Evidence for the Existence of Sulfur-Doped Fullerenes from Elucidation of Their Photophysical Properties

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Evidence is presented that carbon atoms of the hollow fullerene cage can be replaced by sulfur atoms, as has been suggested theoretically. S-doped fullerenes are obtained by arc-vaporization of graphite in the presence of thiophene or 3-methylthiophene. Mass spectra indicate the dominant processes are the substitutions of pairs of carbon atoms by sulfur atoms with the predominant ratios of sulfur to replaced carbon pairs being 1, $^1/_3$, or $^1/_4$. Fractions that contain a large group of such compounds with a substantial S enrichment can be collected by column chromatography, but no single pure compound can be isolated. Since the mass spectra can be interpreted in alternate ways involving S incorporation as an adduct, evidence was sought for their existence from a detailed study of the fluorescence of these species. The fluorescence emission spectra are red-shifted from and consistent with absorption spectra and can be attributed to the emission from symmetry-broken distorted S-doped derivatives of fullerenes. An optical bandgap of 2.5 eV is derived for the S-doped fullerenes resulting from the splitting of the h_u degenerate state. The fluorescence lifetimes of these molecules are 2−7 ns, considerably larger than those of the undoped fullerenes.

Introduction

Because of the discoveries of superconductivity in alkali- and alkaline-earth metal salts of C_{60}[1−3] at critical temperatures almost 2 orders of magnitude higher than the analogous graphite intercalates, it is of interest to attempt to modify the structure to allow for interaction with a wider variety of gegenions. Fullerenes have a closed-shell structure with the surface consisting of 12 pentagons and a varying number of hexagons. In fullerene 60 all atoms are equivalent and lie on the surface of a sphere distributed with the symmetry of a truncated icosahedron. In these closed-shell electronic structures which possess a HOMO−LUMO bandgap of 1.6 eV,[4] electronic transitions are optically forbidden due to the high degree of symmetry.[5,6] This transition is very weak and exhibits a broad absorption band in the visible.[7] Very low yields of fluorescence have been observed in C_{60} and C_{70} reflecting the degree to which optical transitions are allowed in these molecules.[8−11] Thus, an investigation of replacing one or more carbon atoms of the hollow fullerene cage by electron donors and acceptors such as N, B, and S, which should make significant changes in the electronic properties of these molecules, is of considerable interest. These molecules are expected to have novel chemical behavior as well as unusual electronic, magnetic, and optical properties.

In this latter regard, it has recently been demonstrated that doping of the fullerene cage with *N* atoms disturbs the degeneracy of the t_{1u} degenerate state, creating new photophysical effects.[12,13] Such excited-state phenomena are important not only in developing a better fundamental understanding of the energetics of fullerenes but also because distorted fullerene cages are attractive candidates for applications such as optical limiters. C_{60} itself shows optical limiting behavior[14,15] with saturation thresholds equal to or lower than those reported for currently used materials, and N-, S-, or B-doped materials may be able to become involved in charge-transfer transitions that have larger absorption coefficients.

Although some theoretical and experimental work has been devoted to the N- and B-doped fullerenes,[16−19] very little theoretical work has been done so far on the hypothetical $C_{59}S$ molecule. Calculations predict that when a carbon atom of the C_{60} cage is replaced by a sulfur atom, the spherical structure of C_{60} can be distorted, although the electronegativity of these ele-

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ments is about the same.[20] The electronic properties of $C_{59}S$ are thus quite different than those of $C_{59}N$. Thus, theoretical analysis suggests that replacing C with S leads to an energy gap between the HOMO and LUMO of 0.63 eV. A likely structure of $C_{59}S$ is presented in which S is displaced outward from the cage and the distances between S and its nearest-neighbor carbons are about 2 Å. The previous theoretical analysis selected $C_{59}S$ as a possible structure by analogy to the B and N cases, but there was no experimental evidence for the existence of this particular sulfur-doped species. As will be seen later in this paper, in fact one sees no evidence for $C_{59}S$ but does find a number of other sulfur-doped species, the lowest member of which is likely $C_{58}S$.

