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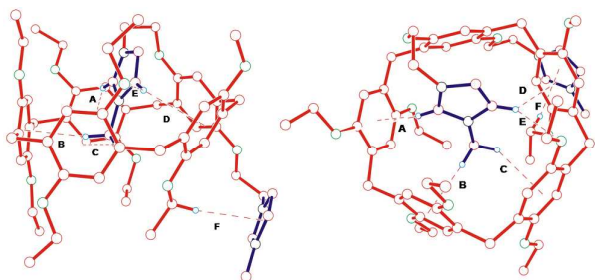


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Pillar[5]arene presented tunable binding ability with different imidazolium-based ionic liquids in chloroform.

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## COMMUNICATION

## Host–guest complexation between 1,4-dipropoxypillar[5]arene and imidazolium-based ionic liquids†

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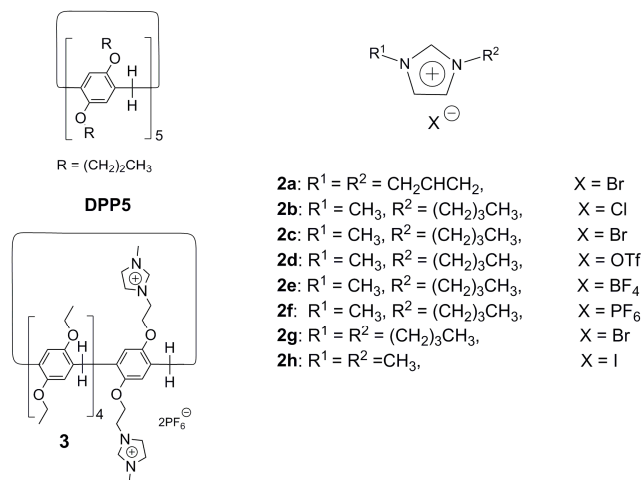
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A series of imidazolium-based ionic liquids with different counterions and alkyl chains were introduced to systematically investigate the host–guest complexation with pillar[5]arene. It was demonstrated that pillar[5]arene presented tunable binding ability with different imidazolium-based ionic liquids in chloroform. Both the counterions and the alkyl chains on the guests played important roles in the host–guest association process.

Threaded structures, such as rotaxanes, pseudorotaxanes and catenanes, act as very important building blocks for advanced supramolecular structures and have been widely applied to prepare supramolecular polymers, molecular devices and sensors.<sup>1</sup> Pseudorotaxanes, considered as the simplest threaded structures, are the basic and crucial precursors for the fabrication of mechanically interlocked structures including rotaxanes and catenanes.<sup>2</sup> Macrocyclic molecules,<sup>3</sup> such as crown ethers, cyclodextrins, calixarenes and cucurbiturils, have been widely used as host molecules to form kinds of inclusion complexes with appropriate guest molecules. For example, dibenzo-24-crown-8 (DB24C8) and benzo-21-crown-7 (B21C7) can bind secondary ammonium salts to form [2]pseudorotaxanes, and these DB24C8/B21C7-based [2]pseudorotaxanes have been applied to construct various supramolecular aggregates, arranging from supramolecular polymers to supramolecular gels.<sup>3b,i</sup> Considering the fascinating structural properties and wide applications of pseudorotaxanes, it is of great significance to develop new molecular recognition systems and build pseudorotaxanes based on these new recognition systems.<sup>4</sup>

Pillar[5]arenes,<sup>5</sup> a new kind of macrocyclic hosts, were first synthesized in 2008 and have achieved quick development over the past several years. Based on their unique rigid molecular structures, pillar[5]arenes have become one of the most perspective candidates to develop new molecular recognition systems and prepare mechanically threaded/interlocked structures.<sup>6</sup> Based on the C–H... $\pi$  interactions between pillar[5]arenes and alkyl chains, a lot of functionalized alkyl chain guests, such as bis(imidazole) derivatives,<sup>5f</sup> alkanedinitriles,<sup>5j</sup> alkanediols,<sup>6a</sup> and secondary dialkylammonium salts<sup>6m</sup> have been explored to investigate the host–guest properties with pillar[5]arenes. Imidazolium-based ionic liquids are a kind of non-volatile salts with melting points below 100 °C. Since their discovery, increasing interest has been

