

Effects of Ionic Liquids on Fluorescence Characteristics of 17 α - and 17 β -estradiol

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Received: 12 April 2012 / Accepted: 24 August 2012 / Published online: 5 September 2012
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Abstract Herein, we report the effects of six different room temperature ionic liquids (RTILs) on fluorescence spectra of 17 α -estradiol (EE1) and 17 β -estradiol (E2). The selected RTILs belonged to the compound classes of 1-alkyl-3-methylimidazolium tetrafluoroborate ($[C_nMIM]BF_4$) and 1-alkyl-3-methylimidazolium hexafluorophosphate ($[C_nMIM]PF_6$). RTILs had a gradual quenching effect on fluorescence intensity (FI) of EE1 and E2, and the quenching process followed the well-known Stern-Volmer theory. The quenching mechanism of EE1 and E2 by RTILs was demonstrated to be dynamic quenching. Additionally, the overall quenching efficiency by $[C_nMIM]BF_4$ was higher than $[C_nMIM]PF_6$. The increased carbon chain length of RTILs did not lead to obvious differences in FI for EE1 and E2. The quenching efficiency showed irregular trend at three different temperatures (25, 35 and 45 °C). RTILs such as $[C_4MIM]PF_6$ had the different fluorescent effects on organic chemicals with different fluorophores. The enhancing effects of $[C_4MIM]PF_6$ were observed on strong fluorescence chemicals (dansyl chloride, rhodamine B, 1,10-phenanthroline, norfloxacin), while quenching effect on weak fluorescence chemicals (EE1 and E2). In theory, these results

provide a theoretical foundation for deep insight into their interaction mechanism between RTILs and estradiol.

Keywords Room temperature ionic liquids · Fluorescence intensity · 17 α -Estradiol · 17 β -Estradiol · Quenching mechanism

Introduction

Room temperature ionic liquids (RTILs) are organic salts that are liquid at ambient temperatures and possess an appreciable liquid range [1]. They have several attractive features, including low-melting temperature (below 373 K), negligible vapor pressure, excellent thermal stability, strong ability to dissolve many chemicals, high electrical conductivity, a wide electro-chemical window, and capacity for repetitive utilization [2]. These properties make RTILs important candidates for the “green chemistry” applications. To date, most research has been focused on different applications of RTILs [3–6]. In the instrumental analytical field, RTILs were used as mobile phase additives in capillary electrophoresis [7] and fluorescence analysis [8–12], and also as the stationary phase in gas chromatography [13]. Devi and coworkers found that the novel ionic liquid $[BMIM][BA]$ could significantly sensitize the fluorescence of Eu^{3+} and Tb^{3+} [14]. The fluorescence intensity (FI) of Eu^{3+} - $[BMIM][BA]/[BMIM][Tf_2N]$ systems was approximately 37,970 times higher than that of Eu^{3+} in aqueous solution. Wu and coworkers found that the ionic liquids, $[C_4MIM]BF_4$, $[C_4MIM]NO_3$, $[C_6MIM]Br$, $[C_4MIM]PF_6$, $[C_6MIM]PF_6$ and $[C_8MIM]PF_6$, could significantly enhance the FIs of four isoquinoline alkaloids [15]. Our previous

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investigation proved that [BMIM]PF₆ quenched the fluorescence of 17 β -estradiol, but enhanced the fluorescence sensitivity of its derivatives with dansyl chloride (DNSCl) [16]. These past studies have shown that RTILs can have varying effects on chemicals with the different fluorophores. Therefore, it is necessary to study the interaction between RTILs and organic chemicals, which can further the application of RTILs to replace traditional organic solvents.

As one of biologically most active steroids, estradiol has two types, 17 α -estradiol (EE1) and 17 β -estradiol (E2), with the α type having stronger biological activity. In recent years, estradiol has been shown to be an endocrine disrupting chemical due to its observed effects on the reproductive systems of fish [17], other wildlife and possibly even humans [18]. Estradiol can enter the human body through diet, inhalation and skin contact resulting in disturbance of

the reproductive system. The estradiol in the environment mainly comes from vertebrate excretion and synthetic hormone medication, and it enters into surface water and sediment through the sewage treatment system [19]. Many countries have set regulatory residue limits for estradiol and its derivatives. In 1991, the food safety administration in the USA set the maximum residue limit of estradiol palmitic acid in poultry edible parts at 2 μgkg^{-1} . In Korea, the highest residual limit of estradiol benzoate in beef was set at 0.12 μgkg^{-1} . Thus, it is necessary to develop a simple and quick and reliable method for the determination of estradiol in environmental matrices.

Fluorescence technique is often used for investigating the interaction mechanisms between RTILs and strongly fluorescent chemicals [20–22]. It was reported by Sarkar and coworkers that the photoinduced intermolecular electron

Fig. 1 The fluorescence spectra of EE1 in six different kinds of RTILs with different concentrations. The added concentrations of RTILs were 1 (0 mM), 2 (10 mM), 3 (30 mM), 4 (60 mM) and 5 (90 mM)

