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# **Temperature Elevation and Fluid Convection Under Optical Trapping Condition as Revealed by Fluorescence Correlation Spectroscopy**

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**Abstract**. Temperature of matter increases under intense photoirradiation owing to photothermal conversion. The photothermal effect is sometimes a significant issue in optical manipulation usually requiring intense optical fields. Quantitative evaluation of local temperature under photo-irradiation can, therefore, provide indispensable information for the optical manipulation. In the previous work, we have applied fluorescence correlation spectroscopy (FCS) to monitor the temperature under the optical trapping condition in water, ethanol and ethylene glycol. We pointed out that analyses of diffusion time of fluorescent dyes could provide information on temperature on the basis of temperature-dependent viscosities of the solvents. In the present work, the FCS thermometry was applied to seven solvents including primary aliphatic alcohols, to examine universal applicability of the method. To verify the experimental results, numerical simulations were performed on the basis of 2D heat conduction at a stationary state. The numerical results on the temperature field satisfactory reproduced the experimental data, proving that the FCS thermometry is applicable to ordinary solvents. In addition, we also performed numerical simulations on velocity fields in the solvent, to evaluate contribution of natural convection under typical optical trapping condition at light intensity of ~MW cm<sup>-2</sup>. It was revealed that the contribution of the natural convection is not negligible for mass transfer in the solvents.

**Keywords**: optical trapping, fluorescence correlation spectroscopy, photothermal effect, temperature measurement, fluid convection.

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#### **1** Introduction

Photons transfer their momenta to matter through absorption and/or scattering. This force acting on the matter is known as radiation force or radiation pressure.<sup>1</sup> In 1970, Ashkin demonstrated that micron-sized particles can be trapped and accelerated in solution by using the radiation pressure from a CW laser under non-resonant photoirradiation condition.<sup>2</sup> Since then, trapping,<sup>3,4</sup> sorting,<sup>5,6</sup> and separation<sup>7,8</sup> of small particles by the radiation pressure have been extensively studied. On the other hand, under resonant photoirradiation condition, some portions of photons are converted into heat via absorption (photothermal conversion), which often causes

the irreversible damage to target materials. A laser beam with non-resonant wavelength has been therefore usually employed for optical manipulation.

In conventional optical tweezers, CW lasers in near infrared (NIR) region are frequently used,<sup>9–11</sup> because the target dielectric particles have smaller scattering and almost no absorption cross sections in the NIR region. In this wavelength region, however, many kinds of solvents (*e.g.* water and alcohols) have weak but non-negligible absorption bands of overtone vibrational transitions due to stretching modes of, *e.g.* CH, OH, and NH bonds.<sup>12</sup> Under typical conditions of optical trapping with a laser beam focused into a diffraction limited spot, a power density at the sample position easily reaches ~ MW cm<sup>-2</sup>. Local temperature at the focal point increases a few tens of Kelvin with such a high power density in water.<sup>13–15</sup> In addition, such significant temperature elevation in the local area induces fluid convection which is undesired for the optical manipulation.<sup>16,17</sup> Therefore, quantitative evaluation of local temperature and fluid convection under optical trapping condition are crucially important for potential applications of the optical manipulation.

For measurements of temperature in a mesoscopic region, spectroscopic properties depending on the temperature have been so far employed because of its non-contact nature, such as, luminescent intensity of rare earth ions,<sup>18,19</sup> spectral shifts of localized surface plasmon resonance,<sup>20</sup> and fluorescent quantum yield of the dyes.<sup>21</sup> On the other hand, we have demonstrated that fluorescence correlation spectroscopy (FCS) can monitor the local temperature elevation under optical trapping condition.<sup>22</sup> FCS can evaluate diffusion coefficients of solute (fluorescent dye) in solvents through the fluctuation of fluorescent intensity originating from the concentration change of the dye in a confocal volume.<sup>23</sup> Information on the temperature can be extracted from temperature dependence of the diffusion coefficient. This FCS thermometry is feasible under the

optical trapping condition because of the following three reasons: i) it scarcely disturbs the system because of a low concentration of the guest dyes, ii) high spatial resolution equivalent to diffraction limit of the confocal fluorescence microscopy, and iii) high temperature accuracy with a few Kelvins.

