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Photoinduced Electron Transfer between C_{60}-Pendant Calixarene and Captured Electron Donor: Improvement of Electron-Transfer Efficiency by Applying Host−Guest Chemistry

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A photoinduced electron transfer between C_{60} connected with calixarene (calix-C_{60}) and a molecule in which aniline and ammonium are connected (ammonium aniline), in which the ammonium moiety is included in the calixarene, has been investigated. By connecting it with calixarene, C_{60} is given the ability to interact with the primary alkylammonium. In the calix-C_{60}/ammonium aniline system, the calixarene moiety of calix-C_{60} is capable of interacting with the ammonium moiety to form a donor−acceptor dyad via the cation-π-type inclusion mechanism in the solution. When a selective pulse laser irradiates the C_{60} moiety of the calix-C_{60}/ammonium-aniline dyad, C_{60} anion radical formation was observed in high quantum yield ($= 0.95$). From transient spectroscopies, it is confirmed that the electron-transfer proceeds through the dissociation of the exciplex of $^3(C_{60}\text{-aniline})^*$ in the calix-C_{60}/ammonium aniline system. By applying interaction between calixarene and ammonium, the electron transfer is accelerated in dyad, greatly increasing the quantum yield for electron transfer. The produced radical anion of the C_{60} moiety persists for about 1 ms, and the back electron-transfer process obeys second-order kinetics, indicating that the radical anion of the C_{60} moiety and the radical cation of the aniline moiety are solvated separately. A novel strategy for constructing a new class of efficient electron-transfer systems by using a calixarene as a reagent capture unit was demonstrated.

Introduction

Intramolecular electron-transfer processes of various donor−acceptor covalently linked systems have been intensely studied in recent research with the intent of applying an effective light-harvesting system to energy conversion/storage, or to generate reactive organic radicals.[1,2] These donor−acceptor dyad and triad molecules are also important as biomimetic model compounds when considering the high-yield photosynthesis systems found in nature. In general, covalently linked intramolecular electron transfer systems exhibit high yields for “forward” photoinduced electron transfer between photoexcited sensitizers and quenchers. However, it is difficult to control the fast intramolecular “back” electron transfer rates between photogenerated radical cation and anion. The fast back-electron-transfer process will suppress the overall quantum yield for reaction systems such as a photocurrent generation. Long-lived charge-separated state formation (establishment of a small rate for back electron transfer) has been reported in high-tactically designed donor−acceptor and electron-mediator systems in only exceptional cases.[2b−e]

Recently, some interesting sensitizing molecules which are connected with functional combination units, such as crown ethers, pyridines, and calixarenes have been reported.[3,4] These sensitizers can be connected further with functional molecules using their combination units (by ligand−metal interaction, hydrogen bonding, etc.), and their photochemical properties and reactivities, which are favorable for electron-transfer systems, can be controlled. In coordinated dyads between metal porphyrin and pyridine-C_{60} systems, for example, effective forward intramolecular electron transfer via ligand−metal interaction and slow intermolecular back electron transfer have been observed.[3a,b,f] These findings suggest that forward- and back-electron-transfer rates can be controlled by introducing the noncovalent bonding between various electron donors and acceptors. For example, in the noncovalently linked dyad molecule, efficient photoinduced electron-transfer systems can be realized by fast intramolecular “forward” electron transfer followed by slow intermolecular “back” electron transfer after breaking the bonding between donor and acceptor.

In the present study, we have constructed a novel noncovalently linked photoreactive dyad by applying supramolecular assembly utilizing host−guest chemistry. Homooxa[3]calixarene-moiety can capture and extract the primary ammonium derivative with high inclusion constants.[5] By connecting C_{60} with a calixarene moiety (calix-C_{60}), the C_{60} moiety gains the ability to capture primary ammonium derivatives of electron donors; the connected molecule is expected to show effective intramolecular “forward” electron transfer and to control intermolecular “back” electron transfer (Scheme 1). In this paper, we will report the enhanced quantum yield and extended lifetime of radical ions by applying host−guest chemistry between a calixarene-

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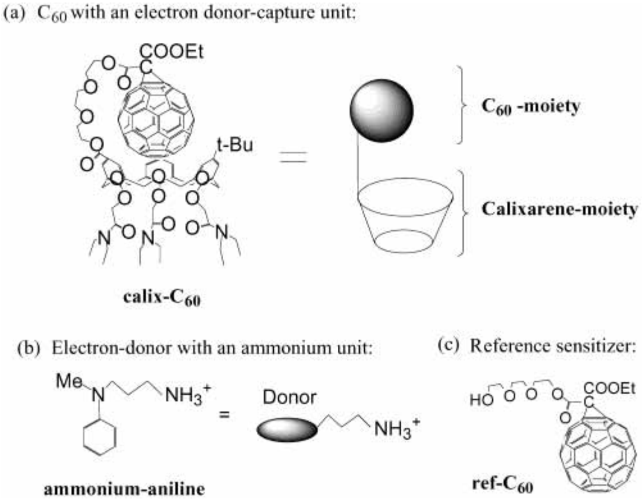
SCHEME 1



