

# Effect of Water on Primary Photocarrier-Generation Process in Y-form Titanyl Phthalocyanine

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We have studied the effect of adsorbed water on the primary photocarrier-generation process in Y-form titanyl phthalocyanine (Y-TiOPc) by using ground-state absorption and time-resolved fluorescence spectroscopy. The water adsorption is the unique feature of Y-TiOPc, which is not observed in the other polymorphs of TiOPc. We report for the first time the water-induced change of the absorption spectrum, that is, the hydrochromism of Y-TiOPc. The fluorescence lifetimes and amplitudes of Y-TiOPc are greatly influenced by adsorbed water. We have found that the mechanism of the fluorescence quenching of Y-TiOPc caused by water adsorption is the same as that by an electric field. Adsorbed water enhances the photocarrier generation of Y-TiOPc in the same way as an electric field does in the picosecond time regime.

## I. Introduction

Titanyl phthalocyanines (TiOPcs) are known as highly photosensitive digital-xerographic pigments.<sup>1,2</sup> Y-form titanyl phthalocyanine (Y-TiOPc) has the highest photosensitivity among various TiOPc polymorphs phase I, phase II, and so on.<sup>3–5</sup> The near-infrared or visible photoexcitation of TiOPc brings about free carrier generation with a high quantum yield. The carrier-generation process in an organic photoconductor is roughly depicted as follows: a singlet molecular exciton generated by photoexcitation partly decays to a geminate bound electron–hole pair or an intermolecular charge transfer (CT) state. The bound pair subsequently dissociates into free carriers with the aid of an external electric field. The latter dissociation process is well described by the Onsager theory<sup>6</sup> or the Noolandi–Hong model.<sup>7</sup> A clear picture as to the details of the former primary process has yet to be reached despite its importance to the photocarrier quantum yield.

The photosensitivity of Y-TiOPc is influenced by environmental factors such as an electric field, temperature, and humidity. An electric field accelerates not only the Onsager dissociation process but also the primary carrier-generation process in the picosecond time regime.<sup>8–11</sup> The temperature dependence of the rate of the Onsager process has been given an analytical expression,<sup>6,7</sup> but we do not yet know how temperature influences the primary process. The effect of an electric field and that of temperature on the Onsager process are not peculiar to Y-TiOPc, but common to all the organic photoconductors including the other polymorphs of TiOPc. On the other hand, the humidity dependence of the photosensitivity is the unique feature of Y-TiOPc. Fujimaki and co-workers<sup>12</sup> have found that Y-TiOPc adsorbs water in air, and that the desorption of water in a vacuum reduces the photoconductivity by 20%. They estimated the ratio of the number of TiOPc molecules to that of adsorbed H<sub>2</sub>O molecules at 1:0.7. In phase I TiOPc, they observed neither adsorbed water nor humidity-dependent photoconductivity. Popovic et al.<sup>8</sup> investigated the humidity dependence of the steady-state and time-resolved