In the previous work, however, the FCS thermometry was demonstrated in small number of solvents.<sup>22</sup> To scrutinize universal applicability of this method, we have applied the FCS thermometry to temperature measurements in seven solvents, which have different thermal and optical properties such as diffusion coefficients, thermal conductivities, and absorption coefficients at the trapping wavelength. In addition, numerical simulations on 2D heat conduction at a steady state were carried out to verify experimental results. The good agreement between the numerical and experimental results has proved that the FCS thermometry can be applied for various kinds of ordinary solvents.

As mentioned in the beginning of this introductory section, fluid convection, which occurs in solutions with steep temperature gradients, is a notable issue for the optical trapping, because it strongly affects motions of target particles in optical manipulation.<sup>17,24–26</sup> To evaluate the contribution of natural convection on mass transfer under optical trapping condition, we have conducted numerical simulations on velocity field on the basis of Navier-Stokes equations. From the spatial distribution of convective flow in a sample chamber, it was revealed that the convection around the focal point of trapping laser light (*i.e.* focal plane of the objective) is minor contribution, but it is not negligible. These results suggest that the whirling motion of convection for the vertical direction may act as a mild mixer for the solvent and the solutes. These findings shed light on heat and mass transfer under optical trapping wavelength of NIR region.

# **2** Experimental

#### 2.1 Thermometry Based on Fluorescent Correlation Spectroscopy

First, we describe in brief how the local temperature can be extracted from FCS measurement. On the FCS measurements, an excitation light source for fluorescence is tightly focused to a diffraction-limited spot in sample solution (Fig. 1a) with an extremely low concentration of fluorescent dyes. For the detection of the fluorescence, a confocal setup is employed to reduce observation volume (*e.g.* on the order of femtoliters). Owing to the low concentration and the very small detection volume, one can observe fluctuation in fluorescent intensity in time domain originating from the local concentration change of the dye due to Brownian motion (Fig. 1a).



Figure 1. (a) Schematic illustrations of fluorescent correlation spectroscopy (FCS). (b) Typical fluorescence autocorrelation curves on FCS measurements; the blue arrow indicates a decrease in diffusion coefficient, while the red arrow represents an increase in the number of molecules in the confocal volume.

Dynamics of the fluctuation is regulated by translational diffusion of the dye molecules. In general, the lateral diffusion of solute depends on its hydrodynamic radius and a viscosity of solvent. Accordingly, the dynamics of the fluctuation involves information on the size of the solute and the viscosity of the solvent. On the other hand, amplitude of the fluctuation compared to the averaged fluorescent intensity is dependent on the number of the dye molecules in the confocal volume. In the FCS measurements, the averaged values of the residence time (diffusion time) and the number of molecules can be determined from an analysis of autocorrelation functions (ACF) of the fluorescence intensity (Fig. 1b). The ACF is given by,<sup>23</sup>

$$G(\tau) = 1 + \frac{1}{N} \left( 1 + \frac{p}{1-p} exp\left(-\frac{\tau}{\tau_{\rm T}}\right) \right) \left(1 + \frac{\tau}{\tau_D}\right)^{-1} \times \left(1 + \frac{\tau}{w^2 \tau_D}\right)^{-1/2} \tag{1}$$

where *N* is the average number of molecules in the confocal volume, *p* and  $\tau_T$  are the fraction of the contribution of triplet state and its lifetime, respectively. *w* is a structural parameter defined by  $w = w_z / w_{xy}$ , where  $w_z$  and  $w_{xy}$  are the axial and radial radii of the ellipsoidal confocal volume, respectively ( $V_{conf} = \pi^{3/2} w_z w_{xy}^2$ ).  $\tau_D$  is the averaged residence time (diffusion time) of a molecule in the confocal volume, which is a function of its translational diffusion coefficient, *D*, as represented by the following equation.

$$\tau_D = \frac{w_{xy}^2}{4D} \tag{2}$$

To extract the information on temperature from above equations, one can apply the Stokes-Einstein model, as represented in eq 3.

$$D = \frac{kT}{6\pi\eta(T)a}$$
(3)  
$$\frac{T}{\eta(T)} = \frac{\gamma}{\tau_D} \left( \gamma = w_{xy}^2 \frac{3\pi a}{2k} \right)$$
(4)

Here *k* is Boltzmann constant,  $\eta(T)$  is the viscosity of the solvent as a function of temperature *T*, and *a* is a hydrodynamic radius of the probe molecule. Eq 4 indicates that temperature in the confocal volume can be determined by the residence time  $\tau_D$  and the reference value of  $T/\eta$ , under the assumption that  $\gamma$  is independent of the temperature in the range of the experiment.<sup>22,27</sup>

