

# New perylene derivative dyes for dye-sensitized solar cells

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## Abstract

We have studied the influence of the spacer alkyl chain length of perylenemonoimide (PMI) dyes on the device performance in dye-sensitized solar cells (DSSCs). We observed that the dyes with longer and branched alkyl chains exhibit higher efficiencies in DSSCs. In line with these statements we now report the highest efficiency obtained under standard conditions for a perylene imide derivative with PMI-DA1 that performs 300 mV open circuit voltage, 9.79 mA/cm<sup>2</sup> short-circuit current and 1.61% overall conversion efficiency.

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**Keywords:** Dye-sensitization; Nanocrystalline TiO<sub>2</sub>; Perylenemonoimide

## 1. Introduction

Dye-sensitized solar cells (DSSCs) based on TiO<sub>2</sub> photoelectrode have been attracting considerable attention since O'Regan and Grätzel [1] and Nazeeruddin et al. [2] reported high solar energy to electricity conversion efficiency,  $\eta$ , up to 11% with ruthenium bipyridyl dyes. The most powerful points of this new technology are simple fabrication process and low production cost respect of silicon technology. In early studies, 9-phenylxanthane dyes were also used as photosensitizers in DSSCs [3,4]. In recent years, various Ru-complexes have been used as efficient photosensitizers [5–7]. In addition to Ru-complexes, coumarin, porphyrine, phthalocyanine, indoline and perylene derivatives have also been reported with  $\eta$  values varying from 1% to 8% [8–13].

Perylene tetracarboxylic derivatives are optoelectronic pigments with high fluorescence quantum yield, high molar absorptivity constant ( $\epsilon \approx 10^5 \text{ M}^{-1} \text{ cm}^{-1}$ ) and chemical stability [14]. The electron injection rate constants ( $k_{\text{inj}}$ ) of perylene and ruthenium dyes into the nc-TiO<sub>2</sub> are relatively similar. Burfeindt et al. [15] reported the  $k_{\text{inj}}$

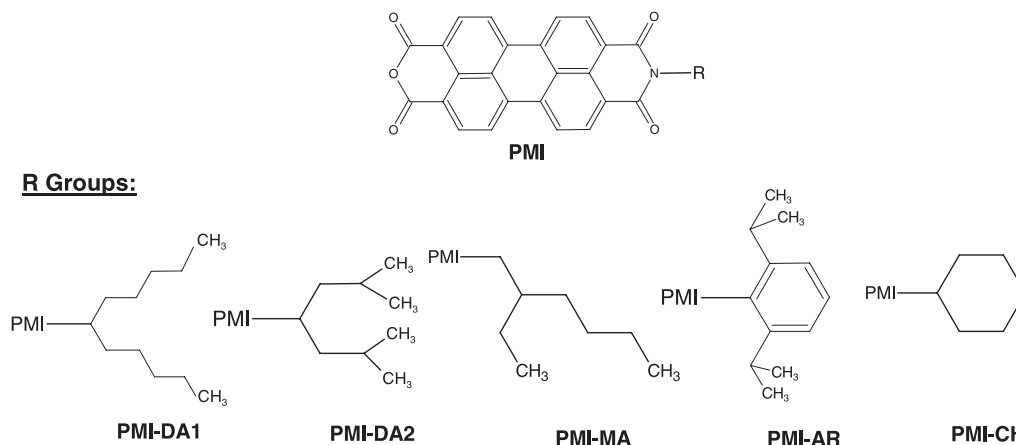
value as  $5 \times 10^{13} \text{ s}^{-1}$  for perylene derivatives, and  $k_{\text{inj}} > 4 \times 10^{14} \text{ s}^{-1}$  for Ru-complexes [16]. Their synthetic chemistry has a potentially wide range of flexibility for altering properties such as color and redox potentials. Kaiser et al. [17], Langhals et al. [18], Quante et al. [19], Geerts et al. [20] have reported various procedures for synthesis of perylene dyes. We now report the performance of DSSCs based on perylenemonoimide (PMI) photosensitizers. The device structure is FTO/nc-TiO<sub>2</sub>/PMI/I<sup>−</sup>/I<sub>3</sub><sup>−</sup>/Pt/FTO. The structures and corresponding abbreviations used throughout the text are given in Scheme 1.

