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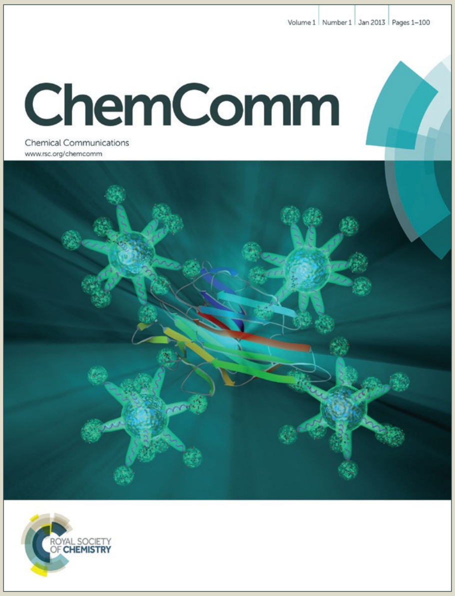

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$[Bmim]_2SbCl_5$: a main group metal-containing ionic liquid exhibiting tunable photoluminescence and white-light emission

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An antimony-based photoluminescent ionic liquid, namely $[Bmim]_2SbCl_5$, has been synthesized and characterized, which exhibited bright yellow and white light emission, with quantum yield as high as 86.3% under UV irradiation.

Materials with luminescence properties are of great importance in many applications, such as LED, fluorescence detection[1] and so on.[2] In recent years, much attention has been paid to the organic-inorganic hybrid photoluminescent (PL) materials. Most of the hybrid PL materials are metal-containing compounds in which the PL can be readily tuned by changing the metal-centre (MC). Currently, the MCs are mostly f-block elements which normally suffer from high cost. Thus it is essential to explore alternative PL materials based on other MCs with low cost and high efficiency. In fact, main group metal ions with electronic configuration of $n\mathrm{S}^2$ such as Sb^{3+}, Bi^{3+} and Sn^{2+},[3] also known as the Hg-like ions, were largely ignored in constructing hybrid PL compounds. However, the scanty researches have provided us the idea that the nitrogen-containing organic bases are effective in tuning the PL properties of the compounds with main group MC, which is related to the matching degree between the organic and the inorganic components.[4]

Ionic liquids (ILs) are a kind of ionic compounds with low melting point, low volatility, and large liquid range. Over the past twenty years, the researches of ionic liquids have experienced an explosion, for the ILs can be widely used not only as green solvents in chemical reactions, but also as versatile materials in catalysis, separations, PL and so on.[5] More importantly, ILs can be custom-tailored to satisfy the functional requirements by changing either the cationic or the anionic components. In the aspect of PL materials, traditional ILs such as imidazolium-based ILs could show intrinsic PL by the π–π^* transitions, but the intensity and quantum yield are normally quite low.[6] In order to improve the PL properties of ILs, both cation and anion have been designed. For instance, the complicated cations or anions with bigger conjugate system have been designed.[7] On the other hand, the introduction of a MC with PL property into anion seems to be more widely used.[8] Until now, both rare earth[9] and transition metal ions, such as Tb^{3+},[9e] Eu^{3+},[9f] Mn^{2+},[10] Au^+ and Ag^+ [11] have been applied to the design of metal-containing PL ILs. By contrast, although some main-group metal containing ILs have been reported,[12] their PL properties were scarcely studied.

Herein, we report on the synthesis, characterizations and PL properties of an antimony(III)-containing IL, namely $[Bmim]_2SbCl_5$ (**1**). Significantly, bright yellow and white light emission of **1** could be achieved under UV light irradiation, with the PL quantum yield (QY) as high as 86.3% in solid state for light-yellow emission.

