Supplementary Material (ESI) for Analyst

Ionic Liquid-Modified Dyes and Their Sensing Performance toward Acids in Aqueous and Non-aqueous Solutions

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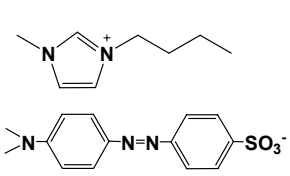
Experimental

General experimental

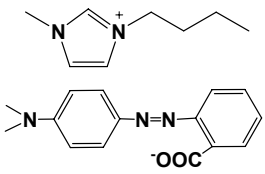
All IL-modified dyes based on $[MR]^-$ and $[MO]^-$ anions were prepared and purified according to a similar method described elsewhere[1]. In a typical procedure, the silver salts of methyl orange (AgMO) and methyl red (AgMR) were firstly prepared freshly before use. The precursors [BMIm]Br, [HMIm]Br, and [BPy]Br could be easily obtained according to the method reported previously[2]. The slightly excess silver salts was added to a dichloromethane solution of the organic bromides (*i.e.* [BMIm]Br, [HMIm]Br, or [BPy]Br), and the solution was stirred for 4 h at room temperature. Silver bromide was removed from the solutions by filtration. To ensure complete removal of silver salts from the product, the filtrate containing the desired product were cooled in a freezer overnight before further filtration. Finally, the desired products with high purities could be obtained with the yields of 84-92%.

^1H and ^{13}C NMR data were recorded on a Bruker AMX FT 400-MHz NMR spectrometer. Chemical shifts were reported downfield in parts per million (ppm, δ) from a tetramethylsilane reference. Electrospray ionization mass spectra were recorded on a Bruker Daltonics APEX II 47e FTMS, and the samples were dissolved in methanol/H_2O. Ultra-Vis spectra were conducted on an Agilent 8453 UV-vis spectrophotometer. Measurements of glass-transition temperatures, melting and freezing points were carried out on a Mettler-Toledo differential scanning calorimeter, model DSC822^e, and the data were evaluated using the Mettler-Toledo STARe software version 7.01. To make sure that water in the nonaqueous systems was excluded as much as possible, three solvents were treated over NaY and the water contents were all < 20 ppm, which were determined by means of a Karl-Fischer titration (Metrohm 831KF coulometer).

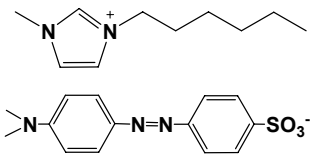
Typical analytical data:



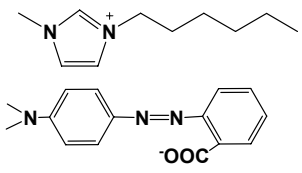
[BMIm][MO]: Orange solid powder; T_m = 189°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.13 (1H, s), 7.82-7.70 (8H, m), 6.85-6.82 (2H, q), 4.16-4.13 (2H, t), 3.85 (3H, s), 3.06 (6H, s), 1.78-1.71 (2H, m), 1.29-1.20 (2H, m) 0.90-0.87 (3H, t). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 152.6, 152.1, 149.1, 142.6, 136.5, 126.5, 124.8, 123.6, 122.2, 121.2, 111.5, 48.5, 35.7, 31.3, 18.7, 13.2. MS (ESI^+) calcd: m/z: 139.1229 ($[BMIm]^+$); found: m/z:139.1232.



[BMIm][MR]: deep red viscous liquid; T_g = -10°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.13 (1H, s), 7.76-7.67 (6H, m), 7.40-7.37 (2H, m), 7.30-7.25 (2H, m), 6.80-6.78 (1H, d), 6.60-6.58 (1H, d), 4.14-4.10 (2H, t), 3.82 (3H, s), 3.03-3.00 (6H, d), 1.76-1.69 (2H, m), 1.27-1.17 (2H, m), 0.86-0.85 (3H, t). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 170.2, 152.1, 149.1, 136.9, 124.6, 123.5, 122.2, 111.3, 48.4, 35.6, 31.3, 18.7, 13.2. MS (ESI^+) calcd: m/z: 139.12 ($[BMIm]^+$); found: m/z:139.12.



