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

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Abstract

The influence of benzimidazole additives on the performance of a bis(tetrabutylammonium)-*cis*-bis(thiocyanato)bis(2,2′-bipyridine-4-carboxylic acid, 4′-carboxylate)ruthenium(II) dye-sensitized TiO_2 solar cell with an I^-/I_3^- redox electrolyte in acetonitrile was investigated by measuring the current–voltage characteristics of more than 20 different benzimidazole derivatives under AM 1.5 (100 mW/cm^2). The benzimidazole additives tested had varying effects on the cell performance. Adding benzimidazole drastically enhanced the open-circuit photovoltage (V_{oc}) and the fill factor (ff), but reduced the short-circuit photocurrent density (J_{sc}) of the solar cell. In order to determine the reasons for the additive effects on cell performance the physical and chemical properties of the benzimidazoles were computationally calculated. Consequently, the greater the calculated partial charge of the nitrogen atoms in position 3 of the benzimidazole groups, the larger the V_{oc}, but the smaller the J_{sc} values. The V_{oc} values also increased as the molecular size of the benzimidazole derivatives decreased. Moreover, the greater the absolute difference between the calculated dipole moment of the benzimidazole and acetonitrile, the larger the J_{sc} value. These results suggest that these properties of the benzimidazoles influenced the extent of interaction between the TiO_2 electrode and electrolyte solvent, which changed the dye-sensitized solar cell performance.

Keywords: Dye-sensitized solar cell; Electrolytic solution; Benzimidazoles; Additive

1. Introduction

Since O’Reganoulos and Grätzel reported a high conversion yield in the last decade, dye-sensitized solar cells have been eagerly investigated [1]. A typical solar cell consists of nanostructured TiO_2 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^-/I_3^-, and a counter electrode such as Pt. In an attempt to improve the 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 an I^-/I_3^- acetonitrile solution increased the photocurrent, but decreased the photovoltage [12]. Frank and co-workers conducted a study on an I^-/I_3^- electrolyte with additives such as NH_3 and pyridine derivatives like 4-*t*-butylpyridine (TBP), which is popular for enhancing dye-sensitized solar cell performance in acetonitrile and found that these additives drastically increased the V_{oc} [13,14].

Quite recently, Boschloo and co-workers reported that like TBP, adding 1-methylbenzimidazole into an I^-/I_3^- electrolyte of a Ru dye-sensitized TiO_2 solar cell increased the voltage output of the cell, but these results were not compared to a cell without an additive [15,16]. Wang et al. also reported adding 1-methylbenzimidazole into I^-/I_3^- quasi-solid-state electrolytes for dye-sensitized solar cells, but did not refer to the role of 1-methylbenzimidazole [17,18]. This work aims to clarify the effects of benzimidazoles on the performance of dye-sensitized solar cells. The influences on cell performance were investigated by examining more than 20 different additives, which were benzimidazole derivatives and included 1-methylbenzimidazole, in an I^-/I_3^- electrolyte and an acetonitrile electrolyte solution and by computationally calculating the physical and chemical properties of the benzimidazole additives.

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2. Experimental

2.1. TiO_2 electrode preparation and dye coating

Titanium(IV) isopropoxide (Kanto Chemical Co.) was rapidly added to an aqueous solution of HNO_3 (Wako Pure 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 TiO_2 paste, which was concentrated by an evaporator.

TiO_2 paste was deposited onto a fluorine-doped stannic oxide conducting glass (FTO, 10 Ω/cm^2, Nippon Sheet Glass Co.) using a screen-printing technique. The resulting layer was calcined for 2 h at 798 K in airflow of 1.5 dm^3/min. This process was repeated three times. The resulting film measured approximately 15 μm thick 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 airflow of 1.5 dm^3/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 S.A.) dye solution. The dye was adsorbed onto the TiO_2 surface by soaking the TiO_2 electrode in a *t*-butanol/acetonitrile (1:1) solution of the N719 dye (concentration: 3×10^{-4} mol/dm^3) 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, composed of a dye-adsorbed TiO_2 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, which was composed of 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide (Tomiyama Pure Chemical Industries Ltd.), 0.1 mol/dm^3 LiI (Aldrich), 0.05 mol/dm^3 I_2 (Wako Pure Chemical Industries Ltd.), and 0.5 mol/dm^3 of the benzimidazole additive and acetonitrile (Kanto Chemical Co.) as solvent, was injected by a microsyringe into the space between the two electrodes.

