Electronic Supplementary Material (ESI) for Lab on a Chip.

Supplementary Information

Monolithic Optofluidic Ring Resonator Lasers Created by Femtosecond Laser Nanofabrication

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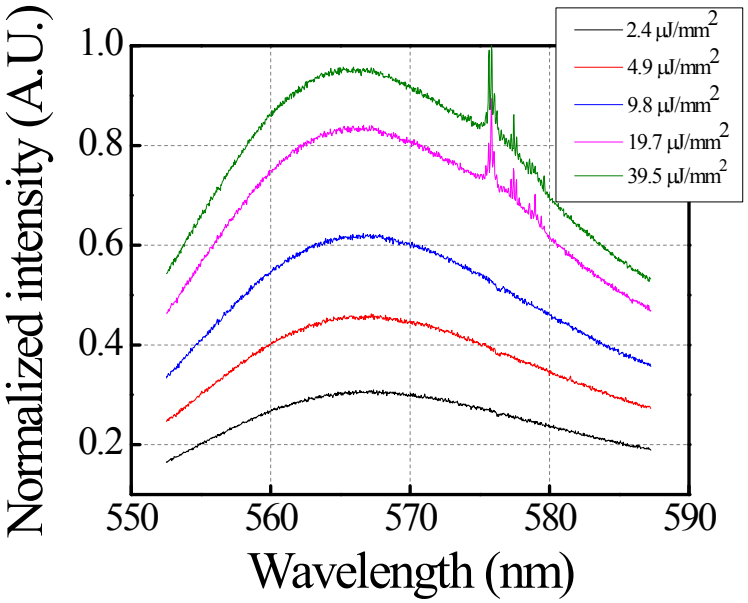


Supplementary Figure 1: Emission spectra as a function of pump fluence below and just above the lasing threshold. A 1200 g/mm grating was used to achieve wider spectral coverage. For comparison purposes, all emission spectra are normalized to the highest peak value. High resolution (0.05 nm) spectra using a 2400 g/mm grating are plotted in Fig. 4(A).

Table 1: Parameters used in the present work

Parameters	Definitions	Units
λ_P	Pump wavelength	nm
λ_L	Lasing wavelength	nm
λ_E	Fluorescence peak wavelength	nm
n_{Sol}	Refractive index of Solvent	-
n_T	Rhodamine 6G (R6G) dye concentration	cm^{-3}
n_X	Dye concentration at excited state	cm^{-3}
$\sigma_a(\lambda_P)$	Absorption cross-section at λ_P	cm^2
$\sigma_a(\lambda_L)$	Absorption cross-section at λ_L	cm^2
$\sigma_e(\lambda_L)$	Emission cross-section at λ_L	cm^2
$E(\lambda)$	Fluorescence quantum distribution	nm^{-1}
q	Quantum yield of RG6 in quinoline	-
q_{Ref}	Quantum yield of RHB in ethanol	-
$FL\text{-}Slope_{Sol}$	Fluorescence efficiency of RG6 in quinoline	nM^{-1}
$FL\text{-}Slope_{Ref}$	Fluorescence efficiency of RHB in ethanol	nM^{-1}
σ	Standard deviation of RG6 fluorescence distribution	ns
ε_{Sol}	Extinction coefficient of RG6	$M^{-1}cm^{-1}$
ε_{Ref}	Extinction coefficient of RHB	$M^{-1}cm^{-1}$
τ_F	Fluorescence lifetime	ns
A	$\sigma_A(\lambda_L)/\sigma_A(\lambda_P)$	-
B	$\sigma_A(\lambda_L)/\sigma_E(\lambda_L)$	-
C	$Q_{Dye}/\eta Q_0$	-
h	Planck constant	Js
c	Speed of light in vacuum	m/s
Δt	Pulse width of the pump laser	ns
η	Light coupling efficiency	-
P_{th}	Lasing photon density threshold	$\#photons/m^2$
Φ_{th}	Lasing fluence threshold	$\mu J/mm^2$
Q_{Dye}	Q-factor due to dye absorption	-
Q_{Sol}	Q-factor due to solvent absorption	-
Q_{Rad}	Q-factor due to radiation loss	-
Q_{Sc}	Q-factor due to scattering loss	-
Q_0	Q-factor of the laser cavity in the absence of gain medium	-

