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Carboxylic ester hydrolysis catalyzed by a host–guest system constructed by cyclodextrin dimer and zinc complex

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ABSTRACT

A new β-cyclodextrin dimer, 2,2′-bipyridyl-4,4′-dimethyl-bridged-bis(6-monodeoxy-6-ammonio-β-cyclodextrin) (BCD, Host) was synthesized and further assembled with a zinc complex containing a hydrophobic group as an inclusion complex, ZnL(BCD) (ZnL, L = 4-(4′-tertbutylbenzyl) diethylenetriamine, Guest). The complex was characterized by elemental analysis and NMR spectra and applied as a new supramolecular system of catalyzing carboxylic ester hydrolysis. In such host–guest system, the two deprotonation constants of the Zn^{II}-coordinated water molecules, 8.38 ± 0.01 and 10.42 ± 0.02 for pK_{a1} and pK_{a2} respectively, were obtained by pH potentiometric titration at 298 ± 0.1 K. The kinetics of *p*-nitrophenyl acetate (pNA) hydrolysis catalyzed by ZnL(BCD) was carried out at pH 7.54–10.56 and 298 ± 0.1 K. The pH profile of observed hydrolysis rate constants catalyzed by ZnL(BCD) exhibits an exponential growth, indicating that the kinetic process is controlled by two acid–base equilibriums. Obtained kinetic results are in good agreement with thermodynamic data for hydroxyl active species in ZnL(BCD) system. Second-order rate constants of 0.15 and 2.64 M^{-1} s^{-1} were calculated for mono- and di-hydroxyl active species in ZnL(BCD) system, respectively. Compared with an unassembled host or guest analogue, Zn(dien) (dien = diethylenetriamine), the supramolecular system exhibits much higher catalytic activity.

1. Introduction

To investigate and better understand the relationship between the structure and activity of metalloenzyme, many zinc complexes were applied to mimic enzymes such as carbonic anhydrase, thermolysin, nucleases and so on [1–3]. Most of model complexes were designed and synthesized only according to the active site of metalloenzyme, such as the structure of $((His)_3Zn(OH_2))$ in the carbonic anhydrase (CA) [4,5]. In fact, the various types of weak interactions between the enzymes and substrates simultaneously play an important role on catalytic process, such as hydrogen bonding and hydrophobic interaction provided by the second coordination sphere around the active site [6]. The introduction of a hydrophobic moiety in a pocket provided by a host molecule is expected to produce active hybrid catalysts with a well defined second coordination sphere provided by the host [7]. Cyclodextrins (CDs) can bind various guest molecules into hydrophobic cavities and have been extensively studied in fields as artificial enzymes, and biomimetic materials [8,9]. Compared with native β-cyclodextrin, bis(β-cyclodextrin)s can significantly enhance the original binding ability and molecular selectivity due to cooperative binding and multiple recognition in aqueous solution and the solid state [10,11]. It was well document that cyclodextrin dimers linked by functional complexes have been investigated in the fields of the molecular recognition and enzyme mimics [12,13]. However, studies on cyclodextrin inclusion complexes, which are constructed by a metal complex binding a CD molecule as metalloenzyme mimics, are still rarely reported. Recently, we have reported the cyclodextrin inclusion complexes as mimics for superoxide dismutase by supramolecular strategy [14,15]. Also, a supramolecular model for a metallohydrolase has been successfully constructed by assembling metal–triamine complex with a pendant side of 4-*tert*-butylbenzyl into β-cyclodextrin cavity [16]. On the basis of the above work, a new approach is to construct a supramolecular catalyst, in which the metal site and its second coordination sphere are provided by the guest and the host respectively. So we design and synthesize a new cyclodextrin dimer linked by 4,4′-dimethyl-2,2′-bipyridyl as host. One of the two cyclodextrin cavities is assembled with guest catalyst, such as a zinc complex, as a supramolecular model for a metallohydrolase. Another cavity will be applied to fix a guest substrate, such as carboxylic acetate, in catalytic process. Herein, we report their synthesis and characterization, thermodynamic properties, and metallohydrolase activities, evaluation of which was based on hydrolysis of *p*-nitrophenyl acetate (pNA).