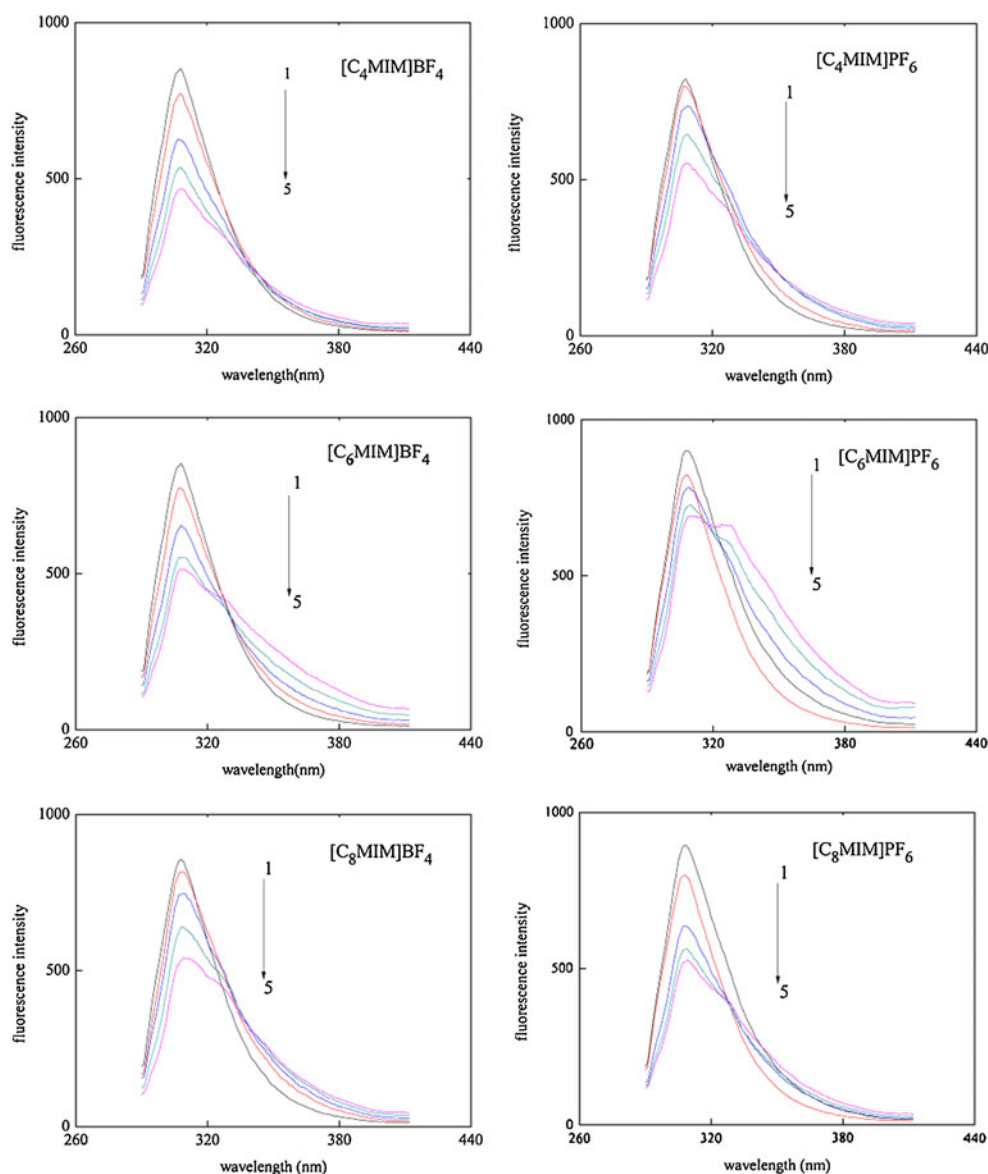
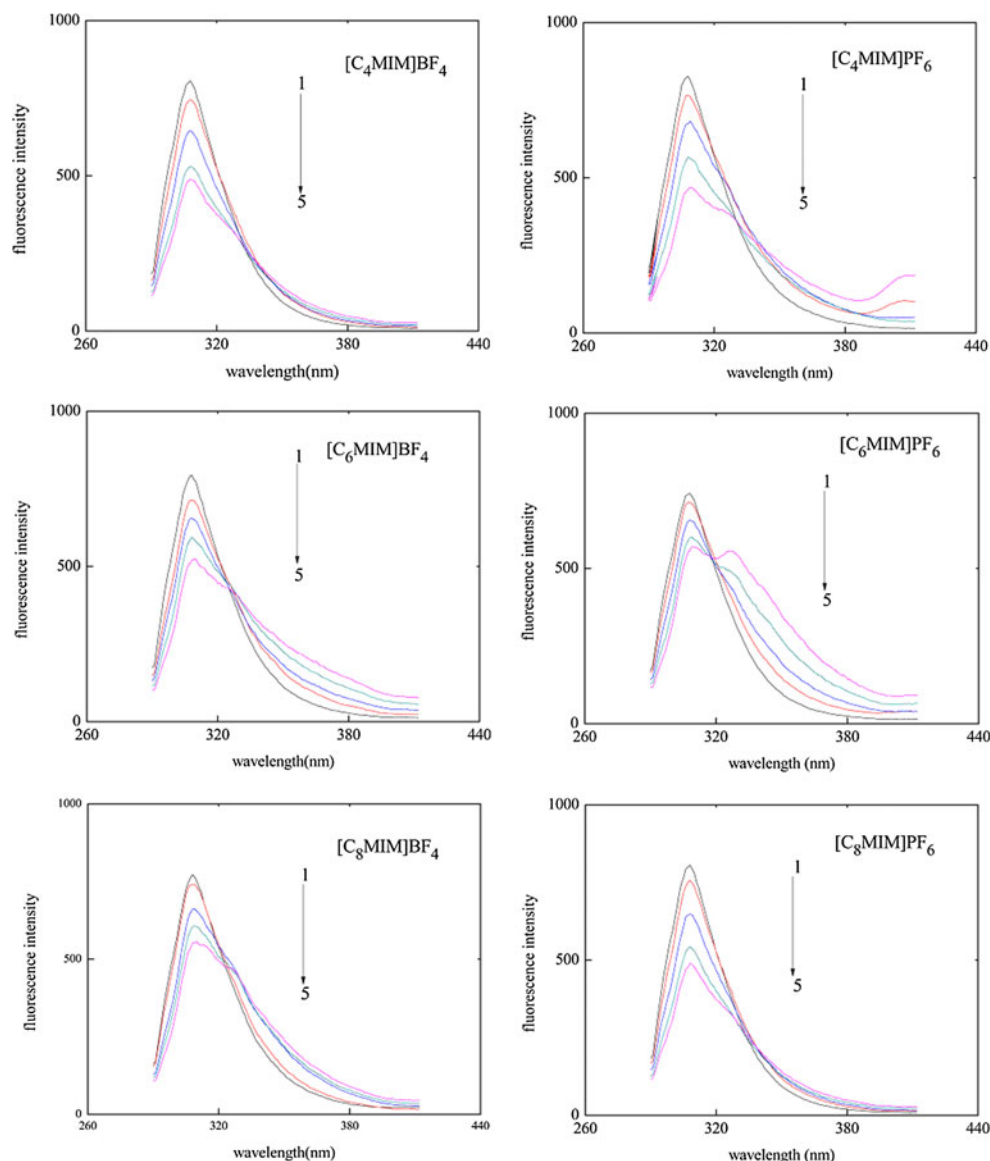


