Photo-induced Electron-transfer Reaction of Naphthalocyanine

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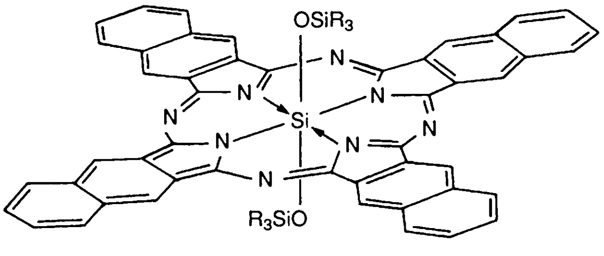
Quenching of fluorescence emission of a series of siloxanes $(R_3SiO)_2SiNc$ by a variety of quenchers ranging from acceptors to donors was studied in dichloromethane solution. The relationship between fluorescence quenching rates and half-wave potentials of the quenchers suggests that quenching results from the photoinduced electron-transfer reaction of substrates $(R_3SiO)_2SiNc$ with quenchers. The results indicate that $(R_3SiO)_2SiNc$ acts as an electron-donating sensitizer for acceptors and as an electron-accepting sensitizer for donors. The small values of the Coulombic attraction (ω_p) obtained from our experiments indicate that the radical-ion pair consisting of $(R_3SiO)_2SiNc$ and a quencher can dissociate easily even in dichloromethane, because $(R_3SiO)_2SiNc$ is an extremely large molecule.

Photo-induced electron-transfer reactions have recently attracted attention because of their use in optical devices using photochemical hole-burning or organic photoconducting mechanisms.[1] Phthalocyanine derivatives are among the most suitable compounds for use in this field because of their high chemical stability in light. Naphthalocyanines,[2] which are derivatives of phthalocyanines, are especially suitable since they effectively absorb semiconductor laser light. Therefore, the photo-induced electron-transfer reactions of phthalocyanines and naphthalocyanines have been extensively studied.[3] However, as is well known, phthalocyanines tend to form molecular aggregates such as dimers, trimers and oligomers even in dilute solutions.[4] Naphthalocyanines generally aggregate more than do phthalocyanines.[5] In photochemical studies of phthalocyanines and naphthalocyanines, the influence of aggregation cannot be neglected because monomers, dimers, trimers and oligomers all have different photochemical characteristics. Fundamental photochemical research on monomeric phthalocyanines and naphthalocyanines has been hampered by these characteristics. While photo-induced electron transfer of the molecular assembly is important in the construction of actual optical devices, it is also helpful to know the photo-induced electron transfer properties of a monomeric compound before studying its molecular assembly. It is convenient that there is a naphthalocyanine [$(Hex_3SiO)_2SiNc$, Fig. 1, R = hexyl, Nc = naphthalocyanine diradical] which possesses monomeric character in solution.[6] However, we know of no previous study of photo-induced electron transfer of the monomeric naphthalocyanines $(R_3SiO)_2SiNc$.

Here we report the photo-induced electron-transfer properties of some monomeric naphthalocyanines, $(R_3SiO)_2SiNc$, with a variety of quenchers ranging from acceptors to donors, using a fluorescence-quenching method.

Results and Discussion

$(Pr_3SiO)_2SiNc$ was synthesized by a slight modification of a previously described method (see Experimental section).[6] $(Pr_3SiO)_2SiNc$ in solution exhibits the following monomeric characteristics: the absorption spectrum in solutions of various concentrations changes according to the Beer–Lambert law, the fluorescence emission spectrum in solution is a mirror image of its Q-band absorption spectrum as depicted in Fig. 2, and the ^1H NMR spectrum shows sharp absorption signals (see Experimental section) which are easily assignable. These monomeric characteristics are derived from the steric bulk of the two trialkylsiloxy groups.



