Bull. Chem. Soc. Jpn., ***74***, 1823–1829 (2001)

Photoexcited State Properties of Silicon Phthalocyanine Monomer, Dimer, and Trimer

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(Received January 30, 2001)

Properties of the excited states of silicon phthalocyanine monomer and its coplanar-stacked dimer and trimer have been investigated. Absorption bands of the oligomers showed blue-shift due to exciton coupling. Weak fluorescence bands of the dimer and trimer appeared in the near-IR region. The lifetimes of the singlet excited states of the dimer and trimer were estimated to be 196 and 53 ps, respectively, from the absorption-time profiles of the singlet excited states. The T–T absorption bands showed decays according to the intermolecular T–T annihilation processes. The rate constants for the intermolecular T–T annihilation processes were one-order smaller than the diffusion-limiting rates of the solvents, indicating some steric hindrance by the substituted group at the axial position. The quantum yields for the intersystem crossing processes of the dimer and trimer were quite small compared to that of the monomer. These findings indicate the extensive contribution of the non-radiative processes in the excited states of the dimer and trimer. The energy transfer rate constants between of the triplet excited phthalocyanines and O_2 decreased in the order of monomer $>$ dimer $>$ trimer. The small rate constants of the dimer and trimers can be attributed to the lower triplet energy levels of the dimer and trimer compared to that of the monomer.

Much attention has been focused on discovering new photophysical and photochemical properties of phthalocyanines and porphyrins.[1] The intramolecular interaction between coplanar-stacked phthalocyanine and porphyrin molecules plays important roles in the energy and electron transfer processes.[2,3] Thus, phthalocyanine oligomers have been studied widely.[4–23] Silicon phthalocyanine has been known to form several oligomers and polymers with a silicon-oxygen backbone.[15–22] The properties of the ground states of silicon phthalocyanine dimer and longer oligomers have been examined by several groups.[15–22] Their results indicate that the electronic states of the coplanar-stacked silicon phthalocyanine oligomers exhibit significant changes compared to the monomer due to the strong interaction among the phthalocyanine rings. Recently, some researchers have reported the excited state properties of silicon phthalocyanine dimer and polymer substituted with alkoxy groups.[20–22] Their results indicate that the excited state properties of these oligomers were quite different from those of the monomer. In order to understand more details of the excited state properties of coplanar-stacked silicon phthalocyanine oligomers, systematic studies by transient absorption measurements are indispensable. The transient absorption measurements are effective to study the excited singlet and triplet properties for the samples, for which the emission studies are not available or difficult to conduct.

In the present paper, we report the results of the transient absorption studies on the monomer, dimer, and trimer of silicon phthalocyanine (Chart 1), which are referred to Pc, $(Pc)_2$, and

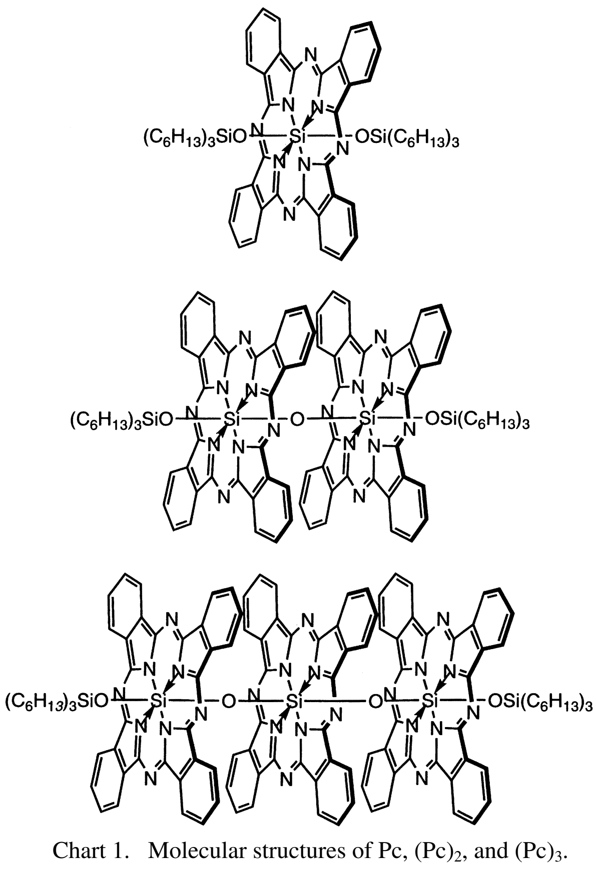

Chart 1. Molecular structures of Pc, $(Pc)_2$, and $(Pc)_3$.

$(Pc)_3$, respectively. Among these oligomers, $(Pc)_3$ is newly prepared in the present study. It would be expected that the interaction between the phthalocyanine moieties will be clearly present in the excited singlet and triplet states as well as in the ground state.

