

Influence of pyrimidine additives in electrolytic solution on dye-sensitized solar cell performance

Hitoshi Kusama*, Hironori Arakawa

Photoreaction Control Research Center (PCRC), National Institute of Advanced Industrial Science and Technology (AIST),
AIST Tsukuba Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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Abstract

The influence of pyrimidine additives on the performance of a bis(tetrabutylammonium)*cis*-bis(thiocyanato)bis(2,2'-bipyridine-4-carboxylic acid, 4'-carboxylate)ruthenium(II) dye-sensitized TiO₂ solar cell with an I⁻/I₃⁻ redox electrolyte in acetonitrile was studied. The current–voltage characteristics were measured for more than 10 different pyrimidine derivatives under AM 1.5 (100 mW/cm²). The pyrimidine additives tested had varying effects on the performance of the cell. The additives drastically enhanced the open-circuit photovoltage (V_{oc}) and the solar energy conversion efficiency (η), but usually reduced the short circuit photocurrent density (J_{sc}) of the solar cell. Physical and chemical properties of the pyrimidines were computationally calculated in order to determine the reasons for the additive effects on cell performance. Consequently, the greater the calculated partial charge of the nitrogen atoms in the pyrimidine groups, the larger the V_{oc} but the smaller the J_{sc} values. The V_{oc} of the cell also increased as the ionization energy of the pyrimidine molecules decreased. Moreover, as the calculated dipole moment of the pyrimidine derivatives increased, the J_{sc} value was reduced, but the V_{oc} value was enhanced. These results suggest that the electron donicity of pyrimidine additives influenced the interaction with TiO₂ electrode and I⁻/I₃⁻ electrolyte, which lead to the changes in dye-sensitized solar cell performance.

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1. Introduction

Dye-sensitized solar cells have been eagerly investigated since the last decade when O'Reganoulos and Grätzel reported a high conversion yield [1]. A solar cell consists of nanostructured TiO₂ film electrodes covered with a monolayer of a sensitizing dye such as bis(tetrabutylammonium) *cis*-bis(thiocyanato)bis(2,2'-bipyridine-4-carboxylic acid, 4'-carboxylate)ruthenium(II), a redox electrolyte like I⁻/I₃⁻, and a counter electrode such as Pt. In an attempt to improve solar cell performance, various studies have examined the dye [2–5] and nanostructured semiconductor electrodes [6–11], but few have investigated the role of the electrolytic solution in enhancing performance. Kang et al. reported that carboxylic acid such as acetic acid in I⁻/I₃⁻ acetonitrile solution increased the photocurrent, but decreased the photovoltage [12]. Frank and co-workers conducted a study on an I⁻/I₃⁻ electrolyte with NH₃ and pyridine derivatives such as 4-*t*-butylpyridine (TBP) as additives in acetonitrile. They found that these additives

drastically increased the V_{oc} [13,14] and suggested that the enhanced V_{oc} by the NH₃ and pyridine derivatives was due to the donating properties of the nitrogen lone pair [13–16].

NH₃ and TBP contain one nitrogen atom, but diazines such as pyrimidine have two nitrogens that can each donate lone pair electrons [17], but diazines have yet to be reported as additives in an electrolytic solution for dye-sensitized solar cells. Moreover, a substituted amino group can increase the number of nitrogen lone pairs in pyrimidines. This paper presents the effects of more than 10 different pyrimidine derivatives including aminopyrimidines in an I⁻/I₃⁻ electrolyte and an acetonitrile electrolytic solution on solar cell performance. Chemical and physical properties of the pyrimidines were also evaluated using molecular orbital calculations in order to elucidate the influence of the pyrimidine additives on the dye-sensitized solar cell performance.

2. Experimental

2.1. TiO₂ electrode preparation and dye-coating

Titanium(IV) isopropoxide (Kanto Chemical Co.) was rapidly added to an aqueous solution of HNO₃ (Wako Pure

* Corresponding author. Tel.: +81-29-861-4643; fax: +81-29-861-6771.
E-mail address: h.kusama@aist.go.jp (H. Kusama).

Chemical Industries Ltd.) and then stirred at 323 K for 12 h. 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 TiO₂ paste, which was concentrated by an evaporator.

