

Ionic Liquid Molecules (ILs) as Novel Guests for Pillar[5]arene: 1:2 Host–Guest Complexes between Pillar[5]arene and ILs in Organic Media

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Pillar[5]arene formed 1:2 host–guest complexes with ionic liquid molecules in organic media. Chemically responsive release of ionic liquid molecules from the cavity of pillar[5]arene is also reported.

Ionic liquid molecules (ILs), which consist of organic cations and counter anions, have become popular due to their potential as a green and recyclable alternative to traditional organic solvents.¹ Macrocyclic hosts such as cyclodextrins,² cucurbiturils,³ and calixarenes⁴ continue to be the focus of considerable research activity because of their interesting conformational, physicochemical, and host–guest properties. It has been reported recently that cyclodextrins⁵ and cucurbiturils⁶ are able to form host–guest complexes with ILs in aqueous media. Since formation of the host–guest complexes increases the solubility of each component and decreases the IL solution viscosity, complexation of ILs with hosts has been studied extensively.

We synthesized a new type of host molecule at the first time and named it “pillar[5]arene” (Figure 1a).^{7,8} The composition of pillar[5]arene is almost the same as that of typical calixarenes.⁴ However, because its repeating units are connected by methylene bridges at the *para*-position, pillar[5]arene has a unique symmetric pillar architecture, which is different from the basket-shaped structure of the *meta*-bridged calixarenes. Since pillar[5]arene is composed of the electron donor hydroquinone, it exhibits very interesting host–guest properties in organic media. For instance, electron-accepting molecules such as viologen and pyridinium derivatives form 1:1 host–guest complexes with pillar[5]arene in acetone.⁷ ILs are cationic electron-accepting molecules similar to viologen and pyridinium derivatives, and we investigated host–guest complexes between pillar[5]arene

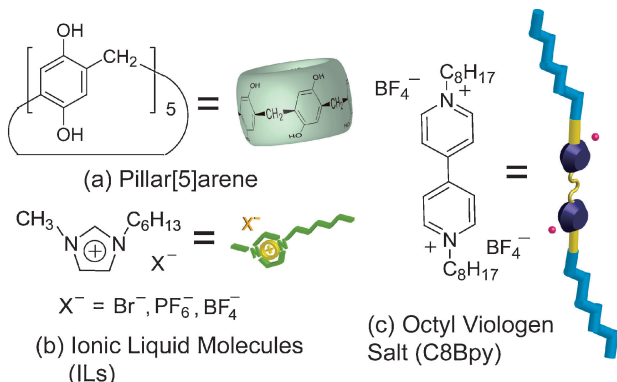


Figure 1. Chemical structures of (a) pillar[5]arene, (b) ionic liquid molecules (ILs), and (c) octyl viologen salt (C8Bpy).

and ILs in organic media. We report the detailed structure and stoichiometry of the host–guest complexes, and release of ILs from the pillar[5]arene upon addition of a competitive guest. While there are several types of ILs, 1-alkyl-3-methylimidazolium cations are among the most widely used. For that reason, in this study 1-hexyl-3-methylimidazolium derivatives⁹ ([C6mim]X, Figure 1b) were employed. By mixing ILs and pillar[5]arene in acetone-*d*₆, we prepared the host–guest complex. Formation of the host–guest complex was investigated by ¹H NMR measurements (Figure 2a). When pillar[5]arene was

