Scandium Ion-Promoted Photoinduced Electron-Transfer Oxidation of Fullerenes and Derivatives by *p*-Chloranil and *p*-Benzoquinone

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Abstract: In the presence of scandium triflate, an efficient photoinduced electron transfer from the triplet excited state of C_{60} to *p*-chloranil occurs to produce C_{60} radical cation which has a diagnostic NIR (near-infrared) absorption band at 980 nm, whereas no photoinduced electron transfer occurs from the triplet excited state of C_{60} ($^3C_{60}$*) to *p*-chloranil in the absence of scandium ion in benzonitrile. The electron-transfer rate obeys pseudo-first-order kinetics and the pseudo-first-order rate constant increases linearly with increasing *p*-chloranil concentration. The observed second-order rate constant of electron transfer (k_{et}) increases linearly with increasing scandium ion concentration. In contrast to the case of the C_{60}/*p*-chloranil/Sc^{3+} system, the k_{et} value for electron transfer from $^3C_{60}$* to *p*-benzoquinone increases with an increase in Sc^{3+} concentration ([Sc^{3+}]) to exhibit a first-order dependence on [Sc^{3+}], changing to a second-order dependence at the high concentrations. Such a mixture of first-order and second-order dependence on [Sc^{3+}] is also observed for a Sc^{3+}-promoted electron transfer from CoTPP (TPP^{2-} = tetraphenylporphyrin dianion) to *p*-benzoquinone. This is ascribed to formation of 1:1 and 1:2 complexes between the generated semiquinone radical anion and Sc^{3+} at the low and high concentrations of Sc^{3+}, respectively. The transient absorption spectra of the radical cations of various fullerene derivatives were detected by laser flash photolysis of the fullerene/*p*-chloranil/Sc^{3+} systems. The ESR spectra of the fullerene radical cations were also detected in frozen PhCN at 193 K under photoirradiation of the fullerene/*p*-chloranil/Sc^{3+} systems. The Sc^{3+}-promoted electron-transfer rate constants were determined for photoinduced electron transfer from the triplet excited states of C_{60}, C_{70}, and their derivatives to *p*-chloranil and the values are compared with the HOMO (highest occupied molecular orbital) levels of the fullerenes and their derivatives.

Introduction

The spherical shape of buckminsterfullerenes makes these carbon allotropes ideal probes for the investigation of electron-transfer reactions, especially in light of aspects regarding the electron-transfer theory of Marcus.[1,2] In the reduction of C_{60}, the first electron is added to a triply degenerate t_{1u} unoccupied molecular orbital to which up to six electrons are accommodated, resulting in a maximum degree of delocalization.[3,4] The small reorganization energy of fullerenes, especially in electron-transfer reactions, and the long triplet excited-state lifetimes have rendered fullerenes as useful components in the design of novel electron-transfer systems in both the ground and excited states.[5−7] In comparison to the facile reduction of C_{60}, however, the oxidation of C_{60} is rendered more difficult with a reported one-electron oxidation potential of 1.26 V versus ferrocene/ferricenium.[8,9] Reed et al. have recently succeeded in oxidizing C_{60} by a strong one-electron oxidant (hexabrominated phenylcarbazole radical cation with inert $CB_{11}H_6X_6^-$ carborane anion) to produce stable $C_{60}^{\bullet+}$ in solution.[10] The electron-transfer oxidation of C_{60} has also been achieved by using the singlet excited state of 10-methylacridinium ion, which has a strong electron acceptor property, or by using the biphenyl radical

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cation produced by photoinduced electron transfer from biphenyl to photosensitizers.[11−13] In this process, the primary acceptor is excited and abstracts an electron from the biphenyl donor. The longer lifetime of the generated biphenyl radical cation enables the occurrence of an electron transfer from C_{60} to produce $C_{60}^{\bullet+}$.[11] Various polycyclic arene π-radical cations can also be produced by pulse radiolysis, and the electron-transfer oxidation of fullerenes by these radical cations has been reported.[14] The oxidation of the triplet excited state of C_{60} ($^3C_{60}$*) has also been studied by using strong electron acceptors such as tetracyano-*p*-quinodimethane (TCNQ),[15] tetracyanoethylene (TCNE),[16] and *p*-chloranil[17] in photolysis experiments of the oxidative quenching of triplet excited fullerenes. In general, very fast quenching reactions of the triplet states of fullerenes are reported in the presence of these electron acceptors, but these processes are not accompanied by a separation of the free radical pairs. A triplet “exciplex” formation has been proposed as a possible mechanism in most cases. Only in the case of a strong oxidant (TCNE) is the exciplex considered as an ion−radical pair.[18] Such a limitation of oxidants has precluded a detailed study of electron-transfer oxidation of the triplet excited states of fullerenes and derivatives. Although the oxidation of fullerenes typically becomes easier upon derivatization,[19] the radical cations of derivatized fullerenes have yet to be characterized. The ionization energies of higher fullerenes are also theoretically suggested to decrease with the cage size.[20,21] This has been shown experimentally by measurements of these compounds using photoionization, photoelectron spectroscopy, and the ion−molecular equilibria−Knudsen cell mass spectrometry.[21,22] However, there has so far been no report on the electron-transfer oxidation reactivities of fullerenes, higher fullerenes, or their functionalized derivatives.

The use of an appropriate metal ion which can accelerate electron-transfer reactions may remove the need of very strong oxidants to accomplish the electron-transfer oxidation of fullerenes. In the presence of such a metal ion, photoinduced electron-transfer reactions, which would otherwise be unlikely to occur, are reported to proceed efficiently.[23,24] We have recently reported that scandium triflate [$Sc(OTf)_3$] acts as the strongest Lewis acid which can effectively accelerate the electron-transfer reactions of oxygen and *p*-benzoquinone.[25]

We report herein that an efficient photoinduced electron transfer from the triplet excited state of C_{60} to *p*-chloranil and *p*-benzoquinone occurs in the presence of $Sc(OTf)_3$ in benzonitrile (PhCN) to produce C_{60} radical cation which has a diagnostic NIR (near-infrared) absorption band at 980 nm. The promoting effect of $Sc(OTf)_3$ is compared with the results for an electron transfer from CoTPP (TPP^{2-} = tetraphenylporphyrin dianion) to *p*-benzoquinone in PhCN. With regard to the derivatized fullerenes, a series of dibenzyl derivatives of C_{60} were synthesized by the reactions of C_{60}^{2-} with alkyl halides.[26,27] We then systematically generated the radical cations of C_{60}, C_{70}, and their derivatives produced by the Sc^{3+}-promoted electron transfer from the fullerene triplet excited states to *p*-chloranil. The electron-transfer oxidation reactivities of a series of fullerenes were determined for the first time and they are compared with the HOMO (highest occupied molecular orbital) levels of the fullerenes.

