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Long-Range Resonant Energy Transfer Using Optical Topological Transitions in Metamaterials

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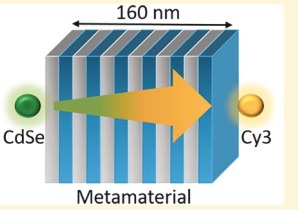
Supporting Information

ABSTRACT: The control and enhancement of resonance energy transfer is highly desirable for a variety of applications ranging from solar cells to spectroscopic rulers. However, the process of direct resonance energy transfer is distance dependent and limited to ∼10 nm for typical donor−acceptor pairs. Here we demonstrate long-range (∼160 nm) direct energy transfer between donor quantum dots and acceptor dye molecules through the use of an optical topological transition (OTT) in a metamaterial. The OTT in a metamaterial, modifies the density of states between the donor and acceptor, resulting in the long-range energy transfer with transfer efficiency of ∼32%. Theoretical calculation based on master-equation formalism is used to model the system and is found to be in good agreement with the experimental observation. The use of OTTs in metamaterials to enhance and control energy transfer process can have wide array of potential applications ranging from organic solar cells to quantum entanglement.



KEYWORDS: *RET, metamaterials, optical topological transitions, long range, energy transfer, lifetime*

Resonant energy transfer in a donor−acceptor system is a ubiquitous process that is of importance across several fields. It is used in structural biology as a spectroscopic ruler in the form of Fluorescence Resonance Energy Transfer (FRET),[1−3] in increasing efficiency of organic LEDs,[4] solar cells,[5] and even in the fundamental process of photosynthesis.[6] A significant limitation of resonance energy transfer through direct dipole−dipole interaction is that it occurs only over very short distances ∼10 nm beyond which the efficiency of the transfer process drops significantly. There have been efforts to increase this distance threshold motivated by the need to study larger molecular systems and to achieve long-range energy transport in solar cells.[7] Most of these efforts utilize photonic structures to confine the electric field and enhance photonic density of states such as in microcavities[8] or through the use of surface plasmons in planar silver films[9,10] and other plasmonic nanostructures[11−13] and hyperbolic metamaterials.[14−16] To demonstrate "true" direct energy transfer, it is necessary to show coupling between the donor and acceptor either through free space or the modified vacuum resulting in change in lifetime of the donor in the presence of the acceptor. In most of the prior demonstrations of long-range energy transfer, such a demonstation has been difficult experimentally as the donor and acceptor molecules are not well separated. The authors in reference 9 do have a well-separated donor-acceptor system; however, they could not observe a donor lifetime reduction. The Optical Topological Transition (OTT) in a metamaterial was theoretically shown to be an ideal regime for enhancing the energy transfer across long distances.[17] Here we demonstrate the direct energy transfer between donor−acceptor pairs that are separated by ∼160 nm mediated through the modified density of states at the OTT in a metamaterial. Evidence of energy transfer is proved through both reduction in the spontaneous emission lifetime of the donor in the presence of the acceptor as well as the increase in the steady-state emission intensity of the acceptor. Theoretical calculations based on the master-equation formalism[18] that include the dynamics of the energy transfer process show reasonable agreement with experiments.

Schematic of the metamaterial used in the experiment is shown in Figure 1a. The structure consists of alternating layers of silver (Ag) and alumina (Al_2O_3) of thicknesses 10 and 36 nm, respectively. A very thin layer of germanium (Ge) was deposited prior to every Ag layer as a wetting layer to improve the smoothness of the Ag films.[19,20] The thickness of the layers is determined by the spectral range over which the OTT, where the real part of either the parallel or perpendicular components of the dielectric permittivity becomes zero, is desired. This in turn is set by the spectral location of the emission maximum of the donor molecules used in the experiment which in our case were CdSe/ZnS core−shell

