

# Further understanding of the multiple equilibria interaction pattern between ionic liquid and $\beta$ -cyclodextrin

Jingjing Zhang · Jianfeng Shi · Xinghai Shen

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**Abstract** The interactions of the ionic liquids 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $C_n\text{mimTf}_2\text{N}$ ,  $n = 2, 4, 6, 8, 10, 12$ ) with  $\beta$ -cyclodextrin ( $\beta$ -CD) in aqueous solutions are investigated in this work. The stoichiometry and apparent association constants are obtained by competitive fluorescence method and isothermal titration calorimetry (ITC). The results show that  $C_2\text{mimTf}_2\text{N}$ ,  $C_4\text{mimTf}_2\text{N}$ , and  $C_6\text{mimTf}_2\text{N}$  mainly form 1:1 (guest:host) inclusion complexes with  $\beta$ -CD, whereas  $C_8\text{mimTf}_2\text{N}$ ,  $C_{10}\text{mimTf}_2\text{N}$ , and  $C_{12}\text{mimTf}_2\text{N}$  form both 1:1 and 1:2 inclusion complexes, the latter of which are mainly attributed to the formation of the  $C_n\text{mim}^+-2\beta$ -CD complexes. Besides,  $\text{Tf}_2\text{N}^-$  only forms the 1:1 complex with  $\beta$ -CD owing to a charge resonance structure that breaks the symmetry of the structure of  $\text{Tf}_2\text{N}^-$ , which is proved by Fourier transform infrared spectra. The thermodynamic parameters obtained by ITC reveal that the formation of the inclusion complexes are enthalpy-controlled for  $C_2\text{mimTf}_2\text{N}$ ,  $C_4\text{mimTf}_2\text{N}$ , and  $C_6\text{mimTf}_2\text{N}$ , while for the  $C_8\text{mimTf}_2\text{N}/\beta$ -CD system, the process becomes entropy and enthalpy driven. Based on high-resolution mass spectrometry used with electrospray ionization results, the interaction between  $C_n\text{mimTf}_2\text{N}$  and  $\beta$ -CD is found to follow the multiple equilibria interaction pattern which was suggested in our previous work.

**Keywords** Cyclodextrin · Ionic liquid ·  $\text{Tf}_2\text{N}^-$  · Inclusion complex · Multiple equilibria

## Introduction

Cyclodextrins (CDs) are a series of macrocyclic oligosaccharides composed of 6, 7, and 8 D-(+)-glucose units named  $\alpha$ -,  $\beta$ -, and  $\gamma$ -CD, respectively, which can encapsulate a number of organic and inorganic guest molecules in their hydrophobic cavity to form inclusion complexes [1–3]. They are commercially available, nontoxic and water soluble, making them widely used in the pharmaceutical industry, foodstuffs and so on [4, 5]. Ionic liquids (ILs) consist of organic cations and appropriate anions, and have been regarded as a good alternative to the conventional and environmentally detrimental volatile solvents. They have intriguing properties such as negligible vapor pressure, nonflammability, tunable physico-chemical properties, high electrical conductivity, and wide electrochemical window, attracting considerable attention in the fields of chemical reactions, separations and electrochemistry [6–11]. Furthermore, ILs are becoming more and more important in the field of supramolecular chemistry, as they can either directly participate in the assembly of supramolecular organizations, or influence the assembly of various supramolecular structures [12]. The combination of CDs and ILs is a key issue in supramolecular chemistry because they can be applied in supramolecular systems with novel structures and properties [13–18]. As a result, the interaction between CD and ILs is of great importance and there have been some reports on this subject [19–24].

Our research group is quite interested in this topic and has been investigating the interaction between imidazolium-based ILs and  $\beta$ -CD in aqueous solutions in the past several years [25–28]. In our previous work, we suggested a detailed multiple equilibria interaction pattern between ILs and CD in aqueous solutions by taking the

J. Zhang · J. Shi · X. Shen (✉)  
Beijing National Laboratory for Molecular Sciences (BNLMS),  
Radiochemistry and Radiation Chemistry Key Laboratory  
of Fundamental Science, College of Chemistry and Molecular  
Engineering, Peking University, Beijing 100871, China  
e-mail: xshen@pku.edu.cn

ILs 1-alkyl-3-methylimidazolium hexafluorophosphate ( $C_n\text{mimPF}_6$ ,  $n = 2, 4, 6, 8$ ) for examples [27]. This interaction pattern successfully demonstrates the existence of contact ion pairs and the dissociated ions of ILs, and indicates how they interact with  $\beta$ -CD respectively. ILs mainly exist as the dissociated ions with a minor percentage of ion pairs in aqueous solutions. The cation or the anion part of the ion pair first interacts with  $\beta$ -CD depending on which part of the ion pair interacts more strongly with  $\beta$ -CD. If both the cation and the anion can interact strongly, the 1:2 ( $\beta$ -CD-cation) $\cdot$ (anion- $\beta$ -CD) inclusion complex will form and thereupon dissociate into  $\beta$ -CD-cation and anion- $\beta$ -CD complexes, of which the cation with long chain will further interact with  $\beta$ -CD to form the 1:2 complexes cation-2 $\beta$ -CD. On the other hand, the dissociated cations and anions of the ILs interact with  $\beta$ -CD randomly to form two kinds of 1:1 inclusion complexes, of which the cation with long chain will also be included in another  $\beta$ -CD [27].