Q-factor analysis

Based on the lasing theory and the experimentally measured lasing threshold, the cavity Q-factor in the absence of the gain medium (*i.e.*, Q_0) can be calculated. The lasing threshold is given by:

$$n_X \sigma_E(\lambda_L) = (n_T - n_X)\sigma_a(\lambda_L) + \frac{2\pi n_{Sol}}{\lambda_L \eta Q_0} \tag{S1}$$

Equation (S1) can be written as:

$$\gamma \equiv \frac{n_X}{n_T} = \frac{\sigma_a(\lambda_L)}{\sigma_e(\lambda_L) + \sigma_a(\lambda_L)} \cdot (1 + \frac{Q_{Dye}}{\eta Q_0}) \tag{S2}$$

The stimulated emission cross section is obtained from the following expression:

$$\sigma_e(\lambda_L) = \frac{{\lambda_L}^4 E(\lambda_L)}{8\pi c {n_{Sol}}^2 \tau_F} \tag{S3}$$

According to the four energy level model, at steady state, γ relates to the dimensionless pump intensity by:

$$\gamma = \frac{I}{I+1}, \tag{S4}$$

and $I = \frac{\gamma}{1-\gamma}$, (S5)

where $I = P \cdot \sigma_a(\lambda_p) \cdot \tau_F$. P is the power density in units of (# of photons per m^2 per second).

Equations (S2) and (S5) can be combined:

$$\frac{P_{th}}{\Delta t} \cdot \sigma_a(\lambda_P) \cdot \tau_F = \frac{\frac{\sigma_a(\lambda_L)}{\sigma_e(\lambda_L) + \sigma_a(\lambda_L)} \cdot [1+C]}{1 - \frac{\sigma_a(\lambda_L)}{\sigma_e(\lambda_L) + \sigma_a(\lambda_L)} \cdot [1+C]} = \frac{1}{\sigma_e(\lambda_L)} \frac{\sigma_a(\lambda_L) \cdot [1+C]}{1 - \frac{\sigma_a(\lambda_L)}{\sigma_e(\lambda_L)} \cdot C} \tag{S6}$$

P_{th} can be expressed in a simpler form as:

$$P_{th} = \frac{\Delta t}{\sigma_e(\lambda_L) \cdot \tau_F} A \frac{1+C}{1 - B \cdot C} \tag{S7}$$

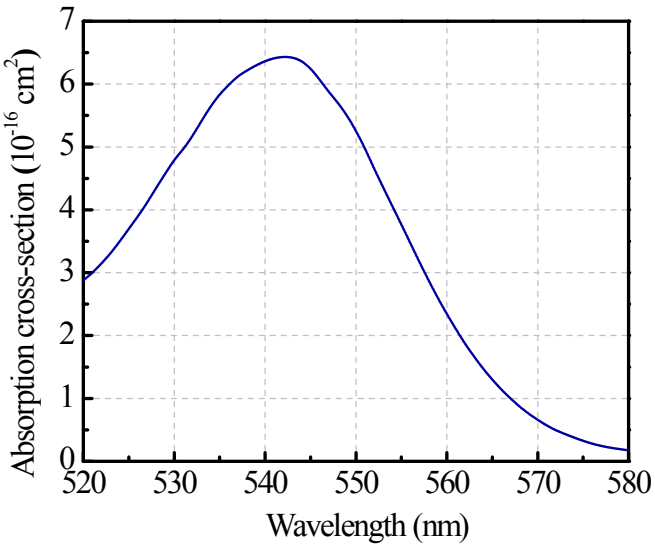
where $A = \frac{\sigma_a(\lambda_L)}{\sigma_a(\lambda_P)}$, $B = \frac{\sigma_a(\lambda_L)}{\sigma_e(\lambda_L)}$, and $C = \frac{Q_{Dye}}{\eta Q_0}$.

