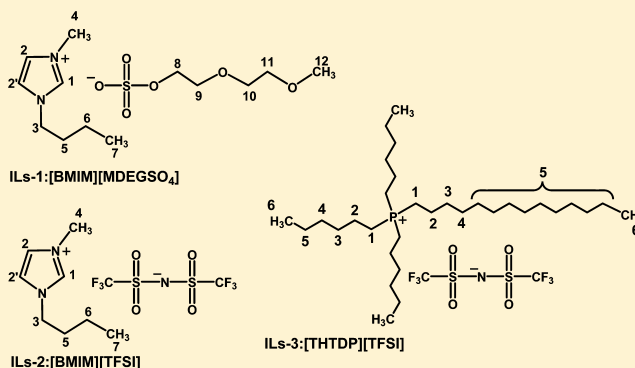


Interactions between Dendrimers and Ionic Liquids Revealed by Pulsed Field Gradient and Nuclear Overhauser Effect NMR Studies

Libo Zhao,[‡] Cai Li,[‡] Jiahai Zhang,^{||} Qinglin Wu,[⊥] Tongwen Xu,^{*,‡} and Yiyun Cheng^{*,†,§}[†]Shanghai Key Laboratory of Regulatory Biology, School of Life Sciences, East China Normal University, Shanghai 200241, People's Republic of China[‡]CAS Key Laboratory of Soft Matter Chemistry, School of Chemistry and Material Science, University of Science and Technology of China, Hefei, Anhui 230026, People's Republic of China[§]Shanghai Key Laboratory of Magnetic Resonance, Department of Physics, East China Normal University, Shanghai 200062, People's Republic of China^{||}Hefei National Laboratory for Physical Sciences at Microscale and School of Life Sciences, University of Science and Technology of China, Hefei, Anhui, 230027, People's Republic of China[⊥]Division of Life Science, The Hong Kong University of Science and Technology, Hong Kong, People's Republic of China

Supporting Information

ABSTRACT: The host–guest interactions of cationic and anionic poly(amidoamine) (PAMAM) dendrimers with three ionic liquids including 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethyl sulfate ([BMIM][MDEGSO₄]), 1-butyl-3-methylimidazolium bis-(trifluoromethylsulfonyl)imide ([BMIM][TFSI]), and trihexyltetradecylphosphonium bis((trifluoromethyl)sulfonyl)imide ([THTDP][TFSI]) were investigated by several NMR techniques such as ¹H and ¹⁹F NMR, pulsed field gradient (PFG) NMR, and 2D nuclear Overhauser enhancement spectroscopy (NOESY). Anionic PAMAM dendrimer interacts with the ionic liquids via ionic interactions. However, almost no interaction is observed between cationic PAMAM dendrimer and the ionic liquids without pH adjustment. Besides, no inclusion formation between the PAMAM dendrimers and the ionic liquids is observed on the basis of NOE NMR studies. The interactions between dendrimers and ionic liquids are very different from those between dendrimers and surfactants or amphiphilic drugs. The results obtained from PFG and NOE studies provide new insights into dendrimer-based host–guest systems.



1. INTRODUCTION

Room-temperature ionic liquids (ILs) as emerging green materials to replace volatile organic solvents have attracted increasing attention during the past decade.^{1–3} These liquid-phase electrolytes are usually composed of organic or inorganic anions and organic cations which form stable ionic pairs.^{4,5} Benefiting from their special compositions, ILs possess several remarkable properties such as negligible vapor pressure, low melting point, high ionic conductivity, and thermal stability when compared to conventional organic and inorganic salts.² These properties make ILs excellent candidates in numerous applications such as electrochemistry, host–guest chemistry, catalysis, green organic synthesis, and separation and purification and in biological systems.^{1,4} For example, ILs used as reaction media in catalytic processes can provide a convenient solution to solvent volatilization and catalyst recovery problems due to the unique low vapor pressure and high stability.^{6–8} Amphiphilic ILs such as alkylimidazolium-based ILs can behave

like conventional surfactants due to their surfactant-like structure with a hydrophobic tail and a hydrophilic headgroup.^{9,10} Also, ILs possess the ability to support the self-assembly of amphiphiles such as surfactants, lipids, and polymers.¹¹

Dendrimer is a class of hyperbranched polymers with excellent monodispersity, globular shape, nanoscale size, interior pockets, and well-defined molecular weight and numbers of surface functionality.^{12–14} These properties endow them with great potential in miscellaneous applications such as catalysis, supramolecular chemistry, host–guest interactions, drug delivery, and gene delivery.^{15–21} According to the unique physicochemical properties of ILs demonstrated above, the interactions between dendrimers and ILs may produce interesting phenomena. For example, (1) there is improved

Received: April 9, 2012

Revised: May 16, 2012

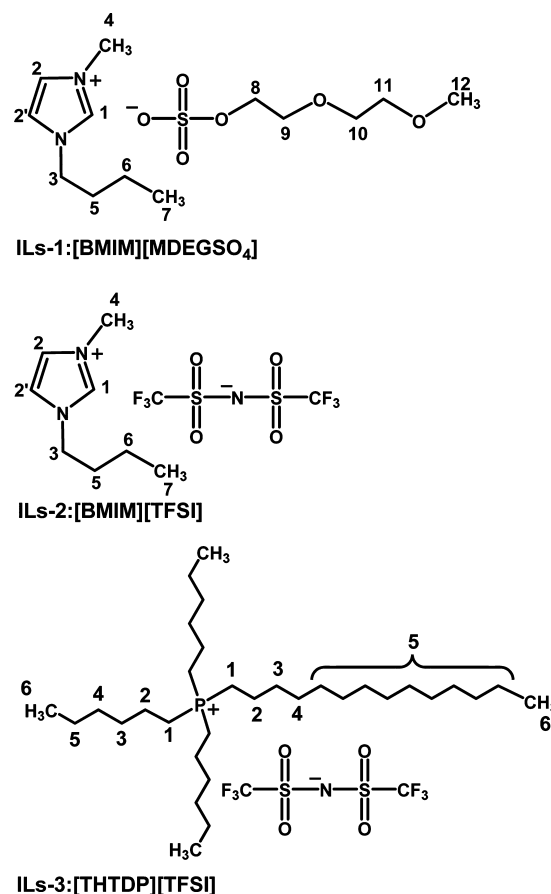
Published: May 31, 2012



proton transport: dendrimer as catalyst or catalyst scaffold is a hot spot in the field of dendrimer due to the so-called “dendritic effect” and nanoscale size.^{12,15} By using dendrimers as synthesis templates, dendrimer-encapsulated metal nanoparticles can be synthesized and used as recyclable catalysis with high performance.^{22–24} Dendrimers and dendrimer-encapsulated platinum nanoparticles were widely used as polymer electrolytes or catalysts in fuel cells.^{22,25} However, proton transport or ionic conductivity of the polymer or polymer composites is of critical importance on the fuel cell performance. In this case, Dai et al. prepared dendritic ILs on the basis of poly(amidoamine) (PAMAM) dendrimer and lithium [TFSI] using a facile strategy.²⁶ The resulting ILs showed high proton conductivity and strong photoluminescence with potential applications in solvent-free electrolyte, organic catalysis, and sensor design. Such dendritic ILs may also have improved thermal stability more than dendrimers and dendrimer-encapsulated metal nanoparticles, maintaining the high catalytic activities of dendrimer-based catalysts at relatively high temperatures.²⁶ (2) There is host–guest behavior: dendrimers can act as hosts of a list of guest candidates such as surfactants, drug molecules, and siRNA.^{27,28} ILs are stable ionic pairs and amphiphiles that are ideal guest molecules for dendrimers. On the other hand, the use of ILs might be limited by their poor solubility and immiscibility with reaction or catalytic media such as water and alcohols.^{29,30} For example, imidazolium-based ILs with chloride, bromide, or methanesulfonate anions are soluble in water, while those with bis((trifluoromethyl)sulfonyl)imide or tetrafluoroborate anions are almost insoluble. Also, the miscibility of imidazolium-based ILs with water decreases with the length of alkyl chains. Recent studies showed that inclusion complexes formed by ILs and cyclodextrin can increase the aqueous solubilities of both components.³¹ The host–guest interactions between dendrimer and ILs may solve the solubility and the immiscibility problems of ILs. On the basis of these potential applications, it is of interest to investigate the host–guest interactions between dendrimers and ILs with different components.