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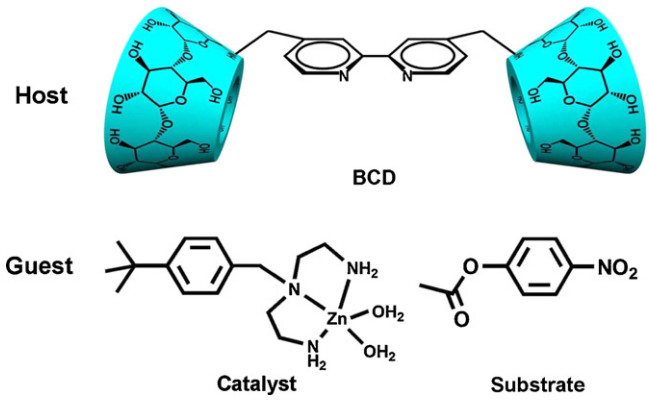


Scheme 1. Host (BCD), catalyst (ZnL) and substrate (pNA).

2. Experimental

2.1. Materials

4,4′-Dimethyl-2,2′-dipyridyl and *p*-nitrophenyl acetate were purchased from Aldrich Chemical Company. β-CD of reagent grade was recrystallized twice from H_2O and dried in vacuo for 12 h at 373 K, DMF were dried over CaH_2 for 2 days and then distilled under reduced pressure prior to use. Common organic reagents were reagent grade and redistilled before use. Water used in all physical measurement experiments was Milli-Q grade. L (L = 4-(4′-tertbutylbenzyl)diethylenetriamine), ZnL (Scheme 1) was prepared by our previous work [14–16], 6-monodeoxy-6-monoamino-β-cyclodextrin was prepared as literatures with minor modification [17,18], and 4,4′-bis(bromomethyl)-2,2′-bipyridyl was obtained according to the literature procedure [19]. 2,2′-bipyridyl-4,4′-dimethyl-bridged-bis(6-monodeoxy-6-ammonio-β-cyclodextrin) (BCD) was prepared as Scheme 2, characterized by EA, ^{1}H NMR, ESI mass and IR spectra (Fig. S1–S4).

Synthesis of 2,2′-bipyridyl-4,4′-dimethyl-bridged-bis(6-monodeoxy-6-ammonio-β-cyclodextrin), BCD.

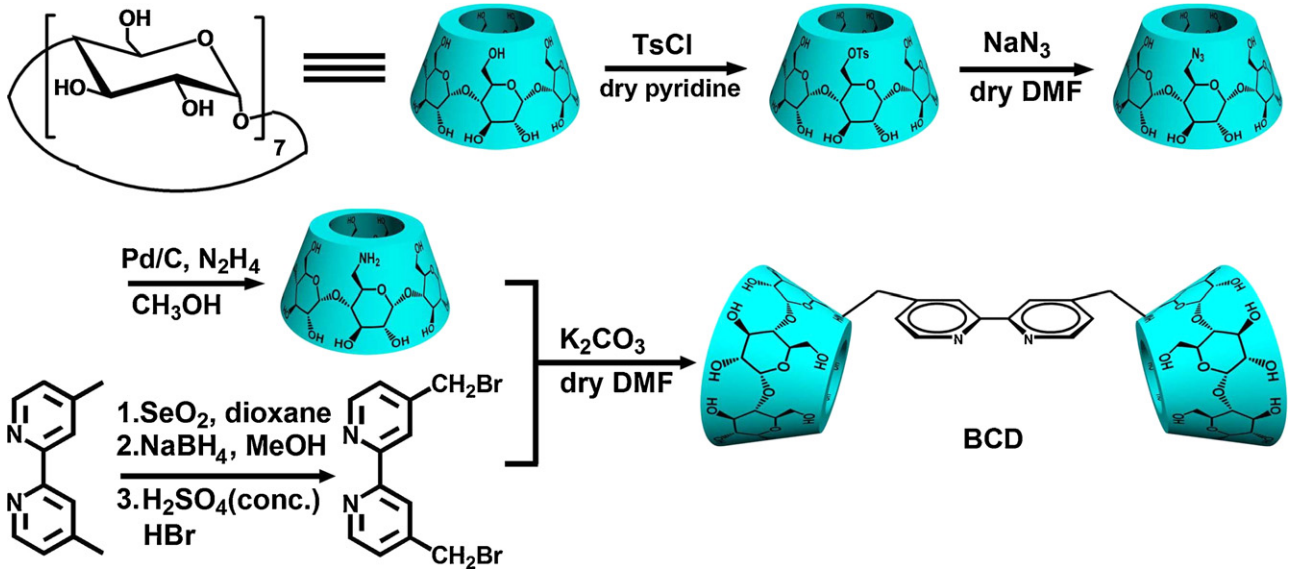
To a solution of 6-monodeoxy-6-monoamino-β-cyclodextrin (2.395 g, 2.112 mmol) and anhydrous potassium carbonate (1.166 g, 8.448 mmol) in dry DMF was dropwisely added a solution of 4,4′-dibromomethyl-2,2′-dipyridyl (0.359 g, 1.056 mmol) in 5 mL dry DMF with vigorous stirring. After heated to 353 K for 8 h under nitrogen, the reaction was cooled to room temperature, and then filtrated and evaporated under a reduced pressure to dryness. The residue was dissolved in a small amount of hot water, and the aqueous solution was poured into acetone (200 mL) to give a white precipitate. The crude product obtained was purified by column chromatography over Sephadex G-25 with distilled deionized water as an eluent to give pure desired compound in 56% yield. ^{1}H NMR(300 MHz, DMSO-d_6): δ 8.56 (d, ^3J(H,H) = 4.87 Hz, 2H; bipyridyl-H-6,6′), δ 8.33 (s, 2H; bipyridyl-H-3,3′), 7.40 (d, ^3J(H,H) = 4.89 Hz, 2H; bipyridyl-H-5,5′), 5.75–5.71 (m, 28H, OH-2,3), 4.90–4.77 (m, 14H, H-1), 4.54–4.45 (m, 12H, OH-6), 3.86–3.46 (m, 60H, H-3,5,6,bpy-CH_2), 3.33–2.73 (m, 28H, H-2,4; overlaps with H_2O), 2.08 (s, 2H, NH); IR (cm^{-1}, KBr) 3376, 2928, 2153, 1707, 1657, 1601, 1560, 1367, 1241, 1157, 1081, 1029, 943, 846, 756, 707, 578, 530; MS(ESI, H_2O, *m*/*z*): $[M+2H]^{2+}$ calcd 1224.4, found 1224.8, $[M+K+H]^{2+}$ calcd 1243.4, found 1243.7; Anal. Calcd for $C_{96}H_{150}N_4O_{68}\cdot 10H_2O$: C 43.87, H 6.52, N 2.13. Found: C 43.56, H 6.72, N 2.18.