Here we try to further investigate the above interaction pattern by using the ILs 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ( $C_n\text{mimTf}_2\text{N}$ ,  $n = 2, 4, 6, 8, 10, 12$ , illustrated in Scheme 1) instead of  $C_n\text{mimPF}_6$ . With the symmetrical structure and two  $\text{SO}_2\text{CF}_3$  groups,  $\text{Tf}_2\text{N}^-$  should be able to form the 1:2 inclusion complex with  $\beta$ -CD, which would expand our multiple equilibria interaction pattern. Ritter and co-workers [14] considered that  $\text{Tf}_2\text{N}^-$  and  $\beta$ -CD form 1:1 inclusion complex, which led to the generation of separated ion pair from the contact ion pair. In our previous work, we suggested that both the cation and the anion part of  $C_{12}\text{mimTf}_2\text{N}$  would interact with  $\beta$ -CD by using  $^1\text{H}$ - $^1\text{H}$  2D ROESY and  $^{19}\text{F}$  NMR [26], and it was supposed that  $\text{Tf}_2\text{N}^-$  interacts with only one  $\beta$ -CD despite two  $\text{CF}_3\text{SO}_2$  groups exists, which may be due to the steric hindrance coming from the separated ion pair ( $\beta$ -CD- $C_n\text{mim}^+$ ) $\cdot$ ( $\text{Tf}_2\text{N}^-$ - $\beta$ -CD) [26]. On the basis of the multiple equilibria interaction pattern [27], we further suggested that the ( $\beta$ -CD- $C_n\text{mim}^+$ ) $\cdot$ ( $\text{Tf}_2\text{N}^-$ - $\beta$ -CD) ion pair will dissociate into separated  $\beta$ -CD- $C_n\text{mim}^+$  and  $\text{Tf}_2\text{N}^-$ - $\beta$ -CD, which breaks the steric hindrance. However, the detailed

interaction mechanism between  $C_n\text{mimTf}_2\text{N}$  and  $\beta$ -CD has not been ascertained yet. So we need to pay more attention to the interaction pattern between  $C_n\text{mimTf}_2\text{N}$  and  $\beta$ -CD, for which we use fluorescence spectra, isothermal titration calorimetry (ITC) and high-resolution mass spectrometry (HRMS) to study the  $C_n\text{mimTf}_2\text{N}/\beta$ -CD systems. We will try to not only validate our multiple equilibria interaction pattern in the  $C_n\text{mimTf}_2\text{N}/\beta$ -CD systems, but also unearth how  $\text{Tf}_2\text{N}^-$  interacts with  $\beta$ -CD. This work will help predict interaction patterns between other ILs and  $\beta$ -CD.

## Experimental section

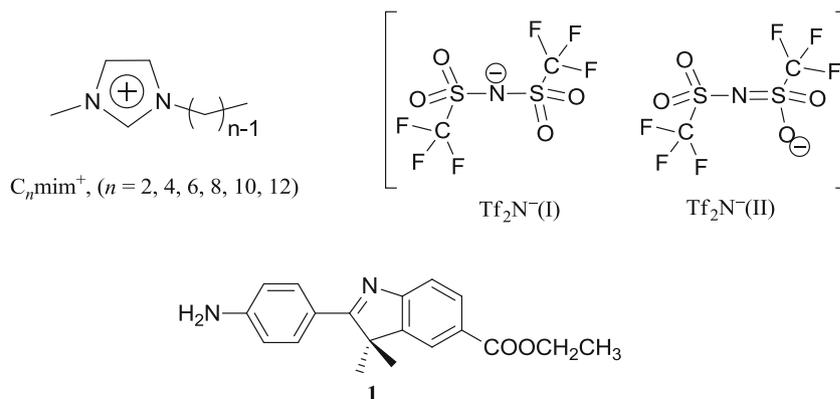
### Materials

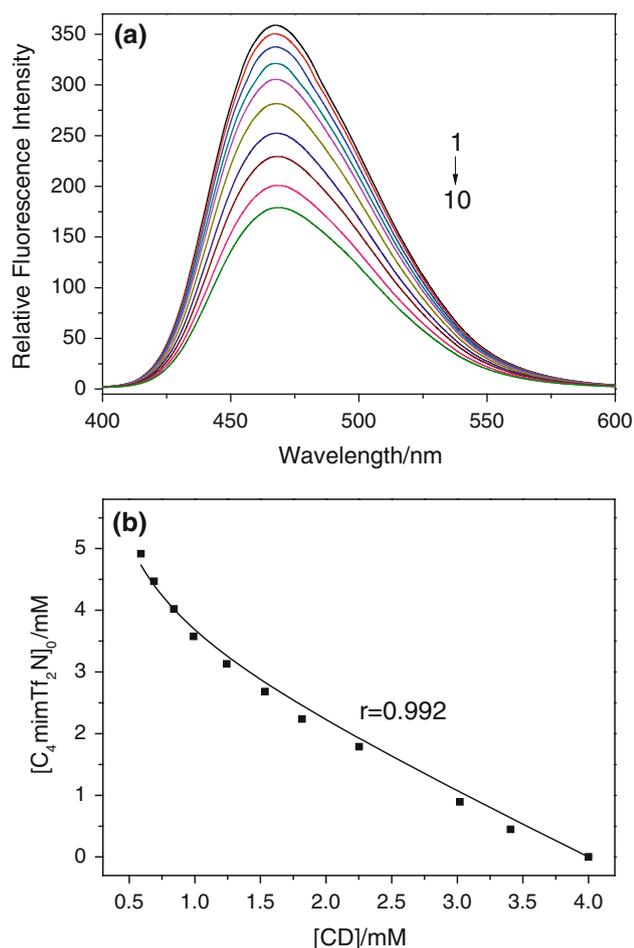
$\beta$ -CD (Beijing Aoboxing, China) was recrystallized twice using tridistilled water and dried under vacuum for 24 h.  $\text{LiTf}_2\text{N}$  (>99 % purity) was purchased from Lanzhou Institute of Chemical Physics, China. The ILs  $C_n\text{mimTf}_2\text{N}$  were synthesized via a metathetical reaction as previously reported [29]. The synthesis and purification of the fluorescent probe 2-(*p*-aminophenyl)-3,3-dimethyl-5-carboethoxy-3*H*-indole (**1**, Scheme 1) were done according to [30, 31]. Spectrographic grade reagent methanol was used as received. Tridistilled water was used throughout the experiments.

### Instruments

Fluorescence spectra were measured on an FL-4500 (Hitachi, Japan) spectrophotometer. The temperature was controlled by placing the sample in a cell compartment whose walls were accessible to water circulation and the final temperature ( $298.0 \pm 0.1$  K) of the sample was obtained by a thermocouple (Check-temp, Hanna, Italy). Fourier transform infrared (FTIR) spectra were recorded on a NICOLET iN10 MX spectrometer. The HRMS used with electrospray ionization (ESI) was performed on a Fourier Transform Ion Cyclotron Resonance. ITC was carried out on a Nano ITC 2G.