## 2. Experimental

### 2.1. Materials and methods

All used reagents were of commercial grade and used without any further purification. PMI-AR was prepared according to a procedure reported by Dincalp et al. [21]. 2,6-diisopropylaniline (3.14 mL, 15 mmol) and Zn(CH<sub>3</sub>COO)<sub>2</sub> · 2H<sub>2</sub>O (0.33 g, 1.5 mmol) were added into a solution of perylene-3,4,9,10-tetracarboxylic dianhydride (0.59 g, 1.5 mmol) in 20 mL of quinoline. The mixture was stirred at 210 °C for 15 h under a nitrogen atmosphere. The reaction solution was cooled to room temperature and then

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Scheme 1.

was added into 400 mL of methanol/10% hydrochloric acid ( $V/V = 2:1$ ) under stirring. The solid precipitate was filtered off and stirred in 100 mL of cold  $\text{Na}_2\text{CO}_3$  solution (10%) for 2 h. Then the precipitate was filtered again and washed with water until the filtrate was colorless. The solid was dried under vacuum at  $90^\circ\text{C}$  for 18 h and purified by silica gel column chromatography with *n*-hexane/ethyl acetate (70:30) as eluent. The product is *N,N'*-bis-(2,6-diisopropylphenyl)-perylene-3,4,9,10-tetracarboxylic diimide. A mixture of perylene diimide (0.28 g, 0.4 mmol), 85% KOH pellets (0.08 g, 1.2 mmol), and 15 mL of *tert*-BuOH was stirred at reflux for 15 h. The mixture was poured into a solution of 15 mL of AcOH and 7 mL of 2 N HCl. The precipitate was washed with water and dried under vacuum at  $90^\circ\text{C}$  for 18 h. Purification of the compound was realized by column chromatography on silica with chloroform/acetic acid (95:05) as eluent. Yield: 55%, m.p.  $> 300^\circ\text{C}$ . Visible (toluene):  $\lambda_1 = 456$ ,  $\lambda_2 = 487$ , and  $\lambda_3 = 523$  nm. FT-IR (KBr,  $\text{cm}^{-1}$ ): 2964, 1775, 1738, 1709, 1666, 1591, 1406, 1360, 1299, 1246, 1023, and 810.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.85$  (2H, doublet, perylene H), 8.75 (2H, doublet, perylene H), and 8.71 (4H, doublet, perylene H); 7.55 (1H, triplet); 7.38 (2H, doublet); 2.69 (2H, heptet); and 1.17 (12H, doublet) ppm.

PMI-MA was synthesized according to procedure reported by Kus et al. [22], PMI-CH, PMI-DA1, and PMI-DA2 were synthesized according to procedure reported by Langhals and Kaiser [17] and Langhals et al. [18] with minor modifications.

Thickness of the films measured using Tencor Alpha Step 500 profilometer. UV-Vis absorption spectra of PMIs in solution and adsorbed on nc- $\text{TiO}_2$  film were measured using Analytic Jena S 600 UV spectrophotometer and fluorescence emission spectra were measured with PTI QM1 fluorescence spectrophotometer. FT-IR measurements were recorded with Perkin Elmer Spectrum BX FTIR spectrometer. Electrochemical measurements were done in a three-electrode cell with Pt wire as the counter, Ag/AgCl as reference, glassy carbon as working electrode

for solution measurements and FTO- $\text{TiO}_2$ -PMI as working electrode for solid-state measurement by using CHI-660B CH Instruments Electrochemical Workstation. The 0.1 M TBAPF<sub>6</sub> in  $\text{CH}_3\text{CN}:\text{CHCl}_3$  (5:1) was used as a supporting electrolyte. For FTO- $\text{TiO}_2$ -PMI electrode preparation,  $\text{TiO}_2$  paste was coated on conductive FTO glasses by doctor blade technique. Coated electrodes sintered at  $450^\circ\text{C}$  for 30 min, then immersed into dye solution for 3 h, and then washed with pure solvent. Dye-sensitized  $\text{TiO}_2$  electrodes were used as working electrode in three-electrode cell for electrochemical measurements.