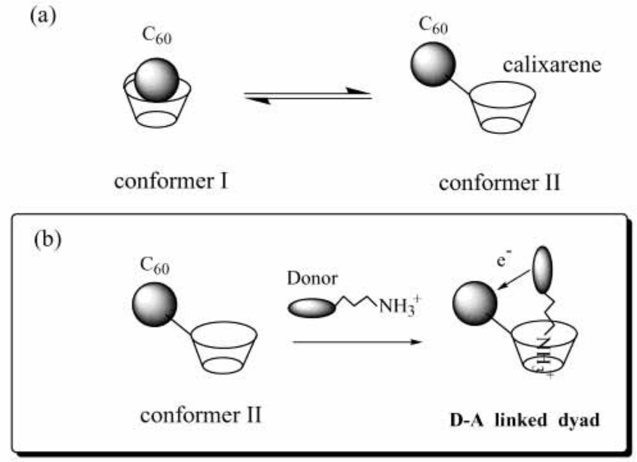
C_{60}-connected molecule and a primary ammonium derivative of methylaniline (ammonium aniline).

Experimental Section

Materials. Homooxa[3]calixarene-C_{60}-connected molecule (calix-C_{60}; Scheme 1a) and a reference C_{60} derivative (ref-C_{60}; Scheme 1c) were prepared by the method described in our previous paper.[6] The primary ammonium derivative of *N*-methylaniline (ammonium-aniline; Scheme 1b) was obtained by the protonation of the corresponding *N*-(3-aminopropyl)-*N*-methylaniline (Tokyo Kasei Kogyo Co. Ltd.) with one equimolar of HCl. The product was recrystallized twice by methanol and ether and dried under vacuo at room temperature in the dark. Anal. Calcd. for $C_{10}H_{17}N_2Cl$: C, 59.84; H, 8.53; N, 13.96. Found: C, 59.88; H, 8.56; N, 14.03 (%). Tetrakis (dimethylamino)ethylene (TDAE) was purchased from Aldrich and used as received. Distilled chloroform was used as solvent.

Instrumentation. The ^{1}H NMR spectra were obtained on a Bruker DRX-600 (600 MHz) spectrometer. Steady-state absorption and emission spectra in the vis/near-IR region were measured with a JASCO V-570DS spectrophotometer and a Shimadzu RF-5300PC spectrophotometer, respectively. The reduction/oxidation potentials were estimated by differential pulse technique with a scan rate of 100 mV/s in dry chloroform saturated with Ar at room temperature. Platinum electrodes were employed as working and counter electrodes. Tetrabutylammonium perchlorate (0.1 M) was used as the supporting electrolyte. A pseudo-reference electrode (Ag/Ag^+) was calibrated by the authentic potential of ferrocene. All electrochemical measurements were carried out in the dark. Time-resolved fluorescence spectra were measured by a single photon counting method using SHG (410 nm) of a Ti:sapphire laser (Spectra Physics, Tsumami 3950-L2s, 1.5 ps fwhm) and a streak scope (Hamamatsu Photonics, C4334−01) equipped with a polychromator. Transient absorption spectra and the absorption−time profiles of transient species were measured by the selective excitation of the C_{60} moiety with 600 nm laser light from an OPO laser (HOYA continuum Surelite OPO, 6 ns fwhm, and 14 mJ /pulse). For the transient absorption spectra in the near-IR region, an InGaAs−PIN photodiode module (Hamamatsu Photonics G5125−10) was employed as a detector for a probe light from a steady 150 W Xe-lamp equipped with cutoff filters to avoid the further photolysis. A sample solution in a rectangular quartz reaction cell (optical path = 1 cm) was deaerated by Ar gas bubbling for 20 min before measurements.

SCHEME 2



Results and Discussion

Structure and Interaction in the Ground State. ^{1}H NMR measurements have been made to confirm the host−guest complex of the calixarene moiety of calix-C_{60} and ammonium moiety of ammonium aniline. Parts a and b of Figure 1 show the ^{1}H NMR spectra of ammonium aniline and calix-C_{60} in $CDCl_3$, respectively. Calix-C_{60} gives a complicated ^{1}H NMR spectrum reflecting the mixture of two environmentally sensitive types of conformers (formation of self-inclusion complex) in $CDCl_3$ (conformers **I** and **II**; Scheme 2a).[6] With the addition of ammonium aniline, the ^{1}H NMR signals of calix-C_{60} and ammonium aniline changed significantly; the ^{1}H NMR signals of conformer **I** decreased and the NMR signals of conformer **II** and ammonium aniline varied as shown in parts c and d of Figures 1. It is reported that homooxacalixarenes can include an ammonium group of *n*-$BuNH_3^+$ from the direction of its phenyl groups (upper rim).[5] From the changes of ^{1}H NMR signals, it can be deduced that the binding species between conformer **II** and ammonium aniline exists as shown in Scheme 2b. The aniline-moiety is arranged in the direction of the upper rim of calixarene moiety. ^{1}H NMR peaks were assigned from observations of ^{1}H−^{1}H 2D COSY and ^{1}H VT NMR.[5,6] These ^{1}H NMR measurements in the presence of sufficient ammonium aniline have shown that calix-C_{60} can make a linked dyad molecule with ammonium aniline and exists predominantly as conformer **II** with its calixarene cavity occupied by the ammonium moiety of ammonium aniline.

