Influence of quinoline derivatives in I^-/I_3^- redox electrolyte solution on the performance of Ru(II)-dye-sensitized nanocrystalline TiO_2 solar cell

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Abstract

The influence of quinoline additives in an I^-/I_3^- redox electrolyte solution on the performance of a bis(tetra-butylammonium)*cis*-bis(thio-cyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II) (N719) dye-sensitized TiO_2 solar cell was studied. The *I–V* characteristics were measured for the cells with 20 types of quinoline derivatives. All of the quinoline additives enhanced the open-circuit photovoltage (V_{oc}) and fill factor (ff), but reduced the short circuit photocurrent density (J_{sc}) of the solar cell. Most of the quinolines also improved the solar energy conversion efficiency (η). The physical and chemical properties of the quinolines were computationally calculated in order to elucidate the reasons for the additive effects on the cell performance. The greater the lowest partial charge of the atoms in the quinoline derivatives, namely nitrogen, the larger the V_{oc}, but the smaller the J_{sc} values. As the dipole moment of the quinoline derivatives increased, the V_{oc} value increased, but the J_{sc} value decreased. The V_{oc} of the cell also increased as the ionization energy of the quinolines decreased. These results suggest that the electron donicity of the quinoline additives affected the interaction with the nanocrystalline TiO_2 photoelectrode, the I^-/I_3^- electrolyte, and the acetonitrile solvent, which changed the Ru(II)-dye-sensitized solar cell performance.
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Keywords: Dye-sensitized solar cell; Electrolytic solution; Quinolines; Additive

1. Introduction

Dye sensitized solar cells have been very intensively studied [1–8] due to its importance as a new energy resource. A typical solar cell consists of nanocrystalline TiO_2 film electrodes covered with a monolayer of a sensitizing dye such as Ru(II) complex (N719), a redox electrolyte like I^-/I_3^- and a counter electrode such as Pt. One method for improving the solar cell performance is to add organic compounds to the electrolyte solution. For example, Kang et al. found that carboxylic acid such as acetic acid in I^-/I_3^- acetonitrile solution enhanced the J_{sc}, but reduced the V_{oc} value [8]. Frank and coworkers conducted a study on an I^-/I_3^- electrolyte with ammonia and pyridine derivatives such as 4-*t*-butylpyridine as additives in acetonitrile. They reported that these additives drastically enhanced both the V_{oc} and η [3,4] and suggested that the enhanced V_{oc} by the NH_3 and pyridine derivatives was due to the donating properties of the nitrogen lone pair [3,4,9,10].

Many benzopyridines and condensed pyridines are known and these have similar electronic structures [11]. However, these compounds have yet to be adoped as additives to the electrolyte solution for dye-sensitized solar cells. It might be possible to determine other pyridine additives that improve solar cell performance. In the present paper, we report results for quinolines or benzo[*b*]pyridines examined in an I^-/I_3^- electrolyte and an in an I^-/I_3^- electrolyte and an acetonitrile electrolytic solution on solar cell performance. Twenty types of quinoline derivatives such as aminoquinoline, alkylquinoline, and alkoxyquinoline were adopted. The chemical and physical properties of the quinoline additives were also evaluated using molecular orbital calculations and compared to dye-sensitized solar cell performance.

2. Experimental

2.1. TiO2 photoelectrode preparation and Ru(II) dye-coating

Titanium(IV) isopropoxide (Kanto Chemical Co.) was rapidly added to an aqueous HNO_3 (Wako Pure Chem-

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ical Industries Ltd.) solution and then stirred for 12 h at 323 K. The colloid was filtered and hydrothermally treated for 12 h in a titanium autoclave at 503 K. The resultant colloidal suspensions were ultrafiltered. The dispersion medium was transferred from water to ethanol (Wako Pure Chemical Industries Ltd.) and filtered again. The colloid was thoroughly dispersed using a high-speed homogenizer by adding ethyl cellulose (Fluka) as a binder and α-terpineol (Wako Pure Chemical Industries Ltd.) as a solvent for the TiO_2 paste, which was concentrated by an evaporator.

