

Exploring Spectroscopic and Physicochemical Properties of New Fluorescent Ionic Liquids

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Abstract In the current study, spectroscopic and physicochemical properties of newly prepared ionic liquids were investigated. Ionic liquids were synthesized via a simple and straightforward route using a metathesis reaction of either N,N-diethyl-p-phenylenediamine monohydrochloride or N-phenacylpyridinium bromide with bis(trifluoromethane) sulfonimide lithium in water. High yield and purity were obtained for the resultant ionic liquids. Data acquired by use of ^1H NMR and FT-IR measurements were consistent with the chemical structures of newly prepared ionic liquids. Results of thermal gravimetric analysis also implied that these ionic liquids have good thermal stability. In addition, UV–vis and fluorescence spectroscopy measurements provided that new ionic liquids are good absorbent and fluorescent. Time-based fluorescence steady-state measurements showed that ionic liquids have high photostability against photobleaching. For a deeper mechanistic understanding of the analytical potential of newly synthesized ionic liquids, spectroscopic and physicochemical parameters, including singlet absorption, extinction coefficient, fluorescence quantum yield, Stokes shift, oscillator strength and dipole moment, were also investigated.

Keywords Ionic liquids · Metathesis · FT-IR · UV–vis · Fluorescence · Photostability

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Introduction

In recent years, room temperature ionic liquids (RTILs) prove to be attractive alternatives for replacing toxic, hazardous and flammable organic solvents [1, 2]. Ionic liquids (ILs) are environmentally benign, nonvolatile, nonflammable with a high thermal stability and wide liquid ranges. These compounds are also good solvents for both inorganic and organic materials [3–5]. The miscibility of ILs in water is heavily based on the type of its anion part. The viscosity of RTILs varies considerably, but they have no effective vapor pressure. RTILs are low-melting salts that form liquids composed entirely of ions, like classical metallic molten salts such as sodium chloride (NaCl) [6]. One of fascinating properties for ILs is that varying the cation or anion may significantly affect physical and chemical properties.

RTILs have been successfully used in several applications, including replacing traditional organic solvents in organic and inorganic synthesis [7]. They have been used in solvent extractions [8, 9], liquid–liquid extractions [10, 11], enzymatic reactions [12], pharmaceutical studies [13], electrochemical studies [14], dye-sensitized solar cells and batteries [15, 16], as buffer additives in capillary electrophoresis [17] and as stationary phases in liquid chromatography [18]. ILs were also utilized as environmentally benign compounds by immobilizing them onto solid supports for extraction of metal ions without the need for partition treatment by the presence of chelating compounds. For example, silica gel modified surface with newly synthesized fluorescent ionic liquid was recently developed by Marwani [19] for a selective extraction of lead from aqueous solutions prior to its determination by use of inductively coupled plasma-optical emission spectrometry.

However, much effort has been directed on studying ILs due to their utility as green solvents and as a host of practical applications to which they are amenable [20, 21]. Moreover,

the interaction and solvation parameters and abilities of ILs have contributed to make them among the most versatile and complex solvents [22–24]. Therefore, several approaches have focused on this topic, and a series of analytical methods have been implemented to explore spectroscopic and physicochemical properties of these novel media [25, 26]. Most of analytical methods involve fast atom bombardment (FAB) mass spectrometry [27], X-ray crystallography and near-infrared Raman spectroscopy [28], and X-ray absorption fine structure (XAFS) [29] and matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) [30]. These methods have shown considerable promise in studying physicochemical and spectroscopic properties of RTILs. However, there are some problems associated with some of these techniques. For example, significant difficulties with MALDI-MS, in particular for quantification, are encountered from the inhomogeneous distribution of the analyte in the matrix-analyte cocrystallite, providing poor spot-to-spot and shot-to-shot reproducibility.

Furthermore, spectroscopic behaviors and physicochemical properties of ILs in relation to their structure were studied by several spectroscopic methods [31–33]. Fluorescence spectroscopy is one of powerful techniques for obtaining information on the structure and function of many molecules [34]. Several approaches have investigated the optical behavior of different substances in the presence of ILs by use of fluorescence measurements [35, 36], providing information on the polarity of ILs, dynamics of ionic diffusion and internal motion of the dissolved solutes. Although optical behaviors of a considerable number of dissolved solutes in the presence of these media have been studied, optical properties of RTILs were not completely understood. Moreover, a great deal of time has been concentrated on either one ionic liquid or one class of ILs, in particular imidazolium salts. Thus, there is still an increasing interest for synthesis and investigation of new ILs.