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/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 by the CAChe program from Fujitsu Limited (Tokyo) implemented on a Windows system. The geometries of the benzimidazole molecule were optimized by a MOPAC (Molecular Orbital Package, PM5) application.

3. Results

3.1. Solar cell performance using benzimidazole additives

I–V measurements were performed on the electrolyte with various substituted benzimidazoles, whose structures are illustrated in Fig. 1. Fig. 2 shows the J_{sc}, V_{oc}, ff and solar energy conversion efficiency (η) results with an additive concentration of 0.5 mol/dm^3 and an illumination source of 100 mW/cm^2. All the cells that contained an additive had a lower J_{sc} value than the cell without an additive. Amino substituted benzimidazoles such as 2-amino-1-methylbenzimidazole and 2-guanidinobenzimidazole yielded a much lower J_{sc} than did other substituents. The highest and lowest J_{sc} were observed for the cells containing 5,6-dimethyl-1-hydroxymethylbenzimidazole and 2-amino-1-methylbenzimidazole, respectively. On the other hand, the V_{oc} values were greater when benzimidazoles were present. Unlike the J_{sc}, amino substituents yielded a higher V_{oc} than other substituents. Among the tested additives, 2-amino-1-methylbenzimidazole had the highest V_{oc}, 0.83 V, but the lowest J_{sc}, 10.3 mA/cm^2. Adding benzimidazole derivatives generally enhanced the ff of the solar cell. The ff trend was similar to that of the V_{oc}. The highest and lowest ff of the cell were observed using 2-amino-1-methylbenzimidazole and 2-cyamnomethylbenzimidazole as the additive, respectively. The benzimidazole derivatives also enhanced the η value. Among the tested additives, 5-chloro-1-ethyl-2-methylbenzimidazole and 2-(1-hydroxyethyl)benzimidazole resulted in the highest η, 7.6%, under 100 mW/cm^2 illumination.

3.2. Computational calculations

As mentioned in Section 3.1, the benzimidazole additives tested had varying effects on the dye-sensitized solar cell performance. In order to investigate the effects of the benzimidazole derivatives on the cell performance the physical and chemical properties of the benzimidazoles were computationally calculated. Numerous correlations between the properties of the additives and solar cell performance were found.

