

# Analysis and Regulation of Unusual Adsorption of Phthalocyanine Zinc(II) into a Nafion Film as Investigated by UV–vis Spectroscopic Techniques

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Phthalocyanine zinc(II) (ZnPc) was found to be adsorbed well into a Nafion (Nf) film. The kinetic analysis suggested that the adsorption of ZnPc into the Nf film is controlled by its diffusion in the Nf film with a diffusion coefficient of  $D = 1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  that is higher than those ( $10^{-9}$ – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ) of cationic redox molecules in the Nf film by 3–6 orders of magnitude. The adsorption isothermal was analyzed by a Brunauer–Emmett–Teller (BET) equation suggesting multilayer adsorption of ZnPc into the film. The BET analysis provided the amount of ZnPc for monolayer adsorption ( $w_m = 1.50 \times 10^{-7} \text{ mol cm}^{-2}$ ), from which the effective area for the ZnPc adsorption was estimated to be larger by a factor of  $1.7 \times 10^3$  than the Nf film area ( $1.0 \text{ cm}^2$ ). The absorption spectra of a Nf film adsorbing ZnPc ((Nf/ZnPc)<sub>ads</sub> film) exhibited two broad absorption bands at 385 and 680–750 nm without any structural features, which is significantly different from the absorption spectra of either ZnPc solution in DMF or a (Nf/ZnPc)<sub>mix</sub> film prepared from a DMF solution containing Nf and ZnPc by solvent evaporation. This is ascribed to the formation of a ZnPc aggregate in the (Nf/ZnPc)<sub>ads</sub> film. Photoluminescence data for the (Nf/ZnPc)<sub>mix</sub> film suggested the presence of a ZnPc monomer and dimer at equilibrium in the film with a concentration of 0.1 M and that energy transfer occurs from the monomer to the dimer in excitation of the monomer (at  $\lambda_{\text{ex}} = 609 \text{ nm}$ ) to yield emission from the dimer. By contrast, photoluminescence data for the (Nf/ZnPc)<sub>ads</sub> film suggested that the excited ZnPc is self-quenched significantly by the formation of the ZnPc aggregate in the film. The lesser electroactivity of ZnPc in the (Nf/ZnPc)<sub>ads</sub> film compared with that in the (Nf/ZnPc)<sub>mix</sub> film could be ascribable to more difficult diffusion of ZnPc in the former film due to the formation of the ZnPc aggregate. The adsorption of ZnPc into the Nf film was significantly regulated by simple pretreatments of the Nf film such as immersion in solvents and storage under solvent vapors. The regulation was explained by controlled physical and chemical properties of a channel for mass and ion transport that is formed by sulfonate groups, counteranions, and solvent molecules in the Nf film.

## Introduction

The use of perfluorosulfonated ionomer films has substantially promoted the development of several important branches of the chemical industry such as electrocatalytic technologies and energy conversion.<sup>1,2</sup> Nafion (Nf) has been studied mainly for the structure and properties as well as application of the perfluorosulfonated ionomer films.<sup>3,4</sup> The chemical structure of Nf consists of a poly(tetrafluoroethylene) backbone with perfluorinated pendant chains terminated by sulfonate groups in either the acidic ( $\text{H}^+$ ) or neutralized form ( $\text{Na}^+$ ,  $\text{K}^+$ , etc.). A Nf film is known to have two fundamentally distinctive structural regions: (1) a hydrophobic region formed by the perfluorinated polymer network and (2) a hydrophilic ionic cluster region comprising the sulfonate groups, counteranions, and water molecules. The neighboring clusters are interconnected through channels that enable the charge and mass transport of the ion and solvent. A Nf film can adsorb easily

cationic molecules and ions by a cation exchange from its solution thanks to the sulfonate groups, and their adsorption has been studied extensively to yield many kinds of functional films.<sup>5–10</sup> Contrastively, functional Nf films based on noncationic molecules are relatively scarce because they cannot be adsorbed into the Nf film by a cation exchange. The scarcity of Nf/noncationic molecule films renders the aspect of such molecules in the Nf film to remain open.

Metal phthalocyanines and the derivatives, exhibiting unique photochemical and electrochemical properties,<sup>11</sup> are attracting much attention as promising materials for designing photonic and electronic nanodevices such as solar cells,<sup>12–14</sup> electrocatalysts,<sup>15</sup> sensors,<sup>16,17</sup> and displays.<sup>18,19</sup> We reported the mechanism of charge transport in the Nf/phthalocyanine zinc(II) (ZnPc) film prepared from a mixture of dimethylformamide (DMF) solution containing Nf and ZnPc by solvent evaporation (denoted as (Nf/ZnPc)<sub>mix</sub> film), revealing that a monomer and dimer of ZnPc are present at equilibrium in the film with a concentration of 0.1–0.3 M and only a monomer works as a hole carrier by its physical displacement.<sup>20</sup> Upon undertaking the extended research, we deal first with the unusual observation that (noncationic) ZnPc is adsorbed well into a Nf film. Herein,

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we present a unique (Nf/ZnPc)<sub>ads</sub> film formed by the adsorption of ZnPc into the Nf film. The presented (Nf/ZnPc)<sub>ads</sub> film is significantly different in a spectroscopic feature and electroactivity from the (Nf/ZnPc)<sub>mix</sub> film. The adsorption process of ZnPc into the Nf film will be analyzed and controlled by some simple pretreatments.

### Experimental Section

**Materials.** Nafion 117 solution (5 wt % alcoholic solution) was purchased from Aldrich Chemical Co. Inc. and diluted with CH<sub>3</sub>OH before use. ZnPc was purchased from Aldrich Chemical Co. Inc. and used as received. The organic solvents CH<sub>2</sub>Cl<sub>2</sub>, DMF, toluene, and CH<sub>3</sub>CN were purified as described in the literature<sup>21</sup> before use.

