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Fluorescent quinolizinium ionic liquids (salts) with unexpectedly high quantum yields up to >99%†

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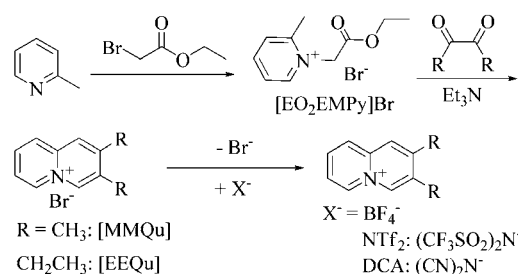
Quinolizinium ionic liquids (salts) featuring an unbranched cation core have been prepared, characterized and found to show extremely high fluorescence quantum yields in solution ($\Phi_f > 99\%$, λ_{em} near 334 nm) and bright cyan fluorescence in molten state (λ_{em} near 465 nm).

Recently, functional materials designed from ionic liquids, which are a class of neoteric solvents composed entirely of ions, are receiving increasing interest, since ionic liquids can be custom-tailored to satisfy the functional requirements for building organic materials by changing either the cation or anion species.¹ Up to now, functionalized ionic liquids have achieved great success in acting as luminescent materials,^{2–4} magnetic fluids,⁵ liquid crystals,⁶ photochromic switches⁷ and many more. The recently reported luminescent ionic liquids could be classified into three structurally distinct types, *i.e.*, protonated polyamidoamine dendrimers,² polycyclic aromatic benzobis(imidazolium),³ and transition metal-containing anions.⁴ The benzobis(imidazolium)-based ionic liquids characteristically exhibit strong fluorescence with quantum yields up to 91% in methanol.³ In many fields, the required quantum yields of fluorescent materials should be as high as possible. In neat ionic liquids, the associated species that are energetically different show excitation wavelength-dependent fluorescence.⁸ Our recent studies show that the fluorescence of the neat ionic liquids can be dramatically enhanced when confined into mesoporous silica gel.⁹

Although a number of cation species of ionic liquids have been developed and studied, all of them are limited to have a common structure with at least one side chain (or proton) in their cation cores, such as dialkylimidazolium. The cationic side chains can be removed by nucleophilic substitution with anions under heating and lead to low thermal stability.¹⁰ So, one possible way to develop novel ionic liquids is to find a substitute for the branched cation cores. The quinolizinium ion, structurally derived from naphthalene, is characterized by a bridgehead quaternary nitrogen atom in the fused

position. Unlike (iso)quinolinium, the quinolizinium ion is symmetric and the π -electron densities are equally distributed over both rings.¹¹ The annelated quinolizinium derivatives have been used as important DNA intercalators.¹² It is of further interest to note that the quinolizinium ion provides a structural motif for designing a new type of ionic liquid with an unbranched cation core.

In this paper, two small-molecule quinolizinium ions were found suitable for making ionic liquids, by incorporating weakly interacting anions (NTf_2 , BF_4 and DCA). Scheme 1 shows the synthesis route of the quinolizinium ionic liquids. First of all, $[\text{EO}_2\text{EMPy}]\text{Br}$ was prepared *via* a quaternization reaction between a methylpyridine and $\text{BrCH}_2\text{COOC}_2\text{H}_5$ in ethanol at 60 °C for 5 h and 80 °C for 15 h. The bromide salt precursors were then synthesized through a Westphal reaction, modified from a previously reported solid-phase procedure.¹³ For example, the mixture of 3,4-hexanedione and 1 equiv. of triethylamine was added dropwise into a THF solution of 1.2 equiv. of $[\text{EO}_2\text{EMPy}]\text{Br}$ under reflux and mechanical stirring. After further stirring for 3 h, a white solid of $[\text{EEQu}]\text{Br}$ was obtained by filtration and recrystallization from methanol by addition of diethyl ether. Finally, an anion metathesis reaction from a bromide ion to NTf_2 (LiNTf_2), BF_4 (NaBF_4) or DCA (AgDCA) in water, afforded the desired ionic liquids or low melting salts. The structures and compositions of the newly prepared compounds were confirmed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FT-IR, electrospray ionization mass spectrometry (ESI-MS, positive ion mode), Br ion-selective electrode and moisture meter. In addition to measuring some basic physicochemical properties such as melting point, thermal stability, density, viscosity and conductivity of these quinolizinium salts, their unexpected and rather interesting fluorescence characteristics were particularly emphasized, *i.e.* high quantum yields up to >99% in solution with λ_{em}