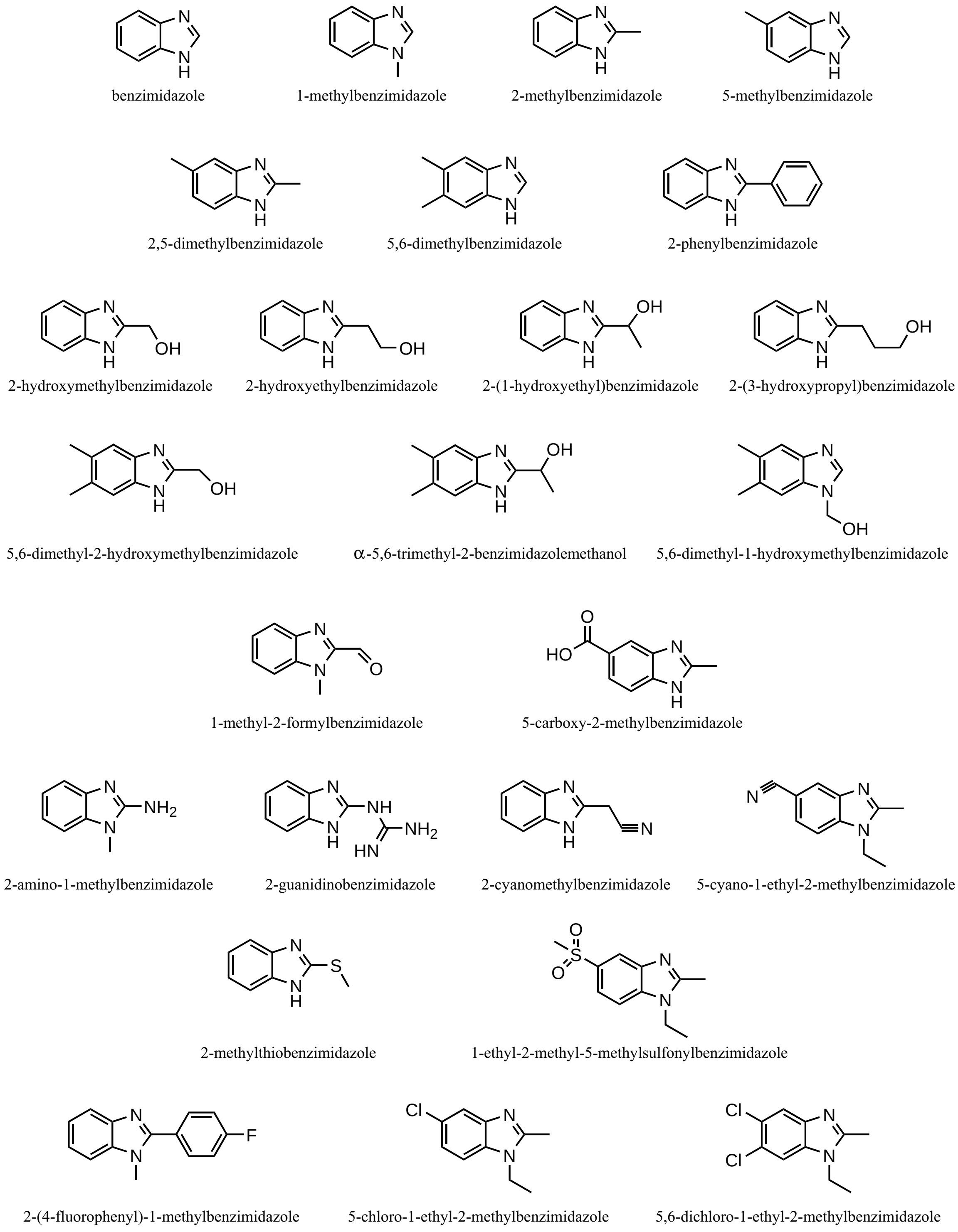
benzimidazole
1-methylbenzimidazole
2-methylbenzimidazole
5-methylbenzimidazole
2,5-dimethylbenzimidazole
5,6-dimethylbenzimidazole
2-phenylbenzimidazole
2-hydroxymethylbenzimidazole
2-hydroxyethylbenzimidazole
2-(1-hydroxyethyl)benzimidazole
2-(3-hydroxypropyl)benzimidazole
5,6-dimethyl-2-hydroxymethylbenzimidazole
α-5,6-trimethyl-2-benzimidazolemethanol
5,6-dimethyl-1-hydroxymethylbenzimidazole
1-methyl-2-formylbenzimidazole
5-carboxy-2-methylbenzimidazole
2-amino-1-methylbenzimidazole
2-guanidinobenzimidazole
2-cyanomethylbenzimidazole
5-cyano-1-ethyl-2-methylbenzimidazole
2-methylthiobenzimidazole
1-ethyl-2-methyl-5-methylsulfonylbenzimidazole
2-(4-fluorophenyl)-1-methylbenzimidazole
5-chloro-1-ethyl-2-methylbenzimidazole
5,6-dichloro-1-ethyl-2-methylbenzimidazole

Fig. 1. The structures of the benzimidazole additives tested.

In order to estimate the extent to which the lone pair electrons of the nitrogen atoms donate, the partial charges of the nitrogen atoms in position 3 of the benzimidazole group were calculated at the PM5 level using the MOPAC system available in the CAChe package. Fig. 3 shows the correlation between the J_{sc} of the cell and the calculated partial charge of position 3 for the benzimidazole derivatives in acetonitrile. The smaller the calculated partial charge, the larger the J_{sc} value becomes. Fig. 4 depicts the correlation between the V_{oc} and the calculated partial charge of the N atom. Contrary to the J_{sc} trend, the smaller the partial charge, the more the V_{oc} was reduced.

