Secondary assembly mechanism of cyclodextrin based on $LiNTf_2@\beta\text{-}CD$ system

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Received: 24 June 2015/Accepted: 22 March 2016/Published online: 30 March 2016 © Springer Science+Business Media Dordrecht 2016 molecules [18–25]. Moreover, we also found the precipitation in the PBD- β -CD, 2,5-bis(5'-*tert*-butyl-2-benzoxazoyl)thiophene (BBOT)- β -CD, and BBOT- γ -CD solutions [23–25]. Further characterization suggested for the first J&K Chemical Company) were used as received. LiNTf₂ (>99 %) was purchased from Lanzhou Institute of Chemical Physics, China. HNTf₂ (99 %) was purchased from J&K Chemical Company. NaNTf₂ and KNTf₂ was obtained by mixing HNTf₂ with NaOH and KOH in the aqueous solution. All other chemicals were analytical grade and used without further purification. Ultrapure water was used throughout the experiments.

Method

Sample preparation

The LiNTf₂@ β -CD aqueous solutions were prepared by weighing desired amount of LiNTf₂ and β -CD, and then heated to obtain transparent solutions, which were kept thermostatically at room temperature for at least 24 h. Then the solutions were freeze-dried for structural characterization. Before freeze-drying, the solutions were quickly freezed by liquid nitrogen to maintain their original self-assembly structure [41, 42].

Dynamic light scattering (DLS)

DLS measurements were performed on an ALV/DLS/SLS-5022F photo correlation spectrometer. The wavelength of laser was 632.8 nm and the scattering angle was 90°. The temperature was controlled at 25 °C. The samples were treated by centrifugating at 10,000 rpm for 30 min before the measurement.

Transmission electron microscope (TEM)

One drop of the sample solution was placed onto a formvar-coated copper grid, and a drop of phosphotungstic acid solution (2 wt%) was used as the negative-staining agent to make the TEM images more clear. For the freeze-fracture TEM (FF-TEM), samples were frozen by liquid propane. The fracturing and replication were carried out on a freezefracture apparatus (Balzers BAF400, Germany) at -140 °C. Pt/C was deposited at an angle of 45° to shadow the replicas, and C was deposited at an angle of 90° to consolidate the replicas. The samples were examined on an FEI Tecnai G2 T20 electron microscope operating at 200 kV.

Powder X-ray power diffraction (XRD)

XRD patterns were obtained on a D/MAX-PC2500 diffractometer with Cu- K_{α} radiation ($\lambda = 0.154056$ nm). The supplied voltage and current were set to 40 kV and 100 mA, respectively. Powder samples were mounted on a sample holder and scanned at a speed of 4°/mim.

Electron spray ionization/mass spectrometry (ESI/MS)

The ESI/MS used with electrospray ionization (ESI) was done on a Fourier transform ion cyclotron resonance mass spectrometer, APEX IV(Bruker, USA).

Fourier transform infrared spectra (FTIR)

FTIR spectra of the grinded xerogel were recorded on a NICOLET iN10 MX spectrometer using infrared microspectroscopy method.

Results

DLS measurements

After being kept thermostatically for at least 24 h, the LiNTf₂@β-CD solutions were still clear and no precipitation happened, even the concentration reached 70 mM@70 mM. The LiNTf₂@β-CD solutions show obvious Tyndall phenomenon, suggesting the existence of self-assembly in the solutions. Figure 1a shows the DLS result of LiNTf2@B-CD (30 mM@30 mM) solution. The hydrodynamic radius $(R_{\rm h})$ ranges from 50 to 300 nm, indicating the existence of large self-assembly. The shape of the self-assembly in the solutions is characterized by TEM method below. α -CD, γ -CD, and DM- β -CD are also utilized (Fig. 1b–d) and only the LiNTf₂@ γ -CD solution shows the signal of large self-assembly. The signals in Fig. 1b and d, whose diameter is about 1-2 nm, probably derive from β -CD or the NTf₂⁻- β -CD inclusion complex [22, 23, 42]. In addition, LiNTf₂ on its own cannot selfassembly so that no self-assembly signal occurs in Fig. 1e.

In contrast, 10 mM β -CD solution shows a signal (Fig. 1f) whose average size is similar to that of the LiNTf₂@ β -CD solution. Bonini et al. characterized that β -CD formed

structure is apparently different from the nanotubes and their SA as reported before [23–29].

Besides, Fig. 4c shows that there exists the mixture of nanosheets and small particles in $\text{LiNTf}_2@\beta\text{-CD}$ (15 mM@30 mM) solution. We propose that the excessive β -CD does not influence the formation of nanosheets, but forms the amorphous aggregates [23, 43].

Moreover, we observed the morphology of the selfassemblies in the NaNTf₂@ β -CD and KNTf₂@ β -CD systems. Figure 4d displays irregular-shaped nanosheets in the KNTf₂@ β -CD system, and this was also observed in the NaNTf₂@ β -CD system. These structures are apparently different from those in the LiNTf₂@ β -CD system and this will be taken into consideration when the self-assembly mechanism is discussed.

