Novel unsymmetrically π-elongated porphyrin for dye-sensitized TiO_2 cells†

Masanobu Tanaka,[a] Shinya Hayashi,[b] Seunghun Eu,[b] Tomokazu Umeyama,[b] Yoshihiro Matano[b] and Hiroshi Imahori*[b]

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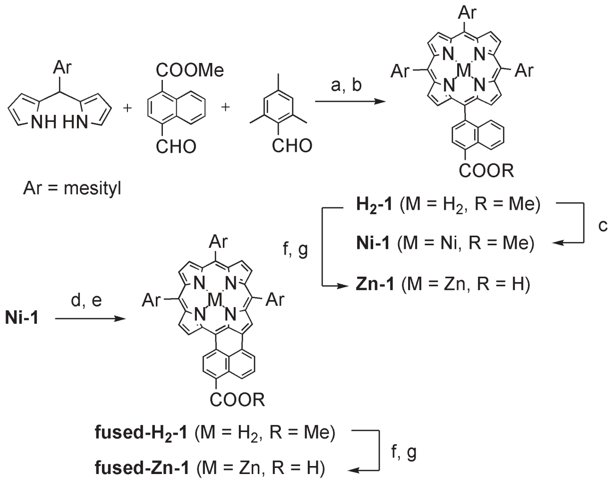
A novel naphthyl-fused zinc porphyrin carboxylic acid has been synthesized and employed successfully in a dye-sensitized TiO_2 solar cell, with a power conversion efficiency of 4.1%, which is improved by 50% relative to the unfused porphyrin reference cell.

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 TiO_2 sensitizers (η = 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 TiO_2 cells are much smaller than those of ruthenium dye-sensitized nanocrystalline TiO_2 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 long-wavelength 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 dye-sensitized 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 TiO_2 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 TiO_2 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 $FeCl_3$.[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).



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).

Fig. 1 displays UV–visible absorption spectra of **fused-Zn-1** and **Zn-1** in CH_2Cl_2. 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** (λ_{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

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[a] *Kyoto University International Innovation Center, Nishikyo-ku, Kyoto 615-8520, Japan*
[b] *Department of Molecular Engineering, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: imahori@scl.kyoto-u.ac.jp; Fax: +81-75-383-2571; Tel: +81-75-383-2566*

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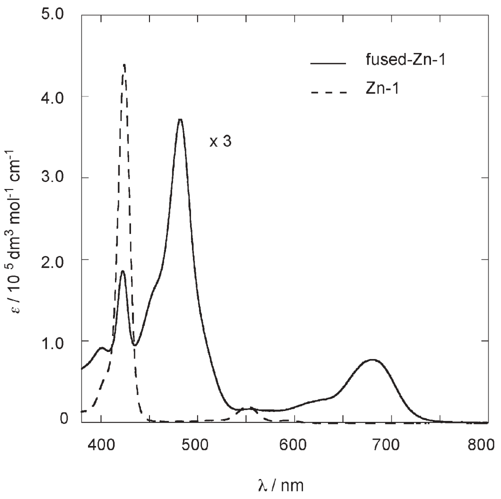

Fig. 1 UV–visible absorption spectra of **fused-Zn-1** (solid line) and **Zn-1** (dashed line) in CH_2Cl_2.

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** (3.3×10^8) 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** (5.0×10^7) is two times larger than that of **Zn-1** (2.5×10^7). 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 CH_2Cl_2 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 ($E_{0\text{-}0}$) are determined (see Table S1). The difference in $E_{0\text{-}0}$ 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 CH_2Cl_2 containing 0.1 M Bu_4NPF_6. 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 TiO_2 (−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 TiO_2 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 TiO_2 films. The TiO_2 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 TiO_2 films were determined by measuring the absorbance of the porphyrins, which were dissolved from the porphyrin-adsorbed TiO_2 films into DMF containing 0.1 M NaOH.[7] Taking into account the surface area of P25 (54 m^2 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 TiO_2 films (**fused-Zn-1**, 7.8×10^{-11} mol cm^{-2}; **Zn-1**, 8.2×10^{-11} mol cm^{-2}). Assuming that the porphyrin molecules are densely packed onto the TiO_2 surface to make a monolayer where the single bond between the carboxyl group and the naphthyl moiety is perpendicular to the TiO_2 surface, the ideal Γ values are estimated to be 9.1×10^{-11} for **fused-Zn-1** and 1.0×10^{-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 TiO_2 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 TiO_2 surface.