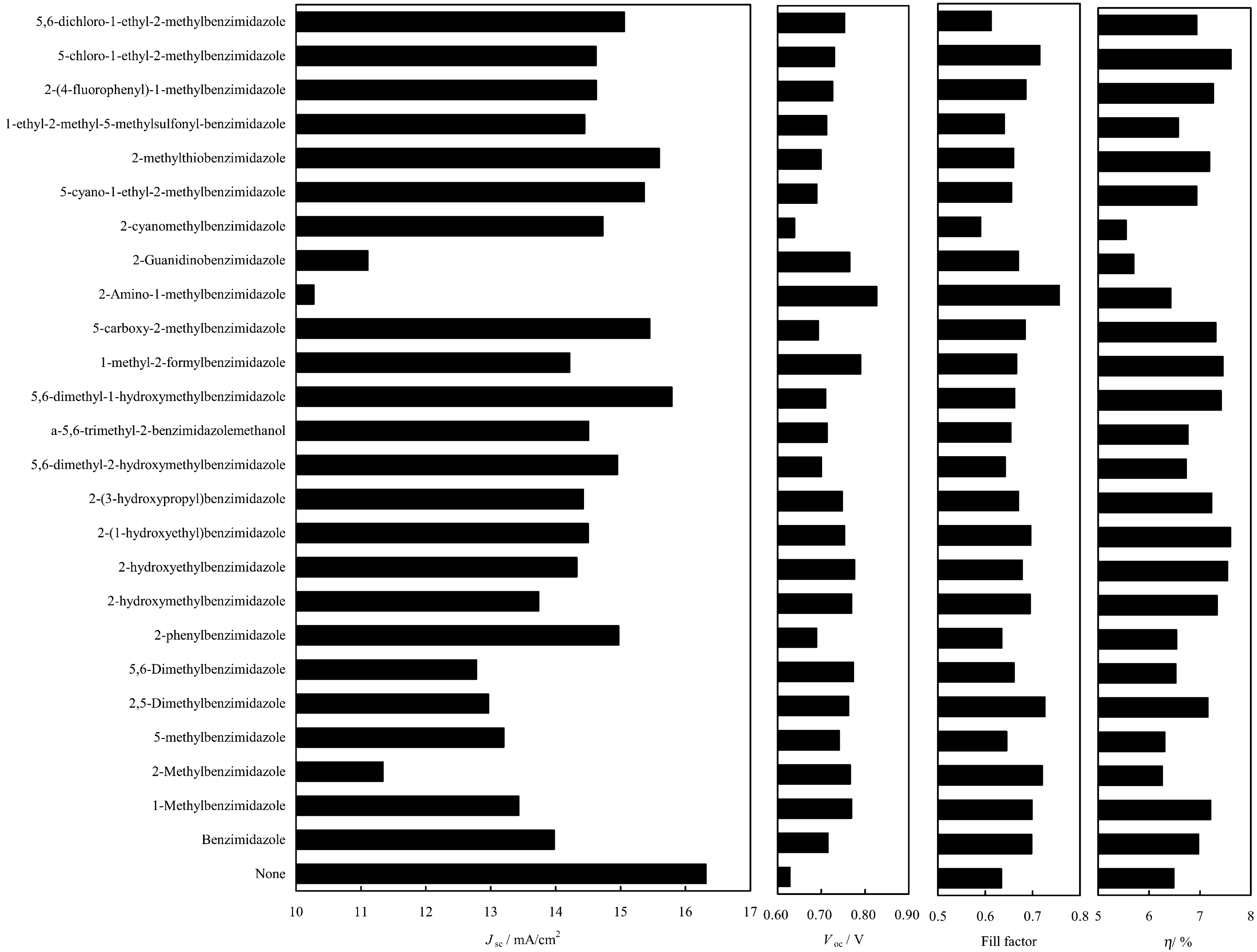

Fig. 2. The influence of the benzimidazole additives in the electrolytic solution on the solar cell performance for a N719 dye-sensitized TiO_2 solar cell. Conditions: electrolyte, 0.6 mol/dm^3 1,2-dimethyl-3-propylimidazolium iodide + 0.1 mol/dm^3 LiI + 0.05 mol/dm^3 I_2 + 0.5 mol/dm^3 benzimidazoles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

