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Drastic Changes in the Lifetime and Electron Transfer and Energy Transfer Reactivity of the Triplet Excited State of *p*-Benzoquinone by Complex Formation with Scandium Ion Salts

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Metal-ion salts such as scandium triflate form strong complexes with the triplet excited state of *p*-benzoquinone, which have extremely long lifetimes as compared with the lifetime of the uncomplexed quinone triplet, whereas no complex is formed with metal-ion salts in the ground state. The absorption maxima (λ_{max}) of triplet−triplet absorption of the metal-ion salt complexes are red-shifted from the λ_{max} value of the uncomplexed quinone triplet and vary depending on the Lewis acidity of the metal-ion salts. The rate of the complexation of the triplet excited state with scandium triflate is determined, obeying pseudo-first-order kinetics. The pseudo-first-order rate constant increases linearly with increasing metal-ion concentration. The transient absorption spectra of donor radical cations produced by photoinduced electron transfer from *N*,*N*-dimethylanilines to the triplet excited state of *p*-benzoquinone are detected by laser-flash photolysis measurements, whereas no such radical cations are detected in the presence of scandium triflate under otherwise the same experimental conditions. Thus, the electron transfer reactivity of the triplet excited state complex of *p*-benzoquinone with scandium triflate toward electron donors is diminished significantly as compared with that of the uncomplexed quinone triplet. In contrast, the energy transfer from the triplet excited state to oxygen is enhanced by complex formation with scandium triflate.

Introduction

The photoexcitation of molecules produces the excited state which has normally a much higher reactivity as compared with that of the ground state. Thus, the use of the excited state has remarkably expanded the scope of chemical reactions, making it possible to develop a huge number of photochemical reactions which would never take place in the ground state.[1−5] The reactivity of the excited state is determined by the excited state energy and the spin multiplicity (singlet or triplet) of the excited molecule.[1−5] If one could control the excited state energy and the spin multiplicity of the molecule, the scope of photochemistry would be further expanded. In this context, it has been reported that the spin state of the lowest excited state of aromatic carbonyl compounds is completely changed from the n,π^* triplet to the π,π^* singlet which becomes lower in energy than the n,π^* triplet due to the complexation with metal-ion salts such as $Mg(ClO_4)_2$ and $Sc(OTf)_3$ ($OTf^- =$ triflate).[6−9] There are a number of examples of singlet excited state lifetimes that are affected by complex formation with metal-ion salts acting as Lewis acids,[10−16] and the photochemical reactions can be accelerated by metal-ion salts.[17−20] Since the lifetimes of singlet excited states are usually too short for the excited states to interact with metal ions via intermolecular collisions in competition with the decay to the ground states, the singlet excited state complexes with metal ions are normally formed by photoexcitation of the ground state complexes with metal ions rather than by interaction between the singlet excited states and metal ions. In contrast to the lifetimes of singlet excited states, however, those of triplet excited states are normally long enough to interact with metal ions via intermolecular collisions. The nature of the lowest excited state of acetophenones (n,π^* or π,π^*) has been shown to be changed by metal-ion−acetophenone interaction in metal-ion-exchanged zeolites.[21] The heavy metal ions in zeolites also facilitate the intersystem crossing, helping to generate triplets from molecules that possess a poor intersystem crossing efficiency.[22,23] However, there has so far been no report on the complex formation between triplet excited states (not ground states) and metal ions, which would change the lifetimes and the reactivities.[24]

We report herein that the triplet excited state of *p*-benzoquinone ($^3Q^*$) forms complexes with metal-ion salts and that the triplet lifetime of the $Sc(OTf)_3$ complex becomes remarkably long by the complexation with metal-ion salts as compared with the lifetime of the uncomplexed quinone triplet. The excited state complex is regarded as a triplet exciplex with $Sc(OTf)_3$.[25] *p*-Benzoquinone is known as a weak base, and there is little interaction between the ground state quinone and metal ions.[18,19,26] Thus, the triplet exciplexes of Q with metal ions are formed by interaction between the triplet excited states and metal ions, the dynamics of which is monitored by the change in the transient absorption spectra of the triplet. The drastic changes in the electron transfer and energy transfer reactivities of the Q triplet are shown to occur by the complex formation with metal ions in comparison with the reactivities of uncomplexed triplet Q. Thus, the present study opens up new perspective for control

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of the excited state lifetimes and reactivities, further expanding the scope of excited state chemistry.

Experimental Section

Materials. Scandium triflate [Sc(OTf)$_3$] was purchased from Pacific Metals Co., Ltd. (Taiheiyo Kinzoku). 1,1,1-Trifluoro-*N*-[(trifluoromethyl)sulfonyl]methane-sulfonamide [Sc(NTf$_2$)$_3$] was obtained from Sigma-Aldrich. Scandium tetrakis(pentafluorophenyl)borate {Sc[B(C$_6$F$_5$)$_4$]$_3$},[27] lutetium triflate [Lu(OTf)$_3$],[28] and cobalt(II) tetraphenylporphyrin (CoTPP)[29] were prepared as described in the literature. Anhydrous magnesium perchlorate [Mg(ClO$_4$)$_2$] was obtained from Wako Pure Chemical Ind., Ltd., and used without further purification. *p*-Benzoquinone (Q), hexamethylbenzene (HMB), *N*,*N*-dimethylaniline (DMA), 4-bromo-*N*,*N*-dimethylaniline (Br-DMA), 4-methyl-*N*,*N*-dimethylaniline (Me-DMA), and butyronitrile were purchased commercially and purified by the standard method.[30] Acetonitrile (MeCN) which was used as a solvent was purified and dried by the standard procedure.[30] [^{2}H$_3$]acetonitrile (CD$_3$CN) was obtained from EURI SO-TOP, France, and used without further purification.

