

Novel concept for contactless all-optical temperature measurement based on diffusion-inspired phosphorescent decay in nanostructured environment

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Introduction

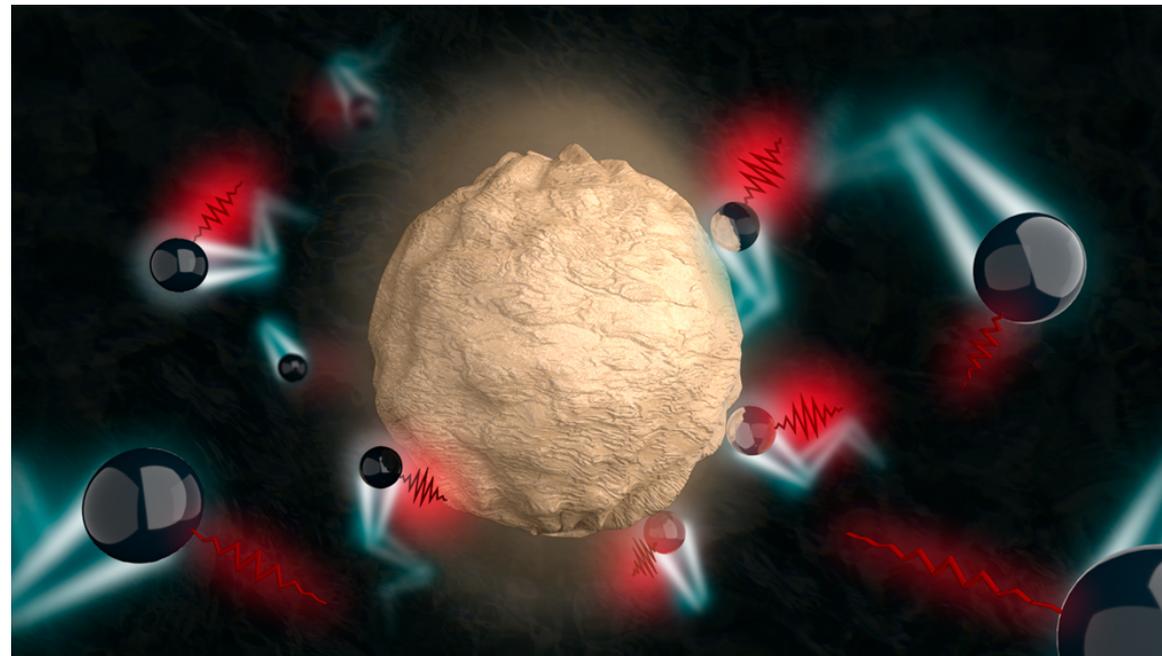
Theory

Simulation

Results

Conclusion

Structured environment controls dynamics of light-matter interaction processes via modified local density of electromagnetic states. In typical scenarios, where nanosecond-scale fluorescent processes are involved, mechanical conformational changes of the environment during the interaction processes can be safely neglected. However, slow decaying phosphorescent complexes (e.g. lanthanides) can efficiently probe micro- and millisecond scale motion via near-field interactions with nearby structures. As the result, lifetime statistics can inherit information about nano-scale mechanical motion. Here we study light-matter interaction dynamics of phosphorescent dyes, diffusing in a proximity of a plasmonic nanoantenna.



The schematics of the system – diffusion of slow-decaying phosphorescent dyes next to a resonant nanoantenna.

