

# Highly Efficient Mesoscopic Dye-Sensitized Solar Cells Based on Donor–Acceptor-Substituted Porphyrins\*\*

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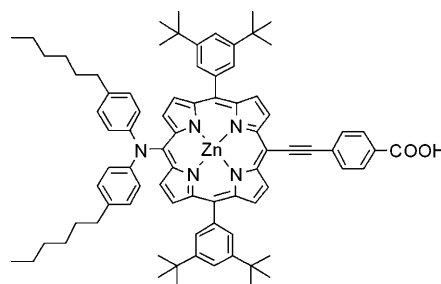
Dye-sensitized solar cells (DSCs) are currently attracting considerable attention because of their high light-to-electricity conversion efficiencies, ease of fabrication, and low production costs.<sup>[1]</sup> Many recent efforts have been devoted to the development of new and efficient sensitizers that are suitable for practical use. Among the investigated compounds, ruthenium sensitizers have been distinguished by attaining more than 11% efficiencies.<sup>[2]</sup> Organic sensitizers have also attracted great interest because of their modest cost, ease of synthesis and modification, large molar absorption coefficients, and satisfactory stability. Organic dyes with conversion efficiencies in the range of 5–10% have been reported.<sup>[3–11]</sup> Porphyrins show strong absorption and emission in the visible region as well as tunable redox potentials. These properties lead to promising applications in many areas, such as optoelectronics, chemosensors, and catalysis.<sup>[12]</sup>

Self-assembled porphyrin molecular structures play a key role in solar energy research as the photosynthetic systems of bacteria and plants contain chromophores based on light-harvesting porphyrins,<sup>[13]</sup> which collect solar energy and convert it efficiently into chemical energy. Various artificial photosynthetic model systems have been designed and synthesized in order to elucidate the factors that control the photoinduced electron-transfer reaction.<sup>[14]</sup> Inspired by the efficient energy transfer in naturally occurring photosynthetic reaction centers, numerous porphyrins<sup>[15]</sup> and phthalocyanines<sup>[16]</sup> have been synthesized and tested in dye-sensitized solar cells. The best-performing porphyrin dyes have been

reported to have conversion efficiencies in DSCs in the range of 5–7%.<sup>[17]</sup> A recently reported series of porphyrin dyes with donor–acceptor (D–A) substituents exhibit promising photovoltaic properties.<sup>[18]</sup>

Herein we report the achievement of an 11% solar-to-electric power conversion efficiency under standard (AM 1.5G, 100 mW cm<sup>-2</sup> intensity) reporting conditions by using a judiciously tailored porphyrin dye, YD-2. To the best of our knowledge, this is the first time such a high efficiency has been obtained with a ruthenium-free sensitizer.

The structure of the YD-2 porphyrin used in this study is shown in Scheme 1. A diarylamino donor group attached to the porphyrin ring acts as an electron donor, and the



Scheme 1. Molecular structure of YD-2.

ethynylbenzoic acid moiety serves as an acceptor. The porphyrin chromophore itself constitutes the  $\pi$  bridge in this particular D– $\pi$ –A structure.<sup>[18]</sup> In a first set of experiments, 2.4  $\mu\text{m}$  thick transparent TiO<sub>2</sub> films loaded with a monolayer of YD-2 were employed in order to accurately measure the spectral response and the internal quantum efficiency of the device. Figure 1 shows the incident photon to current conversion efficiency (IPCE) as a function of the light excitation wavelength. The features of the spectral response of the photocurrent closely match the absorption spectrum of the YD-2 dye. At 460 nm, near the Soret band maximum, the IPCE reaches its highest value of 85%; a second maximum was obtained near 655 nm, where the IPCE is 80%. The value of the absorbance at the latter wavelength was 0.57, thus implying that the sensitizer absorbed 73% of the photons with a wavelength of 655 nm that arrived at the film. By taking into account the light reflection by the counter electrode, the internal quantum efficiency for the generation of an electric current by YD-2 at this wavelength is approximately 100%.

