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## ARTICLE

# Inclusion complexes synthesized from an ABA triblock polymer and $\beta$ -cyclodextrins: Amplification of hydrophobic interaction along a hydrophilic polymer chain†

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Jiangang Gao,<sup>\*ab</sup> Shaobo Yu,<sup>a</sup> Benpei Zheng,<sup>a</sup> Qingping Song,<sup>a</sup> Xingxing Peng,<sup>a</sup> Ying Lin,<sup>a</sup> Gang Zou<sup>b</sup> and Qijin Zhang<sup>\*bc</sup>

A triblock PEG-based polymer (CP1113) with a clear ABA structure was synthesized from 1, 13-tridecanedioic acid (DA13) and mono-methoxy-poly (ethylene glycol) (MePEG) via condensation reaction. An inclusion complex (IC1113) with  $\beta$ -cyclodextrin (CD) was prepared by co-precipitation and the IC formation was confirmed by transmittance determination with a UV-Vis spectrometer. Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetry analysis (TGA) were adopted to characterize IC1113 and the experimental data showed that a channel-type polypseudorotaxane was formed. For further investigating the inclusion behaviors, <sup>1</sup>H-NMR spectroscopy was used to determine the molar ratio between CP1113 and  $\beta$ -CD and 2D ROSEY spectra were recorded to elucidate the IC forming mechanism. The results revealed that  $\beta$ -CD threaded onto the polymer main chain at a molar ratio of 7.8:1 and the molar ratio of EG segments to  $\beta$ -CD in IC1113 was ca. 8.28:1. It was concluded that  $\beta$ -CD accommodated both the methylene and the PEG segments and herein hydrophobic and hydrogen-bonds interactions played the most important roles with a hydrophobic stabilizing and hydrogen-bonding inducing effect, which “amplified” the hydrophobic interaction between  $\beta$ -CD and the methylene segment along the hydrophilic PEG segments.

## Introduction

In recent years, self-assembling supramolecular systems based upon noncovalent binding for example hydrophobic interaction, electrostatic forces or van der Waals interactions have been widely studied due to the potential applications in the areas of molecular devices and biological mimics.<sup>1</sup> The significant developments in supramolecular chemistry especially based on cyclodextrins (CDs) have attracted considerable interests during decades, which could succeed in preparing new particular promising molecular devices such as molecular machines or molecular switches.<sup>2-3</sup>

Since A. Harada *et al.* reported the first “molecular necklace”, a polyrotaxane starting from  $\alpha$ -CD and poly (ethylene glycol) (PEG) in 1992, inclusion complexes (ICs) between CDs and different polymers and CD-based supramolecular polymers have attracted extensive attentions.<sup>4</sup> Besides hydrogen bonding, hydrophobic, electrostatic and van der Waals interactions between CDs and polymers, the size matching between the cross-sectional area of the polymer chains and the cavities of CDs also plays an important role in forming polyrotaxanes or polypseudorotaxanes,<sup>5</sup> which decides that not all polymers can form ICs with any one of three common  $\alpha$ -,  $\beta$ - and  $\gamma$ -CDs.

As a representative guest macromolecule for instance, PEG and its derivative copolymers are the most important research objects for many types of supramolecular structures using host-guest conjugates.<sup>6</sup> Up to now, PEG of molecular weight over

1000 dalton can form complexes with  $\alpha$ -CD to give crystalline polypseudorotaxanes with a channel-type structure and double-stranded ICs with  $\gamma$ -CD, but  $\beta$ -CD has never been found to form stable ICs in solution with PEG of any molecular weight probably due to the poorer size correlation.<sup>5-7</sup>

However,  $\beta$ -CD can form ICs with series of guests from small and thin molecules to large and thick polymers such as poly (propylene glycol) (PPG) from solution or solid state,<sup>8-10</sup> so it is still puzzling that PEG chains can penetrate the beaker-like tunnels of  $\beta$ -CDs yet ultimately slip out resulting in no ICs formation.

Taking into account the inclusion complexation process is a dynamic process with a threading-dethreading equilibrium of  $\beta$ -CDs, there may be other factors at play involving steric fittings, hydrophobic interactions, intermolecular hydrogen bonds and others supramolecular forces, so it is important to determine the most critical rolling factors in complex-forming between CDs and polymers.

It should be noted that H. Fujita *et al.*<sup>11</sup> once reported a molecular piston based on a thermoresponsive polyrotaxane prepared from  $\beta$ -CD and a PEG-*b*-PPG-*b*-PEG copolymer and it might be the first time that  $\beta$ -CD could be deduced to reside on the PEG segments at lower temperature in spite of a hypothesis idea. Soon afterwards in 2000, K.A. Udachin *et al.*<sup>12</sup> produced a solid polypseudorotaxane in a single crystal state between PEG and  $\beta$ -CD for the first time, in which the molar ratio of PEG segments to  $\beta$ -CD was 3:1. However, the preparation process of this polypseudorotaxane took

approximately one month to complete and the achieved inclusion complex was stable only for several hours.

Herein, we report an ABA-type PEG-based triblock polymer with a central hydrophobic methylene segment and PEG segments at both ends, which can form steady ICs with  $\beta$ -CD in aqueous solution based on previous research on IC forming between  $\beta$ -CD and dicarboxylic acids.<sup>13</sup>

## Results and discussion

### The inclusion process of ICs

To elucidate an inclusion process, the time evolution of turbidity, which can be expressed as absorbance or transmittance, is often used to provide interesting IC-forming information at a fixed wavelength of visible light.<sup>14</sup>

As shown in Fig.1, solution transmittance plots of  $\beta$ -CD, CP1113 and their corresponding IC from the initial state were recorded at 600 nm with a temperature falling rate of 15 °C min<sup>-1</sup>. When cooled from 80 °C, the aqueous solutions of  $\beta$ -CD, CP1113 had nearly no decrease in transmittance whereas the transmittance of their mixed solution decreased significantly to almost zero in several minutes, which revealed the formation and aggregation of a inclusion complex<sup>15</sup>. At a interval of 30 s in 3 min, the appearances of turbidity changes of the resulted IC at different intermediate states were shown in the inset pictures in Fig.1, there was a stark contrast between the starting and the final states.

Fig.1 Time dependent solution transmittance curves of  $\beta$ -CD, CP1113 and their inclusion complex (the initial concentration of  $\beta$ -CD, CP1113 were ca. 9.97 and 8.30 mmol L<sup>-1</sup>, respectively)

### Yields of ICs between CP1113 and $\beta$ -CD

Based on the solubility difference of  $\beta$ -CD in water between high and low temperatures of 80 °C and 20 °C, yields of ICs as a function of added amount of CP1113 in a volume-fixed  $\beta$ -CD saturated aqueous solution (expressed in concentration) were revealed in Fig.2 according to the detailed experimental results (see Table S1, ESI†).

