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Ionic liquid-modified dyes and their sensing performance toward acids in aqueous and non-aqueous solutions†

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Six ionic liquid (IL)-modified dyes were synthesized and characterized. Compared to the methyl red and methyl orange, these IL-modified [MR]⁻ or [MO]⁻-based dyes exhibit lower melting points and enhanced solubility, and can be used as sensitive indicators towards free proton in both aqueous and non-aqueous solutions. This work also supplies a new concept of developing novel modified materials with the ILs.

Over the past decade, ionic liquids (ILs) have received great interest in chemistry and industry. Recently, a new trend of IL research and development has been emerging along with the rapid development of IL researches, *i.e.* from media¹ or electrolytes² in 'clean' or 'green' chemical processes to functional soft materials in organic-inorganic hybrids,³ high performance additives in paints,⁴ plastics,⁵ and cleaning agents,⁶ biotechnology,⁷ and luminescence materials,⁸ *etc.* Now, the concept of 'ionic liquid-modified materials' is being established. For example, Rogers and co-workers⁹ presented the concept of combining IL cations with the biologically active anions to produce novel drugs with enhanced performance and delivery options. Another typical example is the development of IL-modified materials based on carborane anions,^{10,11} which not only changed the solubility properties of traditional carboranes but also solved their sublimation problem at high temperature or over vacuum. Very recently, methyl orange was used to synthesize a series of photochromic ionic liquids, and the studies showed that the structure of the cations could affect the rate constant of the *cis* to *trans* thermal isomerisation.¹² Moreover, the poly(ionic liquid)-grafted silica materials were designed as a new chromatographic stationary phase, and the silica phase with methyl orange dye as counter anions exhibited ultra-high selectivity towards shape-constrained isomers.¹³ Therefore, the development of new IL-modified materials or compounds with the aim of acquiring improved properties or enhanced performance, while the material remains the key feature of itself, will be one of new hot topics in the future IL R&D.

The traditional anion dyes, *e.g.* methyl red (MR) and methyl orange (MO), are widely used in the chemistry laboratory and

industrial processes. During the actual applications, however, the use and availability of MR and MO is somewhat limited due to the solubility problem, *e.g.* MO only applies to aqueous solutions while MR is soluble only in some non-aqueous systems. In this paper, we attempt to demonstrate a strategy of modifying the traditional dyes with ionic liquids, *i.e.* to design and synthesize a new class of IL-modified dyes, which are composed of three IL cations ([BMIm]⁺, [HMIm]⁺, and [BPy]⁺) and two dye anions ([MO]⁻ and [MR]⁻) (Fig. 1).

Six IL-modified dyes, *i.e.* [BMIm]MO, [BMIm]MR, [HMIm]MO, [HMIm]MR, [BPy]MO, and [BPy]MR, were obtained with the yields of 84–92%. NMR and ESI-MS analyses showed that all the structures of the salts prepared were in good agreement with that as expected, and their thermal properties, solubilities, p*K*_a values, and the indicating performance in acidic aqueous and non-aqueous solutions were comparatively investigated. The details of ILs synthesis, characterization, and property measurement were given in the electronic supplementary information (ESI†).

In comparison with MR and MO, the properties of six IL-modified dyes have changed greatly. For example, the melting points of MO and MR are 300 °C and 180 °C, respectively; however, the melting points of [BMIm][MO], [HMIm][MO], and [BPy][MO] are 189 °C, 140 °C, and 104 °C, respectively, while [BMIm]MR, [HMIm]MR, and [BPy]MR have no freezing and melting but exhibit a glass transition of <25 °C in a cooling and heating cycle. Such a significant decrease in the melting points after ILs-modification might be explained by the lack of carboxyl dimers in IL-modified [MR]⁻-based dyes due to the replacement of a proton with a bulky and asymmetric cation, which in turn causes the disruption of the crystal packing. For the IL-modified [MO]⁻-based dyes, they also exhibited relatively high melting points of >100 °C, although their melting points also decreased obviously compared to MO. As is known, MR is insoluble in water but partly soluble in many organic solvents, while the MO is almost insoluble in most organic solvents but slightly soluble in cold



Fig. 1 Structure and abbreviations of IL-modified dyes.

