

Dye-sensitized Solar Cells Using Ethynyl-linked Porphyrin Trimers with an Anchoring Group at Long-axis End or Short-axis End

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An ethynyl-linked porphyrin trimer with a carboxyphenyl anchoring group at its long-axis end can be adsorbed more densely on a TiO₂ surface and exhibited better performance in dye-sensitized solar cells than did the trimer with short-axis anchoring, with photoelectric conversion in the near-IR region.

In the course of development of dye-sensitized solar cells (DSSCs),¹ various sensitizing dyes have been studied to enhance their photoelectric conversion efficiencies, because dyes adsorbed on a TiO₂ surface play a significant role in the light-harvesting and charge-separation processes. Among them, porphyrin derivatives have been recently reported as efficient dyes in DSSCs.² On the basis of the characteristic large planar structure of porphyrins, several studies have been performed to investigate the adsorption geometry of porphyrin dyes on the TiO₂ surface, by varying the arrangement of the anchoring groups.³ Recently, we have presented DSSCs using ethynyl-linked porphyrin trimers, aiming to expand the photoabsorption region of porphyrin dyes.⁴ Since three porphyrin units are connected linearly, the molecular length of an ethynyl-linked porphyrin trimer along the ethynyl linkers (long axis) is 3 times the length perpendicular (short axis) to that direction. Therefore, the anchoring direction (longitudinal or horizontal) affects the distance between the porphyrin units and the TiO₂ surface. Adsorption of trimers at the short-axial edge would be beneficial for electron injection from the excited dye to the TiO₂ conduction band, because all porphyrin units of the trimers approach the TiO₂ surface. On the other hand, adsorption of trimers at the long-axial edge would be beneficial to increase the number of adsorbed dyes on the TiO₂ surface, because the trimers occupy a smaller area on the surface. In this study, the effect of adsorption direction has been examined by comparing a trimer with a carboxyphenyl group in the short-axial direction (Zn-ZnA-Zn) and a trimer with a carboxyphenyl group in the long-axial direction (Zn-Zn-ZnA) (Chart 1).

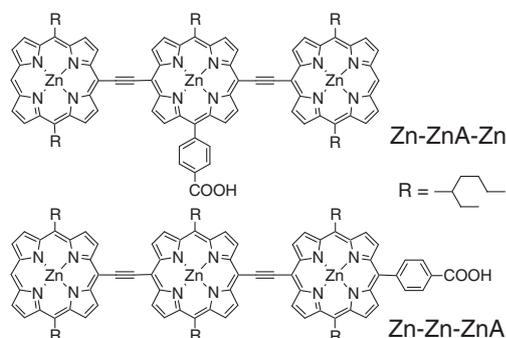
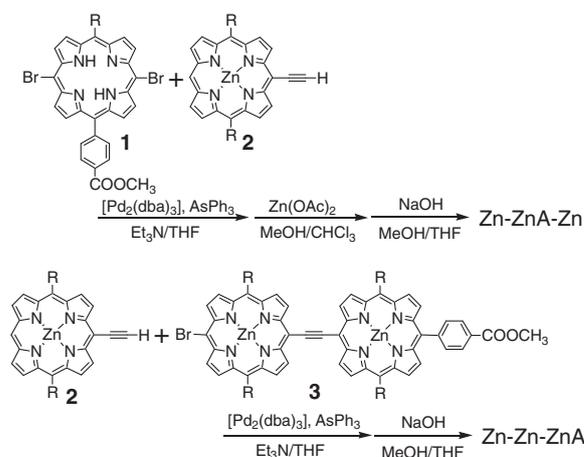


Chart 1.

