Enhanced photoinduced oligomerization of fullerene *via* radical coupling between fullerene radical cation and radical anion using 9-mesityl-10-methylacridinium ion†

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Photocatalytic oligomerization of fullerene in toluene–acetonitrile solution occurs efficiently *via* electron-transfer reactions with the photogenerated electron-transfer state of 9-mesityl-10-methylacridinium ion, followed by the radical coupling reaction between fullerene radical cation and radical anion.

Fullerene polymers have attracted much interest as excellent candidates for molecular conductors, nonlinear optical materials, and components of hydrogen-storage systems.[1,2] The photochemical reaction mechanism of the oligomerization proved to be photochemical [2 + 2]cycloaddition with the formation of four-membered rings between adjacent C_{60} balls.[3,4] However, the polymerization of fullerene in solution reported so far requires high temperature or high pressure and an extremely long photoirradiation time or ionic conditions, which have precluded practical application.[2–9] Alternatively radical cations and radical anions can be produced photochemically by photoexcitation of the charge transfer complex between electron donors and acceptors.[10–12] In particular, photoinduced cycloadditions *via* photoinduced electron transfer provide a new potentially important pathway for controlling synthetic processes which could not be exploited using a classical concerted pathway.[13]

We report herein that photocatalytic oligomerization of C_{60} occurs efficiently *via* electron-transfer oxidation and reduction of C_{60} with the electron-transfer state of 9-mesityl-10-methylacridinium ion (Acr^+-Mes), followed by [2 + 2]cycloaddition between $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ to produce fullerene-oligomers. Photoexcitation of Acr^+-Mes is known to afford the electron-transfer (ET) state of Acr^+-Mes, which has a long lifetime and high oxidation ability as well as high reduction ability, leading to simultaneous formation of both the radical cation of an electron donor and the radical anion of an electron acceptor *via* intermolecular electron transfer.[14–18]

Visible light irradiation (λ = 430 nm) of the absorption band of Acr^+-Mes (1.2×10^{-4} mol dm^{-3}) in a deaerated toluene–acetonitrile (PhMe–MeCN 15 : 2 v/v)[19] solution at 298 K containing C_{60} (9.1×10^{-5} mol dm^{-3}) results in formation of the fullerene-oligomers. Fig. 1a shows the visible–near IR spectral change observed in the photochemical reaction where the appearance of a new absorption band at 710 nm is diagnostic for 1,2-adducts of C_{60}.[20] The quantum yield of the adduct formation (Φ) under photoirradiation with monochromatized light (λ = 430 nm) was determined from an increase in absorbance at 700 nm due to the C_{60} adducts using an actinometer to be 0.75.[21] It should be emphasized that there was no spectral change without Acr^+-Mes under otherwise the same experimental conditions. This indicates that photoexcitation of C_{60} alone results in no photochemical reaction under the present experimental conditions.[22,23] When benzonitrile (PhCN) was used as a solvent, no photochemical reaction occurred (Fig. 1b).

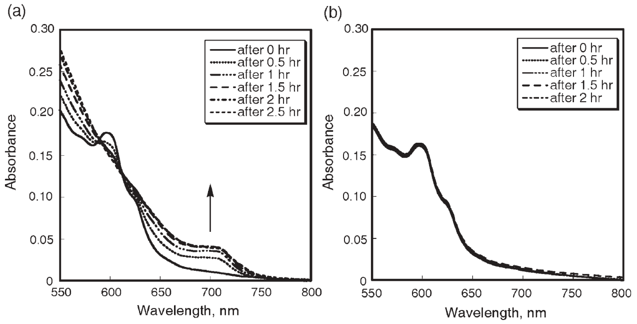

Fig. 1 Vis–near IR absorption spectral change observed in photocycloaddition of C_{60} (9.1×10^{-5} mol dm^{-3}) with Acr^+-$MesClO_4^-$ (1.2×10^{-4} mol dm^{-3}) in deaerated (a) PhMe–MeCN and (b) PhCN at 298 K. Excitation wavelength: λ = 430 nm.

The photoproducts obtained in PhMe–MeCN (15 : 2 v/v) were analyzed by MALDI-TOF-MS. Several peaks were observed from a crude mixture solution after photoirradiation (see electronic supplementary information (ESI) S1†). Soluble components were separated from extracted mixtures on a silica gel or alumina column.[24] The peaks at 1440, 2160 and 2880 were clearly assigned as fullerene-oligomers, C_{120}, C_{180} and C_{240}, respectively (Fig. 2 in which only a linear isomer is shown for C_{180}).