Pulsed field gradient (PFG) and nuclear Overhauser enhancement spectroscopy (NOESY) NMR techniques are powerful tools in the study of inclusion structures and complexes formed by ionic pair and hydrogen-bond.^{27,28,32} PFG NMR can be used to determine the variation of diffusion coefficient or the hydrodynamic size of a target molecule before and after the formation of aggregates or supramolecular complexes.^{28,32} NOESY NMR can provide precise distance information between the host and guest molecules in an inclusion complex.^{27,28} The combination of PFG and NOESY NMR techniques can be used to predict the host–guest chemistry of dendrimer and ILs. Here, generation 5 (G5) cationic PAMAM dendrimer with 128 surface amine groups and generation 4.5 (G4.5) anionic PAMAM dendrimer with 128 surface carboxylate groups were used as model dendrimers. Three ILs including an aqueous soluble IL 1-butyl-3-methylimidazolium 2-(2-methoxyethoxy)ethyl sulfate ([BMIM][MDEGSO₄]) and two insoluble ILs 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([BMIM][TFSI]) and trihexyltetradecylphosphonium bis((trifluoromethyl)sulfonyl)imide ([THTDP][TFSI]) were used as model ILs (Scheme 1). To the best of our knowledge, this is the first study on dendrimer and ILs interaction by NMR studies.

Scheme 1. Chemical Structures of [BMIM][MDEGSO₄] (ILs-1), [BMIM][TFSI] (ILs-2), and [THTDP][TFSI] (ILs-3)



2. EXPERIMENTAL SECTION

2.1. Materials and Solution Preparation. [BMIM]-[MDEGSO₄], [BMIM][TFSI], [THTDP][TFSI], G4 diaminobutane (DAB)-cored and primary amine-terminated poly(propyleneimine) (PPI) dendrimer with 32 surface functionalities and deuterated dimethyl-*d*₆ sulfoxide (DMSO-*d*₆) were purchased from Sigma-Aldrich Co. (St. Louis, MO) and used as received without further purification. [BMIM][TFSI] and [THTDP][TFSI] were freshly dissolved in DMSO-*d*₆ for NMR studies, while [BMIM][MDEGSO₄] was dissolved in deuterated water (D₂O) for NMR studies. G5 amine-terminated and ethylenediamine (EDA)-cored PAMAM dendrimer and G4.5 carboxylate-terminated and EDA-cored PAMAM dendrimer were purchased from Dendritech, Inc. (Midland, MI, USA). The dendrimers were received in methanol, and the solvent was distilled before further use. G4.5 and G5 PAMAM dendrimers and G4 PPI dendrimer stock solutions at 20 mg/mL in D₂O were prepared and stored at 4 °C before NMR studies. D₂O was purchased from Beijing Chongxi High-Tech Incubator Co. (Beijing, China). Pyridine (Py) and sodium fluoride (NaF) used as internal standards in the ¹H and ¹⁹F NMR studies, respectively, were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2. NMR Studies. ¹H NMR spectra were obtained on a Bruker Avance 500.132 MHz NMR spectrometer at 298.2 K for dendrimer/IL solutions with different molar ratios of dendrimer/ILs at 0:1, 1:2, 1:4, 1:8, 1:16, 1:32, and 1:64, respectively. In each sample, the concentration of IL was kept

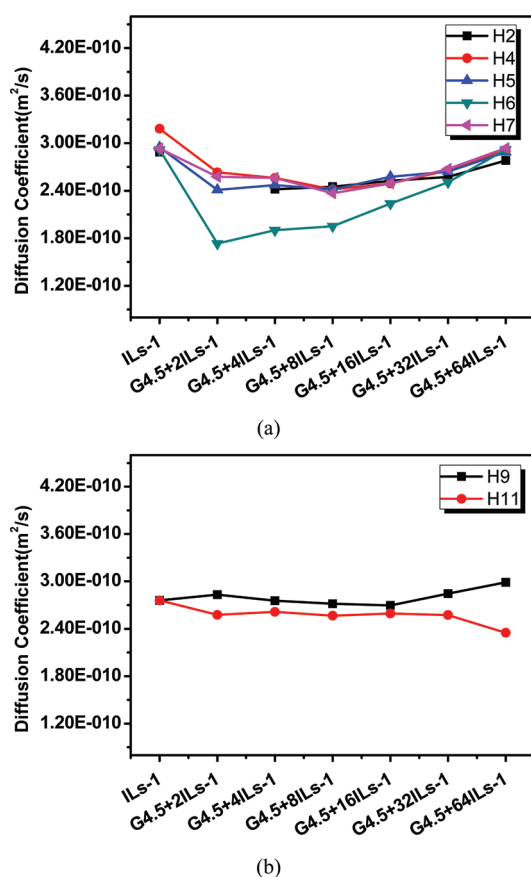


Figure 1. Diffusion coefficients of $[\text{BMIM}]^+$ (A) and $[\text{MDEGSO}_4]^-$ (B) in the mixture of $[\text{BMIM}][\text{MDEGSO}_4]$ (ILs-1) and G4.5 PAMAM dendrimer in D_2O (where, for example, $4.20\text{E-}010$ represents 4.20×10^{-10}). The molar ratio of ILs-1 and G4.5 dendrimer ranges from 2:1 to 64:1. The concentration of ILs-1 is kept constant at 0.5 mg/mL.

constant at 0.5, 0.5, and 1.0 mg/mL for $[\text{BMIM}][\text{MDEGSO}_4]$, $[\text{BMIM}][\text{TFSI}]$, and $[\text{THTDP}][\text{TFSI}]$, respectively.

Diffusion behaviors of the ILs in the dendrimer/IL complexes were measured by PFG NMR experiments which were carried out using a standard Bruker pulse program on the same NMR instrument at 298.2 ± 0.2 K. The time interval (Δ) between gradient pulses is chosen as 100, 100, and 600 ms for systems containing $[\text{BMIM}][\text{TFSI}]$, $[\text{BMIM}][\text{MDEGSO}_4]$, and $[\text{THTDP}][\text{TFSI}]$, respectively. The duration of the gradient pulses (δ) is 1.5 ms. The pulse gradients (g) were increased from 10 to 80% of the maximum gradient strength (50 G/cm) in 16 steps as the spin-echo signal weakened. The self-diffusion coefficient (D) was obtained by fitting these parameters by the following equation:

$$\ln(I_n/I_0) = -\gamma^2 D \delta^2 (\Delta - \delta/3) g^2$$

where I_n and I_0 are the intensities of the spin-echo signal when the sine-shaped field gradient is present and absent and γ is the proton magnetogyric ratio ($26\,753 \text{ rad}\cdot\text{Gauss}^{-1}\cdot\text{s}^{-1}$). All data were processed by Bruker Xwinnmr 3.1 (Bruker Biospin). For all of the PFG NMR studies, a certain amount of pyridine was added into each NMR tube and used as an internal standard.

