

Synthesis of Poly(ethylene glycol) Functionalized Star-shaped Tricationic Imidazolium Based Ionic Liquid*

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Abstract We report on the preparation of a well-defined star-shaped tricationic ionic liquid possessing three arms of poly(ethylene glycol) functionalized imidazolium rings. Remarkable solubility was found in most of the organic solvents we used. Thermogravimetric analysis (TGA) exhibited excellent thermal stability and two distinct decomposition temperatures were attributed to two kinds of chemical degradation. Differential scanning calorimetry (DSC) was further employed to investigate the thermal phase transitions, that three different signals (T_g , T_c , and T_m) were shown upon the second heating process. Moreover, CH₂Cl₂ solution of the ionic liquid expressed an excitation-wavelength dependent fluorescence response, leading to the facile modulation of photoluminescence behavior. This work represents an example of utilizing molecular design to construct novel ionic liquids and endow further potential to be used in the engineering materials.

Keywords: Ionic liquid; Imidazole; Tricationic; Excitation-wavelength dependent; Photoluminescence.

INTRODUCTION

Ionic liquids (ILs) are commonly recognized as a special class of molten salts formed by a wide combination of cations and anions. Because of the independently modified ionic components and favorable properties, such as low volatility^[1–4], high polarity^[5–7], excellent thermal stability^[8–10] and selective dissolving capacity^[1, 11–12], ionic liquid has received a considerable upswing of interest in a variety of applications, including catalysts^[13–17], electrochemistry^[18–20], polymerization^[21–24], engineering fluids^[25–27] or as alternative solvents^[1, 28–31].

In the context of the numerous reported kinds of ionic liquids, 1-alkyl-3-methylimidazolium-based ionic liquids have been widely studied as representative liquids due to their inherent polar or nonpolar segregation^[32–34], which leads to a complex solvation behavior once these ionic liquids are mixed with water or organic solvents. Moreover, increasing interest has been centered on the development of imidazolium-based polymer-containing ionic liquids^[35–38], their novel properties and applications had also been investigated.

It has been known that glycols as well as their derivatives have excellent chemical and physical properties and the ether-derivative ionic liquids are being increasingly studied^[39–42]. In particular, poly(ethylene glycol) (PEG) has been incorporated into cationic or anionic units to produce the ether-derivative ionic liquids, the inclusion of alkoxy moieties always affects the physicochemical properties of relevant products. For example,

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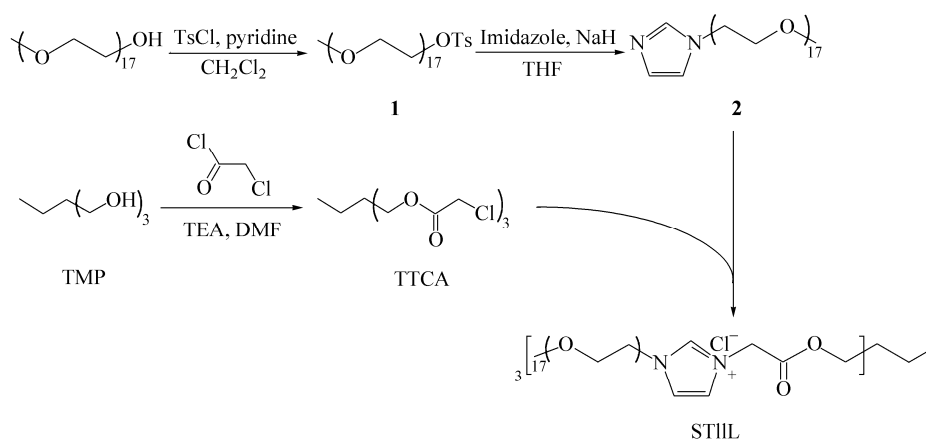
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ionic liquids with a linear-PEG tail attached to the imidazolium ring had been reported by Krishnan *et al.*^[43]. The final products could self-assemble to form a solvent-free ionic gel without assistance, and had been tested to possess a potential application as an electrolyte in dye-sensitized solar cells. In addition, Colacino *et al.*^[44] reported the synthesis of a hydrophilic ammonium based PEG-ionic liquid, which could be used in the application of peptide coupling under microwave activation. The lightspot of this work is that two PEG chains grafted onto the center ammonium cation could lead to a battery of outstanding physicochemical properties compared with the traditional one PEG tail attached ionic liquid, and resulted in the potential usage in some special situations.

Recently, another topological structure of ionic liquids with two cations using poly(ethylene glycol) as a linker has been reported^[45, 46]. Imidazolium-based PEG functionalized dicationic liquids containing alkyl or polyfluoroalkyl groups had been estimated with a thermal decomposition temperature as high as 415 °C^[46], which is much higher than the most common single charged ionic liquids in thermal stability. Moreover, dicationic acidic ionic liquids linked by PEG was also synthesized and could be utilized as catalysts in temperature-dependant phase-separation system to improve product isolation and recycle without loss of catalytic activity^[45, 47].