Laser-Flash Photolysis. Picosecond laser-flash photolysis experiments were carried out with 532 nm laser pulses from a mode-locked, *Q*-switched Quantel YG-501 DP Nd:YAG laser system (pulse width of ~18 ps, 2−3 mJ/pulse). The white continuum picosecond probe pulse was generated by passing the fundamental output through a D$_2$O/H$_2$O solution. Nano- to millisecond laser-flash photolysis experiments were performed by using a continuous xenon lamp (150 W) and an InGaAs−PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions in each laser excitation.

Phosphorescence Experiments. The phosphorescence spectra were measured on a SPEX Fluorolog τ3 fluorescence spectrophotometer. A butyronitrile solution (1 mL) containing *p*-benzoquinone in the absence and presence of Sc(OTf)$_3$ (5.0 $\times$ 10^{-2} M) in the capillary cell was degassed by bubbling with argon gas for 15 min. The solution was irradiated with monochromatized light (λ = 440 nm) from a xenon lamp, and the phosphorescence spectra were measured at 77 K.

Near-IR luminescence emission spectra of singlet oxygen were measured on a Hamamatsu Photonics R5509-72 photomultiplier under irradiation at 462 nm with the use of a Cosmo System LVU-200S monochromator.

Results and Discussion

Formation of Triplet Excited State Complexes with Metal Ions. In picosecond resolved transient absorption measurements, we probed the singlet excited state features of *p*-benzoquinone (^{1}Q*) and its fate in terms of intersystem crossing, which is known to be near quantitative in this class of compounds, in the absence and presence of Sc(OTf)$_3$. For example, following photoexcitation at 355 nm of a concentrated and degassed solution of *p*-benzoquinone (10^{-2} M) led to the observance of a short-lived transient intermediate. The spectral characteristics of this new transient are a broad maximum at 420 nm (see a display of the 400−550 nm region in Figure 1).

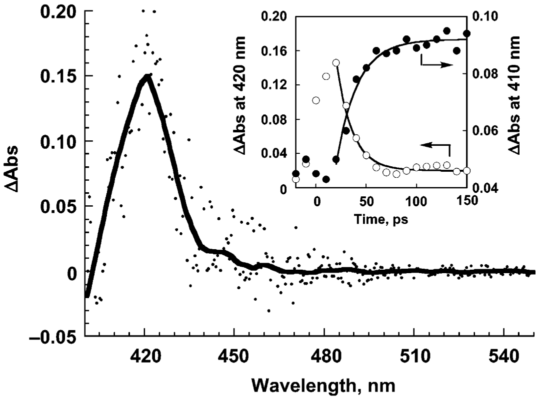
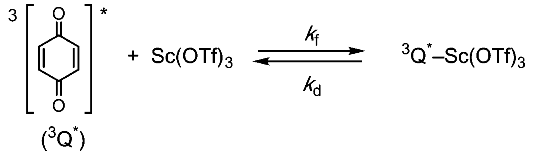


Figure 1. Transient absorption changes corresponding to the singlet excited state of *p*-benzoquinone (^{1}Q*) as recorded immediately after the conclusion of the 18 ps laser pulse. The line shows the fitted line of the data (laser excitation at 355 nm). Inset: Time-absorption decay profile of ^{1}Q* monitored at 420 nm (○) and the triplet excited state of *p*-benzoquinone (^{3}Q*) growth monitored at 410 nm (●) following 355 nm laser excitation.

In parallel to the ^{1}Q* decay at 420 nm, we noticed in the region where the triplet excited state (^{3}Q*) absorbs (see below) a simultaneous growth. This is exemplified in the inset of Figure 1 as solid circles. From the ^{1}Q* decay and the ^{3}Q* growth, we determined the following intersystem crossing rate: 5.0 $\times$ 10^{10} s^{-1}. Due to the time response of our picosecond laser system, we would like to emphasis that this value should be considered as a lower limit. The most important observation is that the addition of Sc(OTf)$_3$ in the concentration range from 9.9 $\times$ 10^{-5} to 3.1 $\times$ 10^{-3} M exerts no discernible effects on the intersystem crossing process and the associated dynamics.

Photoexcitation of *p*-benzoquinone (Q) generates ^{3}Q* with unit efficiency in acetonitrile (MeCN).[31,32] The triplet−triplet (T−T) absorption band appears at λ_{max} = 403 nm. Addition of various concentrations of Sc(OTf)$_3$ to an MeCN solution of Q results in a red shift of the T−T absorption band to 418 nm, as shown in Figure 2. This indicates that the triplet excited state (^{3}Q*) forms a complex with Sc(OTf)$_3$ (eq 1). The time profile of the complex formation is shown in Figure 3a.



(1)

The rate of complex formation obeys pseudo-first-order kinetics, and the pseudo-first-order rate constant increases linearly with increasing metal-ion concentration (Figure 3b). From the slope, we determined the rate constant of the complex formation (k_f) to be 3.6 $\times$ 10^8 M^{-1} s^{-1}. Owing to the large intercept (~10^5 s^{-1}), which relate to the complex dissociation (k_d, s^{-1}) that typical plots of k_{obs} versus Sc(OTf)$_3$ concentrations reveal (see Figure 3b), we postulate an equilibrium between the triplet precursor (^{3}Q*) and the complex [^{3}Q*−Sc(OTf)$_3$]. From this rather crude analysis, we obtain the first estimate for a formation constant (K) of 10^3 M^{-1}.

This led us to pursue a more accurate determination of the K value. The K value of the triplet excited complex of Q with Sc(OTf)$_3$ is determined from the spectral change with variation of the Sc(OTf)$_3$ concentration in Figure 2. The absorbance at 418 nm (ΔAbs) due to the ^{3}Q*−Sc(OTf)$_3$ complex increases with increasing Sc(OTf)$_3$ concentration to reach a constant value (ΔAbs$_\infty$), as shown in Figure 4a.