Experimental Section

Materials. C_{60} (**1**) (>99.95% pure) and C_{70} (**7**) (>99.95% pure) were purchased from Science Laboratories Co., Ltd., Japan, and used as received. Benzonitrile (PhCN) was purchased from Wako Pure Chemical Ind. Ltd., Japan, and distilled over P_2O_5 prior to use.[28] *p*-Benzoquinone and *p*-chloranil were obtained commercially and purified by the standard method.[28] Dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] was prepared according to literature procedures.[29] Scandium trifluoromethanesulfonate, $Sc(OTf)_3$ (99%, FW = 492.16) was obtained from Pacific Metals Co., Ltd. (Taiheiyo Kinzoku). Cobalt(II) tetraphenylporphyrin, CoTPP, was prepared as described in the literature.[30] The examined 1,4-R_2C_{60} derivatives (**2**−**6**) [R = 4-$BrC_6H_4CH_2$ (**2**), 3-$BrC_6H_4CH_2$ (**3**), 2-$BrC_6H_4CH_2$ (**5**), and $C_6H_5CH_2$ (**6**)] and 1,4-(Bu^t)($C_6H_5CH_2$)C_{60} (**4**) were prepared by a reaction of electrogenerated C_{60}^{2-} with RBr as described previously.[26,27] The C_{60}−*N*-methylpyrrolidine derivative (**8**)[31] was synthesized according to literature procedures. To eliminate the problem of multiple isomers in functionalized C_{70}, [1,9]methaofullerene[70] carboxylic acid was prepared selectively according to literature procedures.[32] Condensation of [1,9]-

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methaofullerene[70] carboxylic acid with 4-alkoxyaniline gave [1,9]-methaofullerene[70] (**9**).

Synthesis of [1,9]Methanofullerene[70] (9). To a stirred suspension of sodium hydride (745 mg, 18.6 mmol) in THF (70 mL), 4-cyanophenol (2.13 g, 17.5 mmol) was added in one portion at 0 °C and stirring was continued at 0 °C for 2 h. The solvent was removed under reduced pressure and the residue was resuspended in DMF (70 mL). To the suspension, 1-bromodocosane (7.61 g, 19.5 mmol) was added and the solution was maintained at 70 °C for 2 h. The reaction mixture was allowed to cool to room temperature and then evaporated to dryness at a reduced pressure. The residue was dissolved in $CHCl_3$, washed with brine, dried over anhydrous Na_2SO_4, and evaporated. Reprecipitation from hexane−benzene gave 4-cyano-1-docosanoxybenzene as a pale yellow solid (7.28 g, 17.0 mmol, 97%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.57 (d, $J = 8$ Hz, 2 H), 6.93 (d, $J = 8$ Hz, 2 H), 3.99 (t, $J = 7$ Hz, 2 H), 1.80 (quintet, $J = 7$ Hz, 2 H), 1.50−1.20 (m, 38 H), 0.88 (t, $J = 7$ Hz, 3 H); MS(FAB) 428 ($M + H^+$). To a stirred solution of $LiAlH_4$ (3.17 g, 83.5 mmol) in dry THF (100 mL), a solution of 4-cyano-1-docosanoxybenzene (7.25 g, 16.9 mmol) in dry THF (50 mL) was added dropwise at 0 °C and stirring was continued at 0 °C for 4 h. The reaction mixture was quenched by addition of 5 mL of ethyl acetate followed by addition of 300 mL of 3 M HCl aqueous solution. The organic layer was extracted with benzene, washed with saturated Na_2CO_3, and dried over anhydrous Na_2SO_4 and then the solvent was evaporated. Flash column chromatography on silica gel with ethyl acetate−ethanol (2:1) as an eluent ($R_f = 0.05$) and subsequent reprecipitation from hexane−benzene gave 4-aminomethyl-1-docosanoxybenzene as a white solid (72% yield, 5.27 g, 12.2 mmol). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.20 (d, $J = 8$ Hz, 2 H), 6.86 (d, $J = 8$ Hz, 2 H), 3.94 (t, $J = 7$ Hz, 2 H), 3.79 (s, 2 H), 1.79 (quintet, $J = 7$ Hz, 2 H), 1.50−1.20 (m, 38 H), 0.88 (t, $J = 7$ Hz, 3 H); MS (FAB) 432 ($M + H^+$). To a stirred solution of [1,9]methanofullerene[70] carboxylic acid[32b] (23.5 mg, 0.0261 mmol) and 1-hydroxybenzotriazole hydrate (HOBT) (6.3 mg, 0.0410 mmol) in 5 mL of bromobenzene−DMSO (5:1), was added under nitrogen atmosphere 1,3-dicyclohexylcarbodiimide (DCC) (28.5 mg, 0.138 mmol) followed by 4-aminomethyl-1-docosanoxybenzene (12.2 mg, 0.0282 mmol). The reaction was stirred at room temperature for 20 h, after which the solvent was evaporated to yield a black solid. Flash column chromatography on silica gel with benzene as an eluent ($R_f = 0.15$) and subsequent reprecipitation from benzene−acetonitrile gave **9** as a dark grayish brown solid (25.0 mg, 0.0190 mmol, 73% yield). Mp >300 °C; ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.36 (d, $J = 8$ Hz, 2 H), 6.92 (d, $J = 8$ Hz, 2 H), 6.56 (t, $J = 5$ Hz, 1 H), 4.63 (d, $J = 5$ Hz, 2 H), 3.96 (t, $J = 7$ Hz, 2 H), 3.50 (s, 1 H), 1.78 (quintet, $J = 7$ Hz, 2 H), 1.60−1.20 (m, 38 H), 0.88 (t, $J = 7$ Hz, 3 H); MS (FAB) 1313 ($M + H^+$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.41, 159.04, 155.88, 155.18, 151.45, 151.17, 150.68, 150.61, 150.56, 149.39, 149.27, 149.18, 148.95, 148.60, 148.55, 148.46, 148.35, 148.27, 148.24, 147.71, 147.64, 147.53, 147.38, 147.33, 146.98, 146.87, 145.98, 145.87, 145.53, 145.21, 143.86, 143.43, 143.30, 143.16, 142.84, 142.67, 142.02, 141.95, 141.53, 140.32, 139.15, 138.89, 137.05, 133.82, 133.70, 132.74, 130.86, 130.76, 130.66, 129.64 (C_6H_4), 129.12, 114.97 (C_6H_4), 68.18 (OCH_2), 65.33 (C_{70}-sp^3), 64.13 (C_{70}-sp^3), 44.14 ($CH_2C_6H_4$), 31.92, 30.91, 29.70, 29.62, 29.42, 29.36, 29.26, 26.15, 26.07 (CH), 22.69, 14.12.

Laser Flash Photolysis. The measurements of radical cation absorption spectra in the photochemical reaction of C_{60}, C_{70}, and their derivatives with *p*-benzoquinone and *p*-chloranil in the presence of $Sc(OTf)_3$ (0.11 M) were performed according to the following procedures: The solution was deoxygenated by argon purging for 10 min prior to the measurement. The deaerated PhCN solution containing C_{60}, C_{70}, and their derivatives (1.2×10^{-4} M) and *p*-benzoquinone (0.10 M) or *p*-chloranil (0.04 M) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 532 nm with the power of 10 mJ per pulse. For shorter time-scale measurements (<5 μs), a pulsed xenon flash lamp (Tokyo Instruments, XF80-60, 15 J, 60 ms fwhm) was used for the probe beam, which was detected with a Ge-APD module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10 × 10 mm) and a monochromator. For longer time scale measurements (>5 μs), a continuous xenon lamp (150 W) was used for the probe beam, which was detected with an InGaAs photodiode module (Hamamatsu, G5125-10) after passing through the photochemical quartz vessel (10 × 10 mm) and a monochromator. The outputs from Ge-APD and InGaAs module were recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). The transient spectra were recorded with fresh solutions in each laser excitation. All experiments were performed at 298 K.