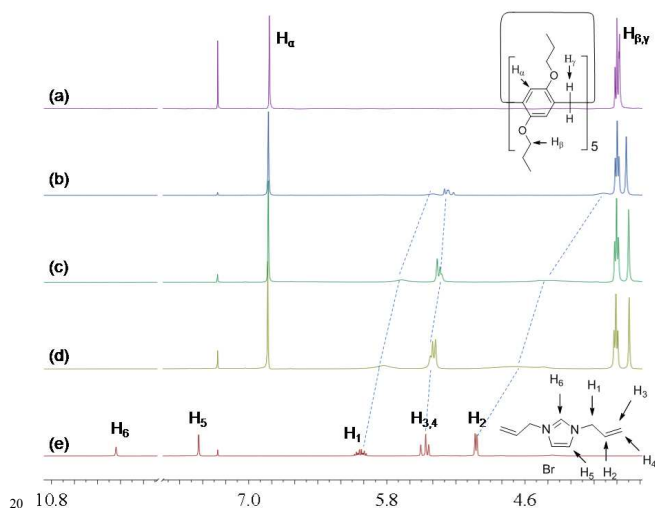
focused on the application of this kind of ionic liquids.<sup>7</sup> Though ionic liquid molecules have been introduced to enrich pillar[5]arene-based supramolecular chemistry,<sup>5c</sup> their attention was mainly focused on dealkylative pillararene derivatives. We have found that the host–guest properties between dialkoxypillararene and imidazolium-based ionic liquid displayed a lower critical solution temperature (LCST) type phase behaviour in chloroform.<sup>8</sup> In order to get an intensive and comprehensive understanding of the nature of the pillar[5]arene/ionic liquid molecular recognition, it is reasonable to investigate the host–guest complexation between pillar[5]arene and different imidazolium-based ionic liquids. Herein, we reported the host–guest complexation properties between a dialkoxypillararene and a series of imidazolium-based ionic liquids.



Scheme 1 Chemical structures of dipropoxypillar[5]arene (DPP5), a series of ionic liquids and 3.

We first investigated the complexation between dipropoxypillar[5]arene (DPP5) and 2a by <sup>1</sup>H NMR (Scheme 1). The <sup>1</sup>H NMR spectrum of a solution of DPP5 and 2a in CDCl<sub>3</sub> showed only one set of peaks, indicating fast-exchange complexation between DPP5 and 2a on the <sup>1</sup>H NMR time scale at 22 °C (Fig. 1b–d). Gradual addition of DPP5 into a solution of ionic liquid 2a in CDCl<sub>3</sub> led to the signal of H<sub>γ</sub> of DPP5 gradually shifting upfield, from 3.77 to 3.69 ppm. Obvious changes in the chemical shifts and peak shapes were observed for

guest molecule **2a**. After complexation,  $H_{1,2,3,4}$  on **2a** all moved upfield and became broad due to the shield effect. For example,  $H_2$  moved from 5.03 to 3.92 ppm, while  $H_1$  moved upfield from 6.02 to 5.42 ppm. Besides, the imidazolium protons of  $H_5$  and  $H_6$  exhibited remarkable complexation-induced broadening effects because their signals could not be observed in Fig. 1b-d, indicating that the imidazolium parts of **2a** were threaded into the cavities of **DPP5**, which was in accordance with the reported changes in the formation of a pillar[5]arene-based [3]pseudorotaxane.<sup>6n</sup> These changes in chemical shifts and shapes of proton signals indicated the existence of the host-guest complexation between **DPP5** and ionic liquid **2a**.<sup>6</sup> The 2D NOESY spectrum of an equimolar mixture of **DPP5** and **2a** was further obtained to investigate the host-guest complexation (Fig. S4, ESI<sup>†</sup>). It showed several correlative peaks between protons on **DPP5** and protons on guest molecule **2a**. For example, correlative peaks between  $H_\beta$  and  $H_\gamma$  of **DPP5** and  $H_2$  of **2a** were observed, which agreed with the formation of a threaded structure.<sup>5,6,9</sup>



**Fig. 1** Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CDCl}_3$ , 22  $^\circ\text{C}$ ) of solutions of **DPP5** and **2a** with different molar ratios (the concentration of **2a** was kept as constant at 10.0 mM): (a) **DPP5**; (b) 1:1; (c) 1:0.6; (d) 1:0.3; (e) **2a**.