Calix-C_{60} (Figure 2) and ref-C_{60} show similar absorption spectra to those typical of C_{60} derivatives. The absorption spectrum of the mixture consisting of calix-C_{60} and ammonium aniline in chloroform is almost identical with the superposition spectrum of each compound, indicating that the charge-transfer (CT) interaction between the C_{60} moiety and the aniline moiety is evidently weak in the ground state. It is reported that the CT interaction between C_{60} and anilines provide relatively small association constants for the complex formation,[7] suggesting that C_{60} and aniline form the CT complex in the ground state only with higher concentrations of ammonium aniline (>0.1 M).

Electron Transfer in the Singlet Excited States of Calix-C_{60}. Contribution of excited singlet states of calix-C_{60} (^{1}(calix-C_{60})*) to the charge separation can be indicated by the measurements of steady-state/time-resolved fluorescence spectroscopy of calix-C_{60} chloroform solution. Figure 3a shows the steady-state fluorescence spectra in the presence of ammonium-

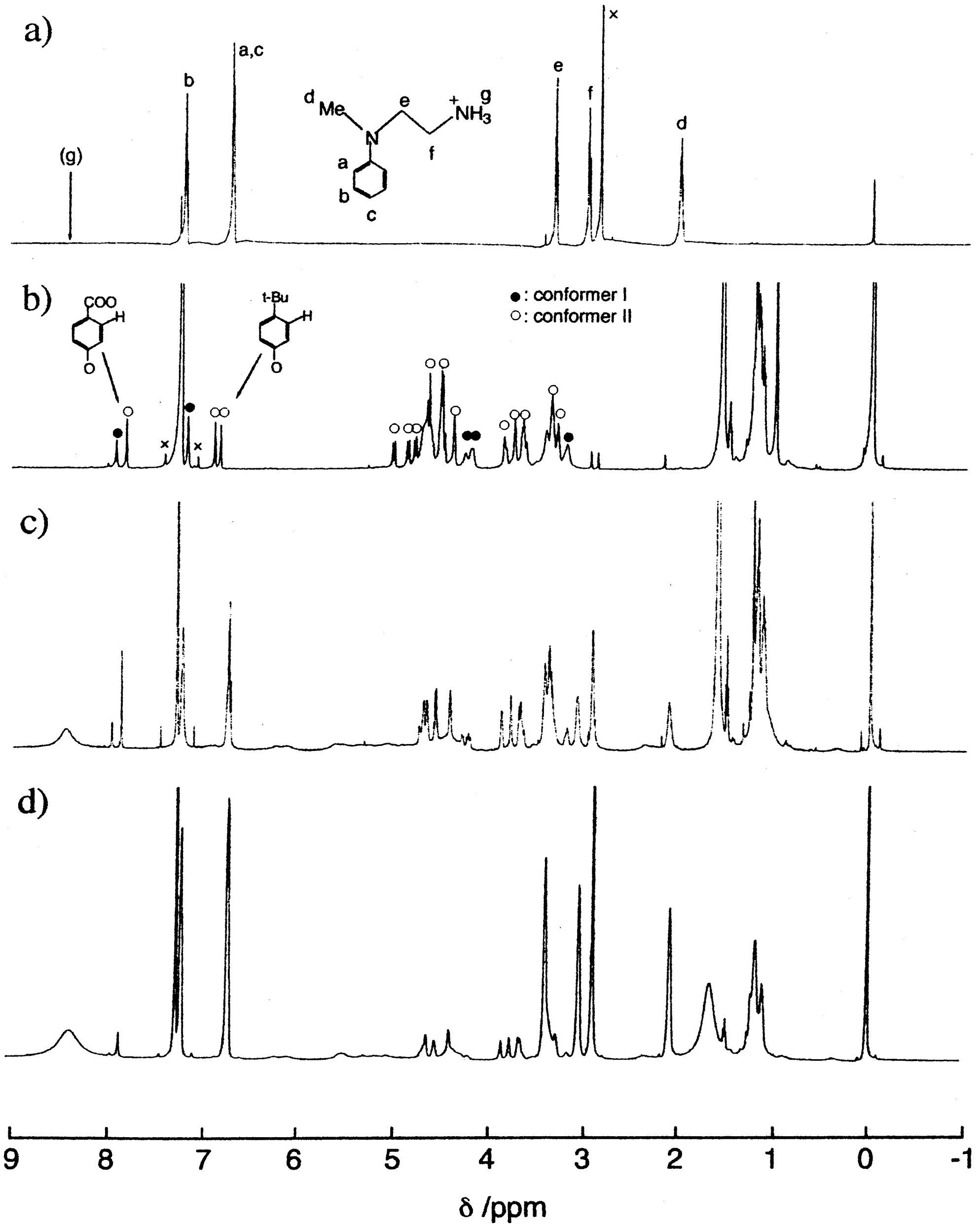


Figure 1. ^{1}H NMR spectra of (a) ammonium aniline, (b) calix-C_{60}, (c) calix-C_{60} and ammonium-aniline mixed solution ([ammonium aniline] = 2.0 mM), (d) calix-C_{60} and ammonium-aniline mixed solution ([ammonium aniline] = 8.0 mM); [calix-C_{60}] = 1.0 mM in $CDCl_3$, room temperature.