Experimental

Materials. Syntheses of Pc, $(Pc)_2$, and $(Pc)_3$ were carried out according to the procedure reported by Wheeler et al.[16] Identifications of the products were carried out using MALDI-TOF MASS.[24] Other chemicals were of the best commercial grade available.

Apparatus. The sub-picosecond transient absorption spectra were observed by the pump and probe method. The samples were excited with a second harmonic generation (SHG, 388 nm) of output from a femtosecond Ti:sapphire regenerative amplifier seeded by SHG of an Er-doped fiber laser (Clark-MXR CPA-2001 plus, 1 kHz, fwhm 150 fs). The excitation laser pulse was depolarized. A white continuum pulse generated by focusing the fundamental light on a flowing H_2O cell was used as the monitoring light. The visible monitoring light transmitted through the sample (optical path length: 2 mm) was detected with a dual MOS detector (Hamamatsu Photonics, C6140) equipped with a polychromator (Acton Research, SpectraPro 150). The spectra were obtained by averaging on a microcomputer.

Nanosecond transient absorption measurements were carried out using a third harmonic generation (355 nm) of a Nd:YAG laser as an excitation source. Probe light from a pulsed Xe lamp was detected with a Si-PIN photodiode equipped with a monochromator after passing through the sample in a quartz cell (1 cm × 1 cm). Sub-millisecond phenomena were observed by using a continuous Xe-lamp and photomultiplier tube as the probe light and the detector, respectively. Sample solutions were deaerated by bubbling Ar through the solutions for 15 min. Details of the transient absorption measurements were described in our previous paper.[25] In all the laser flash photolysis experiments, degradations of the samples due to laser irradiations were checked by the steady-state absorption measurements.

Steady-state fluorescence spectra of the samples were measured on a Shimadzu RF-5300PC spectrofluorophotometer. Fluorescence spectra in the near-IR region were measured by using an argon-ion laser (Spectra-Physics, BeamLok 2060-10-SA, 514 nm, ca. 200 mW) as an excitation source. The emission from sample was focused on to a monochromator (Koken Kogyo, SG-100) equipped with an InGaAs-PIN photodiode (New Focus, 2153). The output signal was recorded using a lock-in amplifier (NF Electronic Instruments, LI 5640).

Fluorescence lifetimes were measured by a single-photon counting method using an argon ion laser, a pumped Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, fwhm 1.5 ps) with a pulse selector (Spectra-Physics, 3980), a second harmonic generator (Spectra-Physics, GWU-23PS), and a streakscope (Hamamatsu Photonics, C4334-01). In the present study, each sample was excited with a 400 nm laser.

Steady-state absorption spectra in the visible and near-IR regions were measured on a Jasco V530 spectrophotometer.

Results and Discussions

Ground State Absorption Spectra. The steady-state absorption spectra of Pc, $(Pc)_2$, and $(Pc)_3$ are shown in Fig. 1. On going from Pc to $(Pc)_2$, the intense Q-band of Pc at 669 nm shifts to shorter wavelength (633 nm). This tendency is in good agreement with the reported spectra for other silicon phthalocyanine oligomers.[15–22] For $(Pc)_3$, a further blue-shift of the Q-band to 620 nm with broadening was observed. Compared with drastic spectral changes between Pc and $(Pc)_2$, the changes between $(Pc)_2$ and $(Pc)_3$ are moderate. Similar shifts were observed in the Soret band region (300–400 nm). These spectral features suggest that appreciable interactions are present among the phthalocyanine rings, probably due to the face-to-face interaction, as explained by the exciton coupling theory.[26] It is interesting to note that the solvent-effect on the ground state absorption bands is small when toluene, $CHCl_3$, and THF were employed as solvents for oligomers; such small solvent-effects for unsubstituted phthalocyanine dimers have been reported in the literature.[15–17] On the other hand, it was reported that the absorption spectra of the silicon phthalocyanine dimers with the alkoxy-substituents in the phthalocyanine rings showed appreciable solvent-effect.[20,21] These findings indicate that the substituent groups of the phthalocyanine ring induce a large solvent-effect.

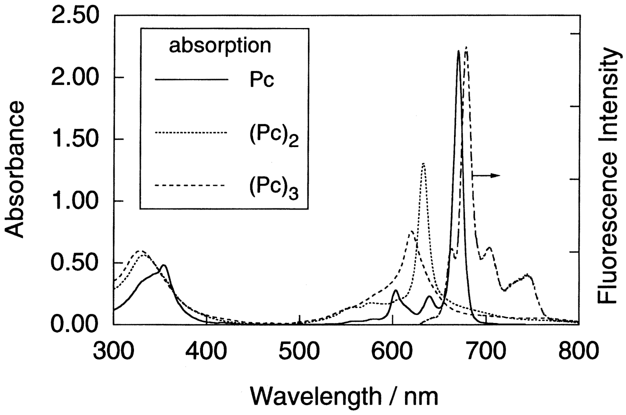

Fig. 1. Steady-state absorption spectra of Pc, $(Pc)_2$, and $(Pc)_3$ in $CHCl_3$. Fluorescence spectrum of Pc is also shown (Excitation: 370 nm).