$(R_3SiO)_2SiNc$
$R = C_3H_7$: $(Pr_3SiO)_2SiNc$
$R = C_6H_{13}$: $(Hex_3SiO)_2SiNc$

Fig. 1 Molecular structure of bis(trialkylsiloxy)silicon 2,3-naphthalocyanine [$(R_3SiO)_2SiNc$]

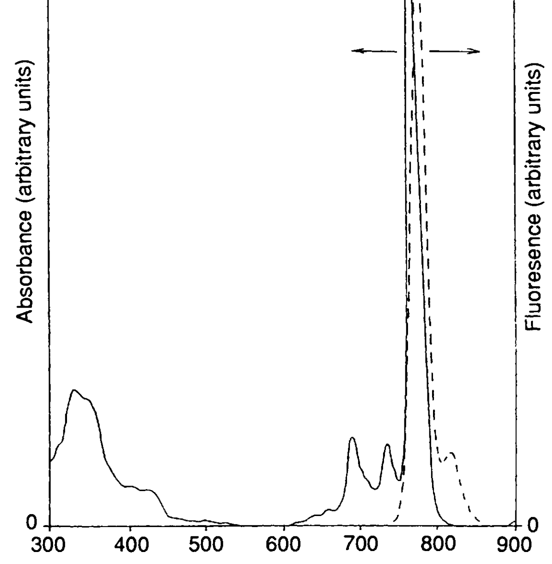


Fig. 2 Absorption (——) and fluorescence emission (----) spectra of $(Pr_3SiO)_2SiNc$ in CH_2Cl_2 at room temperature (2.76×10^{-6} mol dm^{-3}). Excitation wavelength was 690 nm.

The lifetime of the lowest singlet excited state (τ), the zero–zero transition energy [$\Delta E_{0,0}(Nc)$] which is obtained from the frequencies of the absorption (ν) and fluorescence (ν_f) maxima

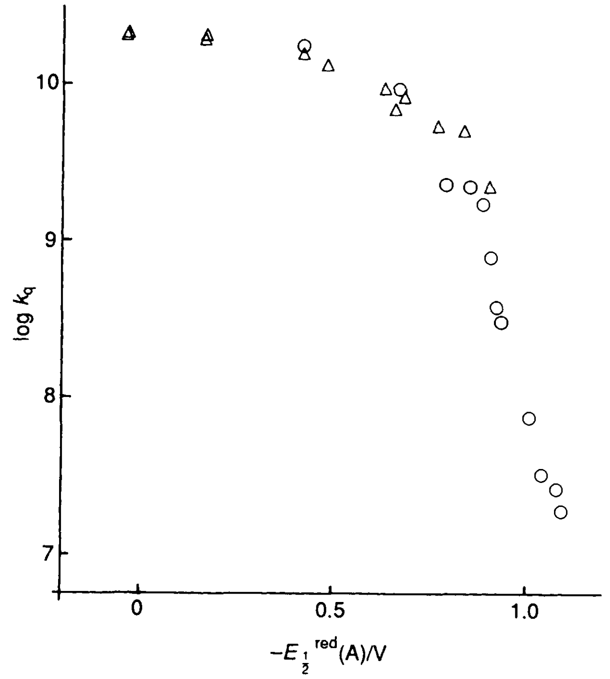


Fig. 3 Plot of log *kq vs.* $E_{\frac{1}{2}}^{\text{red}}$(A) for the quenching of $(Pr_3SiO)_2SiNc^*$ by nitro-compounds (○) and quinones (△)

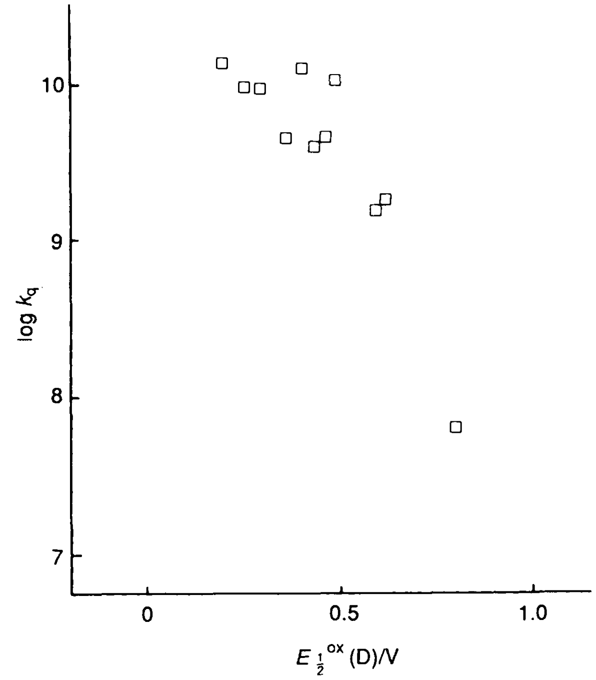


Fig. 4 Plot of log *kq vs.* $E_{\frac{1}{2}}^{\text{ox}}$(D) for the quenching of $(Pr_3SiO)_2SiNc^*$ by donors

