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Soluble Chlorofullerenes $C_{60}Cl_{2,4,6,8,10}$. Synthesis, Purification, Compositional Analysis, Stability, and Experimental/Theoretical Structure Elucidation, Including the X-ray Structure of $C_1\text{-}C_{60}Cl_{10}$

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Abstract: The efficacy of various analytical techniques for the characterization of products of C_{60} chlorination reactions were evaluated by (i) using samples of $C_{60}Cl_6$ of known purity and (ii) repeating a number of literature syntheses reported to yield pure $C_{60}Cl_n$ compounds. The techniques were NMR, UV-vis, IR, and Raman spectroscopy, FAB, MALDI, LDI, ESI, and APCI mass spectrometry, HPLC, TGA, elemental analysis, and single-crystal X-ray diffraction. Most of these techniques are shown to give ambiguous or erroneous results, calling into question the composition and/or purity of nearly all $C_{60}Cl_n$ compounds reported to date. The optimum analytical method for chlorofullerenes was found to be a combination of HPLC and either MALDI or APCI mass spectrometry. For the first time, the chlorination of C_{60} by ICl, ICl_3 , and Cl_2 was studied in detail using dynamic HPLC analysis and APCI mass spectrometry. Suitable conditions were found for the preparation of the new chlorofullerenes $1,7\text{-}C_{60}Cl_2$, $1,9\text{-}C_{60}Cl_2$, $1,6,9,18\text{-}C_{60}Cl_4$, and $1,2,7,10,14,24,25,28,29,31\text{-}C_{60}Cl_{10}$. The latter compound was also studied by ^{13}C NMR spectroscopy and X-ray diffraction, which led to the unambiguous determination of its asymmetric addition pattern. The unusual structure of $C_{60}Cl_{10}$ was compared with other possible isomers using DFT-predicted relative energies. These results, along with additional experimental data and an analysis of the DFT-predicted frontier orbitals of likely intermediates, were used to rationalize the formation of the new compound $C_{60}Cl_{10}$ from $C_{60}Cl_6$ and excess ICl without the rearrangement of any C–Cl bonds. For the first time, the stability of $C_{60}Cl_n$ compounds under a variety of conditions was studied in detail, leading to the discovery that they are, in general, very light-sensitive in solution. The X-ray structure of $C_{60}Cl_6$ was also redetermined with higher precision.

Introduction

The direct addition of substituents to one or more of the double bonds of fullerenes such as C_{60} and C_{70} is the most common way to prepare fullerene derivatives, which are used for both scientific studies and practical applications.¹ Addition-reaction types include cycloaddition, halogenation, and electrochemical reduction followed by alkylation. The “direct-addition” products can sometimes be converted into an even wider array of derivatives by subsequent substitution reactions, including derivatives that cannot be prepared by direct addition reactions. In this regard, the halofullerenes, $C_{60}X_n$, are arguably the most versatile substitution-reaction precursors, and within

this class of compounds chlorofullerenes are far superior to either (i) fluorofullerenes, for which practical amounts are only available for high values of n (i.e., $n \geq 18$), or (ii) bromofullerenes, which are notoriously insoluble. (Note that no iodofullerenes $C_{60}I_n$ have been reported.) Although there are reports of the conversion of $C_{60}F_{18}$ to $C_{60}F_{15}Ph_3$ ² and of $C_{60}Br_{24}$ to $C_{60}F_{24}$ ³ and $C_{60}Cl_{24}$,⁴ there are many more reports of the conversion of the chlorofullerene $C_s\text{-}C_{60}Cl_6$ to many different products, including $C_{60}Me_6$ and $C_{60}Me_5Cl$,⁵ $C_{60}(CH_2CH=CH_2)_6$

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and $C_{60}(CH_2CH=CH_2)_5Cl$,⁶ $C_{60}(OMe)_5OH$ and $C_{60}(OEt)_5OH$,⁷ and $C_{60}Ar_5Cl$ ⁸ ($Ar = Ph$, tolyl, anisyl, *tert*-butylphenyl, fluorophenyl, trimethylsilylphenyl, and thiienyl). The chlorofullerenes $C_sC_{60}Cl_6$ and $C_sC_{70}Cl_{10}$ have been used as precursors for the preparation of derivatives with potentially useful optical⁹ and biomedical properties.¹⁰ There is even one report of the use of $C_sC_{60}Cl_6$ as a chlorinating reagent for organic compounds.¹¹ For all of these reasons, the synthesis of new chlorofullerenes continues to be an important part of our research program.

Compounds of the formula $C_{60}Cl_n$ were among the first derivatives of C_{60} to be reported in the literature. Mixtures of $C_{60}Cl_n$ compounds were prepared in 1991,^{12,13} followed by the synthesis and structure elucidation of the only known isomer of $C_{60}Cl_6$ in 1993.¹⁴ Table 1 lists all $C_{60}Cl_n$ syntheses reported prior to this work,^{4,12–29} including the recent report of two non-isolated-pentagon-rule³⁰ derivatives prepared by adding molec-

ular chlorine to the carbon-arc fullerene-synthesis reactor.²⁹ (Hereinafter, the term chlorofullerene, abbreviated CF, will be used exclusively to denote $C_{60}Cl_n$ derivatives of the one and only isolated-pentagon-rule³⁰ (IPR) isomer of C_{60} (this isomer is sometimes denoted $^{#1812}C_{60}$),^{29,30,35} the two non-IPR $C_{60}Cl_n$ derivatives reported in 2008²⁹ will be denoted $^{#1809}C_{60}Cl_8$ and $^{#1804}C_{60}Cl_{12}$ for clarity). Note that nearly all CFs are soluble in a variety of organic solvents.

The historically important and synthetically useful compound $C_sC_{60}Cl_6$ is properly numbered 1,6,9,12,15,18- $C_{60}Cl_6$. It has the skew-pentagonal-pyramidal addition pattern, and for this reason the IUPAC locant set “1,6,9,12,15,18-” will be abbreviated “SPP-”. Table 1 reveals that several CFs other than SPP- $C_{60}Cl_6$ (hereinafter referred to as $C_{60}Cl_6$, because SPP- $C_{60}Cl_6$ is the only known isomer of this composition) have been reported, and some of these have been characterized by single-crystal X-ray diffraction.^{15–18} However, it is generally acknowledged that the isolation of a crystal or a number of crystals of high compositional and isomeric purity is no guarantee that the bulk product is homogeneous. As discussed below, only one paper reporting the synthesis of practical amounts of one or more CFs (or their X-ray structures) included compelling physicochemical data regarding the molecular composition and isomeric purity of the bulk reaction product (hereinafter the term *molecular composition* will mean the relative amounts of compositionally and/or isomerically different CF molecules present in a reaction product). Since there are, in principle, tens of thousands or hundreds of thousands of possible $C_{60}Cl_n$ isomers for $n > 2$, the burden of proof must be on the authors of synthetic papers to unambiguously establish the purity of their products (there are 23 unique isomers possible for $C_{60}Cl_2$). Until recently, this has been difficult to do and, consequently, has not been done.

In the CF study reported in this paper, the burden-of-proof requirement has been realized, not only for our new synthetic methodology but for several of the synthetic methodologies reported in the literature. We have discovered that the *combination* of HPLC and MALDI- or APCI-MS is the way to reliably analyze CF product mixtures and to determine the purity of individual CFs. Using HPLC and MALDI-MS, we experimentally re-examined reactions 6, 7, 16–18, and 20 listed in Table 1 and found that they produce much more complicated product mixtures than originally reported. In addition, we have studied the chlorination of C_{60} with iodine monochloride, iodine trichloride, and molecular chlorine in chlorobenzene in great detail and have observed two isomers of $C_{60}Cl_2$, one isomer each of $C_{60}Cl_4$ and $C_{60}Cl_6$, and multiple isomers of $C_{60}Cl_8$, $C_{60}Cl_{10}$, and $C_{60}Cl_{12}$ that appear and disappear as a function of time and/or the C_{60} /chlorinating agent mole ratio. One isomer of $C_{60}Cl_{10}$ with an unprecedented addition pattern was structurally characterized by single-crystal X-ray diffraction (an improved X-ray structure of $C_{60}Cl_6$ was also determined). The unusual and seemingly haphazard addition pattern of $C_{60}Cl_{10}$ can be rationalized by inspecting the DFT HOMOs or LUMOs

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Table 1. Compilation of $C_{60}Cl_n$ Chlorofullerene Syntheses, 1991–Present^a

reaction no. [year] ^{ref}	proposed composition ^b	proposed purity [yield]	reagents and rxn conditions	analytical techniques used for characterization ^{b,c}	stability	solvability
1 [1991] ¹²	$C_{60}Cl_{1-24}^d$	mix. [n/r]	Cl_2 , 250–400 °C	WI, EA, IR, (¹³ C NMR, ^e MS (FAB and FI) ^f)	Cl_2 loss at 400 °C	org. solv.
2 [1991] ¹³	$C_{60}Cl_{12-15}^g$	mix. [n/r]	Cl_2 , –35 °C, no light	EA, IR, XPS, (¹³ C NMR ^h)	Cl_2 loss above 200 °C	$PhCH_3$, CH_2Cl_2
3 [1993] ¹⁴	SPP- $C_{60}Cl_6^g$	n/r [100.5%] ⁱ	ICl , C_6H_6 , 3 d ^j	EA, IR, UV-vis, ¹³ C NMR	n/r	org. solv. ^k
4 [1993] ²⁰	$C_{60}Cl_{40}^g$	n/r [n/r]	Cl_2 , CCl_4 , UV	EA, IR, UV-vis	n/r	n/r
5 [1994] ²¹	$C_{60}Cl_{40}^g$	mix. [n/r]	Cl_2 , CCl_4 , UV	EA, IR, UV-vis	Cl_2 loss when heated	CH_2Cl_2 , CCl_4
6 [1996] ²²	$C_{60}Cl_{12}^g$	n/r [n/r]	ICl , C_6H_6 , no light	EA, UV-vis	n/r	C_6H_6 , $C_6H_{12}^l$
7 [1997] ²³	$C_{60}Cl_{24}^m$	n/r [n/r]	Cl_2 , CCl_4 , UV, 44 h	FAB-MS	n/r	CCl_4
8 [1997] ²³	SPP- $C_{60}Cl_6$	n/r [n/r]	ICl , C_6H_6 , 5 d	none	n/r	CCl_4
9 [1998] ³¹	$C_{60}Cl_{24}$	n/r [n/r]	Cl_2 , 327 °C	IR, Raman	n/r	n/r
10 [1999] ²⁴	$C_{60}Cl_{7-45}^n$	mix. ^o [n/r]	Cl_2 , CS_2 , UV	WI, MALDI-MS, PIXE-NMP, EMP, HPLC	possible Cl_2 loss ^p	$PhCH_3$
11 [1999] ²⁵	$C_{60}Cl_{22}^q$	n/r [100%]	Cl_2 , 200–300 °C	WI, IR	n/r	n/r
12 [2001] ³²	$C_{60}Cl_{16}^g$	n/r [42%]	$PhICl_2$, 25 °C, 5 d	EA, IR, LDI-MS (¹³ C NMR)	n/r	$CHCl_2$, $CHCl$
13 [2002] ²⁶	$C_{60}Cl_{30\pm2}^r$	n/r [n/r]	Cl_2 , UV	TG, IR, MALDI-MS (LDI-MS)	n/r	$PhCH_3$
14 [2002] ³³	$C_{60}Cl_{24}$	99.9%[n/r]	Cl_2 , 310 °C	HPLC, WI, UV-vis	n/r	org. solv.
15 [2003] ²⁷	SPP- $C_{60}Cl_6^s$	n/r [n/r]	ICl , ODCB, 7 d ^t	IR, possibly EA	n/r	C_6H_6 , ODCB
16 [2003] ²⁷	$C_{60}Cl_8^u$	“mix. of isomers” [80–99%]	ICl , ODCB, 3 h ^t	EA, IR, (MALDI-MS, ¹³ C NMR ^h)	n/r	C_6H_6 , ODCB
17 [2003] ²⁷	$C_{60}Cl_{10}^u$	same as above	Cl_2 , ODCB, 15 min ^t	same as above	n/r	C_6H_6 , ODCB
18 [2003] ²⁷	$C_{60}Cl_{12}^u$	same as above	ICl , ODCB, 24 h ^t	same as above	n/r	C_6H_6 , ODCB
19 [2003] ²⁷	$C_{60}Cl_{14}^u$	same as above	$KICl_4$, ODCB, 7 d ^t	same as above	n/r	C_6H_6 , ODCB
20 [2003] ²⁷	$C_{60}Cl_{26}^v$	same as above	Cl_2 , ODCB, 7 d ^t	EA, IR, MALDI-MS, (¹³ C NMR ^e)	n/r	C_6H_6 , ODCB
21 [2004] ⁴	$T_h-C_{60}Cl_{24}^w$	~90% ^x [n/r]	VCl_4 , 160–180 °C ^y	EA, IR, ^z TGA-MS, MALDI-MS	“ Cl_2 loss at 280–390 °C” ^{aa}	n/r
22 [2005] ¹⁵	$T_h-C_{60}Cl_{24}^{ab}$	“pure” [n/r]	VCl_4 , 160–180 °C ^y	IR, ^z X-ray	“ Cl_2 loss at 280–390 °C” ^{aa}	n/r
23 [2005] ¹⁶	$D_{3d}-C_{60}Cl_{30}^{ab}$	“pure” [n/r]	ICl , 220–250 °C ^y	IR, ^z X-ray, TGA-MS	“ Cl_2 loss at 450–500 °C” ^{aa}	ODCB ^{ac}
24 [2005] ¹⁷	$C_2-C_{60}Cl_{30}^{ad}$	n/r [n/r]	VCl_4 , 160 °C	IR, ^z X-ray	n/r	n/r
25 [2005] ¹⁷	$C_1-C_{60}Cl_{28}^{ad}$	n/r [n/r]	ICl , 160 °C ^y	IR, ^z X-ray	n/r	n/r
26 [2005] ¹⁹	SPP- $C_{60}Cl_6^{ae}$	90–99% [90%]	ICl , PhCl, 7 min	HPLC, IR, ^z Raman, ^z MALDI-MS, ¹³ C NMR	decomp in solution	$PhCH_3$, $CDCl_3$
27 [2005] ¹⁹	[$C_{60}Cl_5]_2$	n/r [n/r]	ICl , ODCB, 7 d	IR, TGA, (¹³ C NMR)	loses 4.6 ± 0.5 Cl atoms at 270 °C	CS_2
28 [2006] ¹⁸	SPP- $C_{60}Cl_6^{af}$	n/r [n/r]	$POCl_3$, 100–150 °C	IR, X-ray	n/r	n/r
29 [2007] ²⁸	[$C_{60}Cl_5]_2^{ad}$	n/r [40%]	$C_{60}Br_{24} + TiCl_4^{ag}$	IR, X-ray	n/r	n/r
30 [2007] ¹⁰	SPP- $C_{60}Cl_6^{ah}$	“as good...as...” 90% ^{ah} [77%]	ICl , ODCB	¹³ C NMR, IR, (ESI-MS)	n/r	$PhCl$, ODCB, $PhNO_2$
31 [2008] ²⁹	#1809- $C_{60}Cl_8$	n/r [n/r]	carbon-arc + Cl_2	¹³ C NMR, APCI-MS, X-ray	Cl_2 loss at 500 °C	$PhCH_3$, CS_2
32 [2008] ²⁹	#1804- $C_{60}Cl_{12}$	n/r [n/r]	carbon-arc + Cl_2	¹³ C NMR, APCI-MS, X-ray	Cl_2 loss at 500 °C	$PhCH_3$, CS_2
33 [this work]	$\sigma-C_{60}Cl_2$	75% [5%]	ICl , PhCl	HPLC, UV-vis, APCI-MS	n/r	$PhCH_3$, CH_2Cl_2
34 [this work]	$p-C_{60}Cl_2$	75% [5%]	ICl , PhCl	HPLC, UV-vis, APCI-MS	n/r	$PhCH_3$, CH_2Cl_2
35 [this work]	$C_{60}Cl_4$	98% [25%]	ICl , PhCl	HPLC, UV-vis, APCI-MS	n/r	$PhCH_3$, CH_2Cl_2
36 [this work]	SPP- $C_{60}Cl_6$	90–96% [90%]	ICl , PhCl	HPLC, UV-vis, IR, Raman, APCI-MS, ¹³ C NMR, X-ray	Cl_2 loss above 250 °C, light-sensitive	$PhCH_3$, CH_2Cl_2
37 [this work]	$C_{60}Cl_{10}$	98% [30%]	ICl , PhCl	HPLC, UV-vis, IR, Raman, APCI-MS, ¹³ C NMR, X-ray	light-sensitive	$PhCH_3$, CH_2Cl_2

