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Electron transfer reduction of a highly electron-deficient fullerene, $C_{60}F_{18}$

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Electron transfer reduction of a highly electron-deficient fullerene, $C_{60}F_{18}$, to the defluorinated anion, $C_{60}F_{17}^-$ occurs efficiently by a relatively weak one-electron reductant, *p*-chloranil radical anion; the one-electron reduction potential of $C_{60}F_{18}$ is evaluated as 0.04 V (*vs.* SCE) by comparison of the rate constant for electron-transfer from 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine to $C_{60}F_{18}$ with those of other one-electron reductants.

The fluorofullerene $C_{60}F_{18}$ has a unique structure: one half of the [60]fullerene cage is flattened and the hexagonal face at the centre of the fluorinated crown is fully aromatic.[1,2] At the curved face of $C_{60}F_{18}$, the [4 + 2] cycloaddition of anthracene occurs together with the oxidation of anthracene by $C_{60}F_{18}$ to yield anthraquinone as a by-product of the cycloaddition.[3] This indicates that $C_{60}F_{18}$ is a rather strong oxidant because of the very strongly electron-deficient planar region. Other halogenated fullerenes such as $C_{60}Cl_6$, $C_{60}Br_6$ and $C_{60}Br_8$ form charge-transfer complexes with organic donors and it is anticipated that increased electron withdrawal by the halogenated cage would increase electron-transfer reduction.[4,5] However, the actual reactivity of halogenated fullerenes in the electron-transfer reduction has yet to be examined.

We report herein the mechanism and the reactivity of the electron transfer reduction of $C_{60}F_{18}$ in benzonitrile (PhCN). The one-electron reduction potential of $C_{60}F_{18}$ is also reported.

Radical anions of *p*-benzoquinone derivatives are employed as one-electron reductants to reduce $C_{60}F_{18}$. Semiquinone radical anions in PhCN were prepared by comproportionation reactions of *p*-benzoquinone derivatives with the dianions obtained by the reaction of the corresponding hydroquinones with tetrabutylammonium hydroxide.[6] Tetramethyl-*p*-benzosemiquinone radical anion ($Me_4Q^{\cdot-}$) is known to reduce C_{60} to $C_{60}^{\cdot-}$ quantitatively.[7]

Upon mixing a PhCN solution of $C_{60}F_{18}$ with $Me_4Q^{\cdot-}$ (5.0×10^{-5} M), the absorption peak at 346 nm due to $C_{60}F_{18}$ disappears, accompanied by appearance of a new absorption band at 708 nm as shown in Fig. 1. No near-IR band is observed in contrast to the case of the reduction of C_{60} to $C_{60}^{\cdot-}$ which has a near-IR band at 1080 nm.[8]

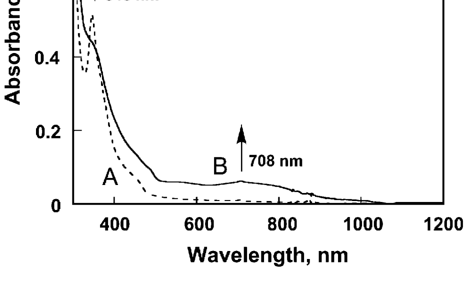
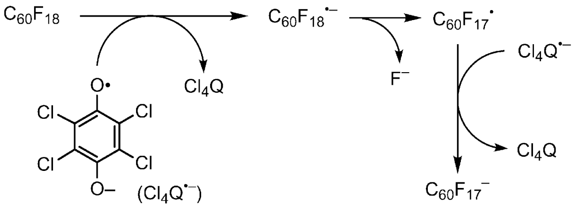


Fig. 1 VIS-NIR spectra of the PhCN solution of (A) $C_{60}F_{18}$ and (B) $C_{60}F_{18}$ with tetramethyl-*p*-benzosemiquinone radical anion (5.0×10^{-5} M) in deaerated PhCN at 298 K.

When $Me_4Q^{\cdot-}$ is replaced by the radical anion of *p*-chloranil ($Cl_4Q^{\cdot-}$) which is a much weaker electron donor, the electron-transfer reduction of $C_{60}F_{18}$ still occurs to afford the same absorption spectrum as observed in the case of the reduction by $Me_4Q^{\cdot-}$ (Fig. 1). Since the one-electron reduction potential (E^0_{red}) of Cl_4Q, (equivalent to the one-electron oxidation potential (E^0_{ox}) of $Cl_4Q^{\cdot-}$), is 0.01 V (*vs.* SCE), the E^0_{red} value of $C_{60}F_{18}$ is expected to be more positive than 0.01 V (*vs.* SCE), which is much more positive than the E^0_{red} value of C_{60} ($E^0_{red} = -0.43$ V *vs.* SCE).[8]

