

Supporting information for

Resonant plasmonic enhancement of single-molecule fluorescence by individual gold nanorods

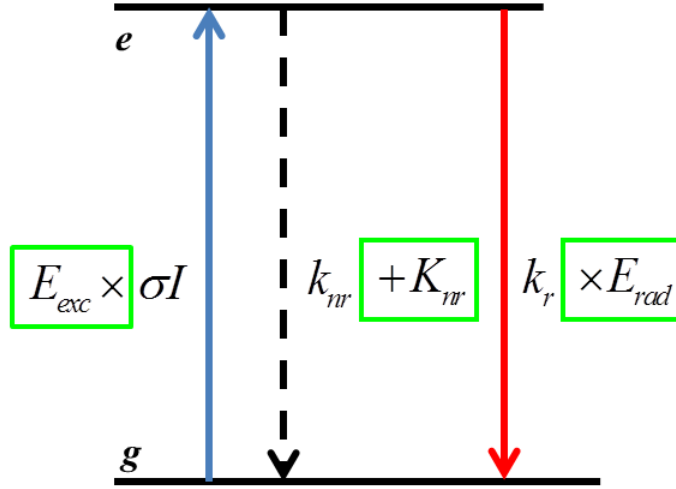
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Section I: Theoretical description of single-molecule fluorescence enhancement near a nano-antenna:



Scheme 1: A simple two-level scheme to describe the transition rates of a molecule without and with gold nanorod antenna (highlighted in green box). σ is the absorption cross section of the molecule and I is the excitation laser intensity.

Based on this scheme, we can write down the rate of population of the excited state (\dot{p}_e) and rate of fluorescence (I_f) when no nanorod is present:

$$\dot{p}_e = \sigma I p_g - (k_{nr} + k_r) p_e$$

$$I_f = p_e k_r$$

Where p_e and p_g are the probabilities of a molecule in the excited and ground state. At steady-state condition:

$$\dot{p}_e = 0$$

$$\Rightarrow \sigma I p_g - (k_{nr} + k_r) p_e = 0$$

$$\Rightarrow \sigma I (1 - p_e) - (k_{nr} + k_r) p_e = 0$$

$$\Rightarrow p_e = \frac{\sigma I}{\sigma I + k_{nr} + k_r} \quad (1)$$

In presence of a nanorod antenna, the rate of population of excited state (\dot{p}'_e) and rate of fluorescence (I'_f) can be written as:

$$\dot{p}'_e = E_{exc}\sigma I p'_g - (k_{nr} + K_{nr} + k_r)p'_e$$

$$I'_f = E_{rad}k_r p'_e ,$$

where p'_e and p'_g are the probabilities of a molecule in the excited and ground state in presence of the antenna. We have assumed emission at a single wavelength. At steady-state conditions:

$$\dot{p}'_e = 0$$

$$p'_e = \frac{E_{exc}\sigma I}{E_{exc}\sigma I + (k_{nr} + K_{nr}) + E_{rad}k_r} \quad (2)$$

The overall fluorescence enhancement (ξ), in presence of the antenna can be given by

$$\xi = \frac{I'_f}{I_f}$$

$$\xi = E_{rad} \frac{p'_e}{p_e}$$

Using equations (1) and (2):

$$\xi = E_{exc}E_{rad} \frac{\sigma I + k_r + k_{nr}}{E_{exc}\sigma I + (k_{nr} + K_{nr}) + E_{rad}k_r} \quad (3)$$