Diffusion Model

The diffusion equation in spherical coordinates for this type of a process can be written as:

$$\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial r^2} + 2 \frac{D}{r} \frac{\partial n}{\partial r} - \gamma(r)n$$

where D is the diffusion coefficient of phosphorescent molecules;

$n(\mathbf{r}, t)$ - concentration of excited molecules;

$\gamma(\mathbf{r}) = \gamma_0 F(\mathbf{r})$ - position-dependent decay rate;

$F(\mathbf{r})$ is the Purcell factor

In free space, without a particle present, the characteristic decay time is

$$\tau_0 = 1 / \gamma_0$$

Diffusion coefficient generally depends on temperature and other parameters of an environment, which can be related to each other via Stokes – Einstein relation:

$$\frac{D_{T_1}}{D_{T_2}} = \frac{T_1}{T_2} \frac{\mu_{T_2}}{\mu_{T_1}}$$

where μ is a solvent's dynamic viscosity and sub-indices correspond to different local temperatures. This dependence can provide a new methodology for local temperature sensing via Purcell-effect-induced luminescence modification, as it will be shown with forthcoming analysis.

Position and orientation averaged Purcell enhancement

$F(r) = \frac{2}{3}F_{\parallel}(r) + \frac{1}{3}F_{\perp}(r)$ - Purcell factor averaged over molecular orientations

$$F_{\parallel}(r) = 1 + \frac{3}{4} \sum_{m=1}^{\infty} (2m+1) \operatorname{Re} \left[B_m \left(\frac{\zeta_m(kr\sqrt{\varepsilon_0})}{kr\sqrt{\varepsilon_0}} \right)^2 + A_m \left(\frac{\zeta'_m(kr\sqrt{\varepsilon_0})}{kr\sqrt{\varepsilon_0}} \right)^2 \right],$$

$$F_{\perp}(r) = 1 + \frac{3}{2} \sum_{m=1}^{\infty} m(m+1)(2m+1) \operatorname{Re} \left[A_m \left(\frac{\zeta_m(kr\sqrt{\varepsilon_0})}{(kr\sqrt{\varepsilon_0})^2} \right)^2 \right],$$

Mie coefficients

$$A_m = - \frac{\sqrt{\varepsilon} \psi_m(ka\sqrt{\varepsilon}) \psi'_m(ka\sqrt{\varepsilon_0}) - \sqrt{\varepsilon_0} \psi'_m(ka\sqrt{\varepsilon}) \psi_m(ka\sqrt{\varepsilon_0})}{\sqrt{\varepsilon} \psi_m(ka\sqrt{\varepsilon}) \zeta'_m(ka\sqrt{\varepsilon_0}) - \sqrt{\varepsilon_0} \psi'_m(ka\sqrt{\varepsilon}) \zeta_m(ka\sqrt{\varepsilon_0})},$$

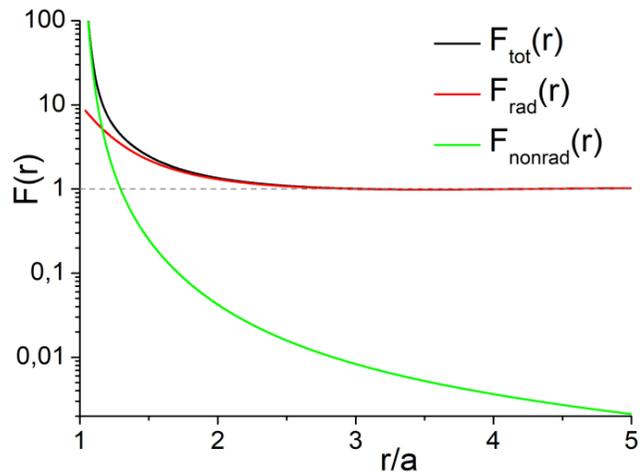
$$B_m = - \frac{\sqrt{\varepsilon_0} \psi_m(ka\sqrt{\varepsilon}) \psi'_m(ka\sqrt{\varepsilon_0}) - \sqrt{\varepsilon} \psi'_m(ka\sqrt{\varepsilon}) \psi_m(ka\sqrt{\varepsilon_0})}{\sqrt{\varepsilon_0} \psi_m(ka\sqrt{\varepsilon}) \zeta'_m(ka\sqrt{\varepsilon_0}) - \sqrt{\varepsilon} \psi'_m(ka\sqrt{\varepsilon}) \zeta_m(ka\sqrt{\varepsilon_0})},$$

$\psi_m(x) = x j_m(x)$, $\zeta_m(x) = x h_m^{(1)}(x)$, $j_m(x)$ и $h_m^{(1)}(x)$ – spherical Bessel and Hankel functions of the first kind, respectively.

