

Reactivity of $C_{60}Cl_6$ and $C_{60}Br_n$ ($n = 6, 8$) in Solution in the Absence and in the Presence of Electron Donor Molecules

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Abstract: The reactivity of halogenofullerenes, $C_{60}Cl_6$ and $C_{60}Br_n$ ($n = 6, 8$), was elucidated in four different solvents, $CHCl_3$, benzene, CS_2 , and cyclohexane, in the absence and in the presence of organic donors of tetrathiafulvalene (TTF) type. In the absence of any electron donors, the stability order in solution was found to be $C_{60}Cl_6 > C_{60}Br_8 > C_{60}Br_6$. The nature of the stability has been considered on the basis of the results of semiempirical molecular orbital calculations. In the presence of any organic donors of TTF type employed in this work, $C_{60}Br_8$ decomposed to form C_{60} in all the solvents. For $C_{60}X_6$ ($X = Cl, Br$), a pronounced difference in the reactivity was observed. For an addition of relatively strong electron donor, the dehalogenation of $C_{60}X_6$ resulting in the formation of cation radical of the donor was observed, while for the relatively weak donors, such a behavior was not observed, and no charge-transfer (CT) interactions between $C_{60}X_6$ and the electron donors were optically detected. According to the difference in reactivity with electron donors, the electrical stability order was found to be $C_{60}Cl_6 > C_{60}Br_6 > C_{60}Br_8$. This order corresponds to that of the electron-accepting ability ($C_{60}Br_8 > C_{60}Br_6 > C_{60}Cl_6$) obtained by cyclic voltammetry measurements. On the basis of the relationship between the electrochemical properties of the halogenofullerenes and the counter donors, the boundary where a certain CT would begin was first predicted for the C_{60} family. X-ray powder diffraction, UV–vis, and elemental analyses revealed that the solid complex prepared in this work by the reaction of $C_{60}Br_8$ with TTF in CS_2 was not $(TTF)_x C_{60}Br_8$ ($x \approx 8$) but instead $TTF \cdot Br_x$ ($x = 0.76–0.86$).

Introduction

The discoveries of the superconducting anion radical salts M_3C_{60} ($M = \text{alkali metal}$)¹ and organic ferromagnetic material $TDAE \cdot C_{60}$ ² have provoked a great interest in the preparation of new charge-transfer (CT) complexes with attractive physical properties based on the C_{60} molecule. Due to the considerably weak electron-accepting ability of C_{60} , however, most of the CT complexes with organic donors so far prepared have exhibited neutral ground state.³ An alternative way to obtain the (partial) ionic CT complex is a functionalization of the C_{60} skeleton by the introduction of a strong electron-withdrawing group.⁴ In view of an interfullerene electron transfer, the sterically bulky substituent is unsuitable as the functional group, because an increase in an interfullerene distance generally tends to localize the unpaired electrons on fullerene molecules.

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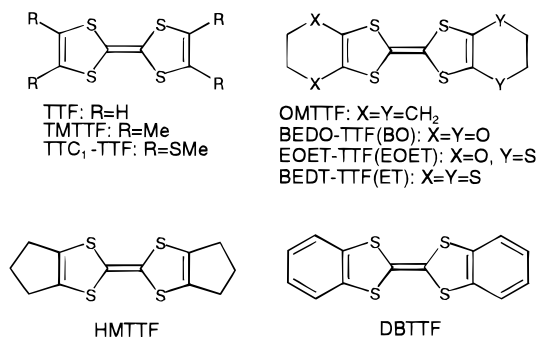
It is well known that halogen atoms are typical electron-withdrawing ones with small size, and several cyclic voltammetry (CV) studies of polyfluorofullerenes, $C_{60}F_n$ ($n = 36, 46$, and 48),⁵ showed that the reduction potentials of these molecules are more positive than that of parent C_{60} . However, both the difficulty in obtaining $C_{60}F_n$ with particular fluorine contents and the presence of some isomers⁶ are unfavorable for isolation and characterization of the CT complex based on $C_{60}F_x$. The functionalization of the C_{60} skeleton by an iodine atom has not been successful so far.⁷ C_{60} and iodine were found to be bound by only the van der Waals force with little CT.⁸ On the other hand, some chlorinated⁹ or brominated¹⁰ fullerenes have been

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Chart 1. Donor Molecules Used in This Study



isolated and structurally characterized, and among them $C_{60}Cl_6$ has already been employed as a starting material of the electrophilic reaction.¹¹ In the present study, we examined the reactivity of $C_{60}Cl_6$ ⁹ and $C_{60}Br_n$ ($n = 6, 8$)^{10a} in the absence and in the presence of several organic donors of TTF type in four kinds of solvent having different polarities. The reactivity of $C_{60}Br_8$ with TTF in CS_2 , which has been reported to give $(TTF)_x C_{60}Br_8$ ($x \approx 8$),¹² was also examined.

Experimental Section

Halogenofullerenes, $C_{60}Cl_6$ and $C_{60}Br_n$ ($n = 6, 8$), were synthesized according to literature procedures.^{9,10a} The donor molecules employed in this study are depicted in Chart 1.¹³ UV-vis-NIR spectra were recorded on a Shimadzu UV-3100 spectrophotometer. IR spectra were taken in KBr pellets with a Perkin-Elmer 1000 series spectrophotometer. Powder X-ray diffraction (XRD) measurements were carried out with an MAC Science M18XHF diffractometer using a Cu rotating-anode generator (Cu $K\alpha$ radiation). Direct current conductivities were measured by a standard four-probe technique attaching gold wires (15 μm diameter) on pellets with gold paint. Raman spectra were taken using a Renishaw Raman grating microscope spectrometer equipped with an Ar laser ($\lambda = 514.5$ nm) in 180° reflective geometry. CV

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(13) Chemicals in text (first half-wave potential ($E_{1/2}^1(D)$), V vs SCE in CH_3CN): TTF, tetrathiafulvalene (0.350); TMTTF, tetramethyl-TTF (0.285); OMTTF, octamethylene-TTF (0.292); HMTTF, hexamethylene-TTF (0.292); BEDO-TTF, bisethylenedioxy-TTF (0.430); EOET-TTF, ethylenedithio-ethylenedioxy-TTF (0.465); TTC₁-TTF, tetrakis(methylthio)-TTF (0.520); BEDT-TTF, bisethylenedithio-TTF (0.520); DBTTF, dibenzo-TTF (0.625); TDAE, tetrakis(dimethylamino)ethylene (-0.75, see ref 41); TDAP, 1,3,6,8-tetrakis(dimethylamino)pyrene (0.018); Cp*₂Ni, decamethylnickelocene (-0.65, see ref 42); Cp*₂Fe, decamethylferrocene (-0.086); Cp₂Fe, ferrocene (0.427).