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water. For six IL-modified dyes, however, they are not only partly soluble in water but also partly dissolved in ethanol, methanol, CH_2Cl_2 , CHCl_3 , DMSO, and DMF, suggesting that the ILs-modification obscures the lines between inorganic salts and organic compounds, and endows them with the characteristics of organic molecules (*i.e.* the enhanced solubility in non-aqueous system), while maintaining the property of inorganic salts (*i.e.* partly soluble in aqueous solution).

As one of the most important properties of the dyes as the indicator, the dissociation constants ($\text{p}K_{\text{a}}$) of six IL-modified dyes in the aqueous solution were determined, Table 1, Fig. S1–S2.† In comparison with MO (3.4), the $\text{p}K_{\text{a}}$ values (3.3~3.4) of three IL-modified [MO]-based dyes only change a little or remain fundamentally unchanged, suggesting that IL-modified [MO]-based dyes exhibit a similar dissociation equilibrium in aqueous solution. For three IL-modified [MR]-dyes, however, their $\text{p}K_{\text{a}}$ values (4.5~4.6) are obviously lower than that of MR (5.0), suggesting that the replacement of $[\text{H}]^+$ by the bulky cations (*i.e.* $[\text{BMIm}]^+$, $[\text{HMIm}]^+$, and $[\text{BPy}]^+$) result in an obvious change in the acidity.

Before and after ILs modification, the changes of the sensing performance towards the acids in aqueous and non-aqueous solutions were studied below. In comparison with MR, it was evident that $[\text{BMIm}][\text{MR}]$ in aqueous solutions with varied pHs exhibited a remarkably enhanced indicating performance with well-differentiated color changes, while, due to insolubility in aqueous solutions, the MR almost did not work under the same conditions (Fig. 2). Only one isosbestic point could be observed at 488 nm (Fig. 2, right picture), indicating that a two-composition equilibrium exists and varies with the acidity. At $\text{pH} = 1$, a band ascribed to the zwitterionic form of the $[\text{MR}]^-$ anion can be exclusively observed at 523 nm with the molar absorption coefficient (ϵ) of $2.28 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$. As the pH increased from 1 to 7, the absorbance at 523 nm decreased gradually, with concomitant appearance and increase of a new absorption band at 415–430 nm, which can be attributed to the azo form of the anionic species. In aqueous solutions of varied pHs and with the naked eye, there are no significant differences in their indicating behavior by changing the cations from $[\text{BMIm}]^+$ to $[\text{HMIm}]^+$ or $[\text{BPy}]^+$. However, the changes of cations indeed influence their UV-vis spectra and thus the indicating behaviour (Fig. S3, S4†). For example, $[\text{HMIm}][\text{MR}]$ and $[\text{BPy}][\text{MR}]$ showed comparable λ_{max} values (530 vs. 531 nm), which is obviously bathochromic shifted as compared to $[\text{BMIm}][\text{MR}]$, but different in corresponding ϵ values (1.40×10^4 and $2.06 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively). Furthermore, their sensitivity to acids is greatly enhanced when the cation changed, particularly in the low pH range. For example, when the pH value increased from 1 to 2, the decrease of the absorbance is about 20% for $[\text{HMIm}][\text{MR}]$ and $[\text{BPy}][\text{MR}]$ (Fig. S3, S4†), larger than the case of $[\text{BMIm}][\text{MR}]$. These suggested that the potential of the IL-modified dyes in aqueous solutions, and their sensitivity towards the free

Table 1 The $\text{p}K_{\text{a}}$ comparison of IL-modified dyes, MR and MO

Dyes	$\text{p}K_{\text{a}}$ values	Dyes	$\text{p}K_{\text{a}}$ values
MO	3.4	MR	5.0
$[\text{BMIm}]\text{MO}$	3.3	$[\text{BMIm}]\text{MR}$	4.5
$[\text{HMIm}]\text{MO}$	3.3	$[\text{HMIm}]\text{MR}$	4.5
$[\text{BPy}]\text{MO}$	3.4	$[\text{BPy}]\text{MR}$	4.6