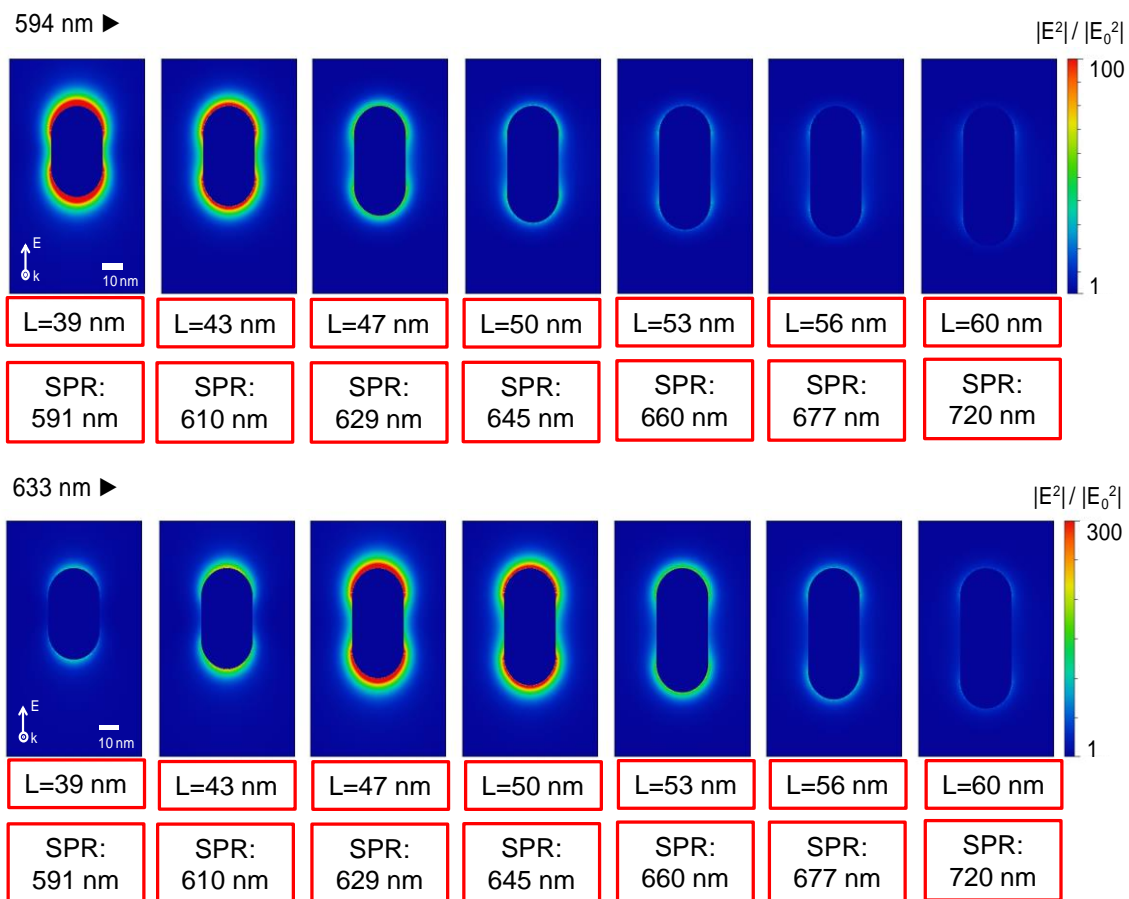
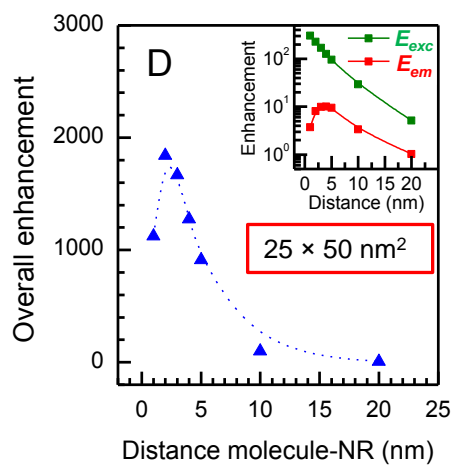
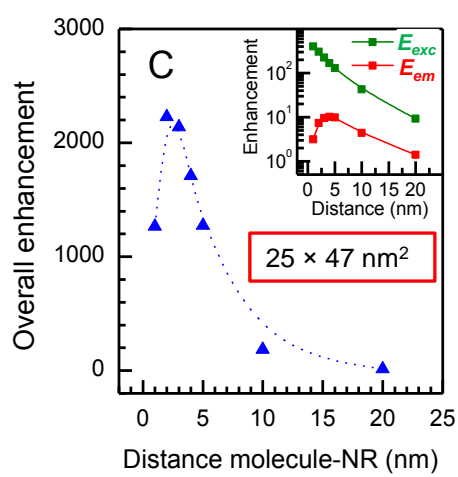
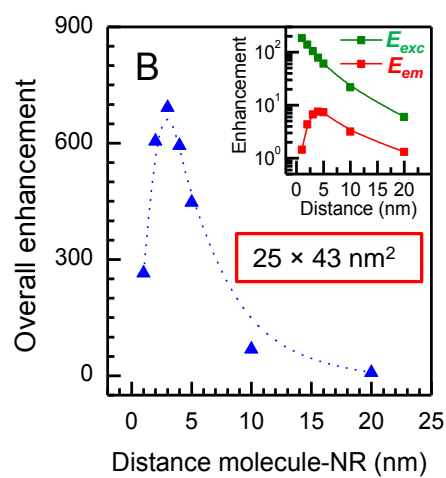
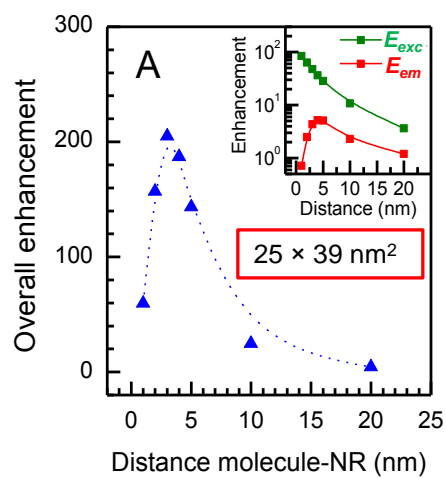


