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COMMUNICATION

Transparent and colourless room temperature ionic liquids having high refractive index over 1.60

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Transparent and colourless ionic liquids with refractive index over 1.60 were synthesised by combining 1-benzyl-3-methylimidazolium or hexyltriphenylphosphonium cations with suitable anions. There is a positive relation between their refractive index and Kamlet-Taft parameters, especially dipolarity/polarisability, suggested as a potential parameter to design ionic liquids with high refractive index.

High refractive index liquids are generally used as reference solution to determine properties of optical materials, such as glasses, minerals, and high molecular weight materials.¹ They have been applied in a variety of fields such as immersion oil of optical microscopic observation to enhance graphic mode, immersion oil of liquid immersion exposure method for preparation of IC chip, and liquid lens. In these applications, transparency, harmless, thermal stability, and chemical stability are required as well as high refractive index. Diodomethane saturated with sulfur, carbon disulphide, and bromonaphthalene are commercially available high refractive index liquids. Although their refractive index is over 1.60, they have some undesired characteristics, such as colouring, pungent smell, toxicity, and low stability, because they contain some reactive atoms such as iodine, arsenic, and sulfur. Therefore, there are strong demands on the development of new liquid materials with refractive index over 1.60, being transparent and colourless in the wavelength range from 380 to 800 nm, low volatility, and high stability.

Ionic liquids are solvents composed entirely of ions with melting points below 100°C.² They have been called “designer solvents” because diversity in combination of cation and anion enables the development of ionic liquids with desired physicochemical properties. Since some ionic liquids may have required properties for ideal high refractive index liquids such as negligibly small volatility, flame retardancy, and high density, there is a potential possibility of ionic liquids as high refractive index liquids. However, for the transparent and colourless ionic liquids, there has been no report on ionic liquids with a refractive index exceeding 1.60.

Previously, Seddon et al. have succeeded in increasing the refractive index of ionic liquids by dissolving bromine or iodine into some ionic liquids.³ This is an easy but effective strategy for dramatically increasing the refractive index of ionic liquids while accompanied by yellow or brown colouration due to the nature of halogen molecules. For the development of “transparent” and “colourless” ionic liquids, it is required to propose a new strategy.

According to Lorentz-Lorenz equation (eqn. (1)), refractive index of materials is a function of molar electric polarisability, α_e , as well as that of the molar volume, V_m .

$$\frac{n^2-1}{n^2+2} = \frac{N_A}{3\epsilon_0} \cdot \frac{\alpha_e}{V_m} = \frac{[R]}{V_m} \quad (1)$$

In this equation, n , ϵ_0 , and $[R]$ are refractive index, dielectric constant in vacuum, and molecular refraction, respectively. This equation clearly indicates that the employment of molecular structures with high molecular refraction and/or containing atoms with high atomic refractions should be effective for developing high refractive index materials. It is known that aromatic rings have high molecular refraction. Also, iodine (13.90), bromine (8.87) and sulphur (7.80) are known as representative atoms having high atomic refraction. The background mentioned above pushed us to design ionic liquids with high refractive index with desired physicochemical properties.

In the present study, we have prepared some ionic liquids based on the following two strategies. One is the use of ions containing aromatic structures.^{4,5} The other is the introduction of iodine atoms onto the component ions.⁶ Based on these two strategies, we have prepared some ionic liquids using following three cations, 1-benzyl-3-methylimidazolium ([BzmIm]), hexyltriphenyl-phosphonium ([P_{p,p,p,δ}]), and 4,5-diiodo-1-butyl-3-methylimidazolium ([BmImI₂]) cations, and a few anions considering the above factors (Fig. 1). Considering high molecular refraction of benzene rings and iodine, the use of these cations is expected to be a rational approach for the design of ionic liquids showing high refractive index. Although a huge number of ionic liquids have been designed and synthesised to date, there are only a limited number of reports on the ionic liquids

