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

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Abstract

The influence of aminotriazole additives in acetonitrile solution of an I^-/I_3^- redox electrolyte on the performance of a bis(tetrabutylammonium)*cis*-bis(thiocyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II) (N719) dye-sensitized TiO_2 solar cell was studied. The current–voltage characteristics were investigated under AM 1.5 (100 mW/cm^2) for 10 different aminotriazole compounds. The aminotriazole additives tested had varying effects on the solar cell performance. Most of the additives enhanced the open-circuit photovoltage (V_{oc}), fill factor (ff) and the solar energy conversion efficiency (η), but reduced the short circuit photocurrent density (J_{sc}) of the solar cell. The highest η of 7.6% was obtained by adding 3-amino-1H-1,2,4-triazole and η was comparable to that of 4-*t*-butylpyridine (TBP). Both the physical and chemical properties of the aminotriazoles were computationally calculated in order to determine the reasons why the additive affects the solar cell performance. The greater the calculated partial charge of the nitrogen atoms in the molecule, the larger the V_{oc} value. The V_{oc} of the solar cell also increased as the size of the aminotriazole molecules decreased. The J_{sc} value increased with increasing the absolute difference in the dipole moments between the calculated aminotriazoles and acetonitrile. These results suggest that the electron donicity of the aminotriazole additives influenced the interaction with the TiO_2 photoelectrode and the solvent, which altered the dye-sensitized solar cell performance.

Keywords: Dye-sensitized solar cell; Electrolytic solution; Aminotriazoles; Additive effect

1. Introduction

Dye-sensitized solar cells have been extensively investigated since O'Reganoulos and Grätzel reported a high solar energy conversion yield [1]. A solar cell consists of nanostructured TiO_2 film photoelectrodes covered with a monolayer of a sensitizing dye such as Ru complex (N719), a redox electrolyte solution of I^-/I_3^- and a counter electrode such as Pt on conducting glass. In an attempt to improve solar cell performance, many studies have examined the nanostructured semiconductor photoelectrodes [2–8] and dye [9–13], but only a few have investigated the role of the electrolytic solution in enhancing performance. Kang and co-workers reported that carboxylic acids such as acetic acid in acetonitrile solution of I^-/I_3^- redox increased the photocurrent, but decreased the photovoltage [14]. Frank and co-workers conducted a study on an I^-/I_3^- electrolyte solution with NH_3 and pyridine derivatives such as TBP as additives in acetonitrile. They found that these additives drastically increased the V_{oc} [15,16] and suggested that the enhanced V_{oc} by NH_3 and pyridine derivatives was due to the donating properties of the nitrogen lone pair [15–18].

Ammonia and TBP have one nitrogen atom in their structure, on the other hand triazoles such as 1,2,4-triazole have three nitrogens that can each donate lone pair electrons [19]. In addition, triazoles have yet to be studied 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 triazoles. This paper presents the influences of 10 different aminotriazole derivatives in acetonitrile solution of an I^-/I_3^- redox electrolyte on solar cell performance and compares the properties of aminotriazoles to that of the TBP additive, which is the most popular additive for the electrolyte solution in a dye-sensitized solar cell. The chemical and physical properties of the aminotriazoles were also investigated using molecular orbital calculations to elucidate the influence of the aminotriazole additives on the dye-sensitized solar cell performance.

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2. Experimental

2.1. TiO_2 photoelectrode preparation and dye-coating

The TiO_2 photoelectrode (thickness: 15 μm) was prepared as described earlier [20]. The dye was adsorbed onto the TiO_2 surface by soaking the TiO_2 photoelectrode in a *t*-butanol/acetonitrile (1:1) solution of the N719 dye (Solaronix S.A., concentration: 3×10^{-4} mol/dm^3) for 100 h at 293 K. The photoelectrode was washed, dried, and immediately used for the measurements of solar cell performance.

2.2. Photovoltaic characterization

A sandwich-type photoelectrochemical cell, which was composed of a dye-adsorbed TiO_2 photoelectrode, 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 using a microsyringe. The electrolytic solution was composed of 0.6 mol/dm^3 of 1,2-dimethyl-3-propylimidazolium iodide (Tomiyama Pure Chemical Industries Ltd.), 0.1 mol/dm^3 of LiI (Aldrich), 0.05 mol/dm^3 of I_2 (Wako Pure Chemical Industries Ltd.), 0.5 mol/dm^3 of the aminotriazole additive and acetonitrile (Kanto Chemical Co.) as the solvent.