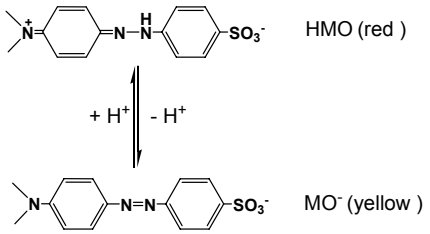
[HMIm][MO]: Orange solid powder; T_m = 140°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.13 (1H, s), 7.82-7.70 (8H, m), 6.85-6.81 (2H, q), 4.15-4.11 (2H, t), 3.85 (3H, s), 3.06 (6H, s), 1.78-1.71 (2H, m), 1.26-1.18 (6H, m), 0.86-0.83 (3H, t). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 152.6, 152.1, 149.1, 136.5, 126.5, 124.8, 123.6, 122.2, 121.2, 111.5, 111.2, 48.7, 35.7, 30.5, 29.3, 25.1, 21.8, 13.8. MS (ESI^+) calcd: m/z: 167.15 ($[HMIm]^+$); found: m/z:167.15.



[HMIm][MR]: deep red viscous liquid; T_g = -3°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.44 (1H, s), 7.80-7.70 (6H, m), 7.40-7.36 (1H, m), 7.30-7.23 (1H, m), 6.79-6.77 (1H, d), 6.60-6.59 (1H, d), 4.15-4.12 (2H, t), 3.84 (3H, s), 3.03-3.00 (6H, d), 1.78-1.73 (2H, q), 1.26-1.24 (6H, m), 0.86-0.85 (3H, t). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.4, 152.7, 152.1, 149.0, 136.8, 132.3, 129.3, 128.7, 124.5, 123.5, 122.2, 118.8, 115.4, 111.3, 48.7, 35.6, 30.5, 29.3, 25.3, 21.8, 13.8. MS (ESI^+) calcd: m/z: 167.15 ($[HMIm]^+$); found: m/z:167.15.

The p*K*a's determination of six IL-modified dyes in aqueous solutions:

Take the [BMIm]MO for an example, in the acidic aqueous solutions, there is an equilibrium as follows:



$$K_a = \frac{[H^+][MO^-]}{[HMO]} \quad (1)$$

$$C_{HMO} = [HMO]+[MO^-] \quad (2)$$

$$A = A'_{HMO} + A'_{MO^-} \quad (3)$$

According to the (1), (2) and (3), the following equation could be obtained.

$$A = \frac{A_{HMO}[H^+] + A_{MO^-} - K_a}{K_a + [H^+]} \quad (4)$$

That is, $$pK_a = \log\frac{(A - A_{MO^-})}{(A_{HMO} - A)} + pH \quad (5)$$

Where C_{HMO} is the total concentration of the [BMIm][MO]; A means the absorbances of the solutions containing the [BMIm][MO]; A_{HMO} means the absorbance of the solution when all the [MO] anion exists in the form of the acid (HMO), and A_{MO^-} is the absorbance of the solution when all the [MO] anion exists in the form of the base ($[MO]^-$).

Keeping the analytical concentration of the [BMIm][MO] and the ionic strength of the solution constant, a series of absorption curves could be obtained when the pH values of the solutions were changed (Fig. S2), and according to the linear graphic method ($\log\frac{(A - A_{MO^-})}{(A_{HMO} - A)}$ vs pH), the pKa value is exactly the intersection point of the line and the pH axis.

Before the experiments of pKa measurements, a series of buffer solutions with the pH of 2.5, 3.0, 3.5, 4.0, 4.5, 7.0 were prepared by sodium citrate, sodium dihydrogen phosphate, and distilled water, respectively, and a [BMIm][MO] solution (2.0×10^{-4} M), a KCl solution (2.5 M), and a HCl solution (2.0 M) were prepared, respectively. Into seven 50 mL volumetric flasks, 5.0 mL [BMIm][MO] solution and 2 mL KCl solution were introduced, respectively. Then, 2 mL HCl

solution (2.0 M) and six buffer solutions with different pHs were added into above seven flasks, respectively, the each solution was diluted with distilled water to the standard scale. Shake well before using, and measure the pH value of each solution. Finally, the absorbance values of these solutions with different pHs could be obtained according to their absorption curves (Fig. S2), and the pKa value could be calculated by the method described above.