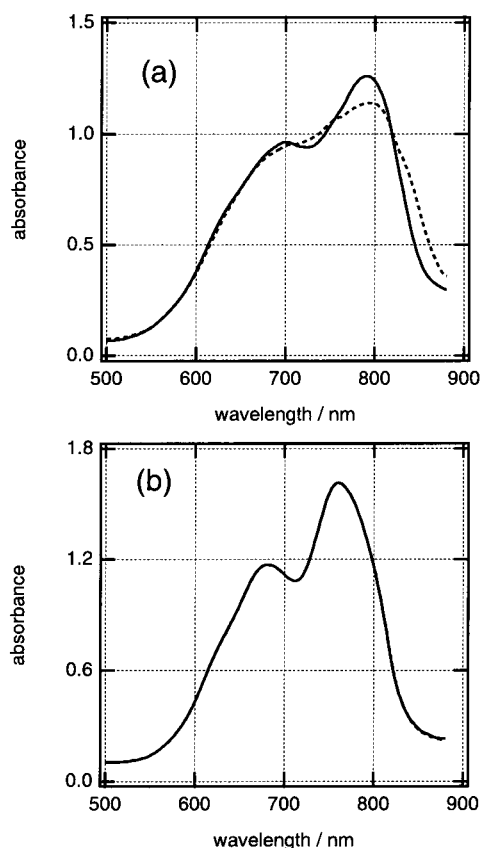
fluorescence of Y-TiOPc. They reported that the steady-state fluorescence intensity decreased with an increase in humidity. In other words, they observed water-induced fluorescence quenching in Y-TiOPc. In their time-resolved measurements, they found two single-exponential components. They reported that the amplitudes of these two components decreased and the time constant of the slower component became shorter with an increase in humidity. We have studied the excited singlet electronic structures of Y-form and phase I TiOPc by using electric-field-modulated picosecond time-resolved fluorescence spectroscopy in our recent papers.<sup>9–11</sup> Two singlet excitons were found in both of the polymorphs. In Y-TiOPc, the shorter lifetime exciton was assigned to an intramolecular CT exciton and the other to a neutral Frenkel exciton. In phase I, on the other hand, both of the excitons were identified as Frenkel excitons. We have regarded the CT exciton as a key to the high photocarrier-generation quantum yield of the Y-form.

The purpose of the present paper is to clarify the origin of the effect of water on the Y-TiOPc photosensitivity. We have measured the ground-state absorption spectra and the picosecond time-resolved fluorescence spectra of Y-form and phase I TiOPc in air and in a vacuum. We have found that Y-TiOPc shows hydrochromism. The mechanisms of the fluorescence quenching and the photosensitivity enhancement induced by adsorbed water in Y-TiOPc will be discussed in detail.

## II. Experimental Section

TiOPc pigments dispersed in a poly(vinylbutyral) matrix were spin-coated on glass substrates and were used as samples. The thickness of the TiOPc-pigment layer was about 0.5  $\mu\text{m}$ . The diameter of the Y-TiOPc microcrystallites was about 0.1  $\mu\text{m}$ , and that of phase I was about 0.2  $\mu\text{m}$ . The samples were held in a cryostat (Oxford, Optistat DN). Measurements in air were performed under about 35% relative humidity. Measurements in a vacuum were performed after evacuating the sample space of the cryostat to about 100 Pa for 30 min. The 100-Pa evacuation was sufficient for water desorption from the Y-TiOPc samples. It has been verified by our gravimetry before and after the evacuation that we obtain the same amount of desorbed

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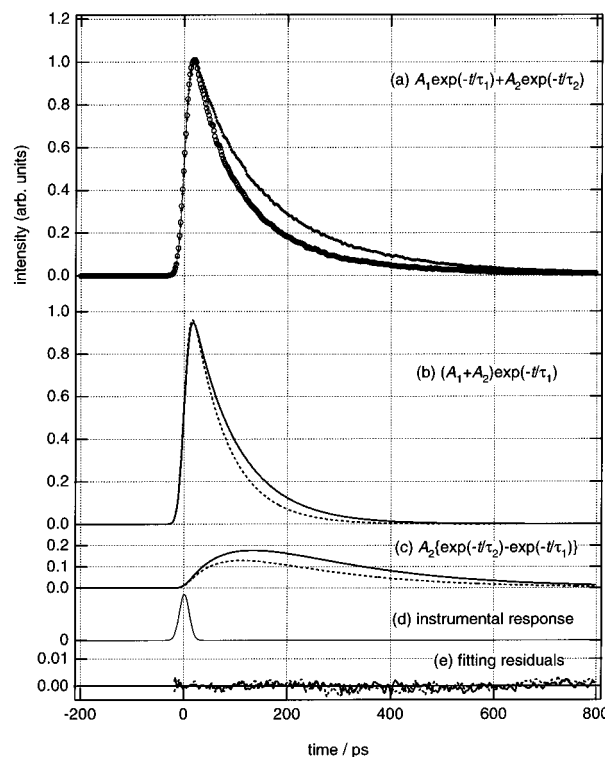