**Scheme 1** The structures of the IL cation  $C_n\text{mim}^+$  ( $n = 2, 4, 6, 8, 10, 12$ ), the two resonance structures of the IL anion  $\text{Tf}_2\text{N}^-$ , and the molecular structure of **1**





**Fig. 1** **a** Fluorescence spectra of **1** in the aqueous solutions of 4 mM  $\beta$ -CD at various initial concentrations of  $C_4\text{mimTf}_2\text{N}$  (from 1 to 10,  $[C_4\text{mimTf}_2\text{N}]_0$  increases from 0.447 to 4.92 mM), **b** initial concentration of  $C_4\text{mimTf}_2\text{N}$ ,  $[C_4\text{mimTf}_2\text{N}]_0$  versus the equilibrium concentration of  $\beta$ -CD,  $[\text{CD}]$ . The solid line is the nonlinear regression fit to the experimental data points following the model of 1:1

## Methods

### Competitive fluorescence measurement

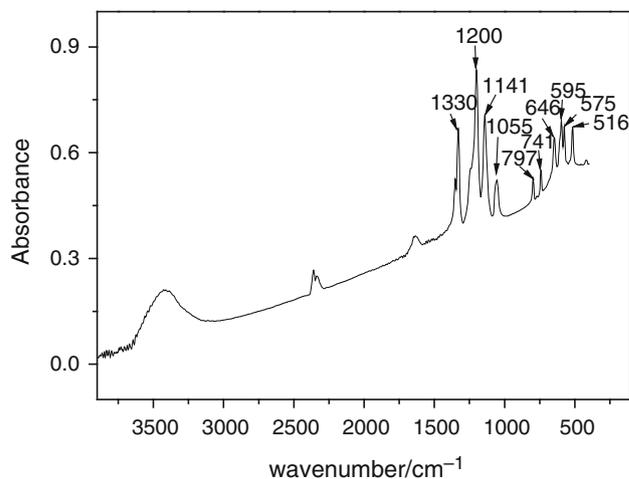
Stock solution of **1** was prepared in methanol and 50  $\mu\text{L}$  aliquots of this stock solution were added into 5 mL volumetric flasks to maintain a final concentration of  $10^{-6}$  M for fluorescence measurements. The pH values of all the solutions with **1** as a probe in this study were adjusted to 9.5 by adding NaOH and no buffer was used [32, 33].

### Isothermal titration calorimetry

In the experimental process of ITC, the IL solution in the syringe was injected over 28 drops with a respective volume of 8  $\mu\text{L}$  into the measuring cell, which was filled with the aqueous solution of  $\beta$ -CD. The temperature was kept at 298.0 K and the stirrer rotational speed was  $250 \text{ min}^{-1}$ . The

**Table 1** Stoichiometry and association constants of  $\text{LiTf}_2\text{N}$ ,  $C_n\text{mimTf}_2\text{N}$  ( $n = 2, 4$ ) with  $\beta$ -CD in water by competitive fluorescence method

	Stoichiometry	$K_1$ ( $\text{M}^{-1}$ )
$\text{LiTf}_2\text{N}$	1:1	$2490 \pm 42$
$C_2\text{mimTf}_2\text{N}$	1:1	$3255 \pm 172$
$C_4\text{mimTf}_2\text{N}$	1:1	$4374 \pm 303$



**Fig. 2** FTIR absorption spectrum of  $\text{LiTf}_2\text{N}$

equilibrium time between two injections was long enough for the signal to return to the baseline. The dilution heat was determined in a separate measurement by injecting the corresponding IL solutions into water and it was subtracted from the determined heat flow. The net reaction heat in each run was analyzed by using the “ligand binding analysis” within the software Digitam 4.1 to simultaneously compute the association constant  $K$  and molar reaction enthalpy ( $\Delta H^\circ$ ), and the standard deviation from the titration curve. Other thermodynamic parameters, i.e., the standard Gibbs free energy of binding ( $\Delta G^\circ$ ) and entropy change ( $\Delta S^\circ$ ) can be obtained by the following equations:

$$\Delta G^\circ = -RT \ln K, \quad (1)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ, \quad (2)$$

where  $R$  is the gas constant and  $T$  is the absolute temperature.