By taking advantage of the fact that polymer-based materials with multicomponent endow them with unique properties and superiority on demand^[48], we get prompted to design a series of novel imidazolium-based ionic liquids functionalized with polymer to form a special topological structure. In this work, we prepared a star-shaped tricationic imidazolium-based ionic liquid (STIIL), the synthetic routes for the synthesis of STIIL are shown in Scheme 1. The procedure of synthesis was started from esterification of trimethylolpropane to form 2-((2-chloroacetoxy)methyl)-2-ethylpropane-1,3-diyl bis(2-chloroacetate) (TTCA) and then followed by the consecutive quaternization reaction with imidazolium functionalized mPEG₇₅₀ (**2**), yielding the final STIIL, containing a imidazolium cationic ring and one PEG chain in each arm, respectively, and connected by central trimethylolpropane. Remarkable solubility was found in most of the organic solvents we used. Thermogravimetric analysis (TGA) exhibited excellent thermal stability and two distinct decomposition temperatures were attributed to two kinds of chemical degradation. Differential scanning calorimetry (DSC) was further employed to investigate the thermal phase transitions, that three different signals (T_g , T_c , and T_m) were shown upon the second heating process. Moreover, CH₂Cl₂ solution of the ionic liquid expressed an excitation-wavelength dependent fluorescence response, leading to the facile modulation of photoluminescence behavior.



Scheme 1 Synthetic routes employed for the preparation of poly(ethylene glycol) monomethyl ether tosylate (**1**), poly(ethylene glycol) monomethyl ether imidazole (**2**), 2-((2-chloroacetoxy)methyl)-2-ethylpropane-1,3-diyl bis(2-chloroacetate) (TTCA) and star-shaped tricationic imidazolium ionic liquid (STIIL)

To the best of our knowledge, imidazolium-based ionic liquids with this kind of star-shaped tricationic topological structure has been rarely reported. The current work represents a proof-of-concept example of utilizing molecular design to produce novel ionic liquids, which have potential to be used in the further engineering materials.

EXPERIMENTAL

Materials

Poly(ethylene glycol) monomethyl ether ($M_w = 750$) was purchased from Aladdin Chemistry Co., Ltd. and with toluene as entrainer before use. Trimethylolpropane, chloroacetyl chloride, imidazole, *p*-toluenesulfonyl chloride and pyridine were purchased from Tianjin Guangfu Fine Chemical Reagent Co., Ltd. and used as received without further purification. Tetrahydrofuran (Sinopharm Chemical Reagent Co., Ltd.) was distilled over sodium before use. Acetonitrile (Sinopharm Chemical Reagent Co., Ltd.) was dried over calcium hydride followed by distillation. Triethylamine (TEA) and sodium hydride (60% in mineral oil) was purchased from Aladdin Chemistry Co., Ltd and used as received. Water was deionized with a Milli-Q SP reagent water system (Millipore) to a specific resistivity of 18.4 M Ω -cm. All other reagents were commercially available and used as received.

Measurements

Molecular weights and molecular weight distributions were determined by GPC equipped with Waters 515 pump and Waters 2414 differential refractive index detector (set at 40 °C). A series of three linear Styragel columns (HR0.5, HR2, and HR4; 7.8 $\times$ 300 mm) were used at an oven temperature of 40 °C. The eluent was THF at a flow rate of 0.3 mL/min. A series of low polydispersity polystyrene (PS) standards were employed for the GPC calibration.

All NMR spectra were recorded on a Bruker AV300 NMR spectrometer (resonance frequency of 300 MHz for ^1H) operated in the Fourier transform mode. CDCl_3 was used as the solvent with tetramethylsilane (TMS) as internal reference at 25 °C.

All FTIR spectra were recorded on a Perkin-Elmer Spectrum 100 IR spectrometer using KBr pellets at room temperature.

TGA test was performed in N_2 atmosphere at a heating rate of 10 K/min from 35 °C to 600 °C using a Netzsch TG 209 F3 instrument.

The viscosity of STIIL was measured over a temperature range of 25–80 °C in step of 5 K using a Brookfield DV-II+Pro viscometer installed with a model LV-4 spindle. Before the viscosity experiment, the STIIL was dried at 70 °C for 24 h in a vacuum oven.

DSC measurements were carried on a Perkin-Elmer DSC-7 instrument. Samples were first heated from 25 to 150 °C at a heating rate of 10 K/min under nitrogen atmosphere and kept constant at 150 °C for 5 min, followed by cooling to –60 °C at 10 K/min and finally heating to 150 °C again at 10 K/min. Glass transition temperature (T_g) was determined as the midpoint of the transition of the second heating sequence.

