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DEPRESSION OF DISPROPORTIONATION OF π-RADICAL ANION OF GOLD PORPHYRIN ELECTROSTATICALLY FIXED IN A POLYMER MATRIX

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ABSTRACT

The electrochemical and photochemical reduction of the fully methylated derivative of gold *meso*-tetrakis-(4-pyridyl)porphine (AuTMPyP) in homogeneous solution gives not only a π-radical anion but also its successive product, phlorin, by disproportionation. The electrostatic fixation of AuTMPyP in a Nafion matrix inhibits the latter undesired reaction against effective charge separation, which is explained by the diffusion constant lower by 8 order of magnitude during electrolytic reduction of AuTMPyP compared to that in homogeneous aqueous solution.

INTRODUCTION

Aiming at the solar energy conversion and storage system industries, much effort [1] has been concentrated on molecular design of superior sensitizers and arrangement of charge-separation fields effective for uphill photoredox reactions. We have also reported the utilization of particulate semiconductor interfaces with dye sensitization [2, 3] and synthesis of water-soluble (metallo)porphyrins with high redox potentials. Especially, the water-

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soluble gold porphyrins had much higher anodically shifted redox potentials and their photoinduced reductive electron transfer cycle was effective for water photoreduction [4, 5]. This photoinduced reduction process involves two kinds of redox cycles. One is between the fully methylated derivative of gold *meso*-tetrakis-(4-pyridyl)porphine (AuTMPyP) and its π-radical anion in alkaline solution, and the other contains those species and the successive product, phlorin, which results from disproportionation and protonation of the π-radical anion, in neutral and acidic solutions. Additionally, we controlled these redox processes during photochemical and electrochemical reduction of the gold porphyrin electrostatically by fixing it in a cation-exchange polymer matrix such as Nafion [6]. While its π-radical anion tends to disproportionate into the energetically unfavorable phlorin in homogeneous aqueous solution, a simple redox cycle between native porphyrin and its π-radical anion was demonstrated in the polymer matrix. These observations provide useful information for designing photochemical redox systems.

Here, we report on 1) a modified chronoabsorptometry method in order to estimate the mobility of the substrate fixed in the polymer matrix and 2), on mechanistic considerations for mobility lowering by electrostatic fixation.

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EXPERIMENTAL

A 5 wt% alcoholic aqueous solution of perfluorinated cation-exchange powder (Nafion 117, Aldrich), which corresponds to 36 meq/L of sulfonic acid residue, was used as polymer matrix for fixing several cationic redox species. The procedure was as follows. 1) Nafion-coated electrodes were prepared by spin-coating the above Nafion solution onto transparent indium-tin (95:5) oxide (ITO) deposited glass electrodes. 2) The cationic redox species was fixed in the Nafion-coated electrode by an ion-exchange method in which the electrode was kept in an aqueous solution containing the cationic redox species for 1 h. The thickness of the coated Nafion membrane was controlled by the concentration of the Nafion solution and the rotation speed on the spin-coating treatment, and was estimated by an interference-color method and electron microscopic observation of the cross section. The amount of the fixed redox species was estimated by spectroscopic measurement with the molar extinction coefficient (ϵ) for aqueous solution. The fixing ratio of AuTMPyP was estimated to be 31% by considering the number of charges per molecule (AuTMPyP has 5 positive charges).

Another method of fixation of the cationic redox species in Nafion for a photochemical microheterogeneous system (colloidal system) was as follows.

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To 0.50 mmol/L of aqueous cationic porphyrin solution was added the equivalent quantity of the above Nafion solution. The colloidal solution was filtered with a Millipore filter (0.45 μm pore size), and the filtrate contained very little porphyrin. The filter cake was washed twice with water and then suspended in the adjusted volume of water. The suspended colloidal solution was very stable, and little precipitate was observed.

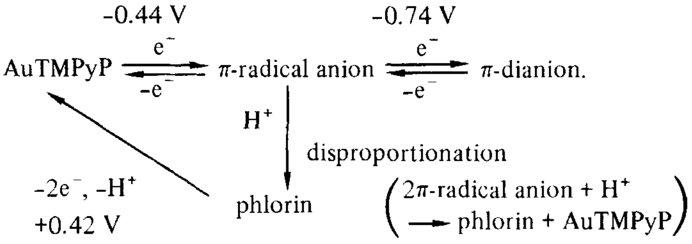
Some cationic porphyrins (i.e., *meso*-tetrakis-(4-pyridyl)porphine (TPyP), its fully methylated derivative (TMPyP), and their gold complexes), methylviologen (MV^{2+}), and *N,N'*-di(propyl-γ-sulfonate)-4,4'-bipyridine (PSV), which behaved as a noncharged redox carrier, were synthesized according to the literature [2, 4, 5, 7-12]. Other chemicals were purchased from Nakarai and Wako.