## Results

### Competitive fluorescence method

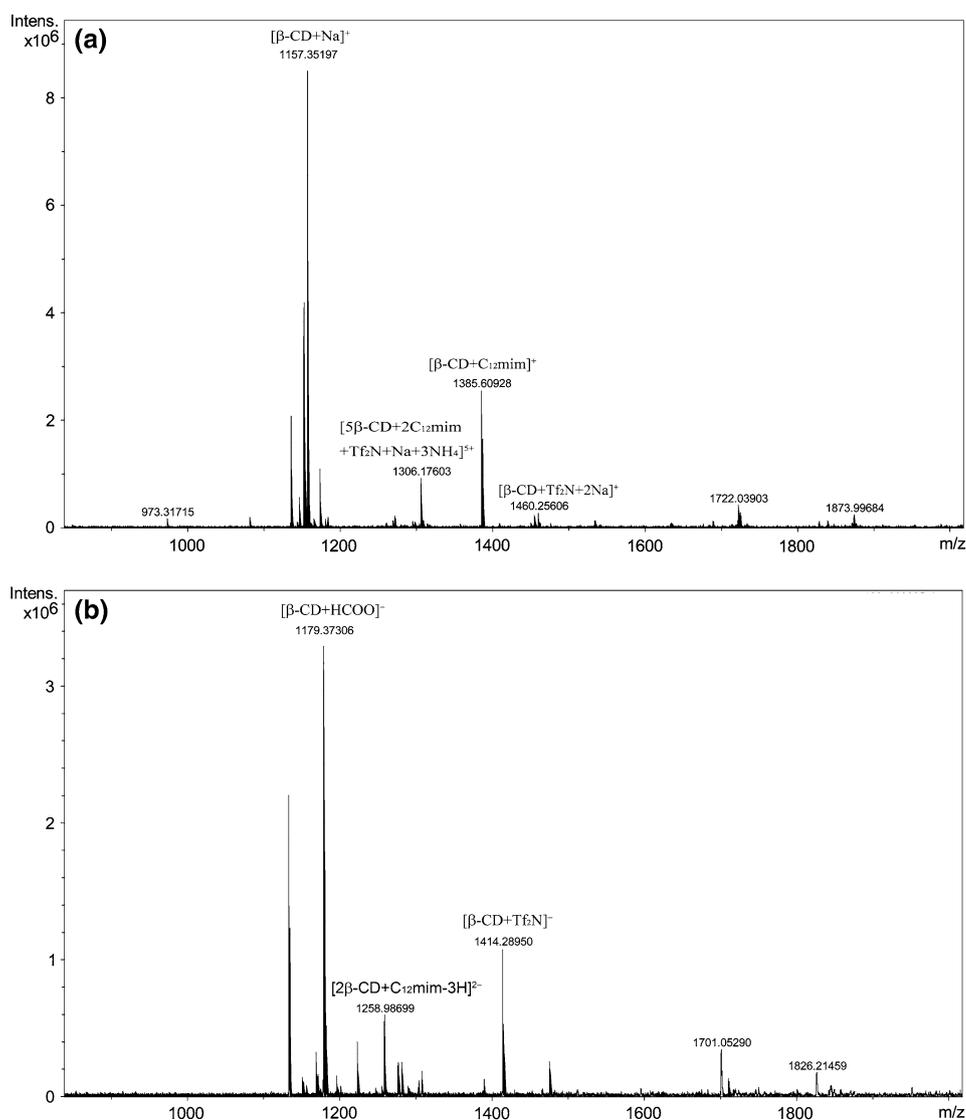
The competitive fluorescence method is suitable for the systems of weak interactions between ILs and  $\beta$ -CD with molecule **1** as fluorescent probe [26, 27]. Here we use it in  $\text{LiTf}_2\text{N}/\beta$ -CD and  $C_n\text{mimTf}_2\text{N}/\beta$ -CD ( $n = 2, 4$ ) systems.

**Table 2** IR spectra peaks and the corresponding vibrational modes of  $\text{LiTf}_2\text{N}$ 

Groups	Wavenumber ( $\text{cm}^{-1}$ )	Corresponding vibrational modes
O=S=O	1330	$\nu_{\text{as}}$
	1141	$\nu_{\text{s}}$
O=S-O <sup>-</sup>	1200	$\nu_{\text{as}}$
	1055	$\nu_{\text{s}}$
S-N-S	646	$\nu_{\text{as}}$
	595	$\nu_{\text{s}}$
S-N=S	797	$\nu_{\text{as}}$
	741	$\nu_{\text{s}}$
Two kinds of S-CF <sub>3</sub>	575	$\nu_{\text{as}}$ and $\nu_{\text{s}}$ of -S-CF <sub>3</sub>
	516	$\nu_{\text{as}}$ and $\nu_{\text{s}}$ of =S-CF <sub>3</sub>

Other  $\text{C}_n\text{mimTf}_2\text{N}$  ( $n = 6, 8, 10, 12$ ) ILs were not studied due to their poor solubility in water. According to the previous report [32], at low fluorescence probe concentrations, the total fluorescence intensity of **1** in  $1/\beta\text{-CD}$  solutions can be expressed by Eq. 3 with different initial concentrations of  $\beta\text{-CD}$  ( $[\text{CD}]_0$ ), and the  $K'_1$ ,  $K'_2$ ,  $I_1/I_0$ , and  $I_2/I_0$  values ( $K'_1$  and  $K'_2$  are the association constants for 1:1 and 1:2 complexes between **1** and  $\beta\text{-CD}$ , respectively, and  $I_0$ ,  $I_1$ , and  $I_2$  stand for the fluorescence intensity of **1** in pure water, in the 1:1 complex, and in the 1:2 complex, respectively) can be estimated by nonlinear regression analysis.

$$I = \frac{(I_0 + I_1 K_1 [\text{CD}]_0 + I_2 K_1 K_2 [\text{CD}]_0^2)}{1 + K_1 [\text{CD}]_0 + K_1 K_2 [\text{CD}]_0^2} \quad (3)$$

**Fig. 3** The positive (a) and negative (b) ESI spectra of equal mole of  $\text{C}_{12}\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$ 

After that, the fluorescence spectra of **1** in the LiTf<sub>2</sub>N/β-CD, C<sub>2</sub>mimTf<sub>2</sub>N/β-CD, and C<sub>4</sub>mimTf<sub>2</sub>N/β-CD systems were measured and that in the C<sub>4</sub>mimTf<sub>2</sub>N/β-CD system is shown in Fig. 1a as an example. Within the range of the ILs concentration studied in this paper, the fluorescence intensity decreases noticeably with the increase of the initial concentration of ILs. The equilibrium concentrations of β-CD, i.e., [CD], at different [C<sub>n</sub>mimTf<sub>2</sub>N]<sub>0</sub> (the initial concentration of C<sub>n</sub>mimTf<sub>2</sub>N) can be calculated using the K'<sub>1</sub>, K'<sub>2</sub>, I<sub>1</sub>/I<sub>0</sub>, and I<sub>2</sub>/I<sub>0</sub> values according to Eq. 3 [34]. The concentration of β-CD binding with ILs can be obtained from [CD]<sub>0</sub> to [CD]. Thus by analyzing the variation of [C<sub>n</sub>mimTf<sub>2</sub>N]<sub>0</sub> as a function of [CD] with Eq. 4 for 1:1 inclusion complexes [25, 27], the results of the interaction between β-CD and C<sub>n</sub>mimTf<sub>2</sub>N are listed in Table 1.

$$[C_n\text{mimTf}_2\text{N}]_0 = \frac{([\text{CD}]_0 - [\text{CD}])(1 + K_1[\text{CD}])}{K_1[\text{CD}]} \quad (4)$$

LiTf<sub>2</sub>N and C<sub>n</sub>mimTf<sub>2</sub>N (n = 2, 4) all form only 1:1 inclusion complexes with β-CD, indicating that C<sub>n</sub>mim<sup>+</sup> (n = 2, 4) and Tf<sub>2</sub>N<sup>-</sup> form 1:1 complexes with β-CD. The 1:1 stoichiometry between C<sub>n</sub>mim<sup>+</sup> (n = 2, 4) and β-CD has been proved in our previous C<sub>n</sub>mimPF<sub>6</sub>/β-CD study [27], while as regarding Tf<sub>2</sub>N<sup>-</sup>, no 1:2 complex Tf<sub>2</sub>N<sup>-</sup>-2β-CD is detected.

