The preparation and characterization of \(n\)-B\(_{18}\)H\(_{22}\)-beta cyclodextrin inclusion complex

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Abstract: Anti- B\(_{18}\)H\(_{22}\) (\(n\)-B\(_{18}\)H\(_{22}\)) is a new class of laser materials. In this paper, \(n\)-B\(_{18}\)H\(_{22}\)-\(\beta\)-cyclodextrin (\(\beta\)-CD) supramolecular inclusion complex was prepared by saturated aqueous solution method for the first time. The characterization of the inclusion complex was studied by FTIR, XRD, and SEM. The results showed that the stability of \(n\)-B\(_{18}\)H\(_{22}\) in water was greatly enhanced due to the formation of the inclusion complex. This paper has opened a new way to improve the stability and extend the application of \(n\)-B\(_{18}\)H\(_{22}\) in aqueous solution. The inclusion compound has potential applications in the preparation of borane liquid laser and the synthesis of \(n\)-B\(_{18}\)H\(_{22}\) derivatives.

1. Introduction

Cyclodextrins (CDs), produced by the enzymatic degradation of starch, are a family of macrocyclic compounds made up of a-D-glucopyranose units linked by \(\alpha\)-1,4 glycosidic bonds\(^{[1]}\). There are many types of cyclodextrins, three of them are commercially available in the form of alpha, beta and gamma cyclodextrins, consisting of 6, 7 and 8 a-D-glucopyranose units and with different cavity sizes (4.5, 7.8, 9.2 Å, respectively)\(^{[2]}\). Cyclodextrins are of great importance in supramolecular chemistry, since cyclodextrins (CDs) are well known to form inclusion complex with a wide variety of hydrophobic molecules having the correct size that are able to penetrate and reside within the CD cavity\(^{[3-7]}\), due to its amphiphilic in nature such as inner hydrophobic cavity and outer hydrophilic shell\(^{[8]}\). The driving forces for forming inclusion complexes include weak van der Waals forces, hydrogen bonding and charge transfer interactions between the host and guest molecule, without forming any covalent bonds\(^{[9]}\). The formation of such complexes improves chemical and physical properties of the guest, such as, enhancement of water solubility of insoluble substances and stability of bioactive molecules, stabilisation of guests against oxidation, light and heat, inhibition of volatility and sublimation, taste modification of drugs and flavours by masking off-flavours and controlled release\(^{[10]}\).

In recent years, there has been considerable interest in studying the spectral properties of cyclodextrin inclusion complexes\(^{[11-13]}\). Spectroscopic studies of CD inclusion complexes have shown that the CDs provide a protective and more constrained hydrophobic cavity for the electronically excited molecule\(^{[14]}\), and it is observed that fluorescence signal increases with increasing concentration of CD and fluorescence maximum is slightly red shifted\(^{[15]}\). The increase in fluorescence intensity during the formation of inclusion complex may be due to (i) the shielding of the fluorescent molecule provided by the hydrophobic cavity reduces the quenching coming from water molecules or solvent-borne quenchers, (ii) increased local viscosity in the CD cavity with concomitant reduction of oxygen quenching, (iii)
lowering of solvent polarity provided by CD cavity and (iv) deaggregation of non-emittive dimer dye into emittive monomer in the case of molecules having a dimer-monomer equilibrium in aqueous solution[15].

B18H22 is a member of a class of boranes that consist of two such clusters fused together in a “macropolyhedral” structure (Fig.1), there are two isomers of B18H22, anti-B18H22 and syn-B18H22. Of all the known binary boranes (compounds consisting only of boron and hydrogen), anti-B18H22 is the only one to have the property of fluorescence. Anti-B18H22 is a highly fluorescent material, anti-B18H22’s fluorescence can withstand the stringent excitation pumping conditions required to achieve laser light emission. In 2015, the first boron hydride laser based on anti-B18H22 was reported[16]. Since then, anti-B18H22, this fine fluorescent material has attracted great attention[17,18]. However, this compound always suffers from poor stability under the influence of water, certain pH levels and temperature, which can cause degradation[19].

![Figure 1. The molecular structure of anti-B18H22](image)

In this study, anti-B18H22 was successfully included in β-CD, and its complex was confirmed using X-ray diffraction (XRD), scanning electron microscope (SEM), and fourier transform infrared spectrum. The molar ratio of inclusion complexes was determined. In addition, the influence of β-CD on anti-B18H22 stability in aqueous solutions was studied by photoluminescence.

