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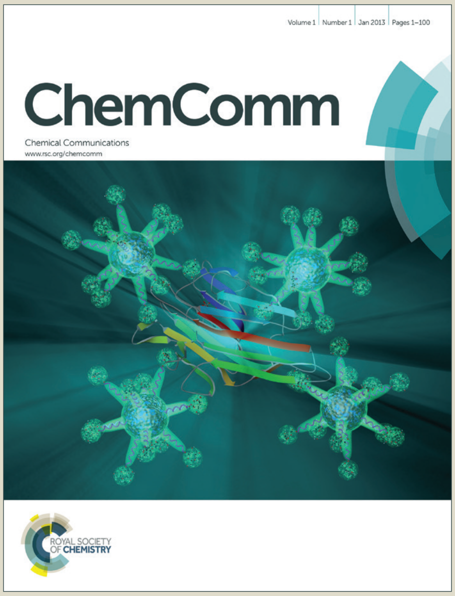

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Modification Effect of *meso*-Hexakis(pentafluorophenyl) [26]Hexaphyrin Aggregates on the Photocatalytic Water Splitting

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Hidehisa Hagiwara[a,b], Motonori Watanabe[b], Takeshi Daio[c], Shintaro Ida[a,b], and Tatsumi Ishihara[a,b]

Water splitting activity of GaN:ZnO photocatalyst was improved by *meso*-hexakis(pentafluorophenyl) [26]hexaphyrin (3). The hexaphyrin (3) assisted the water splitting reaction over the GaN:ZnO photocatalyst by using visible light energy around 600 nm.

Development of a direct conversion process from solar light to fuel is a significant challenge for sustainable development of the global economy. Photosynthesis, which is the most successful solar energy conversion system, has evolved in plants, algae, and cyanobacteria over a long period of time. The photosynthetic system has attracted much interest from scientists in the fields of chemistry, biology, and physics from energetic and environmental viewpoints. In recent years, details of the structures and roles of photosystems I and II have been revealed,[1] and applications for artificial photosynthesis are greatly anticipated. In the research area of artificial photosynthesis, dinuclear complexes or supra-molecular systems have been reported for photocatalytic oxygen formation or light energy harvesting.[2-4] Additionally, many research papers based on inorganic semiconductors, such as metal oxides, nitrides, and oxynitrides, as photocata-lysts for water decomposition have been published.[5-7]

For efficient solar energy conversion, harvesting and utilization of visible light energy are important. In the case of semiconductor photocatalysts, the band-gap energy should be lower than 3.0 eV to absorb visible light. Although there are many small band-gap compounds, most small band-gap semiconductors are unstable in aqueous solution due to photocorrosion.[8] Furthermore, the conduction band (CB) and the valence band (VB) of photocatalysts should sandwich the hydrogen evolution potential (0.0 V vs. NHE, pH 0) and the oxygen evolution potential (1.23 V vs. NHE, pH 0) for photocatalytic water splitting. These requirements restrict the candidate materials for water splitting photocatalysts. Metal complexes and organic dyes have been investigated as light absorbers for dye-sensitized solar cells (DSCs) to harvest visible light energy in sunlight.[9,10] Porphyrins are naturally occurring compounds and are commonly used as photosensitizers for DSCs.[11] While porphyrins have a ring structure consisting of four pyrrole units, so-called expanded porphyrins, which have more than four pyrrole units, have also been synthesized and reported.[12] These expanded porphyrins have the potential for harvesting visible light energy because of their highly-developed π conjugation. In this study, we investigated the modification effects of expanded porphyrins on the photocatalytic water splitting activity of GaN:ZnO solid solution, which has been reported as a highly active photocatalyst for visible light water splitting.[13] In this system, GaN:ZnO and porphyrins were excited by different wavelengths of light, and the water splitting reaction occurred with two-step excitation.[14] This is the first study applying expanded porphyrins to solar energy conversion materials.