Kinetic Measurements. Kinetic measurements of electron-transfer reactions from CoTPP to *p*-benzoquinone in the presence of $Sc(OTf)_3$ were performed on a Unisoku RSP-601 stopped-flow rapid scan spectrophotometer with a Unisoku thermostated cell holder. Typically, a deaerated MeCN solution of CoTPP (2.0×10^{-5} M) and $Sc(OTf)_3$ (5.0×10^{-2} to 2.0×10^{-1} M) was added to a deaerated MeCN solution of *p*-benzoquinone (2.0×10^{-4} to 8.0×10^{-4} M) under Ar with stirring. The rates of electron-transfer reaction from CoTPP (1.0×10^{-5} M) to the *p*-benzoquinone derivatives [$(1.0-4.0) \times 10^{-4}$ M] in the presence of $Sc(OTf)_3$ [$(2.5-1.0) \times 10^{-2}$ M] were monitored in MeCN at 298 K by the rise of the absorption band at 434 nm and the decay of the band at 412 nm due to $CoTPP^+$ and CoTPP, respectively. Kinetic measurements were carried out under pseudo-first-order conditions where the concentrations of electron acceptors were maintained at greater than 10-fold excess of the concentrations of electron donors at 298 K. Pseudo-first-order rate constants were determined by least-squares curve fits of the data using a microcomputer.

ESR Measurements. ESR measurements were carried out to detect the radical ion pair produced in the photoinduced electron transfer from $^3C_{60}{}^*$ to *p*-chloranil in the presence of $Sc(OTf)_3$. These experiments were performed in frozen PhCN at 193 K under irradiation of light with a high-pressure mercury lamp (USH-1005D) focusing at the sample cell in the ESR cavity. The ESR spectra were measured with a JEOL X-band spectrometer (JES-RE1XE). The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (*S*/*N*) ratio of the observed spectra. The *g* values were calibrated with an Mn^{2+} marker.

Theoretical Calculations. Semiempirical MO calculations were performed at the MNDO level with Gaussian 98.[33] Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The heats of formation (ΔH_f) were calculated with the restricted Hartree−Fock (RHF) formalism using a key word "PRECISE".

Results and Discussion

Sc^{3+}-Promoted Electron Transfer from $^3C_{60}{}^*$ to *p*-Benzoquinones. Photoexcitation of C_{60} with 532-nm laser light at which C_{60} has its absorption maximum results in formation of $^3C_{60}{}^*$ via the fast intersystem crossing from the singlet excited state and is characterized by the triplet−triplet absorption band at 740 nm.[34]Although $^3C_{60}{}^*$ is quenched by *p*-chloranil (Cl_4Q) with a rate constant of 2.0×10^7 M^{-1} s^{-1}, no $C_{60}{}^{\bullet +}$ is formed as reported previously[17a] (see Supporting Information S1). This result is reasonable, judging from the positive free energy change (ΔG^0_{et}) obtained from the one-electron oxidation potential of $^3C_{60}{}^*$ ($E^0_{ox} = 0.20$ V vs SCE)[35,36] and the one-electron reduction potential of *p*-chloranil ($E^0_{red} = 0.01$ V vs SCE).[37]

Photoexcitation of *p*-benzoquinone generates its triplet excited state with unit efficiency owing to the ultrafast rate of intersystem crossing.[38] The high energy of the triplet quinone with $E_T = 2.17$ eV[39] is energetically sufficient to accomplish

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[35] The E^0_{ox} value of C_{60} (1.26 V vs ferrocene/ferricenium) is converted to the value vs SCE (1.76 V).[8] Subtraction of the triplet energy of $^3C_{60}{}^*$ (1.56 eV)[36] from the E^0_{ox} value of C_{60} gives the E^0_{ox} value of $^3C_{60}{}^*$ (0.20 V vs SCE).

[36] Hung, R. R.; Grabowski, J. J. *J. Phys. Chem.* **1991**, *95*, 6073.

[37] Fukuzumi, S.; Koumitsu, S.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

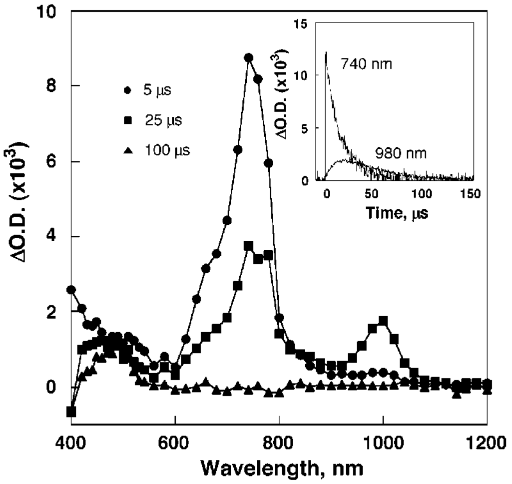


Figure 1. Transient absorption spectra observed in photoinduced electron transfer from C$_{60}$ (1.1×10^{-4} M) to Cl$_4$Q (4.0×10^{-2} M) in the presence of Sc^{3+} (0.11 M) after laser irradiation at $\lambda = 532$ nm in deaerated PhCN at 298 K (black circles = 5 μs, black square = 25 μs, and black triangle = 100 μs). Inset: Time profile of the absorption band at 740 and 980 nm due to ^{3}C$_{60}$* and C$_{60}^{\bullet+}$.

the oxidation of aromatic donors including fullerenes. However, selective photoexcitation with a 440-nm laser light of *p*-benzoquinone in PhCN containing C$_{60}$ results in formation of ^{3}C$_{60}$*, which has a diagnostic band at 740 nm (see Supporting Information S2). This suggests that an efficient energy transfer from the triplet excited state of *p*-benzoquinone to C$_{60}$ (E_T = 1.56 eV)[34] occurs rather than an electron transfer from C$_{60}$.