The TiO_2 paste was deposited onto fluorine-doped stannic oxide conducting glass (FTO, $10\,\Omega/cm^2$, Nippon Sheet Glass Co.) using a screen-printing technique. The resulting layer was calcined for 2 h at 798 K in an airflow of $1.5\,dm^3/min$. This process was repeated three times. The thickness of the resulting film measured approximately 15 μm with a Tencor Alpha-Step 500 surface profiler. The TiO_2 electrode was impregnated with a $0.05\,mol/dm^3$ $TiCl_4$ aqueous solution (Fluka) in a water-saturated desiccator for 0.5 h at 343 K. The electrode was washed with distilled water and then calcined at 723 K for 1 h in an airflow of $1.5\,dm^3/min$. The electrode was cooled to 448 K and immediately soaked in a N719 (Solaronix, SA) dye solution. The dye was adsorbed onto the TiO_2 surface by soaking the TiO_2 electrode in a t-butanol/acetonitrile (Wako Pure Chemical Industries Ltd., 1:1) solution of the dye (concentration: $3 \times 10^{-4}\,mol/dm^3$) for 150 h at 293 K. The photoelectrode was washed, dried, and immediately used to measure solar cell performance.

2.2. Photovoltaic characterization

A sandwich-type electrochemical cell, which was composed of a dye-coated TiO_2 electrode, a 25 μm thick Lumirror spacer film, and a counter electrode was used for the photocurrent measurements. The counter electrode was a Pt sputtered FTO conducting glass. The electrolytic solution was composed of $0.5\,mol/dm^3$ of the quinoline additive (Tokyo Kasei Kogyo Co. Ltd., Wako Pure Chemical Industries Ltd.), $0.6\,mol/dm^3$ 1,2-dimethyl-3-propylimidazolium iodide, $0.1\,mol/dm^3$ LiI, $0.05\,mol/dm^3$ I_2 and acetonitrile (Tomiyama Pure Chemical Industries Ltd.) as the solvent. The electrolyte solution was injected into the space between the two electrodes using a microsyringe.

The dye-coated semiconductor film was illuminated through a conducting glass support. The solar-electric energy conversion efficiency was measured under simulated AM 1.5 solar light (Wacom Co., WXS-80C-3) at $100\,mW/cm^2$ intensity. The photocurrent, photovoltage and I–V curves were measured using a digital source meter (Keithley Model 2400) and a data acquisition system (Eiko Seiki Co.). The apparent cell area of nanocrystalline TiO_2 photoelectrode was $0.25\,cm^2$ ($0.5\,cm \times 0.5\,cm$).

2.3. Computational details

The computational chemical calculations were performed using the CAChe WorkSystem Version 5.04 from Fujitsu Ltd. (Tokyo) implemented on a Windows XP system. The geometries of the quinoline derivatives were optimized by a MOPAC (Molecular Orbital Package, PM5) application.

3. Results

3.1. Solar cell performance using quinoline derivatives as additives

The I–V measurements were performed on the electrolyte with various quinoline additives. Fig. 1 illustrates the structures of quinolines used. Fig. 2 shows the solar cell performances when illuminating with $100\,mW/cm^2$ and an additive concentration of $0.5\,mol/dm^3$. The V_{oc} values for all cells containing quinolines were higher than the cell without an additive. Halogen substituents such as 6-bromoquinoline did not enhance the V_{oc} as much as other substituents such as amino, alkyl and alkoxy groups. Among the tested additives, the highest V_{oc}, 0.89 V, was observed when 4-amino-2-methylquinoline was added to the electrolyte, which is very similar to the maximum V_{oc} value of 0.9 V using a cell that consists of a TiO_2 photoelectrode and I^-/I_3^- redox system [7,12]. Conversely, the J_{sc} values for the cells with quinolines were less than the cell without an additive. Using 4-amino-2-methylquinoline drastically reduced the J_{sc} value. Monosubstituted quinoline derivatives displayed higher J_{sc} than disubstituted and trisubstituted ones. Among the tested quinoline derivatives, 4-amino-2-methylquinoline displayed the lowest J_{sc}, but the largest V_{oc}.

