

Polariton-assisted manipulation of energy relaxation pathways: donor–acceptor role reversal in a tuneable microcavity.

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Abstract: Resonant interaction between excitonic transitions of molecules and localized electromagnetic field allows the formation of hybrid light–matter polaritonic states. This hybridization of the light and the matter states has been shown to significantly alter the intrinsic properties of molecular ensembles placed inside the optical cavity. Here, we have observed strong coupling of excitonic transition in a pair of closely located organic dye molecules demonstrating an efficient donor-to-acceptor resonance energy transfer with the mode of a tuneable open-access cavity. Analysing the dependence of the relaxation pathways between energy states in this system on the cavity detuning, we have demonstrated that predominant strong coupling of the cavity photon to the exciton transition in the donor dye molecule can lead not only to an increase in the donor–acceptor energy transfer, but also to an energy shift large enough to cause inversion between the energy states of the acceptor and the mainly donor lower polariton energy state. Furthermore, we have shown that the polariton-assisted donor–acceptor chromophores’ role reversal or “carnival effect” not only changes the relative energy levels of the donor–acceptor pair, but also makes it possible to manipulate the energy flow in the systems with resonant dipole–dipole interaction and direct energy transfer from the acceptor to the mainly donor lower polariton state. Our experimental data are the first confirmation of the theoretically predicted possibility of polariton-assisted energy transfer reversal in FRET systems, thus paving the way to new approaches to FRET-imaging, remote-controlled chemistry and all-optical switching.

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Materials

6-Carboxyfluorescein (FAM) was selected as a donor dye, and carboxytetramethylrhodamine (TAMRA), as an acceptor dye. The most common way to fix the distance between chromophores required for efficient FRET is to use oligonucleotide-based molecular beacons, because, in this case, the distance between the donor and the acceptor is of the order of the diameter of the DNA double helix, which is 2 nm.

In this study, the donor and acceptor dye molecules were conjugated with a self-complementary oligonucleotide, 5'-TGG AGC GTG GGG ACG GCA AGC AGC GAA CTC AGT ACA ACA TGC CGT CCC CAC GCT CCA-3'.

Donor-only- and acceptor-only-labelled hairpins were also obtained and used as controls (Figure S1). The oligonucleotide sequence of 57 oligonucleotide residues forming a hairpin with an 18-bp stem was so selected as to ensure hairpin stability and a small distance between the donor and the acceptor. The molecular weights of the donor-only-, acceptor-only-, and donor–acceptor double-labelled hairpins were MFAM=17477.47, MTAMRA=17568.68, and MFAM_TAMRA=17945, respectively. All components were obtained from Evrogen (Evrogen Joint Stock Company, Moscow, Russia) and diluted with phosphate-buffered saline (PBS) to a concentration of 100 μ M. For experiments, we used 10 μ L of the solution of each component.

(a) TAMRA

Chemical structure of TAMRA: CN(C)C(=O)NCCc1ccc2c(c1)c3cc(N(C)C)oc4ccccc24

(b) FAM

Chemical structure of FAM: O=C(O)c1ccc2c(c1)c3cc(O)oc4ccccc24

(c) FAM+TAMRA

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The photoluminescence and absorption spectra of the compounds were first studied outside of the cavity (Figure S2). Here, we used different excitation wavelengths, depending on the absorption spectrum of each compound.

