Controlling the Rotation of Porphyrin Units in Ethynyl-linked Porphyrin Trimers for Dye-sensitized Solar Cells by Anchoring onto TiO₂ Surface

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An ethynyl-linked porphyrin trimer bearing carboxyphenyl anchoring groups at all the porphyrin units becomes planar upon adsorption onto TiO₂, showing the Q band absorption and IPCE maximum at longer wavelengths.

Multiporphyrinic chromophores have been studied intentionally from various viewpoints such as the molecular architecture, biomimetic modeling of natural photosynthetic systems, and application for optoelectronic devices.¹ The effect of the arrangement of porphyrin units has been documented well. Monomeric porphyrins have been recently reported as efficient sensitizers in dye-sensitized solar cells (DSSCs),² although their spectral sensitivities are limited to the visible region. By adopting porphyrin oligomers as the sensitizers in DSSCs, the expansion of the light-harvesting region is expected.³ Recently, we have reported DSSCs using ethynyllinked porphyrin trimers.⁴ Ethynyl-linked porphyrin oligomers can have various conformations derived from the rotation along the ethynylene linkers.⁵ Such intramolecular twist may affect the effective π conjugation to expand the absorption region. In this study, the effect of the position of the anchoring groups in ethynyl-linked porphyrin trimers has been investigated, expecting that the rotational motion along the ethynylene linkages could be suppressed by plural anchoring onto the TiO₂ surface. The molecular conformation could be analyzed on the basis of the porphyrin chemistry. Following trimers have been synthesized and investigated in this study: Zn-ZnA-Zn has a carboxyphenyl group at the central porphyrin; ZnA-Zn-ZnA has carboxyphenyl groups at the side porphyrins; and ZnA-ZnA-ZnA has carboxyphenyl groups at all the porphyrins (Chart 1).

The adsorption behavior of these trimers onto TiO₂ was analyzed from the absorption spectra. Figure 1 shows the absorption spectra of the trimers in N,N-dimethylformamide (DMF) solution and on TiO₂. As is characteristic for the ethynyllinked porphyrin oligomers, the split Soret band absorption around 400-500 nm and the Q band absorption around 780 nm were observed for all trimers in DMF. Upon adsorption onto the TiO₂ surface, the absorption maximum of Zn-ZnA-Zn in the Q band region appeared at the shorter wavelength than that in solution, while that of ZnA-ZnA-ZnA on TiO₂ appeared at the longer wavelength than that in solution. The absorption maximum of ZnA-Zn-ZnA on TiO2 was similar with that in solution. By increasing the dipping time from 1 to 14h, the absorbance of ZnA-ZnA-ZnA increased about three times, while the absorbance of Zn-ZnA-Zn did not increase (Figure S2).⁶ Even if the concentration of the solution of Zn-ZnA-Zn was increased to 10 times higher, the absorbance of Zn-ZnA-Zn increased only by 20%.



Chart 1.



Figure 1. Absorption spectra of (a) Zn-ZnA-Zn, (b) ZnA-Zn-ZnA, and (c) ZnA-ZnA-ZnA in DMF (thin lines) and on TiO_2 (thick lines). Inset drawings indicate the typical conformation of the trimers on TiO_2 .

This tendency is interpreted on the basis of the molecular conformation. According to the exciton-coupling theory,⁷ the transition dipole moments perpendicular to the bonding axis afford the shorter-wavelength Soret band absorption peak around 400-420 nm, depending on the dihedral angles between the

porphyrin units. The corresponding absorption peak of Zn-ZnA-Zn on TiO₂ was broadened to both sides from the peak position in solution. On the other hand, the corresponding absorption of ZnA-ZnA-ZnA on TiO₂ was mainly broadened toward the shorter-wavelength direction. This feature indicates the increased ratio of the trimer with high coplanarity between the adjacent porphyrins, where the transition dipole moments are arranged in parallel, leading the blue-shifted absorption. In the case of the coplanar conformation, π conjugation is effectively extended, making the Q band absorption of ZnA-ZnA-ZnA red-shifted.

This tendency is explained by assuming that each porphyrin unit is arranged longitudinally with the carboxy group directing to the surface, as shown in Figure 1 insets. In the case of Zn-ZnA-Zn, the central porphyrin unit is anchored onto the surface, while the side porphyrin units are not anchored. Therefore, the side porphyrin units can rotate, adopting various dihedral angles between the central porphyrin. Because of the steric effect, the side porphyrin units tend to be parallel to the surface. The horizontal arrangement of a porphyrin unit increases the occupying area compared to the vertical arrangement. Therefore, Zn-ZnA-Zn molecules occupy a relatively large area of the surface, adopting various dihedral angles between adjacent porphyrin units. Such arrangement is supported by the fact that the absorbance of Zn-ZnA-Zn on TiO₂ did not increase under the long dipping time condition. In the case of ZnA-ZnA-ZnA, all the porphyrin units can be anchored onto the surface. Therefore, the porphyrin units in ZnA-ZnA-ZnA should adopt the coplanar conformation with each other. This is in accordance with the absorption spectra of ZnA-ZnA-ZnA on TiO₂. If a planar molecule is arranged perpendicular to the surface, the molecule occupies a smaller area of the surface. Therefore, the absorbance of ZnA-ZnA-ZnA on TiO₂ increased along with the increase in the dipping time. As seen here, the experimental results indicate the alteration of the ratio of coplanar and nonplanar conformations upon the adsorption of trimers onto the TiO₂ surface.