Fig. 2 also represents the influences of the quinoline additives in the electrolytic solution on the ff and η of the cell. All of quinolines enhanced the ff of the solar cell. The trend of ff was very similar to the V_{oc}. The highest and lowest ff values were observed when 4-amino-2-methylquinoline and 6-bromoquinoline were used as the additive, respectively. In general, adding quinolines improved the η value. Among the tested quinoline derivatives, 2,4-dimethylquinoline resulted in the highest η, 7.5%.

3.2. Computational calculations

As described above, the tested quinoline additives drastically changed the dye-sensitized solar cell performance. Dye desorption was not observed after the I–V measurements from the nanocrystalline TiO_2 photoelectrode into the electrolyte solution when the quinoline additives were present. Thus, it was determined that the varying effects on the solar cell performance were due to the properties
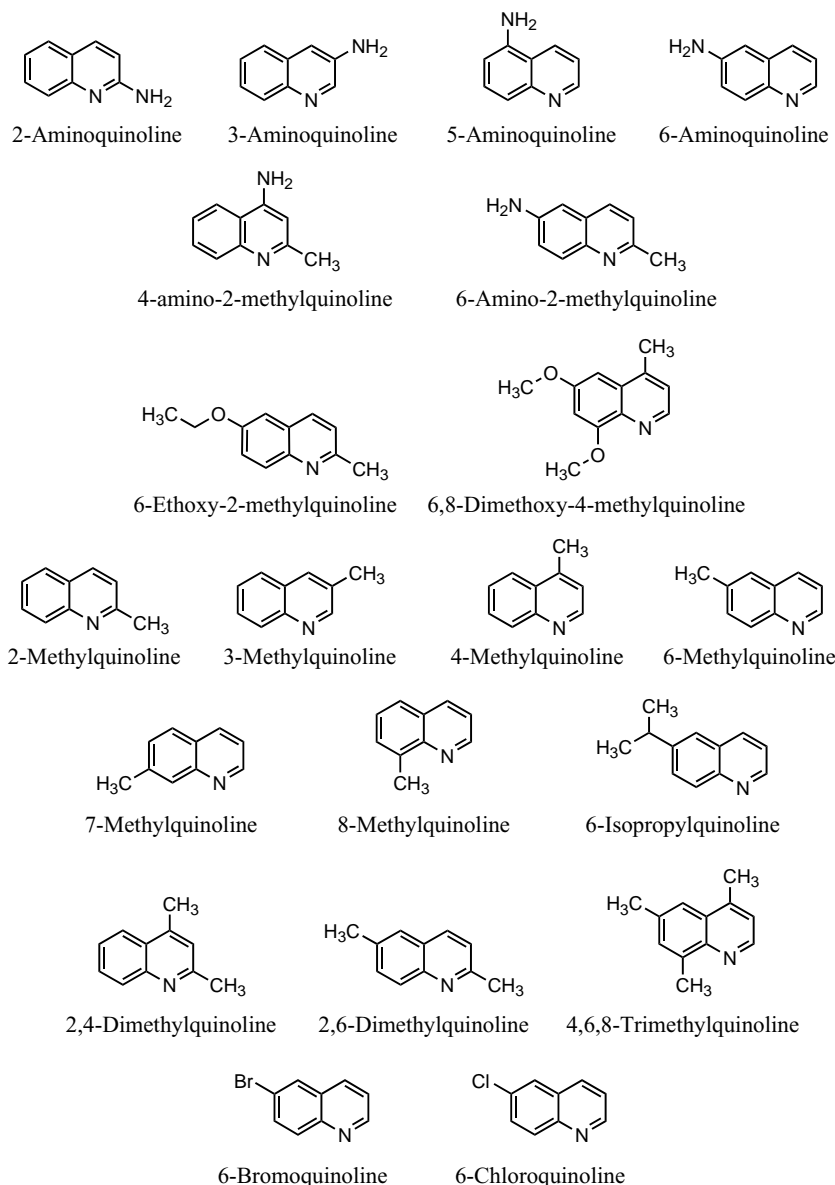
Fig. 1. The structures of the quinoline additives tested.

of the quinolines and not to variations in the amount of adsorbed N719 dye on the TiO$_2$ photoelectrode. Therefore, the physical and chemical properties of the quinoline derivatives were computationally calculated in order to investigate the reasons for the observed influences of the quinoline additives on the cell performance. Various correlations between the properties of the quinolines and solar cell performance such as V_{oc} and J_{sc} were found.

