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Formation of [3]Pseudorotaxanes from β -cyclodextrin and a Series of Dicarboxylic Acids with Their Corresponding α, ω -alkanedicarboxylate AnionsJian-gang Gao^{a,b}, Yu-jie Ding^a, Hong-wei Chen^b, Qing-ping Song^a, Qi-jin Zhang^{b*}*a. Department of Biochemistry and Engineering, Anhui University of Technology and Science, Wuhu 241000, China**b. Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei 230026, China*

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Inclusion complexes between β -cyclodextrin (β -CD) and a series of dicarboxylic acids (DA_n , $n=11-15$) were prepared by co-grinding and co-precipitation methods and the [3]pseudorotaxane structure of them was elucidated by FTIR, DTA and XRD characterizations. Inclusion complexes of β -CD and α, ω -alkanedicarboxylate anions (DA_n^{2-}) were acquired by neutralizing β -CD/ DA_n different inclusion complexes with sodium hydroxide and the structure was also proved to be a pseudorotaxane structure by $^1\text{H-NMR}$ spectra and NOESY spectrum. Both the inclusion complexes of β -CD/ DA_n and β -CD/ DA_n^{2-} adopt the [3]pseudorotaxane structure with β -CD arranged in dimers threaded onto one aliphatic chain and the binding mode of 1:1 inclusion complex was excluded based on the consideration of chain conformations.

Key words: β -cyclodextrin, Inclusion complex, Dicarboxylic acid, α, ω -alkanedicarboxylate anion**I. INTRODUCTION**

Cyclodextrins (CDs) are truncated cone shaped molecules made up of elementary glucopyranose units joined together by α -1,4 linkages forming a torus-shaped ring structure with hydrophobic and nanocavities, within which certain guest molecules can be encapsulated due to the van der Waals' forces, hydrophobic interactions and so on [1-3]. Three commonly available CDs consisting of 6 (α), 7 (β), or 8 (γ) units have a cavity of 5.7, 7.8, or 9.5 Å respectively [4] and different inclusion complexes (ICs) with the above three CDs have been prepared and studied for usages in pharmaceutical, organic, analytic and inorganic chemistry, and in polymer science [5-10].

It is evident that the host-guest recognition of small molecules plays an essential role in the building of supramolecular structures [11]. Self-assembling supramolecular systems based upon noncovalent binding, such as, hydrophobic interaction, electrostatic forces, or van der Waals interactions, have attracted considerable interest due to potential applications in the areas of molecular devices and biological mimics [11-14]. Recently, much attention has been focused on particular promising structures such as pseudorotaxanes, rotaxanes, and catenanes [15-20] originating from the formation of inclusion complexes between CDs and low molecular compounds.

For a long time, many researchers have reported the inclusion behavior of CDs and series of guests such as derivatives of adamantane (e.g. adamantane-1-carboxylic acid) [21-24], naphthenic acids [25,26], and cholic acids [27,28] preferentially grounding on the better molecular size-matching effects between hosts and guests. However, only a few papers have been published concerning inclusion complexes of CDs and aliphatic compounds such as monocarboxylate or dicarboxylate anions or their corresponding aliphatic acids (or diacids) especially for β -CD as the host.

Watanabe *et al.* reported a study of CDs- α, ω -alkanedicarboxylate anion complexes by $^1\text{H-NMR}$ spectroscopy. They argued that α -CD formed but β -CD gave no evidence of complexation with α, ω -alkanedicarboxylates in aqueous solution [29]. However, Wilson *et al.* studied the inclusion behavior of α - or β -CD with alkyl monocarboxylate anions by $^1\text{H-NMR}$ spectroscopy and they found β -CD/alkyl monocarboxylate anions inclusion complex did have complex-induced shift (CIS) [30].

Additional studies have been reported by employing calorimetric [31,32] and potentiometric [33] techniques to investigate the stability of the complexes formed between α - or β -CD and α, ω -alkanedicarboxylate guests under basic or acidic conditions. The conclusions derived from the above works are somewhat divergent as to inclusion or non-inclusion, the binding mode, the magnitudes of the binding constants and the type of host-guest stoichiometry.

Wilson *et al.* further studied the inclusion behavior of β -CD/DM- β -CD (heptakis-(2,6-di-O-methyl)- β -CD) and α, ω -alkanedicarboxylate by a volumetric study

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[34]; they came to the conclusion that in all cases β -CD or DM- β -CD and the α, ω -alkanedicarboxylate formed a stoichiometry of 1:1 inclusion complexes involving the methylene chain threaded through the cavities of CDs.