The present study was aimed to explore spectroscopic and physicochemical properties of newly synthesized ILs via a straightforward route. ILs were synthesized via the metathesis reaction of either N,N-diethyl-p-phenylenediamine monohydrochloride or N-phenacylpyridinium bromide with bis(trifluoromethane)sulfonimide lithium in water. In addition, ILs were characterized by use of ^1H NMR, FT-IR, UV–vis, and fluorescence spectroscopy, thermal gravimetric analysis and elemental analysis. Spectroscopic and physicochemical parameters, including singlet absorption, extinction coefficient, fluorescence quantum yield, Stokes shift, oscillator strength and dipole moment, were investigated for a deeper mechanistic understanding of the analytical potential of newly synthesized ILs.

Experimental

Chemicals and Reagents

N,N-diethyl-p-phenylenediamine monohydrochloride (N,N-EPACl) and N-phenacylpyridinium bromide (N-Phenacyl-PyrBr) were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Bis(trifluoromethane)sulfonimide lithium (LiNTf_2) was also obtained from Sigma-Aldrich. All reagents used were of analytical and spectral purity grade. Doubly distilled deionized water was also used throughout experimental studies.

Synthesis Procedure of ILs

Ionic liquid products were synthesized according to previously recommended procedures reported elsewhere [31]. Briefly, 1 g from the desired salt (N,N-EPACl or N-PhenacylPyrBr) was individually dissolved in 18.2 M Ω -cm distilled deionized water. An equimolar amount of LiNTf_2 was also dissolved separately in water. The two solutions were mixed and stirred for 2 h at room temperature. The reaction resulted in two layers in which the lower layer was separated and dried under vacuum overnight (Scheme 1). The purification by vacuum drying was performed at a drying temperature of 353 K and vacuum of 0.4 kPa.

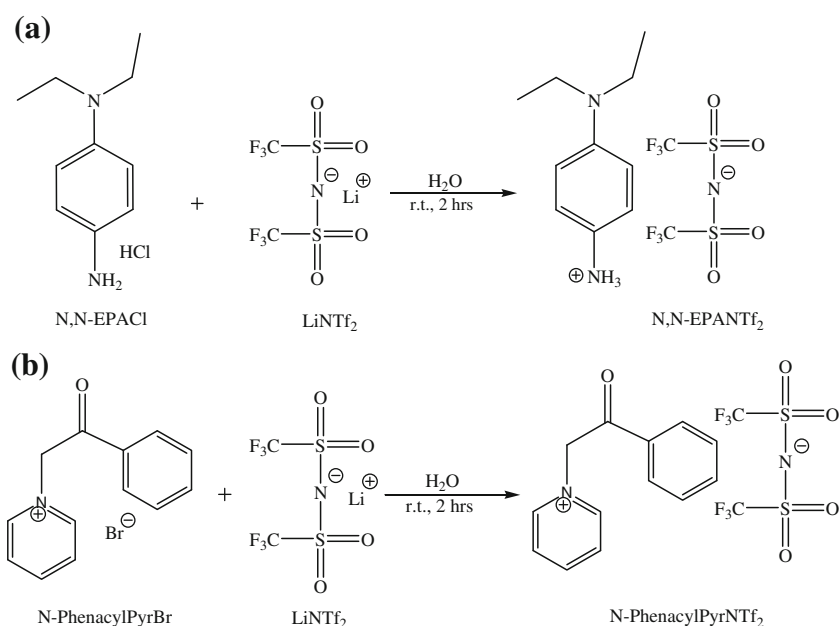
Sample Preparation

Stock solutions of ILs were prepared in ethanol and stored in the dark at 4°C. For both fluorescence and UV–vis spectroscopic studies, standard solutions of 10 μM N,N-EPANTf₂ and N-PhenacylPyrNTf₂ were prepared by adding appropriate amounts of ILs stock solution.