Figure S1: Near-field intensity distribution of nanorods with different aspect ratios under 594 nm and 633 nm excitation. The excitation polarization is along the long axis of the nanorods. The width of the nanorods is fixed at 25 nm and the lengths are shown in the red boxes.



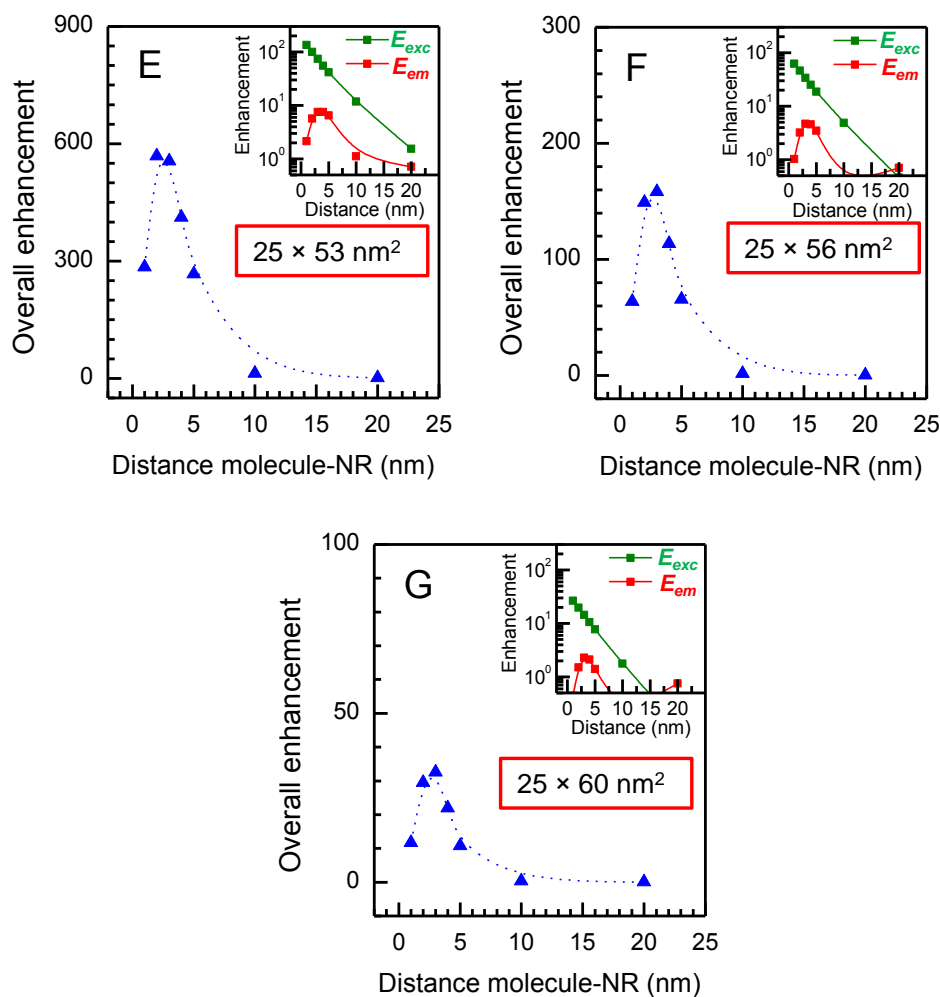


Figure S2: Calculated overall fluorescence enhancements (blue dots) at different distances between CV molecule and the tip of gold nanorods with a length of: (A) 39 nm; (B) 43 nm; (C) 47 nm; (D) 50 nm; (E) 53 nm; (F) 56 nm; and (G) 60 nm. The width was fixed at 25 nm for all rods. The excitation wavelength was selected at 633 nm and emission wavelength at 640 nm. The insets show the excitation (green dots) enhancement and effective emission (red dots) enhancement (taking non radiative relaxation into account) for the same systems. Calculations were performed with the DDA method (see main text for details).

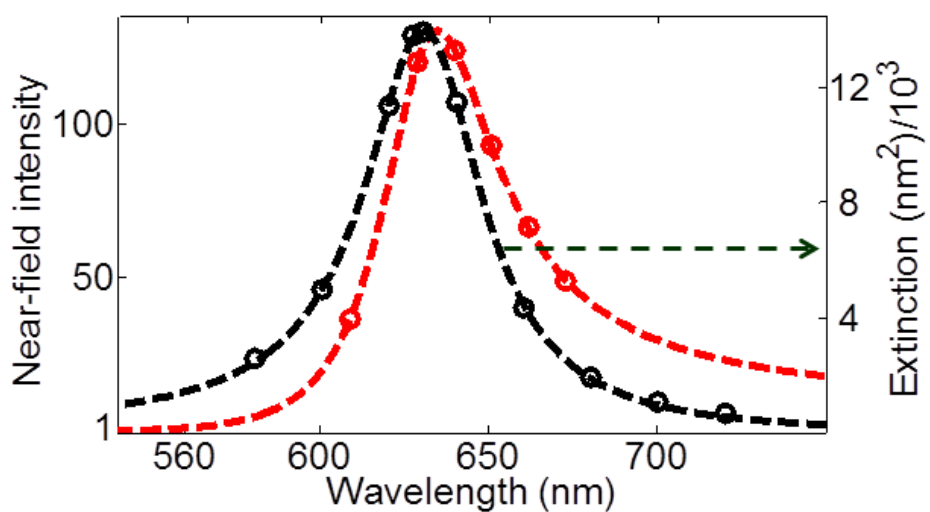