In Fig.2, one can see that the yield of ICs increases gradually with the increase of CP1113 amount and slows down when enough CP1113 is added in 25 mL  $\beta$ -CD saturated aqueous solution. It is probable due to that the amount of CP1113 molecules accelerates the inclusion complexation<sup>14,16</sup> while a balance between complexation and decomplexation exists and works with the increasing amount of guest polymer and the corresponding highest yield is ca. 46.2 %.

Fig.2 IC yields as a function of amounts of added CP1113 with an initial molar concentration of 0.16 mol L<sup>-1</sup> of saturated  $\beta$ -CD solutions at 80 °C

### Fourier transform infrared (FTIR) analysis

FTIR spectra of  $\beta$ -CD, CP1113 and their corresponding inclusion complex IC1113 are presented in Fig.3.

In Fig.3a, the FTIR spectrum of  $\beta$ -CD shows a broad O–H stretching vibration band of hydroxyl at 3383 cm<sup>-1</sup>, a C–H stretching vibration band at 2926 cm<sup>-1</sup>, a bending vibration peak of the O–H bond at 1643 cm<sup>-1</sup>, a C–O symmetric stretching vibration band at 1157 cm<sup>-1</sup> and a C–O in C–O–C stretching vibration band at 1030 cm<sup>-1</sup>.<sup>17</sup>

Fig.3 FTIR spectra for  $\beta$ -CD, CP1113 and IC1113

For CP1113 in Fig.3b, the characteristic absorption bands maxima are assigned to 2872, 1736, 1107, 951 and 843 cm<sup>-1</sup>. At ca. 1736 cm<sup>-1</sup>, a strong infrared band appearing is due to asymmetric stretching vibration of >C=O and the absorption band at 1107 cm<sup>-1</sup> is due to an O–C–C asymmetric stretching vibration of the ester structure.

As can be seen in Fig.3c, all the characteristic absorption bands of CP1113 disappear or lower a lot due to inclusion infrared weakening effects and it reveals that the guest molecule CP1113 has been accommodated into the cavities of  $\beta$ -CD to form inclusion complex.<sup>13,18</sup>

### X-ray diffraction (XRD) analysis

The X-ray diffraction patterns of  $\beta$ -CD, CP1113 and IC1113 are presented in Fig.4, where the pattern of IC1113 is clearly not the simple addition of  $\beta$ -CD and CP1113. In Fig.4c, no characteristic diffraction peaks of  $\beta$ -CD and CP1113 appearing indicates there is no regular crystalline structure of  $\beta$ -CD or CP1113 and a new aggregation phase has been formed.<sup>19</sup>

For the pattern of IC1113, calculated according to the Bragg equation  $2d\sin\theta = n\lambda$  (where  $n$  is assigned to be 1), several new sharp reflections (asterisked in Fig.4c) appear at ca.  $2\theta = 5.91^\circ$ ,  $11.78^\circ$  and  $18.16^\circ$ , among which two main peaks at ca.  $2\theta = 11.78^\circ$  ( $d = 7.52 \text{ \AA}$ ) and  $18.16^\circ$  ( $d = 4.88 \text{ \AA}$ ) are the key features serving as a fingerprint to indicate that IC1113 likely assumes a channel-like pseudorotaxane structure.<sup>20-22</sup>

Fig.4 XRD patterns of  $\beta$ -CD, CP1113 and IC1113

Furthermore, another peak appearing at ca.  $2\theta = 5.91^\circ$ , where the corresponding interplanar spacing  $d$  is 14.95 Å and approximately twice the height of  $\beta$ -CD (7.8 Å), was ever presented in several previous  $\beta$ -CD/polymer correlative works<sup>19,23</sup> yet no detailed explanation was proposed. It may be attributed to the forming of molecular dimmers for a portion of  $\beta$ -CD molecules through intermolecular hydrogen bonds in our opinion.

### Thermogravimetric (TG) analysis

As shown in Fig.5a, the TG curve of  $\beta$ -CD is flat without mass loss below ca. 280 °C and shows a dramatic decomposition at ca. 320 °C with a total mass loss of about 75.0 % when heated to 500 °C.<sup>24</sup>

For CP1113 (Fig.5b), there are two stages for mass losing that can be obviously observed at ca. 25–324 °C and 324–500 °C, which can be attributed to the evaporation of residue water together with the polymer decomposition, the combustion of remnants, respectively. Furthermore, the TG curve of CP1113 has a main reaction zone centred at 397 °C and finally shows a small number of residues of about 1.9 %.

Fig.5 TG curves for (a)  $\beta$ -CD, (b) CP1113, and (c) IC1113

After inclusion complexation, the polypseudorotaxane of IC1113 undergoes two-step thermal degradation at 25–100 °C and 200–500 °C in Fig.5c. The first-stage decomposition with a mass loss of 6.5 % is due to water evaporation, the second stage shows a higher onset temperature for decomposition and a higher proportion of residues than that of CP1113, the better

thermal stability can be attributed to the formation of ICs with channel-type molecular structures.<sup>25</sup>

### Determination of stoichiometry

In order to determine the molar stoichiometry between  $\beta$ -CD and CP1113 in IC1113, <sup>1</sup>H-NMR spectroscopy has been employed and the <sup>1</sup>H-NMR spectrum of IC1113 is shown in Fig.6 in DMSO-*d*<sub>6</sub>, for the IC1113 precipitate derived from water is insoluble in water at room temperature.

In Fig.6, all resonance peaks attributed to  $\beta$ -CD, -CH<sub>2</sub>- and -CH<sub>3</sub> of CP1113 in the spectra are labeled and assigned to the corresponding protons (more details see Fig.S1 and Fig.S2, ESI†). By calculating the integrated areas of two independent peaks with relatively flat baseline, namely H-1 protons of  $\beta$ -CD (7H per molecule) and H-a of methylene protons of CP1113 (14H per molecule), the integral area ratio is ca. 3.9 and then the molar stoichiometry ratio between  $\beta$ -CD and CP1113 is ca. 7.8:1, basically consistent with the calculation results of ca. 8.1:1, based on the mass and yields of ICs (Table S1 and S2, ESI†).

