Photophysical Properties of Fullerenes Prepared in an Atmosphere of Pyrrole

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Samples of C_{60} and C_{70} containing a variety of nitrogen-doped species were prepared by arc vaporization of graphite in the presence of pyrrole. Cage-doped fractions were isolated by column chromatography and characterized by mass spectroscopy, optical absorption, and fluorescence measurements. Mass spectra were consistent with the substitution of an even number of carbon atoms of the C_{60} and C_{70} cages by nitrogen atoms. Carbonaceous clusters including fragmented fullerenes containing hydrogen atoms were also formed. UV–visible spectral analysis indicated that there is an influence of the molecular weight on the fundamental $\pi-\pi^*$ electronic transition. Fluorescence spectra showed a broad band containing vibrational fine structure that is attributed to photoseparated charges in the fragmented fullerenes and a shoulder on the low-energy side that is related to intrinsic excitation in the nitrogen-doped species. Fluorescence results imply a bandgap of 2.36 eV for the N doped fullerenes and the existence of intermediate excitonic transitions below the optical bandgap. Although it has not yet been possible to isolate a pure cage-doped material, the photophysical studies add credence to their existence and the importance of further attempts at their isolation.

Introduction

Because of the exciting discoveries of superconductivity in the alkali and alkaline earth metal salts of C_{60},[1,2] it is of great interest to expand the range of gegenions that can enter such lattices. One approach is to attempt to modulate the structure of the fullerene cage by heteroatom substitution, thus varying the electronic structure and complexing ability. Fullerenes have a closed-shell structure with the surface consisting of 12 pentagons and a varying number of hexagons. The valence electrons of the carbon atoms provide a system that contains a σ-bonding skeleton and a delocalized π-electron cloud. In these closed-shell structures, electronic transitions are optically forbidden due to the high degree of symmetry. The transitions in the visible region of the absorption spectrum are very weak,[3,4] and fluorescence yields are very low.[5,6] Thus, an investigation of replacing one or more carbon atoms of the hollow fullerene cages by electron donors and acceptors such as N, B, and S is of considerable interest, since one may induce important changes in the electronic properties of these molecules and enhance their chemical reactivity. Theoretical studies imply that both nitrogen and boron can be substituted in the fullerene cage to form stable structures.[7,8] The nitrogen-doped C_{60} is characterized as an electron donor, whereas the boron-doped C_{60} is characterized as an electron acceptor.

Synthetic attempts to produce such heteroatom-doped structures have yielded evidence for their existence, but thus far no macroscopic quantity of any pure compound has been reported. In one experiment using boron nitride powder, in the hope that both boron- and nitrogen-doped fullerenes would be produced, only C_nB_m clusters were detected.[9] Presumably this is a result of diatomic N_2 having a much larger binding energy (9.9 eV) than that of B_2 (3.0 eV). Another experiment involved arc vaporization of graphite in the presence of nitrogen or ammonia,[10] and mass spectra revealed such species as $C_{70}N_2$, $C_{59}N_6$, $C_{59}N_6$, and $C_{59}N_2$, albeit in trace amounts.

In this work, N-doped fullerenes were produced by performing an arc vaporization of graphite in the presence of pyrrole vapor. Pyrrole is a quite stable five-membered heterocyclic compound in which the nitrogen atom provides two additional 2π electrons to the four 2π electrons from the carbon atoms making an aromatic system. Pyrrole was chosen as a starting material in the hope that the existence of nitrogen already bound to an aromatic system would allow its capture into a cluster to be more efficient. Nitrogen-doped fractions were isolated via column chromatography, but no single pure species could be isolated. Identification consisted first of mass spectra of these fractions. Because nitrogen doping induces changes in the electronic properties of fullerenes as the 3-fold degenerate t_{1u} lowest unoccupied molecular orbital acts as an acceptor state, a

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detailed study of both the UV–visible and fluorescence spectra was undertaken. The UV–visible spectra can be interpreted in terms of vibrational coupling to the fundamental electronic transition. Information about the photoexcited states is obtained via fluorescence measurements. The behavior of photoexcited states in both N-doped and fragmented fullerenes, and their response to photoexcitation is discussed.