The dye-coated semiconductor photoelectrode 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/cm^2). 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 TiO_2 photoelectrode was 0.25 cm^2 (0.5 cm × 0.5 cm).

2.3. Computational details

The computational chemical calculations were performed using the CAChe program from Fujitsu Limited (Tokyo) implemented on a Windows system. The geometries of the aminotriazole compounds were optimized by a molecular orbital package (MOPAC, PM5) application.

3. Results

3.1. Solar cell performance using aminotriazoles as additives

The *I–V* measurements were performed using electrolyte solutions with various aminotriazole additives. Fig. 1 illustrates the molecular structures of aminotriazole compounds tested. Fig. 2 shows the J_{sc} results when illuminating with 100 mW/cm^2 and an of additive concentration of 0.5 mol/dm^3 if additives were present. The J_{sc} values of the solar cells with aminotriazoles were less than that of the solar cell without additives. The addition of TBP to electrolytic solution also decreased the J_{sc} value.

Fig. 3 illustrates the influence of the aminotriazole additives in the electrolytic solution on the V_{oc} of the solar cell. Similar to TBP, all of the V_{oc} values for solar cells containing aminotriazoles were greater than that of the cell without additives. When comparing isomers, the V_{oc} with 3-amino-1H-1,2,4-triazole was higher than 4-amino-4H-1,2,4-triazole. Among the tested additives, which included TBP, 4-amino-3,5-dimethyl-4H-1,2,4-triazole displayed the largest V_{oc}, 0.78 V.

Fig. 4 represents the influence of the aminotriazole additives in the electrolytic solution on the ff of the solar cell. In general, aminotriazoles enhanced the ff of the solar cell. The highest and lowest ff values were observed when 4-amino-4H-1,2,4-triazole and 3-amino-5-benzylthio-4H-1,2,4-triazole were used as the additive, respectively.

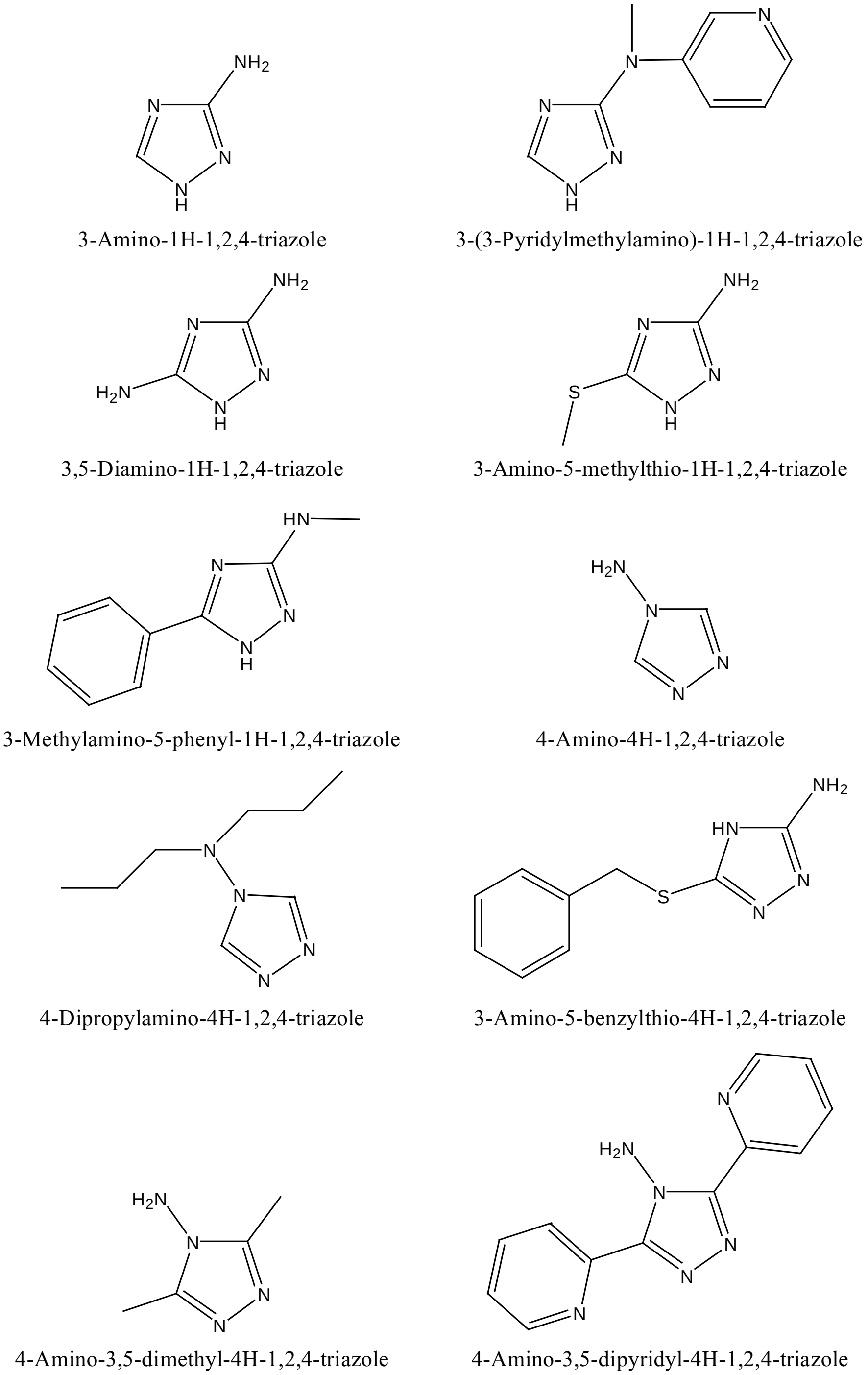
Fig. 5 depicts the influence of the aminotriazoles in the electrolytic solution on η, which was generally enhanced. Among the tested aminotriazoles, 3-amino-1H-1,2,4-triazole resulted in the highest η, 7.6%, and this η was comparable to that of TBP (7.7%).

