

Production and Characterisation of Monomeric $C_{59}N$: A Magnetic Modification of Fullerene

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Abstract. Solid solutions of $C_{59}N$ azafullerene in C_{60} with concentrations up to 10^{-4} were produced in an electric gas discharge tube and by a heat treatment of $(C_{59}N)_2$ dissolved in pure C_{60} . The results on materials produced by the two methods are identical. $C_{59}N$ is a stable monomeric substituent molecule in crystalline C_{60} and may be heated to temperatures as high as 1300K. The concentration of ESR active neutral $C_{59}N$ molecules at ambient temperatures depends on temperature history.

INTRODUCTION

In azafullerene, $C_{59}N$, a simple chemical modification of the fullerene, C_{60} an unpaired electron is added to the lowest unoccupied molecular orbital by substituting a carbon atom for a nitrogen atom[1]. The resulting structure carries magnetic and electric dipole moments and is only slightly deformed[2]. The synthesis in bulk quantities by Hummelen et al.[3] showed that the solid is formed of $(C_{59}N)_2$ dimers. The production of $C_{59}N:C_{60}$ in large quantities allowed to measure the various ^{14}N and ^{13}C hyperfine constants that are a sensitive test of electronic structure calculations. The rotational dynamics of $C_{59}N$ in the solid solution parallels that of C_{60} in the bulk in a broad temperature range below the fcc cubic to sc transition[4].

Here we describe two simple ways to produce solid solutions of $C_{59}N$ in C_{60} ($C_{59}N:C_{60}$). i.) exposing sublimed C_{60} to a N_2 plasma in an electric discharge tube and ii.) heating and subliming a solution of $(C_{59}N)_2$ dimers in C_{60} . The formation of the neutral monomer $C_{59}N$ is verified by comparing the electronic spin resonance (ESR) spectrum to that observed in minute quantities in dimerised $(C_{59}N)_2$ solution exposed to light[5] or in solid $(C_{59}N)_2$ heated to elevated temperatures[6]. Monomeric $C_{59}N$ is stable in the solid solution of C_{60} and as we report here, it can be heated up to temperatures as high as 1300 K without destroying the molecule. The neutral form may easily lose an electron and become an inactive ESR center. The electron is

either temporarily donated to a neighbouring C_{60} molecule[7] or forms metastably pairs at as yet unknown locations. The ease with what $C_{59}N$ is ionised leads to a complex thermal history dependence of the concentration of neutral ESR active $C_{59}N$ molecules.

