

Research Article

Piperidine-Substituted Perylene Sensitizer for Dye-Sensitized Solar Cells

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We have prepared a novel piperidine-donor-substituted perylene sensitizer, **PK0002**, and studied the photovoltaic performance in dye-sensitized solar cells (DSSCs). Physical properties and photovoltaic performance of this new perylene derivative **PK0002** are reported and compared with those of unsubstituted perylene sensitizer, **PK0003**. **PK0002**, when anchored to nanocrystalline TiO₂ films, achieves very efficient sensitization across the whole visible range extending up to 800 nm. The incident photon-to-current conversion efficiency (IPCE) spectrum was consistent with the absorption spectrum and resulted in a high short-circuit photocurrent density (J_{sc}) of 8.8 mA cm⁻². **PK0002** showed higher IPCE values than **PK0003** in the 520–800 nm region. Under standard AM 1.5 irradiation (100 mW cm⁻²) and using an electrolyte consisting of 0.6 M dimethylpropyl-imidazolium iodide, 0.05 M I₂, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile, a solar cell containing sensitizer **PK0002** yielded a short-circuit photocurrent density of 7.7 mA cm⁻², an open-circuit photovoltage of 0.57 V, and a fill factor of 0.70, corresponding to an overall conversion efficiency of 3.1%.

1. Introduction

Dye-sensitized solar cells (DSSCs) have been widely investigated because of their simple structure and potential for low-cost production [1–3]. In this solar cell, a monolayer of dyes is attached to the surface of nanocrystalline TiO₂ film to absorb solar light. The molecular design of dye-sensitizers that can absorb visible light of all colors for nanocrystalline oxide semiconductor solar cells is a challenging task as several requirements have to be fulfilled by the dye which are very difficult to be met simultaneously. Most of current research concerns development of panchromatic sensitizers based on organic dyes and transition metal complexes. Towards this goal, a number of transition metal complexes are used as effective sensitizers, due to their intense charge-transfer

absorption over the whole visible range and highly efficient metal-to-ligand charge-transfer in a dye-sensitized solar cell device. DSSCs with dyes based on ruthenium complexes have achieved energy conversion efficiencies over 11% [4, 5]. In recent years, there has been much effort in replacing the ruthenium complexes with fully organic photosensitizers for environmental reasons, lower cost, and the possibility to obtain very high extinction coefficients, which could also allow application in thinner solar cells as demanded in, for example, solid-state DSSCs.

Derivatives of perylene have been widely applied in various optical devices owing to their outstanding chemical, thermal, and photochemical stability and nontoxicity [6–12]. Several perylene dyes have been used as sensitizers

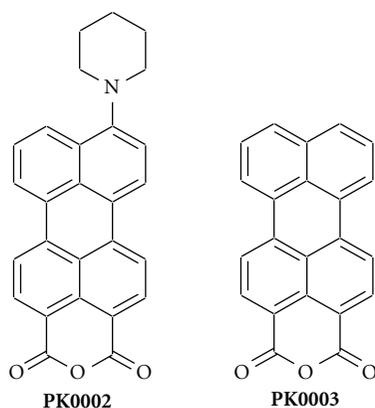


FIGURE 1: Perylene derivatives.

in DSSCs, however, they exhibited very low overall power conversion efficiencies [13–16]. Li and Edvinsson reported diphenylamino-substituted perylene monoanhydrides as sensitizers with power conversion efficiency 3.9% [17], later on they reported 6.8% power conversion efficiency with new perylene sensitizer bearing two thiophenol groups [18]. As our research program in developing the new sensitizers [19], herein, we present a novel piperidine-donor-substituted perylene sensitizer (**PK0002**) and compare with unsubstituted perylene sensitizer (**PK0003**) as shown in Figure 1.