In the present study, the production of S-doped fullerenes is attempted by arc discharge in an atmosphere containing the sulfur-containing compounds thiophene (T) or 3-methylthiophene (3MeT). S-enriched fractions are isolated by column chromatography and identified by mass spectroscopy. However, these analyses in and of themselves are insufficient to argue in favor of the existence of S-doped fullerenes, since they can be interpreted as due to sulfur incorporation as an adduct.[21] Because sulfur doping would be expected to induce changes in the electronic properties of fullerenes as the 5-fold-degenerate h_u highest unoccupied molecular orbital acts as a donor state, UV−visible and fluorescence spectra, and time-resolved fluorescence measurements should yield much more information about the nature of these S-doped species. Multiples of $2n$, $3n$, and $4n$ carbon atoms of C_{60} and C_{70} are replaced by n sulfur atoms. Sulfur doping induces changes in the electronic properties either by disturbing the degenerancy of the h_u state forming excitonic states below the optical gap or by creating defects that disturb the stability of the closed hollow cage. Both types of doping result in creating fluorescence centers. The transitions observed in the absorption spectrum are correlated to those of the fluorescence emission spectrum, indicating that fluorescence is related to intramolecular and banded intermolecular processes.

Experimental Section

Sulfur-doped fullerenes were produced by carrying out electric-arc graphite decomposition in the presence of sulfur-containing species by leaking either T or 3MeT gas simultaneously with helium inside the belljar reaction chamber. During the arc discharge, the temperature of the silicone oil bath (into which the bubbler container with T or 3MeT was placed) was maintained higher than the boiling point of the liquids, which are 84 and 145 °C, respectively. The soot collected from each run was Soxhlet-extracted with either toluene or pyridine, and the fullerene solutions were concentrated with a flash evaporator. The toluene extract was chosen for detailed study because of its higher concentrations of the S-doped derivatives. The yield of the S-doped fullerenes extracted from the soot was as high as 10%. Elemental analysis of a typical sample shows 2.0 wt % sulfur. The yellow-red product gives three bands in column chromatography using neutral alumina as a support phase and toluene as a mobile phase. The first fraction has a yellow-orange color, the second a yellow-green color and the third band has an orange color.

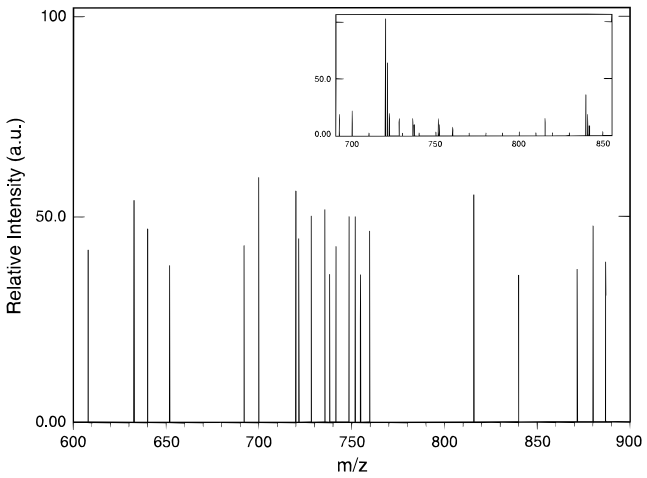

Figure 1. Mass spectrum of S-doped fullerenes at 45 s of the RIC. The insert displays the mass spectrum at 53 s of the RIC.

The materials are stable in toluene and in *n*-hexane solution. All solutions were degassed before each use.

Mass spectral measurements were performed using a Finnigan MAT 4610B mass spectrometer. The material to be tested was vaporized by a direct-exposure probe that was heated from ambient temperature to 700 °C at 20 °C/s. The vapor is bombarded by a stream of high energy electrons (70 eV), generating positive ions, which are then filtered and scanned from 600 to 900 *m*/*z* units. The produced spectrum displays the reconstructed ion chromatograph (RIC) of the sample. The RIC indicates the total number of ions detected during each scan over a specific time interval. For this material, the time interval involved is from 31 to 63 s with a maximum peak at 45 s. Several samples were investigated: the as-produced soot, the product from toluene extraction, the product from pyridine extraction, and the individual fractions obtained from column chromatography.