Experimental Section

Nitrogen-doped fullerenes were produced by carrying out the electric-arc graphite decomposition technique in the presence of nitrogen by leaking pyrrole gas (5–10 mL in liquid phase) simultaneously with helium inside a belljar reaction chamber of essentially the reactor design described by Wudl et al.[11] The reactor used to create the substituted materials consists of a $^1/_8$ in. graphite rod fed against a base anode. The discharge (using an arc welder) was conducted at 90–100 A (ac) in a He (100 Torr) atmosphere. During the arc discharge, the temperature of the silicone oil bath (into which the bubbler container with pyrrole was placed) was maintained higher than the boiling point of pyrrole (131 °C). Soot (3–5 g) collected from each run was Soxhlet-extracted with toluene, and the fullerene solution was concentrated down with a flash evaporator. The yield of the N-doped fullerenes extracted from the soot was as high as 12%. Elemental analysis of the sample shows a 0.92% concentration of nitrogen, a considerable enrichment if one considers that a species such as $C_{59}N$ would have a theoretical N content of 1.94%. The dark-red product gives three bands in column chromatography using neutral alumina as a support phase and toluene or methylene chloride as a mobile phase. The flow rate for the mobile phase was 1 mL/min. The first fraction (toluene) has a yellow-orange color, the second (toluene) a yellow-green color, and the third band that is eluted out with methylene chloride has a dark orange color. The materials are stable in the atmosphere. They are also stable in *n*-hexane solution, while the photophysical properties show some degradation after long (~1 month) storage in toluene.

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. In this case a chromatographic peak from 35 to 78 s with a maximum at 42 s is seen.

UV–visible spectra were recorded on a Perkin-Elmer 330 spectrophotometer in spectroscopic grade *n*-hexane as the solvent. Uncorrected fluorescence spectra were acquired on a Perkin-Elmer MPF-66. Emission spectra were obtained with excitation and emission slit widths of 5 and 3 nm, respectively, excitation wavelengths of 350 and 250 nm, and scanning speeds of 120 nm min.$^{-1}$. The excitation spectra employed 2.5-nm slit widths and emission wavelengths of 430 and 450 nm. All the three fractions have similar absorption and fluorescence spectra but at slightly shifted energies. In the discussion that follows the results of the spectra from the second fraction will be the major focus. Although the other two fractions show similar spectra, the results from fraction two show a better optical resolution that clearly relates to the higher concentrations of N-doped derivatives in this fraction.

Results and Discussion

Mass Spectra. Figure 1 displays the mass spectrum of the N-doped fullerenes obtained at approximately 42 s of the RIC. The spectrum shows peaks at 720 and 840 amu that are due to C_{60} and C_{70} respectively and a number of peaks on the high amu side of the spectrum (above 720 and 840 amu) which are due to substitution of carbon by nitrogen. It also shows a number of peaks below 720 amu which are attributed to fragmentation of C_{60}. The insert contains the mass spectrum at 46 s of the RIC. This mass spectrum shows the typical isotopic distribution of C_{60} and C_{70}. The peaks at 720, 721, and 722 amu which are due to $^{12}C_{60}$, $^{13}C_1{}^{12}C_{59}$, and $^{13}C_2{}^{12}C_{58}$, respectively, are immediately apparent. The ratio of these peaks is 100:63:12, which is very close to the theoretical carbon isotopic abundance. We also observe peaks at 840, 841, and 842 amu which are 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 normalizing to 100 amu is 100:54:28, consistent with theoretical expectations. The odd-numbered peaks associated with ^{13}C isotopes also appear in the mass spectra of the N doped fullerenes at other time frames of the RIC.

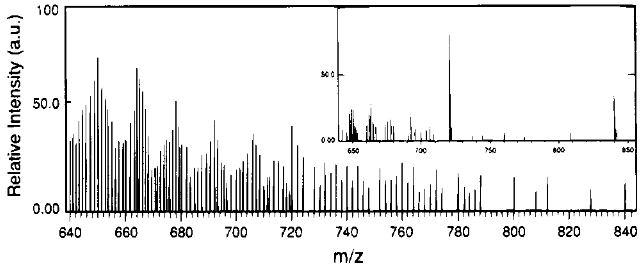

Figure 1. Mass spectrum of N-doped fullerenes at 42 s of the RIC. The insert displays the mass spectrum at 46 s of the RIC.