Figure 1 shows the molecular structures of the *meso*-aryl-expanded porphyrins (**2**-**6**) including *meso*-tetrakis(pentafulorophenyl)porphyrin (**1**) used in this study. All porphyrinoids were prepared according to the reported method.[12] A series of expanded porphyrins were synthesized from pentafluorobenzaldehyde and pyrrole under modified Lindsey conditions,[15] in CH_2Cl_2 with BF_3OEt_2. After oxidation with DDQ, the products were separated by alumina and silica gel column chromatography. Maximum photoabsorption wavelengths of the

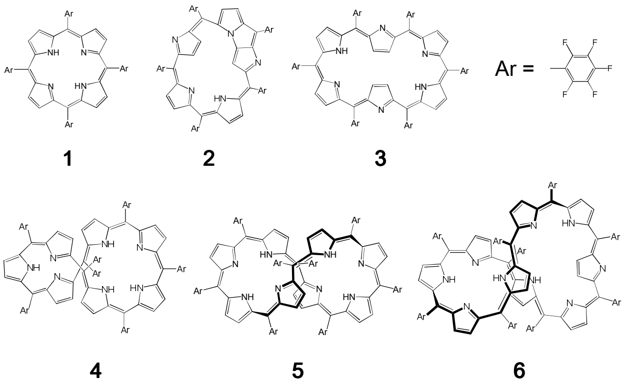

Fig. 1 Molecular structures of porphyrinoids (1-6) used as visible light absorbers in this study.

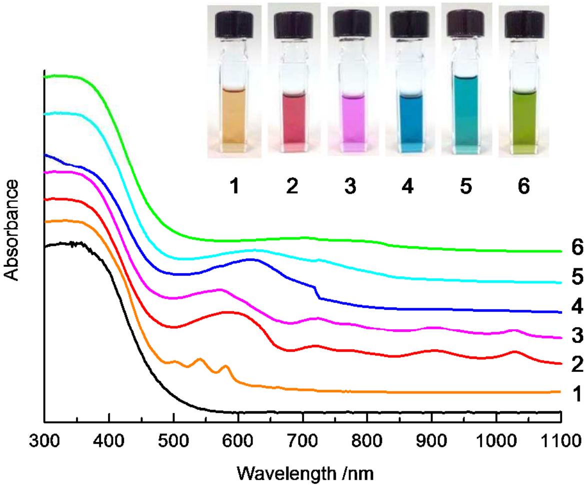

Fig. 2 UV-Vis absorption spectra for GaN:ZnO and RhO_X (0.1 wt%), NiO (0.1 wt%)/porphyrinoid (0.5 wt%)/IrO_2 (0.1 wt%)-GaN:ZnO. Upper pictures are CH_2Cl_2 solutions of compounds **1-6**.

porphyrin in CH_2Cl_2 solutions were red-shifted from 410 nm (1) to 706 nm (6) with expanding ring structure (Fig. S1 and Table S1).

Figure 2 shows the UV-Vis spectra of the GaN:ZnO photocatalyst modified with the porphyrinoids **1-6**. GaN:ZnO absorbed light at wavelengths shorter than 500 nm. Preparation method and characterizations of GaN:ZnO are available in supporting information (Fig. S2). The porphyrinoids **1-6** on the GaN:ZnO surface exhibited absorption peaks in the visible light to near infrared light region. Compared with the absorption spectra of porphyrinoids **1-6** in CH_2Cl_2 (Fig. S1), maximum absorption peaks (Soret or Soret-like band) of the porphyrinoids **1-6** on GaN:ZnO were broad and slightly red-shifted (4-13 nm). Generally, the absorption peak of dye compounds is shifted depending on aggregation states.[16] The aggregation states of the porphyrins are divided into *J* (red-shifted) and *H* (blue-shifted) aggregation, in which the transition dipoles of the porphyrins are aligned parallel and perpendicular, respectively. Thus, it was suggested that the expanded porphyrins formed *J*-like aggregates on the GaN:ZnO surface. Compared to the amorphous states, these aggregates seemed to have an advantage in transporting the photogenerated electrons or holes to reaction sites throughout the dye. Although compound 2 has no absorption peak longer wavelength region than 600 nm in CH_2Cl_2 (Fig. S1), absorption peaks were observed at 722, 770, 905, and 1030 nm in the spectrum of compound **2** modified GaN:ZnO photocatalyst. Molecule structure of compound **2** might be changed during photocatalyst preparation. All of the dye (**1-6**)-modified GaN:ZnO photocatalysts were observed using HR-TEM (Fig. S3). The dyes covered the GaN:ZnO surface with random thickness, and no difference in the structures of the expanded porphyrins was observed in the adsorption states. From TEM-EDX observation, the loaded co-catalysts (IrO_2, RhO_X, and NiO) were 2-5 nm in size and highly dispersed around the GaN:ZnO surface as shown in Fig. S4. In this study, the GaN:ZnO photocatalysts were prepared in the order of IrO_2 loading, dye coating, and RhO_X-NiO loading for GaN:ZnO powder, as previously reported.[17] Although IrO_2 loading was performed before dye coating, IrO_2 contacted the reaction solution directly because the dye did not completely cover the catalyst. Dye amount was optimized as 0.5 wt% in this study, because excess amount of the dyes covered IrO_2 co-catalysts, and decreased gas formation rates (Fig. S5).