Figure S3: Near-field intensity (red, normalized to the incoming intensity) and far-field extinction cross section (black) spectra of a nanorod with SPR wavelength of 629 nm. Near-field intensities are calculated at 5 nm from the surface along the long axis of the nanorod. The excitation wavelength is 633 nm and is polarized along the long axis of the nanorod.

Table 1: results from the DDA simulation.

SPR wavelengths (nm)	591	610	629	645	660	677	700
$E_{exc} (\lambda_{ex} = 594 \text{ nm})$	49.03	31.25	11.76	5.84	3.08	1.71	0.83
$E_{exc} (\lambda_{ex} = 633 \text{ nm})$	28.24	60.88	129.0	95.88	41.47	18.74	7.71
$E_{rad} (\lambda_{em} = 640 \text{ nm})$	9.96	18.76	41.85	45.17	19.58	7.46	2.42
E_r	7.23	12.26	23.04	30.27	34.78	35.78	32.62
$K_{nr}/k_r (\lambda_{em} = 640 \text{ nm})$	38.80	65.95	128.17	155.46	79.69	38.62	15.62
K_{nr}/k_r	23.79	37.61	66.92	84.28	86.83	80.05	61.94
E_{em}	4.60	6.35	8.56	9.58	10.56	11.23	11.74
$\xi (\lambda_{ex} = 633 \text{ nm})$	129.95	386.83	1103.97	918.57	437.90	210.60	90.49
$\xi (\lambda_{ex} = 594 \text{ nm})$	225.54	198.44	100.67	55.95	32.52	19.20	9.74