Fluorescence spectra were recorded using an F-2700 FL spectrofluorometer. The temperature (25 °C) of the water-jacketed cell holder was controlled by a programmable circulation bath. The slit widths were set at 5 nm for excitation and 5 nm for emission. For all experiments, sample concentrations were fixed at 0.01 mol/L.

Sample Preparation

The general approaches to the preparation of 2-((2-chloroacetoxy)methyl)-2-ethylpropane-1,3-diyl bis(2-chloroacetate) (TTCA), poly(ethylene glycol) monomethyl ether tosylate (mPEG₇₅₀-pTs), poly(ethylene glycol) monomethyl ether imidazole and star-shaped tricationic imidazolium ionic liquid (STIIL) are shown in Scheme 1.

Synthesis of 2-((2-chloroacetoxy)methyl)-2-ethylpropane-1,3-diyl bis(2-chloroacetate) (TTCA)

2-((2-chloroacetoxy)methyl)-2-ethylpropane-1,3-diyl bis(2-chloroacetate) (TTCA) was prepared according to literature procedures with little modification^[49, 50]. Into a round-bottom flask equipped with a magnetic stirring bar, trimethylolpropane (6.7 g, 50 mmol), TEA (24.0 mL, 175 mmol) and dry DMF (30 mL) were charged. After cooling to 0 °C in an ice-water bath under N₂ atmosphere, chloroacetyl chloride (13.2 mL, 175 mmol) in 20 mL of dry DMF was added dropwise over 1 h. After stirring for another 12 h at 60 °C, the reaction was essentially complete as monitored by TLC using petroleum ether/ethyl acetate (10/1, *V/V*). Then, the reaction mixture was poured into 300 mL of water. After filtration, the crude product was isolated as brown powder and further purified by silica gel column chromatography using petroleum ether/ethyl acetate (10/1, *V/V*) as eluent, the solvent was then removed under reduced pressure, yielding white powder (11.9 g, yield: 65%). ¹H-NMR (CDCl₃, δ , TMS): 0.92 (3H, CH₃CH₂—), 1.53 (2H, CH₃CH₂—), 4.05 (2H, —CH₂Cl), 4.18 (2H, —OCOCH₂Cl).

Synthesis of Poly(ethylene glycol) Monomethyl Ether Tosylate (mPEG₇₅₀-pTs, 1)

mPEG₇₅₀-pTs was prepared according to literature procedures^[51, 52]. For example, into a round-bottom flask equipped with a magnetic stirring bar, mPEG₇₅₀ (8.0 g, 10.7 mmol), *p*-TsCl (8.1 g, 42.7 mmol), and dry CH₂Cl₂ (50 mL) were charged. After cooling to 0 °C in an ice-water bath under N₂ atmosphere, pyridine (2.0 mL, 24.9 mmol) in 10 mL of dry CH₂Cl₂ was gradually introduced, the reaction mixture was allowed to warm to room temperature and stir for another 24 h at 50 °C. Then, the resulting mixture was poured into 10% hydrochloric solution (100 mL) and extracted with CH₂Cl₂ (3 × 50 mL). The CH₂Cl₂ layer was collected and dried over anhydrous Na₂SO₄, the solvent was then removed under reduced pressure and further dried under vacuum for 3 days, yielding a pale yellow liquid (6.78 g, yield: 67%). ¹H-NMR (CDCl₃, δ , TMS): 2.41 (3H, —ArCH₃), 3.33 (3H, —OCH₃), 3.50–3.65 and 4.12 (68H, —CH₂CH₂O—), 7.32 and 7.77 (4H, ArH).

Synthesis of Poly(ethylene glycol) Monomethyl Ether Imidazole (2)

This compound was prepared according to literature procedures^[53]. For example, into a round-bottom flask equipped with a magnetic stirring bar, NaH (60 mg, 2.5 mmol), and dry THF (10 mL) were charged. After cooling to 0 °C in an ice-water bath, imidazole (0.15 g, 2.2 mmol) in 10 mL of THF was added dropwise and the reaction mixture was allowed to stir at room temperature for 4 h. Then, mPEG₇₅₀-pTs (2.0 g, 2.2 mmol) was added, the resulting mixture was heated to reflux for another 16 h. After cooling to room temperature, the mixture was filtered and the filtrates were evaporated, followed by dissolving the obtained brown oil in methanol and washing with hexane. The methanol layer was collected and the solvent was then removed under reduced pressure, yielding **2** (1.67 g, yield: 95%). ¹H-NMR (CDCl₃, δ , TMS): 3.33 (3H, —OCH₃), 3.42–3.73 and 4.05 (68H, —CH₂CH₂O—), 6.97, 7.26, and 7.49 (3H, imidazole proton).