Synthesis of $[ZnL(H_2O)_2(BCD)](ClO_4)_2.20H_2O$, ZnL(BCD).

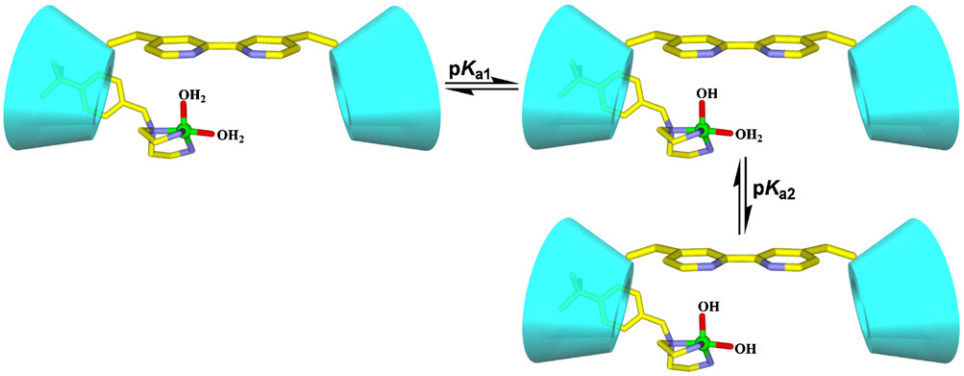
To an aqueous solution of BCD (0.053 g, 0.020 mmol) was slowly added a solution of slight excessive the complex of $ZnL(H_2O)_2(ClO_4)_2$ (0.012 g, 0.022 mmol) in 1 mL H_2O with stirring. After ultrasonic oscillation for 30 min, the mixture solution was kept on magnetic stirring for 60 min at room temperature. Then, the white precipitation was formed by diffusing methanol into the mixed aqueous solution. The pure compound was obtained with 52% yield after filter, washed with methanol and dried with vacuum. ^{1}H NMR(300 MHz, D_2O): δ 8.76 (d, ^3J(H,H) = 4.63 Hz, 2H; bpy-H-6,6′), δ 8.27 (s, 2H; bpy-H-3,3′), 7.66 (d, ^3J(H,H) = 4.63 Hz, 2H; bpy-H-5,5′), δ 7.48 (d, ^3J(H,H) = 7.86 Hz, 2H; ph-H-b), δ 7.42 (d, ^3J(H,H) = 7.86 Hz, 2H; ph-H-c), 5.15–5.03 (m, 14H, H-1), 4.31–3.75 (m, 60H, H-3,5,6,bpy-CH_2), 3.70–3.57 (m, 28H, H-2,4), δ 3.18 (t, 4H; N-CH_2), δ 2.85 (t, 4H; N-CH_2), δ 2.26 (s, 2H; ph-CH_2), δ 1.37 (s, 9H; *t*-butyl-H); Anal. Calcd for $C_{111}H_{181}Cl_2N_7O_{78}Zn\cdot 20H_2O$: C, 39.70; H, 6.63; N, 2.92. Found: C, 39.60; H, 6.27; N, 2.81.