## 2.2. Photovoltaic device preparation and characterization

FTO ( $\text{SnO}_2:\text{F}$ , Pilkington TEC-15;  $R_{\text{sheet}}:15\ \Omega/\square$ ), electrically conductive oxide-coated glasses were used as transparent electrodes.  $\text{TiO}_2$  electrodes consist of an adsorbent mesoporous layer with 20 nm anatase  $\text{TiO}_2$  particle size in 10  $\mu\text{m}$  thicknesses and a second light scattering layer with 400 nm anatase  $\text{TiO}_2$  particle size of 4  $\mu\text{m}$  thicknesses. Preparation and characterization of double-layer  $\text{TiO}_2$  electrode were previously described by Wang et al. [23].

Dye solutions were prepared in  $\text{CH}_3\text{CN}:\text{CHCl}_3$  (1:1) mixture with a concentration of 0.5 mM PMIs.  $\text{TiO}_2$ -coated electrodes, after sintering at  $450^\circ\text{C}$  for 30 min and cooling to  $100^\circ\text{C}$ , were kept overnight in PMI solutions for adsorption. PMI adsorbed  $\text{TiO}_2$ -coated glasses were washed with pure acetonitrile and dried in vacuum.

Platinized FTO glasses were used as a counter electrode. Platinization of counter electrodes were done by coating of FTO glasses with 1% solution of hydrogen hexachloroplatinate (Aldrich) in 2-propanol and annealing at  $400^\circ\text{C}$  for 30 min. Cells were prepared in sandwich geometry. Surlyn-1702 (DuPont) frame was used as a spacer and a thermoplastic sealant between the two electrodes. Prepared cells were sealed by heating at  $100^\circ\text{C}$ . Electrolyte was filled into the space created by Surlyn-1702 between the

electrodes under vacuum using a small hole pre-drilled on the counter electrode with the help of a diamond drill. After filling the electrolyte, a small hole was sealed again using a piece of Surlyn-1702 and a piece of cover glass. The electrolyte consisted of 0.6 M *N*-methyl-*N*-butyl imidazolium iodide (BMII) + 0.1 M LiI + 0.05 M I<sub>2</sub> in acetonitrile. Active areas of the cells were adjusted to 0.157 cm<sup>2</sup> with a special mask.

The so-called prepared DSSCs were characterized by current–voltage (*I*–*V*) measurement and measurements of incident photon to current conversion efficiency (IPCE) spectra. All *I*–*V* measurements were done under 100 mW/cm<sup>2</sup> light intensity and AM1.5 conditions. A 450 W Xenon light source (Oriel) was used to produce an irradiance of various intensities. The spectral output of the lamp was matched in the region of 350–700 nm with the aid of Schott K113 Tempax sunlight filter. *I*–*V* data collection was made by using Keithley 2400 source-meter and Labview data acquisition software.

The overall energy conversion efficiency,  $\eta$ , has been calculated using the equation,  $\eta = P_{\text{max}}/P_{\text{light}} = (V_{\text{mpp}}I_{\text{mpp}})/P_{\text{light}} = (V_{\text{oc}}I_{\text{sc}}\text{FF})/P_{\text{light}}$ , where  $V_{\text{oc}}$  (V) is an open circuit voltage,  $I_{\text{sc}}$  (mA/cm<sup>2</sup>) is a short circuit current, FF the fill factor,  $P_{\text{max}}$  (mW/cm<sup>2</sup>) the maximum power point,  $P_{\text{light}}$  (mW/cm<sup>2</sup>) the incident light power,  $V_{\text{mpp}}$  and  $I_{\text{mpp}}$  the voltage and current at the point of maximum power output of cell, respectively. The IPCE, defined as the number of electrons generated by light in the external circuit divided by the number of incident photons is plotted as function of excitation wavelength. IPCE can be calculated by means of following equation,  $\text{IPCE} (\%) = 1240 I_{\text{sc}}/(\lambda I)$ , where  $I_{\text{sc}}$  (mA/cm<sup>2</sup>) is the short-circuit photocurrent density for monochromatic irradiation and  $\lambda$  (nm) and  $I$  (W/m<sup>2</sup>) are the wavelength and the intensity of the monochromatic light.

