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Application of 9-substituted 3,4-perylenedicarboxylic anhydrides as sensitizers for zinc oxide solar cell

Takuya Dentani [a], Kazumasa Funabiki [a], Ji-Ye Jin [b], Tsukasa Yoshida [c],
Hideki Minoura [c], Masaki Matsui [a,*]

[a] *Department of Materials Science and Technology, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan*
[b] *Department of Chemistry, Faculty of Science, Shinshu University, 3-1-1 Asahi, Matsumoto, Nagano 390-8621, Japan*
[c] *Environmental and Renewable Energy System Division, Graduate School of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan*

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Abstract

A series of 9-substituted 3,4-perylenedicarboxylic anhydrides were examined as sensitizers for the zinc oxide solar cell prepared by a one-step cathode deposition template method. The best performance was obtained for the bromo derivative. The incident photon-to-current efficiency (IPCE) at 431 nm, maximum short-circuit photocurrent density (I_{sc}), open-circuit photovoltage (V_{oc}), fill factor (ff), and solar-light-to-electricity conversion efficiency (η) were observed to be 35.5%, 1.78 mA cm^{-2}, 0.46 V, 0.64, and 0.52%, respectively.

Keywords: Zinc oxide; Dye-sensitized solar cell; Sensitizers; Perylene dyes

1. Introduction

Much attention has been paid to survey of organic sensitizers for dye-sensitized solar cells [1]. The sensitizers are required to have reasonable energy levels to transfer electrons and anchor group(s) to have affinity for semiconductors. Coumarin [2], merocyanine [3], polyene [4], indoline [5], and styryl dyes [6,7] have been reported to show high conversion efficiency for titanium oxide. Perylene derivatives have also been reported to act as sensitizers for titanium oxide solar cells [8,9]. Titanium oxide is generally used as a semiconductor for dye-sensitized solar cells. However, recently, a convenient preparation method of porous zinc oxide thin film at low temperature (70 °C) has been reported [10]. Sensitizers for titanium oxide do not always act for zinc oxide. Therefore, it is of significance to find sensitizers for zinc oxide solar cells. We report herein the application of 9-substituted 3,4-perylenedicarboxylic anhydride as sensitizers for the zinc oxide solar cell prepared by the one-step cathode deposition template method.

2. Experimental

2.1. Instruments

Melting points were measured with a Yanagimoto MP-52 micro-melting-point apparatus. NMR spectra were obtained by a Varian Inova 400 and 500 spectrometers. EI mass spectra (70 eV) were taken with a Shimadzu QP-1000 instrument. UV–vis absorption and fluorescence spectra were taken on Hitachi U-3500 and F-4500 spectrophotometers, respectively. Electrochemical measurements were carried out using a CH Instruments, Inc. electrochemical analyzer. Photoelectrochemical measurements were performed on a Bunko-Keiki CEP-2000 system.

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* Corresponding author. Tel.: +81 58 293 2601; fax: +81 58 230 1893.
E-mail address: matsui@apchem.gifu-u.ac.jp (M. Matsui).

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2.2. Synthesis

Bromine (**2**), dimethylamine (**4c**), dibutylamine (**4d**), dioctylamine (**4e**), and didodecylamine (**4f**) were purchased from Tokyo Kasei Co., Ltd. *N*-[2,5-Di(*t*-butyl)phenyl]-3,4-perylenedicarboximide (**1**), 9-bromo-*N*-[2,5-di(*t*-butyl)phenyl]-3,4-perylenedicarboximide (**3**), 9-dialkylamino-*N*-[2,5-di(*t*-butyl)phenyl]-3,4-perylenedicarboximides (**5c–f**), and 3,4-perylenedicarboxylic anhydride (**6a**) were prepared as described in literature [11].