Scheme 1 Synthesis of quinolizinium ionic liquids (salts).

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around 334 nm and bright cyan fluorescence in molten state with λ_{em} around 465 nm.

Prior to property testing, each salt would be dried at 80 °C and 10^{-2} – 10^{-3} mbar for 20 h, and the water content in these salts could be reduced to 35–302 ppm (see Table S1 in ESI†). The water content was determined by means of Karl-Fischer titration on a Metrohm 831 KF Coulometer. The bromide ion concentration in Br-free salts was estimated to be less than 0.15 wt%, by using a Br ion-selective electrode (DX280-Br, Mettler-Toledo) on a Mettler-Toledo SevenMulti meter. $^1\text{H-NMR}/^{13}\text{C-NMR}$ spectra (ppm, δ) were recorded on a Varian Mercury Plus spectrometer (400 MHz). FT-IR spectra (cm^{-1}) were obtained in KBr discs on a Thermo Nicolet 5700 FT-IR spectrophotometer. ESI-MS spectra (positive ion mode, m/z) were determined in methanol solution on a Bruker Daltonics APEX II 47e FTMS. The melting point was determined on a differential scanning calorimeter model DSC822^c (Mettler-Toledo) with a rate of 10 °C min^{-1} under an N_2 atmosphere. The thermal decomposition temperature was measured on a Pyris Diamond Perkin-Elmer TG/DTA at a rate of 10 °C min^{-1} under an N_2 atmosphere. The density was determined using a 10 mL volumetric flask calibrated with water by mass method. The viscosity was determined on a Stabinger Viscometer SVM 3000/GR. The conductivity was measured on a Mettler-Toledo SevenMulti meter. The temperature for determining density, viscosity and conductivity was maintained to 60 ± 0.1 °C by means of an external temperature controller. The absorption spectra were determined using an Agilent 8453 diode array spectrophotometer with a deuterium lamp as the light source. The emission spectra were recorded on a Hitachi F-7000 FL spectrophotometer equipped with a Xe lamp. The integrating sphere (150 mm diameter, BaSO_4 coating, Edinburgh Instruments) measurements of quantum yields (absolute error < 2.5%) were conducted on an Edinburgh FSL920 spectrofluorimeter equipped with a Xe lamp (Xe900, 230–2000 nm), at an excitation wavelength of 315 nm. The emission lifetime was also determined on the FSL920 with a nanosecond hydrogen flash lamp (nF900, 110–850 nm) as an excitation source, and the lifetime measurements at the peak emission wavelength of (~ 334 nm) were performed at a pulse duration of 1.0 ns and a pulse repetition rate of 40 kHz.

Table 1 shows some basic properties of the quinolizinium salts. Differential scanning calorimetry (DSC) studies reveal that, as expected, replacing the Br anion with NTf_2 , BF_4 or DCA leads to a low melting point (T_m). In particular, three bromide-free salts melt below 100 °C, such as $[\text{MMQu}]\text{NTf}_2$: 60.5 °C, $[\text{EEQu}]\text{NTf}_2$: 50.4 °C and $[\text{EEQu}]\text{DCA}$: 67.9 °C, and thus fall into the ionic liquid class. Thermogravimetric analysis (TGA) shows good thermal stability of

