Fused Five-membered Porphyrin for Dye-sensitized Solar Cells

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Fused five-membered zinc porphyrin carboxylic acid has been synthesized to improve light-harvesting capability in the visible and near-infrared regions. The fused porphyrin-sensitized TiO₂ cell exhibited the photocurrent generation extending over 800 nm, although the power conversion efficiency was found to be moderate (0.30%).

Recently, dve-sensitized solar cells (DSSC) have attracted much attention because of their relatively high power conversion efficiency (η) and potential low-cost production.¹ Ruthenium(II) bipyridyl complexes have proven to be the most efficient TiO₂ sensitizers $(\eta = 9-11\%)^{2}$, whereas it is highly desirable to develop other organic dyes using inexpensive metal or without metal, which exhibit high cell performance.³ Porphyrins have strong absorption at 400-450 nm (Soret band) and relatively weak absorption at 500-700 nm (Q bands), thus they have been regarded as promising sensitizers in DSSC.⁴ The drawback of porphyrins is the insufficient light-harvesting ability in the visible and near-infrared (NIR) regions relative to Ru-based dyes. To surmount this problem, we have synthesized unsymmetrically π -elongated porphyrins for DSSC.⁵ As the results of the elongation of the porphyrin π -system with low symmetry, the absorption of the porphyrins was broadened and red-shifted, leading to improvement of the η value up to 5.2%.⁵ Nevertheless, in terms of the light-harvesting properties of porphyrins in the NIR region there is still room for further improvement.

Here, we report the first application of fused five-membered porphyrin to DSSC. Although fused five-membered porphyrins have been known to reveal broadening and red shift of the absorption, they have yet to be used in DSSC.⁶ The synthetic route to fused-ZnP is shown in Scheme 1. Starting porphyrin (H₂P) was treated with *N*-bromosuccinimide (NBS) to yield monobrominated porphyrin (H₂P-Br). The intramolecular fused



UV-vis absorption spectra of fused-ZnP and ZnP-ref were measured in CH₂Cl₂. The peak positions and molar absorption coefficients (E) are listed in Table S1.8 Compared with ZnPref. fused-ZnP reveals broadening and red shift of Soret and O bands due to expansion of the π system with low symmetry (Figure 1), as seen in fused six-membered porphyrins.^{5a} It is noteworthy that the absorption edge of fused-ZnP is extended to ca. 800 nm. Steady-state fluorescence spectra of fused-ZnP and ZnP-ref were also measured in CH₂Cl₂ by exciting at the Soret band wavelength (Figure S1).⁸ The fluorescence spectrum of fused-ZnP also reveals red-shifted emission with a maximum of 772 nm, relative to ZnP-ref, which is consistent with the results obtained from the UV-vis absorption spectra. The first oxidation potentials (E_{ox}) of fused-ZnP and ZnP-ref were determined by differential pulse voltammetry in CH₂Cl₂ containing Bu₄NPF₆ as a supporting electrolyte (Table S1).⁸ Owing to the elongation of the π system, the E_{ox} value of fused-ZnP (0.93 V vs. NHE) is negatively shifted by 0.07 V in comparison with ZnP-ref (1.00 V vs. NHE). The excited-state oxidation potentials (Eox*) of fused-ZnP (-0.69 V) and ZnP-ref (-1.10 V) were estimated from the respective E_{ox} values and the zeroth-zeroth energy (E_{0-0}) . Taking into account the energy levels of the conduction band (CB) of TiO_2 (-0.5 V vs. NHE)⁵ and I^{-}/I_{3}^{-} couple (0.5 V vs. NHE),⁵ electron injection from the porphyrin excited singlet state to the CB of TiO₂ and charge shift from I⁻ to the resulting porphyrin radical cation are thermodynamically feasible both in the fused-ZnP and ZnP-ref cells



Scheme 1. Reagent and conditions: a) NBS, $CHCl_3$, reflux, 4 h; b) K_2CO_3 , $Pd_2(dba)_3 \cdot CHCl_3$, DMF, reflux, 30 min; c) $Zn(OAc)_2$, $CHCl_3$, MeOH, rt, 2 h; d) NaOH, H₂O, THF, reflux, 1 day.



Figure 1. UV–vis absorption spectra of fused-ZnP (solid line) and ZnP-ref (dashed line) in CH_2Cl_2 .