The electrochemical measurement was carried out in a conventional three-electrode system (modified indium-tin oxide (ITO, 95:5) working electrode, platinum wire counterelectrode, and saturated calomel electrode (SCE)) with an NPGS-301 potentiogalvanostat and an NFG-6 function generator (Nikko Keisoku).

The photochemical reaction of the colloidal system fixing the porphyrin was as follows. The photolysis sample contained 62.5 μmol/L ZnTMPyP in colloidal Nafion, 2.5 mmol/L viologen, and 1.0 mol/L triethanolamine as the sacrificial electron donor. The absorbance at 660 nm, assigned to the viologen radical cation, was monitored with visible light irradiation with a 500-W Xe lamp through UV and near-IR cut-off filters (L42 and IR25s, λ 420-700 nm). The molar extinction coefficients of two kinds of viologen were determined by chemical reduction of the viologen with $Na_2S_2O_4$ in homogeneous aqueous solution.

RESULTS AND DISCUSSION

In our previous reports [4, 5], AuTMPyP was shown to follow two paths of reduction:



While the π-radical anion of AuTMPyP is stable at pH above 10, it disproportionates in neutral and acidic solution. The resulting phlorin, which is a protonated two-electron-reduced porphyrin, is reoxidized completely to AuTMPyP without further successive reactions, but has weaker reducing power than π-radical anion. The photoinduced reductive electron transfer cycle of AuTMPyP was more suitable for use as a sensitizer than any of the other metalloporphyrins, which show more complicated redox processes and include undesired irreversible side reactions [13]. However, additional modification would be required to utilize the high reducing power of the π-radical anion without disproportionation. Therefore, we demonstrated a simple redox cycle that does not go through AuTMPyP phlorin by fixing it electrostatically in a cation-exchange polymer matrix (Nafion) [6]. The disproportionation of the π-radical anion was depressed because of its much low mobility in the matrix.

The present paper describes the quantitative estimation of the mobility in the matrix. The apparent diffusion constant of the redox species fixed in the Nafion-coated ITO electrode was estimated by electrochemical chronoabsorptometry based on homogeneous Cottrell-type analysis [14].

There are some points to be considered in applying the Cottrell-type analysis to the present electrolysis of the Nafion-coated electrode: 1) The electrolytic current contains non-Faradaic processes and a residual current independent of the observable redox process. 2) The Cottrell-type analysis holds good under semi-infinite diffusion conditions where the diffusion thickness (δ) is sufficiently low compared to the membrane thickness. 3) It was hard to make an accurate estimate of the electrode area. 4) It was known that Nafion showed microscopic (in the region of several nanometers) phase separation between hydrophobic and hydrophilic domains, so that the homogeneity of the fixed redox species is a consideration. Therefore, it was also important to evaluate the effective concentration of the redox species in the matrix. In the present study, the above points 1) and 2) were dealt with by assuming that there is an electrolytic time region to satisfy the Cottrell-type analysis in which the diffusion layer is sufficiently thin compared to the film thickness (d), as will be considered below. The other points, 3) and 4) were also overcome by a normalizing technique that uses the mole fraction of the reactant or the product in the total amount of fixed redox species, which was determined by absorption spectra.

Figure 1 shows the absorption spectra of the AuTMPyP fixed in a Nafion-coated ITO electrode during electrolysis. Distinct isosbestic points were observed, which resulted from small side reactions.

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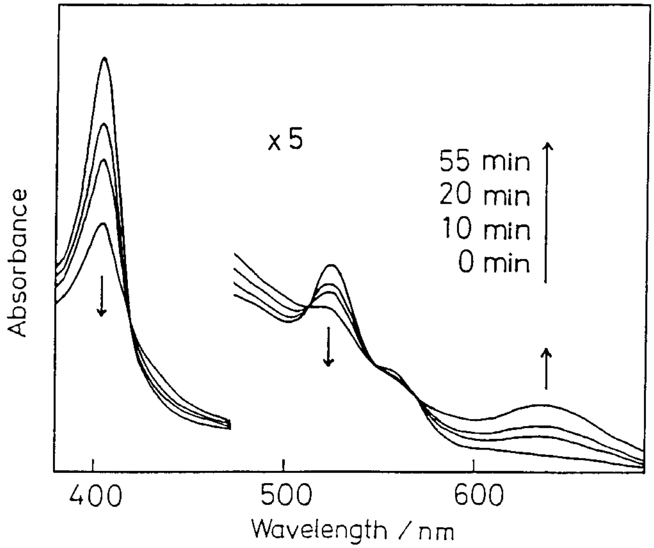

FIG. 1. Absorption spectrum changes of AuTMPyP fixed in a Nafion-coated ITO electrode (0.52 μm thick) in 0.1 *M* Na_2SO_4 aqueous solution during potentiostatic electrolysis for 0, 10, 20, and 55 min at -600 mV vs SCE.