#### FTIR measurement

FTIR spectrum of LiTf<sub>2</sub>N is shown in Fig. 2, and the characteristic peaks and their corresponding vibrational

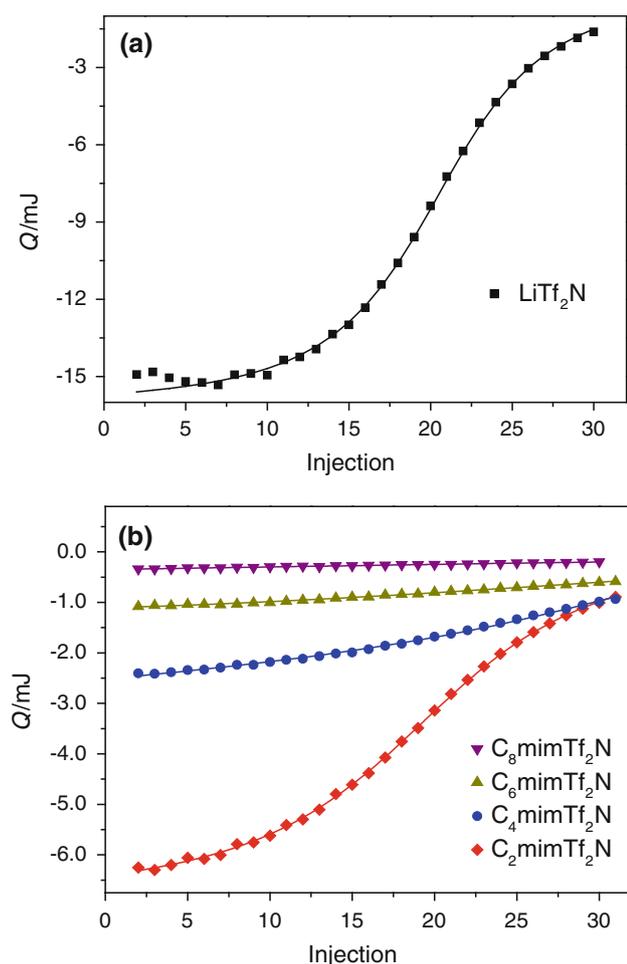
modes are listed in Table 2. The peaks at 1,330 and 1,141 cm<sup>-1</sup> can be assigned to the antisymmetrical and symmetrical stretching modes (ν<sub>as</sub> and ν<sub>s</sub>) of O=S=O in Tf<sub>2</sub>N<sup>-</sup>, while those at 1,200 and 1,055 cm<sup>-1</sup> can be assigned to ν<sub>as</sub> and ν<sub>s</sub> of O=S-O<sup>-</sup>. Moreover, the six peaks between 500 and 800 cm<sup>-1</sup> can be assigned to ν<sub>as</sub> and ν<sub>s</sub> of S-N-S, S-N=S, -S-C(F<sub>3</sub>) and =S-C(F<sub>3</sub>), respectively. These results may indicate the coexistence of the resonance structures of Tf<sub>2</sub>N<sup>-</sup>.

#### ESI/HRMS method

The ESI/HRMS method has been validated effective to study the composition of non-covalent complexes including CD-ILs complexes in our previous work [27], so it is also applied to determine the complex compositions in the systems of this work. The ESI/HRMS spectra of the C<sub>12</sub>mimTf<sub>2</sub>N/β-CD system are shown in Fig. 3 as an example, and after analyzing the signals, the composition of the fragments and their corresponding complexes for the multiple equilibria interaction pattern [27] are listed in Table 3. From the results, it can be seen that C<sub>n</sub>mim<sup>+</sup> (n = 2, 4, 6) with short alkyl side chain and Tf<sub>2</sub>N<sup>-</sup> form the 1:1 complexes (S-4 and S-5), while the 1:2 complexes (S-6) are obtained in C<sub>n</sub>mim<sup>+</sup> (n = 8, 10, 12) systems with longer alkyl side chain. Although the existence of signals corresponding to (β-CD-C<sub>n</sub>mim<sup>+</sup>)-Tf<sub>2</sub>N<sup>-</sup> (S-1) or C<sub>n</sub>mim<sup>+</sup>-(β-CD-Tf<sub>2</sub>N<sup>-</sup>) (S-2) can be observed, no signals of (β-CD-C<sub>n</sub>mim<sup>+</sup>)-(Tf<sub>2</sub>N<sup>-</sup>-β-CD) (S-3) is detected, indicating that both the cation and the anion of the ion pairs will interact with β-CD, and (β-CD-C<sub>n</sub>mim<sup>+</sup>)-(Tf<sub>2</sub>N<sup>-</sup>-β-CD)

**Table 3** The composition of the fragments and their corresponding complexes for the multiple equilibria interaction pattern in equal mole amount of LiTf<sub>2</sub>N/β-CD and C<sub>n</sub>mimTf<sub>2</sub>N/β-CD systems (obtained by ESI/HRMS)

