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Electron-Donating Perylene Tetracarboxylic Acids for Dye-Sensitized Solar Cells

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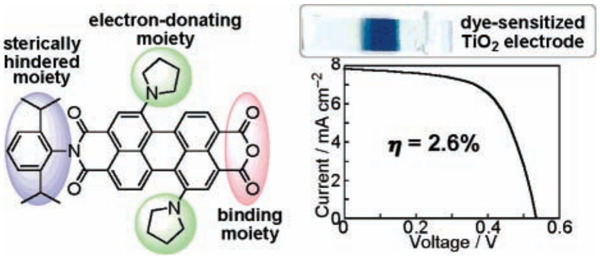
ABSTRACT



Novel perylene imide derivatives with both electron-donating and bulky substituents have been synthesized for dye-sensitized solar cells. The power conversion efficiency reached 2.6%, which is the highest value among perylene-sensitized TiO_2 solar cells.

Recently, a great deal of effort has been devoted to developing efficient solar energy conversion systems.[1] Among them, dye-sensitized solar cells have attracted much attention because of their potential low cost and relatively high power conversion efficiency (η).[2] To date, ruthenium polypyridyl complex sensitized TiO_2 electrodes have shown the highest η value (η = 9−11%).[2] However, in view of cost and environmental demand, metal-free organic dyes are strongly desired. In this context, various organic dyes have been developed for dye-sensitized solar cells.[3−7]

Perylene imides are well-known as chemically, thermally, and photophysically stable dyes and have been utilized in various optical devices.[8−10] So far, several perylene imide sensitized solar cells have been reported, but the η values remain low (η < 1.9%) compared with other organic dyes.[11] The origin of such limited cell performance is the poor

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electron-donating abilities of the perylene imides, which makes it difficult to inject electrons from the excited perylene imide to the conduction band (CB) of the TiO_2 electrode efficiently.

Recently, we[12] and other groups[13] have reported strongly electron-donating perylene tetracarboxylic acid derivatives with amine substituents at their perylene core. The perylene bisimide (PBI) linked to C_{60} has exhibited photoinduced electron transfer from the PBI excited singlet state to C_{60}.[12] On the basis of these results, we designed novel electron-donating perylene tetracarboxylic acid derivatives for dye-sensitized solar cells, as shown in Figure 1. In the molecular design, we consider the following points: (1) Multiple strongly electron-donating substituents (i.e., two pyrrolidines) at the perylene core shift the first oxidation potential in the negative direction considerably.[14] Thus, we can expect a more exothermic electron injection from the excited singlet state to the CB of the TiO_2 electrode, leading to efficient photocurrent generation. Furthermore, such substitution would vary the light-harvesting ability in the red-to-NIR region. (2) The degree of the dye aggregation on the TiO_2 electrode can be modulated by the substituents (i.e., 2,6-diisopropylphenyl and cyclohexyl groups) at one imide end. It should be noted that the electronic structures of the perylene π-systems are not affected by the substituents at the imide nitrogen because the frontier orbitals of these compounds have nodes at the imide nitrogen and the anhydride oxygen atoms.[15] (3) The nature of the anchoring groups (i.e., acid anhydride and carboxylic acid) and the electronic coupling between the perylene core and the TiO_2 surface would affect the cell performance greatly.[16]

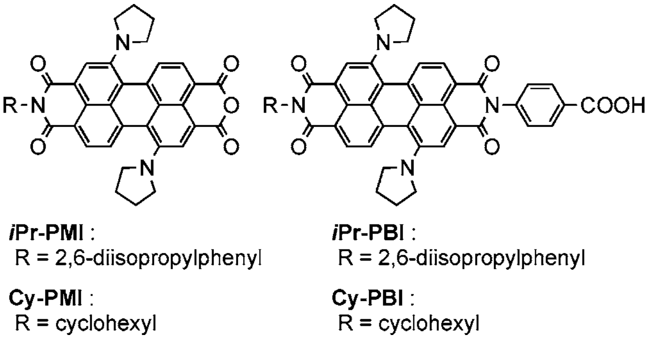

Figure 1. Structures of perylene tetracarboxylic acid derivatives.