2.2. Potentiometric determination

An automatic titrator (Metrohm 702GPD Titrino) coupled to a Metrohm electrode was used and calibrated according to the



Scheme 2. Synthesis route of BCD.



Scheme 3. Deprotonation equilibria of Zn^{II}-coordinated water in solution.

Gran method [20,21]. The electrode system was calibrated with buffers and checked by titration of $HClO_4$ with NaOH (0.10 M). The thermostated cell contained 25 mL of 1.0 mM species in aqueous solutions with I = 0.10 M $NaClO_4$. All titrations were carried out on the aqueous solutions under nitrogen at 298 ± 0.1 K, and initiated by adding fixed volumes of 0.10 M standard NaOH in small increments to the titrated solution. Duplicate measurements were performed, for which the experimental error was below 1%. The titration data were fitted with the Hyperquad 2000 program to calculate the ligand protonation constants K_n, the complex formation constant K_{ML}, and the deprotonation constants of the coordinated water pK_a.

2.3. Kinetic study of pNA hydrolysis

The hydrolysis rate of pNA catalyzed by supramolecular system in aqueous solution was measured by following the enhancement in absorption at 400 nm of the *p*-nitrophenolate released [22,23]. At this wavelength, the absorbance of ester substrate was negligible. The reaction solution was maintained at 298 ± 0.1 K and the ionic strength was adjusted to 0.10 M by sodium perchlorate. 50 mM Tris, pH (7.54–8.56); CHES, pH (8.85–9.49); CAPS, pH (10.03–10.56) were used as buffers. The solutions used in kinetic measurements contained 10% (v/v) CH_3CN. Aqueous solutions of the inclusion compound were prepared by dissolving the inclusion complex in buffer solutions of different pH values and ultrasonic oscillating them ultrasonically for 30 min before testing. The results of the kinetic measurements could be duplicated within ± 5%.

3. Results and discussion

3.1. Complexation and deprotonation constants and species distribution

The protonation constants (K_n) of the ligand and the inclusion complex formation constants (K_{ML}) and the deprotonation constant (pK_a) of the coordinated water molecule (Scheme 3) as well as species distribution in solution were determined by pH potentiometric titration at I = 0.1 M $NaClO_4$ and 298 ± 0.1 K. The pH profiles of the titration curves, including the distribution curves of the Zn^{II} species as a function of pH (Fig. 1), were analyzed by HYPERQUAD program.

$$Zn^{2+} + L = ZnL^{2+} \qquad K_{ZnL} \tag{1}$$

$$Zn^{2+} + L + H^+ = ZnLH^{3+} \qquad K_{ZnLH} \tag{2}$$

$$Zn^{2+} + L + 2H^+ = ZnLH_2{}^{4+} \qquad K_{ZnLH_2} \tag{3}$$

$$Zn^{2+} + L + 3H^+ = ZnLH_3{}^{5+} \qquad K_{ZnLH_3} \tag{4}$$

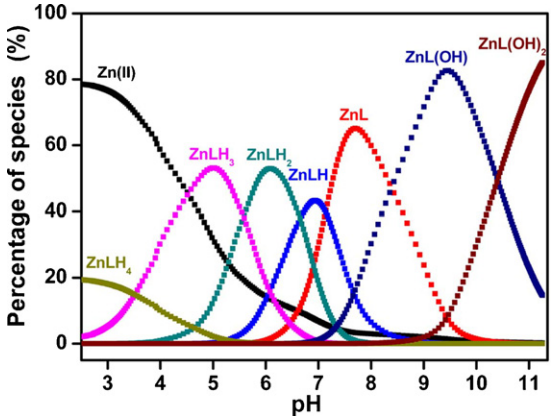


Fig. 1. Distribution plots of species with as a function of pH in 1.0 mM ZnL(BCD) solution at 0.1 M $NaClO_4$ and 298 ± 0.1 K.