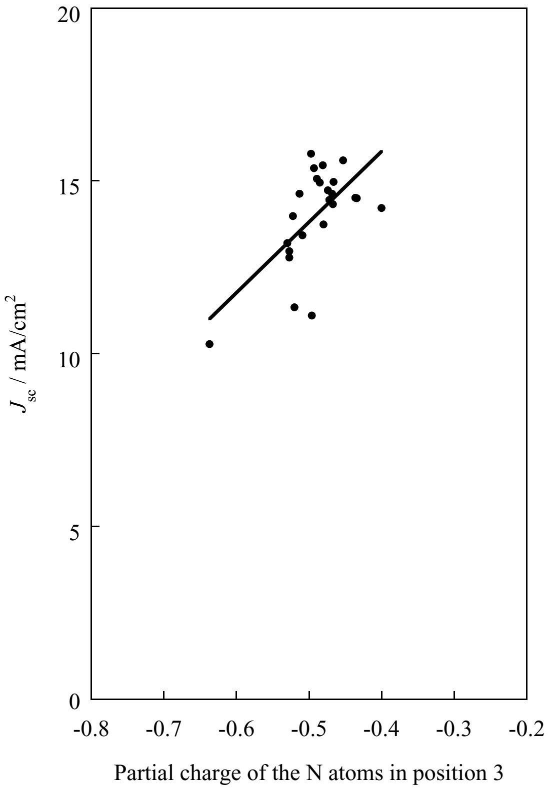

Fig. 3. The correlation between the J_{sc} of the cell and the calculated partial charge of nitrogen atoms in position 3 of the benzimidazole groups in acetonitrile using the MOPAC system available in the CAChe package.

The size and dipole moment of the benzimidazole derivatives were calculated at the PM5 level using the MOPAC system available in the CAChe package. Fig. 5 shows the correlation between the V_{oc} of the cell and the calculated size of the benzimidazole molecules in acetonitrile, which was defined as the maximum distance between the two atoms in the molecule by a molecular orbital calculation. The V_{oc} of the cell decreased as the calculated size of the benzimidazole molecule increased. Fig. 6 depicts the correlation between the V_{oc} of the cell and the calculated solvent accessible surface area of the benzimidazole molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package. The solvent accessible surface area was defined as the molecular surface area accessible to a solvent molecule. The V_{oc} of the cell increased as the surface area accessible to the solvent decreased.

Fig. 7 illustrates the correlation between the J_{sc} of the cell and the calculated dipole moment of the benzimidazole molecules. The larger the absolute difference (solid line) of the dipole moment of benzimidazole is from acetonitrile (3.4 D, dashed line), the larger the J_{sc} value becomes.

4. Discussion

As demonstrated in Fig. 2, the benzimidazole additives in the I^-/I_3^- electrolytic solution influenced the dye-sensitized solar cell performance. In particular, the J_{sc} and V_{oc} values of the cell were drastically altered when an additive was present. The cells containing a benzimidazole additive in the electrolytic solution displayed improved V_{oc} values, but lower J_{sc} values. Computational calculations, which estimated the physical and chemical properties of the benzimidazole derivatives, elucidated the reasons for the various influences on the solar cell performance.

In our previous study, it was suggested that the influence of pyrimidine additives on the dye-sensitized solar cell performance was due to the electron donicity of the nitrogen lone pairs in the pyrimidine ring, which was estimated by the partial charge of N atoms [19]. Based on this finding the donating ability of the N lone pairs was estimated by calculating the partial charges of the N atoms in position

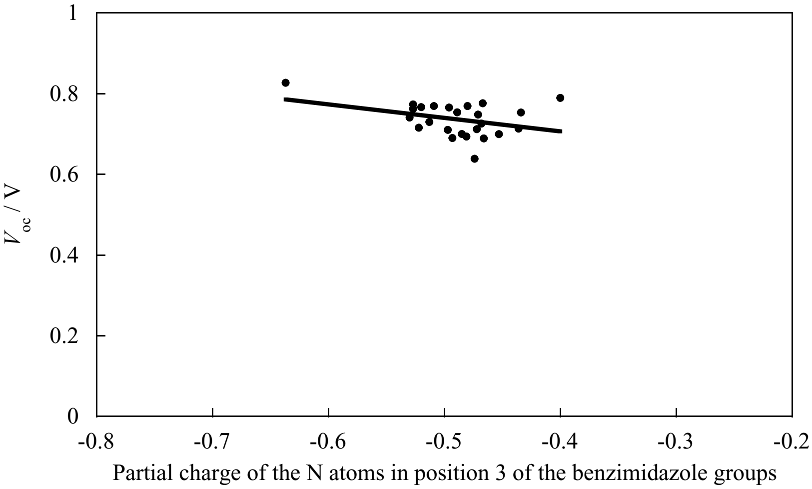

Fig. 4. The correlation between the V_{oc} of the cell and the calculated partial charge of nitrogen atoms in position 3 of the benzimidazole groups in acetonitrile using the MOPAC system available in the CAChe package.