In the presence of scandium triflate [Sc(OTf)$_3$], photoexcitation with 532-nm laser light of C$_{60}$ in PhCN containing Cl$_4$Q results in the appearance of a new absorption band at 980 nm, which is readily assigned to C$_{60}^{\bullet+}$,[9,10,40] as shown in Figure 1.[41] The absorption band due to the *p*-chloranil radical anion (Cl$_4$Q$^{\bullet-}$)$-$Sc^{3+} complex, which should be formed together with C$_{60}^{\bullet+}$ seems to be overlapped at 500 nm with the residual absorption due to ^{3}C$_{60}$*. The decay of ^{3}C$_{60}$* at 740 nm is accompanied by the appearance of C$_{60}^{\bullet+}$ at 980 nm, but this species decays at prolonged reaction time (see inset of Figure 1). This indicates that photoinduced electron transfer from ^{3}C$_{60}$* to Cl$_4$Q (k_{et}) occurs in the presence of Sc^{3+} to produce C$_{60}^{\bullet+}$ and the Cl$_4$Q$^{\bullet-}$$-$Sc^{3+} complex, both of which decay via a back electron-transfer (k_{bet}) process (Scheme 1). The strong binding between Cl$_4$Q$^{\bullet-}$ and Sc^{3+} makes the electron transfer energetically feasible as reported for the Sc^{3+}-catalyzed electron-transfer reduction of *p*-benzoquinone.[25]

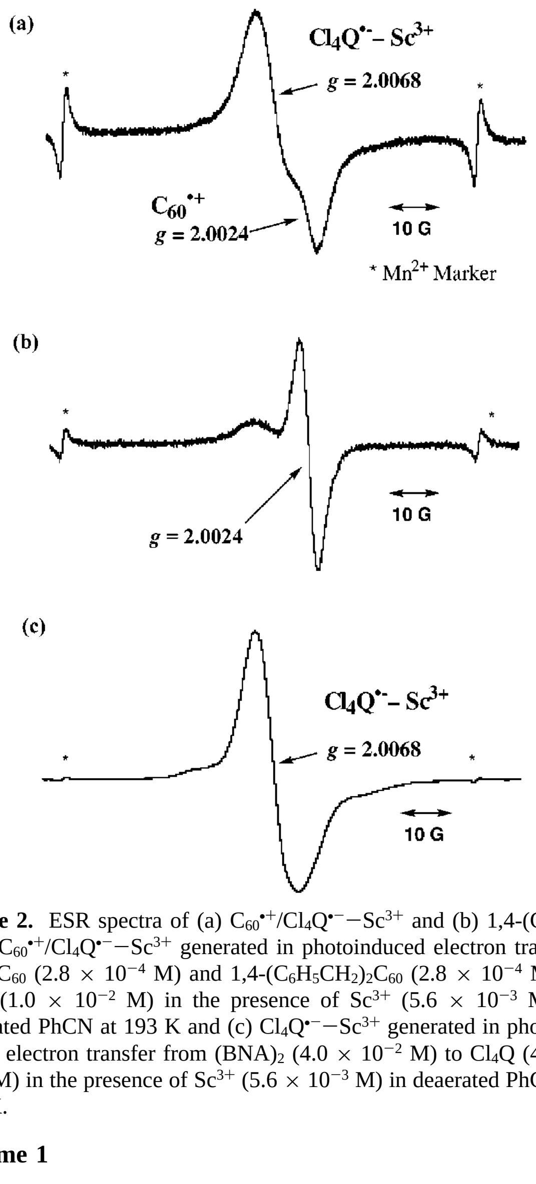
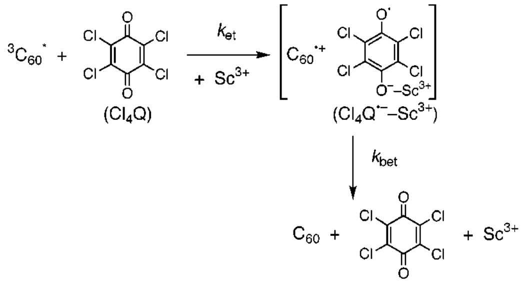


Figure 2. ESR spectra of (a) C$_{60}^{\bullet+}$/Cl$_4$Q$^{\bullet-}$$-$Sc^{3+} and (b) 1,4-(C$_6H_5CH_2$)$_2C_{60}^{\bullet+}$/Cl$_4Q^{\bullet-}$$-$Sc^{3+} generated in photoinduced electron transfer from C$_{60}$ (2.8×10^{-4} M) and 1,4-(C$_6$H$_5$CH$_2$)$_2$C$_{60}$ (2.8×10^{-4} M) to Cl$_4$Q (1.0×10^{-2} M) in the presence of Sc^{3+} (5.6×10^{-3} M) in deaerated PhCN at 193 K and (c) Cl$_4$Q$^{\bullet-}$$-$Sc^{3+} generated in photoinduced electron transfer from (BNA)$_2$ (4.0×10^{-2} M) to Cl$_4$Q (4.0×10^{-2} M) in the presence of Sc^{3+} (5.6×10^{-3} M) in deaerated PhCN at 193 K.

Scheme 1



The formation of the radical intermediate complex [C$_{60}^{\bullet+}$-Cl$_4$Q$^{\bullet-}$$-$Sc^{3+}] in Scheme 1 is confirmed by the ESR spectrum observed in the Sc^{3+}-promoted photoinduced electron transfer from ^{3}C$_{60}$* to Cl$_4$Q in frozen PhCN at 193 K under photoirradiation with a high-pressure mercury lamp. The resulting spectrum is shown in Figure 2a and consists of two overlapping isotropic ESR signals which have different *g* values (g = 2.0068 and 2.0024). However, when C$_{60}$ is replaced by 1,4-(C$_6$H$_5$CH$_2$)$_2$C$_{60}$, the ESR signal at g = 2.0024 (Figure 2b) becomes more prominent as compared to the case of C$_{60}$.

To assign these ESR signals, the Cl$_4$Q$^{\bullet-}$$-$Sc^{3+} complex was independently produced by photoinduced electron transfer from dimeric 1-benzyl-1,4-dihydronicotinamide [(BNA)$_2$][42] to *p*-chloranil in frozen PhCN at 77 K. (BNA)$_2$ is known to act as a unique two-electron donor to produce radical anions of electron acceptors.[43] The ESR spectrum of Cl$_4$Q$^{\bullet-}$$-$Sc^{3+} thus produced (eq 1) is shown in Figure 2c. This signal in the spectrum at

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(38) (a) Rathore, R.; Hubig, S. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 11468. (b) Sun, D.; Hubig, S. M.; Kochi, J. K. *J. Org. Chem.* **1999**, *64*, 2250.

(39) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1996; p 786.

(40) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shinoharu, H.; Yamaguchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *180*, 446.

(41) Since the transient absorption spectra were measured at 20-nm interval, the determined absorption maximum has an uncertainty of 10$-$20 nm.

(42) (a) Patz, M.; Kuwahara, Y.; Suenobu, T.; Fukuzumi, S. *Chem. Lett.* **1997**, 567. (b) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060.

(43) Fukuzumi, S.; Suenobu, T.; Urano, T.; Tanaka, K. *Chem. Lett.* **1997**, 875.