#### 2.2 Optical Setup and Sample Preparation

An optical setup is schematically shown in Appendix A.1. A CW laser (Nd<sup>3+</sup>: YVO<sub>4</sub>) at a wavelength of 1064 nm was employed to induce temperature elevation under optical trapping condition. For the fluorescence excitation, a CW laser at a wavelength of 488 nm (Ar ion laser) was used. Both lasers were focused into diffraction-limited spots by using a high numericalaperture (NA) objective in the sample solution under an inverted optical microscope. For detection of the fluorescent intensity, an avalanche photodiode was used. Other details of the FCS measurements were reported in our previous work.<sup>22</sup> An excitation intensity for the probe molecules was set to 200  $\mu$ W at the backport of the optical microscope.

As sample solutions for the FCS thermometry, seven solvents were used as received: water (distilled water, Wako), ethylene glycol (99%, Wako), 1-pentanol (99 %, Aldrich), 1-

hexanol (99 %, Aldrich), 1-octanol (99 %, Aldrich), 1-nonanol (98 %, Aldrich), and 1-decanol (99 %, Aldrich). As a fluorescent probe, Rhodamine 123 was employed. Sample solutions of the probe molecules were prepared at low concentrations (typically,  $\sim 10^{-9}$  M). For the experiments, the sample solutions were injected into glass-bottom culture dished (Mat-Tek). In all experiments, focusing points of both CW lasers were adjusted 30 µm away from the bottom of the culture dishes.

For the solvent of which temperature dependence of the viscosity is unavailable in the literature, we measured the dependence by using an Ostwald viscometer as shown in Appendix A. 2. In addition, absorption coefficients at 1064 nm were measured for discussion and numerical simulations (see Appendix A. 3).

# **3.** Results and Discussion

#### 3.1 FCS Thermometry in Various Solvents

In general, an increase in temperature at a steady state is determined by generation and conduction of heat, on the basis of Fourier's law. The former process takes place by the absorption of the trapping beam by solvent. The latter process is regulated by thermal conductivities. In the present section, results in water and 1-pentanol are compared as illustrative examples on the latter process. Thermal conductivities of water and 1-pentanol are 0.59 [W m<sup>-1</sup> K<sup>-1</sup>] and 0.15 [W m<sup>-1</sup> K<sup>-1</sup>], respectively and a larger temperature increase is expected for 1-pentanol.

Fig. 2a shows autocorrelation curves (ACCs) in water under irradiation with the NIR laser for different intensities from 0 to 240 mW. Note that these laser intensities were precisely measured values at the focusing points (see Appendix A.1).<sup>28</sup> ACC without NIR irradiation is represented as a black solid line. From this result, the diffusion coefficient of the dye in water at

room temperature was obtained by fitting with a least-square method. With an increase in the intensity of the NIR laser, the ACCs shift to the left-hand side, indicating that the decay of the correlation curves became faster. This laser intensity dependence indicates an increase in the diffusion coefficient by the elevation of temperature. However, degree of the left-shifts was not so remarkable in water even under the intense NIR laser irradiations.



Figure 2. Autocorrelation curves at various NIR laser powers in water, (a), and 1-pentanol, (b).

Fig. 2b shows ACCs in 1-pentanol at various NIR laser intensities. With increasing NIR laser intensity, the ACCs shift to the left-hand side more markedly; degree of the left-shifts was much larger than that in water. This means that 1-pentanol has a greater ratio of the temperature increase per input NIR laser intensity ( $\Delta T/\Delta P$ , [K W<sup>-1</sup>]) compared to that in water. As already mentioned in this section, the thermal conductivity of 1-pentanol is much lower than that of water. Therefore, differences in the ACCs between water and 1-pentanol can be ascribed to the temperature increase per unit input power,  $\Delta T/\Delta P$ . We have carried out same measurements for all

solvents, and obtained the NIR laser intensity dependence of ACCs. The results are summarized in Appendix A. 4. In all solvents, shifts of ACCs to the left-hand side were observed with an increase in NIR laser intensity. However, the solvent showed different values of  $\Delta T/\Delta P$ . As will be discussed later, the primary aliphatic alcohols have quite similar thermal conductivities, while they exhibit considerably different absorption coefficients at 1064 nm. Therefore, the absorption coefficients and the thermal conductivities corresponding to generation and conduction of heat must be taken into account for comparison with numerical simulations.