The synthetic scheme is shown in Scheme 1. The starting material **1** was synthesized in the previously reported manner,[17] but the reaction mixture was found to contain a 1,6-dibromo perylene bisimide derivative. Thus, the substitution reaction by pyrrolidine afforded a mixture of the 1,7-dipyrrolidinyl, 1,6-dipyrrolidinyl, and 1-monopyrrolidinyl perylene bisimide derivatives. The desired product was separated by alumina column chromatography to give **2** in 41% yield. The partial saponification of **2** by an excess amount of KOH in *t*-butyl alcohol gave perylene monoimide monoanhydride (PMI) **_i_Pr-PMI** in 46% yield. The cyclohexyl analogue, **Cy-PMI**, was synthesized as previously described.[14b] On the other hand, the perylene bisimide dyes with a carboxylic group, **_i_Pr-PBI** and **Cy-PBI**, were synthesized by the imidation of the PMI with the protected *p*-carboxyaniline, followed by the acidic hydrolysis by the mixture of sulfuric acid and trifluoroacetic acid. The products were characterized on the basis of their ^1H, ^{13}C, mass, and IR spectra (see Supporting Information S1 and S2).

UV−vis−NIR absorption spectra of **_i_Pr-PMI**, **Cy-PMI**, **_i_Pr-PBI**, and **Cy-PBI** were measured in CH_2Cl_2 (Figure 2 and Supporting Information S3). For instance, **_i_Pr-PMI** exhibits strong absorption at around 700 nm and moderate absorption at 430 nm which are assigned to the charge-transfer (CT) and $\pi-\pi^*$ transition, respectively.[13] The absorption properties are suitable for collecting sunlight, specifically one in the red-to-NIR region. It is noteworthy that the spectra of these compounds are almost identical. This implies that the substituent at the imide nitrogens and the difference in the imide and the acid anhydride have negligible influence on the frontier orbitals of the perylene π-system. The fluorescence spectra were also measured in CH_2Cl_2 with an excitation wavelength of 430 nm where the absorbances of the perylene imide dyes are identical (Supporting Information S4). The peak position and the shape are similar for the perylene imide dyes, showing that there is little difference in the electronic structure of the excited singlet state. The energy levels of the excited singlet state of the perylene imide dyes are determined as 1.73 eV in CH_2Cl_2 from the intercept of the normalized absorption and fluorescence spectra.

The first oxidation potentials of the perylene imide dyes (vs Fc/Fc^+) were measured in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 as a supporting electrolyte by using differential pulse voltammetry. The oxidation potentials were recalculated with respect to NHE (see Supporting Information). The

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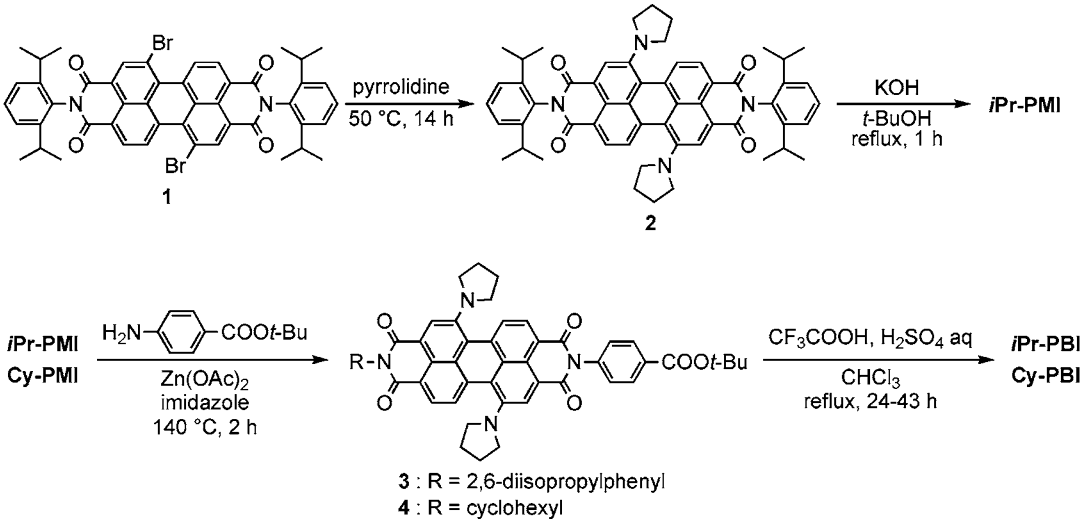
Scheme 1



first oxidation potentials of the perylene imide dyes (***i*Pr-PMI**, 0.90 V; **Cy-PMI**, 0.91 V; ***i*Pr-PBI**, 0.85 V; **Cy-PBI**, 0.88 V vs NHE) are largely similar, which is consistent with the results on the absorption and the fluorescence spectra; that is, the electronic structures are similar for the perylene imide dyes. These values are much lower than that of the dibromoperylene bisimide (>2.25 V vs NHE),[14a] demonstrating the strong electron-donating properties of the pyrrolidine-substituted perylene tetracarboxylic acid. Actually, the energy levels of the perylene imide excited singlet state ($-0.82 \sim -0.88$ V vs NHE) are sufficiently higher than that of the CB of TiO_2 (-0.5 V vs NHE),[2−7] whereas those of the perylene imide radical cations are lower than that of the I^-/I_3^- couple (0.5 V vs NHE).[2−7] Thus, the electron injection from the perylene imide excited singlet state to the CB of TiO_2 and the charge shift from I^- to the resultant perylene imide radical cation are energetically favorable.[18]

