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ANALYSIS OF CLUSTERIZATION OF C_{70} MOLECULES IN BENZENE SOLUTIONS PREPARED BY VARIOUS METHODS

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Abstract

Self-assembling features of molecules of C_{70} in benzene solution prepared in two various ways – equilibrium and non-equilibrium – has been investigated experimentally by method of high-resolution transmission electron microscopy. It was demonstrated, that the formation of densely packed monomolecular fullerene aggregates with a diameter of not more than 30 nm in solutions prepared by the equilibrium method (without the use of external mechanical influences on solution). In the case of solutions C_{70}, which were prepared by the non-equilibrium method (stirring of solution of C_{70} by a mechanical rotator), large quasispherical aggregates of nanoporous structure with fractal size $D \approx 2.19$ were synthesized.

Keywords: fullerene C_{70}, benzene solution, electronic microscopy, clusterization, monomolecular, self-aggregation, morphology, fractal dimension, stability, application.

1 Introduction

Fullerenes C_{60} and C_{70} represent new allotropes of carbon [1] and exhibit unique properties that presently being pursued globally for a wide range of high performance applications. Since then, light C_{60} and C_{70} fullerenes have invited much attention and been extensively investigated. These fullerenes are soluble in many nonpolar organic solvents [2], are insoluble in polar and H-bonding solvents [3]. Light fullerenes are easily transferrable into water [4]. Fullerene C_{70} is extremely valuable for innovative applications in medicine [5–7], chemical synthesis and catalysis [8], biomedical testing [9], electronics [10], solar energy [11] and optics [12]. A number of studies have shown promising potential in using fullerene C_{70} as nonlinear optical laser-radiation limiters [13–16]. The limiters obtained on the base of such nonlinear optical media allow to decrease the laser radiation to an eye-safe level and protect high-sensitive light sensors from damage in the visible, near-, and mid- IR regions in a wide range of laser-pulse widths [17]. Fullerenes are excellent organic semiconductors, with some rather specific features, such as low LUMO level and high electron mobility [18]. C_{70} fullerene is a nontoxic substance and having powerful antioxidant properties due to its high activity as free radicals acceptor [19]. It can be used in photodynamic therapy for treatment of oncological diseases [20–21], in targeted delivery of various drugs in cells [22].

During the last years, new experimental data [23-26] reveal that light fullerenes molecules have tendency to self-assembling and formation of large negatively charged
aggregates of fullerenes of different shapes and sizes in a wide range of mono- and multi-component organic and inorganic solvents. Clusterization of fullerene molecules in solutions may cause significant changes in their physical properties and result in a dramatic change in their technical, medical and other applications. Most scientific articles regarding fullerene aggregation have been focused on the $C_{60}$ behavior in different solvents, and only a few studies were reported on the $C_{70}$ aggregation. In view of the above, development of novel selective methods of synthesis of $(C_{70})_m$ aggregates (where $m$ is a number of fullerene molecules in aggregate) consisting both of intermediate macromolecular $C_{70}$ formations (porous fractal aggregates) and individual $C_{70}$ molecules (densely packed monomolecular aggregate) in solutions with predictable characteristics such as aggregate size and shape, density of packing.

In this work, we exhibit for the first time, the possibility of directed synthesis of both close-packed monomolecular and porous fractal aggregates of $C_{70}$ in benzene. We note that observation of the formation of stable $C_{60}$ aggregate forms in toluene and their electronic absorption behaviors was reported in [27].

2 Experimental details

2.1 Materials

Fullerene $C_{70}$ (99.7 % purity – SES Research, USA) and benzene (99.8 %, analytical grade – Sigma-Aldrich, USA) were used in measurements.

2.2 Preparation of $C_{70}$ solutions

To prepare equilibrium solutions of fullerene of different concentrations, powders of $C_{70}$ were dissolved in benzene and equilibrium mixtures were kept at $\sim 25^\circ C$ in test tubes for 15 days without external mechanical influences.

Non-equilibrium $C_{70}$ solution was prepared by mechanical mixing of $C_{70}$ suspension in benzene in a hermetically sealed flask mounted on the programmable rotator Multi RS-60 (BioSan) in a mechanical swinging mode at a room temperature ($\sim 25^\circ C$), 12 rpm for 14 days.

Before adding to the solution, $C_{70}$ was weighted on an analytical balance EP214C (Ohaus Explorer Pro, Switzerland) with an accuracy of $\leq 0.0001 g$.

2.3 Investigation of structural features of $C_{70}$ solutions

We have used the transmission electron microscope (TEM) LEO-912 AB (ZEISS, Germany) with accelerating voltage of 120 kV and spatial resolution of $\sim 0.34 \text{ nm}$ to determine morphological features and dimensional characteristics of aggregates of fullerenes synthesized in equilibrium and non-equilibrium solutions.