Singlet Excited States of Phthalocyanine Oligomers. The dot-dash line in Fig. 1 shows a steady-state fluorescence spectrum of Pc observed by the excitation at 370 nm. The peak appeared at 678 nm with weak peaks at 703 and 744 nm, which are mirror images of the absorption bands. The fluorescence lifetime (τ_F) of Pc was evaluated to be 5.8 ns, which indicates that Pc has an ordinary lifetime as a monomeric phthalocyanine. As for $(Pc)_2$, broad fluorescence bands appeared at 1060 and 1190 nm (Fig. 2). The observed fluorescence bands are located at similar positions to those reported for the substituted silicon phthalocyanine dimer (around 1000 nm).[21] In the case of $(Pc)_3$, a fluorescence band appeared at 1230 nm. Intensity of the fluorescence band due to $(Pc)_3$ is weaker than that due to $(Pc)_2$ as seen in Fig. 2, in which absorbance of the samples was matched at the excitation wavelength (514 nm), suggesting that the longer oligomers have shorter lifetimes of the singlet excited states. Since these fluorescence bands in the near-IR region were quite weak, the estimation of the fluorescence lifetimes of these oligomers was difficult. Thus, the sub-picosecond laser flash photolysis was employed for these oligomers in the next section.

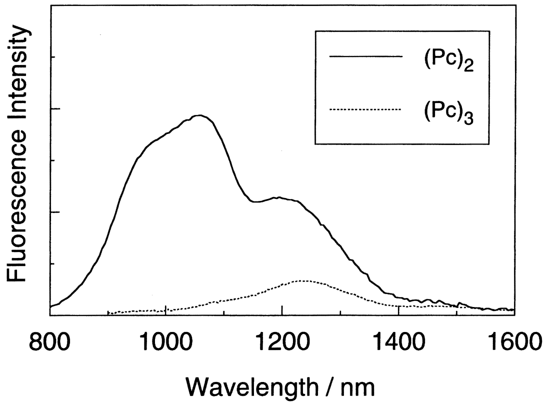

Fig. 2. Fluorescence spectra of $(Pc)_2$ and $(Pc)_3$ in toluene. Absorbance of the samples at the excitation wavelength was matched (Excitation: 514 nm).

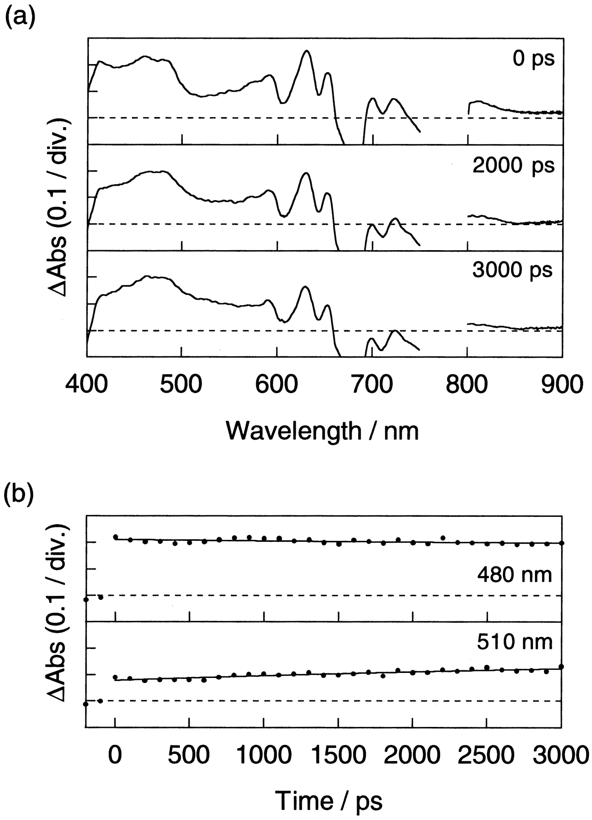

Fig. 3. (a) Transient absorption spectra of Pc in toluene observed by femtosecond laser irradiation at 388 nm. Dash lines indicate ΔAbs = 0. (b) Absorption-time profiles. Solid lines are fitted curves.