ILs	Cation	Anion
LiTf <sub>2</sub> N	(β-CD + LiTf <sub>2</sub> N + Na) <sup>+</sup> (S-2)	(β-CD + Tf <sub>2</sub> N) <sup>-</sup> (S-5)
C <sub>2</sub> mimTf <sub>2</sub> N	(β-CD + C <sub>2</sub> mim) <sup>+</sup> (S-4)	(β-CD + C <sub>2</sub> mim + 2HCOO) <sup>-</sup> (S-4)
	(β-CD + Tf <sub>2</sub> N + Na + H) <sup>+</sup> (S-5)	(β-CD + Tf <sub>2</sub> N) <sup>-</sup> (S-5)
	(β-CD + C <sub>2</sub> mimTf <sub>2</sub> N + NH <sub>4</sub> ) <sup>+</sup> (S-1 or S-2)	(β-CD + C <sub>2</sub> mimTf <sub>2</sub> N + HCOO) <sup>-</sup> (S-1 or S-2)
C <sub>4</sub> mimTf <sub>2</sub> N	(β-CD + C <sub>4</sub> mim) <sup>+</sup> (S-4)	(β-CD + Tf <sub>2</sub> N) <sup>-</sup> (S-5)
	(β-CD + Tf <sub>2</sub> N + Na + H) <sup>+</sup> (S-5)	(β-CD + C <sub>4</sub> mimTf <sub>2</sub> N + HCOO) <sup>-</sup> (S-1 or S-2)
	(β-CD + C <sub>4</sub> mimTf <sub>2</sub> N + Na) <sup>+</sup> (S-1 or S-2)	
C <sub>6</sub> mimTf <sub>2</sub> N	(β-CD + C <sub>6</sub> mim) <sup>+</sup> (S-4)	(β-CD + Tf <sub>2</sub> N) <sup>-</sup> (S-5)
	(β-CD + C <sub>6</sub> mimTf <sub>2</sub> N + Na) <sup>+</sup> (S-1 or S-2)	(β-CD + C <sub>6</sub> mimTf <sub>2</sub> N + HCOO) <sup>-</sup> (S-1 or S-2)
C <sub>8</sub> mimTf <sub>2</sub> N	(β-CD + C <sub>8</sub> mim) <sup>+</sup> (S-4)	(2β-CD + C <sub>8</sub> mim + 2OH + HCOO) <sup>2-</sup> (S-6)
	(β-CD + Tf <sub>2</sub> N + 2 Na) <sup>+</sup> (S-5)	
C <sub>10</sub> mimTf <sub>2</sub> N	(β-CD + C <sub>10</sub> mim) <sup>+</sup> (S-4)	(β-CD + Tf <sub>2</sub> N) <sup>-</sup> (S-5)
	(β-CD + Tf <sub>2</sub> N + 2 Na) <sup>+</sup> (S-5)	(2β-CD + C <sub>10</sub> mim - 3H) <sup>2-</sup> (S-6)
C <sub>12</sub> mimTf <sub>2</sub> N	(β-CD + C <sub>12</sub> mim) <sup>+</sup> (S-4)	(β-CD + Tf <sub>2</sub> N) <sup>-</sup> (S-5)
	(β-CD + Tf <sub>2</sub> N + 2 Na) <sup>+</sup> (S-5)	(2β-CD + C <sub>12</sub> mim - 3H) <sup>2-</sup> (S-6)
	(5β-CD + 2C <sub>12</sub> mim + Tf <sub>2</sub> N + Na + 3NH <sub>4</sub> ) <sup>5+</sup> (S-6 + S-5)	



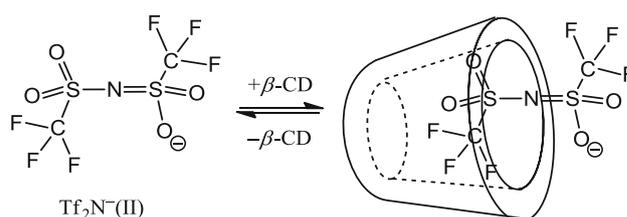
**Fig. 4** The heat caused by the host–guest interaction versus the injection number of LiTf<sub>2</sub>N (a) and C<sub>n</sub>mimTf<sub>2</sub>N (n = 2, 4, 6, 8) (b) into β-CD. The points are obtained from the experiment and the solid lines are the results by regression analysis

(S-3) will dissociate into two kinds of 1:1 complexes (S-4 and S-5).

#### Isothermal titration calorimetry

ITC, which is accurate for the determination of thermodynamic parameters, i.e.,  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  [14, 27, 35–37], can also be used here to study the interaction between C<sub>n</sub>mimTf<sub>2</sub>N and β-CD in aqueous solutions. The fitting curves to obtain the thermodynamic parameters of the formation of LiTf<sub>2</sub>N/β-CD and C<sub>n</sub>mimTf<sub>2</sub>N/β-CD complexes are shown in Fig. 4, and Table 4 shows the results of the complexation (C<sub>10</sub>mimTf<sub>2</sub>N and C<sub>12</sub>mimTf<sub>2</sub>N are not investigated because of their poor solubility in water, leading to weak complex heat).

The negative  $\Delta G$  values for all the systems indicate that the inclusion processes of LiTf<sub>2</sub>N/β-CD and C<sub>n</sub>mimTf<sub>2</sub>N/β-CD are spontaneous. In the case of LiTf<sub>2</sub>N, C<sub>2</sub>mimTf<sub>2</sub>N, C<sub>4</sub>mimTf<sub>2</sub>N, and C<sub>6</sub>mimTf<sub>2</sub>N, the negative  $\Delta H$  and



**Scheme 2** The supposed charge resonance hybrids of Tf<sub>2</sub>N<sup>-</sup> and the inclusion equilibrium of Tf<sub>2</sub>N<sup>-</sup> (II) with β-CD

$\Delta S$  values mean that the inclusion complexations are exothermic and enthalpy-controlled, but not entropy driven. While for C<sub>8</sub>mimTf<sub>2</sub>N/β-CD system, the  $\Delta S$  value of the inclusion complexation becomes positive, indicating that the process turns entropy and enthalpy driven.