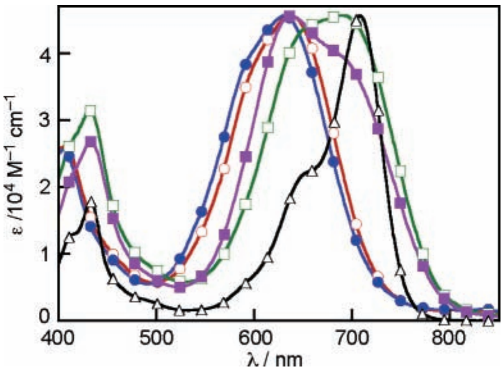


Figure 2. Absorption spectrum of ***i*Pr-PMI** (black line with open triangles) in CH_2Cl_2 and normalized absorption spectra of ***i*Pr-PMI** (red line with open circles), **Cy-PMI** (blue line with closed circles), ***i*Pr-PBI** (green line with open squares), and **Cy-PBI** (purple line with closed squares) on the TiO_2 electrodes. The absorption arising from the TiO_2 electrode was subtracted from the spectrum.

The TiO_2 electrodes with a film thickness of 13 μm were prepared by repeating the following procedure twice.[16c] First, the conducting transparent glass electrodes (FTO) were coated with the mesoporous TiO_2 nanoparticles (P25) by the doctor blade technique. Then, the FTO was calcinated under air at 723 K for 1 h to give the TiO_2 electrodes. The dye-modified TiO_2 electrodes were obtained by immersing the TiO_2 electrodes in the CH_2Cl_2 solution containing ***i*Pr-PMI** or **Cy-PMI** (0.15 mM) and in the mixed solution of *t*-BuOH and CH_3CN (1:1 = v/v) containing ***i*Pr-PBI** or **Cy-PBI** (0.15 mM), respectively, for 15 h at room temperature. The dye-modified TiO_2 electrodes exhibit a blue color for the PMI dyes and a green color for the PBI dyes.

The normalized absorption spectra of ***i*Pr-PMI**, **Cy-PMI**, ***i*Pr-PBI**, and **Cy-PBI** on the TiO_2 electrodes are displayed in Figure 2. A notable increase in the absorption of ***i*Pr-PBI** and **Cy-PBI** at around 650 nm reveals the occurrence of the dye aggregation on the TiO_2 electrode.[19] The broadening of the absorption band that even reveals a band splitting also suggests the dimer formation by reason of excitonic coupling of rotationally displaced PBIs.[20] As expected, the spectral perturbation of ***i*Pr-PBI** is smaller than that of **Cy-PBI** owing to the presence of the bulky substituent at the imide nitrogen. As for the spectra of ***i*Pr-PMI** and **Cy-PMI**, the absorptions arising from both the $\pi-\pi^*$ transition and the CT transition are blue-shifted significantly compared to those of ***i*Pr-PBI** and **Cy-PBI** on the TiO_2 electrode as well as to those of

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***i*Pr-PMI** and **Cy-PMI** in CH_2Cl_2, suggesting that the molecular structures of the PMI dyes are changed by the chemical adsorption on TiO_2. The change can be assigned to the bond opening of the anhydride groups of the PMI dyes[21] because the absorption spectra of the ring-opened PMI dyes in solution are similar to those on TiO_2 (Supporting Information S5). Disappearance of the IR signal due to the anhydride groups after the dye adsorption on the TiO_2 electrode is consistent with the assignment (Supporting Information S6). The slight blue-shift of **Cy-PMI** at around 600 nm relative to that of ***i*Pr-PMI** may result from the presence of the bulky substituent at the imide nitrogen, as in the case of ***i*Pr-PBI** and **Cy-PBI**.