In addition, the inclusion behavior of β -CD and long-chain aliphatic molecules was studied and the binding mode involved the formation of a [3]pseudorotaxanes (two β -CD monomers arranged in dimers) [35]. Further research on dimeric β -CD complexes of aliphatic monocarboxylic or α, ω -dicarboxylic acids having 12-16 carbon atoms gave consistent conclusions [36-39]. In particular, Makedonopoulou *et al.* performed a work on inclusion complex of β -CD and 1,14-tetradecanedioic acid and deduced that a [3]pseudorotaxane was formed, in which a barrel-like dimer of β -CD had been threaded onto a molecule of the aliphatic acid [40]. Csernak studied the H-bonding interactions between half dissociated diethyl malonic (diethyl propanedioic) acid and β -CD then concluded that the protruding functional groups of the guest enhancing the stability of the inclusion complexes [41].

In present work, we report the synthesis of a series of inclusion complexes (ICs) from β -CD and dicarboxylic acids (DA_n , $n=11-15$), the structure of which was elucidated by FTIR, DTA, and XRD characterization. Their corresponding inclusion complexes of β -CD and α, ω -alkanedicarboxylate anion (DA_n^{2-}) were acquired by neutralizing the ICs of β -CD/ DA_n with sodium hydroxide and the pseudorotaxane structure was proved with $^1\text{H-NMR}$ and 2D NOSEY spectrum.

II. EXPERIMENTS

β -CD was purchased from Shanghai Yuanju Biological Science and Technology Co. Ltd. and was used after recrystallization and determined to contain nine water molecules on average after drying. Dicarboxylic acids were received from Shanghai Cathay Biotechnology Co. Ltd. as a gift and used after purification from ethanol.

β -CD and DA_n inclusion complexes were prepared using two methods: co-grinding (kneading) and co-precipitation.

In the co-grinding preparation, β -CD (12.5 mmol, 14.19 g) and DA_n (5 mmol, for DA14, 1.29 g) were uniformly mixed and then co-ground for 30 min in solid state without heating or adding water (dry-grinding) in an agate mortar. Then a white wax-like powder with different appearance from β -CD or DA_n appeared and the mixture was collected and subsequently washed with warm water of temperature 45 °C several times to remove the excess amount of β -CD and acquire ICs.

In the preparation by co-precipitation, an excess amount of β -CD (12.5 mmol, 14.19 g) was dissolved in 75 mL deionized water at 80 °C to form a saturated solution. DA_n (5 mmol) was fully dissolved in 10 mL ethanol then dripped into β -CD saturated solution under strong stirring to form a mixed solution at

80 °C. After refluxing for 12 h, the mixed solution was cooled to 20 °C then a precipitate separated out, which was subsequently filtrated and washed with 45 °C warm water as above. The separated powders revealed white wax-like appearance similar to that of preparation by co-grinding.

All the ICs were dried under vacuum after preparation and separation for further determination.

β -CD/ DA_n^{2-} inclusion complexes were prepared by neutralizing the excess amount of the above β -CD and DA_n inclusion complexes with sodium hydroxide then the ICs were acquired by water-evaporating and dring.

Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 510p FTIR spectrometer with OMNIC software at frequencies from 400 cm^{-1} to 4000 cm^{-1} with a resolution of 2 cm^{-1} . All samples were thoroughly mixed with KBr and pressed into pellets, except for the β -CD and DA_n physical mixture. β -CD and DA_n physical mixture was characterized by triturating two components respectively with KBr and then carefully mixed before pressing into pellets to avoid co-grinding effects. X-ray diffraction (XRD) patterns were taken on an MXP4HF X-ray apparatus equipped with a RKV-86 flat-film camera using a Cu $K\alpha$ radiation filtered on Ni (1.5415 Å) with following parameters: voltage, 30 kV; current, 30 mA; scan rate, 1°/min. β -CD, DA_n , their physical mixture, and ICs were characterized in powder on silicon substrates. Differential thermal analysis (DTA) curves were obtained on a TA-50 (SHIMADZU company) thermalmeter at a heating rate of 10 °C/min under purge gas of nitrogen from 25 °C to 400 °C. $^1\text{H-NMR}$ spectra and NOESY spectrum were recorded on a 400-MHz AVANCE AV-400NMR spectrometer in D_2O solution.