$$Zn^{2+} + L + 4H^+ = ZnLH_4{}^{6+} \qquad K_{ZnLH_4} \tag{5}$$

$$ZnL^{2+} = ZnLH_{-1}{}^{+} + H^+ \qquad K_{a1} \tag{6}$$

$$ZnLH_{-1}{}^{+} = ZnLH_{-2} + H^+ \qquad K_{a2} \tag{7}$$

It is indicated in Fig. 1 that Zn^{2+} species, ZnL^{2+}, $ZnLH^{3+}$, $ZnLH_2{}^{4+}$, $ZnLH_3{}^{5+}$, $ZnLH_4{}^{6+}$, $ZnLH_{-1}{}^{+}$ and $ZnLH_{-2}$, corresponding to Eqs. (1)–(7), respectively, are involved in the complex formation in the range of pH 2–11. Compared with the unassembled analogue Zn(dien) (dien = diethylenetriamine) [24], the formation constant of the ZnL(BCD) complex is higher and the deprotonation constant decreases a little (Table 1, log K = 10.50 and pK_{a1} = 8.38 for ZnL(BCD); log K = 8.92 and pK_{a1} = 8.93 for [Zn(dien)]). The enhancement of complex constant and reduction of deprotonation are probably due to the effect of both the hydrophobic environment around the coordinated water molecule and weak interactions after complexation,

Table 1
Equilibrium constants of ligand and metal complexation in the presence of BCD

Chemical equilibrium		Equilibrium constant
$H_4L^{4+} = H_3L^{3+} + H^+$	pK_1	5.41 ± 0.01
$H_3L^{3+} = H_2L^{2+} + H^+$	pK_2	5.98 ± 0.05
$H_2L^{2+} = HL^+ + H^+$	pK_3	8.21 ± 0.07
$HL^+ = L + H^+$	pK_4	11.23 ± 0.02
$Zn^{2+} + L = [ZnL]^{2+}$	log K_{ML}	10.50 ± 0.01
$[ZnL]^{2+} + H^+ = [ZnLH]^{3+}$	log K_{MLH}	7.12 ± 0.02
$[ZnLH]^{3+} + H^+ = [ZnLH_2]^{4+}$	log K_{MLH_2}	6.60 ± 0.01
$[ZnLH_2]^{4+} + H^+ = [ZnLH_3]^{5+}$	log K_{MLH_3}	5.56 ± 0.02
$[ZnLH_3]^{5+} + H^+ = [ZnLH_4]^{6+}$	log K_{MLH_4}	3.56 ± 0.04
$[ZnL]^{2+} = [ZnL(OH)]^+ + H^+$	pK_{a1}	8.38 ± 0.01
$[ZnL(OH)]^+ = [ZnL(OH)_2] + H^+$	pK_{a2}	10.42 ± 0.02

similar to those in carbonic anhydrase or alkaline phosphatase [25]. The pK_{a2} of Zn(dien) cannot be determined due to easily forming hydroxo-bridged dimer, while the pK_{a2} of $[ZnL(BCD)(H_2O)_2]^{2+}$ deprotonation (Table 1) was determined to be 10.42, which is be close to that of $[ZnL(\beta\text{-CD})(H_2O)_2]^{2+}$(10.44) [16]. It indicates that the large cyclodextrin groups effectively decrease pK_a values and weakening or prevent formation of hydroxo-bridged dimers which occur in other simple mononuclear complex systems [26,27].