(Table S1).⁸ Geometry optimization and vibrational frequency analysis of fused-ZnP and ZnP-ref were performed by DFT methods. Both of the optimized geometries have no negative frequencies. The optimized geometries show that fused-ZnP and ZnP-ref possess planar porphyrin rings (Figure S2).⁸ The electron densities of HOMO and LUMO in fused-ZnP and ZnP-ref are delocalized over the fused five-membered porphyrin and the porphyrin, respectively (Figure S3).⁸

The porphyrin-modified TiO₂ electrodes were prepared by immersing the mesoporous TiO₂ electrodes with 10-µm thickness into 0.2 mM porphyrin MeOH solution at room temperature for 1 h. Given the surface area of P25 $(54 \text{ m}^2 \cdot \text{g}^{-1})$,⁵ the porphyrin densities (Γ) on the actual surface area are determined to be $1.1 \times 10^{-10} \text{ mol} \text{ cm}^{-2}$ for TiO₂/fused-ZnP and 1.2×10^{-10} mol cm⁻² for TiO₂/ZnP-ref. Assuming that the porphyrin molecules are densely packed onto the TiO₂ surface to make a monolayer, the ideal Γ values are calculated to be 1.2 \times 10⁻¹⁰ mol·cm⁻² both for fused-ZnP and ZnP-ref. The experimental Γ values are in good agreement with the calculated Γ values, implying that a well-packed porphyrin monolayer is formed on the TiO₂ surface. UV-vis absorption spectra of $TiO_2/fused$ -ZnP and TiO_2/ZnP -ref electrodes were also measured. The light-harvesting properties of TiO₂/fused-ZnP at around 400-500 and 600-800 nm are remarkably improved compared to those of TiO₂/ZnP-ref (Figure 2) considering the solar energy distribution on the earth.

Cell performances of the TiO₂/fused-ZnP and TiO₂/ZnPref electrodes were evaluated under standard AM 1.5 conditions (100 mW·cm⁻²).⁵ The current–voltage characteristics are given in Figure S4. The η value of the fused-ZnP cell ($J_{SC} =$ 0.88 mA·cm⁻², $V_{OC} = 0.51$ V, ff = 0.67, $\eta = 0.30\%$) is much smaller than that of the ZnP-ref cell ($J_{SC} = 9.4$ mA·cm⁻², $V_{OC} = 0.76$ V, ff = 0.64, $\eta = 4.6\%$). Action spectra of incident photon-to-current efficiency (IPCE) for the porphyrin-sensitized cells are depicted in Figure 2. The action spectra and absorption spectra are virtually similar for TiO₂/fused-ZnP and TiO₂/ ZnP-ref, implying the involvement of the porphyrins for the photocurrent generation. In accordance with the cell performances,



Figure 2. Action spectra (with circles) and UV–vis absorption spectra (without circles) of TiO₂/fused-ZnP (solid line) and TiO₂/ZnP-ref (dashed line) electrodes. Thickness of the TiO₂ films used for the absorption measurements was adjusted to be 0.7–1.0 μ m. The absorption spectra are normalized for comparison.

the IPCE value of the fused-ZnP cell (9.5% at 435 nm) is much smaller than that of the ZnP-ref cell (76% at 420 nm). Nevertheless, owing to the elongation of the porphyrin π system, the photocurrent response is extended over 800 nm in the fused-ZnP cell, which is the longest wavelength among porphyrin-sensitized solar cells.^{4,5} According to a previous paper⁷ at least, more than 0.2 eV of driving force is necessary for efficient electron injection. Accordingly, insufficient driving force for the electron injection (0.19 eV) for the fused-ZnP cell may be responsible for the moderate photovoltaic properties of the fused-ZnP cell. Moreover, the decreased V_{OC} for the fused-ZnP cell may result from fast charge recombination from the electron in the CB of TiO₂ to ZnP⁺⁺ and/or I₃⁻⁻ relative to the ZnP-ref cell.

In conclusion, we have successfully prepared novel fused five-membered porphyrin for DSSC. Although the lightharvesting properties of the fused porphyrin in the visible and NIR regions are remarkably improved relative to the typical tetraphenylporphyrin reference, the photovoltaic properties are moderate. Improvement of the cell performance in fused five-membered porphyrins may be possible by modulating the electronic structure of the porphyrins to optimize the electron injection process.

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- 8 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/ index.html.