^a Abbreviations: SPP- $C_{60}Cl_6 = C_5-C_{60}Cl_6 = 1,6,9,12,15,18-C_{60}Cl_6$; min = minutes; h = hours; d = days; mix. = mixture; n/r = not reported; org. solv. = organic solvents; WI = weight increase; EA = elemental analysis; TGA = thermogravimetric analysis; UV-vis = UV-vis spectroscopy; UV = UV irradiation; ODCB = 1,2-dichlorobenzene; FI = field ionization; PIXE-NMP = particle induced X-ray emission/nuclear microprobe analysis; EMP = electron microprobe analysis; CF(s) = chlorofullerene(s). ^b Comments within quotation marks are verbatim statements from the indicated reference. ^c Methods in parentheses were not suitable for analysis of CFs according to the statements of the authors. ^d Determined by WI and EA. ^e No peaks were observed in the liquid ¹³C NMR spectrum, and only broad peaks were observed in the C(sp²) and C(sp³) regions of the solid-state ¹³C NMR spectrum. ^f No CF ions were observed. ^g Determined by EA. ^h Only broad unresolved peaks in the C(sp²) and C(sp³) regions were observed in the liquid ¹³C NMR spectrum. ⁱ “quantitative yield... 100.5%” was reported in ref 14, which implies that the authors believed the purity of $C_{60}Cl_6$ to be ca. 100%; the authors later corrected the purity to ca. 75% (ref 5); in our 2005 paper (ref 19), we found that this procedure gives 80% pure SPP- $C_{60}Cl_6$. ^j A comparison of different synthetic methods for the preparation of $C_{60}Cl_6$ was reported in ref 19 and is discussed in greater detail in this paper. ^k “The product is very soluble in benzene, carbon disulfide, and tetrachloromethane, moderately soluble in chloroform, dichloromethane, and toluene, and slightly soluble in pentane, hexane, diethyl ether and acetone.” ^l “The crystals readily dissolved in benzene, cyclohexane, and other nonpolar solvents, and they have no solubility in polar solvents.” ^m Determined by FAB-MS. ⁿ Widely different compositions were obtained by different analytical methods for the same samples of chlorofullerenes. ^o HPLC analysis showed that the reaction products contained mixtures of compounds. ^p Chlorofullerene degradation upon standing and/or analysis was reported as one of the possible explanations for widely different values of n determined by different analytical methods (see footnote n). ^q Determined by weight increase. ^r Based on TGA and MALDI-MS. ^s As determined by EA and IR spectroscopy (IR spectrum was in agreement with literature data); see ref 14. ^t Ranges and/or multiple sets of reaction conditions and different chlorinating agents (ICl, ICl_3 , $KICl_4$) were reported to yield these compounds. ^u Determined by EA, which was claimed to be supported by results of chemical modification followed by ESI-MS analysis; the absence of control experiments for the selectivity of the chemical modification step makes it impossible to evaluate these results. ^v Determined by EA and MALDI-MS. ^w Based on EA, TGA, IR (experimental and simulated). ^x Purity estimation was based on IR data. ^y See ref 34 for an alternative preparation procedure. ^z Theoretical simulations of the vibrational spectra were performed along with the experimental measurements. ^{aa} See Section 2 for a reinterpretation of the reported TGA results. ^{ab} Determined by single-crystal X-ray diffraction and experimental and simulated IR data. ^{ac} ¹³C- $C_{60}Cl_{30}$ is insoluble in most common organic solvents such as diethyl ether, 1,4-dioxane, CH_2Cl_2 , $CHCl_3$, and CCl_4 ; it is poorly soluble in CS_2 , toluene, and chlorobenzene; and its solubility in ODCB was estimated at roughly 0.2 mg mL⁻¹. ^{ad} Determined by single-crystal X-ray diffraction study. ^{ae} The relative purity is reported here, as determined by integration of HPLC peaks. ^{af} As determined by single-crystal X-ray diffraction and IR spectroscopy. ^{ag} See ref 19 for an alternative effective synthesis. ^{ah} As determined by ¹³C NMR and IR spectroscopy (the experimental spectra were in agreement with the data reported in ref 14). ^{ai} Reported to be as good as the product of the synthesis reported in ref 19 on the basis of its ¹³C NMR spectrum.

of proposed intermediates leading from $C_{60}Cl_6$ to $C_{60}Cl_{10}$. Finally, we report for the first time that, in general, CFs are photosensitive in solution, even under normal laboratory lighting, and that precautions to exclude light must be taken to avoid decomposition when handling solutions of these interesting and synthetically useful compounds.

Results and Discussion

1. Instrumental Methods for Determining Chlorofullerene Composition and/or Purity. Which Ones Are Reliable and Which Ones Are Not? Careful reading of the literature reports listed in Table 1 revealed that, with one exception, CF molecular compositions and product purities have never been firmly demonstrated.¹⁹ In the majority of the rest of the studies, CF composition and purity were not even discussed explicitly, leaving it for the reader to assume that the reported synthesis or syntheses produced pure products. In some cases, the formation of CF mixtures was qualitatively demonstrated by ^{13}C NMR spectroscopy^{12,13} or HPLC analysis,^{7,24} but in only one paper other than our 2005 publication was the quantitative use of HPLC data for CF mixtures mentioned.⁷ However, even in that case, neither the HPLC data, nor details about the HPLC analysis, nor the procedure they used to interpret their HPLC data were reported.⁷ In this section, we will show that elemental analysis, thermogravimetric analysis, IR, UV-vis, and ^{13}C NMR spectroscopy, and MS ionization methods used in the past are not reliable methods to determine CF composition and purity, alone or in combination.

1.1. Reliability of HPLC as a Method for the Analysis of Chlorofullerenes. HPLC peak areas provide quantitative information on analyte concentrations weighted by their corresponding detector responses. If UV detection is used and analyte extinction coefficients at the detector wavelength are known, then molar concentrations can be determined. However, extinction coefficients for fullerene derivatives are rarely known and are not even knowable for unidentified impurities. Therefore, in most published HPLC analytical work on fullerenes and fullerene derivatives, all that can be reported are integrated peak areas. In many cases, this information can be valuable for comparing the relative purities of two samples. To distinguish between these two situations, we will use HPLC% values to denote percentages calculated from HPLC peak areas and mol % values to denote percentages calculated from molar concentrations. See Supporting Information for more details.³⁶

Surprisingly, HPLC has seen limited use for the study of CFs by others.^{7,24} The reason that most chemists have not considered using HPLC for CFs may be the following statement by the authors of ref 7: “[$C_{60}Cl_6$] was used without further purification in order to avoid degradation” (emphasis added). This statement implies that, in their hands, $C_{60}Cl_6$ degraded during HPLC purification. Despite this statement, we decided to try to purify $C_{60}Cl_6$ by HPLC using a Buckyprep column, and in 2005 we reported that no observable decomposition occurred during HPLC processing of this compound.¹⁹ In order to further demonstrate the reliability of HPLC for the analysis of CFs in this work, we prepared four samples of $C_{60}Cl_6$ of varying purity. These are listed as samples **A–D** in Table 2, and their Buckyprep HPLC traces are shown in Figure 1 (see also Supporting Information Figure S-1). All four samples were prepared using variations of our 7-min synthesis, using chlo-

Table 2. Methods of Analysis Used in This Work To Study $C_{60}Cl_6$ Samples of Varying Purity^a

$C_{60}Cl_6$ sample	HPLC % ^b		mol % ^c		analytical methods used for characterization ^d					
	$C_{60}Cl_6$	C_{60}	$C_{60}Cl_6$	C_{60}	HPLC ^e	IR	UV-vis	^{13}C NMR	MS	TGA ^f
A	95	n/o	95	n/o	+	+	+	+	+	–
B	89	3	86	6	+	+	+	+	+	+
C	67	n/o	67	n/o	+	+	+	+	+	–
D	30	7	27	14	+	+	+	+	+	–

^a In this table, $C_{60}Cl_6$ = SPP- $C_{60}Cl_6$. ^b The HPLC % values in these columns were determined by integration of HPLC peaks (300 nm detection); n/o = not observed. ^c The mol % values in these columns were determined by doubling the C_{60} peak area before calculating the percentages since the ratio of extinction coefficients of $\epsilon(C_{60})/\epsilon(C_{60}Cl_6)$ was found to be 0.49(3) at 300 nm; n/o = not observed. ^d A plus sign indicates that this method was used for this sample; a minus sign indicates that this method was not used for this sample. ^e The same HPLC column (Cosmosil Buckyprep), eluent (50/50 v/v toluene/heptane), and eluent rate (5 mL min^{-1}) were used for all four HPLC analyses. ^f TGA = thermogravimetric analysis.

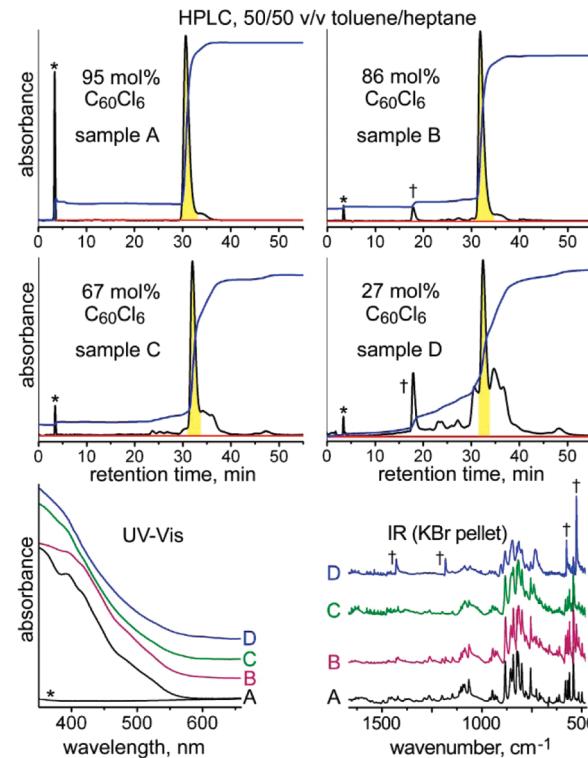


Figure 1. HPLC traces and IR and UV-vis spectra of $C_{60}Cl_6$ samples **A**, **B**, **C**, and **D**, with relative purities ranging from 95 to 27 mol %. The shaded HPLC peaks or portions of peaks are due to SPP- $C_{60}Cl_6$, and peaks marked with daggers are due to C_{60} . The peaks marked with asterisks are due to toluene (the samples were injected as 100% toluene solutions), and their integrated intensities were not included in the quantitative determination of $C_{60}Cl_6$. The IR peaks marked with daggers are due to C_{60} . The same parameters were used for the HPLC analyses (5 mL min^{-1} 50:50 v/v toluene/heptane eluent; 300 nm UV detection). The UV-vis spectrum marked with an asterisk is a toluene blank, and the spectra of samples **B**, **C**, and **D** are offset for clarity (all four samples have virtually no absorptivity at 650 nm).

robenzene (PhCl) as the solvent.¹⁹ Sample **A** was purified by HPLC to 95% $C_{60}Cl_6$ (see below). Sample **B** was from the same reaction as sample **A** but was not purified by HPLC (i.e., it is the crude product of the 7-min synthesis). Samples **C** and **D** were prepared by modifying the 7-min synthesis reaction conditions to intentionally lower the purity of the product. The HPLC traces reveal a much lower purity for sample **C** relative to that of samples **A** and **B** and an even lower purity for sample

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D. As discussed below, the impurities in these $C_{60}Cl_6$ samples were unreacted C_{60} and/or other CFs. No arylfullerene by-products were detected in these samples by mass spectrometry, in contrast to $C_{60}Cl_6$ samples prepared using benzene as the solvent instead of chlorobenzene.¹⁹

In this work, we report CF extinction coefficients (ϵ values) for the first time, for dichloromethane solutions of HPLC-purified $C_{60}Cl_6$ and the asymmetric isomer of $C_{60}Cl_{10}$ that we structurally characterized by X-ray diffraction, as well as ϵ values for C_{60} in both toluene and dichloromethane. These are listed in Supporting Information Table S-1, and the dichloromethane spectra are shown in Supporting Information Figure S-2. The data show that $\epsilon(C_{60})/\epsilon(C_{60}Cl_6) = 0.49(3)$ at 300 nm (the HPLC detector wavelength) and that $\epsilon(C_{60}Cl_6)/\epsilon(C_{60}Cl_{10}) = 1.00(6)$ at 300 nm. If we assume for now that the extinction coefficients at 300 nm for other CF impurities in samples **A–D** are the same as those for $C_{60}Cl_6$ and $C_{60}Cl_{10}$, we can calculate mol % values for $C_{60}Cl_6$ and C_{60} . (The mol % values can be recalculated in the future when extinction coefficients of other CFs become available and when the particular CF impurities in samples **A–D** are identified.) See Supporting Information for more details.^{19,37–39}

1.2. UV-vis Spectroscopy Is Not a Reliable Method of Analysis for Chlorofullerenes. The electronic transitions exhibited by fullerene derivatives are highly dependent on their addition pattern. Interestingly, the nature of the substituents has a much smaller effect on the UV-vis spectra (unless the substituents themselves absorb in the UV-vis region). In favorable cases, one can use UV-vis spectroscopy to elucidate the addition pattern of a fullerene derivative.^{40–45} For example, this was done to verify that a particular isomer of $C_{60}(CF_3)_6$ had the SPP addition pattern⁴⁰ and to determine that $C_{70}(CF_3)_2$ and $C_{1-C_70}(C_2F_5)_2$ have the same addition pattern.⁴¹ However, the purity of these compounds had already been determined by ^{19}F NMR spectroscopy before the UV-vis comparisons were made.

The UV-vis spectra for $C_{60}Cl_6$ samples became more featureless as the sample purity decreased from sample **A** to sample **D**, with the most significant difference between the spectra of samples **A** and **B** (95 mol % and 86 mol % $C_{60}Cl_6$, respectively; this is undoubtedly due to the 6 mol % impurity of C_{60} in sample **B**). However, there is virtually no difference between the spectra of samples **C** and **D**, which have very different levels of purity (67 mol % and 27 mol % $C_{60}Cl_6$, respectively). Furthermore, these UV-vis spectra are essentially

featureless, as is the UV-vis spectrum of the X-ray-characterized isomer of $C_{60}Cl_{10}$ discussed in a later section of this paper. It is quite clear that UV-vis spectroscopy alone is not a reliable method of analysis for CFs.

1.3. Neither IR nor Raman Spectroscopy Is a Reliable Method of Analysis for Chlorofullerenes. As shown by the information listed in Table 1, IR spectroscopy is one of the most common instrumental methods used for the characterization of CFs. When compared with theoretically predicted spectra, experimental IR spectra can sometimes be used to determine the addition pattern of a CF. This was the case for $T_h-C_{60}Cl_{24}$,⁴ the predicted addition pattern of which was later verified by X-ray crystallography.¹⁵ Recording CF Raman spectra is more challenging because the laser excitation of the sample can lead to the loss of Cl atoms (i.e., to sample decomposition). Nevertheless, Raman spectra have been reported for $C_{60}Cl_6$ ¹⁹ and for $T_h-C_{60}Cl_{24}$, $C_{60}Cl_{28}$, and $C_{60}Cl_{30}$.³⁴

However, at issue here is whether vibrational spectroscopy is a reliable method for determining CF purity, and the IR spectra of samples **A–D** demonstrate that it is not. The IR spectra of samples **A**, **B**, and **C** exhibit only minor differences, and even the spectrum of sample **D**, which contains only 27 mol % $C_{60}Cl_6$, is dominated by the bands due to $C_{60}Cl_6$, although they are clearly broader. The IR spectrum of sample **D** also exhibits sharp peaks, marked with daggers in Figure 1, assigned to 14 mol % C_{60} . Note that these bands are obvious only because the IR spectrum of the highly symmetric molecule I_h-C_{60} consists of four intense vibrational bands.⁴⁶ A 14 mol % impurity of a C_{2} - or C_1 -symmetry fullerene derivative might not even be noticed let alone provide quantitative or even qualitative mol % information.

A case in point is the following. In 2004 Troyanov and co-workers reported the synthesis of $T_h-C_{60}Cl_{24}$ and stated that “In view of the elemental analysis and IR spectroscopic data, the purity of the $C_{60}Cl_{24}$ samples should be estimated as rather high, with the major component content of at least 90%.”⁴ However, the results of other analytical methods reported in the same study gave contradictory results: the MALDI mass spectrum exhibited the $C_{60}Cl_{27}^-$ ion as the most intense peak, and the TGA mass loss corresponded to the composition $C_{60}Cl_{26.4}$ assuming that all Cl atoms were eventually lost at high temperature (a reasonable assumption). The presence of the intense $C_{60}Cl_{27}^-$ peak in the MALDI mass spectrum was explained away^{4,47} by invoking the analyte suppression effect, which is known to cause fullerene(X)_{n-1}⁻ ions with a greater number of electron-withdrawing substituents to have MS peak intensities higher than expected from the mol % values of their molecular precursors in a mixture relative to ions in the same mixture with a smaller number of electron-withdrawing substituents.^{48,49} However, the explanation for the inconsistent TGA mass loss, “[This is due to] the presence of a small $C_{60}Cl_{28}$ impurity in the sample”, cannot possibly be true because the sample would have had to contain only 42 mol % $T_h-C_{60}Cl_{24}$ and 58 mol % of $C_{60}Cl_{28}$ if these two were the only components of the TGA sample (furthermore, if CFs with $n \leq 22$ were also present, the

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T_h -C₆₀Cl₂₄ mol % value would have been even lower). It is clear that the authors grossly overestimated the purity of their product based on its IR spectrum.⁴ The high symmetry of T_h -C₆₀Cl₂₄ is probably the reason that it dominated the IR spectrum even though it was present at ≤ 42 mol % (note that the only isomer of C₆₀Cl₂₈ that is known has C_1 symmetry¹⁷).

In conclusion, under favorable conditions, when the IR spectra of at least some components of a CF mixture are known, IR or Raman spectroscopy might reveal the presence of some of the components. For example, an IR spectrum revealed the presence of another high-symmetry CF, D_{3d} -C₆₀Cl₃₀, in a sample of T_h -C₆₀Cl₂₄.³⁶ However, IR and Raman spectroscopy are not, in general, reliable quantitative methods of analysis for CFs.