Fig.6 <sup>1</sup>H-NMR (400MHz) spectrum of IC1113 in DMSO-*d*<sub>6</sub> at 298.15K

Since  $\beta$ -CD and the methylene segment of 11-13 carbon atoms can form channel-like IC structure at a molar ratio of 2:1,<sup>13, 26</sup> there is reason to believe that others at least 5 or 6  $\beta$ -CD molecules (the average number is 5.8) are also located on one CP1113 main chain (more details see Table S2, ESI†). This result verifies the conjecture proposed that some  $\beta$ -CDs may reside on the PEG segments when the supramolecular assembling behaviours between  $\beta$ -CD and a PEG-*b*-PPG-*b*-PEG copolymer has been studied.<sup>11</sup>

Furthermore, if specifically considering the molar ratio between EG segments and  $\beta$ -CD in IC1113 and deducting the  $\beta$ -CD amount possibly resided on the central methylene segment, the value is ca. 8.28:1 and is far greater than the ratio of 3:1 in a monoclinic crystal of PEG and  $\beta$ -CD (see Table S2, ESI†),<sup>12</sup> maybe it is because that  $\beta$ -CDs are more easy to slip when forming ICs in solution and the polymer chains extend in *trans*-conformation in solution rather than bunching-up in the central, wider rims of  $\beta$ -CD dimmers in solid state.<sup>12</sup>

In addition, the molar ratio between  $\beta$ -CD and PEG units in IC1113 is greater than that of ICs between  $\beta$ -CD and PEG-*b*-PPG-*b*-PEG, in which few  $\beta$ -CD molecules reside on PEG segments (see Table S2, ESI†).<sup>11</sup> It may be due to the central methylene segments in CP1113 are more hydrophobic than that of the central PPG segments in PEG-*b*-PPG-*b*-PEG, then the former is more favorable for ICs' forming through hydrophobic interactions.

### Mechanisms of inclusion complex formation between $\beta$ -CD and CP1113

From a macro perspective, about the general mechanisms of inclusion complexation between CDs and polymers, several recent studies summarize and suggest that the inclusion involves an enthalpy-driven and multi-stepped process<sup>14, 15, 27-29</sup> by researching the supramolecular adducts of  $\alpha$ -CD with PEG based polymers. For instance, P. Lo Nostro *et al* recently proposed a two-stepped mechanism consisting of "threading process" and "growth and aggregation",<sup>14</sup> while Travelet *et al* approved a three-stepped one including "threading of CDs", "formation of nanocylinders" and "aggregation of the nanocylinders".<sup>27</sup>

In both cases, no matter what is the difference between the above two views, threading of CDs onto the polymer chains plays the first important role in complex formation because this step is not simultaneous and affected by a lot of internal factors (polymer structure, size correlation, intermolecular interactions, steric restrictions, hydrophilicity or hydrophobicity, molecular weight etc.) and external factors (preparation methods, solvents, concentration, temperature, time etc.).

From a microscopic point of view, if considering the movements, locations of CD molecules and the corresponding intermolecular interactions involved in the process of complex formation and taking the formation of IC1113 as a specific example, one can see a "snapshot photograph" as depicted in Scheme 1, in which the neighboring  $\beta$ -CDs are arranged in a head-to-head or tail-to-tail order in order to maximize the numbers of hydrogen bonds.<sup>30</sup>

In Scheme 1, in a certain intermediate state for forming one pseudopolyrotaxane inclusion complex,  $\beta$ -CDs exist: (1) in the unbound state in aqueous solutions; (2) in threaded state at the ends of polymer chains with a certain degree of reversible de-threading, which can be partially inhibited by hydrophobic interactions and neighbouring threaded CDs; (3) in sliding motion along the polymer chain; (4) in aggregation state as dimmers via intermolecular hydrogen bonds.<sup>14, 28-29</sup>

Scheme 1 Sketch of the preparation process of IC1113

According to the molecular structure of CP1113, regardless of *gauche*- or *trans*- conformations adopted by the polymer backbone, the threading of  $\beta$ -CD onto PEG segments is easier than  $\alpha$ -CD because of the larger cavity size, while  $\beta$ -CD also has a greater tendency to de-thread at the same time. In other words, for  $\beta$ -CDs between states (1) and (2), there exists an equilibrium, which is mainly affected by concentration and temperature because  $\beta$ -CDs need pre-aggregate and the threading process is favoured by decreasing the temperature.<sup>14</sup>

Since the sliding motion is simultaneous when the threaded  $\beta$ -CDs begin interacting with each other,  $\beta$ -CDs in state (4) play an important role in forming pseudopolyrotaxanes in bundles or nanocylinders or even precipitates, thus a more hydrophobic environment is more helpful to stabilize  $\beta$ -CD for its cavity is hydrophobic and the hydrophobic effect is dominating the entire inclusion process.<sup>14</sup>

Although some inclusion complexes of  $\beta$ -CD only dissolve in strongly polar organic solvents such as DMSO and this leads to dissociation of ICs into free individual components,<sup>31</sup> 2D ROSEY spectra were measured to give more experimental evidence about the inclusion mechanism.

In the course of testing 2D ROSEY spectra, it was found that IC1113 dissolved much more difficultly than individual  $\beta$ -CD or CP1113 so that it was supposed that the formed ICs be dissociated or  $\beta$ -CDs tend to slide from the hydrophobic segment to PEG segments or even slide off, which might lead to no obvious chemical shifts or no cross correlation peaks when IC1113 was fully dissolved in DMSO-*d*<sub>6</sub>. Therefore, 2D ROSEY spectra were measured in the case of partial or total dissolution of IC1113 in DMSO-*d*<sub>6</sub> to verify this hypothesis.

As can be seen in Fig.7, there are four kinds of cross correlation peaks with different strengths, which are attributed to the supramolecular interactions between H3, H5 of  $\beta$ -CD and different kinds of protons (marked in the inset of Fig.6) of CP1113, although peaks B and C are weak and not clear enough. Cross correlation peaks A and D involving the central methylene segments and two PEG units close to the ester groups of CP1113 reveals that there are stronger interactions between



H3, H5 of  $\beta$ -CD and H-a, H-d of CP1113, thus it can be deduced that  $\beta$ -CD does form ICs with CP1113 before.

Fig.7 2D ROSEY spectrum of IC1113 partially dissolved in DMSO-d<sub>6</sub> at 298.15K with 5 min of ultrasonication (four kinds of cross peaks with different strength are assigned to the interactions between H3, H5 of  $\beta$ -CD and : A. H-a, B. H-b, C. H-c, D. H-d of CP1113)

However, it is noteworthy that when the IC1113 is fully dissolved, only peaks D in 2D ROSEY spectrum remain appearing (see in Fig.S4, ESI<sup>†</sup>), in case of which  $\beta$ -CDs may tend to slide from the central hydrophobic segment to PEG segments, or some of them may even slide off from the polymer chains to be dissociated.

