A Concept for Controlling Singlet Oxygen ($^1\Delta_g$) Yields Using Nitroxide Radicals: Phthalocyaninatosilicon Covalently Linked to Nitroxide Radicals

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Abstract: In this study, we have investigated the singlet oxygen ($^1\Delta_g$) generation mechanism using phthalocyaninatosilicon (SiPc) covalently linked to nitroxide radicals (NRs), and we succeeded in increasing the singlet oxygen quantum yield (Φ_Δ) by linking the NRs. This originates from both an increase in the triplet quantum yield and excited-state lifetimes long enough to utilize photochemical reactions. Because the electron exchange interactions with paramagnetic species were known to result only in very fast excited-state relaxation, leading to a decrease in photochemical reaction yields, this increase in Φ_Δ is an unusual and precious example for increasing photochemical reaction yields by electron exchange interactions with paramagnetic species. In addition, our experiments and theoretical analyses show that the spin-selective energy transfer rate constant is not influenced by linking the NRs and can be evaluated by the product of spin-statistical factors and matrix elements between the initial and final states.

Introduction

Various kinds of spin-dependent processes are known to play an important role in photophysical and photochemical processes, such as intersystem crossing (ISC) and radical reactions. Because it is crucial to clarify and control these processes in terms of photochemistry and spin chemistry, the heavy atom effects and external magnetic field effects have been investigated not only in the photophysical ISC process between the singlet and triplet states, but also in photochemical and enzyme reactions.[1–5]

On the other hand, while electron exchange interactions with paramagnetic species were known to result only in very fast excited-state relaxation,[6,7] the influences on chemical reaction kinetics have recently been investigated. Turro et al. studied the photolysis of D,L-2,4-diphenylpentan-3-one in the presence of a nitroxide radical and demonstrated that the recombination probability of a radical pair is increased by a paramagnetic nitroxide radical,[8] and this mechanism has been developed as "spin catalysis" by Buchachenko et al.[8–10] Corvaja et al. reported that nitroxide-linked fullerene undergoes an electron transfer reaction with ferrocene.[11] Hayashi et al. have investigated the zinc porphyrin−naphthalenediimide−nitroxide triad in terms of the additional radical effects on the charge-separation and charge-recombination processes.[12] In these photochemical reactions, such as cleavage or electron transfer, electron exchange interactions with paramagnetic species were found to enhance the recombination of products, that is, radicals or separated charges.

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Chart 1
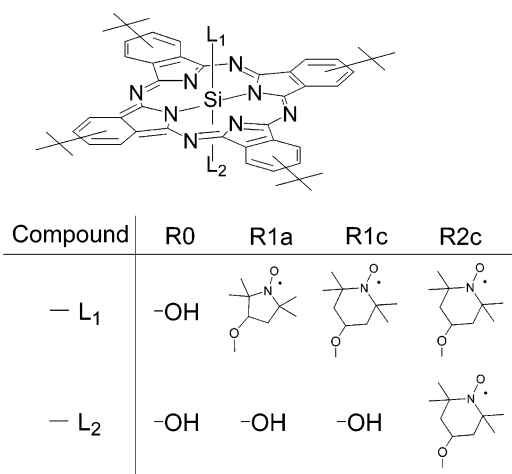
Recently, we investigated phthalocyaninatosilicon (SiPc) covalently linked to nitroxide radicals (NRs) (Chart 1), and we showed that the excited-state lifetimes of these paramagnetic molecules are changeable depending on the electronic interactions between the SiPc and NR moieties.[13,14] In contrast to a conventional knowledge that interactions with paramagnetic species result in very fast excited-state relaxation decreasing photochemical reaction yields,[6,7] these excited-state lifetimes ($0.86-15$ μs) are relatively long enough to utilize for photochemical reactions. This motivated us to try to increase photochemical reaction yields using the electron exchange interactions with NRs.

In this study, we have investigated an energy transfer between NR–SiPc and molecular oxygen, leading to excited singlet oxygen ($^1\Delta_g$). Because singlet oxygen ($^1\Delta_g$) produced by the energy transfer from porphyrinic compounds in the lowest excited triplet (T_1) state to triplet molecular oxygen ($^3\Sigma_g$) is essential for photodynamic therapy of cancer,[15,16] it is important to establish a novel methodology for increasing the singlet oxygen quantum yield (Φ_Δ). While it was shown that complexation with paramagnetic metal ions, such as Cu^{2+}, renders Pcs photoinactive,[7b,16] we have succeeded in increasing the Φ_Δ value using the electron exchange interactions with paramagnetic NRs. Important features are as follows. (1) By linking the NRs, the singlet–triplet ISC of SiPc partially turns into transitions between states having the same spin multiplicity, which results

in ISC enhancements. By comparison between R1a, R1c, and R2c, where the electron exchange interactions with NRs are systematically changeable,[13] it is demonstrated that the ISC enhancements due to NRs are controllable and useful for photochemical reactions. (2) It has been shown that the energy transfer rate constant (k_{ET}) resulting in singlet oxygen ($^1\Delta_g$) is dependent on spin-statistical factors.[17,18] For instance, while a pair of T_1 chromophore and triplet oxygen ($^3\Sigma_g$) provide nine sublevels consisting of the quintet, triplet, and singlet states, the energy transfer resulting in a chromophore in the singlet ground (S_0) state and a singlet oxygen ($^1\Delta_g$) occurs only from the singlet pair, whose probability is $^1/_9$. The linking NRs can change both the spin multiplicity in the excited states and the spin-statistical factors. Thus, the influences of NRs on the energy transfer rate are investigated. Quantum yields of T_1 SiPc and singlet oxygen ($^1\Delta_g$), as well as energy transfer rate constants, are examined by transient absorption and near-infrared red (NIR) luminescence measurements, which are discussed in terms of the spin adduct effects.