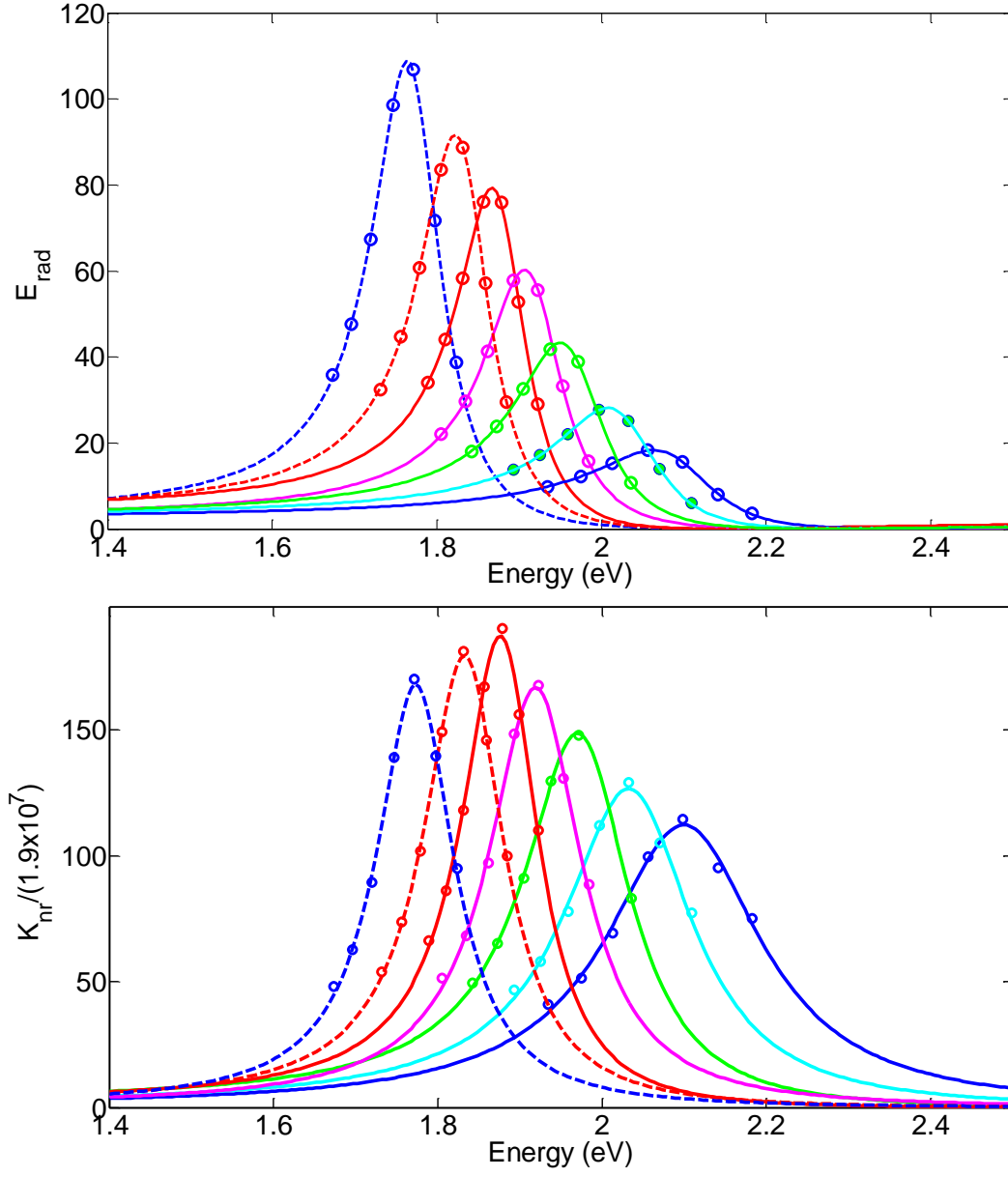


Figure S4: Calculated E_{rad} and K_{nr} as a function of emission energy (circles) for 7 nanorods. E_{rad} and K_{nr} are fitted by solid lines according to the equations below:

$$E_{rad}(\omega) = \left| A + \frac{\alpha\tau}{(\omega - \omega_0) + i\tau} \right|^2$$

$$K_{nr}(\omega) = \left| A' + \frac{\alpha' \tau}{(\omega - \omega_0) + i\tau'} \right|^2$$

where ω_0 is the resonance frequency, τ is FWHM, A and α are constants which describe the shape asymmetry and the amplitude.