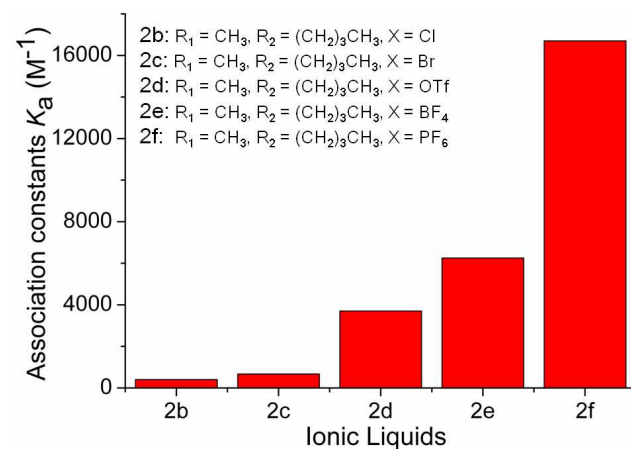
Further experiments were carried out to determine the complexation stoichiometry between **DPP5** and **2a**. By a molar ratio plot based on NMR titration, a 1:1 stoichiometry for the complexation between **DPP5** and **2a** was obtained (Fig. S7, ESI<sup>†</sup>). Electrospray ionization mass spectrum (Fig. S20) of a mixture of **DPP5** and **2a** showed a base peak at  $m/z = 1180.5$ , corresponding to  $[\text{DPP5} \rightarrow \text{2a} - \text{Br}]^+$ , which revealed a 1:1 stoichiometry for the complexation between **DPP5** and **2a**.<sup>5,6</sup> Similar electrospray ionization mass spectrometry results between **DPP5** and other ionic liquids were also got and showed 1:1 stoichiometries for complexations between the host and different guests (Fig. S21–25, ESI<sup>†</sup>).<sup>8</sup>

In the following step, we applied other ionic liquids with different substituent groups and different anions to investigate their influences on the binding ability. Association constants ( $K_a$ ) between **DPP5** and different ionic liquid guests were measured (Table 1, Figs. 2 and S5–19, ESI<sup>†</sup>).<sup>8</sup> As shown in Fig. 2, it was demonstrated that the counterions played a important part in the

formation of host-guest complexes since the  $K_a$  values increased obviously when the counterion varied from  $\text{Cl}^-$  to  $\text{PF}_6^-$  (the  $K_a$  values of **DPP5**→**2d**, **DPP5**→**2e** and **DPP5**→**2f** were obviously higher than that of **DPP5**→**2b** and **DPP5**→**2c**). For example, the  $K_a$  value of **DPP5**→**2f** was  $1.67 (\pm 0.83) \times 10^4 \text{ M}^{-1}$  in  $\text{CDCl}_3$ , about 40 times higher than the value,  $4.04 (\pm 0.29) \times 10^2 \text{ M}^{-1}$ , of **DPP5**→**2b**. Based on the results of association constants, it was indicated that loose ion-pairs can promote the formation of more stable host-guest complexes than intimate ion-pairs.<sup>5,6</sup> Besides, we also found that the alkyl chains on the guest was conducive to the host-guest association process, as ionic liquids with alkyl chains substituents showed higher association constants than that with allyl substituents by comparing the  $K_a$  values of **DPP5**→**2c** and **DPP5**→**2g** with that of **DPP5**→**2a**.<sup>5,6</sup>

**Table 1.** Association constants  $K_a$  ( $\text{M}^{-1}$ ) for host-guest complexations of **2a**–**2h** with **DPP5** ( $\text{CDCl}_3$ , 295 K).