aniline. With the addition of ammonium aniline, a small decrease of fluorescence intensity was observed, which reached the minimum (a decrease of about 20%) at [ammonium aniline] = 2.0 mM. Picosecond time-resolved fluorescence measurements showed that very small quenching of fluorescence of the excited singlet calix-C_{60} (^{1}(calix-C_{60})*) occurs with the addition of 2.0 mM ammonium-aniline (τ_f was changed from 1.27 to 1.17 ns with the addition of ammonium aniline; inset of Figure 3). Slight fluorescence quenching was also observed the in ^{1}(ref-C_{60})*/ammonium-aniline system for the reference C_{60} derivative, which has no calixarene moiety. It is plausible that this decrease of fluorescence intensity is attributed to the intermolecular interaction between ^{1}(ref-C_{60})* and aniline moiety and/or to the conformational change between conformers **I** and **II**. These fluorescence studies suggest that the contribution of intramolecular and intermolecular electron transfer via ^{1}(calix-C_{60})* is very small because of the weak electron-donor ability of the aniline moiety and of the short lifetime of ^{1}(calix-C_{60})*.

$$\text{calix-C}_{60} \xrightarrow{h\nu} {}^1(\text{calix-C}_{60})^* \xrightarrow[\text{slow}]{\text{ammonium-aniline}\;/\!/} (\text{calix-C}_{60})^{\bullet-} + (\text{ammonium-aniline})^{\bullet+} \qquad (1)$$

Electron Transfer of Triplet Excited State of Calix-C_{60} in the C_{60}-Aniline Dyad: Nanosecond Laser Flash Photolysis. Figure 4A shows the transient absorption spectra obtained by 600 nm selective nanosecond pulse laser excitation of C_{60} moiety in the calix-C_{60}/ammonium-aniline Ar-saturated chloroform solution. The transient absorption band at 700 nm that appeared immediately after the laser exposure can be attributed to the triplet excited state of C_{60} moiety.[8] With the decay of ^{3}(calix-C_{60})*, new absorption bands appeared at 410 and 1040 nm, which can be attributed to (ammonium aniline)$^{\bullet+}$ and (calix-C_{60})$^{\bullet-}$, respectively (the assignment of (calix-C_{60})$^{\bullet-}$ transient absorption is described below), indicating that the photo reduction of calix-C_{60} proceeds effectively via ^{3}(calix-C_{60})*.[8]

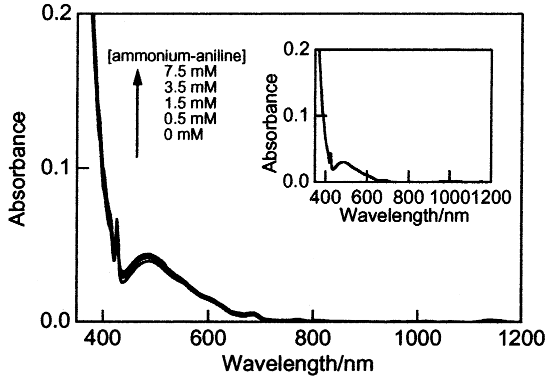


Figure 2. Absorption spectra of calix-C_{60} in the presence of ammonium aniline; [calix-C_{60}] = 0.05 mM in chloroform. Inset: absorption spectra of ref-C_{60}.

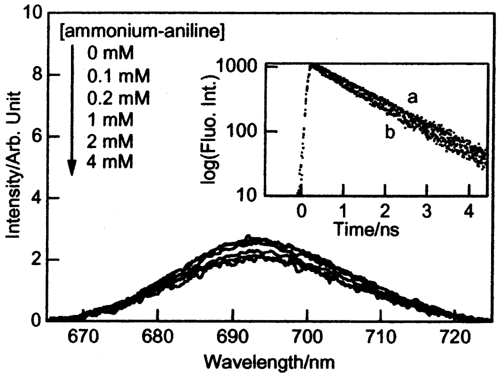


Figure 3. Steady-state fluorescence spectra of calix-C_{60} in the presence of ammonium aniline. [calix-C_{60}] = 0.05 mM. Inset: time-resolved fluorescence profile: (a) fluorescence decay of calix-C_{60}, (b) calix-C_{60} in the presence of ammonium aniline (2.0 mM).

$$\text{calix-C}_{60} \xrightarrow[\text{isc}]{h\nu} {}^3(\text{calix-C}_{60})^* \xrightarrow{\text{ammonium-aniline}} (\text{calix-C}_{60})^{\bullet -} + (\text{ammonium aniline})^{\bullet +} \quad (2)$$

On the other hand, laser flash photolysis of the ref-C_{60}/ammonium-aniline mixed system, which cannot form a donor−acceptor dyad because of the absence of calixarene moiety as a connecting part, gives the similar transient spectrum to the triplet excited state of pristine C_{60} immediately after laser exposure. However, the formations of (ref-C_{60})$^{\bullet -}$ and (ammonium aniline)$^{\bullet +}$ were not observed as shown in Figure 4B. In the simple mixed solution of ref-C_{60} and ammonium aniline, electron transfer between ^{3}(ref-C_{60})* and ammonium aniline rarely occurs in chloroform.