2. Experimental

2.1. General. Dehydrated DMF was purchased from Aldrich. The synthesis of **PK0003** [20] and compound **1** [20, 21] was performed as reported in the literature. ^1H NMR was recorded using a JEOL JNM-ECX-400 spectrometer (400 MHz) and the chemical shifts are referenced to internal tetramethylsilane. Atmospheric pressure chemical ionization (APCI)–HRMS was obtained on an Agilent LC/MSD TOF spectrometer. Absorption and emission spectra were obtained using Shimadzu UV-2400PC and RF-5300PC spectrometers, respectively. Spectroscopic-grade CHCl_3 was purchased from Kanto Chemical. DFT calculations were performed with a Gaussian03 package using B3LYP/6-31G.

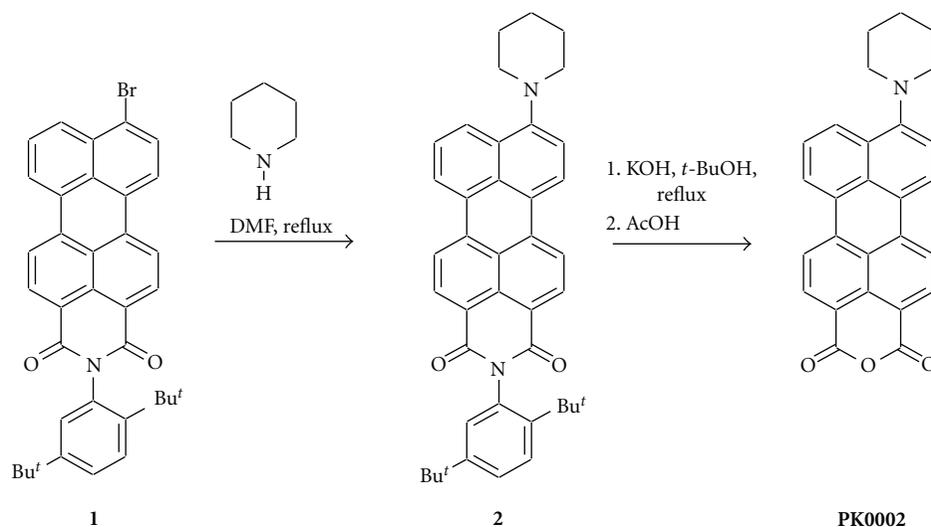
Synthesis of 2. A mixture of compound **1** (100 mg, 0.170 mmol) and piperidine (0.30 mL, 3.6 mmol) in DMF (10 mL) was refluxed under N_2 for 3 h. The reaction mixture turned from bright scarlet to deep blue in color. The solvent was removed on a rotary evaporator. The resulting residue was column chromatographed with silica gel and chloroform, yielding a purple solid (69 mg, 61%). ^1H NMR (CDCl_3): δ (ppm) = 8.61 (2H, m), 8.47 (1H, m), 8.40 (2H, m), 8.33 (1H, m), 8.24 (1H, d, $J = 8.7$ Hz), 7.64 (1H, t, $J = 8.1$ Hz), 7.58 (1H, d, $J = 8.7$ Hz), 7.44 (1H, dd, $J = 8.7, 2.2$ Hz), 7.20 (1H, d, $J = 8.3$ Hz), 7.02 (1H, d, $J = 2.3$ Hz), 3.19 (4H, br), 1.90 (4H, m), 1.73 (2H, br), 1.33 (9H, s), 1.30 (9H, s). APCI-HRMS: calcd for $\text{C}_{41}\text{H}_{41}\text{N}_2\text{O}_2$ (MH^+), 593.3163; found: 593.3008.

Synthesis of PK0002. Crushed KOH pellets (1.5 g) were added to a suspension of **2** (60 mg, 0.11 mmol) in *t*-butanol (50 mL) and the mixture was vigorously refluxed with stirring for 2 hrs (Scheme 1). The blue solid slowly dissolved and the solution turned yellow. While hot, the reaction mixture was cautiously poured into glacial acetic acid (100 mL) with vigorous stirring. The deep blue color returned immediately and a solid precipitated. The suspension was cooled and chloroform was added to dissolve the solid. The organic layer was washed 3 times with water, dried over anhydrous sodium sulfate, stripped on a rotary evaporator and dried overnight in a dessicator. The crude product was column chromatographed on silica gel with chloroform, yielding a purple solid (69 mg, 45%). ^1H NMR (CDCl_3): δ (ppm) = 8.24 (4H, m), 8.21 (1H, d, $J = 8.2$ Hz), 8.02 (1H, d, $J = 7.8$ Hz), 7.92 (1H, d, $J = 8.2$ Hz), 7.56 (1H, t, $J = 7.8$ Hz), 7.08 (1H, d, $J = 8.2$ Hz), 3.21 (4H, br), 1.91 (4H, m), 1.74 (2H, m). APCI-HRMS: calcd for $\text{C}_{27}\text{H}_{20}\text{NO}_3$ (MH^+), 406.1438; found: 406.1342.