To more quantitatively figure out the dependence on NIR laser intensity, the temperature increases were deduced from the ACCs. The results in water and 1-pentanol are shown as illustrative examples in Fig. 3, where the temperature increase,  $\Delta T$ , is plotted as a function of NIR laser intensity. With an increase in NIR laser intensity, the  $\Delta T$  linearly increased. The linear relation is governed by the simple law of heat conduction at a stationary state in which the temperature increase  $\Delta T$  is linearly related to the input energy for the system. To quantitatively compare the slopes of the temperature increases ( $\Delta T/\Delta P$ ) in water and 1-pentanol, both plots in Fig. 3a and -b were analyzed with a linear function. The slopes of 3.4/100 and 6.0/100 were respectively obtained for water and 1-pentanol, and the temperature increase in 1-pentanol was almost twice larger than that in water. Note that the FCS thermometry has high temperature sensitivity (ca.  $\pm 1$  K) and reproducibility in a fixed optical setup. However, once the optical setup is reconstructed, a laser spot diameter at the focusing point varies slightly. This would result in an experimental error in the temperature increase as a function of NIR laser power; the present result in water was 20 % higher than that in our previous work<sup>22</sup> at same experimental condition. To avoid such experimental errors, one should measure the laser spot diameter to estimate a power density (W cm<sup>-2</sup>) at the sample position.



Figure 3. Temperature increase ( $\Delta T$ ) as a function of NIR laser power in water (a), and 1-penatnol (b). The slopes of linear fitting were (3.4/100) and (6.0/100), respectively.

As was mentioned, both processes of generation and conduction of the heat regulate the temperature increase under CW laser excitation. To quantitatively elucidate the solvent dependence of the temperature increase, we introduce a ratio of the absorption coefficient and the thermal conductivity,  $\alpha/\lambda$  [K W<sup>-1</sup>], which represents the total energy stored in the system during photoirradiation. The absorption coefficients, the thermal conductivities, their ratios, and the averaged values of  $\Delta T/\Delta P$  of all solvents are summarized in Table 1. To obtain the averaged  $\Delta T/\Delta P$ , ACCs were accumulated for each of the NIR laser intensities.

solvent	α [m <sup>-1</sup> ]	$\lambda [W m^{-1}K^{-1}]$	$\alpha/\lambda [K W^{-1}]$	$\Delta T/\Delta P$ (averaged)
				[K W <sup>-1</sup> ]
H <sub>2</sub> O	11.2	0.59	25	33
Ethylene Glycol	19.9	0.26	77	74
1-Pentanol	9.14	0.15	61	62
1-Hexanol	8.34	0.15	56	57
1-Octanol	7.99	0.16	50	53
1-Nonanol	7.53	0.16	47	59
1-Decanol	7.36	0.16	46	61

Table 1. Optical/thermal properties of the solvents and the ratios of temperature increase  $(\Delta T/\Delta P)$ 

As will be shown later, plots of  $\Delta T/\Delta P$  and  $\alpha/\lambda$  exhibited clear linear relation. This behavior will be discussed with computational results on the temperature fields.

# 3.2 Discussion with Numerical Simulations

In the present section, numerical simulations are performed to verify the validity of the experimental results in the seven solvents. For the numerical simulation, we modified a previously developed model on nanoscale 2D heat conduction at a stationary state on the basis of finite element method (FEM).<sup>29</sup>

Fig. 4a shows a schematic illustration of a system for the FEM modeling. The geometry consists of a solvent and a glass substrate in x-z space; a microscope objective and a focused laser beam are not considered in calculation of the temperature field. Widths and heights of the solvent