1.4. NMR Spectroscopy Is Not a Reliable Method of Analysis for Chlorofullerenes. ¹³C NMR spectroscopy is a powerful method for the structure elucidation of organic compounds, including fullerene derivatives.⁵⁰ When sufficient sample is available and when the sample is sufficiently soluble in a convenient solvent, the 2D correlation technique ¹³C INADEQUATE can reveal the connectivity of carbon atoms, making a complete peak assignment and addition-pattern determination possible.^{51–56} However, in most cases small sample size and long acquisition times limit ¹³C NMR analysis of fullerene derivatives to revealing whether elements of symmetry are present. The only CF ¹³C NMR spectra reported to date are of C_s -C₆₀Cl₆ (ref 14 and this work), C_s -C₇₀Cl₁₀ (ref 57), and C_1 -C₆₀Cl₁₀ (this work). No ¹³C INADEQUATE studies of CFs have been reported.

The shortcomings of ¹³C NMR spectroscopy as an analytical method for the quantitative determination of CF purity became obvious after the report claiming the “quantitative yield” of C₆₀Cl₆,¹⁴ in which the authors concluded that they had prepared a pure product on the basis of the absence of extra ¹³C NMR resonances, was corrected by the same group in order to explain the presence of phenyl-containing derivatives in the products of methylation of their C₆₀Cl₆.²² The correction stated that the purity of C₆₀Cl₆ prepared by their original method¹⁴ was only ca. 75 mol %; the other 25 mol % consisted of phenylated derivatives and possibly C₆₀Cl_n compounds with $n > 6$.⁵ Our 2005 study confirmed this conclusion;¹⁹ in our hands, the purity of C₆₀Cl₆ obtained using the synthesis reported in ref 14 was 80% based on the integration of HPLC peaks.

Let us assume an ideal situation: a ¹³C NMR spectrum of a CF mixture consisting of a C_1 -symmetry major component and a C_1 -symmetry impurity has been acquired in such a way that peak intensities are proportional to the concentration of each type of cage C atom and that none of the peaks overlap another peak. Let us also assume that peaks are not detectable if their

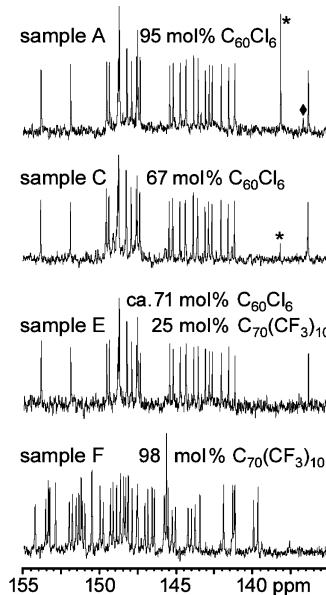


Figure 2. ¹³C NMR spectra in the C(sp²) region of C₆₀Cl₆ samples A and C, a 3:1 mixture of 95 mol % C₆₀Cl₆ and 98% mol % C₁-C₇₀(CF₃)₁₀ (sample E), and 98 mol % C₇₀(CF₃)₁₀ (sample F). Asterisks mark the peaks due to the *ipso* carbon atom of an impurity of toluene. The peak marked with a diamond in the spectrum of sample A is due to an unidentified impurity. Complete spectra, lists of $\delta(^{13}\text{C})$ values, and other information are available in Supporting Information.

signal-to-noise (S/N) ratio is less than or equal to 2. In this case, one can calculate the lower limit of mol % purity (LLMP) of the major component, which depends on the S/N ratio for the major component peaks. If the S/N ratio is 12 (a typical value for a high-quality fullerene-derivative ¹³C NMR spectrum), then the highest possible undetectable concentration of the impurity is only 6 times smaller than the major component concentration. In other words, the LLMP of the major component is 87 mol %. The LLMP drops quickly as the number of impurities increases, as the S/N ratio decreases, or if the symmetry number of the major component increases (see Tables S-2 and S-3 and accompanying text in Supporting Information for more details).

The C(sp²) regions of ¹³C NMR spectra of C₆₀Cl₆ samples A (95 mol % C₆₀Cl₆) and C (67 mol % C₆₀Cl₆) are shown in Figure 2. Also shown is the spectrum of a 3:1 mixture of 95 mol % C₆₀Cl₆ and 98 mol % C₁-C₇₀(CF₃)₁₀ (sample E) and, for comparison, the spectrum of 98% C₁-C₇₀(CF₃)₁₀ (sample F). The $\delta(^{13}\text{C})$ values for C₆₀Cl₆ and C₁-C₇₀(CF₃)₁₀ are listed in Supporting Information Tables S-4 and S-5, respectively, and expansions of the spectra are shown in Supporting Information Figures S-3, S-4, and S-5. The spectra of samples A and C have S/N ratios of 11 ± 2 . Despite their very different C₆₀Cl₆ mol % values, they are nearly indistinguishable. Sample C contains 33 mol % impurity molecules, but the impurities are effectively “NMR silent” under these conditions. An even more dramatic example is sample E, in which the ca. 25 mol % of a single C_1 -symmetry impurity is also effectively NMR silent (i.e., none of the peaks of sample F can be observed in sample E). The S/N ratio is ca. 6 for sample E, in harmony with the calculated LLMP value of 75 mol % for a C_s major component with a single C_1 impurity.

These results show conclusively that ¹³C NMR spectroscopy cannot reliably be used to determine the composition of CF mixtures and therefore the purity of individual CF compounds.

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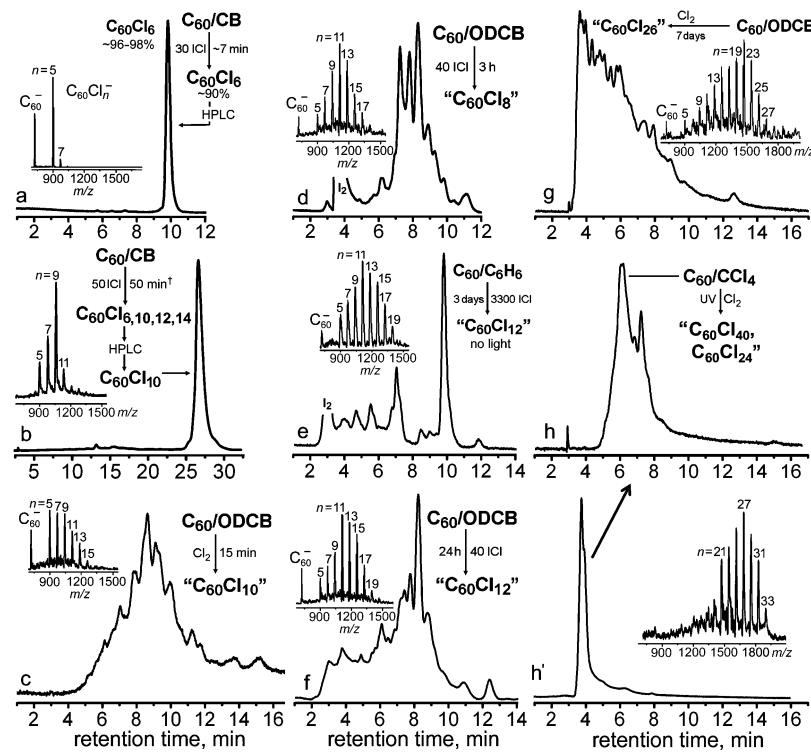


Figure 3. HPLC traces and (as insets) NI-DCTB-MALDI mass spectra of selected CF samples prepared in this work (CB = chlorobenzene; ODCB = 1,2-dichlorobenzene). Except for samples d and h, the HPLC conditions were Buckyprep column, 5 mL min^{-1} toluene, 300 nm detection; for samples d and h, the eluent was 5 mL min^{-1} 60:40 v/v toluene/heptane.

The claims of CF purity in the literature that are based on ^{13}C NMR data^{10,14} are probably incorrect and should be re-evaluated.

1.5. Reliability of Mass Spectrometry (MS) as a Method for the Analysis of Chlorofullerenes. Because of the relatively weak C–Cl bonds in CFs,⁵⁸ they have long been challenging MS analytes. In fact, until recently, MS was thought to be an unsuitable method of analysis for CFs because they underwent either complete loss of Cl atoms under EI or FI conditions¹² or partial loss of Cl atoms under FAB²³ or MALDI conditions.^{24,26,27} In this section of the paper, we review the literature and report the results of our analyses of various samples of C_{60}Cl_6 and $\text{C}_{60}\text{Cl}_{10}$, the relative purities of which had first been determined by HPLC. See also Supporting Information for a discussion of FAB-, LDI-, and ESI-MS results.^{23,26,32}

1.5.1. MALDI-MS. In 1999 Heymann et al. reported the first observation of CF ions, $\text{C}_{60}\text{Cl}_{7,9,11}^-$ and $\text{C}_{70}\text{Cl}_7^-$, in negative-ion-MALDI (NI-MALDI) mass spectra (2,5-dihydroxybenzoic acid was used as the matrix material).²⁴ Other analytical methods used in that study indicated considerably higher n values than 11 ± 1 and 7 ± 1 , respectively. These data suggested that the n values in the sample may have been as high as 45 ± 1 and 31 ± 1 , respectively,²⁴ indicating that extensive fragmentation of these CFs occurred during the MALDI process.

In 2002 we reported that the use of sulfur as a MALDI matrix suppresses halofullerene fragmentation, allowing, for the first time, MALDI-MS observation of high- m -value CF negative ions ($m = 5, 7, 9, \dots, 31$).²⁶ We later demonstrated that *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malonitrile (DCTB) is an even better NI-MALDI matrix material to prevent CF fragmentation.¹⁹ The best spectrum, reproduced in Figure 3a,

was achieved for a 95 mol % sample of C_{60}Cl_6 , which showed a major peak for $\text{C}_{60}\text{Cl}_5^-$ (intensity 100) and a minor peak for $\text{C}_{60}\text{Cl}_7^-$ (intensity ca. 10; this was proposed to result from chloride addition to C_{60}Cl_6).¹⁹ The positive-ion MS showed more substantial fragmentation, with a complete set of closed- and open-shell CF ions $\text{C}_{60}\text{Cl}_m^+$ with $m = 1-7$.¹⁹

In 2003, Troshin et al. reported the synthesis of the putative CF $\text{C}_{60}\text{Cl}_{26}$.²⁷ The authors implied that their product was compositionally pure but, based on ^{13}C NMR spectroscopy, consisted of multiple isomers of $\text{C}_{60}\text{Cl}_{26}$.²⁷ A NI-(9-nitroanthracene)-MALDI mass spectrum showed extremely low-intensity peaks ($S/N \leq 5$) for $\text{C}_{60}\text{Cl}_m^-$ ions with odd $m = 11-25$.²⁷

In this work, NI-DCTB-MALDI-MS was used to analyze several CF samples, including HPLC-purified $\text{C}_{60}\text{Cl}_{10}$. The mass spectra are shown in Figure 3. The spectrum of HPLC-purified $\text{C}_{60}\text{Cl}_{10}$, shown in Figure 3b, consists of a major peak for $\text{C}_{60}\text{Cl}_5^-$, two less intense fragment peaks for $\text{C}_{60}\text{Cl}_5^-$ and $\text{C}_{60}\text{Cl}_7^-$, and a minor peak for $\text{C}_{60}\text{Cl}_{11}^-$. These observations suggest that (i) loss of only a few Cl atoms and (ii) addition of a single chloride ion to the parent molecule C_{60}Cl_n may be general phenomena for NI-DCTB-MALDI mass spectra of CFs. If this is true, then this method of analysis is a suitable method for the determination of n in a highly purified C_{60}Cl_n compound or the highest value of n in a mixture of CFs. However, it could be the case that chloride ion addition is not a very efficient ionization process for high values of n . An example of such an ambiguity is the analysis of the spectrum shown in Figure 3g. The small peak assigned to $\text{C}_{60}\text{Cl}_{27}^-$ could arise from Cl atom loss from the parent ion $\text{C}_{60}\text{Cl}_{28}^-$ (due to a small amount of $\text{C}_{60}\text{Cl}_{28}$ in the sample) instead of chloride ion addition to $\text{C}_{60}\text{Cl}_{26}$. In any event, it is clear that MALDI-MS is not a suitable method for the compositional analysis of CF mixtures and therefore is

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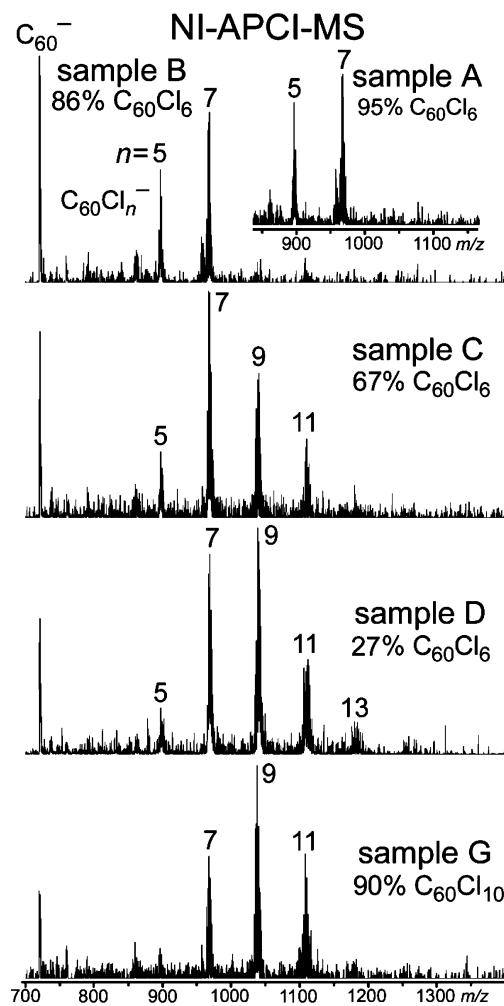


Figure 4. NI-APCI mass spectra of $C_{60}Cl_6$ samples A, B, C, and D and $C_{60}Cl_{10}$ sample G.

not suitable for analyzing the purity of a CF of unknown purity. The other mass spectra in Figure 3 will be analyzed in a later section of this paper.

1.5.2. APCI-MS. The APCI mass spectra of the $C_{60}Cl_n$ CFs studied in this work gave detectable $C_{60}Cl_m^+$ and $C_{60}Cl_m^-$ ions when n was 2, 4, or 6. The positive-ion spectra are shown in Supporting Information Figures S-6 and S-7. They demonstrate extensive fragmentation. For example, the entire set of $C_{60}Cl_m^+$ ions from $m = 1$ to $m = 6$ was observed for $C_{60}Cl_6$. However, no $C_{60}Cl_m^+$ positive ions were observed under APCI conditions for $C_{60}Cl_{10}$ or for any other CF we examined with more than ten Cl atoms. This is probably because CFs with more than six Cl atoms have ionization energies too high for $C_{60}Cl_m^+$ to form.

The negative-ion spectra of $C_{60}Cl_6$ samples A–D and $C_{60}Cl_{10}$ sample G are shown in Figure 4. For sample A (95% $C_{60}Cl_6$), only prominent peaks for $C_{60}Cl_5^-$ and $C_{60}Cl_7^-$ were observed (these peaks had similar intensities). The $C_{60}Cl_7^-$ ion is undoubtedly formed by addition of chloride ion to $C_{60}Cl_6$, as is true under MALDI-MS conditions. Virtually the same APCI mass spectrum was observed for sample B, demonstrating that APCI-MS cannot be used to determine the precise purity of $C_{60}Cl_6$, at least for this range of purities.

Prominent peaks for the $C_{60}Cl_7^-$ and $C_{60}Cl_9^-$ fragment ions were observed in the NI-APCI spectrum of sample G (90+% $C_{60}Cl_{10}$). A prominent peak for $C_{60}Cl_{11}^-$ was also observed, showing that the chloride ion adds to $C_{60}Cl_{10}$ under APCI

conditions as well as under MALDI conditions. However, it may not be the case that the chloride addition ion $C_{60}Cl_{n+1}^-$ will always be observed for a given $C_{60}Cl_n$ compound, especially when n is very large and the addition might be hindered sterically. This cannot be tested at this time because we do not have CF samples for which the composition and purity are unambiguous and were determined by non-MS methods. For now, the observation of a $C_{60}Cl_m^-$ species by MALDI- or APCI-MS indicates that the CF with the highest n value is either $C_{60}Cl_{m-1}$ or $C_{60}Cl_{m+1}$ (these are designated below as $C_{60}Cl_{m\pm 1}$).

1.6. Elemental Analysis (EA) and Thermogravimetric Analysis (TGA) Are Not Reliable Methods of Analysis for Chlorofullerenes. Table 1 shows that EA was the most common technique used to determine the composition of a CF sample. However, EA only gives the average C/Cl mole ratio of a CF sample and therefore is only a suitable method of compositional analysis for a CF that had already been shown to be pure by HPLC. Nevertheless, in the papers reporting reactions 6²² and 16–20²⁷ in Table 1, each product was presumed by the authors, on the basis of EA alone, to be a single compound or to “consist of several isomers” of a single composition. In one paper, the product reported was $C_{60}Cl_{12}$.²² In the other paper, the products reported were $C_{60}Cl_8$, $C_{60}Cl_{10}$, $C_{60}Cl_{12}$, $C_{60}Cl_{14}$, and $C_{60}Cl_{26}$.²⁷ As discussed in a later section, we have repeated these syntheses (except for the synthesis of $C_{60}Cl_{14}$) and have shown by HPLC and MALDI-MS analysis that they consist of CFs with multiple compositions, including compositions with n values greater than and, by implication, less than the single n value originally reported. Any halofullerene composition that was determined by EA alone should be carefully re-evaluated.