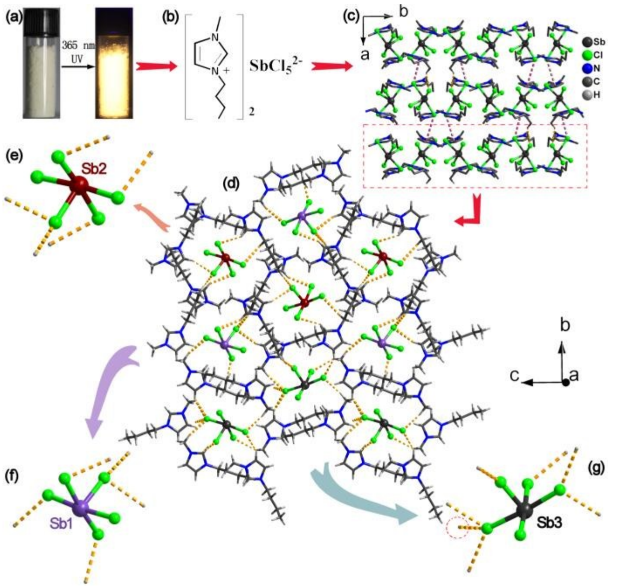

Fig. 1 (a) Photographs of the polycrystalline compound $[Bmim]_2SbCl_5$ (**1**) under the daylight lamp (left) and 365 nm UV lamp (right). (b) Structural diagram of **1**. (c) Packing of the structure of **1** viewed along the *c*-axis; hydrogen atoms are omitted for clarity. (d) A two-dimensional network along the *bc* plane formed by hydrogen bonding among the $[SbCl_5]^{2-}$ and $[Bmim]^+$ ions. (e), (f) and (g) highlight the hydrogen bonds for $Sb(1)Cl_5$, $Sb(2)Cl_5$ and $Sb(3)Cl_5$ anions, respectively.

The light-yellow block-like crystals of **1** were formed by room-temperature (RT) crystallization from a clear and homogeneous solution obtained by heating a mixture of [Bmim]Cl, $SbCl_3$ and ethanol in a vial at 70℃ for 10 minutes (for more details, see ESI†). The crystal structure of $[Bmim]_2SbCl_5$ was determined by single-crystal X-ray diffraction. **1** belongs to the noncentrosymmetric space group of *Cc*, and its structure features a three-dimensional (3D) supramolecular network constructed by hydrogen bonding and anion-π interactions among the $[SbCl_5]^{2-}$ anions and $[Bmim]^+$ cations, Fig. 1. The crystallographic asymmetric unit of **1** consists of six $[Bmim]^+$ cations and three discrete $[SbCl_5]^{2-}$ anions. Each Sb(III) ion is coordinated with five Cl^- ions in the form of quadrangular pyramid, and every pyramid-like anion is surrounded by six imidazole rings (Fig. 1d) in a hamburger-like fashion. Each discrete $[SbCl_5]^{2-}$ anion interacts with neighbouring $[Bmim]^+$ cations via inter-molecular C-H···Cl hydrogen bonds, resulting in a 2D infinite layer along the *bc* plane, Fig. 1d; the C···Cl distances are in the range of 3.481(3) to 3.671(3) Å and the C-H···Cl angles vary from 130 to 169 °, Table S2, ESI†. In fact, the three different anions are in three different modes of hydrogen bonding (for more details, see Figures 1e-g and ESI†). Most of the hydrogen bonds are formed among the Cl^- ions and H atoms in the same layer. While in $[Sb(3)Cl_5]^{2-}$, there is one Cl^- ion that forms a inter-layer hydrogen-bond with the C-H from the adjacent layer (Red cycle in Fig. 1g). Furthermore, There are also two Cl^- ions of $[Sb(3)Cl_5]^{2-}$ in a confortable distance with the electron-deficient imidazole rings from adjacent layers resulting in anion-π interactions, Fig. S3, ESI†. As a result, the inter-layer hydrogen bonds and the inter-layer anion-π interactions lead to a 3D supramolecular network of **1**.

Interesting, **1** exhibited bright yellow light when it was exposed to the illumination of 365 nm UV light at room temperature, which inspired us to study more about the structures and properties of the halogen antimonite(III) compounds. Typically, the halogen antimonite(III) anions exist in the forms of $[SbX_4]^-$, $[SbX_5]^{2-}$ and $[SbX_6]^{3-}$.[4f] Prior to this work, the PL properties at room temperature have always been found in the compounds with discrete anion of $[SbX_6]^{3-}$, whereas seldom was found in compounds with anions of $[SbX_4]^-$ and $[SbX_5]^{2-}$,[4a-e] implying that the PL properties may be closely related to the structure of the anions. In solid state, the $[SbX_6]^{3-}$ always exist in an discrete octahedral form, while the majority of $[SbX_4]^-$ and $[SbX_5]^{2-}$ are dimer or polymers. Taking $[SbX_5]^{2-}$ as an example, Owczarek and co-workers have concluded the formation of $[SbX_5]^{2-}$ recently,[13] that is, during the 67 known anions, only 5 of them are discrete anions, 16 of them are $[Sb_2X_{10}]^{4-}$ or similar dimers, 2 of them are $[Sb_4Cl_{20}]^{8-}$ tetramers, and 44 of them are anionic chains (The structure diagrams of these anions are summarized in Table S4, ESI†). In the dimeric or polymeric $[SbX_5]_n^{2n-}$ ($n > 1$), the adjacent $[SbX_5]^{2-}$ units are close enough to each other so that the intersections may happen between the potential energy surface of excited-state and ground-state, which leads to an increase of the nonradiative energy loss, and thus an efficiency decrease or even quenching of the PL. To our knowledge, there was only one report that described the PL property of a compound containing a truly discrete $[SbCl_5]^{2-}$ anion, but the author claimed that the emission was not originated from $[SbCl_5]^{2-}$.[14]

