Electronic Supplementary Information (ESI)

Large dynamic range dual-mode pH sensor via dye-doped ionic liquid fiber optofluidic lasers

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Supplementary Information List

1. Thermal conductivity measurement

A transient plane thermal conductivity tester (Hot Disk TPS2500S, Sweden) is utilized to obtain the thermal conductivity. The measurements are conducted at room temperature (25 °C) and at a frequency of 1 kHz, respectively. The thermal conductivity of 1-Butyl-3-methylimidazolium hexafluorophosphate ($BmimPF_6$) and glycerol aqueous solution (GAS) are 0.167 and 0.453 $W\cdot m^{-1}\cdot K^{-1}$, respectively. The low thermal conductivity results in a better photobleaching tolerance of RhB-doped $BmimPF_6$ lasing, as shown in Fig. 2b.

2. Quantum yield measurement

To determine the quantum yield of RhB, we measure the absorbance and fluorescence of RhB aqueous solution with different pH value in parallel with Rhodamine 6G (R6G) (in methanol). The absorbance tests are performed with an UV-Visible spectrophotometer (Specord-200, Analytik Jena AG). The fluorescence spectrum is examined using a fluorescence spectrophotometer. The absorption (or excitation) wavelength is fixed at 470 nm. The quantum yield can be calculated as below[1]

$$\Phi_x = \Phi_{ref} \times \frac{F_x}{F_{ref}} \times \left(\frac{n_x}{n_{ref}} \right)^2 \times \frac{f_{ref}}{f_x}, \qquad \textbf{(S1)}$$

where the subscripts x and ref represent the sample to be tested and the standard reference solution, respectively. Φ is the quantum yield, F is the integrated area of the fluorescence emission spectra, n is RI of the solvent, $f = 1\text{-}10^{-A}$, A is the absorbance at the excitation wavelength. Further, we calculate that the Φ increases from 0.89 to 0.48 in the pH range 7.20 -11.17 ($\Phi_{ref} = \Phi_{R6G} = 0.93$ for R6G in methanol).[2]

3. Photophysical parameters of RhB-doped $BmimPF_6$ in acidic environments

The photophysical properties of RhB-doped BmimPF6 in acidic environments, including absorbance (ε), quantum yield (Φ), and fluorescence lifetime (τ) are measured, as shown in Fig. S1.

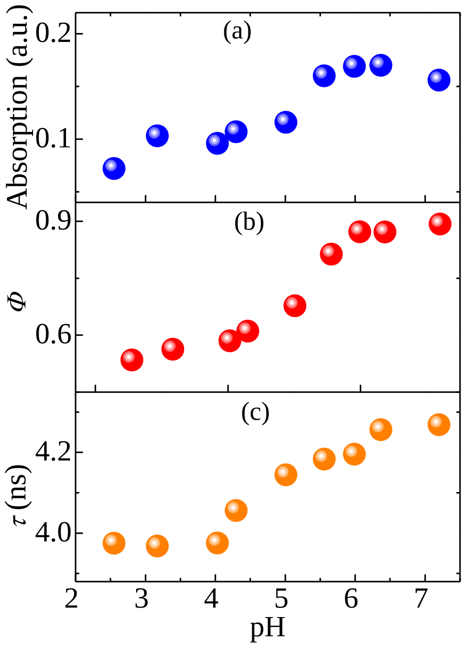

Fig. S1. Photophysical parameters of RhB-doped $BmimPF_6$ in acidic environments. (a) Absorbance (ε), (b) quantum yield (Φ), and (c) fluorescence lifetime (τ) as a function of pH..

4. Absorption cross-section measurement

The measurement of absorbance is used to characterize the dye absorption cross-section. A UV-Visible spectrophotometer (Specord-200, Analytik Jena AG) is used to measure the absorption spectrum.[3] The absorbance spectra of 20 μM RhB with different pHs are measured. The $\sigma_a(\lambda)$ is calculated based on the following equation:[4]

$$\sigma_a(\lambda)=\frac{-\left[\ln\left(10^{-A(\lambda)}\right)\right]}{n\left(\text{molecules}/\text{cm}^3\right)\cdot l\left(\text{cm}\right)}, \quad \textbf{(S2)}$$

where l is the length of light path, n is the concentration of dye, and A is the absorbance, respectively. The absorption cross-section is shown in Fig. S2.