Thermogravimetric analysis (TGA) has also been used to determine the average C/Cl mole ratios of CFs. The relatively low C–Cl bond energies result in decomposition by dechlorination in the temperature range 200–500 °C.^{4,12,13,15,16,19,21} In 1991, Olah et al. reported that a CF sample with an average composition of ca. $C_{60}Cl_{24}$ was completely dechlorinated to C_{60} at 400 °C in an argon atmosphere.¹² In the same year, Tebbe et al. monitored the thermal decomposition of a sample reported to be $C_{60}Cl_{12-15}$ by IR spectroscopy as the sample was heated under vacuum, observing the onset of dechlorination at 200 °C and complete dechlorination at 350 °C.¹³ The compounds T_h - $C_{60}Cl_{24}$ ^{4,15} and D_{3d} - $C_{60}Cl_{30}$,¹⁶ which were characterized by X-ray crystallography, but which were never reliably analyzed for purity according to the criteria discussed above, were also studied by TGA. For T_h - $C_{60}Cl_{24}$, dechlorination occurred between 150 and 400 °C and gave a composition between $C_{60}Cl_{25}$ and $C_{60}Cl_{26}$ (this is our interpretation of the published TGA; the authors claimed that the sample they used was “pure” $C_{60}Cl_{24}$ even though their interpretation of the TGA suggested a ca. 50:50 mixture of $C_{60}Cl_{24}$ and $C_{60}Cl_{28}$). For D_{3d} - $C_{60}Cl_{30}$, dechlorination occurred between 350 and 525 °C and gave a composition between $C_{60}Cl_{32}$ and $C_{60}Cl_{33}$ (again, this is our interpretation of the published TGA figure; the authors stated that “pure $C_{60}Cl_{30}$...decomposes into C_{60} and Cl_2 at 450–500 °C”¹⁶). Finally, the dimeric compound $[C_{60}Cl_5]_2$, characterized by X-ray crystallography in 2007, was reported in 2005 to lose 4.6 ± 0.5 Cl atoms at 270 °C¹⁹ (this is the temperature at which the rate of mass loss was a maximum; the compound lost mass between 150 and 330 °C).

However, TGA is fraught with problems if precise average compositions are desired. For example, consider the TGA trace of $C_{60}Cl_6$ sample B shown in Supporting Information Figure S-9. There is a slow mass loss between 25 and 100 °C that

Table 3. Literature Chlorofullerene Syntheses Investigated in This Work and HPLC and MALDI-MS Results^a

Table 1 reaction no. [year]	composition [purity] reported; ref	reagents ^b and reaction conditions ^c	our HPLC and MALDI-MS results ^d	index to HPLC traces and MALDI mass spectra
7 [1997]	$C_{60}Cl_{24}$ [n/r]; ref 23	xs. Cl_2 , CCl_4 , UV, 44 h ^e	at least 7 $C_{60}Cl_n$ HPLC peaks; $n_{max} = 33 \pm 1$	Figure 3h and 3h'
17 [2003]	$C_{60}Cl_{10}$ [mix. of isomers]; ref 27	xs. Cl_2 , ODCB, 15 min	at least 17 $C_{60}Cl_n$ HPLC peaks; $n_{max} = 15 \pm 1$	Figure 3c
20 [2003]	$C_{60}Cl_{26}$ [mix. of isomers]; ref 27	xs. Cl_2 , ODCB, 7 d	at least 19 $C_{60}Cl_n$ HPLC peaks; $n_{max} = 27 \pm 1$	Figure 3g
6 [1996]	$C_{60}Cl_{12}$ [n/r]; ref 22	3,300 equiv ICl, C_6H_6 , 3 d, (no light)	at least 9 $C_{60}Cl_n$ HPLC peaks; $n_{max} = 19 \pm 1$	Figure 3e
18 [2003]	$C_{60}Cl_{12}$ [mix. of isomers]; ref 27	40 equiv ICl, ODCB, 24 h	at least 19 $C_{60}Cl_n$ HPLC peaks; $n_{max} = 19 \pm 1$	Figure 3f
16 [2003]	$C_{60}Cl_8$ [mix. of isomers]; ref 27	40 equiv ICl, ODCB, 3 h	at least 10 $C_{60}Cl_n$ HPLC peaks; $n_{max} = 17 \pm 1$	Figure 3d

^a Abbreviations: xs. = excess; mix. = mixture of isomers; n/r = not reported; ODCB = 1,2-dichlorobenzene. The reaction numbers shown in the first column are the same as those listed in Table 1. ^b The reagents include C_{60} in every case. ^c The reagents, reagent/ C_{60} mole ratio, solvent, temperature, and reaction time were duplicated as closely as possible according to the published information. ^d HPLC% values are listed.

could be due to the loss of lattice-bound solvent (dichloromethane), but it could also be due to slow loss of Cl atoms from $C_{60}Cl_6$ or the other CF components in the sample. Above 400 °C, there is also a slow mass loss that could be due to sublimation of C_{60} or other factors. The lack of clear temperature regions with no mass loss makes it difficult to determine the mass loss due solely to the decomposition reaction $C_{60}Cl_6 \rightarrow C_{60} + 3Cl_2$. Depending on how the change in mass due to loss of Cl atoms is determined from the experimental data, the average composition can range from $C_{60}Cl_{5.0}$ to $C_{60}Cl_{5.8}$.

To emphasize these problems, we carried out two experiments with different portions of $C_{60}Cl_6$ sample A. One portion was heated at 50 °C under vacuum for 2 h. HPLC analysis showed that the composition of the chlorofullerene sample was unchanged after heating, suggesting that the small mass loss between 25 and 100 °C probably is loss of solvent. Another portion was heated at 220 °C under vacuum for 30 min. At this temperature, the TGA (not shown) exhibited only a slow, gradual change in mass (similar to the TGA for sample B in Supporting Information Figure S-9), but HPLC analysis revealed that the heated sample contained ca. 30 mol % C_{60} . Significantly, only $C_{60}Cl_6$ and C_{60} were observed by HPLC, suggesting that whatever isomers of $C_{60}Cl_m$ may be intermediates in the complete dechlorination are less stable thermally than $C_{60}Cl_m$ ($m = 1–5$). This means that a sample of $C_{60}Cl_6$ will completely decompose to C_{60} at 220 °C, and heating the sample to temperatures between 300 and 400 °C is not necessary. This is relevant because TGA is occasionally used to determine the thermal stability of a CF. The previously cited statement in the literature that “pure $C_{60}Cl_{30}...$ decomposes into C_{60} and Cl_2 at 450–500 °C”¹⁶ can be misleading if the reader does not inspect the TGA, as we did, and discover that the compound actually decomposes at 350 °C.

Both EA and TGA of CFs are also seriously affected by the presence of the impurities in CF samples. For example, we found that $C_{60}Cl_6$ retains a significant amount of solvent when a toluene solution is evaporated to dryness, even if the sample is dried under vacuum for 12 h at 25 °C. In conclusion, EA and TGA are not reliable methods of analysis for chlorofullerenes.

1.7. Single-Crystal X-ray Diffraction Is Not a Reliable Method of Analysis for Bulk Samples of Chlorofullerenes. Whenever single crystals of CFs with sufficiently high quality are obtained, this method can give definitive information on the CF structure.^{15–18} However, the formation of a crop of X-ray quality single crystals does not mean that the bulk product has high purity; in fact, fractional crystallization is a common method of separation and purification. This is illustrated by the following examples. In 2005, the structure of $T_h-C_{60}Cl_{24}$ was determined by single-crystal X-ray diffraction using a crystal grown from a bromine solution of the crude CF sample.¹⁵

However, as discussed below, it is now known that the crude sample was much less pure than the reported 90% purity. In 2007, the structure of $C_{60}Cl_6$ was determined by single-crystal X-ray diffraction.¹⁸ However, the authors reported that the crystals of $C_{60}Cl_6$ were mixed with crystals of unreacted C_{60} (which comprised ca. 40% of the crude product).¹⁸

2. Re-Examination of Reported Chlorofullerene Syntheses and Determination of Product Compositions by HPLC and MALDI-MS. In this section of the paper, we report the results of repeating several of the $C_{60}Cl_n$ syntheses with $n > 6$ listed in Table 1, specifically reactions 6, 7, 16–18, and 20. Literature syntheses of $C_{60}Cl_6$ were previously repeated, and the results discussed, in ref 19 and therefore are not included here. As before,¹⁹ we followed the published procedures as closely as possible. The results are listed in Table 3. In every case a complex mixture of products was observed, casting doubts on the implied purity of the reported composition.

In our hands, a UV-induced chlorination of C_{60} with Cl_2 in CCl_4 solution (reaction 7) gave a light-yellow product that was soluble in CCl_4 , dichloromethane, and toluene. HPLC analysis of this product showed it to be a mixture of several CFs up to $C_{60}Cl_{32/34}$ (according to NI-MALDI-MS; see Figure 3h and h'), similar to the product of the UV-induced chlorination of C_{60} in liquid chlorine.²⁶ The chlorination of C_{60} solution without UV irradiation produced a mixture of CFs with a lower chlorine content up to $C_{60}Cl_{14/16}$ in a 15-min reaction (reaction 17; see Figure 3c) and $C_{60}Cl_{26/28}$ in a 7-day reaction (reaction 20; see Figure 3g). As shown in Table 1, the last two procedures were reported to yield $C_{60}Cl_{10}$ and $C_{60}Cl_{26}$, respectively.²⁷ The wording used in the original report²⁷ may be interpreted as a claim of the compositional purity of these and other CFs: “Most likely, prepared chlorofullerenes $C_{60}Cl_n$ ($n = 8, 10, 12, 14, 26$) consist of several isomers.”²⁷ Our analysis demonstrates that the samples reported to be “ $C_{60}Cl_{10}$ ” and “ $C_{60}Cl_{26}$ ” are in fact mixtures of many CFs that are unlikely to be isomers with the same composition because of (i) a wide range of retention times displayed by the components in HPLC traces and (ii) NI-MALDI-MS showing the presence of higher CFs for the “ $C_{60}Cl_{10}$ ” product. In light of these findings, we suggest that this statement should have been (and should now be reinterpreted to read) “Each of the $C_{60}Cl_n$ reaction products with $n \geq 8$ is very likely to consist of several chlorofullerene compositions.”

In our hands, reactions of C_{60} with ICl under the conditions reported for reactions 6, 16, and 18 also gave complex mixtures of products. For example, Priadarsini et al. reported the synthesis of “ $C_{60}Cl_{12}$ ” by using a very large excess of ICl (ca. 3,300 equiv) in the absence of light (reaction 6).²² However, we found that their procedure yielded $C_{60}Cl_6$ heavily contaminated with many different CFs up to $C_{60}Cl_{19\pm 1}$ (according to HPLC and MALDI-MS; see Figure 3e). Troshin et al. also reported the synthesis

of “C₆₀Cl₁₂”, in this case by using a much higher concentration of C₆₀ but only 40 equiv of ICl (reaction 18).²⁷ However, we found that this published procedure also yielded a complex mixture of C₆₀Cl_n compounds with n_{max} = 18 or 20 (see Figure 3f). When the reaction time was only 3 h (reaction 16) instead of 24 h (reaction 18), the reported product was “C₆₀Cl₈”. In this case, we found that the product was also a complex mixture, with n_{max} = 16 or 18 (see Figure 3d).

The authors of ref 27 also reported that “pure ICl₃ and ICl gave the same results as with KICl₄” when the concentrations of these chlorinating agents were adjusted according to the chlorine content. This conclusion is questionable because the methods used to analyze the products (EA and IR spectroscopy) are not reliable methods. In addition, the results of our study of C₆₀ chlorination, discussed in the next section, show that different CF products are produced when either ICl or ICl₃ were used. Furthermore, the sample of KICl₄ used by Troshin et al.²⁷ was almost certainly not pure for the following reasons: (i) they used an aqueous procedure to prepare KICl₄, and this is known to yield the monohydrate KICl₄·H₂O, which cannot be dried without decomposition unless a Cl₂ atmosphere is present,⁵⁹ and (ii) it is also known that ICl₄⁻ is slowly converted to IO₃⁻ in aqueous solution,⁶⁰ so iodate may also have been present in their sample of KICl₄. For these reasons, reaction 19, reported in ref 27, should be re-examined.

3. Synthesis and Characterization of New Chlorofullerenes.

3.1. General Remarks About ICl, ICl₃, and Cl₂ Chlorination of C₆₀. We investigated the chlorination agents ICl, ICl₃, and Cl₂. Despite its moisture sensitivity and corrosiveness, ICl is easier to manipulate than ICl₃ or Cl₂ because it is a stable liquid and therefore can be added to reaction mixtures with a syringe using air-free techniques. In contrast, ICl₃ is an unstable solid that evolves Cl₂ at 25 °C (the equilibrium pressure of Cl₂ above ICl₃ is ca. 50 Torr at 25 °C and increases rapidly at higher temperatures⁶¹). For this reason, we found it necessary to prepare ICl₃ immediately prior to use (see Experimental Section). Furthermore, in order to simplify the manipulation of Cl₂, we used an unknown excess of it by saturating degassed C₆₀ solutions with gaseous Cl₂. All three chlorinating reagents and their reaction byproducts, ICl or I₂, were easily removed from reaction mixtures under vacuum, which simplified workup procedures. The absence of an aqueous workup and associated multiple extractions, which would have been necessary if chlorinating agents such as VCl₄ had been used,⁴ allowed us to avoid (i) possible CF hydrolysis and (ii) excessively low yields.

A vacuum workup required a volatile solvent. Although benzene had been used for C₆₀ chlorination in the past, we previously found that it reacts with the chlorinating agents we used as well as with CF products under our reaction conditions.¹⁹ Therefore, we used the less volatile but less reactive solvent chlorobenzene (PhCl) in this work, as we previously did for the preparation of 90+% pure C₆₀Cl₆.¹⁹ GC-MS analysis of reaction mixtures showed that the chlorination or iodination of anhydrous, deoxygenated PhCl was detected only when very large concentrations of ICl or ICl₃ were used. Furthermore, both positive- and negative-ion APCI mass spectra of the CF products showed no evidence that reactions between CFs and PhCl had

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 (60) Cason, D. L.; Neumann, H. M. *J. Am. Chem. Soc.* **1960**, *83*, 1822–1828.
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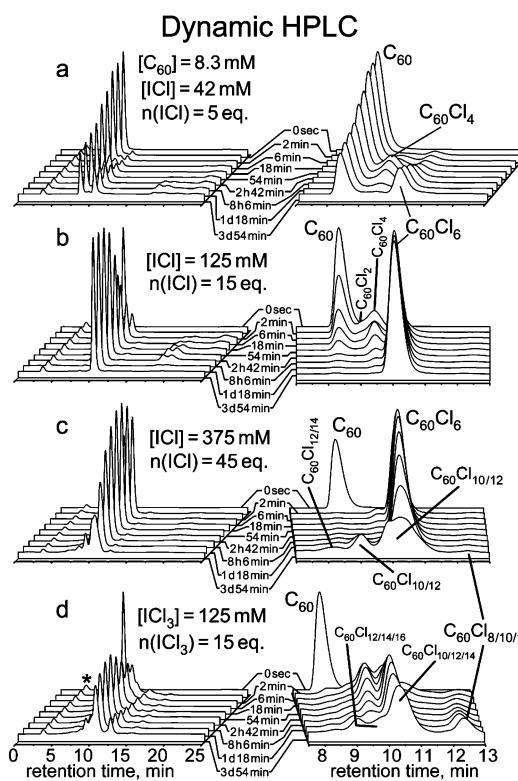


Figure 5. Dynamic HPLC monitoring of C₆₀/PhCl chlorination by ICl and ICl₃. The peak due to the internal standard C₇₀(CF₃)_{10,12} is marked with an asterisk. The CFs were identified by NI-APCI-MS.

taken place. See Supporting Information for more details. We only used homogeneous solutions of C₆₀ in this work: the C₆₀ concentration was 6.0 mg mL⁻¹, slightly below its reported solubility in PhCl of 7.0 mg mL⁻¹.⁶² This choice was based on our previous work on the synthesis of C₆₀Cl₆, which revealed a decrease in selectivity as well as poor C₆₀ conversion when reaction mixtures contained an excess of solid C₆₀.¹⁹

We wanted to monitor the course of the chlorination reactions by dynamic HPLC (i.e., by recording HPLC traces of portions of the reaction mixtures over time). However, the presence of Cl₂, ICl, or ICl₃ did not allow constant-volume reaction-mixture aliquots to be directly injected. Therefore, it was necessary to convert each aliquot to a dry solid, under vacuum, free of chlorinating agent as well as solvent, and redissolve it in a suitable solvent, toluene, for HPLC analysis. This required the presence of an internal standard for normalization of the HPLC traces, one that was not volatile at 25 °C, had a suitable R_f value and extinction coefficient at the detector wavelength, and would not react with the chlorinating agents or the CF products. We found that a mixture of C₇₀(CF₃)_{12,14} derivatives⁴³ was a suitable internal standard: they eluted together as one band with an R_f value of 3.4 min under the HPLC conditions used in this work, and control experiments showed no observable difference in C₆₀ chlorination with and without added C₇₀(CF₃)_{12,14}.