III. RESULTS AND DISCUSSION

FTIR spectra for β -CD, DA_n (for example DA14), β -CD/ DA_n mixture, and β -CD/ DA_n ICs are presented in Fig.1 (FTIR spectra of the others DA_n s can be seen

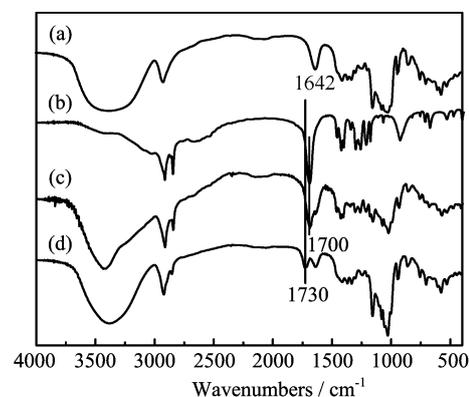


FIG. 1 FTIR spectra of (a) β -CD, (b) DA14, (c) physical mixture of β -CD/DA14, and (d) ICs of β -CD/DA14.

in the supporting information).

As can be seen in Fig.1(c), no new absorption peaks occurs and the band corresponding to the HOH bending mode of water within the β -CD cavity at 1641 cm^{-1} does not overlap the carbonyl band of DA_n . The spectrum of β -CD/ DA_n physical mixture should then correspond to the addition of the spectra of β -CD and DA_n (Fig.1 (a) and (b) respectively) in an adequate ratio.

However, in contrast with the physical mixture, the carbonyl band of ICs (Fig.1(d)) has evidently shifted to a higher frequency (from 1700 cm^{-1} to 1730 cm^{-1}), which does not match that of pure DA_n or its mixture with β -CD. The red shift of 30 cm^{-1} of the carbonyl band can be most probably attributed to the H-bond interactions between carbonyl groups of the guest and the 6-hydroxyl groups of β -CD [42,43] so that the absorbance intensity is significantly lowered [44].

In Fig.2, XRD patterns of β -CD, DA14, their physical mixture, and the inclusion complex are presented. Figure 2 (a) and (b) show the high crystalline properties of pure β -CD and DA14 respectively. An overlapping effect of diffraction patterns between β -CD and DA14 is observed in Fig.2(c) even though not all diffraction peaks precisely match. A comparison of XRD patterns of the complexes with those of the pure parent materials or mixture reveals the formation of a new crystal lattice of the inclusion complexes [45].

In detail, the inter-planar distances in the XRD patterns of β -CD and DA14 were characterized by values which did not occur in the main XRD patterns of the inclusion complex (e.g. d values of 7.51, 4.09, 3.71, 2.96, 2.20 Å for DA14 and 7.08, 6.42, 4.08, 3.89, 3.12, 2.79, 2.45, 2.26 Å for β -CD). Of special interest is the appearing of a new strong diffraction peak at ca. $2\theta=11.52^\circ$ ($d=7.65\text{ Å}$) and 17.71° ($d=5.05\text{ Å}$) suggesting that the β -CD molecules in the complex are in a more ordered state [46]. Actually, the inclusion complex of CDs with low-molecular weight compound can be classified as either "cage-type" or "channel-type" structure [47]. The appearance of two sharp peaks in

inclusion complexes at ca. $2\theta=11.52^\circ$ ($d=7.65\text{ Å}$) and 17.71° ($d=5.05\text{ Å}$) is the key feature serving as a fingerprint to indicate the channel-type structures of inclusion complex [48]. Namely, the β -CD and DA14 IC exhibits packing different from that of the free β -CD and possesses a channel structure similar to those of other β -CD based polypseudorotaxanes [48,49].

The pattern of this complex (Fig.2(d)) is also similar to that of the columnar inclusion complexes between β -CD and adamantane-modified polybenzoxazines [50], poly(1,3-dioxolane) (PDXL) [51], poly(propylene glycol) (PPG) [52], polyaniline (PANI) [53], and poly(neopentyl glycol sebacate) (PNGS) [46]. This implies that the β -CD molecules may be threaded on the chain of DA14. Based on the chemical structures of β -CD and dicarboxylic acids [40], it is deduced that the inclusion complex has a pseudorotaxane structure.

The patterns of IC11-IC15 (ICs corresponding to DA11-DA15 respectively) are similar to each other, which reveals that all the dicarboxylic acids can form a columnar structure with β -CD (seen in supporting information).

