Progress in Solid State Chemistry 44 (2016) 59–74

Contents lists available at ScienceDirect

Progress in Solid State Chemistry

journal homepage: www.elsevier.com/locate/pssc

Fullerenols: Physicochemical properties and applications

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ARTICLE INFO

Article history:
Available online 3 May 2016

Keywords:
Fullerenol
Synthesis
Physicochemical properties of solutions
polymers
Concrete
Paints
Medical application

ABSTRACT

Fullerenols may find the widest application in science and technology. This causes particular interest in developing available and simple methods for the synthesis of water-soluble polyhydroxylated fullerene derivatives on an industrial scale as well as investigating the physicochemical and biological properties and principles of their application. This study systematizes the current literature data on the synthesis, physicochemical properties, and application of polyhydroxylated fullerenes (fullerenols), a class of water-soluble fullerene derivatives. The experimental and theoretical data presented in this study provide a comprehensive overview of these substances and can be valuable to specialists in the fields of nanotechnology, nanomaterials, and nanobiomedicine.

Contents

1. Introduction

Light fullerenes, such as C_{60} and C_{70}, can be applied in various fields, including mechanics, materials science, mechanical engineering, construction, electronics, optics, medicine, pharmacology, food, and cosmetics [1]. However, applications of these fullerenes are limited because of problems associated with mixing the molecules in water-based solutions; solubilities of C_{60} and C_{70} in water at 298 K are 1.3×10^{-11} and 1.1×10^{-13} g l^{-1} [2]. Water-soluble forms of fullerene derivatives may find wide application in mechanical engineering (in water-soluble cooling and antifriction mixtures), building (as soluble additives for cements and concretes), medicine and pharmacy (because of their compatibility

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http://dx.doi.org/10.1016/j.progsolidstchem.2016.04.002
0079-6786/

with water, physiological salt solutions, blood, lymph, stomach juices, etc.), cosmetics (particularly those that have water and water–alcohol bases), as well as science and technology. This increases interest in developing available and simple methods for the synthesis of water-soluble fullerene derivatives on an industrial scale.

Polyhydroxylated fullerenes, or fullerenols, have a simple structure, convenient for practical use (Fig. 1), low toxicity, and possibly further modification. They are considered the most promising water-soluble fullerene derivatives. It should be noted that:

(i) at present, the term "fullerenol" includes both the fullerenols $C_{60}(OH)_X$, which are the derivatives of the fullerene C_{60} (the most accessible fullerene) and hydroxyl derivatives of all other individual fullerenes $C_n(OH)_X$ (n = 60, 70, 76, 78, 84, 90);
(ii) besides hydroxyl groups, fullerenols can include other non-hydroxylic groups, such as oxygen (=O, –O–) $C_n(OH)_XO_Y$, and salt-type groups, such as $[C_n(OH)_XO_Y](ONa)_Z$;
(iii) finally, fullerenols are also referred to as mixtures of individual fullerenols of different composition or low purity (e.g., <95%).

This study aims at describing the synthesis of water-soluble fullerenols and their physicochemical and biological properties as well as analyzing possible applications of fullerenols as nanomodifiers of polymers, construction materials, and in nanobiomedicine.

2. Synthesis of fullerenols

An analysis of the literature reveals many proposed methods for the synthesis of fullerenol from individual light fullerenes (C_{60}, C_{70}), industrial fullerene mixtures of different compositions, and light fullerene derivatives (halogen-, nitro-, sulfo-, etc.). The synthetic strategies proposed for the hydroxyl functionalization of fullerenes can be divided into two groups: (*i*) by the direct reaction of fullerenes and (*ii*) the hydrolysis of fullerene derivatives. Moreover, it should be emphasized that most fullerenol synthesis do not lead to pure $C_{60(70)}(OH)_x$, but to a complex mixture of products with an average composition of $C_{60(70)}(OH)_{x-y}$, $C_{60(70)}O_x(OH)_y$ or $C_{60(70)}(OH)_x(ONa)_y$ [3]. We can conclude that fullerenols obtained by the methods proposed in the literature lead to products of different structures and poor reproducibility, which make it difficult to use them for experimental studies (particularly for biological investigation).

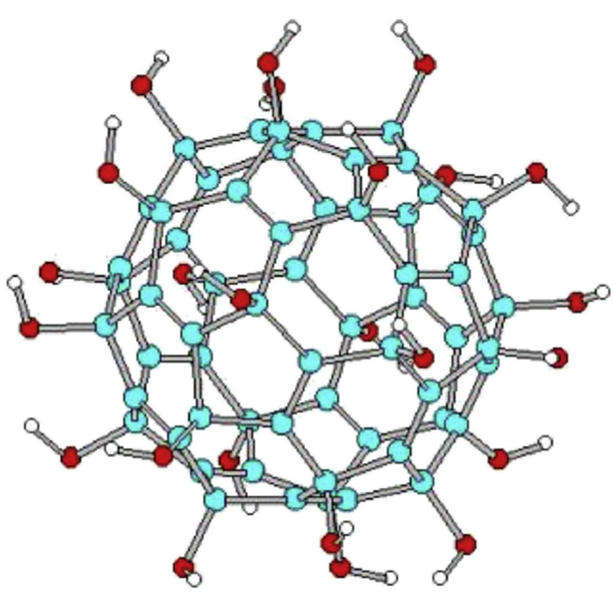

Fig. 1. Structural formula of a $C_{60}(OH)_{24}$ fullerenol (blue circles – carbon atoms, red circles – oxygen atoms, white circles – hydrogen atoms).