Experimental Section

R0, R1a, R1c, and R2c were synthesized following the methods previously reported[13a,19] and were purified carefully before the measurements. As the solvent, spectral grade toluene (Nacalai Tesque Inc.) was used for all measurements, while a 1:1 mixture of toluene and 2-methyltetrahydrofuran (Tokyo Chemical Industry Co, Ltd.) was employed for phosphorescence measurements. For transient absorption and phosphorescence measurements, samples were deaerated by freeze–pump–thaw cycles or nitrogen bubbling, and then the measurements were carried out within 1 day.

Transient absorption measurements were performed at ambient temperature by using a monochromator (JASCO CT-25CP) and a photomultiplier (Hamamatsu Photonics R446) with the continuous wave of a metal halide lamp (Sigma Koki IMH-250) or a He–Ne green laser (543.5 nm, Melles Griot).[13] The signals were integrated using a digital oscilloscope (Iwatsu-LeCroy LT342), where 75 Ω resistance was employed for impedance matching, and thus the time resolution of our instrument was $\sim$10 ns. To gain the voltage, 20 kΩ resistance was used only when an extinction coefficient of triplet–triplet absorption (ϵ_{TSiPc}) was examined for R0.

NIR luminescence measurements were performed using a monochromator (JASCO CT-25CP) and a photomultiplier (Hamamatsu Photonics R5509-42), which was cooled at 193 K by a cold nitrogen gas flow system (Hamamatsu Photonics R6544-20). The photon signals amplified by a fast preamplifier (Stanford Research SR445) were measured by the single photon counting method using a photon counter (Stanford Research SR400).

For these measurements, samples were excited by a Nd:YAG laser (Spectra Physics INDI-30; 355 nm; 7 ns fwhm) or a dye laser (Sirah CSTR-LG532-TRI-T) pumped with a Nd:YAG laser (Spectra Physics INDI 40; 532 nm; 7 ns fwhm). For the singlet oxygen ($^1\Delta_g$) luminescence and transient absorption measurements, laser powers were $0.2-2$ mJ.

Theoretical Background

Excited-State Properties of R0, R1, and R2. To discuss the excited-state dynamics, the excited states of R0, R1, and

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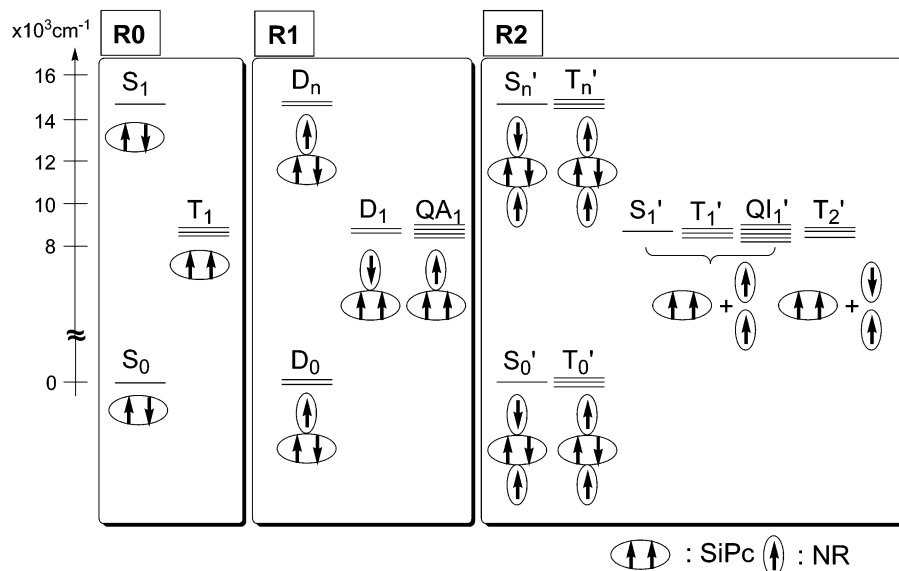
Figure 1. Excited-state energy diagrams of R0, R1, and R2.

R2 are illustrated, together with their excited-state energy diagrams in Figure 1. In the lowest excited singlet (S_1) region of R0 located at 1.47×10^4 cm^{-1},[19c] the S_{1x} and S_{1y} states are doubly degenerate, which are almost entirely derived from the $^1(a_{1u}e_{gy})$ and $^1(a_{1u}e_{gx})$ configurations, respectively (the a_{1u} (π) and e_{gi} (π^*) (i = x or y) orbitals denote the HOMO and LUMO of the Pc ligand, respectively).[7] In the T_1 region, the T_{1x} and T_{1y} states are also doubly degenerate, which are almost entirely derived from the $^3(a_{1u}e_{gy})$ and $^3(a_{1u}e_{gx})$ configurations, respectively.[7] From the phosphorescence spectrum of R0 (Figure 2a, broken line), the T_1 energy is evaluated as 8.90×10^3 cm^{-1}.[20]

For R1, the doublet ground (D_0) state consists of NR in the D_0 state (^{2}NR) and SiPc in the S_0 state (^{1}SiPc). A pair of ^{2}NR and SiPc in the S_1 state (^{1}SiPc*) provide the excited doublet (D_n) state. The lowest excited doublet (D_1) and quartet (QA_1) states are generated by an interaction between ^{2}NR and SiPc in the T_1 state (^{3}SiPc*), which have been confirmed by time-resolved EPR studies.[13a,19b,21]

In the case of R2, the singlet (S_0') and triplet (T_0') ground states are generated by an interaction between the two ^{2}NRs.[22] The excited singlet (S_n') and triplet (T_n') states are constituted by ^{1}SiPc* and two ^{2}NRs. The interactions between ^{3}SiPc* and two ^{2}NRs result in the lowest excited singlet (S_1'), triplet (T_1'), quintet (QI_1'), and second lowest excited triplet (T_2') states.[23,24]