Furthermore, to investigate the effects of hydrophobic segmental lengths on the formation of ICs, three triblock analogues were prepared by reacting MePEG1100 with oxalic acid, succinic acid and adipic acid, respectively. Similar to our previous results,<sup>32</sup> none of them forms ICs with  $\beta$ -CD (see in Fig.S6, ESI<sup>†</sup>).

For triblock polymer CP1102 derived from oxalic acid and MePEG, due to the absence of central hydrophobic segments, it is difficult for the polymer to stabilize  $\beta$ -CDs and make them bind and aggregate, so there is no ICs occurring. For the other two PEG-based polymers CP1104 and CP1106 respectively prepared from succinic acid and adipic acid, both of which nevertheless can form ICs with  $\beta$ -CD in a molar ratio of 1:1,<sup>33-34</sup> the relatively shorter hydrophobic segments can not sufficiently stabilize  $\beta$ -CDs either under the circumstance of relatively poor size correlations. Maybe it can be roughly inferred accordingly that a longer hydrophobic segment is needed to form ICs involving at least one  $\beta$ -CD dimer binding in our opinion.

Moreover, another triblock polymer CP5013 synthesized from Me-PEG5000 and 1, 13-tridecanedioic acid forms no ICs with  $\beta$ -CD either, probably because the two ending PEG segments are too long and the threading, sliding motions of  $\beta$ -CDs become more time-consuming, so that  $\beta$ -CDs cannot effectively thread and aggregate resulting in no ICs.

Therefore, others supramolecular interactions such as hydrogen bonds between neighbouring  $\beta$ -CDs must be considered in addition to hydrophobic interactions. Ross and Rekharsky have proposed that the hydrogen bond stability decreases with increased temperature but the stability of the hydrophobic interaction remains essentially constant.<sup>35</sup> So when decreasing the temperature for preparing ICs, the complex stability caused by the hydrophobic interactions is not influenced however hydrogen bonds become more stable and improve the complex stability.

Although the hydrogen bonding interactions can build cyclodextrins even to fibres,<sup>36-37</sup> limited to the bonding strength and distance in solutions, sole hydrogen bonding interaction is insufficient to aggregate too many  $\beta$ -CDs and need to be coordinated with the hydrophobic interaction resulting in a hydrophobic stabilizing and hydrogen-bonding inducing effect, with which  $\beta$ -CDs bind together via hydrogen bonds based on the hydrophobic interaction with hydrophobic segments of the guest polymer especially in the case of a poor size correlation.

Therefore, it is believed that the reason why PEG with any molecular weight cannot form pseudopolyrotaxanes with  $\beta$ -CDs in aqueous solutions even with the presence of hydrogen bonding interactions, is mainly due to the lack of hydrophobic interactions rather than the poor size correlation between them. Moreover, hydrogen bonds between neighbouring CD cannot drive too many CD all at once to thread onto a hydrophilic

chain starting far from a hydrophobic centre, so it is difficult for all CD to form complexes with some PEG-based copolymers.

Based on the hydrophobic stabilizing and hydrogen-bonding inducing effect, which “amplifies” the hydrophobic interactions along a hydrophilic polymer chain, it is hopeful to achieve more interesting ICs between the relatively inexpensive  $\beta$ -CD and common thin linear polymers by appropriately introducing hydrophobic structures or modification of them, which may open new prospects of pseudopolyrotaxanes and polyrotaxanes.

## Conclusions

In summary, we reported the formation of inclusion complexes between a PEG-based triblock polymer and  $\beta$ -CD in aqueous solution from a relatively high temperature and the highest yield was 46.2%. The achieved IC1113 was characterized and the results revealed that  $\beta$ -CDs threaded onto the polymer main chains to form a channel-type pseudopolyrotaxane, in which  $\beta$ -CDs bind at least on the central hydrophobic segments as well as the PEG units close to the ester groups. When dissolved IC1113 in DMSO,  $\beta$ -CDs may slide off from the polymer chains to be dissociated to free components.

The molar stoichiometry ratio between  $\beta$ -CD and CP1113 in IC1113 was determined to be 7.8:1, so that  $\beta$ -CDs accommodated not only on the methylene segments but more on the PEG segments of CP1113. Eventually, the formation mechanisms of IC1113 were discussed and it was concluded that hydrophobic and hydrogen bonding interactions played the most important roles in this process with a special “hydrophobic amplification” effect.

## Experimental

### Materials

$\beta$ -CD was purchased from Sinopharm Chemical Reagent Co., Ltd and mono-methoxy-poly (ethylene glycol) (MePEG, 1100 and 5000 Da) was purchased from Fluka Company. 1,13-tridecanedioic acid (DA13) was provided by Shanghai Cathay Biotechnology Co., Ltd as a gift and used after purification by ethanol. Oxalic acid, succinic acid and adipic acid were of analytical grade and purchased from Aladdin Industrial Corporation. Other reagents such as absolute ethanol, toluene, concentrated sulfuric acid, sodium hydroxide and so on, were of analytical grade and used as received.

### Synthesis of the ABA-type PEG-based triblock polymers

MePEG (0.01 mol, 11.0 g) and 50 mL newly distilled toluene were put into a 100-mL one-necked round-bottom flask equipped with a Dean-Stark trap, the solution was then heated with stirring to reflux for 24 h at 120 °C to remove the possible hygroscopic water. Then re-crystallized DA13 (1.21g, 0.005 mol) and a few drops of concentrated sulfuric acid as catalyst were added in and the reaction was continued at reflux for 3 days, the water produced in the condensation reaction was also separated with the Dean-Stark trap.

After cooling, an appropriate amount of NaHCO<sub>3</sub> solid powder was added into the solution to neutralize the sulfuric acid and then filtrated off. Finally, toluene was distilled off and the polymer CP1113 (H<sub>3</sub>COEG<sub>24</sub>OOC(CH<sub>2</sub>)<sub>11</sub>COOEG<sub>24</sub>OCH<sub>3</sub>) was achieved as a wax-like solid with a yield of ca. 98 %.

Others four triblock polymers, namely CP1102, CP1104, CP1106 and CP5013, were prepared from two MePEGs and

different diacids by following the above procedures with only specific feeding quality varying.