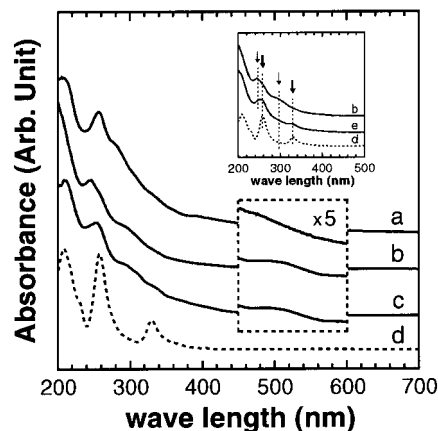


Figure 1. UV-vis spectra of (a) $C_{60}Cl_6$, (b) $C_{60}Br_6$, (c) $C_{60}Br_8$, and (d) C_{60} in cyclohexane immediately after the dissolution. Inset: UV-vis spectra in cyclohexane of (b) $C_{60}Br_6$ for 2 min, (e) $C_{60}Br_6$ for 24 h after the dissolution, (d) C_{60} for comparison. Thin and thick arrows indicate the absorption bands characteristic of $C_{60}Br_6$ and C_{60} , respectively.

experiments were performed in CH_3CN/TOL (TOL , toluene; volume ratio = 1:5) mixture with 0.1 M $TBA \cdot BF_4$ (TBA^+ , tetra(*n*-butyl)-ammonium) at room temperature (ca. 24 °C). Working and counter electrodes were Pt, the reference electrode was saturated calomel electrode (SCE), and the scan rate was 20 mV/s.

The semiempirical molecular orbital calculations were performed using MOPAC 97 with the AM1 parametrization.

The spectroscopic behaviors of halogenofullerenes themselves and also with excess amount of donor molecules ($D/A \approx 3$) were examined in $CHCl_3$ (dielectric constant $\epsilon = 4.81$), benzene (BZ , $\epsilon = 2.28$), CS_2 ($\epsilon = 2.64$), or cyclohexane (CHX , $\epsilon = 2.02$) by UV-vis measurements at room temperature in open air unless otherwise mentioned. Before use, solvents were distilled under N_2 or Ar, except for CS_2 , which was dried by molecular sieves and saturated with Ar by bubbling. The preparation of $(TTF)_8C_{60}Br_8$ was examined by mixing CS_2 solutions of TTF and $C_{60}Br_8$ at ca. 14:1 molar ratio, which resulted in instantaneous deposition of dark purple precipitates. The product was separated by filtration, washed with dry CS_2 and distilled acetone, and then dried in vacuo. The preparation was performed either in open air or under an Ar atmosphere. The latter procedure is essentially the same as that of Rao et al.¹²

Results

In the Absence of Electron Donors. UV-vis spectra of halogenofullerenes immediately after the dissolution in CHX are shown in Figure 1 [$\lambda_{max}/nm = 256$ for $C_{60}Cl_6$ (a), 245 for $C_{60}Br_6$ (b), and 251 for $C_{60}Br_8$ (c)] and compared with that of C_{60} [Figure 1d, $\lambda_{max}/nm = 258$ and 329]. For the solutions of $C_{60}Br_n$ ($n = 6, 8$), exposure to the air for a few hours promoted significant changes in the spectra (see the inset of Figure 1 for $C_{60}Br_6$). Decays of both the band at 245 nm and the shoulder at around 300 nm (indicated by thin arrows) were accompanied by an appearance of new bands at 258 and 329 nm (indicated by thick arrows) ascribed to the intramolecular transition of C_{60} (${}^1T_{1u} \leftarrow {}^1A_{1g}$).¹⁴ The observed spectral changes were thus characterized to be the debromination of $C_{60}Br_6$ into C_{60} in CHX , in which $C_{60}Br_8$ also showed the debromination. On the other hand, $C_{60}Cl_6$ was fairly stable not only in CHX but also in all the other solvents employed in this work. The spectrum of $C_{60}Cl_6$ in CHX resembled very closely that reported previously.⁹ Thus, it is evident that the individual spectrum of halogenofullerenes in Figure 1 is an intrinsic one and is distinguishable from that of parent C_{60} .

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Table 1. Reactivity of $C_{60}Cl_6$ and $C_{60}Br_n$ ($n = 6, 8$) in Four Different Solvents^a

ϵ^b	solvent		donor (D)	acceptor ($E_{red}^1(A)$, V vs SCE)		
	$E_T(30)$, kcal mol ^{-1c}			$C_{60}Br_8$ (+0.14)	$C_{60}Br_6$ (+0.07)	$C_{60}Cl_6$ (-0.07)
2.02	cyclohexane	31.2	no	unstable	unstable	stable
	CS ₂		yes	eq 1 for all D	eq 1 for all D	eq 2 for D \geq BO
2.64	benzene	32.6	no	unstable	unstable	stable
			yes	eq 1 for all D	eq 1 for all D	eq 2 for D \geq BO
2.28	CHCl ₃	34.5	no	stable	stable	stable
			yes	eq 2 for all D	eq 2 for all D	eq 2 for D \geq TTF
4.81	CHCl ₃	39.1	no	stable	stable	stable
			yes	eq 2 for all D	eq 2 for D \geq EOET	eq 2 for D \geq TTF

^a See text for eqs 1 and 2. ^b Dielectric constant. ^c Dimroth-Reichardt's $E_T(30)$ value.

As in the case in CHX, $C_{60}Br_n$ ($n = 6, 8$) was unstable in CS₂ as indicated by the appearance of the vibronic structure characteristic of C_{60} (${}^1T_{1g} \leftarrow {}^1A_{1g}$)¹⁵ at around 600 nm. IR spectrum of a residual product obtained by slow evaporation of the CS₂ solution of $C_{60}Br_8$ showed no trace of $C_{60}Br_8$ and was fully explained by the C_{60} molecule.

In BZ, it has been reported that, on heating, the $C_{60}Br_6$ molecules show a disproportionation into a mixture of $C_{60}Br_8$ and C_{60} ,^{10a} while both bromofullerene solutions are relatively stable at room temperature. All the halogenofullerenes were fairly stable in CHCl₃, so the solvent appeared to be useful for an examination of the essential reactivity of each halogenofullerene with an electron donor. The stability of the halogenofullerenes in four different solvents is summarized in Table 1.