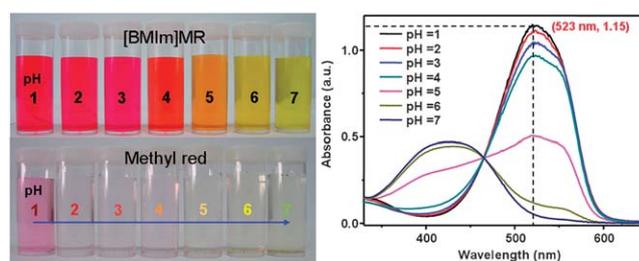


Fig. 2 (Left) pH-dependent color change of $[\text{BMIm}]\text{MR}$ ($5 \times 10^{-5} \text{ M}$) and MR in acidic aqueous solutions (from left to right: $\text{pH} = 1-7$). (Right) UV-vis spectra of $[\text{BMIm}]\text{MR}$ ($5 \times 10^{-5} \text{ M}$) in the aqueous solutions of $\text{pH} = 1-7$.

proton, can be improved *via* the ILs-strategy and further optimized through rational design of the cations.

Since both MR and $[\text{BMIm}][\text{MR}]$ are soluble in ethanol, their sensing performance towards the dissociated proton in ethanol with variation of HOTf ($\text{CF}_3\text{SO}_3\text{H}$) concentrations was further comparatively studied. Although it appears that no significant difference can be observed by the visual discrimination, some substantial differences do exist in their UV-vis spectra (Fig. 3). Firstly, as the HOTf concentration in ethanol solutions increases from 10^{-6} M to 10^{-1} M , the MR only displays one isosbestic point at 488 nm, but two isosbestic points can be observed from the UV-vis spectra of $[\text{BMIm}][\text{MR}]$. Secondly, at the low concentrations of the HOTf (*e.g.* $<10^{-5} \text{ M}$), a new absorption peak at 400 nm could be observed for the $[\text{BMIm}][\text{MR}]$; however, this absorption is not obvious for the MR. This indicates that the former exhibit higher sensitivity towards the dissociated proton of low concentrations. Thirdly, although the same amount of the indicator ($3 \times 10^{-5} \text{ M}$) was employed in the experiments respectively, the molar absorption coefficients of the MR were obviously higher than those of $[\text{BMIm}][\text{MR}]$ under the same conditions. For example, the ϵ values of the MR and $[\text{BMIm}][\text{MR}]$ are $5.08 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$ and $2.73 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively, and their maximum absorption wavelengths all centered on 523 nm. According to above results, we deduce that these IL-modified [MR]-based dyes exhibit a new indicating mechanism towards the dissociated proton, which is obviously different from that of the MR (Fig. S5†). As the HOTf concentration in ethanol increases from 10^{-6} M to 10^{-1} M , the interactions between the proton and the $[\text{BMIm}][\text{MR}]$ pass through two stages. However, for the MR, the azo form directly transfers to the zwitterionic form as the acid concentrations increased. This mechanism is consistent with the experiment results in Fig. 3. As to the reason why only one isosbestic point of

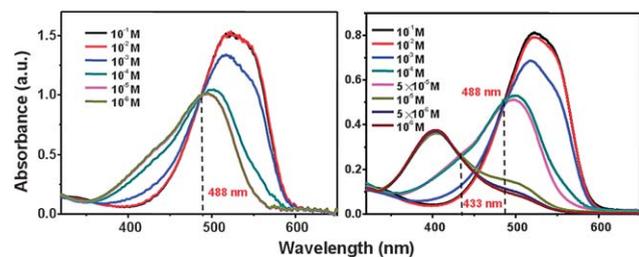


Fig. 3 (Left) UV-vis spectra of the MR ($3 \times 10^{-5} \text{ M}$) in ethanol with varied HOTf concentrations. (Right) UV-vis spectra of $[\text{BMIm}]\text{MR}$ ($3 \times 10^{-5} \text{ M}$) in ethanol with varied HOTf concentrations.

