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Ionic liquidized-naphthalenesulfonamide: successful fabrication of liquid fluorescent materials†

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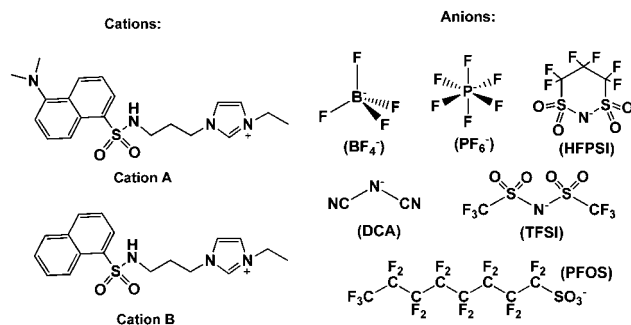
A new class of liquid fluorescent organic salts was designed and prepared through *via* a strategy of ionic liquidization. These new ionic liquid materials exhibited strong green fluorescence and remarkable solvent-dependent photoluminescence under UV irradiation. Their physicochemical properties, especially the fluorescent behaviour, were studied intensively.

As a fascinating class of emissive materials, fluorescent organic salts (FOSs) have received considerable attention in the fields of chemistry, materials, and life science.¹ Compared to molecular emissive materials, FOSs are particularly attractive owing to their unique physicochemical properties, including usually high-temperature and long-term stability, tunable electronic characteristics, solution-based and liquid-state fluorescence, tunable water-solubility, chemoselective sensing to ions or small biomolecules, environmental tolerance, low toxicity, *etc.* These features have endowed the FOSs with great potential in a number of applications, including molecular bioimaging, selective sensing of inorganic anions or small biomolecules, organic electronics, as well as other optical devices.² Currently, a new trend of FOSs studies has focused on the discovery and development of novel fluorescent low melting salts (FLMSs) with liquid-state fluorescent properties, which can be used as a luminescent fluid even at room temperature. For example, the recently reported FLMSs include protonated polyamidoamine dendrimers exhibiting blue photoluminescence,³ phase-tunable fluorophores based upon highly photoluminescent benzobis(imidazolium) salts,⁴ strongly luminescent dialkylimidazolium salts based on europium- or dysprosium-containing anions,⁵ and some gold- or silver-containing imidazolium salts displaying phase-dependent luminescence.⁶ From the viewpoint of chemical materials, the number of luminescent organic salts is theoretically far more than emissive molecule materials, since different combinations of fluorescent cations and emissive anions can give a large amount of possible FLMSs, and meanwhile the possibility of incorporating a highly fluorescent chromophore into the ionic moieties also offers great potential for increased efficiency and versatility in the numerous applications of FOSs in practical science.

But so far, the reported FLMSs are rather limited, mainly due to the difficulty in constructing efficient fluorescent chromophores in the target FLMSs. Thus, the development of novel liquid FLMSs with special properties and strong fluorescent performance is highly desirable.

Recently, an emerging concept of “ionic liquidized materials” is starting to attract interest, and some fascinating ion-type functional materials with low melting points have been reported, including magnetic fluids,⁷ sensitive materials,⁸ ionic liquid crystals,⁹ photochromic switches,¹⁰ and others. In this concept, the ionic liquidization can offer a new opportunity for developing novel FLMSs by introducing a functional group into the organic ionic moieties, which can readily give so-called “task-specific” ionic materials, and more importantly, their physicochemical properties such as melting point, solubility, optical properties, and hydrophilic/hydrophobic ability, *etc.*, can be tuned by altering the combination of their cations and anions. So far, most studies reporting on these ionic liquid-modified materials have focused on the derivatisation of the cationic imidazolium moiety. We also noticed that among the developed FLMSs, the imidazolium moiety was usually chosen as the architectural components to build a desirable FLMS material. Although the imidazolium ring itself has only very weak emission intensities ($\Phi_f < 0.05$)¹¹ in the visible region, it is technically feasible to design a desired liquid FLMS material based on the imidazolium cation *via* a reasonable chromophore design and the selection of a suitable anion.

