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Dye-sensitized Solar Cells Using Supramolecular Porphyrin Arrays Inspired by π -Stacking Structures of Photosynthetic Light-harvesting Complexes

Junko Fujimoto,¹ Kazuhiro Manseki,² and Hidekazu Miyaji*1

¹Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University,

1-1 Yanagido, Gifu 501-1193

²Graduate School of Engineering, Environmental and Renewable Energy System Division, Gifu University, 1-1 Yanagido, Gifu 501-1193

(E-mail: miyaji@gifu-u.ac.jp)

A slipped cofacial π -stacks of bis(4-carboxyphenyl)bis(1methylimidazol-2-yl)porphyrinatomagnesium complex can be self-assembled onto TiO₂ surface as a light-harvesting core. The porphyrin array allows a more favorable light-to-electricity conversion compared to the monomer analogue in dye-sensitized solar cells.

Dye-sensitized solar cells (DSSCs) have received much attention as promising next-generation photovoltaics.¹ Dvedsemiconductor nanoparticle films, wherein electrolytes are embedded in the nanopores of photoelectrodes, play crucial roles in the efficient charge separation of electrons and holes. Porphyrins are an important class of light-absorbing materials owing to their high molar extinction coefficients ($\varepsilon > 10^4$) from UV to visible (or near-IR) region and easy substitution of functional groups to the meso-position.² As for DSSCs incorporating porphyrins, multiporphyrin arrays synthesized via intermolecular covalent bonds have been reported to show improved electron injection as well as light-harvesting efficiency compared to the monomeric sturucture.³ On the other hand, effects of the porphyrin π -stacks on the photovoltaic performance have been poorly understood, although photosynthetic systems benefitting from the light-harvesting porphyrin subunits have been clearly investigated.

From the viewpoint of biomimetics, we focused on porphyrin supramolecules⁴ mimicking the antenna complexes of photosynthetic system.⁵ We synthesized a porphyrin that has 1-methylimidazole and 4-carboxyphenyl groups⁶ for realizing self-organization onto the semiconductor surface. It turned out that the slipped cofacial π -stacking structure of porphyrin can be controlled via the cooperative coordination of 1-methylimidazole to the central metal ion of the porphyrin, both in solutions and in the solid state, i.e., dyed TiO₂ films. We anticipated that the exciton coupling, i.e., transition dipole interactions and the overlapped π orbitals of the porphyrin units allow the efficient electron injection resulting in a marked improvement in the photovoltaic performance.

More specifically, we synthesized a novel magnesium porphyrin **3** that has two 1-methylimidazoles and two carboxyphenyl groups as anchors for TiO_2 (Figure 1). We prepared a methoxycarbonylphenyl-substituted dipyrromethane part as the building blocks for the targeted porphyrins, in which two 1-methylimidazoles are introduced into the *meso*-positions and two carboxyphenyl groups into the other facing *meso*-positions.⁷ Reactions with dipyrromethane and 1-methyl-2-imidazolecar-baldehyde in propionic acid produced free-base porphyrin, which was purified by column chromatography. The substituted



Figure 1. A conceptual drawing of self-organization of 3 on TiO_2 electrode, in which the transition dipole interactions are represented.

methoxycarbonylphenyl groups were then successfully converted to the carboxyphenyl groups by hydrolysis. The obtained free-base porphyrin and magnesium perchlorate were refluxed in pyridine to afford the Mg complex **3**. For comparisons, 5,10,15-tris(4-carboxyphenyl)-20-(1-methylimidazolyl)porphyrinatomagnesium⁶ complex (**2**) and 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrinatomagnesium complex (**1**) were also synthesized (see Supporting Information).⁸

Compounds 1, 2, and 3 showed low solubilities in organic solvents such as dichloromethane and acetonitrile because of their strong hydrogen bonds between the intermolecular carboxylic acid groups. It should be noted that they were soluble in a phosphate buffer solution (pH 7.4) because of the formation of carboxylate salts. Figure 2 shows the UV–vis absorption spectra of 1, 2, and 3 in the buffer solution. Judging from the sharp Soret-band ($\lambda_{max} = 421$ nm), 1 was determined to be a monomer (Figure 2 and Table 1). For 2, the broad Soret-band was observed at around 428 nm, indicating that the interaction of two transition dipoles, i.e., both "face-to-face" and "head-to-tail" dipole interactions, plays a part in the marked peak broadening.⁹ The Soret-band of 3 was found to split into around 380 and 449 nm peaks. Similarly, this band splitting is due to the interaction of transition dipoles by the stacking of 3. The



Figure 2. UV-vis absorption spectra of 1, 2, and 3 in phosphate buffer solutions (pH 7.4).

Table 1. Absorption spectral data of 1, 2, and 3 in solutions (phosphate buffer pH 7.4) and on $\rm TiO_2$

Compound	Solution			On TiO ₂	
	Soret band/nm	Q-band/nm	$\varepsilon_{\alpha}/\varepsilon_{\beta}$	Q-band/nm	$\varepsilon_{\alpha}/\varepsilon_{\beta}$
1	421	564, 604	0.58	566, 608	0.66
2	428	567, 613	0.71	564, 607	0.41
3	380, 427, 449	568, 594, 611	0.50	565, 593, 611	0.30

splitting was found to be 69 nm (4040 cm⁻¹) for **3** and ca. 20 nm (1150 cm⁻¹) for **2**. Thus, it is postulated that the dimer formation of **2** (**2**₂) and the porphyrin array of **3** (**3**_{*n*}) are stable in a phosphate buffer solution.¹⁰ In order to get more insight into the stacking core, we estimated the ratio of $\varepsilon_{\alpha}/\varepsilon_{\beta}$ of Q-bands. The values significantly decreased from 0.71 (**2**) to 0.50 (**3**). In addition, a new peak observed at 594 nm for **3** could be assigned to the Mg site to be a six-coordination structure.¹¹ From these results, it is reasonable to conclude that porphyrin array **3**_{*n*} (J-aggregate) is stabilized via the slipped cofacial π -stacking in a phosphate buffer solution. Such a J-aggregate formation was also supported by the red shift of fluorescence spectrum of **3**, which appeared at 621 nm (**1** at 613 nm). This result also means that the energy gap between HOMO–LUMO becomes smaller for porphyrin array **3**_{*n*}.