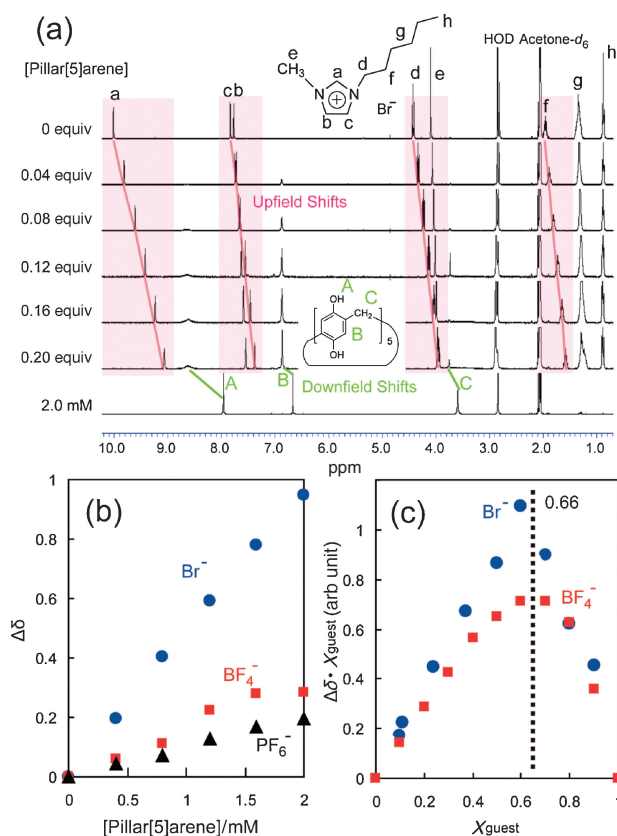


Figure 2. (a) ¹H NMR spectra of [C6mim]Br (10 mM) upon addition of pillar[5]arene (0–0.20 equiv to [C6mim]Br) in acetone-*d*₆ at 25 °C. At the bottom the ¹H NMR spectrum of pillar[5]arene (2.0 mM) in acetone-*d*₆ at 25 °C is shown. (b) Peak shifts of the resonance band attributed to the imidazolium proton at the C2-position of [C6mim]Br (blue circles), [C6mim]BF₄ (red squares) and [C6mim]PF₆ (black triangles); [IL] = 10 mM, [pillar[5]arene] = 0–2 mM. (c) Job plots for pillar[5]arene–[C6mim]Br (blue circles), and pillar[5]arene–[C6mim]BF₄ (red squares); [IL] + [pillar[5]arene] = 10 mM.

added to [C6mim]Br in acetone- d_6 , the proton signals from the imidazolium cation (peaks a–c) and the methylene moieties (peaks d and f) clearly shifted upfield, whereas the resonance bands from the methylene linker (peak g) and methyl moieties (peaks e and h) hardly changed. The peaks of pillar[5]arene shifted downfield by mixing pillar[5]arene with [C6mim]Br. From 2DNOESY analysis (Figure S1),¹⁰ NOE correlation was observed between the phenyl protons of pillar[5]arene and the protons of methylene moieties of [C6mim]Br. These observations indicate that the imidazolium and the methylene moieties adjacent to the N atoms are close to the phenyl moieties of pillar[5]arene. The effect of the counter anion on the host–guest interaction was investigated. Values of the peak shift of the imidazolium proton at the C2 position (peak a) induced by adding pillar[5]arene are shown in Figure 2b. In the case of [C6mim]Br, even with a small amount of pillar[5]arene a large peak shift occurred rapidly. On the other hand, in [C6mim]BF₄ and [C6mim]PF₆, the peak shifts increased gradually with increasing concentration of pillar[5]arene. These data indicate that the host–guest interaction of pillar[5]arene with [C6mim]Br is stronger than with [C6mim]BF₄ and [C6mim]PF₆. Using the Kamlet–Taft method, the dependence on anion of the hydrogen-accepting ability (β value) for a series of [C6mim]cation-based ILs was calculated. The hydrogen-accepting ability increases in the order: [C6mim]PF₆ (0.50) < [C6mim]BF₄ (0.61) \ll [C6mim]Br (0.90).¹¹ The high hydrogen-accepting ability of [C6mim]Br results in the strong host–guest interaction between pillar[5]arene and [C6mim]Br. From the chemical shift of the imidazolium cation at the C2 position (peak a), stoichiometry of the host–guest complex was determined by Job plots (Figure 2c). The peak maximum was observed at the molar fraction $X_{\text{guest}} = 0.66$ in both [C6mim]Br and [C6mim]BF₄. From ESI-MS, 1:1 and 1:2 pillar[5]arene–IL complexes were detected (Figure S2).¹⁰ These data indicate that the stoichiometry of the complexes is 1:2. We also performed a Job plot experiment in [C6mim]PF₆–pillar[5]arene complex. However, due to small peak shift, we could not clearly observe peak tops and determine the stoichiometry. Since the stoichiometry of host–guest complexes such as viologen derivatives–pillar[5]arene and pyridinium–pillar[5]arene reported previously is 1:1, the 1:2 pillar[5]arene–IL complexes are unusual and attractive. Association constants of the complexes could be calculated by fitting the titration curve of the imidazolium cation proton at the C2 position with the nonlinear fitting program WinEQNMR2.¹² The association constants in [C6mim]Br–pillar[5]arene complex were determined to be $K_1 = 110 \text{ M}^{-1}$ and $K_2 = 20 \text{ M}^{-1}$ ($K_1K_2 = 2200 \text{ M}^{-2}$). In [C6mim]BF₄–pillar[5]arene complex, K_1 , K_2 and K_1K_2 were found to be 700, 1.7, and 1190 M^{-2} , respectively (Figure S3).¹⁰