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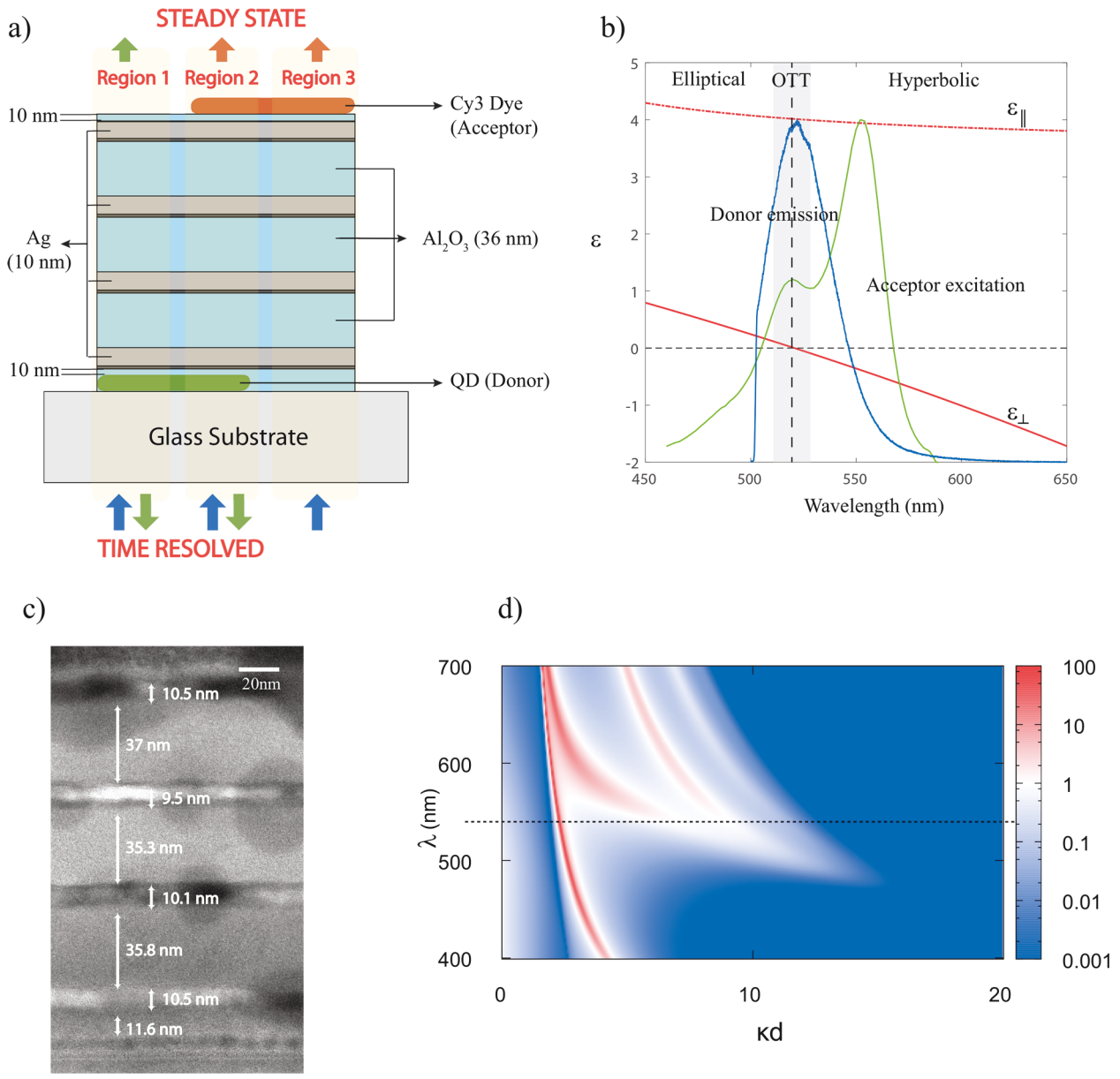

