# Fused Five-membered Porphyrin for Dye-sensitized Solar Cells

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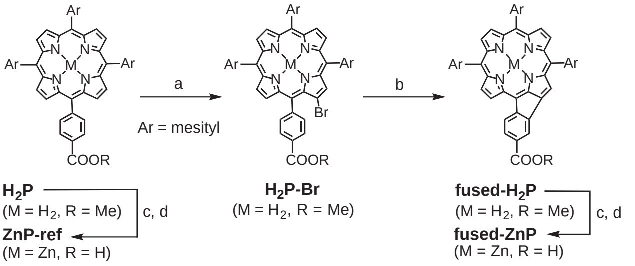
Fused five-membered zinc porphyrin carboxylic acid has been synthesized to improve light-harvesting capability in the visible and near-infrared regions. The fused porphyrin-sensitized $TiO_2$ cell exhibited the photocurrent generation extending over 800 nm, although the power conversion efficiency was found to be moderate (0.30%).

Recently, dye-sensitized solar cells (DSSC) have attracted much attention because of their relatively high power conversion efficiency ($\eta$) and potential low-cost production.[1] Ruthenium(II) bipyridyl complexes have proven to be the most efficient $TiO_2$ 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 $\pi$-elongated porphyrins for DSSC.[5] As the results of the elongation of the porphyrin $\pi$-system with low symmetry, the absorption of the porphyrins was broadened and red-shifted, leading to improvement of the $\eta$ 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 ($H_2P$) was treated with *N*-bromosuccinimide (NBS) to yield monobrominated porphyrin ($H_2P$-Br). The intramolecular fused porphyrin (fused-$H_2P$) was obtained by the treatment of $H_2P$-Br with $Pd^0$ catalysis.[6b] Zinc(II)-metallation and hydrolysis of fused-$H_2P$ gave fused-ZnP. ZnP-ref was also prepared for comparison.[3b] The synthetic details and characterization are provided in Supporting Information.[8]



**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, $H_2O$, THF, reflux, 1 day.

UV–vis absorption spectra of fused-ZnP and ZnP-ref were measured in $CH_2Cl_2$. The peak positions and molar absorption coefficients ($\varepsilon$) are listed in Table S1.[8] Compared with ZnP-ref, fused-ZnP reveals broadening and red shift of Soret and Q bands due to expansion of the $\pi$ 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 $CH_2Cl_2$ 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 $CH_2Cl_2$ containing $Bu_4NPF_6$ as a supporting electrolyte (Table S1).[8] Owing to the elongation of the $\pi$ 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 ($E_{ox}{}^*$) 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 $TiO_2$ and charge shift from $I^-$ to the resulting porphyrin radical cation are thermodynamically feasible both in the fused-ZnP and ZnP-ref cells

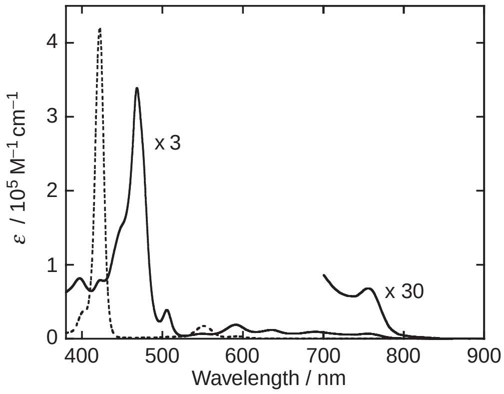


**Figure 1.** UV–vis absorption spectra of fused-ZnP (solid line) and ZnP-ref (dashed line) in $CH_2Cl_2$.

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

Cell performances of the $TiO_2$/fused-ZnP and $TiO_2$/ZnP-ref electrodes were evaluated under standard AM 1.5 conditions ($100\,mW{\cdot}cm^{-2}$).[5] The current–voltage characteristics are given in Figure S4. The $\eta$ value of the fused-ZnP cell ($J_{SC} = 0.88\,mA{\cdot}cm^{-2}$, $V_{OC} = 0.51\,V$, $ff = 0.67$, $\eta = 0.30\%$) is much smaller than that of the ZnP-ref cell ($J_{SC} = 9.4\,mA{\cdot}cm^{-2}$, $V_{OC} = 0.76\,V$, $ff = 0.64$, $\eta = 4.6\%$). 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 $TiO_2$/fused-ZnP and $TiO_2$/ZnP-ref, implying the involvement of the porphyrins for the photocurrent generation. In accordance with the cell performances, 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 $\pi$ 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 paper[7] 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 $TiO_2$ to $ZnP^{+\bullet}$ and/or $I_3^-$ relative to the ZnP-ref cell.

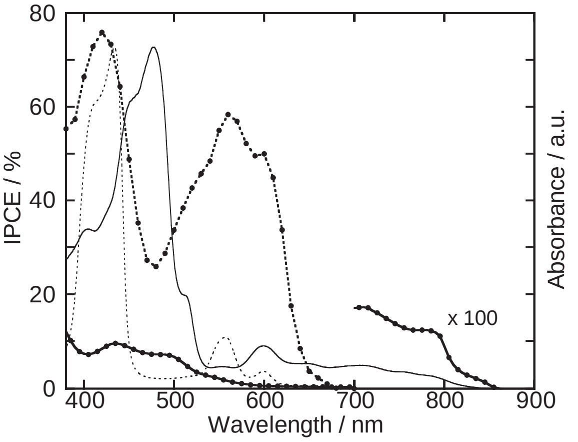


**Figure 2.** Action spectra (with circles) and UV–vis absorption spectra (without circles) of $TiO_2$/fused-ZnP (solid line) and $TiO_2$/ZnP-ref (dashed line) electrodes. Thickness of the $TiO_2$ films used for the absorption measurements was adjusted to be 0.7–1.0 μm. The absorption spectra are normalized for comparison.

In conclusion, we have successfully prepared novel fused five-membered porphyrin for DSSC. Although the light-harvesting 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.