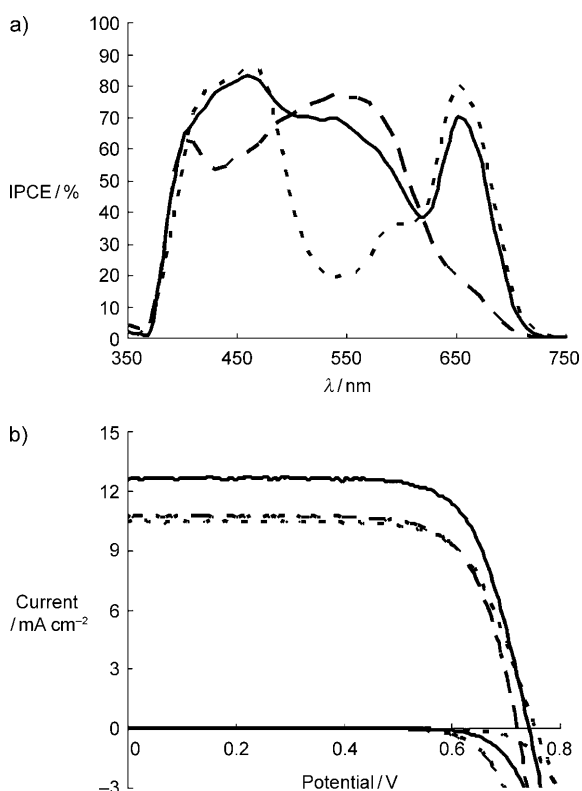
Table 1 shows the short-circuit photocurrent density ( $J_{\text{SC}}$ ), open-circuit photovoltage ( $V_{\text{OC}}$ ), fill factor ( $FF$ ), and power conversion efficiency (PCE) obtained with YD-2 sensitized

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[\*\*] Financial support of this work by the Swiss National Science Foundation and the European Research Council (Advanced Grant no 247404 to M.G.) is gratefully acknowledged. We thank Dr. Carole Grätzel for valuable discussions and editorial help with the manuscript. We also thank Prof. S. Ito and Prof. S. Uchida for the gift of the dye D-205, which was developed and prepared in collaboration with Dr. M. Takata, Dr. H. Miura and Dr. K. Sumioka.



**Figure 1.** a) IPCE action spectra and b)  $J$ - $V$  characteristics of DSC fabricated with YD-2 or D-205 and cosensitized with a YD-2/D-205 mixture. The  $J$ - $V$  curves were measured under 100% sun (AM 1.5G) for YD-2 (---), D-205 (-·-·-), YD-2/D-205 (—).

**Table 1:** Photovoltaic parameters of DSCs based on YD-2.<sup>[a]</sup>

Thickness [μm]	$V_{oc}$ [mV]	$J_{sc}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
2.4	755	10.5	71.2	5.6
4.5	750	13.3	69.8	6.9
6.7	739	15.0	70.9	7.9
8.9	732	16.3	71.0	8.4
11.5	735	16.7	71.5	8.8

[a] DSCs made from YD-2 sensitized transparent nanocrystalline TiO<sub>2</sub> films of various thicknesses by employing a volatile electrolyte (Z960) at full sunlight intensity.

transparent nanocrystalline TiO<sub>2</sub> films, the thickness of which varied from 2.4 to 11.5 μm. Even the thinnest films gave an impressive PCE of 5.6% under illumination by standard AM 1.5G simulated sunlight (100 mW cm<sup>-2</sup>). The PCE reached 8.8% at 11.5 μm mainly because of the increase in  $J_{sc}$  from 10.5 to 16.7 mA cm<sup>-2</sup>, which is accompanied by a small drop in the  $V_{oc}$  value of 20 mV. The fill factor remained remarkably stable at a value of around 0.7, despite a 60% increase in photocurrent and a more than fourfold increase in film thickness, thus showing that any losses in fill factor caused by contributions from the internal resistance of the device must be small. These results are promising for the practical use of YD-2 type sensitizers in transparent dye-sensitized solar cell panels. The sensitizers exhibit a beautiful

green color for windows and glass facades that produce solar electricity.