### 3. Results and discussion

#### 3.1. Absorption and luminescence of PMIs

All PMIs presented in this study show characteristic absorption bands at 459, 488, and 522 nm and fluorescence emission bands at 535, 575, and 622 nm (weak) (Fig. 3). The absorption bands lose structural vibrations and appear to be broad peaks in TiO<sub>2</sub> films. In addition, the fluorescence emission is completely quenched by TiO<sub>2</sub> nanoparticles. Bossman et al. [25] reported that Ru(bpy)<sub>3</sub><sup>2+</sup> complexes located near TiO<sub>2</sub> do not emit light. Since LUMO energy level of PMIs is close to Ru(bpy)<sub>3</sub><sup>2+</sup>, the excited state electrons of PMIs may be injected to the conduction band of TiO<sub>2</sub> or electron traps below the band edge.

#### 3.2. Electrochemistry

Cyclic voltammetry measurements of the PMIs were done in solution and in nc-TiO<sub>2</sub> thin films. Electrochemistry

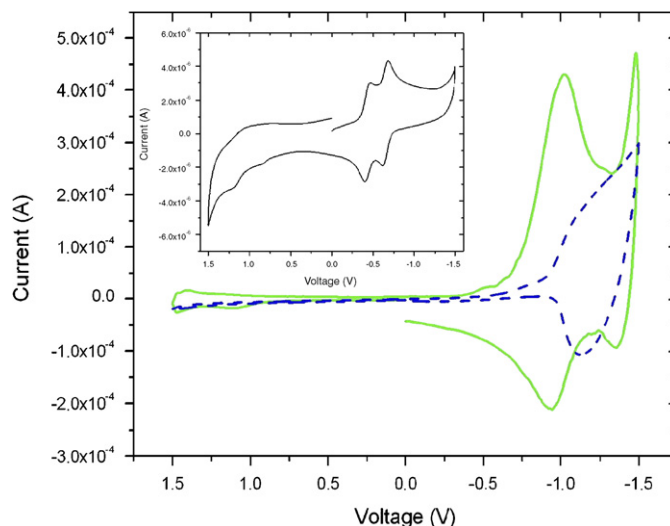


Fig. 1. Cyclic voltammograms of bare nc-TiO<sub>2</sub> film (dashed line), PMI-DA2 adsorbed on nc-TiO<sub>2</sub> electrode (solid line) and PMI-DA2 in solution (inset).

of PMIs in thin films presents some differences in comparison to solution phases. Detected two reversible reduction peaks at −0.4 and −0.6 V in solution phase correspond to the mono and dianion forms of PMIs, respectively. The reduction onsets also shifted slightly toward more positive potentials compared to previous reports of perylenediimides (PDIs) [24]. These shifts may be attributed to the anhydride bonds, which are electrochemically reducible at more positive potentials than imide bonds. Reduction onsets indicate that LUMO energy levels of PMI monoanhydride derivatives are lower than that of PDIs. Although this observation seems to be a disadvantage for DSSCs, PMIs show interesting behavior in the films. One reversible reduction peak was observed in the nc-TiO<sub>2</sub> thin films for PMIs and the reduction onset shifts 30–50 mV more negative potential with respect to potential in solution. This result is attributed to a strong interaction between TiO<sub>2</sub> particles and PMIs. On the dye-adsorbed TiO<sub>2</sub> surface, the anhydride carbonyl vibration of pure PMI at 1770–1750 cm<sup>−1</sup> on FT–IR spectra disappears, but an additional band at 1380 cm<sup>−1</sup> appears and this new signal corresponds to carboxylate stretching. This proves that the anhydride bonds open and anchor to the TiO<sub>2</sub> surface chemically. On the other hand, bare TiO<sub>2</sub> film shows a capacitive current starting from −0.6 V due to the electron flow from FTO electrode to electron traps located between Fermi level and conduction band of TiO<sub>2</sub> (Fig. 1). This negative charge accumulation may lead to a shift at reduction potential of PMIs adsorbed on TiO<sub>2</sub> (Table 1).