The negative-ion electrospray ionization (ESI) mass spectrum of a reaction mixture of $C_{60}F_{18}$ and $Cl_4Q^{\cdot-}$ in acetonitrile shows a prominent signal at *m*/*z* 1043 (relative intensity (*I*) = 70% in the range of *m*/*z* 900 to 1100), which has a characteristic distribution of isotopomers that matches well with the calculated isotopic distribution for $C_{60}F_{17}^-$.[9] This indicates that an electron transfer from $Cl_4Q^{\cdot-}$ to $C_{60}F_{18}$ is followed by defluorination from $C_{60}F_{18}^{\cdot-}$ to give $C_{60}F_{17}^{\cdot}$ which is further reduced by $Cl_4Q^{\cdot-}$ to yield $C_{60}F_{17}^-$ as the final reduced product as shown in Scheme 1.



Scheme 1

The defluorinated position is estimated by PM3 heats of formation of $C_{60}F_{17}^-$ isomers as shown in Fig. 2.[10,11] The heat of formation is the smallest for the $C_{60}F_{17}^-$ isomer where the fluorine at the most distant position from the central aromatic ring (no. 10) is removed.

The electron-transfer reduction of $C_{60}F_{18}$ was also achieved by photoinduced electron-transfer from dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] to $C_{60}F_{18}$ in PhCN. $(BNA)_2$ is known to act as a unique electron donor to produce the radical anions of electron acceptors.[8,12] Under photoirradiation of a

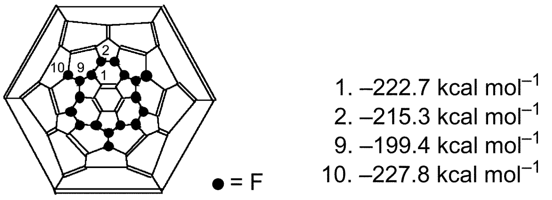


Fig. 2 Schlegel diagram for $C_{60}F_{18}$ with the calculated heat of formation of $C_{60}F_{17}^-$ isomers (the number denotes the defluorinated position).

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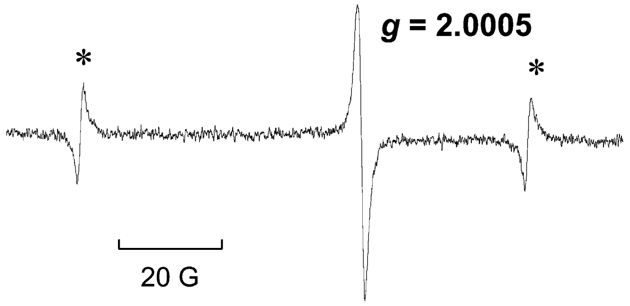


Fig. 3 EPR spectrum of $C_{60}F_{18}{}^{\bullet-}$ generated by the photoinduced electron transfer from $(BNA)_2$ (1.0×10^{-3} M) to $C_{60}F_{18}$ (1.0×10^{-3} M) with a high-pressure Hg lamp in deaerated PhCN at 298 K. * denotes an Mn^{2+} marker.

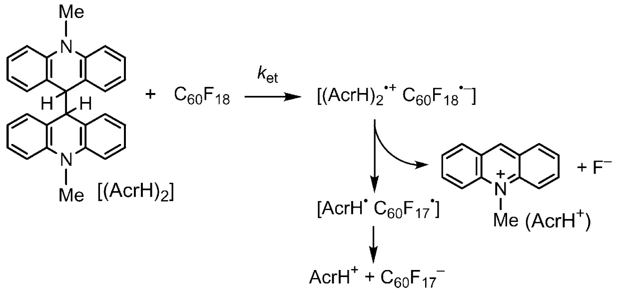
PhCN solution of $(BNA)_2$ and $C_{60}F_{18}$, $C_{60}F_{18}{}^{\bullet-}$ is detected by the EPR spectrum as shown in Fig. 3. The *g* value of the isotropic EPR signal due to $C_{60}F_{18}{}^{\bullet-}$ is 2.0005 which is smaller than the free spin value (2.0023). Small *g* values are characteristic of the EPR spectra of $C_{60}{}^{\bullet-}$ and functionalized $C_{60}{}^{\bullet-}$.[12] No hyperfine splitting due to fluorine atoms of $C_{60}F_{18}{}^{\bullet-}$ is observed. This indicates that the unpaired electron is not delocalised on fluorine atoms in $C_{60}F_{18}{}^{\bullet-}$. Thus, the electron is initially added on the fullerene π-electron system and then intramolecular electron transfer occurs to the antibonding C–F σ* orbital, resulting in the cleavage of the C–F bond. Upon cutting off the light, the EPR signal disappears due to the C–F bond cleavage of $C_{60}F_{18}{}^{\bullet-}$.