Figure 1. (a) Schematic of the sample. 1.5 nm Germanium is used as a wetting layer before each Silver (Ag) layer. Note that the distinct regions within the sample allow for different experiments. Region 1 is used for reflection mode time-resolved experiments for donor lifetimes without acceptor. Region 2 gives time-resolved experiments for donor lifetimes in the presence of acceptor in reflection mode and steady-state experiments for acceptor emission in transmission mode. (b) Effective medium theory calculations showing the OTT regime of the metamaterial (dashed line) overlapping with the transition wavelength (donor emission and acceptor excitation spectrum). (c) Cross-sectional TEM image of the metamaterial showing uniform layers. The Ag (dark layer) has leaked out in some spots during the TEM. Uniform QD layer is also seen at the bottom layer. (d) Plot of transmission coefficient, $|t_p|^2 e^{-2\kappa d}$ in the $\lambda - k$ plane. The dashed line indicates the OTT wavelength.

quantum dots (QDs) that emit at 520 nm. The acceptor molecules used were Cy3 organic dye molecule with absorption overlapping with the QD emission. Shown in Figure 1b is the effective dielectric constant of the metamaterial calculated from experimentally obtained dielectric constants of the individual layers. Also, shown in Figure 1b is the emission and absorption spectrum of the donor QDs and the acceptor dye molecule. The fabrication details of the metamaterial along with the deposition of donor QDs and acceptor molecules are described in detail in the Supporting Information. A transmission electron microscope image of the metamaterial with the layer thicknesses is shown in Figure 1c indicating smooth silver and alumina layers. Figure 1d shows a theoretical plot of the transmission coefficient for the metamaterial structure using S-matrix calculations. These calculations verify that the OTT is indeed in resonance with the maximum of the donor−acceptor energy transfer wavelength range.

The QD and dye molecules were placed on either side of the metamaterial at specific locations as shown in Figure 1a. This was done to facilitate the measurement of spontaneous emission lifetimes and intensities across the same sample to minimize sample to sample variations. Region 1, where only the QD donors are present, allows us to measure the modification of the lifetime just by the proximity to the ENZ metamaterial and acts as the control. Region 2, where both

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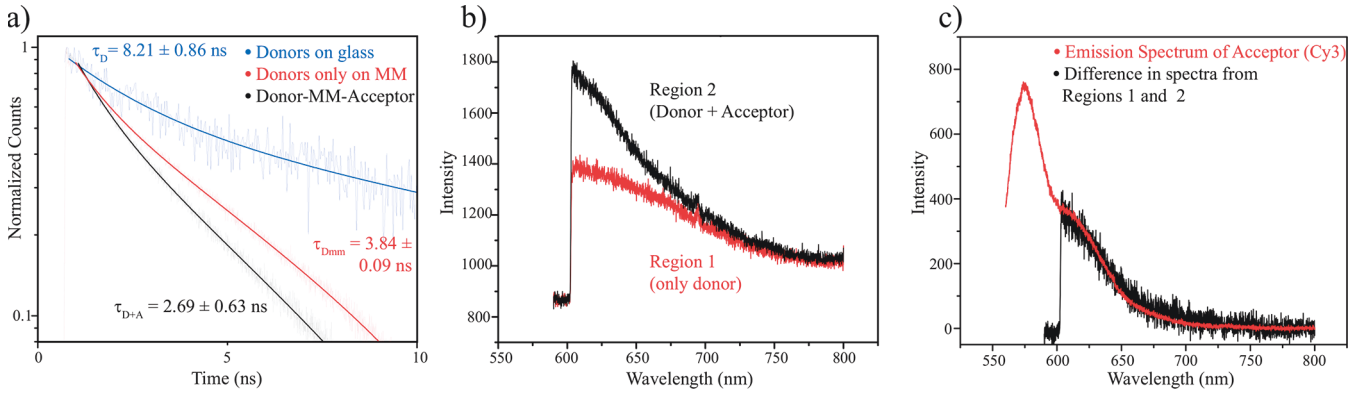