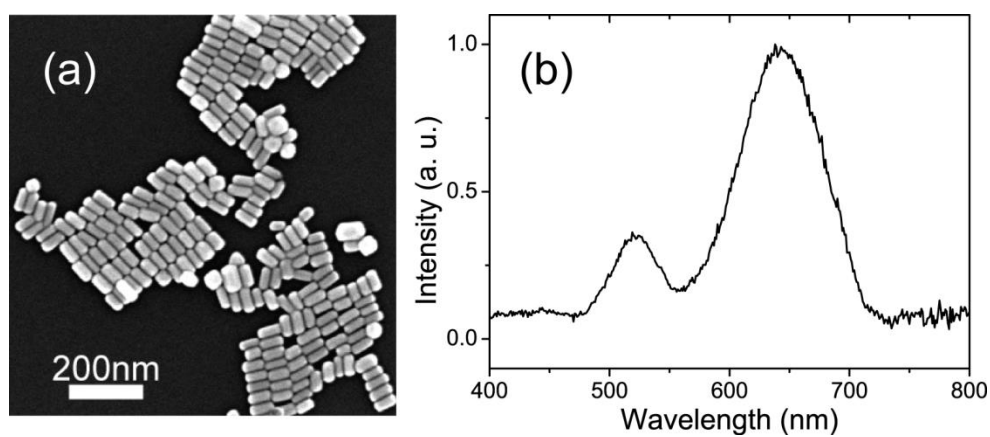


Figure S5: (a) A SEM image of gold nanorods used in present work. (b) Bulk UV-vis spectrum of nanorods in water. The longitudinal surface plasmon resonance is at 650 nm.

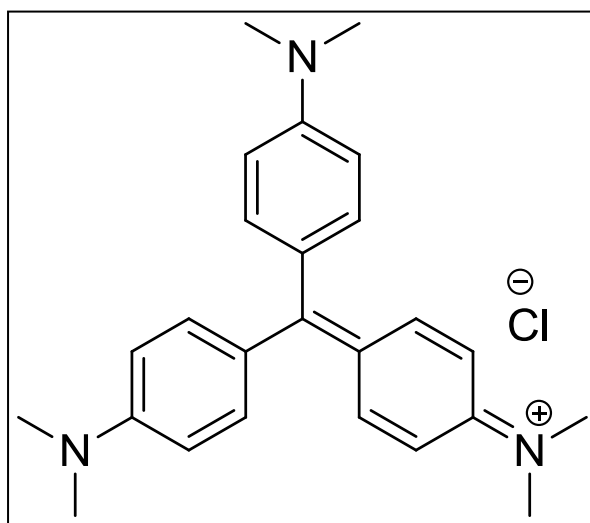


Figure S6: Chemical structure of Crystal Violet (CV).

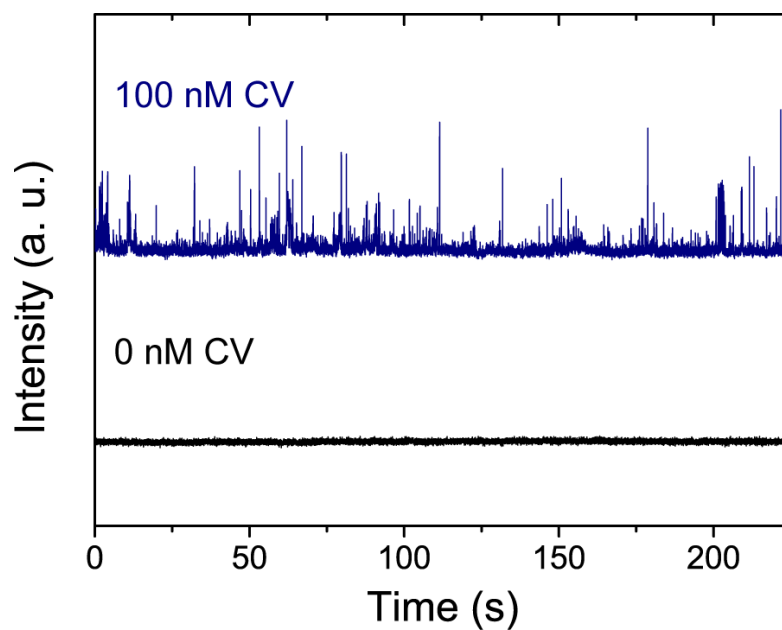


Figure S7: Fluorescence time traces recorded on two single gold nanorods in solutions with different CV concentrations. When there was no CV in glycerol, no fluorescence bursts were observed in the fluorescence timetrace (black). At a CV concentration of 100 nM, fluorescence intensity bursts were visible in the time trace (blue). The excitation power density was 5 kW/cm^2 at 633 nm.