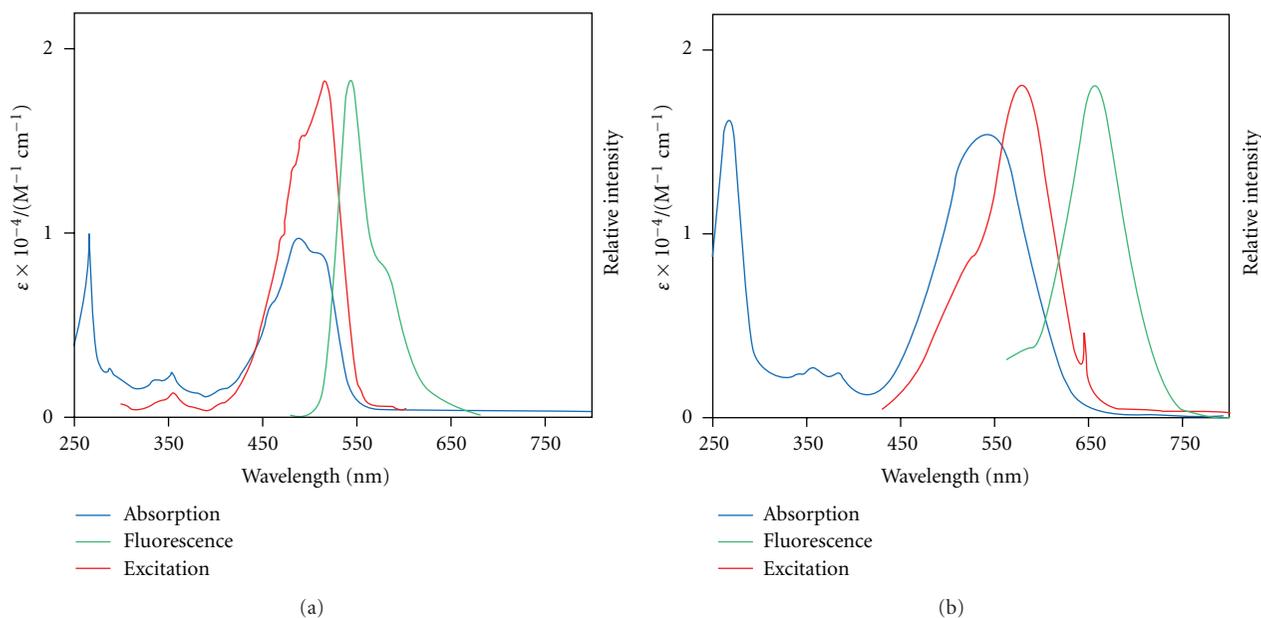
2.2. Fabrication of Dye-Sensitized Solar Cell. A nanocrystalline TiO_2 photoelectrodes of 20 μm thickness (area: 0.25 cm^2) was prepared by screen-printing on conducting glass as previously described [22]. The films were further treated with 0.05 M TiCl_4 and 0.1 M HCl aqueous solutions before examination [23]. Coating of the TiO_2 film was carried out by immersing for 20 h in a sensitizer solution of 3×10^{-4} M dichlorobenzene solution. Deoxycholic acid (20 mM) was added to the dye solution as a coadsorbent to prevent aggregation of the dye molecules [24, 25]. Photovoltaic measurements were performed in a two-electrode sandwich cell configuration. The dye-deposited TiO_2 film and a platinum-coated conducting glass were used as the working electrode and the counter electrode, respectively. The two electrodes were separated by a surlyn spacer (40 μm thick) and sealed by heating the polymer frame. The electrolytes were composed of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I_2 , and 0.1 M LiI in acetonitrile with (0.5 M) or without *tert*-butylpyridine (TBP).