Previous steady-state absorption, transient absorption, and steady-state EPR measurements showed that the electronic
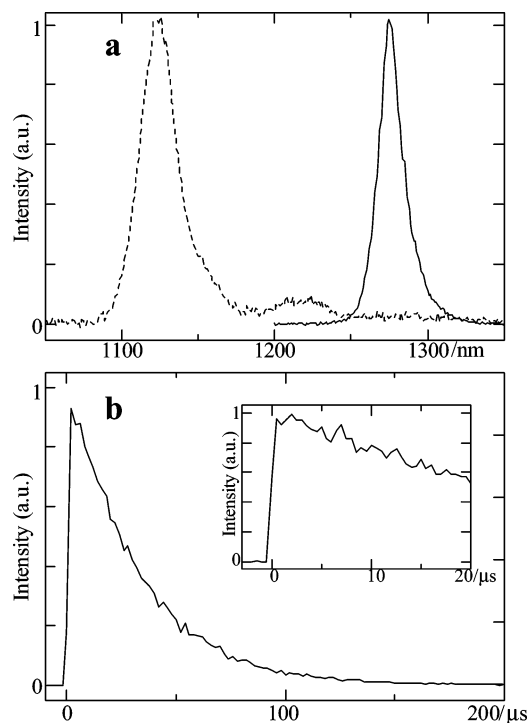

Figure 2. A phosphorescence spectrum of R0 (a; broken line), a singlet oxygen luminescence spectrum (a; solid line), and the decay profile of the singlet oxygen luminescence (b; the inset shows the first 20 μs of the decay). The phosphorescence spectrum of R0 in toluene/2-methyltetrahydrofuran (1:1 v/v, 10^{-6} M) was observed at 77 K, where the photon signals were counted at 40 μs (gate width = 10 ms) after 650 nm laser excitation. The singlet oxygen luminescence measurements were carried out in toluene at ambient temperature, where the spectrum was obtained by counting the photon signals at 1 μs after 650 nm laser excitation of R1c.

interactions between the NR and SiPc moieties are weak, so that the SiPc and NR retain their individual properties.[13,19] Because only the spin quantum number in the excited states can be changed by linking the NRs, these compounds are appropriate for investigating the influences of electron spins on the spin-selective processes.

Free Energy Difference in the Energy Transfer Process. To investigate the energy transfer process, ^{3}SiPc* + O$_2$ ($^3\Sigma_g$)

(20) To determine the T_1 energy of SiPc, phosphorescence measurements were carried out for R0 (Figure 2). Here, a 1:1 mixture of toluene and 2-methyltetrahydrofuran was used as a solvent to prevent aggregation. The T_1 energy of SiPc was determined as 8.90×10^3 cm^{-1} from the phosphorescence peak at low concentration ([R0] = 10^{-6} M).

(21) Previous time-resolved EPR studies have shown that the D_1 and QA_1 states are formed and that an energy splitting ($3J$) between the D_1 and QA_1 states is evaluated as >0.1 cm^{-1}.[13a,19b] Ishii, K.; Ishizaki, T.; Kobayashi, N. *J. Chem. Soc., Dalton Trans.* **2001**, 3227.
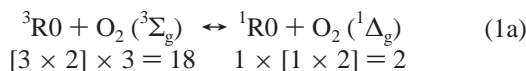
(22) An energy splitting ($2J'$) between the S_0' and T_0' states is evaluated as 9.9×10^{-4} cm^{-1} by a steady-state EPR spectrum.[19a]

(23) Two ^{2}NRs exhibit the triplet and singlet characters in the T_1' and T_2' states, respectively. Energies of the S_1', T_1', T_2', and QI_1' states are calculated as $J - J'$, $-J'$, $-J$, and $-2J - J'$, respectively.[24] Because J (>0.03 cm^{-1}) $\gg$ J' ($\sim$5 $\times$ 10^{-4} cm^{-1}),[13b] they are reevaluated as J, 0, $-J$, and $-2J$, respectively.
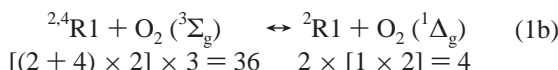
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$\rightarrow$ ^{1}SiPc + O$_2$ ($^1\Delta_g$), the free energy difference (ΔG) between the initial and final states is illustrated. First, from the phosphorescence spectra in Figure 2a, the excited-state energies of ^{3}SiPc* and singlet oxygen ($^1\Delta_g$) are evaluated as 8.90×10^3 and 7.84×10^3 cm^{-1}, respectively, thereby yielding the enthalpy difference (ΔH) as -1.06×10^3 cm^{-1}.
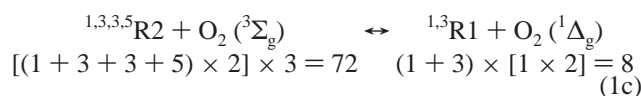
The linking NRs change the spin multiplicity in the ground and excited states, changing the entropy. Because the $^1\Delta_g$ state of molecular oxygen is a doubly degenerate state, the entropy differences (ΔS) between the initial and final states are evaluated as follows.[25]

$$^3R0 + O_2\,(^3\Sigma_g) \;\leftrightarrow\; {}^1R0 + O_2\,(^1\Delta_g) \qquad (1a)$$
$$[3 \times 2] \times 3 = 18 \qquad 1 \times [1 \times 2] = 2$$

$$T\Delta S = RT\ln(2/18)$$

$$^{2,4}R1 + O_2\,(^3\Sigma_g) \;\leftrightarrow\; {}^2R1 + O_2\,(^1\Delta_g) \qquad (1b)$$
$$[(2+4) \times 2] \times 3 = 36 \qquad 2 \times [1 \times 2] = 4$$

$$T\Delta S = RT\ln(4/36)$$

$$^{1,3,3,5}R2 + O_2\,(^3\Sigma_g) \;\leftrightarrow\; {}^{1,3}R1 + O_2\,(^1\Delta_g)$$
$$[(1+3+3+5) \times 2] \times 3 = 72 \qquad (1+3) \times [1 \times 2] = 8 \qquad (1c)$$

$$T\Delta S = RT\ln(8/72)$$

That is, the $T\Delta S$ value is unchanged by linking the NRs and is evaluated as -4.5×10^2 cm^{-1} when $T = 293$ K. Using the ΔH value ($= -1.06 \times 10^3$ cm^{-1}), the ΔG value is calculated as -6.1×10^2 cm^{-1}, indicating that the energy transfer process is exothermic.