In the Presence of Electron Donors. In the following we will first describe the result of $C_{60}Br_n$ in CS₂ to demonstrate the debromination of $C_{60}Br_n$, accompanied by the formation of cation radical of the donor (1). A similar feature was confirmed for $C_{60}Br_n$ in BZ and CHX (2). In CHCl₃, although the debromination of $C_{60}Br_8$ was observed for all TTF donors in Chart 1, that of $C_{60}Br_6$ was found to depend on the strength of the counter donor (3). Such a behavior was also observed in the case of $C_{60}Cl_6$ in all the solvents (4).

(1) Reactivity of $C_{60}Br_n$ ($n = 6, 8$) in CS₂. By addition of TTF into a CS₂ solution of $C_{60}Br_8$ in open air, deep purple precipitates were immediately obtained. The XRD pattern of the product was almost the same as that reported by Rao et al.^{12b} [$2\theta_{max}/^\circ = 16.0s, 18.0s, 25.5s, 26.2vs, 27.4w, 32.3s, 34.3s,$ and $38.4w$]. However, elemental analyses of our product suggested the formula to be TTF \cdot Br_{*x*} ($x \approx 0.76$) but not (TTF)₈C₆₀Br₈. Found: C, 27.45; H, 1.53; S, 48.42; Br, 22.84. Calcd for TTF \cdot Br_{0.76}: C, 27.19; H, 1.52; S, 48.38; Br, 22.91. Calcd for (TTF)₈C₆₀Br₈: C, 43.32; H, 1.08; S, 34.26; Br, 21.35]. Figure 2 shows UV-vis spectra obtained on a KBr pellet [Figure 2a, $\lambda_{max}/10^3$ cm⁻¹ = 4.8, 12.9, 18.3, and 27.0] and in an ethanol solution [Figure 2c, $\lambda_{max}/10^3$ cm⁻¹ = 17.2, 22.8, and 31.5], consistent with those of the mixed-valence salt TTF \cdot Br_{*x*}.¹⁶ The appearance of the low-energy absorption band (4.8×10^3 cm⁻¹, band A in Figure 2a) in a KBr pellet was compatible with both the mixed-valent electronic state and the segregated column structure of constituent molecules in the product.¹⁷ This presumption was also supported by the relatively high conduc-

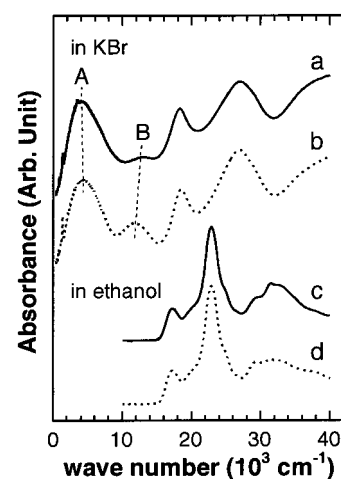


Figure 2. UV-vis-NIR spectra of the product obtained from TTF and $C_{60}Br_8$ in CS₂ both in open air (solid lines: a, in KBr pellet; c, in ethanol) and under Ar (dotted lines: b, in KBr pellet; d, in ethanol). For bands A and B, see text.

tivity (8 S cm^{-1} at 295 K) with a semiconducting temperature dependence. The activation energy observed (82 meV, 79–295 K) is in good agreement with that found in single-crystal TTF \cdot Br_{*x*} (81 meV).¹⁸ The weak peak at 12.9×10^3 cm⁻¹ in KBr (band B in Figure 2a) was ascribed to the intermolecular transition between TTF cation radicals in the crystal. It is known that the intensity of band B is proportional to the density of TTF⁺ pairs in the crystal and vanishes when ρ of TTF⁺ reaches 0.5, based on generalized Wigner lattices.¹⁹ It is therefore reasonable to see a weak intensity at that kind of absorption in TTF \cdot Br_{0.76} ($\rho = 0.76$). In contrast, (TTF⁺)₈C₆₀Br₈⁻⁸ may exhibit a strong absorption at around 13×10^3 cm⁻¹, even if the charge of $C_{60}Br_8$ slightly deviates from -8.

The product prepared under an Ar atmosphere was also found to be the cation radical salt TTF \cdot Br_{*x*}. The absorption spectra for the product in KBr pellet and in ethanol are shown in Figure 2b and d, respectively. The slight increase in the x value (ca. 0.86) obtained by the elemental analyses corresponds to the enhancement of the band B (Figure 2b) compared with that of TTF \cdot Br_{0.76} (Figure 2a).¹⁹ The absorption spectrum in ethanol (Figure 2d) was quite similar to that in Figure 2c. As a summary, our samples obtained by the reaction between TTF and $C_{60}Br_8$ in CS₂ both in open air and under Ar were confirmed to be TTF \cdot Br_{*x*} ($x = 0.76$ –0.86).

In the $C_{60}Br_8$ crystal used for the TTF complex preparation, approximately 1.2 bromine atoms for each molecule were

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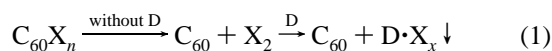
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trapped in the lattice according to the elemental analyses [Found: C, 49.52; H, 0.36; Br, 50.62. Calcd for $C_{60}Br_8 \cdot Br_{1.2}$: C, 49.50; H, 0.00; Br, 50.50], compared with $C_{60}Br_8 \cdot Br_2$ reported previously.^{10a} As a source of bromine, therefore, not only $C_{60}Br_8$ molecules but also the trapped ones were available. However, considering the experimental fact that 11.9 mg (4.49×10^{-2} mmol) of $TTF \cdot Br_{0.76}$ was obtained by the reaction of 13.1 mg (0.90×10^{-2} mmol) of $C_{60}Br_8 \cdot Br_{1.2}$ with a large excess of TTF, it is impossible to cover all the product by the trapped bromine. The instability of $C_{60}Br_8$ in CS_2 in the absence of any electron donors also supported the possibility of the former. Accordingly, it is concluded that the debromination of $C_{60}Br_8$ first occurs in CS_2 , and then $TTF \cdot Br_x$ will be formed if the TTF molecules exist in the solution.