UV-visible spectra were recorded on a Perkin-Elmer 330 spectrophotometer in spectroscopic grade *n*-hexane as the solvent. Fluorescence spectra were acquired on a Perkin-Elmer MPF-66 spectrophotometer. Emission spectra were obtained with excitation and emission slit widths of 3 nm, an excitation wavelength of 350 nm, and scanning speeds of 120 nm min^{-1}. The fluorescence decay was detected by time-resolved fluorescence. The laser source was composed of a mode-locked Nd:YAG laser and a cavity-dumped dye laser. The excitation was of the order of microwatts, and the light pulses were about 10 ps. The fluorescence response was detected with a microchannel plate photomultiplier. For analyzing the data, one utilizes a program developed at the Regional Laser and Biotechnology Laboratories of the University of Pennsylvania, which convolutes the instrumental response function with a trial decay function and compares the resulting calculated curve with the experimental fluorescence decay. One assumes a decay law that has 1, 2, 3, ..., decay contributions in order to perform numerical analysis. Extraction of decay times are possible with the aid of least-squares numerical techniques. An iterative adjustment procedure is used to refine the decay parameters (lifetimes and amplitudes) until the best fit is achieved. From the lifetimes, the average time constants can be calculated. All fractions have similar absorption and fluorescence spectra but at slightly shifted energies. There are only small differences in the materials isolated from gas discharge in 3MeT and T.

Results and Discussion

Mass Spectra. In this section, results are presented for the second chromatographic fraction, which has the highest concentration of S doped derivatives. Figure 1 displays a mass spectrum of the S-doped fullerenes obtained at 45 s of the RIC. The spectrum shows peaks

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at 720, 721, and 840 amu which are due to $^{12}C_{60}$, $^{13}C_1{}^{12}C_{59}$, and $^{12}C_{70}$, respectively. It also shows a number of peaks on the high amu side of the spectrum (above 720 amu) which can be attributed to substitution of even-number multiples of carbon atoms by *n* number of sulfur atoms, and peaks on the low amu side of the spectrum (below 720 amu) which are attributed to the replacement of multiples of larger number of C atoms of C_{60} and C_{70} by S atoms. The insert displays the mass spectrum at 53 s of the RIC, which shows clearly the typical isotopic distribution of C_{60} and C_{70}. The peaks at 720, 721, and 722 amu are due to $^{12}C_{60}$, $^{13}C_1{}^{12}C_{59}$, and $^{13}C_2{}^{12}C_{58}$, respectively. The ratio of these peaks is 100:64:19, which is very close to the carbon isotopic abundance. In addition one observes peaks at 840, 841, and 842 amu due to $^{12}C_{70}$, $^{13}C_1{}^{12}C_{69}$, and $^{13}C_2{}^{12}C_{68}$, respectively. The ratio of these peaks after normalization is 100:54:25, consistent with theoretical expectations. Odd-numbered peaks associated with ^{13}C isotopes appear in the mass spectra of the S-doped fullerenes at other time frames of the RIC. The ratio of the peaks corresponding to C_{60} and C_{70} as compared to the peaks attributed to the substitution of C atoms by S atoms can be as high as 10. This ratio varies depending upon the conditions of the arc vaporization (current, concentration of T or 3MeT in the atmosphere).

