Supplementary material for

Enhanced-fluorescence correlation spectroscopy at micro-molar dye concentration around a single gold nanorod

Saumyakanti Khatua, Haifeng Yuan†, and Michel Orrit*

MoNOS, Huygens-Kamerlingh Onnes Laboratory, Universiteit Leiden, 2300 RA Leiden, The Netherlands

† Present address: Department of Chemistry, KU Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium

* Corresponding author: orrit@physics.leidenuniv.nl

1. Experimental details:

Gold nanorods were synthesized by the seed-mediated growth method reported by El-Sayed et.al[1]. The average size of the gold nanorods used in this study is 25 (± 4) nm × 60 (± 6) nm. A scanning electron microscopy (SEM) image is shown in Fig. S1(a). The longitudinal surface plasmon resonance (LSPR) of these nanorods is approximately at 630 nm when dispersed in water (Fig. S1b). Individual nanorods, coated with cetyl-trimethylammonium bromide (CTAB), were isolated on a PMMA-coated (~ 1μm thick) glass coverslip by spin coating from a water suspension. After spin coating, additional CTAB was removed by washing with deionized water.

Crystal Violet (CV) was used as the fluorophore. It is a positively charged dye with a weak fluorescence quantum yield (QY) of ~0.02[2]. The absorption and emission maxima of CV are at 591 nm and 640 nm respectively in glycerol (Fig. S1c) providing a significant overlap with the SPR of the gold nanorod.
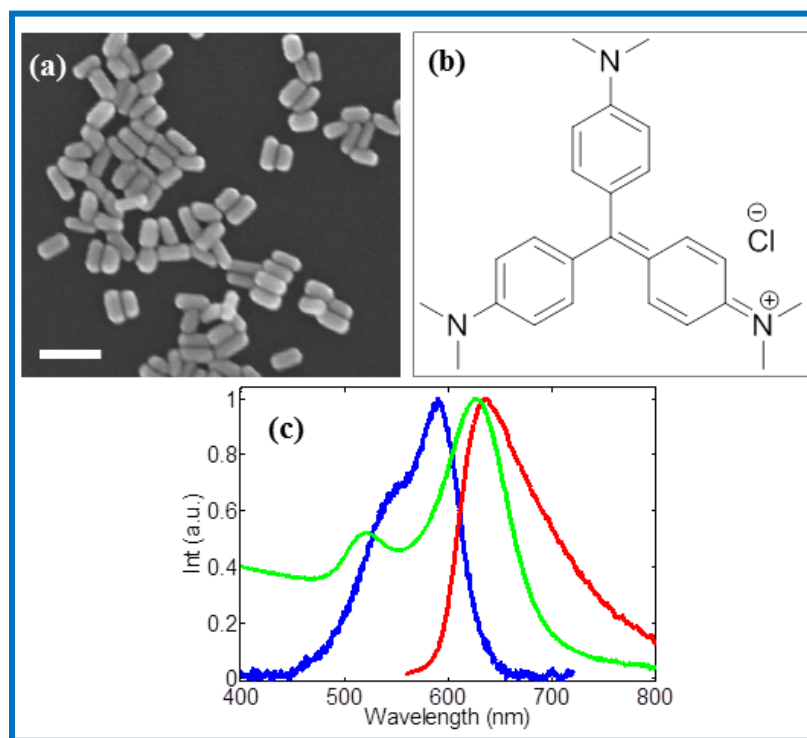
Figure S1: *(a) A scanning electron microscopy (SEM) image of gold nanorods. Averaged dimensions of the nanorods are: 25 nm ×60 nm. (b) Chemical structure of crystal violet (CV). (c) Absorption (blue) and emission (red) spectra of CV in glycerol. Bulk extinction spectrum (green) of gold nanorods dispersed in water.*