These trimers were synthesized as shown in Scheme 1. The monomeric precursors were synthesized by a modified process based on previously reported methods.⁴ The ester derivatives were obtained by the Sonogashira coupling⁵ of monomeric precursors **1** and **2**, followed by zinc insertion, or the Sonogashira coupling of **2** and brominated dimer **3**. Hydrolysis of these ester derivatives afforded the target compounds. Details of syntheses and fabrication of DSSCs are described in Supporting Information.⁶

The adsorption behavior of these trimers on TiO₂ was analyzed on the basis of absorption spectra. The Q-band absorption of these trimers in *N,N*-dimethylformamide solution appeared at 786 (Zn-ZnA-Zn) or 793 nm (Zn-Zn-ZnA). Upon adsorption onto the TiO₂ surface, the absorption peak appeared at 806 (Zn-ZnA-Zn) or 831 nm (Zn-Zn-ZnA), and a shoulder at around 750 nm was observed (Figure 1). With an increase in the dipping time of the TiO₂ film in the dye solution, the Q-band absorption of Zn-Zn-ZnA monotonically increased, while that of Zn-ZnA-Zn showed the maximum value at 2 h. Since the molar extinction coefficients of these trimers are almost the same, the different absorbances at long dipping times (10 h) should be regarded as the difference in the amount of adsorbed dyes on TiO₂. Therefore, the adsorbed amount of Zn-Zn-ZnA is larger than that of Zn-ZnA-Zn at a long dipping time. Since Zn-ZnA-Zn adsorbs on the TiO₂ surface with an anchoring group in the short-axial direction, Zn-ZnA-Zn would occupy a larger area on the surface than does Zn-Zn-ZnA. The shoulder peak at around 750 nm is assigned to H-type aggregates⁷ (stacked aggregates) of the trimers. As shown in Figure 1, the absorbance at these shoulder peaks also increased with an increase in the dipping



Scheme 1. Synthetic routes for the ethynyl-linked porphyrin trimers.

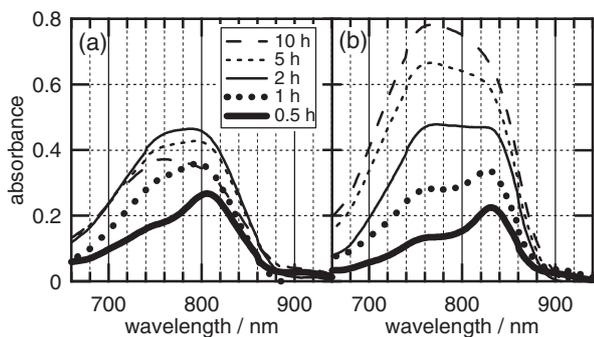


Figure 1. Absorption spectra of (a) Zn-ZnA-Zn and (b) Zn-Zn-ZnA on TiO₂ with various dipping time.

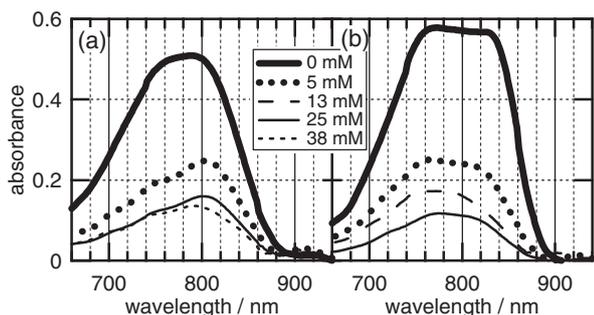


Figure 2. Absorption spectra of (a) Zn-ZnA-Zn and (b) Zn-Zn-ZnA on TiO₂ adsorbed from 5 mM solution containing various concentration of DCA with 2 h dipping.

time, changing the ratio with the Q-band absorption peak. However, the incident photon-to-current conversion efficiency (IPCE) values of the DSSCs adopting these conditions at the peak wavelengths decreased (Figure S4).⁶ This result indicates that the H-type aggregate of these trimers formed on the TiO₂ surface does not contribute to the photoelectric conversion.

To suppress the formation of H-type aggregates of the trimers on the TiO₂ surface, deoxycholic acid (DCA) as a coadsorbent⁸ was added to the dye solution during the immersion process. Figure 2 shows the absorption spectra of the trimers with DCA on TiO₂ under the condition of 2 h immersion. The absorbance of the trimers monotonically decreased with an increase in the amount of DCA, indicating that the coverage of DCA on the TiO₂ surface increased. Meanwhile, the shoulder peaks, which were attributed to H-type aggregates, changed in different ways. By the addition of DCA, the shoulder peak of Zn-ZnA-Zn largely decreased with respect to the Q-band peak, while that of Zn-Zn-ZnA did not. The effect of DCA to suppress the aggregate formation of Zn-Zn-ZnA seems to be slight.