2. Experimental

2.1 Materials

*n*-B18H22 was synthesized in our laboratory according to reference[20,21], and β-CD was obtained from Shanghai chemical reagents Co., Ltd. Acetonitrile was purchased from Aladdin. All other reagents used were of guaranteed analytical grade. Ultrapure water was employed in the preparation of solutions. All working solutions of *n*-B18H22 were prepared by standard procedures and appropriate dilution.

2.2 Preparation of *n*-B18H22-β-CD inclusion complex

*n*-B18H22-β-CD was prepared by a slow and dropwise addition of 0.1 g of *n*-B18H22 dissolved in acetonitrile (2mL) to 20.0 mL of an aqueous solution with 0.477 g of β-CD in 1:1M ratio. After ultrasonic stirring it continuously at room temperature for 2h, the covered flask was frozen unperturbed at -40°C in refrigerator for 12h to yield a yellow precipitate. The yellow precipitate was collected by filtration, and the crystals were washed with ultrapure water and vacuum dried.

2.3 Characterization of *n*-B18H22-β-CD

X-ray diffraction (XRD): XRD measurements were performed with Bruker D8 Advance type X-ray diffractometer using a CuKa radiation source (λ=0.154nm). The diffraction intensities were measured every 0.1° from 20=10 to 80° at scanning speed of 5°/min. The supplied voltage and current were 40 kV and 100 mA, respectively.

Photoluminescence (PL): PL scans were obtained with Hitachi F-4600 fluorescence spectrometer. The sample molecules were excited at 360nm, and the emission spectra was recorded with 10 nm excitation and emission slits. The scan voltage was 700V at scanning interval of 0.5nm and scanning speed of 1500nm/min.

UV - visible spectrum (UV/Vis): UV/Vis analysis was performed with Shimadzu UV2400 spectrophotometer. Ultrapure water as reference, the optical path of color dish is 1cm, a 10⁻⁴ mol/L solution was prepared for experiments.
Fourier transform infrared spectra (FTIR): FTIR analysis was made on a Perkin Elmer Spectrum two infrared spectrometer with a resolution of 4 cm\(^{-1}\) in KBr pellets in the range of 4000-400 cm\(^{-1}\).

Scanning electron microscope (SEM): Crystal morphologies of samples were characterized using a Zeiss Ultra 55 field emission scanning electron microscope operated at 5kV.

3. Results and Discussion

3.1 Determination of inclusion ratio by continuous variation method

In this paper, the continuous variation method was used to determine the inclusion ratio\(^{[22]}\). The total molar concentration of guest (\(\beta\)-CD) and host (\(n\)-B\(_{18}\)H\(_{22}\)) was kept constant, changed the molar concentration ratio of \(n\)-B\(_{18}\)H\(_{22}\) and \(\beta\)-CD. A series of with different molar concentration ratio (\(n\)-B\(_{18}\)H\(_{22}\) and \(\beta\)-CD) mixed solutions were prepared to make molar fraction of \(n\)-B\(_{18}\)H\(_{22}\) varied from 0.1 to 0.9. Determined the absorbance values of mixed solutions (A\(_1\)) and pure \(n\)-B\(_{18}\)H\(_{22}\) solutions (A\(_2\)) at 363nm. \(\beta\)-CD has no absorption peak at 363nm, the absorbance difference of solutions before and after adding \(n\)-B\(_{18}\)H\(_{22}\) was considered to be caused by \(n\)-B\(_{18}\)H\(_{22}\). The value of the absorbance difference (\(\Delta A = A_2 - A_1\)) was plotted against the molar fraction of \(n\)-B\(_{18}\)H\(_{22}\), the position of the x-coordinate at the highest point of the curve can be considered as the location of the inclusion. It can be seen from Fig.2 that the molar fraction of \(n\)-B\(_{18}\)H\(_{22}\) was 0.5 at the highest point of the curve. Therefore, the optimum inclusion ratio can be calculated to be 1:1.

![Figure 2. continuous variation plot](image)

3.2 FTIR measurements

The FTIR spectra of \(n\)-B\(_{18}\)H\(_{22}\), \(\beta\)-CD and the inclusion complex was carried out by a Perkin Elmer Spectrum two infrared spectrometer, the results are shown in Fig.3.