The partial charges of the atoms in the quinoline and substituted groups were calculated at the PM5 level using the MOPAC system available in the CAChe package. Due to the lone pair electrons, the nitrogen atoms were lower than the other atoms such as carbon, oxygen and hydrogen. In addition, the partial charge of the N atom in the quinoline group

was more negative than that in the amino group except for 3-aminoquinoline, 5-aminoquinoline, 6-aminoquinoline and 6-amino-2-methylquinoline. Fig. 3 depicts the correlation between the V_{oc} and the lowest partial charge of the atoms in the quinolines derivatives in acetonitrile. The larger the lowest partial charge of the atoms, the more the V_{oc} was enhanced. Fig. 4 shows the correlation between the J_{sc} of the cell and the lowest partial charge of the atoms in the quinolines. Unlike, the V_{oc} trend, the greater lowest partial charge, the more the J_{sc} value was reduced.

The dipole moment and ionization energy of the quinoline derivatives were also calculated at the PM5 level using the MOPAC system available in the CAChe package. Fig. 5 represents the correlation between the V_{oc} value and the calculated dipole moment of the quinoline derivatives. As the
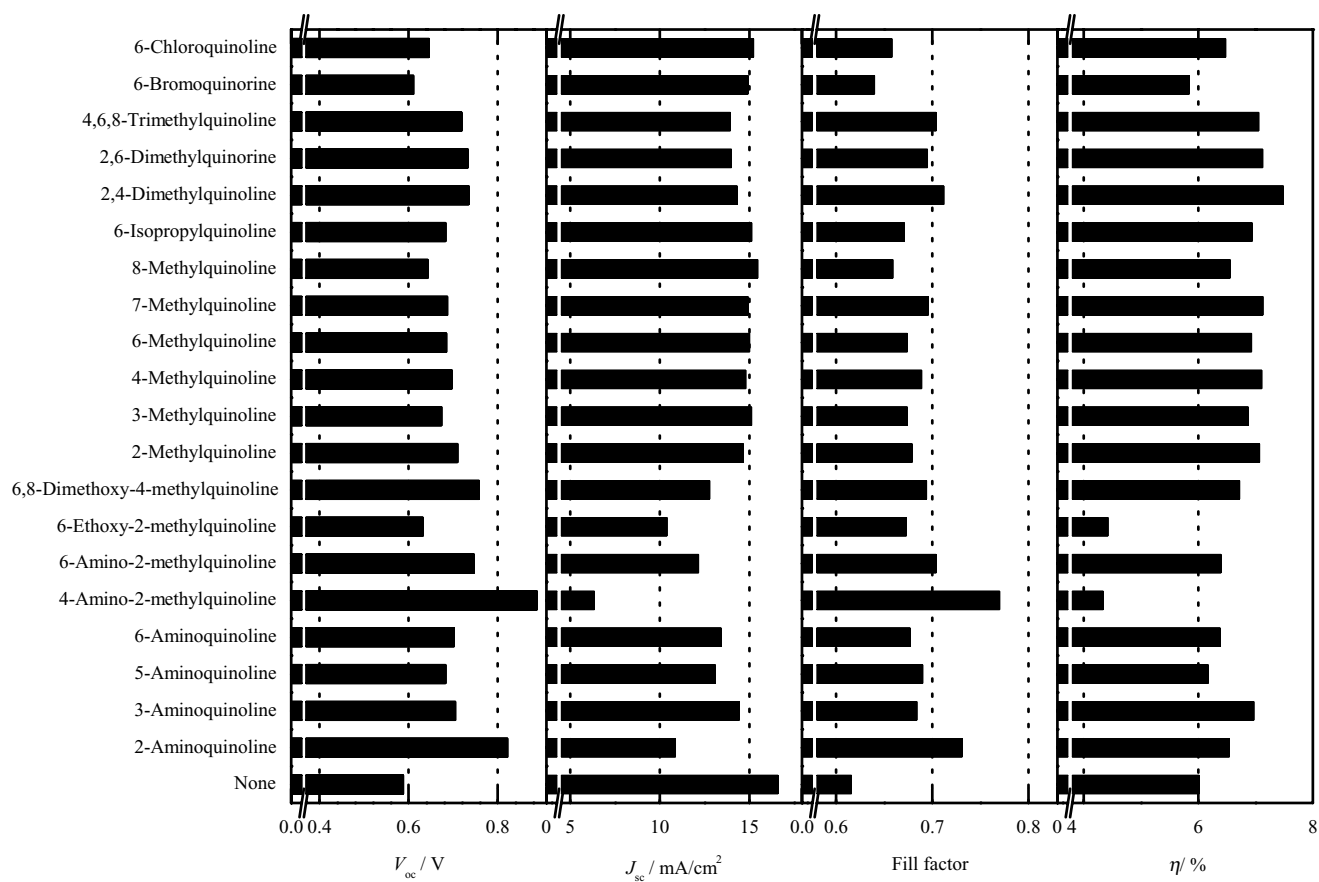
Fig. 2. The influence of the quinoline additives in the electrolytic solution on the solar cell performance for a N719 dye-sensitized TiO$_2$ solar cell. Conditions: electrolyte, 0.5 mol/dm^3 additive + 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I$_2$ in acetonitrile; light intensity, 100 mW/cm^2, AM 1.5.
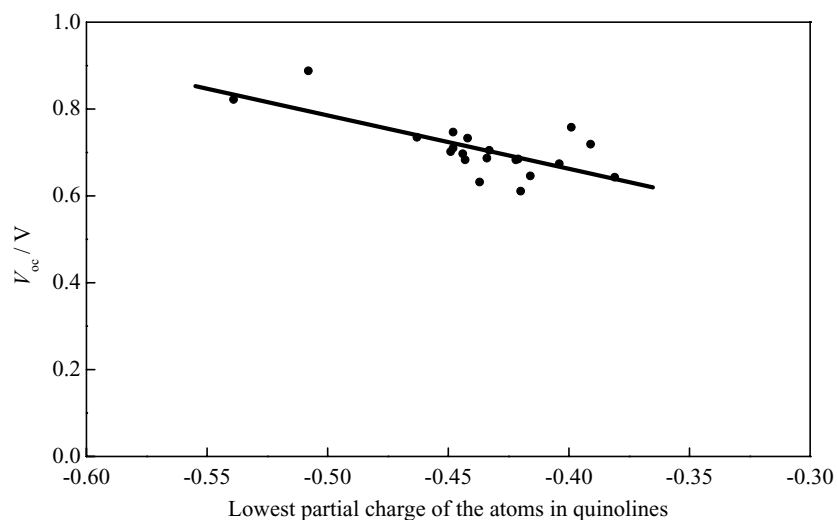