The peaks on the high amu side of 720 at 728, 736, 752, 760, and 816 are attributed to $C_{58}S$, $C_{56}S_2$, $C_{52}S_4$, $C_{50}S_5$, and $C_{36}S_{12}$. All of them obey the $C_{60-2n}S_n$ relationship for $n = 1$, 2, 4, 5, and 12, indicating substitution of an even-number of carbon atoms of the C_{60} cage by sulfur atoms. Complementary peaks appear in other RICs. The chromatograph at 50 s displays, among other peaks which also fit the above relationship, peaks at 800, 824, and 832 which correspond to $C_{40}S_{10}$, $C_{34}S_{13}$, and $C_{32}S_{14}$ for $n = 10$, 13, and 14. The peak at 760 could also be due to $C_{58}S_2$, which is attributed either to the substitution of two carbon atoms by one sulfur atom and the addition of one sulfur atom or to the substitution of two carbon atoms of C_{60} by two sulfur atoms. One also observes peaks related to the substitution of C atoms of C_{70} by S atoms. The peak at 872 is due to the substitution of eight carbon atoms of C_{70} by four sulfur atoms, the peak at 880 to the substitution of 10 carbon atoms of C_{70} by five sulfur atoms, and the peak at 888 to the substitution of 12 carbon atoms by six sulfur atoms. All of them obey the $C_{70-2n}S_n$ relationship. The peak at 880 can also be explained as due to the substitution of two carbon atoms of C_{70} by two sulfur atoms or the substitution of two carbon atoms by one sulfur atom and the addition of one more sulfur atom. The peaks in the high amu side of the spectrum do not appear in the first fraction of the sample. On the low amu side of 720, the mass spectrum displays peaks at 700, 692, and 652 which are related to $C_{45}S_5$, $C_{39}S_7$, and C_9S_{17}. These peaks obey the relationship $C_{60-3n}S_n$ where $n = 5$, 7, and 17. The peak at 640 and 608 are ascribed to $C_{40}S_5$ and $C_{32}S_7$ respectively and follow the $C_{60-4n}S_n$ relationship for $n = 5$ and 7. There are also five lines in the mass spectrum that do not fit the general relationships indicating the complexity of the products.

Optical Properties. Absorption spectra of the S-doped fullerenes in hexane solutions are shown in Figure 2. The $\pi-\pi^*$ absorption band of each of the three fractions are derived from similar underlying structures with important differences in the degree of sulfur substitution. The relative intensities of these peaks gradually decreases with increasing distance from the main peak. The main absorption features are collected in Table 1. The high-energy side of the spectrum contains $\pi-\pi^*$ transitions at 210, 221, and 250 nm which are related to the undoped fullerenes.[6] The absorption peaks at 332, 351, and 404 nm form the major emission bands, and the peaks at 415 and 427 nm are the sources of fluorescence on the low-energy side of the emission spectrum as indicated below. The latter two bands are absent in the first fraction of the sample. From the lower energy absorption edge of the spectrum, a value of the optical bandgap of 2.5 eV can be estimated. The disappearance of the transitions (the bands are very weak as compared to the rest of the spectrum) on the low-energy side of the spectrum at 2.40 eV (516 nm) and 2.10 eV (590 nm) which, according to Hückel molecular orbital calculations,[6] correspond to $h_u \rightarrow t_{1g}$ and $h_u \rightarrow t_{1u}$ absorption bands, may arise from the removal of electron density from the 5-fold-degenerate h_u valence band, that is from p-type doping.

It is assumed that sulfur has been incorporated into the fullerene cage. While the mass spectra do not exclude the alternative interpretation of the formation of clusters, such as S_8, attached on the outside of the fullerene structures, the UV−vis spectral pattern indicate that this is not a valid interpretation and that it is much more likely that S has been incorporated in the fullerene structures. The UV−vis spectra of exohedral sulfur attached to the fullerenes are known to exhibit an additional absorption band which, in the case of S_{16},

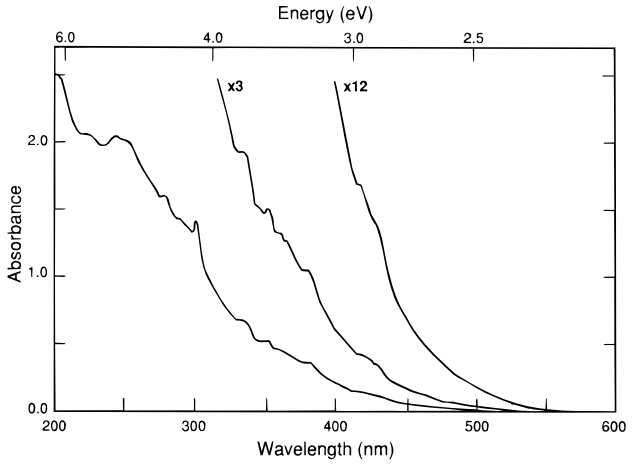

Figure 2. Optical absorption spectrum of S-doped fullerenes in hexane.