and the glass substrate were set to several hundreds of micrometers. To reproduce the experimental conditions, an ellipsoidal shaped heat source as a focused Gaussian beam was put at 30 µm away from the bottom of the glass substrate. The center of the heat source was defined as an origin of xz coordinate. The width of the heat source for x-coordinate  $(FWHM_x)$  was set to 480 nm by assuming the diffraction limit of the trapping laser, which is defined by 0.61 ( $\lambda$ /NA). In the same manner as the  $FWHM_x$ , the height of the heat source for z-coordinate ( $FWHM_z$ ) was assumed to be 2.4 µm. In calculations, heat conduction from the heat source to the solvent and the substrate was considered. Governing equations for the simulation are Laplace and Poisson type heat conduction equations at the steady state.<sup>30</sup> Only one physical parameter required for the calculation with these equations is a thermal conductivity of each material. The thermal conductivity of 1.0 [W m<sup>-1</sup> K<sup>-1</sup>] was obtained from a literature for the glass substrate<sup>20</sup>. The thermal conductivities and the absorption coefficients of other materials are already summarized in Table 1. Thus, the computational variable is only the input NIR laser intensity for the heat source. Calculation was numerically performed with COMSOL Multiphysics, which is a commercially available FEM solver.



Figure 4. (a) Computational modeling of 2D heat conduction at the steady state. (b) Calculated 2D temperature distribution for the system consisting of water and glass substrate at a NIR laser power of 220 mW. (c) Calculated  $\Delta T$  as a function of NIR laser power at the center of the heat source. (d) Relationship between  $\alpha/\lambda$  and  $\Delta T/\Delta P$ . For comparison, experimental results were also plotted.

Fig. 4b shows a 2D temperature mapping in water at a NIR laser intensity of 220 mW. At the center of the temperature mapping, one can recognize a hottest spot ( $\Delta T \sim 5$  K) where the heat source exists. In the solvent adjacent to the heat source, temperature distribution looks like ellipsoidal shapes. But at a distance of 2 µm or more from the heat source, the temperature distribution gradually changes from ellipsoidal shape to concentric one. This distance-dependent behavior is quite similar to that in temperature distribution created by heated individual nanoparticles or microparticles.<sup>31</sup> Accordingly, in the present case, the temperature distribution around the heat source can be recognized as a typical one being created by a point-like heat source.<sup>32,33</sup> On the other hand, the thermal conductivity of the glass substrate is much higher than those of all the solvent employed and, hence, the glass substrate acts as a heat sink for the solvents. Hence, now we focus on the temperature increase at an interface between the solvent and the substrate ( $x = 0 \mu m$ ,  $z = -30 \mu m$ ) and at the upper side of the heat source ( $x = 0 \mu m$ ,  $z = +30 \mu m$ ). While the temperature increase ( $\Delta T$ ) of 2 K was observed at  $z = +30 \mu m$ , the  $\Delta T$  of 1 K was obtained at  $z = -30 \mu m$ . This difference clearly indicates that the solvent between the heat source and the glass substrate was cooled down owing to the higher thermal conductivity of the substrate. This result ensures that it is possible to verify the FCS thermometry with the cooling effect of the substrate on this numerical simulation. In contrast to the temperature distribution in the solvent and the substrate, the temperature was uniform within the heat source.

Next, we discuss the NIR laser intensity dependence of the temperature increase. Fig. 4c shows the maximum temperature at the heat source ( $\Delta T_{max}$ ) as a function of NIR laser intensity. The  $\Delta T_{max}$  linearly increased with the NIR laser intensity, and reached 5 K at 220 mW. The slope of the calculated temperature curve is comparable to the experimental result of water shown in Fig. 3a. This agreement indicates that the temperatures probed by FCS are rationally accounted for by

the heat conduction laws. In the same manner as the result shown in Fig. 4c,  $\Delta T_{max}$  was calculated as a function of NIR laser intensity for all the solvents. To compare the calculated temperature increases to the experimental ones, the relationships between  $\alpha/\lambda$  and  $\Delta T/\Delta P$  are plotted in Fig. 4d. The numerically calculated results exhibited a perfect liner relationship. This behavior is explained by the fundamental law of heat conduction that temperature increase in a system is linearly proportional to total absorbed energy in a heat source. The experimental results (red open squares) are well reproduced by the calculated ones. The numerical simulations ensure that the FCS thermometry is widely applicable to ordinary solvents such as water, ethylene glycol, and primary aliphatic alcohols.

