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Chemical and electrochemical reduction of the highly chlorinated fullerenes $C_{60}Cl_{24}$ and $C_{60}Cl_{30}$

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Fully aromatic $C_{60}Cl_{30}$ is much more difficult to reduce than non-aromatic $C_{60}Cl_{24}$; the anion radicals $C_{60}Cl_n^{\cdot-}$ (n = 24, 30) are unstable and undergo rapid decomposition with loss of Cl^- anions and partial substitution of chlorine atoms by organic groups.

Fullerene C_{60} and its derivatives are widely investigated as electron acceptors. Particularly, parent C_{60} can be easily reduced even to the hexaanion C_{60}^{6-}.[1] Ionic salts of C_{60} trianion M_3C_{60} (M = K, Rb, Cs) exhibited superconducting behaviour up to *ca.* 30 K;[2] the complex $TDAE^{+\cdot}{\cdot}C_{60}^{\cdot-}$ [TDAE = tetrakis(dimethylamino)ethylene] is the only known organic ferromagnetic material that has no *d* or *f* elements in its molecular framework.[3]

The only strong disadvantage of ionic fullerene-based systems is their instability under ambient conditions mostly because of the quenching of C_{60}^{n-} anions by molecular oxygen and moisture.[4] Therefore, there is a need for fullerene-based electron acceptors that can give anion radicals stable in air. This aim can be potentially fulfilled in fullerene derivatives that possess numerous electron-withdrawing groups attached to the carbon cage and, as a sequence, high electron affinity. The fluorinated fullerenes $C_{60}F_{18}$, $C_{60}F_{36}$ and $C_{60}F_{48}$ are strongly electron-deficient molecules that, however, do not give stable anion radicals because of degradation under reduction with loss of F^-.[5,6] Stabilization of halofullerenes can be achieved by arranging all halogen atoms at the fullerene surface in a specific fashion when all remaining sp^2 carbons form aromatic systems integrated in the cage. This is a case of *T*-isomer of $C_{60}F_{36}$ [Figure 1(*a*)] that possesses four aromatic six-memebered rings in the cage that makes this molecule quite inert towards reactions with nucleophiles.[7] However, this stabilization does not prevent this compound from degradation under reduction to the corresponding anion radical. The next generation of aromatic halofullerenes is represented by a family of fluorinated trannulenes, compounds with composition $C_{60}F_{15}R_3$ (R = malonate residue) derived from $C_{60}F_{18}$ and possessing one six-membered and one 18-membered all-*trans* annulene (called trannulene) aromatic rings [Figure 1(*b*)].[8] The compounds $C_{60}F_{15}R_3$ can be reversibly reduced to anion radicals under

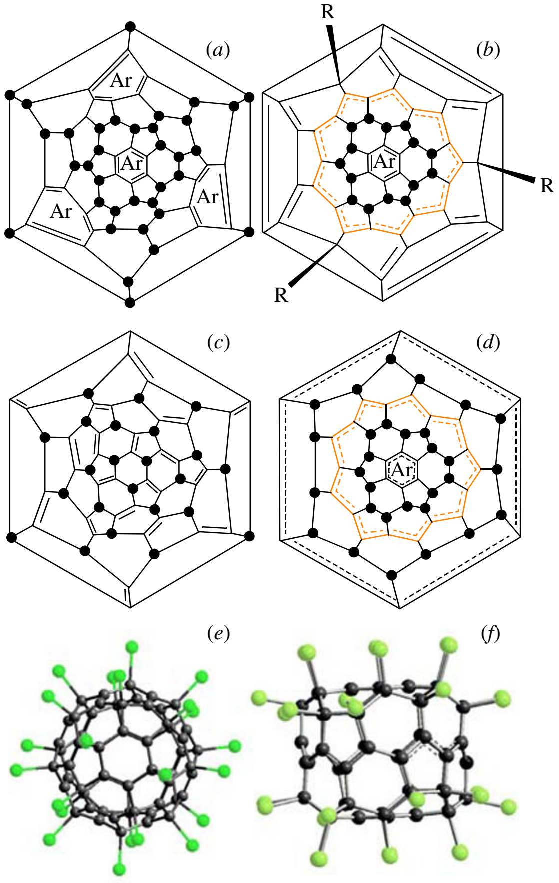


Figure 1 Schlegel diagrams for (*a*) *T*-$C_{60}F_{36}$, (*b*) $C_{60}F_{15}R_3$, (*c*) $C_{60}Cl_{24}$ and (*d*) $C_{60}Cl_{30}$; solid circles denote carbons bearing halogen atoms. Molecular structures of (*e*) $C_{60}Cl_{24}$ and (*f*) $C_{60}Cl_{30}$. Trannulene rings in the diagrams of $C_{60}F_{15}R_3$ and $C_{60}Cl_{30}$ are shown by thin lines.

electrochemical conditions; however, formation of stable ionic salts was not reported.[9]

The synthesis and structural characterization of the most aromatic and stabilised halofullerene $C_{60}Cl_{30}$ were reported recently.[10] This molecule has no isolated double bonds, all sp^2 carbon atoms form two aromatic hexagons and trannulene ring sandwiched between two belts of sp^3 carbons bearing chlorine atoms [Figure 1(*d*),(*f*)]. $C_{60}Cl_{30}$ can be considered as a very promising electron acceptor that can potentially give stable anion radicals due to a high degree of aromatic stabilization and the presence of 30 electron-withdrawing chlorine atoms.