Spin-Statistical Factors in the Energy Transfer Process. It has been shown that the k_{ET} value is represented as follows.[17,18,26]

$$k_{ET} = [(2S+1)_i / \sum_j (2S+1)_j]k_{diff} \qquad (2)$$

Here, k_{diff} denotes the diffusion-controlled rate constant. The initial term results in the spin-statistical factor, whose denominator and numerator denote the total number of initial spin sublevels and number of initial spin sublevels having the same spin multiplicity as the final state, respectively (Figure 3). As described in the Introduction, the spin-statistical factor is known to be $^1/_9$ for the energy transfer process, T$_1$ R0 + O$_2$ ($^3\Sigma_g$) $\rightarrow$ S$_0$ R0 + O$_2$ ($^1\Delta_g$). The spin-statistical factors of this energy transfer process can be changed by linking the NRs, as summarized typically for R1 in Figure 3. A pair of D$_1$ R1 and triplet oxygen ($^3\Sigma_g$) produce quartet and doublet states. Because the energy transfer resulting in D$_0$ R1 and singlet oxygen ($^1\Delta_g$) occurs only from the doublet pair, the spin-statistical factor of D$_1$ R1 is evaluated as $^1/_3$, which is 3 times that ($=^1/_9$) of T$_1$ R0. Because the spin-statistical factor of QA$_1$ R1 is calculated as $^1/_6$, the spin-statistical factor of R1 then becomes $^2/_9$ ($=^1/_3 \times ^1/_3 + ^1/_6 \times ^2/_3$) when [D$_1$]:[QA$_1$] = 1:2. In a similar manner,

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(26) Rodgers et al. have shown that the k_{ET} value depends on ΔG and is expressed by $(^1/_9)k_{diff}/[1 + \exp(\Delta G/RT)]$. In our system, because $[1 + \exp(\Delta G/RT)] \approx 1$, the k_{ET} is represented by eq 2. Ford, W. E.; Rihter, B. D.; Rodgers, M. A. J.; Kenney, M. E. *J. Am. Chem. Soc.* **1989**, *111*, 2362.
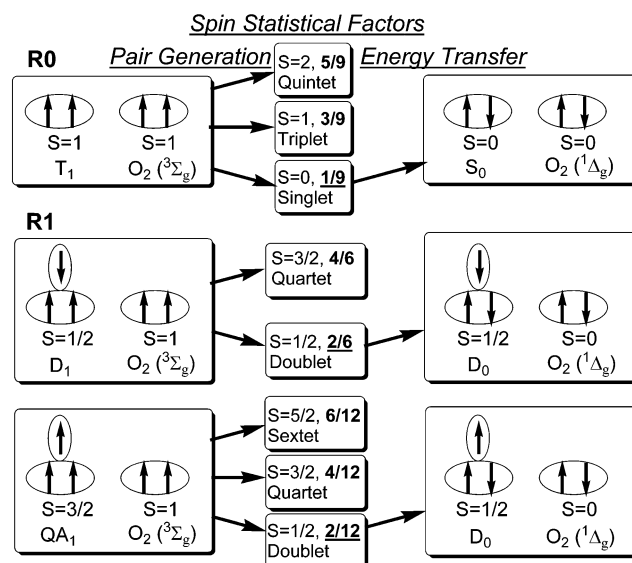
Spin Statistical Factors

Figure 3. Spin-statistical factors in energy transfer processes from T$_1$ R0 (top), D$_1$ R1 (middle), and QA$_1$ R1 (bottom), respectively.

the spin-statistical factor of R2 is calculated as $^7/_{18}$ ($= 1 \times ^1/_{12} + ^4/_9 \times ^3/_{12} + ^4/_9 \times ^3/_{12} + ^3/_{15} \times ^5/_{12}$). Therefore, the k_{ET} values of R1 and R2 will be larger than that of R0, if k_{ET} is controlled by the spin-statistical factors.

Results and Interpretations

Singlet oxygen ($^1\Delta_g$) luminescence was investigated by the NIR luminescence measurements. A decay profile of singlet oxygen ($^1\Delta_g$) luminescence of R1c monitored at 1275 nm is typically shown in Figure 2b. The decay profiles of singlet oxygen ($^1\Delta_g$) luminescence were analyzed with a single-exponential function. The lifetime of singlet oxygen ($^1\Delta_g$) in toluene was evaluated as 32 ± 1 μs, which is similar to the previous studies.[27,28] Therefore, the quenching of singlet oxygen ($^1\Delta_g$) due to the electron exchange interactions with NRs is negligible in our system ([NR] < 6 μM).[29,30] In addition, it has been reported that a pair of singlet oxygen ($^1\Delta_g$) and bacterio-chlorin derivatives form an exciplex in the early stage after photoexcitation,[28] but this kind of exciplex formation could not be observed (Figure 2b, inset). From the singlet oxygen ($^1\Delta_g$) luminescence, singlet oxygen yields (Φ_Δ) were determined by the use of benzophenone ($=0.29$), as summarized in Table 1.[31,32] The Φ_Δ value increases in the order R0 (0.31) < R1c (0.46) $\approx$