Instrumentation

One-dimensional ^1H NMR experiments were performed in the single-pulse mode on a Perkin Elmer 600 MHz spectrometer. All NMR measurements were recorded in CDCl_3 by use of tetramethyl silane (TMS) as an internal standard. ^1H NMR spectra were collected using a 7 μs pulse, 16 scans, and 1 s delay between scans. The spectra were processed by zero filling the FID from 16 to 32 K and applying a line-broadening of 30 Hz. FT-IR spectra were recorded on a Shimadzu FT-IR 470 spectrophotometer in the range 4000–600 cm^{-1} . Thermal gravimetric analyses (TGA) were acquired using a thermal analysis instrument TGA-7 HR V6.1A (module TGA 1400°C). Thermal decomposition temperature (T_{dec}) of ILs was determined at a heating rate of 5°Cmin⁻¹ under nitrogen from 20 to 700°C. UV–vis absorption and fluorescence measurements were performed by use of a Perkin-Elmer UV–vis scanning spectrophotometer and

Scheme 1 Synthetic route of
a N,N-EPANTf₂ and
b N-PhenacylPyrNTf₂



luminescence spectrofluorometer, respectively. Absorption and emission spectra were collected using a 10 mm quartz spectrophotometer and spectrofluorometer cells, respectively. The emission spectra of all ILs were excited at 230 nm excitation wavelength with slit widths set for entrance and exit bandwidths of 3 and 6 nm on both excitation and emission monochromators, respectively. All fluorescence spectra were blank subtracted before proceeding in data analyses. For investigation of photostability of ILs, time-based fluorescence steady-state measurements were acquired with excitation and emission bandpass set at 15 and 5 nm, respectively, in order to induce the photobleaching. The fluence level of the excitation source was open for a period of 30 min. The excitation wavelength for all ILs was set at 230 nm, while the emission wavelength was set at 495 nm for N,N-EPANTf₂ and 370 nm for N-PhenacylPyrNTf₂.

Results and Discussion

Characterization of ILs

Final products obtained for both N,N-EPANTf₂ and N-PhenacylPyrNTf₂ were brown and yellow in color, respectively, and were all liquids at room temperature. However, N,N-EPANTf₂ was extremely more viscous liquid in comparison to N-PhenacylPyrNTf₂. Spectroscopic and physicochemical properties of newly synthesized ILs are recorded in Table 1. The ¹H NMR and FT-IR spectra of ILs were in good agreement with their chemical structure. In addition, synthesized ILs were found to be pure from data obtained by the elemental analysis.

N,N-EPANTf₂ The product of this ionic liquid resulted in brown color of 1.98 g (89.39 % yield) and was liquid at room temperature. ¹H NMR δ (ppm): 1.13 (t, 6H, 2CH₃), 3.27 (q, 4H, 2CH₂), 6.55 (d, 2H, ArH-1 and H-5), 7.21 (d, 2H, ArH-2 and H-4), 7.95 (s, 3H, NH₃). Molecular species were identified by their characteristic absorbance ν_{max} (cm⁻¹): 835, 917, 1015 (C–H); 1160, 1311 (NSO₂); 1195, 1425 (C–S); 1518, 1622 (C=C); 3217, 3317, 3382 (NH), as displayed in Fig. 1. Elemental Anal. Calcd. for C₁₂H₁₇N₃O₄S₂F₆: C (32.35); H (3.82); N (9.43). Found: C (32.12); H (3.46); N (9.20). TGA measurements of this ionic liquid gave a decomposition temperature (T_{dec}) of 290°C (Table 1).

Table 1 Spectroscopic and physicochemical properties of ILs. The symbols rt and T_{dec} represent room and decomposition temperatures, respectively

Parameters	N,N-EPANTf ₂	N-PhenacylPyrNTf ₂
Color	Brown	Yellow
State at rt	Liquid	Liquid
Yield (%)	89.39	94.13
T _{dec} (°C)	290.00	311.00
$\lambda_{max(abs)}$ (nm)	230.00	230.00
$\lambda_{max(em)}$ (nm)	495.00	370.00
$\Delta\bar{\nu}_{ss}$ (cm ⁻¹)	23276.24	16451.23
ϵ (Lmol ⁻¹ cm ⁻¹)	5839.07	6747.52
<i>f</i>	0.50	0.48
μ (Debye)	4.95	4.81
ϕ_F	0.10	0.12