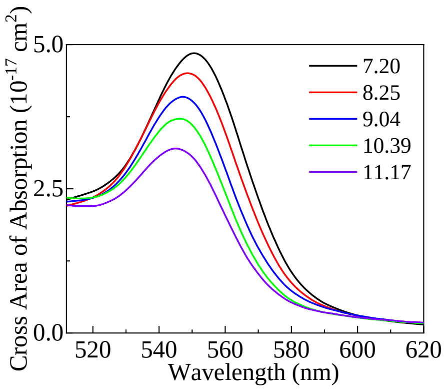

Fig. S2. Absorption cross section of RhB under different pH conditions.

5. Fluorescence lifetime measurement

A fluorescence lifetime measurement system is used to characterize the lifetime of RhB. We measure their transient photoluminescence (PL) decay spectra under different pH values using fluorescence lifetime spectrometer (C11367, Hamamatsu). The processed data is then fitted to an exponential decay function to extract the lifetime value. As shown in Fig. S3 (a), the fluorescence lifetime of RhB in $BmimPF_6$ and GAS are 4.28 and 3.77 ns, respectively. In addition, as shown in Fig. S3 (b), the fluorescence lifetime of RhB increases from 4.28 to 4.09 ns in the pH range 7.20-11.17.

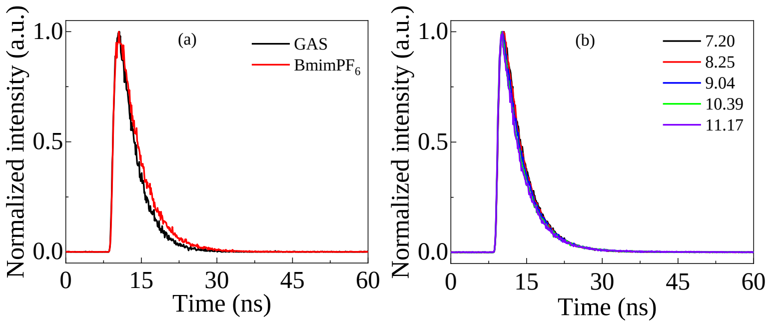

Fig. S3. Fluorescence lifetime measurement. (a) The fluorescence lifetime of RhB in $BmimPF_6$ and GAS. (b) The fluorescence lifetime of RhB under different pH.

6. Emission cross-section measurement

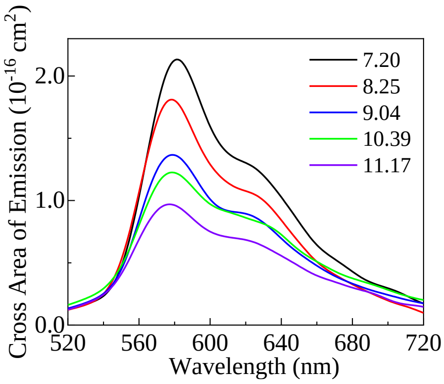

Fig. S4. Emission cross section of RhB under different pH conditions.

The $\sigma_e(\lambda)$ is obtained from the fluorescence emission spectra of RhB aqueous solution using Equation[5]

$$\sigma_e(\lambda) = \frac{g(\lambda)\lambda^4\Phi}{8\pi c\tau_F n_2^{\,2}}, \tag{S3}$$

where c is the speed of light in vacuum, τ_F is the fluorescence lifetime of RhB molecule, $g(\lambda) = I(\lambda)/\int I(\lambda)d\lambda$ is the normalized line-shape function of the fluorescence spectra, and Φ is the fluorescence quantum yield of the dye molecules, respectively. Using experimentally measured data as detailed previously, the emission cross-section under different pH conditions is plotted in Fig. S4.