### Preparation of ICs between CP1113 and $\beta$ -CD

A series of ICs between CP1113 and  $\beta$ -CD were obtained by the co-precipitation method as follows. With constant stirring at 80 °C, different amount of solid CP1113 were respectively added into saturated aqueous solutions of  $\beta$ -CD, which were fixed to be 25 mL containing 4.58 g (ca. 4.0 mmol)  $\beta$ -CD and homogeneous solutions were rapidly formed.

When the above mixed solutions were stopped heating and cooled to 20 °C, each of them turned to white turbid emulsions with pearly lusters accompanied with certain amount of apparent  $\beta$ -CD crystal precipitated at the bottom of the flasks. For one resulted mixture, the whole upper white emulsion was pipeted out, then centrifuged to achieve a white crystalline IC powder, which was washed with cold distilled water of 20 °C for three times and then dried under vacuum for further characterization. The obtained ICs can be stably stored for more than one month at room temperature and has a certain stability below 100 °C despite of the melting point about 41.1 °C of unwrapped CP1113, which is quite different from the several-hour stable polypseudorotaxane of PEG and  $\beta$ -CD prepared with an excess of PEG in case of a very small amount of water.<sup>12</sup>

Eventually, the acquired ICs and the corresponding unbound  $\beta$ -CDs were accurately weighed to calculate the yields and one representative produced IC (IC1113) with the highest yield was subsequently characterized.

### Characterizations and Apparatus

The transmittances of the aqueous solution of CP1113, the initial  $\beta$ -CD solution and their mixing solution before and after the formation of IC1113, were measured at 600 nm to investigate the inclusion process using a Shimadzu UV-2550 UV-VIS spectrophotometer.

Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 510p FTIR spectrometer at frequencies between 400 and 4000  $\text{cm}^{-1}$  at 2  $\text{cm}^{-1}$  resolution.

X-ray diffraction (XRD) patterns of  $\beta$ -CD, CP1113 and IC1113 in powder in the range of  $2\theta = 5^\circ$  and  $70^\circ$  were obtained with a Philips X'Pert PRO diffractometer, using a Ni-filtered  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.5415 \text{ \AA}$ ) on Si substrates with an accelerating voltage of 60 kV and current of 50 mA.

TG curves were obtained on a Shimadzu TGA-50 thermometer at a heating rate of 10 °C  $\text{min}^{-1}$  with nitrogen purging from 25 °C to 500 °C.

<sup>1</sup>H-NMR spectra of IC1113 were recorded on a Bruker Avance-400 NMR spectrometer in DMSO- $d_6$  to elucidate the stoichiometry of the complex.

2D ROSEY spectra were respectively recorded on a Bruker Avance-400 NMR spectrometer with ca. 25mg IC1113 partially or fully dissolved in 0.5 mL DMSO- $d_6$  by ultrasonic dissolution method for different time.

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### Notes

<sup>a</sup>School of Biological and Chemical Engineering, Anhui Polytechnic University, Wuhu, 241000, P.R.China. Email: [gaojiangang@ahpu.edu.cn](mailto:gaojiangang@ahpu.edu.cn); Tel: +86-553-2871254

<sup>b</sup>School of Chemistry and Materials Science, University of Science and Technology of China, Hefei, 230026, P.R.China Email: [zqjm@ustc.edu.cn](mailto:zqjm@ustc.edu.cn)

<sup>c</sup>Anhui Key Laboratory of Optoelectronic Science and Technology, Hefei, 230026, P.R.China

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### References

- J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and J. M. Lehn, *Comprehensive Supramolecular Chemistry*, 1<sup>st</sup> Edn, Oxford: Pergamon, 1996, 1-11.
- A. Harada, *Acc. Chem. Res.*, 2001, **34**, 456-467.
- G. Wenz, *Angew. Chem. Int. Ed. Engl.*, 1994, **33**, 803-822.
- A. Harada, J. Li and M. Kamachi, *Nature*, 1992, **356**, 325-327.
- A. Harada, Y. Takashima and H. Yamaguchi, *Chem. Soc. Rev.*, 2009, **38**, 875-882.
- A. Harada, A. Hashidzume and Y. Takashima, *Adv. Polym. Sci.*, 2006, **201**, 1-43.
- A. Harada, J. Li and M. Kamachi, *Nature*, 1994, **370**, 126-128.
- A. Harada, M. Okada, J. Li and M. Kamachi, *Macromolecules*, 1995, **28**, 8406-8411.
- S.A. Nepogodiev and J. F. Stoddart, *Chem. Rev.*, 1998, **98**, 1959-1976.
- S. Liu, J. Cai, L. Ren, L. Wang and Y. J. Wang. *RSC Adv.*, 2014, **4**, 18608-18611.
- H. Fujita, T. Ooya and N. Yui, *Macromolecules*, 1999, **32**, 2534-2541.
- K. A. Udachin, L. D. Wilson and J. A. Ripmeester, *J. Am. Chem. Soc.*, 2000, **122**, 12375-12376.
- J. G. Gao, Y. J. Ding, H. W. Chen, Q. P. Song and Q. J. Zhang, *Chin. J. Chem. Phys.*, 2008, **21**, 387-392.
- P. Lo. Nostro, L. Giustini, E. Fratini, B.W. Ninham, F. Ridi and P. Baglioni, *J. Phys. Chem. B.*, 2008, **112**, 1071-1081.
- E. Sabadini, F.C. Egidio and T. Cosgrove, *Langmuir*, 2013, **29**, 4664-4669.
- J. Peet, C. C. Rusa, M. A. Hunt and A. E. Tonelli, C.M. Balik, *Macromolecules*, 2005, **38**, 537-541.
- C. Liu, W. Zhang, Q. Wang, Y. Sun and G. W. Diao, *Org. Biomol. Chem.*, 2013, **11**, 4993-4999.
- H. Q. Liu, *China Patent*, 2005, 200410060918.1.
- Y. C. Su, W.C. Chen and F. C. Chang, *Polymer*, 2005, **46**, 1617-1623.
- H. Jiao, S.H. Goh and S. Valiyaveetil, *Macromolecules*, 2002, **35**, 3997-4002.
- A. Harada, *Adv. Poly. Sci.*, 1997, **133**, 141-191.
- B. Wang, J. He, D. H. Sun, R. Zhang, B. X. Han, Y. Huang and G. Y. Yang, *Eur. Polym. J.*, 2005, **41**, 2483-2487.
- J. Huang, Z. Y. Zhou, M. Wei, Y. Chen and P. R. Chang, *J. Appl. Polym. Sci.*, 2008, **107**, 409-417.