Fig. 3. The correlation between the V_{oc} of the cell and the lowest partial charge of the atoms in the quinolines in acetonitrile.

dipole moment increased, the value of V_{oc} increased. Fig. 6 illustrates the correlation between the J_{sc} of the cell and the dipole moment of the quinolines. The J_{sc} value decreased as the dipole moments of the quinolines increased.

Fig. 7 shows the correlation between the V_{oc} of the cell and the calculated ionization energy of the quinolines in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package. The results indicate that the lower
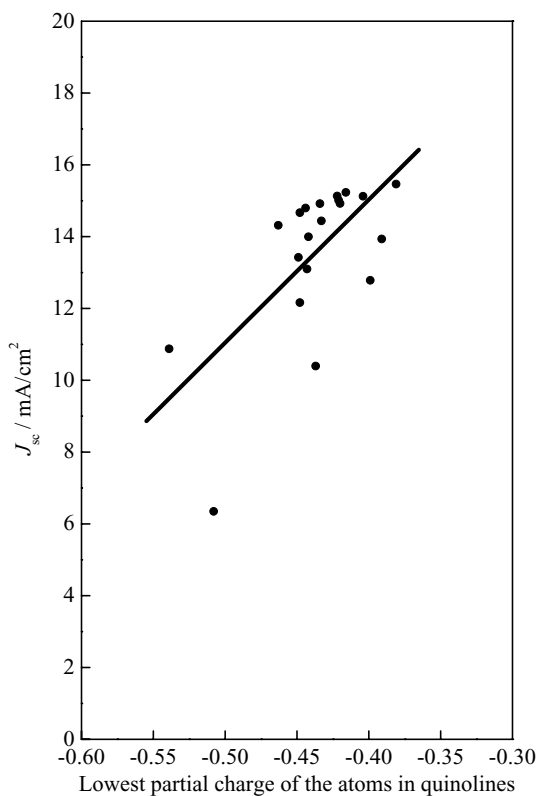
Fig. 4. The correlation between the J_{sc} of the cell and the lowest partial charge of the atoms in the quinolines in acetonitrile.