![Figure 3. FTIR spectra of (a) \(n\)-B\(_{18}\)H\(_{22}\), (b)\(\beta\)-CD, (c) \(n\)-B\(_{18}\)H\(_{22}\)-\(\beta\)-CD inclusion complex.](image)
In the FTIR curve of \( n\)-B\(_{18}\)H\(_{22}\), based on the structure characteristics of \( n\)-B\(_{18}\)H\(_{22}\), 2602 and 2980 cm\(^{-1}\) were assigned to a B–H and B-B stretching vibration, respectively. 980 and 1005 cm\(^{-1}\) to the bending vibration of B-H and B-B, respectively. To \( \beta\)-CD, the infrared absorption peak at 3355 cm\(^{-1}\) was attributed to the stretching (O–H) vibration of hydroxyl group, and this is a broad peak. The stretching (C–O) vibration occur at 1153 cm\(^{-1}\) and 1031 cm\(^{-1}\), the infrared peak intensity of 1031 cm\(^{-1}\) was relatively strong. \( n\)-B\(_{18}\)H\(_{22}\)-\( \beta\)-CD inclusion complex and blank \( \beta\)-CD have a similar infrared absorption curve, it also can be inferred that the structure of \( \beta\)-CD is not changed after packing \( n\)-B\(_{18}\)H\(_{22}\). Encapsulation of \( n\)-B\(_{18}\)H\(_{22}\) only leads to small changes of spectra of \( \beta\)-CD. Compared with the curve of \( \beta\)-CD, the broad peak of the stretching (O–H) vibration of hydroxyl group of \( n\)-B\(_{18}\)H\(_{22}\)-\( \beta\)-CD changed from 3355 to 3320 cm\(^{-1}\). We can found from curve (a) and (c) that the strong characteristic peak at 2602 cm\(^{-1}\) belonging to \( n\)-B\(_{18}\)H\(_{22}\) disappeared completely in the curve of the inclusion complex. Furthermore, the position and shape of the band at 2980, 980, and 1005 cm\(^{-1}\) of \( n\)-B\(_{18}\)H\(_{22}\) changed in the curve of the inclusion complex. These variations in the IR spectrum of the inclusion complex can be attributed to intermolecular interactions between the \( n\)-B\(_{18}\)H\(_{22}\) and \( \beta\)-CD.

3.3 XRD determination

Fig. 4 shows the X-ray diffraction spectra of \( n\)-B\(_{18}\)H\(_{22}\), \( \beta\)-CD, and inclusion complex. Pure \( \beta\)-CD and \( n\)-B\(_{18}\)H\(_{22}\)-\( \beta\)-CD showed similar XRD spectra, but the XRD spectra of \( n\)-B\(_{18}\)H\(_{22}\) was significantly different. In general, some changes of the characteristic peak of \( \beta\)-CD and \( n\)-B\(_{18}\)H\(_{22}\) were observed due to the formation of inclusion complex, such as, some peak disappeared, peak intensity decreased, some new peaks appeared. The powder XRD patterns of \( n\)-B\(_{18}\)H\(_{22}\) and \( \beta\)-CD had typical crystal phase characteristics. The sharp and intense peaks at 2\( \theta\)=29.3, 39.1, 40.3 attributed to \( n\)-B\(_{18}\)H\(_{22}\) and 2\( \theta\) =35.1 attributed to \( \beta\)-CD (Fig. 3). These peaks were disappeared almost in the XRD spectra of \( n\)-B\(_{18}\)H\(_{22}\)-\( \beta\)-CD, instead broad and weak peaks emerged. In addition, some new, sharp and intense peak was observed in the spectra of \( n\)-B\(_{18}\)H\(_{22}\)-\( \beta\)-CD. These changes are the result of the interaction between \( n\)-B\(_{18}\)H\(_{22}\) and \( \beta\)-CD. The changes in diffractogram confirmed the formation of inclusion complex and similar results were observed in other experiments, such as SEM, etc.