7. The effect of concentration on the lasing behaviors of RhB-doped $BmimPF_6$

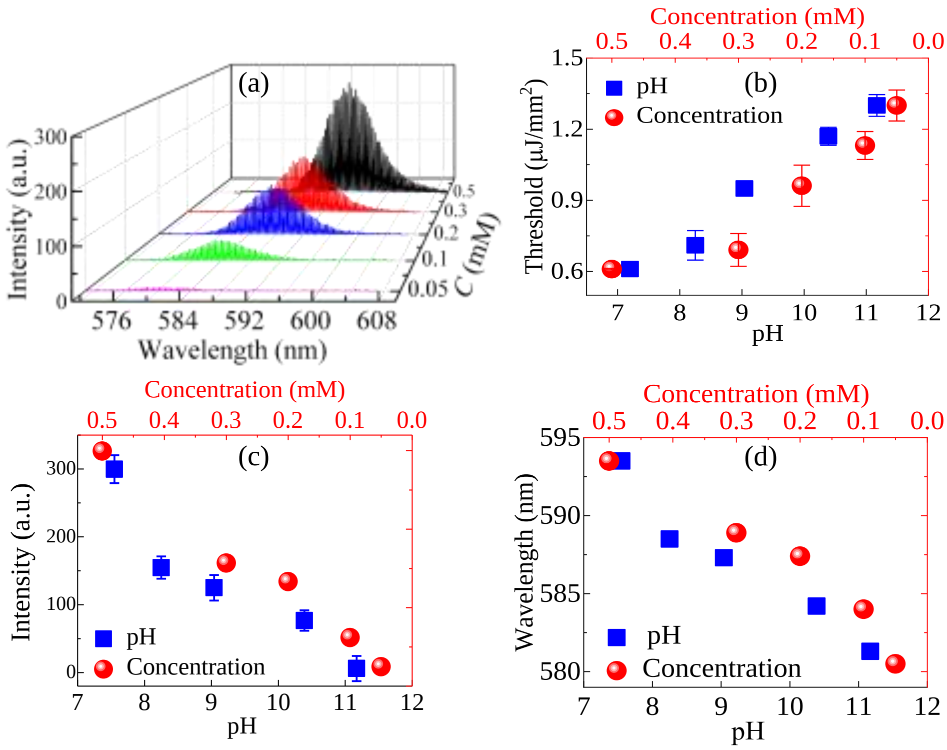

Fig. S5. (a) Lasing spectra of RhB-doped $BmimPF_6$ with various concentrations. The pH value of the $BmimPF_6$ solution is kept at pH= 7.20, while the pump energy density (PED) = 1.77 μJ mm^{-2}. (b) Comparison of lasing threshold of RhB-doped $BmimPF_6$ (pH =7.20) at various concentrations and 0.5 mM RhB-doped $BmimPF_6$ at various pH values. (c) Comparison of the lasing intensity of RhB-doped $BmimPF_6$ (pH =7.20) at various concentrations and 0.5 mM RhB-doped $BmimPF_6$ at various pH values. (d) Comparison of the lasing center wavelength of RhB-doped $BmimPF_6$ (pH =7.20) at various concentrations and 0.5 mM RhB-doped $BmimPF_6$ at various pH values.

In order to verify the hypothesis of dye concentration quenching caused by the aggregation of dye molecules in the alkaline aqueous solvent. We carry out a control experiment, *i.e.* the lasing emission properties of RhB-doped $BmimPF_6$ (pH =7.20) at different concentrations (0.05 to 0.5 mM) are investigated. As shown in Fig. S5 (a), the lasing emission behaviors under different dye concentrations are very similar to that under various pH values in alkaline environments in Fig. 3. *i.e.*, when the dye concentration decreases from 0.5 mM to 0.05 mM, the lasing center wavelength blueshifts from 592.9 nm to 580.5 nm with a sharp decrease in the lasing emission intensity. The maximal lasing intensity attenuation factor (I_{max}/I_{min}) is ca. 78-fold at 0.05 mM. Further, the effects of concentration (from 0.5 mM to 0.05 mM) and pH (7.20-11.17) on the lasing characteristics (lasing threshold, lasing intensity, central wavelength) are also investigated, respectively. As shown in Fig. S5, the effects of concentration and the effects of pH on lasing emission are shown a very good agreement.

References

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