Although aesthetically pleasing, the green coloration of the YD-2 sensitized TiO<sub>2</sub> films results in a lack of light harvesting in the 480–630 nm range, which leads to the reduction of the  $J_{sc}$  and PCE values of the device. This result is clearly apparent from the IPCE spectrum, which shows a pronounced dip with a minimum at around 530 nm, where the IPCE value decreases to a mere 20% (Figure 1). Hence, cosensitization by the D-205 dye, which shows complementary spectral responses in the visible spectral range was attempted in order to increase the light harvesting in the green-wavelength region. The D-205 dye has an absorption maximum at 532 nm that coincides with the minimum of the IPCE response of the YD-2 dye. The absorption maxima of D-205 in THF and for YD-2 in ethanol are 532 nm (53 000 M<sup>-1</sup> cm<sup>-1</sup>) and 644 nm (31 200 M<sup>-1</sup> cm<sup>-1</sup>), respectively.<sup>[18,19]</sup> The photovoltaic performance of cosensitized dyes was enhanced in comparison to that of a solar cell containing a single dye. The IPCEs of devices made with individual dyes and by cosensitization are shown in Figure 1 a. For cosensitization, the TiO<sub>2</sub> surface was initially coated with a monolayer of the YD-2 dye by dipping the TiO<sub>2</sub> into a solution of the dye for 16 hours, followed by immersion of the electrode in a solution of the D-205 dye for 30 minutes and then washing with acetonitrile to remove any excess dye. The peaks corresponding to two different dyes are clearly shown in the IPCE spectra of the cosensitized devices. The cosensitization of the TiO<sub>2</sub> electrode by D-205 results in a dramatic enhancement of the photocurrent response in the spectral region of 480–580 nm, where the IPCE spectrum of the YD-2 dye shows a dip.

The photovoltaic parameters of these solar cells are given in Table 2. It is emphasized that the D-205 and YD-2 dyes gave almost identical efficiencies and  $J_{sc}$  values when measured separately. Devices based on the coadsorbed dyes

**Table 2:** Photovoltaic parameters of DSCs based on YD-2 and D-205.<sup>[a]</sup>

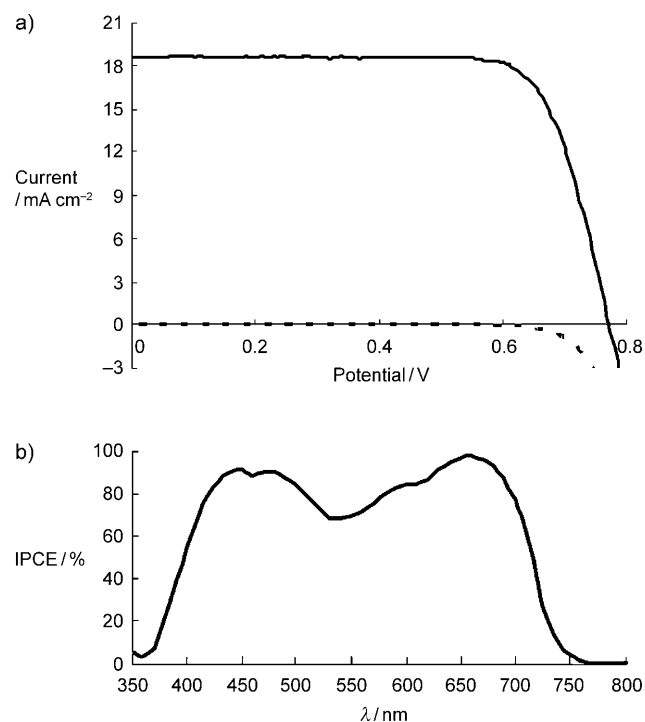
Sensitizer	$V_{oc}$ [mV]	$J_{sc}$ [mA cm <sup>-2</sup> ]	FF [%]	PCE [%]
YD-2/D-205	742	12.6	73.2	6.9
D-205	720	10.8	73.2	5.7
YD-2	755	10.5	71.2	5.6

[a] DSCs made from YD-2 and D-205 as cosensitizers under full sunlight intensity by employing a volatile electrolyte (Z960) and a 2.4 μm thick film.

D-205 and YD-2 showed a 20% increase in  $J_{sc}$  values with a concomitant 20% increase in efficiency (Figure 1). These enhanced values result from filling the dip in the IPCE spectrum of the YD-2 device. The PCE attains a value close to 7% for the cosensitized device, which is the highest reported to date for a 2.4 μm thick transparent titania film, hence showing that effective panchromatic light harvesting is achieved by the combination of the two sensitizers despite the short optical path length. This approach reveals an

important feature for solid-state DSCs where the diffusion length of the device becomes a limiting factor.<sup>[20]</sup>

To further increase the light-harvesting capacity of these devices, an 11  $\mu\text{m}$  transparent  $\text{TiO}_2$  film was coated with a 5  $\mu\text{m}$  thin layer of 400 nm reflecting particles. The characteristic  $J$ - $V$  curve of the solar cell containing YD-2 is shown in Figure 2a. The IPCE spectrum of the YD-2 device exhibits a broad absorption from 400 nm to 750 nm with a peak maximum over 90% at 675 nm (Figure 2b). A  $J_{\text{SC}}$  of  $18.6 \text{ mA cm}^{-2}$ , a  $V_{\text{OC}}$  of 0.77 V, and a  $FF$  of 0.764 were derived