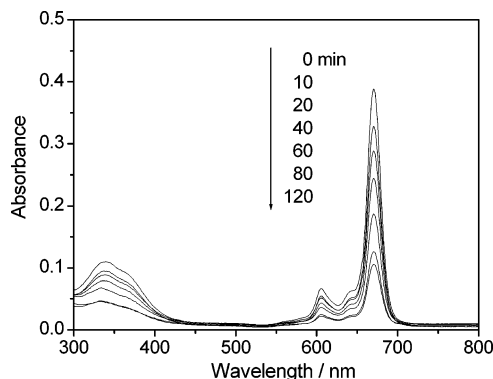
**Preparation of a Nf Film and Adsorption of ZnPc into the Film.** A Nf film was prepared by casting 10  $\mu$ L of a 2.5 wt % Nf solution onto a glass substrate (1.0 cm<sup>2</sup>) or indium tin oxide (ITO) electrode (effective area, 1.0 cm<sup>2</sup>). The film thickness (*L*) was calculated as 1.0  $\mu$ m by eq 1:

$$L = \frac{0.025Vd_{\text{sol}}}{Ad_{\text{Nf}}} \quad (1)$$

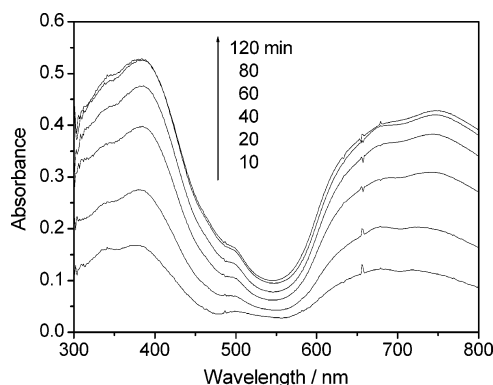
where *V* is the volume ( $1.0 \times 10^{-2}$  cm<sup>3</sup>) of the cast Nf solution, *d*<sub>sol</sub> is the density (0.83 g cm<sup>-3</sup>) of the Nf solution, *d*<sub>Nf</sub> (2.0 g cm<sup>-3</sup>)<sup>22</sup> is the density of the Nf film, and *A* (1.0 cm<sup>2</sup>) is the substrate area. The Nf-film-coated glass substrate or ITO electrode was immediately (within a few minutes) used for the experiments of ZnPc adsorption unless otherwise mentioned. In some cases, several pretreatments were employed involving either immersion into solvents of water, toluene, CH<sub>2</sub>Cl<sub>2</sub>, and CH<sub>3</sub>CN for 3 h at 25 °C or storage in air or in the vapor of these solvents under the pressure of saturated vapor at 25 °C for 1–7 days. The Nf-film-coated glass substrate or ITO electrode was dipped in a ZnPc solution ( $(0.1\text{--}1.25) \times 10^{-4}$  M, 2.5 mL) in CH<sub>2</sub>Cl<sub>2</sub> for ZnPc adsorption. The amount of ZnPc adsorbed into the film was calculated from the visible absorption spectral change of the ZnPc solution before and after the ZnPc adsorption and the molar absorption coefficient ( $\epsilon_{671} = 155\,300$  M<sup>-1</sup> cm<sup>-1</sup>) at  $\lambda_{\text{max}} = 671$  nm. The ZnPc concentration in the film was obtained from the amount of ZnPc adsorbed in the film and the film volume.

**Preparation of the (Nf/ZnPc)<sub>mix</sub> Film.** DMF solution (10 mL) containing 0.78–2.90 mg of ZnPc was prepared, and then, a portion of the solution was mixed with a 5 wt % Nf solution in a weight ratio of 9:1 (ZnPc solution/Nf solution) to obtain a mixture solution containing the known amount of ZnPc and 0.5 wt % Nf. The mixture solution (42.5  $\mu$ L) was cast onto a glass substrate (1.0 cm<sup>2</sup>) or an ITO electrode (effective area, 1.0 cm<sup>2</sup>) and then air-dried at room temperature for 24 h to form a ZnPc-containing Nf film. The thickness of the film coated was estimated to be 1.0  $\mu$ m using  $V = 42.5$   $\mu$ L, *d*<sub>sol</sub> = 0.942 g cm<sup>-3</sup>, *d*<sub>Nf</sub> = 2.0 g cm<sup>-3</sup>, and *A* = 1.0 cm<sup>2</sup> according to eq 1. The ZnPc concentration in the film was obtained from its amount in the film and the film volume.

**Measurements.** Absorption spectra of the ZnPc solution were measured in a quartz cell with 1 mm or 1 cm of a light pass length using a photodiode array spectrophotometer (Shimadzu, Multispec-1500). The absorption spectra of the ZnPc-containing Nf film were measured using the same appliance. Photoluminescence spectra of the ZnPc solution were measured in a quartz cell (1 cm  $\times$  1 cm) using a fluorescence spectrophotometer (Hitachi F-4010). Photoluminescence spectra of the ZnPc-containing Nf film in water were taken from the rear side of



**Figure 1.** Absorption spectral change of  $3.0 \times 10^{-5}$  M ZnPc solution (2.5 mL) in CH<sub>2</sub>Cl<sub>2</sub> when dipping a Nf film in the solution. The light path length of the spectrophotometric cell is 1 mm. The dipping times are indicated in the figure.

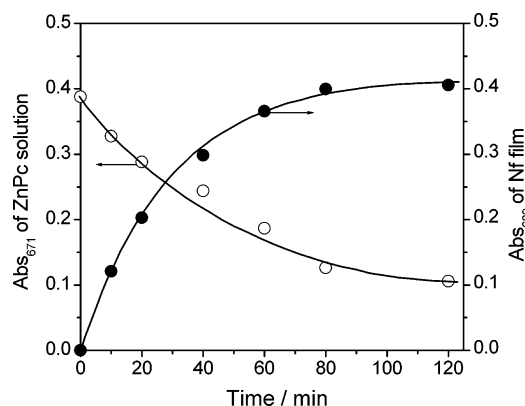


**Figure 2.** Absorption spectral change of a Nf film when dipped in  $3.0 \times 10^{-5}$  M ZnPc solution (2.5 mL) in CH<sub>2</sub>Cl<sub>2</sub>. The dipping times are indicated in the figure.

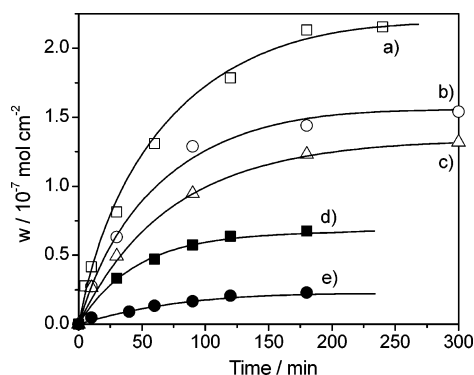
the glass substrate at an angle of 45° to minimize the light scattering effect using the same appliance. All the photoluminescent measurements were carried out at 25 °C under an argon atmosphere. Cyclic voltammograms of the ZnPc-containing Nf film coated on the ITO electrode were measured in an aqueous solution of 0.1 M KNO<sub>3</sub> (pH 6.3) at a scan rate of 20 mV s<sup>-1</sup> using a conventional single-compartment electrochemical cell equipped with a modified ITO working electrode, a saturated calomel reference electrode (SCE), and a platinum wire counter electrode. Distilled ion-exchange water was used for all the experiments.