Table 1 Modification effect on the photocatalytic water splitting activity of GaN:ZnO.[a, b, c, d]

Compound	Amount of compound /µmol	Formation rate /µmol h^{-1}		Ratio (H_2/O_2)	Residual ratio /%
		H_2	O_2		
1	25.7	35.6	12.3	2.9	82.5
2	20.5	14.5	5.3	2.7	60.2
3	17.1	46.0	22.3	2.1	95.2
4	14.7	20.6	9.6	2.1	92.1
5	12.3	16.7	7.0	2.4	77.8
6	10.6	14.4	6.1	2.4	62.9
None	-	23.3	10.0	2.3	-

[a] Catalyst: RhO_X (0.1 wt%), NiO (0.1 wt%)/Porphyrinoid (0.5 wt%)/IrO_2 (0.1 wt%)-GaN:ZnO (50 mg). [b] Reaction solution: distilled water (30 mL, pH 11). [c] Light source: 300 W Xe lamp (full arc, 622 mW). [d] Reaction time: 5 h.

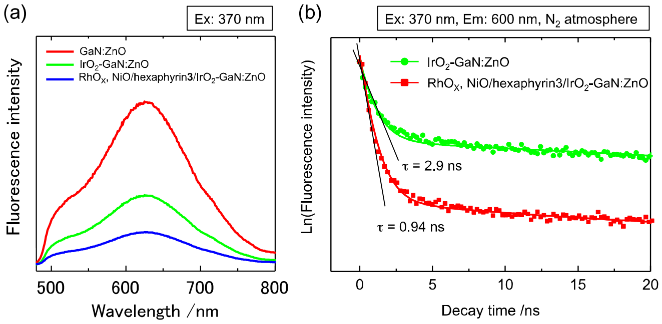

Fig. 3 (a) Fluorescence spectra and (b) fluorescence life-time measurements for GaN:ZnO and RhO_X, NiO/compound **3**/IrO_2-GaN:ZnO photocatalysts.

Table 1 shows H_2 and O_2 formation rates for photocatalytic water splitting on the GaN:ZnO photocatalysts modified with compounds **1-6**. Compared with the result for the non-modified catalyst, *meso*-tetrakis(pentafluorophenyl)porphyrin (**1**) and *meso*-hexakis(pentafluorophenyl) [26] hexaphyrin (**3**) exhibited positive effects on the photocatalytic activity. The formation ratio seems to relate to the dye residual ratio, which was calculated from the absorbance of the dyes before and after the photocatalytic reaction. Clearly, **3** was the most stable and effective dye among the expanded porphyrins examined for improving the activity of GaN:ZnO photocatalyst. The stability of **3** was also confirmed by ^{1}H-NMR measurements (Figs. S6, S7). Figure S8 shows the photocatalytic water splitting on RhO_X, NiO/compound **3**/IrO_2-GaN:ZnO photocatalyst. The formation of H_2 and O_2 was observed immediately after light irradiation, and amounts of gases increased linearly with increasing reaction time. Furthermore, the formation ratio of H_2:O_2 was almost 2:1, thus a stoichiometric water splitting reaction occurred on the GaN:ZnO photocatalyst modified with compound **3**.