Synthesis of Star-shaped Tricationic Imidazolium Ionic Liquid (STIIL)

STIIL was prepared by a quaternization reaction according to literature procedures with little modification^[54]. Into a round-bottom flask equipped with a magnetic stirring bar, **2** (1.24 g, 1.5 mmol), TTCA (0.12 g, 0.3 mmol), and dry CH₃CN (10 mL) were charged. After complete dissolving, the reaction mixture was heated to reflux at 80 °C under N₂ atmosphere for 7 days. Then, the reaction mixture was cooled to room temperature and CH₃CN was removed *via* rotary evaporation. The crude product was redissolved in methanol, and cold diethyl ether was poured into the methanol solution. The top layer was decanted off and this procedure was repeated for three times. The collected solution was then washed with diethyl ether, followed by drying under vacuum for 6 h to yield STIIL (3.0 g, yield: 88%). ¹H-NMR (CDCl₃, δ , TMS): 0.85 (3H, CH₃CH₂—), 1.42 (2H, CH₃CH₂—), 3.35 (9H, —OCH₃), 3.50–3.65 (200H, —CH₂CH₂O—), 3.86 (6H, —NCH₂CH₂O—), 4.10 (6H, —COOCH₂—), 4.48 (6H, —NCH₂CH₂O—), 5.69 (6H, —NCH₂COO—), 7.54, 8.15, and 10.17 (9H, imidazole proton).

RESULTS AND DISCUSSION

Synthetic routes employed for the preparation of STIIL is shown in Scheme 1. The TTCA was prepared by reacting trimethylolpropane with chloroacetyl chloride; mPEG₇₅₀ was activated by *p*-TsCl at first, followed by

the reaction with imidazole in the presence of NaH to afford compound **2**; finally, STIIL was obtained by the quaternization reaction of **2** with TTCA in CH₃CN. GPC analysis, shown in Fig. 1, was first employed to confirm the chemical regularity of this kind of ionic liquids. Obviously, GPC analysis of STIIL revealed a monomodal and almost symmetric elution peak, yielding a M_n of 2.1 kDa and an M_w/M_n of 1.20 (Fig. 1). The curves for each precursor, mPEG₇₅₀-OH, mPEG₇₅₀-pTs, and mPEG₇₅₀-imidazole, were also presented.

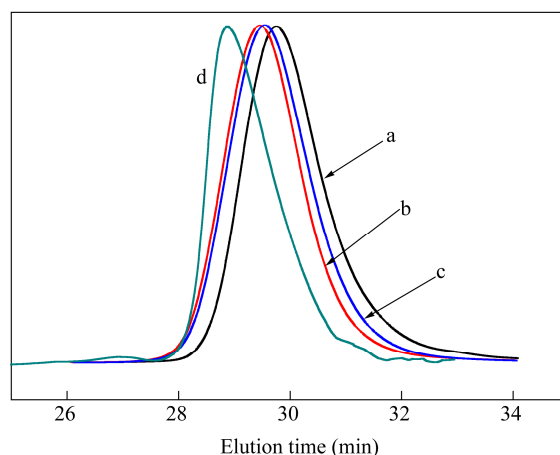


Fig. 1 GPC traces recorded for (a) mPEG₇₅₀-OH, (b) mPEG₇₅₀-pTs (**1**), (c) mPEG₇₅₀-imidazole (**2**) and (d) star-shaped tricationic imidazolium ionic liquid (STIIL)

The accurate chemical structure of mPEG₇₅₀-pTs (**1**), mPEG₇₅₀-imidazole (**2**), TTCA and STIIL were then confirmed by ¹H-NMR analysis (Fig. 2). Compared the ¹H-NMR spectrum of STIIL with that of compound **2**, the chemical shift of the acidic proton in the 2-position on the imidazolium ring, $-N^+CHN-$, moved to 10.17, and the protons in the 4, 5-position resonated at $\delta = 8.22$ and 7.53, respectively. Previously, Xu *et al.*^[55] found once the PEG wrapped around the imidazolium ring to form a shielded environment, “solvation” of the imidazolium ring of IL by the PEG chain occurred, same phenomenon was also reported by Krishnan *et al.*^[56]. The imidazolium ring was located within the hole of the coiled PEG, leading to an obviously upfield shift of the protons on the imidazolium ring in ¹H-NMR spectrum. However, in our situation, the star-shaped topological structure of STIIL hindered PEG chains wrapping around the imidazolium ring, the PEG chains could not be able to construct a shielded environment. Furthermore, the chemical shift of protons in $-N^+CH_2COO-$ moved up to $\delta = 5.73$ compared to the proton of $-CH_2Cl-$ in TTCA at $\delta = 4.07$, indicating the electron-withdrawing effect of the ester group and imidazolium cation increased the acidity of the hydrogen atoms significantly.^[57]