### Results and Discussion

**Investigation and Analysis of the Adsorption Process of ZnPc into a Nf Film.** The UV–vis absorption spectrum of the ZnPc solution in CH<sub>2</sub>Cl<sub>2</sub> exhibits a well-defined Soret band and Q band of ZnPc at 337 and 671 nm, respectively. When dipping the Nf film in the ZnPc solution, the absorbances of the solution decreased with the dipping time, as shown in Figure 1. Simultaneously, the color of the Nf film turned blue. This is illustrated by the absorption spectral change of the Nf film shown in Figure 2. The absorption spectra of the Nf film showed characteristically two broad absorption bands at 340–385 and 680–750 nm, which are very different from those in solution. (The difference in the spectral shape will be discussed later.) The absorbances of the film increased with an almost unchanged spectral shape, as the dipping time went on. The absorbances at 689 nm of the Nf film (*Abs*<sub>689</sub>) and at 671 nm of the solution (*Abs*<sub>671</sub>) were plotted with the dipping time in Figure 3. The



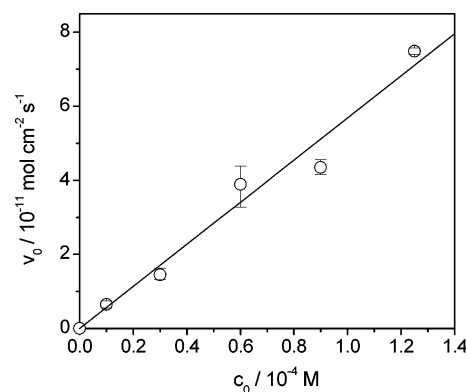
**Figure 3.** Plots of absorbances at 671 nm of the ZnPc solution ( $Abs_{671}$ , open circles) and at 689 nm of the Nf film ( $Abs_{689}$ , closed circles) vs dipping time. The conditions are indicated in Figures 1 and 2.



**Figure 4.** Time courses of the amount ( $w$ ) of ZnPc adsorbed into the Nf film when dipped in the ZnPc solution with various concentrations. The ZnPc concentrations in the solution are (a)  $1.25 \times 10^{-4}$  M, (b)  $9.0 \times 10^{-5}$  M, (c)  $6.0 \times 10^{-5}$  M, (d)  $3.0 \times 10^{-5}$  M, and (e)  $1.0 \times 10^{-5}$  M.

$Abs_{689}$  value of the Nf film increased in response to the decrease of the  $Abs_{671}$  value of the solution, showing that ZnPc is adsorbed into the Nf film. Similar adsorption of ZnPc into the Nf film was observed from its solution in toluene and benzene aside from  $CH_2Cl_2$ . Adsorbed ZnPc was not desorbed from the Nf film when the ZnPc-adsorbing film was immersed in  $CH_2Cl_2$ , toluene, and benzene, suggesting the irreversible adsorption of ZnPc. The irreversibility is not caused by a chemical change of ZnPc in the Nf film because, when immersing the ZnPc-adsorbing Nf film in DMF, ZnPc can be quantitatively retrieved as its solution in DMF by dissolution of the film.

Figure 4 shows time courses of the amount ( $w$ /mol  $cm^{-2}$ ) of ZnPc adsorbed into the Nf film from the ZnPc solution with various concentrations. For each concentration,  $w$  increased with time and saturated in more than 3 h. The saturated  $w$  value increased from  $2.3 \times 10^{-8}$  to  $2.1 \times 10^{-7}$  mol  $cm^{-2}$  with an increase in the ZnPc concentration in the solution from  $1.0 \times 10^{-5}$  to  $1.25 \times 10^{-4}$  M. When adsorbing  $2.1 \times 10^{-7}$  mol  $cm^{-2}$  of ZnPc, the concentration ( $c_{Nf}$ ) of ZnPc in the Nf film (film volume,  $1.0 \times 10^{-4}$   $cm^3$ ) is extremely high (2.1 M). The initial adsorption rate ( $v_0$ /mol  $cm^{-2}$   $s^{-1}$ ) was estimated from the tangent of the initial change of  $w$ , and it increased linearly with the ZnPc concentration ( $c_0$ /M) in the solution, as shown in Figure 5. This indicates that the adsorption of ZnPc is a first-order process with respect to the ZnPc concentration. This could suggest that the adsorption of ZnPc is most possibly diffusion-controlled in the Nf film. The first-order kinetics of the ZnPc



**Figure 5.** Plots of the initial rate ( $v_0$ ) of ZnPc adsorption from the  $CH_2Cl_2$  solution into the Nf film vs the ZnPc concentration ( $c_0$ ) in the solution.

adsorption was analyzed on the basis of Fick's diffusion law (eq 2):

$$v_0 = -D \left( \frac{dc_0}{dx} \right) \times 10^{-3} \quad (2)$$

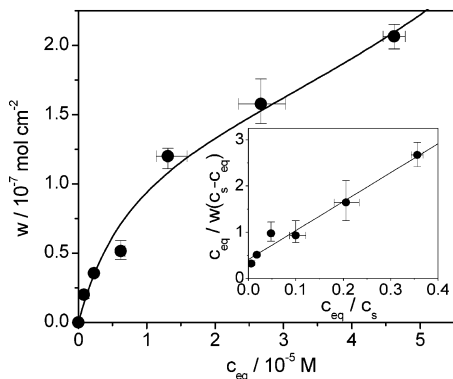
where  $D$  and  $x$  are the diffusion constant ( $cm^2$   $s^{-1}$ ) and the thickness (cm) of the diffusion layer and  $dc_0/dx$  represents a concentration gradient. If assuming  $dx$  as the diffusion length,  $\sqrt{6Dt}$  at  $t = 1$  s, the concentration gradient is represented as  $c_0/\sqrt{6D}$ , and eq 3 can be derived from eq 2.