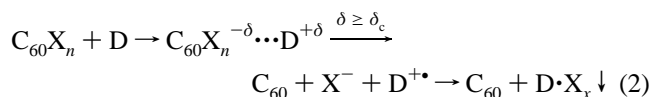
Raman spectroscopy measurements were performed for $TTF \cdot Br_x$ prepared in open air to compare it with the result reported by Rao et al.¹² It was found that the compound we obtained was very sensitive to the laser power and the spectrum changed its shape with time of laser irradiation. A band at 1442 cm^{-1} , being expected in mixed-valence salt $TTF \cdot Br_{0.76}$,²⁰ was observed by a light irradiation (2×10^{-3} mW) for 100 s. However, an additional irradiation for 1000 s or an enhancement of the laser power by a factor of 30 (7×10^{-2} mW) led to the appearance of a new band at 1416 cm^{-1} , which is expected in $TTF \cdot Br_{1.0}$.²¹ The spectral change observed is very similar to that reported previously²⁰ and is reminiscent of that observed by the irradiation of an electron beam on the $TTF \cdot Br_x$.²² Tomkiewicz et al. reported that a heavy dose of irradiation caused evaporation of bromine from the $TTF \cdot Br_x$ to produce neutral TTF, followed by its sublimation due to local heating, while a light dose resulted in the polymerization of TTF^{+} .²² Thus, it is likely that the additional band at 1416 cm^{-1} observed in our work may originate from the polymerization of TTF^{+} . Consequently, the spectral pattern obtained with a laser power of 7×10^{-2} mW per 0.01 mm spot (1416s, 1433sh, 1481w, weak triplet at 1500, 1508, and 1513 cm^{-1}) closely resembled that published by Rao et al. (strong doublet at 1414 and 1421, and weak peaks at 1483, 1504, and 1519 cm^{-1}),¹² although a much stronger power (ca. 1 mW, focused spot ca. 0.04 mm) was reportedly used.

With any electron donors of TTF type in Chart 1, the $C_{60}Br_n$ ($n = 6, 8$) in CS_2 afforded cation radical salts, as represented by eq 1.



(2) Reactivity of $C_{60}Br_n$ ($n = 6, 8$) in CHX or BZ. In CHX, $C_{60}Br_n$ was unstable even in the absence of donor molecules, as described above. As a result, all the mixtures of $C_{60}Br_n$ with organic donors of TTF type exhibited the characteristic band of C_{60} (eq 1), similar to the mixing in CS_2 .

On the other hand, the addition of any organic donors of TTF type in the BZ solution of $C_{60}Br_n$ initiated the debrominations of $C_{60}Br_n$ to afford radical salts ($D \cdot X_x$ in eq 2),



where δ_c is a certain degree of CT required to break C–X bonds

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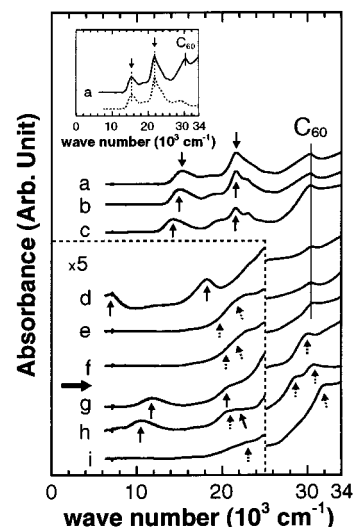


Figure 3. UV-vis spectra of the mixtures of $C_{60}Br_6$ with TTF system donors (a, TMTTF; b, OMTTF; c, HMTTF; d, TTF; e, BO; f, EOET; g, TTC₁-TTF; h, ET; i, BEDT-TTF) in $CHCl_3$. The vertical line indicates the absorption characteristic of the C_{60} molecule (${}^1T_{1u} \leftarrow {}^1A_{1g}$). The vertical solid and dotted arrows indicate the absorption characteristic of ionized and neutral constituent molecules, respectively. The horizontal arrow is the boundary of $\delta = \delta_c$. Inset: The spectra of the mixture with TMTTF in $CHCl_3$ (solid line) and TMTTF·Br in methanol (dotted line).

in $C_{60}X_n$. Such a reaction has been previously observed in dichloromethane solution of $C_{60}Br_{24}$ ^{10b} and Cp_2Fe , which initiated both the debromination of $C_{60}Br_{24}$ and the formation of $Cp_2Fe^{+} \cdot FeBr_4^{-}$.²³

(3) Reactivity of $C_{60}Br_n$ ($n = 6, 8$) in $CHCl_3$. Figure 3 demonstrates UV-vis spectra up to $34 \times 10^3 \text{ cm}^{-1}$ for the mixtures of $C_{60}Br_6$ with organic donors of TTF type in $CHCl_3$ (in the order of electron-donating ability from the top). With a variation in the electron-donating ability of the counter donors, a pronounced change of the absorption spectra was observed.

An absorption band characteristic of C_{60} appeared at $30.3 \times 10^3 \text{ cm}^{-1}$ by the addition of the relatively strong donors of TMTTF (a), OMTTF (b), HMTTF (c), TTF (d), BEDO-TTF (BO, e), and EOET-TTF (EOET, f). For the mixture with TMTTF, OMTTF, or HMTTF, the bands observed below $25 \times 10^3 \text{ cm}^{-1}$ were ascribed to the monomer of cation radicals (indicated by vertical solid arrows). As an example, the spectrum of the mixture with TMTTF was compared with that of TMTTF·Br in methanol¹⁶ in the inset of Figure 3. It is noticeable that both spectra below $25 \times 10^3 \text{ cm}^{-1}$ are very similar to each other. The corresponding bands for TTF should be due to the partially ionized one suspended in $CHCl_3$, since band A was observed as in the case of $TTF \cdot Br_x$ in a KBr pellet (Figure 2a,b). These results indicated that the presence of the strong donor initiated the loss of bromine of $C_{60}Br_6$ to form cation radical followed by a precipitation of cation radical salt (eq 2).

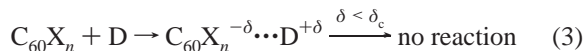
For the mixture with BO or EOET, on the other hand, the formation of each cation radical has not been observed, despite the occurrence of the debromination. The broad band that appeared at around $22 \times 10^3 \text{ cm}^{-1}$ was ascribed to pristine $C_{60}Br_6$ (indicated by vertical dotted arrows). No reasonable explanation for the absence of cation radical is clear at present.

The spectrum of the mixture with TTC₁-TTF (g) or BEDT-TTF (ET, h) also exhibited the characteristic bands of each cation radical, along with those of each neutral component

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(vertical dotted arrows). However, the band of C₆₀ at 30.3 × 10³ cm⁻¹ due to the debromination was absent. A possible explanation for the discrepancy is the formation of cation radical by the reaction of each donor with bromine atom trapped in the C₆₀Br₆ crystal. As in the case of C₆₀Br₈, there was one bromine atom trapped in the lattice per C₆₀Br₆ molecule [Found: C, 56.40; H, 0.21; Br, 43.37%. Calcd for C₆₀Br₆·Br: C, 56.30; H, 0.00; Br, 43.70%], consistent with the earlier work.^{10a} If the cation radical salt is formed by the reaction with the trapped bromine, it is then probable that the characteristic bands of each cation radical are present, whereas that of C₆₀ is absent.

