Fullerene acting as an electron donor in a donor–acceptor dyad to attain the long-lived charge-separated state by complexation with scandium ion†

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A long-lived charge-separated (CS) state of fullerene–trinitrofluorenone linked dyad in which fullerene acts as an electron donor is formed by photoinduced electron transfer from C_{60} to TNF in the presence of $Sc(OTf)_3$; the CS lifetime is determined as 23 ms in PhCN at 298 K.

Fullerene, which has a highly delocalized three-dimensional π-system, is suitable for efficient electron transfer (ET) because the uptake or release of electrons results in minimal structural and solvation changes upon ET.[1] Consequently, a formation of the long-lived CS state has been examined by using fullerene-based D–A linked dyad systems in which fullerene acts as an electron acceptor.[2–5] However, fullerene has so far been used only as an electron acceptor in D–A systems, because the ET oxidation of fullerene is much more difficult than the ET reduction.[6–8]

We have recently reported that photoinduced *intermolecular* ET oxidation of fullerene with *p*-benzoquinone is made possible by the addition of $Sc(OTf)_3$ (OTf^- = triflate) which can bind with the product of ET.[9] Such a strong binding of $Sc(OTf)_3$ with the radical anions of electron acceptors results in ET from electron donors to acceptors even though photoinduced *intramolecular* ET is energetically impossible in the absence of metal ion.[10,11] The elongation of the CS state lifetime of D–A linked dyads has been achieved by the addition of metal ions.[12,13] However, there has so far been no report on formation of the CS state of D–A dyads using fullerene as an electron donor in the presence of metal ions.

We report herein the photodynamics of a fullerene–trinitrofluorenone dyad (C_{60}–TNF as shown in Fig. 1)[14] in the absence and presence of $Sc(OTf)_3$. A long-lived CS state is formed by photoinduced ET from C_{60} to TNF in the presence of $Sc(OTf)_3$ upon photoexcitation of C_{60}–TNF, whereas only the triplet excited state of C_{60} ($^3C_{60}^*$) is formed in absence of $Sc(OTf)_3$.

The synthesis of C_{60}–TNF has been reported previously.[14] The differential pulse voltammograms (DPV) of C_{60}–TNF in deaerated benzonitrile (PhCN)[15] are shown in Fig. 2. The ratio of the current of DPV of the three reduction peaks is 1 : 2 : 1. By comparison

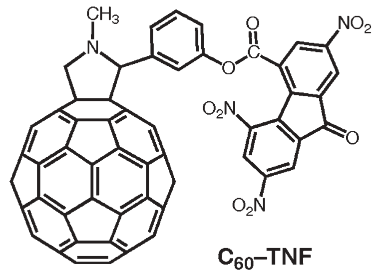

Fig. 1 Chemical structure of C_{60}–TNF dyad.

with those of the unlinked compounds, the first and second one-electron reduction processes occur at the TNF moiety. The second reduction peak due to $TNF^{•-}/TNF^{2-}$ is overlapped with the peak due to $C_{60}/C_{60}^{•-}$. The third peak is assigned to $C_{60}^{•-}/C_{60}^{2-}$.[14] On the other hand, the one-electron oxidation occurs at the C_{60} moiety of C_{60}–TNF. When $Sc(OTf)_3$ (30 mmol dm^{-3}) is added to a deaerated PhCN solution of C_{60}–TNF, a large positive shift is observed at the first one-electron reduction due to $TNF/TNF^{•-}$ as shown in Fig. 2(b).[16,17] The E_{red} value of TNF is changed from −0.40 V *vs.* SCE to +0.01 V in the presence of $Sc(OTf)_3$. Thus, $TNF^{•-}$ forms a strong complex with $Sc(OTf)_3$, which induces a decrease of the CS state energy.