$$v_0 = -\sqrt{\frac{D}{6}} \times c_0 \times 10^{-3} \quad (3)$$

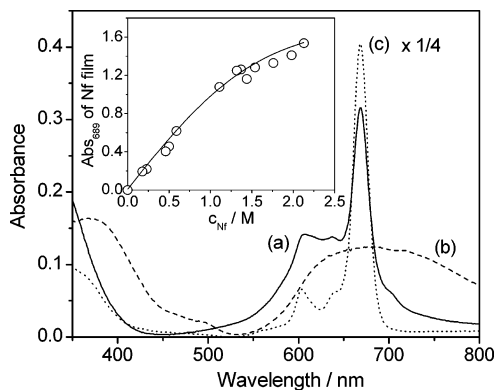
The slope of the straight line in Figure 5 provided  $D = (1.9 \pm 0.2) \times 10^{-6}$   $cm^2$   $s^{-1}$  as the diffusion constant of ZnPc in the Nf film. This value is somewhat lower than that ( $(0.66-1.1) \times 10^{-5}$   $cm^2$   $s^{-1}$ ) of the macrocyclic complex of porphyrin derivatives in organic solvent.<sup>23</sup> It is higher by 3–6 orders of magnitude than those ( $10^{-9}$ – $10^{-12}$   $cm^2$   $s^{-1}$ ) of cationic Ru complexes in the Nf films dipped in an aqueous electrolyte solution as measured by electrochemical techniques.<sup>6,24</sup> The diffusion of cationic molecules is electrostatically restricted by sulfonate groups of Nf in the film.<sup>6</sup> Hydrophobic and noncationic ZnPc could be adsorbed onto the Nf film, possibly by hydrophobic interaction between ZnPc and the perfluorinated polymer network of Nf. ZnPc is supposed to be incorporated from the mass transport channel for ions and solvents, and ZnPc could possibly diffuse through an interface region between the hydrophobic perfluorinated polymer network and a hydrophilic mass transport channel in the Nf film. ZnPc is not subjected to electrostatic restriction from sulfonate groups of Nf in diffusion in the film. This could account for the very fast diffusion of ZnPc in the Nf film.

Adsorption isotherms were examined in order to evaluate the adsorption process of ZnPc into the Nf film. The plot of  $w$  versus the equilibrium ZnPc concentration ( $c_{eq}$ /M) in the solution is shown in Figure 6. The adsorption isotherm could not be analyzed using a Langmuir adsorption isotherm assuming a monolayer adsorption mode. A Brunauer–Emmett–Teller (BET) adsorption isotherm (eq 4) was applied to the isothermal curve in Figure 6 assuming a multilayer adsorption mode:

$$w = \frac{Bw_m c_{eq}}{(c_s - c_{eq}) \left\{ 1 + (B - 1) \frac{c_{eq}}{c_s} \right\}} \quad (4)$$



**Figure 6.** Adsorption isotherm of ZnPc from its  $\text{CH}_2\text{Cl}_2$  solution into the Nf film.  $w$  and  $c_{\text{eq}}$  are the amount of ZnPc adsorbed and concentration in the solution at equilibrium, respectively. The solid line is a simulated curve based on the BET adsorption isotherm (eq 4). The inset shows a plot of  $c_{\text{eq}}/w(c_s - c_{\text{eq}})$  vs  $c_{\text{eq}}/c_s$  and a simulated straight line based on eq 5.



**Figure 7.** Absorption spectra of (a) the  $(\text{Nf/ZnPc})_{\text{mix}}$  film, (b) the  $(\text{Nf/ZnPc})_{\text{ads}}$  film, and (c)  $3.0 \times 10^{-6}$  M ZnPc solution in DMF. The ZnPc concentration ( $c_{\text{Nf}}$ ) is 0.1 M for both films. The inset shows the absorbance ( $\text{Abs}_{689}$ ) at 689 nm of the  $(\text{Nf/ZnPc})_{\text{ads}}$  film vs  $c_{\text{Nf}}$ .

where  $w_m$  ( $\text{mol cm}^{-2}$ ),  $B$ , and  $c_s$  are the amount of ZnPc for a monolayer adsorption, a constant related to the heat of adsorption, and the saturated ZnPc concentration ( $1.3 \times 10^{-4}$  M) in the solution, respectively. Equation 4 can be transformed into eq 5.

$$\frac{c_{\text{eq}}}{w(c_s - c_{\text{eq}})} = \frac{1}{Bw_m} + \frac{(B-1)}{Bw_m} \times \frac{c_{\text{eq}}}{c_s} \quad (5)$$

According to eq 5, the plot of  $c_{\text{eq}}/w(c_s - c_{\text{eq}})$  versus  $c_{\text{eq}}/c_s$  for experimental data gave a straight line, as shown in the inset of Figure 6. This indicates that ZnPc is adsorbed into the Nf film in a multilayer mode obeyed by the BET adsorption isotherm. The intercept and slope provided  $w_m = (1.5 \pm 0.2) \times 10^{-7}$   $\text{mol cm}^{-2}$  and  $B = 16 \pm 6$ . The effective area for ZnPc adsorption in a unit area ( $1.0 \text{ cm}^2$ ) of the Nf film can be estimated to be  $1.7 \times 10^3 \text{ cm}^2$  from  $w_m$  and a space ( $1.89 \text{ nm}^2$ ) per ZnPc molecule assumed as a circle with the diameter of molecular size ( $1.55 \text{ nm}$ ).<sup>25</sup> It means that the effective area for ZnPc adsorption is larger by a factor of  $1.7 \times 10^3$  than the Nf film area.

**Spectroscopic Comparison of the  $(\text{Nf/ZnPc})_{\text{ads}}$  and  $(\text{Nf/ZnPc})_{\text{mix}}$  Films.** We now compare spectroscopically the present  $(\text{Nf/ZnPc})_{\text{ads}}$  film with a  $(\text{Nf/ZnPc})_{\text{mix}}$  film. The visible absorption spectra of both of the films are shown in Figure 7 including that in a DMF solution, and the spectroscopic features are summarized in Table 1. The spectrum of the  $(\text{Nf/ZnPc})_{\text{mix}}$  film

**TABLE 1: Summary of the Visible Absorption Spectroscopic Features of ZnPc in Nafion Films, DMF, and  $\text{CH}_2\text{Cl}_2$  Solution**