Thus we further studied the PL properties of **1**. As shown in Fig. 2a, there are two emission peaks found at 583 and 460 nm, respectively upon excitation of different wavelengths. Excitation spectra show that the emission at 583 nm has a quite wide range of excitations from 250 nm to 420 nm, peaking at 368 nm and with a shoulder peak at 283 nm, while the emission peak at 460 nm corresponds to an excitation peak of 303 nm, Fig. 2b. The Stocks shift of this magnitude has been reported before.[4k] As the excitation wavelengths were changed from 270 to 303 nm or from 368 to 303 nm, the intensity of the 460 nm emission increased, accompanied by a decrease of the intensity of the 583 nm emission. It means that the compound can display tunable PL properties via varying the excitation wavelength. The colours of the emissions can be better quantified with the CIE chromaticity diagram, as depicted in Fig. 2c. The coordinates were (0.409, 0.411), (0.376, 0.375) and (0.483, 0.489), when the compound was excited at 285 nm, 303 nm and 368 nm, respectively. The point (0.376, 0.375) falls within the colour gamut of white-light, and the other two are all located at yellow colour region. In other words, with the increase of the excitation wavelengths from 250 to 450 nm, the emission colours of compound **1** can be changed from yellow to white, and finally to yellow again.

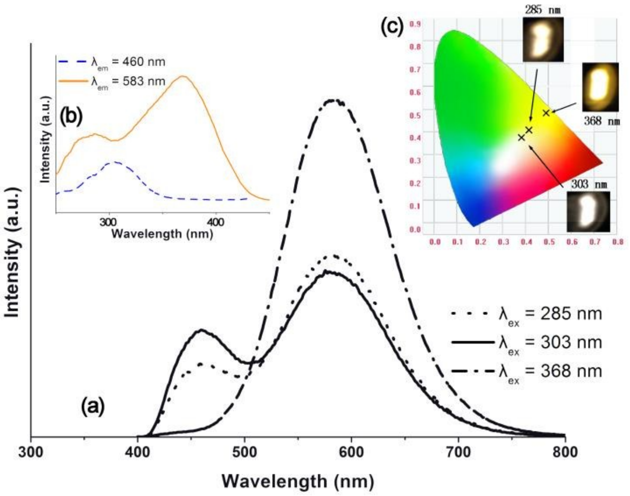

Fig. 2 (a) Emission spectra of $[Bmim]_2SbCl_5$ (**1**) at different excitation wavelengths. (b) Excitation spectra of **1** at different emission wavelengths. (c) CIE coordinates of the emission colours and corresponding PL images (inset) of **1** at different excitation wavelengths.

The decay time of **1** was measured as 4.26 μs ($\lambda_{ex,em}$ = 397, 583 nm), Fig. S11, ESI†. Such a value is totally different from that of most of the $[Bmim]^+$-containing salts, which were in nanosecond order of magnitude.[6b,6c] According to literatures,[4l, 4m] the $[SbX_n]^{3-n}$-based compounds normally exhibit a variety of emission bands from 500 nm to 700 nm, implying that the emission peak of **1** at 583 nm may be ascribed to $[SbCl_5]^{2-}$. As for the emission band at around 460 nm, it has an independent excitation band peaking at 303nm (Fig. 2b), while it is also found that most of the $[Bmim]^+$-containing salts have nonnegligible absorption around 300 nm,[6b, 6c] indicating that such a emission band came from $[Bmim]^+$. Further theory calculations supported the inferences, and ascribed the emission band in 460 nm and 583 nm to intraligand charge transfer (ILCT)[15] of $[Bmim]^+$ and chlorine-to-metal charge transfer (XMCT)[16] of $SbCl_5^{2-}$, respectively (For more details, see ESI†). The hydrogen bonding and anion-π interactions between anions and cations may increase the electron densities of $[Bmim]^+$, which probably makes the anion act as an electron-donor and enhance the intensity of the emission at 460 nm along with a decrease of the PL intensity in 580 nm. Finally, the tunable PL spectra were observed.