DTA curves of β -CD, DA_n (for example DA14), β -CD/ DA_n physical mixture, and β -CD/ DA_n ICs are shown in Fig.3. The endothermic peak at $229.32\text{ }^\circ\text{C}$, present in Fig.3 (a) and (c), was assigned to a reversible transformation between two crystal-types of β -CD [54]. For DA14 molecules, there are two endothermic peaks at 128.79 and $292.5\text{ }^\circ\text{C}$ attributed to the melting and decomposition point respectively.

Figure 3(c) is almost the mathematical addition of Fig.3 (a) and (b), which indicates there is no interaction between β -CD and DA14 molecules. As is seen from Fig.3(d), the peak of crystal-types transformation of β -CD disappears and the decomposition temperature is higher than both pure β -CD and DA14. This implies that DA14 molecules included inside the β -CD channels can improve β -CD thermal stability and the encapsulating effect also stabilized DA14 molecules [54]. The broad transition between $70\text{--}100\text{ }^\circ\text{C}$ was attributed to

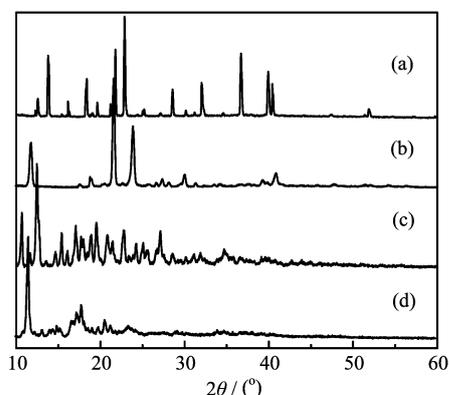


FIG. 2 XRD patterns of (a) β -CD, (b) DA14, (c) physical mixture of β -CD/DA14, and (d) ICs of β -CD/DA14.

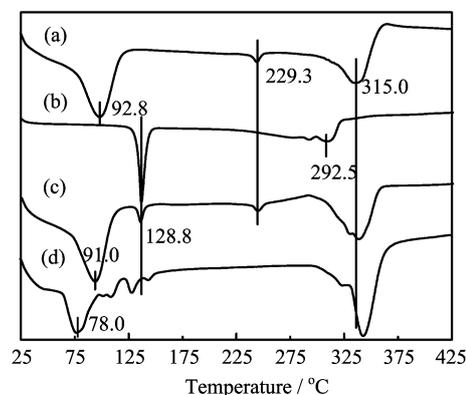


FIG. 3 DTA curves of (a) β -CD, (b) DA14, (c) physical mixture of β -CD/DA14, and (d) ICs of β -CD/DA14.

the evaporation of residue ethanol and small amount of water left in the co-precipitation process.

Inclusion complexes of β -CD/ DAn^{2-} were prepared by neutralizing excess amount of β -CD/ DAn ICs with 10 mol/L sodium hydroxide aqueous solution for tens of days. After filtration the inclusion complex of β -CD/ DAn^{2-} was obtained in solution form.

$^1\text{H-NMR}$ spectra of β -CD, DA14^{2-} and their ICs in D_2O are displayed in Fig.4.

Figure 4(a) gives protons' signals of pure β -CD, in which the chemical shifts of H1-H6 are 5.008, 3.587, 3.903, 3.522, 3.791, and 3.816 ppm respectively. For the pure DAn^{2-} in Fig.4(d), chemical shifts of Ha-Hc are 2.107, 1.480, and 1.230 ppm.

In Fig.4(c), significant shifts to upfield of β -CD interior protons in 2:1 ICs are observed in the case of H3 (3.867 ppm, $\Delta\delta = -0.036$ ppm) and H5 (3.711 ppm, $\Delta\delta = -0.080$ ppm), which is probably due to the shielding effect of the encapsulated aliphatic chains of DA14^{2-} . However, the resonance of H1, H2, H4, and H6 located in the exterior has almost no chemical shift, which indicates that supramolecular interactions exist between DAn^{2-} and β -CD interior protons other than exterior ones [55]. Although J values could not be measured with precision, the changes observed in the H3 and H5 region [56] suggest a distortion of the β -CD three-dimensional structure associated with the formation of inclusion complex.