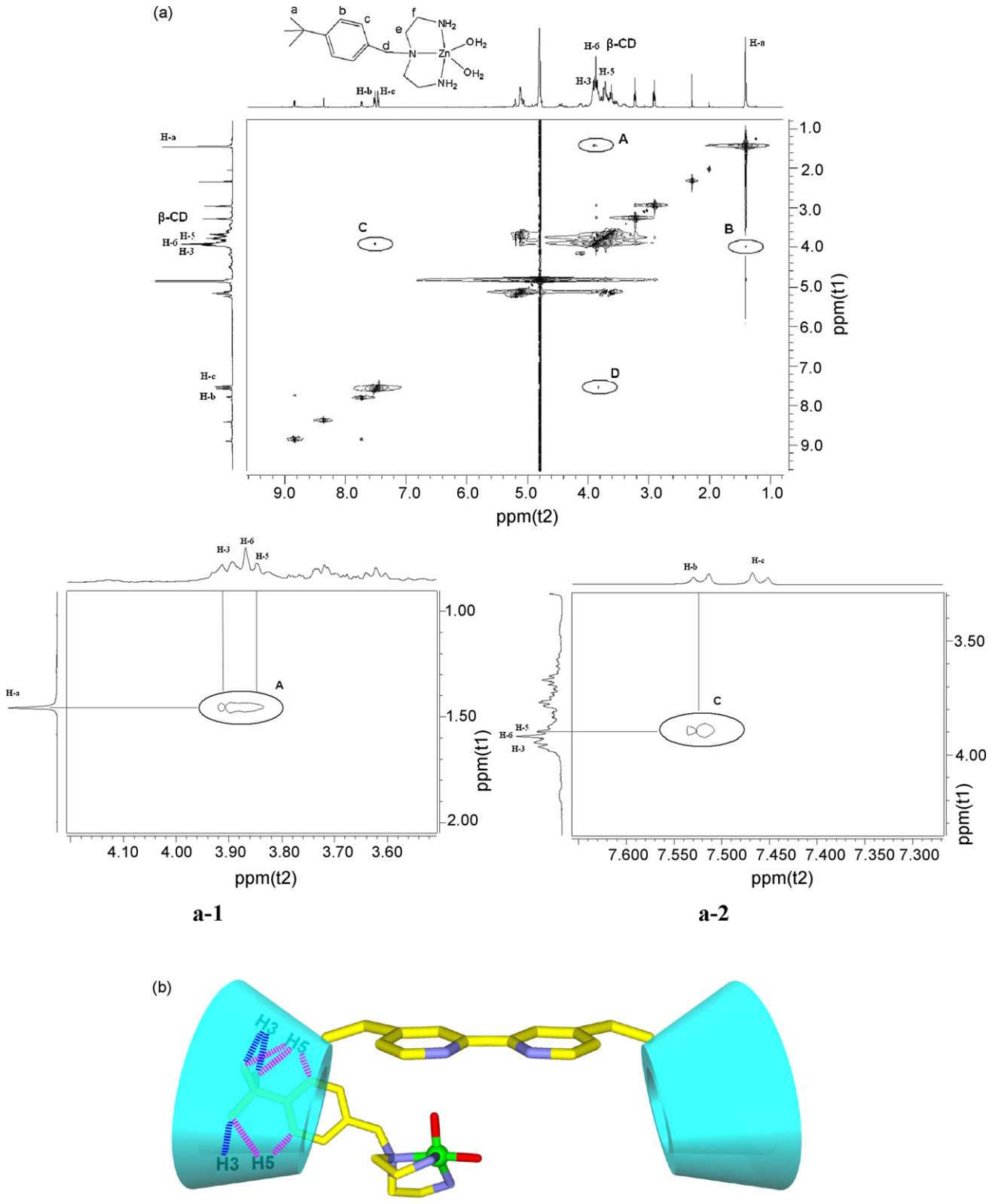


Fig. 2. (a) ROESY spectrum of ZnL(BCD) (10 mM) in D_2O at 298 ± 0.1 K with a mixing time of 200 ms and (b) the possible binding manner of ZnL(BCD) in aqueous solution.

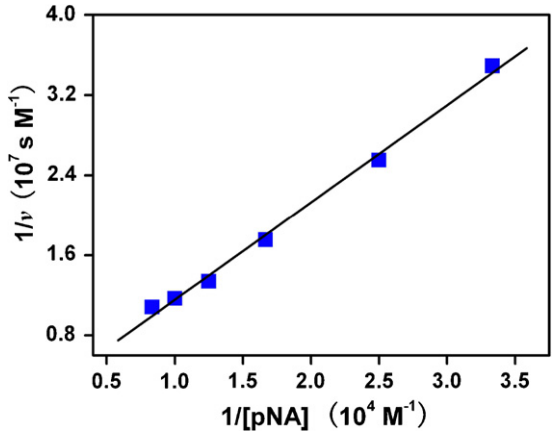


Fig. 3. Lineweaver–Burk plot obtained for the ZnL(BCD) catalytic reaction in the presence of different substrate concentration [pNA] at pH 7.0 and 298 ± 0.1 K.

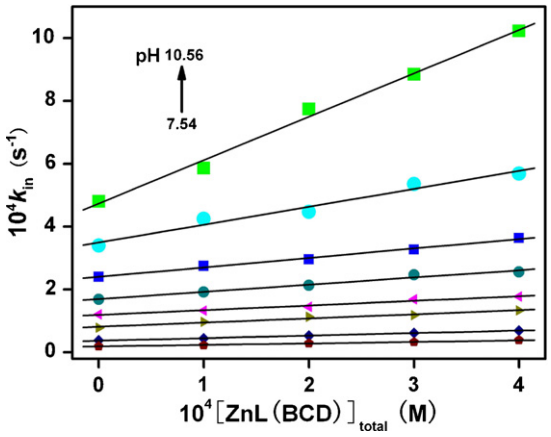


Fig. 4. The $[ZnL(BCD)]_{total}$ dependence of the initial rate constants (k_{in}) at pH 7.54–10.56, 0.1 M $NaClO_4$ and 298 ± 0.1 K in the presence of 10% (v/v) CH_3CN.