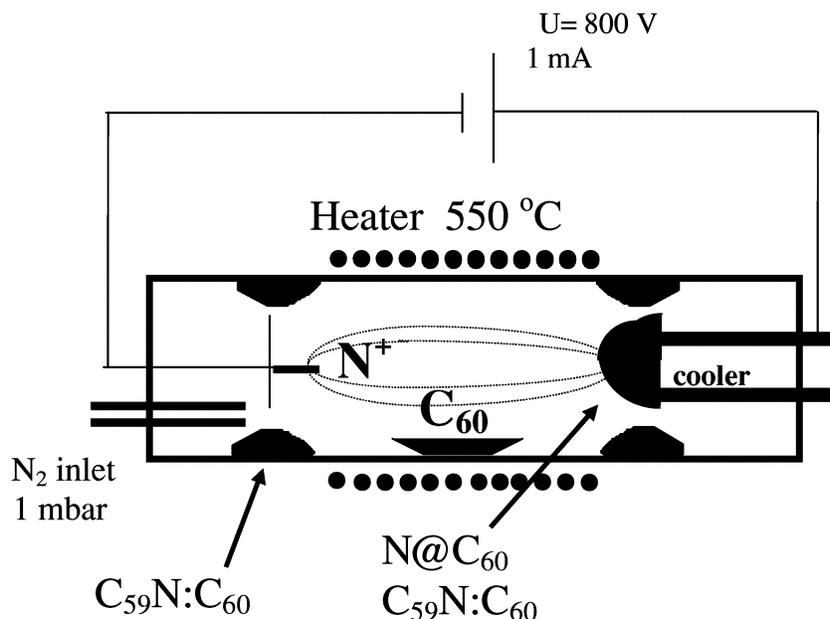


FIGURE 1. Production of $C_{59}N$ by exposing sublimed C_{60} to a nitrogen plasma of a gas discharge tube. $C_{59}N$ is produced in the plasma and deposited with C_{60} all over the quartz tube and cooled electrode but at the cooler parts it is in an ESR inactive form, probably as $C_{59}N^+$. Endohedral $N@C_{60}$ is deposited at the cooled electrode, N atoms escape from the cage at hotter regions.

PRODUCTION OF $C_{59}N:C_{60}$

In the first method $C_{59}N$ is formed from C_{60} reacting with the N plasma in a gas discharge tube (Figure 1) originally designed for the production[8] of endohedral $N@C_{60}$. A 10 cm long section of the 6 cm diameter quartz tube is heated to about 550°C. In the quartz tube the cathode is water-cooled and is at ambient temperature. C_{60} powder placed between the electrodes at the bottom of the tube is sublimed and deposited onto both the cooler ends of the quartz tube and onto the water cooled electrode. As the electric discharge is turned on, N^+ ions in the plasma react with C_{60} and form $N@C_{60}$ and $C_{59}N$ simultaneously. Unlike $N@C_{60}$ from which N escapes at temperatures above[8] 200 °C, $C_{59}N$ once formed is extremely stable. Endohedral $N@C_{60}$ dissolved in C_{60} with a concentration of 100 ppm is collected from the water-cooled electrode. $C_{59}N$ dissolved in C_{60} is collected from both the heated surface and

the cathode of the quartz tube. The intensity of the ESR signal (proportional to the neutral $C_{59}N$ free radical molecules) depends strongly on the temperature of the substrate onto which it is deposited. Only part of the $C_{59}N$ molecules is neutral and thus ESR active in the as formed material. The other part is ESR inactive, most probably in the form of $C_{59}N^+$ ions. The material with the largest concentration of ESR active centers is found in a narrow stripe at the hottest region (approximately 400°C) where there is still deposition. Initially the deposition at the cathode contains little or no ESR active $C_{59}N$ centers. A further heat treatment or sublimation shows, however, that it contains a large concentration of ESR inactive centers; probably in the form of $C_{59}N^+$ ions with electrons trapped in pairs at some other location. Thus the concentration of neutral and ionised $C_{59}N$ together is rather homogeneous and is independent of the temperature of the surface where it is deposited. Like $N@C_{60}$, $C_{59}N$ is formed in the plasma and is not the result of a reaction of deposited C_{60} with the plasma.

After deposition, the discharge tube was opened to air before sealing the samples into quartz tubes in vacuum or under helium. The material is stable in He atmosphere at ambient temperatures for at least several months. In air the ESR of $C_{59}N$ disappears at ambient temperatures in about a week, however, it may be regenerated by resublimation of the material. The ESR spectrum of the sublimed material shows almost no other free radicals than $C_{59}N$ formed during the production. There is, however, a small intensity, narrow line (at 334.9 mT on Figure 2) which is intrinsic to the system and arises from C_{60} -ions[7].

A second method that is potentially useful to produce $C_{59}N:C_{60}$ in larger $C_{59}N$ concentrations has been successfully applied also. Here, pure $(C_{59}N)_2$ dimer powder was dissolved together with pure C_{60} in toluene and extracted at low temperatures. The mixture was heated in vacuum to 730 K for a few hours. Subsequently, it was placed into a temperature gradient and partially sublimed to the colder part of a quartz tube in dynamic vacuum. In the material left behind at the high temperature end most of $C_{59}N$ remains in the dimerized form. The sublimed material has high purity and has about the same concentration of ESR active $C_{59}N$ monomers as the unsublimed part left behind. Although various starting $C_{60} : (C_{59}N)_2$ mass ratios between 500 to 5 and various heat treatments were used, the highest ESR active concentration $C_{59}N$ did not exceed 10^{-4} and for the same heat treatment it was proportional to the initial $(C_{59}N)_2$ content.