Fig. 2 The fluorescence spectra of E2 in six different kinds of RTILs with different concentrations. The added concentrations of RTILs were 1 (0 mM), 2 (10 mM), 3 (30 mM), 4 (60 mM) and 5 (90 mM)



transfer was enhanced from *N,N*-dimethylaniline to different Coumarin dyes in a neat RTIL, ([Emim][Tf₂N]) [23]. Geng and coworkers proved that [C₁₄mim]Br binds to bovine serum albumin through electrostatic attraction at low concentrations and through hydrophobic interaction at high concentrations [24]. The FIs of norfloxacin were decreased with increasing alkyl chain length on imidazolium ring of RTILs, and the main interaction between the ionic liquid [C_nmim]Br and norfloxacin was proved to be not by hydrogen bond [25]. Regretfully, so far very little data are available on interactions between RTILs and weakly fluorescent chemicals, which may hinder the most efficient utilization of these “green” solvents. Therefore, the aim of this study was to evaluate the effects of RTILs on fluorescent behavior of EE1 and E2 as weakly fluorescent chemicals, and to lay the foundation for deep insight into the interactions between RTILs and weakly fluorescent chemicals,

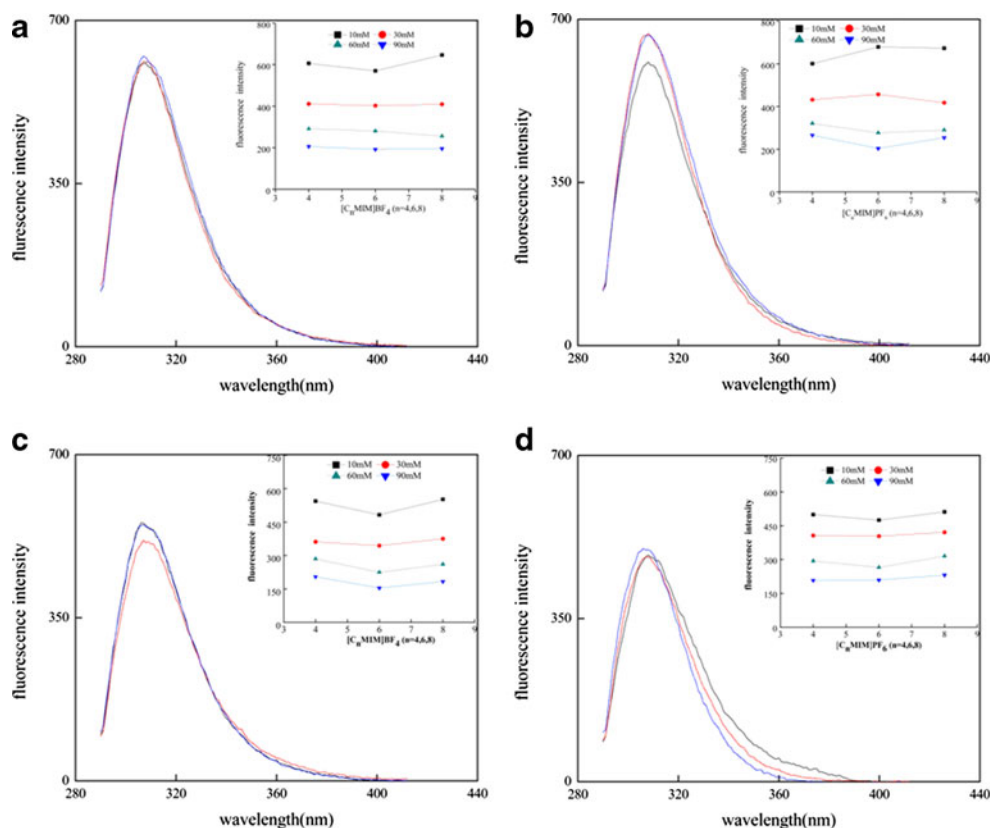
or for their application in analysis of weakly fluorescent chemicals. In this study, we chose six ionic liquids as the representative species of RTILs to analyze for their effects on the fluorescence spectra and FIs of EE1 and E2.

Material and Methods

Chemicals and Reagents

Reference compounds of 17 α -estradiol (EE1) and 17 β -estradiol (E2) were purchased from Sigma-Aldrich (St. Louis, MO, USA). RTILs with stated purities of 99.0 % were obtained from Shanghai Chengjie Chemical Co., Ltd. (Shanghai, China). The six RTILs were 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄MIM]BF₄), 1-hexyl-3-methylimidazolium

Fig. 3 Fluorescence emission spectra and FI (*inset*) of EE1 (a,b) and E2 (c,d) in RTILs with different carbon chain length. (a,c) in $[C_n\text{MIM}]\text{BF}_4$, (b,d) in $[C_n\text{MIM}]\text{PF}_6$



tetrafluoroborate ($[C_6\text{MIM}]\text{BF}_4$), 1-octyl-3-methylimidazolium tetrafluoroborate ($[C_8\text{MIM}]\text{BF}_4$), 1-butyl-3-methylimidazolium hexafluorophosphate ($[C_4\text{MIM}]\text{PF}_6$), 1-hexyl-3-methylimidazolium hexafluorophosphate ($[C_6\text{MIM}]\text{PF}_6$) and 1-octyl-3-methylimidazolium hexafluorophosphate ($[C_8\text{MIM}]\text{PF}_6$). These six standard compounds were used as received. Methanol used in this study was LC-grade and purchased from Jinshan Reagent Corporation, Wenzhou, China.

Fluorescence Spectroscopy

Fluorescence spectra were recorded using a model RF-5301PC spectrofluorometer (Shimadzu Corporation, Tokyo, Japan) with a 150 W Xenon arc lamp as the excitation source and single-grating monochromators as wavelength selection devices with a slit width of 5 nm. The excitation

and emission wavelength for EE1 and E2 were 280 nm and 308 nm, respectively. The samples were excited at 280 nm and the emission spectra recorded from 290 to 412 nm. All fluorescence spectra were corrected for the solvent blank.

