Novel unsymmetrically π -elongated porphyrin for dye-sensitized TiO₂ cells[†]

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Received (in Cambridge, UK) 16th February 2007, Accepted 11th April 2007 First published as an Advance Article on the web 26th April 2007 DOI: 10.1039/b702501g

A novel naphthyl-fused zinc porphyrin carboxylic acid has been synthesized and employed successfully in a dye-sensitized TiO_2 solar cell, with a power conversion efficiency of 4.1%, which is improved by 50% relative to the unfused porphyrin reference cell.

Since the first report on a high power conversion efficiency (η) in dye-sensitized solar cells by Grätzel and coworkers, they have been extensively investigated.¹ To date, ruthenium(II) bipyridyl complexes have proven to be the most efficient TiO₂ sensitizers ($\eta = 9 - 11\%$).² On the other hand, the use of porphyrins as light harvesters on solar cells is particularly attractive given their primary role in photosynthesis.³ However, the η values of porphyrin-sensitized nanocrystalline TiO₂ cells are much smaller than those of ruthenium dye-sensitized nanocrystalline TiO₂ cells because of their insufficient light-harvesting properties in the visible region.³

Porphyrins have very strong absorption in the 400-450 nm region (Soret band) and weak absorption in the 500-700 nm region (Q bands).⁴ Both Soret and Q bands arise from π - π^* transitions and can be explained in terms of a linear combination of transitions from slightly splitting HOMO and HOMO-1 to a degenerate pair of LUMOs. The configuration interaction leads to the intense short-wavelength Soret band and the weak longwavelength Q bands. The elongation of π -conjugation and loss of symmetry causes splitting in the π and π^* levels and reduces the HOMO-LUMO gap, resulting in broadening of the absorption and an increasing intensity of Q bands. More importantly, the Soret and Q bands are red-shifted, which improves the overlap between the absorption and solar energy distribution on the earth. Although there have been several reports on the synthesis of aromatic ring-fused, π -extended porphyrins with low symmetry,⁵ they have never been applied to dye-sensitized solar cells.

Here we report the first application of aromatic ring-fused, π -extended porphyrins with low symmetry (**fused-Zn-1**) to dyesensitized solar cells. We designed a novel naphthyl-fused zinc porphyrin carboxylic acid (Scheme 1). The unsymmetrically π -elongated porphyrin is expected to collect visible light efficiently, leading to the improvement of the photovoltaic properties. To facilitate electron injection from the porphyrin excited singlet state to the conduction band (CB) of a TiO₂ electrode, a carboxyl group is attached to the fused naphthyl moiety in the porphyrin ring. Bulky mesityl groups are also introduced at the three *meso* positions of the porphyrin ring to reduce the aggregation of the porphyrin molecules on the TiO₂ surface.^{6,7}

The synthetic route to **fused-Zn-1** is shown in Scheme 1. 5-(4-Carbomethoxynaphth-1-yl)-10,15,20-tris(2,4,6-trimethylphenyl) porphyrin (**H**₂-1) was synthesized by the cross-condensation of mesityldipyrromethane with 4-carbomethoxynaphthylaldehyde and 2,4,6-trimethylbenzaldehyde. Ni(II)-metallation was carried out by the treatment of **H**₂-1 with Ni(acac)₂ at 110 °C to yield **Ni-1**. Ring-closure was achieved by the treatment of **Ni-1** with FeCl₃.^{5e} Subsequent demetallation, hydrolysis, and Zn(II)-metallation gave **fused-Zn-1**. Porphyrin reference **Zn-1** was also prepared from **H**₂-1. Their structures were verified by spectroscopic analyses including ¹H NMR and MALDI-TOF mass spectra (see Supporting Information).

Fig. 1 displays UV–visible absorption spectra of **fused-Zn-1** and **Zn-1** in CH₂Cl₂. As we expected, the light-harvesting properties of **fused-Zn-1** are improved by the expansion of the π -system and loss of symmetry. The absorption of **fused-Zn-1** ($\lambda_{max} = 482$ nm, $\varepsilon = 1.24 \times 10^5$; 682 nm, $\varepsilon = 2.46 \times 10^4$) is red-shifted and broadened compared to that of **Zn-1** (422 nm, $\varepsilon = 4.33 \times 10^5$; 551 nm, $\varepsilon = 2.07 \times 10^4$). The molar absorptivity at the Soret band



Scheme 1 Reagents and conditions: a) $BF_3(OEt_2)$, $CHCl_3$, r.t., 2 h; b) DDQ, 1 h, 9% (2 steps); c) Ni(acac)_2, toluene, reflux, 20 h, 82%; d) FeCl_3, CH_2Cl_2, CH_3NO_2, r.t., 30 min; e) TFA, H_2SO_4, 16% (2 steps); f) KOH, H_2O, THF, EtOH, reflux, 4 h; g) Zn(OAc)_2, CHCl_3, r.t., 4 h, 77% for fused-Zn-1 (2 steps).

