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The self-assembly and aqueous solubilization of [60]fullerene with disaccharides

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ABSTRACT

Solubilization of [60]fullerene in water by complexation with disaccharides in mixed homogeneous solvent system, is described for the first time. The complexation of extremely water-insoluble [60]fullerene dissolved in non-polar solvent toluene and extremely water-soluble disaccharides dissolved in polar solvent DMSO resulted in an unique self-assembled highly crystalline water-soluble [60]fullerene–disaccharide complex. The interaction between [60]fullerene and disaccharides was found to be non-covalent and were characterized by FTIR, UV–Vis, NMR, XRD, and thermogravimetric analysis. The particle size of the lactose–C_{60} complex was found to be monodisperse ~60 nm from Transmission Electron Microscopy (TEM) and matched with the size obtained from Static Light Scattering (SLS). Preliminary studies of radical scavenging on the most stable free radical 2,2′-diphenyl-1-picrylhydrazyl (DDPH) suggested that complex has potential biological applications.

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1. Introduction

Since the discovery of the novel biomedical applications[1] of [60]fullerene, attempts have been made to make it water-soluble. Various techniques have been applied to make it water-soluble that include covalent functionalization,[2] emulsion formation,[3] complexation with biomaterials,[4] interaction with amphiphilic molecules,[5] and non-covalent guest–host[6] systems. Among the guest–host systems, cyclodextrins are widely studied and successfully utilized including several patents.[7] One of the fundamental logic of guest–host system is that the fullerene molecule occupies the hydrophobic cavity of the cyclodextrins. Based on this premise it was argued that only γ-cyclodextrin (cavity size = 0.950 nm) could include the [60]fullerene (diameter = 0.7 nm) thus forming a 1:1 inclusion complex which was subsequently modified to show that even β-cyclodextrin (cavity size = 0.78 nm) could include a [60]fullerene molecule forming a 2:1 inclusion complex.[8] This was possible due to the formation of a self-assembled structure which included the [60]fullerene in the cavity formed by two cyclodextrin units.[9] If one were to look at the cyclodextrin structure closely, the glucose units are linked by the α-1,4-glycoside linkages.[10] How important is it for the [60]fullerene molecule to sit inside a cavity made by these bucket structures? If two β-cyclodextrins could include the [60]fullerene molecule then by the same logic it should be possible for a disaccharide to encircle a [60]fullerene molecule due to the same hydrophobic interactions. In fact some early studies have shown that fullerene/carbohydrates compositions were possible by mechanochemical method that led to fullerene aggregates in carbohydrate shell and that surface carbohydrate layer formed a van der Waals complex with fullerene.[11] Subsequent molecular modeling studies and theoretical calculations have shown that the enthalpy of formation of fullerene/sucrose complex was 3.5 kcal/mole.[12] If that is the case a few number of disaccharides could be used to isolate [60]fullerene in aqueous media or in other words solubilize [60]fullerene.

This paper describes the preparation of a crystalline highly water-soluble [60]fullerene by complexation with very inexpensive, naturally and commercially available, nontoxic disaccharides (lactose, maltose, and sucrose) in comparison to the very expensive and difficult to synthesize, toxic host molecules. Disaccharides can easily interact with [60]fullerene and convert this highly water-insoluble molecule into a highly water-soluble complex. Enthalpy and entropy calculation of interaction between [60]fullerene and disaccharides also support the formation of non-covalent complex.[12] The non-covalent interaction between [60]fullerene and disaccharides was characterized by using conventional characterization techniques like UV–Vis, FTIR, NMR, XRD, and TGA analysis. The morphology and particle size of the complex was determined by Transmission Electron Micrograph (TEM) and Static Light Scattering (SLS). The radical scavenging properties of this water-soluble complex was estimated from in vitro experiments using radical scavenging of most stable free radical 2,2′-diphenyl-1-picrylhydrazyl.

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2. Results and discussion

[60]Fullerene is an extremely water-insoluble molecule. Solubilizing the [60]fullerene in polar solvents is difficult and its solubility in non-polar organic solvents is also limited.[13] The lack of genuine water-solubility and availability of macroquantities of [60]fullerene and disaccaharides inspired us to prepare water-soluble [60]fullerene–disaccharides complex for the requirement of biological applications. Highly water-soluble [60]fullerene–disaccharide complex was prepared by simple complexation of reactants in homogeneous solvent system as shown in Scheme 1. Among the commercially available disaccharides, the complex of [60]fullerene with lactose was fully characterized and reported here.

2.1. Aqueous solubility of complexes

As expected, after complexation of [60]fullerene with different disaccharides, the aqueous solubility of [60]fullerene increased significantly as shown in Table 1. The complex of maltose with [60]fullerene has high water-solubility as maltose has the highest water-solubility than the other disaccharides. The complex of maltose–C_{60} has more [60]fullerene concentration due to the higher solubilizing power of maltose. Moreover, it was found that aqueous solution of the complex was stable for several months and does not aggregate like β-cyclodextrin/[60]fullerene complex after some days. The amount of [60]fullerene/mg of the complex was determined by UV–Vis after extraction with toluene.