Here, we report the reduction of $C_{60}Cl_{30}$ under electrochemical conditions and in the presence of strong organic donors such as TDAE and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Newly prepared highly symmetrical [Figure 1(*c*),(*e*)] non-aromatic $C_{60}Cl_{24}$[11] was studied for comparison.

Table 1 Electrochemical reduction potentials (*vs.* SCE) for $C_{60}Cl_{30}$ and $C_{60}Cl_{24}$ in comparison with data reported for other halogenated fullerenes and C_{60}.

Compound	$E_{1/2}$ (V *vs.* SCE)			Ref.
$C_{60}Cl_{24}{}^{a}$	0.00^{b}	-0.30^{b}	-0.66^{b}	This work
$C_{60}Cl_{30}{}^{a}$	-0.25^{b}	-0.62^{b}	-1.05^{b}	This work
$C_{60}F_{18}$	-0.33^{b}			12
$C_{60}F_{15}[C(COOEt)_3]_3$	−0.09			9
C_1-$C_{60}F_{36}$	0.07	-0.38^{b}	-0.98^{b}	12
C_3-$C_{60}F_{36}$	0.12	-0.39^{b}	-1.03^{b}	12
T-$C_{60}F_{36}$	0.04	-0.43^{b}	-0.97^{b}	12
$C_{60}F_{48}$	0.78^{b}	0.34^{b}	-0.15^{b}	13
C_{60}	−0.60	−1.07	−1.87	14

[a]The data collected for *ca.* 0.2 mM solutions of $C_{60}Cl_n$ in 0.1 M $TBAPF_6$–1,2-$C_6H_4Cl_2$ at 0.2 V s^{-1} at 20 °C. A glassy carbon working electrode had a size of 0.2 mm^2; a platinum wire was used as a reference electrode; all potentials were measured against SCE. [b]E_p for quasi-reversible or totally irreversible peaks.

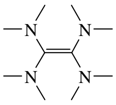
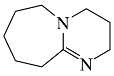
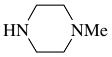
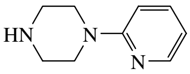
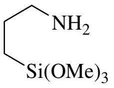
Both $C_{60}Cl_{30}$ and $C_{60}Cl_{24}$ undergo irreversible electrochemical reduction in 1,2-dichlorobenzene even at high scan rates of 500 mV s^{-1} (Table 1, potentials are given *vs.* SCE). However, the first reduction potential of $C_{60}Cl_{30}$ is much lower than that of $C_{60}Cl_{24}$ in spite of the presence of a higher number of electron-withdrawing chlorine atoms in $C_{60}Cl_{30}$ molecule. Difficulty of reduction of $C_{60}Cl_{30}$ with respect to $C_{60}Cl_{24}$ and instability of corresponding anion can be rationalised if we assume that conversion of $C_{60}Cl_{30}$ to $C_{60}Cl_{30}^{\bullet-}$ is accompanied by loss of aromaticity. The non-aromatic anion $C_{60}Cl_{30}^{\bullet-}$ can gain back stabilization after elimination of Cl^- and formation of the aromatic radical $C_{60}Cl_{29}^{\bullet}$, which can further degrade *via* different pathways. Similar trends were observed in reduction of fully aromatic *T*-$C_{60}F_{36}$ (four aromatic hexagons in the cage) in comparison with partially aromatic (three aromatic hexagons and three isolated double bonds) C_3 and C_1 isomers of this fluoride.[12] Thus, the first reduction potential of *T*-$C_{60}F_{36}$ was 0.04 V (*vs.* SCE) with respect to 0.07 and 0.12 V for C_1 and C_3 isomers, respectively. Loss of aromaticity of *T*-$C_{60}F_{36}$ under reduction shifts the reduction potential to more negative values. This shift is much more pronounced for $C_{60}Cl_{30}$ (compared with $C_{60}Cl_{24}$) because reduction seems to destroy a 18-electron aromatic system, which is larger than a six-electron aromatic ring in *T*-$C_{60}F_{36}$.