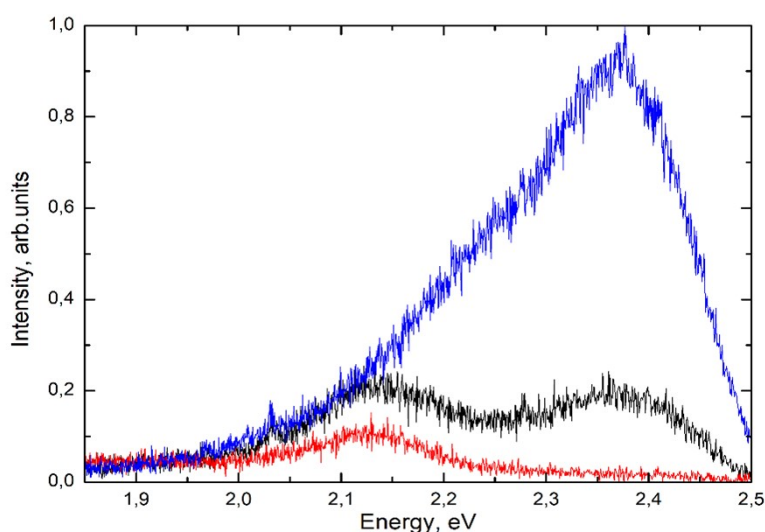


Figure S3. The photoluminescence spectra of the solutions containing molecular beacons labelled with FAM alone (blue), TAMRA alone (red), and both FAM and TAMRA (black). All samples were located outside the microcavity. The photoluminescence was excited at 450 nm. The concentrations of the dye molecules in the sample solutions were about 100 μM in all experiments.

In order to estimate the FRET efficiency via dipole–dipole interaction, we placed the solutions containing the beacons labelled with FAM, TAMRA, and FRET pair alternately on the lower mirror of the microcavity without the upper one and excited them non-resonantly with a 450-nm laser. In this way, we ensured the same experimental conditions as in the experiments with the medium placed inside the cavity. The measured photoluminescence (PL) spectra are shown in Figure S3.

It can be seen from these spectra that FAM-only-labelled hairpins exhibited a high PL intensity (probably due to the high quantum yield of FAM, 97%) with a peak at 525 nm, while the TAMRA-only counterpart exhibited a low-intensity PL. These results correspond to a more efficient excitation of FAM at 450 nm ($\sim 20\%$ of the maximum at 495 nm) compared to TAMRA ($\sim 2\%$ of the maximum at 546 nm). The hairpins labelled with both the donor and the acceptor exhibited a significant decrease in the donor PL intensity and a simultaneous increase in the acceptor PL intensity, a result that indicates energy transfer from the donor to the acceptor. From these data, the FRET efficiency can be estimated using the following expression:^[1,2]

$$E = 1 - \frac{F_{DA}}{F_D}, \quad (\text{S1})$$

where E is the efficiency of FRET, F_{DA} and F_D are the donor fluorescence intensities in the presence and absence of the acceptor, respectively. The above data lead to an estimated FRET efficiency value of 80%.

Experimental setup

The experimental setup is shown in Figure S4. In order to enter the strong coupling regime, the approach originally described in Ref. [3] was used. Briefly, our versatile tuneable microcavity cell (VTMC)^[4] is composed of plane and convex mirrors that form an unstable $\lambda/2$ Fabry–Perot microcavity. One mirror is made convex (curvature radius, 77.3 mm) in order to satisfy the plane-parallelism condition and minimize the mode volume. The plane mirror is mounted on top of a Z-piezopositioner to provide fine tuning of the microcavity length in a range of up to 10 μm with a nanometre precision, and the landing procedure is carried out with a DRV3 high-precision differential micrometre (Thorlabs), which is indirectly connected to the convex mirror.

The alignment of the plane-parallelism point and the sample is performed by moving the convex mirror in the lateral direction by means of an XY precision positioner. A sample is deposited directly onto the plane mirror, which consists of standard (18×18 mm) glass coverslips with a ~35-nm layer of aluminium metallization on their upper side. The VTMC is mounted onto an inverted confocal microspectrometer consisting of an Ntegra-base (NT-MDT) with a 100X/0.80 MPLAPON lens (Olympus) on a Z-piezopositioner, an XY scanning piezostage, and a homemade confocal unit. The fluorescence spectra of all samples were excited with an L450P1600MM 2.1-W, 450-nm laser (Thorlabs) with an LDS5-EC power supply (Thorlabs); for the transmission spectra, an MCWHF2 white LED (Thorlabs) with a homemade optical condenser was used. It should be noted that the laser power was far from saturation in our experiments.

The recording system included an Andor Shamrock 750 monochromator equipped with an Andor DU971P-BV CCD (Andor Technology Ltd.) and two 488-nm RazorEdge® ultrasteep long-pass edge filters (Semrock).