2.3. 9-Bromo- and 9-dialkylamino-3,4-perylenedicarboxylic anhydrides **6b–f**

To *t*-butyl alcohol (20 mL) were added **3** or **5c–f** (0.204 mmol) and potassium hydroxide (716 mg, 10.9 mmol). The mixture was refluxed for 1.5 h. After cooling to the mixture, was added acetic acid (80 mL) and stirred at room temperature overnight. After evaporating the solvent, water was added. The precipitate was filtered. Then, to the precipitate was added aqueous 10% potassium carbonate solution (200 mL). The mixture was refluxed for 30 min. The precipitate was filtered. To the filtrate was added acetic acid to make the solution acidic. The solution was refluxed for 10 min and filtered. The precipitate was washed with water, chloroform, and hexane. Compounds **6b–f** were purified by column chromatography (SiO_2, CH_2Cl_2:AcOEt = 10:1).

2.3.1. 9-Bromo-3,4-perylenedicarboxylic anhydride (**6b**)

Yield: 33%; mp > 300 °C; ^{1}H NMR (DMSO-d_6) δ: 7.92 (t, 1H, $J = 8.1$ Hz), 8.13 (d, 1H, $J = 8.1$ Hz), 8.32 (d, 1H, $J = 8.3$ Hz), 8.51 (d, 1H, $J = 8.1$ Hz), 8.52 (d, 1H, $J = 8.1$ Hz), 8.64 (d, 1H, $J = 8.1$ Hz), 8.78 (d, 1H, $J = 8.3$ Hz), 8.81 (d, 1H, $J = 8.3$ Hz), 8.86 (d, 1H, $J = 8.3$ Hz); MS *m/z* (rel intensity): 402 ($M^+ + 2$; 100), 400 (M^+; 97), 358 (22), 356 (24), 330 (31), 328 (31), 249 (32), 248 (47), 165 (19), 164 (20), 125 (36), 124 (75), 123 (32).

2.3.2. 9-Dimethylamino-3,4-perylenedicarboxylic anhydride (**6c**)

Yield: 64%; mp > 300 °C; ^{1}H NMR ($CDCl_3$) δ: 3.08 (s, 6H), 7.15 (d, 1H, $J = 8.5$ Hz), 7.64 (dd, 1H, $J = 8.5$ and 7.6 Hz), 8.18 (d, 1H, $J = 8.2$ Hz), 8.29 (d, 2H, $J = 8.2$ Hz), 8.32 (d, 1H, $J = 8.5$ Hz), 8.43 (d, 1H, $J = 8.5$ Hz), 8.61 (d, 1H, $J = 8.2$ Hz), 8.63 (d, 1H, $J = 8.5$ Hz); MS *m/z* (rel intensity): 365 (M^+; 100), 278 (53), 250 (41).

2.3.3. 9-Dibutylamino-3,4-perylenedicarboxylic anhydride (**6d**)