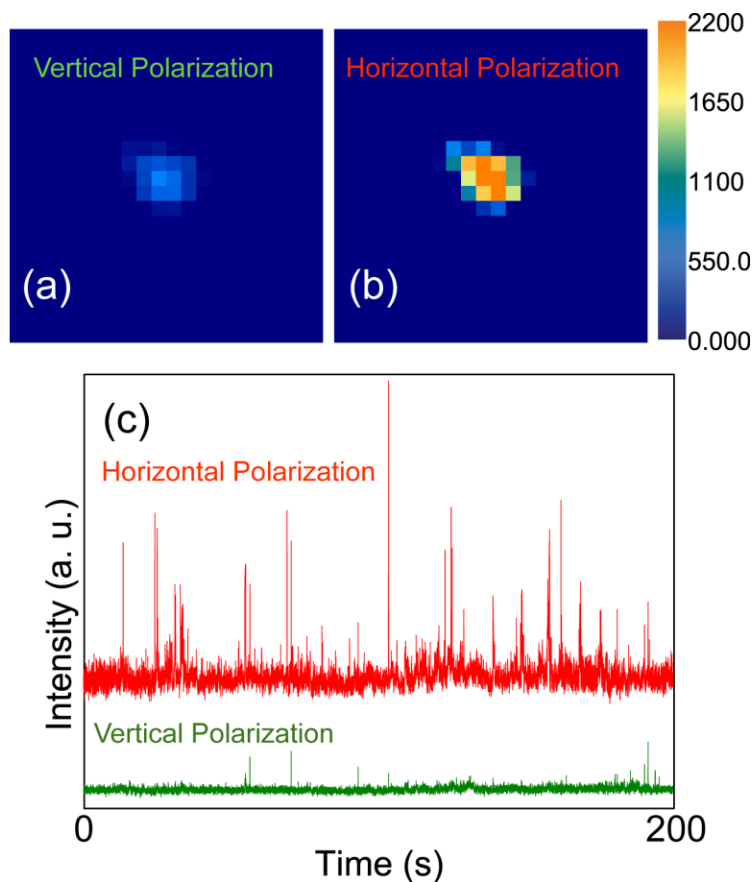


Figure S8: (a) and (b) $2\ \mu\text{m} \times 2\ \mu\text{m}$ images of a nanorod for two perpendicular detection polarizations (vertical and horizontal). A circularly polarized 633 nm laser was used as the excitation source. The nanorod of interest is located at the centre of image. Note that the long axis of the nanorod is oriented along the horizontal polarization detection. (c) Fluorescence time trace on the same GNR in the presence of CV for vertical (green) and horizontal (red) polarization. We can clearly see the fluorescence with horizontal polarization is more enhanced than fluorescence with vertical polarization. This indicates that the fluorescence enhancement is strongly polarization dependent.

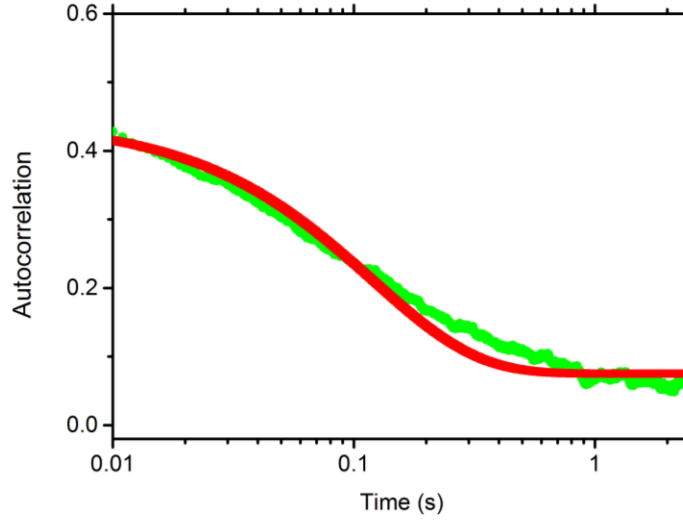


Figure S9: A typical autocorrelation curve of the fluorescence bursts, fitted with a single exponential (red curve). The correlation decay is clearly non-exponential, but the fit allows us to extract an average decay time of 124 ms, clearly longer than expected for molecular diffusion.