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In the case of such a simple redox process, one can normalize the absorbance changes by using mole fractions as follows:

$$A(t,\lambda) = [1 - f(t)]A(0,\lambda) + f(t)A(\infty,\lambda), \tag{1}$$

$$f(t) = [A(t,\lambda) - A(0,\lambda)]/[A(\infty,\lambda) - A(0,\lambda)], \tag{2}$$

where $A(t,\lambda)$ and $f(t)$ are the absorbance at electrolytic time t and wavelength λ, and the mole fraction of the AuTMPyP π-radical anion at electrolysis time t, respectively. The boundary conditions $A(0,\lambda)$ and $A(\infty,\lambda)$ represent the absorbances of AuTMPyP and its π-radical anion. Here, the normalization is quite reasonable with respect to omission of any other redox processes in the electrolysis.

Figure 2 shows the time dependence of $f(t)$ for various membrane thicknesses, obtained from the absorbances at 405, 524, and 640 nm, which were

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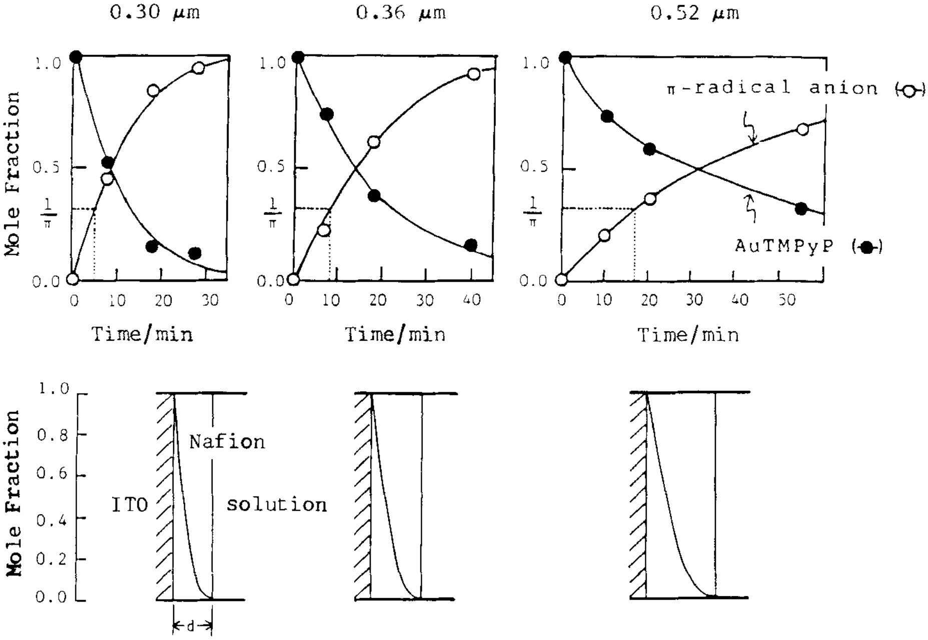

FIG. 2. Rate of change of mole fraction (f) of reduced AuTMPyP (○) and the remaining AuTMPyP (●) fixed in Nafion-coated ITO electrodes, obtained from the spectral changes in Fig. 1. Nafion membrane thickness (left to right): 0.30, 0.36, and 0.52 μm.

assigned to the Soret band, the Q-band of AuTMPyP, and its π-radical anion, respectively. On the other hand, the quantity of electricity during the electrolysis, $Q(t)$, involves an integrated Cottrell-type term, $q(t)$, and the non-Faradaic term, $N(t)$:

$$Q(t) = q(t) + N(t), \tag{3}$$

$$q(t) = 2FAC_0(D_{\mathrm{app}}t/\pi)^{1/2}, \tag{4}$$

where F, A, C_0, D_{app}, and t are the Faraday constant, the effective area of the modified electrode, the effective concentration of AuTMPyP in Nafion ($= m_0/(Ad)$, with m_0 the amount of AuTMPyP in Nafion and d the thickness of the modified electrode), the apparent diffusion constant of AuTMPyP during reductive electrolysis in the Nafion-coated electrode, and the electrolytic time, respectively.