by using eqn. (1), the half-wave reduction potential [$E_{\frac{1}{2}}^{\text{red}}$(Nc)], and the half-wave oxidation potential [$E_{\frac{1}{2}}^{\text{ox}}$(Nc)] for $(Pr_3SiO)_2SiNc$ and $(Hex_3SiO)_2SiNc$ are shown in Table 1. Physical properties of the two $(R_3SiO)_2SiNc$ species as shown in Table 1 exhibit no significant differences resulting from the difference in the alkyl-chain length R.

$$\Delta E_{0,0} = (h\nu + h\nu_f)/2 \qquad (1)$$

The fluorescence emission of $(Pr_3SiO)_2SiNc$ in Ar-saturated CH_2Cl_2 solution was quenched by a wide variety of quenchers (acceptors and donors). In each case, the quenching followed the well known Stern–Volmer equation (2),[8] where I and I_0 are

$$I_0/I = 1 + k_q\tau[Q] \qquad (2)$$

the relative fluorescence intensities with and without a quencher (Q), respectively, k_q is the bimolecular quenching rate constant, and [Q] is the concentration of Q. Plots of I_0/I *vs.* [Q] gave straight lines with intercepts of 1.0. From the slopes ($k_q\tau$) of these plots and τ, the k_q-values for a large number of quenchers were obtained. The k_q-values for nitro compounds, quinones and donors are shown in Tables 2, 3 and 4, respectively, together with half-wave potentials of the quenchers.

Plots of log k_q *vs.* half-wave potentials for acceptors and donors are shown in Fig. 3 and Fig. 4, respectively. These plots strongly suggest that the bimolecular quenching of the lowest singlet state of $(Pr_3SiO)_2SiNc$ by both kinds of quencher in solution takes place by an electron-transfer mechanism.

For the acceptors (A), according to Rehm and Weller,[7] the electron-transfer quenching mechanism can be described by eqn. (3) where Nc is $(Pr_3SiO)_2SiNc$, the asterisk stands for the

$$\text{Nc}^* + \text{A} \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} \underset{\text{encounter complex}}{(\text{Nc}^*\,\text{A})} \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} \underset{\text{ion-radical pair}}{(\text{Nc}^{\bullet+}\,\text{A}^{\bullet-})} \xrightarrow{k_{30}} \text{Nc} + \text{A} \qquad (3)$$

excited state, k_{12} and k_{21} are the diffusion-controlled association and dissociation rate constants, respectively, k_{23} and k_{32} are the rate constants of forward electron transfer for the actual electron-transfer process and back electron transfer to the excited state, respectively, and k_{30} is the rate constant of back electron transfer to the ground state.

The thermochemical cycle for reaction (3) is depicted by eqn. (4), where ΔG_{23} is the free-energy change of the actual electron-transfer process (Nc* A) ⟶ (Nc•+ A•−), ω_p is the work term required for bringing the free-radical ions, Nc•+ and A•−, together, and ω_r, which is the corresponding work term for the neutral reactant, can be neglected.[7] Therefore, ΔG_{23} is given by eqn. (5).[7] The values of $E_{\frac{1}{2}}^{\text{ox}}$(Nc), $E_{\frac{1}{2}}^{\text{ox}}$(A) and $\Delta E_{0,0}$(Nc) can be measured directly.