2.3. Photovoltaic Characterization. The working electrode was illuminated through a conducting glass. The current-voltage characteristics were measured using a solar simulator (AM-1.5, 100 mW/cm^2 , WXS-155S-10; Wacom Denso Co. Japan). Monochromatic incident photon-to-current conversion efficiency (IPCE) for the solar cell, plotted as a function of excitation wavelength, was recorded on a CEP-2000 system (Bunkoh-Keiki Co. Ltd.). Incident photon-to-current conversion efficiency (IPCE) at each incident wavelength was calculated from (1), where I_{sc} is the photocurrent density at short circuit in mA cm^{-2} under monochromatic irradiation, λ is the wavelength of incident radiation in nm, and ϕ is the incident radiative flux in mW cm^{-2}

$$\text{IPCE}(\lambda) = 1240 \left(\frac{I_{\text{sc}}}{\lambda \phi} \right). \quad (1)$$



SCHEME 1: Preparation of PK0002.

FIGURE 2: Absorption, fluorescence, and excitation spectra of PK0003 (a) and PK0002 (b) in CHCl_3 .

3. Results and Discussion

3.1. Photophysical Properties. The absorption, excitation, and fluorescence spectra for PK0003 and PK0002 are shown in Figure 2, and the numerical data are summarized in Table 1. The absorption maxima (λ_{max}) of PK0003 and PK0002 were observed at 489 nm and 544 nm, respectively. Their molar absorption coefficients (ϵ) were calculated to be $1.0\text{--}1.6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. The fluorescence emission maxima (λ_{flur}) of PK0003 and PK0002 were observed at 543 nm and 655 nm, respectively. It is noticed that on going from PK0003 without a donor group to PK0002 with the donor group, the structured absorption and fluorescence bands become broader and are shifted to longer wavelengths, and

the Stokes shift becomes larger. These observations imply that the more charge-transfer character is involved in the $\pi\text{-}\pi^*$ transition of the donor-substituted PK0002. PK0003 and PK0002 show a blue-shifted absorption when adsorbed onto TiO_2 (Figure 3). This effect is attributed to the ring opening of the anhydride group on perylene to form two carboxylates, providing interactions with the oxide surface.

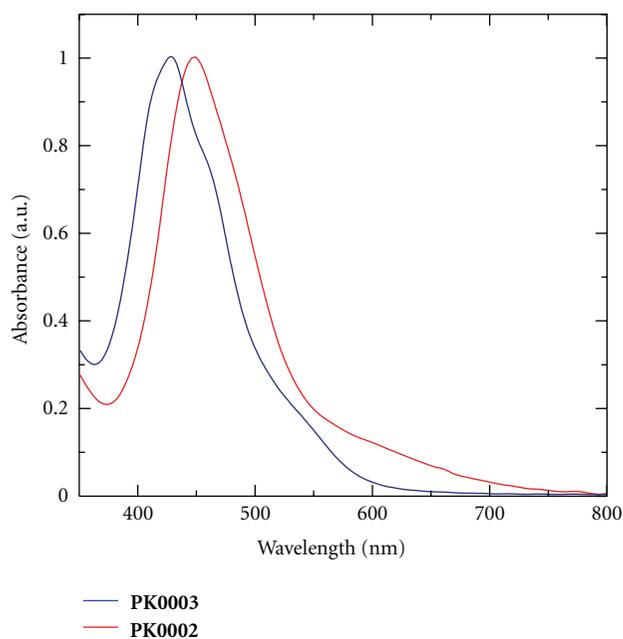
To obtain an insight into the electron distribution and relative energy level of PK0003 and PK0002 for better understanding of the charge injection and dye regeneration process, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of PK0003 and PK0002 were calculated with B3LYP/6-31G implemented in a Gaussian-03 program package (Figure 4).