Figure 2. (a) Donor (QD) lifetimes for control (blue), on the metamaterial in absence of acceptor (red), and on the metamaterial in the presence of acceptor (black). A clear reduction in lifetime of the donor QDs is observed in the presence of the acceptor. (b) Steady state PL spectrum collected from region 1 (donor only) and region 2 (donor + acceptor) in transmission mode using a 600 nm long pass filter. No PL was observed in region 3 where the donor was absent. (c) Difference in emission spectra between the regions 1 and 2 (black) along with the PL spectrum of the bare acceptor showing that the PL emission enhancement observed in (b) is due to emission arising from the acceptor.

donors and acceptors are present, is used to establish the modification of spontaneous emission lifetime of the donor and the intensity of the acceptor due to the donor−acceptor coupling. Region 3 allows us to account for any direct excitation of the acceptor by the pump. The direction of pump and emission collected are also shown in the schematic figure, Figure 1a.

To demonstrate long-range energy transfer, we obtained time-resolved photoluminescence (PL) spectra from the QDs for the cases with and without the acceptor (dye molecules). Time Correlated Single Photon Counting (TCSPC) measurements were carried out at a 480 nm wavelength excitation using a 500 fs pulsed laser operating at 80 MHz (Toptica). The measurements were performed in the reflection geometry, as shown in the schematic (Figure 1a) in the regions 1 and 2, as defined previously. A 550 nm short pass filter ensured that the obtained signal was purely from the donor QDs. The results of the time-resolved PL measurements are shown in Figure 2a, along with the time-resolved PL measurements for a control sample of spin-coated QDs on glass. As can be seen, the lifetime of the QDs under the metamaterial is decreased as compared to the control sample due to the combination of enhanced photonic density of states (PDOS) at the OTT in the metamaterial as well as nonradiative quenching.[21,22] More interestingly, the lifetime of the QDs is further reduced in the presence of the acceptor. In contrast, when the experiment was repeated with control samples of bulk silver of the same thickness as the metamaterial, we observed no donor lifetime decrease in the presence of the acceptor (Supporting Information). This is in agreement with our previous theoretical work where the energy transfer enhancement in bulk silver is only observable close to the plasmon resonance ($\lambda \sim 300$ nm).[17] There was also no decrease in donor lifetimes in the presence of acceptor for control samples of bulk alumina (Supporting Information). Thus, the decrease in the spontaneous emission lifetime of the donor QDs observed in the presence of the acceptor for the metamaterial system unambiguously indicates their direct coupling through the modified density of states at the OTT.

The time-resolved PL data were fit using a biexponential decay function having a fast lifetime component less than 1 ns and a longer component of the order of several ns. The lifetimes were calculated as a weighted average of these two components and were found to be 8.21 ± 0.86 ns for the control, 3.93 ± 0.09 ns (τ_{Dmm}) for the QDs under the metamaterial in the absence of acceptor and 2.69 ± 0.52 ns (τ_{D+A}) for the complete donor-metamaterial-acceptor system. The energy transfer rate Γ_{ET} can be estimated from the efficiency of the FRET process obtained from the time-resolved data using the following relationship:[23−25] $\eta_{FRET} = 1 - \tau_{D+A}/\tau_D$. The energy transfer efficiency is calculated to be 32% and the energy transfer rate to be $\Gamma_{ET} \sim 0.12$ ns^{-1}. Here we use the lifetimes of the donor already modified by the metamaterial (τ_{Dmm}) as τ_D, and hence, this gives us the absolute direct energy transfer rate. Instead, if we were to use the lifetime of the donor on glass as τ_D, we will obtain efficiency of 65% which includes the lifetime modification from the metamaterial and, hence, is not the true measure of the enhanced direct energy transfer to the acceptor.