In Fig.4(f), in the presence of β -CD, the remarkable splitting of Hc signals shows that DA14^{2-} has indeed been included in the inner cavity of the β -CD host and

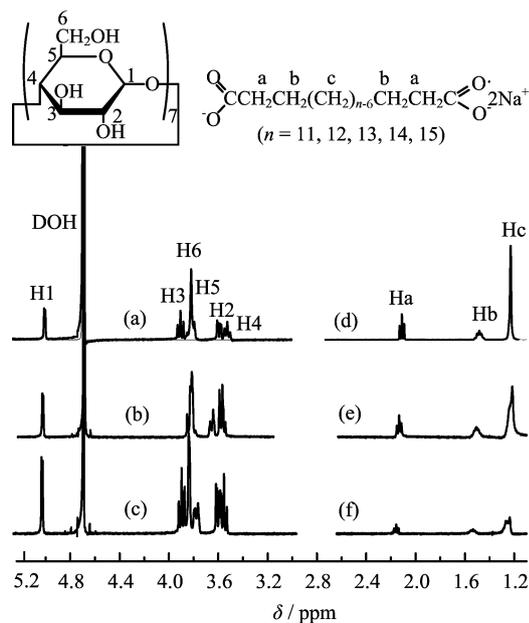


FIG. 4 400-MHz $^1\text{H-NMR}$ spectra of β -CD and DAn^{2-} at 298 K in D_2O . (a) β -CD only. (b) β -CD and DAn^{2-} in 1:1 mixture. (c) β -CD and DAn^{2-} in 2:1 ICs. (d) DAn^{2-} only. (e) DAn^{2-} in 1:1 mixture. (f) DAn^{2-} in 2:1 ICs.

all these anionic DAn^{2-} compounds form stable complexes with β -CD [20].

Moreover, perceptible chemical shift to lower magnetic fields of Ha (2.156 ppm, $\Delta\delta = +0.049$ ppm), Hb (1.533 ppm, $\Delta\delta = +0.053$ ppm), and Hc (1.255 ppm, $\Delta\delta = +0.025$ ppm) also reveals that the aliphatic chain of DA14^{2-} is included in the interior of β -CD to form an inclusion complex and the carboxylic anions were likely to be included in the narrower side of the β -CD cavity [57]. Considering H-bonds interaction in adjacent β -CD molecules, the head-to-tail conformation occupied only a small fraction and the head-to-head was the most probable structure in the ICs [58].

$2\text{D}^1\text{H-NMR}$ experiments were performed in neutral D_2O at 25 $^\circ\text{C}$ for further elucidating the structural features. In NOESY spectra of the 2:1 β -CD/ DAn^{2-} inclusion complex (Fig.5), clear NOE cross-peaks (peaks A, B, and C) between H3 (somewhat weak) and H5 of β -CD and the alkyl protons Ha, Hb, and Hc of DAn^{2-} were observed, suggesting that the whole alkyl chain resides in the cavity of the host.

All possible encapsulated modes of DAn^{2-} molecules in the β -CD cavity are summarized and revealed in Fig.6 [34,40].

The binding mode of Fig.6(a) is a non-inclusion complex involving ion-dipole interaction of the inclusion mode for the 1:1 β -CD/ DAn^{2-} . In Fig.6 (b) and (c), the structures of a folded alkyl chain included in the cavity of β -CD and a pseudorotaxane conformation are proposed, respectively. Figure 6(d) renders the inclusion mode of 2:1 β -CD/ DAn^{2-} with two β -CD monomers arranged in dimers threaded onto one methylene chain

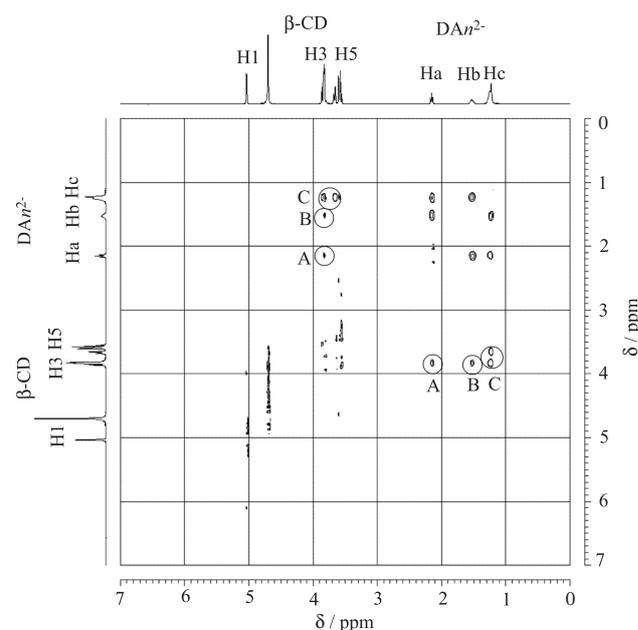


FIG. 5 2D NOESY spectrum (400 MHz) of a 2:1 β -CD/ DAn^{2-} inclusion complex with a mixing time of 1.5 s in D_2O solution at 298 K.