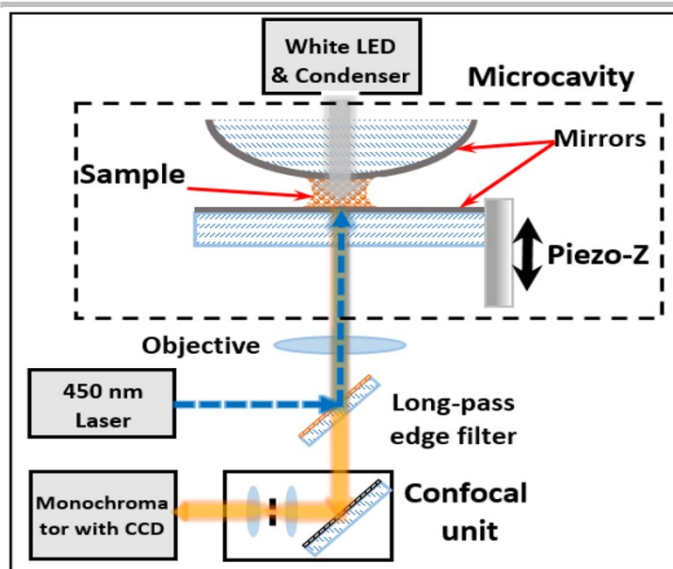


Figure S4. The experimental setup.

Numerical calculations of spatial mode distributions.

The finite elements method (FEM) was used to calculate the spatial and spectral mode distributions inside the cavity. In these calculations higher transverse modes of the microcavity were also taken into account (Figure S5).

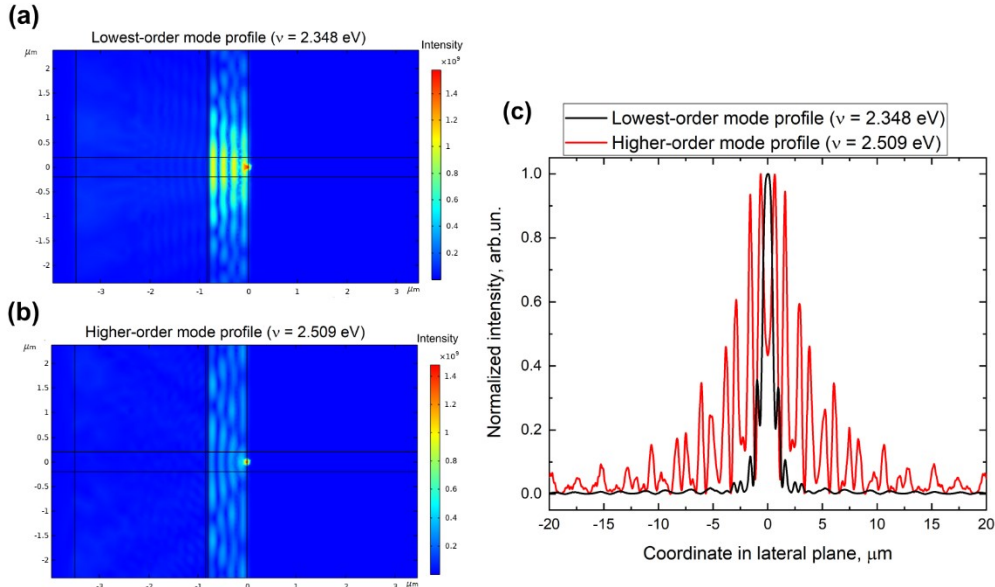


Figure S5. Colour maps of the spatial mode distribution for (a) the lowest-order and (b) the higher-order mode. (c) Comparison between the lateral profiles of the two modes in one of the lateral directions.

It can be seen from Fig. S5 that the lowest-order transverse mode is much stronger confined than the higher-order mode. Thus, when measuring the emission from the small region between the mirrors being at closest one to each other we effectively limit the influence of higher-order transverse modes and investigate the coupling with the mode having very small volume.