The dynamic HPLC results are shown in Figures 5 and 6 (see also Supporting Information Figures S-10 and S-11). The HPLC peak assignments were made using APCI mass spectra of different HPLC fractions. These mass spectra are shown in Supporting Information Figures S-12 and S-13. Figure 5a shows that ICl chlorination with [ICl] = 42 mM and [ICl]/[C₆₀] = 5

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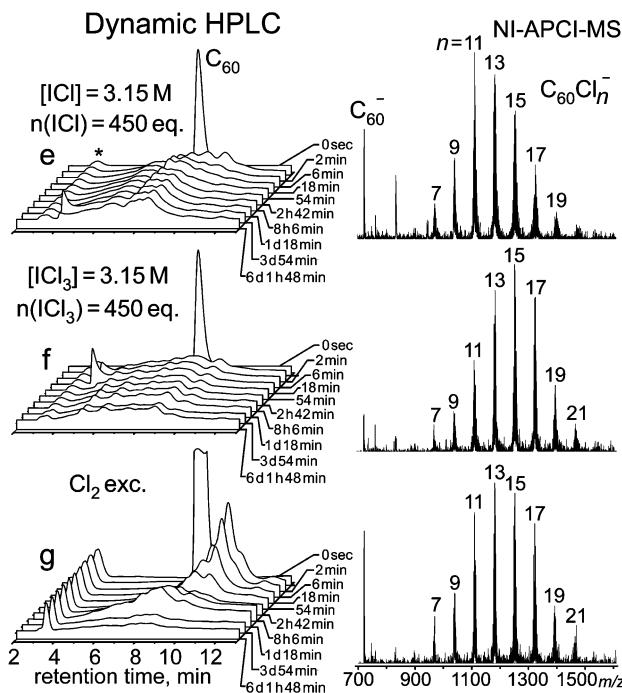


Figure 6. (Left) HPLC monitoring of C_{60}/PhCl chlorination with large excesses of ICl, ICl_3 , or Cl_2 . The peak of the $C_{70}(\text{CF}_3)_{12,14}$ internal standard is marked with an asterisk. (Right) NI-APCI-MS of the reaction mixtures after a reaction time of 6.075 d (i.e., 6 d + 1 h + 48 min) and after removal of $C_{70}(\text{CF}_3)_{12,14}$ by HPLC.

produced the single isomer 1,6,9,18- $C_{60}\text{Cl}_4$ (hereinafter referred to as $C_{60}\text{Cl}_4$; see below for characterization), which was slowly converted to $C_{60}\text{Cl}_6$. Chlorination with $[\text{ICl}] = 125 \text{ mM}$ and $[\text{ICl}]/[\text{C}_{60}] = 15$ (Figure 5b) revealed a shoulder on the low- R_f side of the $C_{60}\text{Cl}_4$ HPLC peak, which was later shown to be due to a mixture of 1,9- and 1,7- $C_{60}\text{Cl}_2$ (hereinafter referred to as *o*- and *p*- $C_{60}\text{Cl}_2$, respectively), both of which are precursors to $C_{60}\text{Cl}_4$ without rearrangement. Note that a significant amount of $C_{60}\text{Cl}_4$ was formed within the first 2 min with 125 mM ICl; in contrast, a similar amount of $C_{60}\text{Cl}_4$ was formed only after ca. 1 h with 42 mM ICl. This was the first indication that the ICl chlorination of C_{60} was probably second order or higher in ICl. When the concentration of ICl and the ICl/ C_{60} mole ratio were increased again by a factor of 3, to 375 mM and 45, respectively (Figure 5c), a solution containing 90+% $C_{60}\text{Cl}_6$, with only a small amount of $C_{60}\text{Cl}_4$, was formed within 2 min. The HPLC data also show that the further chlorination of $C_{60}\text{Cl}_6$ is very slow under these conditions.

Two other aspects of ICl chlorination of C_{60} were discovered in the experiments shown in Figure 5. First, a red precipitate of the dimeric compound $(\text{C}_{60}\text{Cl}_5)_2^{19,28}$ was formed when the concentration of ICl was 125 mM. However, the precipitate was not observed when the concentration of ICl was either 15 or 375 mM. Presumably, the bimolecular formation of the dimer only occurred to a significant extent when the putative monomer radical C_{60}Cl_5 was present above a critical concentration. At 15 mM ICl, the immediate precursor of $C_{60}\text{Cl}_5$, viz. $C_{60}\text{Cl}_4$, formed too slowly, and at 375 mM, $C_{60}\text{Cl}_4$ (and presumably $C_{60}\text{Cl}_5$) was converted to $C_{60}\text{Cl}_6$ too quickly. Second, these results allowed us to prepare 90+% $C_{60}\text{Cl}_6$ on a 155 mg scale in 7 min using the conditions shown in Figure 5c (see Experimental Section for more details).

Figure 5d shows that ICl_3 chlorination with $[\text{ICl}_3] = 125 \text{ mM}$ and $[\text{ICl}_3]/[\text{C}_{60}] = 15$ was much less selective than any of the

three ICl chlorinations discussed above. A wide variety of C_{60}Cl_n compounds with $n = 8, 10, 12, 14$, and 16 were formed. Interestingly, the HPLC peak with an R_f value of ca. 12.5 min may contain an isomer of C_{60}Cl_8 that is only slowly chlorinated further (this is based on the observation that the most intense NI-APCI-MS peaks for the fraction containing this HPLC peak are for $\text{C}_{60}\text{Cl}_7^-$ and $\text{C}_{60}\text{Cl}_9^-$; see Supporting Information Figure S-13). Note that chlorination with the same concentration of ICl instead of ICl_3 produced predominantly C_{60}Cl_6 ; ICl is clearly a more selective chlorinating agent than ICl_3 . As discussed above, Troshin et al. reported that ICl_3 and ICl gave similar results for C_{60} chlorination when the reaction mixtures contained equal concentrations of Cl atoms.²⁷ The results in Figure 5c and d show that this is clearly not the case, at least when $[\text{ICl}] = 375 \text{ mM}$ and $[\text{ICl}_3] = 125 \text{ mM}$.

Figure 6 shows the results of chlorination with large excesses of the chlorinating agents Cl_2 , ICl (3.15 M), and ICl_3 (3.15 M). In all three cases, complex mixtures of C_{60}Cl_n compounds were formed; the highest m/z NI-APCI-MS peak observed was for $\text{C}_{60}\text{Cl}_{21}^-$, consistent with the presence of $\text{C}_{60}\text{Cl}_{20}$, $\text{C}_{60}\text{Cl}_{22}$, or both. When Cl_2 was used, a black precipitate was also formed, which is under further investigation. These experiments were performed to see if the four structurally characterized compounds $T_h\text{-C}_{60}\text{Cl}_{24}$,¹⁵ $C_1\text{-C}_{60}\text{Cl}_{28}$,¹⁷ $C_2\text{-C}_{60}\text{Cl}_{30}$,¹⁷ and $D_{3d}\text{-C}_{60}\text{Cl}_{30}$ ¹⁶ could be prepared at 25 °C with a large excess of chlorinating agent (the published syntheses of these compounds all involved temperatures above 150 °C). It is clear from the results shown in Figure 6 that chlorination at 25 °C is too slow for compounds with 24 or more Cl atoms to be formed in a reasonable amount of time. In addition, the formation of these higher CFs probably involves Cl atom rearrangements during the chlorinations, and such rearrangements are also slow at 25 °C. (There are no reports demonstrating Cl atom rearrangement in a CF at 25 °C; there is one report that chlorination of $T_h\text{-C}_{60}\text{Cl}_{24}$ with SbCl_5 at 300 °C produces $D_{3d}\text{-C}_{60}\text{Cl}_{30}$, and the $D_{3d}\text{-C}_{60}\text{Cl}_{30}$ addition pattern cannot be derived by simply adding six Cl atoms to $T_h\text{-C}_{60}\text{Cl}_{24}$; however, $T_h\text{-C}_{60}\text{Cl}_{24}$ decomposes to C_{60} and Cl_2 at temperatures above 280 °C, so it is not clear that $D_{3d}\text{-C}_{60}\text{Cl}_{30}$ is formed in this reaction by chlorination of intact $T_h\text{-C}_{60}\text{Cl}_{24}$.¹⁵)

3.2. Synthesis, Isolation, and Characterization of *o*- $C_{60}\text{Cl}_2$, *p*- $C_{60}\text{Cl}_2$, and $C_{60}\text{Cl}_4$. The large-scale synthesis of a mixture of the lower CFs *o*- $C_{60}\text{Cl}_2$, *p*- $C_{60}\text{Cl}_2$, and $C_{60}\text{Cl}_4$ was accomplished by using the “Figure 5b” reaction conditions ($[\text{ICl}] = 125 \text{ mM}$, $[\text{ICl}]/[\text{C}_{60}] = 15$). Since $C_{60}\text{Cl}_6$ is formed rapidly from the lower CFs under these conditions, it was necessary to quench the reaction at the shortest possible time but without the addition of reagents that could complicate and interfere with the subsequent HPLC purification. Therefore, we used a reaction vessel of local design that allowed vacuum drying of ca. 20 mL of PhCl to occur within minutes at 25 °C or below. This apparatus, a modified version of the reaction vessel we previously used for the synthesis of $C_{60}\text{Cl}_6$,¹⁹ is shown in Supporting Information Figure S-14.

The PhCl solution of C_{60} and 15 equiv of ICl was stirred at 15 °C for only 1 min. At that time, vacuum evaporation was initiated and was complete in ca. 4 min for a nominal reaction time of 5 min. The resulting solid was dissolved in toluene and purified using a two-stage HPLC procedure, which is shown in Figure 7. Toluene was the eluent for the first stage and 50:50 v/v toluene/heptane was the eluent for the second stage. This procedure yielded 99% pure $C_{60}\text{Cl}_4$. However, *o*- $C_{60}\text{Cl}_2$ and *p*- $C_{60}\text{Cl}_2$ were each obtained with only ca. 75% purity. The

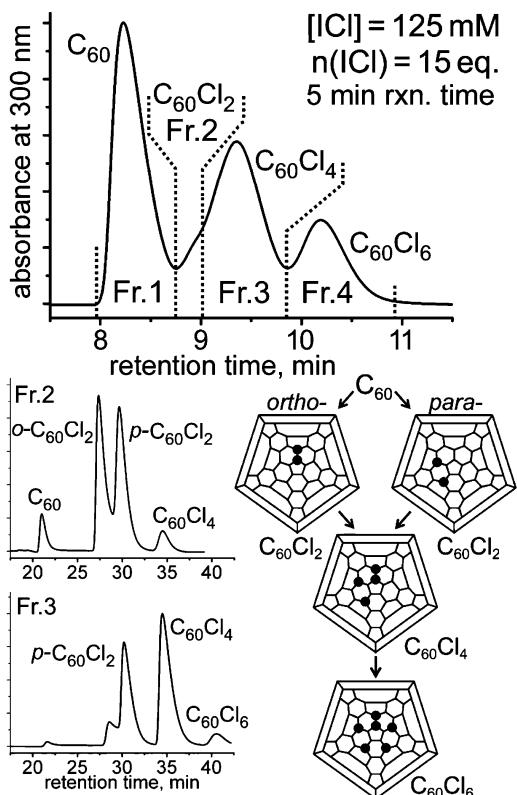


Figure 7. HPLC purification of *o*-C₆₀Cl₂, *p*-C₆₀Cl₂, C₆₀Cl₄, and C₆₀Cl₆. The proposed reaction pathway from C₆₀ to C₆₀Cl₆ is shown using Schlegel diagrams.

structural relationships between the C₆₀Cl₂ isomers, C₆₀Cl₄, and C₆₀Cl₆ are shown as Schlegel diagrams in Figure 7.

The compounds *o*-C₆₀Cl₂, *p*-C₆₀Cl₂, and C₆₀Cl₄ were analyzed by positive-ion APCI mass spectrometry, which was used to assign their molecular compositions (see Supporting Information Figures S-15 and S-16). The most likely addition patterns for the two isomers of C₆₀Cl₂ are (i) the one with adjacent cage C(sp³) atoms that form a hexagon–hexagon edge (*o*-C₆₀Cl₂) and (ii) the one with cage C(sp³) atoms in *para* positions on one of the 20 fullerene hexagons (*p*-C₆₀Cl₂). The other 21 possible isomers of C₆₀Cl₂ are predicted to have much higher energies.⁶³ Furthermore, the UV–vis spectrum of the C₆₀Cl₂ compound with an *R*_f value of ca. 28 min in 50:50 v/v toluene/heptane is virtually identical to the spectrum of the *ortho* cycloadduct of C₆₀, as shown in Supporting Information Figures S-17 and S-18, (see also Table S-6),^{64,65} which strongly suggests that this C₆₀Cl₂ compound is also an *ortho* isomer, viz., *o*-C₆₀Cl₂. In a similar vein, the UV–vis spectrum of the C₆₀Cl₂ compound with an *R*_f value of ca. 30 min in 50:50 v/v toluene/heptane is virtually identical to the spectrum of *p*-C₆₀(CF₃)₂,⁴² the structure of which was first elucidated by ¹⁹F NMR and DFT calculations⁶⁶ and

has recently been confirmed by X-ray diffraction⁶⁷ (see Supporting Information Figures S-19 and S-20 and Table S-7). Therefore, we propose that this C₆₀Cl₂ compound is also a *para* isomer, viz., *p*-C₆₀Cl₂. However, the spectrum of *p*-C₆₀Cl₂ has an additional feature at 490 nm not observed in the spectrum of *p*-C₆₀(CF₃)₂, which could be a bona fide spectral feature of *p*-C₆₀Cl₂ or could be due to an unidentified impurity. The *ortho* and *para* assignments for the two isomers of C₆₀Cl₂ are also supported by their APCI mass spectra. The spectrum assigned to *p*-C₆₀Cl₂ exhibits peaks for both C₆₀Cl₂⁺ and C₆₀Cl⁺, but the spectrum assigned to *o*-C₆₀Cl₂ exhibits peaks only for C₆₀Cl⁺. This is consistent with a more crowded environment for the Cl atoms in *o*-C₆₀Cl₂ than in *p*-C₆₀Cl₂.

The 1,6,9,18 addition pattern of C₆₀Cl₄, shown in Figure 7, was assigned as follows. First, as discussed above, it is reasonable to assume that Cl migration on the fullerene cage is unlikely to occur at a significant rate at 25 °C. Second, there is only one isomer of C₆₀Cl₄, so it must be formed from both *o*-C₆₀Cl₂ and *p*-C₆₀Cl₂ and must have an addition pattern that is part of the C₆₀Cl₆ addition pattern. However, the UV–vis spectrum of C₆₀Cl₄, shown in Supporting Information Figure S-21, is essentially featureless and is indistinguishable from the spectra of the structurally characterized compounds 1,6,9,18-C₆₀(CH₂Ph)₄,⁶⁸ 1,6,11,18-C₆₀(CH₂Ph)₄,⁶⁸ and 1,6,11,18-C₆₀(CF₃)₄^{42,67} (see Supporting Information Figures S-22 and S-23). Note that the 1,6,11,18 addition pattern is not a substructure of the 1,6,9,12,15,18 addition pattern of C₆₀Cl₆. Nevertheless, the 1,6,9,18 addition pattern of C₆₀Cl₄, although probable, has not been rigorously established. For completeness, the UV–vis spectrum of C₆₀Cl₆ is shown in Figure S-24.

3.3. Synthesis, Isolation, and Spectroscopic Characterization of C₆₀Cl₁₀. In order to obtain a C₆₀Cl_n compound with *n* > 6, we increased the concentration of ICl from 375 to 660 mM (80 equiv based on C₆₀). This resulted in the isolation of a mixture of CFs with *n* = 10, and possibly with *n* = 8 and 12, after only 6 h of reaction (cf. the 3 d 54 min/[ICl] = 375 mM HPLC trace in Figure 5c). A single isomer of C₆₀Cl₁₀ was isolated, as shown in Figure 8. It appears to be ca. 25 mol % of the mixture of CFs formed in this reaction. Considering that it is formed by the sequential addition of four Cl atoms to C₆₀Cl₆, this is a remarkably selective reaction. There may be other isomers of C₆₀Cl₁₀ in the reaction mixture. The isomer we have isolated was simply (i) the most abundant and (ii) the easiest to purify.