Fluorescence Quenching Measurements

A stock solution ($100 \text{ mg}\cdot\text{L}^{-1}$) was prepared by dissolving 5 mg of EE1 or E2 in 50 mL methanol and stored at 4°C before use. Working solutions were obtained by appropriate dilution of the stock solution with ionic liquids or methanol. The final concentrations of all ionic liquids were 0, 10, 30, 60 and 90 mM, and the tested concentration of estradiol was $0.5 \text{ mg}\cdot\text{L}^{-1}$. Two milliliters of the test solution were added to 1 cm^2 quartz cuvettes for fluorescence determination at 25, 35 and 45°C .

Table 1 FI of EE1 ($0.5 \text{ mg}\cdot\text{L}^{-1}$) for RTILs with different anions

C_{RTILs} ($\text{mmol}\cdot\text{L}^{-1}$)	$[C_4\text{MIM}]\text{BF}_4$	$[C_4\text{MIM}]\text{PF}_6$	$[C_6\text{MIM}]\text{BF}_4$	$[C_6\text{MIM}]\text{PF}_6$	$[C_8\text{MIM}]\text{BF}_4$	$[C_8\text{MIM}]\text{PF}_6$
10	605.9	600.5	570.4	679.3	646.0	672.8
30	411.5	431.9	402.3	457.1	409.3	417.4
60	290.6	320.7	280.5	276.8	255.4	289.5
90	205.7	265.2	192.0	203.9	195.9	253.9

Table 2 FI of E2 (0.5 mg·L⁻¹) for RTILs with different anions

C _{RTILs} (mmol·L ⁻¹)	[C ₄ MIM]BF ₄	[C ₄ MIM]PF ₆	[C ₆ MIM]BF ₄	[C ₆ MIM]PF ₆	[C ₈ MIM]BF ₄	[C ₈ MIM]PF ₆
10	544.7	499.8	483.1	475.1	552.1	510.9
30	361.6	407.1	344.4	403.8	375.1	421.2
60	284.9	293.8	225.3	265.6	260.7	315.5
90	204.7	208.1	154.3	209.5	182.9	231.4

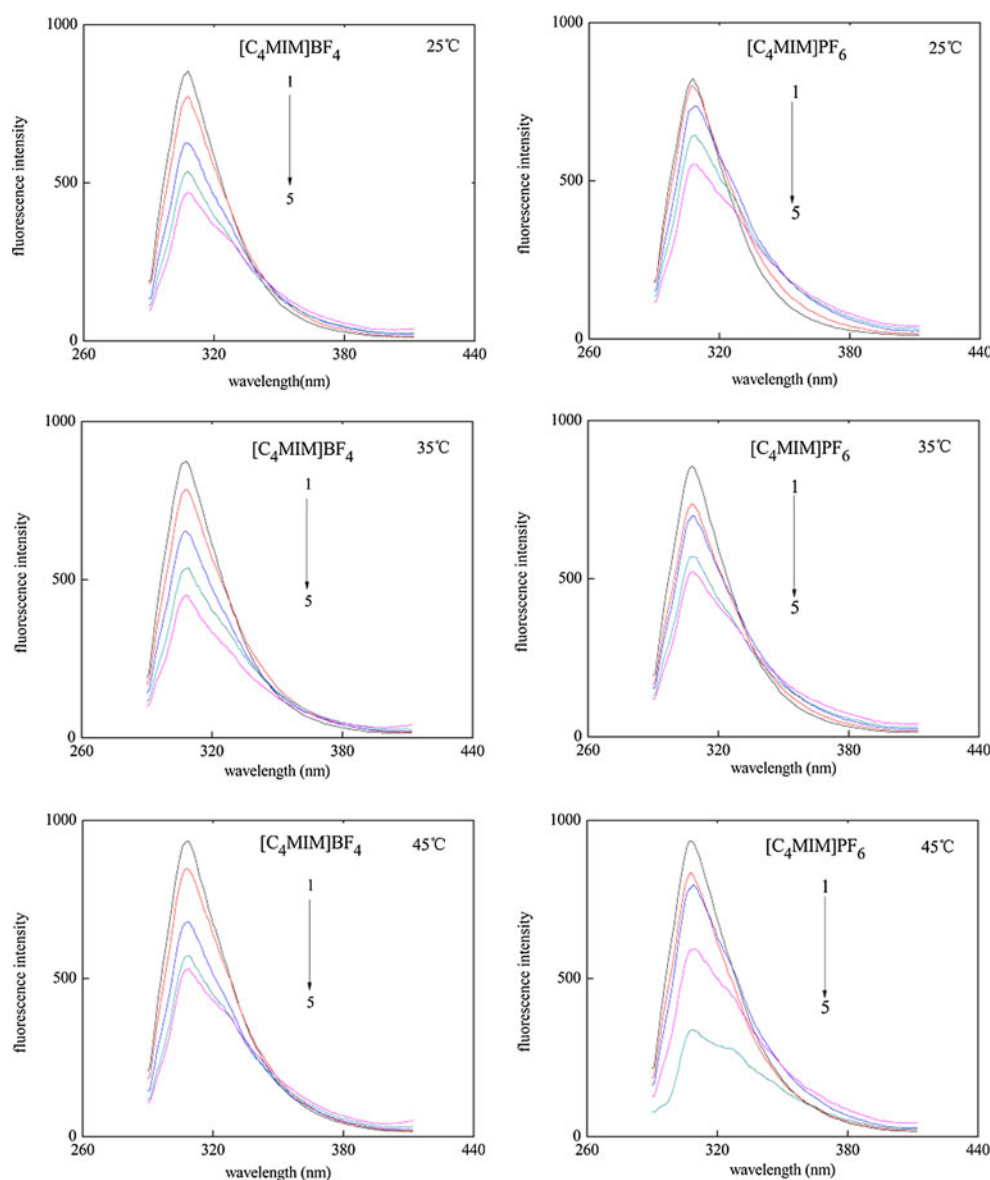
Results and Discussion

Effects of RTILs on Fluorescence Behavior of EE1 and E2

The different concentrations of RTILs in solvents resulted in a complex interplay with EE1 or E2 due to their physicochemical properties (e.g. viscosity, static dielectric constant, refractive index, density and polarizability), which affects their steady-

state emission behavior. At ambient conditions, ionic liquids were much more viscous than the organic solvents such as methanol. The viscosity of methanol was 0.58 mPas at 20 °C, while the viscosity of [C₄MIM]PF₆ and [C₄MIM]BF₄ was reported to be 430 mPas and 154 mPas, respectively, at the same temperature. Also for the same type of ionic liquid, the viscosity increased with increasing substituent atomic number [26]. Considering the vast differences between the

Fig. 4 The fluorescence spectra of EE1 in six different kinds of RTILs at different temperatures. The added concentrations of RTILs were 1 (0 mM), 2 (10 mM), 3 (30 mM), 4 (60 mM) and 5 (90 mM)



viscosity values of RTILs and of the common organic solvents, a series of RTIL concentrations (10, 30, 60 and 90 mM) were prepared in methanol. As shown in the Figs. 1 and 2, the FIs of EE1 and E2 decreased gradually with increasing RTILs concentrations from 0 to 90 mM. Therefore, the six RTILs had a significant quenching effect on the fluorescence of EE1 and E2. In addition, no obvious hypsochromic or bathochromic phenomenon of the emission maxima was observed in the quenching processes.

