This is the peer reviewed version of the following article: Hamza, A.O., Bouillard, J.G. and Adawi, A.M. (2022), Förster Resonance Energy Transfer Rate and Efficiency in Plasmonic Nanopatch Antennas. ChemPhotoChem. Accepted Author Manuscript., which has been published in final form at https://doi.org/10.1002/cptc.202100285. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited.

## **RESEARCH ARTICLE**

# Förster Resonance Energy Transfer Rate and Efficiency in Plasmonic Nanopatch Antennas

Abdullah O. Hamza<sup>a,b,c</sup>, Jean-Sebastien G. Bouillard<sup>\*,a,b,</sup> and Ali M. Adawi<sup>\*,a,b</sup>

- [a] Dr A. O. Hamza, Dr J-S. G. Bouillard and Dr A. M. Adawi, Department of Physics and Mathematics, University of Hull, Cottingham Road, HU6 7RX, UK E-mail: <u>a.adawi@hull.ac.uk</u> and <u>j.bouillard@hull.ac.uk</u>
- [b] Dr A. O. Hamza, Dr J-S. G. Bouillard and Dr A. M. Adawi
  G. W. Gray Centre for Advanced Materials, University of Hull, Cottingham road, HU6 7RX, UK
  E-mail: <u>a.adawi@hull.ac.uk</u> and <u>j.bouillard@hull.ac.uk</u>
  [c] Dr A. O. Hamza

[c] Dr A. O. Hamza Department of Physics, College of Science, Salahaddin University-Erbil, Iraq.

**Abstract:** Successful control of Förster resonance energy transfer (FRET) through the engineering of the local density of states (LDOS) will allow us to develop novel strategies to fully exploit this phenomenon in key enabling technologies. Here we present an experimental and theoretical study on the effect of the LDOS on the FRET rate and efficiency in plasmonic nanopatch antennas formed between a gold nanoparticle and an extended silver film. Our results reveal that plasmonic nanopatch antennas of similar levels of LDOS exhibit comparable levels of FRET rate and FRET efficiency, demonstrating that LDOS plays an important part in controlling both FRET rate and efficiency. Our findings contribute to the ongoing debate about the relation between the FRET process and the LDOS, as well as directly impacting the development of novel FRET based light harvesting and sensing devices.

### Introduction

Förster resonance energy transfer (FRET) is a short range energy transfer from an excited donor to a nearby ground-state acceptor molecule<sup>[1,2]</sup>. The typical FRET length scale is ~10 nm, and the FRET rate between an isolated donor-acceptor pair separated by a distance *r* is given by<sup>[1,3]</sup>

$$\Gamma_{ET} = \Gamma_0 \left(\frac{R_0}{r}\right)^6 \tag{1}$$

where  $\Gamma_0$  is the spontaneous emission rate of the donor in free space and  $R_0$  is the Förster radius.

Based on the work of Dung et al<sup>[4]</sup>, the FRET rate depends on the total Green function between the donor-acceptor pair, or in terms of the electric field, the FRET rate is proportional to the square of the donor field,  $E_D$ , at the location of the acceptor,  $r_A$ ,  $(\Gamma_{ET} \propto |\mathbf{E}_{\rm D}(\mathbf{r}_{\rm A})|^2)$ . Accordingly, the FRET rate is affected by the electromagnetic field in the vicinity of the donor-acceptor pair and thus can be controlled. Understanding how to modify the FRET rate via controlling the electromagnetic environment of the donoracceptor pair will allow to develop novel strategies to fully exploit this phenomenon in key enabling technologies such as light harvesting systems<sup>[5]</sup>, Lasers<sup>[6]</sup>, colour-tuning LEDs<sup>[7]</sup>, optical networks<sup>[8]</sup> and sensing systems<sup>[9,10]</sup>. In order to fully capitalise on FRET phenomena, it is crucial to relate the FRET rate into a readily measurable field related physical quantity such as the spontaneous emission rate of the donor,  $\Gamma_{\!\scriptscriptstyle D}.$  The spontaneous emission rate,  $\Gamma_D$ , depends on the local density of optical states (LDOS), a quantity that is directly proportional to the imaginary part of the Green function at the donor location  $(\mathbf{r}_D)^{[3,4,11]}$  or in terms of the donor field  $\Gamma_D \propto LDOS \propto Im\{E_D(r_D)\}$ . It is therefore essential to correlate the FRET rate,  $\Gamma_{ET}$ , with the spontaneous emission rate of the donor,  $\Gamma_D$ . From the work of Dung *et al*<sup>[4]</sup>, however, there is no obvious relation between the two. Consequently, seeking an answer to the nature of the dependency of the FRET rate on the spontaneous emission rate of the donor,  $\Gamma_D$ , and thus the LDOS, has attracted much attention from both a fundamental physics point of view, as well as its potential technological applications<sup>[12-19]</sup>. Despite intensive research in this area, the exact relation between the FRET rate,  $\Gamma_{ET}$ , and the spontaneous emission rate of the donor,  $\Gamma_D$ , is still the subject of an ongoing debate. For example, studies based on all dielectric optical resonators<sup>[12,14,20-22]</sup> show no correlation between  $\Gamma_{ET}$  and  $\Gamma_D$ . Similarly, Bidault *et al*<sup>[23]</sup> reported no direct correlation between FRET rate and LDOS using 40 nm and 60 nm gold nanoparticle dimer antennas. In parallel, Bohlen et al<sup>[24]</sup> reported that a single plasmonic nanoparticle of size in the range 5 nm to 20 nm has a negligible effect on the FRET rate. By contrast Aissaoui et al<sup>25</sup> showed that using a 5 nm gold nanoparticle, the FRET rate depends linearly on  $\Gamma_{D}$  (thus the LDOS). Furthermore, a series of plasmonic based resonators