$$\begin{tikzcd}
\text{Nc}^* + \text{A} \arrow[r, "\omega_r"] \arrow[d, "\begin{array}{l}E_{\frac{1}{2}}^{\text{ox}}(\text{Nc}) - E_{\frac{1}{2}}^{\text{red}}(\text{A}) - \\ \Delta E_{0,0}(\text{Nc})\end{array}"'] & (\text{Nc}^*\,\text{A}) \arrow[d, "\Delta G_{23}"] \\
\underset{\text{solvated ion-radical}}{\text{Nc}^{\bullet+} + \text{A}^{\bullet-}} \arrow[r, "\omega_p"] & (\text{Nc}^{\bullet+}\,\text{A}^{\bullet-})
\end{tikzcd} \qquad (4)$$

$$\Delta G_{23} = E_{\frac{1}{2}}^{\text{ox}}(\text{Nc}) - E_{\frac{1}{2}}^{\text{red}}(\text{A}) - \Delta E_{0,0}(\text{Nc}) + \omega_p \qquad (5)$$

By using our experimental results and previously published information,[9] the ω_p-value can be calculated from the intercept of the linear correlation between $\Delta G_{23}^{\ddagger} + E_{\frac{1}{2}}^{\text{red}}(\text{A}) + \Delta E_{0,0}(\text{Nc})$ and $(\Delta G_{23}^{\ddagger})^{-1}$ based on eqn. (6), where $\Delta G_{23}^{\ddagger}$ is the free energy

$$\Delta G_{23}^{\ddagger} + E_{\frac{1}{2}}^{\text{red}}(\text{A}) + \Delta E_{0,0}(\text{Nc}) = (\Delta G_0^{\ddagger})^2/(\Delta G_{23}^{\ddagger}) + [E_{\frac{1}{2}}^{\text{ox}}(\text{Nc}) + \omega_p] \qquad (6)$$

of activation between the encounter complex and the ion-radical pair, and $\Delta G_0^{\ddagger}$ is the free energy of activation for when $\Delta G_{23} = 0$. The $\Delta G_{23}^{\ddagger}$-value can be estimated using k_q-values obtained in our experiments and eqn. (7),[9] where Z is the

$$\Delta G_{23}^{\ddagger} = (RT/F)\ln[Z(1/k_q - 1/k_{12})] \qquad (7)$$

Table 1 Spectroscopic and electrochemical properties of $(R_3SiO)_2SiNc$

$(R_3SiO)_2SiNc$	τ[a]/ns	$\Delta E_{0,0}(\mathrm{Nc})$[b]/eV	$E_{1/2}^{\mathrm{red}}(\mathrm{Nc})$[c]/V	$E_{1/2}^{\mathrm{ox}}(\mathrm{Nc})$[d]/V
$(Pr_3SiO)_2SiNc$	4.25	1.60	−0.925	0.645
$(Hex_3SiO)_2SiNc$	4.29	1.60	−0.940	0.640

[a] Lifetime of the fluorescence excited state in CH_2Cl_2 solution. [b] The zero–zero transition energy. [c] Half-wave reduction potential *vs.* SCE in CH_2Cl_2. [d] Half-wave oxidation potential *vs.* SCE in CH_2Cl_2.

Table 2 Fluorescence quenching rates (k_q) and half-wave reduction potentials [$E_{1/2}^{\mathrm{red}}(\mathrm{A})$] for nitro-compounds

Nitro-compounds	$E_{1/2}^{\mathrm{red}}(\mathrm{A})$[a]/V	$k_q/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
2,4,7-Trinitrofluoren-9-one	−0.420	1.853×10^{10}
p-Dinitrobenzene	−0.675	9.686×10^{9}
o-Dinitrobenzene	−0.798	2.376×10^{9}
p-Nitrobenzonitrile	−0.861	2.259×10^{9}
m-Dinitrobenzene	−0.893	1.765×10^{9}
p-Nitroacetophenone	−0.910	8.259×10^{8}
Methyl *p*-nitrobenzoate	−0.930	3.906×10^{8}
m-nitrobenzonitrile	−0.939	3.141×10^{8}
m-Nitrobenzaldehyde	−1.016	7.906×10^{7}
m-Nitroacetophenone	−1.051	3.341×10^{7}
p-Chloronitrobenzene	−1.089	2.682×10^{7}
Methyl *m*-nitrobenzoate	−1.105	1.929×10^{7}

[a] Half-wave reduction potential *vs.* SCE in CH_2Cl_2.