The fullerene-oligomers were also characterized by IR spectroscopy (Fig. 3). The IR peaks of the photoproducts were observed at 1430, 1454 and 1493 cm^{-1}, which agree with the reported values for C_{120} (1431, 1428, 1261 cm^{-1})[3] and fullerene polymer (1493, 1458, 1423 cm^{-1}).[4a]

Nanosecond laser excitation at 430 nm of a deaerated PhCN solution containing Acr^+-Mes and C_{60} results in the appearance of new transient absorption bands in the NIR region, which are the superposition of those due to $C_{60}^{\bullet+}$ (960 nm) and $C_{60}^{\bullet-}$ (1080 nm) as shown in Fig. 4a.[25–29] The transient absorption bands of $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ disappear, accompanied by the appearance of a new absorption band at 740 nm due to the triplet excited state of C_{60}

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† Electronic supplementary information (ESI) available: Spectral information and MALDI-TOF-MS results. See DOI: 10.1039/b705289h

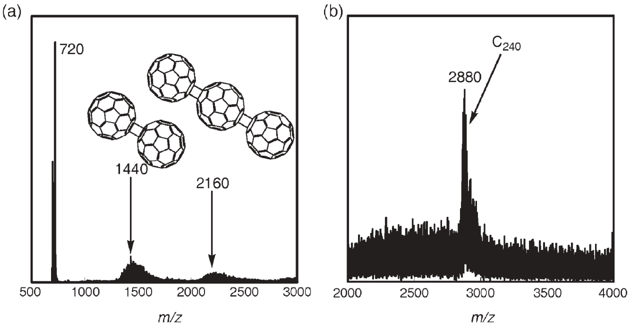


Fig. 2 MALDI-TOF-MS spectra of solution containing C_{60} oligomers through (a) silica gel and (b) alumina column chromatography.

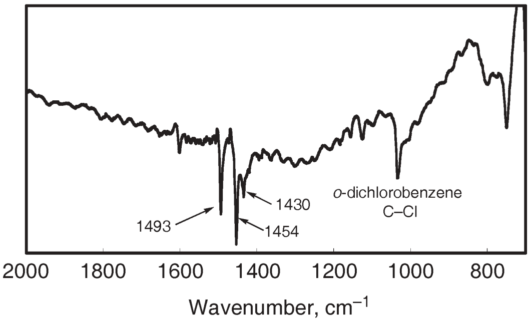


Fig. 3 IR spectrum of C_{60} oligomers in KBr disk purified by silica gel column chromatography.

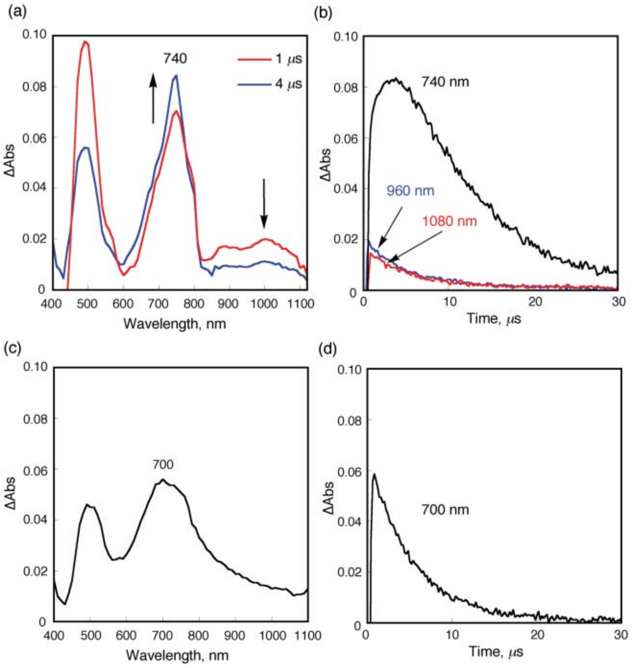


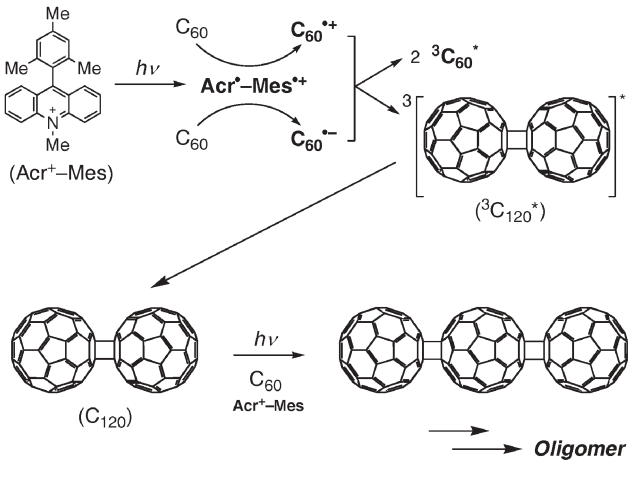
Fig. 4 (a) Transient absorption spectra in PhCN observed in photoinduced oligomerization of C_{60} (1.0×10^{-4} mol dm^{-3}) with Acr$^+$-MesClO$_4^-$ (1.0×10^{-4} mol dm^{-3}) taken 1 and 4 μs after laser excitation at 430 nm at 298 K. (b) Time profiles at 740, 960 and 1080 nm in PhCN. (c) Transient absorption spectra in PhMe–MeCN (15 : 2 (v/v)) observed in photoinduced electron-transfer oxidation of C_{60} (1.0×10^{-4} mol dm^{-3}) with Acr$^+$-MesClO$_4^-$ (1.0×10^{-4} mol dm^{-3}) taken 1 μs after laser excitation at 430 nm at 298 K. (d) Time profile of absorbance at 700 nm in PhMe–MeCN (15 : 2 (v/v)).