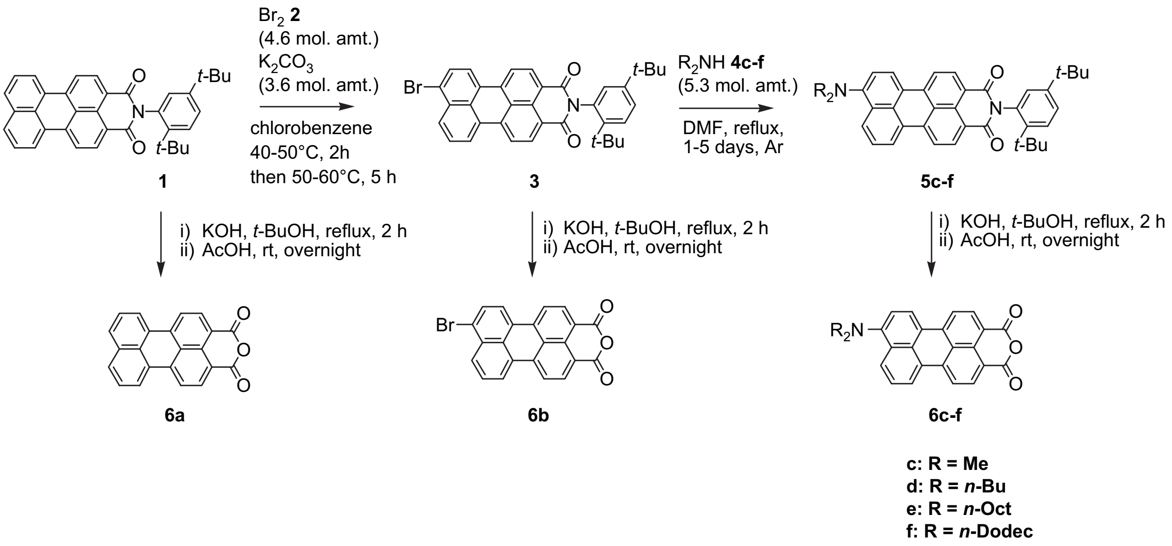
Yield: 18%; mp 223–227 °C; ^{1}H NMR ($CDCl_3$) δ: 0.90 (t, 6H, $J = 7.5$ Hz), 1.33 (q, 4H, $J = 7.6$ Hz), 1.60–1.63 (m, 4H), 3.34 (t, 4H, $J = 7.5$ Hz), 7.23 (d, 1H, $J = 7.9$ Hz), 7.62 (t, 1H, $J = 7.9$ Hz), 8.17 (d, 1H, $J = 8.4$ Hz), 8.27 (d, 1H, $J = 7.9$ Hz), 8.31 (d, 1H, $J = 8.4$ Hz), 8.32 (d, 1H, $J = 8.4$ Hz), 8.41 (d, 1H, $J = 8.0$ Hz), 8.42 (d, 1H, $J = 8.4$ Hz), 8.44 (d, 1H, $J = 8.4$ Hz); MS *m/z* (rel intensity): 449 (M^+; 29), 406 (100).

2.3.4. 9-Dioctylamino-3,4-perylenedicarboxylic anhydride (**6e**)

Yield: 13%; mp 145–149 °C; ^{1}H NMR ($CDCl_3$) δ: 0.84 (t, 6H, $J = 7.4$ Hz), 1.23–1.25 (m, 20H), 1.59–1.63 (m, 4H), 3.32 (t, 4H, $J = 7.5$ Hz), 7.22 (d, 1H, $J = 8.4$ Hz), 7.62 (t, 1H, $J = 7.9$ Hz), 8.16 (d, 1H, $J = 8.4$ Hz), 8.28 (d, 1H, $J = 7.9$ Hz), 8.31 (d, 1H, $J = 8.4$ Hz), 8.33 (d, 1H, $J = 8.4$ Hz), 8.42 (d, 1H, $J = 8.0$ Hz), 8.44 (d, 1H, $J = 8.0$ Hz), 8.46 (d, 1H, $J = 7.9$ Hz); MS *m/z* (rel intensity): 561 (M^+; 100), 462 (77), 349 (34), 277 (24).

2.3.5. 9-Didodecylamino-3,4-perylenedicarboxylic anhydride (**6f**)

Yield: 59%; mp 137–139 °C; ^{1}H NMR ($CDCl_3$) δ: 0.85 (t, 6H, $J = 7.0$ Hz), 1.22–1.30 (m, 36H), 1.63–1.67 (m, 4H), 3.35 (t, 4H, $J = 7.5$ Hz), 7.15 (d, 1H, $J = 8.4$ Hz), 7.55



Scheme 1.