Such an absorbance change due to the complex formation is expressed by eq 2, which is rewritten by eq 3, where ΔAbs$_0$ is

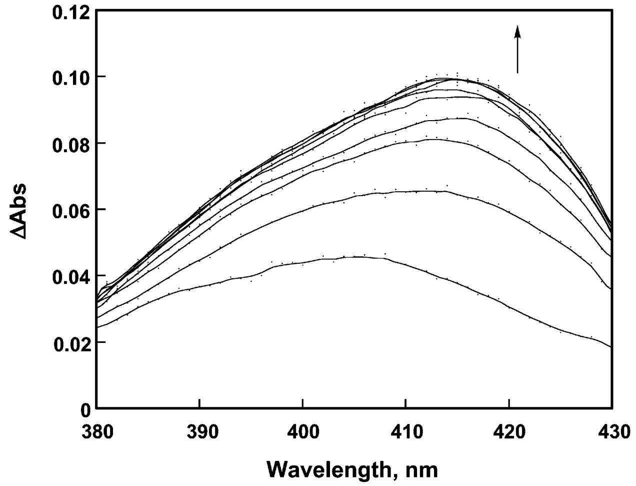


Figure 2. T−T absorption spectra by laser-flash photolysis of Q (1.2×10^{-2} M) in the absence of Sc(OTf)$_3$ and the presence of Sc(OTf)$_3$ (2.1×10^{-4}, 4.2×10^{-4}, 6.3×10^{-4}, 8.3×10^{-4}, 1.0×10^{-3}, 1.2×10^{-3}, 1.4×10^{-3}, and 1.6×10^{-3} M) in deaerated MeCN at 298 K at 1 μs (absence of Sc(OTf)$_3$) and 6 μs (presence of Sc(OTf)$_3$) after laser excitation at $\lambda = 355$ nm.

the absorbance at 418 nm in the absence of

$$\Delta\mathrm{Abs} - \Delta\mathrm{Abs}_0 = K[\mathrm{Sc}^{3+}](\Delta\mathrm{Abs}_\infty - \Delta\mathrm{Abs}_0)/(1 + K[\mathrm{Sc}^{3+}]) \quad (2)$$

$$(\Delta\mathrm{Abs} - \Delta\mathrm{Abs}_0)^{-1} = (\Delta\mathrm{Abs}_\infty - \Delta\mathrm{Abs}_0)^{-1} + (K[\mathrm{Sc}^{3+}](\Delta\mathrm{Abs}_\infty - \Delta\mathrm{Abs}_0))^{-1} \quad (3)$$

Sc(OTf)$_3$. According to eq 3, a linear correlation is obtained between $(\Delta\mathrm{Abs} - \Delta\mathrm{Abs}_0)^{-1}$ and $[\mathrm{Sc}^{3+}]^{-1}$ (Figure 4b). From the slope and intercept of the linear plot is determined the formation constant as K $(=k_\mathrm{f}/k_\mathrm{d}) = 3.0 \times 10^3$ M^{-1} in MeCN at 298 K, which is in reasonable agreement with the kinetic analysis (see above).

The heat of formation (ΔH) of the ^{3}Q*−Sc(OTf)$_3$ complex is determined as −25.8 kJ mol^{-1} (−0.27 eV) from the temperature dependence of K (Figure 5). This indicates that there is significant interaction between ^{3}Q* and Sc(OTf)$_3$.

^{3}Q* also forms complexes with other metal-ion salts, and the T−T absorption band is red-shifted as the Lewis acidity of the metal-ion salts[27,33−35] increases in the following order: 409 nm [Mg(ClO$_4$)$_2$], 412 nm [Lu(OTf)$_3$], 417 nm [Sc(NTf$_2$)$_3$, NTf$_2^-$ = N(SO$_2$CF$_3$)$_2^-$], 418 nm [Sc(OTf)$_3$], and 421 nm {Sc[B(C$_6$F$_5$)$_4$]$_3$}, as shown in Figure 6. We have recently reported that the fluorescence maxima of the singlet excited states of 10-methylacridone with metal ions (^{1}AcrCO*−M^{n+}) are red-shifted as the Lewis acidity of the metal-ion salts increases.[33] Figure 7 shows a plot of the $h\nu$ values of the T−T absorption of the triplet excited state complexes of Q with metal ions versus the rate constants of the metal-ion-salt-promoted electron transfer from cobalt(II) tetraphenylporphyrin (CoTPP) to Q.[34] A good linear correlation in Figure 7 indicates that in both cases the binding of metal ions with the triplet and singlet excited states is much stronger than the binding with the ground states and that the difference in the binding energy between the ground and excited states increases with increasing Lewis acidity. Thus, the basicity of both the triplet and singlet excited states is enhanced as compared to that of the ground states.