Effects of RTIL Structures on FIs of EE1 and E2

Effects of Cation

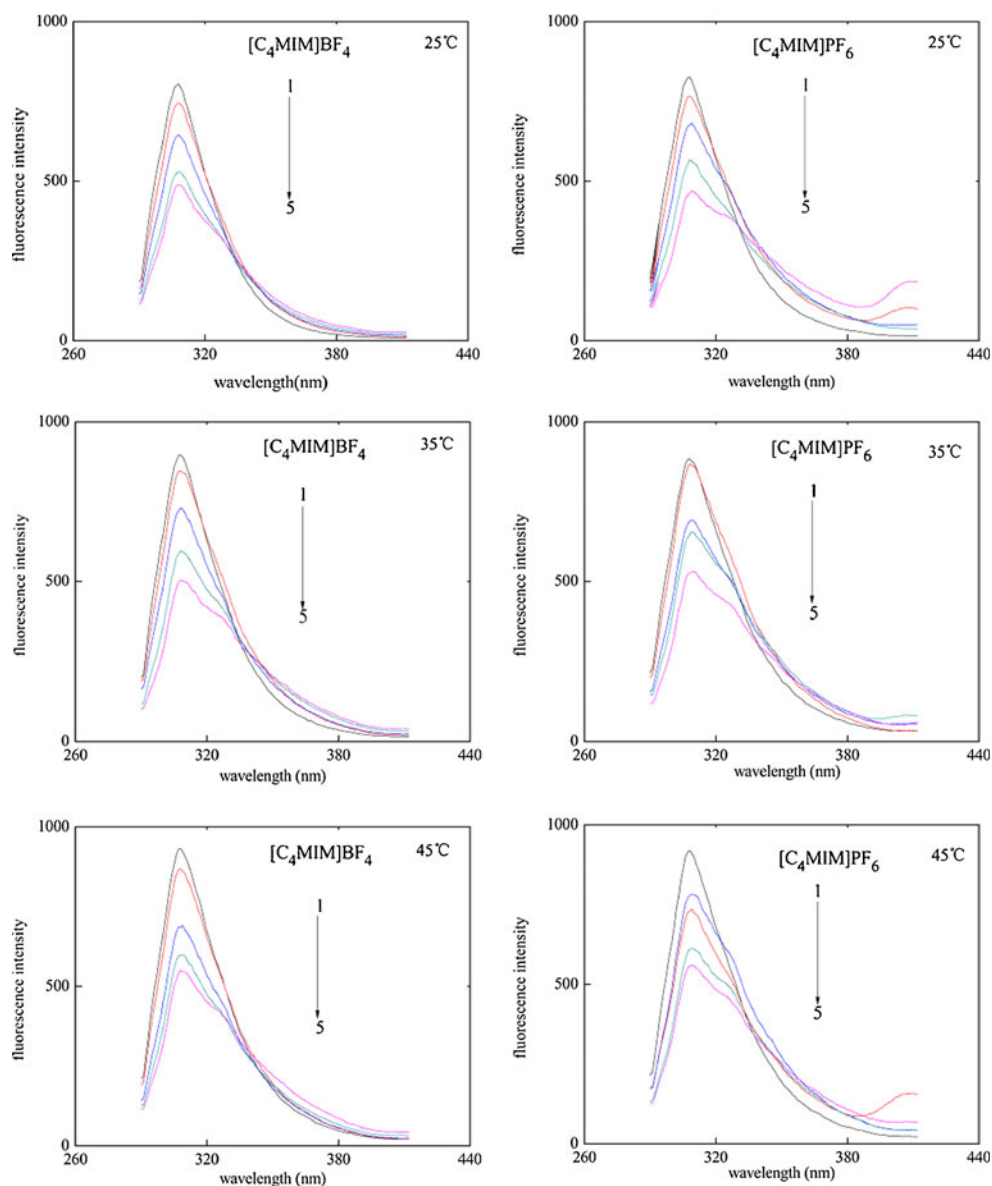
The effects of different RTIL cations on FIs of EE1 and E2 were investigated and are shown in Fig. 3. The viscosity

increases with increasing alkyl chain length on the imidazolium ring when RTILs contain the same anion [26]. In theory, FIs of EE1 and E2 should follow the order: $[C_4MIM]^+ < [C_6MIM]^+ < [C_8MIM]^+$. However in this investigation, no consistent trend or obvious differences for FIs of EE1 and E2 (0.5 mgL^{-1}) were observed with the increase in the carbon chain length on the imidazolium ring. These results might be due to solvent physicochemical property differences between RTILs and estradiol, such as electrostatic dielectric constant, refractive index, density and polarization.

