Supporting Information

Gold nanorods as multifunctional probes in liquid crystalline DNA matrix

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Extinction spectrum of gold nanorods

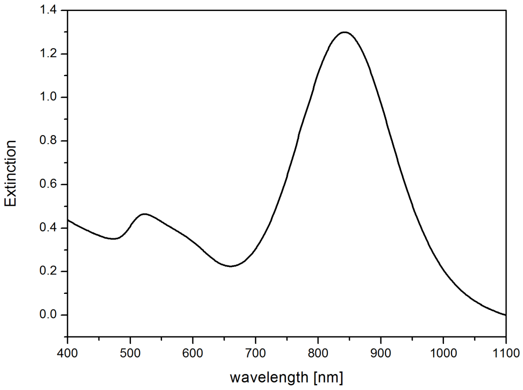

Figure S1. Extinction spectrum of gold nanorods solution.

The model of two-photon excited fluorescence in DNA-dye system

The model of the angular dependence of ps-2PFM of liquid crystalline DNA can be found in [1]. It takes into account the orientation of a DNA strand and the direction of the emission dipole of a fluorescent dopant in the macroscopic XY framework of the scan plane (Fig. S2). The rotation of DNA in the XY plane is accounted by the angle φ. Averaging the binding angle of a dye or a NR, i.e. the rotation of the emission dipole by 360° around the long axis of DNA strand, leads to formation of a cone with an opening angle Ψ. Small variations in the orientation of DNA helix and deviations of the binding angle are taken into account by thickening the cone by an angle $\Delta\Psi$. On the basis of our previous examination [1], the relative angle between the DNA chain and a bound molecule of EB is constant and equals to $\Psi_{EB} = 80^{\circ}$.

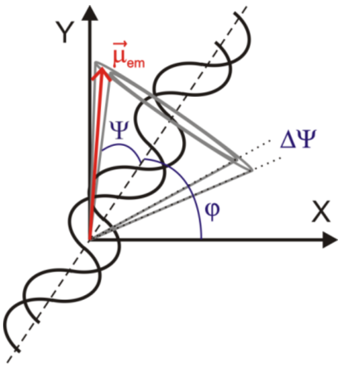

Figure S2. Model of the orientation of the emission dipole of a DNA marker, $\vec{\mu}_{em}$, with respect to a DNA double helix in the macroscopic XYZ framework of the sample. The dipoles $\vec{\mu}_{em}$ are located in a cone of half-angle Ψ with the origin on a long axis of a DNA helix (denoted by the dashed line). The variable thickness of the cone is defined as $\Delta\Psi$, and the position of DNA in the XY plane of the sample is described by angle φ.

The determination of optimum illumination conditions

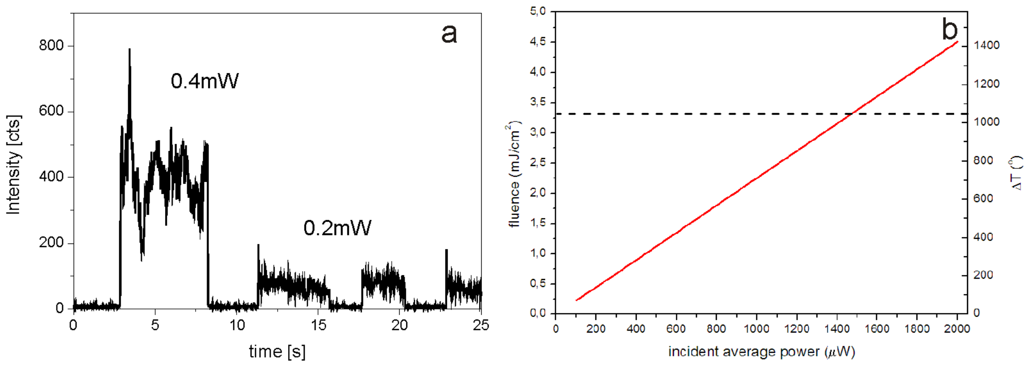

Figure S3. a) Temporal profile of 2PL of a NR excited at l-SPR maximum wavelength, P = 0.4 mW and P = 0.2 mW; b) Calculated fluence and temperature increase as a function of the incident laser power measured at the entrance to the microscope; dashed line denotes the threshold energy of gold melting;

