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Reversible surface activity and self-assembly behavior and transformation of amphiphilic ionic liquids in water induced by a pillar[5]arene-based host-guest interaction

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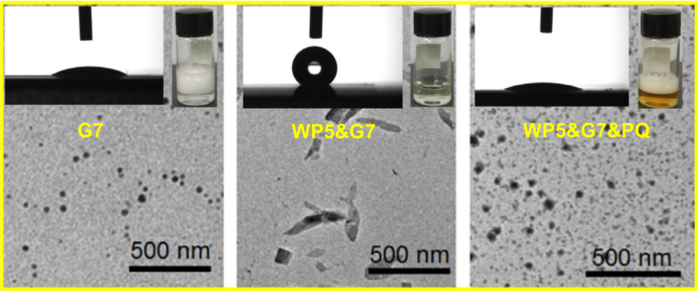
GRAPHICAL ABSTRACT



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ABSTRACT

In this paper, we aimed to develop a reversible and effective method to control the surface activity and self-assembled morphology of amphiphilic imidazolium-type ionic liquids (**G**) in water. For this purpose, a series of pillar[5]arene/imidazolium supramolecular complexes were designed and prepared. Before the formation of the host-guest complex, the surface activity of **G7** worked well, and foams could be generated easily. However, after the addition of water-soluble pillar[5]arene (**WP5**), the rigid **WP5** platform caused steric hindrance that prevented the hydrophobic chains on **G7** from getting close to each other, inducing the change in surface activity. On the other hand, because paraquat (**PQ**) has a larger association constant with **WP5** than **G7**, the surface activity of the solution can be recovered after the addition of **PQ**. TEM confirmed that self-assembled morphologies of this reversible system transformed from nanoparticles to nanosheets then to nanoparticles. It is anticipated that this supramolecular method for controlling the surface activity of amphiphiles in a reversible way may find application in fields where fast foaming and defoaming are needed.

1. Introduction

Ionic liquids are a form of liquid salts at room temperature that consist entirely of anions and cations. Compared with traditional organic solvents and electrolyte solutions, ionic liquids have some advantages, such as wide liquid state range, high electrical conductivity, and low vapor pressure [1,2]. Amphiphilic ionic liquids are a new type of ionic liquids that contain a large hydrophobic portion. Because amphiphilic ionic liquids combine both the properties of an amphiphile and ionic liquid, they have some advantages, such as higher surface activity, stronger self-assembly tendency in water, and better application in phase-transfer catalysis [3,4].

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Pillar[*n*]arenes, the newest type of macrocyclic compounds prepared first by Ogoshi in 2008,[5] linked hydroquinone and its derivatives by —CH_2— at the *2* and *5* positions [6–12]. Compared with other macrocyclic compounds (crown ethers [13,14], cyclodextrins [15–17], calixarenes [18–21], cucurbiturils [22–28]), pillar[*n*]arenes have some unique advantages, such as easy synthesis and functionalization, symmetrical pillar-like structures, controllable cavity size, and planar chirality [29–34]. During the past 10 years, the application of pillar[*n*]arenes has developed rapidly both in fields of chemistry and materials. Numerous guest molecules can complex with pillar[*n*]arene though host-guest interactions to fabricate unique supramolecular systems, such as polymers [35–37], nanotubes [38,39], chemosensors,[40,41] drug delivery systems,[42–45] and others [46–52].

Herein, we utilize the host-guest chemistry of water-soluble pillar[5]arene **WP5** for controlling the surface activity and self-assembled morphology of a series of amphiphilic imidazolium-type ionic liquids (**G**). As shown in Scheme 1, the alkyl chain on **G7** can penetrate into the cavity of **WP5** to form a host-guest complex, and the hindering effect of **WP5** not only prevents alkyl chains from moving close between **G7** molecules but also enhances the solubility of the whole system. As a result, the surface activity and self-assembled morphology of **G7** will be changed. Additionally, when the solution is mixed with paraquat **PQ**, which has a higher association constant with **WP5** and acts as a competitive guest molecule, the alkyl chain is expelled from the cavity of **WP5**. Therefore, this host-guest system can be used to control the surface activity and self-assembled morphology of **G7** in a reversible and effective way.