**Figure 2.** a) Photocurrent density–voltage ( $J$ - $V$ ) characteristics of a device (2.4  $\mu\text{m}$  thick film) using YD-2 as sensitizer under AM 1.5G illumination ( $100 \text{ mW cm}^{-2}$ ). Values for dark current (-----) and 100% sun (—) are shown. b) Incident photon-to-current conversion efficiency (IPCE) spectrum of the same device.

from the  $J$ - $V$  curve, thus giving an overall power conversion efficiency ( $\eta$ ) of 11% under illumination with standard AM 1.5G simulated sunlight ( $100 \text{ mW cm}^{-2}$ ). The  $J_{\text{SC}}$  value obtained from integrating the product of the IPCE spectrum with the AM 1.5G spectral solar photon flux was  $17.6 \text{ mA cm}^{-2}$ . This value lies within 5% of the measured  $J_{\text{SC}}$  value, thus showing that any spectral mismatch of the simulated sunlight with regard to standard AM 1.5G emission is small.

In conclusion, the integration of a porphyrin chromophore as  $\pi$  bridge into a D- $\pi$ -A dye resulted in a new conjugated porphyrin dye that exhibits an unprecedented efficiency of 11% when used as a photosensitizer on a double-layer  $\text{TiO}_2$  film under standard illumination test conditions. It has also been demonstrated that this novel porphyrin dye shows a greatly enhanced photovoltaic performance when cosensitized on a thin  $\text{TiO}_2$  film (2.4  $\mu\text{m}$ ) with a metal-free

dye that has a complementary spectral response. Testing of cosensitization for various  $\text{TiO}_2$  film designs are the next step in our investigation. The present study has opened new possibilities for the improvement of photovoltaic performance through a judicious design of the donor–acceptor substitution on porphyrin dyes.

### Experimental Section

**Device fabrication:** Screen-printed layers of  $\text{TiO}_2$  films were prepared as previously reported.<sup>[3c]</sup> The transparent film was prepared with a  $\text{TiO}_2$  nanoparticle paste (DSL-18NRT) obtained from Dysol, Australia. After sintering at  $500^\circ\text{C}$  and cooling to  $80^\circ\text{C}$ , the sintered  $\text{TiO}_2$  electrodes were sensitized by immersion in a solution of the YD-2 dye (0.2 mM in ethanol with 0.4 mM chenodeoxycholic acid, CDCA) for 18 h, and then assembled using a thermally platinized FTO/glass (Tec 7) counter electrode. For the cosensitization experiments,  $\text{TiO}_2$  electrodes were first immersed in a solution of YD-2 (0.2 mM in ethanol with 0.4 mM CDCA) for 18 h, rinsed with acetonitrile, and then immersed in a solution of D-205 (0.2 mM in *tert*-butanol/acetonitrile (1:1) with 0.4 mM CDCA) for 30 min. Following the immersion procedure, the dye-sensitized electrode was rinsed with acetonitrile and dried in air. The working and counter electrodes were separated by a 25  $\mu\text{m}$  thick hot melt ring (Surlyn, DuPont) and sealed by heating. The cell internal space was filled with a volatile electrolyte (Z960: 1.0 M 1,3-dimethylimidazolium iodide, 0.03 M iodine, 0.5 M *tert*-butylpyridine, 0.05 M LiI, 0.1 M guanidinium thiocyanate), in an 85:15 acetonitrile/valeronitrile mixture through a pre-drilled hole using a vacuum pump. The electrolyte injection hole on the thermally platinized FTO glass counter electrode was finally sealed with a Surlyn sheet and a thin glass cover by heating.

**Photovoltaic characterization:** A 450 W xenon light source (Oriel, USA) was used to characterize the solar cells. The spectral output of the lamp was matched in the region of 350–750 nm with the aid of a Schott K113 Tempax sunlight filter (Präzisions Glas & Optik GmbH, Germany) so as to reduce the mismatch between the simulated and true solar spectra to less than 2%. The current–voltage characteristics of the cell measured under these conditions were obtained by applying external potential bias to the cell and by measuring the generated photocurrent with a Keithley model 2400 digital source meter (Keithley, USA). The devices were masked to attain an illuminated active area of  $0.16 \text{ cm}^2$ .

Received: April 9, 2010

Published online: August 4, 2010

**Keywords:** donor–acceptor systems · dyes/pigments · energy conversion · porphyrinoids · solar cells

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