The disappearance of the EPR signal obeyed first order kinetics.[13] The decay rate constant of defluorination of $C_{60}F_{18}{}^{\bullet-}$ was determined as 2.8 s^{-1} at 298 K. The temperature dependence of the rate constant (268–298 K) afforded the activation enthalpy (75 kJ mol^{-1}) and activation entropy (13 J mol^{-1} K^{-1}) for the C–F bond dissociation.[14]

In order to evaluate the E^0_{red} value of $C_{60}F_{18}$, we examined the electron-transfer reduction of $C_{60}F_{18}$ by 10,10′-dimethyl-9,9′,10,10′-tetrahydro-9,9′-biacridine [$(AcrH)_2$].[15] The $(AcrH)_2$ is known to act as a two-electron donor in the outer-sphere electron transfer reactions with various inorganic and organic one-electron acceptors.[16] The logarithm of rate constants of electron transfer is linearly related to the E^0_{red} values of one-electron acceptors in the region of E^0_{red} value between −0.2 and 0.3 V (*vs.* SCE) as eqn. (1).

$$\log k_{et} = (F/2.3RT)E^0_{red} + \text{const.} \qquad (1)$$

Electron transfer from $(AcrH)_2$ to $C_{60}F_{18}$ occurs to yield 10-methylacridinium ion ($AcrH^+$) and $C_{60}F_{17}{}^-$. The rate-determining electron transfer from $(AcrH)_2$ to $C_{60}F_{18}$ is followed by the facile cleavage of C–C bond of $(AcrH)_2{}^{\bullet+}$ and the cleavage of C–F bond of $C_{60}F_{18}{}^{\bullet-}$ to give the radical pair ($AcrH^{\bullet}$ $C_{60}F_{17}{}^{\bullet}$) in which electron transfer from $AcrH^{\bullet}$ to $C_{60}F_{17}{}^{\bullet}$ occurs to yield $AcrH^+$ and $C_{60}F_{17}{}^-$ as shown in Scheme 2.



Scheme 2

The electron transfer rate was determined by an increase in the absorption band due to $AcrH^+$ or $C_{60}F_{17}{}^-$. The rate obeyed pseudo-first-order kinetics in the presence of excess $(AcrH)_2$ and the pseudo-first-order rate constant increased linearly with increasing $(AcrH)_2$ concentration. The second-order rate constant of electron transfer (k_{et}) is determined as 1.2 M^{-1} s^{-1}. This value is between the k_{et} values of *p*-methoxy-substituted trityl cation ($(p\text{-MeOC}_6H_4)Ph_2C^+$: 1.9 M^{-1} s^{-1}) and 7,7,8,8-tetracyanoquinodimethane (TCNQ: 3.8×10^3 M^{-1} s^{-1}).[16,17] Based on the linear correlation between $\log k_{et}$ and E^0_{red} [eqn. (1)], the E^0_{red} value of $C_{60}F_{18}$ is determined as 0.04 V (*vs.* SCE) from the k_{et} value of $C_{60}F_{18}$ (1.2 M^{-1} s^{-1}) and the E^0_{red} values of cation $(p\text{-MeOC}_6H_4)Ph_2C^+$ (0.05 V *vs.* SCE) and TCNQ (0.19 V). The E^0_{red} value of $C_{60}F_{18}$ (0.04 V *vs.* SCE) is by 0.47 V more positive than the value of C_{60} (−0.43 V *vs.* SCE). This value is consistent with the reported E^0_{red} values of $C_{60}F_{48}$ and $C_{60}F_{36}$.[5] Based on the known correlation between E^0_{red} and gas-phase electron affinity (EA), the EA value of $C_{60}F_{18}$ is estimated as 3.1–3.2 eV.

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10 The unique geometry of $C_{60}F_{18}$ revealed by the X-ray structure has been reported to be reproduced well by quantum chemistry calculations on a semi empirical PM3 level[2].

11 Theoretical calculations were performed on a COMPAQ DS20E computer using the PM3 Hamiltonian. Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The DFT calculations gave similar results.

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13 The observed first-order decay of the EPR signal indicates that the detected radical species is $C_{60}F_{18}{}^{\bullet-}$ rather than $C_{60}F_{17}{}^{\bullet}$ which would decay obeying a bimolecular second-order kinetics.

14 The Eyring plot gave a good linear correlation, from which the activation enthalpy and entropy were determined.

15 The small quantity of isolated $C_{60}F_{18}$ precluded determination of the E^0_{red} value by the conventional electrochemical method.

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