3.2. Computational calculations

As mentioned in Section 3.1, the tested aminotriazoles remarkably affected the dye-sensitized solar cell performance. Dye desorption was not observed after the photovoltaic measurements from the TiO_2 photoelectrode to the electrolytic solution when the aminotriazoles were present. Thus, it was determined that the varying effects on the solar cell performance were due to the properties of the aminotriazoles and not due to variations in the adsorbed amount of N719 dye on the TiO_2 photoelectrode. Therefore, the physical and chemical properties of the aminotriazoles were computationally calculated in order to investigate the reasons for the observed influences of the aminotriazole additives on the cell performance. Several correlations between the properties of the additives and solar cell performance such as J_{sc} and V_{oc} were found.

The donating ability of the lone pair electrons in the nitrogen atoms was estimated by calculating the partial charges of the nitrogen atoms in the molecule at the PM5 level using the MOPAC system available in the CAChe package. Fig. 6 depicts the correlation between the V_{oc} value of the cell and the maximum partial charge of the N atoms in the molecule in acetonitrile. The larger the maximum partial charge, the more the V_{oc} was enhanced.

The size and dipole moment of the aminotriazole derivatives were also calculated at the PM5 level using the MOPAC system available in the CAChe package. Fig. 7 shows the correlation between V_{oc} of the cell and the calculated size of the aminotriazole molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.



3-Amino-1H-1,2,4-triazole

3-(3-Pyridylmethylamino)-1H-1,2,4-triazole

3,5-Diamino-1H-1,2,4-triazole

3-Amino-5-methylthio-1H-1,2,4-triazole

3-Methylamino-5-phenyl-1H-1,2,4-triazole

4-Amino-4H-1,2,4-triazole

4-Dipropylamino-4H-1,2,4-triazole

3-Amino-5-benzylthio-4H-1,2,4-triazole

4-Amino-3,5-dimethyl-4H-1,2,4-triazole

4-Amino-3,5-dipyridyl-4H-1,2,4-triazole

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

The size of an aminotriazole molecule was defined as the maximum distance between the two atoms in the molecule by a molecular orbital calculation. The V_{oc} of the cell increased as the calculated size of the aminotriazole molecule decreased. Fig. 8 depicts the correlation between the V_{oc} of the cell and the solvent accessible surface area of the aminotriazole molecules in acetonitrile. The solvent accessible surface area was defined as the molecular surface area accessible to a solvent molecule. As the surface area accessible to the solvent decreased, the V_{oc} of the cell increased. Fig. 9 illustrates the correlation between the J_{sc} of the cell and the calculated dipole moment of the aminotriazoles. The J_{sc} value increased as the absolute difference (solid line) in the dipole moments of the calculated aminotriazoles and acetonitrile, which was 3.4 D (dashed line) increased.