The dye-sensitized solar cells were fabricated with 0.05 M I_2/0.1 M LiI/0.6 M 2,3-dimethyl-1-propylimidazolium iodide/0.5 M 4-*t*-butylpyridine in acetonitrile solution as an electrolyte. The current−voltage characteristics were measured under AM 1.5 conditions (100 mW cm^{-2}) (Supporting Information S7). The η values are derived from the equation $\eta = V_{OC} \times J_{SC} \times ff$, where V_{OC} is open circuit potential (V), J_{SC} is short circuit current density (mA cm^{-2}), and ff is the fill factor (Table 1). The η value of the ***i*Pr-PMI** cell (2.6%) is larger by ca. 70% than that of the **Cy-PMI** cell (1.5%), showing that the larger substituent at the imide nitrogen inhibits the dye aggregation on the surface of the TiO_2, leading to suppression of the unfavorable deactivation of the dye-excited state. The η value of the ***i*Pr-PMI** cell (2.6%) is remarkably high compared to that (<0.1%) of the TiO_2 cell with the similar PMI derivative without an electron-donating substituent.[11a] It should be emphasized here that the η value of the ***i*Pr-PMI** cell is the largest one among the perylene-sensitized solar cells.[11] Thus, the excited singlet state of the perylene imide dye with both strongly electron-donating and bulky substituents can inject electrons to the CB of the TiO_2 electrode, resulting in the efficient photocurrent generation. The η values of ***i*Pr-PBI** and **Cy-PBI** (<0.02%) cells are smaller than that of the TiO_2 reference cell without the dyes and are 2 orders of magnitude smaller than those of ***i*Pr-PMI** and **Cy-PMI** cells. More importantly, the comparison of ***i*Pr-PMI** and ***i*Pr-PBI** cells shows that changing the coupling moiety to the TiO_2 electrode yields a remarkable difference (100 times) in device efficiency, despite the fact that both electron-donating and sterically hindering groups are present in both molecules. Such a large difference may be explained by the difference in the electronic coupling between the dyes and TiO_2. The smaller electronic coupling between the perylene core and the TiO_2 surface through the carboxylphenyl group in the PBI-based TiO_2 cells would be responsible for the slow electron injection from the PBI excited singlet state to the CB of the TiO_2 electrode, leading to the extremely low η values. Thus, the coupling group between the perylene core and the TiO_2 electrode is of utmost importance in determining dye performance.

Table 1. Cell Performance of PMI-Sensitized TiO_2 Cells[a]

dye	V_{OC}/V	J_{SC}/mA cm^{-2}	ff	η/%
***i*Pr-PMI**	0.54	7.8	0.63	2.6
Cy-PMI	0.51	4.6	0.64	1.5

[a] Thickness of the TiO_2 film: 13 μm. Irradiation area: 0.25 cm^2. Condition: AM 1.5 (100 mW cm^{-2}).

Action spectra of incident photon−current efficiency (IPCE) are depicted in Figure 3. The action spectra of ***i*Pr-PMI**- and **Cy-PMI**-sensitized solar cells match the corresponding absorption spectra on the TiO_2 electrodes (Figure 2). The IPCE of a ***i*Pr-PMI**-sensitized TiO_2 cell reaches ca. 40%, and the photocurrent response extends up to 800 nm. The relatively high IPCE values at 600−800 nm are particularly intriguing because of their possible applications in transparent solar cells for windows and tandem cells.

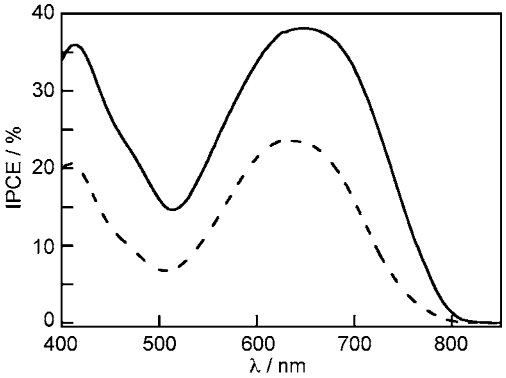

Figure 3. Action spectra of ***i*Pr-PMI** (solid line) and **Cy-PMI** (dashed line) sensitized TiO_2 cells.

In conclusion, we have successfully synthesized novel perylene imide derivatives with a strongly electron-donating moiety, bulky substituents, and an acid anhydride as the strong coupling group for dye-sensitized solar cells. The power conversion efficiency reached 2.6%, which is the highest value among perylene-sensitized TiO_2 solar cells. These results unequivocally corroborate that the introduction of the two pyrrolidine moieties, 2,6-diisopropylphenyl groups, and acid anhydride into the perylene imide is responsible for the significant improvement of the cell performance.

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Supporting Information Available: Experimental details (S1 and S2), absorption (S3) and fluorescence (S4) spectra, absorption spectra of ring-opened ***i*Pr-PMI** and **Cy-PMI** (S5), IR spectra (S6), and current−voltage characteristics (S7). This material is available free of charge via the Internet at http://pubs.acs.org.

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