#### 3.3. Photovoltaic device performance

Photovoltaic performances of investigated PMIs in DSSC are given in Table 2. Current density–voltage (*I*–*V*) curves measured under standard conditions (AM1.5

Table 1  
Electrochemical redox potentials of PMIs

Dye	$E_0-E_{-1}$ (V)	$E_{-1}-E_{-2}$ (V)	$E_{\text{TiO}_2}$ (V)	$E_{\text{Fc}}$ (V)
PMI-AR	−0.73	−0.96	−1.02	0.41
PMI-MA	−0.45	−0.65	−1.02	0.41
PMI-CH	−0.46	−0.66	−0.98	0.44
PMI-DA1	−0.41	−0.64	−1.02	0.42
PMI-DA2	−0.43	−0.64	−1.02	0.42

Redox potentials are given versus Ag/AgCl reference electrode.

Table 2  
 $I$ – $V$  measurement results of DSSs sensitized with PMI-DA1, PMI-DA2, PMI-MA, PMI-AR, PMI-CH, and standard dye Z-907 under illumination with 100 mW/cm<sup>2</sup> light intensity by AM 1.5 solar simulator

	PMI-DA1	PMI-DA2	PMI-MA	PMI-AR	PMI-CH	Z-907
$V_{\text{oc}}$ (V)	0.300	0.300	0.26	0.251	0.273	0.550
$I_{\text{sc}}$ (mA/cm <sup>2</sup> )	9.79	8.40	6.73	4.1	0.24	18.02
$V_{\text{mpp}}$ (V)	0.200	0.190	0.15	0.169	0.190	0.310
$I_{\text{mpp}}$ (mA/cm <sup>2</sup> )	8.09	6.12	4.37	3.6	1.9	13.64
MPP (mW)	1.61	1.16	0.65	0.60	0.367	4.22
FF	0.55	0.46	0.37	0.58	0.6	0.42
$\eta$ (%)	1.61	1.16	0.65	0.60	0.37	4.22

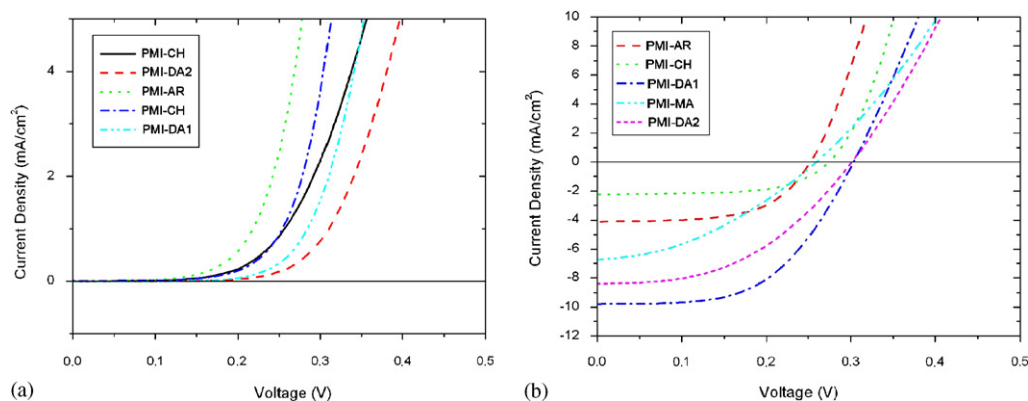


Fig. 2.  $I$ – $V$  curves of PMIs (a) in the dark, (b) under 100 mW/cm<sup>2</sup> AM1.5 illumination.