On the high amu side of the spectrum the main peaks at 722, 724, 728, 732, 736, 740, 744, 752, 760, 764, 772, 780, 788, 800, and 812 amu are attributed to $C_{59}N$, $C_{58}N_2$, $C_{56}N_4$, $C_{54}N_6$, $C_{52}N_8$, $C_{50}N_{10}$, $C_{48}N_{12}$, $C_{44}N_{16}$, $C_{40}N_{20}$, $C_{38}N_{22}$, $C_{34}N_{26}$, $C_{30}N_{30}$, $C_{26}N_{34}$, $C_{20}N_{40}$, and $C_{14}N_{46}$. All of them obey the $C_{60-2n}N_{2n}$ relationship for $n = {}^1/_2$, 1, 2, 3, 4, 5, 6, 8, 10, 11, 13, 15, 17, 20, and 23. Several smaller peaks are also observed in the spectrum following the same relationship. With the exception of $C_{59}N$, it is clear that only even-numbered ratios of C to N atoms are present. Complementary peaks appear in other mass spectra of the RIC. The mass spectrum at 45 s of the RIC contains, among other peaks that again fit the above relationship, a peak at 804 that corresponds to $C_{18}N_{42}$ ($n = 21$). Also observed is the appearance of peaks related to the substitution of C atoms of C_{70} by N atoms. For example, peaks are seen at 842 and 864 which may correspond to $C_{69}N$ and $C_{58}N_{12}$, respectively. These higher amu peaks do not appear in the third fraction of the sample which contains only the lower amu clusters. Further attempts at isolation and identification of macroscopic quantities of these fractions are underway.

The large number of peaks that can be explained as 60 atom clusters by evoking combinations of carbon and nitrogen atoms following a $C_{60-2n}N_{2n}$ rule is a strong argument favoring interpretation of the data as due to fullerene type molecules. Alternatively, one would have to envision a wide variety of polycyclic heteroaromatics, but one might expect there to be a considerably broader distribution of masses in such materials. Also the high solubility of these materials seems more consistent with cluster compounds than with polycyclics.

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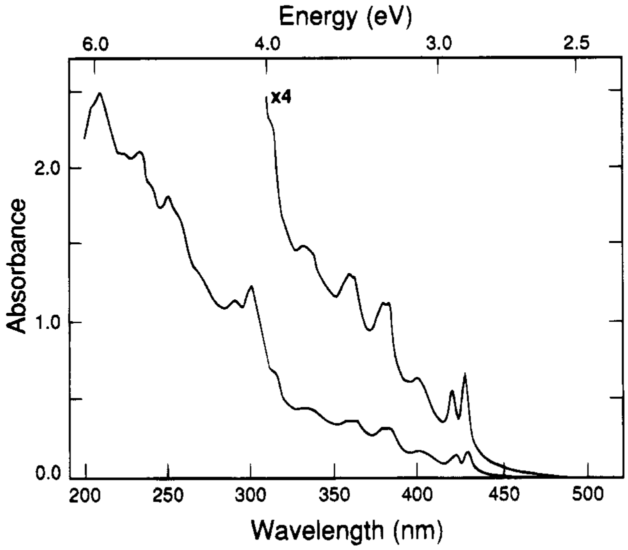

Figure 2. Optical absorption spectrum of N-doped fullerenes in hexane.

The lower amu materials in these samples result from the fragmentation of C_{60}. This effect may be a result of breaking the fullerene cage generating non-fullerene carbonaceous clusters which include linear and ring structures.[12] The clusters are present in all mass spectra and display peak maxima at 650, 664, 678, 692, and 706 amu. There is extensive substructure within each cluster that appears to differ by 14 (CH_2) amu from the next cluster and follows the relationship $C_{60-2n}-2n$ providing evidence of hydrogen entities in these clusters. Elemental analysis of these clusters gives a 6.1% concentration of hydrogen. 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 N atoms and the fragmented fullerenes can be as high as 10. This ratio varies depending upon the arc current and concentration of pyrrole during the preparation.

Optical Properties. The absorption spectrum of the second fraction of the N-doped fullerenes in a solution of hexane is shown in Figure 2, and exhibits broad structured $\pi-\pi^*$ transitions in the visible and UV. The $\pi-\pi^*$ absorption band of each of the three fractions has a similar intensity profile. The relative intensities of these peaks gradually decrease with increasing distance from the main peak. The main absorption features are given in Table 1. Four main bands are observed. The first band, on the high-energy side of the spectrum (from 200 to 270 nm), exhibits seven equally spaced absorption peaks separated by approximately 10 nm. The optical transitions at 210, 232, 250, and 270 nm correspond according to Huckel molecular orbital calculations to $h_u \rightarrow g_g$, $h_g \rightarrow t_{2u}$, $g_g \rightarrow t_{2u}$, and $h_u \rightarrow h_g$ transitions of undoped C_{60}.[13] The second band consists of peaks at 282, 289, and 300 nm, while the third band contains peaks from 315 to 399 nm that are separated by approximately 17 nm. The peaks in the third band exhibit a further splitting. Peaks are also observed at 420 and 428 nm that constitute a fourth band.