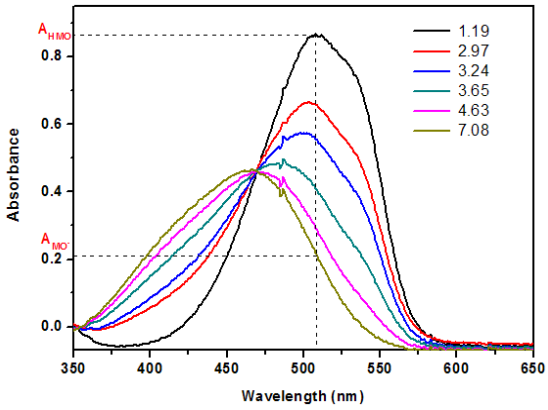


Fig. S1. The absorbance determination (A_{HMO} and A_{MO}) of [BMIm][MO] in the buffer solutions with different pHs

Take the case of [BMIm][MO], its p*K*a value (3.3) could be easily obtained by a linear graphic method (Fig. S1).

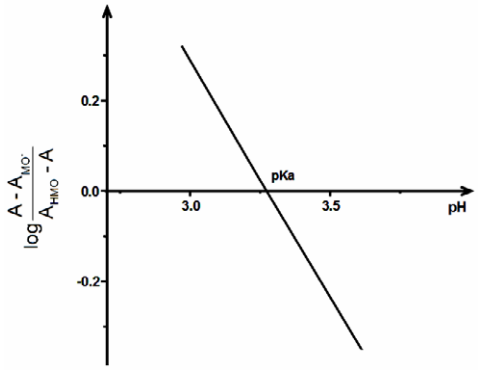


Fig. S2. The p*K*a determination of [BMIm][MO] by the linear graphic method.

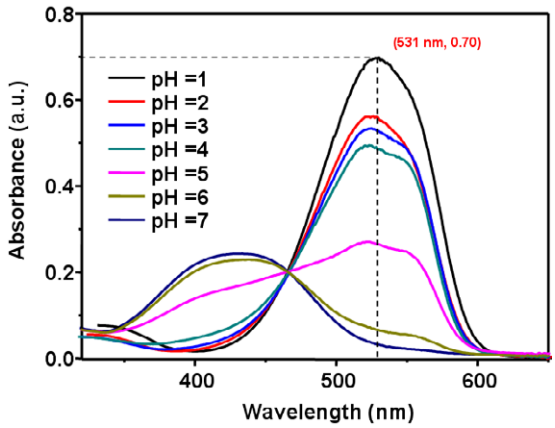


Fig. S3. UV-vis spectra of [HMIm][MR] (5×10^{-5} M) in the aqueous solutions of pH= 1-7.

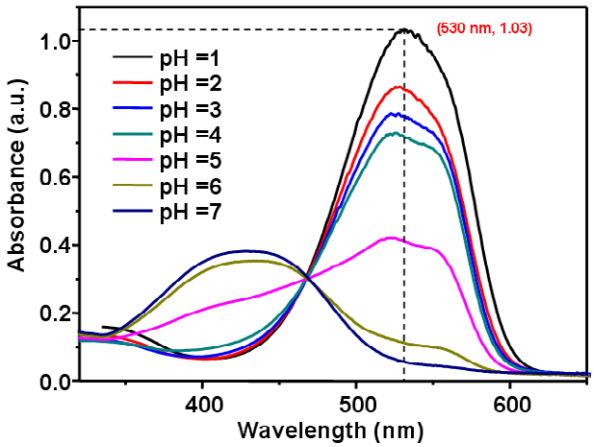


Fig. S4. UV-vis spectra of [BPy][MR] (5×10^{-5} M) in the aqueous solutions of pH= 1-7.