The solar cell performance parameters of the DSSCs using the trimers were plotted versus DCA concentrations, as shown in Figure 3. In spite of the decrease in absorbance, the short-circuit photocurrent density (J_{SC}) of the DSSCs using the trimers drastically increased, indicating that the charge-separation efficiency was improved by the addition of DCA. In the case of Zn-Zn-ZnA, J_{SC} further increased with an increase in the DCA concentration, while J_{SC} of the DSSCs using Zn-ZnA-Zn reached the maximum value at around 10 mM DCA. The tendency for Zn-ZnA-Zn is in accord with the suppression of

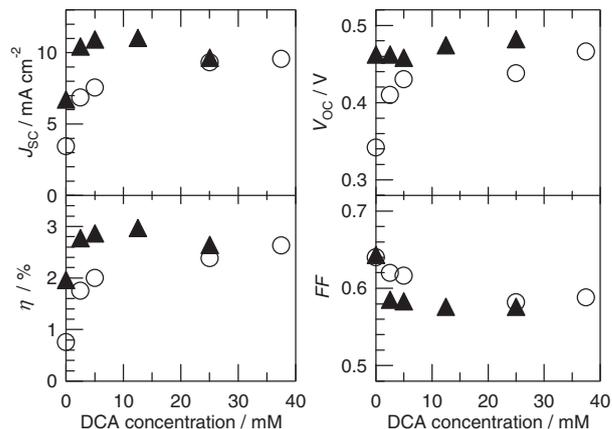


Figure 3. Solar cell performance parameters of the DSSCs using Zn-ZnA-Zn (circles) and Zn-Zn-ZnA (triangles).

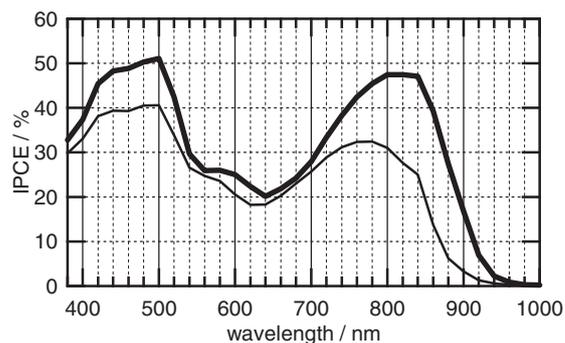


Figure 4. IPCE spectra of the DSSCs using Zn-ZnA-Zn (thin line, DCA 38 mM) and Zn-Zn-ZnA (thick line, DCA 13 mM).

aggregation, as seen in the absorption spectra. Further, there was a large difference in the tendency of the open-circuit photovoltage (V_{OC}) upon the addition of DCA. V_{OC} of the DSSCs using Zn-ZnA-Zn drastically increased with an increase in the DCA concentration, while that of Zn-Zn-ZnA was almost the same, regardless of the DCA concentration. Interestingly, the maximum values of V_{OC} were almost the same. The fill factor (FF) of Zn-ZnA-Zn and Zn-Zn-ZnA was almost constant, regardless of the concentration. Reflecting the tendencies of J_{SC} and V_{OC} , the maximum photoelectric conversion efficiency (η) of Zn-Zn-ZnA (η : 2.91%; V_{OC} : 0.47 V; J_{SC} : 10.8 mA cm⁻²; FF : 0.57) exceeded that of Zn-ZnA-Zn (η : 2.63%; V_{OC} : 0.47 V; J_{SC} : 9.57 mA cm⁻²; FF : 0.59).