Table 1. Optical Absorption and Fluorescence Emission Bands of S-Doped Fullerenes in Hexane Solution

absorption		emission	
λ (nm)	E (eV)	λ (nm)	E (eV)
300.5	4.126	374	3.316
332	3.735	384	3.229
336	3.690	392	3.163
351	3.533	402	3.085
359	3.454	418	2.966
364	3.407	422	2.938
378	3.280	435	2.850
398	3.116	456	2.719
404	3.069	472	2.627
415	2.988	500	2.480
427	2.904	506	2.450

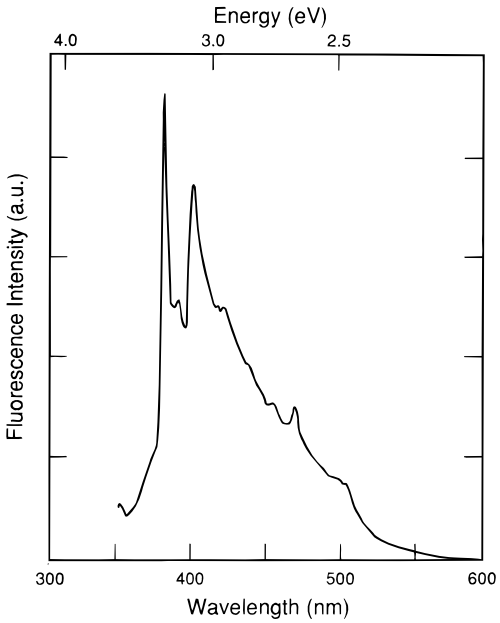

Figure 3. Fluorescence emission spectrum of S-doped fullerenes in hexane (excitation $\lambda = 350$ nm).

is located at ~488 nm and is characteristic of the exohedral sulfur chain.[22] Quite to the contrary, the absorption spectrum of the S-doped fullerenes exhibits a considerably different, much broader spectrum indicating new transitions in the visible and the UV that can be interpreted in terms of cage substitution. The 488 nm peak is conspicuously absent.

Excited-State Properties. The fluorescence emission spectrum for the second chromatographic fraction of the S doped fullerenes at room temperature excited at 350 nm is shown in Figure 3, and is red-shifted relative to absorption indicating the importance of relaxation effects after excitation. The excitation spectrum of the S-doped fullerenes was also performed and has similar wavelength dependence as the absorption spectrum. The emission spectrum is very broad from 350 to 600 nm and overlaps with the absorption spectrum, and the transitions are correlated (Table 1), indicating that the fluorescence is related to intramolecular processes. The emission spectrum is the result of the intramolecular transitions and the interaction between the excitation energy with various molecular weight S-doped fullerenes. This interaction leads to the molecular levels forming a band, accompanied by a broadening of the emission profile and a shift to lower energies. The bands in the spectral region from 350 to 480 nm are ascribed to the species observed below the 720 amu mass spectral region. These bands are attributed to the energetic disorder which arises from charge separation in these molecules. When multiples of 3*n* or 4*n* carbon atoms are replaced by *n* sulfur atoms, the stable structure of C_{60} may be distorted. Such sulfur-doped fullerenes species act as defects, which in turn act as fluorescence centers.