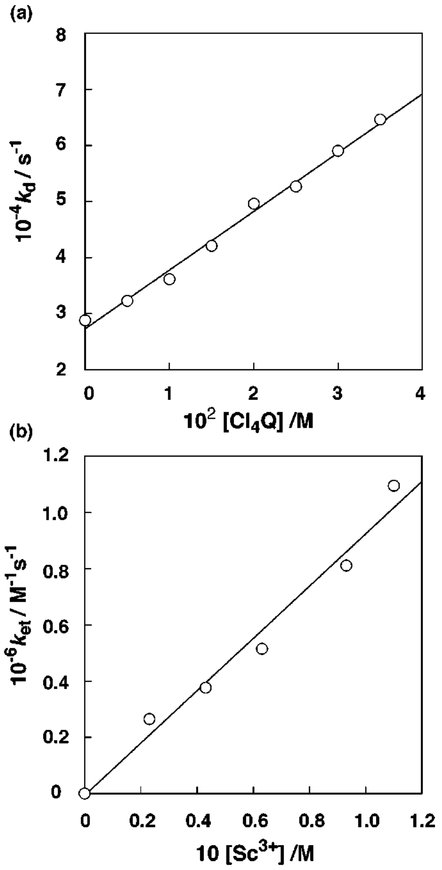
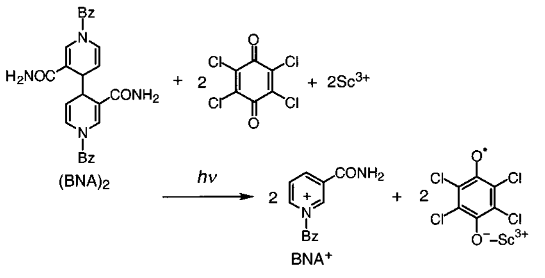


Figure 3. (a) Plot of decay rate constants (k_d) of $^3C_{60}$* vs [Cl_4Q] in the presence of Sc^{3+} (0.11 M) in deaerated PhCN at 298 K. (b) Plot of k_{et} vs [Sc^{3+}] for electron transfer from $^3C_{60}$* to Cl_4Q in deaerated PhCN at 298 K.

$g = 2.0068$ agrees with the ESR signal with the g value of 2.0068 in Figure 2a. The other ESR signal at $g = 2.0024$ in Figure 2a agrees with that reported for $C_{60}^{\bullet+}$.[10,44]



(1)

The decay rate of the absorbance due to $^3C_{60}$* at 740 nm (inset of Figure 1) obeys pseudo-first-order kinetics and the pseudo-first-order rate constant (k_d) increases linearly with increasing the p-chloranil concentration [Cl_4Q] as shown in Figure 3a. From the slope of the linear correlation in Figure 3a is obtained the second-order rate constant of electron transfer (k_{et}) in Scheme 1. The k_{et} value increases linearly with increasing the Sc^{3+} concentration as shown in Figure 3b.

When p-chloranil is replaced by p-benzoquinone (Q), the k_{et} value for electron transfer from $^3C_{60}$* to Q, which was evaluated from the slope of the line in Figure 4a, increases with an increase in [Sc^{3+}] to exhibit a first-order dependence on [Sc^{3+}] at low concentrations, changing to a second-order dependence at high concentrations as shown in Figure 4b (open circles).

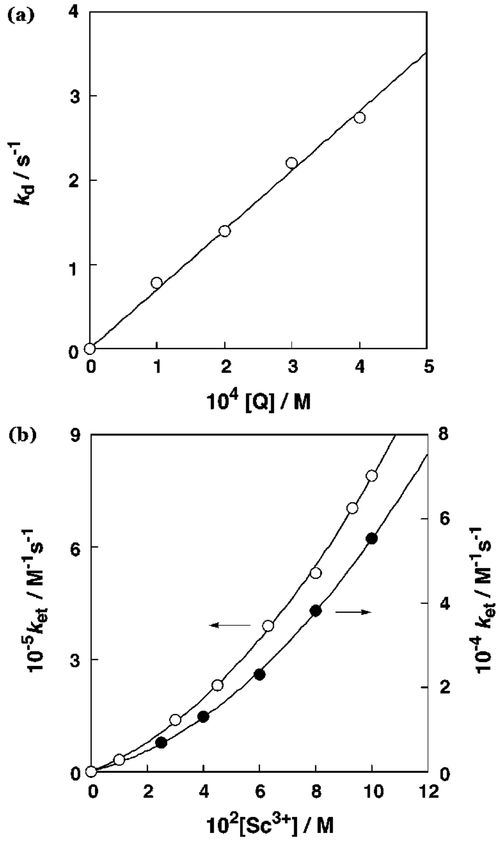
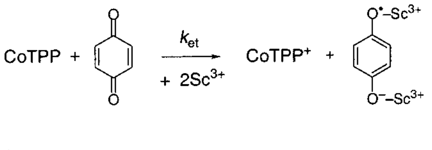


Figure 4. (a) Plot of decay rate constant (k_d) of $^3C_{60}$* vs [Q] in the presence of Sc^{3+} (0.10 M) in deaerated PhCN at 298 K. (b) Plot of k_{et} vs [Sc^{3+}] for electron transfer from $^3C_{60}$* to Q (white circles) and from CoTPP (1.0×10^{-5} M) to Q (1.0×10^{-2} M) (black circles) in the presence of Sc^{3+} in deaerated PhCN at 298 K.

Such a mixture of first-order and second-order dependence on [Sc^{3+}] is also observed in electron transfer from CoTPP (TPP^{2-} = tetraphenylporphyrin dianion) to Q. No electron transfer from CoTPP to Q occurs in PhCN at 298 K. In the presence of Sc(OTf)$_3$, however, efficient electron transfer from CoTPP to Q occurs to yield CoTPP$^+$ (see Supporting Information S3). The electron-transfer rates obey second-order kinetics, showing a first-order dependence on each reactant concentration. The dependence of the observed electron-transfer rate constant (k_{et}) on [Sc^{3+}] was examined for electron transfer from CoTPP to Q at various concentrations of Sc^{3+}. The results are shown in Figure 4b (black circles), where the k_{et} value increases linearly with [Sc^{3+}] to show a first-order dependence on [Sc^{3+}] at low concentrations, changing to a second-order dependence at high concentrations as is the case of the Sc^{3+}-promoted electron transfer from $^3C_{60}$* to Q in Figure 4b (open circles).



(2)

A mixture of first-order and second-order dependence on [Sc^{3+}] is ascribed to formation of 1:1 and 1:2 complexes between the semiquinone radical anion and Sc^{3+} at the low and high concentrations of Sc^{3+} (eqs 3 and 4, respectively), which results in acceleration of the rate of electron transfer. The complex formation of $Q^{\bullet-}$ and Sc^{3+}

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(44) Siedschlag, C.; Torres-Garcia, G.; Wolff, C.; Mattay, J.; Fujitsuka, M.; Watanabe, A.; Ito, O.; Dunsch, L.; Ziegs, F.; Luftmann, H. *J. Inform. Res.* **1998**, *24*, 265.

$$\mathrm{Q}^{\bullet-} + \mathrm{Sc}^{3+} \overset{K_1}{\rightleftharpoons} \mathrm{Q}^{\bullet-}\text{−}\mathrm{Sc}^{3+} \quad (3)$$

$$\mathrm{Q}^{\bullet-} + \mathrm{Sc}^{3+} + \mathrm{Sc}^{3+} \overset{K_2}{\rightleftharpoons} \mathrm{Q}^{\bullet-}\text{−}2\mathrm{Sc}^{3+} \quad (4)$$

should result in the positive shift of the one-electron reduction potential of Q (E_{red}) and the Nernst equation is given by eq 5, where E^0_{red} is the one-electron reduction potential

$$E_{\mathrm{red}} = E^0_{\mathrm{red}} + (2.3RT/F) \log K_1[\mathrm{Sc}^{3+}](1 + K_2[\mathrm{Sc}^{3+}]) \quad (5)$$

of Q to $\mathrm{Q}^{\bullet-}$ in the absence of Sc^{3+} and K_1 and K_2 are the formation constants for the 1:1 and 1:2 complexes between $\mathrm{Q}^{\bullet-}$ and Sc^{3+}, respectively. Since Sc^{3+} has no effect on the oxidation potential of CoTPP and $^3\mathrm{C}_{60}{}^*$, the free energy change of electron transfer in the presence of Sc^{3+} (ΔG_{et}) can be expressed by eq 6, where ΔG^0_{et} is the free energy change in the absence of Sc^{3+}. Thus, electron transfer from CoTPP and $^3\mathrm{C}_{60}{}^*$ to Q and

$$\Delta G_{\mathrm{et}} = \Delta G^0_{\mathrm{et}} - (2.3RT) \log(K_1[\mathrm{Sc}^{3+}] + K_1K_2[\mathrm{Sc}^{3+}]^2) \quad (6)$$