the quinolizinium salts, with decomposition temperature (T_d) ranging from 265 to 408 °C. Interestingly, the quinolizinium bromides exhibit comparable thermal stability to their BF_4 -based counterparts (~ 350 °C), nevertheless, in traditional ionic liquids, the nucleophilic Br anion is much less thermally stable than BF_4 , e.g. $[\text{EMIm}]\text{Br}$ (311 °C) vs. $[\text{EMIm}]\text{BF}_4$ (450 °C).¹⁰ This finding should be attributed to the unbranched cation core in the quinolizinium ion, offering no side chain to react with anions. However, not all anions can take advantage of the quinolizinium ion's resistance to heating. For example, $[\text{EEQu}]\text{DCA}$ is thermally stable only up to 281 °C, in spite of 408 °C for $[\text{EEQu}]\text{NTf}_2$. Hence, the thermal decomposition of the quinolizinium salts depends on the nature of both the cation and anion. The two NTf_2 -based ionic liquids were determined to show moderate density, viscosity and conductivity, like $[\text{MMQu}]\text{NTf}_2$: 1.49 g mL^{-1} , 37.2 cP and 8.42 mS cm^{-1} at 60 °C.

Intense photoluminescence is the most attractive feature of the quinolizinium compounds. A preliminary study was carried out to investigate their UV-Vis absorption and fluorescence emission characteristics in solution. As shown in Fig. 1a, the absorption and emission spectra of $[\text{EEQu}]\text{NTf}_2$ in ethanol each consist of two vibrational bands, and are roughly in a mirror-image relation to each other. The fluorescence peak located at 334 nm (3.713 eV) is close to the corresponding absorption peak at 329 nm (3.769 eV), resulting in a small Stokes shift ($\Delta\nu$) of 445 cm^{-1} (0.056 eV). The small Stokes shift indicates that there is only small geometry modification between the ground state (S_0) and the first excited state (S_1).¹⁴

Table 2 summarizes the observed λ_{abs} and λ_{em} values, which suffer no significant impact from altering the alkyl chain length (methyl and ethyl), anion species (Br, NTf_2 , BF_4 and DCA) and solvent type (ethanol, CH_3CN and THF). In addition, the fluorescence decay of

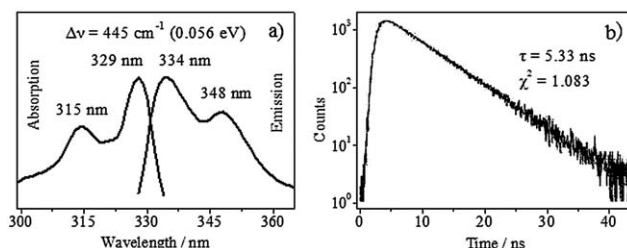


Fig. 1 The absorption and emission spectra (a) and fluorescence decay (b) of $[\text{EEQu}]\text{NTf}_2$ in 5×10^{-6} mol L^{-1} ethanol solution at ambient conditions. $\Delta\nu$ (cm^{-1}) = $10^7 \times (1/\lambda_{\text{abs}} - 1/\lambda_{\text{em}})$ is the Stokes shift, τ the lifetime, and χ^2 the linear fitting parameter.

Table 1 Some basic properties of quinolizinium salts

Salt	T_m^a (°C)	T_d^b (°C)	ρ^c (g mL^{-1})	η^d (cP)	κ^e (mS cm^{-1})
$[\text{MMQu}]\text{Br}$	237.1	346			
$[\text{MMQu}]\text{NTf}_2$	60.5	408	1.49	37.2	8.42
$[\text{MMQu}]\text{BF}_4$	186.4	347			
$[\text{MMQu}]\text{DCA}$	137.5	265			
$[\text{EEQu}]\text{Br}$	221.6	347			
$[\text{EEQu}]\text{NTf}_2$	50.4	405	1.44	49.3	4.70
$[\text{EEQu}]\text{BF}_4$	115.5	353			
$[\text{EEQu}]\text{DCA}$	67.9	281			

^a Melting point. ^b Decomposition temperature at 5% weight loss. ^c Density at 60 °C. ^d Viscosity at 60 °C. ^e Conductivity at 60 °C.