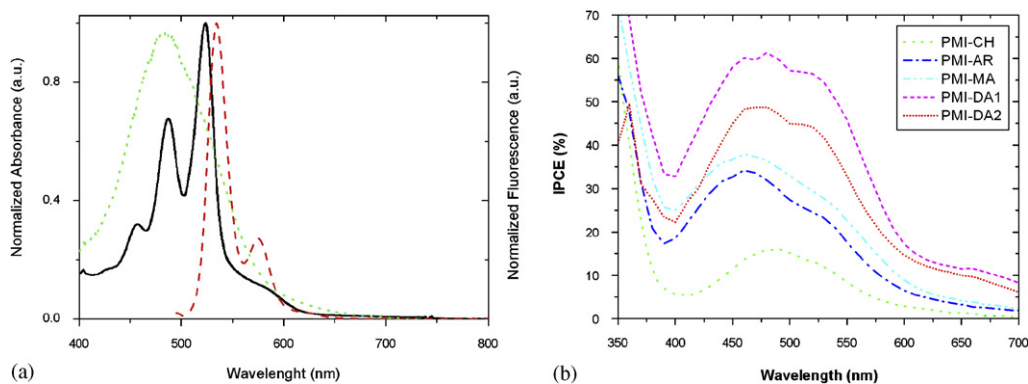


Fig. 3. (a) Normalized UV–vis absorption (—) and fluorescence (---) spectra of PMI-AR solution in toluene and absorption spectrum of PMI-AR adsorbed on nc-TiO<sub>2</sub> surface (····) and (b) IPCE spectra of PMIs.



and 100 mW/cm<sup>2</sup> light intensity) and in the dark (Fig. 2). Monochromatic IPCE spectra of PMIs are shown in Fig. 3. As seen in Table 2, efficiencies improves significantly from the dye PMI-CH to PMI-AR, PMI-MA, PMI-DA2, and PMI-DA1, as 0.37%, 0.60%, 0.65%, 1.16%, and 1.60%, respectively.

The short circuit current densities,  $I_{sc}$ , as well the open circuit voltages,  $V_{oc}$ , increase significantly with three-dimensional mobility-free rotations capacities of the side-chains. As proven at PMI, morphology studies that the three dimensional alkyl side-chains with free rotation capacities, prevent aggregation that enhances the photo-electron transfer injection from dye to titania. Efficiency increases from PMI-MA to PMI-DA2 and to PMI-DA1 are clear demonstrations of such behavior, which may be named as better spacer properties that prevent the charge recombination of electron to electrolyte from the conduction band of TiO<sub>2</sub>. The spacer quality increases starting from 2-ethylhexyl to 2,6-dimethyl-4-heptyl and 6-undecyl groups. In line with these statements, we now report the highest efficiency under standard conditions obtained for a perylene imide derivative with PMI-DA1 that performs 300 mV open circuit voltage, 9.79 mA/cm<sup>2</sup> short-circuit current and 1.61% overall conversion efficiency.

The DSSC with cyclohexyl derivative of PMI-CH exhibits 2.24 mA/cm<sup>2</sup> short circuit current, 273 mV open circuit voltage, and 0.6 fill factor yielding 0.37% efficiency. Another derivative with geometrically similar spacer is 2,6-diisopropylphenyl derivative, PMI-AR, yields about twice better efficiency of  $\eta = 0.60\%$ . This difference may not be attributed to mobility differences, but rather the efficiency differences of electrochemical potentials. Aromatic ring in PMI-AR is a stronger electron donor in comparison to cyclohexyl. Due to higher electron density of the PMI-AR molecule, the LUMO level is higher than PMI-CH. This effect may result in better electron injection to TiO<sub>2</sub> conduction band from PMI-AR.

As seen from the IPCE spectra of PMIs given in Fig. 3(b), there is a complete linearity with comparison to overall conversion efficiencies and short circuit currents as well in Table 2. IPCEs at max. wavelengths for PMI-DA1, PMI-DA2, PMI-MA, PMI-AR, and PMI-CH are 15%, 34%, 38%, 48%, and 61%, respectively.

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