Q_{Dye} can be calculated by:

$$Q_{Dye} = \frac{2\pi n_{Sol}}{\lambda_L n_T \sigma_a(\lambda_L)} \tag{S8}$$

P_{th} is related to the excitation fluence at the pump wavelength by:

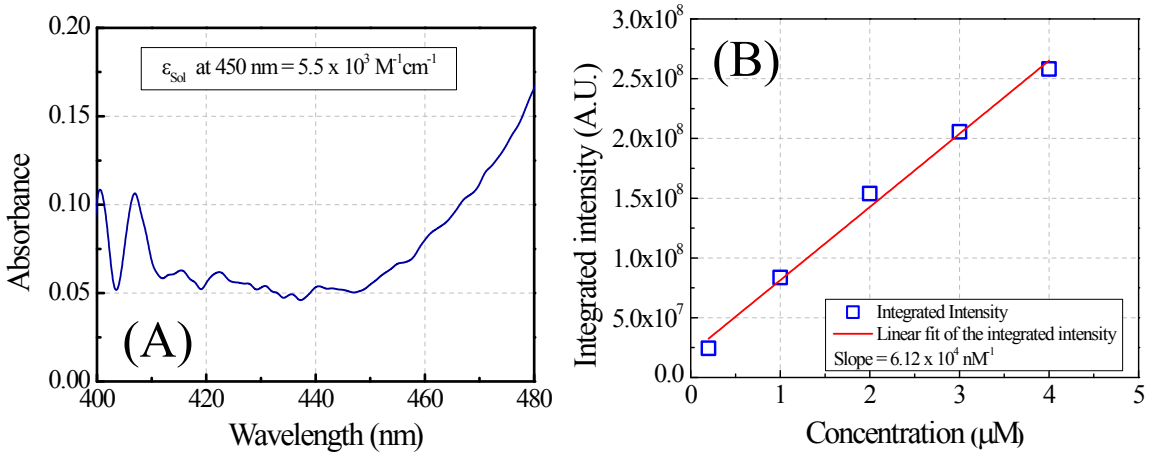
$$\Phi_{th} = P_{th} \cdot \frac{h \cdot c}{\lambda_P} = \frac{h \cdot c \cdot \Delta t}{\sigma_e(\lambda_L) \cdot \lambda_P \cdot \tau_F} A \frac{1+C}{1 - B \cdot C} \tag{S9}$$



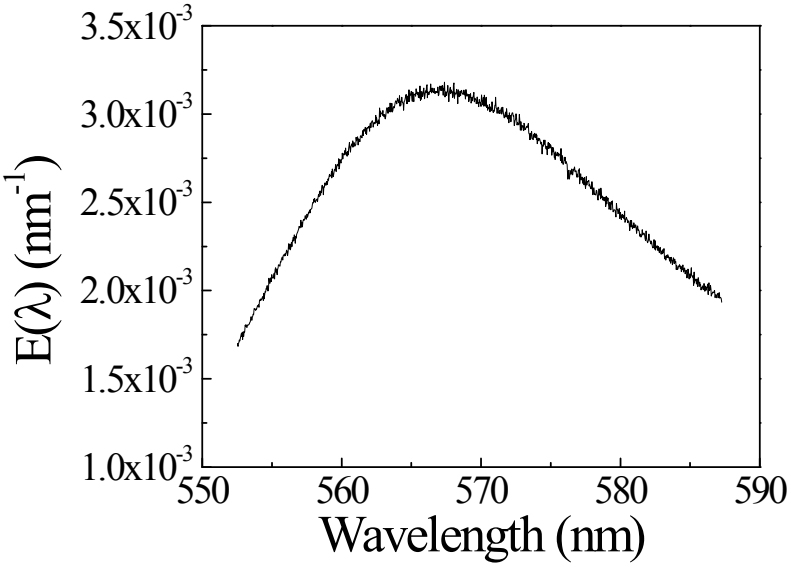
Supplementary Figure 2: Absorption cross-section of RG6 in quinoline based on absorbance measurement with 10 μM solution.