**Figure 1.** Ground-state absorption spectra of TiOPc. (a) Y-form in the vacuum (line) and in air (broken line). (b) Phase I in the vacuum (line) and in air (broken line).

water by the evacuation as done by Fujimaki et al.<sup>12</sup> in their thermogravimetric measurements. All the measurements were done at room temperature (297 K). Ground-state absorption spectra were measured with a monochromator (Acton, SP150) and a thermoelectrically cooled photon-counting photomultiplier (Hamamatsu, R-2949). The spectral resolution was 2 nm. A xenon lamp was used as a light source. Picosecond time-resolved fluorescence spectra were measured with a conventional system based on a streak scope (Hamamatsu, C4334) with an imaging spectrograph (Chromex, 250is). The streak scope was driven in a photon-counting mode. The fluorescence excitation source was a mode-locked Ti:sapphire laser (Coherent, MIRA900) at a repetition rate of 75.5 MHz. The time resolution was about 10 ps, which was limited by the streak scope. The excitation wavelength was 800 nm. The excitation density was 0.3 mW mm<sup>-2</sup> (average power) or 4 pJ mm<sup>-2</sup> (pulse energy).

### III. Results

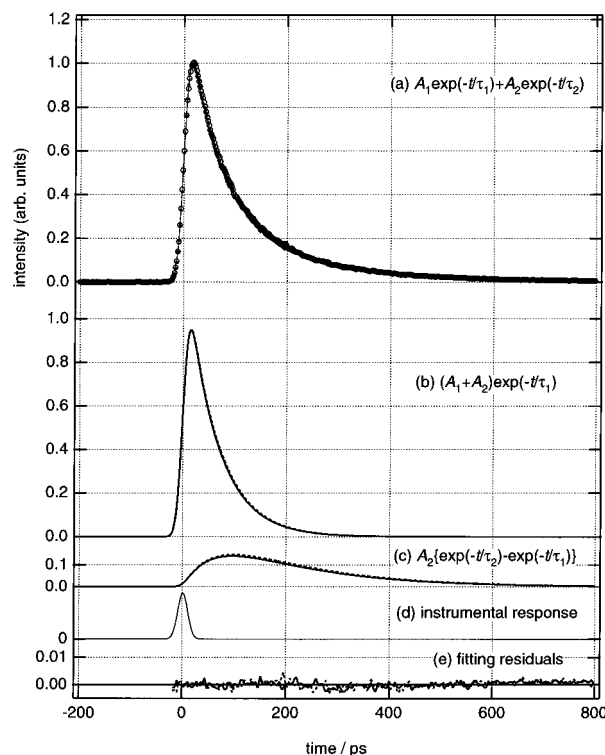
Figure 1 shows the ground-state absorption spectra of TiOPc in air and in the vacuum. The spectrum of the Y-form in the vacuum is significantly different from that in air as shown in Figure 1a. The absorption band of aerated Y-TiOPc is broader than and slightly red-shifted compared to that of the degassed pigments. We have verified that the change of the Y-TiOPc spectrum is reversible. The aeration of the degassed pigments for about 2 h makes the spectrum change back into that in air. As mentioned in the previous section, adsorbed water in aerated Y-TiOPc is desorbed by the evacuation. The adsorption of another gas such as nitrogen and oxygen has never been observed. Popovic et al.<sup>8</sup> have reported that the presence of oxygen does not influence the fluorescence of Y-TiOPc. We