NOESY NMR experiments were performed on the same NMR instrument as described above. ^1H - ^1H NOESY spectra of the samples containing $[\text{BMIM}][\text{MDEGSO}_4]/\text{G4.5 PAMAM}$, $[\text{BMIM}][\text{TFSI}]/\text{G4.5 PAMAM}$, $[\text{BMIM}][\text{MDEGSO}_4]/\text{G5}$

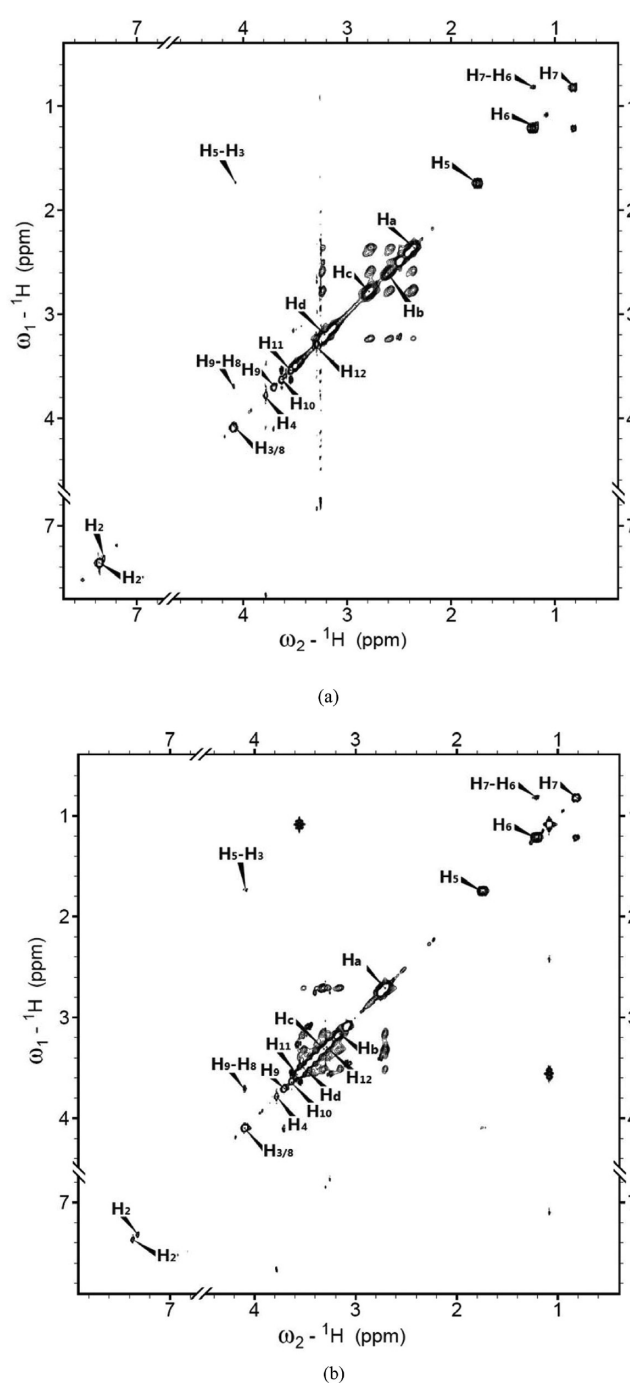


Figure 2. ^1H - ^1H NOESY spectra of $[\text{BMIM}][\text{MDEGSO}_4]/\text{G4.5 PAMAM dendrimer}$ complex in D_2O without pH adjustment (A) and at pH 4.0 (B). The molar ratio of $[\text{BMIM}][\text{MDEGSO}_4]$ and G4.5 PAMAM dendrimer is 40:1. The G4.5 dendrimer concentration is 2 mg/mL.

PAMAM, $[\text{BMIM}][\text{TFSI}]/\text{G5 PAMAM}$, and $[\text{BMIM}][\text{MDEGSO}_4]/\text{G4 PPI}$ at different IL/dendrimer molar ratios (16–64) were obtained at a mixing time of 300 ms and $8.2 \mu\text{s}$ ^1H 90 pulse width. The NOESY spectra of the $[\text{BMIM}][\text{MDEGSO}_4]/\text{G4.5}$ and $[\text{BMIM}][\text{MDEGSO}_4]/\text{G5}$ complex at different pH conditions were conducted. The relaxation delay and acquisition time were set at 2 s and 205 ms, respectively. All data were processed with NMRPipe software on a Linux workstation.