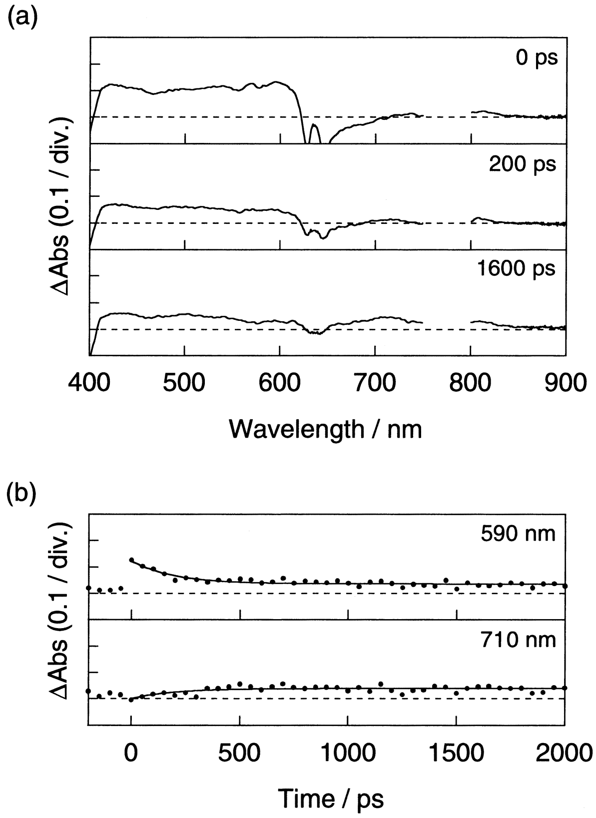

Fig. 4. (a) Transient absorption spectra of $(Pc)_2$ in toluene observed by femtosecond laser irradiation at 388 nm. Dash lines indicate ΔAbs = 0. (b) Absorption-time profiles. Solid lines are fitted curves.

Figure 3a shows transient absorption spectra of Pc in toluene upon femtosecond laser excitation at 388 nm. Absorption bands appeared at 810, 722, 700, 653, 630, 591, 479, 460, and 412 nm immediately after the laser excitation. These absorption bands will be attributed to the singlet excited state of Pc. At 3000 ps after the laser irradiation, intensities of these absorption bands became small, while the absorbance around 510 nm increased, as indicated in an absorption-time profile at 510 nm (Fig. 3b). The absorption band at 510 nm can be attributed to absorption band of triplet excited Pc, as shown later. Thus the rise of the absorption band at 510 nm can be attributed to the intersystem crossing process of Pc. The decay rate constant (k_S) of the singlet excited state (480 nm of Fig. 3b) was estimated to be 2.1×10^8 s^{-1}, which agreed well with the decay rate constant of the fluorescence band (= $1/\tau_F$) of Pc, 1.7 $\times$ 10^8 s^{-1}. This agreement supports the identification of the absorption bands of the singlet excited state of Pc.

In the case of $(Pc)_2$, the transient absorption bands due to the singlet excited state, which appeared immediately after the laser excitation, were quite broad, in contrast to those of Pc (Fig. 4a). The broadening of the absorption bands is a similar tendency to that of the ground state absorption spectrum of $(Pc)_2$. The absorption bands appeared at 595, 569, 539, and 422 nm. As shown in Fig. 4b, the absorption bands due to the singlet excited state decreased over a few hundred ps. At 1600 ps after the laser excitation, the absorption bands were observed around 710 and 510 nm; these may be attributed to the triplet excited state of $(Pc)_2$. The decay rate constant of the singlet excited state (= k_S) was estimated to be 5.1×10^9 s^{-1} (Fig. 4b), which corresponds to 196 ps of the decay lifetime.

As for $(Pc)_3$, the transient absorption bands due to the singlet excited states appeared at 684 and 520 nm (Fig. 5a); the decay rate constant was as fast as 1.9×10^{10} s^{-1} (Fig. 5b), which corresponds to 53 ps of the decay lifetime. The fast decays of the singlet excited dimer and trimer can be attributed to the fast non-radiative deactivation to the ground state via low-

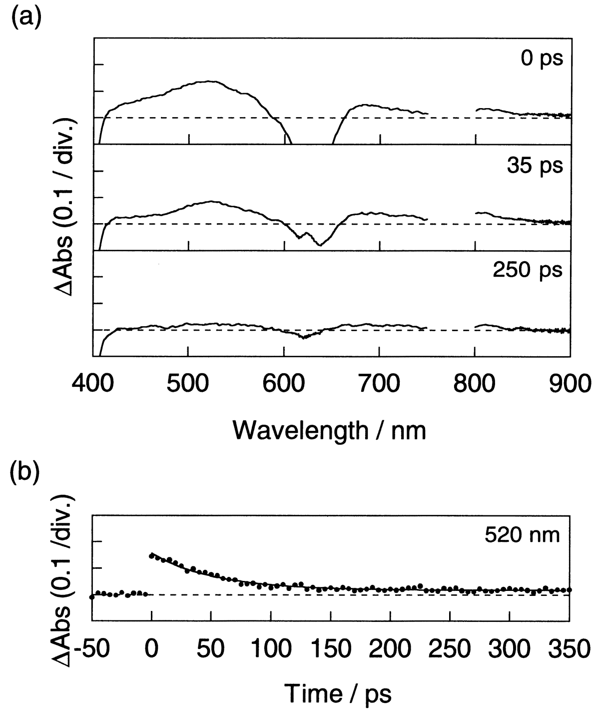

Fig. 5. (a) Transient absorption spectra of $(Pc)_3$ in toluene observed by femtosecond laser irradiation at 388 nm. Dash lines indicate ΔAbs = 0. (b) Absorption-time profile. Solid line is a fitted curve.