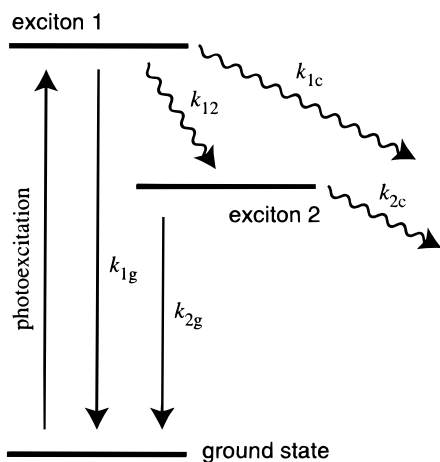
**Figure 2.** (a) Fluorescence decay curves of Y-TiOPc at  $870 \pm 20$  nm in the vacuum (small solid circles, data; line, fitting) and in air (large open circles, data; broken line, fitting). (b) Fitting curves of the population decay of the shorter lifetime exciton (line, in the vacuum; broken line, in air). (c) Fitting curves of the population decay of the longer lifetime exciton (line, in the vacuum; broken line, in air). (d) Instrumental response function as determined by a Rayleigh scattering measurement. (e) Residuals of the fitting shown in (a) normalized by each fitting curve (line, in the vacuum; broken line, in air).

have verified by an X-ray powder diffraction measurement that the Y-form crystal structure does not change upon the evacuation. Therefore it is natural to ascribe the spectrum change upon the evacuation in Figure 1a to water desorption. We should call this phenomenon, the water-induced change of the Y-TiOPc absorption spectrum, hydrochromism. On the other hand, we see in Figure 1b that the spectrum of phase I TiOPc does not change upon the evacuation. The phase I TiOPc pigments do not adsorb water.<sup>12</sup> It is consistent that we observe no water effect on the phase I spectrum in Figure 1b.

Unfortunately the present streak scope does not have enough sensitivity in the near-infrared region longer than 900 nm. Consequently the TiOPc fluorescence spectrum in air and that in the vacuum were nearly identical and we could not obtain meaningful spectral information, because a real TiOPc-fluorescence peak lies at about 1  $\mu$ m. In other words, the shapes of the obtained fluorescence spectra did not reflect the pigment property, but were determined by a Rayleigh-cut filter and the spectral sensitivity of the streak scope. Hereafter we focus our attention on the temporal behavior of the TiOPc fluorescence. Figures 2 and 3 show the fluorescence decay curves of TiOPc in air and in the vacuum. The fluorescence intensity is integrated in the wavelength region  $870 \pm 20$  nm, and is normalized by the number of absorbed photons at the photoexcitation. We have already clarified in our previous papers<sup>9-11</sup> that the fluorescence decay curves of Y-form and phase I TiOPc in air are very well fitted to a sum of two exponentials,  $A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2)$ . We have found in the present study that the decay curves of the degassed pigments are also very well fitted to the same model function.



**Figure 3.** (a) Fluorescence decay curves of phase I TiOPc at 870  $\pm$  20 nm in the vacuum (small solid circles, data; line, fitting) and in air (large open circles, data; broken line, fitting). (b) Fitting curves of the population decay of the shorter lifetime exciton (line, in the vacuum; broken line, in air). (c) Fitting curves of the population decay of the longer lifetime exciton (line, in the vacuum; broken line, in air). (d) Instrumental response function as determined by a Rayleigh scattering measurement. (e) Residuals of the fitting shown in (a) normalized by each fitting curve (line, in the vacuum; broken line, in air).



**Figure 4.** Schematic diagram of the primary process after photoexcitation in TiOPc. Straight arrows stand for radiative transitions, and wavy arrows represent nonradiative relaxation process.

Figure 4 schematically shows the diagram of the exciton dynamics proposed on the basis of this model function in our previous papers.<sup>9,11</sup> The shorter lifetime species is labeled as exciton 1 whose population is proportional to  $(A_1 + A_2) \exp(-t/\tau_1)$ , and the longer lifetime one as exciton 2 whose population is proportional to  $A_2 \{ \exp(-t/\tau_2) - \exp(-t/\tau_1) \}$ . The decay rate of exciton 1 ( $k_1 = \tau_1^{-1}$ ) is the sum of the radiative decay rate ( $k_{1g}$ ), the internal conversion rate ( $k_{12}$ ), and the rate of the other decay ( $k_{1c}$ ). The carrier-generation pathway is included in the other decay. Exciton 2 decays either to the ground state radiatively with a rate of  $k_{2g}$  or to the other state