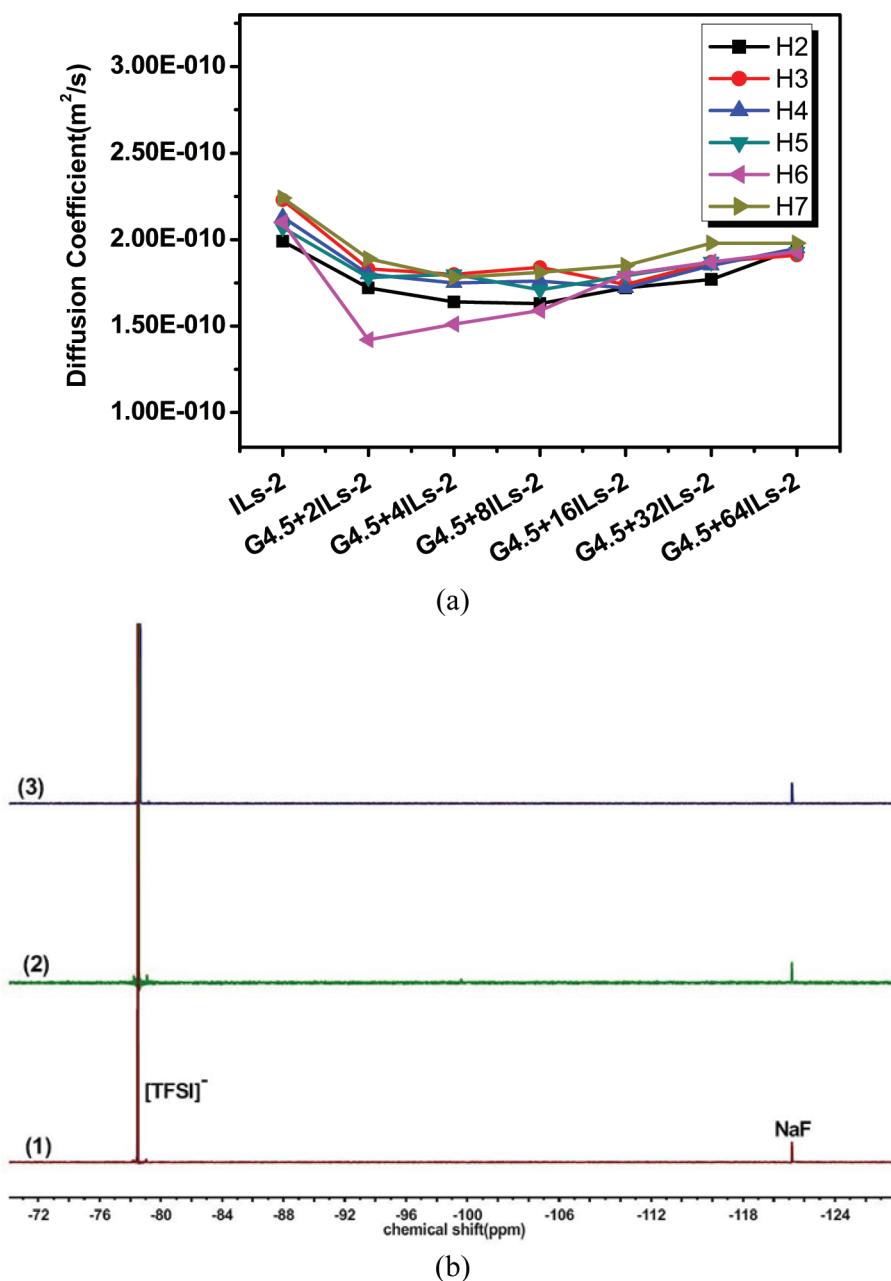


Figure 3. (A) Diffusion coefficient of $[\text{BMIM}]^+$ in the mixture of $[\text{BMIM}][\text{TFSI}]$ (ILs-2)/G4.5 PAMAM dendrimer in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (20/80, v/v) (where, for example, $3.00\text{E-}010$ represents 3.00×10^{-10}). The molar ratio of ILs-2/G4.5 dendrimer ranges from 2:1 to 64:1, and the concentration of ILs-2 was kept constant at 0.5 mg/mL. (B) ^{19}F NMR spectra of ILs-2 in the absence (1) and presence of G4.5 (2) and G5 (3) PAMAM dendrimers in $\text{DMSO-}d_6/\text{D}_2\text{O}$ (20/80, v/v) using NaF as an internal reference. The G4.5 and G5 dendrimer concentration was kept constant at 8.68×10^{-5} M and the molar ratio of ILs-2/dendrimer is 16:1.

The ^{19}F NMR spectra were obtained on a Bruker AVANCE AV III 400 MHz NMR spectrometer at 298.2 ± 0.2 K. $[\text{BMIM}][\text{TFSI}]$ dissolved in $\text{DMSO-}d_6$ solution was mixed with G5 and G4.5 PAMAM dendrimer at a molar ratio of 16:1. The dendrimer concentrations are fixed at $86.8 \mu\text{M}$. A certain amount of NaF was added into the dendrimer/ $[\text{BMIM}][\text{TFSI}]$ complex solutions as an internal standard before the ^{19}F NMR experiments.

3. RESULT AND DISCUSSION

3.1. Interactions between Anionic Dendrimers and ILs. Diffusion NMR techniques including PFG and DOSY are widely used in the characterization of dendrimer-based

host–guest systems.²⁸ As shown in Figure 1A, the addition of G4.5 PAMAM dendrimer into $[\text{BMIM}][\text{MDEGSO}_4]$ aqueous solution at a IL/dendrimer molar ratio of 2:1 significantly decreased the diffusion coefficients of the cation $[\text{BMIM}]^+$ of the IL, suggesting increased hydrodynamic size of $[\text{BMIM}]^+$ and the presence of interactions between G4.5 PAMAM dendrimer and $[\text{BMIM}]^+$. At higher IL/dendrimer molar ratios above 2:1, the diffusion coefficient of $[\text{BMIM}]^+$ increases with the IL/dendrimer molar ratio. The ILs in dendrimer/IL complexes are in a fast exchange of free and bound state on the NMR time scale; therefore, the diffusion coefficient is a time-weighted average of the diffusion coefficients in each state.

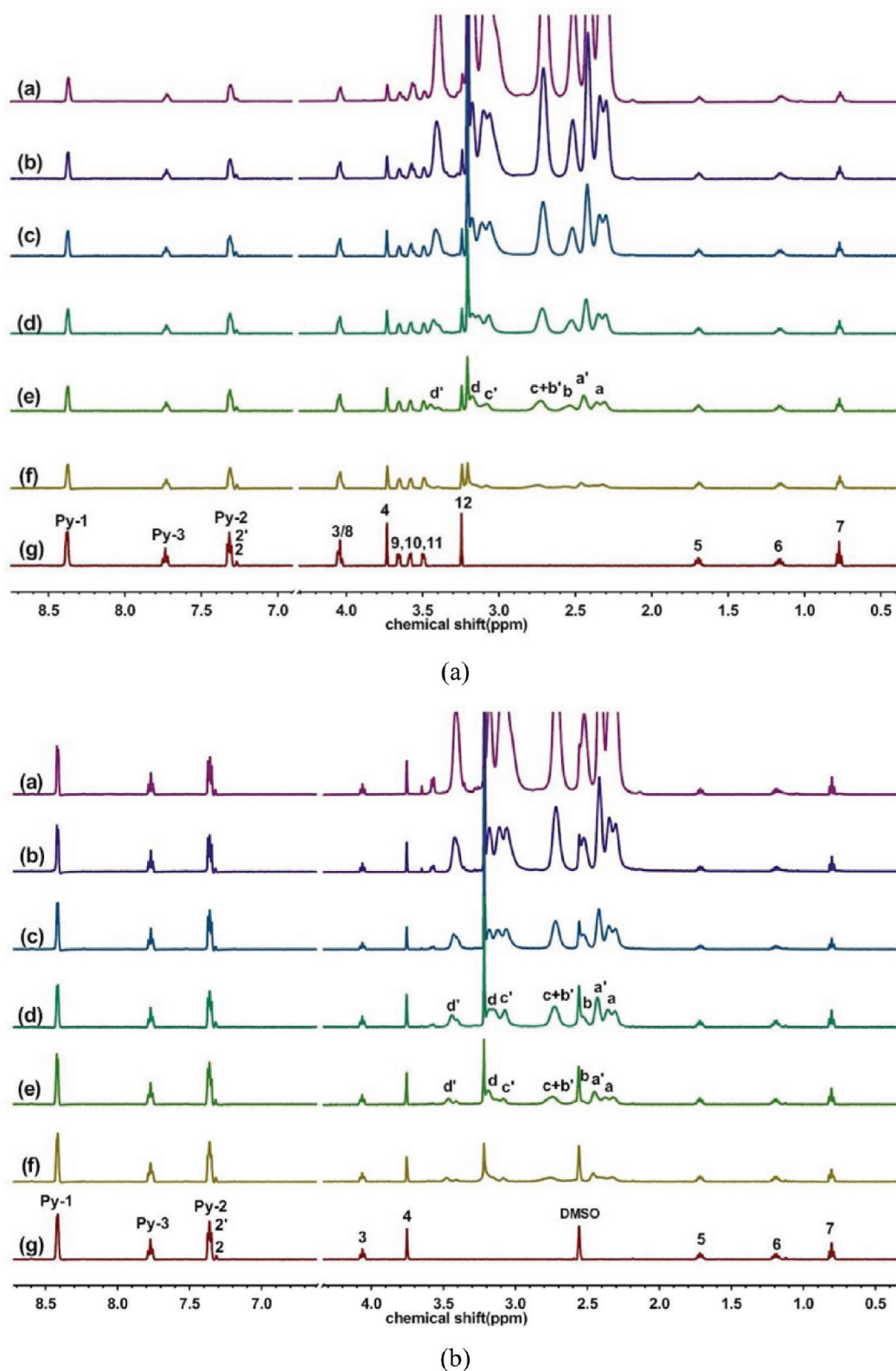


Figure 4. ^1H NMR spectra of G4.5 PAMAM dendrimer with [BMIM][MDEGSO₄] (ILs-1; A) and [BMIM][TFSI] (ILs-2; B) in D₂O and DMSO-*d*₆/D₂O (20/80, v/v), respectively. The concentrations of ILs-1 and ILs-2 were kept constant at 0.5 mg/mL, and the molar ratio of IL/G4.5 ranges from 2:1 to 64:1 (a–f). Spectra g are the ^1H NMR spectra for pure IL.