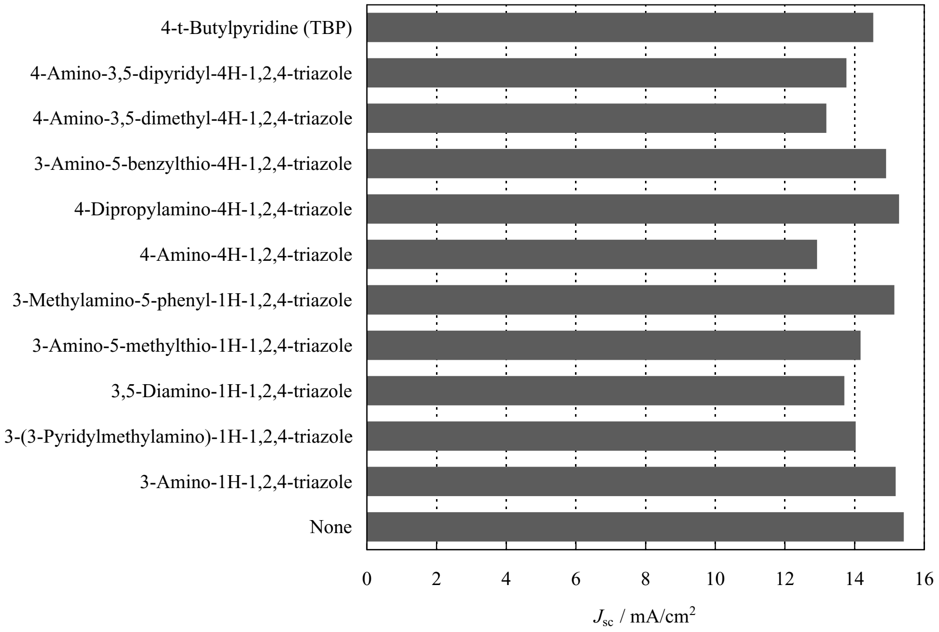


Fig. 2. The influence of the aminotriazoles in the electrolytic solution on the J_{sc} for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 additive in acetonitrile; light intensity, 100 mW/cm^2, AM 1.5.