with a rate of  $k_{2c}$ . The decay rate of exciton 2 is expressed as  $k_2 (= \tau_2^{-1})$ . In Y-TiOPc, exciton 1 has been assigned to an intramolecular CT exciton and exciton 2 to a neutral Frenkel exciton.<sup>9</sup> Both of the excitons have been assigned to Frenkel excitons in phase I TiOPc.<sup>11</sup> In Figures 2 and 3, the fitting results are shown together. The fluorescence decay of Y-TiOPc in air is definitely faster than that in the vacuum as shown in Figure 2a. We see in Figure 2b that water adsorption makes the lifetime of the CT exciton ( $\tau_1$ ) shorter. Figure 2b also shows that the amplitude of the decay curve of the CT exciton ( $A_1 + A_2$ ) is almost independent of humidity. The amplitude of the decay curve of the Frenkel exciton ( $A_2$ ) decreases upon water adsorption as shown in Figure 2c. On the other hand, Figure 3 indicates that there is no prominent difference between the decay curve of the phase I TiOPc fluorescence in air and that in the vacuum. It is consistent that we observe no water effect on the phase I TiOPc decay curves, because phase I TiOPc does not adsorb water.

It has been shown in our previous papers<sup>9,11</sup> that the rate of the internal conversion from exciton 1 to exciton 2 ( $k_{12}$ ) is proportional to  $A_2(k_1 - k_2)$ . Then we can estimate the water-adsorption effect on the internal conversion rate. The water-induced changes of  $k_{12}$  and the other fitting parameters of Y-form and phase I TiOPc are summarized in Table 1. The listed values of the parameters were obtained from four measurements. The experimental uncertainties of the fluorescence lifetimes and amplitudes in Table 1 are about  $\pm 5\%$ . These uncertainties are larger than those in the electric-field-modulated time-resolved fluorescence measurements of our previous works,<sup>9–11</sup> because it is not possible to measure the fluorescence of the degassed and aerated pigments at the same time. Consequently the uncertainties of the water-induced changes of the parameters in the fifth column of Table 1 are also about  $\pm 5\%$ . Because the water-induced parameter changes of phase I TiOPc are all within  $\pm 5\%$  as shown in Table 1, we conclude that the fluorescence kinetics of phase I TiOPc in air is nearly identical with that in the vacuum within the experimental uncertainties.

The water-induced changes of the kinetics parameters of Y-TiOPc, on the other hand, are deemed to be significant. The radiative decay rate of exciton 1 ( $k_{1g}$ ) is regarded as independent of humidity, because the area of the absorption spectrum of Y-TiOPc (Figure 1a) changes less than 1% upon water adsorption. The internal conversion rate ( $k_{12}$ ) decreases by 30% upon water adsorption as shown in Table 1. In other words, adsorbed water decelerates the internal conversion process from the shorter lifetime CT exciton to the longer lifetime Frenkel exciton in Y-TiOPc. Then the  $k_1$  increase as large as 18% should be ascribed to the increase of  $k_{1c}$ , which must be much more than 18%. The decay pathway denoted by  $k_{1c}$  includes the pathway from the CT exciton to a bound electron–hole pair. The  $k_{12}$  decrease and the  $k_{1c}$  increase bring about the  $A_2$  decrease as large as 45%. This means that adsorbed water decreases the quantum yield of the Frenkel exciton.  $A_1 + A_2$  corresponds to the initial population of the CT exciton prepared by the photoexcitation, and naturally remains unchanged upon water adsorption. We can ascribe the changes of  $A_1$  and  $A_2$  solely to those of  $k_1$ ,  $k_2$ , and  $k_{12}$ . In short, the fluorescence quenching caused by adsorbed water in Y-TiOPc is attributable to the changes of the excited-state decay rates.