Single-particle spectroscopy was performed on a home-built confocal sample-scanning microscope as shown in Fig. 2a. A 633 nm Helium-Neon laser or a 532 nm Nd-YAG laser were used as excitation source. The excitation laser was tightly focused on the sample with a high numerical aperture (1.2) oil immersion objective. The luminescence signal was collected by the same objective, filtered from the excitation laser using appropriate notch filters and detected either by an avalanche photodiode (APD) or by a liquid-nitrogen-cooled CCD spectrometer. Photoluminescence images were recorded by scanning the sample across the laser focus using a XYZ piezo scanning stage. Fluorescence time traces were acquired by a photon counting module (Time-Harp). The fluorescence correlation function, $G(\tau)$ was calculated and fitted to a two-component diffusion model using SynPhoTime software, with two characteristic times τ_1 and τ_2.
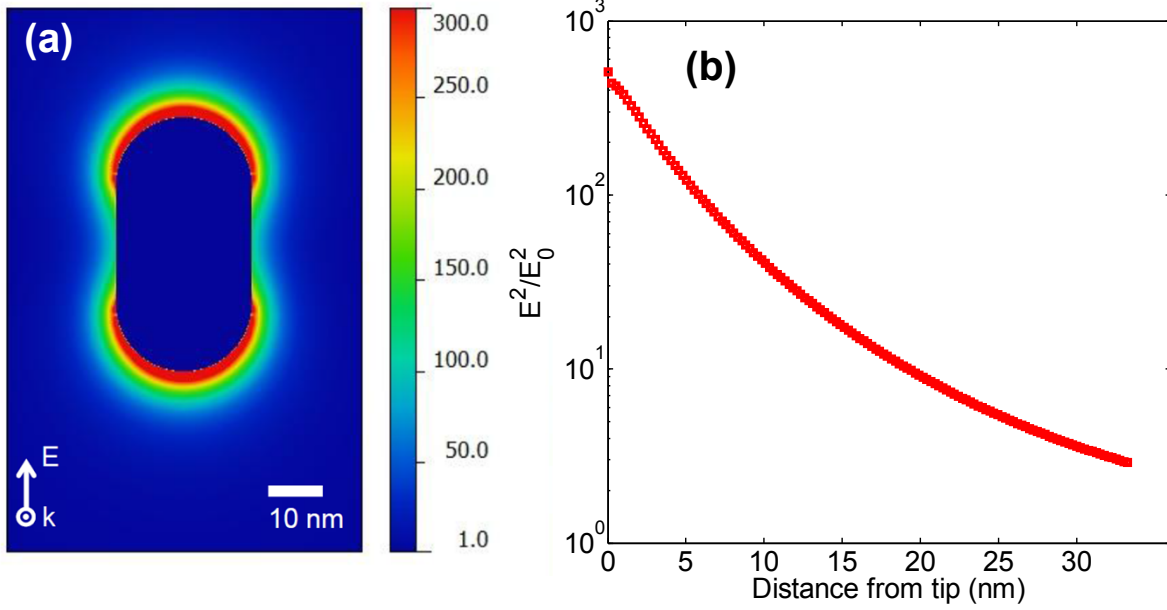
2. Near-field intensity distribution around a gold nanorod

Figure S2: *(a) Calculated near-field intensity map of a 25 nm × 47 nm gold nanorod using discrete dipole approximation (DDA) method. The excitation wavelength was 633 nm and the incident polarization was along the long axis of the nanorod. (b) Near-field intensity as a function of distance from the tip of the nanorod. The field intensity decreases by a factor of 10 from its maximum value at a distance of 10 nm from the tip.*

3. *Temperature distribution around a gold nanorod*

The steady state temperature at a given point ξ near an ellipsoid representing a gold nanorod can be expressed by equation (1) which is an analytical solution of Poisson's equation of heat conductivity around an ellipsoid.

$$T(\xi) = T_0 + \phi(\xi) = T_0 + \frac{1}{8\pi K_m \sqrt{a^2 - b^2}} \frac{P_d}{} log \frac{\sqrt{\xi + a^2} + \sqrt{a^2 - b^2}}{\sqrt{\xi + a^2} - \sqrt{a^2 - b^2}} \quad , (1)$$

where P_d is the dissipated power, K_m is the thermal conductivity of the medium, T_0 is the temperature of the medium at infinite distance from the nanorod, a and b are the length of the major and minor axis of the nanorod and ξ is an ellipsoidal coordinate given by

$$\xi$$

$$= \frac{1}{2}\{(x^2 + y^2 + z^2) - (a^2 + b^2)\} + \frac{1}{2}\sqrt{(a^2 + b^2) + (x^2 + y^2 + z^2)^2 - 2x^2}$$

The surface temperature of the nanorod is found at $\xi = 0$. We note that equation (1) is based on several assumptions: (a) the temperature over the entire nanorod is uniform. This is a valid approximation as the heat conductivity of gold ($\sim 318 \, Wm^{-1}K^{-1}$ at $300 \, K$) is three orders of magnitude higher than that of glycerol ($\sim 0.29 \, Wm^{-1}K^{-1}$ at $300 \, K$). (b) The thermal conductivity of the medium K_m is constant through the temperature range. K_m of glycerol changes by only ~2% within the range between 300 K and 350 K. (c) the system is in steady state, i.e. $\delta T/\delta t = 0$. This is valid as the heating source is stationary in this case and the typical heat diffusion time is several nanoseconds only. We also mention that no effect of substrate was considered.