Nanosecond laser excitation (λ = 430 nm) of C_{60}–TNF in deaerated PhCN results in formation of the triplet excited state of C_{60} ($^3C_{60}^*$; λ_{max} = 750 nm)[18] as shown in Fig. 3(a). The transient absorption disappeared completely 180 μs after laser excitation. The decay rate constant of $^3C_{60}^*$ is determined as 3.2×10^4 s^{-1}, which agrees with the reported value for $^3C_{60}^*$. The CS energy is

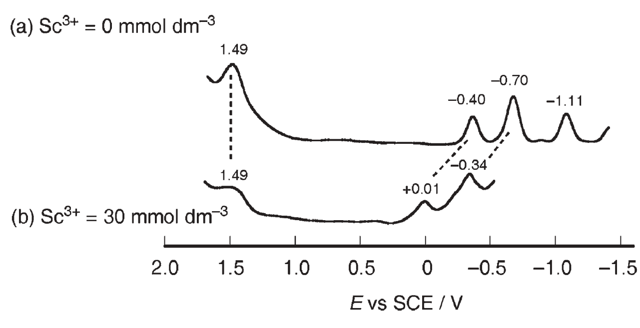

Fig. 2 (a) Differential pulse voltammograms of C_{60}–TNF dyad in deaerated PhCN containing Bu_4NClO_4 (0.1 mol dm^{-3}) in the absence and (b) in the presence of $Sc(OTf)_3$ (30 mmol dm^{-3}) at 298 K.

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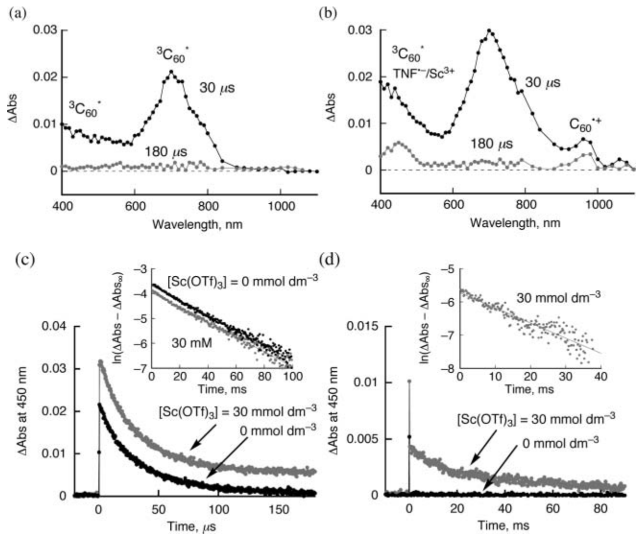
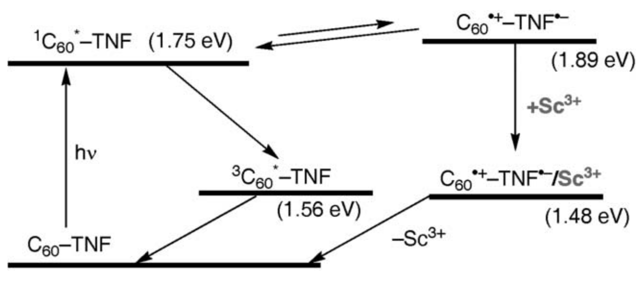


Fig. 3 Transient absorption spectra of C_{60}–TNF (0.1 mmol dm^{-3}) obtained by nanosecond laser flash photolysis in deaerated PhCN (a) in the absence and (b) in the presence of $Sc(OTf)_3$ (30 mmol dm^{-3}) taken at 30 and 180 μs after laser excitation (430 nm) at 298 K. Decay profiles of transient absorption at 450 nm in the absence (black) and the presence of $Sc(OTf)_3$ (30 mmol dm^{-3}, gray) in the (c) 100 μs and (d) 10 ms ranges. Inset: First-order plots for decay in the presence of $Sc(OTf)_3$.

determined from the one-electron redox potentials of C_{60}–TNF as 1.89 eV, which is larger than the values of the singlet and the triplet excited energy of C_{60} ($^1C_{60}$*: 1.75 eV; $^3C_{60}$*: 1.56 eV).[18] Thus, no photoinduced ET occurs from the C_{60} moiety to the TNF moiety as shown in the energy diagram in Scheme 1.

