. Dimethyl-3-propylenimidazolium iodide (600 mM), I₂ (50 mM, 0 mM), and LiI (100 mM, 0 mM) in acetonitrile were used to prepare the redox electrolyte for the present investigation. Figure 8 and Table 5 show the J-V curves and corresponding photovoltaic parameters for DSSCs with mixed dyes (SQ-77/SQ-80 = 1:1, 1:4, 4:1) and reference dye SQ-4 at different concentrations of I₂ and LiI in the electrolyte, respectively. There was no significant difference in the PCE of the four DSSCs with normal iodine electrolytes (I₂ 50 mM, LiI 100 mM). However, in I₂ and LiI-free electrolytes, there was a marked difference between the mixed dyes (SQ-77, SQ-80) and the reference dye SQ-4. DSSCs with mixed dyes (SQ-77/SQ-80 = 1:4) showed Jsc, Voc, and FF of 4.60 mA/cm², 0.73 V, and 0.453, respectively, and 1.53% under simulated solar.
irradiation, while DSSCs with SQ-4 showed highly hampered PCE of only 0.24% under simulated solar irradiation. This significant decrease in FF could be due to a lack of iodine in the electrolyte [63,64]. From these results, we can say that I₂ and Lil played a role in the electrolyte in the mixed dyes (SQ-77, SQ-80). In addition, the conversion efficiency increased as the ratio of SQ-80 increased in three different dye mixtures (SQ-77/SQ-80 = 1:1, 1:4, 4:1). This is because SQ-80 played the role of I⁻ source, as shown in Equation (1), and an increase in the concentration of I⁻ promoted the formation of I₃⁻, facilitating the formation of an I⁻/I₃⁻ redox couple. When 500 mM Lil and 50 mM I₂ were added to acetonitrile, as shown in Equation (2), K was high, I₂ reacted with I⁻ to form I₃⁻, and the free iodine concentration was very low [65,66].

\[ \text{I}_2 + \text{I}^- = \text{I}_3^- \]  
(1)

\[ K = \frac{[\text{I}_3^-]}{[\text{I}_2][\text{I}^-]} = 10^{6.76} \]  
(2)

![Figure 8. J-V curves of mixed dye sensitizers (SQ-77 and SQ-80) and SQ-4 DSSCs with different concentrations of I₂ and Lil electrolyte injection. (Solid line: normal iodine electrolyte; dotted line: I₂ and Lil free electrolyte.).](image-url)
Table 5. Summarized photovoltaic parameters for DSSCs estimated from the J–V characteristics shown in Figure 8.

<table>
<thead>
<tr>
<th>SQ-77:SQ-80</th>
<th>I2 and LiI Conc. (mM)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>50, 100</td>
<td>10.1</td>
<td>0.58</td>
<td>0.59</td>
<td>3.48</td>
</tr>
<tr>
<td>1:4</td>
<td></td>
<td>10.0</td>
<td>0.62</td>
<td>0.60</td>
<td>3.68</td>
</tr>
<tr>
<td>4:1</td>
<td></td>
<td>10.2</td>
<td>0.58</td>
<td>0.59</td>
<td>3.46</td>
</tr>
<tr>
<td>SQ-4</td>
<td></td>
<td>9.30</td>
<td>0.66</td>
<td>0.60</td>
<td>3.70</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SQ-77:SQ-80</th>
<th>I2 and LiI Conc. (mM)</th>
<th>Jsc (mA/cm²)</th>
<th>Voc (V)</th>
<th>FF</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>0, 0</td>
<td>4.05</td>
<td>0.71</td>
<td>0.51</td>
<td>1.45</td>
</tr>
<tr>
<td>1:4</td>
<td></td>
<td>4.60</td>
<td>0.73</td>
<td>0.45</td>
<td>1.52</td>
</tr>
<tr>
<td>4:1</td>
<td></td>
<td>3.87</td>
<td>0.70</td>
<td>0.52</td>
<td>1.41</td>
</tr>
<tr>
<td>SQ-4</td>
<td></td>
<td>3.43</td>
<td>0.64</td>
<td>0.11</td>
<td>0.24</td>
</tr>
</tbody>
</table>

4. Conclusions

In this study, the terminal modification of the alkyl chain in the squaraine dye was carried out, aiming towards successfully demonstrating their multifunctional role as sensitizer and electrolyte component source. This is expected to reduce the number of materials used in DSSCs, leading to lower costs and process savings. Three symmetrical SQ dye sensitizers with various modifications at their alkyl chain terminal, like iodine and 1-methylimidazole, were made and used as dye sensitizers for the use of DSSCs. Multiple investigations were conducted on their photophysical, electrochemical, and photovoltaic characteristics. SQ-80 (modified alkyl chain terminal by 1-methylimidazole) demonstrated the prevention of dye molecule aggregation. The highest PCE in DSSCs prepared with these dyes was 4.2% with SQ-4 (unmodified), although the PCE of SQ-80 was only about 10% lower than SQ-4. On the other hand, DSSCs with SQ-80 demonstrated higher PCE than SQ-4 after 450 h of storage and improved binding strength to the TiO₂ surface. These findings demonstrate that the interfacial charge transport and durability of squaraine dye are influenced by the architectures of alkyl chain terminal functionalization. The blend dyes SQ-77 and SQ-80 demonstrated about 1.5% PCE, which was five times higher than SQ-4 when iodine and Li were not included in the electrolyte. This is likely to be attributed to the $I^-/I_3^-$ redox couple generated by the iodine and 1-methylimidazole modified at the alkyl chain terminals of the dyes when DSSCs operated normally.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/colorants3030014/s1, Figure S1: ¹³C-NMR spectra of SQ-80; Figure S2: ¹H-NMR spectra of SQ-80; Figure S3: Cyclic voltammograms of Fc and symmetrical SQ-4 dyes in $I_3^-/I^-$ redox electrolyte (Scan rate was 50 mVs⁻¹); Figure S4: Cyclic voltammograms of Fc and symmetrical SQ-77 dyes in $I_3^-/I^-$ redox electrolyte (Scan rate was 50 mVs⁻¹); Figure S5: Cyclic voltammograms of Fc and symmetrical SQ-80 dyes in $I_3^-/I^-$ redox electrolyte (Scan rate was 50 mVs⁻¹); Figure S6: The absorption spectra of dye adsorbed transparent TiO₂ (4 µm) from optical band edge calculation.

Author Contributions: Conceptualization, K.M. and S.S.P.; methodology, K.M.; validation, K.M. and Y.K.; formal analysis, K.M. and Y.K.; investigation, K.M. and Y.K.; data curation, Y.K. and S.S.P.; writing—original draft preparation, K.M.; writing—review and editing, Y.K. and S.S.P.; supervision, S.S.P. All authors have read and agreed to the published version of the manuscript.

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References


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