- 24 F. Giordano, C. Novak, J. R. Moyano, *Thermochim. Acta.*, 2001, **380**, 123-151.
- 25 J. C. Huang, X. Li, T. T. Lin, C. B. He, K.Y. Mya, Y. Xiao and J. Li, *J. Polym. Sci. Part B: Polym. Phys.*, 2004, **42**, 1173-1180.
- 26 S. Makedonopoulou, A. Tulinsky and I. M. Mavridis, *Supramol. Chem.*, 1999, **11**, 73-81.
- 27 C. Travelet, G. Schlatter, P. Hébraud, C. Brochon, A. Lapp and G. Hadziioannou, *Langmuir*, 2009, **25**, 8723-8734.
- 28 A. Becheri, P. Lo Nostro, B.W. Ninham and P. Baglioni, *J. Phys. Chem. B.*, 2003, **107**, 3979-3987.
- 29 M. Ceccato, P. Lo Nostro and P. Baglioni, *Langmuir*, 1997, **13**, 2436-2439.
- 30 C. P. A. Anconi, C. S. Nascimento Jr., W. B. De Almeida and H. F. Dos Santos, *J. Phys. Chem. C.*, 2012, **116**, 18958-18964.
- 31 G. Wenz, B. H. Han and A. Muller, *Chem. Rev.*, 2006, **106**, 782-817.
- 32 J. G. Gao, *Ph.D. Thesis*, University of Science and Technology of China, 2007.
- 33 Y. V. Lisnyak, A.V. Martynov, V.N. Baumer, O.V. Shishkin and A.V. Gubskaya, *J. Incl. Phenom. Macrocycl. Chem.*, 2007, **58**, 367-375.
- 34 O. Csernak, A. Buvári-Barcza, J. Samu and L. Barcza, *J. Incl. Phenom. Macrocycl. Chem.*, 2005, **51**, 59-63.
- 35 P. D. Ross and M.V. Rekharsky, *Biophys. J.*, 1996, **71**, 2144-2154.
- 36 A. Celebioglu and T. Uyar, *RSC Adv.*, 2013, **3**, 22891-22895.
- 37 Y. J. Ahn, Y. W. Kang, M. K. Ku, Y. H. Yang, S. H. Jung and H. S. Kim, *RSC Adv.*, 2014, **4**, 8200-8208.

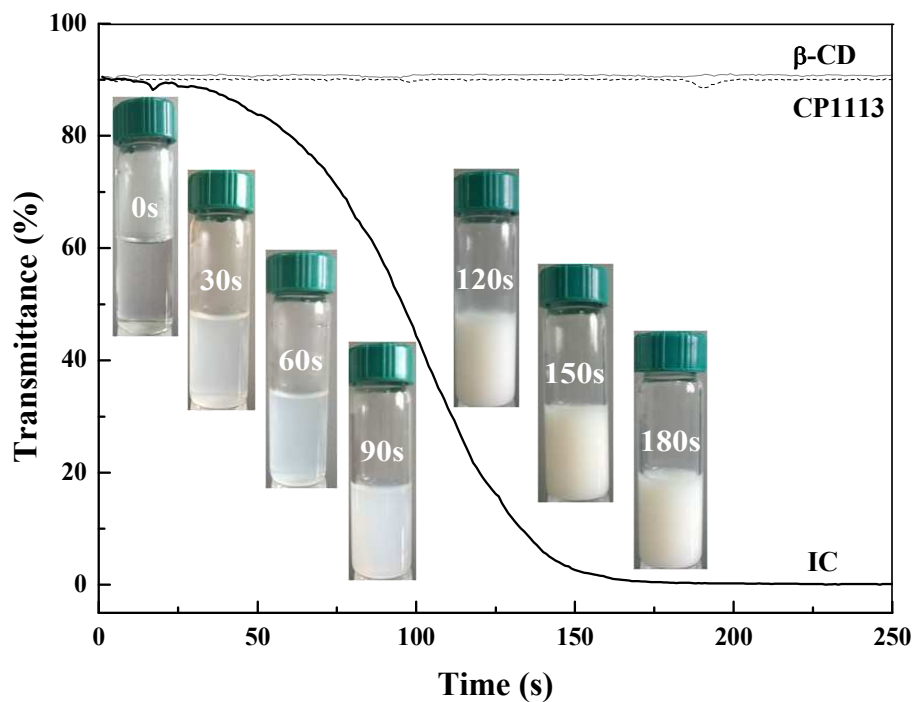


Fig.1 Time dependent solution transmittance curves of  $\beta$ -CD, CP1113 and their inclusion complex (the initial concentration of  $\beta$ -CD, CP1113 were ca. 9.97 and 8.30  $\text{mmol L}^{-1}$ , respectively)

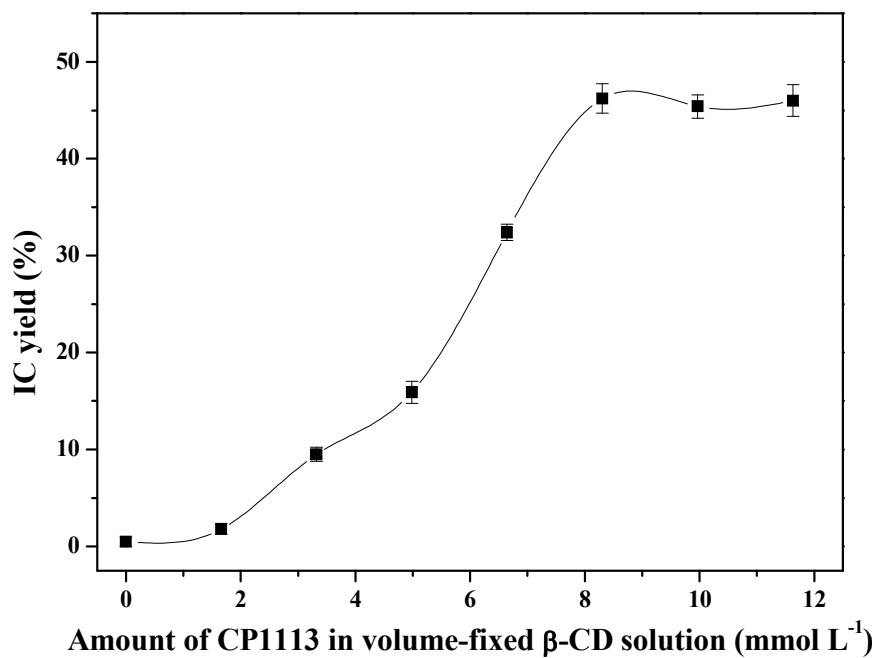


Fig.2 IC yields as a function of amounts of added CP1113 with an initial molar concentration of 0.16  $\text{mol L}^{-1}$  of saturated  $\beta$ -CD solutions at 80  $^{\circ}\text{C}$