Hydroxylation of fullerenes can produce various mixtures of polyhydroxylated fullerenes. For example, hydroxylation of the C_{60} fullerene in the presence of a quaternary ammonium base (particularly tetrabutylammonium hydroxide (TBAH)) results in $C_{60}(OH)_{26.5}$ derivative [4]. Moreover, it has been shown that the fullerenol obtained by the reaction of the C_{60} fullerene with TBAH in toluene in the presence of oxygen and water solution of NaOH is a stable anion radical $Na^{n+}[C_{60}O_xOH_y]^-{}_n$ (where n = 2–3, x = 7–9, and y = 12–15) [5]. When HNO_3/H_2SO_4 mixture was used, $C_{60}(OH)_{18-20}$ derivative was formed [6,7]. Yang et al. [8] described a convenient and effective method of fullerenol synthesis; as a catalyst, polyethylene glycol 400 (PEG) was added to the reaction mixture containing fullerenes, aqueous solution of NaOH, and an oxidizing agent. Sheng et al. [9] synthesized fullerenols by the direct reaction of fullerene dredge and H_2O_2 + NaOH mixture. The low solubility of nonhydroxylated fullerenes reduces the rate of the direct reaction between C_{60} and hydrogen peroxide. Therefore, it is more convenient to add the complementary hydroxyl groups to the hydroxylated fullerenol with 12 hydroxyl groups. Kokubo et al. [10] carried out a reaction between the fullerenol with 12 hydroxyl groups and H_2O_2 (1) + H_2O (2) with ω_1 = 0.13 at 60 °C with shaking to produce the fullerenols $C_{60}(OH)_{36}\cdot 8H_2O$ and $C_{60}(OH)_{40}\cdot 9H_2O$ with different compositions and structures over several days. The 11 methods for the synthesis of water-soluble fullerenols ($C_{60}(OH)_1$, $C_{60}(OH)_6$, $C_{60}(OH)_8$, $C_{60}(OH)_{x<12}$, $C_{60}(OH)_{12}$, $C_{60}(OH)_{x>15}$, $C_{60}(OH)_{15}$, $C_{60}(OH)_{x<21}$, $C_{60}(OH)_{24}$, etc.) were described in a US patent [11]. Kokubo et al. [12] developed two methods for the synthesis of water-soluble fullerenol. A water-soluble polyhydroxylated fullerene, that is, a fullerenol, containing 44 hydroxyl groups and eight secondary bound water molecules, $C_{60}(OH)_{44}\cdot 8H_2O$, was synthesized in a simple one-step reaction from pristine C_{60} by hydroxylation with hydrogen peroxide in the presence of a phase-transfer catalyst (TBAH), under organic/aqueous bilayer conditions. Semenov et al. [13] synthesized a mixed fullerenol (fullerenol-mix-ss) by direct one-stage oxidation of fullerene black from H_2O + NaOH mixture. Arrais and Diana [14] developed a new method for the synthesis of water-soluble fullerenols, involving the reduction of C_{60} with Na/K alloy and successive stirring in the presence of O_2 and H_2O. By the hydrolysis of the products of RuO_4 and fullerenes reaction, the diols 1,2-$C_{60}(OH)_2$, 1,2-$C_{70}(OH)_2$, and 5,6-$C_{70}(OH)_2$ can be synthesized. Because of the instability of such derivatives, their application in biological experiments becomes impracticable [15]. Chiang et al. developed a high-yield method of $C_{60}(OH)_{10-12}$ fullerenol synthesis by the hydrolysis of polycyclosulfated fullerene derivative in the presence of water or in an aqueous solution of NaOH [16]. Schneider et al. synthesized fullerenol by the reaction between fullerene C_{60} and an excess of BH_3–tetrahydrofuran (THF) complex, followed by hydrolysis with glacial acetic acid, sodium hydroxide/hydrogen peroxide, or sodium hydroxide [17]. Troshin et al. used halogenated fullerenes as reagents to prepare fullerenols. Depending on the reaction conditions, two types of substances (complex mixtures of products with average compositions $C_{60}O_nH_m$, n = 10–26, m = 14–30 and $C_{60}O_nH_mM_k$, M = K, Na; n = 17–24, m = 16–28, k = 3–8) with different levels of water solubility were obtained [18].