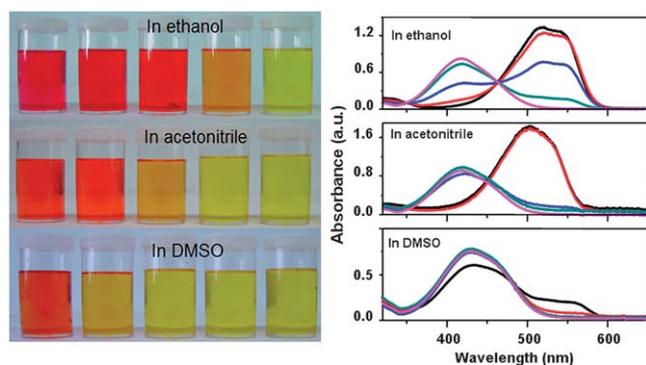


Fig. 4 (Left) Indicating pictures of [BMIm]MO (3×10^{-5} M) in ethanol, acetonitrile and DMSO with varied HOTf concentrations, from left to right: [HOTf] = 10^{-1} M \sim 10^{-5} M. (Right) UV-vis spectra of [BMIm]MO (3×10^{-5} M) in ethanol, acetonitrile and DMSO with varied HOTf concentrations, respectively. Black line: 10^{-1} M, red line: 10^{-2} M, blue line: 10^{-3} M, green line: 10^{-4} M, magenta line: 10^{-5} M.

[BMIm][MR] is seen in the aqueous solutions (Fig. 2), we attribute it to the insolubility of the trace resulting MR in aqueous solutions.

MO is mainly used for acid–base titration in aqueous solutions, since it cannot be dissolved in most non-aqueous systems. However, after the IL modification, the IL-modified [MO]-based dyes are soluble or partly soluble in non-aqueous solutions. Therefore, the sensing performance of [BMIm]MO towards the dissociated proton in organic solvents was also investigated. A typical strong acid HOTf ($\text{CF}_3\text{SO}_3\text{H}$) and a weak acid AcOH (acetic acid) were chosen as the acid sources (concentration: 10^{-1} M to 10^{-5} M), respectively. For three solvents, ethanol exhibits the characteristics of an amphoteric solvent similar to water, while DMSO and acetonitrile possess the ability of weakly accepting a proton through hydrogen bonding.

It can be seen that, from Fig. 4, the indicating performance of [BMIm]MO in the three solvents is obviously different. Firstly, the color change points of [BMIm]MO in three solvents are different. When the HOTf concentration was 10^{-3} M, the colours of the [BMIm]MO in ethanol, acetonitrile, and DMSO solutions are red, orange, and yellow, respectively. Since the colour changes of the solutions are mainly caused by the transformation between the azo form and the zwitterionic form, which is unrelated to the dissociation degree of the [BMIm]MO, the differences in indicating performance might be caused by different dissociation degrees of the strong acid HOTf in non-aqueous solutions. That is, the dissociations of HOTf strongly depend on the deprotonation ability of the solvent itself. When the HOTf is replaced with a weak acid AcOH in the three solutions with varied acidic concentrations, almost no colour changes and even the changes in the absorption wavelength or the absorption intensity can be observed (Fig. S11, S12[†]), suggesting that the weak acid AcOH in the three solvents almost does not dissociate. Therefore, these IL-modified [MO]-based dyes should be potentially sensitive materials to evaluate the dissociations of acids in non-aqueous solvents. Secondly, excepting that some difference in the absorption wavelengths and the absorption intensity could be clearly observed from their UV-vis spectra shown in Fig. 4, the [BMIm]MO in three solvents only exhibited one isosbestic point, *i.e.* at 464 nm in ethanol, at 452 nm in acetonitrile, and at 485 nm in DMSO. This suggested

that the indicating mechanism of these IL-modified [MO]-derivatives might be similar to that of MO, as shown in Fig. S13.[†] This point can also be proven to a certain extent from the slight changes of their pK_a values in the aqueous solution before and after the IL modification.

In conclusion, a new class of IL-modified dyes was synthesized and characterized. After ILs modification, the physicochemical properties of these dyes including the melting point, solubility, and the dissociation constants were changed or enhanced greatly. Among them, the IL-modified [MR]-based dyes exhibited enhanced sensing performance towards the acids than MR in aqueous solution and a different indicating mechanism from MR in non-aqueous solutions, while the IL-modified [MO]-based dyes displayed good sensitivity toward the dissociated proton in non-aqueous systems. This work will expand the application of indicator materials towards the acids in potential fields such as sensory systems, protein determination, and fluorescence resonance energy transfer, and more importantly, a new concept of developing novel modified materials with the ILs is presented.

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