TABLE 1: Physical properties of **PK0003** and **PK0002**.

Compound	Absorption ^(a)		Fluorescence ^(a)		Absorption on TiO ₂ film	IP	E^{0-0} ^(c)	LUMO ^(d)
	λ_{\max}/nm	$\epsilon \times 10^{-4}/\text{M}^{-1} \text{cm}^{-1}$	$\lambda_{\text{ex}}/\text{nm}$ ^(b)	$\lambda_{\text{fluor}}/\text{nm}$ ^(b)	λ_{\max}/nm	(eV)	(eV)	(eV)
PK0003	489	1.0	516	543	450	-5.88	2.07	-3.81
PK0002	544	1.6	580	655	500	-5.60	1.77	-3.83

^(a)In CHCl₃.^(b)At emission maximum.^(c) E^{0-0} values were estimated from the 5% intensity level of the absorption spectra on TiO₂.^(d)Calculated from $E^*(\text{LUMO}) = E(\text{IP}) - E^{0-0}$.TABLE 2: The photovoltaic data of DSSCs based on **PK0003** and **PK0002**.

Dye	TBP	J_{sc} [mA cm ⁻²]	V_{oc} [V]	F.F.	Eff. [%]
PK0003	0	7.6	0.45	0.63	2.2
PK0003	0.5 M	4.1	0.56	0.69	1.6
PK0002	0	8.8	0.41	0.59	2.1
PK0002	0.5 M	7.7	0.57	0.70	3.1

FIGURE 3: Absorption spectra of **PK0003**- and **PK0002**-adsorbed TiO₂ film.

The HOMO and LUMO energies are -5.88 eV and -3.18 eV, respectively, for **PK0003**. The corresponding energies for **PK0002** are -5.31 eV and -2.88 eV, respectively. These values are positively shifted due to the introduction of the donor moiety, piperidine, at the 9th position. The influence of the introduction of the donor group is larger on the HOMO, which is shifted by +0.57 eV, than on the LUMO, which is shifted by +0.30 eV. Upon adsorption on the TiO₂ surface, the carboxylic anhydride group is believed to be cleaved to become dicarboxylate. Therefore, the DFT calculations were also conducted for disodium salts of the dicarboxylate as models for the adsorbed molecules. The HOMO and LUMO energies for **PK0002** are -4.33 eV and -1.63 eV, respectively [20]. The major effect is rise in energy of both of the HOMO

and LUMO. The effect is more pronounced for the LUMO, resulting in an increase in the HOMO-LUMO gap from 2.43 eV for the anhydride to 2.70 eV for the dicarboxylate. This result agrees with the blue-shifted absorption spectra of **PK0003** and **PK0002** when adsorbed onto TiO₂ (Figure 3).

The ionization potential (IP) of **PK0003** and **PK0002** bound to nanocrystalline TiO₂ film was determined using a photoemission yield spectrometer (Riken Keiki AC-3E). The ground-state oxidation potential (IP) values of -5.88 eV and -5.60 eV obtained for sensitizer **PK0003** and **PK0002**, respectively, were low enough for efficient regeneration of the oxidized dye through reaction with iodide [26]. The excited-state oxidation potential, LUMO, of sensitizers **PK0003** and **PK0002** was estimated at -3.81 eV and -3.83 eV, respectively, which lies above the conduction band edge (-4.2 eV) [2] of nanocrystalline TiO₂. Efficient electron injection into the conduction band of TiO₂ is therefore expected to occur with both sensitizers **PK0003** and **PK0002**.