The TiO₂ paste was deposited onto fluorine-doped stannic oxide conducting glass (FTO, 10 Ω /cm², 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 dm³/min. This process was repeated three times. The thickness of the resulting film measured approximately 15 μ m with a Tencor Alpha-Step 500 surface profiler. The TiO₂ electrode was impregnated with a 0.05 mol/dm³ TiCl₄ 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 dm³/min. The electrode was cooled to 448 K and immediately soaked in a bis(tetrabutylammonium)*cis*-bis(thiocyanato)bis(2,2'-bipyridine-4-carboxylic acid, 4'-carboxylate)ruthenium(II) (N719, Solaronix, SA) dye solution. The dye was adsorbed onto the TiO₂ surface by soaking the TiO₂ electrode in a *t*-butanol/acetonitrile (1:1) solution of the N719 dye (concentration: 3×10^{-4} mol/dm³) for 100 h at 293 K. The electrode was washed, dried, and immediately used for photochemical measurements.

2.2. Photovoltaic characterization

A sandwich-type electrochemical cell, which was composed of a dye-adsorbed TiO₂ electrode, a 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 injected into the space between the two electrodes by a microsyringe. The electrolytic solution was composed of 0.62 mol/dm³ 1,2-dimethyl-3-propylimidazolium iodide (Tomiya Pure Chemical Industries Ltd.), 0.1 mol/dm³ LiI (Aldrich), 0.05 mol/dm³ I₂ (Wako Pure Chemical Industries Ltd.), and 0.5 mol/dm³ of the pyrimidine additive and acetonitrile (Kanto Chemical Co.) as solvent.

The dye-coated semiconductor film was illuminated through a conducting glass support. The solar-to-electric energy conversion efficiency was measured under simulated solar light (Wacom Co., WXS-80C-3, AM 1.5, 100 mW/cm²). The photocurrent, photovoltage, and *I*-*V* curves were measured using a Keithley Model 2400 digital source meter and a data acquisition system (Eiko Seiki Co.). The apparent cell area of TiO₂ photoelectrode was 0.25 cm² (0.5 cm \times 0.5 cm).

2.3. Computational details

The computational chemical calculations were performed by the CAChe program from Fujitsu Limited (Tokyo) implemented on a Windows system. The geometries of the pyrimidines were optimized by a Molecular Orbital Package (MOPAC, PM5) application.

3. Results

3.1. Solar cell performance using pyrimidine additives

I-*V* measurements were performed on the electrolyte with various pyrimidine additives, whose structures are illustrated in Fig. 1. Fig. 2 shows the *J*_{sc} results when illuminating with 100 mW/cm² and an additive concentration of 0.5 mol/dm³. Except for 2-amino-4,6-dimethoxypyrimidine, the *J*_{sc} value for cells containing a pyrimidine additive was less than the cell without an additive. Monoamino substituents such as 5-aminopyrimidine yielded a higher *J*_{sc} than diamino substituent such as 4,5-diaminopyrimidine. Alkyl substituted aminopyrimidines such as 2-amino-4-methylpyrimidine and 2-amino-4,6-dimethylpyrimidine and non-substituted aminopyrimidines such as 2-aminopyrimidine displayed similar *J*_{sc} values. The highest and lowest *J*_{sc} were obtained in the cells using 2-amino-4,6-dimethoxypyrimidine and 2,4-diaminopyrimidine, respectively.

Fig. 3 illustrates the influence of the pyrimidine additives in the electrolytic solution on the *V*_{oc} of the cell. The *V*_{oc} values for cells containing pyrimidines were greater than the cell without an additive. Substituents of the amino group enhanced the *V*_{oc} more than pyrimidine. In contrast to the *J*_{sc}, diamino substituents yielded a higher *V*_{oc} than monoamino substituent. Alkyl substituted and non-substituted aminopyrimidines showed comparable *V*_{oc} values. Among the tested additives, 2,4-diaminopyrimidine had the highest *V*_{oc}, 0.85 V, but the lowest *J*_{sc} (Fig. 2).

Fig. 4 represents the influence of the pyrimidine additives in the electrolytic solution on the ff of the cell. In general, adding pyrimidine derivatives enhanced the ff of the solar cell. Unlike the *J*_{sc} and *V*_{oc} trends, alkyl substituted aminopyrimidines showed lower ff values than non-substituted ones. The highest and lowest ff values were observed using 2,4-diaminopyrimidine and 4,5-diaminopyrimidine as the additive, respectively.

Fig. 5 depicts the influence of the pyrimidine additives in the electrolytic solution on η . Remarkable enhancement of the η value was observed for all the pyrimidine derivatives except for 4,5-diaminopyrimidine. Similar to the *J*_{sc} trend, monoamino substituents yield a higher η than diamino substituent. Alkyl substituted and non-substituted aminopyrimidines displayed similar η values. 2-Aminopyrimidine resulted in the highest η of the cell among the tested additives.