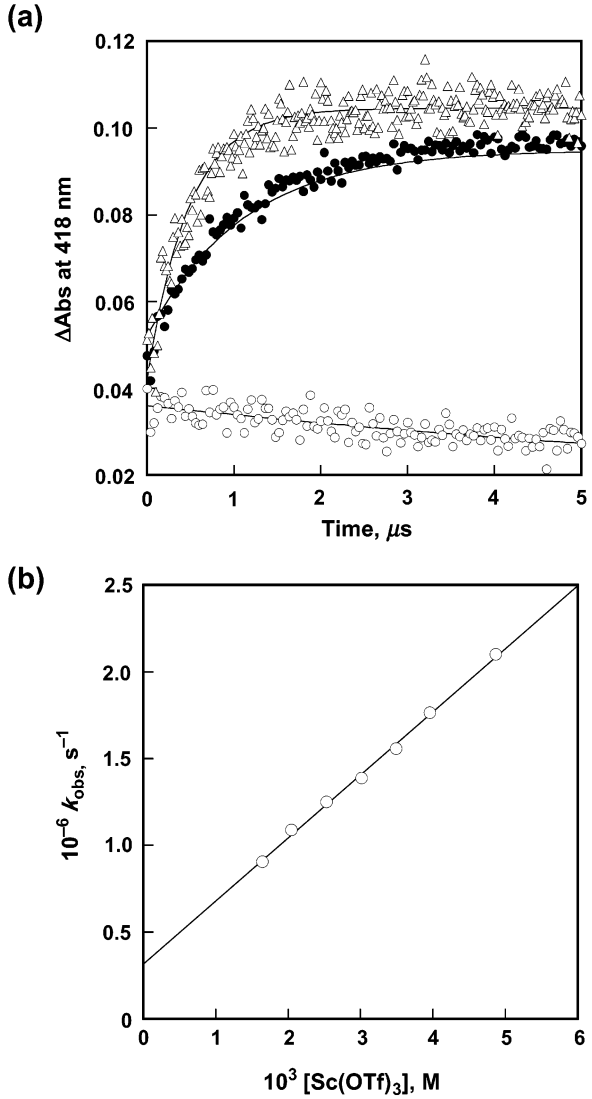


Figure 3. (a) Time course of the absorption change at 418 nm due to the complex formation of ^{3}Q* with Sc(OTf)$_3$ [0 M (○), 1.6×10^{-3} M (●), and 4.9×10^{-3} M (△)] in deaerated MeCN at 298 K. (b) Plot of the pseudo-first-order rate constant (k_obs) vs [Sc(OTf)$_3$].

The formation constants and the rate constants of the complex formation of Q with various metal-ion salts were determined for the case of the ^{3}Q*−Sc(OTf)$_3$ complex. The results are summarized in Table 1.

The T−T absorption spectrum of ^{3}Q* decayed to the spectral baseline on the microsecond time scale with a lifetime of 2.1×10^{-4} s.[36] In the presence of Sc(OTf)$_3$, however, the T−T absorption decay becomes much slower and, moreover, depends on the Sc(OTf)$_3$ concentration, as shown in Figure 8. The decay dynamics consists of both first-order and second-order processes, which correspond to the unimolecular decay to the ground state and the T−T annihilation, respectively. The first-order decay constant (k_T) and the second-order decay constant ($k_\mathrm{T-T}$) were determined separately from the first-order and second-order plots (see Supporting Information Figure S1). The second-order rate constants ($k_\mathrm{T-T}$ values) were determined including the mole absorption coefficient (ϵ) of the triplet absorption.

Plots of k_T versus [Sc(OTf)$_3$] and $\epsilon^{-1}k_\mathrm{T-T}$ versus [Sc(OTf)$_3$] are shown in parts a (circles) and b (circles) of Figure 9, respectively. In each case, the decay rate constant decreases with increasing Sc(OTf)$_3$ concentration to reach a constant value which is much smaller than the value without the metal ion.

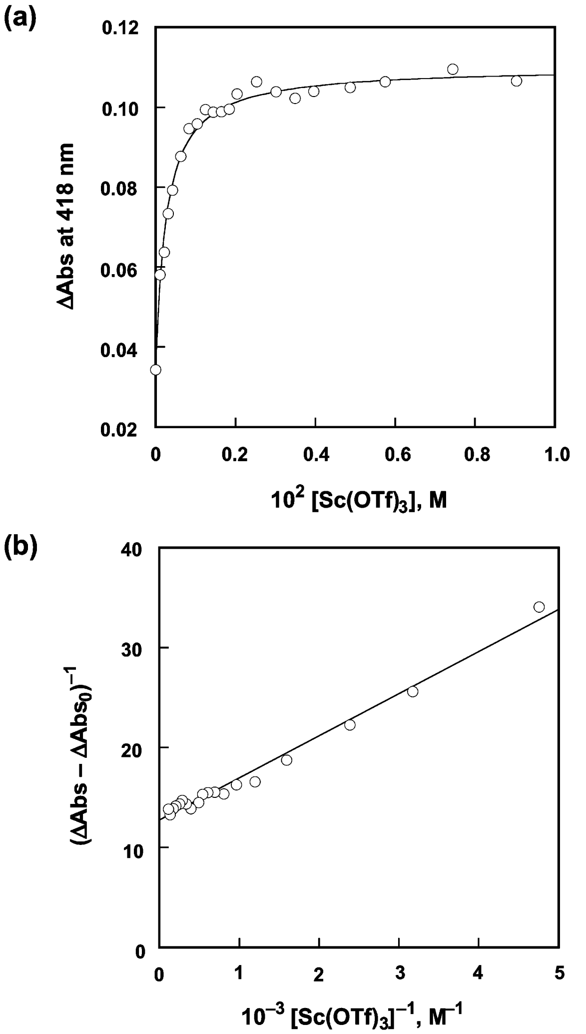


Figure 4. (a) Plot of the T−T absorption at 418 nm vs [Sc(OTf)$_3$] by laser-flash photolysis of Q (1.2 × 10^{-2} M) in the absence of Sc(OTf)$_3$ and the presence of Sc(OTf)$_3$ (0−9.0 × 10^{-3} M) in deaerated MeCN at 298 K at 1 μs (absence of Sc(OTf)$_3$) and 6 μs (presence of Sc(OTf)$_3$) after laser excitation at λ = 355 nm. (b) Plot of (ΔAbs − ΔAbs$_0$)$^{-1}$ vs [Sc(OTf)$_3$]$^{-1}$.

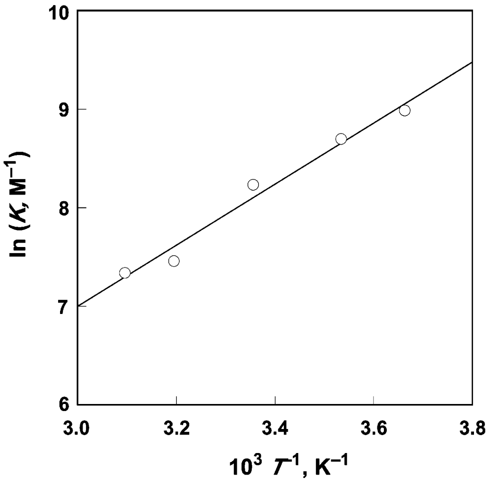


Figure 5. Plot of ln *K* of the complex formation between ^{3}Q* and Sc(OTf)$_3$ vs T^{-1}.