In order acquire necessary parameters to analyze Q_0 in equation (S9), we performed several measurements and data extractions. We measured the Rhodamine 6G (R6G) dye absorption cross-section as presented in Fig. S2 and obtained $\sigma_a(\lambda_P)$ and $\sigma_a(\lambda_L)$. Q_{Dye} was calculated to be 9.07×10^3 according to equation (S8).

Next, we need to determine the fluorescence quantum distribution $E(\lambda)$ and fluorescence lifetime (τ_F) of the RG6 in quinoline to calculate $\sigma_e(\lambda_L)$ in equation (S3). In order to compute $E(\lambda)$, we need to first calculate the quantum yield (q) and measure the fluorescence spectrum of the dye solution. To determine the quantum yield, we performed absorption and fluorescence measurements of RG6 dye in quinoline and compared the results against a reference dye solution (Rhodamine B (RhB) in ethanol) which has a known q_{Ref} value[1]. Fluorescence test was done with FluoroMax-4



Supplementary Figure 3: (A) Absorbance of RG6 dye in quinoline as a function of wavelength. (B) Integrated fluorescence intensity as a function of RG6 dye concentration.



Supplementary Figure 4: Fluorescence quantum distribution, E(λ).

spectrofluorometer (Horiba Scientific). Absorption test was performed with NanoDrop 2000c spectrophotometer (Thermal Scientific). The excitation wavelength for the absorption measurement was 450 nm. The measurement results shown in Fig. S3 indicate ε_{Sol} and FL-Slope$_{Sol}$ of 5.5 x 10^3 $M^{-1}cm^{-1}$ and 6.12 x 10^4 nM^{-1}, respectively.

Using the equation:

$$q = q_{Ref} \times \frac{FL - Slope_{Sol}}{FL - Slope_{Ref}} \times \frac{n_{Sol}^2}{n_{Ref}^2} \times \frac{\varepsilon_{Ref}}{\varepsilon_{Sol}} \quad , \tag{S10}$$

the fluorescence quantum yield, q, of 0.12 was obtained.

RG6 fluorescence quantum distribution, E(λ), can be obtained through the fluorescence spectrum in Fig. S1(B) by considering that

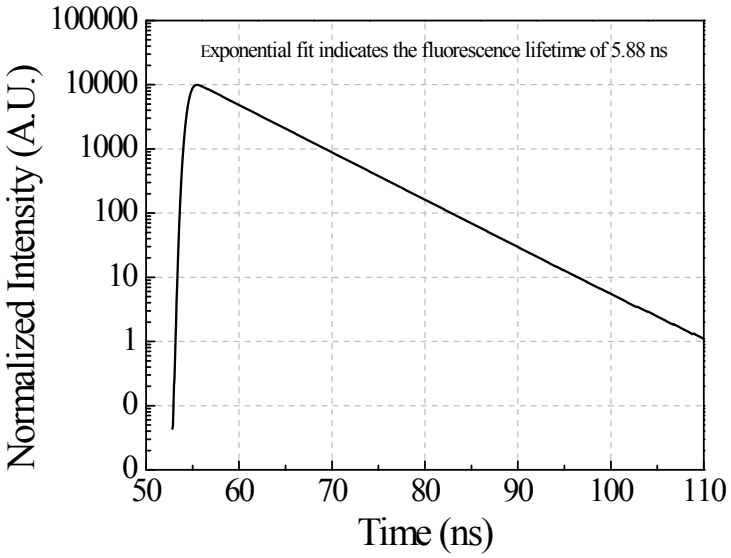
$$\int E(\lambda) \cdot d\lambda = q. \tag{S11}$$