Table 2 Absorption and emission data of quinolizinium salts

Salt	Solvent	λ_{abs}^a (nm)	λ_{em}^a (nm)	τ^a (ns)	$\Phi_f^{a,b}$ (%)
[EEQu]NTf ₂	Ethanol	329	334	5.33	>99
[EEQu]BF ₄	Ethanol	329	334	5.38	>99
[EEQu]DCA	Ethanol	329	334	—	>99
[MMQu]NTf ₂	Ethanol	328	334	—	95
[MMQu]BF ₄	Ethanol	328	334	—	94
[MMQu]DCA	Ethanol	328	334	—	96
[EEQu]Br	Ethanol	329	334	—	89
[MMQu]Br	Ethanol	328	334	—	82
[EEQu]NTf ₂	CH ₃ CN	328	333	5.40	95
[EEQu]NTf ₂	THF	330	336	4.87	86

^a Measured in 5×10^{-6} mol L⁻¹ solutions at room conditions. ^b The absolute quantum yield measured by integrating sphere method.

[EEQu]NTf₂ in ethanol follows a single exponential function, with a typical fluorescence lifetime of 5.33 ns, as shown in Fig. 1b.

Moreover, the fluorescence intensity of the quinolizinium compounds is several times stronger than that of naphthalene ($\Phi_f = 20\%$)¹⁵ at the same condition (see Fig. S2 in ESI†). This finding prompted us to determine their absolute fluorescence quantum yields (Φ_f) using integrating sphere method. To our surprise, the Φ_f values of the only bicyclic naphthalene-like quinolizinium fluorophore range up to 82–99%, as listed in the last column in Table 2. In particular, three Br-free [EEQu] compounds in ethanol are all capable of giving the highest Φ_f value of >99%, close to the theoretical maximum (100%). Three Br-free [MMQu] compounds also maintain a high level of Φ_f (94–96%). As for the two bromides, their Φ_f values are relatively low, 82% for [MMQu]Br and 89% for [EEQu]Br respectively, on account of heavy atom (Br)-induced fluorescence quenching. In other solvents, high Φ_f s could also be obtained from [EEQu]NTf₂, i.e. CH₃CN (95%) and THF (86%). In theory, high fluorescence yields require polycyclic aromatic systems. To our knowledge, the quinolizinium ring should be the first small aromatic system (bicyclic) that gives a Φ_f value near 100%.

Computer simulations were conducted to better understand the unprecedented high fluorescence quantum yields of the only bicyclic quinolizinium fluorophore. As shown in Fig. 2a, the optimized ground-state geometry of the [MMQu] cation adopts a planar conformation, and the three C–N bonds are fully delocalized to be almost of the same length 1.384–1.389 Å, close to these C–C bond lengths (1.364–1.438 Å). When excited to the S₁ state (see Fig. S5 in ESI†), only a modest change in the bond lengths (–0.024–+0.029 Å) of [MMQu] occurs, without perceivable distortion of the aromatic plane, answering for the above-mentioned small Stokes shift value. As seen from the electron density surface of [MMQu] in Fig. 2b, the positive charge is highly delocalized into the aromatic system, leaving only +0.208 e charge located at the quaternary nitrogen atom (see Table S2 in ESI†). Likewise, two frontier orbitals (HOMO and LUMO, Fig. 2c, d) are also substantially delocalized over the entire ring. The HOMO–LUMO gap was overrated to be 4.15 eV, relative to the experimental value of absorption energy: 3.78 eV (328 nm). In fact, the quaternary nitrogen atom is an electron-withdrawing group, which helps to transfer about –1.08 e from the hydrogen atoms and methyl groups into the [MMQu] ring (see Table S2†), resulting in an electron-rich aromatic system. To sum up, the high quantum yields of the quinolizinium fluorophore should be related to the following structural reasons: 1) no significant structural difference between S₀ and S₁ states; 2) the well-delocalized positive charge and frontier orbitals; and 3) the electron-rich system.