$\mathrm{Cl}_4\mathrm{Q}$ becomes more favorable energetically with an increase in the concentration of Sc^{3+}. If such a change in the energetics is directly reflected in the transition state of electron transfer, the dependence of the observed rate constant of electron transfer (k_{et}) on $[\mathrm{Sc}^{3+}]$ can be derived from eq 6 as given by eq 7, where k_0 is the rate constant in the absence of Sc^{3+}.

$$k_{\mathrm{et}}/[\mathrm{Sc}^{3+}] = k_0K_1(1 + K_2[\mathrm{Sc}^{3+}]) \quad (7)$$

The validity of eq 7 is confirmed by the linear plot of $k_{\mathrm{et}}/[\mathrm{Sc}^{3+}]$ vs $[\mathrm{Sc}^{3+}]$ for the Sc^{3+}-promoted electron transfer from $^3\mathrm{C}_{60}{}^*$ and CoTPP to Q as shown in Figure 5 (part a and b, respectively). From the slopes and intercepts in Figures 5a and 5b are obtained the K_2 values as 1.7 and 2.0, respectively. The agreement of these two K_2 values supports the validity of the analysis.

Since there is no interaction between Q and Sc^{3+} as indicated by the lack of spectral change of Q in the presence of Sc^{3+}, the acceleration of electron transfer from CoTPP to Q is ascribed to the complexation of Sc^{3+} with $\mathrm{Q}^{\bullet-}$. The formation of the 1:2 complex between $\mathrm{Q}^{\bullet-}$ and Sc^{3+} (eq 4) is confirmed by the ESR spectrum of $\mathrm{Q}^{\bullet-}\text{−}2\mathrm{Sc}^{3+}$, which shows superhyperfine structure due to the interaction of $\mathrm{Q}^{\bullet-}$ with two Sc nuclei. Since $\mathrm{Q}^{\bullet-}\text{−}2\mathrm{Sc}^{3+}$ is unstable because of the facile disproportionation reaction, the $\mathrm{Q}^{\bullet-}\text{−}\mathrm{Sc}^{3+}$ complex was generated in photoinduced electron transfer from $[(\mathrm{BNA})_2]$[38] to Q at low temperatures. The photochemical reaction was carried out in an ESR cavity where an ESR tube containing a propionitrile (EtCN) solution of $(\mathrm{BNA})_2$, Q, and Sc^{3+} was irradiated with a mercury lamp at 203 K. Propionitrile was used instead of PhCN to avoid freezing the solvent at 203 K. The observed ESR spectrum of the semiquinone radical anion ($\mathrm{Q}^{\bullet-}$) in the presence of Sc^{3+} (4.4×10^{-2} M) is shown in Figure 6a. The well-resolved 19 lines of the spectrum clearly indicate the hyperfine splitting (a(4H)) due to four protons of semiquinone radical anions and superhyperfine splitting (a(2Sc)) of two equivalent Sc^{3+} nuclei ($I = {}^7/_2$). The hyperfine splitting constants are almost the same between a(4H) and a(2Sc), resulting in the overall nuclear spin = 9, which causes 19 lines. The computer simulation spectrum with $a(4\mathrm{H}) = 1.15$ G, $a(2\mathrm{Sc}) = 1.15$ G with the line width ($\Delta H_{\mathrm{msl}}) = 0.50$ G is shown in Figure 6b for comparison. The agreement between the observed and simulation spectra confirms the formation of the 1:2 complex between $\mathrm{Q}^{\bullet-}$ and Sc^{3+}.[45]

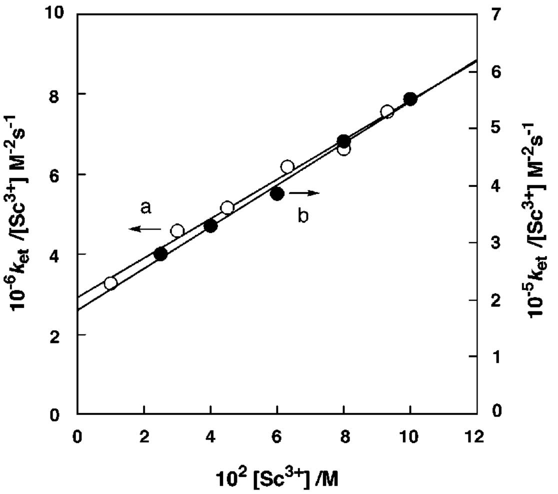

Figure 5. (a) Plot of $k_{\mathrm{et}}/[\mathrm{Sc}^{3+}]$ vs $[\mathrm{Sc}^{3+}]$ for electron transfer from C_{60} to Q in the presence of Sc^{3+} in deaerated PhCN at 298 K (white circles). (b) Plot of $k_{\mathrm{et}}/[\mathrm{Sc}^{3+}]$ vs $[\mathrm{Sc}^{3+}]$ for electron transfer from CoTPP to Q in the presence of Sc^{3+} in deaerated PhCN at 298 K (black circles).

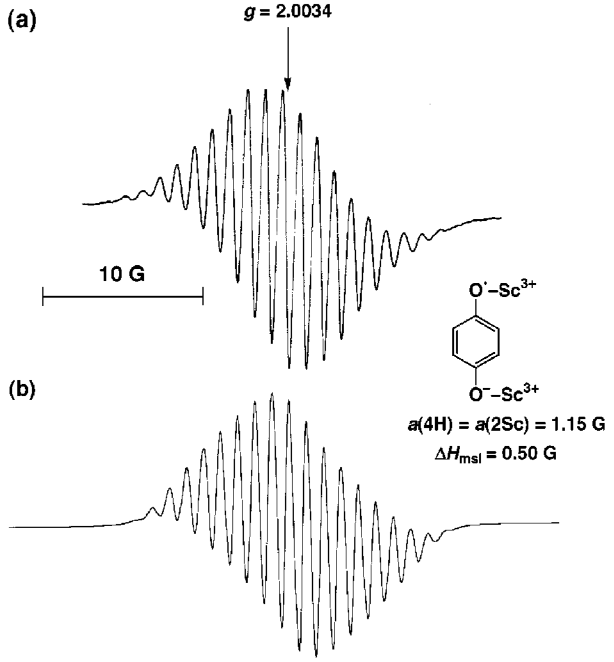

Figure 6. (a) ESR spectrum of propionitrile solution containing $(\mathrm{BNA})_2$ (1.6×10^{-2} M), *p*-benzoquinone (4.9×10^{-2} M), and $\mathrm{Sc(OTf)}_3$ (4.4×10^{-2} M) with irradiation of a high-pressure mercury lamp at 203 K. (b) Computer simulation spectrum with $g = 2.0034$, $a(4\mathrm{H}) = a(2\mathrm{Sc}) = 1.15$ G, $\Delta H_{\mathrm{msl}} = 0.50$ G.