Fig. 6. The correlation between the J_{sc} of the cell and the dipole moment of the quinolines.

ionization energy of the quinoline derivatives, the larger V_{oc} of the cell.

4. Discussion

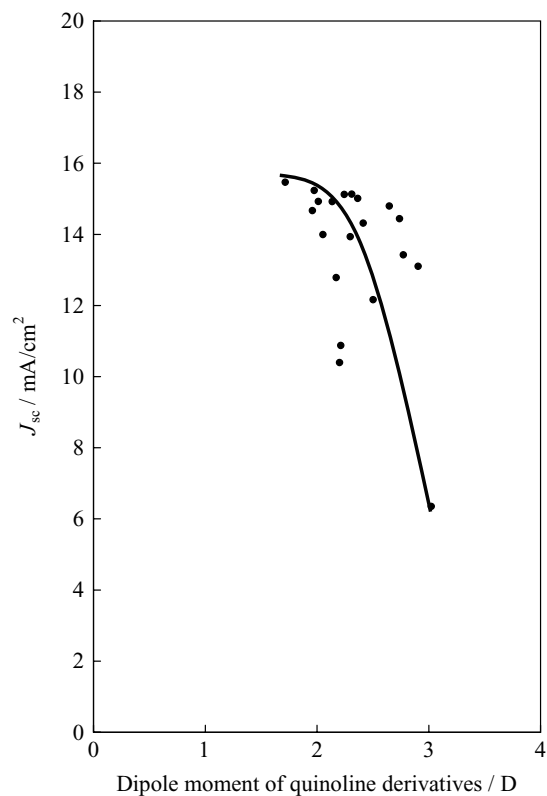The quinoline additives in the I^-/I_3^- electrolytic solution influenced Ru(II)-dye-sensitized nanocrystalline TiO$_2$ solar cell performance and in particular, the V_{oc} and J_{sc} values were drastically altered (Fig. 2). All of the cells with quinoline derivatives, displayed larger V_{oc} values, but smaller J_{sc} values compared to the cell without an additive. Why did the quinolines enhance V_{oc} and reduce J_{sc}? Grätzel and coworkers hypothesized that the adsorption of the additive onto the free area of the TiO$_2$ photoelectrode exposed to redox electrolyte suppressed the dark current arising from the I_3^-
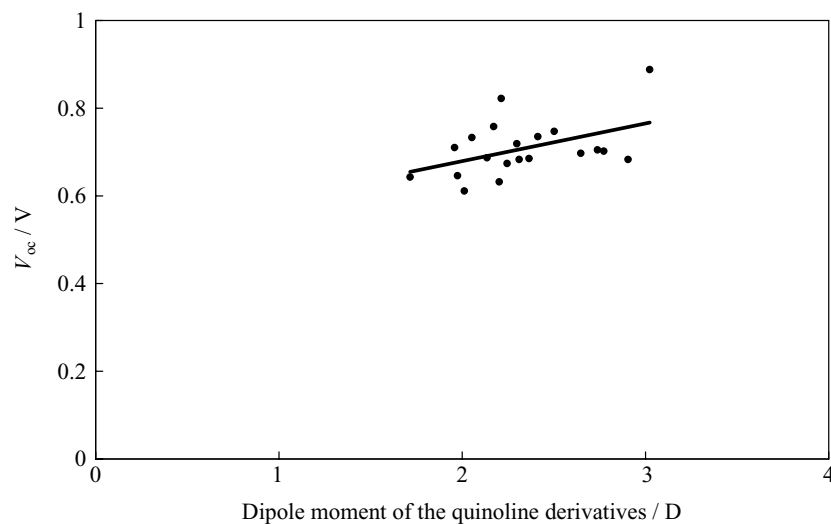