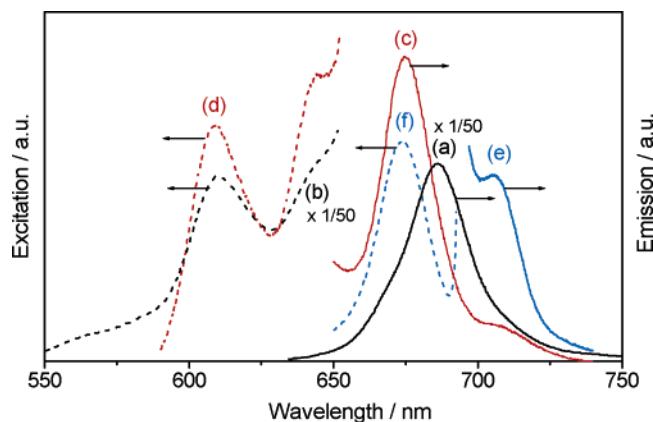
film or solution	$\lambda_{\text{max}}/\text{nm}$	$\epsilon/10^4 \text{ M}^{-1} \text{ cm}^{-1}$
(Nf/ZnPc) <sub>mix</sub>	607	1.30
	637	1.35
	669	3.16
(Nf/ZnPc) <sub>ads</sub>	689	0.97
	DMF solution	603
CH <sub>2</sub> Cl <sub>2</sub> solution	637	2.28
	669	14.6
	606	2.66
	645	2.54
	671	15.5

exhibited maximum peaks at  $\lambda_{\text{max}} = 607$ , 637, and 669 nm which are almost identical to the well-defined maximum peaks ( $\lambda_{\text{max}} = 603$ , 637, and 669 nm) in the DMF solution. However, the ratio ( $\epsilon_{637}/\epsilon_{669} = 0.44$ ) of the molar absorption coefficients at 637 and 669 nm for the  $(\text{Nf/ZnPc})_{\text{mix}}$  film is higher than that ( $\epsilon_{637}/\epsilon_{669} = 0.15$ ) for the DMF solution, indicating the formation of a ZnPc dimer with an absorption maximum at  $\lambda_{\text{max}} = 635 \text{ nm}$ .<sup>20,26</sup> Absorption spectroscopic data suggest that the ZnPc monomer and dimer are present at equilibrium in the  $(\text{Nf/ZnPc})_{\text{mix}}$  film under the conditions of  $c_{\text{Nf}} = 0.1 \text{ M}$ . The absorption spectrum of the  $(\text{Nf/ZnPc})_{\text{ads}}$  film is significantly different from that of the  $(\text{Nf/ZnPc})_{\text{mix}}$  film with the same  $c_{\text{Nf}}$ , and the former afforded two broad absorption bands at 370 and 689 nm without any structural features in a visible region. The broad absorption spectroscopic feature could suggest that ZnPc is aggregated to a great extent in the  $(\text{Nf/ZnPc})_{\text{ads}}$  film, which is consistent with the multilayer adsorption of ZnPc into the film suggested by the BET analysis. ZnPc could be locally concentrated in the interface region between the hydrophobic perfluorinated polymer network and the hydrophilic mass transport channel in the  $(\text{Nf/ZnPc})_{\text{ads}}$  film. The locally concentrated ZnPc would be favorable to be aggregated in the film.

The spectral shape of the  $(\text{Nf/ZnPc})_{\text{ads}}$  film did not change appreciably with the ZnPc concentration (refer to Figure 2), and the plot of absorbance ( $\text{Abs}_{689}$ ) at 689 nm of the film versus  $c_{\text{Nf}}$  exhibited a linear relationship to the extent of 1.2 M (shown in the inset of Figure 7), showing that the formation of the aggregated ZnPc is hardly dependent on  $c_{\text{Nf}}$  under the conditions employed ( $c_{\text{Nf}} = 1.8 \times 10^{-1} - 1.2 \text{ M}$ ). The  $c_{\text{Nf}}$  value could be high enough for ZnPc to be aggregated in the  $(\text{Nf/ZnPc})_{\text{ads}}$  film. The molar absorption coefficient of ZnPc in the  $(\text{Nf/ZnPc})_{\text{ads}}$  film was calculated as  $9700 \pm 20 \text{ M}^{-1} \text{ cm}^{-1}$  from the slope of the straight line.

A photoluminescence spectroscopic technique was used in order to characterize the ZnPc species in both of the films. The emission and excitation spectra are shown in Figure 8 for the films and DMF solution, and the maximum wavelength ( $\lambda_{\text{max}}$ ) for the emission spectra and emission yields ( $\Phi_{\text{rel}}$ ) relative to that of ZnPc in the DMF solution are summarized in Table 2. For the ZnPc solution, the excitation at  $\lambda_{\text{ex}}$  (excitation wavelength) = 609 nm gave emission spectrum a with  $\lambda_{\text{max}} = 686 \text{ nm}$  that is well-defined fluorescence of the ZnPc monomer. For the  $(\text{Nf/ZnPc})_{\text{mix}}$  film, excitation at  $\lambda_{\text{ex}} = 609 \text{ nm}$  yielded emission spectrum c with a maximum and shoulder at  $\lambda_{\text{max}} = 675$  and 708 nm, respectively. Although the emission peak at  $\lambda_{\text{max}} = 675 \text{ nm}$  was shorter than that ( $\lambda_{\text{max}} = 686 \text{ nm}$ ) for the DMF solution, excitation spectrum d for emission at  $\lambda_{\text{em}}$  (emission wavelength) = 675 nm for the  $(\text{Nf/ZnPc})_{\text{mix}}$  film was similar to that for DMF solution (excitation spectrum b at  $\lambda_{\text{em}} = 686 \text{ nm}$ ), showing that the emission band at  $\lambda_{\text{max}} = 675 \text{ nm}$  (in spectrum c) can be assigned to emission from the ZnPc





**Figure 8.** Photoluminescence (solid lines) and excitation (dashed lines) spectra of the (Nf/ZnPc)<sub>mix</sub> film ( $c_{\text{Nf}} = 0.1$  M, red and blue) and  $1.0 \times 10^{-5}$  M ZnPc solution in DMF (black): (a) emission spectrum of the ZnPc solution at  $\lambda_{\text{ex}} = 609$  nm; (b) excitation spectrum of the ZnPc solution at  $\lambda_{\text{em}} = 686$  nm; (c) emission spectrum of (Nf/ZnPc)<sub>mix</sub> at  $\lambda_{\text{ex}} = 609$  nm; (d) excitation spectrum of (Nf/ZnPc)<sub>mix</sub> at  $\lambda_{\text{em}} = 675$  nm; (e) emission spectrum of (Nf/ZnPc)<sub>mix</sub> at  $\lambda_{\text{ex}} = 675$  nm (for dimer); (f) excitation spectrum of (Nf/ZnPc)<sub>mix</sub> at  $\lambda_{\text{em}} = 708$  nm (for dimer). For the (Nf/ZnPc)<sub>ads</sub> film ( $c_{\text{Nf}} = 0.1$  M), neither excitation at  $\lambda_{\text{ex}} = 609$  nor excitation at  $675$  nm yielded any emission.