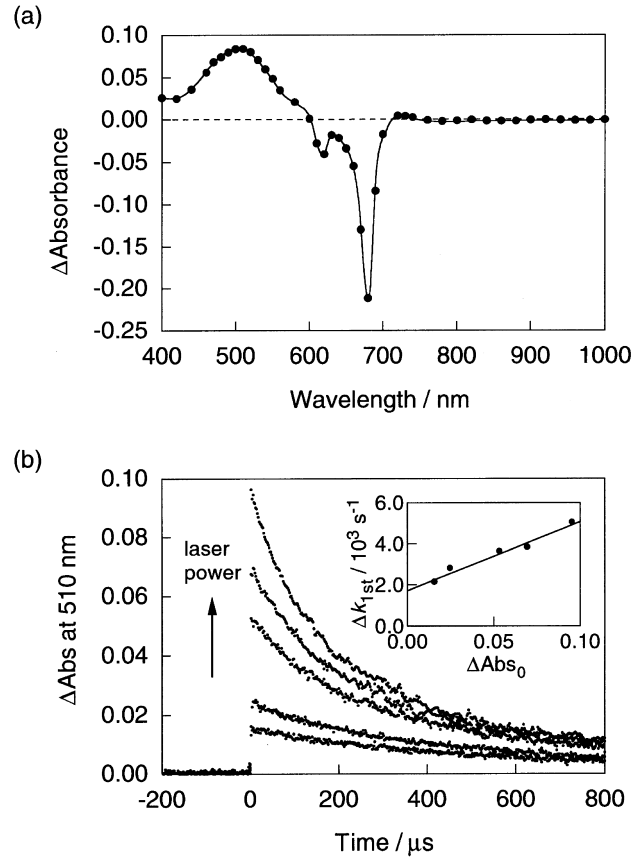

Fig. 6. (a) Transient absorption spectra of Pc in toluene at 250 ns after the nanosecond laser irradiation at 355 nm. (b) Absorption-time profiles at 510 nm obtained by various laser power. Inset: Plots of Eq. 1 for Pc.

er-energy states such as ring-to-ring charge transfer, as suggested for the previously reported silicon phthalocyanine dimers.[21] The contribution of the fast non-radiative deactivation is supported by the fact that the quantum yields for the intersystem crossing processes of the oligomers decreased drastically, as discussed later in the present paper. Furthermore, the quite small quantum yields for fluorescence of dimer and trimer (ca. 10^{-3} for dimer)[21] support the dominant non-radiative processes in the singlet excited states of dimer and trimer.

From the fluorescence intensity, Oddos-Marcel et al. estimated the lifetime of the singlet excited state to be 24 ps for silicon phthalocyanine dimer substituted with the alkoxy groups.[21] The shorter lifetime of their dimer than the present study indicates that the alkoxy substitution to the phthalocyanine rings of the dimer changes the excited properties as well as the ground state properties. On the other hand, Ern et al. reported the transient absorption study on silicon phthalocyanine polymer, which consists of an average of 32 cofacially stacked phthalocyanine rings.[22] They observed that the excited state of the polymer decayed within 20 ps, which is shorter than the decay lifetime of $(Pc)_3$ in the present study. Thus, shorter lifetimes of the singlet excited state seem to be a general trend in longer phthalocyanine oligomers.

Triplet Excited States of Phthalocyanine Oligomers. In order to evaluate the contribution of the intersystem crossing process, the nanosecond laser-flash photolysis studies were carried out. For Pc in toluene, the transient absorption band appeared at 510 nm with the depletion of the Pc absorption in the region of 610–700 nm (Fig. 6a). The transient absorption band observed by the nanosecond laser irradiation can be attributed to the transition from the lowest triplet excited state to the upper triplet excited states (T–T absorption), since the absorption band was quenched in the presence of the triplet energy quencher such as oxygen. The decay of the transient absorption band at 510 nm changed to mixed order kinetics of the first- and second-order when the excitation laser power became strong, as shown in Fig. 6b. This finding indicates the contribution of the triplet–triplet (T–T) annihilation to the decay process of the triplet excited state of Pc. For a quantitative analysis of the decay profiles, the first order decay rate constant (k_{1st}) and the second order decay rate constant (k_{2nd}) were separated by using the following equation:[27]

$$-\mathrm{d}[\ln(\Delta \mathrm{Abs}_0)]/\mathrm{d}t = \Delta k_{1st} = k_{1st}{}^0 + (2k_{2nd}/\varepsilon_T)\Delta \mathrm{Abs}_0 \qquad (1)$$