We also carried out steady-state PL measurements in the transmission mode where a 460 nm continuous wave excitation laser was directly incident on the donor QDs through the substrate side. As seen from Figure 1b, at this excitation wavelength the acceptor dye absorption is negligible. The PL emission from the sample was collected on the opposite side in the three regions. Region 3 showed no PL signal, ruling out the direct excitation of the dye molecules with the laser. Thus, any signal seen in region 2 could only have been obtained from the excitation of the dye molecules by the donor QDs, and donor QD emission itself leaking through the metamaterial into the far field. This QD emission is treated as the background and is quantified by the PL from region 1. This background signal can be subtracted from the signal from region 2. A 600 nm long pass filter was used before the detector in this case. Although not ideal, it was necessary to cut off the tail from the QD emission spectrum which was overpowering the dye emission due to the larger concentration. When compared to the PL from region 1, PL from region 2 clearly shows an increase in the part of the spectrum where the dye is expected to emit as seen in Figure 2b). This increase is plotted in Figure 2c) and matched with an appropriately scaled emission spectrum from the acceptor dye to good agreement. We thus have satisfactory evidence of the increase in acceptor emission in the presence of the donor molecule. A fraction of the increase in PL could be attributed to direct photon excitation from the donor QDs. However, this would not result

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in donor lifetime changes and it is precisely this lifetime decrease, taken in conjunction with the steady-state PL modification that proves direct energy transfer through the high-k modes in the metamaterial.

To substantiate our experimental claims, we have carried out theoretical modeling of the experimental system using a dynamical description based on the master-equation formalism.[18] The complete decay profile of the donor QDs in the presence of the acceptors located on the other side of the metamaterial is obtained using this approach. Physically the problem reduces to the interaction of two two-level atoms (donor and acceptor) mediated through the modified vacuum in the presence of the metamaterial.[18,26,27] Details of the calculation are described in the Supporting Information.

Assuming that at $t = 0$ the donor is in the excited state and the acceptor in the ground state, we find the probability, $P(t)$ of finding the donor and acceptor in their initial states

$$P(t) = \frac{1}{2}e^{-\Gamma_s t}[\cos(\Omega_c t) + \cosh(\Gamma_c t)] \quad (1)$$

where Γ_s is the emission rate of the single donor in front of the metamaterial film and Γ_c and Ω_c are the collective emission rate and level shift of the donor−acceptor pair connected by the metamaterial film (detailed expressions can be found in Supporting Information). In the absence of the acceptor, the above expression simplifies to

$$P^{\text{single}}(t) = e^{-\Gamma_s t} \quad (2)$$

In order to compare the theoretical model with the experiment, we evaluate Γ_s, Γ_c, and Ω_c for the given hyperbolic multilayer structure by means of the S-matrix method using the geometrical parameters, as sketched in Figure 1a and using experimental values for the permittivites of the Al_2O_3 and Ag/Ge layers. We further average the above probabilities over the measured emission spectrum of the donor $\sigma^{\text{em}}(\omega)$ and the absorption spectrum of the acceptor $\sigma^{\text{abs}}(\omega)$ according to

$$P_{\text{av}}(t) = \frac{\int d\omega \sigma^{\text{em}}(\omega)\sigma^{\text{abs}}(\omega)P(t)}{\int d\omega \sigma^{\text{em}}(\omega)\sigma^{\text{abs}}(\omega)} \quad \text{and}$$

$$P_{\text{av}}^{\text{single}}(t) = \frac{\int d\omega \sigma^{\text{em}}(\omega)P^{\text{single}}(t)}{\int d\omega \sigma^{\text{em}}(\omega)} \quad (3)$$