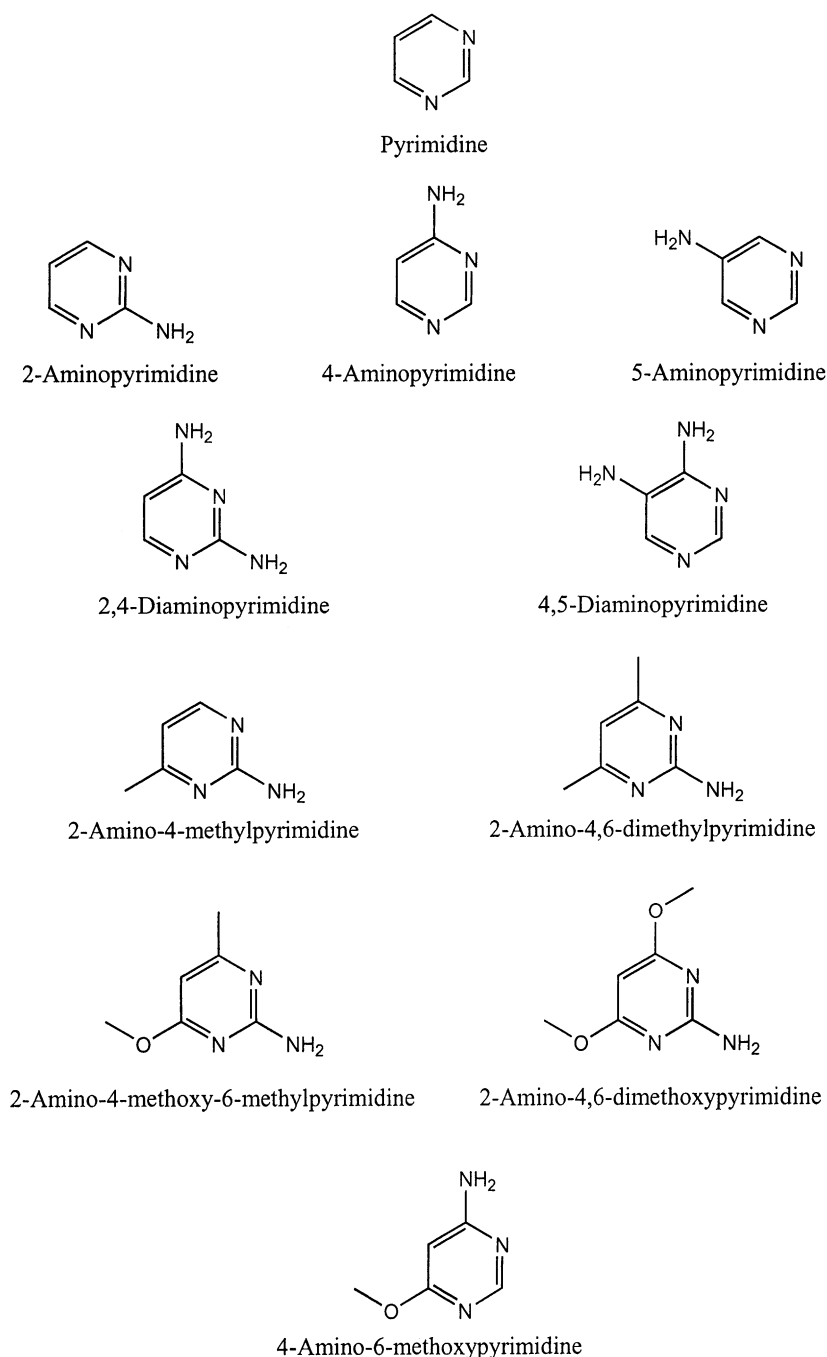


Fig. 1. The structures of the pyrimidine additives tested in this study.

3.2. Computational calculations

As mentioned in Section 3.1, the pyrimidine additives tested had varying effects on the dye-sensitized solar cell performance. After the photovoltaic measurements, dye desorption was not observed from the TiO_2 electrode to the electrolytic solution when pyrimidine additives were present. Thus, it was determined that the varying effects on performance were due to the properties of the pyrimidine additives and not variations in the adsorbed dye amount on the TiO_2

electrode. Therefore, the physical and chemical properties of the pyrimidines were computationally calculated in order to investigate the reasons that the pyrimidine derivatives had varying effects on the cell performance. Various correlations between the properties of the additives and solar cell performance such as J_{sc} and V_{oc} were found.