With our continuous efforts to develop novel ionic liquid materials with special properties and functions,¹² herein a series of ionic



Scheme 1 Structures and abbreviations of cations and anions composing eight FLMSs.

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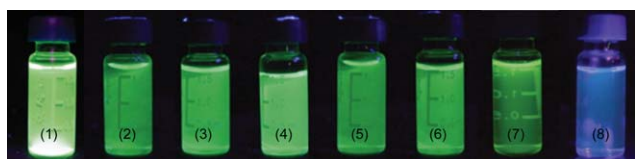


Fig. 1 Photograph of FLMSs 1–8 in methanolic solution (10^{-5} M) under irradiation from a 365 nm lamp (5 W).

liquidized naphthalenesulfonamides was prepared as a new class of FLMS material (Scheme 1). All the resulting FLMSs showed strong photoluminescence both in the solutions and in the condensed phases. The studies involving their absorption and emission characteristics, as well as the solvent-dependent photoluminescence, will be particularly emphasized.

Eight FLMSs were obtained as waxy solids or highly viscous liquids with yields of 55–68%. All the FLMSs are moisture-stable. Among them, FLMSs 1, 2, 4 are water-soluble, whilst the other salts are hydrophobic. DSC analysis showed that all FLMSs had no melting or crystallization in a cooling and heating cycle, and only exhibited glass-forming characteristics at the temperatures of -22.9 to 18.9 °C. TGA analysis showed that these novel organic salts possessed excellent thermal stabilities ($T_d > 320$ °C).

With these new FLMSs in hand, more attention was turned towards their photophysical properties because the fluorescence is the most remarkable feature of these new materials. A preliminary study was performed to investigate their UV absorption and fluorescence emissions in solution. As Fig. 1 showed, under the irradiation from a 365 nm cold light source, FLMSs 1–7 with a naphthalenesulfonamide group in the cation structure exhibited strong green fluorescence in dilute methanolic solution (10^{-5} M), and moderate blue fluorescence was observed for the methanolic solution of FLMS 8 with a naphthyl group in the cation.

To further study how structural, substituent, and anionic variations influence the photophysical properties, their absorptions and fluorescence were investigated in detail. A summary of key photophysical properties including the absorption maximum (λ_{abs}), the molar extinction coefficient (ϵ), the maximum excitation wavelength (λ_{ex}), the maximum emission wavelength (λ_{em}), as well as the quantum efficiency (Φ_f) is shown in Table 1. In methanol, except that FLMS 8 displays a λ_{abs} at 324 nm, FLMSs 1–7 exhibit relatively narrow ranges of λ_{abs} (333–341 nm). A unique feature is that, in theory, the fluorescent behaviour of these FLMSs is mainly determined by the chromophores on the imidazolium ring, *viz.* the

naphthalenesulfonamide or the naphthyl moiety, while the anion only plays a role in tuning the physicochemical properties such as melting point, water-solubility, viscosity, *etc.* Similarly, for these salts, the absorption maximum in the UV region is mainly attributed to the π -electron excitation of the chromophores, and the imidazolium ring itself has only a small contribution to their absorptions; however, in addition to the difference in hydrophilic or hydrophobic characteristics, FLMSs 1–7 with different anions gave some difference in the λ_{abs} s. That means, the anion may also play a role through ion-pairing interactions because the minor changes of the cationic clusters, which are readily caused by the electrostatic forces or the hydrogen bonding interactions, can influence the electron transfer from the donor (anion) to the excited acceptor (the chromophores).¹³ For example, the λ_{abs} of FLMS 3 with a $[\text{PF}_6]^-$ anion is 330 nm, while a λ_{abs} of 341 nm was obtained for FLMS 5 with a $[\text{TFSI}]^-$ anion. To explore the effects of differential anionic factors, the fluorescence emissions of FLMSs 1–7, which have the same cation, were comparatively studied in methanol at a concentration of 10^{-5} M, Table 1. The results showed that the six salts displayed very similar λ_{em} s (515–517 nm), while the corresponding λ_{ex} s are in the range of 333–338 nm, indicating that the anion variation had only a little effect on their λ_{ex} s and λ_{em} s. However, FLMSs 2–7 displayed different Φ_f s ranging from 0.18–0.36, although they possessed the same chromophore on the imidazolium ring. This may be explained by the difference of cationic clusters through the ion-pairing interactions. These interactions are related to the structure of the anions and their affinity for the cation, and consequently influence the quantum efficiency. As compared to the FLMSs 2–7, FLMS 8 with a naphthyl group only gave a small Φ_f of 0.01, indicating that the electron-donating dimethylamino group