The NI-APCI mass spectrum shown in Figure 8 is the same as the spectrum of sample G shown in Figure 4 and was previously discussed. The ¹³C NMR spectrum shown in Figure 8 indicates that the isomer of C₆₀Cl₁₀ we have isolated has C₁ symmetry. A larger scale NMR spectrum is shown in Supporting Information Figure S-25 and the ¹³C δ values are listed in Supporting Information Table S-9. The UV–vis spectrum of C₆₀Cl₁₀ is shown in Supporting Information Figure S-26 and relative absorbance values are listed in Supporting Information Table S-10. Derivatives of C₆₀ with 10 substituents are not common. The known examples are seven isomers of C₆₀(CF₃)₁₀⁴² and two isomers of C₆₀(C₂F₅)₁₀.⁶⁹ Therefore, C₆₀Cl₁₀ represents the only example of a well-characterized C₆₀X₁₀ compound in which the X groups are atoms. The experimental

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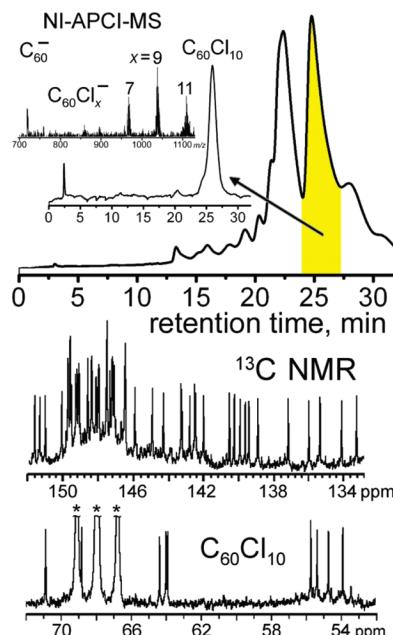


Figure 8. HPLC purification and characterization of $C_{60}Cl_{10}$ by NI-APCI-MS and ^{13}C NMR spectroscopy (peaks marked with asterisks are due to unidentified impurities). The mass spectrum shown is of the purified sample (i.e., 90+% $C_{60}Cl_{10}$). The HPLC eluent was 30:70 v/v toluene/heptane, and the eluent flow rate was 7 mL min⁻¹.

and DFT-predicted IR spectra of $C_{60}Cl_{10}$ are shown in Supporting Information Figure S-27.

3.4. X-ray Structures of $C_{60}Cl_6$ and $C_{60}Cl_{10}$. A poor-quality X-ray structure of $C_{60}Cl_6$ was reported in 2006.¹⁸ We were able to grow good-quality crystals and redetermine the structure of this compound. The final R indices are $R_1 = 0.085$ and $wR_2 = 0.229$ (the literature values are 0.197 and 0.382, respectively¹⁸). A comparison of other relevant data collection parameters for the two X-ray structure determinations of $C_{60}Cl_6$ is shown in Supporting Information Table S-12. Partial thermal ellipsoid drawings of $C_{60}Cl_6$ and $C_{60}Cl_{10}$ are shown in Figure 9 (complete thermal ellipsoid plots are shown in Supporting Information Figure S-28). The final R indices for $C_{60}Cl_{10}$ are $R_1 = 0.089$ and $wR_2 = 0.225$. The structure of $C_{60}Cl_{10}$ is of sufficient quality that there is no doubt as to its addition pattern but is not of sufficient quality for a detailed analysis of the interatomic distances and angles. For that, we will rely on the DFT-predicted structural parameters for this isomer of $C_{60}Cl_{10}$.

The unprecedented and unexpected addition pattern of $C_{60}Cl_{10}$ could not have been determined in the absence of the X-ray structure. It consists of the SPP addition pattern of $C_{60}Cl_6$ with four additional Cl atoms. Its asymmetric structure is consistent with the ^{13}C NMR spectrum discussed above. Furthermore, the fact that the $C_{60}Cl_{10}$ addition pattern includes the SPP- $C_{60}Cl_6$ addition pattern is consistent with our hypothesis that isomers of $C_{60}Cl_8$ and $C_{60}Cl_{10}$ are formed by the addition of two or four Cl atoms to the common intermediate SPP- $C_{60}Cl_6$ without rearrangement. The four Cl atoms were added to SPP- $C_{60}Cl_6$ in such a way that they form two-thirds of a second SPP addition pattern. These four Cl atoms, Cl14, Cl28, Cl29, and Cl31, form an *o,m,p*- $C_{60}Cl_4$ fragment that is the same as the proposed addition pattern of the new compound $C_{60}Cl_4$. As discussed below, the *o,m,p*- $C_{60}Cl_4$ fragment of $C_{60}Cl_{10}$ is “attached” to the SPP- $C_{60}Cl_6$ fragment so that Cl14 and Cl15 are on adjacent cage $C(\text{sp}^3)$ atoms on one fullerene pentagon and Cl28 and Cl29 are on

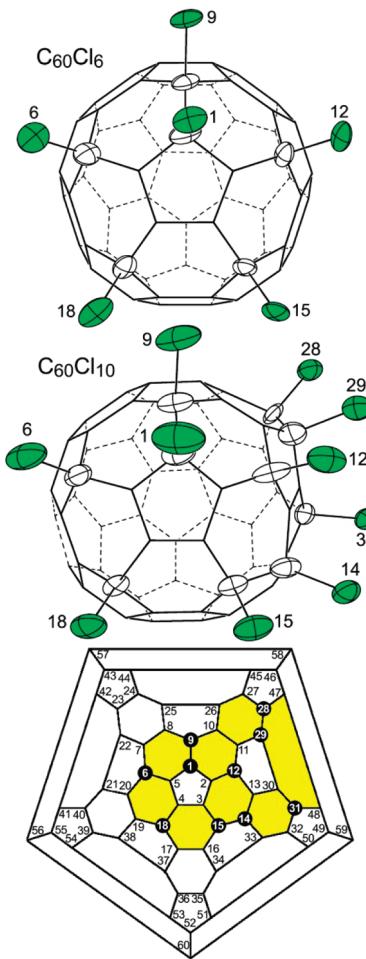


Figure 9. Drawings of the structures of 1,6,9,12,15,18- $C_{60}Cl_6$ (SPP- $C_{60}Cl_6$) and 1,6,9,12,14,15,18,28,29,31- $C_{60}Cl_{10}$ (14,28,29,31,SPP- $C_{60}Cl_{10}$; 50% probability ellipsoids shown only for Cl atoms and the cage C atoms to which they are attached) and the Schlegel diagram for 14,28,29,31,SPP- $C_{60}Cl_{10}$. The locants used for 14,28,29,31,SPP- $C_{60}Cl_{10}$ are not the lowest set of IUPAC locants possible for this addition pattern; they are the lowest set if the locants for the C–Cl vertexes on 1,6,9,12,15,18- $C_{60}Cl_6$ keep their original designations (the correct IUPAC locant set for $C_{60}Cl_{10}$ is 1,2,7,10,14,24,25,28,29,31).

$C(\text{sp}^3)$ atoms on another fullerene pentagon but are separated by a $C(\text{sp}^2)$ atom (i.e., this is a 1,3- C_5Cl_2 pentagon). Note that Cl12 is on a $C(\text{sp}^3)$ atom that shares its three fullerene polygons with five other $C(\text{sp}^3)$ atoms.

4. Relative Stability and Stepwise Formation of $C_{60}Cl_{10}$. **4.1. Thermodynamic Considerations Based on DFT-Predicted Relative Energies.** The addition to C_{60} or higher fullerenes of H, F, Cl, or Br atoms or CF_3 groups, each of which forms a 2c–2e⁻ bond to a single cage C atom, has been extensively studied experimentally and theoretically.^{1,42,67,70–72} The smaller addends H and F tend to add so that all of the newly formed $C(\text{sp}^3)$ atoms are contiguous (one notable exception is an isomer of $C_{60}F_8$;³⁹ here we only include compounds formed by direct addition to fullerenes, not by substitution of fullerene-derivative precursors). For $n \leq 12$, the larger addends Br and CF_3 tend to form derivatives with the addends *meta* or *para* to one another, with *ortho* cage $C(\text{sp}^3)$ atoms being rare. For example, the only bromofullerenes with adjacent cage $C(\text{sp}^3)$ atoms are $C_{60}\text{Br}_6$ (one

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ortho pair)⁷³ and C₇₀Br₁₀ (one *ortho* pair).⁷⁴ Fullerene(CF₃)_n compounds tend to have addition patterns that are referred to as ribbons or loops of edge-sharing *m*- and *p*-C₆₀(CF₃)₂ hexagons.^{42,75} Chlorine atoms are sterically in between. For *n* > 2, CFs in which all of the C–Cl vertexes are contiguous (e.g., D_{3d}-C₆₀Cl₃₀) or in which none of them are contiguous (e.g., C₆₀Cl₂₄,¹⁵ C₇₈Cl₁₈⁷⁶ and C₈₀Cl₁₂⁷⁷) are rare. Chlorofullerenes with some C–Cl vertexes *ortho* and with some *meta* and/or *para* to one another are the rule, including C₁-C₆₀Cl₄ (this work), C₅-C₆₀Cl₆,¹⁸ #1809C₆₀Cl₈,²⁹ C₆₀Cl₁₀ (this work), #1804C₆₀Cl₁₂,²⁹ C₆₀Cl₂₈,¹⁷ C₂-C₆₀Cl₃₀,¹⁷ C₇₀Cl₁₀,⁷⁴ C₇₀Cl₁₆,⁷⁸ C₇₀Cl₂₈,⁷⁹ C₇₆Cl₁₈,⁸⁰ C₇₈Cl₃₀,⁸¹ and C₉₀Cl₃₀.⁸²

Before we had determined the structure of C₆₀Cl₁₀ by X-ray crystallography, we tried to prepare a “short list” of plausible C₆₀Cl₁₀ addition patterns to begin our computational study. The only structurally characterized C₆₀X₁₀ compounds that are known are six isomers of C₆₀(CF₃)₁₀ and two isomers of C₆₀(C₂F₅)₁₀, none of which have contiguous cage C(sp³) atoms.^{42,69,83} The “in-between” steric requirements of Cl atoms meant that we could not consider these addition patterns as very likely. Furthermore, none of them are derived by adding four addends, without rearrangement, to SPP-C₆₀(CF₃)₆ (which, incidentally, is a known compound⁴⁰). Nevertheless, one isomer of C₆₀(CF₃)₁₂ does have two SPP addition-pattern fragments on opposite poles.⁸⁴ Initially, therefore, it seemed reasonable to propose that one possible stable isomer of C₆₀Cl₁₀ might have the addition pattern of SPP,SPP-C₆₀(CF₃)₁₂ minus the Cl atoms on one of the *ortho* pairs of C(sp³) atoms in the hypothetical molecule SPP,SPP-C₆₀Cl₁₂ (this would leave a ribbon of three edge-sharing *p*-C₆Cl₂ hexagons on the pole opposite the remaining SPP fragment). In a DFT study of the early stages of addition to C₆₀, Clare and Kepert calculated selected isomers of C₆₀Cl_n for *n* = 2, 4, 6, 8, 12, 18, and 24. Plausible isomers of C₆₀Cl₁₀ were not mentioned, even in passing. At the HF/6-31G* level of theory, Zhao and co-workers calculated isomers of C₆₀Cl_n for *n* = 2, 4, 6, and 8. In that paper, they stated that “the HOMO [of SPP-C₆₀Cl₆]...almost evenly spread over the equator belt, implying...no preferred site for further addition.”⁸⁵

With this limited information as a starting point, we decided that our computational study had to be as inclusive as possible.

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We performed an exhaustive search of all isomers of C₆₀Cl₁₀ formed by adding four Cl atoms to SPP-C₆₀Cl₆. We believe that this limitation was justified because there are no reports demonstrating Cl atom rearrangement in a CF at 25 °C (see above). More than 30,000 isomers were studied at the semiempirical AM1 level. The 1,100 lowest-energy isomers from that set were recalculated at the PBE/TZ2P//AM1 level, and the 44 lowest-energy isomers from that set were recalculated at the PBE/TZ2P//PBE/TZ2P level and again at the B3LYP/6-311G*//PBE/TZ2P level. The nine lowest-energy isomers from that set are shown in Figure 10, along with their PBE/TZ2P//PBE/TZ2P and their B3LYP/6-311G*//PBE/TZ2P relative energies. Supporting Information Table S-13 is list of the 44 DFT-predicted lowest-energy isomers and their relative energies (0.0–23.8 kJ mol⁻¹ with the PBE functional).

The unusual and unexpected results are as follows. First, the third most stable isomer of C₆₀Cl₁₀ that can be made by adding four Cl atoms to SPP-C₆₀Cl₆ is the abundant isomer we have isolated and characterized by X-ray crystallography, 14,28,29,31, SPP-C₆₀Cl₁₀. Second, the addition pattern of 14,28,29,31,SPP-C₆₀Cl₁₀ is not a fragment of a known or proposed addition pattern of any C₆₀X_n compound with *n* > 10. Third, all but one of the nine lowest-energy isomers are asymmetric (the least-stable of the nine isomers has C_s symmetry). Fourth, all nine involve the creation of one or two *ortho* pairs of C(sp³) atoms in addition to the *ortho* pair in the original SPP array (in fact, only one of the 44 lowest-energy isomers does not have an additional *ortho* pair). Fifth, there are no isolated C₆Cl₂ hexagons and no *pmp* or *p*³ ribbon of edge-sharing C₆Cl₂ hexagons that is isolated from the SPP Cl atoms for the first nine isomers. The 14th isomer (not shown), with a relative energy of 13.1 kJ mol⁻¹, is the lowest-energy isomer in which none of the four added Cl atoms share a hexagon (or pentagon) with any of the six Cl atoms in the SPP array. Finally, the isomer referred to earlier, with an SPP array on one pole, an isolated *p*³ ribbon on the other, and overall C_s symmetry, is not even among the 44 lowest-energy isomers; its DFT-predicted relative energy is 34.2 kJ mol⁻¹. One thing is now clear. The “flexible” steric requirements of Cl atoms will make it much more challenging to make a short list of plausible low-energy addition patterns based on previously reported structures, for a given value of *n*, than for fullerene(X)_n derivatives with X = H, F, Br, or CF₃.

To better understand the transformation of SPP-C₆₀Cl₆ into 14,28,29,31,SPP-C₆₀Cl₁₀, we considered all possible C₆₀Cl₈ isomers formed by adding two Cl atoms to SPP-C₆₀Cl₆ without any rearrangement. All 626 isomers were studied at the AM1 level, and the 50 lowest-energy isomers at the PBE/TZ2P level. Nine of the first 19 lowest-energy isomers are shown in Figure 11, along with their PBE/TZ2P relative energies. Interestingly, the most stable isomer is 14,31,SPP-C₆₀Cl₈, and the 28,29,SPP and 28,31,SPP isomers are no more than 21 kJ mol⁻¹ higher in energy. (Note that 13,32,SPP-C₆₀Cl₈ is the second lowest-energy isomer.) It is now clear that the formation of 14,28,29,31,SPP-C₆₀Cl₁₀ is not only among the kinetically favored products of the further chlorination of SPP-C₆₀Cl₆, it is one of the three most-thermodynamically favored products as well.

Significantly, 28 of the 44 lowest-energy isomers of C₆₀Cl₁₀ have a Cl atom on either C13 or C14, including all of the first 13 isomers and 20 of the first 28 isomers. The C13–C14 bond in DFT-optimized C₆₀Cl₆, at 1.379 Å, is among the shortest and presumably the most electron-rich double bonds in this molecule (only the unique bonds and atoms in C_s-symmetric C₆₀Cl₆ are mentioned in this paragraph; see Supporting Information Figure

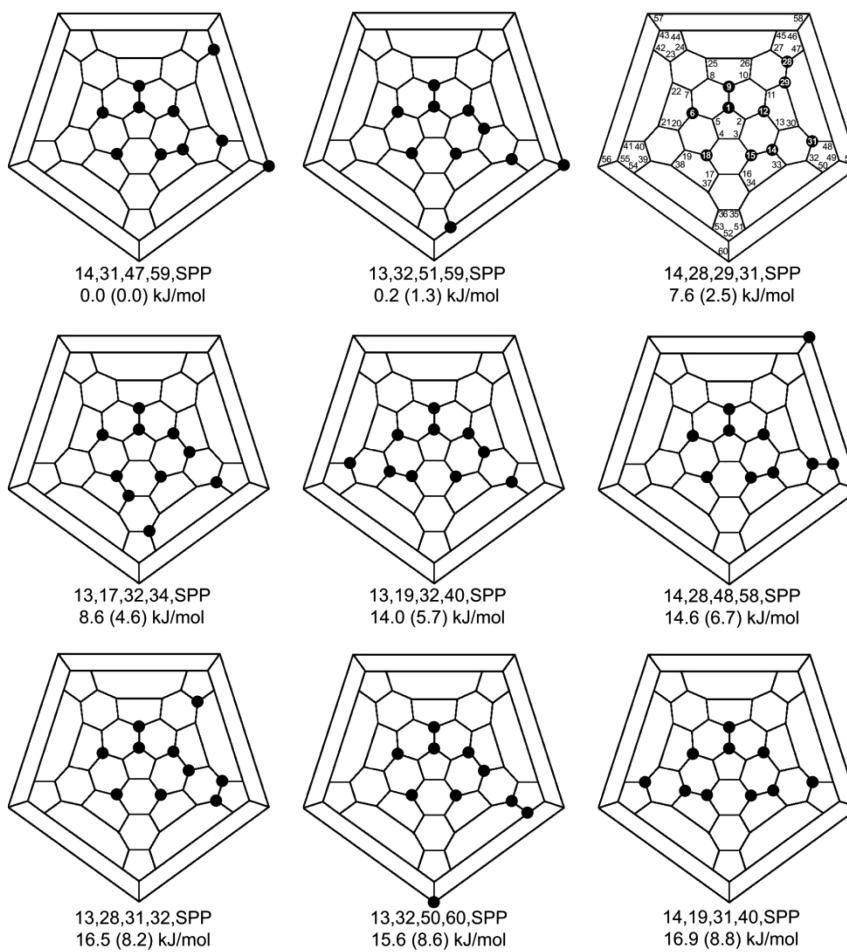


Figure 10. Schlegel diagrams of the nine lowest-energy DFT-optimized isomers of $C_{60}Cl_{10}$ that include an SPP array of six Cl atoms (SPP = 1,6,9,12,15,18). The locants used for the 14,28,29,31,SPP- $C_{60}Cl_{10}$ compound are not the lowest locants possible for this addition pattern (see Figure 9 for a larger drawing of the numbered Schlegel diagram for 14,28,29,31,SPP- $C_{60}Cl_{10}$). The locants for the other isomers are not necessarily the lowest sets of locants; they too were chosen to simplify comparisons with SPP- $C_{60}Cl_6$ and 14,28,29,31,SPP- $C_{60}Cl_{10}$. The relative energies shown were determined at the B3LYP/6-311G*//PBE/TZ2P level (for comparison, the values in parentheses were determined at the PBE/TZ2P/PBE/TZ2P level).