Figure 3a shows a proposed model of IL–pillar[5]arene complex. From Job's plots, two IL formed the complex with pillar[5]arene. Since the inner cavity size of pillar[5]arene is ca. 5 Å, it seems quite difficult that two imidazolium rings could fit inside. Thus, the proposed model of interactions of the IL ionic pairs through hydrogen bonding on the OH rims of the pillar[5]arene could be considered to justify the results obtained from the Job plots. Since the imidazolium protons (Ha, Hb, and Hc) and first methylene groups on the hexyl protons (Hd and Hf) shifted upfield whereas the methyl (He) and terminal butyl portions of the hexyl chain (Hg and Hh) do not appear to shift

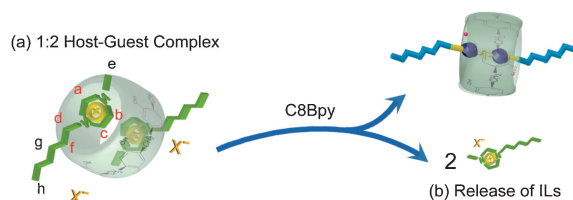


Figure 3. Proposed structure of 1:2 pillar[5]arene–IL complex, and (b) release of ILs upon addition of the competitive guest C8Bpy.

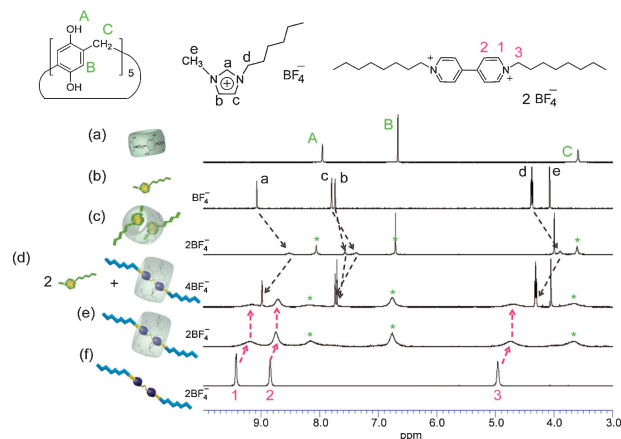


Figure 4. Partial ¹H NMR spectra of (a) pillar[5]arene (5 mM), (b) [C6mim]BF₄ (10 mM), (c) the mixture of pillar[5]arene (5 mM) and [C6mim]BF₄ (10 mM), (d) the mixture of pillar[5]arene (5 mM), [C6mim]BF₄ (10 mM), and C8Bpy (10 mM), (e) the mixture of pillar[5]arene (5 mM) and C8Bpy (10 mM), (f) C8Bpy (10 mM) in acetone- d_6 at 25 °C. The peaks from pillar[5]arene that formed complexes are shown with asterisks.

upfield at all, the imidazolium and first methylene moieties should be located around the pillar[5]arene rim.

To dissociate the IL–pillar[5]arene complexes, a competitive guest octyl viologen salt (C8Bpy, Figure 1c) was used. Figure 4d shows the ¹H NMR spectrum of the mixture of pillar[5]arene, [C6mim]BF₄, and C8Bpy. Chemical shifts of the peaks from [C6mim]BF₄ were similar to those of free [C6mim]BF₄ (Figure 4b). In contrast, the peaks from C8Bpy were the same as those from the C8Bpy–pillar[5]arene complex (Figure 4e). Addition of C8Bpy dissociated the host–guest complex between [C6mim]BF₄ and pillar[5]arene because the electron acceptor C8Bpy interacts more strongly than [C6mim]BF₄ with pillar[5]arene.⁷

In conclusion, we investigated the host–guest complex structure between pillar[5]arene and ILs. Pillar[5]arene formed 1:2 host–guest complexes with ILs in organic media. To the best of our knowledge, formation of host–guest complexes between ILs and macrocyclic hosts in organic media is little known, while complexation of ILs with macrocyclic hosts in aqueous media has been reported.^{5,6} The stoichiometry of the host–guest complexes between pillar[5]arene and guests previously reported has been 1:1, thus formation of 1:2 pillar[5]arene–guest complexes is a first example. Since 1:2 host–guest complexes have been applied as supramolecular crosslinker for construction of supramolecular polymers,¹³ the 1:2 pillar[5]arene–IL com-

plexes will be utilized for construction of chemically responsive supramolecular polymer and network structures. This is now under investigation.

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