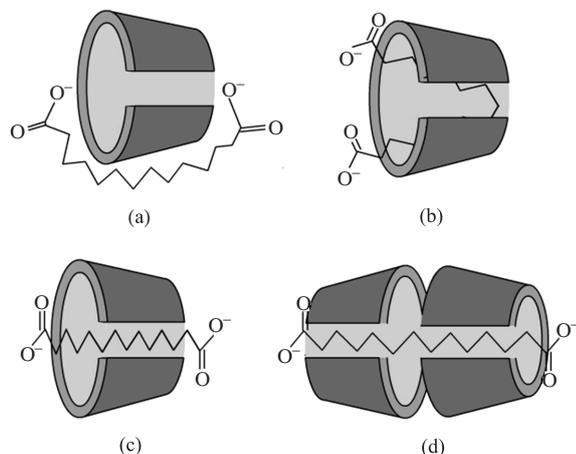


FIG. 6 Illustration of ICs structures of 1:1 β -CD/ DA_n^{2-} inclusion complex (a), (b), (c), and 2:1 β -CD/ DA_n^{2-} inclusion complex (d).

of dicarboxylate to form a [3]pseudorotaxane [40].

The binding modes shown in Fig.6 (a) and (b) could be excluded in the previous volumetric study performed by Wilson [34] and the results of shielding-desielding interaction between β -CD and DA_n^{2-} in $^1\text{H-NMR}$, NOSEY spectra (Fig.4 and Fig.5 respectively), the proposed columnar structure according to XRD patterns presented in Fig.2 can also reach this result.

The alkyl chain conformation of DA_n^{2-} residing in the cavity of β -CD has been taken into account, especially the gauche kinks effects when $n > 11$ [59], based on comparison of $^1\text{HNMR}$ spectra of the β -CD/ DA_n^{2-} inclusion complex and β -CD/ DA_n^{2-} 1:1 mixture (as seen in Fig.4).

In β -CD/ DA_n^{2-} 1:1 mixed solutions, a 1:1 inclusion complex with a pseudorotaxane structure was put forward [34]. In consideration of the gauche kink effect of the aliphatic hydrocarbon chain based on the depth, height, and the cavity volume of β -CD molecules, the maximum number of carbon atoms that can be included in one β -CD cavity is 8 [60] based on the formula $L/A = 1.5 + 1.265(n-1)$ and $V/A^3 = 27.4 + 26.9(n-1)$ proposed by Tanford [59].

There are four methylenes on average residing in the β -CD cavity according to the packing mode of the β -CD/1,14-tetradecanedioic acid complex molecules [40]. Different shielding-desielding effects between β -CD and DA_n^{2-} assuming two different binding modes would be observed in $^1\text{H-NMR}$ spectra. As seen in Fig.4 (b) and (c), H3 and H5 of β -CD of β -CD/ DA_n^{2-} ICs in this study shifted upfield and the chemical shift decreased by half compared to 1:1 β -CD and DA_n^{2-} mixture, probably due to the half shielding effect of the DA_n^{2-} chains according to the above deduction (seen in the supporting information). Then a [3]pseudorotaxane structure is probably adopted by 2:1 β -CD/ DA_n^{2-} inclusion complexes with sodium hydroxide treatment

from β -CD and DA_n ICs.

IV. CONCLUSION

Inclusion complexes between β -cyclodextrin (β -CD) and a series of dicarboxylic acids (DA_n , $n=11-15$) were prepared by co-grinding and co-precipitation and the [3]pseudorotaxane structure of them was elucidated by FTIR, DTA, and XRD characterization. Inclusion complexes of β -CD and DA_n^{2-} were acquired by neutralization β -CD/ DA_n ICs with sodium hydroxide and the structure was proved to be also a pseudorotaxane structure by $^1\text{H-NMR}$ spectra and NOESY spectrum. Both the inclusion complexes of β -CD/ DA_n and β -CD/ DA_n^{2-} adopt a [3]pseudorotaxane structure with β -CD arranged in dimers threaded onto one aliphatic chain and the binding modes of 1:1 inclusion complex were excluded based on the consideration of chain conformations.

V. ACKNOWLEDGMENTS

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