#### Discussion

##### The inclusion pattern of Tf<sub>2</sub>N<sup>-</sup>/β-CD

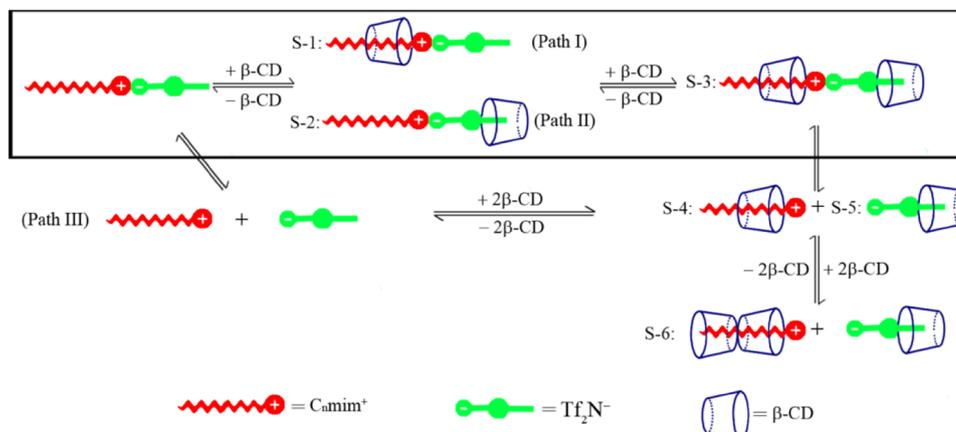
The competitive fluorescence method is the most sensitive method for the systems of weak interactions between ILs and β-CD. According to the results, Tf<sub>2</sub>N<sup>-</sup> only forms 1:1 complex with β-CD despite its symmetrical structure and two SO<sub>2</sub>CF<sub>3</sub> groups. As regards ESI/HRMS results of equal mole of ILs and β-CD in Table 4, no signals corresponding to the 1:2 inclusion complexes between Tf<sub>2</sub>N<sup>-</sup> and β-CD occur, while those corresponding to the Tf<sub>2</sub>N<sup>-</sup>-β-CD, C<sub>n</sub>mim<sup>+</sup>-β-CD, and C<sub>n</sub>mim<sup>+</sup>-2β-CD (when n = 8, 10, 12) inclusion complexes can be seen. Even in LiTf<sub>2</sub>N/β-CD system where there is little steric hindrance between the cation Li<sup>+</sup> and Tf<sub>2</sub>N<sup>-</sup>, no Tf<sub>2</sub>N<sup>-</sup>-2β-CD inclusion complexes are detected. This also confirms that Tf<sub>2</sub>N<sup>-</sup> only forms the 1:1 complex with β-CD.

One of the reasons for this phenomenon shall be the steric hindrance between β-CD molecules. Moreover, considering the structure of Tf<sub>2</sub>N<sup>-</sup>, we suggest to explain the phenomenon with a charge resonance structure according to the FTIR results which indicate the coexistence of the resonance hybrids of Tf<sub>2</sub>N<sup>-</sup> (I and II, shown in Scheme 1). The resonance tautomer Tf<sub>2</sub>N<sup>-</sup> (II) loses the structural symmetry, so when another β-CD molecule gets close to the 1:1 Tf<sub>2</sub>N<sup>-</sup> (II)-β-CD complex, both the poor symmetry of Tf<sub>2</sub>N<sup>-</sup> (II) and the steric hindrance will obstruct the resonance tautomer from further forming the 1:2 complex (Scheme 2).

This supposed resonance equilibrium can get support from the similar mechanism mentioned in a previous study about imidodisulfuryl fluoride ion (SO<sub>2</sub>F)<sub>2</sub>N<sup>-</sup> [38]. The inductive effect of the SO<sub>2</sub>F group will greatly reduce the electron density on the nitrogen in (SO<sub>2</sub>F)<sub>2</sub>N<sup>-</sup>, thus forming the (SO<sub>2</sub>F)N-S(=O)(F)O<sup>-</sup> structure with a

**Table 4** Thermodynamic parameters  $\Delta G$ ,  $\Delta H$ ,  $\Delta S$  and association constant  $K$  for the complex formed by  $\text{LiTf}_2\text{N}$ ,  $\text{C}_n\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$  in aqueous solution

ILs	Stoichiometry	$K$ ( $\text{M}^{-1}$ )	$\Delta H$ ( $\text{kJ mol}^{-1}$ )	$\Delta G$ ( $\text{kJ mol}^{-1}$ )	$\Delta S$ ( $\text{J mol}^{-1} \text{K}^{-1}$ )
$\text{LiTf}_2\text{N}$	1:1	$2836 \pm 116$	$-30.0 \pm 1.3$	-19.7	-34.5
$\text{C}_2\text{mimTf}_2\text{N}$	1:1	$2740 \pm 92$	$-31.1 \pm 1.6$	-19.6	-38.6
$\text{C}_4\text{mimTf}_2\text{N}$	1:1	$2921 \pm 119$	$-31.2 \pm 0.4$	-19.8	-38.2
$\text{C}_6\text{mimTf}_2\text{N}$	1:1	$9808 \pm 595$	$-28.8 \pm 0.2$	-22.8	-20.1
$\text{C}_8\text{mimTf}_2\text{N}$	1:1	$12069 \pm 1088$	$-20.5 \pm 0.3$	-23.3	9.39

**Scheme 3** The multiple equilibria interaction pattern between  $\text{C}_n\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$  in aqueous solution

sulfur–nitrogen  $\pi$  bonding [38]. This phenomenon has also been considered by Cruickshank [39], who concluded that it occurs to an appreciable extent in sulfamates and other relative derivatives. X-ray data of the imidodisulfonate ion,  $\text{HN}(\text{SO}_3)_2^{2-}$ , also indicates that appreciable sulfur–nitrogen  $\pi$  bonding occurs in this kind of species indeed [40].