Although the third fraction of the sample exhibits similar intensity profiles, the two peaks of the fourth band are absent in this fraction. These two absorption peaks are sources of fluorescence on the low energy side of the emission spectrum, as is further discussed below. The structure observed in the absorption spectra of the N-doped fullerenes can be interpreted in terms of an influence of the molecular weight on the fundamental electronic transition. Another interpretation, however, is that there is vibrational coupling of the fundamental $\pi \rightarrow \pi^*$ electronic transition with vibrational levels of the excited state. This interpretation is supported by the occurrence of constant spacing between peaks in the bands.

Table 1. Optical Absorption, Fluorescence Excitation, and Fluorescence Emission Fine Structure for N-Doped Fullerenes in Hexane Solution

absorption		excitation		emission[a]	
λ (nm)	E (eV)	λ (nm)	E (eV)	λ (nm)	E (eV)
210	5.90	210	5.90	306	4.05
221	6.61	220	5.64	319	3.89
232	5.34	234	5.30	329	3.77
240	5.17	248	5.00	341	3.64
250	4.96	250	4.96	349	3.56
257	4.82	257	4.82	358	3.46
270	4.59	271	4.58	379	3.27
282	4.40	284	4.37	389	3.19
289	4.29	296	4.19	403	3.08
300	4.13	308	4.03	412	3.01
313	3.96	319	3.89	423	2.93
330	3.76	332	3.73	430	2.88
337	3.68	340	3.65	437	2.84
358(362)	3.46	360(364)	3.44	456(464)	2.72
378(382)	3.26	380(384)	3.26	472(479)	2.63
399(404)	3.11	401(405)	3.09	499(504)	2.48
420	3.95	422	2.94	528	2.35
428	2.90	430	2.88	536	2.31

[a] The data on the fluorescence emission from 306 to 358 nm are from excitation at 250 nm. Other data are from excitation at 350 nm.

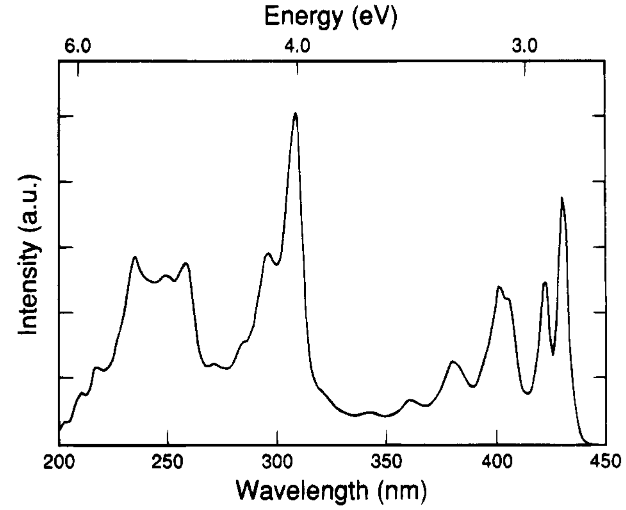

Figure 3. Fluorescence excitation spectrum of N-doped fullerenes in hexane (emission λ = 430 nm).

Excited-State Properties. The fluorescence excitation spectrum of the N-doped fullerenes in a solution of hexane is shown in Figure 3. To a first approximation, the excitation spectrum should have the same dependence on wavelength as the absorption spectrum. The excitation spectrum exhibits major peaks at 296, 308, and 422, 430 nm corresponding to absorptions at 289, 300, and 420, 428 nm, respectively. The peaks at 422 and 430 nm that correspond to the fourth band of the absorption spectrum do not appear in the excitation spectra of the third fraction of the sample. The transi-

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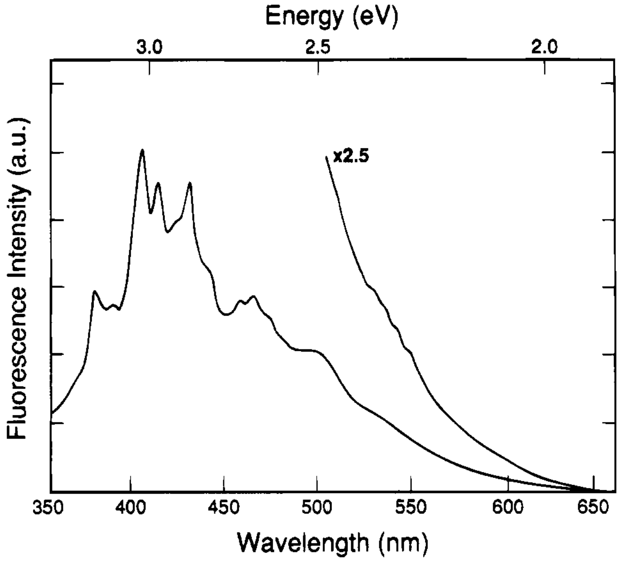

Figure 4. Fluorescence emission spectrum of N-doped fullerenes in hexane (excitation $\lambda = 350$ nm).

tions associated with the third absorption band are shown in the excitation spectrum between 319 and 405 nm (Table 1). The falloff on the high-energy side of the spectra is attributed to the increasing role of recombination for carriers generated by strongly absorbed light.