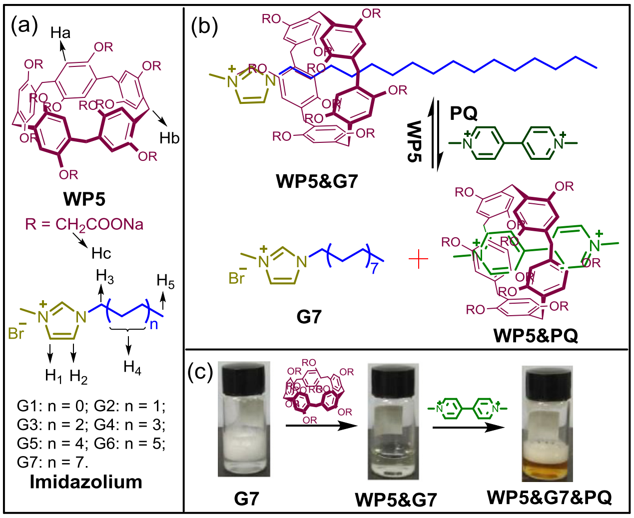
2. Experimental

Syntheses of WP5 and G. WP5 was synthesized according to the published procedure [53]. The synthetic route to amphiphilic imidazolium-type ionic liquids is shown in Scheme 2. Taking **G7** as an example, 0.82 g (10 mmol) of 1-methyl-1*H*-imidazole and 33.8 g (11 mmol) of 1-bromohexadecane were mixed in 50 mL of toluene. The mixture was heated at 100 °C for 12 h. Then, the solvent was decanted leaving a pale brown oil. The oil was washed with diethyl ether 3 times to afford pure product. All NMR data were acquired using a BRUKER AVANCE-III HD400 spectrometer. ^1H NMR (400 MHz, D_2O, room temperature) δ (ppm): 7.51 (s, 1H), 7.49 (s, 1H), 4.19 (t, $J = 8$ Hz, 2H), 3.84 (s, 3H), 1.80 (s, 2H), 1.26–1.15 (m, 26H), 0.74 (t, $J = 6$ Hz, 3H). ^{13}C NMR (100 MHz, D_2O, room temperature) δ (ppm): 129.75, 126.51, 120.56, 47.61, 31.73, 29.15, 29.04, 27.64, 27.46, 23.16, 13.86. Mass spectral data were acquired through the electron spray ionization (ESI) technique on a QTOF-micro quadrupole mass spectrometer (Micromass). LRESIMS is shown in Fig. S10: m/z 307.6 $[M-Br]^+$ (100%).

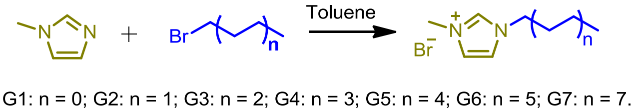
Surface tension investigation. Aqueous solutions of **G7**, **WP5&G7** and **WP5&G7&PQ** at different concentrations were first prepared and the surface activity of the solutions was investigated by a Jzhy1-180 surface tension meter at 25 °C.

Transmission Electron Microscopy (TEM) Studies. The self-assembly behavior of the system was studied using TEM. The solutions of 1.25×10^{-4} M of **G7, G7&WP5,** and **G7&WP5&PQ** were first made in water. These samples were prepared by drop-coating the three solutions onto a carbon-coated copper grid. TEM experiments were performed on a JEM-1200EX instrument with an accelerating voltage of 80 kV.

Contact angle measurement. Aqueous solutions of **G7** (1.25×10^{-4} M), **WP5&G7** (1.25×10^{-4} M) and **WP5&G7&PQ** (1.25×10^{-4} M) were first prepared and the contact angle data of the solution were recorded using an OCA20 instrument (DataPhysics Instruments GmbH, Filderstadt) at 25 °C.



Scheme 1. (a) Chemical structures of water-soluble pillar[5]arene **WP5** and amphiphilic imidazolium-type ionic liquids G. (b) Complex formed by **G7** and **WP5**. (c) Reversible foam generated from **G7**, **WP5&G7** and **WP5&G7&PQ**.



Scheme 2. Synthesis of amphiphilic imidazolium-type ionic liquids (n = 0, 1, 2, 3, 4, 5, 6, 7).

Dynamic light scatting experiments. The mean diameters of the assemblies of **G7** (1.25×10^{-4} M), **WP5&G7** (1.25×10^{-4} M) and **WP5&G7&PQ** (1.25×10^{-4} M) were measured by DLS experiments on a Nano-ZS ZEN3600 instrument at 25 °C. The scattering intensity was measured at an angle of 175°. An average of three successive measurements was noted for each sample.

Isothermal titration calorimetry studies. Isothermal titration calorimetric (ITC) measurements were performed on a VP-ITC microcalorimeter (Microcal, USA) in aqueous solutions at 25 °C. Raw ITC data for 27 sequential injections (10 μL per injection) of a **G7** solution (2.00 mM) into a **WP5** solution (0.100 mM).

3. Results and discussion

Host-guest interactions between amphiphilic ionic liquids and WP5. The host-guest interaction between **WP5** and **G7** was first investigated by ^1H NMR spectroscopy and ITC. As shown in Fig. 1, compared with free **WP5** and **G7** (Fig. 1a and c), the hydrogen signals of **G7** shifted significantly upon the addition of equimolar **WP5** (Fig. 1b). The overlapped peaks related to H_4 on the alkyl chain shifted upfield and obviously split into five separate peaks ($\Delta\delta$ = 0.12, 0.03, −0.47, −0.76, and −0.83 ppm, respectively). This phenomenon indicated that H_4 was located within the cavity of **WP5** and was shielded by the electron-rich pillar-like structure because of the complex formed between **WP5** and **G7**.[54] In addition, a 2D NOESY NMR experiment was also performed, which showed that the signals related to H_4 were close to the signals related to the pillar-like platform, which is in accordance with the ^1H NMR results (Fig. S12). The association constant (K_a) of this host-guest complex was determined by isothermal titration calorimetry (ITC). The K_a value was estimated to be $9.19 \pm 1.14 \times 10^5\ M^{-1}$ for **WP5** $\supset$ **G7** in a 1:1 complex (Fig. S11). All the phenomena above provided convincing evidence for the