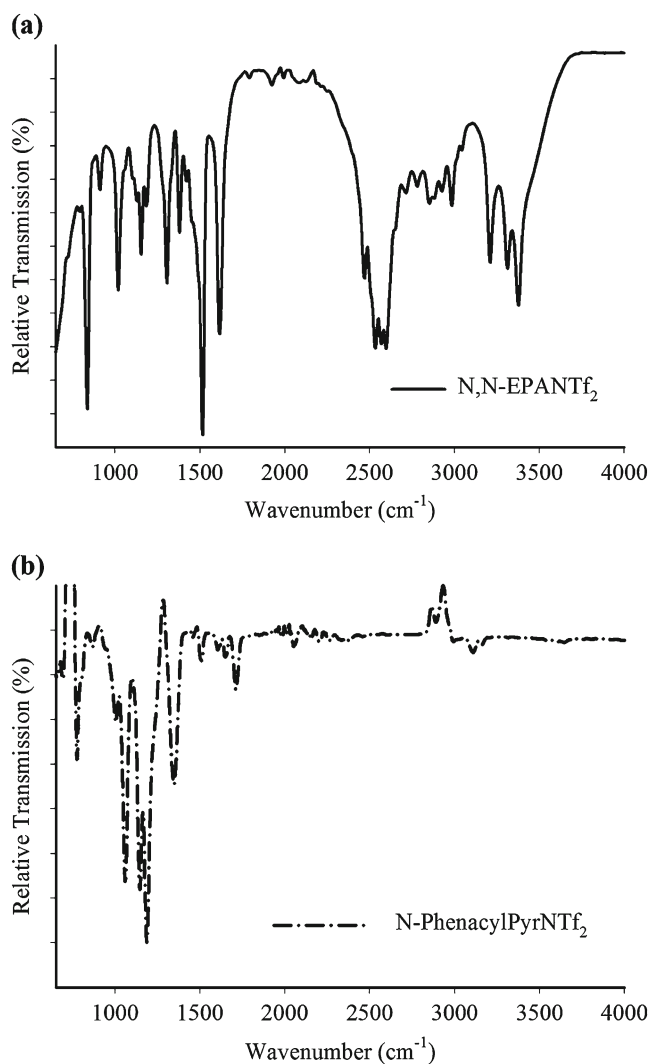


Fig. 1 FT-IR spectra of **a** N,N-EPANTf₂ and **b** N-PhenacylPyrNTf₂

N-PhenacylPyrNTf₂ This ionic liquid was yellow in color and liquid at room temperature, resulted in 1.62 g (94.13 % yield). ¹H NMR δ (ppm): 2.54 (s, 2H, CH₂CO), 7.33–7.87 (m, 5H, ArH), 8.5–9.3 (m, 5H, PyridiniumH). FT-IR characteristic absorbances ν_{max} (cm⁻¹): 772, 859, 999, 1051 (C–H); 1138, 1348 (NSO₂); 1182, 1496 (C–S); 1636 (C=C); 1705 (CO), as shown in Fig. 1. Elemental Anal. Calcd. for C₁₅H₁₂N₂O₅S₂F₆: C (37.65); H (2.51); N (5.86). Found: C (36.94); H (2.35); N (5.70). This compound was thermally stable up to 311°C (Table 1).

Spectroscopic Investigation of ILs

UV–vis and Fluorescence Spectroscopic Study

UV–vis absorption spectra of both N,N-EPANTf₂ and N-PhenacylPyrNTf₂ show two broad characteristic bands appeared at 230 and 280 nm for N,N-EPANTf₂ and at 230

and 270 nm for N-PhenacylPyrNTf₂ (Fig. 2). The optical behavior of newly prepared ILs not only displays that these ILs are good absorbent, but it also brings into light a very interesting fluorescence behavior. Generally, high background fluorescence was noticed in the emission spectra of ILs (Fig. 3). Fluorescence spectra of both N,N-EPANTf₂ and N-PhenacylPyrNTf₂ display two broad characteristic bands appeared at 400 and 495 nm for N,N-EPANTf₂ and at 370 and 450 nm for N-PhenacylPyrNTf₂. Results of UV–vis and fluorescence further supported the purity of ILs and were consistent with data of elemental analysis.