based on these cations.^{4,5} Because van der Waals interactions, π - π interaction and/or halogen-bonding between these cations are so strong, they formed organic salts with high crystallinity. For the development of ionic liquids with these cations to show melting point or glass transition temperature below room temperature, it is strongly suggested to use anions having ability to considerably diminish these interactions. As these anions, we have selected saccharinate ([Sac])^{7,8} and 2-iodobenzenesulfonate ([Bz-I-SO₃]) anions because these anions have asymmetric structure and their negative charges are highly delocalised. Moreover, since they contain a benzene ring, sulfur atom, and/or iodine atom, these anions are expected to be effective to increase the refractive index of the ionic liquids. On the other hand, as counter anions for [BmIm]₂ cation, we have selected bis(trifluoromethane)sulfonimide ([N(Tf)₂]) and dicyanamide ([N(CN)₂]) anions, because these anions are known to provide ionic liquids with low glass transition temperature.^{9,10} The preparation of these ionic liquids was achieved by ion exchange reaction and suitable purification (see ESI). Thermal properties of these ionic liquids were examined with differential scanning calorimetric measurements. Their transparency was evaluated from transmittance at wavelength of 400 nm. Refractive index, n_D , of these ionic liquids was measured at wavelength of 589 nm using Abbe refractometer. Thermal properties of the prepared organic salts are shown in Table 1. The glass transition temperature (T_g) and melting temperature (T_m) of these organic salts are greatly influenced by the anion species. For example, while [P_{p,p,p,6}]Br shows T_m at 202 °C, the employment of [Sac] and [Bz-I-SO₃] anions, that largely help to decrease the crystallinity of [P_{p,p,p,6}] cation, provides ionic liquids showing T_g below room temperature. Similarly, a room temperature ionic liquid was obtained by combining [Sac] anion with [BzmIm] cation. These results indicate that aromatic anions are potential counter anions for cations having aromatic rings for reducing crystallinity of the formed ionic liquids.

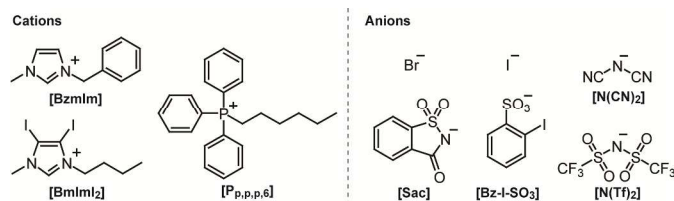


Fig. 1 Structure of cations and anions employed for the design of ionic liquids in this study.

In a series of [BmIm]₂ salts, a room temperature ionic liquid has only been obtained by combining it with [N(Tf)₂] anion. On the other hand, the employment of iodine, [N(CN)₂] and [Bz-I-SO₃] anions provides organic salts with high T_m as seen in Table 1. It is assumed that their high crystallinity is attributed to both van der Waals interaction and dipole-dipole interaction between these cations and anions. These results indicate that it is important to select suitable ion pair to reduce interaction among cations and/or anions without forming specific interaction to elevate T_m .

Fig. 2 shows a picture of three vials containing water, 1-butyl-3-methylimidazolium bis(trifluoromethane)sulfonimide ([Bmim]₂[N(Tf)₂]), and [P_{p,p,p,6}][Sac] in front of equally-spaced vertical stripes. It is visually presented that the ionic liquids prepared in this study are transparent and colourless as good as water. The spaces of lines are enlarged by the liquids and the magnitude of enlargement is proportional to the refractive index of the liquids. It is noteworthy that the line space enlarged by [P_{p,p,p,6}][Sac] is significantly larger than that by water. Compared with the magnitude of enlargement by conventional ionic liquid such as

Table 1 Refractive index, transmittance and thermal properties of prepared ionic liquids

Ionic liquid	T_g (°C)	T_m (°C)	n_D at 25 °C	T_{400} (%)
[BzmIm]Br	-12	-	1.61	98.5
[BzmIm][Sac]	-16	-	1.60	89.9
[P _{p,p,p,6}]Br	-	202	- ^a	- ^a
[P _{p,p,p,6}][N(Tf) ₂]	-	90	- ^a	- ^a
[P _{p,p,p,6}][Sac]	11	-	1.63	99.7
[P _{p,p,p,6}][N(CN) ₂]	-27	-	1.61	- ^a
[P _{p,p,p,6}][Bz-I-SO ₃]	7	-	1.64	- ^a
[P _{p,p,p,6}][Bz-SO ₃]	-5	-	1.61 (50 °C)	- ^a
[P _{4,4,4,4}][Sac]	-41	-	1.53	99.9
[Bmim] ₂ I	-	230	- ^a	- ^a
[Bmim] ₂ [N(Tf) ₂]	-42	-	1.50	- ^a
[Bmim] ₂ [N(CN) ₂]	-	130	- ^a	- ^a
[Bmim] ₂ [Bz-I-SO ₃]	-	174	- ^a	- ^a

^anot examined.

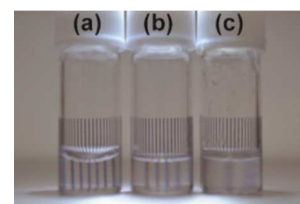


Fig. 2 A picture of vials containing (a) water, (b) [Bmim]₂[N(Tf)₂], and (c) [P_{p,p,p,6}][Sac].

[Bmim]₂[N(Tf)₂], that by [P_{p,p,p,6}][Sac] is evidently larger. This clearly shows larger refractive index of [P_{p,p,p,6}][Sac] than that of conventional ionic liquids and water.