Fluorescence emission was also observed in the condensed quinolizinium salts. For example, the emission spectrum from the solid

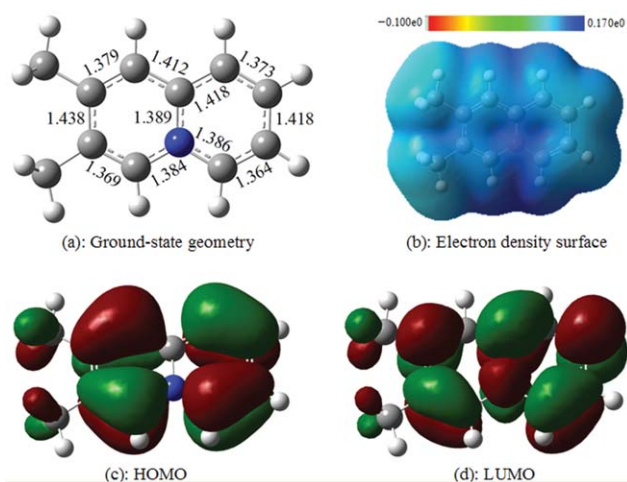


Fig. 2 Optimized ground-state geometry of the [MMQu] cation (a, bond length Å), color-coded electron density surface (b) and frontier molecular orbitals: HOMO (c) and LUMO (d). The calculations were performed in the gas phase at B3LYP/6-31 + G(d,p) level of theory.

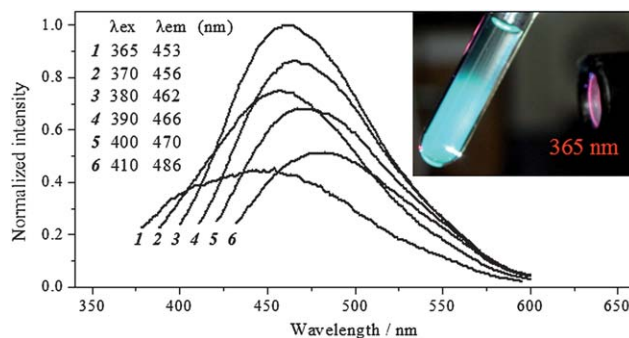


Fig. 3 Excitation wavelength dependent emission spectra in the molten [EEQu]NTf₂ at 60 °C and cyan fluorescence under irradiation by a 365-nm cold light source (136 mW cm⁻²).

[EEQu]NTf₂ is composed of two overlapping bands peaked at 350 nm (see Fig. S3 in ESI†), in a shape similar to the case in solution. However, the molten [EEQu]NTf₂ exhibits structureless emission bands, as shown in Fig. 3. Unlike the cases in solution and the solid state, the emission peak in the liquid state increases with excitation wavelength, in agreement with the previous studies on imidazolium ionic liquids.⁸ In detail, the emission peak in Fig. 3 would vary from 453 to 486 nm, when the excitation wavelength was shifted from 365 to 410 nm. The emission wavelength of the molten salt falls within the visible range, and a bright cyan fluorescence could be seen under irradiation by an ultraviolet cold light source (365 nm). A plausible explanation for the cyan fluorescence should be the presence of a large number of associated species (such as ion clusters), which are energetically different and naturally occurring in ionic liquids *via* hydrogen-bonding, π - π stacking and/or electrostatic interactions.^{8,16} Similar results were also obtained from [MMQu]NTf₂ (see Fig. S3 and S4 in ESI†).

In conclusion, with [MMQu]NTf₂ and [EEQu]NTf₂ *etc.* we present a new type of quinolinizinium ionic liquid featuring an unbranched cation core. The key structural feature makes the small bicyclic quinolinizinium fluorophore exhibit very strong fluorescence (~334 nm) with quantum yields up to >99% in solution, which raises the possibility of designing and fabricating high-efficiency fluorescent compounds with small molecular weights. The emission properties of these quinolinizinium salts can be dramatically tuned by altering the phase state, and bright cyan fluorescence (~465 nm) in the molten state was observed.

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