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Very Convenient and Efficient Purification Method for Fullerene (C_{60}) with 5,11,17,23,29,35,41,47-Octa-*tert*-butylcalix[8]arene-49,50,51,52,53,54,55,56-octol

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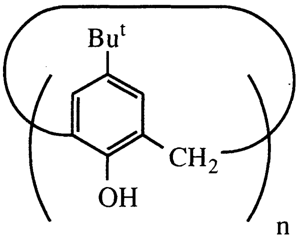
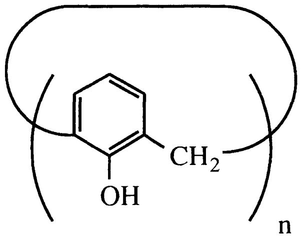
The gram-order of fullerene (C_{60}) with 99.8 wt% purity was isolated from carbon soot by fractional precipitation with 5,11,17,23,29,35,41,47-octa-*tert*-butylcalix[8]arene-49,50,51,52,53,54,55,56-octol. This is a very convenient and efficient C_{60} purification method without any precious apparatus.

Buckminsterfullerene (C_{60}) is a novel compound which has a variety of scientific potentials as electron-carriers, π-basic donors and acceptors, caged host molecules, *etc.*[1] In spite of a broad demand for and a scientific interest in C_{60} the progress of this chemistry has been suppressed and hampered by its very extensive commercial price. This situation prompted us to develop a convenient purification method which might enable us to procure C_{60} in a reasonable price. The survey of past literatures taught us that the most promising among the methods reported so far is column chromatography using polystyrene gel, silica gel, activated charcoal, neutral alumina, *etc.*[2-4] The difficulty of C_{60} purification is related to the separation of C_{60} from C_{70} and higher fullerene homologues, but the separation is not achieved to a satisfactory level by these chromatographic methods.

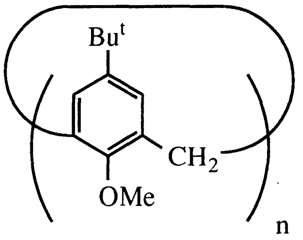
More recently, Williams and Verhoeven[5] reported that certain water-soluble calix[n]arenes are capable of solubilizing C_{60} in water. It thus occurred to us that host-guest chemistry using calix[n]arenes might provide a breakthrough for facile purification of C_{60}. Examination with CPK molecular models suggests that the size of the inner cavity of calix[8]arene (8.6 Å when it adopts a regular cone conformation) is comparable with the size of C_{60} (7.1 Å). We thus synthesized various calix[8]arene derivatives as well as calix[4]arene and calix[6]arene derivatives and investigated how they interact with C_{60} in solution. Quite accidentally, we discovered that the starting material, 5,11,17,23,29,35,41,47-octa-*tert*-butylcalix[8]arene-49,50,51,52,53,54,55,56-octol ($\mathbf{1}_8$) selectively forms a 1:1 complex with C_{60}. Since this complex is sparingly soluble in most organic solvents, one can very easily and very efficiently purify C_{60} as the precipitate. C_{60} can be readily isolated from the complex by dispersing the precipitate into chloroform.



$\mathbf{1}_n$



$\mathbf{2}_n$



$\mathbf{3}_n$

Compounds $\mathbf{1}_n$, $\mathbf{2}_n$, and $\mathbf{3}_n$ were prepared according to literatures.[6-8] The typical isolation method is as follows. Carbon soot [9] (200 mg) containing 72 wt% of C_{60}, 13 wt% C_{70}, and 15 wt% others was dissolved in toluene (60 ml). The solution was mixed with a toluene solution (200 ml) of $\mathbf{1}_8$ (389 mg, 0.30 mmol) and the combined solution was left at room temperature for 15 h. The precipitate was recovered by filtration and subjected to HPLC analysis. As shown in Fig. 1, the purity of C_{60} can be enhanced up to 96.0 wt% by this simple fractional precipitation method. The sole concomitant impurity was C_{70} (4.0 wt%). The precipitate was dissolved in hot toluene (200 ml) and left at room temperature for 15 h. The HPLC analysis showed that the precipitate thus formed contains C_{60} in 99.0 wt% purity. The same operation was repeated once again; the C_{60} purity was enhanced up to 99.8 wt%. Elemental analysis of this precipitate established that the complex has a 1:1 stoichiometry (Found: C 87.96%, H 5.79%. Calcd for $C_{88}H_{112}O_8$+C_{60}: C 88.07%, H 5.59%). When this precipitate was stirred in chloroform (30 ml) at room temperature for 1 h, C_{60} was precipitated while $\mathbf{1}_8$ was dissolved in chloroform. We could recover 102 mg (70.8 %) of C_{60} with 99.8 wt% purity.