FTIR spectroscopy was also employed to confirm the chemical structures of all the precursors and final STIIL, and the results are shown in Fig. 3. The representative FTIR spectrum of TTCA (spectrum a) clearly revealed the presence of absorbance peaks at 786 and 690 cm⁻¹, which are characteristic of stretching vibration of C—Cl bonds^[58–60]. Moreover, compared with spectrum b, the newly presented signal at 3110 cm⁻¹ in spectrum c represented the stretching vibration of C—H aromatic groups and indicated the presence of the imidazole ring. Nearly complete disappearance of the two characteristic peaks of 786 and 690 cm⁻¹ in spectrum d apparently indicated that almost all the C—Cl bonds were consumed and participated in the quaternization reaction to build STIIL. It should be noted that the observed broad band at 3177 cm⁻¹ in spectrum d clearly confirmed the existence of extensive H-bonds in the structure of STIIL, which was in agreement with the results reported by Dyson *et al.*^[61]. They pointed out that oxygen atoms in the PEG chains could act as H-bond acceptors towards the imidazolium protons. In addition, the electron-withdrawing effect of ester group increased the acidity of the hydrogen atoms in the $-CH_2COO-$ moieties attached to the imidazolium cation, which also made an important contribution to H-bond probably^[57, 62]. On the basis of chemical intuition, the expected star-shaped topological structure of STIIL has been successfully obtained by considering all the factors above.

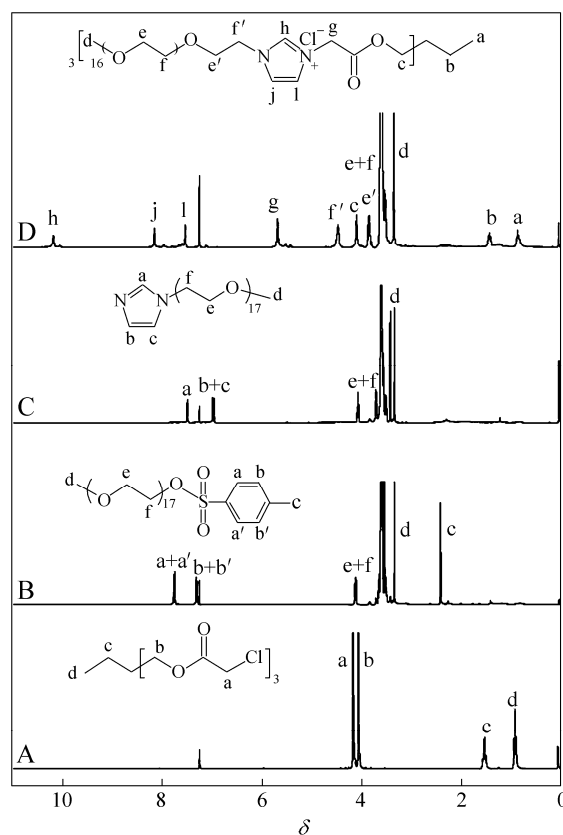


Fig. 2 ^1H -NMR spectra recorded in CDCl_3 for (A) TTCA, (B) mPEG_{750} -pTs (**1**), (C) mPEG_{750} -imidazole (**2**) and (D) star-shaped tricationic imidazolium ionic liquid (STIIL)

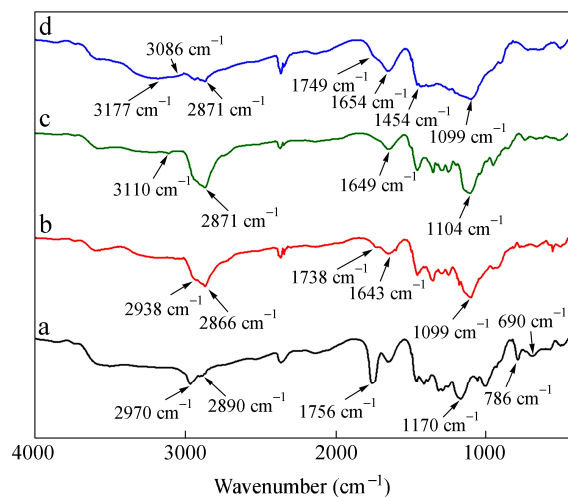


Fig. 3 FTIR spectra recorded for (a) TTCA, (b) mPEG_{750} -pTs (**1**), (c) mPEG_{750} -imidazole (**2**) and (d) star-shaped tricationic imidazolium ionic liquid (STIIL)