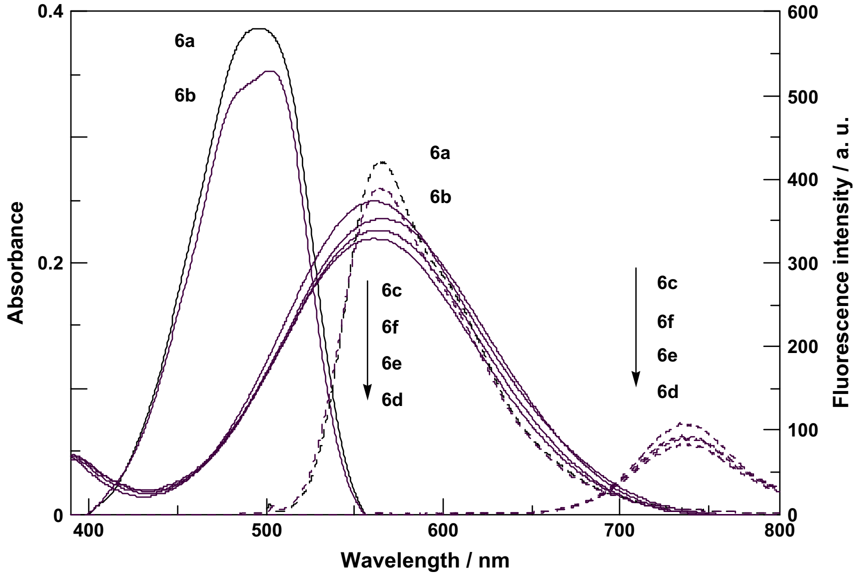


Fig. 1. UV–vis absorption and fluorescence spectra of **6a–f** in DMSO. Solid and dotted lines show the UV–vis absorption and fluorescence spectra, respectively. The concentration of **6a–f** is 1.0×10^{-5} mol dm^{-3}.

(t, 1H, $J = 7.9$ Hz), 7.83 (d, 1H, $J = 8.4$ Hz), 7.93 (d, 1H, $J = 7.9$ Hz), 8.11 (d, 2H, $J = 8.4$ Hz), 8.13 (d, 1H, $J = 8.4$ Hz), 8.18 (d, 1H, $J = 7.9$ Hz), 8.25 (d, 1H, $J = 8.4$ Hz); MS *m*/*z* (rel intensity): 673 (M^+; 66), 518 (40), 281 (74), 207 (100).

3. Results and discussion

3.1. Synthesis

Synthesis of 9-substituted 3,4-perylenedicarboxylic anhydrides **6** is shown in Scheme 1. *N*-[2,5-Di(*t*-butyl)phenyl]-3,4-perylenedicarboximide (**1**) reacted with bromine (**2**) to afford the 9-bromo derivative **3**, which reacted with secondary amines **4c–f** to give the 9-dialkylamino imido derivatives **5c–f**, followed by hydrolysis to provide the 9-dialkylamino-3,4-perylenedicarboxylic anhydrides **6c–f**. Compounds **6a** and **6b** were obtained by the hydrolysis of the imido derivatives **1** and **3**, respectively.

3.2. UV–vis absorption and fluorescence spectra

The UV–vis absorption and fluorescence spectra of **6a–f** in DMSO are shown in Fig. 1. The absorption maxima (λ_{max}) of **6a** and **6b** were observed at around 500 nm. Their molar absorption coefficients (ε) were calculated to be ca. 36,000 dm^3 mol^{-1} cm^{-1}. Their emission maxima (λ_{em}) were observed at 564 nm. Meanwhile, the λ_{max} of 9-dialkylamino derivatives **6c–f** were observed at around 560 nm, being more bathochromic than those of **6a** and **6b** due to the push–pull chromophoric system. The λ_{ex} of **6c–f** were observed at around 737 nm. The relative fluorescence intensities (RFI) of **6c–f** were less than those of **6a** and **6b**. The UV–vis absorption and fluorescence spectral data are listed in Table 1.

3.3. Electrochemical measurement

Since compounds **6a–f** were less soluble in acetonitrile, the electrochemical measurement was carried out in DMSO.