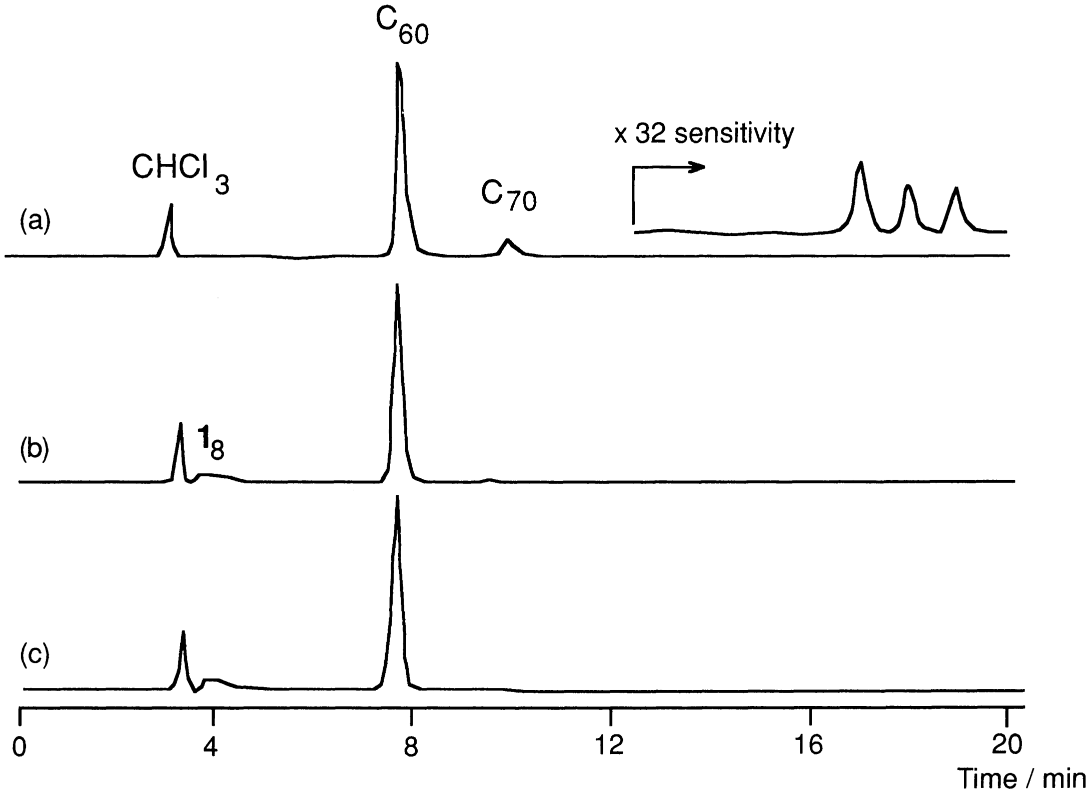


Fig.1. HPLC chromatograms of (a) carbon soot, (b) the first precipitate, and (c) the third precipitate. Column, CAPCELL PAK C18 UG120: mobile phase, toluene:methanol = 1:1 v/v; λ = 340 nm.

