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Supporting Information

High sensitivity pH sensing by using a ring resonator laser integrated into a microfluidic chip

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I. Theoretical analysis of optofluidic ring resonator dye lasers

The optofluidic dye laser can be modeled as a four-energy-level laser system. Let \( N_1 \) be dye concentration in the exited state and \( n_t \) be total dye concentration. \( Q_{\text{abs}}, Q_{\text{leak}}, \) and \( Q_{\text{scat}} \) are the quality factors of a ring resonator related to the energy losses caused by the cavity absorption, light leakage, and scattering, respectively. The total quality factor \( (Q_{\text{tot}}) \) of a Whispering Gallery Mode (WGM) in a ring resonator can be written as: 

\[
Q_{\text{tot}} = Q_{\text{abs}} + Q_{\text{leak}} + Q_{\text{scat}} \quad [1].
\]

Then, the population inversion condition can be expressed as \([2-4]\]

\[
N^e(\lambda) \geq \left( n_t - N_1 \right) \sigma_a(\lambda) + \frac{2\pi m}{\lambda \sigma_{\text{leak}}},
\]

where \( \sigma_a(\lambda) \) and \( \sigma_e(\lambda) \) are the dye absorption cross-section and the dye emission cross-section at the lasing wavelength \( \lambda_l \), respectively. \( m = n_1/n_2 \) is the effective refractive index (RI) of the WGMs, where \( n_1 \) and \( n_2 \) are the RIs of the optical fiber and the gain cladding solution, respectively. At threshold, Eq. (S1) can be written as:

\[
\gamma = \frac{N_1}{n_1} = \frac{\sigma_a(\lambda)}{\sigma_a(\lambda) + \sigma_e(\lambda)} \left( 1 + \frac{Q_{\text{abs}}}{Q_{\text{tot}}} \right),
\]

where \( \gamma \) is defined as the fraction of gain molecules in the excited state at the threshold. \( Q_{\text{abs}} = 2\pi m/\eta n_0 \sigma_a(\lambda) \), \( \eta \) is the ratio of the evanescent-field volume to that of the whole WGM, which is estimated to around 0.02 \([1]\).

In our experiment, \( n_1 = 1.458, n_2 = 1.333 \), and the diameter of the optical fiber is 200 \( \mu \)m. Then, the calculated \( Q_{\text{tot}} \) will be beyond \( 10^{19} \) \([1]\), which can be neglected as compared to the \( Q_{\text{abs}} \approx 10^9 \). According to Ref. \([5]\), \( Q_{\text{scat}} \) is of the order of \( 10^{12} \) and can also be neglected. Figure S2 presents the calculated \( Q_{\text{abs}} \) under different pH conditions.

According to the laser theory, the lasing threshold, \( I_{\text{th}} \), is determined by:

\[
I_{\text{th}} = \frac{\gamma}{1 - \gamma} \quad (S3)
\]

Through Eqs. (S2)-(S3), one can calculate the lasing threshold, in which the \( \sigma_a(\lambda) \) and \( \sigma_e(\lambda) \) of disodium fluorescein (DSF) aqueous solution are measured in the experiments detailed below in section II and V, respectively.

II. 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 \([6]\). The absorbance spectra of 20 \( \mu \)M DSF with different pHs are measured \([7]\). The \( \sigma_a(\lambda) \) is calculated based on equation:

\[
\sigma_a(\lambda) = \frac{-\ln(10^{10A(\lambda)})}{n(\text{molecules/cm}^3)l(\text{cm})},
\]

where \( l \) is the length of light path, \( n \) is the concentration of dye, and \( A \) is the absorbance. The absorption cross-section is shown in Figure S1. The \( \sigma_a(\lambda) \) at the lasing wavelength (523 nm) is estimated to be \( 5.31 \times 10^{-18} \) to \( 7.96 \times 10^{-18} \) in the pH range 6.51-12.30.
III. Fluorescence lifetime measurement

A fluorescence lifetime measurement system is used to characterize the lifetime of DSF. 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 Figure S3, the fluorescence lifetime of DSF increases from 4.92 to 5.38 ns in the pH range 6.51-12.30.