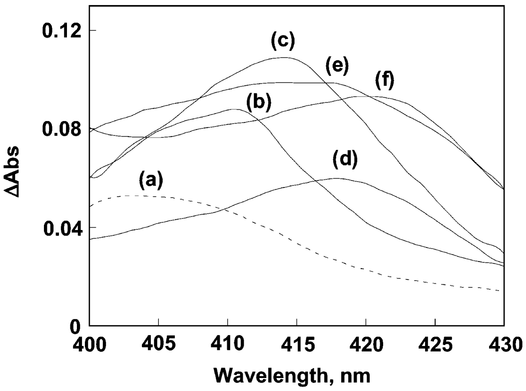


Figure 6. T−T absorption spectra by laser-flash photolysis of Q (1.2 × 10^{-2} M) (a) in the absence of and the presence of (b) Mg(ClO$_4$)$_2$ (5.0 × 10^{-2} M), (c) Lu(OTf)$_3$ (1.5 × 10^{-2} M), (d) Sc(NTf$_2$)$_3$ (5.0 × 10^{-3} M), (e) Sc(OTf)$_3$ (5.0 × 10^{-3} M), and (f) Sc[B(C$_6$F$_5$)$_4$]$_3$ (5.0 × 10^{-3} M) in deaerated MeCN at 298 K at 6 μs after laser excitation at λ = 355 nm.

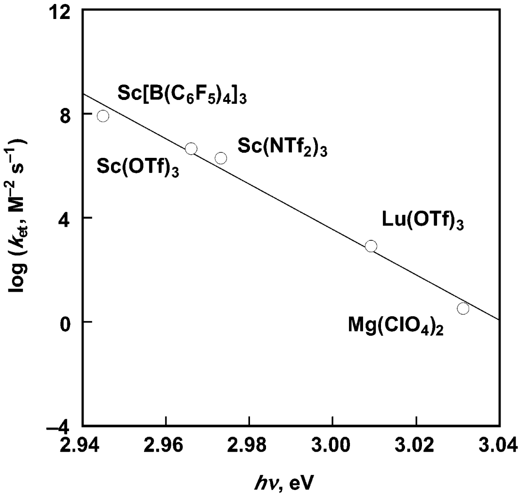


Figure 7. Plot of log k_{et} for metal-ion-promoted electron transfer from CoTPP to Q vs $h\nu$ of the T−T absorptions of the ^{3}Q*−metal-ion complexes.

This indicates again that ^{3}Q* is in equilibrium with the Sc(OTf)$_3$ complex [^{3}Q*−Sc(OTf)$_3$] and that the triplet lifetime of the ^{3}Q*−Sc(OTf)$_3$ complex is much longer than the lifetime of free ^{3}Q* (Scheme 1). According to Scheme 1, k_{T} and $k_{\mathrm{T-T}}$ are given as a function of [Sc(OTf)$_3$] by eqs 4 and 5, respectively.

$$k_{\mathrm{T}} = \frac{k^0{}_{\mathrm{T}} + k^1{}_{\mathrm{T}}K[\mathrm{Sc}^{3+}]}{1 + K[\mathrm{Sc}^{3+}]} \tag{4}$$

$$k_{\mathrm{T-T}} = \frac{k^0{}_{\mathrm{T-T}} + k^1{}_{\mathrm{T-T}}K^2[\mathrm{Sc}^{3+}]^2 + k^2{}_{\mathrm{T-T}}K[\mathrm{Sc}^{3+}]}{(1 + K[\mathrm{Sc}^{3+}])^2} \tag{5}$$

Hereby, $k^0{}_{\mathrm{T}}$ and $k^1{}_{\mathrm{T}}$ are the first-order decay rate constants of ^{3}Q* and the ^{3}Q*−Sc(OTf)$_3$ complex and $k^0{}_{\mathrm{T-T}}$, $k^2{}_{\mathrm{T-T}}$, and $k^1{}_{\mathrm{T-T}}$ are the second-order decay rate constants of ^{3}Q* and the ^{3}Q*−Sc(OTf)$_3$ complex. The $k^1{}_{\mathrm{T}}$ value can be readily determined by the fit of the data to eq 4, since $k^0{}_{\mathrm{T}}$ and the *K* values have already been determined independently. The second-order rate constants ($k_{\mathrm{T-T}}$ values) were determined including the mole absorption coefficient (ϵ) of the triplet absorption (vide supra). The decay rate constants, on the other hand, were determined from the reasonable fit of all the data of k_{T} and $k_{\mathrm{T-T}}$ to eqs 4 and 5 (solid lines for the circles in Figure 9a and b). The rate constants of the ^{3}Q*−Sc(NTf)$_2$ and ^{3}Q*−Mg(ClO$_4$)$_2$ complexes were also determined, as shown in Figure 9a and b (rectangles and triangles, respectively). The rate constants thus determined

TABLE 1: First- and Second-Order Decay Rate Constants of $^3Q^*$ and $^3Q^*$−Metal-Ion Salt Complexes[a]

metal ion	K (M^{-1})	k^0_T (s^{-1})	k^1_T (s^{-1})	$\epsilon^{-1}k^0_{T-T}$ (cm s^{-1})	$\epsilon^{-1}k^1_{T-T}$ (cm s^{-1})	$\epsilon^{-1}k^2_{T-T}$ (cm s^{-1})
$Sc(OTf)_3$	3.0×10^3	4.8×10^3	1.8×10	1.0×10^6	7.0×10^3	2.5×10^4
$Sc(NTf_2)_3$	3.2×10^2	4.8×10^3	2.1×10	1.0×10^6	1.5×10^4	5.0×10^4
$Mg(ClO_4)_2$	2.3×10	4.8×10^3	4.8×10	1.0×10^6	2.0×10^4	8.0×10^5

[a] k^0_T and k^1_T are the first-order decay rate constants of $^3Q^*$ and the $^3Q^*$−metal-ion salt complexes, and k^0_{T-T}, k^2_{T-T}, and k^1_{T-T} are the second-order decay rate constants of $^3Q^*$ and the $^3Q^*$−metal-ion salt complexes. ϵ is the mole absorption coefficient of the triplet absorption.