Effect of Anion

It is important to note that the fluorescence enhancement or quenching effect depends on the type and concentration of fluorescent substances and features of the ionic liquids. FIs of

Fig. 5 The fluorescence spectra of E2 in six different kinds of RTILs at different temperatures. The added concentrations of RTILs were 1 (0 mM), 2 (10 mM), 3 (30 mM), 4 (60 mM) and 5 (90 mM)

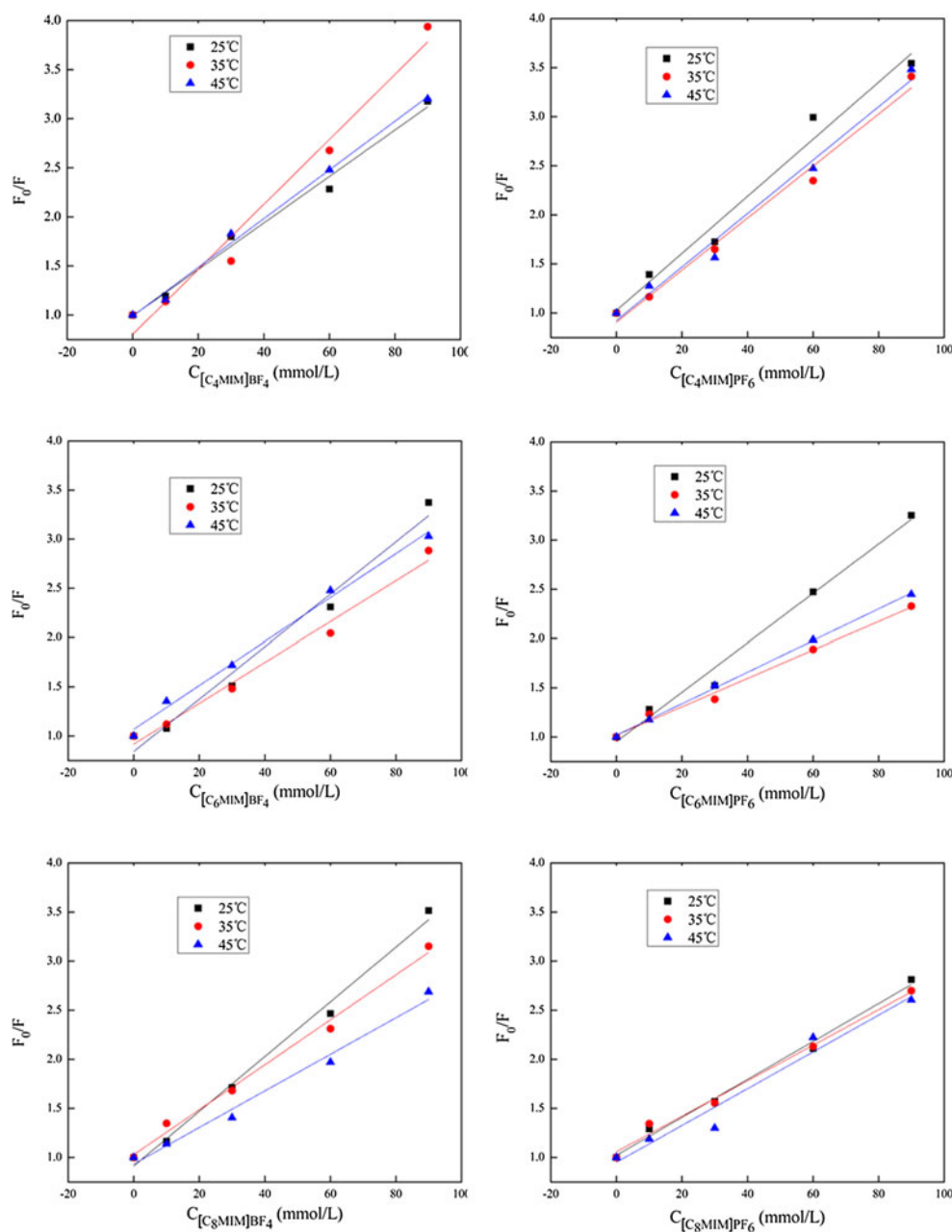


EE1 and E2 with respect to RTILs with different anions are shown in Tables 1 and 2. All RTILs showed quenching effects on FIs of EE1 with lower fluorescence intensities for $[C_nMIM]BF_4$ compared to $[C_nMIM]PF_6$ (Table 1). Similar results were observed for E2 (Table 2). Generally, the higher the symmetry of the anion, the higher the viscosity of RTILs [27]. The PF_6^- anion with an octahedral structure is better dispersed around the ions to provide more solvent action. This higher symmetry of negative charge provides better dispersion, which leads to the increase of viscosity. Thus, the viscosity of $[C_nMIM]PF_6$ was greater than that of $[C_nMIM]BF_4$ because of the stronger Coulomb force [28].

Effect of Temperature on the Fluorescence Intensity of EE1 and E2

Temperature had a significant influence on the FIs of EE1 and E2 solutions. Generally, FI would decrease with increasing temperature because of molecular internal energy conversion [29]. In order to investigate the effects of different temperature on the FIs of EE1 and E2 in the absence and presence of RTILs, we conducted a series of experiments at three different temperatures (25, 35 and 45 °C). As shown in Figs. 4 and 5, FIs of EE1 and E2 decreased with the increasing concentrations of RTILs within the investigated temperature range. No

Fig. 6 The Stern-Volmer plot for the binding of ionic liquid to EE1 at different temperatures



significant hypsochromic or bathochromic shift of the emission maxima was observed with increasing of temperature. Finally, there was a weak trend of FI increasing for EE1 and E2 in the absence of RTILs with the increase in temperature. This might be an inverse process of $T_1 \sim S_1$ due to the thermal excitations, leading to the occurrence of fluorescent hysteresis.

Fluorescence Quenching Mechanism

Fluorescence quenching is an important technique used to obtain adequate information about the structure and dynamics of fluorescent molecules. Fluorescence intensity of the solute can be decreased by variety of molecular interactions including

excited state reactions, molecular rearrangements, energy transfer, ground-state complex formation, collisional quenching and so on [30]. The FI of estradiol decreased because of molecular interaction with RTILs, and thus RTILs act as a fluorescence quencher. There exist two kinds of fluorescence quenching, i.e., static and dynamic quenching. Static quenching refers to formation of a ground state fluorophore-quencher complex which does not emit a photon. Dynamic quenching refers to formation of an excited state fluorophore-quencher complex [24]. Fluorescence quenching is generally described by the Stern-Volmer equation:

$$F_0/F = 1 + K_q\tau_0[Q] = 1 + K_{sv}[Q]$$

Fig. 7 The Stern-Volmer plot for the binding of ionic liquid to E2 at different temperatures