II. Estimation of $E_{exc}\sigma I$:

Estimated E_{exc} by a nanorod with SPR at 629 nm (which shows the maximum enhancement) is 129. Absorption cross section of a CV molecule (σ) is 1 nm^2 . Excitation intensity is 5 kW/cm^2 . Using these values one can estimate the enhanced rate of excitation:

$$E_{exc}\sigma I = 2 \times 10^8 \text{ excitations/s}$$

Including the radiative decay rate enhancement E_{rad} and the additional non-radiative decay rate (K_{nr}) we estimate the enhanced decay rate:

$$k_{nr} + K_{nr} + E_r k_r = 3 \times 10^9 \text{ s}^{-1}$$

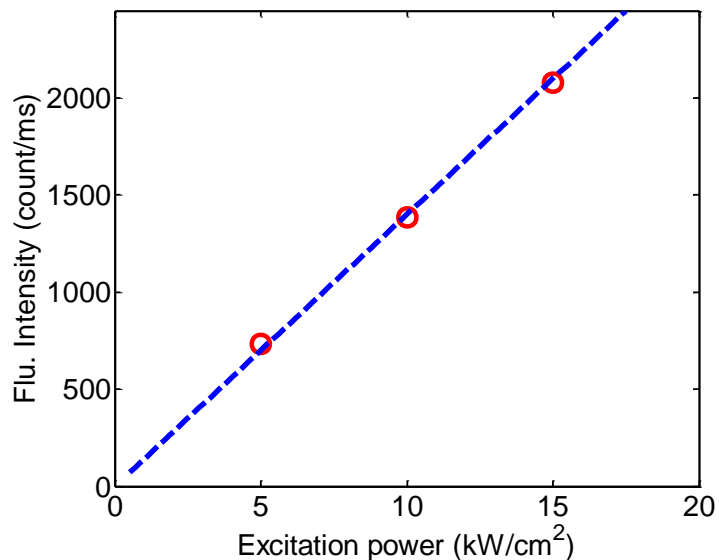


Figure S10: Maximum fluorescence burst intensities (from fluorescence time traces recorded on a nanorod) are shown as a function of excitation laser power (red circles). A linear fit to the data is shown as blue line. The linear dependence of fluorescence intensities shows that the enhanced molecule is below saturation.

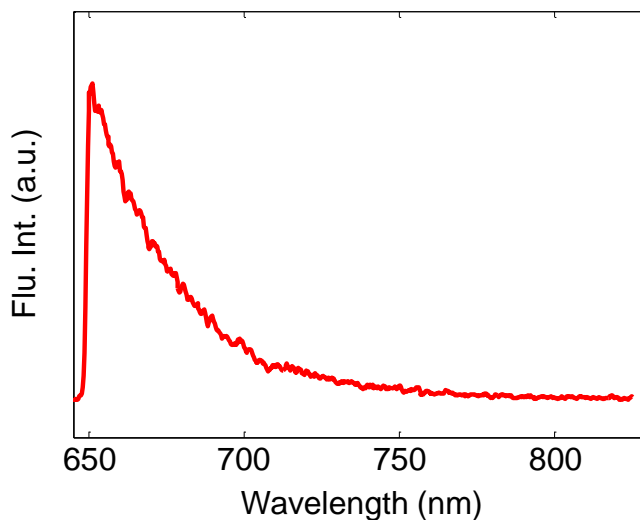


Figure S11: Luminescence spectrum of a gold nanorod covered with 50 nM CV solution in glycerol using 633 nm excitation. The fluorescence is much brighter than that of the nanorod without CV, but its spectrum is very similar, confirming that CV fluorescence is strongly enhanced only around the SPR of the nanorod. In particular, the absence of any sharp lines excludes significant contributions from surface-enhanced Raman scattering (SERS) to the observed bursts.