The fluorescence emission spectrum of the N-doped fullerenes at room temperature excited at 350 nm is shown in Figure 4. The same emission spectrum was obtained with excitation at 250 nm, suggesting that the emission occurs from the same electronic states. Solutions of C_{60} in hexane and benzene do not exhibit fluorescence at room temperature,[14,15] and very weak fluorescence has been observed in C_{70} solutions.[6] A weak fluorescence at room temperature in solutions of fullerenes in toluene has been observed.[5] The fluorescence spectrum of N-doped fullerenes is red-shifted relative to the absorption indicating the importance of relaxation effects after excitation. The occurrence of spectral diffusion implies that energy transfer is faster than structural relaxation following excitation. The usual explanation is that excitation generates a Frenkel exciton that subsequently migrates by hopping among molecules differing in excitation energy, giving rise to spectral diffusion. An alternate explanation is that primary excitation generates a pair of charge carriers with distortion of their local environment. Upon recombination, red-shifted fluorescence may be emitted.

The emission spectrum displays a large band that contains a number of peaks between 350 and 505 nm and a shoulder in the low-energy side of the spectrum from 525 to 565 nm. The large band exhibits distinct transitions between 379 and 504 nm (Table 1), all of them related to the absorption spectrum. The excitation energy migrates among the fullerene chromophores in solution and emission occurs from a variety of sites. The presence of these peaks suggests an extrinsic origin, with fragmented C_{60} species acting as defects. Furthermore, the presence of nitrogen in conjugated systems results in the enhancement of fluorescence. This effect is correlated to the increase in protonation of the nitrogen atoms upon excitation.[16] This fluorescence is exhibited in the high-energy side of the spectrum and can be explained as being the result of the increases of the HOMO–LUMO transition energy arising from ionization of neutral fullerenes.

The shoulder in the low-energy side of the spectrum that peaks at 525 nm (2.36 eV) is attributed to fluorescence from N-doped fullerenes and is indicative of an optical bandgap of 2.36 eV related to energy relaxation to the lowest excited vibronic level followed by fluorescence to the ground-state vibronic manifold. This shoulder also shows oscillations, which can be attributed to the split $h_u \rightarrow t_{1u}$ transition. Pristine C_{60} has a closed-shell electronic structure with a HOMO–LUMO (h_u–t_{1u}) optical bandgap of 1.6 eV.[17] Upon doping with N atoms the icosahedral symmetry of C_{60} is lost, as the addition of electrons in the t_{1u} degenerate state of C_{60} disturbs the degeneracy, resulting in a splitting into three nondegenerate levels. In $C_{59}N$ one of these levels should be half-occupied and, according to theoretical calculations, is located below the LUMO level at about 0.27 eV.[7] The presence of fluorescence on the low-energy side of the spectrum is associated with excitonic transitions into a manifold of localized states. These states, which are produced upon doping with nitrogen, are energetically inequivalent and are localized in the bandgap. Transitions may involve triplet states that are created via intersystem crossing from photoexcited single states. The fluorescence in this spectral region is assigned to Frenkel-like excitons in the range 2.36–2.20 eV that correspond to intramolecular excitation in the N-doped fullerenes in solution.

Conclusions

Nitrogen-doped fullerenes and carbonaceous clusters produced by arc vaporization in the presence of pyrrole possess interesting photophysical properties. Compounds form that follow the $C_{60-2n}N_{2n}$ relationship with a resultant splitting of the degenerate levels of C_{60} as the icosahedral symmetry is lost. Spectral properties are quite different from those of undoped fullerenes in solution. The absorption spectrum contains families of equally spaced peaks and closely matches the fluorescence excitation spectrum.

Fluorescence emission is attributed to intrinsic excitation of N-doped fullerenes and extrinsic charge separation of fullerene fragments. From the fluorescence results, an optical bandgap of 2.36 eV is derived and the intragap fluorescence is explained in terms of excitonic transitions in the energy range 2.36–2.20 eV. The photophysical properties lend further credence to the existence of a variety of N-doped fullerene cages.

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