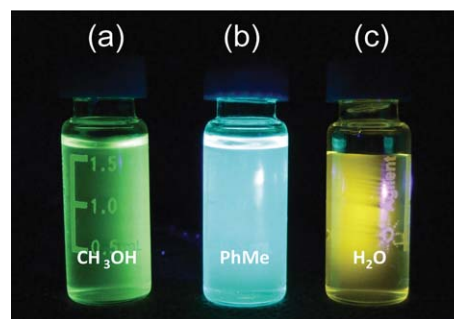


Fig. 2 Photograph of FLMS 4 in three different solvents under a 365 nm cold light source, (a) in methanol, (b) in toluene, (c) in H_2O . The concentration of FLMS 4 is 10^{-5} M.

Table 1 Physicochemical properties of fluorescent low melting salts (FLMSs)

FLMS	[Cation][Anion]	Yield (%)	Hydrophilic/hydrophobic	T_g (°C)	T_d (°C)	λ_{abs} (nm) ^a	$\log(\epsilon)$ ^a	λ_{ex} (nm) ^a	λ_{em} (nm) ^a	Φ_f ^b
1	[A][Br]	68	hydrophilic	18.9	384	338	3.36	338	511	0.24
2	[A][BF ₄]	61	hydrophilic	7.6	406	336	3.75	337	515	0.36
3	[A][PF ₆]	63	hydrophobic	11.4	401	330	3.92	333	515	0.18
4	[A][DCA]	57	hydrophilic	-1.8	328	335	4.05	335	517	0.27
5	[A][TFSI]	62	hydrophobic	-9.7	414	339	3.67	337	515	0.32
6	[A][HFPSI]	60	hydrophobic	-9.2	425	341	2.58	336	516	0.33
7	[A][PFOS]	55	hydrophobic	16.4	392	337	3.97	338	517	0.24
8	[B][TFSI]	66	hydrophobic	-22.9	436	324	3.37	324	344	0.01

^a Data taken in MeOH under ambient conditions, the concentration is 10^{-5} M. ^b Quantum efficiencies (Φ_f) were determined relative to dansylamide (for FLMSs 1–7) or naphthalene (for FLMS 8).

Table 2 Solvent effects on photophysical properties of FLMS **4**^a

Solvents	ET(30) ^b	DN ^c	DC ^d	λ_{abs} (nm)	λ_{em} (nm)	Stokes shift ^e (cm ⁻¹)
H ₂ O	63.1	33	78.4	335	518	11276
MeOH	55.4	19	32.7	335	511	10281
EtOH	51.9	31.5	24.8	339	509	9852
n-BuOH	50.2	18	17.3	337	507	9950
MeCN	45.6	14.1	36.6	338	515	10168
DMSO	45.1	29.8	45.0	341	515	9908
DMF	43.8	26.6	38.3	339	509	9852
CH ₃ COCH ₃	42.2	17	20.7	339	506	9736
CH ₂ Cl ₂	40.7	1	8.93	342	502	9319
CHCl ₃	39.1	4	4.71	341	500	9326
THF	37.4	20	7.58	336	501	9802
PhMe	33.9	0.01	2.37	339	494	9256