To evaluate the kinetic parameters and the possible reaction mechanisms for electron transfer, the dependence of the pseudo-first-order decay rate constants of ^{3}(C_{60} moiety)* (k_{obs}) on the ammonium-aniline concentration was analyzed (Figure 5). In the ref-C_{60}/ammonium-aniline system, the decay of ^{3}(ref-C_{60})* obeys pseudo-first-order kinetics, and the pseudo-first-order plot of ^{3}(ref-C_{60})* gives a straight line. The second-order quenching rate constant for ^{3}(ref-C_{60})* (k_q) was estimated from a slope of the fitted calculation line to be a very small value ($k_q = 5.0 \times 10^4$ M^{-1}s^{-1}), which indicates that the intermolecular electron transfer between ^{3}(ref-C_{60})* and ammonium aniline is not feasible. The ref-C_{60}/ammonium aniline/homooxa[3]calixarene (Scheme 3) mixed system leads to the same observation.

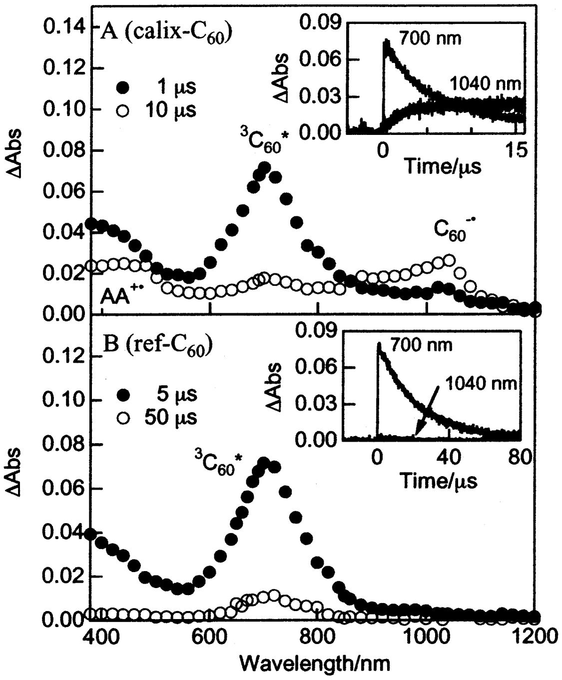


Figure 4. Transient absorption spectra obtained by nanosecond laser light; (A) calix-C_{60}/ammonium-aniline system, (B) ref-C_{60}/ammonium-aniline system. [C_{60} derivatives] = 0.05 mM, [ammonium aniline] = 2.0 mM. Inset: time−absorption profiles. AA$^{+\bullet}$ = cation radical of ammonium aniline.

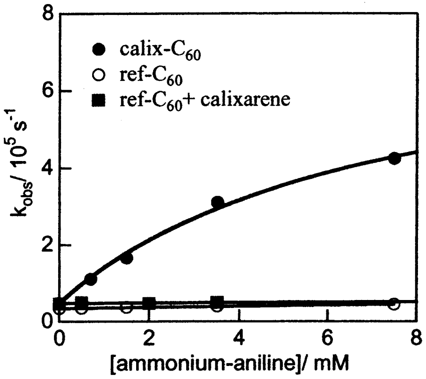
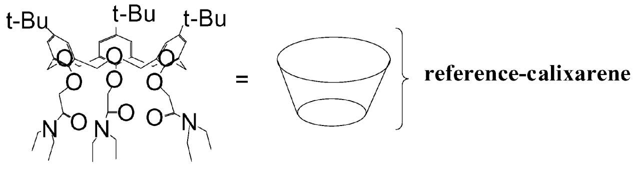


Figure 5. Pseudo-first-order plot for ^{3}(C_{60} derivatives)* decay obtained by time-resolved analysis. [C_{60} derivatives] = 0.05 mM; [calixarene] = 0.05 mM.