The current–voltage characteristics were measured using the 10 μm-thick TiO_2 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 $\eta = J_{SC} \times V_{OC} \times ff$, where J_{SC} is short circuit current density (mA cm^{-2}), V_{OC} is open circuit potential (V), and ff is fill factor. For the **fused-Zn-1**-sensitized cell, J_{SC} of 10.6 mA cm^{-2}, V_{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-to-current efficiency (IPCE) for the **fused-Zn-1**- and the **Zn-1**-sensitized cells are depicted in Fig. 2. The action spectra are similar to the corresponding absorption spectra on the TiO_2 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%,

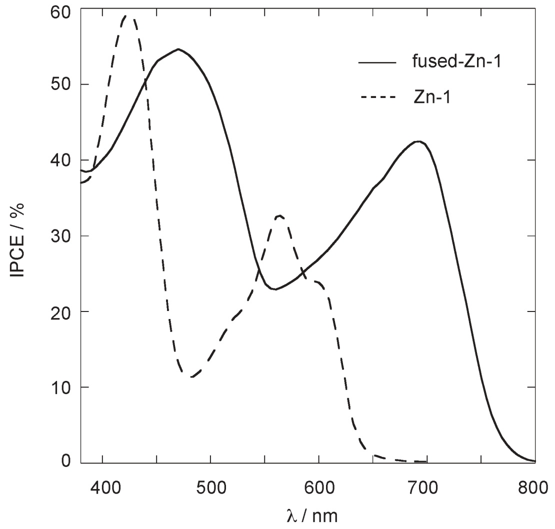

Fig. 2 Action spectra of **fused-Zn-1** (solid line) and **Zn-1** (dashed line)-sensitized solar cells. Conditions: electrolyte 0.1 M LiI, 0.05 M I_2, 0.6 M 2,3-dimethyl-1-propylimidazolium iodide, and 0.5 M 4-t-butylpyridine in CH_3CN; input power: AM 1.5 under simulated solar light (100 mW cm^{-2}).

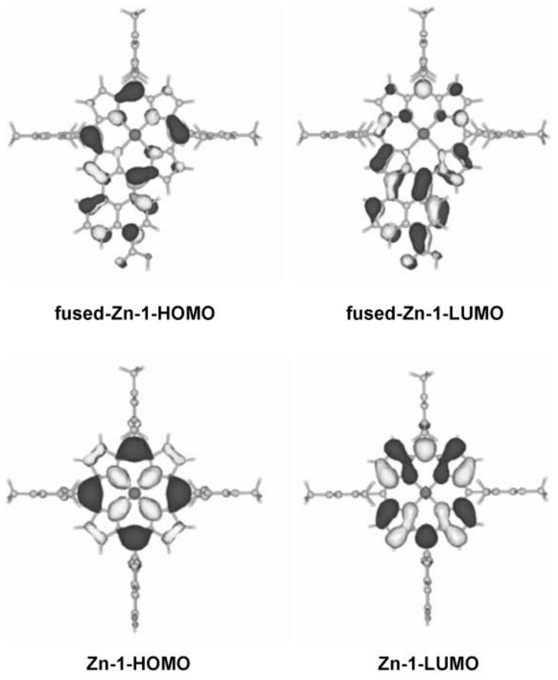

Fig. 3 Molecular orbitals of **fused-Zn-1** and **Zn-1** calculated at the B3LYP/3-21G* level.

extending the response of the photocurrent generation close to 800 nm. The improved photocurrent generation of the **fused-Zn-1**-sensitized 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 TiO_2 electrode in the **fused-Zn-1**-sensitized cell owing to the strong electronic coupling between the porphyrin and the TiO_2 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 dye-sensitized TiO_2 solar cell for the first time. The porphyrin-sensitized TiO_2 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 TiO_2 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.

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