In order to estimate the extent that the lone pair electrons in nitrogen atoms donate, the partial charges of the nitrogen atoms in the pyrimidine group were calculated at the PM5 level using the MOPAC system available in the CAChe

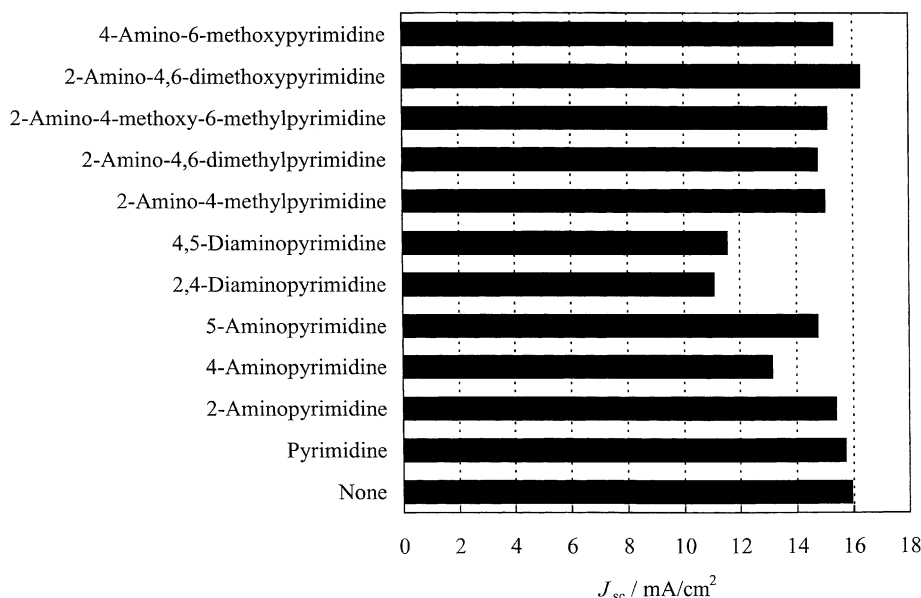


Fig. 2. The influence of the pyrimidine additives in the electrolytic solution on the J_{sc} for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.62 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 pyrimidines in acetonitrile; light intensity, 100 mW/cm^2 , AM 1.5.

package. Fig. 6 shows the correlation between the J_{sc} of the cell and the calculated partial charge of the N atoms in the pyrimidine groups in acetonitrile. For N atoms at the 1 and 3 positions in the pyrimidine groups, the smaller the calculated partial charge, the more the J_{sc} value was enhanced. Fig. 7 depicts the correlation between the V_{oc} and the calculated partial charge of N atom. Contrary to the J_{sc} trend, the smaller the calculated partial charge, the more the V_{oc}

was reduced regardless of where the lone pair is located in the pyrimidine group.

Then the dipole moment and ionization energy of the pyrimidine derivatives were calculated at the PM5 level using the MOPAC system available in the CAChe package. Fig. 8 illustrates the correlation between the J_{sc} of the cell and the calculated dipole moment of the pyrimidine molecules. In general, the J_{sc} value increased as the

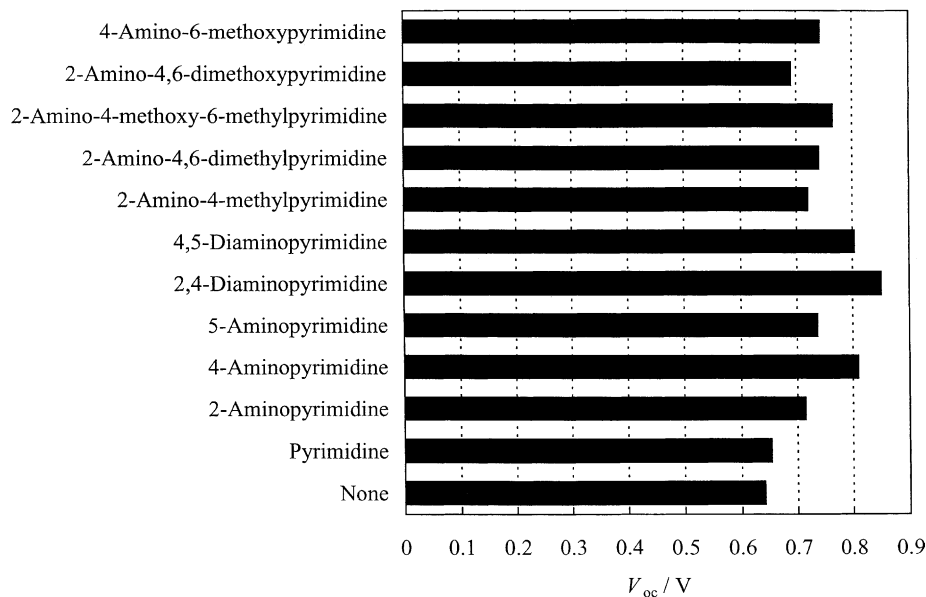


Fig. 3. The influence of the pyrimidine additives in the electrolytic solution on the V_{oc} for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.62 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 pyrimidines in acetonitrile; light intensity, 100 mW/cm^2 , AM 1.5.