According to Fig. S4

$$E(575\ nm) = 0.0028\ nm^{-1}. \tag{S12}$$

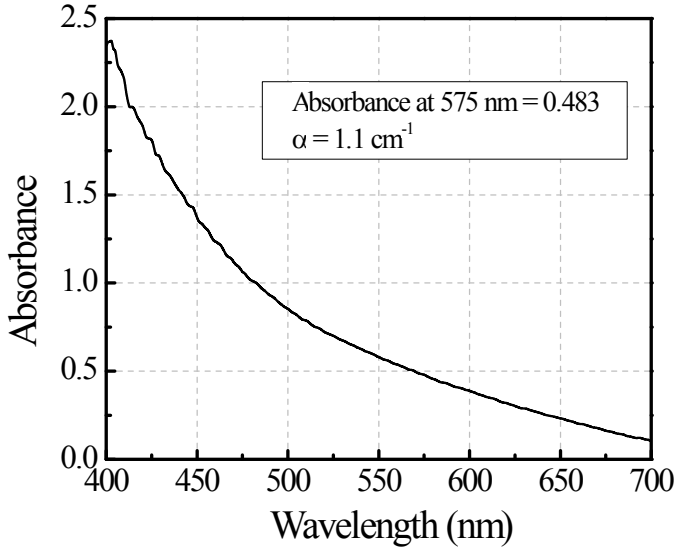
In the next step, we measured the fluorescence lifetime, τ_F of the RG6 in quinoline. The measurement result of the time correlated photon counting experiment performed using a fluorescence lifetime spectrometer (TemPro, Horiba) is shown in Fig. S4. An exponential fit reveals 5.88 ns fluorescence lifetime of RG6 dye in quinoline. We substituted the measured parameters to equation (S3), and determined the stimulated emission cross-section, σ_e, of 2.61x10^{-17} cm^2.

We have now all the parameters needed to extract Q_0 from equation (S9). Considering an input pump fluence threshold (Φ_{TH}) of 15 μJ/mm^2 during experiment, we calculate Q_0 to be 3.3x10^4.



Supplementary Figure 5: Fluorescence decay curve obtained with 500 μM RG6 dye in quinoline. The exponential fit reveals 5.88 ns fluorescence lifetime.

In order to validate the method used here to extract the Q-factor (*i.e.*, Q_0), we employ the same theoretical model to estimate the lasing threshold of an optofluidic ring resonator laser reported in Ref. 2., which Q-factor is known (*i.e.*, $\eta Q_0 = 4x10^6$). Table 2 tabulates several key parameters used for this work and the work reported in reference[2]. Based on the parameters listed on the right column of Table 2, an estimated lasing fluence threshold of 22 nJ/mm^2 is obtained, very close to the experimentally measured result of 25 nJ/mm^2. Therefore, our current approach to extract $Q_0 = 3.3x10^4$ using the lasing fluence threshold is justified.



Supplementary Figure 6: Absorbance measurement of quinoline as a function of wavelength.

Table 2: Comparisons of the current work and the work in Ref. 2.

Parameters	Current work (1 mM R6G in quinoline)	Ref. 2 (2 mM R6G in ethanol)
λ_P	532 nm	532 nm
λ_L	575 nm	600 nm
n	1.62	1.40
n_T	6×10^{17} cm^{-3}	1.2×10^{18} cm^{-3}
$\sigma_a(\lambda_P)$	5.18×10^{-16} cm^2	2×10^{-16} cm^2
$\sigma_a(\lambda_L)$	3.25×10^{-17} cm^2	1×10^{-19} cm^2
$\sigma_e(\lambda_L)$	2.61×10^{-17} cm^2	1×10^{-16} cm^2
$E(\lambda)$	2.8×10^{-3} nm^{-1}	5.7×10^{-3} nm^{-1}
q	0.12	0.9
τ_F	5.88 ns	4.08 ns
A	6.27×10^{-2}	5×10^{-2}
B	1.25	1×10^{-3}
C	0.28	0.3
Δt	5 ns	5 ns
Q_{Dye}	9.07×10^3	1.2×10^6
ηQ_0	3.3×10^4	4×10^6
Φ_{th}	15 μJ/mm^2	22 nJ/mm^2