Table 1
Physical properties of 3,4-perylenedicarboxylic anhydrides **6a–f** and their cell performance on zinc oxide

Compound	$\lambda_{max}(\varepsilon)$[a] (nm)	λ_{em}[a] (nm)	RFI[a]	E_{red}[b] (V)	E_{ox}[b] (V)	λ_{max}[c] (nm)	Absorbance[d]	IPCE[e] (%)	I_{sc}[e] mA cm^{-2}	V_{oc}[e] (V)	ff[e]	η[e] (%)
6a	495 (38,100)	564	100	−0.93	1.58	424	1.62	29.5	1.44	0.45	0.65	0.42
6b	503 (35,200)	564	92	−0.98	1.49	431	1.11	35.5	1.78	0.46	0.64	0.52
6c	561 (25,000)	736	26	−1.05	1.16	444	1.38	9.2	0.66	0.37	0.67	0.16
6d	561 (22,100)	737	20	−0.96	1.26	462	1.14	14.0	0.81	0.41	0.64	0.21
6e	564 (22,700)	736	21	−0.98	1.22	457	1.19	12.3	0.77	0.41	0.63	0.20
6f	566 (23,400)	738	22	−1.09	1.10	458	1.32	12.3	0.70	0.44	0.63	0.20

[a] Measured in DMSO.
[b] vs SCE in acetonitrile.
[c] Measured on zinc oxide film.
[d] On zinc oxide.
[e] Action spectrum under monochromatic light with 0.2×10^{16} photon cm^{-2} s^{-1} and *I*–*V* characteristics under white light with 100 mW cm^{-2}.

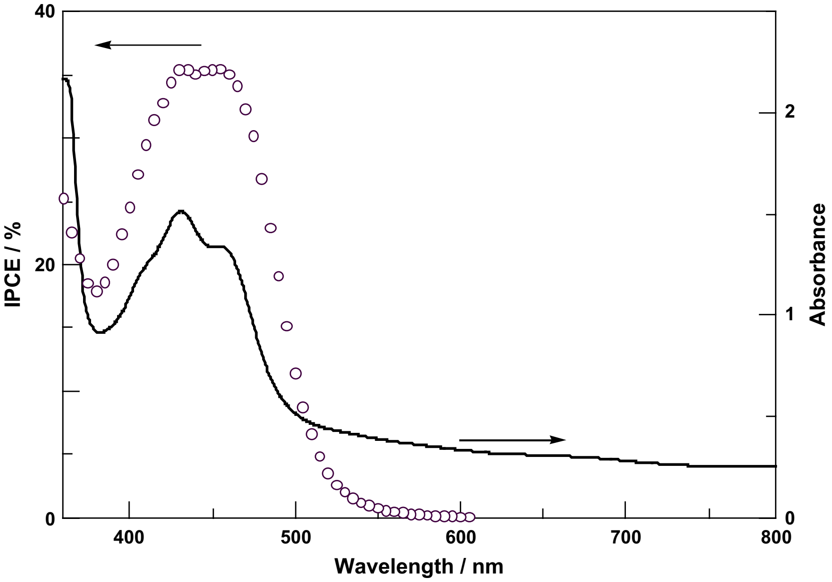


Fig. 2. UV–vis absorption and action spectra of **6b**.

A silver wire was used as a *pseudo*-reference electrode to avoid contamination of the analyte. Only the reduction potential (E_{red}) of **6a–f** was observed. The measured E_{red} vs Ag in DMSO was calibrated to E_{red} vs SCE in acetonitrile on the basis of the oxidation potential (E_{ox}) of ferrocene. Then, the E_{ox} of **6a–f** was calibrated on the basis of the E_{red} and λ_{max} in DMSO. The E_{red} and E_{ox} of **6a–f** are shown in Table 1. The E_{red} of **6a–f** was negative enough to sensitize zinc oxide (0.7 V vs SCE in acetonitrile). The E_{ox} of **6a–f** was positive to accept electrons from electrolyte triiodide/iodide (I_3^-/I^-, 0.29 V vs SCE in acetonitrile). Thus, 3,4-perylenedicarboxylic anhydrides can act as sensitizers for zinc oxide from thermodynamic point of view.