Table 3 Fluorescence quenching rates (k_q) and half-wave reduction potentials [$E_{1/2}^{\mathrm{red}}(\mathrm{A})$] for quinones

Quinones	$E_{1/2}^{\mathrm{red}}(\mathrm{A})$[a]/V	$k_q/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
p-Chloranil	+0.035	2.099×10^{10}
p-Bromanil	+0.030	2.212×10^{10}
2,6-Dichloro-*p*-benzoquinone	−0.165	2.000×10^{10}
2,5-Dichloro-*p*-benzoquinone	−0.168	2.078×10^{10}
2,3-Dichloro-1,4-naphthoquinone	−0.422	1.595×10^{10}
p-Benzoquinone	−0.482	1.367×10^{10}
9,10-Phenanthraquinone	−0.636	9.541×10^{9}
2,5-Dimethyl-*p*-benzoquinone	−0.663	7.282×10^{9}
1,4-Naphthoquinone	−0.682	8.517×10^{9}
2-Methyl-1,4-naphthoquinone	−0.773	5.459×10^{9}
1,5-Dichloro-9,10-anthraquinone	−0.841	5.224×10^{9}
Duroquinone	−0.905	2.259×10^{9}

[a] Half-wave reduction potential *vs.* SCE in CH_2Cl_2.

Table 4 Fluorescence quenching rates (k_q) and half-wave reduction potentials [$E_{1/2}^{\mathrm{ox}}(\mathrm{D})$] for donors

Donors	$E_{1/2}^{\mathrm{ox}}(\mathrm{D})$[a]/V	$k_q/\mathrm{dm^3\,mol^{-1}\,s^{-1}}$
N,*N*,*N*′,*N*′-Tetramethyl-*p*-phenylenediamine	+0.194	1.388×10^{10}
N,*N*-Diethyl-*p*-phenylenediamine	+0.249	9.882×10^{9}
N,*N*-Dimethyl-*p*-phenylenediamine	+0.290	9.353×10^{9}
p-Phenylenediamine	+0.355	4.706×10^{9}
Tetrathiafulvalene	+0.399	1.282×10^{10}
4-Aminodiphenylamine	+0.433	4.071×10^{9}
N,*N*-Diphenyl-*p*-phenylenediamine	+0.466	4.610×10^{9}
N,*N*,*N*′,*N*′-Tetramethylbenzidine	+0.487	1.082×10^{10}
Phenothiazine	+0.598	1.553×10^{9}
Phenoxazine	+0.621	1.824×10^{9}
N,*N*-Dimethyl-*p*-toluidine	+0.802	6.635×10^{7}

[a] Half-wave oxidation potential *vs.* SCE in CH_2Cl_2.

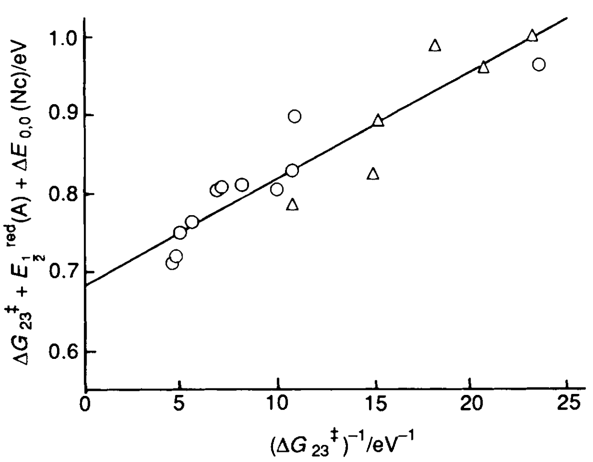


Fig. 5 Plot of $\Delta G_{23}^{\ddagger} + E_{1/2}^{\mathrm{red}}(\mathrm{A}) + \Delta E_{0,0}(\mathrm{Nc})$ *vs.* $(\Delta G_{23}^{\ddagger})^{-1}$ for the quenching of $(Pr_3SiO)_2SiNc^*$ by nitro-compounds (○) and quinones (△)

collision frequency which is generally taken as 1×10^{11} dm^3 mol^{-1} s^{-1}, *F* is the Faraday constant, the k_{12}-value has been reported as 2×10^{10} dm^3 mol^{-1} s^{-1} for neutral organic molecules, *R* is the Rydberg constant, and *T* is absolute temperature (usually 293 K). Plots of $\Delta G_{23}^{\ddagger} + E_{1/2}^{\mathrm{red}}(\mathrm{A}) + \Delta E_{0,0}(\mathrm{Nc})$ *vs.* $(\Delta G_{23}^{\ddagger})^{-1}$ as depicted in Fig. 5 gave a straight line described by eqn. (8). From this equation, we estimated the ω_p-value for acceptors to be +0.039 (eV).