The miscibility of STIIL was then investigated by mixing it with a variety of common organic solvents. It was found that STIIL was miscible in most of the organic solvents we used, such as CH_2Cl_2 , EtOAc, CH_3CN , DMF, CH_3OH and H_2O . However, it found out to form a biphasic system and immiscible in petroleum ether (PE) and diethyl ether (Et_2O), which was coincidence with the miscibility of a hydrophilic ammonium-based

poly(ethylene glycol)-ionic liquid (PEG-IL) reported by Colacino *et al.*^[44]. Interestingly, compared the ionic liquid immiscible or partially miscible in ethyl acetate with previously reported literature^[45], the STIIL reported here could be well miscible in ethyl acetate. This difference should be ascribed to the presence of three PEG arms in STIIL, which enhanced the solubility of STIIL in ethyl acetate^[44].

The combination of imidazolium moieties and PEG chains as well as the thermal decomposition behavior of STIIL was further proved by thermogravimetric analysis (TGA) under N₂ atmosphere at a heating rate of 10 K/min, shown in Fig. 4(a). There existed ~3.6 wt% decrease in the weight retentions before 140 °C, corresponding to the physical volatilization of water removal. Subsequently, the STIIL exhibited high thermal stability up to at least about 200 °C and an obvious two distinct weight loss was observed. The weight loss started at 235 °C, estimated to be ~12.8%, could be ascribed to the introduction of three ester linkages in STIIL, which had slight lower thermal stability. This decomposition behavior compared well with that previously reported determined by Kim and Lee and Yang *et al.*^[63, 64]. They also found two distinct decomposition temperatures during their TGA test of ILs and attributed the weight loss at lower temperatures to the presence of methyl acetate group in their samples, resulting in the decrease of thermal stability of ILs remarkably. The onset decomposition temperature corresponding to 5% mass loss (~266 °C) of STIIL here was slight lower than that of other reported PEGylated imidazolium ILs^[56]. This should be due to the star-shaped topological structure of STIIL hinders PEG chains wrapping around the imidazolium ring, the nucleophilic attack of Cl⁻ on the imidazolium ring would become easier and resulted in the forward of onset of chemical degradation. Similarly, several examples also demonstrated that incorporating short length PEG chains to quaternary cations led to worse thermal stability than those with one or no ether groups^[65, 66]. The second weight loss step, started at ~302 °C, comprising a significant fraction of 77 wt%, could be assigned to chemical degradation of STIIL, and kept constant after 400 °C. However, it should be noted that the maximum decomposition temperature (400 °C) was much higher than that of reported PEG functionalized imidazolium ionic liquids^[43, 56].

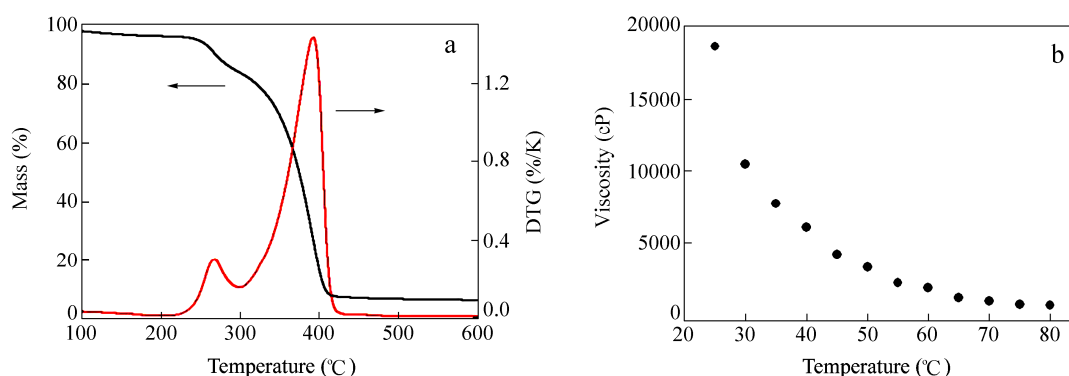


Fig. 4 (a) Thermogravimetric analysis of STIIL performed under inter N₂ atmosphere at a heating rate of 10 K/min; (b) Temperature dependence of viscosity of STIIL

Moreover, STIIL exhibited a soft gel state with a rather low fluidity at room temperature, that is, it is hard to flow out of an inverted tube, accompanying a viscosity as high as 19000 cP (Fig. 4b). With the temperature increasing, the viscosity of STIIL showed a dramatically decrease to ~560 cP at 80 °C and then kept constant. The high viscosity displayed by STIIL here is resulting from the reduced rotational freedom induced by the presence of three PEG chains (*n*-mers = 17 each), as well as by the strong intermolecular forces of interactions arising between the polar PEG chains. Even the temperature increased up to 80 °C, the value remained higher than that of reported PEG functionalized ionic liquids^[44, 56].

