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Azo dye/cyclodextrin: New findings of identical nanorods through 2:2 inclusion complexes

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ABSTRACT

Inclusion complexation behavior of 4-aminoazobenzene (AAB) and 4-amino-2,3′-dimethyl azobenzene (GBC, fast grant GBC) with α- and β-cyclodextrins (α-CD, β-CD) is analyzed by scanning electron microscope, transmission electron microscope, Fourier transform infrared spectroscopy, differential scanning calorimetry, powder X-ray diffraction, and proton nuclear magnetic resonance spectroscopy techniques. Transmission electron microscope analysis suggests that identical nanorods formed in AAB/CD inclusion complexes while different dimension nanostructures were observed in GBC/CD inclusion complexes. The nanostructures confirmed that the ratio of 2:2 (guest:host) inclusion complex has been developed to a miniature nanorod. Nanosecond time-resolved fluorescence studies indicated that AAB/GBC have fast life time in water, whereas slow life time in CDs corresponds to a higher-order structure of 2:2 complexes. Thermodynamic parameters and binding affinity of the inclusion complex formation were determined and discussed. van der Waals interactions are mostly responsible for enthalpy-driven complex formation of AAB and GBC with cyclodextrins.

1. Introduction

Cyclodextrin (CD) is a cyclic oligomer of α-D-glucose obtained by the action of certain enzymes on starch (Szejtli, 1998). In general CDs have shallow truncated cones; these carbohydrates present a hydrophobic cavity, whose size depends on the number of basic glucose units and two different rims, a wider (named head, H) having all secondary hydroxyl groups and a narrower (named tail, T) having all primary hydroxyl groups. The application of CD in chemistry is strongly associated to its ability to form inclusion complexes with a variety of guest molecules basically in aqueous solutions (Anconi, Nascimento, De Almeida, & Dos Santos, 2012; Connors, 1997). Because of CDs notable structure, CDs have also been used as a cyclic component in the assembly of supramolecular architectures (Harada, 2001). In supramolecular field, the cyclodextrins (CDs) are perfect host system for studying nano- and micro-structures through self-assembly of inclusion complexes. Mainly four models are responsible to form the linear type of nanostructures, head to head, tail to tail, head to tail and secondary self-assembly into stack way layer by layer arrangement. The CD nanorods form their secondary assembly through the hydrogen bonding between CDs (Miyake et al., 2003; Wu, Shen, & He, 2006). The hydrogen bond between the OH groups present along the rim of the CD is also an essential driving force leading to the formation of stable inclusion complex and nanostructure (Anconi et al., 2012; Ceccato, Lo Nostro, & Baglioni, 1997).

The application of molecular modeling techniques (Mohsen & Mina, 2009; Sherrod, 1992; VD'Souza & Lipkowitz, 1998) can help reinforce experimental results, such as stoichiometry, geometry and thermodynamics parameters accompanying the complexation process, and they also provide information on the driving forces responsible for such processes (Madrid, Mendicuti, & Mattice, 1998; Madrid, Pozuelo, Mendicuti, & Mattice, 1997). Further, molecular modeling studies on 1:1 inclusion complexes (Madrid et al., 1997) demonstrated that the formation of both inclusion complexes was complimentary with the nonbonded van der Waals interactions as the major participation to the stabilization. Moreover we merged the experimental and molecular modeling analysis leads to successful consequences in designing structure, energetic, enthalpy and entropy difficulties (Antony Muthu Prabhu, Sankaranarayanan, Venkatesh, & Rajendiran, 2012; Rajendiran & Siva, 2014; Sivasankar, Antony Muthu Prabhu, Karthick, & Rajendiran, 2012). We reported self-assembly of nanorod formation through the inclusion complex, nanorod formation mechanism was proposed based on the molecular modeling studies (Sankaranarayanan & Rajendiran, 2013).

In this study, the formation of identical nanorods between α-CD and β-CD with 4-aminoazobenzene (AAB) and 2,3-dimethyl-4-aminoazobenzene (GBC, fast grant GBC) molecules was discussed (Fig. 1). The formation of the nanorods layer by layer (LbL)