For the mixture with DBTTF (i), the spectrum did not exhibit the bands ascribable to either C₆₀ or DBTTF^{•+} (eq 3).



Thus, the boundary between eqs 2 and 3 ($\delta = \delta_c$) exists between EOET (f) and TTC₁-TTF (g), as indicated by a horizontal arrow in Figure 3. A CT absorption band due to the interaction between the donors and C₆₀Br₆ or debrominated C₆₀, which would be expected to appear in the range of (13–16) × 10³ cm⁻¹ ^{3a} in solution, has apparently not been observed.

For C₆₀Br₈ in CHCl₃, the mixtures with any electron donors of TTF type in Chart 1 exhibited the characteristic band of C₆₀ at 30.3 × 10³ cm⁻¹, indicating the occurrence of the debromination of C₆₀Br₈ and the formation of C₆₀ (eq 2).

(4) Reactivity of C₆₀Cl₆ in CHCl₃, BZ, CS₂, or CHX. For C₆₀Cl₆, UV–vis spectra for the mixtures with organic donors of TTF type in CHCl₃ revealed features slightly different from those for C₆₀Br₆. An absorption band characteristic of C₆₀ appeared at 30.3 × 10³ cm⁻¹ by the addition of the relatively strong donors of TMTTF, OMTTF, HMTTF, and TTF. Furthermore, additional bands originating from each cation radical¹⁶ were also observed for these donors below 25 × 10³ cm⁻¹. These results indicate that the presence of the strong donor initiates the loss of chlorine of C₆₀Cl₆ to form cation radical (eq 2), which is similar to the case of C₆₀Br₆. A CT absorption band due to the interaction between the donors and C₆₀Cl₆ or dechlorinated C₆₀ has not apparently been observed.

For relatively weak donors such as BO, EOET, TTC₁-TTF, ET, and DBTTF, on the other hand, the spectra exhibited no trace of C₆₀ and were approximated as a superposition of the constituent molecules (eq 3). In addition, no CT absorption bands between each donor and C₆₀Cl₆ were detected. Accordingly, the boundary between eqs 2 and 3 for C₆₀Cl₆ shifted to the stronger donor side compared with the result for C₆₀Br₆ and exists between TTF and BO. This indicates that C₆₀Cl₆ is less susceptible than C₆₀Br₆ to the attack by electron donors.

Although the boundary in the BZ solution was observed between TTF and BO just like in CHCl₃, in CHX or CS₂ the boundary shifted to the weaker donor side. In CHX, a characteristic band of C₆₀ was observed in the mixture with BO, in contrast to the case in CHCl₃ or BZ. On the other hand, the spectrum of the mixture with TMTTF, OMTTF, TTF, or BO below 25 × 10³ cm⁻¹ showed a different feature not observed in CHCl₃. The spectrum of the mixture with TMTTF or OMTTF corresponds to that observed in assembly of each completely ionized cation radical, while for the mixture with TTF or BO, the bands observed below 25 × 10³ cm⁻¹ were fully ascribed to each partially ionized one.^{17a,c} In fact, the spectrum of the mixture with TTF resembled closely that of TTF·Br_x in KBr (see Figure 2a,b). These observed spectra, being apparently inconsistent with those in CHCl₃ or BZ, were likely caused by the presence of the Coulomb interaction between the suspended

Table 2. Heats of Formation and Related Data for C₆₀Cl₆, C₆₀Br_n (n = 6, 8), and C₆₀^a

	C ₆₀ Br ₈	C ₆₀ Br ₆	C ₆₀ Cl ₆	C ₆₀
ΔH _f ⁰ , kJ mol ⁻¹	3777	3822	3542	4069
dipole, D	<10 ⁻²	0.74	0.27	<10 ⁻²
-ε _{HOMO} , eV	9.62	9.58	9.63	9.64
-ε _{LUMO} , eV	3.02	2.76	2.80	2.95
Δε, eV	6.60	6.82	6.83	6.69

^a Heat of formation ΔH_f⁰, orbital energies ε_{HOMO} and ε_{LUMO}, and HOMO–LUMO energy gap Δε.

donor cations in CHX, which has a lower polarity (ε = 2.02) compared with that of CHCl₃ (ε = 4.81).

The shift of the boundary observed by changing the solvent indicates that a certain degree of CT (δ_c) from donor to C₆₀Cl₆ should be critical whether the dehalogenation takes place or not. The degree of CT in solution depends not only on the ionization potential of donor and electron affinity of acceptor, but also on both the Coulomb energy and the solvation energy. The total energy of the latter two are not linearly related with dielectric constants of solvent, so that the relation between the occurrence of dehalogenation and the dielectric constant of solvent used would not be simple. The relation will be discussed in the Discussion.

Redox Potentials. In our preliminary CV measurements, a broad irreversible wave was observed at -0.07, +0.07, and +0.14 V for C₆₀Cl₆, C₆₀Br₆, and C₆₀Br₈, respectively. After the appearance of the irreversible wave, three reversible ones, which were very similar to those of parent C₆₀, were detected in all halogenofullerenes. Similar voltammograms were reported in C₆₀Cl_{11.6} (-0.2 V vs Ag/AgCl)²⁴ and C₆₀Br₂ (+0.05 V vs SCE).²⁵ Tebbe et al. assigned the irreversible wave to be a reduction of halogen (X) bonded with a C₆₀ skeleton to halide (X⁻),²⁴ indicating that at these potentials the addition of an electron to C₆₀X_n occurs. It is then apparent that the addition of an electron to C₆₀X_n strongly accelerates the instability of the C–X bond. Regarding those potentials as the first reduction ones (E¹_{red}(A)) intrinsic to each halogenofullerene, the order of the electron-accepting ability was found to be C₆₀Br₈ > C₆₀Br₆ > C₆₀Cl₆ > C₆₀, so it is evident that the enhancement of the electron-accepting ability by an introduction of halogen atoms is surely present. With regard to electrical stability, C₆₀Br₈ is less stable than C₆₀Br₆, and both bromofullerenes are unstable compared with C₆₀Cl₆. This stability order is in good agreement with that obtained by the reactivity with organic donors of TTF type.