3.2. Photovoltaic Performance. The photovoltaic properties of the solar cells fabricated with these organic dyes were measured under simulated AM 1.5G irradiation (100 mW cm⁻²). The open-circuit photovoltage (V_{oc}), short-circuit photocurrent density (J_{sc}), fill factor (ff), and solar energy-to-electricity conversion efficiencies (η) were listed in Table 2. Figure 5 shows the photocurrent action spectra for the cells with sensitizers **PK0003** and **PK0002** where the incident photons-to-current conversion efficiency (IPCE) values are plotted as a function of wavelength. **PK0003** achieved efficient sensitization of nanocrystalline TiO₂ across the whole visible range and displayed the highest IPCE value of 80% at around 450 nm. Under similar conditions, **PK0002** showed higher IPCE values than **PK0003** in the 520–800 nm region. This result is consistent with the absorption spectra of the sensitizers on the TiO₂ surface (Figure 3). **PK0002** shows the highest IPCE value of 70% at around 470 nm. One possible explanation for this low IPCE value of sensitizer **PK0002** is the aggregation of sensitizer molecules on the

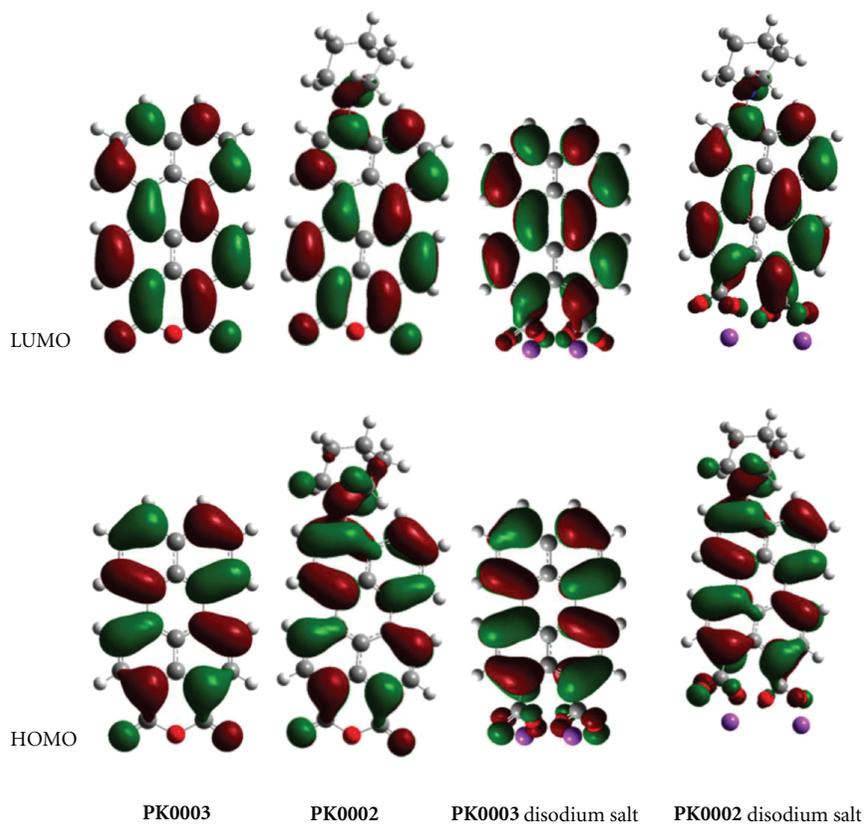


FIGURE 4: Frontier orbitals of PK0003 and PK0002.

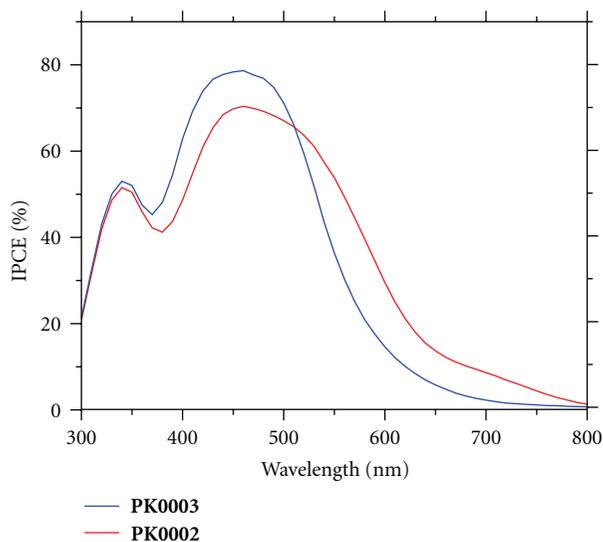


FIGURE 5: Photocurrent action spectra (IPCE) of nanocrystalline TiO₂ film sensitized by PK0003 (blue line) and PK0002 (red line). The redox electrolyte solution was a mixture of 0.6 M DMPII, 0.05 M I₂, and 0.1 M LiI in acetonitrile.