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(30) Moore and colleagues have shown that the quenching rate constant and initial luminescence enhancement of singlet oxygen ($^1\Delta_g$) by TEMPO derivatives were $(1-6) \times 10^4$ M^{-1} s^{-1} and $6-13$ M^{-1}, respectively. Using these values, the quenching rate and initial luminescence enhancement were evaluated as <0.4 s^{-1} and $<8 \times 10^{-5}$ in our system ([NR] < 6 μM), which are negligible. Belford, R. E.; Seely, G.; Gust, D.; Moore, T. A.; Moore, A.; Cherepy, N. J.; Ekbundit, S.; Lewis, J. E.; Lin, S. H. *J. Photochem. Photobiol., A: Chem.* **1993**, *70*, 125.
(31) In the Φ_Δ measurements, concentrations of samples were ~3 μM, where the singlet oxygen ($^1\Delta_g$) luminescence intensities were proportional to the optical density at 355 nm. Photon signals were counted at 4 μs (gate width $= 5$ μs) after 355 nm laser excitation to remove fluorescence influences.[27a] The Φ_Δ value of 0.29 for benzophenone in benzene, which has been most often used, was employed as a standard by considering solvent dependence.[27a,32]

Table 1. Excited-State Properties of R0, R1a, R1c, and R2c

compound	R0	R1a	R1c	R2c
Φ_F	0.57	0.16	0.21	0.012
$\Phi_\Delta{}^{a-c}$	0.31	0.47	0.46	0.61
$\Phi_{TSiPc}{}^c$	0.34	0.54	0.59	0.67
$k_{ET}/10^9\,M^{-1}\,s^{-1\,d}$	1.9	2.1	2.0	2.0
$\tau_{TSiPc}/\mu s$	500^e	0.86^f	7.6^e	3.7^e

[a] Φ_Δ measurements were carried out with various laser powers (over 10 times), and the average Φ_Δ values were employed. [b] Sample solutions were bubbled with oxygen gas. [c] Experimental errors were within 15%. [d] Experimental errors were within 10%. [e] From ref 13b. [f] From ref 13a.

R1a (0.47) < R2c (0.61), thereby indicating increases of ∼50% and ∼100% as a result of substituting one and two NRs, respectively. Thus, we succeeded in increasing the Φ_Δ value by linking the NRs.

To clarify this origin, quantum yields of ^{3}SiPc* (Φ_{TSiPc}) were investigated by transient absorption measurements, where a broad triplet−triplet absorption band at around 400−600 nm and a bleaching of the ground-state Q absorption band (∼680 nm) were monitored.[13,19] The ϵ_{TSiPc} of R0 was determined as 3.1 (± 0.3) × 10^4 dm^3 mol^{-1} cm^{-1} at 500 nm using the singlet depletion method,[33] and then the Φ_{TSiPc} of R0 was evaluated using (tetraphenylporphinato)zinc as a standard.[34,35] In the cases of R1a, R1c, and R2c, the ϵ_{TSiPc} values of R1a, R1c, and R2c were assumed to be identical to that of R0 because of the very weak electronic interaction between the SiPc and NR moieties,[36] and thus the Φ_{TSiPc} values were determined by comparison with R0 (Table 1).[35] The Φ_{TSiPc} value increases in the order R0 (0.34) < R1a (0.54) ≈ R1c (0.59) < R2c (0.67) and increases by ∼50% and ∼100% through linkage of one and two NRs, respectively. These Φ_{TSiPc} values are close to the corresponding Φ_Δ values within the experimental errors, indicating that the energy transfer efficiency is almost 100% even with the linking NRs. This is consistent with the previous studies on Pc derivatives.[25,37] The similarity in the Φ_{TSiPc} and Φ_Δ values between R1a and R1c indicates that the increase in the electronic interaction between the SiPc and NR moieties is invalid for increasing Φ_{TSiPc} and Φ_Δ. On the other hand, because the Φ_{TSiPc}

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(33) Using the singlet depletion method, a difference absorption spectrum of R0 measured at 400−750 nm was corrected for bleaching of the ground state, which resulted in a plausible absolute triplet−triplet absorption spectrum of R0. Thus, the ϵ_{TSiPc} value was correctly evaluated. The ϵ_{TSiPc} measurements were carried out with various laser powers (0.2−1 mJ). Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(34) The Φ_{TSiPc} value of R0 was determined by comparison with (tetraphenylporphinato)zinc ($\epsilon_T(470) = 74\,000$ dm^3 mol^{-1} cm^{-1}, $\Phi_T = 0.83$). Hurley, J. K.; Sinai, N.; Linschitz, H. *Photochem. Photobiol.* **1983**, *38*, 9.

(35) For determining the Φ_{TSiPc} values, concentrations of samples were ∼3 μM. The decay profiles of transient absorption signals were fitted by a least-squares method, from which the initial intensities were evaluated.