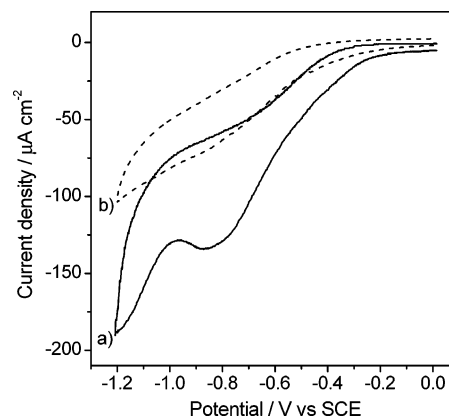
**TABLE 2: Summary of Photoluminescence Data of ZnPc in Nf Films and DMF Solution**

film or solution	$\lambda_{\text{ex}}^a/\text{nm}$	$\lambda_{\text{max}}^b/\text{nm}$	$\Phi_{\text{rel}}^c$	assignment
(Nf/ZnPc) <sub>mix</sub>	609	675 p	3.6	monomer
		708 sh	0.50	dimer
		708 p	2.6	dimer
(Nf/ZnPc) <sub>ads</sub>	609		0.0	
	675		0.0	
DMF solution	609	686 p	100	monomer

<sup>a</sup>  $\lambda_{\text{ex}}$  is the excitation wavelength. <sup>b</sup>  $\lambda_{\text{max}}$  is the maximum wavelength of emission spectra, and p and sh represents a peak and shoulder, respectively. <sup>c</sup>  $\Phi_{\text{rel}}$  was calculated by  $\Phi_{\text{rel}} = I_{\text{em}}/(1 - 10^{-A_{\text{abs}}})$ , where  $I_{\text{em}}$  and  $A_{\text{abs}}$  are the relative emission intensities at  $\lambda_{\text{max}}$  and the absorbances at  $\lambda_{\text{ex}}$ , respectively, and it was normalized by  $\Phi_{\text{rel}} = 100$  for the DMF solution.

monomer. The difference in the emission maximum between the (Nf/ZnPc)<sub>mix</sub> film ( $\lambda_{\text{max}} = 675$  nm) and ZnPc solution ( $\lambda_{\text{max}} = 689$  nm) could be ascribed to stabilization of the excited ZnPc monomer by solvation of DMF. The emission band at  $\lambda_{\text{max}} = 708$  nm (shoulder) in spectrum c could be assigned to fluorescence of the ZnPc dimer based on literature reporting the emission at  $\lambda_{\text{max}} = 699\text{--}704$  nm from a dimer of a ZnPc derivative in a  $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  solution.<sup>27</sup> This result corroborates an equilibrium between ZnPc monomer and dimer in the (Nf/ZnPc)<sub>mix</sub> film under the conditions of  $c_{\text{Nf}} = 0.1$  M. The excitation at  $\lambda_{\text{ex}} = 675$  nm for the (Nf/ZnPc)<sub>mix</sub> film results in emission spectrum e with a maximum at  $\lambda_{\text{max}} = 708$  nm for the dimer. Excitation spectrum f for the emission at  $\lambda_{\text{em}} = 708$  nm is considerably overlapped with the emission band ( $\lambda_{\text{max}} = 675$  nm) from the monomer in spectrum c. The overlap indicates that energy transfer occurs from the monomer to the dimer in excitation of the monomer (at  $\lambda_{\text{ex}} = 609$  nm) to yield emission from the dimer (as the shoulder at 708 nm in spectrum c).

Upon excitation at  $\lambda_{\text{ex}} = 609$  nm for the (Nf/ZnPc)<sub>mix</sub> film, the  $\Phi_{\text{rel}}$  values for emissions at  $\lambda_{\text{max}} = 675$  and 708 nm were  $\Phi_{\text{rel}} = 3.6$  and 0.50 as normalized by  $\Phi_{\text{rel}} = 100$  for the DMF solution, respectively. The low  $\Phi_{\text{rel}}$  values compared with that for the DMF solution could result from a self-quenching of the excited monomers and dimers due to a high concentration (0.1 M) that is higher by 4 orders of magnitude than that in the

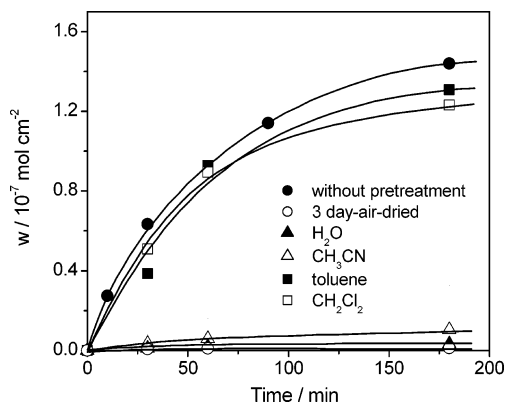


**Figure 9.** Cyclic voltammograms of (a) the (Nf/ZnPc)<sub>mix</sub> film and (b) the (Nf/ZnPc)<sub>ads</sub> film coated on an ITO electrode dipped in a 0.1 M  $\text{KNO}_3$  aqueous solution (pH 6.3) as measured at  $20 \text{ mV s}^{-1}$ .

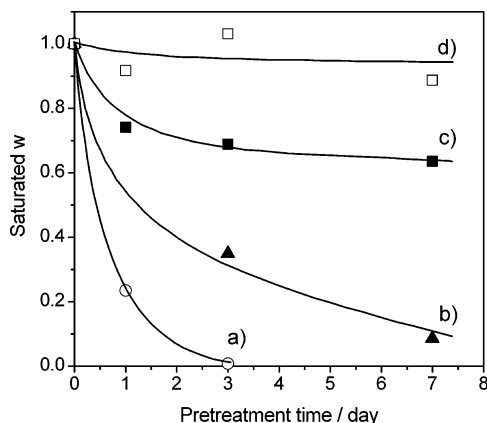
solution ( $1.0 \times 10^{-5}$  M). For the (Nf/ZnPc)<sub>ads</sub> film ( $c_{\text{Nf}} = 0.1$  M), neither excitation at  $\lambda_{\text{ex}} = 609$  nor excitation at  $\lambda_{\text{ex}} = 675$  nm yielded any emission. This suggests that the excited ZnPc is self-quenched significantly by aggregation of the ZnPc in the (Nf/ZnPc)<sub>ads</sub> film.