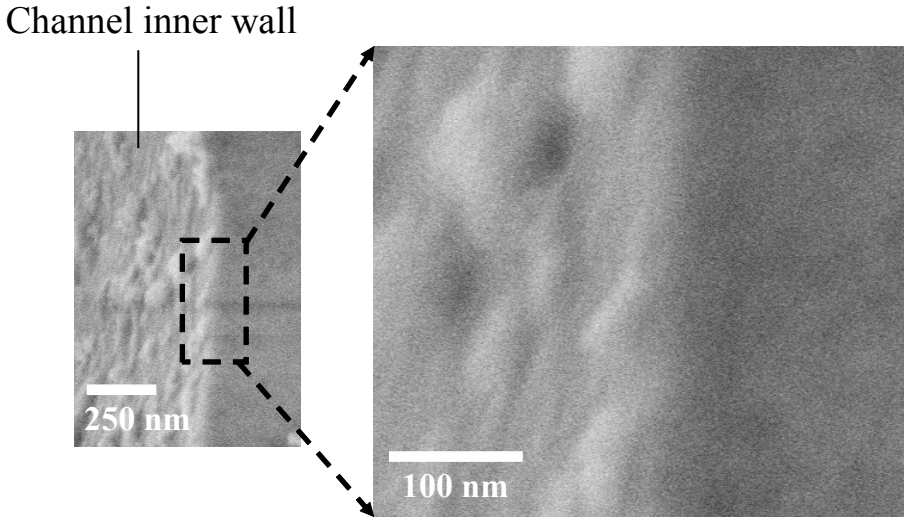
Estimation of Q_{Sc}

The surface roughness of a pre-annealing device fabricated by the 3-D femtosecond laser writing process has previously been characterized to be 40-50 nm[3]. Fig. S6 shows the SEM image of the ring resonator inner wall taken after the ring resonator underwent thermal annealing. The roughness was reduced to approximately 30 nm.

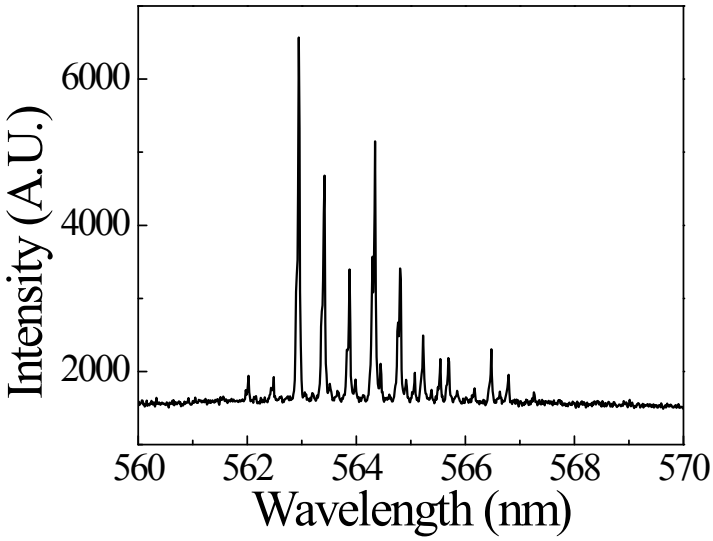
The roughness is related the Q-factor by[4]:

$$Q \propto \frac{1}{\sigma_{rough}^{\ 2} \cdot (n_{core}^{\ 2} - n_{cladding}^{\ 2})}, \tag{S13}$$

where σ_{rough} is the surface roughness. n_{core} and $n_{cladding}$ are the refractive index for the ring and the cladding, respectively. Previous work on polymer ring resonators, whose surface roughness and the Q-factor have been well characterized and directly measured, provides a means to estimate the scattering loss related Q-factor of our ring resonator. According to Ref. 4,5, a Q-factor of $5x10^5$ was obtained at 780 nm for a polymer ring resonator with the surface roughness of 5-10 nm. Based on equation S13, the scattering loss related Q-factor of our ring resonator should range between $3.2x10^4$ and $1.3x10^5$, in agreement with the scattering related Q-factor estimation ($Q_{Sc} = 4.2x10^4$) that we extract based on the lasing threshold.



Supplementary Figure 7: SEM images of the channel inner wall. The surface roughness (rms) is about 30 nm.



Supplementary Figure 8: Lasing emission from 1 mM R6G in chlorobenzene (n=1.524) at a pump fluence of 90 μJ/mm^2. Flow rate was 3 μL/min.

References

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