In order to examine the self-organization on the TiO₂ electrode, **1**, **2**, and **3** were adsorbed by immersing the TiO₂ electrode in each methanol solution of the porphyrin.¹² Figure 3 shows the absorption spectra of **1**, **2**, and **3** on the TiO₂ electrode. The amount of dye adsorbed on TiO₂ was controlled by the adsorption time for 18–24 h, which can be estimated from the absorption spectra of anound 0.4 at 565 nm corresponding to the Q-bands. The $\varepsilon_{\alpha}/\varepsilon_{\beta}$ value of Q-bands on TiO₂ decreased from 0.66 (**1**) to 0.30 (**3**), which was similar to that observed in solution. Furthermore, a new peak also appeared at 593 nm. We found that the organized structure of porphyrin array **3**_n could be controlled on the TiO₂ surface. The red shift of Q-band from 608 to 611 nm could be explained by the splitting of LUMO (S1) due to the intermolecular interactions of J-aggregates.

The photovoltaic performance of DSSCs fabricated with porphyrins 1, 2, and 3 was evaluated (Table 2). The short-circuit current density (J_{sc}) of dimer (2₂) was found to be 1.7 times higher than that of 1, whereas 1.8 times higher J_{sc} was observed



Figure 3. Absorption spectra of 1, 2, and 3 on TiO_2 .

 Table 2. Photovoltaic properties of 1, 2, and 3

Compound	$J_{\rm sc}/{ m mAcm^{-2}}$	$V_{\rm oc}/{ m V}$	F.F.	$\eta/\%$
1	1.25	0.231	0.65	0.18
2	2.14	0.431	0.65	0.60
3	2.26	0.391	0.68	0.60



Figure 4. Photocurrent action spectra of DSSCs consisting of light-harvesting porphyrins 1-3 on TiO₂ electrodes.

for porphyrin array 3_n . It is likely that the π -stacking formation of porphyrin array 3_n (J-aggregate) contributed to the improved photocurrent. The open circuit voltage (V_{oc}) for both dimer 2_2 and porphyrin array 3_n was significantly higher than that of 1. This can be explained by the suppressed electron recombination reaction at the interface of TiO₂ electrodes and I₃⁻ in electrolyte as being due to the densely packed structure on TiO₂ for π -stacking dimer and porphyrin arrays. As a consequence, conversion efficiency (η) for 2 and 3 increased by a factor of 3.3 compared to that for 1 (from 0.18% to 0.60%). Higher (10–20%) incident photon to current conversion efficiency (IPCE, Figure 4) at the Soret-band of the dimer 2_2 and the porphyrin array 3_n , as well as the peak broadenings, was observed compared to 1.¹³ It is likely that the broadening of IPCE at the Soret-band is attributed to the splitting LUMO (S2) by transition dipole interactions of "face-to-face" and "head-to-tail" modes that are defined as allowed transitions. At the Q-band, the IPCE of the dimer 2_2 and porphyrin array 3_n significantly increased by a factor of 2.0–2.8, as compared to 1. In addition to the broadening of the IPCE of 3_n by transition dipole interactions, the quantum yields of electron injection also seemed to improve. It is postulated that the electron recombination from TiO₂ to 3_n was effectively suppressed by hole trapping (i.e., hole migration¹⁴) due to the continuous π -stacking structure (via the overlapped π orbitals) of the porphyrin array.

In summary, we successfully synthesized the Mg porphyrin that has two 1-methylimidazoles and two carboxyphenyl groups. The DSSC incorporating the supramoleclular porphyrin array had positive effects on the increased photocurrent, which could be explained by the strong exciton coupling, i.e., transition dipole interactions and π -stacking of the oriented porphyrins, leading to the favorable electron injection. We believe that this result will provide a new strategy for the design and synthesis of dyes for fabricating highly efficient DSSCs. Further applications of DSSCs using exciton coupling and π -stacking system are in progress.

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- 10 It seemed to exist as equilibrium mixtures of monomer, dimer, trimer,...oligomer (3_n) in a phosphate buffer solution because of coordination of water to Mg. However, the porphyrin array seemed to exist stable, considering from the band splitting at 380 and 449 nm ($\Delta E = 4040 \text{ cm}^{-1}$) and the peak broadenings. The Co porphyrin which has two 1methylimidazoles and two alkyl chains was reported to form 90–500mer in an organic solvent, showing the band splitting at 474 and 404 nm ($\Delta E = 3650 \text{ cm}^{-1}$).^{4c} Therefore, our supramolecular porphyrin array ($\Delta E = 4040 \text{ cm}^{-1}$) also seemed to form a same level or higher levels of the porphyrin array. It was considered that the formation of such stable porphyrin array in water came from the effective hydrophobic interaction and π -stacking, in addition to the cooperative coordination from 1-methylimidazole to Mg.
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