THERMAL HISTORY DEPENDENCE

The concentration of ESR active neutral $C_{59}N$ molecules, n , depends on thermal history in samples prepared by both methods described. Figure 2 shows a typical example. In samples cooled slowly (i.e. 1 K/min) from temperatures above 700 K, n is strongly reduced. The ESR reappears if the sample is heated rapidly to temperatures, T_Q , above 700 K, kept at this temperature for a few minutes and subsequently quenched into liquid nitrogen. The thermal cycle is repeatable. The higher T_Q , the larger is the ESR signal, i.e. the concentration of neutral $C_{59}N$. Quenching to ambient

temperatures is less effective than quenching into liquid nitrogen. The concentration of $C_{59}N$ may be reduced to n as small as 10^{-6} and this rules out any mechanism where the formation of $(C_{59}N)_2$ dimers from diffusion of monomers in the solid were involved. Moreover, in one case a sample enclosed in a relatively small evacuated quartz tube and quenched from $T_Q = 1300$ K became stable, i.e. it is no more dependent on heat treatments below 1100 K.

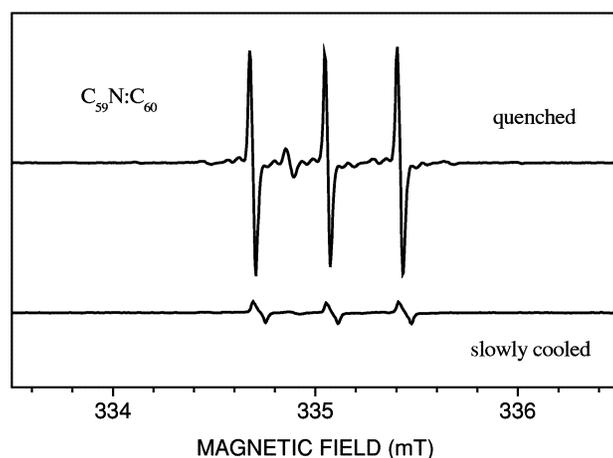


FIGURE 2. ESR spectra of a $C_{59}N:C_{60}$ solid solution at ambient temperatures. Quenched: rapid cool from 730 K into liquid nitrogen. Slow cooled: from 730K to 300 K in 8 hours. The thermal cycle may be repeated. The decrease of ESR is attributed to ionisation of $C_{59}N$ radicals into ESR silent $C_{59}N^+$. There is no ESR of a corresponding anion, thus the electrons are believed to form pairs at an unknown location.

Thus, most probably the histeretic behavior depends on some defects which trap electrons hopping at high temperatures from $C_{59}N$ radicals through neighboring C_{60} sites into the solid. As shown elsewhere[7], the extra electron hops between $C_{59}N$ and its first neighbour C_{60} molecules with a slow but well measurable rate. Strangely, however, during the cooling process this electron may escape entirely from $C_{59}N$ ions to as yet unidentified locations. The electrons seem to be trapped in pairs, since with the reduction of n there is no corresponding increase or decrease of another ESR line which would signal radicals formed or annihilated by the trapped electrons (Figure 2). Clearly, the total paramagnetic susceptibility is decreased during the slow cooling experiment and increased in the quench experiment; suggesting the respective formation and break-up of electron pairs.

CONCLUSIONS

$C_{59}N$ is a very stable molecule but in the pure solid it forms dimers. Dilute solutions of $C_{59}N$ in pure C_{60} maybe produced in a N discharge tube or by dissolving the dimer in C_{60} . The thermal history dependence suggests that the radical $C_{59}N$ may easily loose an electron and form $C_{59}N^+$ ions. Thus it is expected that at higher concentrations $(C_{59}N)_{1-x}(C_{60})_x$ alloys are metallic.

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