(36) This assumption is reasonable and persuasive because of the following reasons. (1) It is well-known that the transient absorption signals at around 400−600 nm originate almost entirely from the triplet−triplet absorption of the SiPc moiety, which is consistent with the fact that the transient absorption spectra are similar between R0, R1a, R1c, and R2c.[13] (2) The electronic interaction between the SiPc and NR moieties is very small, because the NR substituents scarcely influence triplet−triplet absorption and ground-state absorption spectra (the Q-band shifts were within 70 cm^{-1}), respectively.[13,19] (3) Extinction coefficients in steady-state absorption spectra are not changed by the NR substituents. For instance, the ϵ differences in the sharp Q absorption bands between R0, R1a, R1c, and R2c are within 3%.[13,19]

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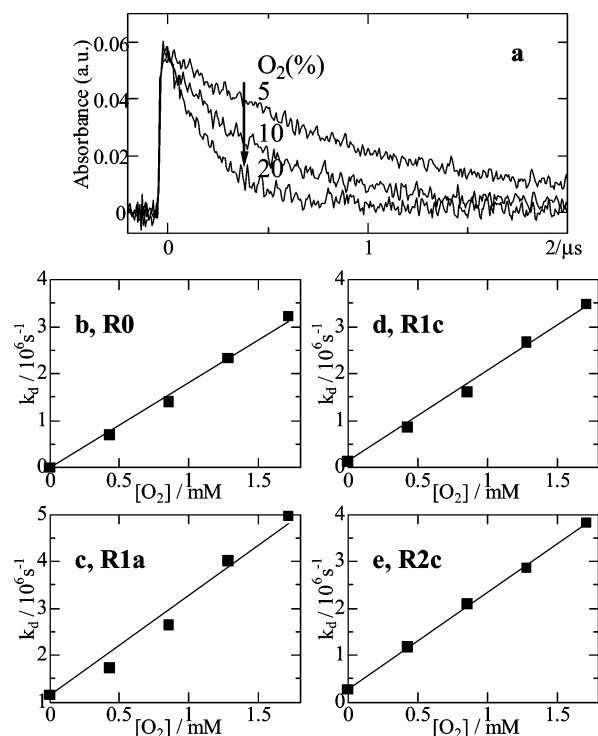
Figure 4. Decay profiles of transient absorption signals of R1c with O$_2$ (a) and relationships between transient absorption decay rates (k_d) and concentration of molecular oxygen ([O$_2$]) for R0 (b), R1a (c), R1c (d), and R2c (e). The concentration of SiPc was ∼15 μM, while the [O$_2$] values were changed by bubbling sample solutions with a mixed gas of oxygen and nitrogen (O$_2$/N$_2$ = 0.20:0.80, 0.15:0.85, 0.10:0.90, and 0.05:0.95, respectively).[38] Fitted solid lines were calculated by a least-squares method.

and Φ_Δ values of R2c are larger than those of R1a and R1c, the increase in number of NRs is efficient for generating ^{3}SiPc* and singlet oxygen ($^1\Delta_g$).

To investigate the energy transfer process quantitatively, energy transfer rate constants, k_{ET}, were examined by transient absorption measurements. Because the back energy transfer rate constant, k_{BET}, is expressed as $k_{ET} \times \exp(-\Delta G/RT)$ (=0.05 × k_{ET}), the back energy transfer rate (=k_{BET}[^{1}SiPc][O$_2$($^1\Delta_g$)]) is negligibly small as compared to the forward energy transfer rate (=k_{ET}[^{3}SiPc*][O$_2$($^3\Sigma_g$)]) under our experimental conditions, where [O$_2$] (>0.4 mM) is much larger than [SiPc] (∼15 μM).[25,38] Because $\Phi_{TSiPc} \approx \Phi_\Delta$, the transient absorption decay rate (k_d) is expressed as $1/\tau_{TSiPc} + k_{ET}$[O$_2$] (τ_{TSiPc} denotes the lifetime of ^{3}SiPc* in the absence of molecular oxygen).[18] For all of our compounds, the k_d values exhibited a good linear relationship with [O$_2$], as shown in Figure 4. From these slopes, the k_{ET} values were evaluated as 1.9 × 10^9, 2.1 × 10^9, 2.0 × 10^9, and 2.0 × 10^9 M^{-1} s^{-1} for R0, R1a, R1c, and R2c, respectively. These $1/(k_{ET}$[O$_2$]) values (∼60 ns when [O$_2$] = 8.54 mM) are much faster than the τ_{TSiPc} values (>0.8 μs), indicating the efficient energy transfer. This is consistent with the fact that the Φ_Δ values are close to the corresponding Φ_{TSiPc} values. The k_{ET} values evaluated experimentally are independent of the linking NRs in contrast to the spin-statistical factors calculated. These results will be investigated in detail in the following section.

(38) In our experiments, concentrations of molecular oxygen were 0.427, 0.854, 1.28, 1.71, and 8.54 mM, which were changed by bubbling sample solutions with a mixed gas of oxygen and nitrogen (O$_2$/N$_2$ = 0.05:0.95, 0.10:0.90, 0.15:0.85, 0.20:0.80, and 1:0, respectively). Wilhelm, E.; Battino, R. *Chem. Rev.* **1973**, *73*, 1.

Discussion

Increase in Singlet Oxygen Yields. We have succeeded in increasing the Φ_Δ value by linking the NRs. This NR effect can be interpreted by the large Φ_{TSiPc} and long τ_{TSiPc} values, as follows.

(1) In the case of R1, the electron exchange interaction between the SiPc and NR moieties changes the spin quantum number, such as $S_0 \rightarrow D_0$, $S_1 \rightarrow D_n$, $T_1 \rightarrow D_1$ and QA_1, which has been confirmed by the QA_1 observations using time-resolved EPR.[13,19] Because ISC between the S_1 and T_1 states of the SiPc moiety partially turns into the fast $D_n \rightarrow D_1$ transition, the ISC enhancements due to the linking NR result in both the increase in Φ_{TSiPc} and the decrease in fluorescence quantum yield.[13,19]

(2) One of the most important features is that our paramagnetic NR–SiPc compounds exhibit relatively long lifetimes ($=0.87$–7.6 μs) despite the generation of the $D_1 \rightarrow D_0$ transition,[13] while paramagnetic molecules generally exhibit very short excited-state lifetimes, for example, CuPc ($\tau = 35$ ns),[7b] making the compounds photoinactive.[16] These relatively long lifetimes originate from the weak electronic interactions between the SiPc and NR moieties. Because these τ_{TSiPc} values are longer than $1/(k_{ET}[O_2])$ (~ 60 ns, when $[O_2] = 8.54$ mM), the energy transfer efficiency is close to 100%.