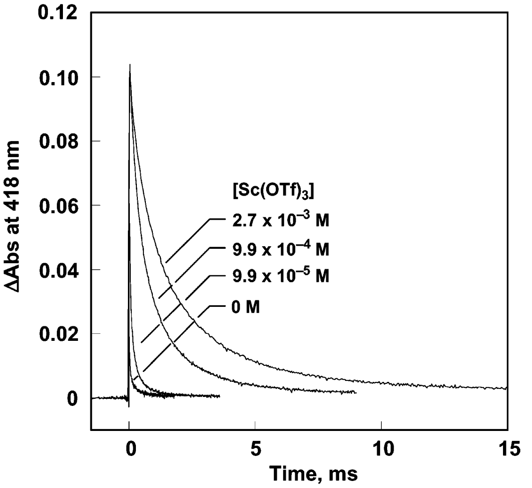


Figure 8. Decay dynamics of T−T absorption change at 418 nm by laser-flash photolysis of *p*-benzoquinone (1.2×10^{-2} M) in the absence and presence of $Sc(OTf)_3$ (9.9×10^{-5}, 9.9×10^{-4}, and 2.7×10^{-3} M) in deaerated MeCN at 298 K.

are listed in Table 1 together with the K values. In the case of the $^3Q^*$−$Sc(OTf)_3$ complex, the k^1_T value is 270 times smaller than the k^0_T value. Thus, the triplet lifetime of $^3Q^*$ becomes remarkably longer once complexation with $Sc(OTf)_3$ takes place.

Following photoexcitation of Q, the singlet excited state (S_1) is formed and an efficient intersystem crossing generates the lowest triplet excited state (T_1). The triplet lifetime may be determined by the energy gap between the S_1 and T_1 states, since the larger the mixing of the singlet state, the faster is the triplet decay. The T_1 state becomes lower in energy due to the binding of metal-ion salts with $^3Q^*$. In contrast, virtually no complex formation may occur between the S_1 state of $^1Q^*$ and metal-ion salts because of the extremely short lifetime of the S_1 state of $^1Q^*$ (<20 ps).[31] In such a case, the stronger the binding of $^3Q^*$ with the metal-ion salt, the larger is the S_1−T_1 energy gap and, thus, the longer is the triplet lifetime. This may be the reason the triplet lifetime of the $^3Q^*$−$Sc(OTf)_3$ complex (5.7×10^{-2} s) is longer than the lifetime (2.1×10^{-2} s) of the $^3Q^*$ complex with $Mg(ClO_4)_2$, the Lewis acidity of which is weaker than that of $Sc(OTf)_3$. Since the first-order decay process of the $^3Q^*$−$Sc(OTf)_3$ complex is expressed as a single-exponential function, there are no multiple relaxation processes as reported in a doublet exciplex.[24]

Change in the Electron Transfer Reactivity of the Triplet Quinone by Complexation with Metal-Ion Salts. Photochemical reactions of *p*-benzoquinone derivatives have been extensively studied because of the high reactivities of quinone triplets.[37−40] The energy diagram of $^3Q^*$ and the $^3Q^*$−$Sc(OTf)_3$ complex is summarized in Scheme 2, where the energies were determined from the one-electron redox potentials and the triplet excited energies were determined from the phosphorescence spectrum of Q in the absence and presence of $Sc(OTf)_3$ observed in deaerated frozen butyronitrile at 77 K (see Supporting Information Figure S2).[41]

The free energy change of photoinduced electron transfer (ΔG^0_{et}) from 4-bromo-*N*,*N*-diemthylaniline (Br-DMA) to the triplet excited state of Q is exergonic (−0.45 eV), judging from the one-electron oxidation potential of Br-DMA (E^0_{ox} vs saturated calomel electrode (SCE) = 0.92 V)[42,43] and the one-electron reduction potential of $^3Q^*$ (E^0_{red} = 1.37 V vs SCE).[44,45] In fact, a transient absorption band due to the Br-DMA radical cation (λ_{max} = 492 nm)[46] is observed together with that of $Q^{\bullet-}$ (λ_{max} = 422 nm with a shoulder at 450 nm)[47] in the photoexcitation of an MeCN solution of Q and Br-DMA, as shown in Figure 10a (open circles). In the presence of $Sc(OTf)_3$, however, no electron transfer from Br-DMA to $^3Q^*$−$Sc(OTf)_3$ occurs, as shown in Figure 10a (solid circles). This is ascribed to the