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[†] Electronic supplementary information (ESI) available: Experimental, electrochemical data. See DOI: 10.1039/b702501g



Fig. 1 UV-visible absorption spectra of fused-Zn-1 (solid line) and Zn-1 (dashed line) in CH_2Cl_2 .

of fused-Zn-1 is lower than that of Zn-1, however, the integrated molar absorptivity with respect to wavenumber at the Soret band region (400–530 nm) is rather comparable for fused-Zn-1 (3.3 \times 10^8) and **Zn-1** (4.2 × 10^8). More importantly, the integrated value of the molar absorptivity at the Q band region (530-750 nm) of **fused-Zn-1** (5.0 \times 10⁷) is two times larger than that of **Zn-1** (2.5 \times 10^7). These results ensure that the incident light is absorbed intensively in the visible and near-infrared regions by fused-Zn-1. The fluorescence spectra of fused-Zn-1 and Zn-1 were also measured in CH₂Cl₂ excited at the peak position of the Soret band (see Fig. S1). The emission maximum of fused-Zn-1 (716 nm) is red-shifted relative to that of Zn-1 (601 nm), which is consistent with the results on the UV-visible absorption spectra. From the intercept of the normalized absorption and emission spectra, the zeroth-zeroth energies (E_{0-0}) are determined (see Table S1). The difference in E₀₋₀ values of fused-Zn-1 (1.80 eV) and Zn-1 (2.15 eV) implies a small HOMO-LUMO gap of the π -elongated porphyrin. Cyclic voltammetry was used to determine the first oxidation potentials of the porphyrins. All porphyrins exhibited reversible waves for a one-electron oxidation in CH2Cl2 containing 0.1 M Bu₄NPF₆. The first oxidation potential of fused-Zn-1 (0.99 V vs. NHE) is shifted by 0.05 V in the negative direction compared to that of Zn-1 (1.04 V vs. NHE) as a result of the π -elongation. The energy levels of the porphyrin excited singlet state for fused-Zn-1 (-0.78 V vs. NHE) and Zn-1 (-1.11 V vs. NHE) are higher than the CB of TiO₂ (-0.5 V vs. NHE),⁷ whereas the energy levels of the porphyrin radical cation for fused-Zn-1 (0.99 V vs. NHE) and **Zn-1** (1.04 V vs. NHE) are lower than those of the I^{-}/I_{3}^{-} couple (0.5 V vs. NHE).⁷ Thus, charge separation from the porphyrin excited singlet state to the CB of TiO₂ and charge shift from the I^{-}/I_{3}^{-} couple to the porphyrin radical cation are thermodynamically feasible.8

Nanoporous films were prepared from a colloidal suspension of TiO_2 nanoparticles (P25) dispersed in distilled water.⁹ The suspension was deposited on a transparent conducting glass by using a doctor blade technique. The films were annealed at 673 K for 10 min, followed by similar deposition and annealing (723 K, 2 h) for the 10 µm-thick TiO₂ films. The TiO₂ electrodes were immersed in MeOH containing 0.2 mM **fused-Zn-1** for 0.5 h or

Zn-1 for 1 h at room temperature. The total amounts of the porphyrins adsorbed on the TiO₂ films were determined by measuring the absorbance of the porphyrins, which were dissolved from the porphyrin-adsorbed TiO₂ films into DMF containing 0.1 M NaOH.7 Taking into account the surface area of P25 $(54 \text{ m}^2 \text{ g}^{-1})$,^{7,9} the porphyrin densities (Γ) on the actual surface area were determined from the total amount of the porphyrins adsorbed on the TiO₂ films (fused-Zn-1, 7.8 \times 10⁻¹¹ mol cm⁻²; **Zn-1**, 8.2 \times 10⁻¹¹ mol cm⁻²). Assuming that the porphyrin molecules are densely packed onto the TiO₂ surface to make a monolayer where the single bond between the carboxyl group and the naphthyl moiety is perpendicular to the TiO₂ surface, the ideal Γ values are estimated to be 9.1 \times 10⁻¹¹ for **fused-Zn-1** and 1.0 \times 10^{-10} for **Zn-1**, which largely agree with the experimental values. Reflecting the distorted structure of **fused-Zn-1**, the ideal Γ value of fused-Zn-1 is smaller than that of Zn-1 (see Fig. S2). Immersion of the TiO₂ electrode into the porphyrin solutions for a longer time (>1 h) did not increase the Γ value, showing saturated behavior of the porphyrin adsorption on the TiO₂ surface.