$$D_{\text{obs}} = D_b P_b + D_f P_f$$

where P_b and P_f are molar fractions of bound- and free-state ILs, respectively, D_b and D_f are diffusion coefficients of

bound- and free-state ILs, respectively, and D_{obs} is the observed diffusion coefficient of IL in the dendrimer/IL complex. In the dendrimer/IL complexes, P_b decreases with increasing IL/dendrimer molar ratio. Therefore, increased

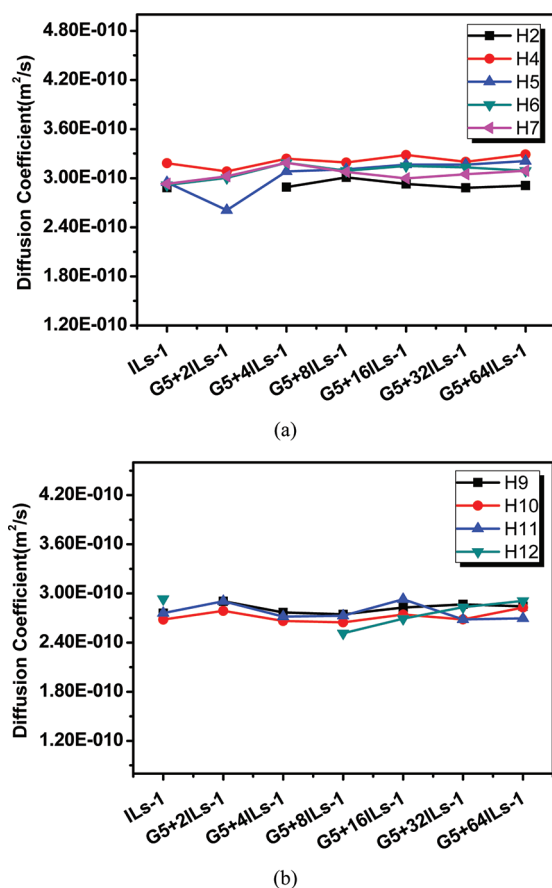


Figure 5. Diffusion coefficients of $[\text{BMIM}]^+$ (A) and $[\text{MDEGSO}_4]^-$ (B) in the mixture of $[\text{BMIM}][\text{MDEGSO}_4]$ and G5 PAMAM dendrimer in D_2O (where, for example, $4.80\text{E}-10$ represents 4.80×10^{-10}). The molar ratio of ILs-1 /G5 dendrimer ranges from 2:1 to 64:1, and the concentration of ILs-1 is kept constant at 0.5 mg/mL .

diffusion coefficients of the ILs were observed at higher IL/dendrimer ratios. On the other hand, the diffusion coefficients of the anion $[\text{MDEGSO}_4]^-$ are scarcely changed in the presence of G4.5 PAMAM dendrimers, indicating that $[\text{MDEGSO}_4]^-$ does not interact with the G4.5 dendrimer (Figure 1B).

Previous studies demonstrated that amphiphilic surfactant such as sodium dodecyl sulfate (SDS) and drug molecules such as phenylbutazone simultaneously bind on dendrimer surface and localize in dendrimer interior pockets,^{32,33} while sodium deoxycholate mainly forms inclusion complexes with dendrimer.³⁴ Here, the NOESY spectra of G4.5/ $[\text{BMIM}][\text{MDEGSO}_4]$ complexes at different pH conditions were conducted to reveal the interaction mechanisms between G4.5 and the IL. Surprisingly, no NOE cross-peak between the $[\text{BMIM}][\text{MDEGSO}_4]$ protons and the G4.5 pocket protons was observed even when the condition of the complex solution was adjusted to pH 4.0 (Figure 2), suggesting that neither $[\text{BMIM}]^+$ nor $[\text{MDEGSO}_4]^-$ localizes in the G4.5 interior pockets. The interactions between G4.5 and $[\text{BMIM}]^+$ proven in PFG studies in Figure 1A should be ionic pairs between G4.5 anionic surface and the cationic $[\text{BMIM}]^+$. It is worth noting that the interactions between PAMAM dendrimer and $[\text{BMIM}]^+$ are relatively weaker than that between PAMAM dendrimer and SDS. For example, the complexation of SDS to PAMAM or PPI dendrimer caused the decrease of SDS diffusion coefficient

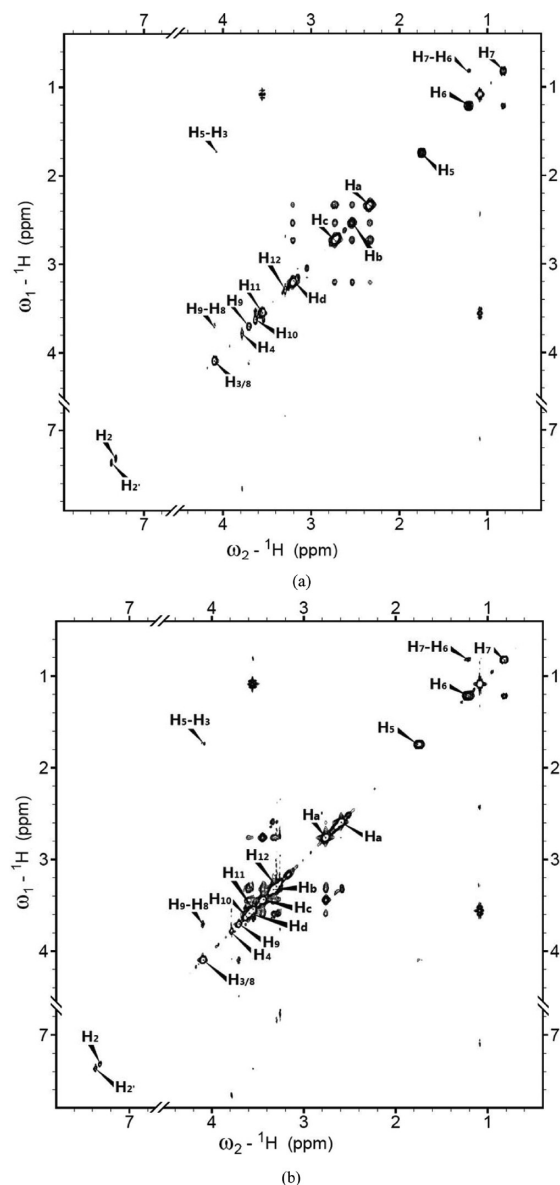


Figure 6. ^1H - ^1H NOESY spectra of $[\text{BMIM}][\text{MDEGSO}_4]$ /G5 PAMAM dendrimer complex in D_2O without pH adjustment (A) and at pH 4.0 (B). The molar ratios of ILs-1 and G5 are 64 and 40, respectively. The dendrimer concentration is 2 mg/mL .

from $4.3 \times 10^{-10} \text{ m}^2/\text{s}$ to a minimum D value of $1.2 \times 10^{-10} \text{ m}^2/\text{s}$ (28%) for PAMAM and to $8.0 \times 10^{-11} \text{ m}^2/\text{s}$ (19%) for PPI dendrimer.³² In the dendrimer/IL complex, the diffusion coefficient of $[\text{BMIM}]^+$ decreases from $2.1 \times 10^{-10} \text{ m}^2/\text{s}$ to a minimum value of $1.7 \times 10^{-10} \text{ m}^2/\text{s}$ (81%) during this period (Figure 1).

