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Nanoscale self assembly of cyclodextrin capped 4-aminobenzophenone via non-covalent interactions

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ABSTRACT

Formation of nanoscale self-assemblies of 4-aminobenzophenone (4ABP) with α-CD and β-CD was analyzed by spectral and morphological techniques. 4ABP:CD inclusion complexes are analyzed by SEM, TEM, FT-IR, DSC, XRD, and ^{1}H NMR methods. TEM images show that both α-CD and β-CD inclusion complexes formed nanovesicles and nanorods respectively. Upfield chemical shift observed for 'A' ring protons reveals that phenyl ring (without amino group substitution ring) entered into the CD cavities and the aniline ring of 4ABP present in the exterior part of the CD cavities. Absorbance and emission fluorescence spectral shifts of 4ABP with α-CD and β-CD indicate the formation of supramolecular assemblies in an aqueous solution. The spectral results shows that (i) 4ABP is partially incorporated into the CD nanocavities and (ii) "A" ring of 4ABP is deeply present in the β-CD cavity than in α-CD. Molecular modeling offered better approaching of the noncovalent interactions on the inclusion complex 4ABP:CDs. The negative ΔH and ΔS values specified that the inclusion process was an exothermic and thermodynamically much favorable.

1. Introduction

Cyclodextrins are doughnut-fashioned oligosaccharides [1] consisting of 6(α-), 7(β-) or 8(γ-CD) D-(+)-glucopyranose units connected by α-(1,4) bonds with a hydrophobic cavity that is competent of forming inclusion complex with hydrophobic guests of appropriate dimensions and an external hydrophilic surface. A number of the additional compensation of cyclodextrins application contains the potential for the development of drug's stability, protection, organoleptic properties and stability [2–4]. Among several factors that can manipulate the quality of drug–CD interaction, the majority significant is the nature of the CD employed [5,6]. An entire guest molecule or parts of a guest molecule can be incorporated in the CD cavity. The threading of numerous CDs onto a linear guest consequences in a supramolecular "nanowire" frequently named pseudopolyrotaxane (PPR) [7,8]. This threading of several CD units onto a linear guest and close packing of CDs is assisted by hydrogen bonding among the hydroxyl groups located beside the rims of the adjacent CDs. The included guest segments are separated from the adjacent linear guest via the walls of the CD cavities and are required to accept highly extensive conformations by the narrow host CD channels.

Several researches have reported self assembly nanoarchitectures [9] from CD and linear guest molecules. Harada et al. [10] accounted the opening example of an inclusion complex formed through the self-assembly of α-CD and poly(ethylene glycol) and since then, other researchers have reported outcome achieved by using various types of CDs and guest molecules [11–13]. While the formation of CD–benzophenone derivative inclusion complexes and their shape [14,15] have already been reported by us before, the effect of the CD type on the aggregation behavior of these self assembly nanostructures has been fully addressed. Although the formation of host:guest inclusion complexes in solution can result in significant alterations to the spectral, chemical and physical functionality of the guest. For instance, the aqueous solubility of hydrophobic molecules can be extensively improved leading inclusion into a water-soluble host [16]. Further, most important, the host inclusion can have major effects on the fluorescence of polarity-sensitive guest molecules, during effects on the guest excited state. Recently, we reported successful consequences on self-assembly of nanorod formation through the inclusion complex and the system was projected based on the molecular modeling and spectroscopic studies [17–19].

In this paper, we have studied the spectral characteristics of 4-aminobenzophenone (4ABP) with α-CD and β-CD. The cyclodextrin capped 4ABP:CD inclusion complex spectral properties in solution are studied by UV–visible, fluorescence and fluorescence lifetime measurements. The 4ABP:CD inclusion complex nanomaterials are investigated by SEM, TEM, FTIR, DSC, Powder X-RD, ^{1}H NMR techniques and