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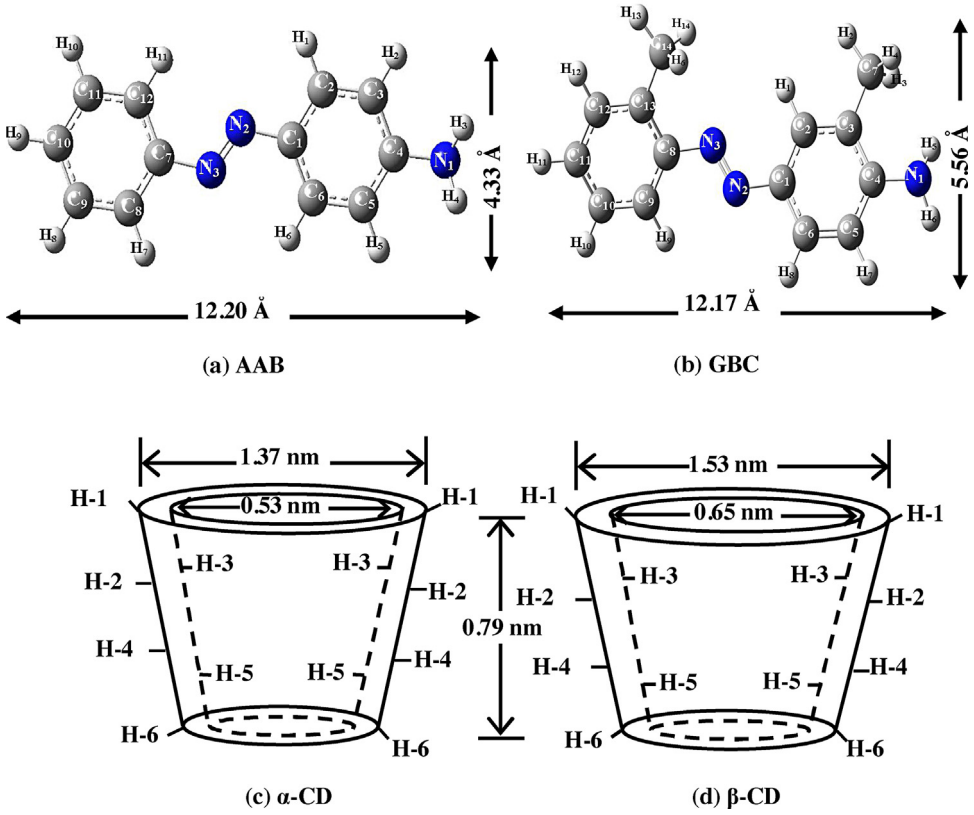

Fig. 1. The optimized structure with the numbering system of (a) AAB and (b) GBC obtained by PM3 level of theory and truncated cone shaped molecular structure of (c) α-CD and (d) β-CD.

method was proposed. The inclusion complexes were subsequently analyzed by absorption, fluorescence, fluorescence lifetime, FTIR, differential scanning calorimeter (DSC), powder X-ray diffraction (PXRD) and ^{1}H NMR techniques. The study of α-CD and β-CD with AAB and GBC is the extension of our earlier work (Antony Muthu Prabhu, Venkatesh, & Rajendiran, 2010; Antony Muthu Prabhu, Venkatesh, Sankaranarayanan, Siva, & Rajendiran, 2010; Premakumari et al., 2011; Venkatesh, Antony Muthu Prabhu, & Rajendiran, 2011).

2. Experiments

2.1. Reagents and materials

AAB, GBC, 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 2×10^{-5} M. The concentration of α-CD and β-CD solutions was varied from 1×10^{-3} to 10×10^{-3} M.

2.2. Preparation of nanomaterials

The α-CD or β-CD (1 mmol) was dissolved in 40 ml distilled water and AAB or GBC (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 AAB/CD and GBC/CD inclusion complexes were recovered by filtration and washed with little amount of ethanol and water to remove uncomplexed dyes 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.

2.3. 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-Vyon IBH. Scanning electron microscopy (SEM) photographs were collected on a JEOL JSM 5610LV instrument. The morphology of AAB and GBC dyes encapsulated with CD inclusion complexes was 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 AAB, GBC, α-CD, β-CD and the inclusion complexes were measured between wave numbers 4000 cm^{-1} and 400 cm^{-1} on Nicolet Avatar 360 FT-IR spectrometer using KBr pellets. One-dimensional ^{1}H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer using DMSO-d_6 (99.9%) as a solvent. The DSC was recorded using Mettler Toledo DSC1 fitted with STR^e software, 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 and the pattern was measured in the 2θ angle range between 5° and 80° with a scan rate 5°/min.

2.4. Molecular modeling studies

The theoretical calculations were performed using Gaussian 09 W. The initial geometries of the dye and CD molecules were constructed with Spartan 08 and then optimized by the PM3 method. α-CD and β-CD were fully optimized by PM3 without any