The addition of $Sc(OTf)_3$ (30 mmol dm^{-3})[17] to a PhCN solution of C_{60}–TNF, however, results in drastic change in the photodynamics from the formation of $^3C_{60}$* to ET to produce the CS state in which $TNF^{\bullet-}$ forms a complex with Sc^{3+} ($TNF^{\bullet-}/Sc^{3+}$; λ_{max} = 450 nm) at 180 μs after laser excitation, as shown in Fig. 3(b). The assignment of the absorption band at 450 nm due to the $TNF^{\bullet-}/Sc^{3+}$ complex was confirmed by that observed in the photoinduced ET reduction of the unlinked TNF with dimeric 1-benzyl-1,4-dihydronicotinamide[19] in the presence of Sc^{3+} (see ESI,† S1). The absorption spectrum of $TNF^{\bullet-}$ is significantly blue-shifted from 548 and 970 nm to 450 nm by the complexation with Sc^{3+} (see ESI,† S1). The appearance of the absorption band at 960 nm is clear indication of formation of $C_{60}^{\bullet+}$.[9] The quantum yield of the CS state was determined from the $C_{60}^{\bullet+}$ absorbance as 35%.[20,21]



Scheme 1

An external electron donor (*trans*-stilbene) was added to a PhCN solution of C_{60}–TNF in order to confirm the oxidizing ability of the CS state of C_{60}–TNF. The laser photoirradiation of a PhCN solution containing C_{60}–TNF, $Sc(OTf)_3$ (30 mmol dm^{-3}) and *trans*-stilbene (10 mmol dm^{-3}) results in formation of new transient absorption bands due to *trans*-stilbene radical cation (λ_{max} = 480 and 760 nm)[22] instead of the absorption band due to the radical cation of the C_{60} moiety, whereas the absorption band due to the $TNF^{\bullet-}/Sc^{3+}$ moiety is overlapped with that of *trans*-stilbene radical cation as shown in Fig. 4(a) (closed circles). No formation of *trans*-stilbene radical cation was observed in the absence of $Sc(OTf)_3$ as shown in Fig. 4(a) (open circles). This indicated that intermolecular ET from *trans*-stilbene to the $C_{60}^{\bullet+}$ moiety in $C_{60}^{\bullet+}$–$TNF^{\bullet-}/Sc^{3+}$ occurs to give *trans*-stilbene radical cation, because the one-electron oxidation potential of *trans*-stilbene (E_{ox} = 1.47 V *vs.* SCE)[23] is less positive than the one-electron reduction potential of the $C_{60}^{\bullet+}$ moiety (E_{red} = 1.49 V *vs.* SCE). When *trans*-stilbene is replaced by 1,2-dimethoxybenzene (E_{ox} = 1.45 V *vs.* SCE), the ET oxidation by $C_{60}^{\bullet+}$–$TNF^{\bullet-}/Sc^{3+}$ also occurs to give 1,2-dimethoxybenzene radical cation (λ_{max} = 410 and 1100 nm)[22c] as shown in Fig. 4(b). On the other hand, no ET oxidation was observed in the case of naphthalene (1.60 V) and pentamethylbenzene (1.58 V),[24] because the ET oxidation by the CS state is energetically impossible. Thus, it has clearly been shown that the CS state $C_{60}^{\bullet+}$–$TNF^{\bullet-}/Sc^{3+}$ can act as a strong oxidant.

The CS lifetime of $C_{60}^{\bullet+}$–$TNF^{\bullet-}/Sc^{3+}$ was determined by the decay profile of the transient absorption. The transient absorption at 450 nm due to $^3C_{60}$* decays to zero in the absence of Sc^{3+} (black line in Fig. 3(c)), whereas the absorption at 450 nm in the presence

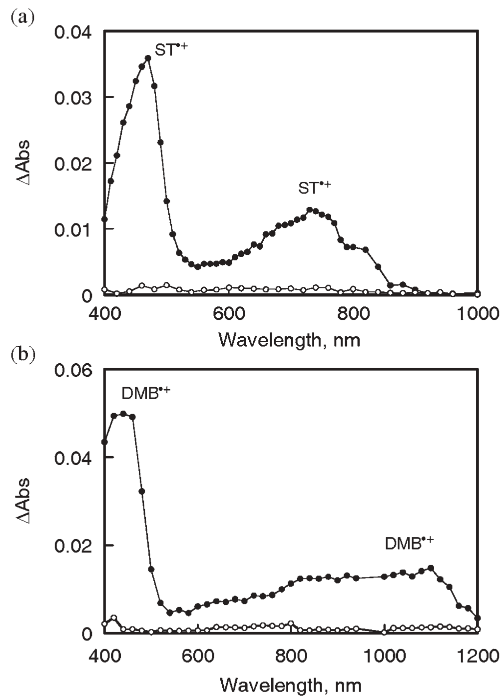


Fig. 4 Transient absorption spectra of C_{60}–TNF (0.1 mmol dm^{-3}) obtained by laser flash photolysis in a deaerated PhCN containing (a) *trans*-stilbene (ST) and (b) 1,2-dimethoxybenzene (DMB) in the absence (○) and presence of $Sc(OTf)_3$ (30 mmol dm^{-3}, ●) taken at 180 μs after laser excitation (430 nm) at 298 K.