where ΔAbs_0, $k_{1st}{}^0$ and ε_T are referred to T–T absorbance at t = 0, an intrinsic first-order decay rate constant, and an extinction coefficient of the T–T absorption band, which were estimated by energy transfer from anthracene.[28] In the inset of Fig. 6b, the plots for Pc in toluene are shown as an example. From the slope of the plot, the k_{2nd} value (= k_{TT}, the rate constant of T–T annihilation process) of Pc in toluene was estimated to be 9.2 × 10^8 dm^3 mol^{-1} s^{-1}, which is one-order smaller than the diffusion limiting rate of the solvent (k_{diff}, 1.2 × 10^{10} dm^3 mol^{-1} s^{-1} for toluene).[29] Furthermore, the $k_{1st}{}^0$ value was estimated

Table 1. Spectroscopic and Dynamic Properties of Pc, $(Pc)_2$, and $(Pc)_3$

	Solvent	Pc	$(Pc)_2$	$(Pc)_3$
τ_F/ps	toluene	5800	$196^{a)}$	$53^{a)}$
k_S/s^{-1}	toluene	2.1×10^8	5.1×10^9	1.9×10^{10}
$\tau_{T0}/\mu s$	toluene	578	126	103
	$CHCl_3$	386	92	61
	THF	420	128	77
$k_{TT}/dm^3\ mol^{-1}\ s^{-1}$	toluene	9.2×10^8	1.0×10^9	$(1.8 \times 10^9)^{b)}$
	$CHCl_3$	1.4×10^9	9.8×10^8	—$^{c)}$
	THF	1.7×10^9	1.5×10^9	$(3.2 \times 10^9)^{b)}$
Φ_T	toluene	0.19	0.092	0.013
	$CHCl_3$	0.19	0.055	0.010
	THF	0.18	0.077	0.014
$k_{O2}/dm^3\ mol^{-1}\ s^{-1}$	toluene	1.7×10^9	1.2×10^7	2.1×10^6
	$CHCl_3$	1.1×10^9	7.9×10^7	1.6×10^6
	THF	1.6×10^9	1.2×10^7	2.6×10^6

a) These values were estimated from the k_S value. b) These values include large estimation error due to weak signal. c) Estimation was difficult due to weak signal.

to be $1.8 \times 10^3\ s^{-1}$, which corresponds to 578 μs of the intrinsic lifetime (τ_{T0}). Essentially the same T–T absorption bands were observed in other solvents such as $CHCl_3$ and THF. In these solvents, decays of the T–T absorption bands were also governed by the mixed-order decay kinetics. The treatment according to Eq. 1 gave k_{2nd} and $k_{1st}{}^0$ values, which are summarized in Table 1 as the k_{TT} and τ_{T0} ($= 1/k_{1st}{}^0$) values. The τ_{T0} value in $CHCl_3$ is smaller than that in other solvents. The finding can be attributed to an irreversible reaction of the sample with $CHCl_3$: Repeated laser irradiations of the $CHCl_3$ solution caused substantial changes in the ground state absorption spectrum, indicating the photoinduced reaction of the sample, while the transient absorption measurements were carried out always with fresh samples. As for k_{TT} values, each value was one-order smaller than the each k_{diff} value, as in the case of Pc in toluene.

As mentioned above, the T–T absorption bands of Pc were quenched in the presence of oxygen, the triplet energy quencher. The bimolecular quenching rate (k_{O2}) was determined to be $1.7 \times 10^9\ dm^3\ mol^{-1}\ s^{-1}$ in toluene. The k_{O2} values in other solvents are also summarized in Table 1. It is interesting to note that the k_{O2} values in these solvents are one-order smaller than the k_{diff} values of the solvents, as in the case of the k_{TT} values. The fact that the k_{TT} and k_{O2} values are smaller than the k_{diff} values results from steric hindrance due to $(n\text{-}C_6H_{13})_3Si$-groups at the axial position of the phthalocyanine-moiety, since the lowest triplet energy (T_1) of Pc (120 kJ mol^{-1}) is higher than that of O_2 (94.1 kJ mol^{-1}),[29] indicating a sufficient driving force for the energy transfer process.