The band on the low-energy side of the spectrum from 495 nm (2.50 eV) to 520 nm (2.38 eV) is related to fluorescence from S-doped fullerenes. This band is absent in the first fraction of the sample, which does not contain the peaks above 720 amu in the mass spectrum, and is centered at 500 nm with a clear shoulder at 505 nm. The value of 2.50 eV corresponds to the gap derived from the onset of the occupied h_u valence band and the t_{1u} conduction band. This band-gap value agrees well with that estimated from the absorption spectrum. In the S-doped C_{60} the $h_u \rightarrow t_{1u}$ transition is split. Doping with S atoms results in disturbing the degeneracy of the h_u state of C_{60} leading to the formation of intermediate states localized in the band gap. The fluorescence in this spectral region should be related to Frenkel-like excitons in the range 2.50−2.38 eV and corresponds to an intramolecular excitation in the S-doped fullerenes in solution.

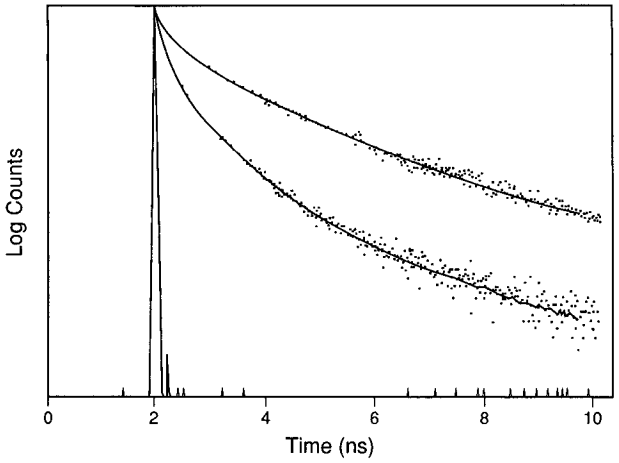

Figure 4. Fluorescence decay curves for S-doped fullerenes at room temperature: upper curve, decay at 500 nm, lower curve, decay at 400 nm (excitation $\lambda = 295$ nm).

The fluorescence decay curves of the second chromatographic fraction at 400 and 500 nm (both excited at 295 nm) are shown in Figure 4. In both curves one detects three exponential decay elements providing evidence for multiple components of the time-resolved fluorescence. This is consistent with the presence of multiple S-doped fullerenes. From the fluorescence decay and curve fitting, average lifetimes of 2.1 ± 0.05 and 7 ± 0.05 ns, respectively, were determined. The different lifetime values may be due to separate sources (extrinsic or intrinsic) of fluorescence and are larger than those reported for C_{60}(1.2 ns)[23] and C_{70}(0.67 ns).[24] This is consistent with the increase in the bandgap of the S-doped fullerenes relative to C_{60} and C_{70}. The increases in the band gap in turn result in increases of the lifetimes of the photoexcited states. In addition, the lifetimes of the photoexcited states are influenced by the presence of defects, especially as these defects cause charge separation. Thus, the presence of defects in the S doped fullerenes which are located below 720 amu in the mass spectrum, increases the distance between the lowest unoccupied and the highest occupied molecular orbitals arising from the ionization of the undoped fullerenes.

Conclusions

The synthesis of S-doped fullerenes has been attempted by arc vaporization in the presence of thiophenes

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and the materials have been characterized by mass spectroscopy, optical absorption, and fluorescence measurements. There is good evidence that doping fullerenes with S results in the formation of molecules which follow predominantly the $C_{60-2n}S_n$, $C_{60-3n}S_n$, and $C_{60-4n}S_n$ relationships. Compounds corresponding to the first of these relationships result in splitting the degenerate energy levels of C_{60}, whereas compounds obeying the second and third of these relationships result in considerable structural distortion as a consequence of the large defects introduced. These molecules exhibit fluorescence, which has its origin in the symmetry-broken forbidden optical processes and in charge separation in the distorted molecules. The intermolecular interactions lead to a broadening and red shifting of the emission spectrum, relative to absorption. A value of the bandgap of 2.5 eV was deduced from optical absorption measurements and compares well with that obtained from fluorescence results. The average lifetimes are larger than those observed in the undoped fullerenes.

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