of Sc^{3+} does not decay completely at 180 μs after the laser excitation (gray line in Fig. 3(c)). The residual absorption corresponds to that due to the CS state, decaying at prolonged reaction time as shown in Fig. 3(d). The first-order decay rate constant of the fast component in the presence of Sc^{3+} agrees with the value in the absence of Sc^{3+} (3.2×10^4 s^{-1}) as shown in the first-order plots (the inset of Fig. 3(c)). This indicates that no ET from $^3C_{60}*$ to the TNF moiety occurs in both the absence and presence of Sc^{3+}. In the absence of Sc^{3+}, ET from $^3C_{60}*$ to the TNF is highly endergonic and thereby energetically impossible as mentioned above (Scheme 1). The ET from $^3C_{60}*$ to TNF in the presence of Sc^{3+} becomes exergonic (−0.08 eV in Scheme 1), but the ET rate, which requires intermolecular ET activation by Sc^{3+}, may be much slower than the decay of $^3C_{60}*$ because of the small ET driving force.

On the other hand, ET from $^1C_{60}*$ to TNF is still energetically impossible, but the ET becomes highly exergonic (−0.27 eV) by the addition of 30 mmol dm^{-3} $Sc(OTf)_3$. Femtosecond laser excitation (λ = 430 nm) of C_{60}–TNF in deaerated PhCN results in formation of the $^1C_{60}*$ at 3 ps after laser excitation. The transient absorption of $^1C_{60}*$ is completely changed to $^3C_{60}*$ at 3000 ps (see ESI,† S3). The formation rate constant of $^3C_{60}*$ at 700 nm is determined to be 9.0×10^8 s^{-1}. The addition of $Sc(OTf)_3$ (30 mmol dm^{-3}) to a PhCN solution of C_{60}–TNF also results in formation of $C_{60}^{\bullet+}$ overlapped with the shoulder of absorption of $^3C_{60}*$, since the absorption change at 700 nm in the presence of Sc^{3+} is larger than that in the absence of Sc^{3+} (see ESI,† S2). The formation rate in the presence of Sc^{3+} is also determined as 9.0×10^8 s^{-1}, which is same as in the absence of Sc^{3+}. Thus, the CS state ($C_{60}^{\bullet+}$–$TNF^{\bullet-}$/Sc^{3+}) may be formed *via* ET from $^1C_{60}*$ to TNF and the subsequent strong binding of $TNF^{\bullet-}$ with Sc^{3+}, which makes the CS process possible (Scheme 1).

The slow decay component (Fig. 3(d)) results from the charge-recombination process. The lifetime of CS state is determined as 23 ± 4 ms in PhCN at 298 K from the first-order plot in the inset of Fig. 3(d). The CS lifetime remains the same irrespective of difference in concentrations of Sc^{3+} (1–30 mmol dm^{-3}).[25]

The activation enthalpy for the *intramolecular* back ET (BET) was determined from the slope of the Eyring plot as 24 kJ mol^{-1} (see ESI,† S3). Such a large temperature dependence of the BET rate indicates that the *intra*molecular BET process with the driving force of 1.48 eV is deeply in the Marcus inverted region, since the reorganization energy of BET is determined as 0.67 eV from the activation enthalpy using the Marcus theory.[26] No *inter*molecular BET of the CS state was observed because the *inter*molecular BET process is also slowed down in the Marcus inverted region as reported previously for the *inter*molecular ET oxidation of C_{60}.[27]

In summary, C_{60} has successfully been used as an electron donor that is linked with an electron acceptor in the presence of Sc^{3+} to attain the longest CS lifetime at 298 K (23 ± 4 ms) ever reported for electron donor–acceptor linked systems.

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