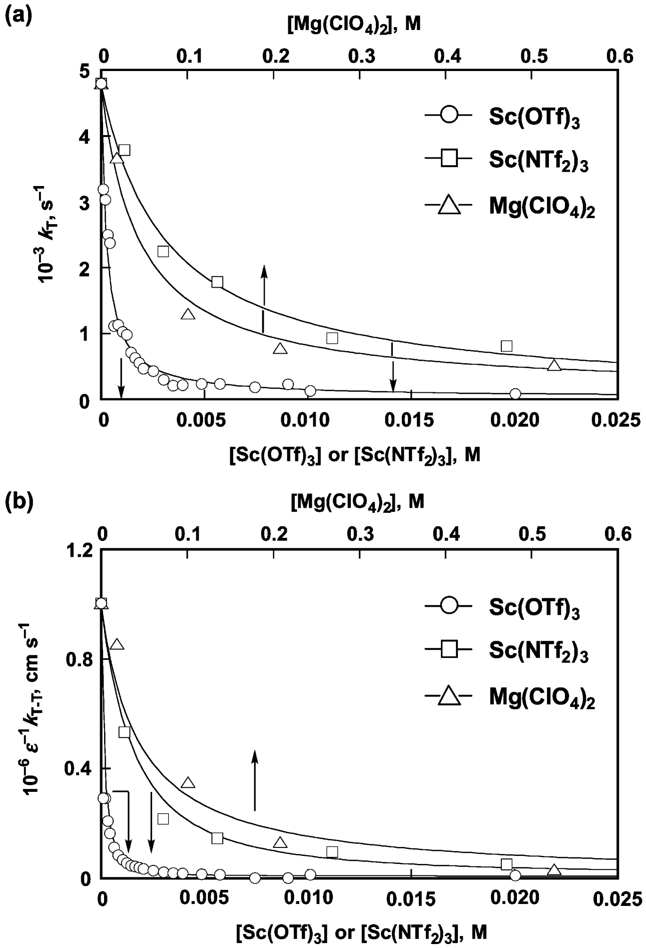
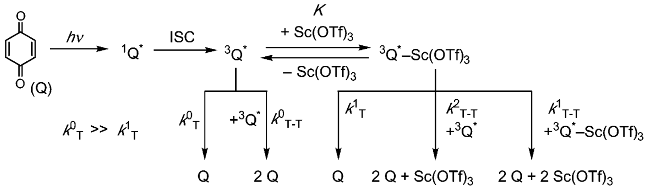
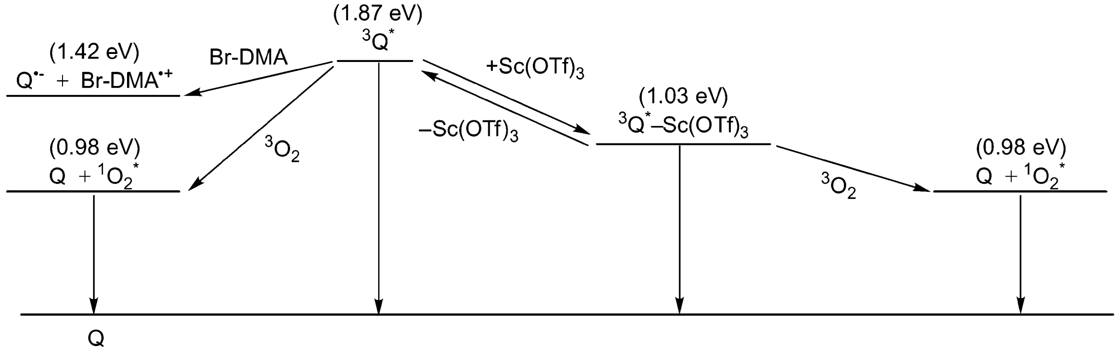


Figure 9. Plots of (a) first-order (k_T) and (b) second-order (k_{T-T}) rate constants vs the concentrations of metal-ion salts for T−T absorption change of Q in the presence of $Sc(OTf)_3$ (○), $Sc(NTf_2)_3$ (□), and $Mg(ClO_4)_2$ (△) in deaerated MeCN at 298 K.

SCHEME 1



SCHEME 2



change in the free energy change of electron transfer which becomes positive (+0.39 eV) when $^3Q^*$ forms the complex with Sc(OTf)$_3$, which has a much less positive E^0_{red} value (0.53 V vs SCE) than that of $^3Q^*$ (1.37 V vs SCE).[44] Similarly, photoinduced electron transfer from *N*,*N*-dimethylaniline (DMA, E^0_{ox} = 0.76 V vs SCE)[42] and 4-methyl-*N*,*N*-dimethylaniline (Me-DMA, E^0_{ox} = 0.69 V vs SCE)[42] to $^3Q^*$ occurs to produce DMA$^{\bullet +}$ and Me-DMA$^{\bullet +}$ as well as $Q^{\bullet -}$, whereas no such radical ions are produced in the case of the $^3Q^*$−Sc(OTf)$_3$ complex (see Supporting Information Figure S3).[48]

When hexamethylbenzene (HMB, E^0_{ox} = 1.49 V vs SCE) is employed as an electron donor, neither $^3Q^*$ nor the $^3Q^*$−Sc(OTf)$_3$ complex gives the HMB radical cation (λ_{max} = 490 nm),[49] as shown in Figure 10b, where only the T−T absorptions of $^3Q^*$ and $^3Q^*$−Sc(OTf)$_3$ are seen upon photoexcitation of the Q−HMB system in the absence of Sc(OTf)$_3$ (open circles) and in the presence of Sc(OTf)$_3$ (solid circles). This is consistent with the endergonic photoinduced electron transfer in the absence of Sc(OTf)$_3$ (ΔG^0_{et} = 0.12 eV) as well as in the presence of Sc(OTf)$_3$ (ΔG^0_{et} = 0.96 eV).[50]

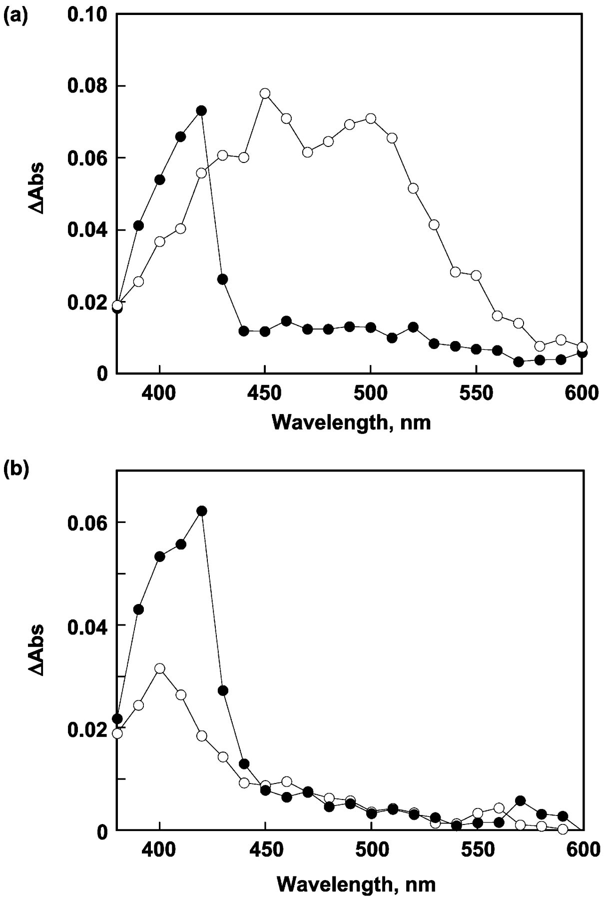


Figure 10. (a) Transient absorption spectra by laser-flash photolysis of Q (1.4 × 10^{-2} M) and Br-DMA (7.3 × 10^{-3} M) in the absence (○) and presence (●) of Sc(OTf)$_3$ (9.3 × 10^{-3} M) in deaerated MeCN at 298 K at 1 μs after laser excitation at λ = 355 nm. (b) Transient absorption spectra by laser-flash photolysis of Q (1.4 × 10^{-2} M) and HMB (3.3 × 10^{-3} M) in the absence (○) and presence (●) of Sc(OTf)$_3$ (9.3 × 10^{-3} M) in deaerated MeCN at 298 K at 1 μs after laser excitation at λ = 355 nm.