Finally, we use an ensemble average to account for the distribution in the orientations of the dipole moment of the donor and acceptor molecules (parallel and perpendicular to the interface.) The numerically obtained values for $P_{\text{av}}(t)$ and $P_{\text{av}}^{\text{single}}(t)$ are shown in Figure 3 for different distances from the interface z. It can be seen that for any time $P_{\text{av}}(t) < P_{\text{av}}^{\text{single}}(t)$, indicating a super-radiant emission due to the interaction of the donor with the acceptor via the metamaterial film as also found in the experiment. While these numerical calculations include averaging over the dipole orientations, they do not account for the spatial variation in the donor and acceptor positions. A full modeling of the experimental situation would necessitate such an averaging over all the different horizontal and vertical positions within the layers. Nonetheless, the main feature of the experimental result is captured by our simple model. Given the distribution in distance of the donor and acceptors from the interface in the experimental scenario, we find an effective distance, $z = 30$ nm to show closest agreement with experiments. The simulations (see Supporting Information) show an emission rate $2\Gamma_{\text{glass}}$ and $2.5\Gamma_{\text{glass}}$, for the donor in the absence and presence of the acceptor, respectively. These values are close to the experimentally found values of $2.1\Gamma_{\text{glass}}$ and $3.1\Gamma_{\text{glass}}$.

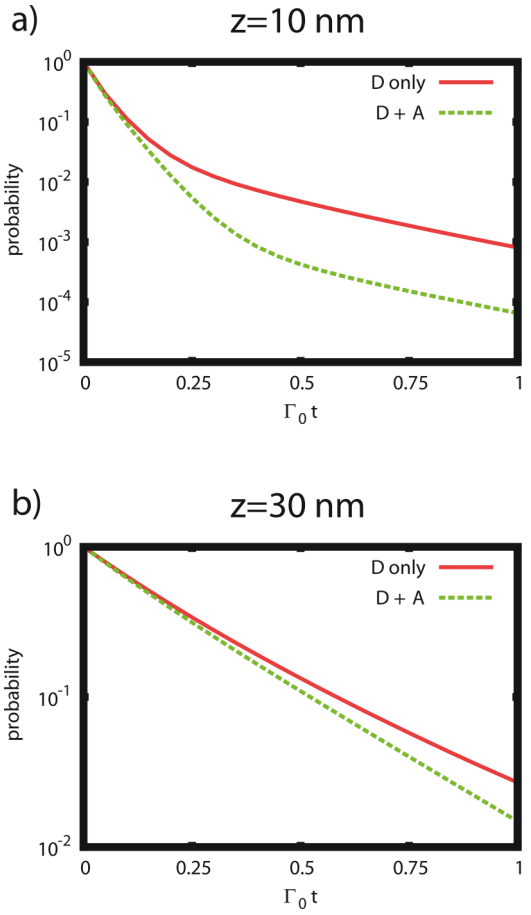

Figure 3. Dynamics of the donor lifetimes: Calculated probabilities of finding the donor in its excited state in the presence of acceptor, P_{av} (green) and absence of acceptor, $P_{\text{av}}^{\text{single}}$ (red) for different distances from the interface. The donor lifetimes are extracted from these probabilities and compared with the experimental results.

In summary, we have demonstrated experimentally, direct energy transfer between donor QDs and acceptor dye molecules across a 160 nm thick metamaterial at the OTT. The evidence of long-range energy transfer going far beyond the typical FRET distances is proven through reduction in spontaneous emission lifetime of the donor in the presence of the acceptor as well as the increase in spontaneous emission intensity of the acceptor. The dynamics of the donor−acceptor pair is modeled within the master-equation framework using experimental parameters for the emission and absorption spectrum of donor and acceptor, respectively. The theoretical calculations are found to be in reasonable agreement with experimentally observed decay dynamics. The observation of direct long-range energy transfer mediated through the modified density of states at the OTT within the metamaterial has implications in studies of long chain molecules, organic solar cells, and even quantum entanglement.[16,28]

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■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsphotonics.8b00484.

Discussions on sample preparation, control experiments and the detailed theoretical model (PDF).

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Notes

The authors declare no competing financial interest.

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