**Electroactivity of ZnPc Adsorbed into a Nf Film.** The electroactivity of ZnPc is also different between the (Nf/ZnPc)<sub>ads</sub> and (Nf/ZnPc)<sub>mix</sub> films. This is illustrated by cyclic voltammograms (CVs) of both the films coated on the ITO electrodes dipped in a 0.1 M  $\text{KNO}_3$  aqueous solution. The reduction wave from  $\text{Zn}^{\text{II}}\text{Pc}$  to  $\text{Zn}^{\text{I}}\text{Pc}^-$  was distinctly observed at  $-0.86$  V versus SCE for the (Nf/ZnPc)<sub>mix</sub> film (Figure 9a). For the (Nf/ZnPc)<sub>ads</sub> film, it was observed at a similar potential but was not as clear as that for the (Nf/ZnPc)<sub>mix</sub> film despite having the same  $c_{\text{Nf}}$  (Figure 9b). The observed electrochemical response of ZnPc indicates that ZnPc is surely present in the interface between the film and the ITO substrate. This result shows that ZnPc is adsorbed not only on the surface but also in the interior of the film. The lesser electroactivity of ZnPc in the (Nf/ZnPc)<sub>ads</sub> film compared with that in the (Nf/ZnPc)<sub>mix</sub> film could be ascribed to difficult diffusion of the aggregated ZnPc. It could explain the irreversibility of the ZnPc adsorption to the Nf film (vide supra). The lower diffusion coefficient for the (Nf/ZnPc)<sub>ads</sub> film than that for the (Nf/ZnPc)<sub>mix</sub> film was supported by preliminary impedance measurements of both of the films. The quantitative electrochemical parameters provided by the impedance measurements will be described elsewhere.

**Regulation of ZnPc Adsorption into a Nf Film.** A pretreatment for the Nf film can change drastically the ability of the film for ZnPc adsorption. The time courses of  $w$  for the Nf films with different pretreatments are shown in Figure 10. When the Nf film was dipped in the ZnPc solution in  $\text{CH}_2\text{Cl}_2$  without any pretreatment (within a few minutes after preparation of the Nf film), ZnPc was adsorbed into the film with a adsorption profile shown by the plot of closed circles. However, when it was air-dried for 3 days before dipping, ZnPc was not adsorbed into the Nf film during dipping in the ZnPc solution for 3 h (plot of open circles). The loss of the ZnPc adsorption ability of the air-dried Nf film could be explained by the narrowed mass transport channel due to evaporation of the solvent molecules (alcohol and water, which are contained in the Nf solution cast) from the Nf film.<sup>28</sup> Upon immersion of the Nf film in water or  $\text{CH}_3\text{CN}$  for 3 h as a pretreatment, the channel is swelled by these solvent molecules to keep it from narrowing,<sup>28</sup> but ZnPc was hardly adsorbed into the Nf film during dipping in the ZnPc solution for 3 h (plots of closed and open triangles). This could be ascribed to the decreased affinity of



**Figure 10.** Time courses of the amount ( $w$ ) of ZnPc adsorbed from the  $9.0 \times 10^{-5}$  M ZnPc solution in  $\text{CH}_2\text{Cl}_2$  into the Nf film with various pretreatments. The pretreatments are as follows: without pretreatment (closed circles); stored in air for 3 days (open circles); immersed in  $\text{H}_2\text{O}$  (closed triangles); immersed in  $\text{CH}_3\text{CN}$  (open triangles); immersed in toluene (closed squares); immersed in  $\text{CH}_2\text{Cl}_2$  (open squares) for 3 h.



**Figure 11.** Plots of the saturated amount ( $w$ ) of ZnPc adsorbed from the  $9.0 \times 10^{-5}$  M ZnPc solution in  $\text{CH}_2\text{Cl}_2$  into the Nf film with various pretreatments vs pretreatment time. The pretreatments are as follows: (a) stored in air (open circles); stored in vapors of (b)  $\text{H}_2\text{O}$  (closed triangles), (c) toluene (closed squares), and (d)  $\text{CH}_2\text{Cl}_2$  (open squares) under the pressure of saturated vapor at  $25^\circ\text{C}$ . The saturated  $w$  values were normalized by  $w$  for without pretreatment.

the channel swelled by water or  $\text{CH}_3\text{CN}$  for ZnPc adsorption, if taking into account that ZnPc is insoluble in both solvents. The swelling  $\text{CH}_3\text{CN}$  or water molecules in the channel would not be easily substituted by  $\text{CH}_2\text{Cl}_2$  molecules during dipping in the ZnPc solution in  $\text{CH}_2\text{Cl}_2$  for at least 3 h due to their strong interactions with sulfonate groups of Nf relative to  $\text{CH}_2\text{Cl}_2$ . As shown by the plots of closed and open squares, the pretreatment of immersing the Nf film in toluene or  $\text{CH}_2\text{Cl}_2$  for 3 h allowed the film to adsorb ZnPc from its solution with a similar adsorption profile to that without any pretreatment (plot of closed circles).

The adsorption of ZnPc into the Nf film is also affected by pretreatments with vapors of solvents in a gas phase. Figure 11 shows the plots of the saturated  $w$  value (normalized by the  $w$  value without any pretreatment) versus pretreatment time, when using the Nf films with various vapor pretreatments before the ZnPc adsorption from its  $\text{CH}_2\text{Cl}_2$  solution. The saturated  $w$  value decreased to 0.23 for 1 day air-dryness and reached less than 0.01 for 3 day air-dryness (plot a). When the Nf film was stored under the pressure of saturated water vapor at  $25^\circ\text{C}$ , it also decreased to 0.35 for 3 days (plot b). However, the comparison with the 3 day air-dried film shows that the adsorption ability

of the film can be 35% retained by moisture, most likely due to keeping the mass transport channel of the Nf film from narrowing. When stored for 7 days in  $\text{CH}_2\text{Cl}_2$  or toluene vapors, the saturated  $w$  value was 0.89 or 0.64, respectively (plot d or c). These vapors could also be incorporated into the mass transport channel to keep its affinity for ZnPc adsorption. This result demonstrates that the ZnPc adsorption into the Nf film is significantly regulated by the vapor of solvents.