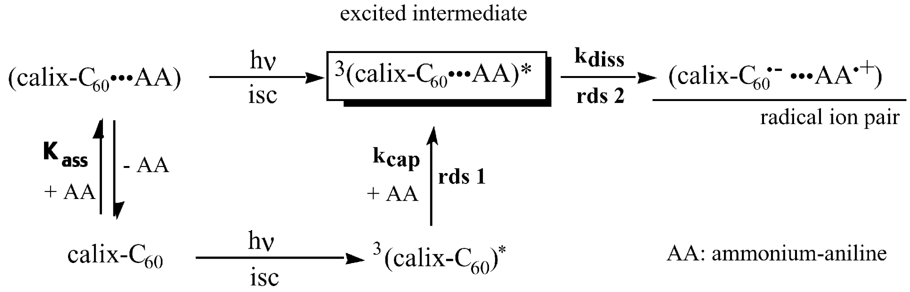
SCHEME 3



In contrast, for the calix-C_{60}/ammonium-aniline dyad system, the k_{obs} values were defined as large values compared with that of the ref-C_{60}/ammonium-aniline system, and the pseudo-first-order plot results in a saturating curve. This saturation curve indicates that the k_q values contain a dynamic formation process of a reactive photoexcited intermediate (exciplex) before electron transfer.[9] In this case, with assistance of inclusion property between calixarene and ammonium, the complexation ability of excited-intermediates between ^{3}(calix-C_{60})* and aniline units is greatly increased. Therefore, an intramolecular electron transfer can be reasonably expected as shown in Scheme 4.

With the lower concentration of ammonium aniline, there exists the empty cavity species of calix-C_{60} in the solution; however, the photoexcitation of calix-C_{60} to ^{3}(calix-C_{60})* will increase the electron-acceptor ability of C_{60} moiety, resulting

SCHEME 4



in the capturing of ammonium aniline to form exciplex (^{3}(calix-C_{60}•••AA)*), which dissociates into the radical ion pair (calix-$C_{60}^{\bullet-}$•••$A^{\bullet+}$). Thus, the AA capture of ^{3}(calix-C_{60})* may be the rate-determining step for the decay of empty ^{3}(calix-C_{60})* in low concentration of ammonium aniline (**rds 1** in Scheme 4).

With the higher concentration of ammonium aniline, the pseudo-first-order rate constants (k_{obs}) were obtained for the decay of ^{3}(calix-C_{60}•••A)*; such k_{obs} values in the pseudo-first-order plot begin to saturate, which indicates that kinetic rate-determining step will change to the dissociation of the excited intermediate (^{3}(calix-C_{60}•••A)*) into (calix-$C_{60}^{\bullet-}$•••$AA^{\bullet+}$) as shown in **rds 2** in Scheme 4. On assuming equations (3.1 and 3.2) for reaction Scheme 4, the two rate constants for ^{3}(calix-C_{60})* quenching are estimated to be 4.4×10^7 $M^{-1}s^{-1}$ (**rds 1**, capturing of ammonium aniline, second-order rate constant; k_{cap}) and 4.3×10^5 s^{-1} (**rds 2**, deactivation of triplet calix-C_{60}-ammonium-aniline complex by electron transfer, first-order rate constant; k_{diss}) by curve fitting. The association constant (K_{ass}) between calix-C_{60} and ammonium aniline was estimated to be 150 M^{-1} from the fitting calculation of the saturating curve.

$$k_{obs} = \left(\frac{[\text{calix-}C_{60}\cdots\text{AA}]}{[\text{calix-}C_{60}]_{init}}\right)k_{diss} + \left(\frac{[\text{calix-}C_{60}]_{init} - [\text{calix-}C_{60}\cdots\text{AA}]}{[\text{calix-}C_{60}]_{init}}\right)k_{cap}[\text{AA}] \quad (3.1)$$

$$K_{ass} = \frac{[\text{calix-}C_{60}\cdots\text{AA}]}{([\text{calix-}C_{60}]_{init} - [\text{calix-}C_{60}\cdots\text{AA}])([\text{AA}] - [\text{calix-}C_{60}\cdots\text{AA}])} \quad (3.2)$$

where AA is ammonium aniline and $[\text{calix-}C_{60}]_{init} = 0.05$ mM.

From the oxidation potential of ammonium aniline (+0.320 V vs ferrocene/ferrocenium in chloroform), the reduction potentials of ref-C_{60} and calix-C_{60} (−1.18, and −1.14 V vs ferrocene/ferrocenium in chloroform, respectively) and the lowest triplet energies of ref-C_{60} and calix-C_{60} (1.50 eV in 77 K-toluene:CH_2I_2 = 1:1 (v/v)),[10] the free energy changes of electron transfer (ΔG_{et}) were estimated as +9.87 (kcal mol^{-1}; ref-C_{60}/ammonium-aniline) and +8.95 (kcal mol^{-1}; calix-C_{60}/ammonium aniline). From these ΔG_{et} values, very small k_q (k_{obs}) values were predicted. The kinetic findings about the evaluated small k_q (k_{obs}) value for ref-C_{60}/ammonium-aniline system are in good agreement with this prediction. On the other hand, the k_{obs} value for calix-C_{60}/ammonium-aniline dyad system is far larger than the predicted k_{obs} value derived from electrochemical parameters, which also indicates that the reaction intermediate exists in the intramolecular electron-transfer process of the C_{60}-aniline dyad molecule. These observations clearly imply the enhanced ability of calixarene moiety for the intramolecular electron transfer by forming the reactive photoexcited intermediates.