The temporal profile of NRs luminescence excited with our setup depends quadratically on the incident laser power, which confirms that the luminescence is caused by two-photon absorption (Fig. S3 a). When an NR is excited close to its l-SPR the collected signal is stable only in the low-power excitation regime. In an NR subjected to the long-term illumination (in seconds regime), the NR heating may contribute strongly to the instability. To evaluate the significance of thermal effects, we estimated the focused peak intensity and the corresponding energy incident on a single NR. One-photon absorption cross section σ_{1PA} of an NR, determined from the absorption spectra of NRs solution with known concentration, equals 2.26 x 10^{-12} cm^2. We estimated the temperature increase of a nanoparticle after the absorption of a single fs laser pulse according to the formula:

$$\Delta T_{NP} = \frac{\sigma_{1PA} F}{V c_{Au} \rho_{Au}} \qquad \text{(S1)}$$

where F is the incident laser fluence, V denotes nanoparticle volume, ρ_{Au} and c_{Au} are bulk gold density and specific heat capacity, respectively. The obtained results are presented in Fig. S3 b. The melting point of gold nanoparticles depends on the particle size, but for nanoparticles bigger than ~15 nm it is usually assumed to be similar to the melting temperature of bulk gold T_m = 1337 K. [2] Effective diameter of our NRs equals d_{eff} = 18 nm, thus T_m is expected not to be very different from the bulk value. With the assumption of absence of cumulative effects, the energy of the focused beam is below the melting threshold at the illumination power less than 1.5 mW. In addition to nanoparticles melting, gold nanorods may undergo shape transformation before the melting temperature is reached, which changes their optical properties. However, in the experiments with fs laser in the range of average powers applied in this work (up to 0.5 mW), and when the nanorods were embedded in a matrix with good thermal conductivity, NRs did not stay hot for the time long enough for significant structural changes to occur. [3]

Investigation of the nanorods under irradiation

We performed a thorough analysis of a single NR behavior under laser irradiation in a function of the laser power. Images below present a variation of 2PL intensity when a nanorod is irradiated with a laser of an average power equal 20-30 μW (Fig. S4 a, b, d) and from 15 to 100 μW (Fig. S4 b, c, e). The gradual decrease of 2PL intensity is observed with the power values up to 50 μW, whereas a significant deviation from a linearly polarized 2PL emission is observed in the case of P = 100 μW. Shift in the Z direction increases the 2PL intensity (Fig. S5). Laser illumination with the average power of 5 μW does not introduce any change neither in the angular distribution nor the maximum intensity of the 2PL signal (Fig. S6). The discussion of the observations is given in the main text.

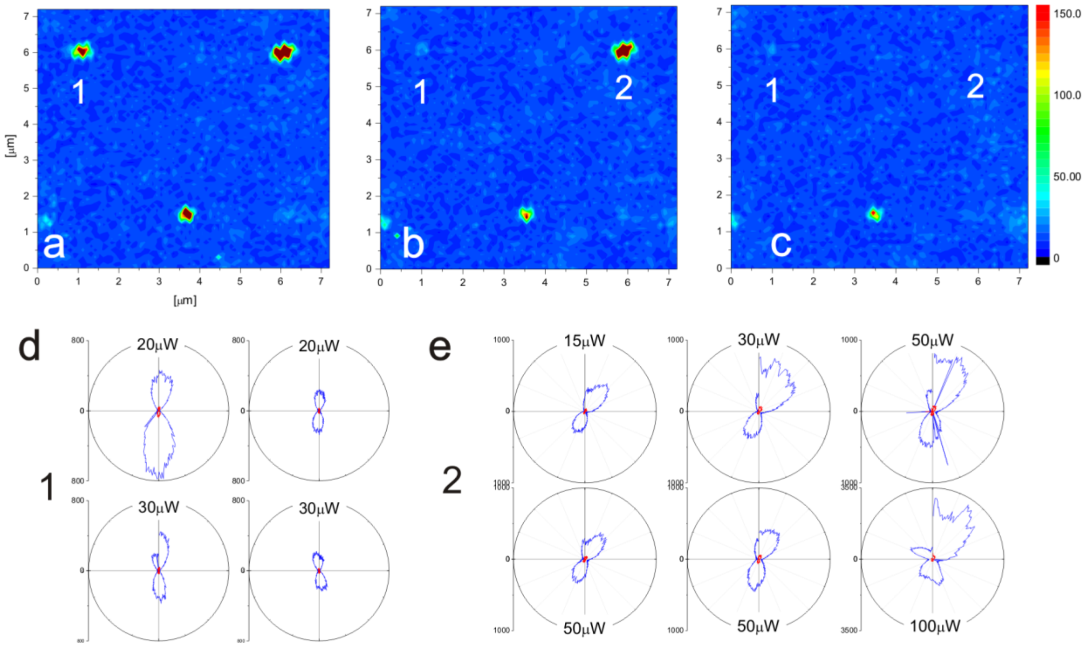

Figure S4. a-c) Scans of 2PL intensity of gold NRs in DNA LC matrix, P = 15 μW: a) scan before the polarization analysis of individual NRs, b) scan after the analysis of the NR no.1, c) scan after the analysis of the NR no. 2. d-e) polarization analyses of the NR no. 1 (d) and no. 2 (e); the incident laser powers are indicated in the figures.