Accounting for changes in pumping intensity

For correct calculation of the lower polariton branch population, it was necessary to account for changes in pumping intensity during the tuning of the cavity length. When the exciting field was in resonance with one of the cavity eigenmodes, a significant rise of the field intensity inside the cavity was observed. To account for this effect, we used a numerical model^[5] developed for calculating the spectral and spatial properties of the microcavity electromagnetic modes by the finite elements method.^[6] It should be noted that higher transverse modes of the microcavity were also taken into account. This was necessary because, during the excitation, the radiation of the pumping laser was focused by an objective lens with quite a large numerical aperture ($\text{NA}=0.95$), and the pumping radiation excited the higher transverse modes (Figure S6a).

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In the transmission experiments, the illuminating light had an approximately planar wavefront (Figure S6b); therefore, there were no signs of higher transverse modes in the transmission spectra (Figure S7a).

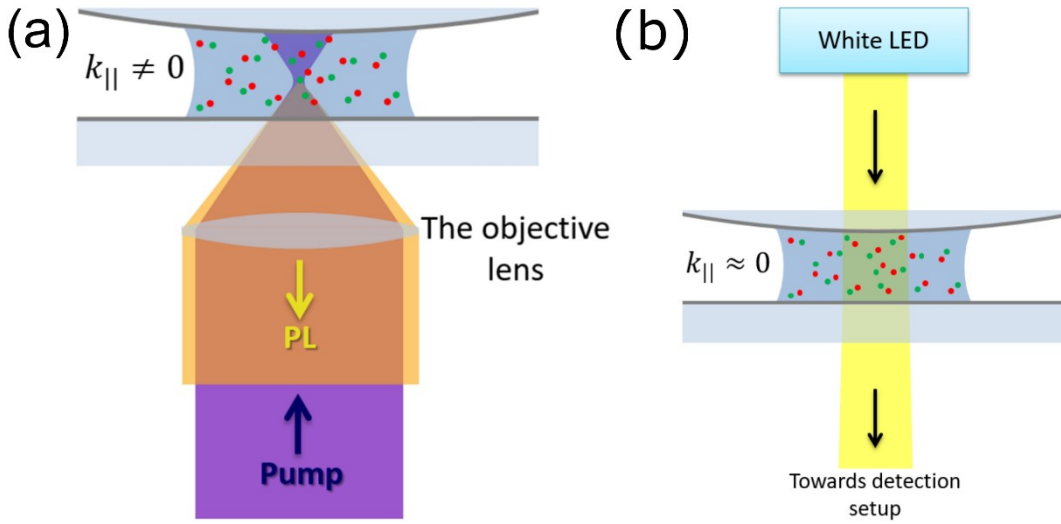


Figure S6. The principal configuration of the excitation (a) and transmission (b) experiments.

Using the model developed, we calculated the spectral distribution of the electromagnetic energy for the experimental set of cavity lengths. Then, for all these spectra, the points corresponding to the excitation laser frequency were determined. These values were used as the pumping intensities at the given cavity lengths (Figure S7b).