## Conclusion

The present paper reports the first unusual observation that noncations phthalocyanine zinc(II) (ZnPc) is adsorbed well into the Nf film. It was revealed that ZnPc diffuses very fast in the Nf film with a diffusion coefficient of  $D = 1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  that is higher than those ( $10^{-9}$ – $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ ) of cationic redox molecules in the Nf film by 3–6 orders of magnitude. The analysis of the adsorption isothermal using a BET equation showed multilayer adsorption of ZnPc, providing  $w_m = 1.50 \times 10^{-7} \text{ mol cm}^{-2}$  as the amount of ZnPc for a monolayer adsorption. The absorption and photoluminescence spectroscopic features of a  $(\text{Nf}/\text{ZnPc})_{\text{ads}}$  film are significantly different from those of either a  $(\text{Nf}/\text{ZnPc})_{\text{mix}}$  film or DMF solution, suggesting that ZnPc is aggregated in the  $(\text{Nf}/\text{ZnPc})_{\text{ads}}$  film. The adsorption of ZnPc into the Nf film was significantly regulated by simple pretreatments of the Nf film such as immersion in solvents and storage under solvent vapors. This illustrates that the adsorption of ZnPc is controlled by sensitive physical and chemical properties of a channel for mass and ion transport in the Nf film. The adsorption of an electroneutral molecule into a Nf film undoubtedly results in a wide range of functional Nf films that are applicable to many kinds of electronic and photoelectronic nanodevices. We are undertaking extended studies on Nf/phthalocyanine or porphyrin derivative films prepared by an adsorption technique to develop new functional films.

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## References and Notes

- (1) Doyle, M.; Rajendran, G. Part 3: Polymer electrolyte membrane fuel cell systems (PEMFC). In *Handbook of Fuel Cells: Fundamentals, Technology and Applications*; Vielstich, W., Lamm, A., Gasteiger, H., Eds.; John Wiley & Sons: Chichester, U.K., 2003; Vol. 3; p 351.
- (2) Deng, W.-Q.; Molinero, V.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2004**, *126*, 15644.
- (3) Heitner-Wirguin, C. *J. Membr. Sci.* **1996**, *120*, 1.
- (4) Mauritz, K. A.; Moore, R. B. *Chem. Rev.* **2004**, *104*, 4535.
- (5) Yagi, M.; Kaneko, M. *Adv. Polym. Sci.*, in press.
- (6) Yagi, M.; Sato, T. *J. Phys. Chem. B* **2003**, *107*, 4975.
- (7) Yagi, M.; Takahashi, M.; Teraguchi, M.; Kaneko, T.; Aoki, T. *J. Phys. Chem. B* **2003**, *107*, 12662.
- (8) Yagi, M.; Kaneko, M. *Chem. Rev.* **2001**, *101*, 21.
- (9) Yagi, M.; Kinoshita, K.; Kaneko, M. *J. Phys. Chem.* **1996**, *100*, 11098.
- (10) Yagi, M.; Kinoshita, K.; Kaneko, M. *J. Phys. Chem. B* **1997**, *101*, 3957.
- (11) *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guillard, R., Eds.; Academic Press: New York, 2003; Vols. 15–17.
- (12) Huisman, C. L.; Goossens, A.; Schoonman, J. *J. Phys. Chem. B* **2002**, *106*, 10578.
- (13) He, J.; Benko, G.; Korodi, F.; Polivka, T.; Lomoth, R.; Akerman, B.; Sun, L.; Hagfeldt, A.; Sundstrom, V. *J. Am. Chem. Soc.* **2002**, *124*, 4922.
- (14) Yoshida, T.; Tochimoto, M.; Schlettwein, D.; Woehrle, D.; Sugiura, T.; Minoura, H. *Chem. Mater.* **1999**, *11*, 2657.
- (15) Zhao, F.; Zhang, J.; Woehrle, D.; Kaneko, M. *J. Porphyrins Phthalocyanines* **2000**, *4*, 31.

- (16) Spadavecchia, J.; Ciccarella, G.; Stomeo, T.; Rella, R.; Capone, S.; Siciliano, P. *Chem. Mater.* **2004**, *16*, 2083.
- (17) Sauer, T.; Caseri, W.; Wegner, G.; Vogel, A.; Hoffmann, B. *J. Phys. D: Appl. Phys.* **1990**, *23*, 79.
- (18) Locklin, J.; Shinbo, K.; Onishi, K.; Kaneko, F.; Bao, Z.; Advincula, R. C. *Chem. Mater.* **2003**, *15*, 1404.
- (19) Lelievre, D.; Bosio, L.; Simon, J.; Andre, J. J.; Bensebaa, F. *J. Am. Chem. Soc.* **1992**, *114*, 4475.
- (20) Yagi, M.; Fukiya, H.; Kaneko, T.; Aoki, T.; Oikawa, E.; Kaneko, M. *J. Electroanal. Chem.* **2000**, *481*, 69.
- (21) Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*, 4th ed.; Reed Education and Professional Publishing Ltd: Oxford, U.K., 1996.
- (22) White, H. S.; Leddy, J.; Bard, A. J. *J. Am. Chem. Soc.* **1982**, *104*, 4811.
- (23) Saiki, H.; Takami, K.; Tominaga, T. *Phys. Chem. Chem. Phys.* **1999**, *1*, 303.
- (24) Yagi, M.; Yamase, K.; Kaneko, M. *J. Electroanal. Chem.* **1999**, *476*, 159.
- (25) Scheidt, W. R.; Dow, W. *J. Am. Chem. Soc.* **1977**, *99*, 1101.
- (26) Kaneko, Y.; Nishimura, Y.; Arai, T.; Sakuragi, H.; Tokumaru, K.; Matsunaga, D. *J. Photochem. Photobiol., A* **1995**, *89*, 37.
- (27) Kaneko, Y.; Arai, T.; Tokumaru, K.; Matsunaga, D.; Sakuragi, H. *Chem. Lett.* **1996**, 345.
- (28) Lin, R.-J.; Onikubo, T.; Nagai, K.; Kaneko, M. *J. Electroanal. Chem.* **1993**, *348*, 189.