Fig. 5. The correlation between the V_{oc} of the cell and the dipole moment of the quinolines.
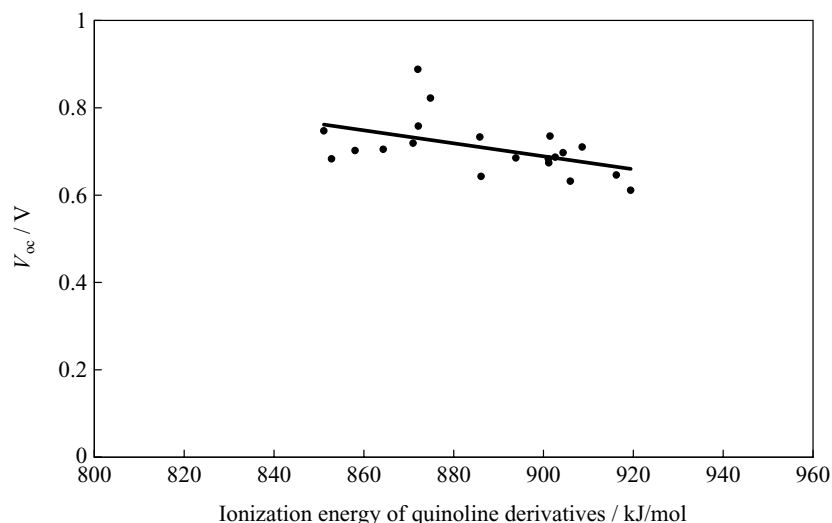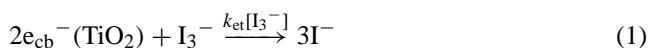
Fig. 7. The correlation between the V_{oc} of the cell and the ionization energy of the quinolines in acetonitrile.

reduction by the conduction band electrons at the semiconductor electrolyte junction [2]:

$$2e_{cb}^-(TiO_2) + I_3^- \xrightarrow{k_{et}[I_3^-]} 3I^- \tag{1}$$

For regenerative photoelectrochemical systems:

$$V_{oc} = \left(\frac{kT}{e}\right) \ln \left(\frac{I_{inj}}{n_{cb}k_{et}[I_3^-]}\right) \tag{2}$$

where k and T are the Boltzmann constant and the absolute temperature, respectively. I_{inj} is the charge flux that results from the sensitizing dye injecting an electron and n_{cb} is the concentration of electrons at the TiO$_2$ surface, while k_{et} is the rate constant for the reduction of I_3^- by the conduction band electrons. Thus, the V_{oc} increases as k_{et} decreases [13,14].

More recently, Kim and coworkers proposed that the influence of the additives on V_{oc} and J_{sc} was due to raise the flatband potential (V_{FB}) of the TiO$_2$ photoelectrode [8]. Absorbing additives in the electrolytic solution on the TiO$_2$ surface may raise the flatband potential (V_{FB}) of the TiO$_2$ electrode [15]. Under Fermi level pinning, these two parameters are linked by:

$$V_{oc} = |V_{FB} - V_{red}| \tag{3}$$

where V_{red} is the standard reduction potential of a redox coupling. According to the literature [16], the change in V_{red} was negligible when pyridines were added in acetonitrile. Consequently, if V_{red} remains constant upon the addition of an additive, then a negative shift in V_{FB} by adsorbing additives on the TiO$_2$ surface should increase the V_{oc}. Raising the V_{FB} would also cause a negative shift in the conduction band edge of TiO$_2$, which would decrease the electron injection rate from the exiting dye and explain the reduction in the J_{sc} upon adding additives.