Change in the Energy Transfer Reactivity of the Triplet Quinone by Complexation with Metal-Ion Salts. Since both $^3Q^*$ (1.87 eV) and $^3Q^*$−Sc(OTf)$_3$ (1.03 eV) are higher in energy than the singlet oxygen ($^1O_2^*$) (0.98 eV),[51,52] energy transfer from both $^3Q^*$ and $^3Q^*$−Sc(OTf)$_3$ to $^3O_2$ is expected to occur. In fact, the characteristic singlet oxygen ($^1\Delta_g$) phosphorescence is observed at 1270 nm[51,52] by irradiation of Q (1.2 × 10^{-4} M) in both the absence and presence of Sc(OTf)$_3$ (1.0 × 10^{-2} M) (see Supporting Information Figure S4). Figure 11 shows the decay time profiles of $^3Q^*$ and $^3Q^*$−Sc(OTf)$_3$ in air-saturated

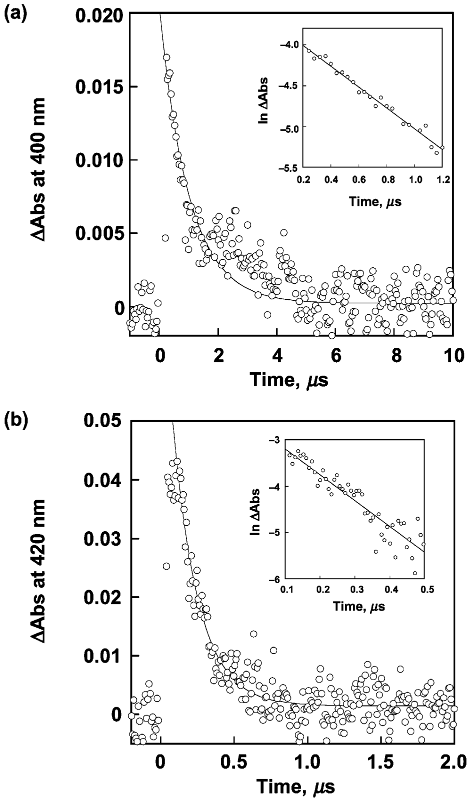


Figure 11. (a) Decay time profiles of absorbance at 400 nm observed by photoexcitation of an air-saturated MeCN solution of Q (1.2 × 10^{-2} M). (b) Decay time profiles of absorbance at 420 nm observed by photoexcitation of an air-saturated MeCN solution of Q (1.2 × 10^{-2} M) in the presence of Sc(OTf)$_3$ (1.0 × 10^{-2} M).

MeCN ($[O_2] = 2.6 \times 10^{-3}$ M). The decay rates of $^3Q^*$ and $^3Q^*-Sc(OTf)_3$ increase linearly with increasing O_2 concentration (see Supporting Information Figure S5). The rate constants (k_{EN} values) of the energy transfer from $^3Q^*-Sc(OTf)_3$ and $^3Q^*$ to O_2 were determined to be 1.9×10^9 and 3.1×10^8 M^{-1} s^{-1}, respectively. The energy transfer rate of $^3Q^*-Sc(OTf)_3$ is ~6 times faster than that of $^3Q^*$. It is known that the k_{EN} value decreases with increasing triplet excited state energy as the energy gap increases.[53] When strong electron donors are employed, the singlet oxygen is quenched by charge transfer from electron donors to $^3O_2$.[54,55] In the present case, $^3Q^*$ is an electron acceptor rather than an electron donor, and thereby, the triplet excited energy determines the k_{EN} value. Thus, the acceleration effect of $Sc(OTf)_3$ on the energy transfer is ascribed to the lower energy of the $^3Q^*-Sc(OTf)_3$ complex than that of $^3Q^*$ in Scheme 2.

Summary and Conclusions

The triplet excited state of *p*-benzoquinone forms complexes with metal-ion salts such as $Sc(OTf)_3$, whereas no such complexes are formed in the ground state. The triplet lifetimes are significantly elongated and the triplet energy is lowered by the complex formation with $Sc(OTf)_3$. The electron transfer reactivity of the triplet quinone with electron donors is diminished, whereas the energy transfer reactivity toward $^3O_2$ is enhanced because of the change in the triplet excited state energy by the complex formation with $Sc(OTf)_3$. Such complex formation of the triplet excited state with metal-ion salts provides a new and versatile methodology to control the lifetime and reactivity of the triplet excited state, leading to expansion of the scope of the excited state reactions.

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Supporting Information Available: Figures showing first-order and second-order plots for the decay of $^3Q^*-Sc(OTf)_3$ (Supporting Information Figure S1), phosphorescence spectra of $^3Q^*$ and $^3Q^*-Sc(OTf)_3$ (Supporting Information Figure S2), transient absorption spectra of the DMA−Q and Me-DMA−Q systems in the absence and presence of $Sc(OTf)_3$ (Supporting Information Figure S3), emission spectra of $^1O_2^*$ (Supporting Information Figure S4), and the dependence of k_{obs} on $[O_2]$ for the energy transfer from $^3Q^*$ and $^3Q^*-Sc(OTf)_3$ to O_2 (Supporting Information Figure S5). This material is available free of charge via the Internet at http://pubs.acs.org.

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