The dissipated power P_d is given by:

$$P_d = \sigma I \qquad (1)$$

σ is the absorption cross-section. The absorption cross section of a 25×60 nm gold nanorod is 10^4 nm^2 at 633 nm. I is the excitation laser intensity.
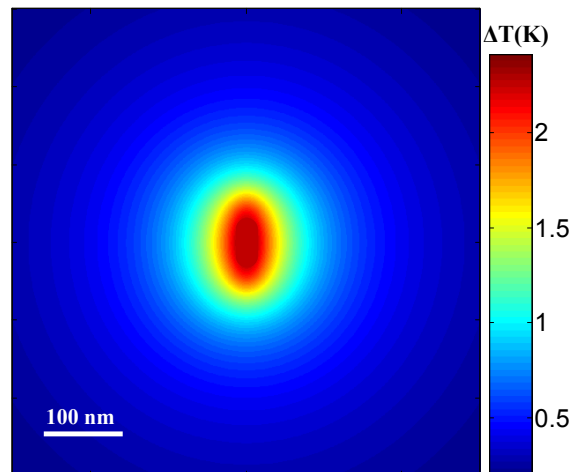
Figure S3: *Temperature distribution profile around an ellipsoidal gold nanoparticle (25 ×60 nm) using equation 1 in the main text. For an excitation power of 10 µW, the temperature rise at the surface of the nanorod was 2.4 K. Note that substrate effect was not included in this calculation.*
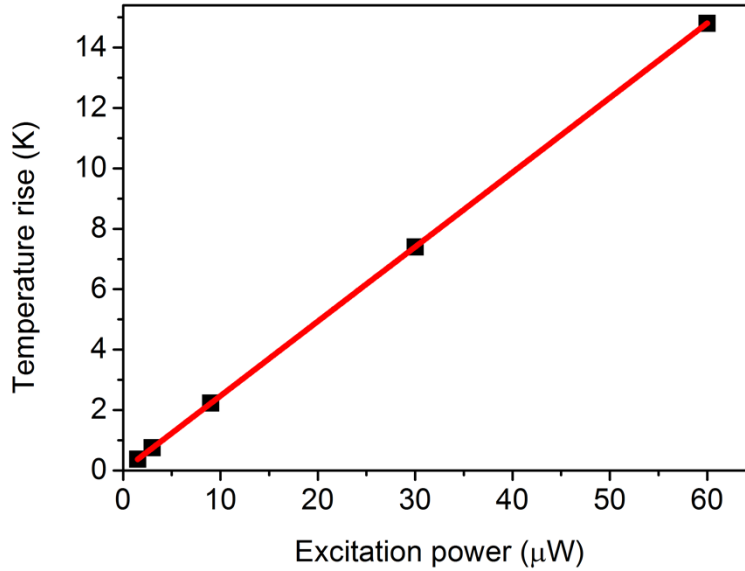

Figure S4: *Temperature rise (averaged between temperature rises at the surface and at a distance of 10 nm from the surface) as a function of excitation power (black squares). A linear fit (red line) yields a slope of 0.24 K/µW.*

4. Calculation of diffusion time (τ_d):

The diffusion time is given by:

$$\tau_d = \frac{L^2}{D}$$

where L= 10 nm, the dimension of steepest variation (thickness) of the near-field. D is the molecular diffusion coefficient:

$$D = \frac{k_B T}{6\pi\eta(T)r}$$

k_B is the Boltzmann's constant. r is the hydrodynamic radius (1 nm). The viscosity of glycerol as a function of temperature $\eta(T)$ can be expressed as[3]:

$$\eta(T) = \eta_0 10^{\frac{B}{T-T_0}} \text{.......}(1)$$

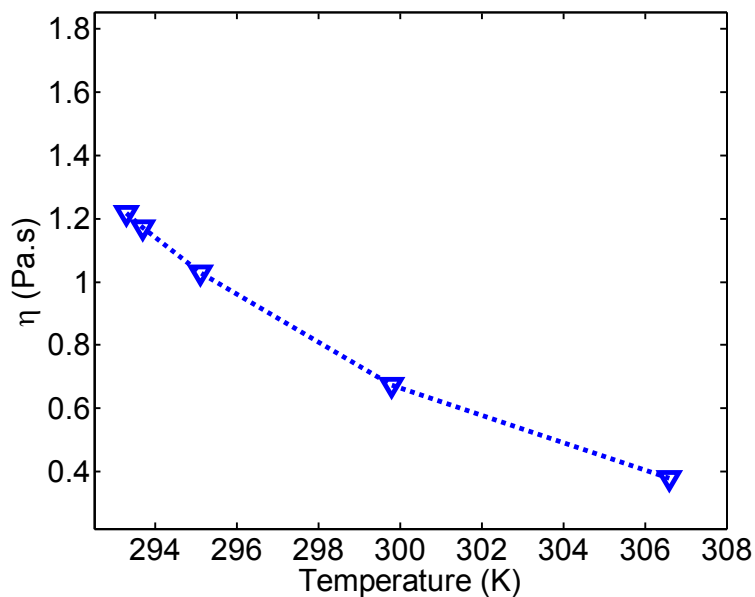with $\eta_0 = 7.9 \times 10^{-8} Pa.s$, $B = 1260\,K$, and $T_0 = 118\,K$.

Figure S5: *Calculated local viscosity of glycerol as a function of temperature according to equation 1. The room temperature was 293 K. Connecting dots are used as a guide to the eye.*
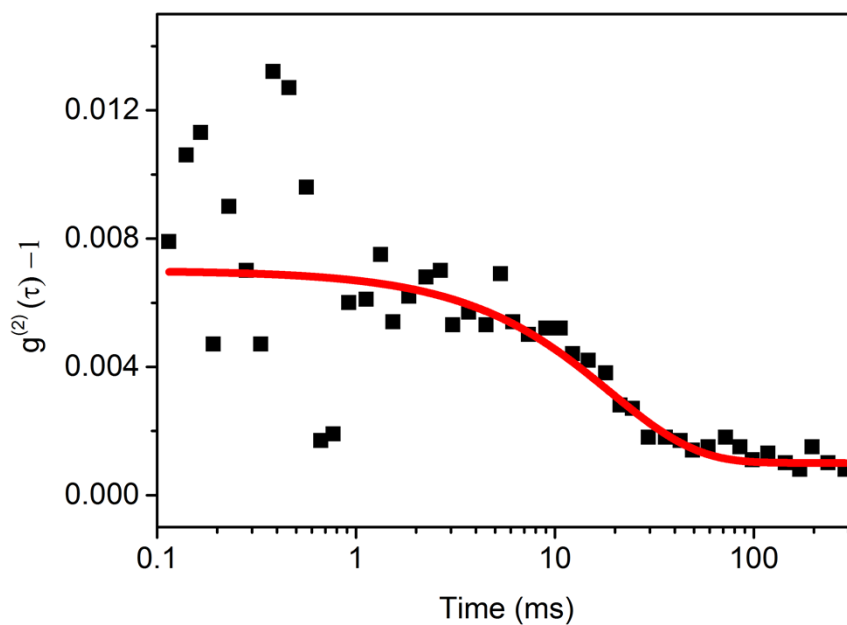

Figure S6: *FCS curve of 10 pM CV in glycerol. A single exponential fit (red curve) yields a correlation time of 17 ms.*

At 10 μW excitation power, the temperature increase is: $\Delta T = 2.05\ K$, $\eta = 1.03\ Pa.s$ according to equation 1.

$$D = 2.1 \times 10^{-13} m^2/s$$

$$\tau_d = 0.5\ ms$$

The correlation of the fluorescence of a CV solution in glycerol at room temperature, observed in a standard confocal microscope, shows a weak correlation (Fig. S6). As the correlation time is too short for translational diffusion and too long for rotational diffusion, we attribute it to triplet blinking. The associated fluctuations may influence the short correlation component observed in enhanced fluorescence correlation spectroscopy.

References:

1. B. Nikoobakht and M. A. El-Sayed, *Chemistry of Materials*, 2003, **15**, 1957-1962.
2. L. A. Brey, G. B. Schuster and H. G. Drickamer, *Journal of Chemical Physics*, 1977, **67**, 2648-2650.
3. R. Zondervan, F. Kulzer, G. C. G. Berkhout and M. Orrit, *Proceedings of the National Academy of Sciences of the United States of America*, 2007, **104**, 12628-12633.
4. J. A. Balderas-Lopez, A. Mandelis and J. A. Garcia, *Review of Scientific Instruments*, 2000, **71**, 2933-2937.