Calculations. Standard heats of formation (ΔH_f⁰), dipole moments, HOMO and LUMO energy levels (ε_{HOMO} and ε_{LUMO}), and HOMO–LUMO energy gaps (Δε) calculated for C₆₀Cl₆ and C₆₀Br_n (n = 6, 8) and C₆₀ are listed in Table 2. ΔH_f⁰ values obtained are very similar to those reported previously^{26,27} except for that of C₆₀Cl₆, which has not been reported to our knowledge. The thermodynamical stability order was found to be C₆₀Cl₆ > C₆₀Br₈ > C₆₀Br₆, consistent with that in solution without any electron donors. The energy difference between C₆₀Cl₆ and C₆₀Br₆ (280 kJ mol⁻¹) was in good agreement with that between 1,4-added C₆₀Cl₂ and C₆₀Br₂ (94 kJ mol⁻¹)^{26,28} in

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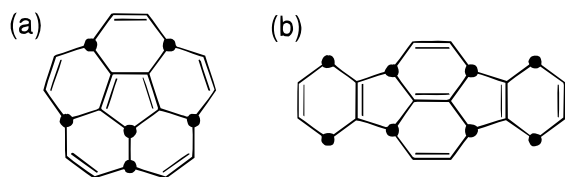


Figure 4. Addition patterns of halogens in (a) $C_{60}X_6$ ($X = Cl, Br$) and (b) $C_{60}Br_8$.

terms of the number of halogen atoms added. This correlation is most likely caused by the fact that $C_{60}X_6$ ($X = Cl, Br$) are evidently produced by a sequence of 1,4-additions rather than 1,2-additions because of the steric hindrance,²⁹ as shown in Figure 4.^{9,10a} It should be noted that both addition patterns suffer double bonds in pentagon ring(s), which is energetically unfavorable as suggested by Mills and Nixon.³⁰ In addition to the 1,4-addition, both $C_{60}Br_6$ and $C_{60}Cl_6$ (C_s symmetry) involve a sterically unfavorable 1,2-addition, and relatively large dipole moments. In contrast to $C_{60}X_6$, $C_{60}Br_8$ (C_{2v} symmetry) showed a negligibly small dipole moment due to the high symmetry of the addition pattern. The order of the ϵ_{LUMO} value was predicted to be $C_{60}Br_6 \sim C_{60}Cl_6 > C_{60} > C_{60}Br_8$. Since ϵ_{LUMO} is equal to $-E_A$ (E_A is electron affinity) when Koopmans theorem is applied, then the order of E_A would be $C_{60}Br_8 > C_{60} > C_{60}Cl_6 \sim C_{60}Br_6$. The larger E_A value predicted for $C_{60}Br_8$ appears to correspond well to the experimental results both of the reactivity with electron donors and of CV measurements, and can be explained in the view of aromaticity. On the other hand, the comparable ϵ_{LUMO} of $C_{60}Br_6$ with that of $C_{60}Cl_6$ may conflict with the experimental characters. A consideration will be described in the following section.

Discussion

The reactivity of $C_{60}X_n$ in four different solvents with or without electron donor molecules is summarized in Table 1. Combined with the previous experiment, in which $C_{60}Br_6$ disproportionates into a mixture of $C_{60}Br_8$ and C_{60} in BZ or CCl_4 by heating,^{10a} the present results led to the stability orders in solution with $C_{60}Cl_6 > C_{60}Br_8 > C_{60}Br_6$ and $C_{60}Cl_6 > C_{60}Br_6 > C_{60}Br_8$ in the absence and in the presence of electron donors, respectively. Here we consider the origin of the stability orders.

In the Absence of Electron Donor. ΔH_f^0 values obtained by AM1 calculations indicated the thermodynamical stability order of $C_{60}Cl_6 > C_{60}Br_8 > C_{60}Br_6$, consistent with that in solution without any electron donors. The greater stability of chlorofullerenes compared to bromofullerenes was also supported by the dehalogenation temperatures of halogenofullerenes: 400 °C for $C_{60}Cl_x$ (av $x = 24$, including less than 10% of C_{70}),³¹ 200–350 °C for $C_{60}Cl_x$ (av $x = 12.0$),²⁴ 150 °C for $C_{60}Br_x$ ($2 \leq x \leq 4$),³¹ and 150–200 °C for $C_{60}Br_{24}$.^{10b} The energy difference between $C_{60}Cl_6$ and $C_{60}Br_6$ is mainly caused by the greater stiffness of C–Cl bond than that of the C–Br one. On the other hand, the difference between $C_{60}Br_6$ and $C_{60}Br_8$ may be explained by the difference in addition patterns as shown in Figure 4. For $C_{60}Br_6$, which takes the addition pattern of Figure 4a, there is the eclipsing interaction between two bromine atoms on a hexagon junction (1,2-addition). The significant strain of a C_{60} skeleton would also occur due to the presence of the sp^3 – sp^3 adjacency. It is thus evident that $C_{60}Br_6$

is less stable than $C_{60}Br_8$, because such a 1,2-addition across the hexagon junction does not exist in the addition pattern of Figure 4b. The X–X repulsion in $C_{60}X_6$ ($X = Cl, Br$) may also reflect the stability order between $C_{60}Cl_6$ and $C_{60}Br_6$.

In solution, furthermore, the dipole moment of the solute also influences the stability remarkably, since the solvation energy for the solute would increase with an increase in the polarity of the solute. The calculation predicted that the order of dipole moment would be $C_{60}Br_6 > C_{60}Cl_6 \gg C_{60}Br_8$ as seen in Table 2. This indicates that in solution $C_{60}Br_6$ would gain more stability due to the solvation energy. However, the order of the stability in solution ($C_{60}Cl_6 > C_{60}Br_8 > C_{60}Br_6$) was apparently different from that of the dipole moment. The discrepancy is likely due to the fact that both ϵ and Dimroth–Reichardt parameters ($E_T(30)$)³² of the solvent used in this work are fairly small. Then the dipole moment of the solute would have relatively little effect on the solvation energy in such a solvent. The stability order in solvent used would be, therefore, dominated by the thermodynamical stability of $C_{60}X_n$.

Although the thermodynamical stability of halogenofullerenes would be a predominant factor in the stability in the solvent used, a contribution of the polarity of the solvent was also observed in the case of $C_{60}Br_n$ ($n = 6, 8$). In the present work, it was found that both bromofullerenes were fairly stable in $CHCl_3$ ($\epsilon = 4.81$, $E_T(30) = 39.1$ kcal mol⁻¹) or BZ ($\epsilon = 2.28$, $E_T(30) = 34.5$), but not in CS_2 ($\epsilon = 2.64$, $E_T(30) = 32.6$) or CHX ($\epsilon = 2.02$, $E_T(30) = 31.2$). The observed dependency may be ascribed to the difference in the polarity of the solvent used. Since the first two solvents have relatively large $E_T(30)$'s, resulting in larger solvation energies, both bromofullerenes would be stable in the solvents, while they would be unstable and decompose to form C_{60} in the latter two solvents.