Glass transition temperature (T_g) is one of the basic physical parameters of natural or synthetic polymers. Both molecular weights, particularly in the low MW range, and chain topology can considerably affect T_g values^[67–71]. Differential scanning calorimetry (DSC) was further employed to investigate the thermal phase transition of bulk STIIL, typical DSC thermograms of STIIL are shown in Fig. 5. It has been found that many

types of ILs were observed to be significantly super-cool without crystallization, even melting points^[72]. In Fig. 5, DSC scan of the second heating process at a rate of 10 K/min showed that the STIIL displayed three different signals: a glass transition at $-49.1\text{ }^{\circ}\text{C}$, a cold crystallization peak at $-14.5\text{ }^{\circ}\text{C}$, and a melting peak at $28.5\text{ }^{\circ}\text{C}$, respectively. Compared with the thermal phase transition of mPEG₇₅₀-imidazole, the cold crystallization temperature of STIIL decreased and the glass transition and melting temperatures were slightly affected. With the consideration of the composition, these peaks should be corresponding to transitions of the PEG chains. Moreover, the enthalpy change, ΔH_c , during the crystallization of STIIL can be calculated to be $(37.9 \pm 3.8)\text{ J/g}$ from the integration area of the strong exothermic peak (T_c), lower than that of 100% crystalline PEG polymer ($\Delta H^0 = 196.8\text{ J/g}$) reported by previous literature^[73]. Thus, an attempt to estimate the degree of crystallinity (X_c) of mPEG chains in STIIL was made according to this equation^[74],

$$X_c = \Delta H_c / (f_{\text{mPEG}} \times \Delta H^0)$$

where ΔH^0 (196.8 J/g) is the heat of fusion of 100% crystalline PEG; f_{mPEG} (79.6%) is the weight fraction of the mPEG chains in the STIIL, obtained from $^1\text{H-NMR}$. Combined all these factors, the X_c value could be calculated to be $\sim 24.2\%$, which was notably lower than that of a bulk PEG₁₀₀₀ (86.0% crystallinity)^[75]. This result indicated that there might exist some defects in the solid crystalline structure of STIIL, due to the restricted alignment of the star-shaped polymer to form an ordered array^[76].

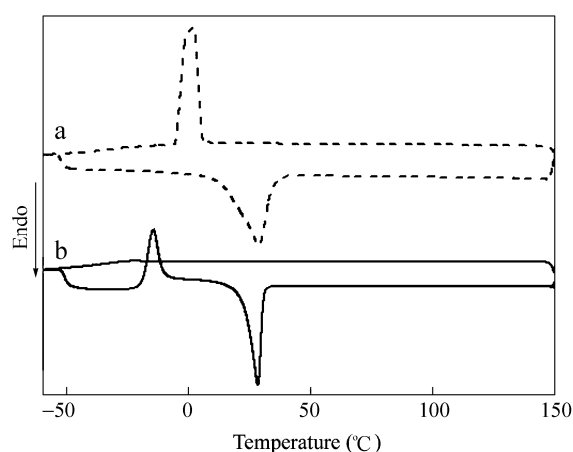


Fig. 5 Differential scanning calorimetry (DSC) curves recorded for (a) mPEG₇₅₀-imidazole and (b) STIIL

Finally, the optical behavior of STIIL in CH_2Cl_2 was investigated. A representative emission spectrum of STIIL in CH_2Cl_2 upon excited at 370 nm is shown in Fig. 6(a). As can be seen, the emission spectrum covered the visible range of wavelength from 400 to 600 nm with a maximum emission peak at 439 nm. The photographs shown in Fig. 6(b) displayed the color change of STIIL in CH_2Cl_2 before and after exposed under UV irradiation. We can clearly discern the light yellow to bright cyan transition upon UV irradiation (365 nm) by naked eyes directly. In addition, the emission wavelength of the CH_2Cl_2 sample was strongly dependent on the excitation wavelength (Fig. 6c). In our experiment, the sample was excited at various wavelengths (280 nm to 420 nm) from short to long wavelengths with an interval of 10 nm, the emission peaks displayed a synchronous red shift. For example, the first emission peak, excited at 280 nm, exhibited in a wide range from 300 to 600 nm with a maximum emission peak at 398 nm. However, once excited the same sample at 420 nm, the newly present emission peak became narrower, ranging from 430 to 600 nm, accompanied by a maximum emission peak at 495 nm, red-shifted $\sim 100\text{ nm}$ relative to that of excited at 280 nm (Fig. 6d). To the best of our knowledge, several papers had reported this phenomenon on imidazolium-based ionic liquids, our results agree well with them^[77–80].

