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Nanostructures formed by cyclodextrin covered aminobenzophenones through supramolecular self assembly

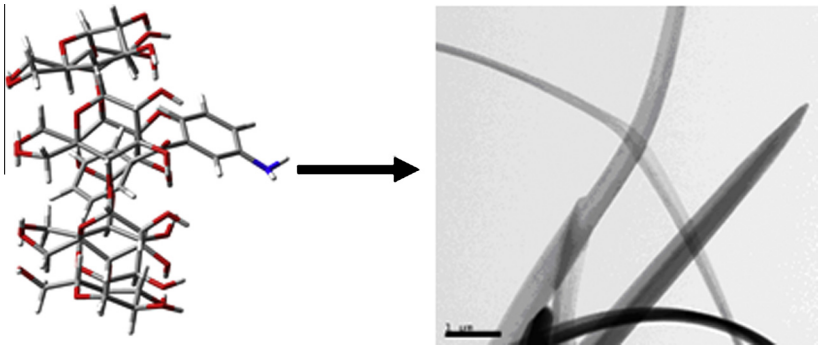
N. Rajendiran *, R.K. Sankaranarayanan, J. Saravanan

Department of Chemistry, Annamalai University, Annamalai Nagar 608 002, India

HIGHLIGHTS

- 2ABP and 3ABP guest molecule form 1:1 inclusion complex.
- Intermolecular hydrogen bonding play a vital role in the formation of nanostructure.
- 2ABP/α-CD complex show the self assembly hierarchical thread nanostructures.
- β-CD complexes displays a nanobrick nanostructure.
- Solvent study demonstrate the ESIPT and TICT in both molecules.

GRAPHICAL ABSTRACT



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ABSTRACT

Cyclodextrin (**α** and **β**) based nanostructures formed with 2-aminobenzophenone, 3-aminobenzophenone through the supramolecular self assembly are studied by absorption, fluorescence, time-resolved fluorescence, SEM, TEM, FT-IR, DSC, PXRD and ^{1}H NMR. The unequal layer by layer nanosheets and nanoribbons are formed through self assembly of 3ABP/CD inclusion complexes. 2ABP/α-CD complex nanostructures show the self assembly hierarchical thread structure and β-CD complexes displays a nanobrick structure. The formation of nanostructures are prearranged to H—O···H, NH_2···O and H_2N···H intermolecular hydrogen bond between individual complexes. The absorption and fluorescence spectral changes explicit formation of 1:1 inclusion complexes and solvent study demonstrate the ESIPT and TICT present in both molecules. The thermodynamic parameters (**Δ*H***, **Δ*G*** and **Δ*S***) of 2ABP and 3ABP molecule and the inclusion complexes were determined from semiempirical PM3 calculations.

Introduction

The design of organic molecules permeates with specific structural sequence that decides their spontaneous assembly into organized nanoscale structures is a remarkable goal in supramolecular chemistry [1,2]. The morphology of the assembly is regularly determined by the structure of the individual components [3]. The molecular encapsulation and molecular assembly or self-assembly of CDs and their derivatives are give more attention in chemical, polymer and biological systems [4–9]. The molecular assembly based on α-CD necklace in the polyrotaxane, which is reversibly shuttled using a STM under ambient circumstances [10]. The formation of nanotubes with γ-CD indicated that the length of guest molecule is a key factor in the route of nanotube formation [11]. Further, CD based nano-structures of linking β- and γ-CD molecular nanotube aggregates by the encapsulation of diphenyl-hexatrienes. These cyclodextrin-nanotubes were found to consist of 20 β-CDs and 30–35 γ-CDs, respectively [12]. Furthermore, based on its dimension, CD cavity has to accommodate one

* Corresponding author. Tel.: +91 94866 28800; fax: +91 4144 238080.
E-mail address: drrajendiran@rediffmail.com (N. Rajendiran).

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or two guest molecules in the majority cases; if the guest is long enough, three [13–15] or more numerous CD rings [16,17] can be threaded along it. The micro rod formed by the secondary assembly of β-CD nanotube induced by the guest molecule, the nanotube of β-CD occupied by the guest molecule acted as a center for the aggregation of β-CD to form the unfilled nanotube [18].

In this paper, the cyclodextrin covered 2ABP and 3ABP inclusion complexes spectral properties are determined by UV–visible and fluorescence measurements. Further, we summarize research on nanomaterials formed by CDs with 3ABP and 2ABP possibly reflecting the thought of nanoarchitectonics, according to classification of unit nanostructures (nanorod, nanobelt, nanosheet, nanobrick), prearranged assemblies (layer-by-layer (LbL) self-assembly) and hierarchical structures, where research on inclusion complex is developed into nanostructures through self-assembly is highlighted. The wrapping characteristics of 2ABP and 3ABP (Fig. 1) onto CD nanomaterials are investigated by SEM, TEM, FTIR, DSC, Powder X-RD and ^{1}H NMR.