References

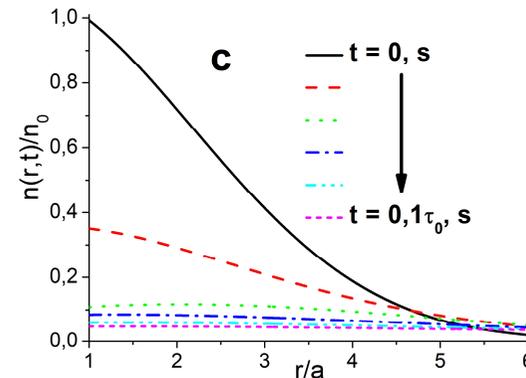
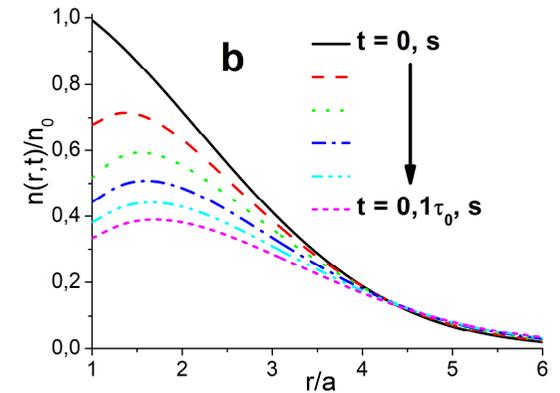
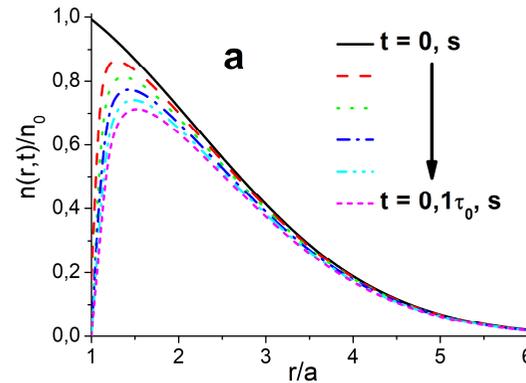
[1] Gaponenko, S. V. et al. // Sci. Rep. 2019, 9 (1).

Purcell factor



Purcell enhancement next to a gold (50nm radius) nanoparticle. Orientation-averaged total, radiative and nonradiative enhancements (black, red and green lines respectively) as a function of the normalized distance (to the particle's radius) between the dipole and particle's surface. The phosphorescent emission central wavelength is 690 nm.

Analysis of the diffusion-inspired emission dynamics



Radial distribution of excited dye molecules density in a vicinity of the particle. Different times, elapsed from the pump pulse are represented with color lines (in captions – $[0:6:0.1\tau_0]$ the interval is equidistantly divided into 6 sections). Diffusion coefficients (D [$\mu\text{m}^2 / \text{ms}$]) are: a) 0, b) 0.2, c) 1.6. Other parameters: $a=50\text{nm}$ $R_b=4.8a$ $\tau_0=300\mu\text{s}$