3.2. Conformation analysis of ZnL(BCD)

It is well known that elucidation of the crystal structure is one of the most convincing methods of unequivocally illustrating the geometrical structure of CD inclusion complex [14,15]. Unfortunately, our repeated attempts to prepare single crystals of the inclusion complex ZnL(BCD) were unsuccessful. Whereas, 2D NMR spectroscopy has recently become a powerful qualitative method that has previously been used to monitor weak through space proton coupling interactions in cyclodextrin inclusion complexes, since the NOE cross-peaks between the protons that are closer than 0.4 nm in space will be observed in the ROESY spectrum [28]. To investigation the binding geometry between the BCD and ZnL, 2D ROESY NMR spectroscopy of the inclusion complex ZnL(BCD) was determined at 298 K in D_2O. As shown in Fig. 2a, the ROESY spectra of the inclusion complex displayed clear NOE cross-peaks between the H3/H5 of BCD and *p-tert*-butyl protons Ha of ZnL as well as between the H5 of BCD and aryl protons Hb of ZnL. This result indicates that the *p-tert*-butyl-phenyl moiety of ZnL was included into the hydrophobic cavity from the primary side of BCD. According to these results, a possible conformation of ZnL(BCD) was shown in Fig. 2b. The binding manner is similar to the case in the inclusion complex ZnL(CD), which has been characterized by the X-ray crystallography in our previous work [16].

3.3. Acetate hydrolysis

The hydrolysis of *p*-nitrophenyl acetate has been widely used to examine catalytic abilities of various mimics of metallohydrolase [29]. The initial rate (υ) was determined by monitoring formation of the *p*-nitrophenolate anion at 400 nm. We found that the initial rate (8.72×10^{-8} M s^{-1}) of pNA hydrolysis in the presence of ZnL(BCD) was one order of magnitude higher than the corresponding value (5.52×10^{-9} M s^{-1}, Fig. S5) in the presence of BCD at pH 8.33 Tris–HCl buffer and 298 ± 0.1 K. Therefore the contribution of BCD for hydrolysis acceleration can be neglected.

To assess the hydrolysis ability of ZnL(BCD) system, Michaelis–Menten saturation kinetics was undertaken at pH 8.33 and 298 ± 0.1 K (Fig. 3). The value of K_m (5.3×10^{-4} M), which was obtained from Lineweaver–Burk double reciprocal plot in our work, was 14-fold lower than the K_m value (7.6×10^{-3} mM) for the pNA hydrolysis catalyzed by the simple ZnN_3 complex, analogue of ZnL [30]. This reduction in the value of K_m is probably due to the enhancement on the stability of the 'catalyst–substrate' intermediate due to hydrophobic environment provided by the cyclodextrin dimer. The result is in agreement with a study in which site-directed mutagenesis was used to alter the nature of the hydrophobic cavity of the carbonic anhydrase [31].

When the substrate concentration was kept constant during the measurement, the initial first-order rate constant (k_{in}, in = initial) of the total inclusion complex was calculated as $\upsilon/[pNA]_{total}$ [32].

$$\begin{aligned} v &= k_{in}[pNA] \\ &= (k_{obs}[catalyst]_{total} + k_{OH^-}[OH^-] + \ldots)[pNA] \end{aligned} \quad (8)$$

At a given pH value, the k_{in} values were measured at different concentrations of catalyst. For each kinetic measurement, the k_{in} value increased linearly with the total concentration of catalyst. The linear plots were extended to a wide pH range (7.54–10.56) (Fig. 4). Thus, from Eq. (8) the slope of k_{in} versus $[catalyst]_{total}$ resulted in the observed second-order rate constant (k_{obs}).

In ZnL(BCD) system, the second-order rate constant was found to increase exponentially with the increase of pH value (Fig. 5) in good agreement with the calculated percentage of both $[ZnL(BCD)(OH)(H_2O)]^+$ and $[ZnL(BCD)(OH)_2]$ species (Fig. 1). The result indicates that the hydroxyl complexes are the kinetically active species and thus the kinetic process of pNA hydrolysis is controlled by two acid–base equilibria. A complete rate can therefore