### 3.3 Contribution of Natural Convection

In the previous sections, we have discussed the temperature field under the optical trapping condition. Though the FCS thermometry is applicable to ordinary solvents, the  $\Delta T$  on the order of a few tens of Kelvins may induce fluid convection driven by buoyancy force, called as natural or free convection.<sup>16</sup> This convection has been recognized as a significant issue in the optical manipulation in solution phase.<sup>17,24</sup> So as to more quantitatively figure out the heat and mass transfer under optical trapping condition, we performed numerical simulations of the fluid convection. For the simulation on the velocity field, we again employed the FEM geometry as was shown in Fig. 4a. For fluid flow, the governing equations are Navier-Stokes equations; this problem was numerically solved with COMSOL Multiphysics based on the temperature field calculated in the previous section. The details on numerical modeling and boundary conditions have been described in previous works.<sup>34,35</sup> In principle, driving force of the natural convection is the buoyancy force arising from the temperature gradient in solvent; an origin of the buoyancy is

a decrease in density of the fluid with increasing temperature. In this section, we focus on the natural convection in water because of the availability of its temperature-dependent physical properties. A volumetric expansion coefficient ( $\beta$ ) of  $3.0 \times 10^{-4}$  [K<sup>-1</sup>] was used for the calculation.



Figure 5. (a) Computational 2D velocity distribution for the system consisting of water and glass substrate at a NIR laser power of 220 mW. (c) Calculated convective velocity as a function of NIR laser power at the center of the heat source ( $v_{sourve}$ ) and the center of the sample chamber ( $v_{max}$ ).

Fig. 5a shows a calculated 2D velocity mapping of the natural convection at a NIR laser intensity of 220 mW; the red arrows represent velocity vectors. In the sample chamber, one can see a whirling motion of the convection flow from the bottom to top. The highest convective velocity ( $v_{max}$ ) is found at the upper side of the heat source ( $x = 0 \mu m$ ,  $z = 100 \mu m$ ). In the vicinity of the glass surface ( $x = \pm 120 \mu m$ ,  $z = 20 \mu m$ ), convection flows are accelerated by the large temperature gradient compared with that in the upper part of the sample chamber. These whirling motion and velocity profiles are characteristics of the natural convection in a thin sample chamber.<sup>16,17,34</sup>

Next, we examined the NIR laser intensity dependence on the convective velocity. Fig. 5b shows the convective velocities at the point of  $v_{max}$  and at the heat source ( $v_{source}$ ). The convective velocities at both points linearly increases with NIR laser intensity. This linear behavior can be ascribed to the constant expansion coefficient<sup>34</sup>  $\beta$ . At the heat source, the v<sub>source</sub> is at most about 500 nm s<sup>-1</sup>. This low-velocity flow is expected to play a minor role on optical manipulation, because most of colloidal nano or microparticles to be trapped exhibit active Brownian motion. On the FCS measurements, too fast flow may affect translational diffusion of guest dye molecules. However, as already shown in Fig. 5b, the convection velocity in the confocal volume is at most 500 nm s<sup>-1</sup>. Therefore, in the present case, it is presumed that the translational diffusion of the dyes was not affected by the convection flow because acquisition times for each autocorrelation curve were less than a few hundreds of milliseconds. In contrast, the  $v_{max}$  reached a maximum of 1.8 µm s<sup>-1</sup> at a NIR laser intensity of 250 mW. At this velocity, colloidal spheres with diameters of nanometers to micrometers can be transported by the drag force of solution. Hence, one can devise following two conclusions on the natural convection. i) Although the natural convection is induced under the present condition of optical trapping (typically  $\Delta T \sim 5$  K), the contribution of the convection is negligible because of the low convective velocity at the focal point of the objective. ii) At the center of the sample chamber, the convective velocity can exceed 1.0  $\mu$ m s<sup>-1</sup>. This speed is not high enough to disturb the optical manipulation through, the convective flow can stir the inside of the sample chamber mildly. Thus, the FCS thermometry and the numerical simulations on temperature and velocity field shed light on heat and mass transfer under optical trapping condition.

#### 4. Conclusion

In the present work, universal applicability of the FCS thermometry was examined. Experimental results were discussed with numerical simulations on 2D mesoscopic heat conduction at the steady state. As a result, the experimental and the numerical results exhibited satisfactory agreement, demonstrating that the FCS thermometry is applicable for many solvents. In addition to the discussion on the temperature field, contribution of the natural convection under optical trapping condition was evaluated with numerical simulations; spatial profiles of the natural convection were clearly visualized. It has been revealed that the contribution of the natural convection is not negligible in the present case. These findings quantitatively clarified temperature elevation and natural convection under optical trapping condition.

#### Disclosures

The authors declare no competing financial interest.