In the case of insoluble IL $[\text{BMIM}][\text{TFSI}]$, similar results were obtained from PFG and NOE studies. As shown in Figure 3A, ionic interactions between G4.5 and $[\text{BMIM}]^+$ cause the decrease of the diffusion coefficient of $[\text{BMIM}]^+$ at low IL/dendrimer molar ratios. Again, no encapsulation of $[\text{BMIM}]^+$ within G4.5 PAMAM dendrimer was observed in the NOESY spectrum of G4.5/ $[\text{BMIM}][\text{TFSI}]$ complex (Figure S1 of the Supporting Information). To investigate the interactions between G4.5 and $[\text{TFSI}]^-$, ^{19}F NMR spectra were used. As shown in Figure 3B, the $[\text{TFSI}]^-$ peak is scarcely shifted (from -78.49 to -78.53 ppm) before and

after complexation with G4.5 PAMAM dendrimer. Also, the ^1H NMR spectra of $[\text{BMIM}][\text{TFSI}]$ and $[\text{BMIM}][\text{MDEGSO}_4]$ in Figure 4 showed that both dendrimer and IL peaks remain unchanged during the titration of G4.5

PAMAM dendrimer into both IL solutions. Therefore, only weak ionic interactions occur between G4.5 PAMAM dendrimer surface and the ILs including $[\text{BMIM}][\text{TFSI}]$ and $[\text{BMIM}][\text{MDEGSO}_4]$. Perhaps, the strong ionic pairing