IV. Quantum yield measurement

To determine the quantum yield of DSF, we measured the absorbance and fluorescence of DSF 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 [8].
\[ \Phi_x = \Phi_{\text{ref}} \times \frac{F_x}{F_{\text{ref}}} \times \left( \frac{n_x}{n_{\text{ref}}} \right)^2 \times \frac{f_{\text{ref}}}{f_x}, \quad (S5) \]

where the subscripts \( x \) and \( \text{ref} \) represent the sample to be tested and the standard reference solution, respectively. \( \Phi \) is the quantum yield, \( F \) is the integrated area of the fluorescence emission spectra, \( n \) is RI of the solvent, \( f = 1 - 10^{-A} \), \( A \) is the absorbance at the excitation wavelength. We calculate that the \( \Phi \) increases from 0.29 to 0.92 in the pH range 6.51 - 12.3 (\( \Phi_{\text{ref}} = \Phi_{\text{R6G}} = 0.93 \) for R6G in methanol) [9].

V. Emission cross-section measurement

The \( \sigma(\lambda) \) is obtained from the fluorescence emission spectra of DSF aqueous solution using equation [10]

\[ \sigma_x(\lambda) = \frac{g(\lambda) \lambda^4 \Phi}{8\pi c \tau_x n_x^2}, \quad (S6) \]

where \( c \) is the speed of light in vacuum, \( \tau_x \) is the fluorescence lifetime of DSF molecule, \( g(\lambda) = \int \lambda f(\lambda) \text{d}\lambda \) is the normalized line-shape function of the fluorescence spectra, and \( \Phi \) is the fluorescence quantum yield of the dye molecules. Using experimentally measured data as detailed previously, the emission cross-section under different pH conditions is plotted in Figure S4. The \( \sigma(\lambda) \) at the lasing wavelength (523 nm) is estimated to be \( 3.83 \times 10^{-17} \) to \( 1.61 \times 10^{-16} \) in the pH range 6.51-12.30.

![Fig. S4. Emission cross section of DSF under different pH conditions.](image)

VI. Sensitivity analysis

According to the laser theory, a normalized pumping rate relative to threshold value is given by [11]

\[ r \equiv \frac{R_p}{R_{p,\text{th}}}, \quad (S7) \]

where \( R_p \) is pumping rate in atoms per second, \( R_{p,\text{th}} \) is threshold pumping rate in atoms per second. The below-threshold region\( (r<1) \) is then described by the approximate results [11]

\[ n_{\text{ss}} = \frac{r}{1-r}, \quad \text{below threshold, } r<1 \quad (S8) \]

The approximate formulas for the laser behavior above threshold are thus [11]
\[ n_{ss} = r - 1, \quad \text{above threshold, } r > 1 \quad (S9) \]

where \( n_{ss} \) is the number of output photons.

We can rewrite \( r = I_P/I_{th} \), where \( I_P \) is the pump power, and \( I_{th} \) is the threshold pump power. So the intensity of the output light \( I \propto n_{ss} \).

\[
I \approx \begin{cases} 
\frac{r}{1-r} \frac{I_p}{I_{th}} & \text{when } r < 1, \text{ below threshold} \\
1 - \frac{I_p}{I_{th}} & \text{when } r > 1, \text{ above threshold} 
\end{cases} \quad (S10)
\]

The sensitivity capabilities of optofluidic sensing can be predicted by calculating the effect of the dye parameters on the lasing threshold, defined as \([12]\)

\[
S_\alpha = \left| \frac{dI/I}{d\alpha/\alpha} \right|, \quad (S11)
\]

where \( \alpha \) is the parameter examined \((\alpha = \sigma_a, \tau, \Phi)\).

Through Eqs. (S10)-(S11), the sensitivity below and above the threshold can be calculated by

\[
S_\alpha = \begin{cases} 
\left| \frac{d\alpha}{d\alpha} \left( \frac{\alpha}{(1-\gamma) \frac{I_p}{I_{th}} (1-\gamma)} \right) \right| & \text{below threshold} \\
\left| \frac{d\alpha}{d\alpha} \left( \frac{I_p \cdot \alpha}{\gamma(1-\gamma) \frac{I_p}{I_{th}} (1-\gamma)} \right) \right| & \text{above threshold} 
\end{cases} \quad (S12)
\]

To assess the effect of the dye parameters \((\sigma_a, \tau, \Phi)\) on the pH sensitivity, we consider them independently to isolate their role. Therefore, the effect of various parameters on sensitivity can be obtained by calculating Eq. (S12).

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