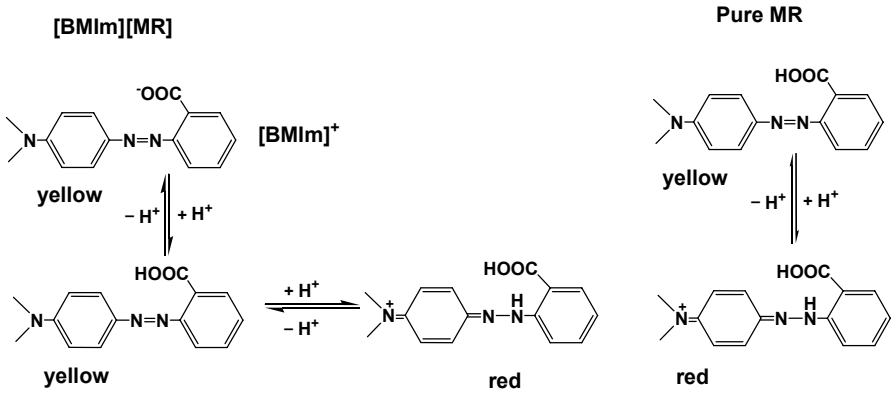


Fig. S5. Possible indicating mechanism of [BMIm]MR and pure MR in ethanol solution.

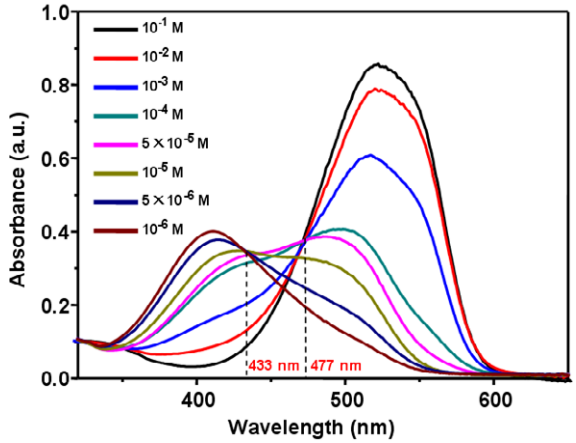


Fig. S6. UV-vis spectra of [HMIm][MR](3×10^{-5} M) in ethanol with varied HOTf concentrations

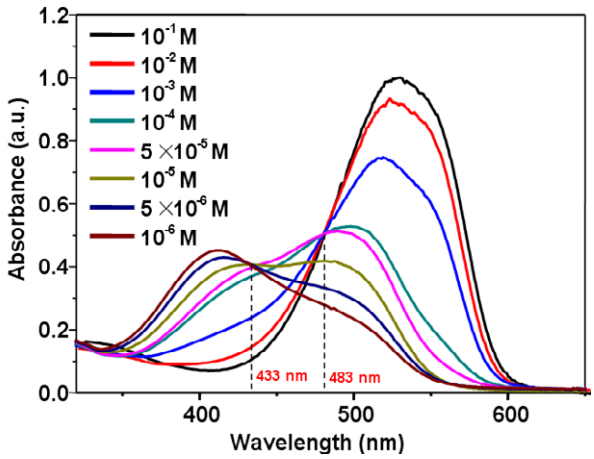


Fig. S7. UV-vis spectra of [BPy][MR] (3×10^{-5} M) in the ethanol with varied HOTf concentrations

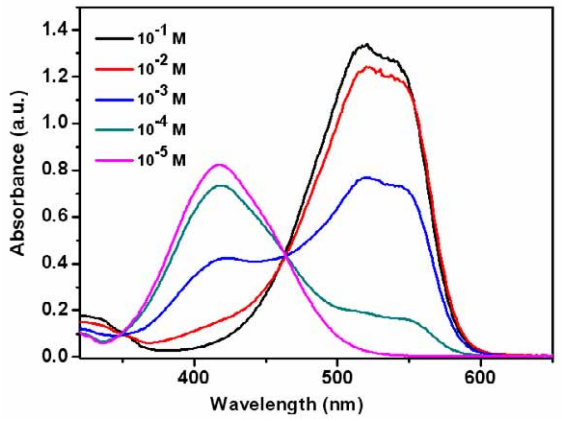


Fig. S8. UV-vis spectra of [BMIm]MO (3×10^{-5} M) in ethanol with different HOTf concentrations