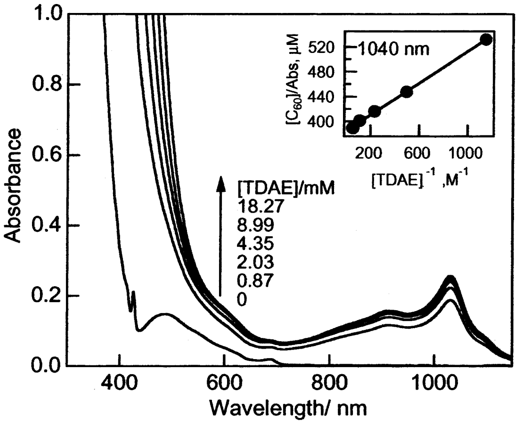


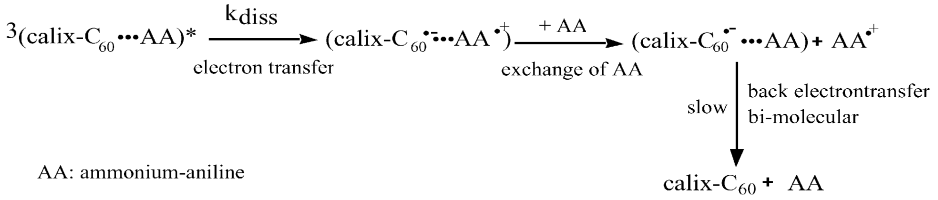
Figure 6. Spectral-changing of calix-C_{60} by the addition of TDAE in Ar-saturated chloroform. [calix-C_{60}] = 0.05 mM. Inset: Benesi−Hildebrand plot of steady-state absorption of C_{60} anion radical.

Efficiency for Intramolecular Electron Transfer. The efficiency for electron transfer via ^{3}(calix-C_{60})* can be evaluated from the saturated ratio values of $[\text{calix-}C_{60}^{\bullet-}]_{max}$:$[^3(\text{calix-}C_{60})^*]_{initial}$, which are calculated by using the molar absorption coefficients of the transient species.[11] Unknown spectroscopic parameters for the transient species were estimated as described below.

The assignment of (calix-C_{60})$^{\bullet-}$ and (ref-C_{60})$^{\bullet-}$ absorption bands and molar absorption coefficients were performed by the observation of steady-state absorption spectra of calix-C_{60} in the presence of tetrakis(diethylamino)ethylene (TDAE) in Ar-saturated chloroform (Figure 6). Tetrakis(diethylamino)ethylene is a known reductant for fullerene derivatives, and produces 1:1 ion pairs in less polar solvents.[12] The molar absorption coefficient of (calix-C_{60})$^{\bullet-}$ can be estimated by the Benesi−Hildebrand fitting calculation assuming a 1:1 complex formation (inset of Figure 6; estimated ϵ of (calix-C_{60})$^{\bullet-}$ at 1040 nm = 4000 $M^{-1}cm^{-1}$). The observation of (ref-C_{60})$^{\bullet-}$ gives the same absorption bands as that of (calix-C_{60})$^{\bullet-}$. The ^{3}(calix-C_{60})* molar absorption coefficient was estimated at 7000 M^{-1} cm^{-1} (at 700 nm) by considering a yield for intersystem crossing (isc) from ^{1}(calix-C_{60})* to ^{3}(calix-C_{60})* and comparing a transient absorption intensity of $^3C_{60}$* (ϵ at 740 nm = 18800 M^{-1} cm^{-1})[10] under optical/instrumental conditions that are critically the same.[13] The yield for intersystem crossing (ϕ_{isc}) from ^{1}(calix-C_{60})* to ^{3}(calix-C_{60})* was indirectly calculated to be 0.95 from the quantum yield for singlet oxygen ($^1O_2$*) formation via T−T energy transfer from ^{3}(calix-C_{60})* to O_2 by monitoring an emission of $^1O_2$* at the peak of 1270 nm.[13,14] This approach was supported by the fact of quantitative energy transfer from ^{3}(calix-C_{60})* to O_2 (obtained rate constant for energy transfer; k_{en} = 3.0×10^9 M^{-1} s^{-1}).

Figure 7 shows the efficiency curve for electron transfer from ammonium aniline to ^{3}(calix-C_{60})* with the intramolecular

SCHEME 5



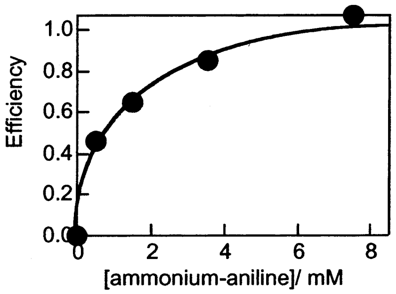


Figure 7. The efficiency plot for photoinduced electron transfer via ^{3}(calix-C_{60})* obtained by laser flash photolysis. Efficiency = [(calix-C_{60})$^{•-}$]$_{max}$/[^{3}(calix-C_{60})*]$_{initial}$.