$$\Delta G_{23}^{\ddagger} + E_{1/2}^{\mathrm{red}}(\mathrm{A}) + \Delta E_{0,0}(\mathrm{Nc}) = 0.0133\,(\Delta G_{23}^{\ddagger})^{-1} + 0.684 \quad (8)$$
$$(\mathrm{cc} = 0.930)$$

Analogously the electron-transfer quenching mechanism for donors (D) can be described by reaction (9) according to Rehm–Weller.[7]

$$\mathrm{Nc^* + D} \xrightleftharpoons[k_{21}]{k_{12}} \underset{\text{encounter complex}}{(\mathrm{Nc^*\,D})} \xrightleftharpoons[k_{32}]{k_{23}} \underset{\text{ion-radical pair}}{(\mathrm{Nc^{\bullet-}\,D^{\bullet+}})} \xrightarrow{k_{30}} \mathrm{Nc + D} \quad (9)$$

Based on a thermochemical cycle similar to that described by equation (4), the free-energy change (ΔG_{23}) of the actual electron-transfer process $(\mathrm{Nc^*\,D}) \longrightarrow (\mathrm{Nc^{\bullet-}\,D^{\bullet+}})$ in reaction (9) is given by eqn. (10). The ω_p was evaluated to be −0.018 (eV) for donors from the intercept of the linear correlation between $\Delta G_{23}^{\ddagger} - E_{1/2}^{\mathrm{ox}}(\mathrm{D}) + \Delta E_{0,0}(\mathrm{Nc})$ and $(\Delta G_{23}^{\ddagger})^{-1}$ (Fig. 6).[9]

$$\Delta G_{23} = E_{1/2}^{\mathrm{ox}}(\mathrm{D}) - E_{1/2}^{\mathrm{red}}(\mathrm{Nc}) - \Delta E_{0,0}(\mathrm{Nc}) + \omega_p \quad (10)$$

Because these ω_p-values for acceptors and donors are extremely small, we believe the radical-ion pair can dissociate easily even in a non-polar medium such as dichloromethane. On the other hand, the ω_p-term is generally described by eqn. (11) according to the Rehm–Weller equation,[7] where *a* is the

$$\omega_p = -e_0^2/\varepsilon a \quad (11)$$

assumed centre-to-centre distance of the solvated radical ions

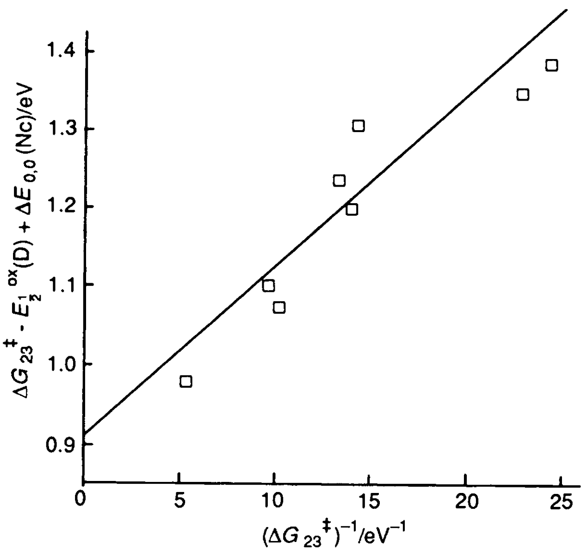


Fig. 6 Plot of $\Delta G_{23}{}^{\ddagger} - E_{\frac12}^{ox}(D) + \Delta E_{0,0}(Nc)$ *vs.* $(\Delta G_{23}{}^{\ddagger})^{-1}$ for the quenching of $(Pr_3SiO)_2SiNc^*$ by donors

in the pair and ε is the relative permittivity of the solvent. In a polar medium such as acetonitrile ($\varepsilon = 37$), when a is assumed to be 7 Å, ω_p is estimated to be -0.03 eV (by Rehm–Weller). This small ω_p-value in acetonitrile is almost identical with our experimental ω_p values for $(Pr_3SiO)_2SiNc$ in dichloromethane, although the ε-values of dichloromethane and acetonitrile are *ca.* 7 and *ca.* 37, respectively.