We also tested $\mathbf{1}_n$ (n=4 and 6), $\mathbf{2}_n$ (n=4, 6, and 8), and $\mathbf{3}_n$ (n=4, 6, and 8) but the precipitation complexed with C_{60} was not observed. The results suggest that the cavity size and the OH and *tert*-butyl groups play important roles. Why can only $\mathbf{1}_8$ form a sparingly-soluble 1:1 complex with C_{60}? The preparation of a single crystal for X-ray analysis is so far unsuccessful. Hence, we tried to characterize the complex in the solid state by spectroscopic methods. In IR spectra (KBr disk) C_{60} gives strong peaks at 526, 576, 1183, and 1429 cm^{-1}. In the complex these peaks were scarcely changed. $\mathbf{1}_8$ gives a ν_{OH} band at 3240 cm^{-1}, characteristic of the intramolecularly hydrogen-bonded OH group. In the complex this band shifted to 3304 cm^{-1}, suggesting that the intramolecular hydrogen-bonds are partially disrupted or weakened. In UV-visible spectra (KBr disk) C_{60} has the λ_{max} at 260, 348, and 450 - 550 (broad) nm. In the complex the broad absorption band at 450 - 550 nm disappeared, suggesting that the interaction among C_{60} molecules is suppressed by the isolation effect of **1**$_8$. The most useful information was obtained from CP-MAS ^{13}C NMR spectra. The large up-field shift was observed for the *tert*-butyl carbons whereas the large down-field shift was observed for the $ArCH_2Ar$ methylene carbons. This change suggests that the *tert*-butyl groups exist on the C_{60} sphere whereas some C_{60}-induced conformational change causes the unusual down-field shift of the $ArCH_2Ar$ methylene groups.

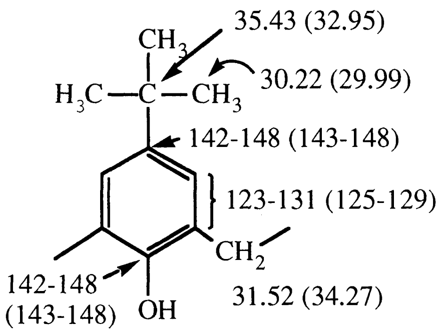


Fig. 2. Chemical shifts (ppm) of **1**$_8$ and the complex (given in parentheses) in CP -MAS ^{13}C NMR spectra.

From the foregoing results it seems most reasonable to propose that C_{60} is included in the cavity of **1**$_8$. Through X-ray crystallographic studies of calix[n]arenes including aromatic guest molecules Ungaro *et al.*[10-12] repeatedly emphasized the importance of a CH-π interaction between the *tert*-butyl groups and included aromatic guest molecules. In the present system the CH-π interaction between the *tert*-butyl groups in **1**$_8$ and the π-system in C_{60} may play a crucial role. In fact, **2**$_8$ without the *tert*-butyl groups cannot form such a precipitate complex. This proposal is further corroborated by the spectroscopic data. The CP-MAS ^{13}C NMR spectra support the view that C_{60} is bound to the upper edge of the calix[8]arene cavity, interacting with the *tert*-butyl groups substituted at the *p*-positions. This inclusion mode isolates C_{60} molecules in the solid state and suppresses the mutual interaction of C_{60} molecules. The change is well reflected by the UV-visible spectra. The inclusion mode is also in line with the IR spectra: **1**$_8$ tends to adopt a flattened conformation to enjoy an efficient intramolecular hydrogen-bonding interaction,6) so that the hydrogen-bonds should be partially disrupted or weakened when it adopts a cavity-forming conformation. The contribution of the OH-π interaction between the OH groups on the lower rim and C_{60} 13) is not thoroughly ruled out because **3**$_8$ cannot form such a precipitate. We consider, however, that this is due to the high solubility of **3**$_8$ brought forth by *O*-methylation. Meanwhile, the dissociation of the complex is readily effected by dispersing the complex into chloroform. This is ascribed to competitive substitution of C_{60} in the cavity with chloroform because alkyl halides are also included in the cavity.14)

In conclusion, the present method was accidentally found in our laboratory in the course of our studies on inclusion chemistry of calix[n]arenes. The method has enabled us to obtain the gram-order of high-purity C_{60} without using any precious apparatus. It is our hope that this unexpected discovery would contribute to the progress of C_{60} chemistry and at the same time, provide a fruitful cross-link between calixarene chemistry and C_{60} chemistry.

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