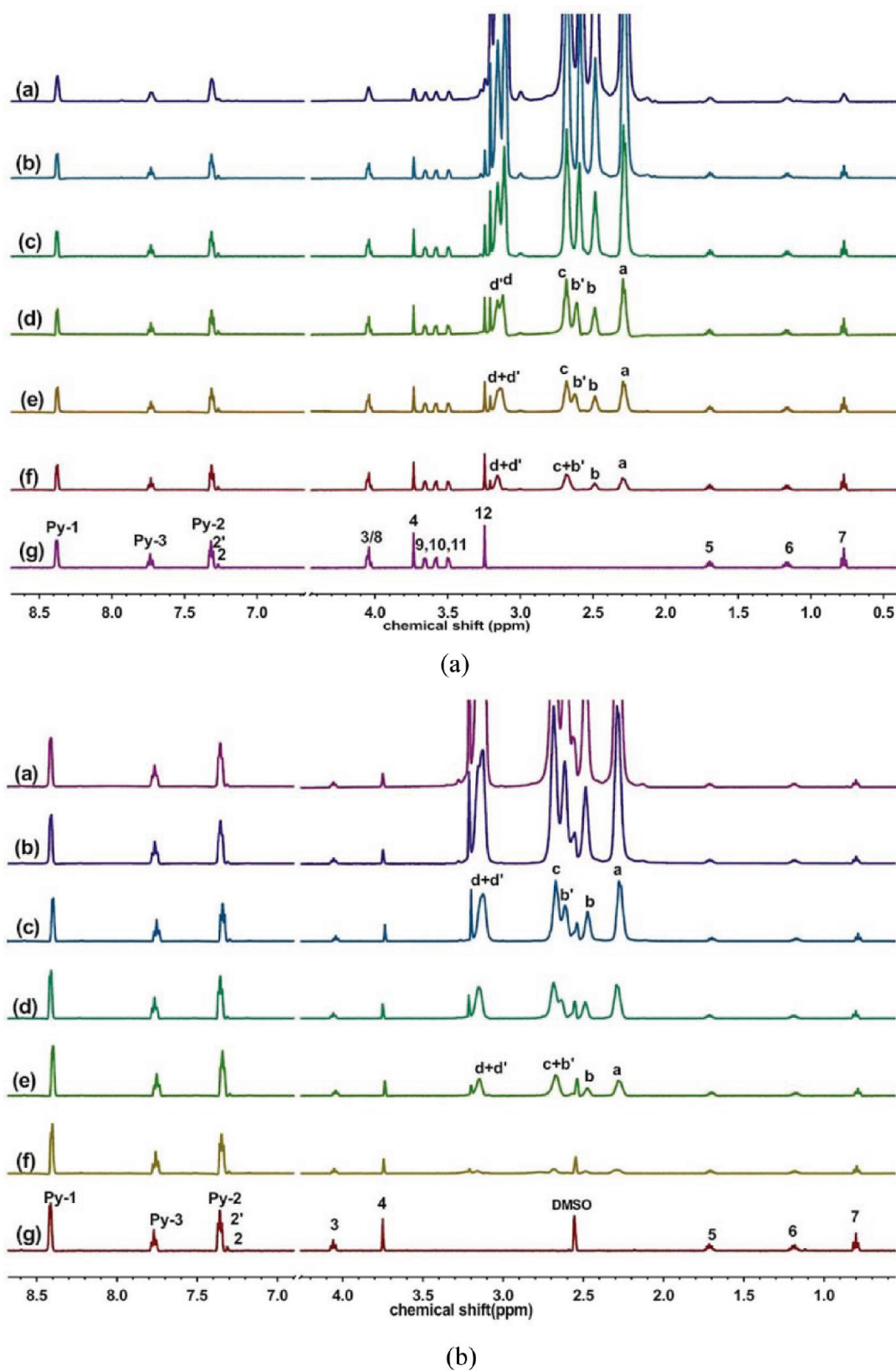


Figure 7. continued

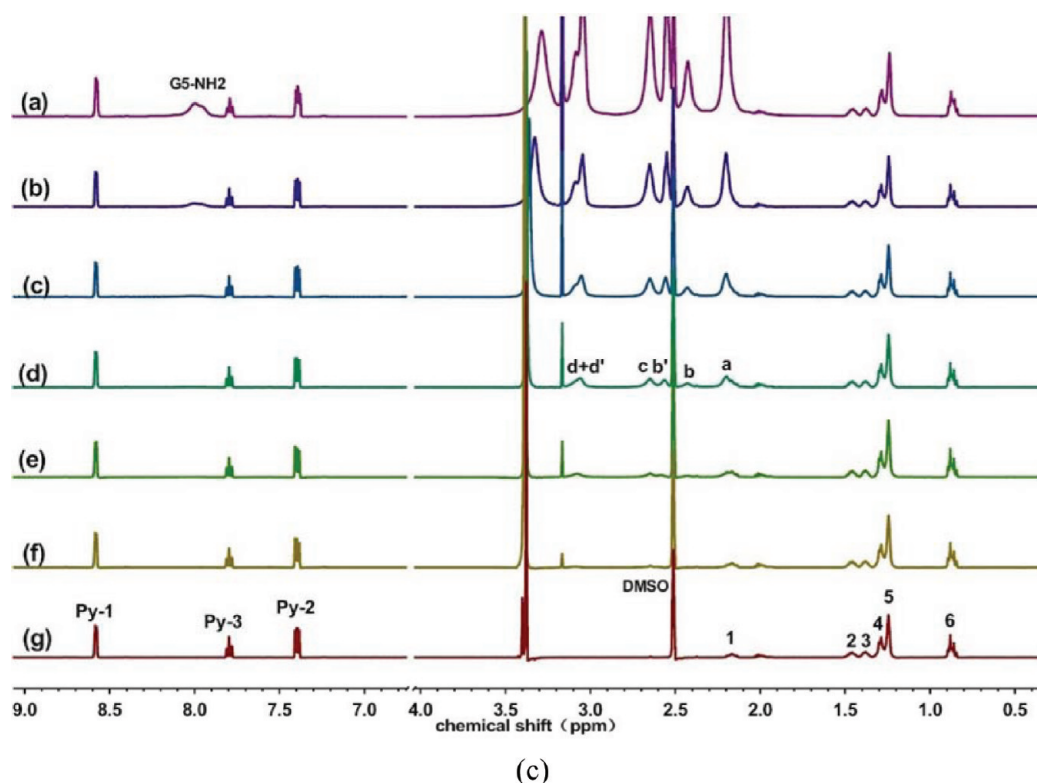


Figure 7. ^1H NMR spectra of G5 dendrimer with [BMIM][MDEGSO₄] (A), [BMIM][TFSI] (B), and [THTDP][TFSI] (C) in D₂O, DMSO-*d*₆/D₂O (20/80, v/v) and DMSO-*d*₆/D₂O (20/80, v/v), respectively. The molar ratio of IL/GS dendrimer ranges from 2:1 to 64:1 (a–f). Spectra g are the ^1H NMR spectra for pure ILs. The concentrations of ILs-1, ILs-2, and ILs-3 are kept constant at 0.5, 0.5, and 1 mg/mL, respectively.

between the anion and cation in the ILs prevents the ionic interactions and inclusion formation between dendrimer and ILs. As a result, the host–guest behavior of dendrimer with ILs is much different from that of dendrimer with surfactant and amphiphilic drugs.^{28,32}

3.2. Interactions between Cationic Dendrimers and ILs. Surprisingly, G5 PAMAM dendrimer with 128 cationic surface functionalities showed distinct interaction behaviors with the ILs compared with G4.5 PAMAM dendrimer. As shown in Figure S5, the diffusion coefficients of both [BMIM]⁺ and [MDEGSO₄][−] are scarcely changed during the addition of G5 PAMAM dendrimer (IL/dendrimer molar ratio ranges from 2:1 to 64:1). Also, no encapsulation of [BMIM]⁺ and [MDEGSO₄][−] within the interior pockets of G5 PAMAM dendrimer is observed at different pH conditions (Figure 6). These results suggest extremely weak interactions between G5 and [BMIM][MDEGSO₄]. This phenomenon is also observed for insoluble ILs including [BMIM][TFSI] and [THTDP][TFSI] (Figure S2 and Figure S3 of the Supporting Information). The lack of interactions between G5 PAMAM dendrimer and the three ILs is further confirmed by ^1H NMR titration experiments. As shown in Figure 7, no shift of both dendrimer peaks and IL peaks is observed at all IL/dendrimer molar ratios. Besides, a slight change in the [TFSI][−] peak in ^{19}F NMR spectra of dendrimer/[BMIM][TFSI] complex compared to free [BMIM][TFSI] (from −78.49 ppm to −78.65 ppm) is observed in Figure 3B. The distinct binding behavior of G4.5 and G5 dendrimers with the ILs might be attributed to the presence of sodium ions on the surface of G4.5 dendrimer. These sodium ions may bind with the anions in the ILs such as [MDEGSO₄][−] and [TFSI][−] which helps the ionic interactions between the G4.5 anionic surface and the

cation [BMIM]⁺. To confirm this speculation, we investigated the interactions between G5 PAMAM dendrimer and [BMIM][MDEGSO₄] under acidic conditions. As shown in Figure S4 of the Supporting Information, interactions between [MDEGSO₄][−] and cationic G5 dendrimer were observed at pH 5.0, suggesting that counterions play an important role in the interactions between dendrimers and ionic liquids.

In previous studies, G5 PAMAM dendrimer showed a strong ability to encapsulate SDS molecules within its interior cavities.³⁵ Here, [MDEGSO₄][−] has a similar amphiphilic structure as SDS but failed to localize within the G5 interior pockets. To help with the formation of inclusion complexes between cationic dendrimer and ILs, a G4 amine-terminated PPI dendrimer with a much more hydrophobic interior than PAMAM dendrimer was used. As shown in Figure 8, no NOE cross-peaks were observed between PPI pocket protons and [MDEGSO₄][−] protons, suggesting that the fail of inclusion complex between IL and G5 is not attributed to the relatively polar pockets of PAMAM dendrimer. The weak interactions between cationic PPI dendrimer and [BMIM][MDEGSO₄] are further confirmed by PFG studies in Figure S5 of the Supporting Information. A recent study has demonstrated the formation of several inclusion complexes consisted of ILs and β -cyclodextrin.³⁶ The cation and anion in the IL 1-dodecyl-3-methylimidazolium [TFSI] simultaneously exhibited strong interactions with β -cyclodextrin. NMR studies confirmed that the alkyl chain on the imidazolium ring instead of the imidazolium ring itself enters into the hydrophobic cavity of β -cyclodextrin.³⁶ The interior pocket of PPI dendrimer is more hydrophobic than that of β -cyclodextrin; however, the IL 1-dodecyl-3-methylimidazolium [TFSI] used in ref 36 is more

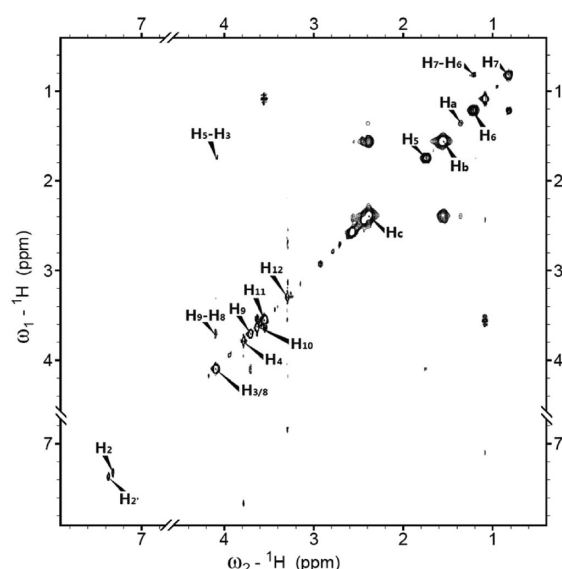


Figure 8. ^1H – ^1H NOESY spectrum of $[\text{BMIM}][\text{MDEGSO}_4]/\text{G4 PPI}$ dendrimer complexes in D_2O . The molar ratio ILs-1 and G4 PPI is 16:1, and the dendrimer concentration is 2 mg/mL.

hydrophobic than the ILs $[\text{BMIM}][\text{MDEGSO}_4]$ and $[\text{BMIM}][\text{TFSI}]$ used in the current study due to the long aliphatic chain in 1-dodecyl-3-methylimidazolium. The ions such as $[\text{BMIM}]^+$ and $[\text{MDEGSO}_4]^-$ are energetically unfavorable for forming inclusion complexes with G5 or G4.5 PAMAM dendrimer. Though the cation in $[\text{THTDP}][\text{TFSI}]$ is hydrophobic, a size limit is a problem for the encapsulation of this large cation within a dendrimer pocket because of steric hindrance effect. Therefore, the lack of inclusion formation between the three ILs and G5/G4.5 dendrimer is observed in this study.