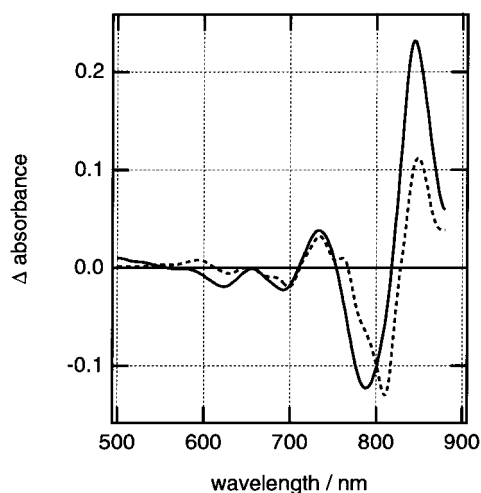
#### IV. Discussion

The electric-field-induced changes of the fluorescence-kinetics parameters of TiOPcs reported in our previous papers<sup>9–11</sup> are

**TABLE 1: Effect of Adsorbed Water on Fitting Parameters of Fluorescence Kinetics in Y-form and Phase I TiOPc**

polymorph	fitting parameter $X$	$X(\text{degassed})$	$X(\text{aerated})$	water-induced change of $X^a$ (%)	electric-field-induced change of $X^b$ (%)
Y-form	$k_1$	$(85 \text{ ps})^{-1}$	$(72 \text{ ps})^{-1}$	+18	+4
	$k_2$	$(185 \text{ ps})^{-1}$	$(175 \text{ ps})^{-1}$	+5	+5
	$k_{12}$			-30	-5
	$A_1$	0.50	0.72	+45	+2
	$A_2$	0.50	0.28	-45	-8
	$A_1 + A_2$	1.0	1.0	-0.4	-1
phase I	$k_1$	$(50 \text{ ps})^{-1}$	$(50 \text{ ps})^{-1}$	-1	+4
	$k_2$	$(156 \text{ ps})^{-1}$	$(157 \text{ ps})^{-1}$	-1	+4
	$k_{12}$			+3	+2
	$A_1$	0.71	0.70	-2	+1
	$A_2$	0.29	0.30	+5	-2
	$A_1 + A_2$	1.0	1.0	+0.4	+0.5

<sup>a</sup> The water-induced change of  $X$  is  $[X(\text{aerated}) - X(\text{degassed})]/X(\text{degassed}) \times 100$ . <sup>b</sup> The electric-field-induced change of  $X$  is  $[X(30 \text{ V } \mu\text{m}^{-1}) - X(0 \text{ V } \mu\text{m}^{-1})]/X(0 \text{ V } \mu\text{m}^{-1}) \times 100$ .



**Figure 5.** Difference absorption spectrum of Y-TiOPc. Line, ground-state spectrum in air minus that in the vacuum. Broken line, second derivative of the ground-state spectrum in the vacuum with respect to photon energy.

added to the sixth column of Table 1 as a reference. The experimental uncertainties of the rates and the amplitudes in the electric-field-modulated measurements were limited to  $\pm 1\%$  by our original method.<sup>9–11</sup> The  $30\text{-V } \mu\text{m}^{-1}$  electric field reduces  $k_{12}$  by 5% and increases  $k_1$  and  $k_2$  by 4% or 5% in Y-TiOPc. The decay process indicated by  $k_{1c}$  in Figure 4 is accelerated by the electric field. The directions of these field-induced rate-constant changes in Y-TiOPc are exactly the same as those of the water-adsorption-induced changes revealed in the present study. This means that the mechanism of the fluorescence quenching brought about by water adsorption is the same as that by an electric field. An electric field accelerates the decay process from the CT exciton to the bound electron–hole pair, and increases  $k_{1c}$ . Adsorbed water also increases  $k_{1c}$  as shown above. Because water adsorption enhances the photocurrent of Y-TiOPc by 20%,<sup>12</sup> it is natural to ascribe the water-induced  $k_{1c}$  increase to the fact that the decay process from the CT exciton to the bound pair is accelerated by adsorbed water. We conclude that the water effect on the exciton dynamics of Y-TiOPc is similar to the electric-field effect.