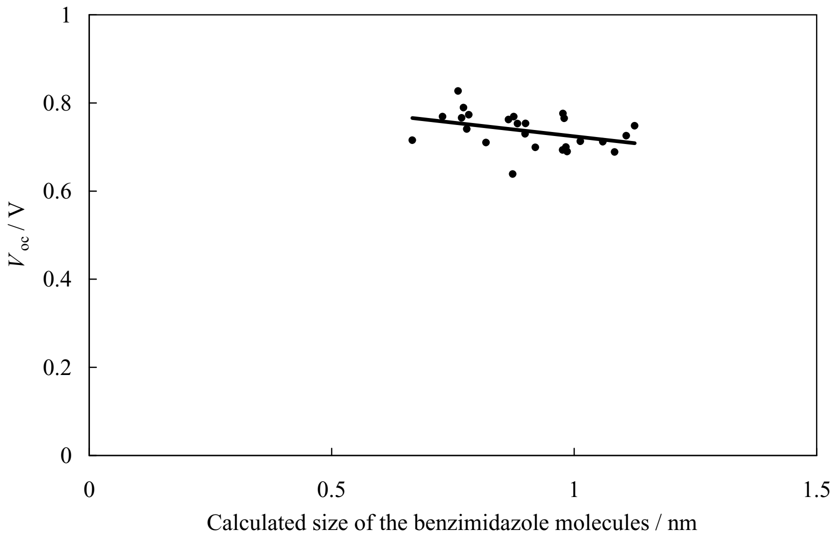

Fig. 5. The correlation between the V_{oc} of the cell and the calculated size of the benzimidazole molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.

3 of the benzimidazole group. 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. 3 and 4). These results suggest that the benzimidazole molecules adsorb onto the free Lewis acid sites of the TiO_2 electrode [20], which would increase the V_{oc}, but decrease the J_{sc} value. Two different mechanisms have been suggested for the adsorption of additives on the TiO_2 surface. One is to suppress the dark current arising from the I_3^- reduction by the conduction band electrons at the semiconductor electrolyte junction (Eq. (1)):

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

For regenerative photoelectrochemical systems, Eq. (2) holds

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

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. Decreasing k_{et} increases the V_{oc} [2,3]. The higher the partial charge of the N atom in position 3 of the benzimidazole group, the easier and more often benzimidazoles can adsorb onto the Lewis acid sites of the TiO_2 surface

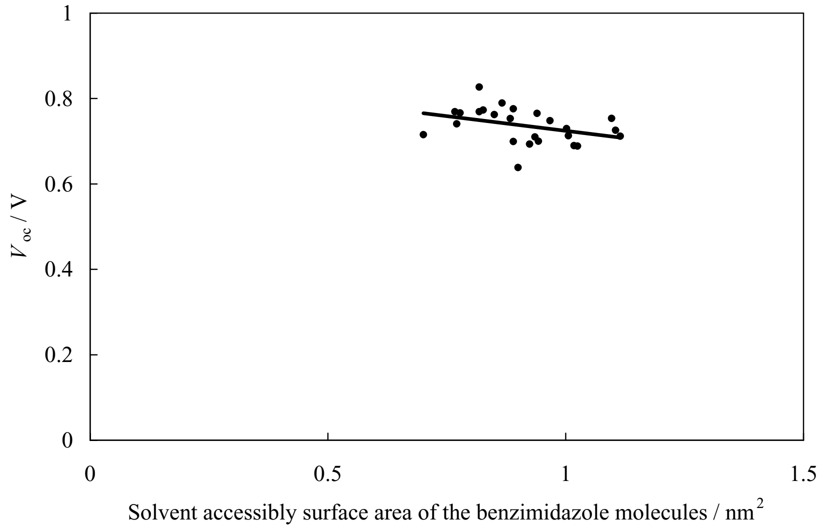

Fig. 6. The correlation between the V_{oc} of the cell and the solvent accessible surface area of the benzimidazole molecules in acetonitrile at the PM5 level using the MOPAC system available in the CAChe package.