There are some points to be considered in using Cottrell-type chronoamperometry and chronocoulometry. Under conditions of a diffusion layer that is enough thinner than the film thickness and reductive electrolysis at a cathodic potential (-600 mV vs SCE) sufficiently higher than the half-wave potential of -440 mV, there should be an appropriate electrolytic time region where the $q(t)$ relation holds. In the present study the following conditions allow us to apply the Cottrell $q(t)$ relation to the electrolysis of AuTMPyP. 1) The reductive electrolysis of AuTMPyP gave only its π-radical anion with no side reactions, as Fig. 2 shows. 2) The condition where Eq. (2) holds is that δ is smaller than $d/2$. Then the mole fraction $f(t)$ can be written as

$$f(t) = q(t)/(m_0 F), \tag{5}$$

where the electrolysis involves a one-electron reduction process. By combining the Eqs. (4) and (5), one obtains

$$f(t) = (2/d)(D_{\mathrm{app}}/\pi)^{1/2} t^{1/2}. \tag{6}$$

There is a linear relationship between d and square root of the electrolysis time, t^*, when $f(t)$ is comparatively small. This time region means that $\delta \ll d$. Now, we adopt t^* where $f(t) = 1/\pi$, and then

$$d = 2(\pi D_{\mathrm{app}})^{1/2} (t^*)^{1/2}. \tag{7}$$

In Fig. 3 a good straight line is obtained according to Eq. (7), and the slope leads to the apparent diffusion coefficient, of AuTMPyP in the Nafion matrix D_{app}, as 2.3×10^{-13} cm^2/s. This value is much smaller than that in homogeneous aqueous solution ($D_{\mathrm{app}} = 1.6 \times 10^{-5}$ cm^2/s) which was obtained from the linear relationship between the peak currents and the square root of the sweeping rate of the electrode potential in the conventional cyclic voltammogram, i.e., the fixed AuTMPyP had a markedly lower mobility in the Nafion matrix. The latter resulted in no successive disproportionation of the AuTMPyP π-radical anion.

Table 1 shows the apparent formation rates of one-electron-reduced viologen in bulk aqueous solution in the presence of ZnTMPyP fixed in colloidal Nafion under visible light irradiation. Triethanolamine was used as an electroneutral sacrificial electron donor. The anion radical of AuTMPyP does not have the thermodynamic capability to reduce viologen, so that AuTMPyP was replaced by ZnTMPyP in the photolysis experiment.

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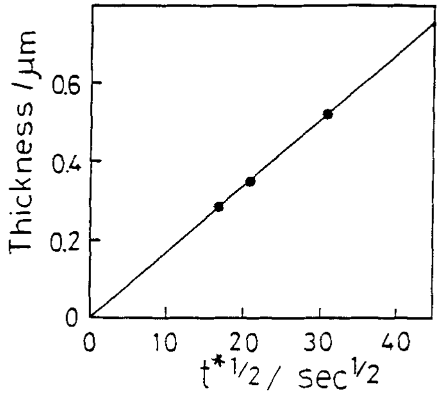

FIG. 3. Relationship between the Nafion membrane thickness d and $(t^*)^{1/2}$ when the mole fraction $f = 1/\pi$. Each point was obtained from Fig. 2 for AuTMPyP-fixed Nafion-coated ITO electrodes of various membrane thicknesses.

Similar to the case of AuTMPyP, ZnTMPyP was fixed strongly in the Nafion matrix, and its D_{app} was also depressed compared to the homogeneous aqueous solution. The reduction rate of MV^{2+} in the colloidal system was lowered by one-fifth, as was expected, since the cationic electron carriers are also concentrated in the Nafion matrix, and the resulting viologen cation radical undergoes reoxidation at a much faster rate than its escape rate from the matrix. In contrast, electroneutral viologen, PSV, was a superior electron carrier for the transfer of the reducing power from the Nafion matrix to the bulk solution. This

TABLE 1. Relative Photoreduction Rate of Viologen by ZnTMPyP Bound in Nafion[a]

	Relative rate	
	PSV	MV^{2+}
0.6 wt% in Nafion	105	62
No Nafion	100	315

[a] [ZnTMPyP] = 62.5 μmol/L, [viologen] = 2.50 mmol/L. The deaerated solution was irradiated with a 500-W Xe lamp through UV and IR cutoff filters.

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preliminary result promises to extend the present colloidal charge separation unit to successive electron relays for solar energy conversion and storage systems.

The present study quantitatively supports the previous conclusion that the cationic porphyrin fixed in Nafion had much lowered mobility and that the undesired disproportionation process was reduced in the matrix [6].

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