There is another example that shows the similarity between the water effect and the electric-field effect. Figure 5 shows the difference spectrum between the Y-TiOPc absorption spectrum in air and that in the vacuum. We have found that this difference spectrum looks similar to the electroabsorption spectrum of Y-TiOPc reported by Saito and co-workers.<sup>5</sup> They have shown that the CT character or the permanent dipole moment of the excited singlet state of Y-TiOPc is much larger

than that of the ground state, and that the electroabsorption spectrum in the near-infrared region resembles the second derivative of the absorption spectrum with respect to photon energy. We have calculated the second derivative of the Y-TiOPc spectrum in the vacuum (Figure 1a), and present it in Figure 5. We see that the positive and negative peaks of the difference spectrum are well reproduced by the second-derivative spectrum. We conclude that the effect of water is similar to that of an electric field not only on the exciton dynamics but also on the ground-state absorption spectrum.

We have two ideas regarding the origin of the water effect in Y-TiOPc. First, the similarity between the water effect and the electric-field effect leads to a simple idea that adsorbed water makes a local electric field in the Y-TiOPc microcrystallites. Let us estimate the local field of adsorbed water. We know well the electric-field dependence of electroabsorption signals.<sup>5,13</sup> On the basis of the electroabsorption spectrum presented by Saito and co-workers,<sup>5</sup> we can estimate the difference between the permanent dipole moment of the excited state and that of the ground state at  $6.7 \times 10^{-29} \text{ C m}$ . Then we compare the difference spectrum with the second-derivative spectrum in Figure 5, and estimate the local electric field of adsorbed water at  $1 \times 10^2 \text{ V } \mu\text{m}^{-1}$ . This field strength appears to be too large, but note that the strength of the dipole electric field of a water molecule is as large as  $1.1 \times 10^2 \text{ V } \mu\text{m}^{-1}$  at 1 nm away from the water molecule dipole ( $6.47 \times 10^{-30} \text{ C m}$ ). The ratio of the  $k_{12}$  decrease caused by water adsorption to that caused by the  $30\text{-V } \mu\text{m}^{-1}$  field in Y-TiOPc is 6 as shown in Table 1. If the field dependence of the  $k_{12}$  change is linear, the local field is estimated at  $180 \text{ V } \mu\text{m}^{-1}$ . The quadratic field dependence of the  $k_{12}$  change leads to the local field of about  $70 \text{ V } \mu\text{m}^{-1}$ . We cannot calculate the local field accurately at the present stage, but we think that the local-field model is a promising idea to account for the water effect. It is noted that the data of  $k_1$  and  $k_2$  in Table 1 are not useful for estimating the local field, because these rates are the sum of the rates of elementary decay pathways and their field dependence will be more complicated.

Second, it is also possible that the water effect originates from the formation of an intermolecular compound between TiOPc and  $\text{H}_2\text{O}$ . TiOPc is a p-type photoconductor, that is to say, an electron-donating molecule, and  $\text{H}_2\text{O}$  possibly works as an electron acceptor. There is a good chance of CT-complex formation. A hydrogen-bonding complex is also possible because of an interaction between  $\text{Ti}=\text{O}$  and  $\text{H}-\text{O}$ . Fujimaki et al.<sup>12</sup> estimated the activation energy of water desorption from Y-TiOPc at  $67 \text{ kJ mol}^{-1}$ , which is compatible with a CT or hydrogen-bonding complex. How can we understand the water-induced changes of the absorption spectrum and the fluorescence kinetics of Y-TiOPc on the basis of the intermolecular-complex



model? In the case of the CT complex, it is possible to expect that intermolecular polarization induced by a CT interaction enhances the carrier-generation process. If the intermolecular polarization accelerates the decay process from the singlet excitons to the bound pair, the CT-complex model is compatible with the water-induced fluorescence quenching. However, it is not easy to interpret the difference spectrum (Figure 5) in terms of the CT-complex model. In the difference spectrum, we cannot point out any clear CT band that is generally brought about by CT-complex formation. In the case of the hydrogen-bonding complex model, TiOPc acts as a proton acceptor. A hydrogen-bonding interaction may have an effect similar to that of a CT interaction.