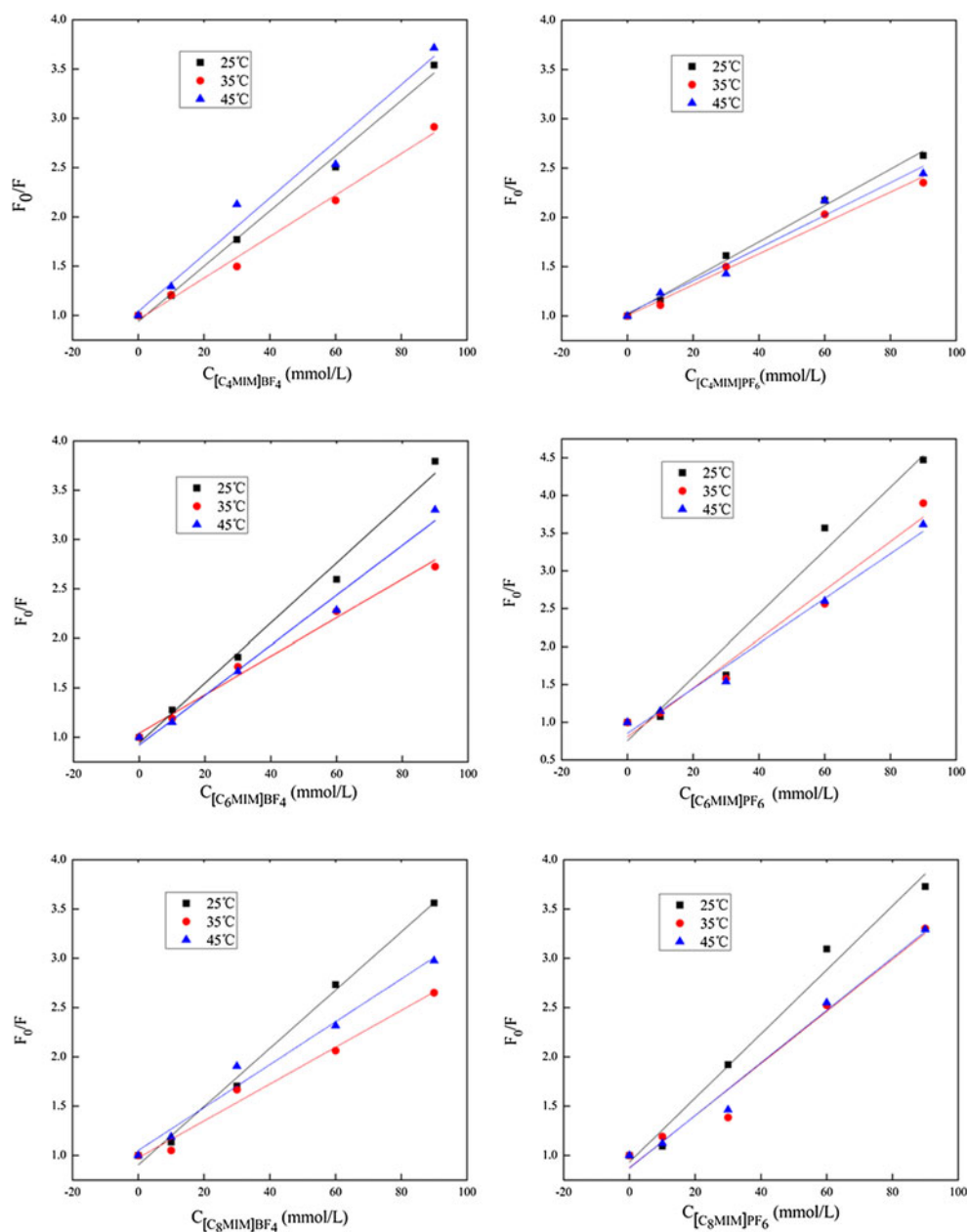


Table 3 The Stern-Volmer equation of EE1 at different temperatures

RTILs	T/°C	Stern-Volmer equation	R ²	K _{sv} /(×10 ⁴ L·mol ⁻¹)
[C ₄ MIM]BF ₄	25	y=0.0237x+0.9921	0.9902	0.0237
	35	y=0.0331x+0.803	0.9779	0.0331
	45	y=0.0248x+0.9893	0.9951	0.0248
[C ₆ MIM]BF ₄	25	y=0.0266x+0.8423	0.9805	0.0266
	35	y=0.0207x+0.9179	0.9858	0.0207
	45	y=0.0223x+1.0684	0.9941	0.0223
[C ₈ MIM]BF ₄	25	y=0.0279x+0.9132	0.9925	0.0279
	35	y=0.0229x+1.0283	0.9923	0.0229
	45	y=0.0186x+0.9332	0.9871	0.0186
[C ₄ MIM]PF ₆	25	y=0.0291x+1.0265	0.9799	0.0291
	35	y=0.0265x+0.9077	0.9878	0.0265
	45	y=0.0272x+0.9245	0.985	0.0272
[C ₆ MIM]PF ₆	25	y=0.0251x+0.9538	0.9877	0.0251
	35	y=0.0144x+1.0202	0.9912	0.0144
	45	y=0.016x+1.0186	0.9991	0.016
[C ₈ MIM]PF ₆	25	y=0.0193x+1.0224	0.9928	0.0193
	35	y=0.0181x+1.0579	0.9906	0.0181
	45	y=0.0187x+0.9513	0.9631	0.0187

where F₀ and F are the fluorescence intensities of the fluorophore in the absence and presence of quenchers, respectively; K_{sv} and K_q are the Stern-Volmer quenching constant and the bimolecular quenching constant, respectively; τ₀ is the lifetime of the fluorophore in the absence of a quencher, and [Q] is the quencher concentration. Plots of F₀/F versus concentrations of

RTILs at three temperatures are shown in Figs. 6 and 7. The strong linear correlation coefficient (R²>0.96) and the quenching constant (K_{sv}) are shown in Tables 3 and 4. As reported by Geng et al. [24], the Stern-Volmer quenching constant for dynamic quenching was less than 1.0×10³L·mol⁻¹. Therefore, it could be inferred that fluorescence quenching of EE1 and E2