This result could have been due to deviation of our actual centre-to-centre distance for $(Pr_3SiO)_2SiNc$ from the assumed centre-to-centre distance (a) in equation (11). Since this naphthalocyanine molecule has a large, macromolecular conjugated ring system as well as two sterically hindered trialkylsiloxy groups, the actual centre-to-centre distance for $(Pr_3SiO)_2SiNc$ should be much larger than *ca.* 7 Å. The actual centre-to-centre distance for this naphthalocyanine was estimated to be 30–40 Å using the ε values of dichloromethane and acetonitrile, eqn. (11), and the a value (7Å) assumed for acetonitrile solvent by Rehm–Weller.

A quenching experiment with $(Hex_3SiO)_2SiNc$ was performed using several acceptors and donors in order to evaluate the influence (if any) of the size of the trialkylsiloxy groups. The results are summarized in Table 5. Since the quenching-rate constants of $(R_3SiO)_2SiNc$ species (R = Pr and Hex) with each quencher were not significantly different, the size of the trialkylsiloxy group has no significant effect on the electron-transfer reaction under these conditions in solution. This result also indicates that the actual centre-to-centre distance for $(R_3SiO)_2SiNc$ could be as much as 30–40 Å.

The possibility that there is electron transfer from the triplet state of $(R_3SiO)_2SiNc$ species after intersystem crossing remains to be studied. However, the triplet energy of $(Hex_3SiO)_2SiNc$ has been reported to be 0.93 eV (21.5 kcal mol^{-1}).[10,*] Since this energy is too low to cause an electron-transfer reaction from the lowest triplet state, the electron transfer probably proceeds directly from the lowest singlet state.

Conclusions.—Quenching studies of the fluorescence emission of $(R_3SiO)_2SiNc$ species by a variety of quenchers ranging from acceptors to donors indicate that quenching occurs through photo-induced electron transfer. In the photo-induced electron transfer from the lowest singlet state, $(R_3SiO)_2SiNc$ is an electron-donating sensitizer to acceptors and an electron-accepting sensitizer to donors. Radical-ion pairs derived from $(R_3SiO)_2SiNc$ can dissociate even in a non-polar medium such as dichloromethane. The alkyl-chain length of R in $(R_3SiO)_2SiNc$ did not affect the electron-transfer process in solution as long as R was propyl or hexyl. The actual centre-to-centre distance of the solvated radical ions in the pair for $(R_3SiO)_2SiNc$ could be as long as 30–40 Å.

Experimental

Apparatus.—M.p.s were determined with a Yanagimoto micro melting point apparatus and were uncorrected. Electronic spectra were obtained using an Hitachi 150–20 spectrometer. Fluorescence emission spectra were observed using an Hitachi 850 fluorescence spectrophotometer. ^{1}H NMR spectra were taken using an Hitachi R-250 spectrometer, and chemical shifts were recorded in parts per million (ppm) downfield from tetramethylsilane as internal standard (δ-scale). J-Values are given in Hz. Elemental analyses were performed at the microanalytical laboratory of the Sagamihara Chemical Research Center.

Materials.—$(Hex_3SiO)_2SiNc$ was synthesized according to a previously described method.[6]