S-29 for a Schlegel diagram of $C_{60}Cl_6$ showing the DFT-predicted double-bond distances). The only shorter bonds in $C_{60}Cl_6$ are C2–C3, at 1.356 Å, and C10–C11, at 1.377 Å. However, none of the 44 isomers have a Cl atom on C2 or C3 and only three of the 44 isomers has a Cl atom on C10 or C11 (and one of these also has a Cl atom on C14). The next shortest double bond in $C_{60}Cl_6$ is C16–C17, at 1.383 Å, but only six of the 44 isomers have a Cl atom on C16 or C17, and two of these also have a Cl atom on C13 or C14. All of the remaining C–C bonds in $C_{60}Cl_6$ are 1.401 Å or longer.

4.2. Kinetic Considerations Based on DFT-Predicted Frontier Orbitals. In this section we use frontier-orbital arguments to rationalize the observation that 14,28,29,31,SPP- $C_{60}Cl_{10}$ is one of the most abundant isomers to be formed from SPP- $C_{60}Cl_6$. In general, the addition of ICl to olefins is first order in olefin and either second⁸⁶ or third order⁸⁷ in ICl. This suggests an iodonium intermediate followed by addition of a Cl^- ion from the putative ICl_2^- anion, as shown in Scheme 1.⁸⁶ Two experiments were performed to probe the possible mechanism of chlorination of C_{60} , $C_{60}Cl_6$, and $C_{60}Cl_8$ by ICl. First, to determine that salts of ICl_2^- with large cations such as $C_{60}I^+$,

$C_{60}Cl_6I^+$, and $C_{60}Cl_8I^+$ could be soluble in chlorobenzene, a slurry of sparingly soluble $N(n\text{-Bu})_4Cl$ in chlorobenzene was treated with 1 equiv of dark brown ICl, producing a light-orange solution with no solid present. (The solubility in low-dielectric-constant solvents is also demonstrated by the fact that crystals of $PPN^+ICl_2^-$ can be grown from chloroform solution.⁸⁸) Second, two ICl chlorinations of C_{60} were studied as follows. The initial concentration of C_{60} was the same in both reactions, but the initial concentrations of ICl were 42 and 125 mM, a 1:3 ratio. If the reaction was second order in ICl, then the ratio of the initial rates of disappearance of C_{60} should be 1:9. The consumption of C_{60} was monitored by HPLC after 2 min and after 6 min of reaction. The ratio of the rates of disappearance of C_{60} was 1:7.3 after 2 min, 1:8.4 after 6 min, and 1:11 for the period of time from 2 to 6 min. This demonstrates that the chlorination of C_{60} by ICl is higher than first order in ICl and is probably second order in ICl (this ignores the possibility of parallel mechanisms with different orders).

A possible mechanism of dichlorination of a fullerene double bond by ICl is shown in Scheme 2. The iodonium intermediate is shown with the I atom bound to a single cage $C(sp^3)$ atom because our DFT calculations indicate that this structure for $C_{60}I^+$ is more stable than the structure with the I atom bridging

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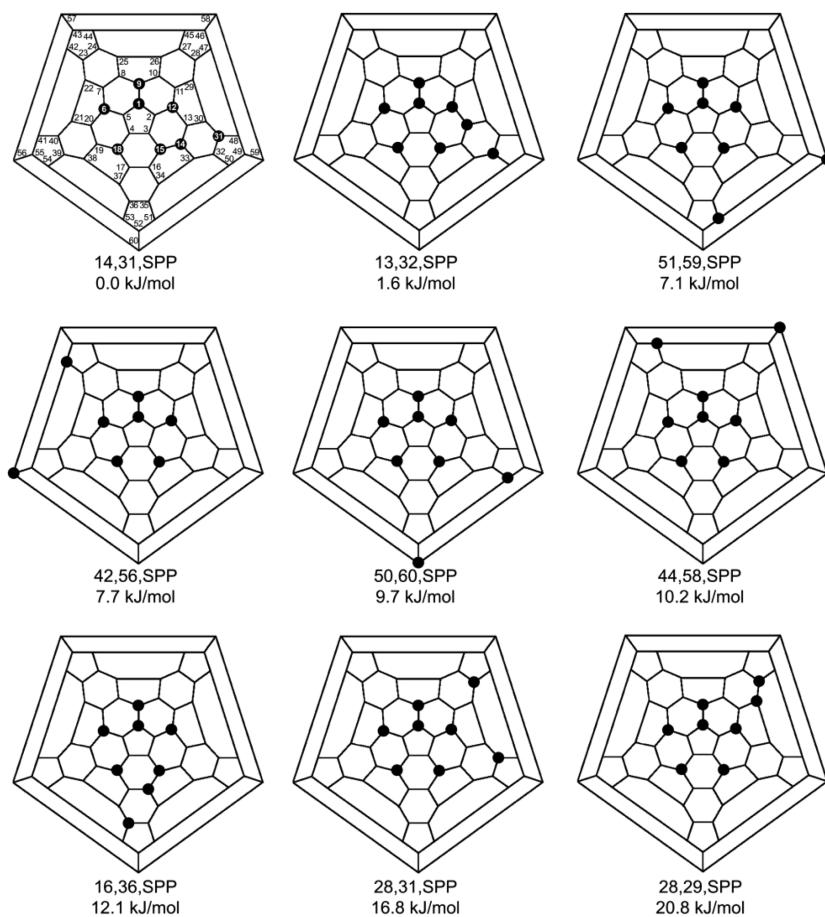
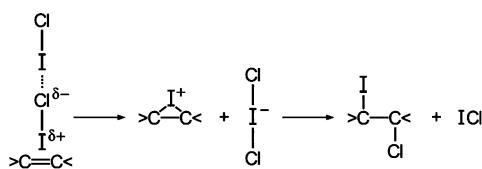
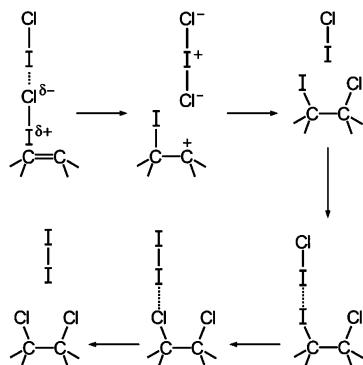


Figure 11. Schlegel diagrams of nine of the 19 lowest-energy DFT-optimized isomers of $C_{60}Cl_8$ that include an SPP array of six Cl atoms (SPP = 1,6,9,12,15,18). The locants for the other isomers are not necessarily the lowest set of locants; they were chosen to simplify comparisons with SPP- $C_{60}Cl_{10}$ and 14,28,29,31,SPP- $C_{60}Cl_{10}$. The relative energies shown were determined at the PBE/TZ2P level of theory.

Scheme 1



Scheme 2



two adjacent C atoms. This scheme suggests that the partially positively charged I atom of ICl attacks the HOMO of the fullerene and one of the partially negatively charged Cl atoms of the resulting ICl_2^- anion then attacks the LUMO of the fullerene(I)⁺ iodonium cation.

The proposed stepwise transformation of C_{60} into 14,28,29,31, SPP- $C_{60}Cl_{10}$ is shown in Supporting Information Figure S-29. The Schlegel diagrams for $C_{60}Cl_6$ and the three isomers of $C_{60}Cl_8$ also show, schematically, their HOMOs, the orbitals that would be attacked by ICl. The sequence of reactions leading to the overall addition of two Cl atoms is (i) electrophilic attack of ICl on the HOMO of the precursor, leading to the formation of the fullerene(I)⁺ cation; (ii) nucleophilic attack of ICl_2^- on the LUMO of the fullerene(I)⁺ cation, leading to the fullerene(I)(Cl) intermediate; and (iii) substitution of the I atom by another Cl atom, possibly by electrophilic attack of ICl on the HOMO of fullerene(I)(Cl), which has a large contribution on the I atom.

Analysis of the relevant HOMOs and LUMOs, some of which are shown in Figure 12, supports our proposal that 14,28,29,31, SPP- $C_{60}Cl_{10}$ should be a kinetically viable product. Consider the HOMO of $C_{60}Cl_6$. There are 10 unique cage C atoms that have the most significant contributions, C26–C35. The atoms C26, C29, C30, C33, and C34 share a hexagon or pentagon with a C–Cl vertex, leaving C27, C28, C31, C32, and C35 as the sterically most likely points of attack for the ICl molecule. Are there significant differences in the “double-bond” distances involving these five atoms? The answer is no; the DFT-optimized distances span the narrow range 1.399–1.404 Å (see Supporting Information Figure S-30). Do the five cage C atoms differ in their POAV^{30,89} angles? The answer is also no; all five are $12.0 \pm 0.1^\circ$. Finally, the relative energies of the five

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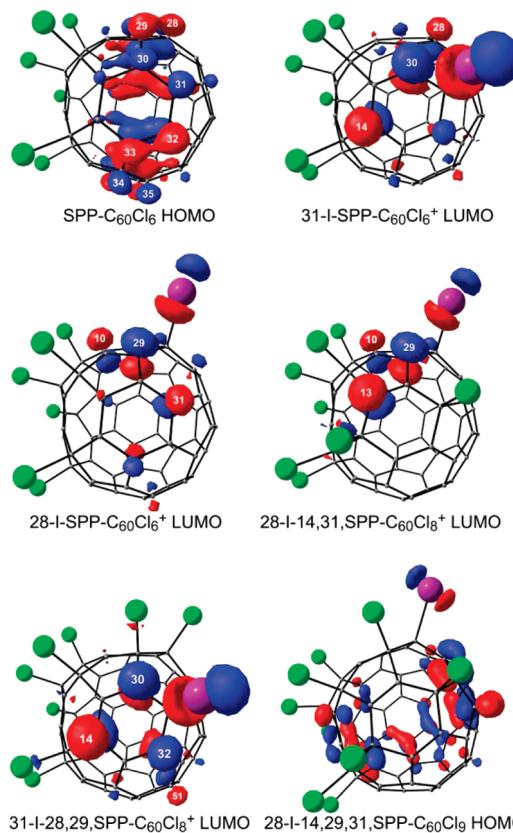


Figure 12. HOMOs and LUMOs for selected compounds and iodonium cations. The blue (+) and red (−) lobes of the π atomic orbitals for each carbon atom are scaled approximately to their coefficients in these molecular orbitals.

$C_{60}Cl_6I^+$ cationic intermediates are all within 3.3 kJ mol^{-1} of one another (the isomer with I^+ on C31 is the lowest).

Next consider the LUMOs of 28-I-SPP- $C_{60}Cl_6^+$ and 31-I-SPP- $C_{60}Cl_6^+$, also shown in Figure 12. It is clear that these iodonium intermediates would naturally lead to the three isomers of $C_{60}Cl_8$ on the path to 14,28,29,31,SPP- $C_{60}Cl_{10}$, viz., 28,29,SPP- $C_{60}Cl_8$, 28,31,SPP- $C_{60}Cl_8$, and 14,31,SPP- $C_{60}Cl_8$. Furthermore, note that the LUMOs of 28-I-14,31,SPP- $C_{60}Cl_8^+$ and 31-I-28,29,SPP- $C_{60}Cl_8^+$ justifies the prediction that these iodonium intermediates would naturally lead to the final product, 14,28,29,31, SPP- $C_{60}Cl_{10}$. Finally, consider the HOMO of the neutral intermediate, 28-I-14,29,31,SPP- $C_{60}Cl_9$. With such a significant contribution from a p orbital on the I atom, it is possible that the cage I atom could attack the σ^* orbital of ICl , which could provide a facile path for the substitution of a cage I atom for a Cl atom.

Rogers and Fowler proposed a sequential mechanism for the addition of six Cl atoms to C_{60} to form $C_{60}Cl_6$.⁹⁰ Their calculations suggested that Cl atoms should add to the cage C atoms with the highest free valence index (in closed-shell intermediates) or to the C atoms with the highest spin density (in radical intermediates). Furthermore, they proposed that the cage $C(sp^2)$ atoms adjacent to cage $C(sp^3)$ atoms (i.e., adjacent to C–Cl vertexes) are not, in general, available for the addition of Cl atoms. They suggested that addition to such sites occurs only when a radical intermediate cannot be converted to a closed-shell product by adding the Cl atom to any other C atom (as in the final addition to the 6,9,12,15,18- $C_{60}Cl_5$ radical to

form SPP- $C_{60}Cl_6$). However, isolation of 1,9- $C_{60}Cl_2$ and 1,6,9,18- $C_{60}Cl_4$ in this work clearly shows that fullerene C(sp^2) atoms adjacent to C(sp^3) atoms are available for the addition of “Cl atoms,” at least for a mechanism involving cationic iodonium intermediates.

5. Stability and Photodegradation of Chlorofullerenes. In order for CFs to be used reliably for a variety of applications, including as starting materials for further derivatization, their stabilities under a wide range of conditions must be known. The few cases that report CF stability deal almost exclusively with their thermal decomposition in the solid state (see Table 1 for examples). In this section of the paper, we report the stabilities of pure CFs, including the four new CFs reported here for the first time, in solutions of organic solvents and in the presence and absence of air, water, and light.

5.1. Comparison of the Thermal Stabilities of Chlorofullerenes with Fluorofullerenes and Bromofullerenes in the Solid State. The thermal stabilities of $C_{60}Cl_6$, T_h - $C_{60}Cl_{24}$, and D_{3d} - $C_{60}Cl_{30}$ in the solid state were discussed above. Recall that we did not observe any isomerization products when $C_{60}Cl_6$ was heated under vacuum. In this work we also examined the thermal stability of T_h - $C_{60}F_{24}$.⁹¹ When this compound was sublimed at 300°C under vacuum, we observed both loss of F atoms and isomerization, since the compound C_{3v} - $C_{60}F_{18}$ ⁹² was detected in the sublimate by ^{19}F NMR. The contiguous addition pattern of C_{3v} - $C_{60}F_{18}$ is not part of the addition pattern of T_h - $C_{60}F_{24}$ (which consists of a noncontiguous arrangement of F atoms), demonstrating that the T_h - $C_{60}F_{24} \rightarrow C_{3v}$ - $C_{60}F_{18}$ process required F-atom rearrangement, either intramolecular, intermolecular, or both. Note that T_h - $C_{60}F_{24}$ is a kinetically stable isomer of this composition (it was predicted to have an energy that is 340 and 280 kJ mol^{-1} higher than that of putative D_2 and D_{3d} isomers with contiguous addition patterns⁹¹). Its high energy may provide the driving force for the thermal isomerization that occurs during the loss of six F atoms. Therefore, it is possible that kinetically stable CFs might undergo similar thermally induced isomerizations.

However, in general, the CFs studied to date are less thermally stable than the fluorofullerenes $C_{60}F_{18}$, $C_{60}F_{36}$, and $C_{60}F_{48}$, which sublime unchanged at 200 – 400°C but are more stable than bromofullerenes, which rapidly lose Br atoms at only 100 – 220°C .⁹³ This order follows the experimental bond-energy trend $C_{60}\text{-F}$ (ca. 290 kJ mol^{-1}) > $C_{60}\text{-Cl}$ (167 kJ mol^{-1}) > $C_{60}\text{-Br}$ (83 kJ mol^{-1}).^{58,94} Moreover, our HPLC analysis of solid, solvent-free samples of $C_{60}Cl_6$ and $C_{60}Cl_{10}$ did not show any detectable changes even after months of storage in air at room temperature in ambient light. This demonstrates the high stability of at least some CFs upon storage, which is important for the further use of these compounds as synthons.

5.2. Photosensitivity of Chlorofullerenes in Solution. A portion of $C_{60}Cl_6$ sample **A** was used to prepare a 0.14 mM solution in degassed anhydrous toluene. It was split into four aliquots (samples **I**–**IV**) that were stored for 35 d in Pyrex flasks under different conditions. Sample **I** was stored in the dark under a

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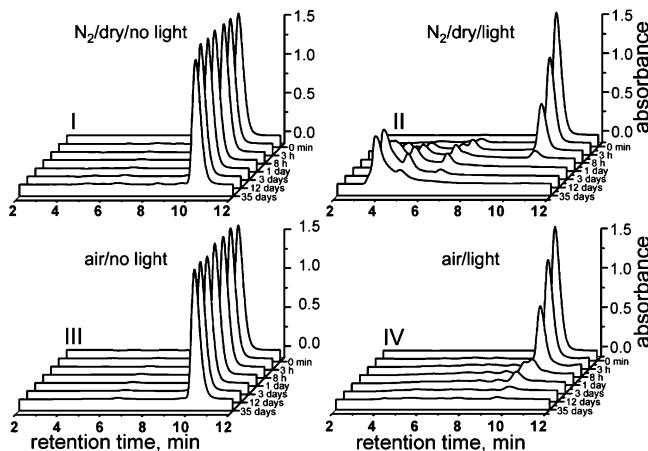


Figure 13. Dynamic HPLC plots of $C_{60}Cl_6$ /toluene samples **I**–**IV**.

nitrogen atmosphere; sample **II** was stored in ambient laboratory fluorescent light under nitrogen; sample **III** was stored in the dark in the presence of ambient air; and sample **IV** was stored under light in the presence of air (the solutions stored in air were saturated with ambient air by bubbling). The temperature was 22 ± 1 °C throughout the experiment.