Table 4 The Stern-Volmer equation of E2 at different temperatures

RTILs	T/°C	Stern-Volmer equation	R ²	K _{sv} /(×10 ⁴ L·mol ⁻¹)
[C ₄ MIM]BF ₄	25	y=0.028x+0.9399	0.9946	0.028
	35	y=0.021x+0.9583	0.9925	0.021
	45	y=0.0288x+1.0407	0.9753	0.0288
[C ₆ MIM]BF ₄	25	y=0.0303x+0.9434	0.9905	0.0303
	35	y=0.0195x+1.0418	0.9903	0.0195
	45	y=0.0252x+0.9222	0.9882	0.0252
[C ₈ MIM]BF ₄	25	y=0.0296x+0.9039	0.995	0.0296
	35	y=0.0187x+0.9766	0.984	0.0187
	45	y=0.0218x+1.0508	0.9801	0.0218
[C ₄ MIM]PF ₆	25	y=0.0184x+1.0141	0.9954	0.0184
	35	y=0.0157x+1.0036	0.9893	0.0157
	45	y=0.0166x+1.0245	0.9745	0.0166
[C ₆ MIM]PF ₆	25	y=0.0419x+0.7544	0.9687	0.0419
	35	y=0.0323x+0.8053	0.9755	0.0323
	45	y=0.0297x+0.8533	0.9852	0.0297
[C ₈ MIM]PF ₆	25	y=0.0325x+0.9334	0.9841	0.0325
	35	y=0.0264x+0.8764	0.9734	0.0264
	45	y=0.0267x+0.8723	0.9833	0.0267

by the six RTILs was a dynamic quenching mechanism. In addition, the quenching efficiency showed an irregularly trend at the three different temperatures.

The Different Effects of RTILs on Chemicals with Different Fluorophores

In this investigation, the six RTILs all showed significantly quenching effects on EE1 and E2, with weak fluorescence. In order to compare the different effects of ionic liquids on organic chemicals with different fluorophores, we studied characteristics of strong fluorescent chemicals in RTILs. Under the conditions of the maximum emission wavelength of 412 nm, FI of norfloxacin (NFLX) increased approximately by 12.0–19.0-fold in $[C_nMIM]BF_4$ /methanol and 1.5–17.0-fold in $[C_nMIM]PF_6$ /methanol solutions (Fig. 8a), when compared to that of NFLX in methanol [25]. Also, RTILs had a significant enhancement effects on FIs of DNSCI over those in water. At 5-mgL^{-1} , $[C_4MIM]PF_6$, $[C_6MIM]PF_6$ and $[C_8MIM]PF_6$ increased approximately 8.5, 7.6 and 6.1 times, respectively, FI of DNSCI in water. Similarly, at 50 mgL^{-1} , three kinds of ionic liquids increased 7.9, 7.6 and 7.0 times FI of DNSCI in comparison with that in water (Fig. 8b). The fluorescence enhancement or quenching was dependent on the types and concentrations of fluorescent substances and the features of

RTILs. The increase in quantum yields of rhodamine B, pyronine B, and 1,10-phenanthroline in the presence of $[C_4MIM]PF_6$ demonstrated fluorescent enhancement of ionic liquids. Especially, the most significantly sensitizing effects on fluorescent chemicals were observed in micelles of $[C_4MIM]PF_6$ with an obviously hypsochromic shift [8]. The above results demonstrated that RTILs such as $[C_4MIM]PF_6$ possibly had the different effects on strong or weak fluorescence chemicals, namely, enhancing effect for strong fluorescence chemicals (DNSCI, rhodamine B, 1,10-phenanthroline, NFLX), while quenching effect for weak fluorescence chemicals (EE1 and E2) [8, 16, 25]. The former phenomenon was in agreement with Fletcher's observations, who reported that the emission from alternant PAHs was quenched while that from nonalternant PAHs was not [9]. However, further research is required to understand the mechanism on the previous phenomenon.

Conclusions

In this study, we analyzed in detail the effects of six RTILs on fluorescence characteristics of EE1 and E2. The main conclusions are summarized as follows: (i) FIs of EE1 and E2 were decreased with increasing concentration of RTILs; (ii) The quenching efficiency on EE1 and E2 by RTILs was $[C_nMIM]BF_4 > [C_nMIM]PF_6$ and showed an irregular trend with the increase of the carbon chain length on the imidazolium ring; (iii) The quenching mechanism by the six RTILs was dynamic quenching and (iv) The different temperatures ($25\text{--}45\text{ }^\circ\text{C}$) led to an irregularly varying trends for EE1 and E2. $[C_4MIM]PF_6$ had the different fluorescent effects on organic chemicals with different fluorophores, namely, enhancing effect for strong fluorescence chemicals (DNSCI, rhodamine B, phenanthroline, norfloxacin), while quenching effect for weak fluorescence chemicals (EE1 and E2).

Acknowledgements This work was jointly funded by National Natural Science Foundation of China (21077079), International Cooperation Project of Wenzhou City (H20100053, H20100054) and Public Benefit Project of Zhejiang Province (2011C23114, 2011C37006, 2011B25).

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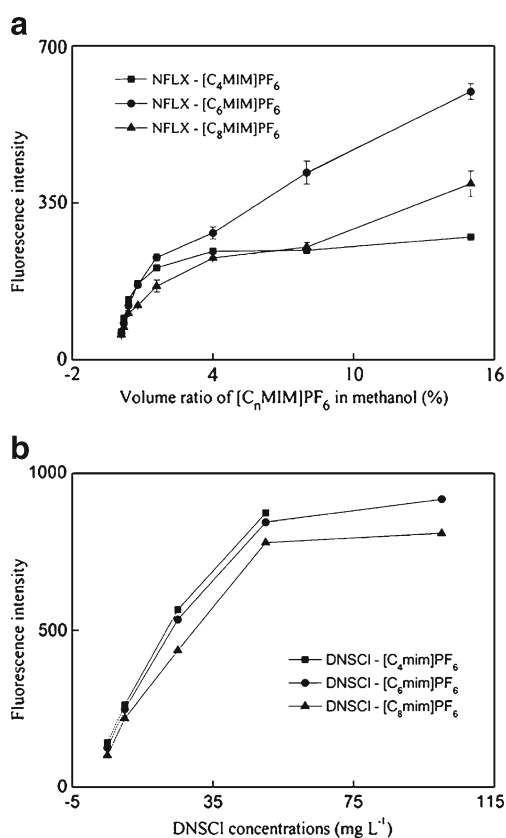


Fig. 8 The effects of $[C_nMIM]PF_6$ on FIs of NFLX and DNSCI

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