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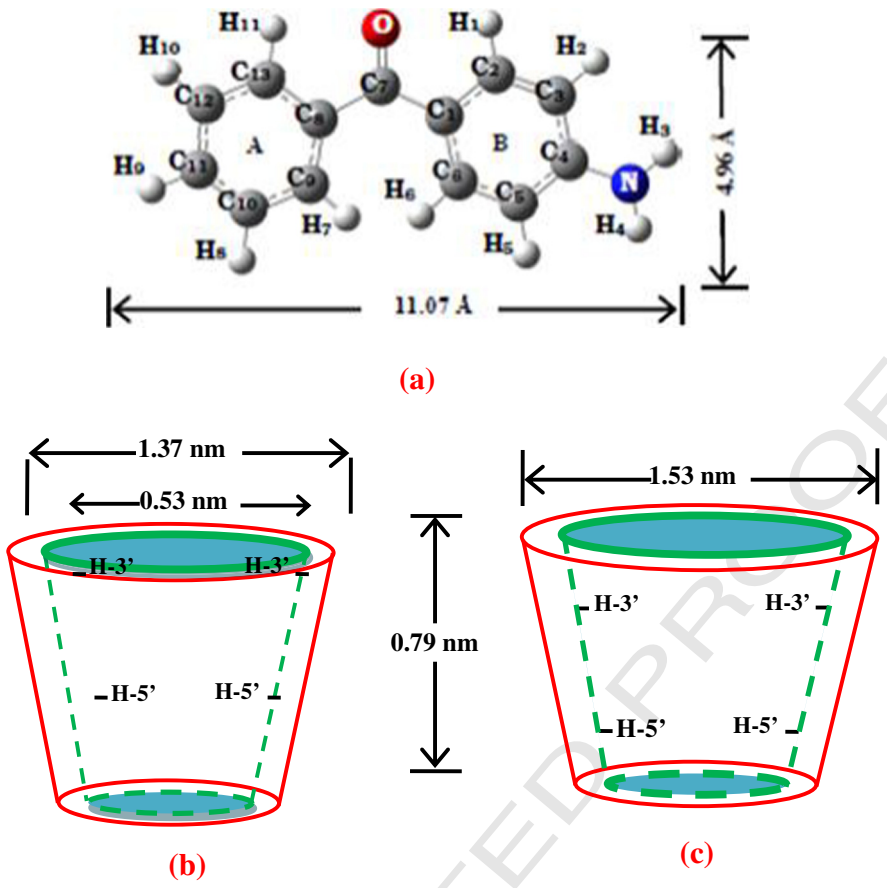

Fig. 1. (a) 4ABP (obtained by the PM3 method) and molecular dimensions of (b) α-CD and (c) β-CD.

molecular modeling methods. The optimized structures of 4ABP, α-CD and β-CD are shown in Fig. 1.

2. Experimental

2.1. Instruments

Absorption spectral measurements were carried out with a Shimadzu (Model UV 2600) UV–visible spectrophotometer and steady-state fluorescence measurements were analyzed using a Shimadzu spectrofluorimeter (Model RF-5301). The fluorescence lifetime measurements were performed using a picosecond laser and single photon counting setup from Jobin-Yvon IBH. Scanning electron microscopy (SEM) photographs were collected on a JEOL JSM 5610LV instrument. The morphology of 4ABP molecule encapsulated with CD inclusion complexes was investigated by TEM using a TECNAI G2 microscope with an accelerating voltage of 200 kV, using carbon coated copper TEM grid (200 mesh). FT-IR spectra of the inclusion complexes were measured between wave numbers 4000 cm^{-1} and 400 cm^{-1} on a Nicolet Avatar 360 FT-IR spectrometer using KBr pellets. One-dimensional ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using DMSO-d_6 (99.9%) as a solvent. DSC was recorded using Mettler Toledo DSC1 fitted with STR^e software; the temperature scanning range was from 298 K to 523 K with a heating rate of 10 K/min. PXRD spectra were recorded with a Bruker D8 advance diffractometer and the pattern was measured in the 2θ angle range between 5 and 80° with a scan rate of 5°/min.

2.2. Reagents and materials

4ABP, α-CD and β-CD were purchased from Sigma-Aldrich chemical company, USA and used without further purification. Triply distilled water was used for the preparation of aqueous solutions. All solvents were used of the highest grade (spectrograde) and all the spectral measurements were performed at the solute concentrations of 2×10^{-5} M. The concentration of α-CD and β-CD solutions was varied from 1×10^{-3} to 10×10^{-3} M.

2.3. Preparation of nanomaterials

α-CD and β-CD (1 m mol) was dissolved in 40 mL distilled water and 4ABP (1 m mol) in 10 mL methanol was slowly added to the CD solution. This mixture was sonicated at 313 K for 2 h. Then the solution was refrigerated overnight at 278 K. The precipitated 4ABP:CD inclusion complexes were recovered by filtration and washed with a little amount of ethanol and water to remove uncomplexed 4ABP and CDs, respectively. This precipitate was dried in vacuum at room temperature for two days and stored in an airtight bottle. These powder samples were used for further analysis.

2.4. Molecular modeling studies

Theoretical calculations were performed using Gaussian 09W. Theoretical geometries of the 4ABP and CD molecules were constructed with Spartan 08 and then optimized by the PM3 method. α-CD and

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