XRD patterns

We freeze-dried a series of samples for structural characterization of the self-assembly in the LiNTf₂@ β -CD aqueous solution. Figure 5d shows the XRD pattern of the freeze-dried product of LiNTf₂@ β -CD (30 mM@30 mM) solution, which differs from the XRD patterns of the freeze-dried β -CD (Fig. 5f). The structure of β -CD and its complexes are mainly classified into cage-type and channel-type ones. Here the major peaks at $2\theta = 9.5$, 12.6, and 18.2° in Fig. 5f are observed, indicating the cage-type structure of the original β -CD. While the major peaks at $2\theta = 11.5$ and 17.6° in Fig. 5d and e are characteristic of the channel-type of β -CD [48–50]. It can thus be deduced that the β -CD molecules form the channel-type structure in

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by organic molecules with poor solubility, the organic molecules first induce β -CDs to form rigid nanotubes, and with these nanotubes as recrystallization centers, other empty β -CDs are packed together to form the rodlike structures [23–25]. Here most β -CDs tend to form inclusion complexes with NTf₂, so the SA can be well-organized through the stacking of the NTf₂- β -CD nanotubes. The concentration of the guest molecule leads to the difference of the SA mechanism between the LiNTf₂@ β -CD SA system and our previous ones.

Driving forces for self-assembly

The addition of urea influences the self-assembly by weakening the inclusion complexation between NTf_2^- and β -CD, suggesting that hydrophobic interaction is an

essential driving force for the self-assembly between LiNTf₂ and β -CD. Besides, we replaced β -CD with α -CD, γ -CD, and DM- β -CD for further investigation on the mechanism. The DLS results show that LiNTf₂ can selfassemble with β -CD and γ -CD, but not with α -CD. In Park's dye- γ -CD hydrogel system, gelation occurred only in the complex with γ -CD but was absent with α -CD and β -CD [36]. We consider that a cavity with proper size is also important for the binding of the CD into nanotubes, thus no self-assembly occurs in the LiNTf₂@ α -CD system. As for DM- β -CD, a large part of the hydroxyl groups are replaced by methyl, so the hydrogen-bonding interaction is weakened. The hydrogen-bonding interaction probably contributes to both the binding of β -CD into nanotubes and the SA of the nanotubes into nanosheets, just like our previous studies about the SA [23–25].





Fig. 7 FTIR absorption spectra of *a* the freeze-dried products of LiNTf₂@ β -CD (30 mM@30 mM), *b* physical mixture of LiNTf₂ and β -CD, and *c* β -CD

In the self-assembly, the arrangement of the nanotubes is perfectly achieved and nanosheets with regular shape are obtained consequently. The thickness of the nanosheets is about 30–40 nm, so it should be noted that the nanosheet is not a single layer but a bulk aggregation of nanotubes. In comparison, Rajendiran et al. also fabricated nanosheets using a series of non-ionic drug molecules and CDs [30– 32]. They also proposed the "secondary self-assembly" mechanism [32] while the shape of their nanosheets was irregular. Here the DLS results of the HNTf₂, NaNTf₂, and KNTf₂ systems demonstrate that the undissociated NTf₂⁻ is unfavorable for self-assembly, and Na⁺ and K⁺ cannot act the same role as Li⁺ in the self-assembly. We attribute these results to the special ability of Li⁺ in forming hydrogen-bonding interactions between CDs and water molecules [36, 54–56]. Here Li⁺ not only acts as the cation but also makes sure to closely pack the nanotubes into the SA by participating in inducing hydrogen-bonding network between the adjacent β -CDs and water molecules [36, 54–56].

Conclusions

The self-assembly behavior of LiNTf₂ and β -CD in the concentrated aqueous solution was investigated on the basis of our previous study about their interaction pattern in the diluted solution. Nanosheets with regular shape were obtained in the LiNTf₂@β-CD system. We confirmed that LiNTf₂ self-assembles with β -CD in a 1:1 molar ratio. A supramolescular self-assembly mechanism was proposed, that LiNTf₂@β-CD firstly forms one dimensional nanotubes, after which the nanotubes further stack with each other to form 3D nanosheets by SA. It was demonstrated that the hydrogen-bonding interaction between adjacent β -CDs molecules is necessary for the formation of the nanotubes and the SA, and Li⁺ shows a special effect in the SA by inducing stable hydrogen-bonding network between the adjacent β -CDs and water molecules. By this work we further illustrated our SA mechanism in the concentrated aqueous solution, and obtained a novel self-assembly structure by the SA mechanism. This SA system is helpful in constructing CD self-assembly structures based on inclusion complexation in water. Besides, as NTf₂ is an important anion of ILs, this work may bring in a new way for the application of IL-CD system, such as synthesis, catalysis, separation, reaction medium, etc.

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