To investigate the excitation energy transfer in the dye-modified GaN:ZnO photocatalyst, fluorescence spectra were measured as shown in Fig. 3(a). Under excitation light at a wavelength of 370 nm, broad photoluminescence from GaN:ZnO was observed from 550 nm to 800 nm. The photoluminescence intensity was decreased by IrO_2 loading. As-prepared GaN:ZnO contains many surface vacancies and defects, and these lattice defects acted as recombination centers to generate fluorescence.[18] In

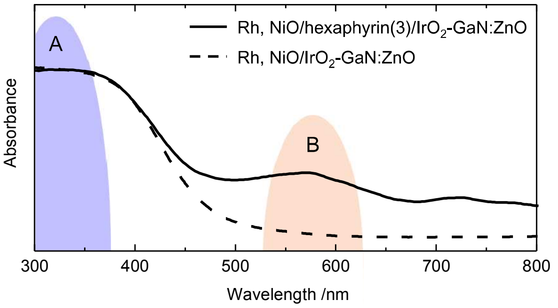

Fig. 4 UV-vis absorption spectra for GaN:ZnO photocatalysts and wavelength regions of external light sources in Table 2.

Table 2 Wavelength dependence of the activity of RhO_X, NiO /hexaphyrin (**3**) /IrO_2-GaN:ZnO. [a, b]

Dye	Light[c, d]	Formation rate /μmol h^{-1}		Ratio
		H_2	O_2	(H_2/O_2)
3	A + B	8.3	3.9	2.13
3	A	2.8	1.3	2.15
3	B	0.0	0.0	-
None	A+B	2.2	1.1	2.00

[a] Catalyst: RhO_X (0.1 wt%), NiO (0.1 wt%)/Dye (0.5 wt%) /IrO_2 (0.1 wt%)-GaN:ZnO. [b] Amount of dye: 0.17 μmol. [c] 300W Xe lamp (80 mW). [d] A: 250 nm < λ < 385 nm; B: 530 nm < λ < 630 nm.

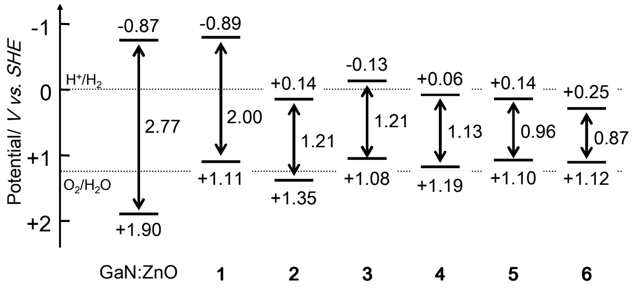

Fig. 5 Energy band levels for GaN:ZnO and porphyrinoids used in this study.

the IrO_2 loading process, GaN:ZnO was calcined at 673 K for 1 h in air. This process promoted the crystallization of GaN:ZnO, and lattice defects decreased as a post-calcination effect of GaN:ZnO reported by Maeda et al.[13] Therefore, the fluorescence intensity from GaN:ZnO decreased by IrO_2 loading. Furthermore, the fluorescence from IrO_2-loaded GaN:ZnO was also quenched by modification with **3**. Although **3** has an absorption band around 600 nm, its fluorescence lifetime decreased due to modification with **3** [Fig. 3(b)]. These results suggest that the excitation energy of GaN:ZnO transferred to **3**. It was also suggested from the photocurrent measurements of **3**-modified GaN:ZnO photoelectrode (Fig. S9). The photo-current direction was reversed by the modification with **3**, thus photoexcited electrons in the valence band of GaN:ZnO transferred to LUMO or HOMO levels of **3**. The wavelength dependence of the water splitting activity was investigated to confirm the necessity of visible light excitation of **3** for the water splitting reaction. Figure 4 shows the relationship between the absorption spectra for GaN:ZnO photocatalysts and the wavelength regions of Xe lamps with a band-pass glass filter, which was used in the experiment of wavelength dependency. Light at the bands of A and B in Fig. 4 was used for excitation of GaN:ZnO and compound **3**, respectively. The lamps were adjusted to the same intensity (80 mW). Although water splitting was achieved on dye-modified GaN:ZnO under the irradiation by both Xe lamps, the water-splitting reaction hardly proceeded under visible light irradiation (530 nm < λ < 630 nm) as shown in Table 2. The excitation of **3** was insufficient to decompose water, and thus the charge transfer mechanism in **3**-modified GaN:ZnO photocatalyst is different from that in DSCs. The formation rates on the dye-modified GaN:ZnO under UV light irradiation (250 nm < λ < 385 nm) were almost the same as those for RhO_X and NiO/IrO_2-GaN:ZnO. These results suggest that the photoexcitation of both GaN:ZnO and **3** were necessary to yield a positive effect of dye-modification on the photocatalytic activity. The **3**-modified GaN:ZnO photocatalyst successfully achieved water splitting by using light around 600 nm in wavelength. In our previous study, we found that the charge transfer mechanism of GaN:ZnO modified with chloro-(5,10,15,20-tetraphenylporphyrinato)chromium(III) involved a two-step excitation of both GaN:ZnO and porphyrin.[14] Thus, photocatalytic water splitting on the expanded porphyrin modified GaN:ZnO photocatalysts may also occur with a two-step excitation process, which is similar to photosynthesis.