It is known that [60]fullerene can be reduced to anion radicals by strong amine-based organic donors such as TDAE[3] and DBU.[15] The difference between these two donors is in the character of reduction. TDAE does not undergo addition to the carbon cage thus forming truly ion-radical salt $TDAE^{+\bullet}C_{60}^{\bullet-}$. The reduction of fullerene by DBU is accompanied by addition of amine to double C=C bond of the fullerene cage with formation of the diamagnetic zwitter ion DBU^{+}–C_{60}^{-}. Reactions of both $C_{60}Cl_{30}$ and $C_{60}Cl_{24}$ with an excess of TDAE or DBU (35 equiv. for $C_{60}Cl_{30}$ and 30 equiv. for $C_{60}Cl_{24}$) were conducted under stirring in an argon atmosphere at room temperature for 2 h. The addition of amine was accompanied by an immediate change in the colour of the reaction mixture from yellow-orange ($C_{60}Cl_{24}$) or red ($C_{60}Cl_{30}$) to dark brown; precipitation of insoluble reaction products was observed within 20–40 min. The amorphous precipitates formed were washed initially with hexane, next with chloroform and finally with diethyl ether. The obtained solids were polar compounds (soluble in DMSO, sparingly soluble in MeOH and water), whose composition determined from chemi-cal analysis data corresponded to $C_{60}(-N^{+}R_3)_xCl_y^-$ ($x = 2.3$–6.4, $y = 3.5$–8.1, NR_3 denotes DBU or TDAE). Thus, the test reactions resulted in elimination of chlorine atoms from the fullerene cage accompanied by their partial substitution with tertiary amine groups.

The ^{1}H NMR spectra exhibited only broad humps corresponded to the signals from numerous non-equal amine groups attached to the cage. The ESR spectra of all $C_{60}(-N^{+}R_3)_xCl_y^-$ compounds (solutions and powders) were represented by single signals that can be fitted by superposition of two or more Lorenz curves. The average *g*-factor ($g_{av} = 2.004$–2.005 G) and line width ($H_{pp} = 3$–7 G) depend on sample composition (Table 2) but remain almost the same at lower temperatures (down to 77 K). The signals with similar ESR parameters were observed for samples of $C_{60}Cl_6$ treated with DBU under conditions described above (7 equiv. of amine were added). The appearance of signals in the ESR spectra of halofullerenes reduced by TDAE or DBU can correspond to the presence of the $C_{60}(-N^{+}R_3)_xCl_y^-$ species with odd x values (1, 3, 5, 7, *etc.*). Probably, such compounds can exist as stable radicals at room temperature since their recombination (dimerisation of two fullerene cages bearing bulk addends) should be extremely hindered.

Surprisingly, reactions of chlorofullerenes with small amounts of amines (DBU, TDAE, 1–5 equiv.) afforded the precipitation of products that possess compositions and ESR spectral parameters very similar to the samples obtained using a large excess of amines. At the same time, a considerable part of the pristine halofullerenes remains unchanged and can be recovered even after a long reaction time (*ca.* 12–24 h). The degradation of $C_{60}Cl_{30}$ was monitored by changes in the absorption spectrum of this chlorofullerene in the visible region (Figure 2). Thus, the addition of 4 equiv. of DBU results in immediate decrease in

Table 2 Bulk composition of products prepared in the reactions of halofullerenes with amines.[a]

Amine	$C_{60}Cl_{24}$	$C_{60}Cl_{30}$	$C_{60}F_{36}$
 TDAE	$C_{60}(amine)_{4.9}Cl_{5.7}$	$C_{60}(amine)_{6.4}Cl_{8.1}$	—
 DBU	$C_{60}(amine)_{2.3}Cl_{4.3}$	$C_{60}(amine)_{1.8}Cl_{3.5}$	—
	$C_{60}(Amine)_{5.6}{}^{b}$	$C_{60}(Amine)_{8.4}{}^{b}$	$C_{60}(Amine)_{7.9}F_{7.3}{}^{b}$
	$C_{60}(Amine)_{7.1}{}^{b}$	$C_{60}(Amine)_{6.6}{}^{b}$	$C_{60}(Amine)_{6.6}F_{5.1}{}^{b}$
	$C_{60}(Amine)_{12.8}{}^{b}$	—	—

[a] Bulk compositions were calculated from chemical microanalysis data. The contents of C, H and N were determined for all samples; Cl, Si and F were analysed depending on the composition of the starting halofullerene (Cl or F) and reagent (presence of Si). Two or three measurements were performed to determine content of specified element in every sample; deviations between measurements were below ±0.15%. [b] 'Amine' means the residue of starting amine without hydrogen atom at nitrogen.