To suppress the aggregate formation on the TiO₂ surface, deoxycholic acid (DCA) as coadsorbents was added to the dye solution during the immersion process. Figure 2a shows the DCA concentration dependence of the absorbance of the trimers on 3-µm-thick TiO₂ films. The absorbance of the trimers monotonically decreased along with the increase in the amount of DCA, indicating the increase of the coverage of DCA on the TiO₂ surface. Compared to the trimer with single-anchoring group, the absorbance of the trimers with plural-anchoring groups decreased moderately along with the increase in the amount of DCA. This result indicates that the increase in the number of anchoring groups enhances the adsorbability of the trimers onto the TiO₂ surface. DSSCs were prepared with ca. 10um-thick TiO₂ electrode. The IPCE values of the DSSCs using the trimers at the corresponding wavelength were plotted with respect to various DCA concentrations, as shown in Figure 2b. In spite of the decrease in the absorbance, the IPCE values of these DSSCs increased by the addition of DCA, indicating that the charge-separation efficiency of the trimers were improved by the addition of DCA.

Figure 3 shows the solar cell performance parameters of the DSSCs using the trimers, plotted versus the DCA concentrations. The short-circuit photocurrent density (J_{SC}) of ZnA-Zn-ZnA reached the maximum value at the higher concentration than that of Zn-ZnA-Zn, while that of ZnA-ZnA-ZnA monotoni-



Figure 2. DCA concentrations dependence of (a) absorbance at 500 nm and (b) IPCE values of Zn-ZnA-Zn (triangles), ZnA-Zn-ZnA (circles), or ZnA-ZnA-ZnA (squares).



Figure 3. DCA concentration dependence of the solar cell performance parameters of the DSSCs using Zn-ZnA-Zn (triangles), ZnA-Zn-ZnA (circles), or ZnA-ZnA-ZnA (squares).

cally increased under this condition. These tendencies were in accord with the results of the IPCE values. The open-circuit photovoltage ($V_{\rm OC}$) of the trimers increased by the addition of DCA. The fill factor (FF) was almost constant, regardless of the DCA concentrations. Reflecting the tendencies of $J_{\rm SC}$ and $V_{\rm OC}$, the photoelectric conversion efficiency (η) of ZnA-Zn-ZnA showed the highest value.

As shown in Figure 4, the IPCE maximum of the DSSC using Zn-ZnA-Zn with a large amount of DCA in the Q band region appeared at the shorter wavelength than that without DCA. This tendency is opposite from the absorption maxima, which appeared at the longer wavelengths along with the increase in the amount of DCA. In the case of ZnA-ZnA-ZnA, the IPCE maximum in the Q band region appeared at the longer wavelength than the absorption maximum. These results are interpreted as follows. The change in the absorption of Zn-ZnA-Zn upon the addition of DCA is caused by the suppression of the formation of H-type aggregates and/or the increased portion



Figure 4. IPCE spectra of the DSSCs using (a) Zn-ZnA-Zn, (b) ZnA-Zn-ZnA, or (c) ZnA-ZnA-ZnA without DCA (thin lines) or with DCA (thick lines, a: 150 mM; b, c: 300 mM).

of the coplanar conformers. In general, the suppression of aggregates improves the charge-separation efficiency. The improvement of IPCE might be such an effect. However, this contribution should be enhanced at the longer wavelength region. Therefore, the appearance of the IPCE maximum at the shorter wavelength indicates that the nonplanar conformers contribute mainly to the charge-separation process. On the other hand, the coplanar conformers should contribute mainly in the cases of ZnA-Zn-ZnA and ZnA-ZnA.

This tendency is explained by the distribution of LUMO at the porphyrin unit with the anchoring group in each conformer (Figure S6). In the case of Zn-ZnA-Zn, the distribution of LUMO in the central porphyrin unit is larger for the nonplanar conformer with respect to the coplanar conformer. This is the reason for the effective charge separation in the nonplanar conformation. In the case of ZnA-Zn-ZnA, the LUMO is distributed to the porphyrin unit with the anchoring group only in the coplanar conformation. Therefore, the effective charge separation should occur from the coplanar conformation. In the case of ZnA-ZnA-ZnA, the LUMO is distributed to the porphyrin unit with the anchoring group in any conformations. Therefore, the charge separation should occur in any conformation. Because the coplanar conformer is the main product of the adsorption process, the IPCE maximum of the DSSC using ZnA-ZnA appeared at the longer-wavelength region. As seen here, the intramolecular twist along the ethynylene linkers causes the difference in the distribution of the LUMO, leading to the difference in the charge-separation process.

In summary, the conformation of the porphyrin units in the ethynyl-linked porphyrin trimers (Zn-ZnA-Zn, ZnA-Zn-ZnA, and ZnA-ZnA-ZnA) on TiO₂ was found to depend on the position of the anchoring groups. Because Zn-ZnA-Zn with DCA showed the absorption maximum at longer wavelength than those without DCA, the effect of the formation of H-type aggregation should not be excluded, even though it is a minor contribution. In the case of Zn-ZnA-Zn, in which only the central porphyrin unit has the anchoring group, the side porphyrin units can be twisted along the ethynylene linkers. On the other hand, all the porphyrin units of ZnA-ZnA-ZnA can be anchored on TiO₂, leading the coplanar conformation with the effective π conjugation. Under this situation, ZnA-ZnA-ZnA seems the most advantageous for the charge-separation process. However, the electronwithdrawing effect of the anchoring groups makes the oxidation potential of the excited state of ZnA-ZnA the most anodic among these three trimers. Because of this disadvantage of ZnA-ZnA in the energy-level matching, the photovoltaic performance of the DSSCs using ZnA-Zn-ZnA was the best.

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