In the case of $(Pc)_2$, transient absorption spectra were estimated in three solvents, as shown in Fig. 7. The T–T absorption spectra are essentially the same in these solvents. The transient absorption bands appeared at 720, 600, and 500 nm with the depletion of the ground state absorptions at 620–700 nm and 780–860 nm. These absorption bands correspond well with those observed in the sub-picosecond transient absorption spectrum (Fig. 4a, 1600 ps). Essentially the same spectra in these solvents are quite reasonable for the present phthalocyanine dimers, since the ground state absorption spectra did not show any large changes in these solvents. This finding is in contrast to the previously reported T–T absorption spectra of the dimer of silicon phthalocyanine substituted by the alkoxy groups: The T–T absorption spectra of the substituted dimer showed extensive solvent-dependence, as in the case of its ground state absorption spectra.[20] The T–T absorption bands of $(Pc)_2$ showed the decay according to the mixed order kinetics, as for Pc. The k_{TT} values of the $(Pc)_2$ in the various solvents were similar to those of Pc, indicating that the T–T annihilation process of $(Pc)_2$ was also affected by the steric hindrance due to $(n\text{-}C_6H_{13})_3Si$-groups at the axial position. It should be noted that the τ_{T0} values of $(Pc)_2$ are about 1/3–1/5

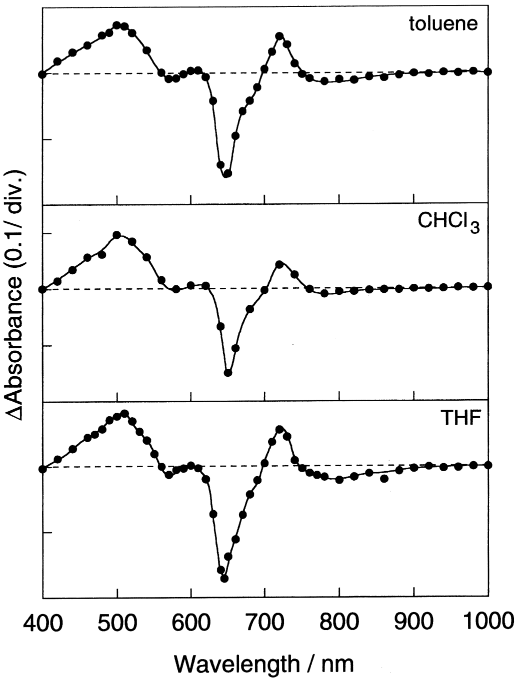

Fig. 7. Transient absorption spectra of $(Pc)_2$ in toluene, $CHCl_3$, and THF at 250 ns after the nanosecond laser irradiation at 355 nm. Dash lines indicate ΔAbs = 0.

of Pc in the corresponding solvents. The estimated τ_{T0} values were similar to those of the substituted silicon phthalocyanine dimer.[20]

It is interesting to note that the intensity of the transient absorption band of $(Pc)_2$ is somewhat smaller than that of Pc, even though the ground state absorbance of the samples was matched at the excitation wavelength. By the relative actinometry method, the quantum yields for the intersystem crossing process (Φ_T) were estimated, as summarized in Table 1: The Φ_T values of $(Pc)_2$ are about 1/2–1/4 of Pc. The smaller Φ_T values of $(Pc)_2$ indicate the contribution of the fast non-radiative process and the intersystem crossing process of the singlet excited state of $(Pc)_2$.

The transient absorption bands of $(Pc)_2$ were quenched in the presence of oxygen, while the k_{O2} values for $(Pc)_2$ were about 1/100 of Pc in the corresponding solvents (Table 1). This finding indicates that the T_1 level of $(Pc)_2$ is lower than that of Pc.

For $(Pc)_3$, the T–T absorption bands appeared at 680 and 500 nm with the depletion of the ground state absorptions at 640 nm and 720–880 nm in toluene, $CHCl_3$, and THF (Fig. 8). The observed absorption bands correspond well with that observed in the sub-picosecond transient absorption spectrum (Fig. 5a, 250 ps). The identification of the T–T absorption bands of $(Pc)_3$ is supported by the fact that the observed absorption bands were also generated by the energy transfer from the triplet energy donor.[28] The spectral features were essentially the same in the examined solvents as in the cases of Pc and $(Pc)_2$. The transient absorption bands of $(Pc)_3$ were quite weak; the absorbance of the T–T bands of $(Pc)_3$ was 1/15–1/20 of Pc. The Φ_T values of $(Pc)_3$ are summarized in Table 1. From the Φ_T and k_S values, the rate constants of the intersystem crossing processes of Pc, $(Pc)_2$, and $(Pc)_3$ were estimated to be 4.0×10^7, 4.7×10^8, and 2.5×10^8 s^{-1}, respectively, indicating enhancement of the intersystem crossing processes of the oligomers. On the other hand, the rate constants of the non-radiative processes of $(Pc)_2$ and $(Pc)_3$ were estimated to be as large as 4.6×10^9 and 2.5×10^{10} s^{-1}, respectively, indicating that the non-radiative processes of oligomers have substantial effects on the deactivation processes of their singlet excited states. The efficient non-radiative process of $(Pc)_3$ accords with the fact that the decay of the singlet excited state of $(Pc)_3$ is faster than that of $(Pc)_2$. The efficient non-radiative processes of dimer and trimer accord with the prediction by the neutral exciton model based on the strong coupling limit, in which the transition from the lowest excited state to the ground state is forbidden.[21] Furthermore, the contribution of the ion-pair configuration such as a ring-to-ring charge transfer provides an efficient deactivation pathway, which also increases the non-radiative process.