3.4. Preparation of zinc oxide solar cell

A template zinc oxide thin film (thickness: ca. 3 μm) was prepared as described in the report [10]. The film was dried at 150 °C for 1 h before use. The zinc oxide thin film was immersed in the DMF solution of dye (5×10^{-4} mol dm^{-3}) at 25 °C for 4 days. The optimized immersion conditions were obtained in advance. After drying, the film was set in the solar cell as shown in our previous paper [12]. An acetonitrile–ethylenecarbonate (v/v = 1:4) mixed solution containing tetrabutylammonium iodide (0.5 mol dm^{-3}) and iodine (0.05 mol dm^{-3}) was used as an electrolyte.

3.5. Photoelectrochemical properties of zinc oxide solar cell

Typical UV–vis absorption and action spectra of 3,4-perylenedicarboxylic anhydrides are shown in Fig. 2. The action spectrum was followed by the absorption band of **6b** on zinc oxide, indicating the photosensitization of zinc oxide by **6b**. The IPCE of **6b** was observed to be 35.5% at 431 nm.

Typical photocurrent density–photovoltage (I–V) curve is shown in Fig. 3. The I_{sc} and V_{oc} of **6b** were observed at 1.78 mA cm^{-2} and 0.46 V, respectively. The ff and η were calculated to be 0.64 and 0.52%, respectively.

The cell performance of 9-substituted 3,4-perylenedicarboxylic anhydrides **6a–f** is shown in Table 1. Compounds **6a–f** were not desorbed from the zinc oxide film by the addition of ammonia, indicating that these compounds were tightly adsorbed and/or chemically bonded with zinc oxide.

The amount of dye on zinc oxide film can affect the cell performance. In our experience, when the absorbance is larger than 1.0, indicating more than 90% of photon is absorbed, the film performance can be evaluated. The absorbance of **6a–f** on zinc oxide was observed in the range of 1.14–1.62, indicating that sufficient amount of **6a–f** was doped on the zinc oxide film.

The introduction of long alkyl group into merocyanine dyes [3] and semisquaric acids [12] have been reported to improve the cell's performance. However, no remarkable difference in

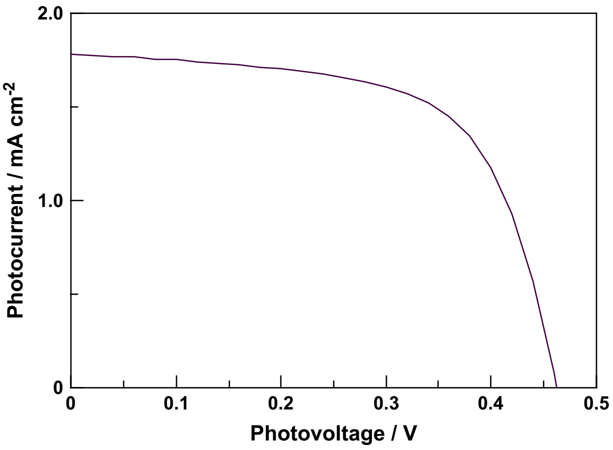


Fig. 3. Photocurrent density–photovoltage curve of **6b**.

the performance among the dialkylamino derivatives **6c–f** was observed.

The dialkylamino derivatives **6c–f** were supposed to show better performance than the unsubstituted and bromo derivatives **6a** and **6b**, due to stronger push–pull chromophoric system. However, interestingly, compounds **6c–f** showed less performance than **6a** and **6b**, which might be attributed to less fluorescence intensity of **6c–f** than **6a** and **6b**.