That is, the electronic interactions between the SiPc and NR moieties resulting in relatively long lifetimes are suited for both the effective generation of ^{3}SiPc* and the efficient energy transfer to molecular oxygen. In general, the electron exchange interactions with paramagnetic species had been known to result only in very fast excited-state relaxation,[6,7] which decreases photochemical reaction yields.[16] Therefore, this increase in Φ_Δ is an unusual and precious example for increasing photochemical reaction yields by the electron exchange interactions with paramagnetic species. In addition, the Φ_Δ value ($=0.61$) of R2c is close to that ($=0.54$) of ZnPc,[37a] indicating that interactions with paramagnetic species are useful for controlling photochemical reaction from the T_1 state, similar to the heavy atom effects.

Energy Transfer Process. It is found that the k_{ET} values are independent of the linking NRs. Because this energy transfer process is known to depend on the spin-statistical factors (R0 = $^1/_9$, R1 = $^2/_9$, and R2 = $^7/_{18}$), it is noteworthy that the k_{ET} value is not changed by linking the NRs. To clarify this origin, the energy transfer process between R1 and O_2 is investigated in detail.

Under another approach for evaluating the energy transfer rate, the nonresonance energy transfer rate constant is represented as follows.[18,39]

$$k_{ET} = (2\pi/\hbar)F\beta^2[(2S+1)_i/\sum_j (2S+1)_j] \tag{3}$$

Here, β^2 is the electronic matrix element for mixing between the initial and final states, and F is the Franck–Condon factor for the transition. Because the ΔG value is scarcely changed by linking the NRs,[13,19] the $(2\pi F/\hbar)$ value is reasonably assumed to be a constant C between R0, R1, and R2. Thus, the β^2 value is investigated. In the case of R0, a pair of T_1 R0 and O_2 ($^3\Sigma_g$) generate the excited quintet, triplet, and singlet states. The

(39) (a) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1962**, *37*, 1962. (b) Robinson, G. W.; Frosch, R. P. *J. Chem. Phys.* **1963**, *38*, 1187.

energy transfer resulting in S_0 R0 and O_2 ($^1\Delta_g$) occurs only from the singlet pair. Using the wave functions of R0 and O_2 shown in the Supporting Information, the initial and final singlet states are represented as follows.

$$|S_0 + {}^1\Delta_g\rangle = |a_{1u}\bar{a}_{1u}\pi_x{}^*\bar{\pi}_x{}^*| \tag{4a}$$

$$|T_1 + {}^3\Sigma_g\rangle = \{|a_{1u}e_{gx}\bar{\pi}_x{}^*\bar{\pi}_y{}^*| + |\bar{a}_{1u}\bar{e}_{gx}\pi_x{}^*\pi_y{}^*|\}/\sqrt{3} - \{|\bar{a}_{1u}e_{gx}\bar{\pi}_x{}^*\pi_y{}^*| + |a_{1u}\bar{e}_{gx}\bar{\pi}_x{}^*\pi_y{}^*| + |\bar{a}_{1u}e_{gx}\pi_x{}^*\bar{\pi}_y{}^*| + |a_{1u}\bar{e}_{gx}\pi_x{}^*\bar{\pi}_y{}^*|\}/\sqrt{12} \tag{4b}$$

Using eq 4, the matrix element is evaluated as follows.

$$\beta^2 = |\langle S_0 + {}^1\Delta_g|e^2/r|T_1 + {}^3\Sigma_g\rangle|^2 = 3|\langle a_{1u}\pi_x{}^*|e^2/r|\pi_y{}^*e_{gx}\rangle|^2$$
$$= 3K^2 \tag{5}$$

Because the probability of singlet pair generation is $^1/_9$, a theoretical k_{ET} value was evaluated as $CK^2/3$ ($=C \times 3K^2 \times ^1/_9$) for R0.

On the other hand, while a pair of O_2 ($^3\Sigma_g$) and R1 in the excited states (D_1, QA_1) form the excited sextet, quartet, and doublet states, the energy transfers only via the doublet pair. In this case, the wave functions of the initial and final doublet states ($Ms = +^1/_2$) are represented as follows.

$$|D_0 + {}^1\Delta_g, +^1/_2\rangle = |a_{1u}\bar{a}_{1u}r\pi_x{}^*\bar{\pi}_x{}^*| \tag{6a}$$

$$|D_1 + {}^3\Sigma_g, +^1/_2\rangle = \{-2|\bar{a}_{1u}\bar{e}_{gx}r\pi_x{}^*\pi_y{}^*| + |\bar{a}_{1u}e_{gx}\bar{r}\pi_x{}^*\pi_y{}^*| + |a_{1u}\bar{e}_{gx}\bar{r}\pi_x{}^*\pi_y{}^*|\}/3 - \{2|a_{1u}e_{gx}\bar{r}\pi_x{}^*\bar{\pi}_y{}^*| - |a_{1u}\bar{e}_{gx}r\pi_x{}^*\bar{\pi}_y{}^*| - |\bar{a}_{1u}e_{gx}r\pi_x{}^*\bar{\pi}_y{}^*| + 2|a_{1u}e_{gx}\bar{r}\pi_x{}^*\pi_y{}^*| - |a_{1u}\bar{e}_{gx}r\bar{\pi}_x{}^*\pi_y{}^*| - |\bar{a}_{1u}e_{gx}r\bar{\pi}_x{}^*\pi_y{}^*|\}/6 \tag{6b}$$