4. CONCLUSION

The interactions of three ILs with cationic and anionic dendrimers in aqueous solution were studied by several NMR techniques. It can be deduced from the PFG studies that weak ionic interactions occur between anionic PAMAM dendrimer and the ILs, and that no interaction exists between cationic dendrimers and the three ILs without pH adjustment. Counterion plays an important role in the interactions between dendrimers and ionic liquids. NOESY spectra proved that no inclusion complex forms between the two dendrimers and the three ILs at different pH conditions. It is reasonable to suggest that ionic interaction is the major driving force for the formation of anionic dendrimer/ILs complexes. The findings obtained in this study are interesting due to the distinct host–guest behavior as compared to previous dendrimer/drug and dendrimer/surfactant systems. The combination of PFG and NOE NMR techniques provides new insights into dendrimer-based host–guest systems.

■ ASSOCIATED CONTENT

Supporting Information

Figures showing further information on ^1H NMR and ^1H – ^1H NOESY spectra of the complexes of dendrimer with ILs and diffusion coefficients. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: twxu@ustc.edu.cn (T.X.); yycheng@mail.ustc.edu.cn (Y.C.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the Science and Technology of Shanghai Municipality (Grant 11DZ2260300), the Talent Program of East China Normal University (Grant No.77202201), the Program for New Century Excellent Talents in University of Ministry of Education of China, and the Innovation Program of Shanghai Municipal Education Commission (Grant No.12ZZ044) for financial support on this project, and the USTC&CAS Special Grant for Postgraduate Research, Innovation and Practice.

■ REFERENCES

- (1) Petkovic, M.; Seddon, K. R.; Rebelo, L. P.; Silva Pereira, C. *Chem. Soc. Rev.* **2011**, *40*, 1383.
- (2) Tariq, M.; Freire, M. G.; Saramago, B.; Coutinho, J. A.; Lopes, J. N.; Rebelo, L. P. *Chem. Soc. Rev.* **2012**, *41*, 829.
- (3) Wang, H.; Gurau, G.; Rogers, R. D. *Chem. Soc. Rev.* **2012**, *41*, 1519.
- (4) Walsh, D. A.; Lovelock, K. R.; Licence, P. *Chem. Soc. Rev.* **2010**, *39*, 4185.
- (5) Giernoth, R. *Top. Curr. Chem.* **2010**, *290*, 263.
- (6) Podgoršek, A.; Salas, G.; Campbell, P. S.; Santini, C. C.; Pádua, A. A.; Costa Gomes, M. F.; Fenet, B.; Chauvin, Y. *J. Phys. Chem. B* **2011**, *115*, 12150.
- (7) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. *Nat. Mater.* **2009**, *8*, 621.
- (8) Campbell, P. S.; Podgoršek, A.; Gutel, T.; Santini, C. C.; Pádua, A. A.; Costa Gomes, M. F.; Bayard, F.; Fenet, B.; Chauvin, Y. *J. Phys. Chem. B* **2010**, *114*, 8156.
- (9) Aerov, A. A.; Khokhlov, A. R.; Potemkin, I. I. *J. Phys. Chem. B* **2010**, *114*, 15066.
- (10) Zech, O.; Thomaier, S.; Bauduin, P.; Rück, T.; Touraud, D.; Kunz, W. *J. Phys. Chem. B* **2009**, *113*, 465.
- (11) Greaves, T. L.; Drummond, C. J. *Chem. Soc. Rev.* **2008**, *37*, 1709.
- (12) Tomalia, D. A. *New J. Chem.* **2012**, *36*, 264.
- (13) Tomalia, D. A. *Soft Matter* **2010**, *6*, 456.
- (14) Tomalia, D. A. *Prog. Polym. Sci.* **2005**, *30*, 294.
- (15) Astruc, D.; Boisselier, E.; Ornelas, C. *Chem. Rev.* **2010**, *110*, 1857.
- (16) Tomalia, D. A.; Reyna, L. A.; Svenson, S. *Biochem. Soc. Trans.* **2007**, *35*, 61.
- (17) Cheng, Y. Y.; Zhao, L. B.; Li, Y. W.; Xu, T. W. *Chem. Soc. Rev.* **2011**, *40*, 2673.
- (18) Caminade, A. M.; Majoral, J. P. *Chem. Soc. Rev.* **2010**, *39*, 2034.
- (19) Caminade, A. M.; Hameau, A.; Majoral, J. P. *Chem.—Eur. J.* **2009**, *15*, 9270.
- (20) Caminade, A. M.; Servin, P.; Laurent, R.; Majoral, J. P. *Chem. Soc. Rev.* **2008**, *37*, 56.
- (21) Caminade, A. M.; Turrin, C. O.; Majoral, J. P. *Chem.—Eur. J.* **2008**, *14*, 7422.
- (22) Yancey, D. F.; Carino, E. V.; Crooks, R. M. *J. Am. Chem. Soc.* **2010**, *132*, 10988.
- (23) Gomez, M. V.; Guerra, J.; Myers, V. S.; Crooks, R. M.; Velders, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 14634.
- (24) Gomez, M. V.; Guerra, J.; Velders, A. H.; Crooks, R. M. *J. Am. Chem. Soc.* **2009**, *131*, 341.
- (25) Raghu, S. C.; Berchmans, S.; Phani, K. L.; Yegnaraman, V. *Chem.—Asian J.* **2007**, *2*, 775.
- (26) Huang, J. F.; Luo, H.; Liang, C.; Sun, I. W.; Baker, G. A.; Dai, S. *J. Am. Chem. Soc.* **2005**, *127*, 12784.

- (27) Zhao, L. B.; Wu, Q. L.; Cheng, Y. Y.; Zhang, J. H.; Wu, J. H.; Xu, T. W. *J. Am. Chem. Soc.* **2010**, *132*, 13182.
- (28) Hu, J. J.; Xu, T. W.; Cheng, Y. Y. *Chem. Rev.*, in press (doi: 10.1021/cr200333h).
- (29) Vreekamp, R.; Castellano, D.; Palomar, J.; Ortega, J.; Espiau, F.; Fernández, L.; Penco, E. *J. Phys. Chem. B* **2011**, *115*, 8763.
- (30) Domańska, U.; Zawadzki, M.; Tshibangu, M. M.; Ramjugernath, D.; Letcher, T. M. *J. Phys. Chem. B* **2011**, *115*, 4003.
- (31) Gao, Y. A.; Li, Z. H.; Du, J. M.; Han, B. X.; Li, G. Z.; Hou, W. G.; Shen, D.; Zheng, L. Q.; Zhang, G. Y. *Chem.—Eur. J.* **2005**, *11*, 5875.
- (32) Fang, M.; Cheng, Y. Y.; Zhang, J. H.; Wu, Q. L.; Hu, J. J.; Zhao, L. B.; Xu, T. W. *J. Phys. Chem. B* **2010**, *114*, 6048.
- (33) Yang, W. J.; Li, Y. W.; Cheng, Y. Y.; Wu, Q. L.; Wen, L. P.; Xu, T. W. *J. Pharm. Sci.* **2009**, *98*, 1075.
- (34) Wu, Q. L.; Cheng, Y. Y.; Hu, J. J.; Zhao, L. B.; Xu, T. W. *J. Phys. Chem. B* **2009**, *113*, 12934.
- (35) Cheng, Y. Y.; Li, Y. W.; Wu, Q. L.; Xu, T. W. *J. Phys. Chem. B* **2008**, *112*, 12674.
- (36) He, Y. F.; Cheng, Q. D.; Xu, C.; Zhang, J. J.; Shen, X. H. *J. Phys. Chem. B* **2009**, *113*, 231.