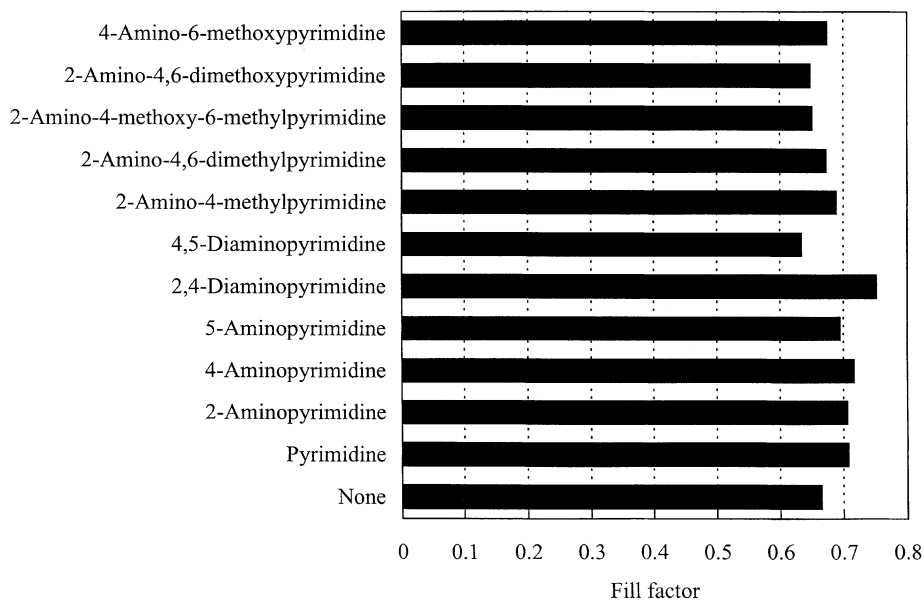


Fig. 4. The influence of the pyrimidine additives in the electrolytic solution on the ff for a N719 dye-sensitized TiO₂ solar cell. Conditions: electrolyte, 0.62 mol/dm³ 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm³ LiI + 0.05 mol/dm³ I₂ + 0.5 mol/dm³ pyrimidines in acetonitrile; light intensity, 100 mW/cm², AM 1.5.

calculated dipole moment of the pyrimidines decreased. Fig. 9 shows the correlation between the V_{oc} and the calculated dipole moment of the pyrimidine molecules and indicates that the greater the calculated dipole moment of the pyrimidine derivatives, the larger the observed V_{oc} value.

Fig. 10 represents the correlation between the V_{oc} of the cell and the calculated ionization energy of the pyrimidine molecules in acetonitrile at the PM5 level using the MOPAC system available in the CACHE package. The results indicate

that as the calculated ionization energy of the pyrimidine molecules is decreased, the V_{oc} of the cell is increased.

4. Discussion

As shown in Figs. 2–5, the pyrimidine additives in the I⁻/I₃⁻ electrolytic solution influenced dye-sensitized solar cell performance. In particular, the J_{sc} and V_{oc} values were