$$|QA_1 + {}^3\Sigma_g, +^1/_2\rangle = |a_{1u}e_{gx}r\bar{\pi}_x{}^*\bar{\pi}_y{}^*|/\sqrt{2} - \{|a_{1u}e_{gx}\bar{r}\pi_x{}^*\bar{\pi}_y{}^*| + |a_{1u}\bar{e}_{gx}r\pi_x{}^*\bar{\pi}_y{}^*| + |\bar{a}_{1u}e_{gx}r\pi_x{}^*\bar{\pi}_y{}^*| + |a_{1u}e_{gx}\bar{r}\bar{\pi}_x{}^*\pi_y{}^*| + |a_{1u}\bar{e}_{gx}r\bar{\pi}_x{}^*\pi_y{}^*| + |\bar{a}_{1u}e_{gx}r\bar{\pi}_x{}^*\pi_y{}^*|\}/\sqrt{18} + \{|\bar{a}_{1u}\bar{e}_{gx}r\pi_x{}^*\pi_y{}^*| + |\bar{a}_{1u}e_{gx}\bar{r}\pi_x{}^*\pi_y{}^*| + |a_{1u}\bar{e}_{gx}\bar{r}\pi_x{}^*\pi_y{}^*|\}/\sqrt{18} \tag{6c}$$

Using eqs 6, the β^2 values of R1 are evaluated as follows.

$$\beta^2 = |\langle D_0 + {}^1\Delta_g, +^1/_2|e^2/r|D_1 + {}^3\Sigma_g, +^1/_2\rangle|^2 = K^2 \tag{7a}$$

$$\beta^2 = |\langle D_0 + {}^1\Delta_g, +^1/_2|e^2/r|QA_1 + {}^3\Sigma_g, +^1/_2\rangle|^2 = 2K^2 \tag{7b}$$

The electron exchange matrix elements of R1 are K^2 and $2K^2$ for the D_1 and QA_1 states, respectively, and are smaller than that ($=3K^2$) of T_1 R0. Using the probabilities of doublet pair generation ($^1/_3$ and $^1/_6$ for the D_1 and QA_1 states, respectively), the theoretical k_{ET} value of R1 was calculated as $CK^2/3$ ($=C \times K^2 \times ^1/_3$ or $C \times 2K^2 \times ^1/_6$), which is the same as that ($=C \times 3K^2 \times ^1/_9$) of R0. Thus, the linking NRs do not influence the energy transfer rates, when the Franck–Condon factor and electronic wave functions of SiPc are unchanged by linking the NRs. This originates from the fact that the NRs result in both the increase in the spin-statistical factors and the decrease in the electron exchange interaction (Figure 5). Under the Dexter
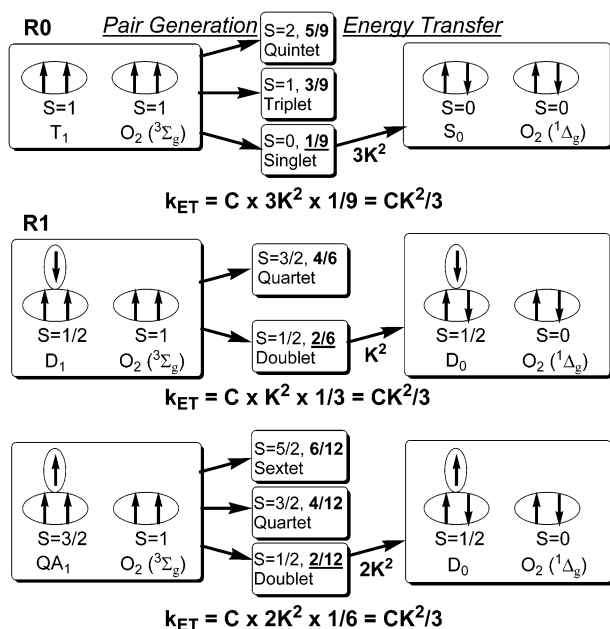
Figure 5. Summary of energy transfer processes from T_1 R0 (top), D_1 R1 (middle), and QA_1 R1 (bottom), respectively. K^2 denotes the electron exchange matrix element described in the text.

Figure 6. Summary of the NR effects on the singlet oxygen generation mechanism.

mechanism,[1,40] this energy transfer occurs accompanying electron exchange processes, $e_g \rightarrow \pi_y^*$, $\pi_x^* \rightarrow a_{1u}$. Therefore, the SOMO of NR hardly influences the electron exchange processes, when the electronic interactions between the SiPc and NR moieties are small.

Conclusion

In this study, we have investigated the singlet oxygen ($^1\Delta_g$) generation mechanism in terms of the NR effects, as summarized in Figure 6. We have succeeded in increasing the Φ_Δ value by linking the NRs, which originates from both the increase in the triplet quantum yield and excited-state lifetimes long enough to utilize photochemical reactions. Because the electron exchange interactions with paramagnetic species had been known to result in very fast excited-state relaxation,[6,7] decreasing photochemical reaction yields,[16] this increase in Φ_Δ is an unusual and precious example for increasing photochemical reaction yields by the electron exchange interaction with paramagnetic species.

From the viewpoint of photodynamic therapy, because heavy elements are generally harmful to health, our methodology, where the Φ_Δ value is controllable by paramagnetic species without heavy elements, is promising. Indeed, the combined use of a photoradical generation and the efficient singlet oxygen

generation in radical−chromophore systems will be a novel approach for exhibiting high photoactivity in the tumor site, with low photoactivity in other parts of the body.[41]

Our experiments and theoretical analyses show that the spin-selective energy transfer rate constant is not influenced by linking the NRs and can be evaluated by the product of the spin-statistical factors and matrix elements between the initial and final states.

Supporting Information Available: Electronic wave functions of R0, R1, and O_2 (PDF).[42] This material is available free of charge via the Internet at http://pubs.acs.org.

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