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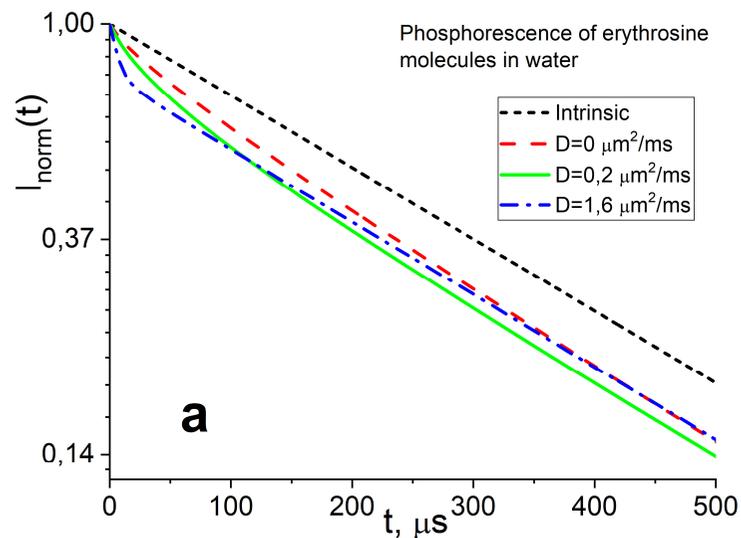
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Intensity decay of the dye molecules in a vicinity of the particle

The diffusion kinetics has a direct replica on the lifetime distribution, which can be measured at the far-field. Intensity, collected at the far-field, has the following time dependence:

$$I(t) \sim \int_a^{R_{\text{collection}}} \int_0^\pi \int_0^{2\pi} F^{\text{rad}}(r) \gamma_0 n(r,t) r^2 \sin^2(\vartheta) dr d\vartheta d\varphi$$

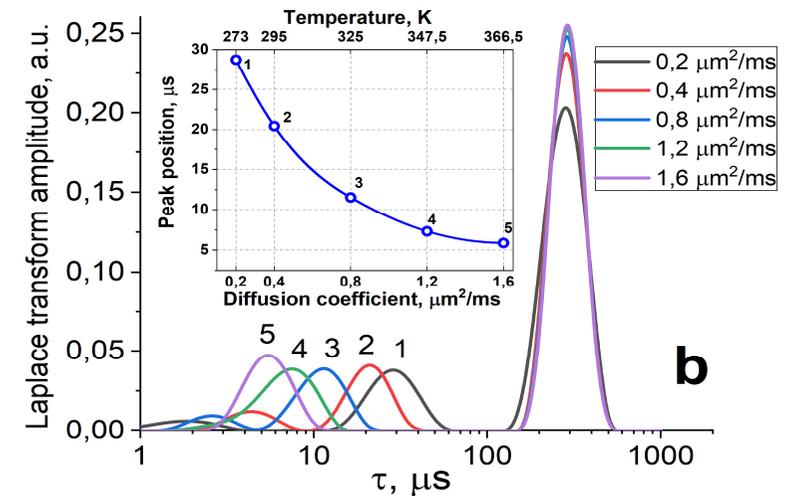


Lifetime distribution analysis

The kinetics of the collected intensity can be used as a tool for diffusion and, hence, temperature detection. To demonstrate this, we apply the inverse Laplace transformation on the function $I(t)$:

$$I(t) = \int_0^\infty g(s) e^{-st} ds$$

where $s = 1/\tau$ is the inverse relaxation time.





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1. We developed a novel concept for contactless all-optical temperature and diffusion measurements, which are enabled by dynamic time-dependent Purcell effect in a solution of phosphorescent molecules interfacing resonant nanoantennae.
2. Dynamics of the long life-time phosphorescent molecules decay is shown to be strongly dependent on the Brownian motion next to a resonator.
3. Subsequently, far-field radiation emitted from diffusing molecules is analyzed via the inverse Laplace transform and exploited to recover local properties of a fluid environment.
4. An efficient contact-free approach to measure required hydrodynamical characteristics of a liquid in a broad temperature range with nano-scale spatial resolution is demonstrated.
5. The proposed method can utilize biologically compatible compounds demonstrating new capabilities in a variety of lab-on-a-chip realizations and expanding the range of microfluidics applications.

D. Kislov, D. Novitsky, A. Kadochkin, D. Redka, A.S. Shalin, P. Ginzburg // Phys.Rev.B, 101, 035420 (2020).

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