In the Presence of Electron Donors. The reactivity with organic donors of TTF type indicated the stability order of $C_{60}Cl_6 > C_{60}Br_6 > C_{60}Br_8$, corresponding to that of the electron-accepting ability ($C_{60}Br_8 > C_{60}Br_6 > C_{60}Cl_6$) obtained by CV measurements. Alternatively, $C_{60}X_n$ was more reactive with electron donors as the $E_{red}^1(A)$ value increased. Taking into account the electrochemical results that $C_{60}X_n$ dehalogenated at such a potential that $C_{60}X_n$ would be reduced first, it is evident that the electron-accepting ability of $C_{60}X_n$ influences significantly the stability in the presence of electron donors. The origin of the electron-accepting ability of $C_{60}X_n$ used will hereinafter be considered.

As seen in Table 2, the AM1 calculations predicted the higher ϵ_{LUMO} level of $C_{60}Br_6$ (–2.76 eV) than that of $C_{60}Br_8$ (–3.02 eV), indicating that the electron affinity (E_A) of $C_{60}Br_6$ would be lower than that of $C_{60}Br_8$ when Koopmans theorem is applied. Since, in general, $E_{red}(A)$ is equal to the half-wave potential ($E_{1/2}(A)$) within experimental error, $E_{red}^1(A)$ would depend both on E_A and on the solvation energy difference between the ionic and neutral molecules (ΔG_{solv})³³ as

$$E_{1/2}^1(A) \sim E_{red}^1(A) = E_A - \Delta G_{solv} + C_1 \quad (4)$$

where C_1 is the constant mainly based on the absolute potential of the reference electrode used. It is known that the larger E_A disperses the extra charge in the anion radical over the conjugated system, and such a charge delocalization is accompanied by the increase in ΔG_{solv} (i.e., the decrease in

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absolute value ($|\Delta G_{\text{solv}}|$).³⁴ Then eq 4 can be approximated as

$$E_{\text{red}}^1(\text{A}) = \alpha E_{\text{A}} + C \quad (5)$$

It is thus evident that the lower E_{A} of C_{60}Br_6 than of C_{60}Br_8 would result in the lower $E_{\text{red}}^1(\text{A})$, consistent with the experimental results. The larger number of C atoms in the conjugated system in C_{60}Br_6 (50 atoms) than that in C_{60}Br_8 (46 atoms), which affords the greater extent of charge delocalization,³⁵ may have some influences on the smaller $E_{\text{red}}^1(\text{A})$ of C_{60}Br_6 .

The higher ϵ_{LUMO} level of C_{60}Br_6 predicted can be explained on the basis of a theoretical method described by Aihara and Takata.³⁶ They pointed out the higher aromaticity of C_{60}Br_6 compared with that of C_{60}Br_8 , mainly caused by the decreasing ratio of pentagons to hexagons in the conjugated system. Then the HOMO–LUMO energy gap ($\Delta\epsilon$) of C_{60}Br_6 would be enhanced accompanied by the rise of the ϵ_{LUMO} level, consistent with our AM1 calculations. Accordingly, since the pentagon/hexagon ratio in the conjugated system on the C_{60} skeleton strongly depends on the addition pattern of the addends, it is then evident that the difference in the addition pattern between C_{60}Br_6 and C_{60}Br_8 (see Figure 4) strongly influences the difference in the electron-accepting ability between both bromofullerenes.

For C_{60}X_6 ($\text{X} = \text{Cl}, \text{Br}$), which are isostructural with each other, theoretical predictions listed in Table 2 indicate that the ϵ_{LUMO} level of C_{60}Br_6 (-2.76 eV) is slightly higher than that of C_{60}Cl_6 (-2.80 eV). This seems to conflict with the experimental results both of the reactivity with electron donors and of CV measurements, in which it was found that the electron-accepting ability of C_{60}Br_6 was apparently higher than that of C_{60}Cl_6 . The discrepancy observed appears to be explainable on the basis of the difference in ΔG_{solv} between C_{60}Br_6 and C_{60}Cl_6 . Since the electronegativity of the Cl atom is higher than that of the Br one, the extent of the charge delocalization in the transient $\text{C}_{60}\text{Cl}_6^-$ molecule would be greater than that in $\text{C}_{60}\text{Br}_6^-$. As described above, the delocalization of the extra charge prevents the stability of the anion radical in solution, so that the ΔG_{solv} value for C_{60}Cl_6 would be apparently larger than that for C_{60}Br_6 . It is then evident that the $E_{\text{red}}^1(\text{A})$ value of C_{60}Cl_6 is smaller than that of C_{60}Br_6 (eq 4), consistent with the CV measurements.

Boundary of CT. Figure 5 demonstrates the correlation between the electron-accepting ability of C_{60}X_n and the reactivity with electron donors in CHCl_3 , where the upper left is the area for strong CT interaction between donor and acceptor molecules, and the lower right is the area for a weak one.^{17b} For comparison, CT complexes based on C_{60} ($E_{\text{red}}^1(\text{A}) = -0.44$ V vs SCE), including those with rather strong donors of $\text{Cp}^*\text{Fe}^{3+}$ and TDAP,³⁸ were also added in this figure. All the C_{60} complexes employed were found to be neutral (represented by an open circle).^{3,37–39} For halogenofullerenes, a closed circle indicates the presence of the dehalogenation (eq 2) and an open circle

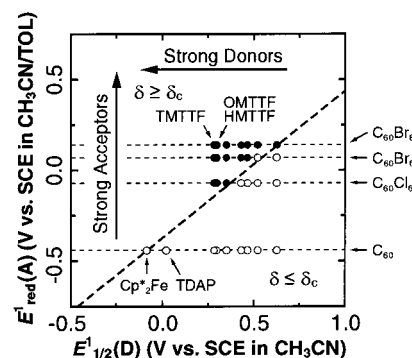


Figure 5. Dependence of the reactivity with organic donors of TTF type on the electron-accepting ability of C_{60}Cl_6 and C_{60}Br_n ($n = 6, 8$) and C_{60} .

indicates the absence of the dehalogenation (eq 3). It is then obvious that there is a universal boundary whether a certain CT occurs or not:

$$0.81E_{1/2}^1(\text{D}) - E_{\text{red}}^1(\text{A}) = +0.37 \text{ V} \quad (6)$$

The positive slope indicates that the reactivity of C_{60}X_n with electron donors would increase with an increase in the reduction potential of C_{60}X_n . The deviation of the slope from unity is likely due to the difference in polarity among C_{60} and C_{60}X_n molecules. Consequently, the distinct boundary whether a certain CT occurs or not was first derived for the C_{60} family from the viewpoint of both electron-accepting and -donating abilities.