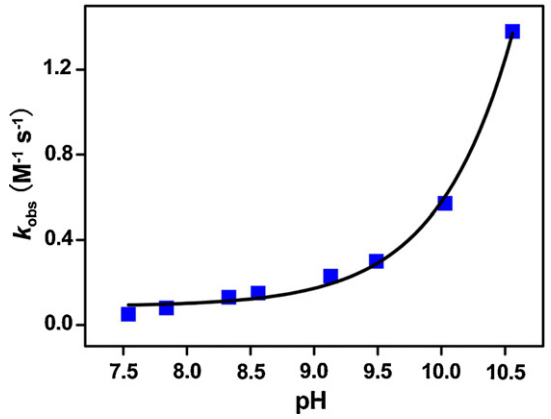
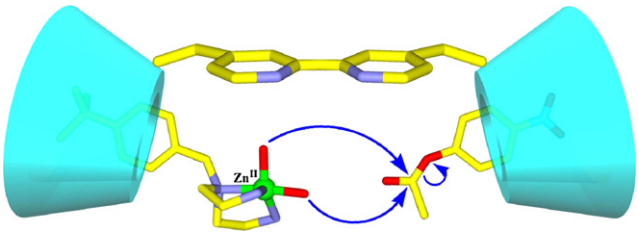


Fig. 5. The pH dependence of the second-order rate constants (k_{obs}) for pNA hydrolysis catalyzed by $[ZnL(BCD)]_{total}$.



Scheme 4. Suggested intermediate of pNA hydrolysis catalyzed by ZnL(BCD).

be expressed as Eq. (9).

$$k_{obs} = \frac{k^{I}_{cat}[LZnOH] + k^{II}_{cat}[LZn(OH)_2] + \dots}{[Zn(II)species]_{total}} = \frac{k^{I}_{cat}K_{a1}[H^+] + k^{II}_{cat}K_{a1}K_{a2}}{[H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2}} \quad (9)$$

Subsequently, the k_{cat} and pK_a values were found by curve-fitting to be 0.15 M^{-1} s^{-1} and 8.12 for $[ZnL(BCD)(OH)]^+$, and 2.64 M^{-1} s^{-1} and 10.60 for $[ZnL(BCD)(OH)_2]$, respectively (R = 0.989). The k^{I}_{cat} of the monohydroxyl active species $[ZnL(BCD)(OH)]^+$ is located in the normal range with similar pK_a values [29], which is about 2 times higher than that of its simple unassembled analogue $[Zn(dien)(OH)(H_2O)]^+$ (k_{cat} = 0.08 M^{-1} s^{-1}) [33]. While the k^{II}_{cat} of the first-order dihydroxyl active species $[ZnL(BCD)(OH)_2]$ is about 33 times higher than that of $[Zn(dien)(OH)(H_2O)]^+$.

It is well known that *p*-nitrophenyl group can be included into the cyclodextrin cavity with hydrophobic interaction in aqueous solution [12,34], resulting that the cyclodextrin dimer acts as the catalytic reaction location with one cavity fixing the catalyst and the other cavity fixing the substrate. This spatial favorableness enhances the odds of nucleophilic attack on the carboxylic carbon with the hydroxyl species, so that the k_{cat} of the mono- and di-hydroxyl active species enhance. As two coordinated water molecules dissociating protons were shown in Scheme 3, the hydroxyl group in an equatorial position of the trigonal bipyramid in ZnL(BCD) system attacks the carboxylic carbon directly at low pH, and the axial one with higher nucleophilicity attacks the carboxylic carbon at high pH [16]. Formation of dihydroxyl species led to a decrease in the positive charge distribution of the whole nucleophilic agent, which is propitious to nucleophilic attack. Compared with monohydroxyl species, dihydroxyl species have a lower oxidation number and more nucleophilic groups, resulting in higher nucleophilicity. All of these factors have significant effects on their catalytic activity for hydrolysis of the carboxylic ester. Thus, a possible intermediate involving nucleophilic attacks by the first and second hydroxyl groups is proposed in Scheme 4.

Therefore, it can be drawn the conclusion from the above experiments that zinc hydroxyl species are effectively active to catalyze the hydrolysis of ester and the hydrophobic interactions between the two cavities and catalyst/substrate are helpful to hydrolysis. In this work, kinetic results are in good agreement with thermodynamic data for hydroxyl active species in ZnL(BCD) system.

4. Conclusions

A new cyclodextrin dimer has been synthesized, characterized and assembled with Zn^{II}-triamine complex containing a pendant side of 4-*tert*-butylbenzyl to form supramolecular system as ester hydrolysis catalyst. The supramolecular system can stabilize hydroxyl species in solution. For pNA hydrolysis, supramolecular system exhibits the kinetic behavior of dihydroxyl species, behaving much higher catalytic activity than unassembled analogue. In such host–guest system, the cooperative hydrophobic interactions between the two CD cavities and catalyst/substrate play a vital role on pNA hydrolysis, and all obtained kinetic results are in good agreement with thermodynamic data for hydroxyl active species.

Supplementary information

^{1}H NMR, IR and ESI-MS spectra of BCD and kinetics data of pNA catalytic hydrolysis can be found.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.07.010.

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