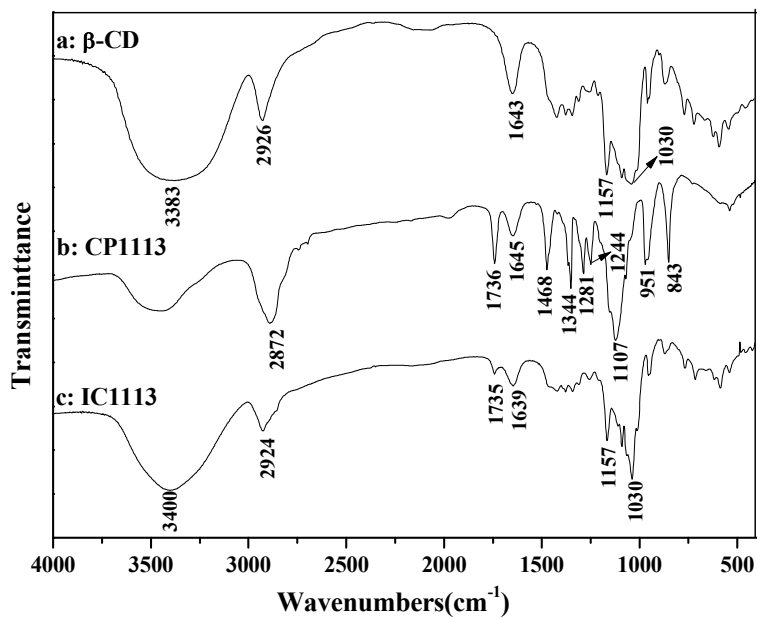


Fig.3 FTIR spectra for  $\beta$ -CD, CP1113 and IC1113

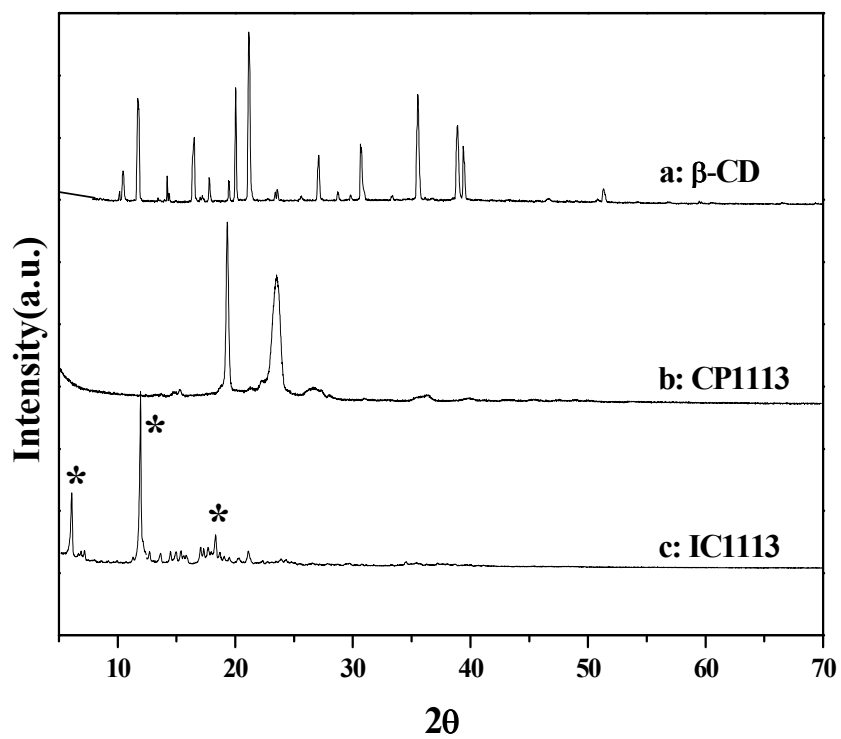


Fig.4 XRD patterns of  $\beta$ -CD, CP1113 and IC1113

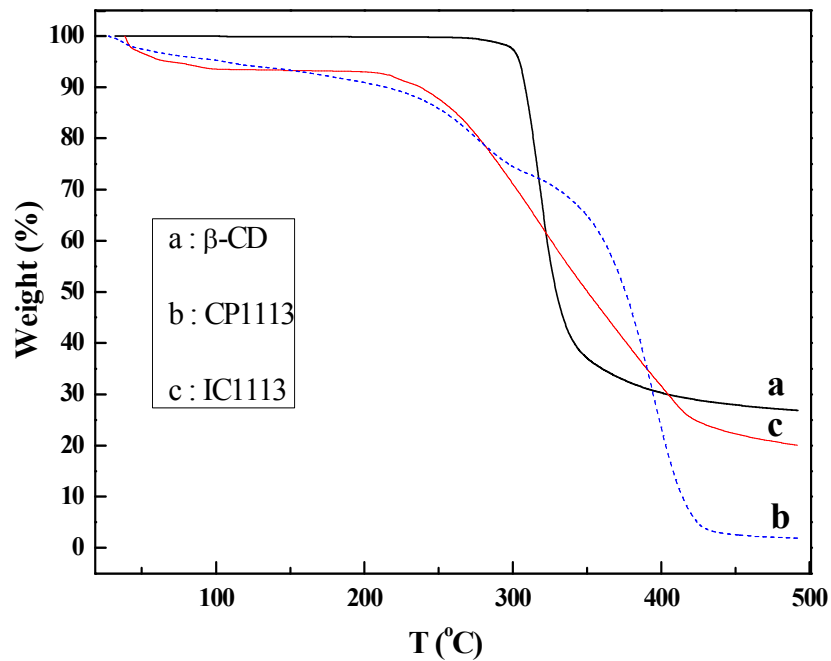


Fig.5 TG curves for (a)  $\beta$ -CD, (b) CP1113, and (c) IC1113

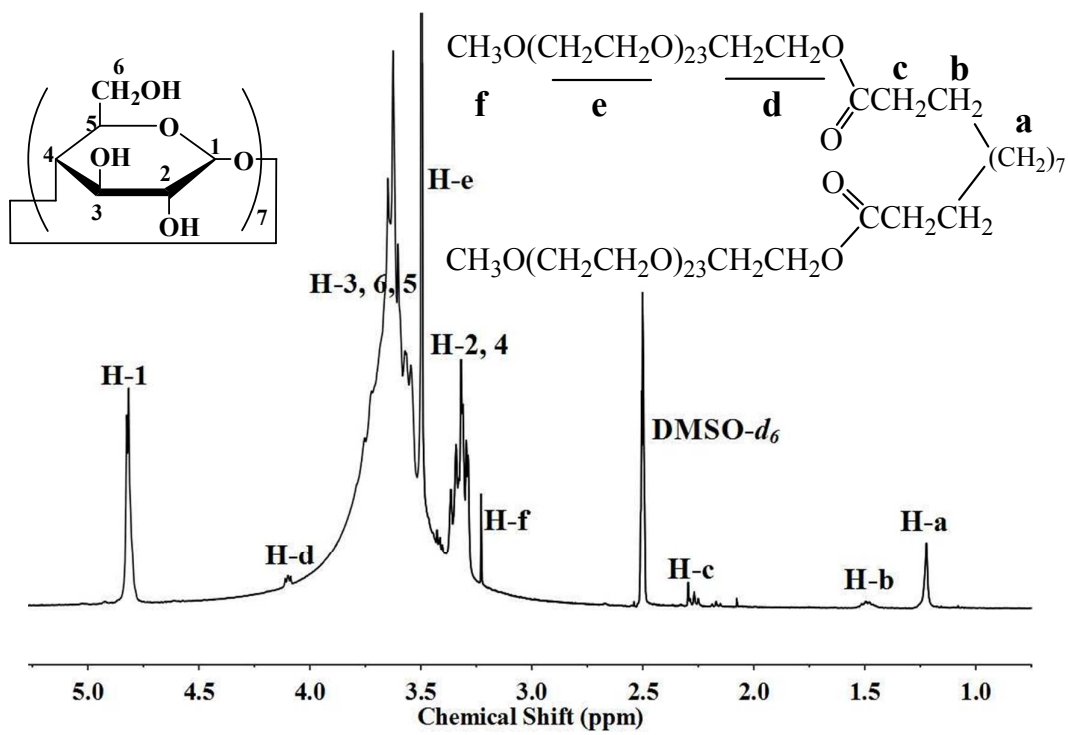
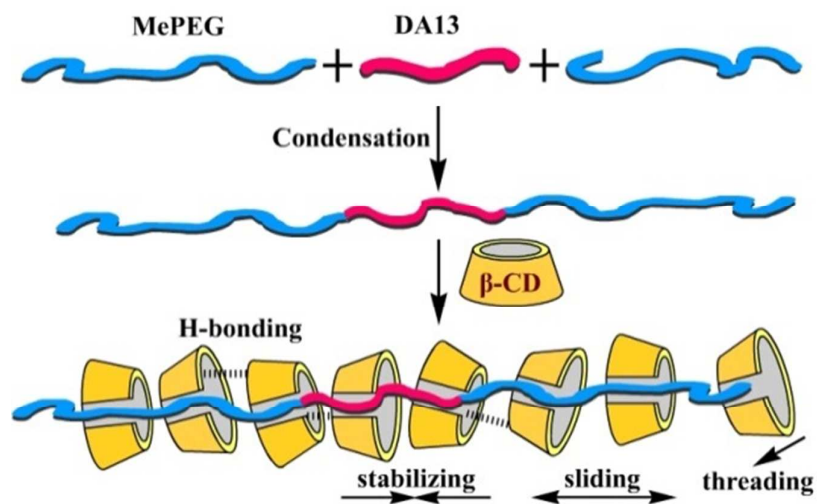


Fig.6  $^1\text{H-NMR}$  (400MHz) spectrum of IC1113 in  $\text{DMSO-}d_6$  at 298.15 K