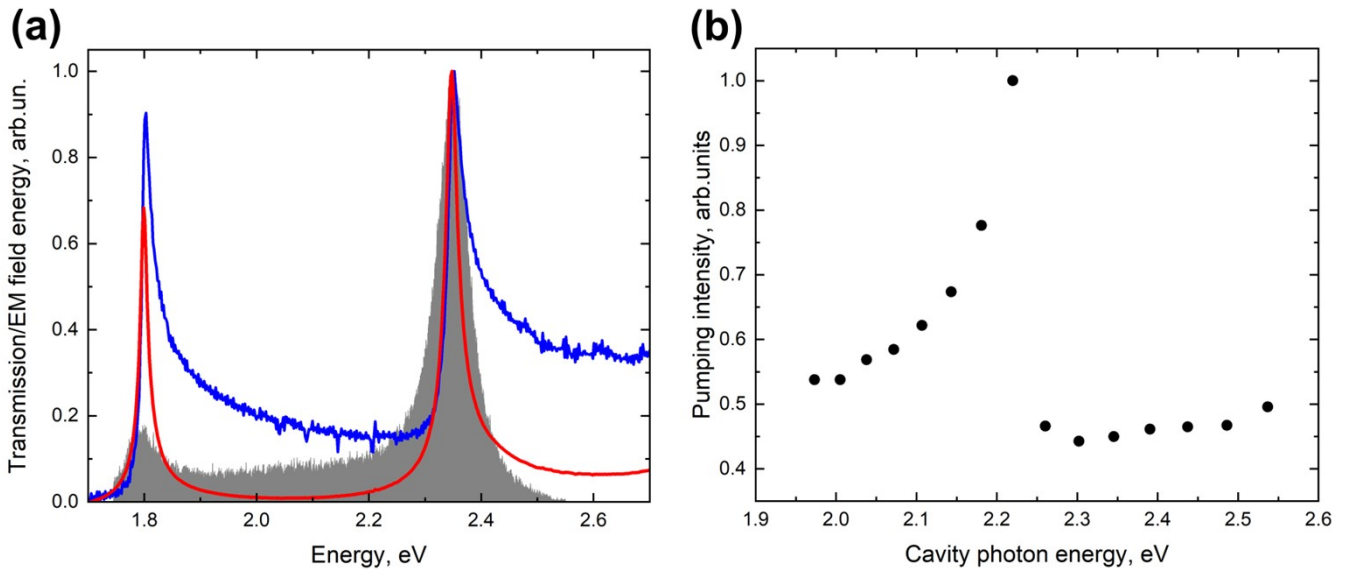


Figure S7. Panel (a) shows the calculated spectrum of electromagnetic energy inside the microcavity with (red) and without (blue) mode selection. The grey area represents the corresponding experimental

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transmission spectrum. Panel (b) shows the pumping intensity dependence on the cavity mode frequency.

Calculation of the coupling strengths and Hopfield coefficients

The spectral properties of the experimental system based on the donor–acceptor pair placed inside the microcavity were researched using the Jaynes–Cummings Hamiltonian describing the interaction between the cavity mode and the dipole moments of the emitters. For our hybrid system, this Hamiltonian is as follows:

$$H_{JC} = \hbar\omega_{cav}a^+a + \frac{1}{2}\hbar\omega_D\sigma_D^z + \frac{1}{2}\hbar\omega_A\sigma_A^z + \hbar g_{D-cav}(a^+\sigma_D^- + a\sigma_D^+) + \hbar g_{A-cav}(a^+\sigma_A^- + a\sigma_A^+), \quad (S2)$$

where $\hbar\omega_c$, $\hbar\omega_D$, and $\hbar\omega_A$ are the energies of the microcavity electromagnetic mode and the donor and acceptor excitons, respectively; $a(a^+)$ is the photon annihilation (creation) operator; $g_{j-cav}(j = A, D) = d_j\sqrt{\hbar\omega_c/2\varepsilon_0V}$ is the coupling strength, where d_D and d_A are the dipole moments of energy transition of the donor and acceptor, respectively, ε_0 is the vacuum permittivity, and V is the volume of the electromagnetic mode; $\sigma_i^z = |e_i\rangle\langle e_i| - |g_i\rangle\langle g_i|$, $\sigma_i^+ = |e_i\rangle\langle g_i|$, $\sigma_i^- = |g_i\rangle\langle e_i|$ ($i = A, D$), and $|g_i\rangle$ and $|e_i\rangle$ are the wavefunctions of the ground and excited states of the emitters. It should be noted here that expression (S1) has no term describing direct interaction between the dipole moments of the chromophores. This is because this process is much slower than energy exchange between the emitters and cavity mode at the coupling strengths taking place in the current research.^[7,8] The Hamiltonian also can be written in a matrix representation:

$$H_{JC} = \begin{pmatrix} \hbar\omega_{cav} & \hbar g_{D-cav} & \hbar g_{A-cav} \\ \hbar g_{D-cav} & \hbar\omega_D & 0 \\ \hbar g_{A-cav} & 0 & \hbar\omega_A \end{pmatrix} \quad (S3)$$

We diagonalized this matrix using QuTiP,^[9] which allowed us to obtain the eigenstates and eigenvalues of this Hamiltonian. The values of the energies of the microcavity electromagnetic mode and the donor and acceptor excitons were extracted from the experimental data. For finding the coupling strengths of our hybrid system, we used the differential evolution method,^[10] a stochastic method for obtaining the extrema of a function of several variables. In order to correctly estimate the experimental coupling strengths, we minimized the absolute values of the differences between the Hamiltonian eigenvalues and the energies corresponding to the maxima of the experimental spectra. As a result of this procedure, we obtained the values of g_{D-cav} and g_{A-cav} equal to 435 and 41 meV, respectively.