Under the conditions that afforded the best efficiency (DCA 38 mM for Zn-ZnA-Zn, 13 mM for Zn-Zn-ZnA), the IPCE spectra of the DSSCs using the trimers were compared. As shown in Figure 4, the IPCE values of Zn-Zn-ZnA were higher than that of Zn-ZnA-Zn in all wavelength regions. The obtained IPCE value in the NIR region (Zn-Zn-ZnA: 47% at 840 nm) is the highest among the reported porphyrin-sensitized DSSCs. Even though there is a slight difference in absorbance (Figure S6),⁶ the internal quantum efficiency of Zn-Zn-ZnA should be higher than that of Zn-ZnA-Zn. Therefore, Zn-Zn-ZnA was found to be more favorable than Zn-ZnA-Zn in terms of the charge-separation efficiency.

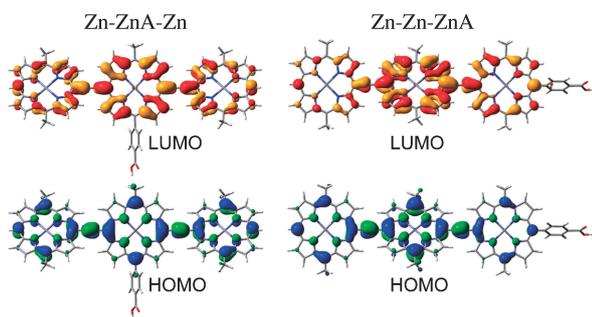


Figure 5. Frontier orbitals of Zn-ZnA-Zn and Zn-Zn-ZnA calculated by B3LYP/6-31G(d) on Gaussian09.⁹

To investigate the difference in charge separation between these trimers, the electronic structures of Zn-ZnA-Zn and Zn-Zn-ZnA were compared based on the results of DFT calculations. Figure 5 shows the frontier orbitals of these trimers. Basically, the photoexcited electron is regarded to reside in the LUMO of the ground state. Therefore, the distribution of the LUMO in Figure 5 can be related to the density of the photoexcited electron. If the electron injection process proceeds by a through-bond scheme, the excited electron should reside around the anchoring position. Although the LUMO is distributed over the entire molecule, the *meso*-position of the central porphyrin, where the carboxyphenyl group is connected in Zn-ZnA-Zn, is a node of the LUMO. Therefore, overlap of the orbitals between the dye and TiO₂ is minimized. On the other hand, the LUMO of Zn-Zn-ZnA is distributed on the *meso*-position of the porphyrin bonded to the anchoring group. Although the distribution of the LUMO on the anchoring group is faint, overlap of the orbitals between the dye and TiO₂ is possible, facilitating electron injection.

After injecting the photoexcited electron, the dye in the oxidized state has a vacancy of an electron, which is regarded to be distributed along the HOMO of the original state. As seen in Figure 5, the HOMO of these trimers is distributed over the whole molecule. If the vacancy of the electron caused by the electron injection is distributed near TiO₂, charge recombination from the electrons in TiO₂ to the oxidized dyes would be facilitated. The arrangement of Zn-ZnA-Zn offers such a possibility. Since Zn-Zn-ZnA with an anchoring group in the long-axial direction enables two of the three porphyrin units to recede from the TiO₂ surface, the rate of charge recombination from the electrons in TiO₂ to the oxidized Zn-Zn-ZnA would be lower than that to the oxidized Zn-ZnA-Zn.

In summary, the photoelectric conversion efficiency of DSSCs using Zn-Zn-ZnA, which has a carboxyphenyl group in the long-axial direction, was higher than that using Zn-ZnA-Zn with a carboxyphenyl group in the short-axial direction. One possible reason for the difference in the photovoltaic properties was suggested based on the phase of their frontier orbitals, calculated by DFT. The experimental result indicates that the unanchored porphyrins need not be present near the TiO₂ surface. The short distance between the dye and TiO₂ may rather facilitate charge recombination between the photoinjected electron in the TiO₂ conduction band and the oxidized dye. These results would be beneficial findings on the adsorption geometry for efficient DSSCs using porphyrin arrays.

This work was supported by the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST program) on the development of organic photovoltaics toward a low-carbon society, from the Japanese Government, and the Research Fellowships of the Japan Society for the Promotion of Science (JSPS) for Young Scientists.

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