Scheme 1 Sketch of the preparation process of IC1113

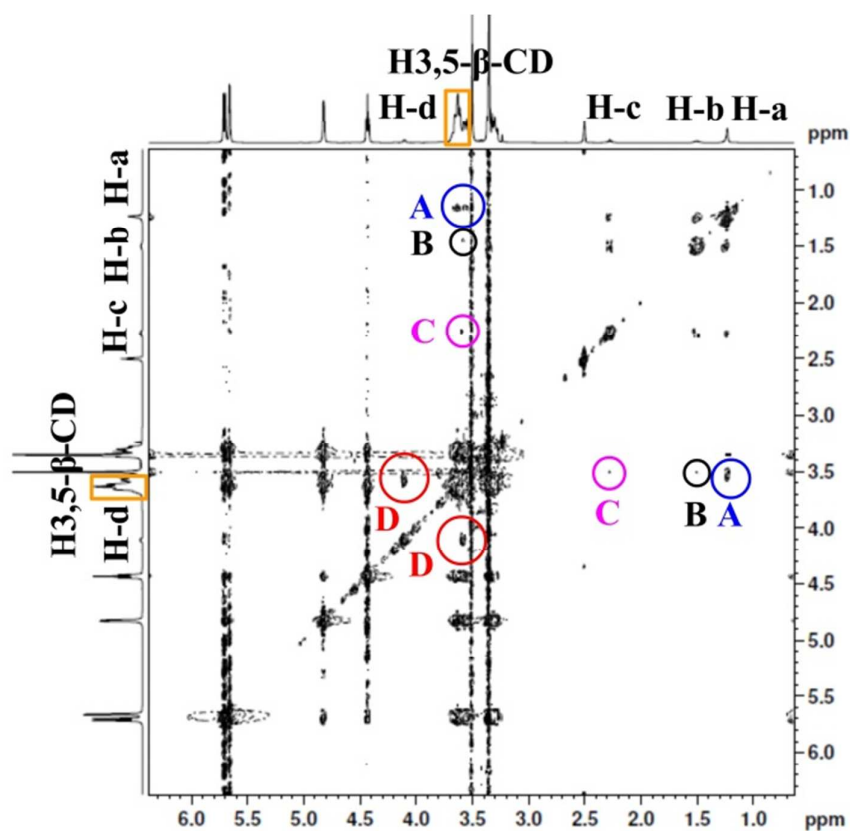


Fig.7 2D ROSEY spectrum of IC1113 partially dissolved in DMSO-d<sub>6</sub> at 298.15K with 5 min of ultrasonication (four kinds of cross peaks with different strength are assigned to the interactions between H<sub>3</sub>, H<sub>5</sub> of  $\beta$ -CD and : A. H-a, B. H-b, C. H-c, D. H-d of CP1113)