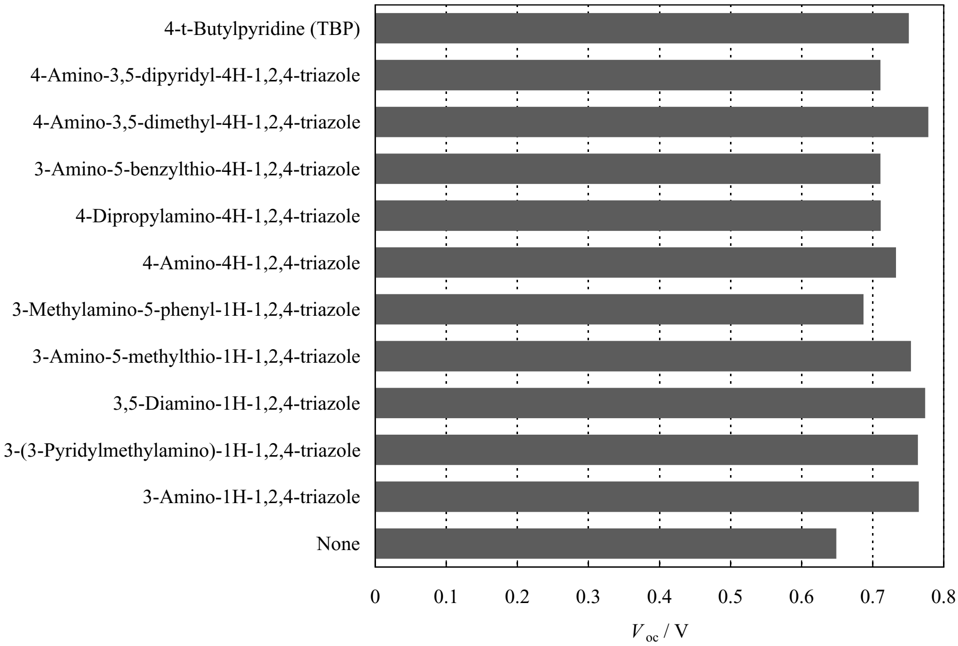


Fig. 3. The influence of the aminotriazoles in the electrolytic solution on the V_{oc} for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 additive in acetonitrile; light intensity, 100 mW/cm^2, AM 1.5.

4. Discussion

As shown in Figs. 2–5, the aminotriazole additives in the I^-/I_3^- electrolytic solution influenced dye-sensitized solar cell performance and in particular, the J_{sc} and V_{oc} values were drastically altered. Most of the cells with aminotriazoles displayed higher V_{oc} values, but typically showed lower J_{sc} values compared to those of a cell without an additive. These trends were also observed in the cell using TBP. Computational calculations investigated the reasons

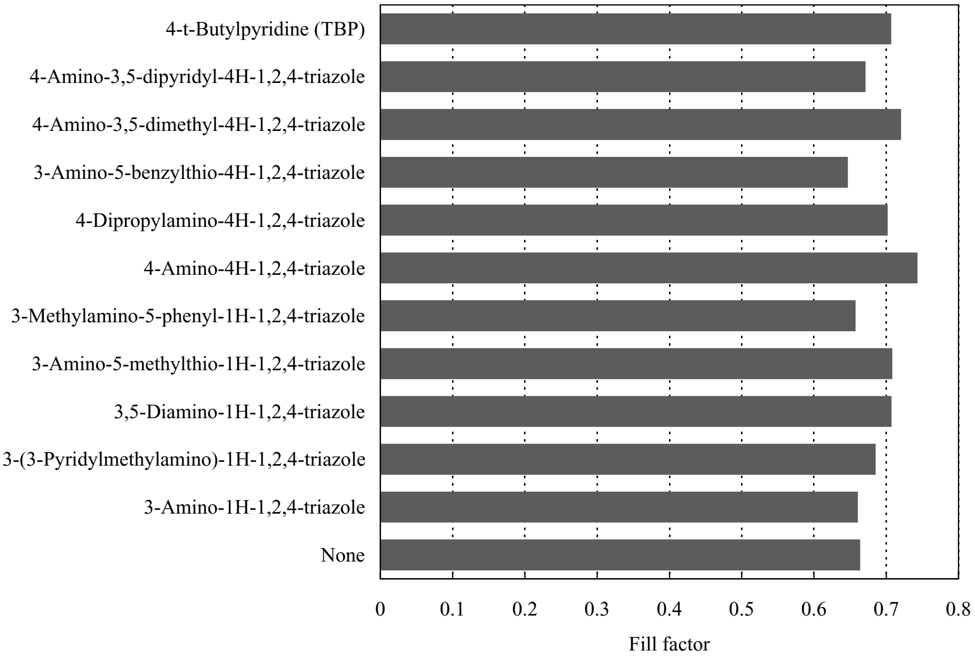


Fig. 4. The influence of the aminotriazoles in the electrolytic solution on the ff for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 additive in acetonitrile; light intensity, 100 mW/cm^2, AM 1.5.

