Harnessing Förster energy transfer

Our fascination with light, matter and their mutual interactions has been the driving force behind the advent of new optical materials, ranging from a variety of organic and inorganic dielectrics to tailored metals, photonic crystals and more recently, metamaterials. Photonic metamaterials are engineered composite materials consisting of structures much smaller than the wavelength of light, designed to exhibit counterintuitive properties such as negative index of refraction and invisibility cloaking. One such property called hyperbolic dispersion, where the material's dielectric permittivity is negative in one direction (like in metals) and positive in an orthogonal direction (like in dielectrics), has particularly striking applications. These *hyperbolic* metamaterials enable propagation of waves with nominally unlimited wavevectors and have a broadband singularity in the density of photonic states (which are the optical modes available for light propagation). Owing to the ability to strongly modify the photonic environment, hyperbolic metamaterials enable the control of several physical and optical phenomena, such as spontaneous emission and reflection, leading to potential applications in sensing, efficient LEDs, solar cells and stealth technology.

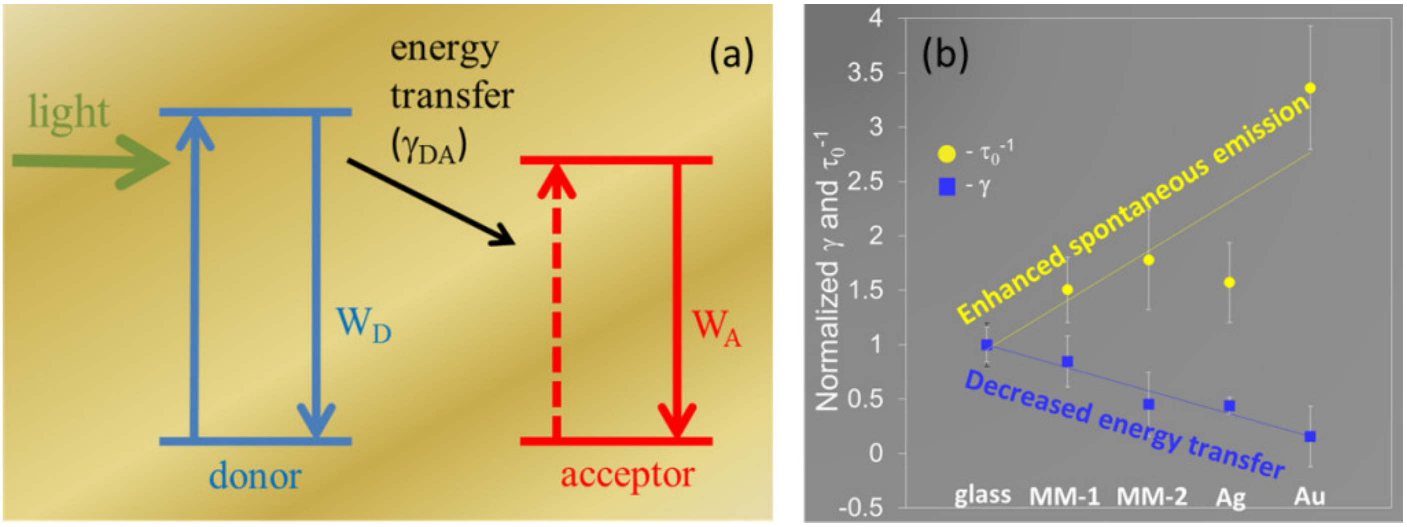

Fig. 1. (a) Schematic of Förster donor–acceptor energy transfer showing the absorption of light in the donor, a combination of radiative and non-radiative relaxation processes in the donor (WD), donor–acceptor energy transfer (?DA), and the relaxation processes in the acceptor (WA). (b) Emission decay rates ?0?1 and Förster energy transfer constants ? in dye-doped films deposited on top of glass, a metamaterial with magnesium fluoride as the outermost layer (MM-1), a metamaterial with silver as the outermost layer (MM-2), a silver film (Ag), and a gold film (Au).

In this work, the effect of modified photonic environments in the vicinity of metals and hyperbolic metamaterials on the Förster energy transfer has been investigated. Named after Theodor Förster, who first provided a quantitative insight into the process in 1946, the incoherent transfer of energy from an excited donor (such as an atom, molecule or a fluorophore) to a nearby acceptor (Fig. 1a) is an enabling process behind scores of important phenomena in physics and biology. One such process is photosynthesis in plants, where chromophores excited by sunlight relay energy for effective functioning of the plant. Typically, energy transfer occurs at distances of the order of a few nanometers and finds applications in microscopy, spectroscopy and biochemical tracking of cells and proteins. However, the effect of the dielectric/photonic environment on the Förster energy transfer has been widely debated in the literature. Several contradictory theoretical and experimental studies have claimed that the rate of energy transfer can be enhanced, suppressed or unchanged by modifying the photonic environment. This broad range of claims and findings makes the observations in this work particularly important.

The experimental samples studied in this work consisted of a mixture of two dyes deposited onto different substrates like glass, silver, gold and hyperbolic metamaterials. The dyes were chosen such that there was a good overlap between the emission spectrum of one dye (the donor), with the absorption spectrum of the other (the acceptor), which is a prerequisite for efficient Förster energy transfer. A combination of spectroscopic and time-resolved emission measurements was used to determine the emission decay rates (t_o) of the dye molecules and the rates of Förster energy transfer (g) between dye molecules on different substrates. The main takeaways from the study were two-fold: 1) Förster energy transfer is inhibited in the vicinity of metals and hyperbolic metamaterials – the photonic environments with high local densities of photonic states and 2) the same dielectric environments that boost spontaneous emission, also inhibit the Förster energy transfer (Fig. 1b).

The authors infer that a variety of other physical phenomena, which in regular dielectric media depend on the local dielectric environment, can be controlled in custom tailored systems such as hyperbolic metamaterials, plasmonic structures and cavities. The concept can even be extended to biological processes and chemical reactions (such as rusting and oxidation), which could potentially be controlled by simply modifying the dielectric environment, in which the reaction occurs.

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