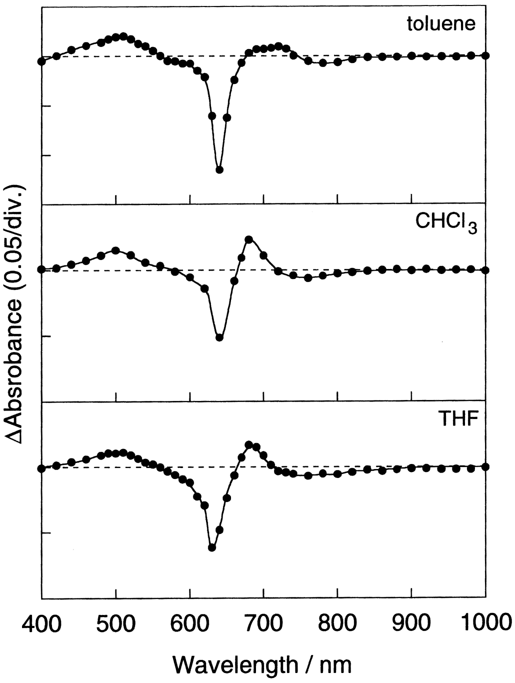

Fig. 8. Transient absorption spectra of $(Pc)_3$ in toluene, $CHCl_3$, and THF at 250 ns after the nanosecond laser irradiation at 355 nm. Dash lines indicate $\Delta Abs = 0$.

The τ_{T0} values of $(Pc)_3$ were estimated to be 57–103 μs, which are smaller than those of $(Pc)_2$ in the corresponding solvents, while the estimation of the k_{TT} values was difficult due to the weak signals of T–T absorption bands of $(Pc)_3$. The short τ_{T0} values of $(Pc)_2$ and $(Pc)_3$ accord with the fast intersystem crossing processes of these oligomers, as discussed above.

The k_{O2} values were on the order of 10^6 dm^3 mol^{-1} s^{-1}; this indicates that T_1 of $(Pc)_3$ becomes even lower. From the Sandrofy equation,[29] the T_1 level of $(Pc)_3$ is expected to be lying below the excitation energy of oxygen by 21 kJ mol^{-1}, i.e. the T_1 level of $(Pc)_3$ is 73 kJ mol^{-1} above its ground state. The estimated value is reasonable, since the excited singlet energy of $(Pc)_3$ is 97 kJ mol^{-1} from the fluorescence spectrum (Fig. 3). Increase of the steric hindrance of $(Pc)_3$ is also a possible explanation for the quite small k_{O2} values on going from $(Pc)_2$ to $(Pc)_3$. However, the observation of T–T annihilation process of $(Pc)_3$ shows that the triplet state will not be localized on the central Pc-moiety, indicating that the triplet state of $(Pc)_3$ is also reactive to the molecule in the solution. Therefore, the lower T_1 level of $(Pc)_3$ seems to be a plausible explanation for the lower k_{O2} values. As for $(Pc)_2$, the T_1 level was estimated to be 77 kJ mol^{-1} by using the Sandrofy equation. The lower T_1 level can explain the fact that the reactivity of triplet excited $(Pc)_2$ with oxygen is lower than that of Pc.

In Table 1, Φ_T and τ_{T0} values of $(Pc)_2$ and $(Pc)_3$ in $CHCl_3$ are somewhat smaller than those in toluene and THF, while the dielectric constant of $CHCl_3$ is intermediate between those of toluene and THF. This finding suggests the photoinduced process of oligomers with $CHCl_3$, since $CHCl_3$ is known as an electron acceptor for the oligomers with high donor-abilities.[30] The electron transfer with solvent may decrease the Φ_T and τ_{T0} values.

Conclusion

The excited state properties of the dimer and trimer of the silicon phthalocyanine were much different from those of the monomer. The fast non-radiative deactivation to the ground state via lower-energy states of the dimer and trimer resulted in the fast decay rate of the singlet excited states and the small quantum yields for the intersystem crossing process. Furthermore, the interaction between the phthalocyanine rings of the dimer and the trimer caused small singlet and triplet excited state energies, which appeared as near-IR fluorescence and slow reaction rates with oxygen of these oligomers, respectively. These properties of oligomers are interesting for the prediction of the properties of polymers.

The present work was partly supported by a Grant-in-Aid on Scientific Research from the Ministry of Education, Science, Sports and Culture (No. 10207202, 11740380, and 12875163). The authors are also grateful to financial support by Core Research for Evolutional Science and Technology (CREST) of Japan Science and Technology Corporation. One of the authors (M. F.) thanks the Ogasawara Foundation for the Promotion of Science & Engineering for financial support.

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