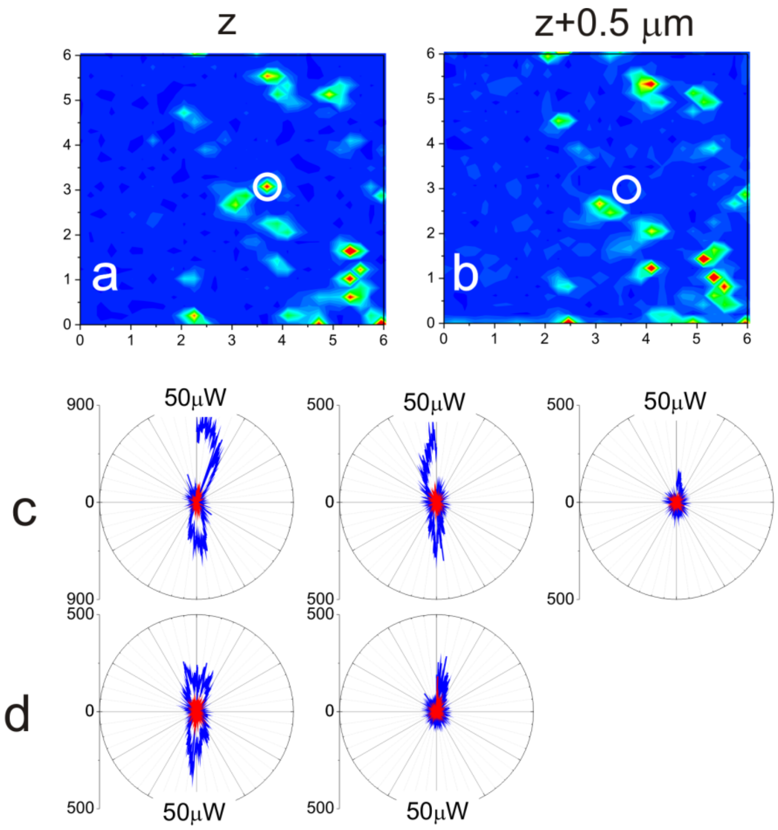

Figure S5. a, b) Scans of 2PL intensity of gold NRs in DNA LC matrix before and after polarization analysis of a single NR indicated with a white circle, respectively (P = 15 μW); c,d) polar graphs of 2PL of a NR indicated with a white circle in the scan a, in a position (x, y, z) (c); in the position (x, y, z+0.5μm) (d); the incident laser powers are indicated in the figures.

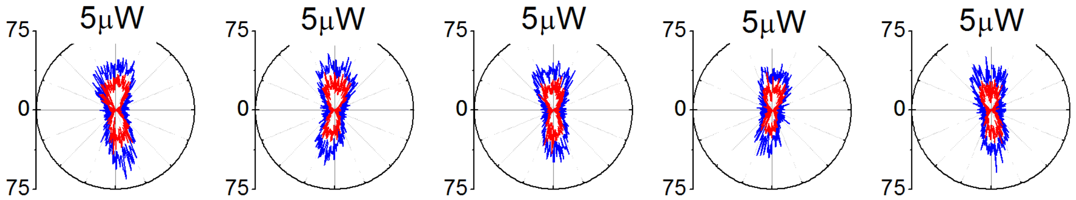

Figure S6. 2PL polar graphs of a single NR illuminated six times with a laser of P = 5 μW.

References

1. (a) Mojzisova, H.; Olesiak, J.; Zielinski, M.; Matczyszyn, K.; Chauvat, D.; Zyss, J., Polarization-Sensitive Two-Photon Microscopy Study of the Organization of Liquid-Crystalline DNA. *Biophys J* **2009,** *97* (8), 2348-2357; (b) Olesiak-Banska, J.; Mojzisova, H.; Chauvat, D.; Zielinski, M.; Matczyszyn, K.; Tauc, P.; Zyss, J., Liquid crystal phases of DNA: evaluation of DNA organization by two-photon fluorescence microscopy and polarization analysis. *Biopolymers* **2011,** *95*, 365-375.
2. (a) Buffat, P.; Borel, J. P., Size effect on the melting temperature of gold particles. *Phys Rev A* **1976,** *13* (6), 2287-2298; (b) Hashimoto, S.; Werner, D.; Uwada, T., Studies on the interaction of pulsed lasers with plasmonic gold nanoparticles toward light manipulation, heat management, and nanofabrication. *J Photoch Photobio C* **2012,** *13* (1), 28-54.
3. Petrova, H.; Perez Juste, J.; Pastoriza-Santos, I.; Hartland, G. V.; Liz-Marzan, L. M.; Mulvaney, P., On the temperature stability of gold nanorods: comparison between thermal and ultrafast laser-induced heating. *Phys Chem Chem Phys* **2006,** *8* (7), 814-21.