^a Data taken in methanol under ambient conditions, the concentration of FLMS **4** in the methanol solution is 10⁻⁵ M. ^b The polarity scale for a solvent, ET(30), is the electronic transition energy of the betaine dye 4-(2,4,6-triphenylpyridinium)-2,6-diphenylphenoxide in that solvent, in units of kcal/mol. ^c DN means the donor numbers of the solvent used at 25 °C. ^d DC means the dielectric constants (ϵ) of the solvent used at 25 °C. ^e Stokes shifts, in various solvents, given in cm⁻¹ by $-10^7(1/\lambda_{\text{em}} - 1/\lambda_{\text{abs}})$; all the data about ET(30), DN, and DC of the solvents were drawn from ref. 15, 16 and 17, respectively.

on the 5 position of the naphthyl ring is crucially important for the improvement in fluorescence efficiency of the resulting FLMSs. In general, the fluorescence of traditional imidazolium-based ionic liquids is strongly dependent on the excitation wavelengths, since their very weak fluorescence is mainly contributed by the π - π^* electronic transitions of the imidazolium moiety.¹¹ For these FLMSs, however, when the excitation wavelengths varied, no obvious shifts for the emission wavelengths were observed (Fig. S3[†]), suggesting that the fluorescence excited mechanism of these new FLMSs was very different from the traditional imidazolium-based salts.

For some emissive compounds, sometimes solvent-dependent photoluminescence can be observed. This feature offers an excellent handle for tuning the photophysical characteristics of a solution.¹⁴ To our delight, the new FLMS materials obtained in this study exhibited obvious solvent-dependent photoluminescence. In Fig. 2, the marked colour difference in the photoluminescent properties of FLMS **4** can be clearly observed under UV lamp irradiation in three different solvents, indicating the great potential for solvent effects to influence the emission behaviour of these new FLMS materials.

Commonly, λ_{abs} and λ_{em} respond to the changes in solvent dielectric in a manner consistent with changes in the polarity of the chromophore as it transitions from the ground state to an excited state. Therefore, to further investigate the solvent effects on photophysical properties, the absorption and emission properties of FLMS **4** were studied in twelve solvents with different polarities. As was shown in Table 2, as compared to the insignificant changes of λ_{abs} (from 335 to 342 nm) with increasing solvent polarity, the λ_{em} of the FLMS **4** was strongly dependent on the nature of the solvent, displaying a very obvious shifts with λ_{em} ranging from 494 to 518 nm when the solvent was changed. However, no discernible trends were observed between the λ_{em} and the solvents' DN (donor number) or ϵ (dielectric constant). Moreover, the Stokes shifts of FLMS **4** in twelve solvents ranged from 9256 to 11276 cm⁻¹, which is very dependent on the DN of the solvent used. These values are in the range of unusually large Stokes shifts (5000–15000 cm⁻¹), commonly ascribed to structural reorganization of the fluorophore or excited-state reactions.¹⁸ Similar to the solvent effects on λ_{em} , no clear trends can be deduced between the Stokes shift and the DN or ET(30) or ϵ from the data in Table 2 since many factors related to the solvent nature can influence or greatly alter them.

In conclusion, the successful fabrication of liquid fluorescent materials *via* ionic liquidization has been carried out, and their physicochemical properties, especially the fluorescent behaviour, were studied. Among them, most salts are liquids at room temperature. FLMSs **1–7** show green photoluminescence characteristics in both the solution and pure liquid states under UV irradiation. Furthermore, they also display remarkable solvent-dependent photoluminescence. The new strategy of "ionic liquidized materials" endows the target FLMS materials with improved properties such as lower melting point, enhanced solubility, controlled hydrophilic/hydrophobic behaviour, optional solution-based liquid-state fluorescence, *etc.* This will offer new opportunities for the preparation and application of liquid fluorescent materials.

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