Optical properties of these ionic liquids are also summarised in Table 1. A most noteworthy result is that n_D of ionic liquids having [BzmIm] or [P_{p,p,p,6}] cations are over 1.60. Those of [P_{p,p,p,6}]Br and [P_{p,p,p,6}][N(Tf)₂] have not been examined due to their high melting temperature. Considering the facts that the n_D of conventional ionic liquids ranges from 1.4 to 1.5 and the highest n_D value for colourless ionic liquid is reported to be 1.59,⁷ the ionic liquids prepared in this study were categorised into high refractive index ones. These results suggest that the introduction of aromatic rings is one of effective approaches for the design of high refractive index ionic liquids in spite of a fear of elevation of T_m . For example, n_D of [BzmIm]Br is 1.61, which is 0.06 higher than that of 1-butyl-3-methylimidazolium bromide, [Bmim]Br. Increase of n_D upon the introduction of aromatic rings was also observed for the case of phosphonium-based ionic liquids, namely, n_D of [P_{p,p,p,6}][Sac] is 1.63, which is 0.10 higher than that of [P_{4,4,4,4}][Sac].

Substitution of imidazolium protons with iodine atoms also increased the n_D of the ionic liquids. For example, n_D of [Bmim]₂[N(Tf)₂] is 1.50, which is 0.07 higher than that of an analogous imidazolium salt, [Bmim]₂[N(Tf)₂]. A positive effect of iodine-substitution was also observed in the comparison of the n_D of [P_{p,p,p,6}][Bz-SO₃] with that of [P_{p,p,p,6}][Bz-I-SO₃]. Since, in these ionic liquids, iodine atoms are introduced not as an anion but as a part of ions, these ionic liquids are colourless. It is also important to mention that both [Bmim]₂[N(Tf)₂] and [P_{p,p,p,6}][Bz-I-SO₃] keep their colourless state and transparency even after heating at 100 °C for 6 h. Design of ionic liquids through substitution of protons with iodine atoms is also a potential strategy to design highly refractive ionic liquids. Based on the above-mentioned results, we have synthesised [Bmim]₂[Bz-I-SO₃], but it was obtained as a solid with T_m of 174 °C. Lowering T_m without lowering n_D is another task to be solved.

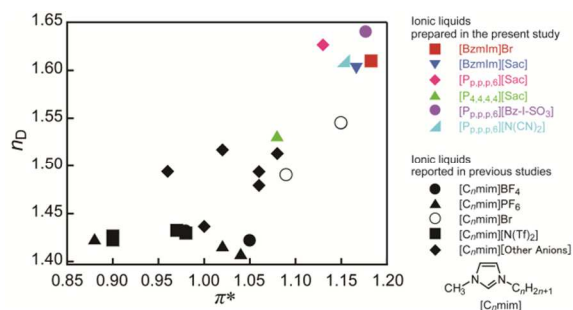


Fig. 3 Relation between n_D and Kamlet-Taft parameter, π^* value, of ionic liquids prepared in this study and reported in previous studies.

Next, we have tried to make a protocol to design ionic liquids having higher refractive index. Kamlet-Taft parameters are useful for evaluating polarity of ionic liquids as well as that of organic solvents. Recently, these Kamlet-Taft parameters were strongly suggested to be standard polarity parameters for ionic liquids.¹¹ As Kamlet-Taft parameters, there are such three parameters as α , β , and π^* , which indicate hydrogen-bonding acidity, hydrogen-bonding basicity, and dipolarity, respectively. Since refractive index of materials is a function of molar electric polarisability, α_e as seen in eqn. (1), we hypothesised that there might be some correlations between refractive index of ionic liquids and their π^* values. To examine our hypothesis, refractive index^{3,12-17} of some known ionic liquids are plotted as a function of their π^* values.¹⁸⁻²⁸ As shown in Fig. 3, there is a positive relation between them including a few exceptions. Some of our data mentioned in this paper were also plotted (in colour) in Fig. 3. Focusing on exceptional ionic liquids that are away from the correlation, it is found that refractive indexes of imidazolium salts having anions with F atoms such as BF_4^- and PF_6^- are lower than that expected from their π^* values. In spite of large dipole moment due to strong electron withdrawing effect of F atoms, highly symmetric anion structure suppressed the overall polarisability to cause lower refractive index than that expected from the π^* values. However there are multiple factors to affect the n_D of the ionic liquids, the π^* value of these ionic liquids should be a top priority factor. This finding may be an important insight for designing ionic liquids with higher refractive index.

In conclusion, we have succeeded in developing room temperature colourless ionic liquids with high refractive index and high transparency by employing cations having benzene rings and/or iodine-substituted ions. Refractive index of some of prepared ionic liquids is over 1.60, higher than those of any other transparent and colourless ionic liquids previously reported. It is also an important fruit that their refractive index is positively correlated with their Kamlet-Taft π^* parameter.

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Notes and references

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