Either way, the key factor is the adsorption of additives onto the TiO$_2$ surface. It was reported that the surface of nanocrystalline TiO$_2$ photoelectrode was positively charged (Ti^{4+}) due to their Lewis acidity [2,7,17–20]. Accordingly, the atoms bearing the lowest partial charge in the compounds could be preferential points for their adsorption on TiO$_2$ surface [20–22]. In fact, as the lowest partial charge in the atoms of quinoline derivatives (nitrogen) increased, V_{oc} increased (Fig. 3), but the J_{sc} decreased (Fig. 4). The greater the negative charge of the N atom in the quinoline derivatives, the easier and more often the quinolines can adsorb onto the Lewis acid sites of the free areas of the TiO$_2$ electrode, which would increase the V_{oc} and decrease the J_{sc}, as explained by the above mechanisms.

The other results support this hypothesis. Fig. 5 illustrates the correlation between the V_{oc} of the cell and the calculated dipole moment of the quinoline derivatives. The V_{oc} value increased as the dipole moment of the additives increased. The larger the dipole, the easier and more often the quinolines can adsorb on the TiO$_2$ surface since the adsorption energy become more negative [23,24], which results in a larger V_{oc} and a lower J_{sc}.

The other effect on the V_{oc} is explained by the electron donicity of the quinoline additives. As represented in Fig. 7, the V_{oc} value increased as the ionization energy of the quinoline derivatives decreased. Quinolines react with iodine in the solvent to form charge-transfer complexes between the N and I atoms [25–28]. The chemical reactions are written as:

$$quinolines + I_3^- \rightleftarrows quinolinesI_2 + I^- \tag{4}$$
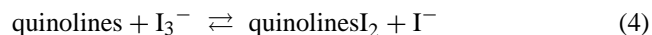
This reaction decreases the I_3^- concentration, but increases the I^- concentration, which raises the hole collection by I^- [9,29] and enhances the V_{oc} of the cell. A lower I_3^- concentration may also slow the reaction between the injected electrons and I_3^-, which would increase the electron concentration in the TiO$_2$ film and improve the V_{oc} [10,13]. The theory of intermolecular charge-transfer com-

plexes is explained by the interaction between the HOMO of the donors (quinolines) with the LUMO of the acceptors (iodine). The greater the overlap and/or the smaller energy difference of the donor HOMO and the acceptor LUMO, the greater the stabilization energy (Δ) and the greater the extent of mixing, which causes a greater charge transfer from the donor to the acceptor. Therefore, it is easier to form a charge-transfer complex when the ionization energy of the donor is small and the electron affinity of acceptor is large [30]. Thus, the lower the ionization energy of the quinoline derivatives, the more efficiently the holes are collected and/or the electron concentration in the TiO_2 photoelectrode is increased, which enhances the V_{oc} value.

Molecular orbital calculations also explain the other effects on the J_{sc}. As illustrated in Fig. 6, the J_{sc} value reduced as the calculated dipole moment of the quinoline derivatives increased. This correlation is consistent with the previously proposed idea. The more the additive dipole moment screens the acetonitrile dipoles (calculated to be 3.4 D), the smaller the dielectric constant of the electrolyte solution [31–34] and the lower the dielectric constant, the smaller the J_{sc} value of the cell [12,35].

Therefore, the reason that quinoline additives significantly influenced the Ru(II)-dye-sensitized nanocrystalline TiO_2 solar cell performance was due to the interaction of the additives with the photoelectrode, redox electrolyte, and electrolyte solvent, which all relate to the electron donating properties of the quinolines.

5. Conclusion

The influence of 20 different quinoline additives on the performance of a Ru(II) complex dye-sensitized nanocrystalline TiO_2 solar cell was investigated for an I^-/I_3^- redox electrolyte in acetonitrile. Typically, adding quinoline derivatives reduced the J_{sc} of the solar cell, but enhanced the V_{oc}, ff and η. As the lowest partial charge of the atoms in the quinolines increased, the V_{oc} was enhanced, but the J_{sc} value was reduced. The greater the dipole moment of quinolines, the higher the V_{oc} but the lower the J_{sc} value. Moreover, as the ionization energy of the quinoline derivatives was reduced, the V_{oc} value was enhanced. These correlations suggest that the electron donicity of quinoline additives influenced the interaction with the photoelectrode, the redox electrolyte, and solvent, which caused the changes in solar cell performance.

Acknowledgements

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