intensities of the 350–550 nm bands; this observation proves that a part of $C_{60}Cl_{30}$ was consumed in some reaction accompanied by destruction of the trannulene ring in the molecule of this chloride. This process becomes slower with time, but the degradation of $C_{60}Cl_{30}$ is still evident even after 12 h after initiation of the reaction. The complete disappearance of $C_{60}Cl_{30}$ trannulene absorption bands was achieved after three days when extra 30 equiv. of DBU were added to the reaction mixture. The resulting absorption spectrum is similar to the spectra of polyaminofullerenes prepared by a direct reaction of C_{60} with an amine in air.[16]

The chlorofullerenes $C_{60}Cl_{30}$ and $C_{60}Cl_{24}$ also react with primary and secondary amines in the presence of K_2CO_3 (1 equiv. of amine per halogen atom in the substrate molecule, stirring at room temperature for 12 h followed by heating at reflux for 1 h). These reactions yield mixtures of neutral polyaminofullerenes $C_{60}[NRR']_x$, whose average composition was determined by chemical analysis (Table 2). Piperazine-containing polyaminofullerenes readily give water-soluble salts under treatment with organic or inorganic acids. These salts were isolated as brownish solids under slow concentration of their acidic solutions in a vacuum at room temperature. Concentration at elevated temperature is accompanied by hydrolysis and formation of water insoluble fullerenols $C_{60}(OH)_x$ and salts of corresponding piperazines.

As it is seen in Table 2, the composition of the product depends on the structure of reagent but the number of amine addends is always much lower than the number of chlorine atoms in starting halofullerene. It is also surprising that the prepared aminofullerenes contain no chlorine atoms attached to the fullerene cage. This feature is in a sharp contrast with the reactivity of $C_{60}F_{36}$, which also undergoes partial substitution and elimination of fluorine atoms but still leaves part of them attached to the fullerene cage. For example, reaction of $C_{60}F_{36}$ with *N*-methylpiperazine yields a product mixture with bulk composition C_{60}(4-methylpiperazin-1-yl)$_{7.9}F_{7.3}$. This material is unstable under continuous (1 month) storage in air and undergoes hydrolysis to form the water-soluble salts C_{60}(4-methylpiperazin-1-yl)$_x$-$(OH)_y(HF)_z$.

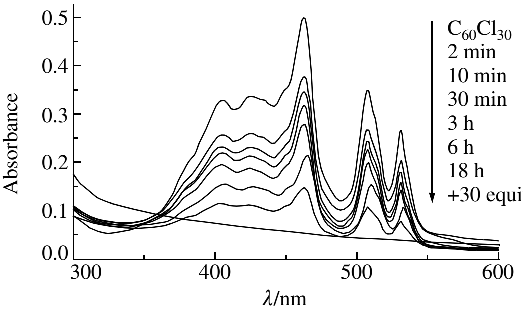


Figure 2 Evolution of absorption spectrum of $C_{60}Cl_{30}$ + 4DBU reaction mixture with time.

To investigate the possibility of photoinduced electron transfer reduction of $C_{60}Cl_{30}$, this chlorofullerene was mixed with polyconjugated polymer poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-*p*-phenylene vynilene] (MDMO-PPV) and the resulting blend was studied by light-assisted ESR. Photoinduced electron transfer yielding long-lived charge-separated states occurs with outstanding efficiency between C_{60} or its simple derivatives (monoaddition products like PCBM) and polyconjugated polymers.[17] In contrast, no signals from polymer 'back-bone' cation and chlorofullerene anion were detected by this method in $C_{60}Cl_{30}$–MDMO-PPV blend probably due to a short lifetime of the charge-separated state. The fluorinated trannulene $C_{60}F_{15}[C(COOEt)_3]_3$,[†] which was a reference compound in the blend with MDMO-PPV, exhibited extremely low-intensity signals presumably from the photogenerated polymer 'back-bone' radical cation.

Thus, we investigated the chemical and electrochemical reduction of the $C_{60}Cl_{30}$ electron-deficient fullerene derivative (with respect to C_{60}) with a high degree of aromatic stabilization. It was shown for the first time that an increase in electron affinity of the fullerene cage by addition of multiple electron-withdrawing groups does not result in a similar increase in the stability of the corresponding anion radicals. The reason is in almost complete destruction of the fullerene π-system in such derivatives as $C_{60}Cl_{30}$; even high degree of charge delocalization that is hypothetically possible in the 18-electron trannulene system of $C_{60}Cl_{30}^{\bullet-}$ does not save this anion radical from degradation *via* loss of Cl^-.

Supplementary materials including CVA plot for $C_{60}Cl_{30}$ and ESR spectrum of the $C_{60}Cl_{30}$ + DBU product are available free of charge *via* http://www.turpion.org/suppl/mc/2346/suppl2346.pdf.

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[†] Sample of $C_{60}F_{15}[C(COOEt)_3]_3$ was provided by Professor R. Taylor.