($^3C_{60}$*) (Fig. 4b). The formation rate constant of $^3C_{60}$* generated from $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ was determined as 5.2×10^5 s^{-1}. The decay at 740 nm obeys first-order kinetics. The decay rate constant of $^3C_{60}$* is determined as 1.0×10^5 s^{-1}, which is similar to the reported value.[30,31] Thus, no further reaction from $^3C_{60}$* may occur in PhCN.

When PhCN was replaced by PhMe–MeCN, neither $C_{60}^{\bullet+}$ nor $C_{60}^{\bullet-}$ was detected as shown in Fig. 4c. Instead, a new broad absorption band is observed at around 600–1100 nm (λ_{max} = 700 nm) at 1 μs after nanosecond laser excitation. This broad NIR transient band agrees well with that due to the triplet excited state of [2 + 2]cycloadduct, C_{120} ($^3C_{120}$*).[31] The formation rate constant of $^3C_{120}$* was determined to be 1.6×10^7 s^{-1}, which is much faster than the formation of $^3C_{60}$* in PhCN. This indicates that fast C–C bond formation between $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ may occur in PhMe–MeCN to produce $^3C_{120}$* rather than C_{120} (*vide infra*). The decay rate constant of $^3C_{120}$* was determined as 2.2×10^5 s^{-1}, which is similar to the reported value (4.3×10^5 s^{-1}).[30,31]

According to the above-mentioned results, the reaction mechanism of photoinduced oligomerization of C_{60} is summarized in Scheme 1, where only a linear isomer is shown for C_{180}. Since the free energy change of electron transfer (ΔG°_{et}) from C_{60} (E°_{ox} = 1.73 V *vs.* SCE)[32] to the Mes$^{\bullet+}$ moiety of the electron-transfer state of Acr$^+$-Mes (E°_{ox} = 1.88 V)[14] is negative ($\Delta G^\circ_{et} = -0.15$ eV), the electron-transfer oxidation of C_{60} is energetically feasible to form $C_{60}^{\bullet+}$. On the other hand, the electron-transfer reduction of C_{60} ($E^\circ_{red} = -0.43$ V)[25] with the Acr$^\bullet$ moiety ($E^\circ_{red} = -0.49$ V)[14] is also thermodynamically feasible to give $C_{60}^{\bullet-}$ ($\Delta G^\circ_{et} = -0.06$ eV). Thus, C_{60} acts as both an electron donor and acceptor in electron-transfer reactions of the ET state (Acr$^\bullet$-Mes$^{\bullet+}$) with C_{60} to produce $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ at the same time. The [2 + 2]cycloaddition occurs efficiently between $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ to afford $^3C_{120}$* rather than C_{120}, because the driving force of back electron transfer in PhCN (2.16 eV) is larger than the triplet excited state energy of C_{120} (*ca.* 1.5 eV).[31,33] The radical coupling between $C_{60}^{\bullet-}$ and $C_{60}^{\bullet+}$ also affords the triplet excited state of C_{60} ($^3C_{60}$*). Further oligomerization may occur by the same process.

The formation of $C_{60}^{\bullet-}$ and $C_{60}^{\bullet+}$ in the photocatalytic oligomerization of C_{60} with Acr$^+$-Mes in PhMe–MeCN was confirmed by ESR (electron spin resonance) measurements under photoirradiation at low temperature. A deaerated PhMe–MeCN (15 : 2



Scheme 1

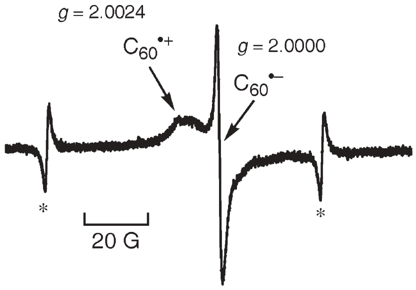


Fig. 5 ESR spectrum of C_{60} radical cation and radical anion observed under irradiation of a deaerated PhMe–MeCN (15 : 2 (v/v)) solution containing C_{60} (91 μmol dm^{-3}) and Acr$^+$-MesClO$_4^-$ (120 μmol dm^{-3}) measured at 143 K (frozen). Asterisk denotes an Mn^{2+} marker.

(v/v)) solution of Acr$^+$-Mes with C_{60} was irradiated by a high-pressure Hg lamp at 223 K. The resulting ESR spectrum observed at 143 K, which is shown in Fig. 5, exhibits signals at $g = 2.0024$ and 2.0000, which agree well with the reported g values of $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$, respectively.[26,27]

In conclusion, Acr$^+$-Mes acts as an efficient photocatalyst for the cycloaddition of fullerene, which proceeds *via* the radical coupling between $C_{60}^{\bullet+}$ and $C_{60}^{\bullet-}$ to yield the fullerene-oligomers in PhMe–MeCN. In PhCN, back electron transfer from $C_{60}^{\bullet-}$ to $C_{60}^{\bullet+}$ results in formation of $^3C_{60}$*, since bond formation between a radical ion pair is slower in a polar solvent.

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