#### The interaction pattern involved multiple equilibria

Based on the results above, when the interaction pattern between  $\text{C}_n\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$  in aqueous solutions is discussed, both the dissociation equilibrium of  $\text{C}_n\text{mim}^+\cdot\text{Tf}_2\text{N}^-$  ion pairs and the complexation of the dissociated ions by  $\beta\text{-CD}$  should be considered. From the competitive fluorescence method and ESI/HRMS results, the  $\text{C}_n\text{mim}^+$  forms the 1:1 or 1:2 complexes due to different length of alkyl side chains. That is,  $\text{C}_2\text{mim}^+$ ,  $\text{C}_4\text{mim}^+$ , and  $\text{C}_6\text{mim}^+$  form the 1:1 complexes with  $\beta\text{-CD}$ , while  $\text{C}_8\text{mim}^+$ ,  $\text{C}_{10}\text{mim}^+$ , and  $\text{C}_{12}\text{mim}^+$  form the 1:2 complexes. In addition, the signals of 1:2 complexes in HRMS mainly correspond to  $\text{C}_n\text{mim}^+-2\beta\text{-CD}$  ( $n = 8, 10, 12$ ), which indicates that the intermediate 1:2 complex ( $\beta\text{-CD}-\text{C}_n\text{mim}^+\cdot(\text{Tf}_2\text{N}^--\beta\text{-CD})$ ) will dissociate into  $\text{C}_n\text{mim}^+-\beta\text{-CD}$  and  $\text{Tf}_2\text{N}^--\beta\text{-CD}$ . With regard to the anion moiety,  $\text{Tf}_2\text{N}^-$  forms the 1:1 complex with  $\beta\text{-CD}$ . The interaction pattern between  $\text{C}_n\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$  successfully validates our multiple equilibria interaction pattern (Scheme 3), and the association constants  $K_1$  of

$\text{C}_n\text{mimTf}_2\text{N}/\beta\text{-CD}$  complexes should be attributed to the weighting average of the association constants of 1:1  $\text{C}_n\text{mim}^+\cdot\text{Tf}_2\text{N}^--\beta\text{-CD}$  (S-1 or S-2), 1:1  $\text{C}_n\text{mim}^+-\beta\text{-CD}$  (S-4), and 1:1  $\text{Tf}_2\text{N}^--\beta\text{-CD}$  (S-5) complexes, while  $K_2$  of  $\text{C}_n\text{mimTf}_2\text{N}/\beta\text{-CD}$  complexes originates from that of  $\text{C}_n\text{mim}^+-2\beta\text{-CD}$  (S-6).

#### Thermodynamic parameters of the inclusion complexes

When the ILs are  $\text{C}_2\text{mimTf}_2\text{N}$  and  $\text{C}_4\text{mimTf}_2\text{N}$ , both the association constants (by competitive fluorescence method and ITC method) and the thermodynamic parameters (by ITC method) are close to those of  $\text{LiTf}_2\text{N}/\beta\text{-CD}$  (Tables 1, 3). This conforms to the strength order of  $\text{C}_2\text{mim}^+$ ,  $\text{C}_4\text{mim}^+$ , and  $\text{Tf}_2\text{N}^-$  interacting with  $\beta\text{-CD}$ , that is,  $\text{Tf}_2\text{N}^- > \text{C}_4\text{mim}^+ > \text{C}_2\text{mim}^+$ , which we previously suggested [26]. For  $\text{C}_6\text{mimTf}_2\text{N}$  and  $\text{C}_8\text{mimTf}_2\text{N}$ , the association constants in Table 3 are bigger than that of  $\text{LiTf}_2\text{N}/\beta\text{-CD}$ , indicating that the  $\text{C}_6\text{mim}^+$  and  $\text{C}_8\text{mim}^+$  interact much more strongly with  $\beta\text{-CD}$ .

The processes of the inclusion complexation of  $\text{LiTf}_2\text{N}$ ,  $\text{C}_2\text{mimTf}_2\text{N}$ ,  $\text{C}_4\text{mimTf}_2\text{N}$ , and  $\text{C}_6\text{mimTf}_2\text{N}$  with  $\beta\text{-CD}$  are exothermic and enthalpy-controlled, but not entropy driven. The unfavorable effect of the negative  $\Delta S$  values can be overcome by the more negative values of  $\Delta H$ , leading to energetically favorable values. This is the common situation concerning the formation of inclusion complexes

between CDs and various guest molecules, similar to  $C_n\text{mimPF}_6/\beta\text{-CD}$  systems [27].

However, for  $C_8\text{mimTf}_2\text{N}/\beta\text{-CD}$  system, the  $\Delta S$  value of the inclusion complexation becomes positive, that is, the process is entropy and enthalpy driven. Before association, both the host CD and guest are highly solvated, and the solvent molecules around the host and the guest are highly ordered. During the association, the solvation shells of both the host and the guest undergo reorganization accompanied by the loss of some solvent molecules. This process creates disorder in the system and thus leads to a favorable entropic gain [41], and the positive  $\Delta S$  of the  $C_8\text{mimTf}_2\text{N}/\beta\text{-CD}$  system is just the combined result.

## Conclusions

We have investigated the interactions between  $C_n\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$  in aqueous solutions. The competitive fluorescence measurement, ITC and ESI/HRMS results show that the interaction between  $C_n\text{mimTf}_2\text{N}$  and  $\beta\text{-CD}$  is just like the  $C_n\text{mimPF}_6/\beta\text{-CD}$  solution, following our multiple equilibria interaction pattern. Both the cation and anion moiety of  $C_n\text{mimTf}_2\text{N}$  can form 1:1 complex with  $\beta\text{-CD}$ , and the result complex  $(\beta\text{-CD}-C_n\text{mim}^+)(\text{Tf}_2\text{N}^--\beta\text{-CD})$  dissociates into  $C_n\text{mim}^+-\beta\text{-CD}$  and  $\text{Tf}_2\text{N}^--\beta\text{-CD}$ . The cation moiety  $C_n\text{mim}^+-\beta\text{-CD}$  ( $n = 8, 10, 12$ ) with long alkyl side chain will further form 1:2 complexes with another  $\beta\text{-CD}$ , while the anion moiety  $\text{Tf}_2\text{N}^--\beta\text{-CD}$  will not because of a charge resonance structure in the structure. These results successfully validate our multiple equilibria interaction pattern and will help predict interaction patterns between other ILs and  $\beta\text{-CD}$ .

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