On the other hand, the boundary whether a complete CT ($\delta = 1$) occurs or not has still been characterized poorly, since such a strong donor is rare in organic materials. Among them, $\text{TDAE}\cdot\text{C}_{60}^2$ or $\text{Cp}^*\text{Ni}\cdot\text{C}_{60}\cdot\text{CS}_2$ ⁴⁰ seems to be the closest one to the boundary, where the $E_{1/2}^1(\text{D})$ values were estimated to be -0.75 V (vs SCE) for TDAE ⁴¹ and -0.65 V for Cp^*Ni .⁴² Although the relatively high conductivity in both complexes^{2a,40} is likely caused by the partial CT, the downshift of the $A_g(2)$ Raman-active mode by 6 cm^{-1} in $\text{TDAE}\cdot\text{C}_{60}$ ⁴³ indicated the almost complete monovalency of C_{60} molecules. The complete CT was also supported both by the observation of the UV–vis absorption bands characteristic of the monoanion of C_{60} in solution⁴⁴ and by the absence of the metallic behavior.⁴⁵ Unlike $\text{TDAE}\cdot\text{C}_{60}$, the degree of CT in the $\text{Cp}^*\text{Ni}\cdot\text{C}_{60}$ compound has not yet been clarified, although the Jahn–Teller distortion of the C_{60} molecule from I_h to D_{2h} symmetry has been observed.⁴⁰ This indicated that a considerable amount of CT

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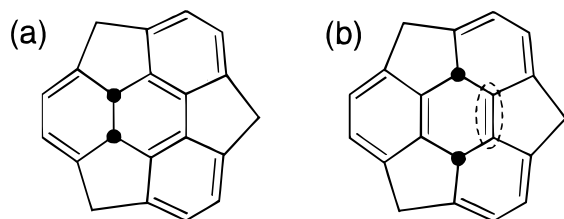


Figure 6. Addition patterns at (a) 1,2- and (b) 1,4-positions. The double bond introduced into a pentagon ring is encircled by the dotted line.

occurs in this compound. One can then expect that the boundary of $\delta = 1$ exists in the vicinity of Cp^*Ni-C_{60} compounds. Assuming that the boundary of $\delta = 1$ is parallel to that of $\delta = \delta_c$ (eq 6), substitutions of -0.65 V for $E_{1/2}^1(D)$ and -0.44 V for $E_{red}^1(A)$ in eq 6 give a line:

$$0.81E_{1/2}^1(D) - E_{red}^1(A) = -0.09 \text{ V} \quad (7)$$

Therefore, the possibility of the partial ionic CT may be present between eqs 6 and 7 as

$$-0.09 \text{ V} \leq 0.81E_{1/2}^1(D) - E_{red}^1(A) \leq +0.37 \text{ V} \quad (8)$$

Interestingly, despite the large difference in the molecular size, the requirement of the partial CT predicted here is very similar to that reported for the TTF–TCNQ system with the segregated stacks ($-0.02 \text{ V} \leq E_{1/2}^1(D) - E_{1/2}^1(A) \leq +0.34 \text{ V}$).^{17b}

Instability of $C_{60}X_n$ ($X = Cl, Br$). The absence of the reversible redox waves intrinsic to halogenofullerenes contrasts with the successful observations of them in $C_{60}H_2$,⁴⁶ $C_{60}(CN)_2$,⁴⁷ and $C_{60}F_n$,⁵ in which 1,2-addition is preferred to 1,4-addition due to the small size of addends. The difference in electrical stability observed may be explained by the difference of the addition patterns of the addend. In general, in 1,2-addition that is favorable for the small addend, H, F, or CN, double bonds are found only in hexagon rings, while in 1,4-addition that preferentially occurs for the sterically bulky addend such as Cl or Br, double bonds are found not only in hexagon rings but also in pentagon one, as shown in Figure 6.²⁹ Since the introduction of a double bond into a pentagon ring causes a considerable destability,³⁰ chloro- and bromofullerenes easily lose halogen atoms by both thermodynamical and electrical perturbations.

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Conclusion

The reactivity of halogenofullerenes, $C_{60}Cl_6$ and $C_{60}Br_n$ ($n = 6, 8$), was examined in $CHCl_3$, BZ, CS_2 , and CHX in the absence and in the presence of nine kinds of organic donors of TTF type. The order of stability in solution without any donors was $C_{60}Cl_6 > C_{60}Br_8 > C_{60}Br_6$, consistent with that of thermodynamical stability predicted by the AM1 calculation. In the presence of any electron donors in Chart 1, $C_{60}Br_8$ debrominated, giving rise to the formation of cation radicals. One of the representatives of the reaction was the formation of $TTF \cdot Br_x$ as a result of mixing $C_{60}Br_8$ with TTF in CS_2 , contrary to the result reported previously. Unlike $C_{60}Br_8$, a distinct change of the spectra was observed for $C_{60}X_6$ ($X = Cl, Br$) with a variation in electron-donating ability of the counter donors. The mixture with the relatively strong donors exhibited a characteristic absorption band of C_{60} due to the dehalogenation, while such a behavior was not observed for the weak donors. According to the difference in the reactivity with electron donors, the electrical stability order was found to be $C_{60}Cl_6 > C_{60}Br_6 > C_{60}Br_8$, consistent with the CV measurements, in which all halogenofullerenes used were surely confirmed to be stronger acceptors than the parent C_{60} . Based on the relationship between the electrochemical properties of the halogenofullerenes and the counter donors, the distinct boundary of $\delta = \delta_c$ was first derived for the C_{60} family: $0.81E_{1/2}^1(D) - E_{red}^1(A) = +0.37 \text{ V}$, which resembled quantitatively that obtained for the TTF–TCNQ family. For the preparation of the (partial) ionic CT complex, therefore, one should employ such a combination of the fullerene derivative and the counter donor meeting the requirement above. The electrical instabilities observed are caused by the presence of double bonds in pentagon ring(s), suggesting that the appropriate choice of the fullerene derivatives, in which there are no double bonds in a pentagon ring, should be essential.

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Supporting Information Available: UV–vis spectra of the mixtures of $C_{60}Cl_6$ with TTF system donors in $CHCl_3$ and CHX (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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