Importantly, the compound **1** exhibits a high quantum yield of 86.3% in solid state (λ_{ex} = 370 nm), presumably due to the multiple hydrogen bonds in the supramolecular network of **1** that make the structure more rigid and thus the thermal vibration of atoms are reduced.[17]

Thermal behaviour of **1** was studied by TGA and DSC on the polycrystalline pure sample of **1** (Fig. S6, ESI†), indicating that the melting point of **1** is 349 K, and the weight loss started at ~240℃ due to the decomposition of **1**. Temperature-dependent powder X-ray diffraction (PXRD) indicated that compound **1** was stable and remained highly crystalline from RT to 338 K (Fig. S10, ESI†). Then the temperature-dependent PL spectra on the polycrystalline sample of **1** were measured and the QYs were calculated accordingly (Figs. S11 and S12, ESI†), indicating negligible changes which suggests that **1** is a high-efficiency solid state PL material from RT to ~345 K. However, the PL of compound **1** was quenched when it was melted at 349 K, perhaps due to the thermal collision deactivation and destruction of the crystal structure.[9d] Like some other ionic liquids, however, in the process of cooling, solidification progress did not happen immediately when the temperature was below the melting point, unless there were some seed crystals in the melt, or the melt was stirred; PXRD indicated that the structure of **1** remained intact after solidification (Fig. S6, ESI†).

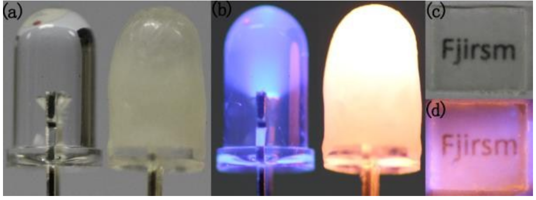

Fig. 3 Photographs of UV-LED lamp (left) and the LED coated with a thin layer of compound **1** (right) both in states of turned off (a) and on (b). (c) and (d) are the photographs of the film coated on a piece of glass in daylight lamp and under UV-LED lamp, respectively.

After obtaining an efficient PL material with the ability to form a stable melt at low temperature, we shift our focus towards possible applications. By a simple procedure of dipping a UV-LED lamp into the melt of **1**, a LED that emitted bright yellow light was obtained after the solidification of the melt on the lamp. Due to the low heat-emitting property of LED, the new LED could emit stable yellow light at ambient conditions, with an ignorable temperature variation.

Unsurprisingly, once the environmental temperature crosses a threshold of 349 K, i.e. the melting point of **1**, the emission light of LED was changed back to violet, that was, the light of LED itself. However, when the temperature was decreased well below 349 K, the LED emitted yellow light again. Such cycle can be repeated, meaning that the LED is a temperature sensing color-changing LED which can be used as high temperature alert device. To the best of our knowledge, such kind of temperature sensor based on the luminescence quenching by a melting process is seldom reported.[2g]

The ability to form a stable melt also provides an opportunity to prepare the film of **1**. In a typical process, the polycrystalline sample of **1** was firstly dispersed on a piece of glass of 10 mm × 10 mm × 1 mm, and heated above the melting point to obtain a melt on the glass. Then a plastic sheet and another piece of glass were deposited in turn on top of the melt. By applying pressure gently on the top of the glass, the melt spread uniformly between the sheet and glass. After being cooled down to room temperature and stayed for a while, a transparent film with a thickness of ~20 μm was formed. The thinner film could be obtained by applying more pressure. As seen in Fig. 3d, the film could emit the characteristic PL of **1**. PXRD pattern of the film indicated the high degree of crystallinity, and preferred orientation of some higher order reflections, Fig. S6, ESI†. Quantum yield of the film was measured as 82.6%, comparable with that of polycrystalline **1**.

Conclusions

In conclusion, we have prepared the compound $[Bmim]_2SbCl_5$, an main group metal-containing ionic liquid that contains an discrete $[SbCl_5]^{2-}$ anion in the structure. With features of easy preparation, tunable PL with high quantum yield and easy-processing, the compound has potential application as PL material in temperature sensing color-changing LED and so on. More importantly, the study sheds a light on obtaining efficient PL materials via combining various imidazolium cations with discrete MX_n anions (M = main-group metal ion, X = halogen).

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Notes and references

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† *Crystal data for compound* **1**: Intensity data were collected on a Super Nova diffractometer equipped with CCD detector using Mo-*Kα* radiation (λ = 0.71073 Å). $C_{16}H_{30}N_4SbCl_5$, M = 577.44, monoclinic, Cc, a = 15.3778(3), b = 27.5062(5), c = 17.4435(3) Å, β = 102.004(2)°, V = 7217.0(2) $Å^3$, T = 100(2) K, Z = 12, Dc = 1.594 g cm^{-3}, μ(Mo-$K\alpha$) = 1.711 mm^{-1}, F(000) = 3480, crystal size 0.20 × 0.15 × 0.15 mm, 14256 independent reflections (R_{int} = 0.0267). Final R = 0.0227 for 13621 reflections with $I > 2\sigma(I)$ and wR_2 = 0.0526 for all data.

Electronic Supplementary Information (ESI) available: Crystallographic data in CIF format, synthetic procedures, more structural details, PXRD, TGA curves, DSC curves, and elemental analyses results. CCDC number 1031043. See DOI: 10.1039/c000000x/

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