Determination of Fluorescence Quantum Yield

In order to evaluate the fluorescence efficiency of ILs, the fluorescence quantum yield (ϕ_F) of ILs was calculated using an optically diluted solution to avoid reabsorption effect

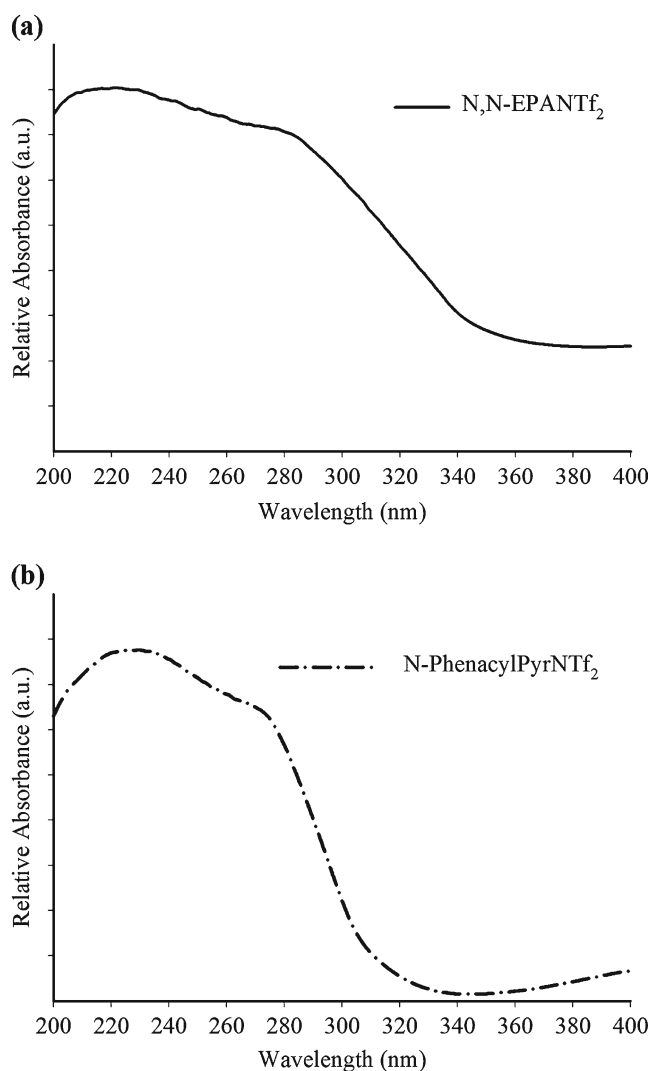


Fig. 2 UV–vis absorption spectra of 10 μM **a** N,N-EPANTf₂ and **b** N-PhenacylPyrNTf₂ in ethanol

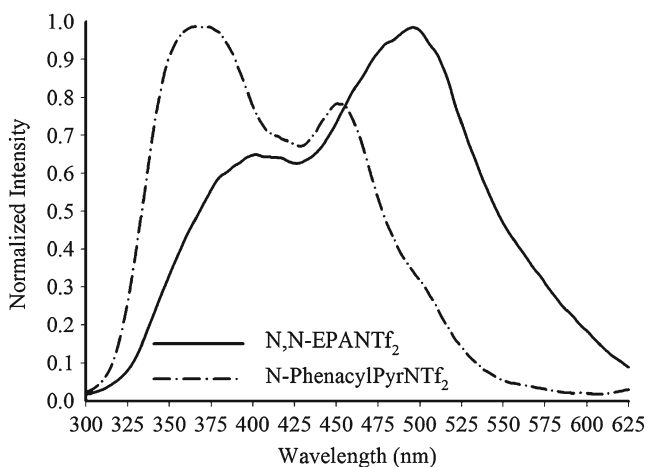


Fig. 3 Emission spectra of 10 μM N,N-EPANTf₂ and N-PhenacylPyrNTf₂ in ethanol, excited at 230 nm for both N,N-EPANTf₂ and N-PhenacylPyrNTf₂

(absorbance at excitation wavelength ≤ 0.1) [34]. L-tryptophan ($\phi_F=0.14$ in water) was chosen as a standard sample because L-tryptophan absorbs at 280 nm [37, 38], which is near the excitation wavelength of ILs. Thus, it is expected that the same number of photons are absorbed by both samples (L-tryptophan and ionic liquid). The fluorescence efficiency of ILs can be related to that of the standard by the following equation [39]:

$$\phi_{F(x)} = \left(\frac{A_s}{A_x}\right) \left(\frac{F_x}{F_s}\right) \left(\frac{n_x}{n_s}\right)^2 \phi_{F(s)}$$

where A corresponds to the absorbance at the excitation wavelength (expressed in number of absorbed photons), F is the area under the corrected emission curve (expressed in number of emitted photons) and n refers to the refractive index of solvents used. Subscripts s and x refer to the standard and unknown, respectively. Based on the above equation, fluorescence quantum yields of both N,N-EPANTf₂ and N-PhenacylPyrNTf₂ were determined to be 0.10 and 0.12 in ethanol (Table 1), respectively.