In order to find the Hopfield coefficients, we obtained the eigenfunctions of the Hamiltonian with the coupling strengths corresponding to our experimental data. Each eigenfunction was represented as a superposition of the functions of the pure photon and exciton states. The coefficients of the decomposition determine the Hopfield fractions of the polaritonic states.

Fitting of the emission spectra from the weakly coupled states

In order to fit the spectral position of short wavelength maximum in the experimental PL spectra we used Fermi Golden rule.^[11] According to this, the probability of emission is proportional to the local density of photonic states (LDOS). For calculation of this quantity we used numerical model developed earlier via Finite Elements Method.^[5,6] As a result of computation we got spectral distribution of electromagnetic energy inside the cavity. For planar Fabry-Perot cavity this quantity is equal to LDOS scaled by the constant factor, which can be easily proved using, for example, Transfer Matrix Method.^[12] Since energy of the field in our cavity is mostly localized within plane-parallel zone (See supplementary information), we assume that LDOS provided by our cavity can be approximated with spectral distribution of energy inside the cavity. Thus, emission intensity of dye molecules weakly coupled to the cavity was calculated via the following formula:

$$I_{cav}(\omega) = I_{fs}(\omega) \cdot \frac{\rho_{cav}(\omega)}{\rho_{fs}(\omega)},$$

where I_{fs} – emission intensity in free space, ρ_{cav} and ρ_{fs} – LDOS inside the cavity and in free space, respectively. Using the described approach, we modelled spectra corresponding to each cavity thickness used in experiments. Spectral positions of maxima in these spectra were in turn exploited for fitting presented in Fig. 2d.

References

- [1] R. M. Clegg, in *Fluorescence Imaging Spectroscopy and Microscopy*, Vol. 137 (Eds.: X.F. Wang, B. Herman) John Wiley & Sons, New York, **1996**, pp. 179–251.
- [2] G. W Gordon, G. Berry, X. H. Liang, B. Levine and B. Herman, *Biophys. J.* **1998**, *74*, 2702–2713.
- [3] A. Konrad, A. M. Kern, M. Brecht and A. J. Meixner, *Nano Lett.* **2015**, *15*, 4423–4428.
- [4] K. E. Mochalov, I. S. Vaskan, D. S. Dovzhenko, Y. P. Rakovich and I. Nabiev, *Rev. Sci. Instrum.* **2018**, *89*, 053105.
- [5] M. A. Lednev, D. S. Dovzhenko, Y. P. Rakovich and I. Nabiev, *J. Phys: Conf. Ser.* **2019**, *1410*, 012160.
- [6] J. Jin, *The Finite Element Method in Electromagnetics*, Wiley, Hoboken, **1993**.
- [7] J. Feist and F. J. Garcia-Vidal, *Phys. Rev. Lett.* **2015**, *114*, 196402.
- [8] R. Sáez-Blázquez, J. Feist, A. I. Fernández-Domínguez and F. J. García-Vidal, *Phys. Rev. B* **2018**, *97*, 241407(R).
- [9] J. Johansson, P. Nation and F. Nori, *Comput. Phys. Commun.* **2012**, *183*, 1760–1772.
- [10] R. Storn and K. Price, *J. Glob. Optim.* **1997**, *11*, 341–359.
- [11] R. Alicki, *Int. J. Theor. Phys.*, **1977**, *16*, 351–355.
- [12] B. E. A. Saleh and M. C. Teich, *Fundamentals of Photonics*, Wiley Series in Pure and Applied Optics

(John Wiley & Sons, New York), **1991**.