For transmission electron microscopy, copper grids (diameter 3.05 mm, 300 mesh, Ted Pella Inc., USA) without formvar coating were used. Digital micrographs of samples were analysed using UTHSCSA Image Tool software (UTHSCSA, USA).
3 Results and discussions

Figure 1 represents electron microscopic images of \((C_{70})_m\) aggregates synthesized in benzene solutions of \(C_{70}\) at fullerene concentration of \(\sim 1.0 \text{ mg/ml}\) prepared by equilibrium method.

![Transmission electron microscope image of \((C_{70})_m\) aggregates](image)

Figure 1. Transmission electronic microscope image show the formation of \((C_{70})_m\) aggregates of fullerenes synthesized in \(C_{70}\) benzene solution prepared by equilibrium method (without using of external mechanical influences on the solution). The initial concentration of \(C_{70}\) in solution is \(\sim 1.0 \text{ mg/ml}\).

It has been shown that processes of self-organization of \(C_{70}\) molecules in solutions prepared by equilibrium method is synthesized close-packed aggregate with a diameter of \(d \sim 25\) nm. Additional morphological investigations of a peripheral part of an individual \(C_{70}\) aggregate using high resolution TEM have allowed to find out that \((C_{70})_m\) aggregate has a close-packed monomolecular dispersion (see Fig-1). \(C_{70}\) molecules have unique electronic properties that make them attractive candidates for diagnostic and therapeutic applications.

Figure 2 shows a TEM image of \((C_{70})_m\) aggregate, which has been synthesized in the benzene solvent prepared by other "non-equilibrium method" of preparation of \(C_{70}\) solution. In a solution prepared by non-equilibrium method, self-aggregation of fullerene molecules and synthesis of large porous fractal aggregates of quasispherical shape with a diameter of \(d \sim 220 \pm 10\) nm, consisting of smaller intermediate "discrete" aggregates of \(C_{70}\) with a diameter of \(d_0 \sim 20 \pm 35\) nm were observed during 12 ÷ 15 days (see Fig-2).

It has been established [28] that the minimum of free energy \((E)\) of the system "fullerene cluster + benzene solution" (normalised to one molecule of fullerene) at the room temperature can only be achieved when a fractal aggregate \((C_{70})_{55}\) with a radius \(R = 2.3\) nm is formed (symmetry group \(D_{5h}\)). According to the fractal concept [29], the relationship between number of fullerene molecules in the cluster \((m)\), its radius \((R)\) and the fractal dimension \((D)\) can be expressed as

\[
D = \ln m \cdot (\ln R - \ln r_0)^{-1}
\]

(1)
where \( r_0 \) is average radius of \( C_{70} \) molecule. Fractal dimension of the aggregate synthesized in the solution does not depend on the initial concentration of fullerene, however, geometrical dimension of the aggregate increases proportionally with the concentration of \( C_{70} \) in the solution.

Using Eq. 1 and the numbers \( m = 55, R = 2.3 \) nm and \( r_0 = 0.37 \) nm, we found that the fractal dimension of the synthesized \((C_{70})_m\) aggregate in benzene is \( D \approx 2.19 \) (see Fig-2).

Figure 1. Transmission electronic microscope image show the formation of large \((C_{70})_m\) aggregates of fullerenes synthesized in \( C_{70} \) benzene solution prepared by non-equilibrium method (mechanical mixing of \( C_{70} \) solution using rotator).

Precise measurements of the inner structure of fractal \((C_{70})_m\) aggregate performed using high-resolution TEM and analysis using UTHSCSA Image Tool software have shown that the shortest distance (i.e. spatial gap) between neighbouring discrete structural units of "small dimension" located inside fullerene aggregate does not exceed \( \Delta L \approx 1.8 \) nm (Fig-2).

4 Conclusions

TEM microscopic investigations of \( C_{70} \) solutions in benzene revealed the possibility of synthesis of both fractal and closed-packed \((C_{70})_m\) aggregates. It was observed that in solutions prepared by the non-equilibrium method at the room temperature, mainly large quasispherical aggregates of fullerene with a diameter of \( \sim 220 \pm 10 \) nm having porous structure with fractal dimension \( D \approx 2.19 \) are synthesized. In equilibrium solutions of \( C_{70} \) of the same initial concentration, the formation of densely packed monomolecular fullerene aggregates with \( D \approx 3 \) was observed. In both cases, the finite geometrical dimensions of the synthesized nano-porous \((C_{70})_m\) aggregates are determined by the initial concentration of fullerene. Higher initial concentration of \( C_{70} \) in the solution requires a greater number of iterations of self-assembly of fullerene molecules which leads to an increase in the geometrical dimension of the synthesized \((C_{70})_m\) aggregates.
Fractal \((C_{70})_m\) aggregates synthesized in benzene are stable to external mechanical (for instance, intensive mixing of solution, repeated transfusion from flask to flask) and thermal influences (heating up to \(\leq 50^\circ C\) in the water bath followed by slow cooling to a room temperature).

Experimental results obtained in this study may be used for a wide range of practical applications of \(C_{70}\) fullerene dispersions in nanotechnologies, chemistry and biomedicine.

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