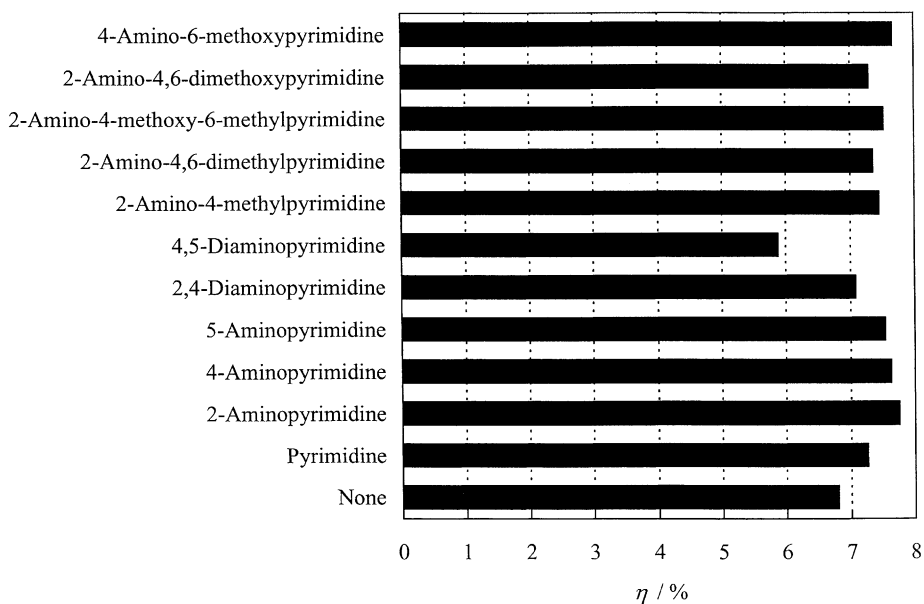


Fig. 5. The influence of the pyrimidine additives in the electrolytic solution on η for a N719 dye-sensitized TiO₂ solar cell. Conditions: electrolyte, 0.62 mol/dm³ 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm³ LiI + 0.05 mol/dm³ I₂ + 0.5 mol/dm³ pyrimidines in acetonitrile; light intensity, 100 mW/cm², AM 1.5.

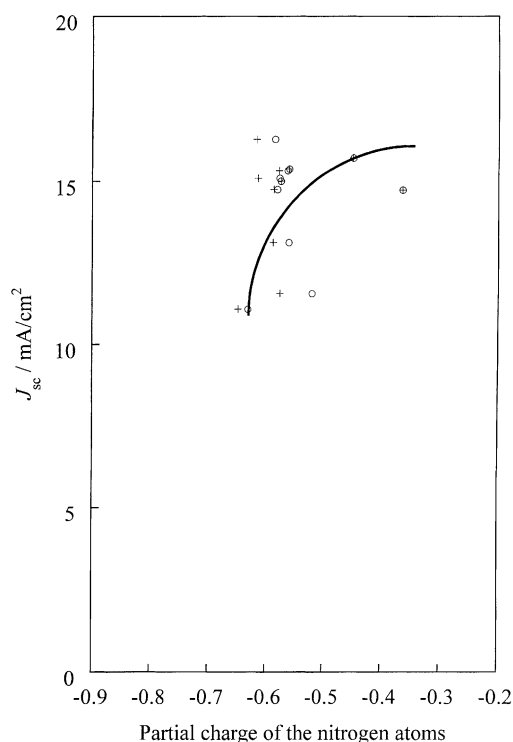


Fig. 6. The correlation between the J_{sc} of the cell and the calculated partial charge of nitrogen atom in the pyrimidine groups in acetonitrile: (○) position 1 and (+) position 3.

drastically altered by the pyrimidine derivatives. The cells containing a pyrimidine additive in the electrolytic solution displayed higher V_{oc} values, but typically showed lower J_{sc} values compared to a cell without additives. In order to investigate the reasons that the pyrimidine additives influenced the cell performance, computational calculations were performed. First, the partial charges of the N atoms in the

pyrimidine group were calculated to estimate the donating ability of the N lone pairs. The calculations were compared to the experimental results of the solar cell performance and it was determined that as the partial charge of the N atoms increased, the J_{sc} decreased, but the V_{oc} increased (Figs. 6 and 7). These results suggest that the pyrimidine molecules adsorb into the free areas of the TiO_2 electrode, which would increase the V_{oc} , but decrease the J_{sc} values. The adsorption of the additives in the electrolytic solution onto the TiO_2 surface may raise the flatband potential (V_{FB}) of the TiO_2 electrode [12]. Under Fermi level pinning, these two parameters are linked by Eq. (1):

$$V_{oc} = |V_{FB} - V_{red}| \quad (1)$$

where V_{red} is the standard reduction potential of a redox coupling. Assuming that V_{red} remains constant when pyrimidines are added, increasing the V_{FB} by adsorbing pyrimidines onto the TiO_2 surface should increase the V_{oc} . The larger the partial charge of the N atom in the pyrimidine group, the easier and more often the pyrimidines can adsorb onto the Lewis acid sites of the TiO_2 surface [18], which would cause a higher V_{oc} . Raising the V_{FB} would also lead to a negative shift in the conduction band edge of TiO_2 , which decreases the electron injection rate from the exiting dye and explains the reduction in the J_{sc} upon adding pyrimidine derivatives. The other results from the molecular orbital calculations support this hypothesis. As illustrated in Fig. 9, the V_{oc} increases as the calculated dipole moment of the pyrimidines increases. The larger the dipole, the easier and more often the pyrimidine derivatives can adsorb onto TiO_2 surface [19,20], which leads to a higher V_{oc} of the cell.