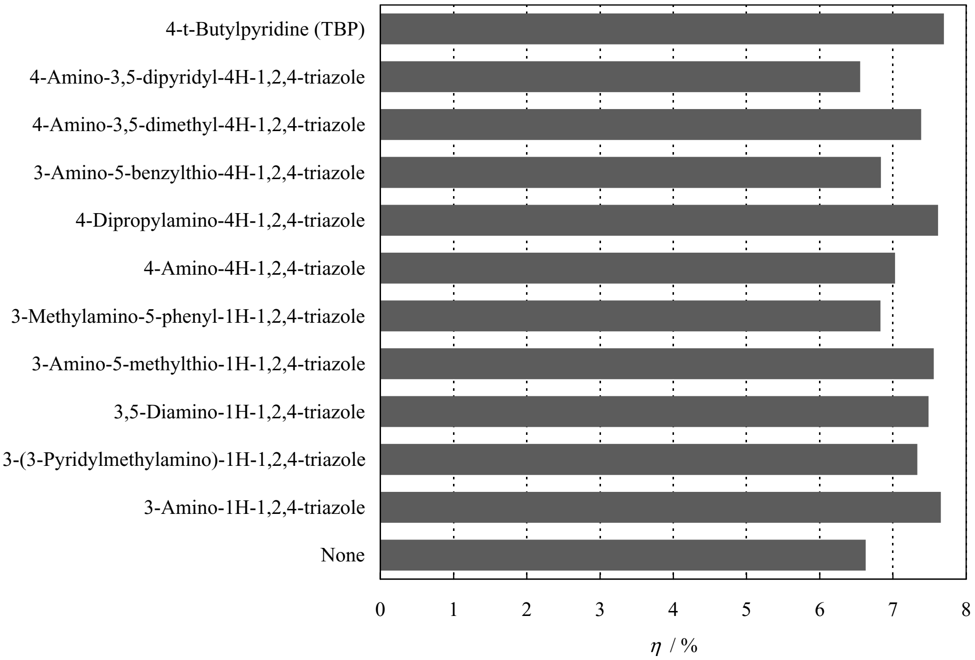


Fig. 5. The influence of the aminotriazoles in the electrolytic solution on η for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 additive in acetonitrile; light intensity, 100 mW/cm^2, AM 1.5.

why the aminotriazole additives influenced the cell performance. The calculated partial charges of the N atoms in the molecule estimated the donating ability of the N lone pairs and these calculations were compared to the experimental results. It was determined that the V_{oc} value of the cell increased as the maximum partial charge of the N atoms increased (Fig. 6). This result suggests that the molecules of aminotriazoles adsorb onto the free areas of the TiO_2 photoelectrode, which would increase the V_{oc} value. Two different mechanisms have been suggested for additive adsorption on TiO_2 surface. One is to suppress the dark current arising from the I_3^- reduction by the electrons in conduction band

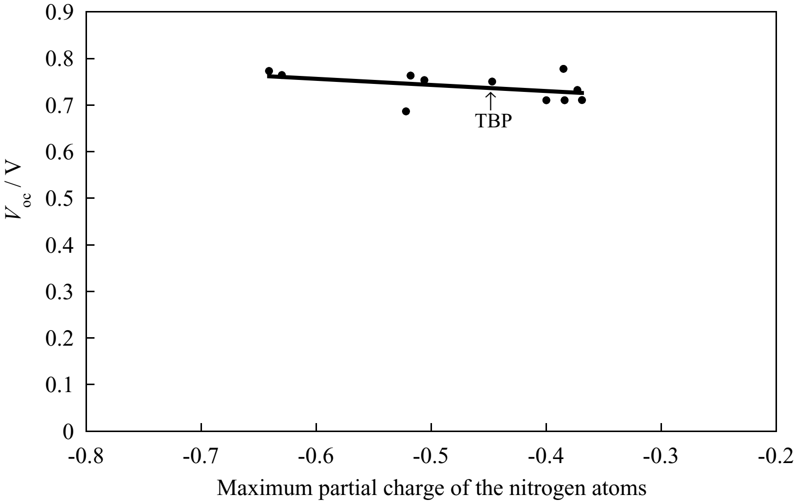


Fig. 6. The correlation between the V_{oc} of the cell and the maximum partial charge of the nitrogen atom in the molecule in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.