Determination of Oscillator Strength and Dipole Moment

Stokes shifts ($\Delta\bar{\nu}_{ss}$) of ILs were calculated, Table 1, using the following equation [40]:

$$\Delta\bar{\nu}_{ss} = \bar{\nu}_{em} - \bar{\nu}_{ex}$$

where $\bar{\nu}_{ex}$ and $\bar{\nu}_{em}$ are the wavenumbers of excitation and emission maxima in cm^{-1} , respectively. The oscillator strength represents the effective number of electrons transition from the ground to excited state and provides the absorption area in the electronic spectrum. The oscillator

strength, f , is obtained, Table 1, according to the following equation [41]:

$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu})d\bar{\nu}$$

where ϵ corresponds to the extinction coefficient measured in $\text{Lmol}^{-1}\text{cm}^{-1}$ and $\bar{\nu}$ refers to the numerical value of wave-number measured in cm^{-1} . The transition dipole moment (μ) from ground to excited state of ILs in Debye was calculated, Table 1, using the following equation [42]:

$$\mu^2 = \frac{f}{4.72 \times 10^{-7} \times \bar{\nu}}$$

Photostability Study

Time-based fluorescence measurements were implemented for evaluation of ILs photostability against photobleaching (Fig. 4). Both N,N-EPANTf₂ and N-PhenacylPyrNTf₂ were exposed to the greatest amount of radiation for 30 min, and time-based fluorescence measurements were performed on air-saturated samples in order to induce the photobleaching. The excitation and emission bandpass set was at 15 and 5 nm, respectively. Figure 4 clearly displays the behavior of these ILs in terms of their susceptibility to photobleaching over a 30 min time span. It can be observed that there is minimal to no loss in fluorescence intensities of ILs with an increase in the exposure time. The decrease in fluorescence intensities (% photobleaching) of ILs was calculated from the difference between the area under the emission peak of each ionic liquid before and after photobleaching (Fig. 5a, b and c). The calculated % photobleaching of N,N-EPANTf₂ and N-PhenacylPyrNTf₂ was determined to be 3.14 and 12.10 %, respectively, as can be depicted in Fig. 5c. Results

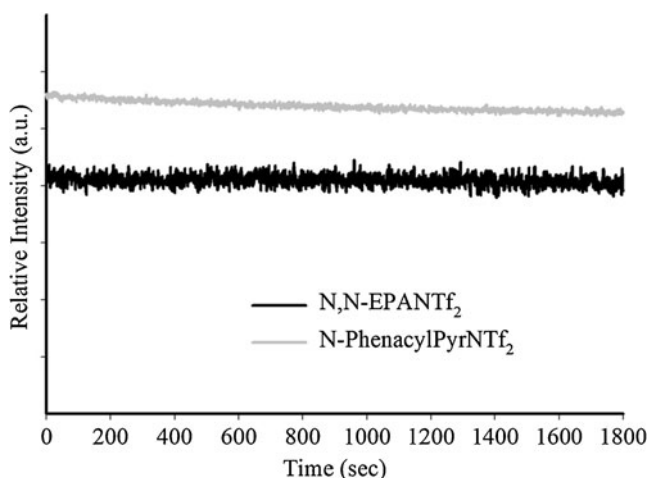


Fig. 4 Time-based fluorescence steady-state measurements of 10 μM N,N-EPANTf₂ and N-PhenacylPyrNTf₂ in ethanol, acquired with excitation and emission bandpass set at 15 and 5 nm, respectively