Unlike the trend of V_{oc} , the J_{sc} value was enhanced as the calculated dipole moment of the pyrimidines decreased (Fig. 8). The calculated dipole moment of acetonitrile, the electrolyte solvent, was 3.4 D. This correlation is explained by an idea previously proposed. The more the dipole

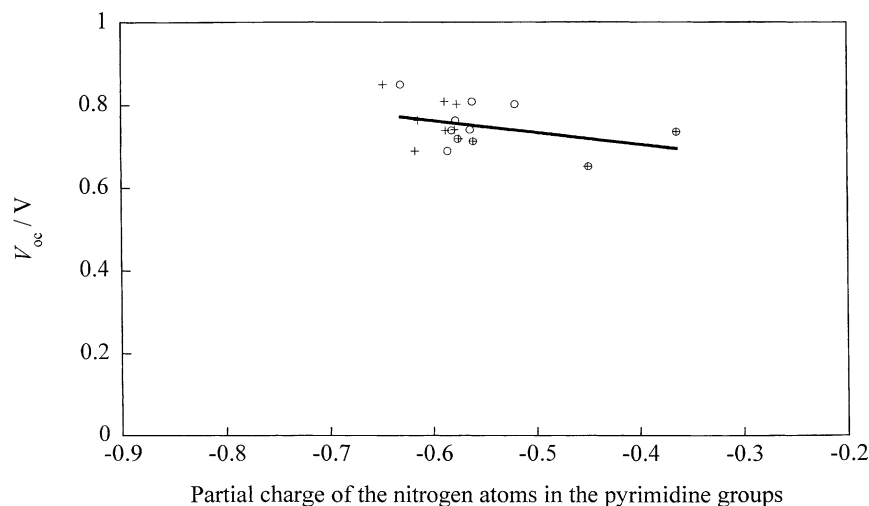


Fig. 7. The correlation between the V_{oc} of the cell and the calculated partial charge of nitrogen atom in the pyrimidine groups in acetonitrile: (○) position 1 and (+) position 3.

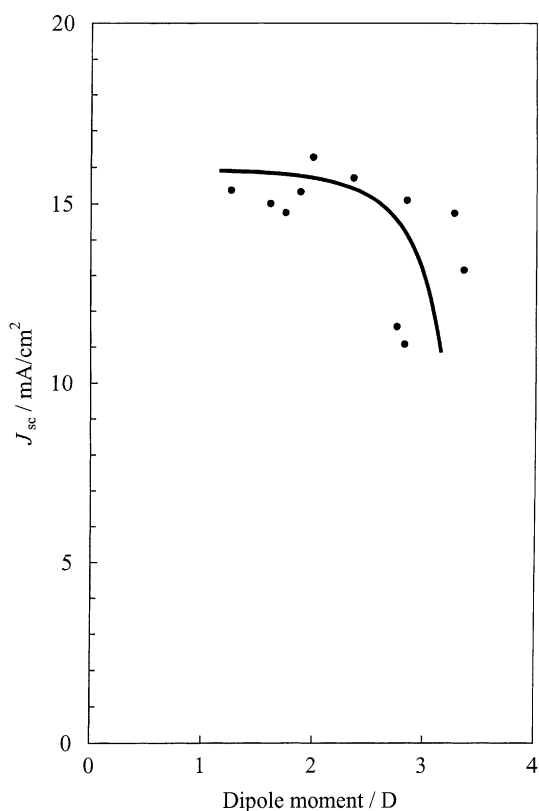
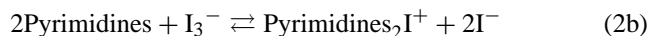
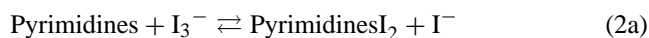


Fig. 8. The correlation between the J_{sc} of the cell and the calculated dipole moment of the pyrimidine molecules at the PM5 level using the MOPAC system available in the CAChe package.

moment of the additive shields the solvent dipoles, the greater the reduction of the dielectric constant of the electrolytic solution [21,22] and the lower the dielectric constant, the less photocurrent in the cell [23,24].

The other effect on the V_{oc} is explained by electron donicity of pyrimidines. As shown in Fig. 10, the V_{oc} increased as the calculated ionization energy of the pyrimidine molecule decreased. It is known that pyrimidine derivatives react with iodine in the solvent to form charge-transfer complexes between the N of pyrimidine and I atoms [25–27]. The chemical reactions are written as Eqs. (2a) and (2b):



These reactions decrease the I_3^- concentration while increasing the I^- concentration. Increasing the I^- concentration improved hole collection by I^- [15,28] and increases the V_{oc} of the cell. Decreasing the I_3^- concentration may reduce the reaction between the injected electrons and I_3^- , which increased the electron concentration in the TiO_2 film. The increase in electron concentration improves the V_{oc} [3,16]. The theory of intermolecular charge-transfer complex formation is explained by the interaction between the HOMO of donors (pyrimidine) with the LUMO of acceptors (iodine). The greater the overlap and/or the smaller energy difference of the HOMO of donors and the LUMO of acceptors, the greater the stabilization energy, Δ and the greater the extent of mixing. This leads to more charge-transfer from the donors to the acceptors. 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 [29]. Thus, the lower the ionization energy of the pyrimidine derivatives, the more efficiently the hole is collected [15,28] and/or the electron concentration in the TiO_2 film increases, which results in a higher V_{oc} .