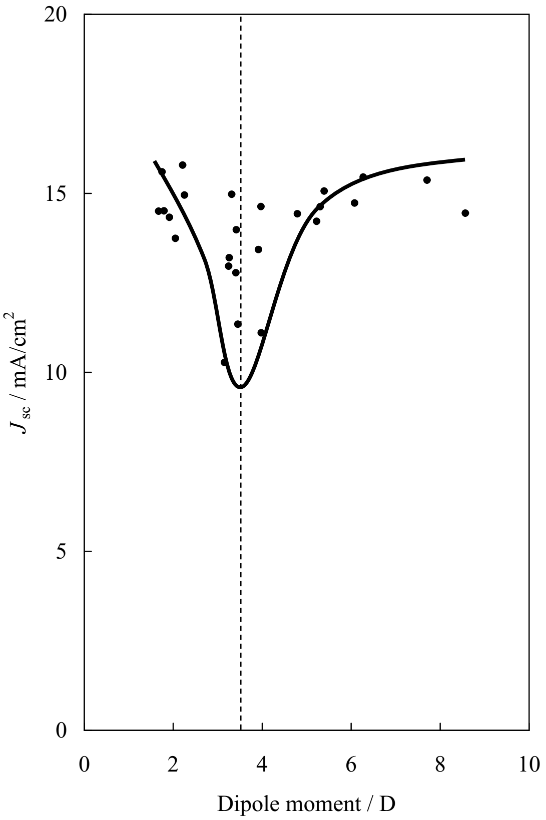

Fig. 7. The correlation between the J_{sc} of the cell and the calculated dipole moment of the benzimidazole molecules at the PM5 level using the MOPAC system available in the CAChe package.

[20], which more efficiently suppresses the dark current arising from the I_3^- reduction by the conduction band electrons at the semiconductor electrolyte junction. The other mechanism is to raise the flatband potential (V_{FB}) of the TiO_2 electrode. The adsorption of the additives in the electrolytic solution onto the TiO_2 surface may raise the V_{FB} of the TiO_2 electrode [12]. Under Fermi level pinning, these two parameters are linked by Eq. (3):

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

where V_{red} is the standard reduction potential of a redox coupling. Assuming that V_{red} remains constant upon adding benzimidazoles, adsorbing benzimidazole onto the TiO_2 surface would increase V_{FB}, which should increase the V_{oc}. The greater the partial charge of the N atom in the benzimidazole group, the easier and more often the benzimidazoles can adsorb onto the Lewis acid sites of the TiO_2 surface [12]. Raising the V_{FB} also causes a negative shift in the conduction band edge of TiO_2, which decreases the electron injection rate from the exiting dye and explains the lower J_{sc} values upon adding benzimidazole derivatives.

The other results from the molecular orbital calculations support these hypotheses. The V_{oc} values increased as both the calculated size of the benzimidazole molecule (Fig. 5) and the solvent accessible surface area decreased (Fig. 6). The smaller the molecule, the more often and the easier the benzimidazole can adsorb onto the free Lewis acid sites of the TiO_2 surface, which leads to a higher V_{oc} of the cell.

Molecular orbital calculations also explain the other effects on the J_{sc}. The J_{sc} values decrease as the absolute difference of the calculated dipole moment of the benzimidazole from acetonitrile, which is 3.4 D, decreases (Fig. 7). This correlation is consistent with the previously proposed idea. The dielectric constant of an electrolytic solution decreases as the difference in the dipole moments of the additive and solvent decreases because the additive screens more of the solvent dipoles, which lowers the dielectric constant [21,22]. Thus, there is less photocurrent in the cell [23,24].

Therefore, it was concluded that the interactions of the benzimidazoles with the TiO_2 electrode and electrolyte solvent had a significant influence on the dye-sensitized solar cell performance.

5. Conclusion

The influence of more than 20 different benzimidazole 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. Adding benzimidazoles reduced the J_{sc} of the solar cell, but enhanced the V_{oc} and ff. As the partial charge of the nitrogen atoms in the benzimidazole group increased, the V_{oc} was enhanced, but the J_{sc} value was reduced. The V_{oc} of the cell increased as the molecular size of the benzimidazole derivatives decreased. In addition, the greater the absolute difference between the dipole moment of the benzimidazole and the solvent, the more the J_{sc} value increased. These correlations suggest that the electron donicity and size of benzimidazole derivatives influence the interaction with TiO_2 electrode and electrolyte solvent, which changes the solar cell performance.

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