Host-guest complexes	$K_a$
<b>DPP5</b> → <b>2a</b>	$9.50 (\pm 0.16) \times 10$
<b>DPP5</b> → <b>2b</b>	$4.04 (\pm 0.29) \times 10^2$
<b>DPP5</b> → <b>2c</b>	$6.71 (\pm 0.36) \times 10^2$
<b>DPP5</b> → <b>2d</b>	$3.70 (\pm 0.27) \times 10^3$
<b>DPP5</b> → <b>2e</b>	$6.25 (\pm 0.78) \times 10^3$
<b>DPP5</b> → <b>2f</b>	$1.67 (\pm 0.83) \times 10^4$
<b>DPP5</b> → <b>2g</b>	$3.32 (\pm 0.38) \times 10^2$
<b>DPP5</b> → <b>2h</b>	$1.04 (\pm 0.15) \times 10^3$

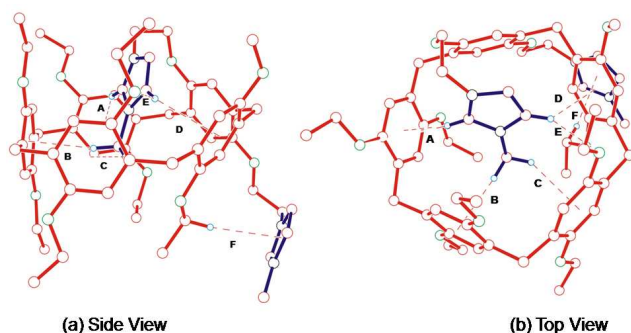


**Fig. 2** Association constants between **DPP5** and ionic liquids.

Though we did not get the single crystal structures of host-guest complexes discussed above (Table. 1), we serendipitously obtained the single crystal structure of an imidazolium-containing pillar[5]arene **3** which could also give us useful information about the host-guest interactions between pillar[5]arenes and imidazolium ion-based ionic liquids. This single crystal was grown by slow evaporation of its  $\text{CH}_3\text{COOC}_2\text{H}_5/\text{CH}_3\text{CN}$  ( $v/v = 4:1$ ) solution at room temperature (Fig. 3). From this crystal structure, it was clear that one of the two imidazolium cation located in the cavity of the pillar[5]arene. The imidazolium cation inside the cavity has four  $\text{C-H} \cdots \pi$  interactions with the neighbouring benzene rings and one  $\text{C-H} \cdots \text{O}$  interaction with an oxygen atom on the neighbouring benzene ring. The  $\text{C-H} \cdots \pi$  distances,  $2.54 \sim$



2.94 Å, were shorter than 3.05 Å, indicating the existence of the C-H... $\pi$  interactions (A, B, C and D in Fig. 3).<sup>5d,5g,6h,6i</sup> The C-H...O distance was 2.51 Å and its angle was 135.59° (E in Fig. 3). Interestingly, the imidazolium unit outside the cavity had one C-H... $\pi$  interactions with the alkyl chain in neighbouring benzene ring with the C-H... $\pi$  distance of 2.83 Å (F in Fig. 3). The X-ray crystallographic analysis revealed that the imidazolium could indeed thread into the cavity of the pillar[5]arene, which also gave strong support for the complexation between host DPP5 and guests 2a–2h mentioned above.



**Fig. 3** Ball-stick views of the crystal structure of **3**. Hydrogens except ones that are involved in host-guest interactions and PF<sub>6</sub> anions were omitted for clarity. Carbon atoms are red, oxygen atoms are green, and nitrogen atoms are black. The red dashed lines indicate C-H... $\pi$  interactions (A, B, C, D, F) and C-H...O interaction (E). C-H... $\pi$  interaction parameters: C-H... $\pi$  distance (Å), C-H... $\pi$  angle (deg) A, 2.54, 159; B, 2.55, 170; C, 2.94, 133; D, 2.76, 128; F, 2.83, 172. C-H...O interaction parameters: C-H...O distance (Å), C-H...O angle (deg) for E, 2.51, 136.

In conclusion, the host–guest complexation between a series of imidazolium ion-based ionic liquids with different counterions and alkyl chains and dipropoxypillar[5]arene were systematically investigated by multiple characterization methods, including NMR, MS and single X-ray crystal analysis. It was demonstrated that dipropoxypillar[5]arene presented tunable binding ability with different imidazolium-based ionic liquids in chloroform. In particular, loose ion-pairs on the guest can promote the formation of more stable host–guest complexes than intimate ion-pairs. Besides, the alkyl chains on the guests induced positive effects for the host–guest association process. With the better understanding and development of this molecular recognition motif, it will give us a more comprehensive guidance in construction of sophisticated interlocked structures and functional supramolecular systems based on ionic liquids and pillararenes.

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## Notes and references

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