The current-voltage characteristics were measured using the 10 µm-thick TiO₂ electrode modified with each porphyrin and a Pt counter electrode under AM 1.5 conditions (100 mW cm⁻²).⁷ The η value is derived from the equation $\eta = J_{\rm SC} \times V_{\rm OC} \times ff$, where $J_{\rm SC}$ is short circuit current density (mA cm⁻²), $V_{\rm OC}$ is open circuit potential (V), and ff is fill factor. For the fused-Zn-1-sensitized cell, $J_{\rm SC}$ of 10.6 mA cm⁻², $V_{\rm OC}$ of 0.62 V, and *ff* of 0.62 yield η of 4.1%, while for the Zn-1-sensitized cell, J_{SC} of 6.7 mA cm⁻², V_{OC} of 0.61 V, and ff of 0.68 yield η of 2.8% (see Fig. S3). Thus, the η value of the fused-Zn-1-sensitized cell is larger by 50% than that of the Zn-1-sensitized cell. Action spectra of incident photon-tocurrent efficiency (IPCE) for the fused-Zn-1- and the Zn-1sensitized cells are depicted in Fig. 2. The action spectra are similar to the corresponding absorption spectra on the TiO₂ electrode (Fig. S4) as well as in CH_2Cl_2 (Fig. 1). It is noteworthy that the fused-Zn-1-sensitized cell reveals high IPCE values of up to 55%,



Fig. 2 Action spectra of **fused-Zn-1** (solid line) and **Zn-1** (dashed line)-sensitized solar cells. Conditions: electrolyte 0.1 M LiI, 0.05 M I₂, 0.6 M 2,3-dimethyl-1-propylimidazolium iodide, and 0.5 M 4-t-butyl-pyridine in CH₃CN; input power: AM 1.5 under simulated solar light (100 mW cm⁻²).



Fig. 3 Molecular orbitals of fused-Zn-1 and Zn-1 calculated at the B3LYP/3-21G* level.

extending the response of the photocurrent generation close to 800 nm. The improved photocurrent generation of the fused-Zn-1sensitized cell relative to that of the Zn-1-sensitized cell parallels the results on the η values. To shed light on the electronic structures of fused-Zn-1 and Zn-1, DFT calculations were performed. Geometry optimization and vibration frequency analysis were carried out at the B3LYP/3-21G* level. The optimized structures have no negative frequencies. The electron densities of HOMO and LUMO in fused-Zn-1 are delocalized over the elongated π system (Fig. 3), which is in good agreement with the UV-visible absorption and fluorescence spectra and the electrochemical studies. It should be noted here that there are significant electron densities on the carboxyl group in LUMO of fused-Zn-1, whereas no apparent electron densities are seen on the carboxy group in LUMO of Zn-1. The comparison supports efficient electron injection from the porphyrin excited singlet state to the CB of the TiO₂ electrode in the fused-Zn-1-sensitized cell owing to the strong electronic coupling between the porphyrin and the TiO2 surface through the carboxyl group. Thus, the strong electronic coupling also rationalizes the higher η value of the **fused-Zn-1**-sensitized cell in comparison with the Zn-1-sensitized cell. On the other hand, the porphyrin plane of fused-Zn-1 is strained due to the steric hindrance between the β -proton and that of the fused naphthalene ring compared to that of Zn-1. The strain of the porphyrin ring is likely to cause fast nonradiative relaxation in the porphyrin excited singlet state, resulting in moderate improvement of the power conversion efficiency.

In conclusion, we have successfully synthesized a novel unsymmetrically π -elongated porphyrin to apply it to a dyesensitized TiO₂ solar cell for the first time. The porphyrinsensitized TiO₂ cell exhibited a power conversion efficiency of 4.1%, which was improved by 50% relative to the unfused porphyrin reference cell. These results clearly show that the elongation of a porphyrin π -system with low symmetry is a useful tactic for collecting solar light in the visible and near infrared regions, leading to improved cell performance of porphyrin-sensitized solar cells. Further improvement of the power conversion efficiency in porphyrin-sensitized TiO₂ cells will be possible by designing a planar fused porphyrin in which a larger aromatic ring is used as a fused moiety instead of a naphthalene ring.

This work was supported by the Strategic University/Industry Alliance of the International Innovation Center, Kyoto University. We gratefully acknowledge Prof. Susumu Yoshikawa (Kyoto University) and Prof. Shozo Yanagida (Osaka University) for the use of equipment for photovoltaic measurements. Computation time was provided by the Supercomputer Laboratory, Institute for Chemical Research, Kyoto University, and the Academic Center for Computing and Media Studies, Kyoto University.

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