2.2. Fourier transform infrared spectroscopy (FTIR)

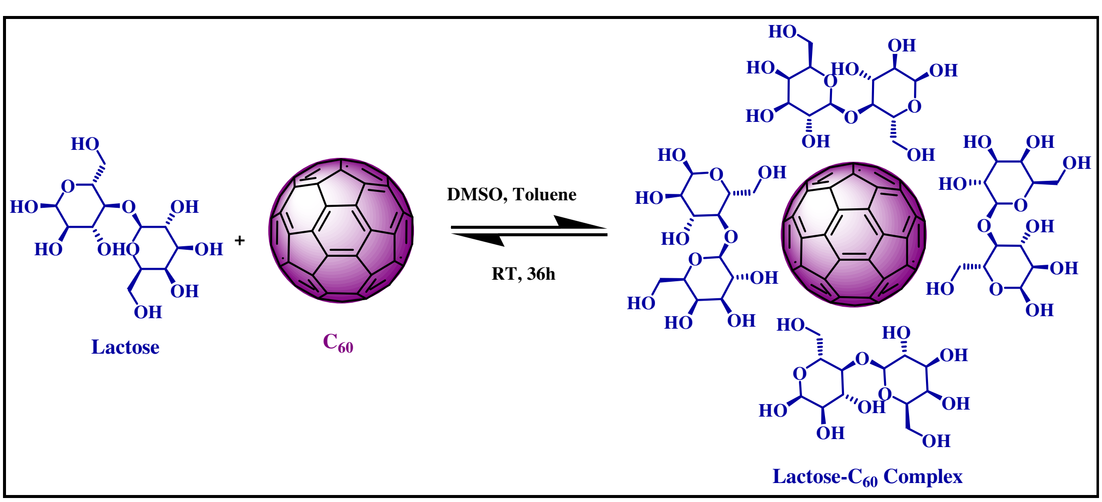
FTIR spectroscopy is an effective tool to characterize the non-covalent interactions between two molecules. The FTIR absorption spectra of C_{60}, lactose, and C_{60}–lactose are shown in Figure 1. The spectrum of pristine C_{60} (Fig. 1 a) shows four characteristic absorption bands at 1429 cm^{-1}, 1183 cm^{-1}, 578 cm^{-1}, and 527 cm^{-1}. The spectrum of lactose (Fig. 1b) shows absorption bands at 3335 cm^{-1}, 1653 cm^{-1}, 1038 cm^{-1}, and 779 cm^{-1}, the positions and relative intensities of a few bands are affected by the formation of non-covalent complex between lactose and C_{60}. The spectrum of C_{60}–lactose complex (Fig. 1c) shows bands at 3334 cm^{-1}, 1653 cm^{-1}, 1035 cm^{-1}, and 777 cm^{-1} of lactose and also shows distinct IR absorption bands of C_{60} at 578 cm^{-1} and 527 cm^{-1} and it is observed that the lactose peaks remain strong in the spectrum. These results indicate the modification of environment of lactose due to the formation of lactose/C_{60} complex. If it were not so then the spectra would resemble that of a physical mixture of C_{60} and the lactose with no shift in the characteristic bands.

2.3. UV–visible spectroscopy (UV–Vis)

The visible evidence for the formation of lactose–C_{60} complex and stability of the lactose–C_{60} complex in polar and non-polar solvents comes from simple extraction experiment conducted in vials and UV–Vis absorbance spectroscopy. [60]Fullerene in toluene shows beautiful deep purple color and shows maximum absorbance at 334 nm and 406 nm (Fig. 2A) and it is completely insoluble in water and other polar solvents. Lactose is completely soluble in DMSO and does not show any absorbance in this region (Fig. 2B). When these two miscible solutions are mixed together in an inert atmosphere and after evaporation of organic solvents, result in a water-soluble yellowish brown color lactose–C_{60} complex that shows maximum absorbance at 348 nm and widening of absorbance band after 400 nm in water as compared to typical absorbance at 334 nm and 406 nm for the pristine fullerene in toluene (Fig. 2C). When toluene was added to the solid lactose–C_{60} complex, it was observed that [60]fullerene easily goes into the toluene solution and lactose settled down at the bottom of vial. The toluene layer shows absorbance similar to that of pristine [60]fullerene in toluene (Fig. 2D). However, when toluene was added to the aqueous solution of lactose–C_{60} complex (Fig. 2E), it was observed that aqueous solution of lactose–C_{60} complex was stable enough and the [60]fullerene does not go into the toluene layer. The aqueous layer shows absorbance similar to that of lactose–C_{60} complex in water and toluene layer does not show any absorbance. Thus, the aqueous solution of lactose–C_{60} complex was stable enough that [60]fullerene was not extractable. However, this is completely in contrast to that of the non-covalent cyclodextrin–[60]fullerene inclusion complex.[14]

2.4. Thermogravimetric analysis (TGA)

The stoichiometry of the lactose–C_{60} complex was evaluated from the thermogravimetric analysis as shown in Figure 3. A small mass loss due to the loss of structural water molecules at the beginning was found in the lactose and lactose–C_{60} complex, followed by a larger mass loss corresponding to the decomposition of the glucose units of the lactose. The second mass loss for the lactose–C_{60} complex was observed to be at lower temperature compared to pristine lactose, due to the modification of glucose



Scheme 1. Complexation of lactose–C_{60} in mixed solvent system.

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