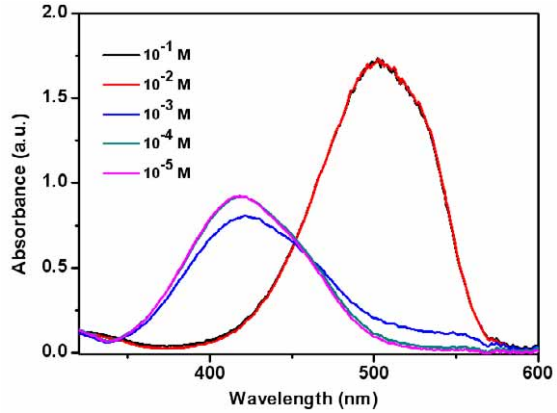


Fig. S9. UV-vis spectra of [BMIm]MO (3×10^{-5} M) in CH_3CN with different HOTf concentration

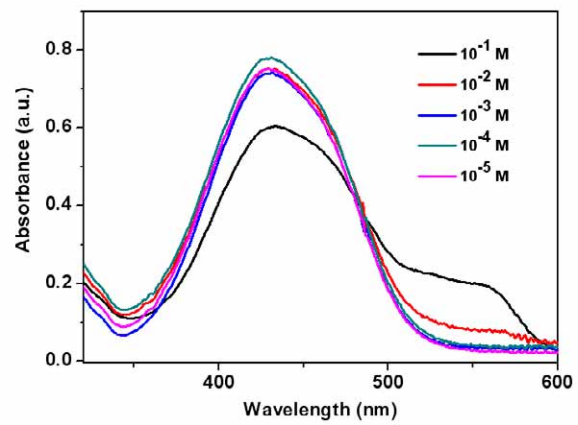


Fig. S10. UV-vis spectra of [BMIm]MO (3×10^{-5} M) in DMSO with different HOTf concentration

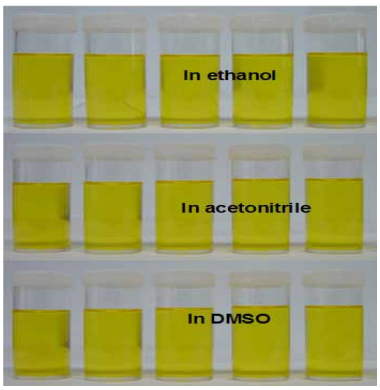


Fig. S11. Color changes of [BMIm]MO (3×10^{-5} M) in ethanol, acetonitrile and DMSO along with the concentration changes of AcOH. From left to right: [AcOH] = 10^{-1} M ~10^{-5} M

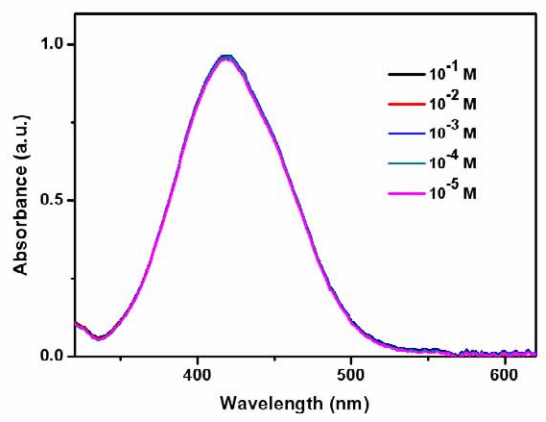


Fig. S12. UV-vis spectra of [BMIm]MO (3×10^{-5} M) in ethanol with different AcOH concentration

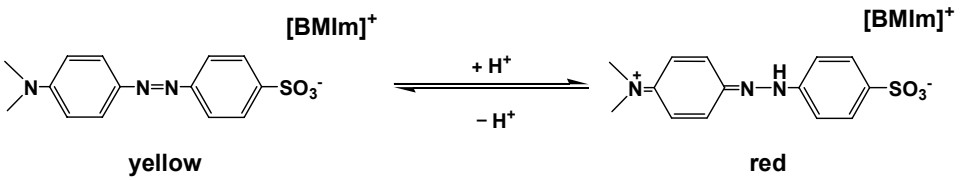


Fig. S13. The indicating mechanism of the [BMIm][MO] in ethanol, acetonitrile, or DMSO.

1 a) D. Gerhard, S. C. Alpaslan, H. J. Gores, M. Uerdingen, P. Wasserscheid, *Chem. Commun.* **2005**, 5080-5081; b) Y. Tzeng, C. Shen, T. Yu, *J. Chromatogr. A*, **2008**, 1193, 1-6.

2 P. Bonhôte, A. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, *Inorg. Chem.* **1996**, 35, 1168-1178.