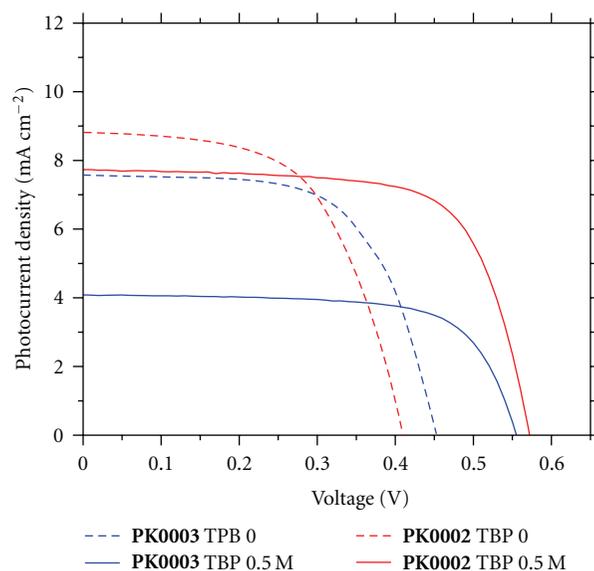


FIGURE 6: Photocurrent voltage characteristics of a nanocrystalline photoelectrochemical cell sensitized with the dye PK0003 and PK0002 at AM 1.5 illuminations (light intensity: 100 mW cm⁻²).

TiO₂ surface, which could not be completely suppressed by addition of deoxycholic acid (DCA) as a coadsorbent.

Figure 6 shows photocurrent voltage curves of a sandwich-type sealed solar cell based on PK0003 and

PK0002 at standard AM 1.5 irradiation with using an electrolyte of 0.6 M dimethylpropyl-imidazolium iodide (DMPII), 0.05 M I₂ and 0.1 M LiI in acetonitrile with (0.5 M) or without *tert*-butylpyridine (TBP). PK0003 and

PK0002-sensitized cell gave a short-circuit photocurrent density (J_{sc}) of 7.6 mA cm^{-2} and 8.8 mA cm^{-2} , and an overall conversion efficiency (η) of 2.2% and 2.1%, respectively, using electrolytes with no TBP. The short-circuit photocurrent density decreased by adding TBP in the electrolyte. In contrast, the open-circuit voltage and the fill factor increased significantly with the presence of TBP. TBP probably adsorbed on the bare TiO_2 surface and suppress the recombination between the injected electrons and I_3^- ions [27]. As shown in Table 2, the solar cell sensitized with **PK0002** showed a photocurrent density of 7.7 mA cm^{-2} , an open-circuit potential of 0.57 V, and a fill factor of 0.70, corresponding to an overall conversion efficiency (η) of 3.1% with the electrolyte containing 0.5 M TBP under standard AM 1.5 irradiation (100 mW cm^{-2}). Thus, this class of piperidine-substituted perylene sensitizer serves as a basis for further design of new potential sensitizers by introducing suitable substituents on the perylene to improve the light harvesting efficiency of the sensitizer.

4. Conclusion

We have synthesized a novel perylene derivative with a piperidine donor substituent, **PK0002**, for dye-sensitized solar cells. **PK0002** achieved very efficient sensitization of nanocrystalline TiO_2 over the whole visible range extending into the near-IR region (ca. 800 nm). The photovoltaic data of this new sensitizer show 3.1% power conversion efficiency under standard AM 1.5 irradiation (100 mW cm^{-2}). Further study will target the development of a high-performance solar cell through modification of the electronic and steric environments of the sensitizers on the basis of alteration of the substituent on the perylene moiety.

Acknowledgments

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