Preparation of $(Pr_3SiO)_2SiNc$. To a solution of dihydroxysilicon naphthalocyanine[6] (3 g, 3.9 mmol) in β-picoline (3-methylpyridine) (420 cm^3) were added tributylamine (12 cm^3, 50.4 mmol) and chloro(tripropyl)silane (10.8 cm^3, 49.2 mmol). The mixture was refluxed for 2 h. After cooling, the reaction mixture was poured into an ethanol–water (1:1) mixture (600 cm^3) and kept overnight. The resulting precipitate was collected by filtration, washed successively with water and methanol, and then dried. The precipitate was then treated with hot chloroform (~600 cm^3) to extract the soluble fraction. The chloroform solution was concentrated to ~50 cm^3 and cooled to crystallize the product. The crystals were filtered off and washed with chloroform. Recrystallization of the product from chloroform gave $(Pr_3SiO)_2SiNc$ as dark green crystals (1.45 g, 34%), m.p. >300 °C (Found: C, 72.7; H, 6.1; N, 10.3. $C_{66}H_{66}N_8O_2Si_3$ requires C, 72.89; H, 6.12; N, 10.30%); δ_H(250 MHz; $CDCl_3$) -2.06 (12 H, t, J 7.32, CH_2CH_2Me), -0.85 (12 H, sextet, J 7.32, CH_2CH_2Me), -0.28 (18 H, t, J 7.32, CH_2CH_2Me), 7.93 (8 H, dd, J 6.10 and 3.35, naphthalene ring 6- and 7-H), 8.68 (8 H, dd, J 6.10 and 3.35, naphthalene ring 5- and 8-H and 10.03 (8 H, s, naphthalene ring 1- and 4-H; $\lambda_{max}(CHCl_3)$/nm 311 (log ε = 4.98), 333 (5.22), 349 (5.19), 400 (4.67), 425 (4.64), 689 (5.04), 734 (4.99) and 774 (5.84).

$(R_3SiO)_2SiNc$, acceptors, and donors were purified by recrystallization and/or sublimation before use.

Measurement of Oxidation and Reduction Potentials.—The reduction potentials of acceptors $[E_{\frac12}^{red}(A)]$ and $(R_3SiO)_2SiNc$ $[E_{\frac12}^{red}(Nc)]$ as well as the oxidation potentials of donors $[E_{\frac12}^{ox}(D)]$ and $(R_3SiO)_2SiNc$ $[E_{\frac12}^{ox}(Nc)]$ were obtained by cyclic voltammetry using a Hokuto Denko HB-104 function generator and a Hokuto Denko HA-501 potentiostat/galvanostat. The working and counter electrodes were of platinum wire. An SCE electrode was used as the reference and 0.1 mol dm^{-3} tetrabutylammonium perchlorate was the supporting electrolyte. All measurements were performed in a CH_2Cl_2 solution of the sample (1 mmol cm^{-3}) after deaeration by bubbling with Ar.

Fluorescence-quenching Experiments.—In the dark, a solution of Nc (2.76×10^{-6} mol dm^{-3}) and quencher (0–1×10^{-1} mol dm^{-3}) in CH_2Cl_2 was deaerated by bubbling with Ar for 1 min. Fluorescence measurements of the solution were carried out by

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[*] 1 cal = 4.184 J.

Table 5 Quenching rate constant of $(R_3SiO)_2SiNc^*$ for some quenchers

	$\log k_q$					
	p-Dinitrobenzene	*m*-Nitrobenzonitrile	*p*-Bromanil	2-Methyl-1,4-naphthoquinone	*p*-Phenylenediamine	Phenothiazine
$(Pr_3SiO)_2SiNc$	9.986	8.497	10.345	9.737	9.673	9.191
$(Hex_3SiO)_2SiNc$	9.859	8.461	10.281	9.667	9.454	8.926

excitation at 690 nm followed by observation of the fluorescence emission at ~781 nm maximum.

Fluorescence Lifetime Measurements.—Fluorescence lifetimes were measured using a Horiba NAES-1100 time-resolved spectrofluorimeter (Horiba NFL-111 nanosecond lamp filled with hydrogen gas, Horiba SCU-111 optical chamber, Horiba SGM-111 monochromator, Horiba SSU-111 photomultiplier unit and Horiba NAES-1100 data acquisition and processing unit). Emission was resolved with a monochromator set at the peak emission wavelength ~781 nm. Adulteration of the fluorescence lifetimes by reabsorption was avoided by using highly diluted samples ($\sim 10^{-6}$ mol dm^{-3}). Spectroscopic grade CH_2Cl_2 was used as solvent. The CH_2Cl_2 solution was deaerated by bubbling with Ar for 1 min before measurements. Those fluorescence decays which were all single-exponential were recorded. The fluorescence lifetimes were computed using the least-squares iterative deconvolution method. Tabulated fluorescence lifetimes in Table 1 are the average values of several measurements. Each fluorescence lifetime has $\pm 1.30 \times 10^{-2}$ ns deviation.

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