Formation of Radical Cations of Fullerene Derivatives. The formation of $\mathrm{C}_{60}{}^{\bullet+}$ by Sc^{3+}-promoted photoinduced electron-transfer oxidation of $^3\mathrm{C}_{60}{}^*$ by *p*-chloranil (vide supra) enables us to examine the oxidation reactivities of a series of fullerene derivatives quantitatively, because oxidation of fullerenes is expected to be easier upon derivatization.[19] The examined fullerene derivatives are shown in Chart 1.

As is the case for C_{60} (Figure 1), the transient absorption maxima of other fullerene radical cations were determined by

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[45] The 1:2 complex between $\mathrm{Q}^{\bullet-}$ and Sc^{3+} is exclusively formed at 203 K probably because of the large K_2 value at the low temperature as compared to the value at 298 K.

Chart 1

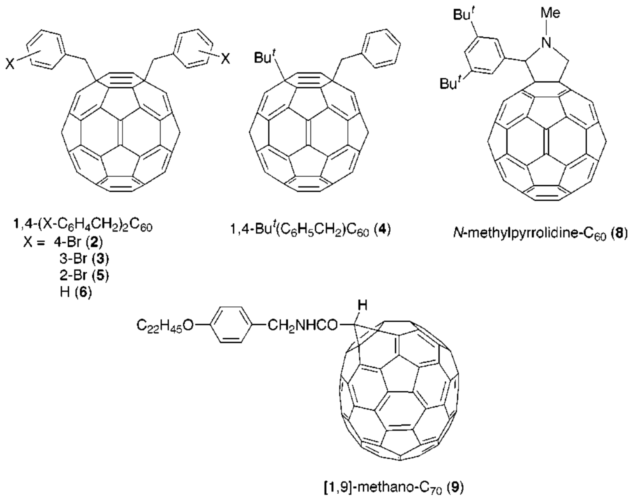

Table 1. Absorption Maxima (λ_{max}) and g Values of Fullerene Radical Cations, Rate Constants of Electron Transfer (k_{et}) from Fullerene Triplets to p-Chloranil in the Presence of $Sc(OTf)_3$ (0.11 M), and Relative HOMO Level of Fullerenes (ΔE_{HOMO})

	compound	λ_{max}, nm	g value	k_{et}, $M^{-1} s^{-1}$	ΔE_{HOMO},[a] eV
1	C_{60}	980	2.0024	1.1×10^6	0
2	$1,4\text{-}(4\text{-}BrC_6H_4CH_2)_2C_{60}$	920	2.0024	2.3×10^6	0.22
3	$1,4\text{-}(3\text{-}BrC_6H_4CH_2)_2C_{60}$	920	2.0024	2.5×10^6	0.24
4	$1,4\text{-}(Bu^t)(C_6H_5CH_2)C_{60}$	900	2.0024	2.6×10^6	0.31
5	$1,4\text{-}(2\text{-}BrC_6H_4CH_2)_2C_{60}$	900	2.0024	2.7×10^6	0.32
6	$1,4\text{-}(C_6H_5CH_2)_2C_{60}$	920	2.0024	3.0×10^6	0.32
7	C_{70}	1400	2.0017	4.0×10^6	0.46
8	N-methylpyrrolidine-C_{60}	960	2.0026	5.9×10^6	0.51
9	[1,9]methano-C_{70}	1400	2.0012	8.4×10^6	0.60

[a] Calculated by the MNDO semiempirical method in reference to C_{60}.

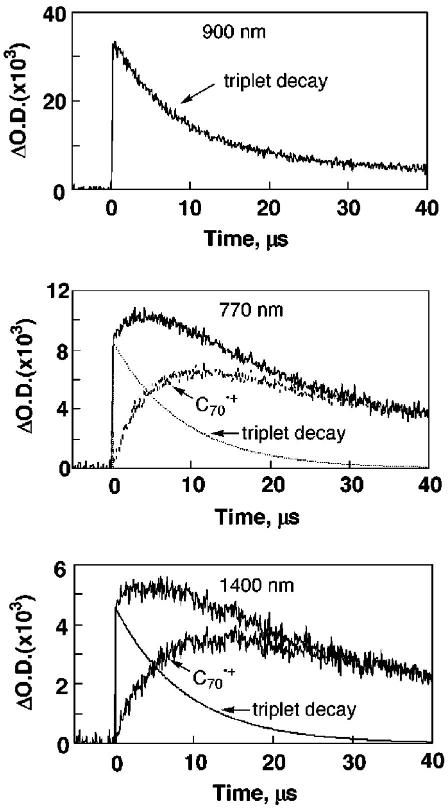

Figure 7. Time profiles observed in the photoinduced electron transfer from C_{70} (1.1×10^{-4} M) to Cl_4Q (4.0×10^{-2} M) in the presence of Sc^{3+} (0.11 M) at (a) 900, (b) 770, and (c) 1400 nm. Time profile at 900 nm is mainly due to $^3C_{70}{}^*$. The time profile of $C_{70}{}^{\bullet +}$ is obtained by subtracting the time profile of $^3C_{70}{}^*$ (the dotted line) from the observed time profile at 770 and 1400 nm (part b and c, respectively).

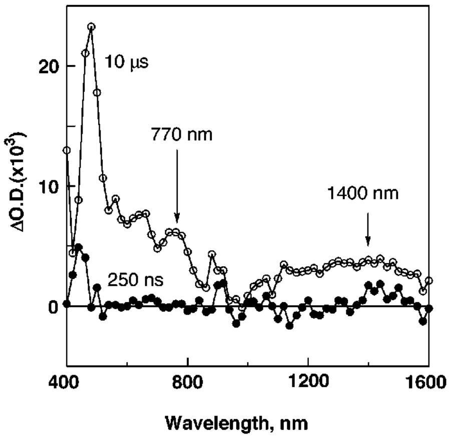

Figure 8. Transient absorption spectra after subtraction of the absorption due to $^3C_{70}{}^*$ in the photoinduced electron transfer from C_{70} (1.1×10^{-4} M) to Cl_4Q (4.0×10^{-2} M) in the presence of Sc^{3+} (0.11 M) at 250 ns and 10 μs after laser excitation at $\lambda = 532$ nm in deaerated PhCN at 298 K.

laser flash photolysis experiments for the Sc^{3+}-promoted photoinduced electron-transfer reactions from the triplet excited states of the fullerene derivatives to p-chloranil (e.g., see Supporting Information S4). The λ_{max} values of the fullerene radical cations are listed in Table 1 (vide infra).