Constant-volume aliquots of the four solutions were analyzed by injecting them directly into the HPLC instrument. Dynamic HPLC plots are shown in Figure 13. The results convincingly demonstrate that exposure to fluorescent light causes decomposition of $C_{60}Cl_6$ in toluene solution. The presence of oxygen or water vapor did not cause decomposition when the solution was stored in the dark (Sample **III**). The half-life of $C_{60}Cl_6$ in toluene was found to be ca. 5 h when exposed to light under nitrogen or in the presence of air (Sample **II**). In the absence of air, C_{60}^- and $C_{60}(C_6H_4CH_3)_n^-$ ions with $n = 2, 3, 4$, and 5 were observed by APCI mass spectrometry, as shown in Supporting Information Figure S-31. No negative ions with Cl atoms were observed. In the presence of air (Sample **IV**), only C_{60}^- was observed, which is consistent with known reactions of arylfullerenes with air.^{8,95–98} The CF $C_{60}Cl_6$ was also found to be photosensitive when dissolved in dichloromethane (0.17 mM). An analogous series of experiments showed that the rate of photodecomposition of $C_{60}Cl_6$ is ca. 15 times slower in dichloromethane than in toluene, as shown in Supporting Information Figure S-32.

Similar experiments with toluene solutions of CF mixtures containing $C_{60}Cl_{6–12}$ and a 90+% sample of $C_{60}Cl_{10}$ (0.06 mM) showed that these compounds are also photosensitive. For example, the half-life of $C_{60}Cl_{10}$ dissolved in toluene under ambient light was similar to that of $C_{60}Cl_6$, as shown in Supporting Information Figure S-33. This shows that photosensitivity is likely to be a generic property of CFs. This can be attributed to photoinduced homolytic cleavage of C–Cl bonds, which was previously shown to occur during 366 nm

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irradiation of benzene and toluene solutions of $C_{60}Cl_6$ (radical species were observed by ESR spectroscopy).⁹⁹

As far as we are aware, this work is the first study demonstrating the photosensitivity of CFs in solution under ambient light. In one previous report, however, a CF synthesis was performed in the dark (but without further comment as to why). All other previous instances of the use of CF solutions may therefore have involved some degree of photodecomposition, and the chlorofullerene literature should be interpreted with this in mind.

Experimental Section

Reagents and Solvents. The following ACS Reagent grade solvents were purchased from the indicated vendor, dried with the indicated drying agent, and stored under a nitrogen atmosphere prior to use: benzene (Sigma-Aldrich, Na); toluene (Fisher Scientific, Na); chlorobenzene (Sigma-Aldrich, CaH₂); 1,2-dichlorobenzene (Sigma-Aldrich, CaH₂); tetrachloromethane (Sigma-Aldrich, used as received). HPLC grade toluene, heptane, and dichloromethane were used as received from Fisher Scientific. The compounds C_{60} (99.9%, Term-USA), chlorine (UHP, Matheson), iodine monochloride (Sigma-Aldrich, 99.998% trace metals basis), *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]-malononitrile (Fluka), tris(acetylacetone)chromium(III) (Sigma-Aldrich), and KBr (Sigma-Aldrich, 99+% FTIR grade) were used as received. All syntheses were carried out under a purified nitrogen atmosphere using standard Schlenk techniques with vigorous stirring. The compound $C_{70}(CF_3)_{10}$ (98+% pure) was prepared as previously described.⁴³ A sample containing a mixture of isomers of $C_{70}(CF_3)_{12}$ and $C_{70}(CF_3)_{14}$ was isolated during the HPLC purification of $C_{70}(CF_3)_{10}$ (the fraction eluting at 2.5–3.5 min was collected (20:80 v/v toluene/heptane, 5 mL min⁻¹)).

Physical Methods. HPLC analyses and purifications were performed using Shimadzu liquid chromatography instrumentation (CBM-20A control module, SPD-20A UV detector, LC-6AD pump, manual injector valve) equipped with a 10 mm i.d. × 250 mm Nacalai Tesque Cosmosil Buckyprep column. Electronic spectra were recorded using a Varian Cary 500 spectrophotometer with a digital resolution of 1 nm per data point. ¹³C NMR spectra were recorded at 25 °C using a Varian UNITY INOVA 400 or a Varian UNITY INOVA 500 spectrometer operating at 100 or 126 MHz, respectively. MALDI mass spectra were recorded on a Kratos Analytical Kompact MALDI IV time-of-flight spectrometer in the linear mode. A 337 nm N₂ laser was used for target activation. Each mass spectrum was the average of 50–100 laser shots. The CF samples and the *trans*-2-[3-(4-I-butylphenyl)-2-methyl-2-propenylidene]malononitrile matrix material (DCTB) were dissolved separately in toluene and were mixed in a 1:10 (mol sample)/(mol DCTB) ratio. A drop of each sample/DCTB solution was deposited on a stainless steel slide with a capillary and dried under a strong stream of cool air from an airsprayer/brush in order to achieve a uniform sample surface. APCI mass spectra were recorded on a Finnigan LCQ-DUO mass spectrometer (acetonitrile carrier solvent, 0.3 mL min⁻¹ flow; the CF sample was injected as a toluene solution; N₂ carrier gas; corona voltage, 3.5 kV; evaporator temp, 400 °C). Thermogravimetric analysis was performed using a TA Instruments TGA-2950 Thermogravimetric Analyzer (platinum sample pans, ca. 5 mg sample size, 25–500 °C).

X-ray diffraction data from a red-orange needle of $C_{60}Cl_6$ grown from a saturated toluene solution were collected at 173 K on a Bruker AXS 1000 CCD diffractometer employing Mo K α radiation. Selected crystallographic parameters are listed in Table 4. Absorption and other corrections were applied by using SADABS. The structure was solved by using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least-squares process. All

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Table 4. X-ray Parameters for $C_{60}Cl_6$ and $C_{60}Cl_{10}$

	$C_{60}Cl_6$	$C_{60}Cl_{10}$
molecular formula	$C_{60}Cl_6$	$C_{60}Cl_{10}$
formula weight, g mol ⁻¹	933.30	1075.10
crystal system	orthorhombic	orthorhombic
space group	<i>Cbc</i> a	<i>C222</i> ₁
<i>Z</i>	16	8
color of crystal	dark red	red-orange
unit cell dimensions		
<i>a</i> , Å	19.639(9)	9.9970(14)
<i>b</i> , Å	17.258(10)	20.717(4)
<i>c</i> , Å	40.11(2)	39.968(6)
α , deg	90	90
β , deg	90	90
γ , deg	90	90
temperature, K	173(2)	150(2)
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0845, <i>wR</i> ₂ = 0.2291	<i>R</i> ₁ = 0.0888, <i>wR</i> ₂ = 0.2251
goodness-of-fit on <i>F</i> ²	1.096	1.072

atoms were refined by using anisotropic atomic displacement parameters. Standard Bruker control and integration software was employed, and Bruker SHELXTL software was used for structure solution, refinement, and graphics. The asymmetric unit contains two $C_{60}Cl_6$ molecules, each of which is disordered over two positions. This was obvious only from the Cl atom positions. The C atom positions overlap so well that they cannot be described by split positions. Two occupational parameters were refined for the chlorine atoms, one for each molecule. In molecule 1 the occupational parameter refined to almost exactly 0.75 (3:1), and in molecule 2 to almost exactly 0.5 (1:1).

X-ray diffraction data from a red-orange needle of $C_{60}Cl_{10}$ grown from a saturated toluene/heptane solution was collected at 150 K on a D8 goniostat equipped with a Bruker APEXII CCD detector at Beamline 11.3.1 at the Advanced Light Source (Lawrence Berkeley National Laboratory) using synchrotron radiation tuned to $\lambda = 0.7749$ Å. A series of 4 s data frames measured at 0.2° increments of ω were collected to determine the unit cell parameters, which were refined by least-squares using 1060 reflections and are listed in Table 4. For data collection frames were measured for a duration of 4 s at 0.3° intervals of ω with a maximum 2θ value of ~60°. Absorption and other corrections were applied by using SADABS. The structures were solved by using direct methods and refined (on F^2 , using all data) by a full-matrix, weighted least-squares process. Standard Bruker control and integration software (APEX II) was employed, and Bruker SHELXTL software was used for structure solution, refinement, and graphics. The solvent molecules (without heavy atoms, therefore probably heptanes and toluene molecules) were severely disordered. Since no disorder model was successful, the program SQUEEZE was used to generate a data set that ignores the contribution with these disordered solvent molecules. All non-hydrogen atoms were refined by using anisotropic displacement parameters.

Handling of ICl. In a typical experiment, the storage container with solid ICl (a storage tube equipped with a Teflon valve and a side arm) was warmed to 35–40 °C, and the resulting liquid was measured using warm 50, 250, or 500 μL gas-tight syringes equipped with a Teflon straw of sufficient volume to accommodate the sample of ICl without direct contact of it with the stainless steel needle. [WARNING: ICl is volatile, toxic, extremely corrosive, and moisture-sensitive and should be handled only by trained personnel.]

Preparation of $C_{60}Cl_3$. Degassed samples of ICl (either 12.5 μL (0.246 mmol) or 376 μL (7.41 mmol)) were treated with excess chlorine at ca. -50 °C in the small greaseless reactor of local design shown in Supporting Information Figure S-34. The reactor was allowed to warm up to room temperature [WARNING: Cl_2 is extremely toxic, and an excess of liquid Cl_2 (b.p. -35 °C) condensed at -50 °C can lead to pressures at 25 °C high enough to rupture even a thick-walled glass reactor; this procedure should only be carried out by trained personnel and only with an adequate

pressure release system attached to the apparatus]. The color changed from dark brown (ICl) to bright yellow (ICl_3) within 30 min. Excess chlorine was then removed under vacuum at -50 °C, and the product was used immediately. [WARNING: ICl_3 is volatile, toxic, extremely corrosive, moisture-sensitive, and evolves chlorine upon standing, which can lead to a dangerous pressure buildup; it should be handled only by trained personnel.]

Handling of Chlorofullerenes. All operations involving solutions of CFs were performed either in the dark or with minimal exposure to light. However, the literature syntheses of CFs that were repeated in this work (see Table 3) were performed under ambient laboratory light to reproduce as closely as possible the original procedures (the one exception was the synthesis of $C_{60}Cl_{12}$ (Table 3, no. 6). Nevertheless, handling and analysis of the products of the literature syntheses were performed in the dark or with minimal exposure to light.

Synthesis of $C_{60}Cl_6$ Samples A, B, C, and D. Samples A and B were prepared by adding ICl (1.600 g, 0.500 mL, 9.8 mmol, 60 equiv) to a vigorously stirred solution of C_{60} (0.122 g, 0.169 mmol) in degassed chlorobenzene (20 mL) at ca. 15 °C in the glass reactor of local design (see Figure S-14 in Supporting Information).¹⁹ The reactor was evacuated to remove all volatiles immediately after the addition of ICl, for a total reaction time of 5 min. The dried product residue was dissolved in a minimum volume of dichloromethane, which was then removed under vacuum to yield $C_{60}Cl_6$ sample B (0.155 g, 0.166 mmol, 98% yield based on C_{60}). Sample A was prepared by HPLC purification of 0.04 g of sample B (toluene eluent).

Sample C was prepared by addition of ICl (0.800 g, 0.25 mL, 4.9 mmol, ca. 60 equiv) to a vigorously stirred solution of C_{60} (0.0600 g, 0.083 mmol) in degassed chlorobenzene (10 mL) at room temperature in a 50 mL Schlenk flask. The flask was evacuated to remove all volatiles immediately after the addition of ICl, for a total reaction time of 1 h (the longer time was due to the small diameter of the stopcock bore). The residue was dried for an additional 6 h to ensure complete removal of I_2 . The product was used without further purification.

Sample D was prepared by addition of ICl (0.467 g, 0.146 mL, 2.9 mmol, ca. 80 equiv) to a vigorously stirred solution of C_{60} (0.0263 g, 0.036 mmol) in degassed chlorobenzene (4 mL) at room temperature in a 50 mL Schlenk flask. The flask was evacuated to remove all volatiles immediately after the addition of ICl, for a total reaction time of 40 min. The residue was dried for an additional 6 h to ensure complete removal of I_2 . The product was used without further purification.

Investigation of Literature Chlorofullerene Syntheses.

Table 3, no. 16 (“ $C_{60}Cl_8$ ”). The reaction conditions were chosen in order to duplicate the original preparation²⁷ as closely as possible. The compound ICl (0.0576 g, 0.018 mL, 0.35 mmol, 40 equiv) was added to a vigorously stirred solution of C_{60} (0.0075 g, 10 μmol) in 1,2-C₆H₄Cl₂ (0.25 mL) at 20 °C in a 25 mL Schlenk flask. After 3 h, the reaction mixture was flash evaporated under vacuum yielding an orange product that was a mixture of CFs.

Table 3, no. 17 (“ $C_{60}Cl_{10}$ ”). The reaction conditions were chosen in order to duplicate the original preparation²⁷ as closely as possible. The compound C_{60} (0.0075 g, 10 μmol) was dissolved in degassed 1,2-C₆H₄Cl₂ (0.25 mL) in a 25 mL Schlenk flask and treated with an excess of chlorine at 20 °C. A dark precipitate was formed, which redissolved after ca. 10 min. After 15 min, the reaction mixture was flash evaporated under vacuum, yielding an orange product that was a mixture of CFs.

Table 3, no. 6 (“ $C_{60}Cl_{12}$ ”). The reaction conditions were chosen in order to duplicate the original preparation²² as closely as possible. The compound ICl (1.600 g, 0.500 mL, 9.8 mmol, 3300 equiv) was added to a vigorously stirred solution of C_{60} (0.0022 g, 0.003 mmol) in 1,2-C₆H₄Cl₂ (15 mL) at 20 °C in a 50 mL Schlenk flask. The reaction was performed in the dark. After 3 d, the reaction mixture was evaporated under vacuum yielding an orange mixture of CFs.

Table 3, no. 18 (“C₆₀Cl₁₂”). The reaction conditions were chosen in order to duplicate the original preparation²⁷ as closely as possible. The compound ICl (0.0576 g, 0.018 mL, 0.35 mmol, 40 equiv) was added to a vigorously stirred solution of C₆₀ (0.0075 g, 10 μmol) in 1,2-C₆H₄Cl₂ (0.25 mL) at 20 °C in a 25 mL Schlenk flask. After 24 h, the reaction mixture was flash evaporated under vacuum yielding an orange mixture of CFs.

Table 3, no. 20 (“C₆₀Cl₂₆”). The reaction conditions were chosen in order to duplicate the original preparation²⁷ as closely as possible. The compound C₆₀ (0.0075 g, 10 μmol) was dissolved in degassed 1,2-C₆H₄Cl₂ (0.25 mL) in a 25 mL Schlenk flask and treated with an excess of chlorine at 20 °C. A dark precipitate was formed, which redissolved after ca. 10 min. After 7 d, the reaction mixture was flash evaporated under vacuum, yielding an orange mixture of CFs.

Table 3, no. 7 (“C₆₀Cl₂₄”). The reaction conditions were chosen in order to repeat the original preparation^{21,23} as closely as possible. A vigorously stirred suspension of C₆₀ (0.0050 g, 0.007 mmol) in tetrachloromethane (4 mL) in a 25 mL Schlenk flask was treated with an excess of chlorine at 20 °C for 16 h. The yellow-green solution was then irradiated using a Hanovia PC451050 mercury vapor lamp for an additional 24 h. The resulting solution, which was still yellow-green, was evaporated to dryness under vacuum yielding a yellow-orange mixture of CFs.

Synthesis of o-C₆₀Cl₂, p-C₆₀Cl₂, and C₆₀Cl₄. The compound ICl (75 μL, 0.2400 g, 1.48 mmol, 15 equiv) was added to a vigorously stirred solution of C₆₀ (0.0705 g, 0.0979 mmol) in degassed chlorobenzene (12 mL) at ca. 15 °C in the glass reactor shown in Supporting Information Figure S-14.¹⁹ The reactor was evacuated to remove all volatiles 1 min after the addition of ICl, for a total reaction time of 5 min. The dried product residue was dissolved in a minimum volume of toluene, which was filtered and

separated into 75% *o*-C₆₀Cl₂, 75% *p*-C₆₀Cl₂, and 98% C₆₀Cl₄ by HPLC (see Figure 7).

Synthesis of C₆₀Cl₁₀. The compound ICl (0.700 mL, 2.2400 g, 13.8 mmol, 83 equiv) was added to a vigorously stirred solution of C₆₀ (0.1200 g, 0.167 mmol) in degassed chlorobenzene (16 mL) at ca. 15 °C in the same glass reactor used for the previous synthesis. The reactor was evacuated to remove all volatiles 45 min after the addition of ICl, for a total reaction time of 50 min. The dried product residue was dissolved in a minimum volume of toluene, which was filtered and HPLC processed to yield 90+% of red-orange C₆₀Cl₁₀ (ca. 25% yield based on C₆₀; see Figure 8).

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Supporting Information Available: Crystallographic information files for C₆₀Cl₆ and C₆₀Cl₁₀ and additional text, figures, and tables; complete ref 39. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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