We do not think that water is adsorbed only on the surface of the Y-TiOPc microcrystallites. It is unlikely that surface-adsorbed water has an important influence on the absorption spectrum and the fluorescence kinetics of the Y-TiOPc microcrystallites as large as 0.1  $\mu\text{m}$ . We have no idea where or in what kind of site water molecules exist inside the Y-TiOPc microcrystallites. As mentioned above, adsorbed water in Y-TiOPc is easily desorbed, and the Y-form crystal structure does not change upon water desorption. These facts may indicate that adsorbed water should be regarded as zeolitic water. Oka et al.<sup>14</sup> reported the existence of a void between two adjacent molecules in Y-TiOPc, but we do not know whether this void provides enough room for adsorbed zeolitic water. We need another experiment such as NMR and IR measurements to know the site and the state of adsorbed water. It is also left to future studies to know why only the Y-form adsorbs water.

Finally we make comments on two discrepancies between our results and those of the pioneering work of Popovic et al.<sup>8</sup> First, they reported that the time constant of the shorter lifetime exciton of Y-TiOPc hardly depended on humidity. We have shown in the present study that  $\tau_1$  becomes shorter by 18% upon water adsorption. Second, they showed that the fluorescence amplitude of the shorter lifetime component ( $A_1$ ) and that of the longer lifetime component ( $A_2$ ) were both reduced by water adsorption. In the present study,  $A_1$  increases and  $A_2$  decreases upon water adsorption, and  $A_1 + A_2$  remains unchanged. We can make two plausible explanations for these discrepancies. First, the photoexcitation wavelength of our experiments (800 nm) is longer than that of Popovic et al. (590 nm). Khan and co-workers<sup>15</sup> has found in a conjugated polymer that higher energy excitons are more easily dissociated into bound pairs by an electric field. They have shown that the field-induced changes of fluorescence kinetics depend on photoexcitation wavelength. We have to conduct more experiments in the future to know whether Y-TiOPc also shows excitation-energy-dependent fluorescence kinetics. Second, it is possible to ascribe the discrepancies to the fact that the time resolution of the measurements of Popovic et al. was insufficient. They obtained the fluorescence-kinetics parameters by using the time-correlated single-photon-counting method whose best time resolution is

generally about 30 ps. We are sure that it is not easy to obtain exactly the time constant of the shorter lifetime exciton with this method. When the time resolution is not sufficient in a fluorescence-decay-curve measurement, lifetime shortening can be easily mistaken for amplitude quenching. On the other hand, the streak scope that we used has a time resolution of 10 ps as mentioned above. There is no difficulty in measuring a 70-ps decay and observing the lifetime shortening as large as 20% with the streak scope. It is generally accepted that a streak scope is the best instrument for time-resolved fluorescence spectroscopy in all respects. From a spectroscopic point of view, our data are more reliable than those by Popovic et al.

## V. Summary

The effect of water on the primary process of the Y-TiOPc photocarrier generation has been studied. We have found that the water effect on both the exciton dynamics and the ground-state absorption of Y-TiOPc is similar to the electric-field effect. Water adsorption accelerates the decay process from the shorter lifetime CT exciton to the bound electron-hole pair, and decelerates the internal conversion from the CT exciton to the longer lifetime Frenkel exciton. The mechanism of the fluorescence quenching induced by water adsorption is found to be the same as that by an electric field. Adsorbed water enhances the carrier generation of Y-TiOPc in the same way as an electric field does. We have proposed two possibilities for the origin of the water effect: a water-induced local electric field and a CT or hydrogen-bonding complex between TiOPc and  $\text{H}_2\text{O}$ . Clarification of the site and the state of adsorbed water in Y-TiOPc will require additional studies.

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