Figure 5 shows energy band levels of GaN:ZnO and porphyrinoids determined by cyclic voltammetry, spectroscopic measurements, or from the literature.[19] The LUMO energy levels of the expanded porphyrins tended to shift to higher potential with expanding ring structure. Compounds **1** and **3**, which have more negative LUMO energy levels than the hydrogen formation potential, showed positive effects on the photocatalytic activity of GaN:ZnO. It was reported that the photocatalytic water splitting activity of dye-modified photocatalysts is related to the LUMO energy levels of dyes.[20] Therefore, it is suggested that the excited electrons in the LUMO level of compounds contributed to the reduction reaction of water (hydrogen formation reaction) in water splitting on the dye-modified GaN:ZnO photocatalyst. Furthermore, the water splitting activity might be influenced by dye conformation. It is thought that the π-π interaction of molecules in dye aggregates of compounds **1** and **3** is relatively developed than that of distorted porphyrinoids (**4**-**6**). Well-developed π-π stacking may contribute to the high electrical conductivity.[21] In the case of dye-modified photocatalyst, the electrical conductivity of dye aggregate is also important for the photocatalytic activity, because a number of photogenerated charges (electrons and holes), which can reach the reaction site without recombination, depend on the conductivity of dye aggregate. In addition, compound **3** has large absorption coefficient, which is one order of magnitude larger than those of other porphyrinoids (Table S1). Thus, compound **3** is more suitable for converting light energy than compound **1**. Compound **3** was the most effective dye for improving the photocatalytic activity of GaN:ZnO in this study because it has a suitable LUMO energy level, good stability under water splitting conditions, and a large absorption band in the visible light region.

Consequently, this study revealed the modification effect of expanded porphyrins on the photocatalytic water split-ting activity of GaN:ZnO. Among the expanded porphyrins examined, *meso*-hexakis(pentafluorophenyl) [26]hexaphyrin (**3**) showed the most positive effect in improving the photocatalytic activity. Unlike the dye sensitization, the excitation of both GaN:ZnO and dye was necessary to achieve efficient water splitting. Compound **3** assisted the water splitting reaction over the GaN:ZnO photocatalyst by using visible light around 600 nm, which is a wavelength region abundantly contained in solar light. This study indicates that surface modification of expanded porphyrins has the potential to improve the photocatalytic activity of inorganic semiconductor photocatalysts under solar light irradiation and the expanded porphyrins, especially hexaphyrin, are applicable for solar energy conversion.

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[a] Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Japan. E-mail: h.hagiwara@cstf.kyushu-u.ac.jp

[b] International Institute for Carbon-Neutral Energy Research, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Japan.

[c] International Research Center for Hydrogen Energy, Kyushu University 744 Motooka, Nishi-ku, Fukuoka, Japan.

Electronic Supplementary Information (ESI) available: [Experimental procedures, UV-vis absorption spectra, TEM-EDX analysis, ^{1}H NMR spectra, and X-ray diffractions]. See DOI: 10.1039/c000000x/

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