3.4 SEM analysis

Fig. 5 shows the structure and physical appearance of \( n\)-B\(_{18}\)H\(_{22}\), \( \beta\)-CD, \( n\)-B\(_{18}\)H\(_{22}\)/\( \beta\)-CD physical mixture and \( n\)-B\(_{18}\)H\(_{22}\)-\( \beta\)-CD inclusion complex by SEM. Some obvious changes can be seen from Fig. 5 after forming the inclusion complex. \( n\)-B\(_{18}\)H\(_{22}\) appeared as irregular shape crystals with different sizes (Fig. 5a) whereas the surface of \( \beta\)-CD was compact and smooth (Fig. 5b). Physical mixture had the characteristics of \( n\)-B\(_{18}\)H\(_{22}\) and \( \beta\)-CD (Fig. 5c). The structure of the inclusion was completely different, with tight structure and regular morphology (Fig. 4d). The morphological changes which appeared in
SEM images confirmed the existence of interaction between \( n\text{-B}_{18}\text{H}_{22} \) and \( \beta\text{-CD} \).

### 3.5 Stability Analysis
Free \( n\text{-B}_{18}\text{H}_{22} \) in water is particularly easy to degrade, so it is important to stabilize the free \( n\text{-B}_{18}\text{H}_{22} \). The properties of \( n\text{-B}_{18}\text{H}_{22} \) and the inclusion complexes solutions were evaluated through stability experiments of pH tolerance (alkali solution used only, \( \beta\text{-CD} \) can be decomposed by acids.) and temperature. The performance comparisons were carried out by investigating the variations of fluorescence intensity with pH and temperature. Fluorescence measurements were performed by the F-4600 fluorescence spectrophotometer (Hitachi). The inclusion complex was dissolved in water (0.005g/3mlH_{2}O), 1.5x10^{-2}mol.L^{-1} free \( n\text{-B}_{18}\text{H}_{22} \) aqueous solution was elected to be compared. The fluorescence intensity of the samples was measured at 415 nm. Fig. 6 and Fig.7 show the stability of \( n\text{-B}_{18}\text{H}_{22} \) and the inclusion complex under different pH. It can be seen that the fluorescence intensity of \( n\text{-B}_{18}\text{H}_{22} \) reduced rapidly at the test. At 25°C, \( n\text{-B}_{18}\text{H}_{22} \) reached the degradation percentage of 75% in 9h. On the contrary, the fluorescence intensity of the inclusion complex reduced slowly, hardly any change can be observed in the pH range of the experiment.

![Figure 5. Scanning electron microscope of (a) \( n\text{-B}_{18}\text{H}_{22} \), (b)\( \beta\text{-CD} \), (c) \( n\text{-B}_{18}\text{H}_{22}/\beta\text{-CD} \) physical mixture, and (d) \( n\text{-B}_{18}\text{H}_{22} - \beta\text{-CD} \) inclusion complex.](image)

The heat stability of the inclusion complex in water are shown in Fig. 8, the similar results can be obtained within in the temperature of 25°C, 40°C, 50°C, 60°C for 3h. The results showed when \( n\text{-B}_{18}\text{H}_{22} \) and \( \beta\text{-CD} \) were formed into the inclusion complex, the stability of \( n\text{-B}_{18}\text{H}_{22} \) in water was greatly enhanced. The reason was probably that the inclusion complexation with \( \beta\text{-CD} \) can affect the physical and chemical properties of guest molecules, the formation of an inclusion complex usually leads to the retardation of degradation processes, the inclusion of \( n\text{-B}_{18}\text{H}_{22} \) into \( n\text{-B}_{18}\text{H}_{22}/\beta\text{-CD} \) protected the guest from chemical, photochemical stresses, damage caused by other molecules. Thus, the stability of \( n\text{-B}_{18}\text{H}_{22} \) against elevated temperature, hydrolysis, was effectively increased through its complexation with \( \beta\text{-CD} \).
4. Conclusion
The β-cyclodextrin inclusion complex with the eighteen borane was successfully formed and characterized by means of various analytical techniques such as X-ray diffraction, SEM and FTIR. The formation of a 1:1 inclusion complex between β-CD and \( n\text{-B}_{18}\text{H}_{22} \) by UV/Vis analysis. The degradation process was carefully compared with \( n\text{-B}_{18}\text{H}_{22} \) through PL analysis. The stability studies indicated β-CD can greatly improve the chemical stability of free \( n\text{-B}_{18}\text{H}_{22} \) in the form of inclusion complex. Thus, the inclusion complexation with β-CD is a promising method to develop a new class of \( n\text{-B}_{18}\text{H}_{22} \)-loaded material with improved stability and extended application.

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