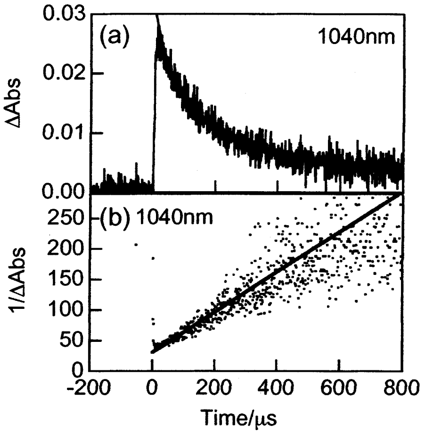


Figure 8. Time profiles of radical ion in 100-μs-order time scale: (a) time-absorption profile of (calix-C_{60})$^{•-}$, (b) second-order kinetic analysis for the back-electron-transfer rate monitored at (calix-C_{60})$^{•-}$.

electron-transfer mechanism. The curve shows a tendency to saturate at higher concentrations of ammonium aniline. From the maximal ratio ([calix-$C_{60}$$^{•-}$]$_{max}$:[^{3}(calix-$C_{60}$)*]$_{initial}$), the efficiency ($\phi_{et}$) for electron transfer via ^{3}(calix-C_{60})* can be evaluated to be 1.0. This ϕ_{et} value is more than 50 times larger than the ϕ_{et} for ref-C_{60}/ammonium-aniline system ($\phi_{et} < 0.02$), and we can deduce that the acceleration effect of calixarene-ammonium host−guest inclusion is very large. The observed $\phi_{et} = 1.0$ implies that all ^{3}(calix-C_{60})* species converge to the exciplex, which dissociates completely into radical ion pair in chloroform. The quantum yield (Φ_{et}) for electron transfer from ^{1}(calix-C_{60})* to (calix-C_{60})$^{•-}$ (photon to radicals) can be evaluated by the relation $\Phi_{et} = \phi_{isc}\phi_{et}$. The Φ_{et} value of calix-C_{60}/ammonium-aniline system can thus be evaluated as 0.95.

The Lifetime of Radical Ions. After the intramolecular electron transfer, each radical ion, (calix-C_{60})$^{•-}$ and (ammonium aniline)$^{•+}$, persisted up to 1 ms (half-life = 0.4 ms) as shown in Figure 8. This value is larger than those of typical donor−acceptor covalently linked dyad systems such as C_{60}-triphenylamine (220 ns) and C_{60}-aniline dyad (60 μs in clusters).[15,16] The lifetimes of radical ions in our present system are long enough for use as an effective electron pool, which can be applied to the second electron transfer in some photoenergy storage/conversion systems. These radical species decayed in several hundred microsecond-order time scales; since the time profile according to second-order kinetics indicate that the back electron transfer occurs as bimolecular reactions, one can regard that (calix-C_{60})$^{•-}$ and (ammonium-aniline)$^{•+}$ act as independent species. This suggests that (calix-C_{60})$^{•-}$ and (ammonium aniline)$^{•+}$ are solvated separately, but are not the contact radical ion pair which leads to intramolecular back electron transfer with the first-order kinetics. Since the solvation ability of chloroform is weak owing to its low dielectric constant, the presence of solvent separated ion pair and free radical ions in the inclusion complex is hardly conceivable. As another possibility, one may consider some release process of (ammonium-aniline)$^{•+}$ from ion-pair dyad in the calixarene inclusion complex after the electron transfer. From the observed kinetics of ion radicals, it seems likely that the calixarene moiety of the ion-pair dyad dynamically exchanges the guest molecule unit (ammonium aniline). This dynamic exchange may lead to the release and dispersion of (ammonium aniline)$^{•+}$ to the bulk solution, because the population of ammonium-aniline which is not oxidized by excited calix-C_{60} is quite higher than that of (ammonium aniline)$^{•+}$. The proposed mechanism of the back electron transfer is summarized in Scheme 5. The reciprocal plot (second-order plot) of transient absorption of (calix-C_{60})$^{•-}$ is a straight line and derives the rate constant for back electron transfer ($k_{bet} = 1.3 \times 10^9$ M^{-1} s^{-1}), which is far smaller than the diffusion-controlled limit in chloroform ($k_{diff} = 1.1 \times 10^{10}$ M^{-1} s^{-1}).

Concluding Remarks

A new strategy for constructing highly effective electron transfer systems utilizing noncovalently linked donor−acceptor interaction is established. By applying the C_{60}-connected calixarene as a host for ammonium-aniline, the intramolecular-type forward electron transfer via the triplet exciplex takes place between the C_{60} moiety and aniline moiety, producing (calix-C_{60})$^{•-}$ and (ammonium aniline)$^{•+}$ ($\Phi_{et} = 0.95$), while electron transfer via the singlet excited state is less effective and no substantial electron transfer takes place between the triplet excited state of ref-C_{60} and aniline in the mixture system in chloroform ($\Phi_{et} < 0.02$). In the host−guest system, the back electron transfer between (calix-C_{60})$^{•-}$ and (ammonium-aniline)$^{•+}$ is slow; thus, the lifetimes of ion radicals are surprisingly extended compared to that of the covalent dyad system and persist for more than 1 ms. From these results, we have concluded that the introduction of host−guest inclusion property between calixarene and ammonium as a connection unit of donor (aniline)−acceptor (C_{60}) system is very meaningful in improving the quantum yield (total yield) for photoinduced electron transfer.

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References and Notes

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