Therefore, it was concluded that the electron donating property of pyrimidine additives to the electrolytic solution

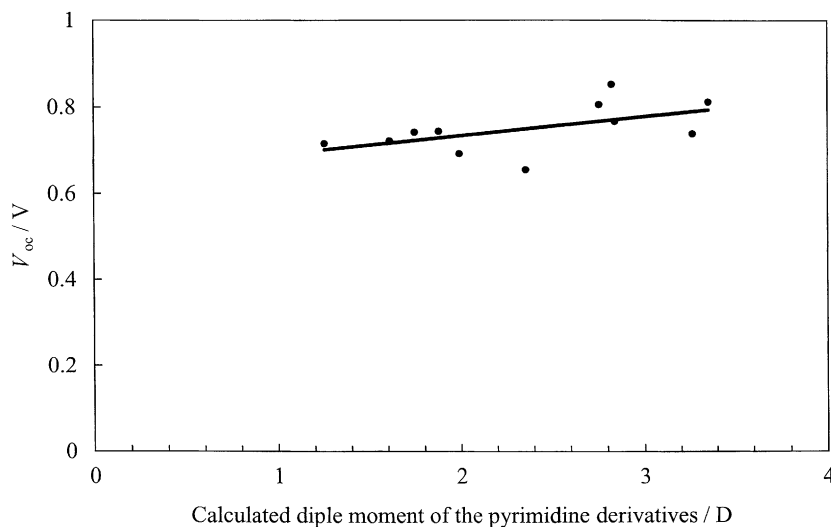


Fig. 9. The correlation between the V_{oc} of the cell and the calculated dipole moment of the pyrimidine molecules at the PM5 level using the MOPAC system available in the CAChe package.

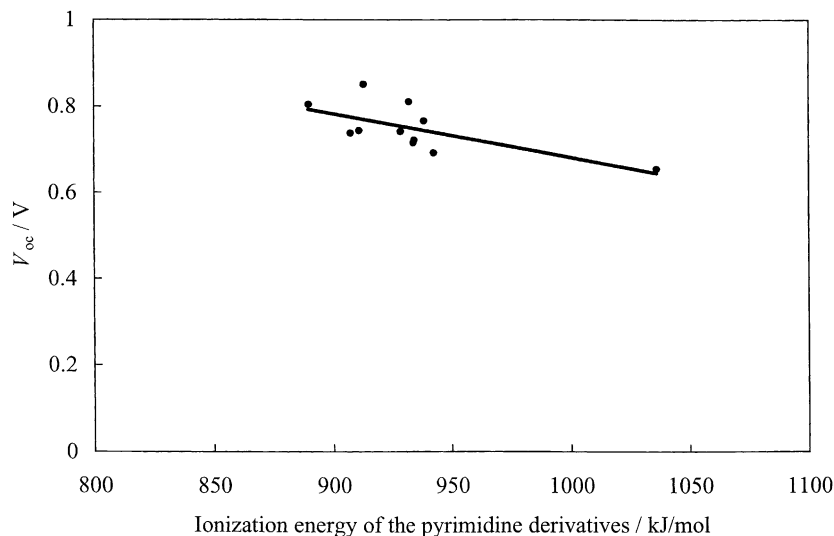


Fig. 10. The correlation between the V_{oc} of the cell and the calculated ionization energy of the pyrimidine molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.

had a significant influence on the dye-sensitized solar cell performance.

5. Conclusion

The influence of more than 10 different pyrimidine additives on the performance of a Ru complex (N719) dye-sensitized TiO_2 solar cell was investigated for an I^-/I_3^- redox electrolyte in acetonitrile. Typically, adding pyrimidines reduced the J_{sc} of the solar cell, but enhanced the V_{oc} and η . As the partial charge of the nitrogen atoms in the pyrimidine group increased, the V_{oc} was enhanced, but the J_{sc} value was reduced. The V_{oc} also increased as the ionization energy of the pyrimidine molecules decreased. The larger the dipole moment of the pyrimidine derivatives, the smaller the J_{sc} value and the larger the V_{oc} value. These correlations suggest that the electron donicity of pyrimidine derivatives influenced the interaction with TiO_2 electrode and I^-/I_3^- electrolyte and lead to the changes in solar cell performance.

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