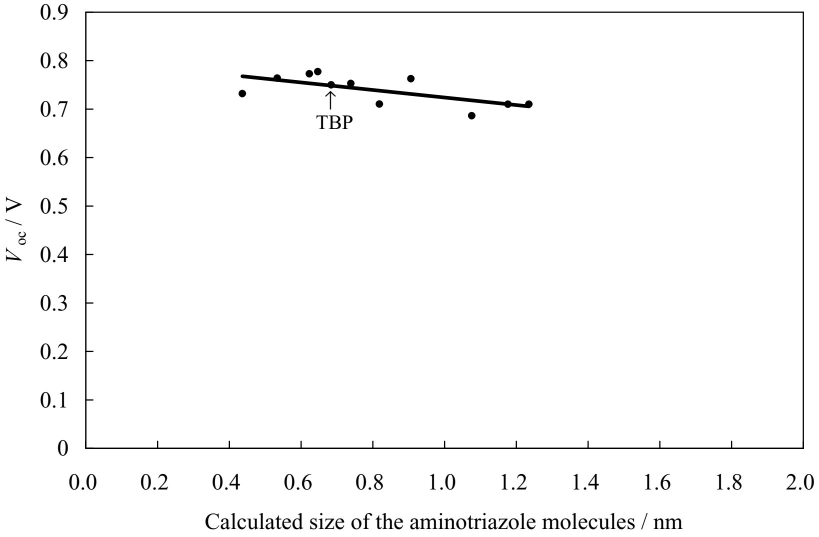


Fig. 7. The correlation between the V_{oc} of the cell and the calculated size of the aminotriazole molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.

at the semiconductor electrolyte junction:

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

For regenerative photoelectrochemical systems, Eq. (2) holds:

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

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. The V_{oc} increases as the k_{et} decreases [9,10]. The higher the partial charge of the N atom in the molecule, the easier and more often the aminotriazoles can adsorb onto the free area on the TiO_2 surface [21–23], which more efficiently suppresses the dark current. The other mechanism is to raise the flatband potential (V_{FB}) of the TiO_2 photoelectrode. Adsorbing additives in the electrolytic solution onto the TiO_2 surface may raise the flatband potential (V_{FB}) of the TiO_2 electrode [14,24]. Under Fermi level pinning, these two parameters are linked by

$$V_{oc} = |V_{FB} - V_{red}| \qquad (3)$$

where V_{red} is the standard reduction potential of a redox coupling. If V_{red} remains constant when aminotriazoles are added, then increasing the V_{FB} by adsorbing aminotriazoles onto the TiO_2 surface should increase the V_{oc}. Raising the

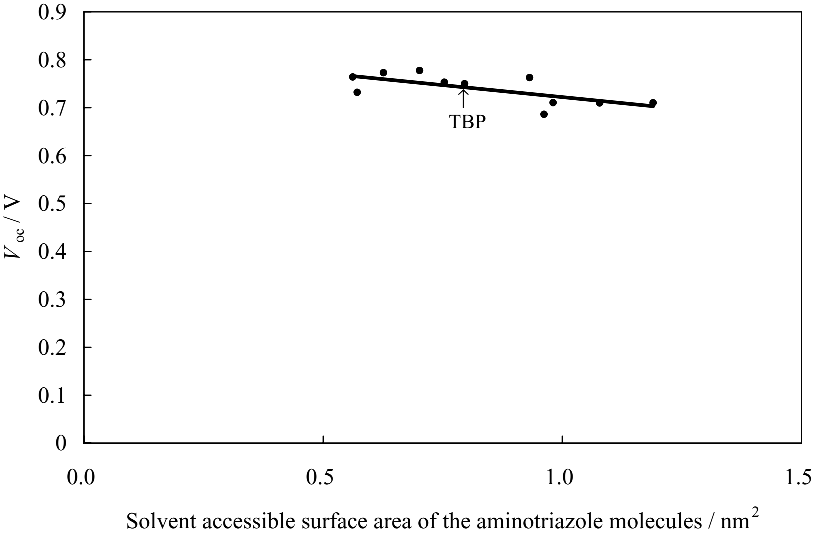


Fig. 8. The correlation between the V_{oc} of the cell and the solvent accessible surface area of the aminotriazole molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.