Experiments

Instruments

Absorption spectral measurements were carried out with a Shimadzu (Model UV 2600) UV–visible spectrophotometer and steady-state fluorescence measurements were made by using a Shimadzu spectrofluorometer (Model RF-5301). The fluorescence lifetime measurements were performed using a picoseconds laser and single photon counting setup from Jobin–Vyon IBH (Madras University, Chennai). Scanning electron microscopy (SEM) photographs were collected on a JEOL JSM 5610LV instruments. The morphology of 2ABP and 3ABP encapsulated CD inclusion complexes were investigated by TEM using a TECNAI G2 microscope with accelerating voltage 100 kV and 200 kV, using carbon coated copper TEM grid (200 mesh). FT-IR spectra of 2ABP, 3ABP, α-CD, β-CD and the inclusion complexes were measured from 4000 cm^{-1} to 400 cm^{-1} on Nicolet Avatar 360 FT-IR spectrometer using KBr to pellets. ^{1}H NMR spectra was recorded on a Bruker AVANCE 400 MHz spectrometer (Germany) using D_2O (99.9%) as a solvent. The DSC were recorded using Mettler Toledo DSC1 fitted with STR^e software (Mettler Toledo, Switzerland), temperature scanning range was from 25 to 250 °C with a heating rate of 10 °C/min. PXRD spectra were recorded with a BRUKER D8 advance diffractometer (Bruker AXS GmbH, Karlsruhe, Germany) and the pattern was measured in the 2θ angle range between 5° and 80° with a scan rate 5°/min.

Reagents and materials

2ABP, 3ABP, α-CD and β-CD were purchased from Sigma–Aldrich chemical company 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 4×10^{-5} M. The concentration of α-CD and β-CD solutions were varied from 1×10^{-3} to 10×10^{-3} M.

Preparation of nanomaterials

α-CD or β-CD (1 mmol) was dissolved in 40 ml distilled water and 2ABP or 3ABP (1 mmol) in 10 ml methanol was slowly added to the CD solution. This mixture was sonicated at 40 °C for 2 h. Then the solution was refrigerated overnight at 5 °C. The precipitated 2ABP/CD and 3ABP/CD inclusion complexes were filtered and the precipitate was washed with little amount of ethanol and water to remove uncomplexed ABPs and CDs, respectively. These precipitates were dried in vacuum at room temperature for two days and stored in an airtight bottle. These powder samples were using for further analysis.

Molecular modeling studies

The theoretical calculations were performed with Gaussian 03W. The preliminary geometry of the guest and CDs were

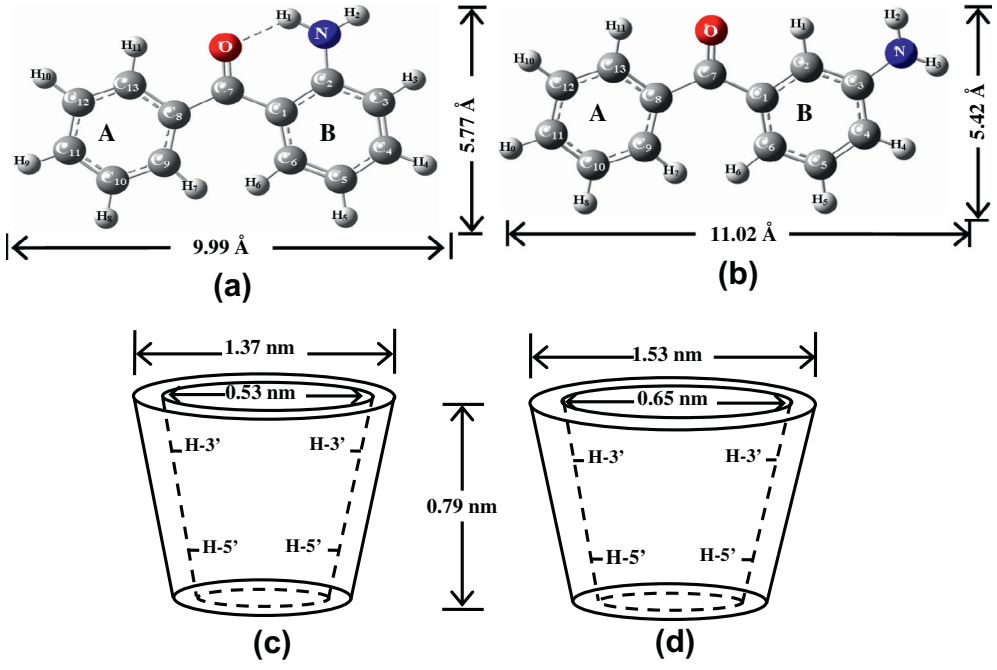

Fig. 1. The optimized structure with the numbering system of (a) 2ABP and (b) 3ABP obtained by PM3 level of theory and truncated cone shaped molecular structure of (c) α-CD and (d) β-CD. The values represent dimensions of the corresponding molecules.