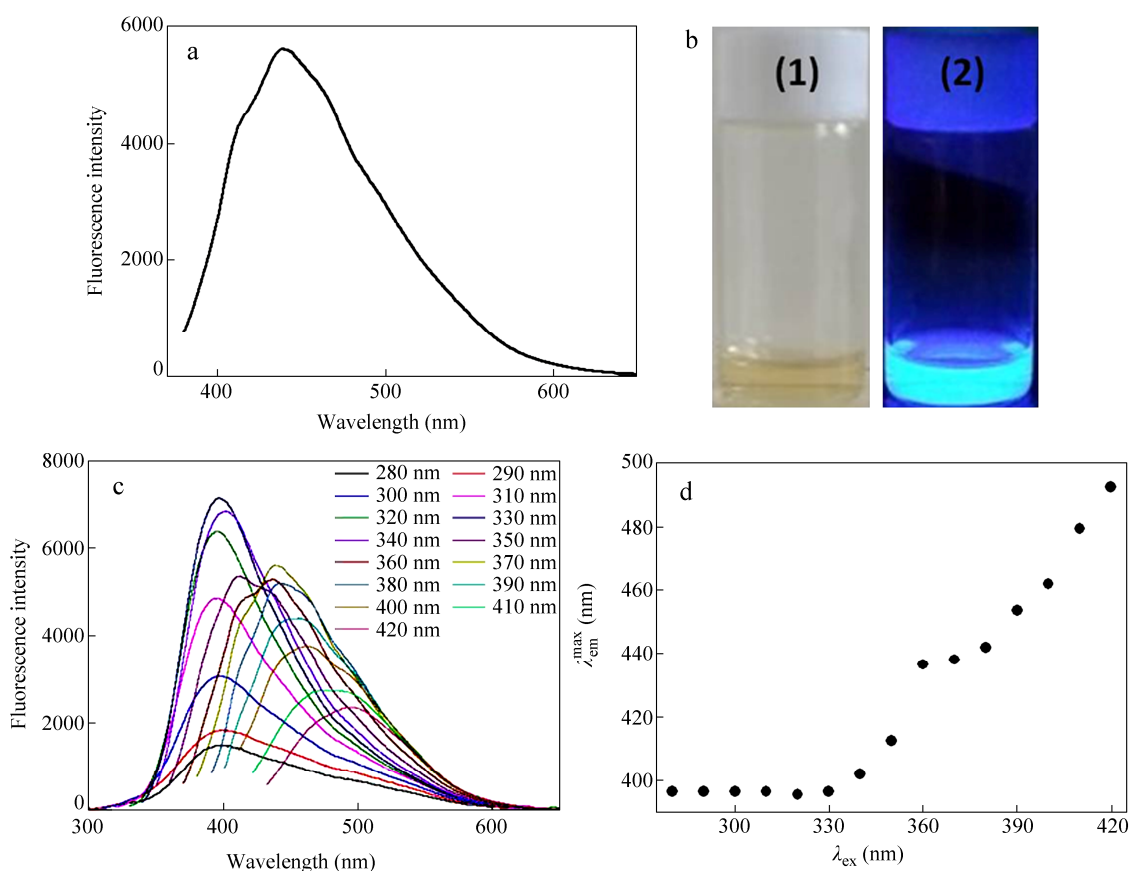


Fig. 6 (a) Typical fluorescence emission spectrum ($\lambda_{\text{ex}} = 370$ nm; slit widths: Ex. 5 nm, Em. 5 nm) obtained for STIIL in CH_2Cl_2 ; (b) Photographs of the CH_2Cl_2 solution of STIIL before (1) and after (2) irradiation under a 365 nm UV lamp; (c) Excitation wavelength dependent fluorescence emission spectra of STIIL in CH_2Cl_2 and (d) Variation of the fluorescence peak position with the excitation wavelength

CONCLUSIONS

In summary, we have successfully prepared a well-defined star-shaped tricationic ionic liquid with three arms of poly(ethylene glycol) functionalized imidazolium rings, possessing excellent solubility in most of the organic solvents, especially in EtOAc, which is immiscible or partially miscible with most of other ionic liquids. Although introduction of PEG chains reduces the onset decomposition temperature of STIIL, resulting from the easier nucleophilic attack of Cl^- on the imidazolium ring, the maximum decomposition temperature (400 °C) was much higher than that of reported PEG functionalized imidazolium ionic liquids. Photoluminescence behavior of STIIL in CH_2Cl_2 can be observed by naked eyes upon UV irradiation. The excitation wavelength dependent fluorescence response gives rise to the facile modulation of fluorescence emission. This work represents a potential engineering materials rooting in a PEG-functionalized tricationic imidazolium based ionic liquid.

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