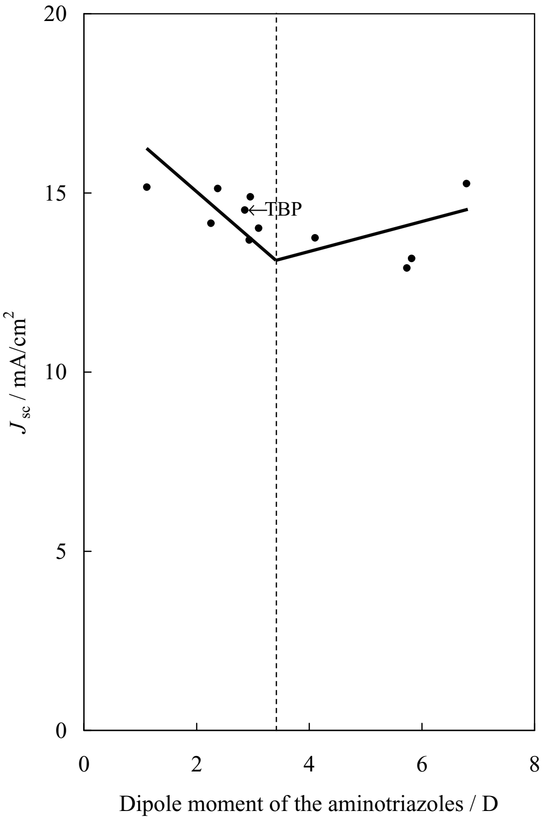


Fig. 9. The correlation between the J_{sc} of the cell and the calculated dipole moment of the aminotriazoles at the PM5 level using the MOPAC system available in the CAChe package.

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 aminotriazole derivatives. The higher the partial charge of the N atom in the molecule, the easier and more often the aminotriazoles can adsorb onto the Lewis acid sites of the TiO_2 surface, which would increase the V_{oc} and decrease the J_{sc}.

The other results support this hypothesis. As depicted in Fig. 7, the V_{oc} of the cell increased as the calculated size of the aminotriazole molecule decreased. As represented in Fig. 8, the V_{oc} of the cell increased as the surface area accessible to the solvent decreased. These findings also suggest that the aminotriazole additives adsorb onto the free areas of the TiO_2 photoelectrode. Electrolytes that have smaller aminotriazole additives more readily adsorb onto the free areas of the TiO_2 photoelectrode. Therefore, the smaller the molecule, the more often and the easier the aminotriazoles can adsorb onto the free Lewis acid sites of the TiO_2 surface, which leads to a larger V_{oc} of the cell. Moreover, as described in Section 3.1, for the isomers, the V_{oc} with 4-amino-4H-1,2,4-triazole was lower than 3-amino-1H-1,2,4-triazole since in the former two N atoms (1,2-position) can interact with the TiO_2 surface, but the latter cannot (2,4-position). Therefore, twice as many 3-amino-1H-1,2,4-triazole molecules may be absorbed onto the free area of the TiO_2 as 4-amino-4H-1,2,4-traizaole, which results in a lower V_{oc} value for the latter.

Molecular orbital calculations also explain the other effects on the J_{sc}. The J_{sc} value increased as the absolute difference of the calculated dipole moment of the aminotriazoles from acetonitrile, which was 3.4 D (dashed line in Fig. 9), increased and is represented by the solid line in Fig. 9. This correlation is consistent with the idea previously proposed. The dielectric constant of an electrolytic solution decreases as the difference in dipole moments between the additive and solvent decreases since the additive screens more of the solvent dipoles [25,26], and the lower the dielectric constant, the less photocurrent in the cell [27,28].

The values for TBP are also shown in Figs. 6–9. All the correlations between the V_{oc} or J_{sc} and the properties of aminotriazoles are also applicable to the properties of TBP. In addition, these correlations are also observed using pyrimidine additives [20]. It was suggested that the electron donicity of pyrimidine additives influenced the interaction with photoelectrode as well as solvent and led to the changes in the V_{oc} or J_{sc} values. Therefore, it was concluded that the electron donating properties of the aminotriazoles on the electrolytic solution significantly influenced the dye-sensitized solar cell performance in a similar manner as TBP and pyrimidine.

5. Conclusion

The influence of 10 different aminotriazole additives on the performance of a N719 dye-sensitized TiO_2 solar cell was investigated for an $I^-/I_3{}^-$ redox electrolyte in acetonitrile. Typically, adding aminotriazoles reduced the J_{sc} of the solar cell, but enhanced the V_{oc}, ff, and η. The highest η of 7.6%, which was comparable to that of TBP, was obtained by adding 3-amino-1H-1,2,4-triazole. As the maximum partial charge of the nitrogen atoms in the molecule increased, the V_{oc} value was enhanced. The V_{oc} also increased as the size of the aminotriazoles decreased. As the absolute difference of the calculated dipole moment of the aminotriazoles from solvent increased, the J_{sc} value increased. These correlations suggest that the electron donicity of aminotriazoles influenced the interaction with the TiO_2 electrode as well as the solvent and caused the changes in solar cell performance.

Acknowledgements

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