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# **Appendix A: Experimental Details**

# A.1 Experimental Setup

Figure 6 shows an Optical setup. We employed an inverted optical microscope (IX-70, Olympus), and a microscope objective with a numerical aperture of 1.3. To induce local temperature elevation,  $Nd^{3+}$ : YVO<sub>4</sub> CW laser was used. For the excitation of fluorescence, Ar+ laser was used. To evaluate the laser power at a sample position, the NIR laser beam was focused by using the microscope objective then re-collimated by the same type of objective. The gap between the two objectives was filled with immersion oil. The diameter of the incident laser beam to the objective was adjusted to the same size as the back aperture of the objective. The fraction of the input laser power (I<sub>in</sub>) and output laser power (I<sub>out</sub>) was measured with a power meter.



Figure 6. Experimental setup.

# A.2 Temperature-dependent Viscosity of the Solvent

Figure 7 shows temperature dependence of the viscosities of the solvents. The viscosity was measured by using an Ostwald viscometer. Experimental plots were fitted with an 8th degree polynomial.



Figure 7. Temperature-dependent viscosities of all solvents: (a) 1-pentanol, (b) 1-hexanol, (c) 1octanol, (d) 1-nonanol, and (e) 1-decanol.

# A.3 Absorption Coefficients at 1064 nm

Figure 8 shows the relationship between the transmitted NIR laser power and the optical path length. This experiment was performed under an optical microscope with a cylindrical quartz cell. The absorption coefficient at 1064 nm was determined from the Lambert-Beer's law.



Figure 8. Transmitted NIR laser power as a function of optical path length in all solvents: (a) 1-pentanol, (b) 1-hexanol, (c) 1-octanol, (d) 1-nonanol, and (e) 1-decanol.

#### A.4 Autocorrelation Curves in All Solvents at various NIR laser intensities

Figure 9 shows dependence of autocorrelation curves on the NIR laser power in each solvents. In all solvents, the autocorrelation curves shifted to left hand side, indicating that the diffusion coefficient increased with NIR laser power.



Figure 9. Autocorrelation curves at various NIR laser power in ethylene glycol (a), 1-hexanol (b), 1-octanol (c), 1-nonanol (d), and 1-decanol (e).

#### **Caption List**

**Fig. 1** (a) Schematic illustrations of fluorescent correlation spectroscopy (FCS). (b) Typical fluorescence autocorrelation curves on FCS measurements; the blue arrow indicates a decrease in diffusion coefficient, while the red arrow represents an increase in the number of molecules in the confocal volume.

Fig. 2 Autocorrelation curves at various NIR laser powers in water, (a), and 1-pentanol, (b).

**Fig. 3** Temperature increase ( $\Delta T$ ) as a function of NIR laser power in water (a), and 1-penatnol (b). The slopes of linear fitting were (3.4/100) and (6.0/100), respectively.

**Table 1** Optical/thermal properties of the solvents and the ratios of temperature increase  $(\Delta T/\Delta P)$ **Fig. 4** (a) Computational modeling of 2D heat conduction at the steady state. (b) Calculated 2D temperature distribution for the system consisting of water and glass substrate at a NIR laser power of 220 mW. (c) Calculated  $\Delta T$  as a function of NIR laser power at the center of the heat source. (d) Relationship between  $\alpha/\lambda$  and  $\Delta T/\Delta P$ . For comparison, experimental results were also plotted. **Fig. 5** (a) Computational 2D velocity distribution for the system consisting of water and glass substrate at a NIR laser power of 220 mW. (c) Calculated  $\Delta T$  as a function for the system consisting of water and glass substrate at a NIR laser power of 220 mW. (c) Calculated convective velocity as a function of NIR laser power at the center of the heat source ( $v_{sourve}$ ) and the center of the sample chamber ( $v_{max}$ ).

Fig. 6 Experimental setup.

**Fig. 7** Temperature-dependent viscosities of all solvents: (a) 1-pentanol, (b) 1-hexanol, (c) 1-octanol, (d) 1-nonanol, and (e) 1-decanol.

**Fig. 8** Transmitted NIR laser power as a function of optical path length in all solvents: (a) 1-pentanol, (b) 1-hexanol, (c) 1-octanol, (d) 1-nonanol, and (e) 1-decanol.

**Fig. 9** Autocorrelation curves at various NIR laser power in ethylene glycol (a), 1-hexanol (b), 1-octanol (c), 1-nonanol (d), and 1-decanol (e).