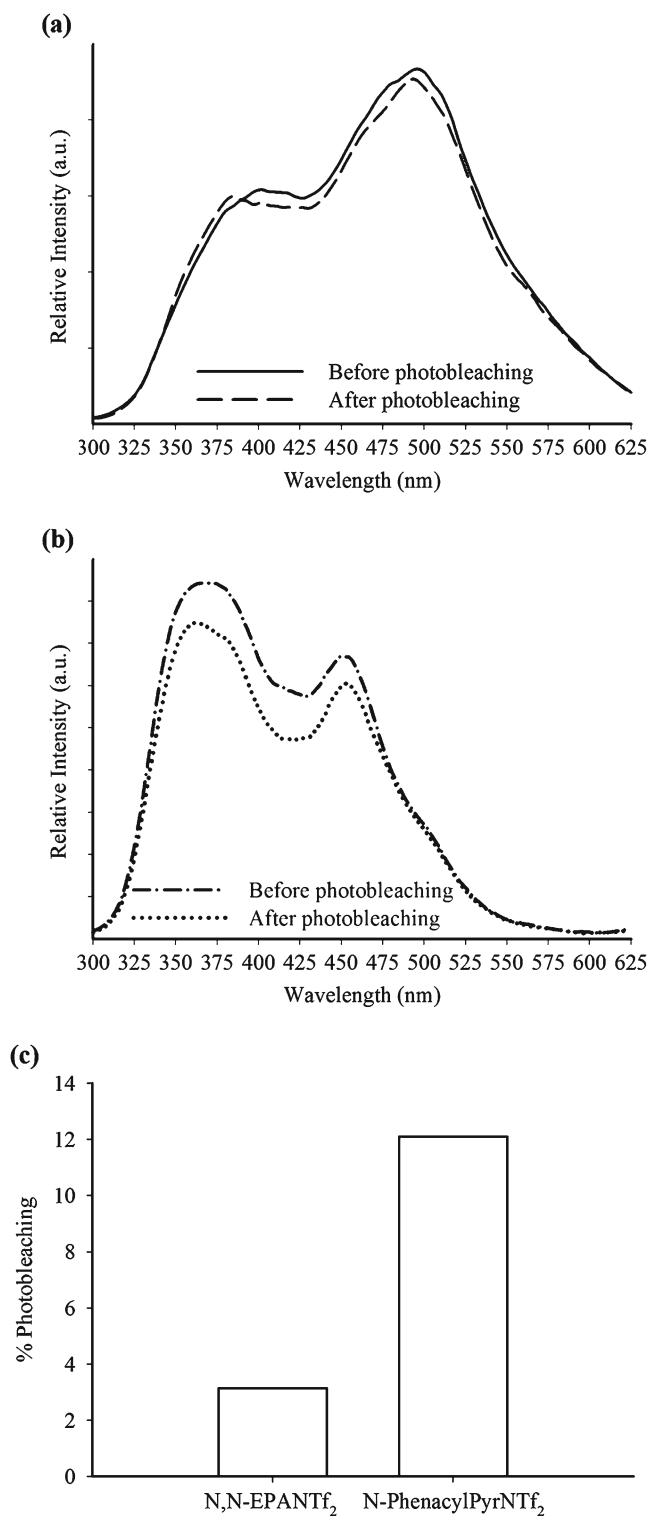


Fig. 5 Emission spectra of 10 μ M **a** N,N-EPANTf₂ and **b** N-PhenacylPyrNTf₂ in ethanol before and after photobleaching. **c** Calculated % photobleaching of ILs after exposure to the greatest amount of radiation for 30 min

of photostability study clearly indicated that N,N-EPANTf₂ was more photostable than N-PhenacylPyrNTf₂. In general,

information is so limited about the photostability relationship to the structure that the conclusion remains open.

Conclusion

In this study, new ILs were successfully prepared using a simple and straightforward route via metathesis reaction. Both N,N-EPANTf₂ and N-PhenacylPyrNTf₂ are liquids at room temperature and have high thermal stability, which can be used in gas chromatography or in high temperature reactions. In addition, resulted ILs were found to be good absorbent and fluorescent. Time-based fluorescence measurements demonstrated that new ILs have high photostability against photobleaching. These results illustrated the future potential of fluorescent ILs by, for example, fabrication of optoelectronic devices such as solar cells or organic light-emitting diodes (OLEDs). Alternatively, ILs may be used as solvents in organic reactions or liquids which dissolve naturally occurring macromolecules such as cellulose. Finally, the preparation and investigation of spectroscopic and physicochemical properties of these ILs may play an important role towards exploring their potential applications.

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