In the case of C_{70} (**7**), the triplet−triplet absorption band of C_{70}, which appears at $\lambda_{max} = 900$ nm, decays to reach a residual absorbance due to $C_{70}{}^{\bullet +}$ as shown in Figure 7a. At other wavelengths the rise in absorbance due to $C_{70}{}^{\bullet +}$ is significantly mixed with the decay in absorbance due to $^3C_{70}{}^*$ as shown in a time profile at 770 nm (Figure 7b) and at 1400 nm (Figure 7c). The decay of $^3C_{70}{}^*$ obeys first-order kinetics and the pseudo-first-order rate constant increases linearly with increasing Cl_4Q concentration $[Cl_4Q]$ as in the case of $^3C_{60}{}^*$. The second-order rate constant of electron transfer (k_{et}) is determined from the slope of the linear correlation and is listed in Table 1. To extract the time profile of $C_{70}{}^{\bullet +}$ at 770 and 1400 nm, the time profile of $^3C_{70}{}^*$ (dotted line) is subtracted from the observed time profile as shown in parts b and c of Figure 7, respectively. This procedure is repeated at each wavelength to obtain the time-resolved absorption spectrum due to $C_{70}{}^{\bullet +}$. The maximum absorbance due to $C_{70}{}^{\bullet +}$ is obtained at 10 μs (Figure 7b,c). The transient absorption spectra thus obtained at 250 ns and 10 μs are shown in Figure 8, where a broad absorption band is observed in the NIR region (1400 nm) together with the bands at 770 and 500 nm in the spectrum at 10 μs.[46] Reed et al.[10] have recently reported that $C_{70}{}^{\bullet +}$ has an absorption band at 770 nm which corresponds to the band observed at 770 nm in Figure 8. Since the time profile at 1400 nm (Figure 7c) is the same as the profile at 770 nm after subtraction of the absorbance due to $^3C_{70}{}^*$ (Figure 7b), the long-wavelength absorption band in the NIR region ($\lambda_{max} = 1400$ nm) is clearly attributed to $C_{70}{}^{\bullet +}$. A similar broad NIR band is observed for [1,9]methanofullerene-[70] (**9**) (Table 1, see also Supporting Information, S5).

The formation of the radical ion pair $[C_{70}{}^{\bullet +}Cl_4Q^{\bullet -}{-}Sc^{3+}]$ is confirmed by the ESR spectrum observed in Sc^{3+}-promoted

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[46] The absorption bands at shorter wavelengths than 700 nm may be overlapped with the bands due to $Cl_4Q^{\bullet -}{-}Sc^{3+}$, since these absorption bands are commonly observed for other fullerene derivatives (e.g., see Figure 1).

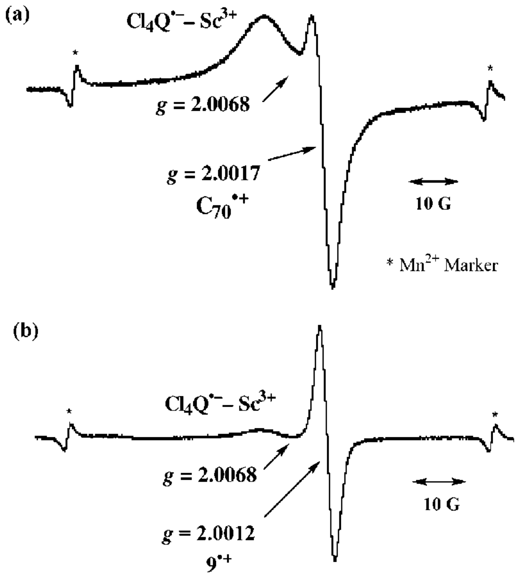

Figure 9. ESR spectra of (a) $C_{70}^{•+}/Cl_4Q^{•-}-Sc^{3+}$ and (b) $\mathbf{9}^{•+}/Cl_4Q^{•-}-Sc^{3+}$ generated in photoinduced electron transfer from C_{70} (2.8×10^{-4} M) and **9** (2.8×10^{-4} M) to Cl_4Q (1.0×10^{-4} M) in the presence of Sc^{3+} (5.6×10^{-3} M) in deaerated PhCN at 193 K.

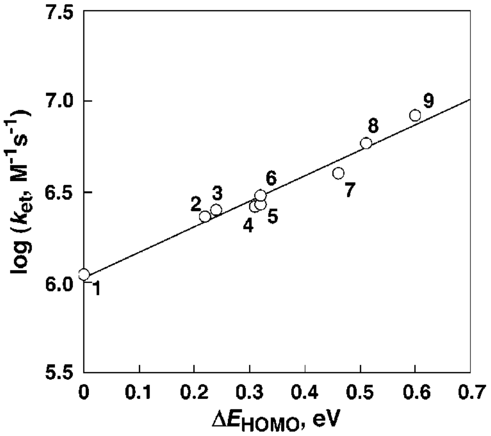

Figure 10. Plot between log k_{et} and ΔE_{HOMO} based on the data in Table 1.

photoinduced electron transfer from $^3C_{70}$* to Cl_4Q in frozen PhCN at 193 K under photoirradiation with a high-pressure mercury lamp as shown in Figure 9a. As is the case for C_{60} (Figure 2a), two isotropic ESR signals ($g = 2.0068$ and $g = 2.0017$) are observed in Figure 9a. The former is attributed to $Cl_4Q^{•-}$ and the latter is assigned to $C_{70}^{•+}$. In contrast to the case of $C_{60}^{•+}$ ($g = 2.0024$ in Figure 2), the g value of $C_{70}^{•+}$ is smaller than the free spin value (2.0023). When C_{70} is replaced by a functionalized C_{70} (**9**), the g value of $\mathbf{9}^{•+}$ (2.0012) becomes even smaller as compared to $C_{70}^{•+}$. These g values are listed in Table 1 together with those of other fullerenes obtained in a similar manner.

Relationship between Rates of Electron-Transfer Oxidation of Fullerene Triplet Excited States and the HOMO Energies. The k_{et} values of Sc^{3+}-promoted photoinduced electron transfer from the triplet excited states of a series of fullerenes to *p*-chloranil were determined as for the case of C_{60} and C_{70} (vide supra) and these values are listed in Table 1. The k_{et} value also increases with increasing the cage size of the fullerenes (Table 1). Such an increase in the k_{et} value may be primarily ascribed to the higher HOMO energies upon the derivatization of C_{60} and C_{70} since the ionization energies of fullerenes are reported to decrease for derivatized C_{60} and higher fullerenes.[19−22] Since the HOMO levels of fullerenes calculated by the semiempirical MNDO method are shown to be well-correlated with the one-electron oxidation potentials of fullerenes,[5] an increase in the HOMO energy relative to C_{60} (ΔE_{HOMO}) has been calculated for each fullerene in Table 1 (see Experimental Section). A plot between log k_{et} and ΔE_{HOMO} is shown in Figure 10, where there is a good linear correlation between them. Such a linear correlation suggests that the electron-transfer oxidation reactivities of the triplet excited states of fullerenes to *p*-chloranil are largely determined by the HOMO energies of fullerenes when the triplet energies remain virtually the same among the fullerenes.

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Supporting Information Available: Transient absorption spectra of $^3C_{60}$* (S1, S2), UV−vis spectral changes in electron transfer from CoTPP to Q in the presence of Sc^{3+} (S3), transient absorption spectra of $\mathbf{5}^{•+}$ (S4), and time-profile and transient absorption spectra observed in the photoinduced electron transfer from $^3\mathbf{9}$* to Cl_4Q in the presence of Sc^{3+} (S5) (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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