The cell performance of 3,4-perylenedicarboxylic anhydride derivatives on titanium oxide has been reported to show the η values in the range of 0.052–0.92%, which were improved by UV-irradiation, showing 0.45–1.92% [8]. Perylene tetracarboxylic acid and its monoimido derivative have been reported to show the IPCE value 38.8 and 13.6%, respectively [9]. Thus, perylene derivatives have been reported to show lower performance than the other organic dyes such as coumarins, merocyanines, polyenes, indolines, and styryls. Though the cell performance is not high enough, in a series of our study on the survey of sensitizers for zinc oxide prepared by the one-step deposition template method, 9-bromo-3,4-perylenedicarboxylic anhydride showed the highest results: IPCE 35.5% and η value 0.52%.

4. Conclusion

A series of 3,4-perylenedicarboxylic anhydrides were examined as sensitizers for the zinc oxide solar cell prepared by a one-step cathode deposition template method. These derivatives showed strong affinity for zinc oxide. 9-Bromo-3,4-perylenedicarboxylic anhydride showed the best performance, the IPCE at 431 nm 35.5%, I_{sc}, 1.78 mA cm^{-2}; V_{oc}, 0.46 V; ff, 0.64; and η, 0.52%.

References

[1] Arakawa H. New technology in dyes-sensitized solar cells. Tokyo: CMC; 2001 and literatures cited therein.

[2] Hara K, Kurashige M, Dan Y, Kasada C, Shinpo A, Saga S, et al. Design of new coumarin dyes having thiophene moieties for highly efficient organic-dye-sensitized solar cells. New J Chem 2003;27(5):783–5.

[3] Sayama K, Tukagoshi S, Hara K, Ohga Y, Shinpo A, Abe Y, et al. Photoelectrochemical properties of J aggregates of benzothiazole merocyanine dyes on a nanostructured TiO_2 film. J Phys Chem B 2002;106(6): 1363–71.

[4] Hara K, Kurashige M, Ito S, Shinpo A, Suga S, Sayama K, et al. Novel polyene dyes for highly efficient dye-sensitized solar cells. Chem Commun 2003;2:252–3.

[5] Horiuchi T, Miura H, Uchida S. Highly-efficient metal-free organic dyes for dye-sensitized solar cells. J Am Chem Soc 2004;126:12218–9.

[6] Wang ZS, Li FU, Huang H. Photocurrent enhancement of hemicyanine dyes containing RSO3– group through treating TiO_2 films with hydrochloric acid. J Phys Chem B 2001;105(38):9210–7.

[7] Sayama K., Arakawa H., Hara K., Suga S., Shinho A., Oga Y. Semiconductor electrode using styryl dye photosensitizer, photoelectric conversion device, and solar cell, JP 2003234133. Chem Abstr 182865 2003; 139.

[8] Wang S, Li Y, Du C, Shi Z, Xiao S, Zhu D, et al. Dye sensitization of nanocrystalline TiO_2 by perylene derivatives. Synth Met 2002; 128(3):299–304.

[9] Ferrere S, Gregg BA. New perylenes for dye sensitization of TiO_2. New J Chem 2002;26(9):1155–60.

[10] Yoshida T, Iwaya M, Andoh H, Oekermann T, Nonomura K, Schelettwein D, et al. Improved photoelectrochemical performance of electrodeposited ZnO/eosinY hybrid thin films by dye re-adsorption. Chem Commun 2004;4:400–1.

[11] Feiler L, Langhals H, Polborn K. Synthesis of perylene-3,4-dicarboximides – novel highly photostable fluorescent dyes. Liebigs Ann Chem 1995;7:1229–44.

[12] Matsui M, Nagasaka K, Tokunaga S, Funabiki K, Yoshida T, Minoura H. 3-Aryl-4-hydroxycyclobut-3-ene-1,2-diones as sensitizers for TiO_2 solar cell. Dyes Pigments 2003;58(3):219–26.