Fig. 1 Schematic representation of the studied plasmonic nanopatch antenna.

show linear<sup>[15–17,26–28]</sup> and even superlinear<sup>[13]</sup> dependency of  $\Gamma_{ET}$  on  $\Gamma_D$  (thus LDOS).

Several studies<sup>[23,29–37]</sup> investigated the modification of the FRET efficiency using plasmonic or photonic nanostructures. For example, the works of Bidault *et al*<sup>(23)</sup>, Sanz-Paz *et al*<sup>(29)</sup> and Asgar *et al*<sup>(30)</sup> showed that the FRET efficiency deteriorates in the presence of plasmonic nanostructures, while Torres *et al*<sup>(31)</sup>, Lunz *et al*<sup>(32)</sup> and Zambrana-Puyalto *et al*<sup>(33)</sup> reported on the improvement of the FRET efficiency with plasmonic structures. Collison *et al*<sup>(34)</sup> showed that the FRET efficiency can be either enhanced or suppressed relative to the FRET efficiency in air using plasmonic surface lattice resonances. These results are attributed to Purcell enhancement and its role in modifying the rates of the donor's decay processes; specifically the radiative and non-radiative decay rates enhancements.

In this work we investigate both the FRET rate and FRET efficiency in mixed gold-silver nanopatch antennas<sup>[38–40]</sup> formed between a gold nanoparticle of diameter *D* and an extended silver film separated by a gap of width 30 nm (see Fig. 1). In particular, the nanopatch antennas are designed to exhibit a comparable level of spontaneous emission rate,  $\Gamma_D$  (thus LDOS). Both finite difference time domain (FDTD) calculations and experimental measurements show that the FRET rate,  $\Gamma_{ET}$  and FRET efficiency remain unchanged in nanopatch antennas, independently of the gold particle diameter *D*, as they exhibit a similar level of LDOS. These findings reveal that LDOS plays an important part in controlling both FRET rate and efficiency.



Fig. 2 (a) The chemical structure of the used donor-acceptor pair (Pyridine1-Rhodamine800) in this work. (b) Normalised absorption and emission spectra of the experimentally used donor-acceptor pair.

#### **Results and Discussion**

The spontaneous emission rate of the donor,  $\Gamma_D$  (thus LDOS), was calculated as a function of the nanopatch antennas gold particle diameter, *D*, by treating the donor emitter as a classical point dipole oscillating along the z-direction (see Figure 1) and

located at the centre of the nanogap. In this framework, the donor spontaneous emission decay rate,  $\Gamma_D$ , can be written as<sup>[3]</sup>

$$\Gamma_{\rm D} = \Gamma_0 \frac{P_{\rm D}}{P_0} \qquad (2)$$

where  $P_{\rm D} = \frac{\omega}{2} {\rm Im} \{ \boldsymbol{\mu}_D^* \cdot \boldsymbol{E}_{\rm D}(\mathbf{r}_{\rm D}) \}$  is the power emitted by the donor coupled to the nanopatch antenna,  $\boldsymbol{\mu}_{\rm D}$  is the donor dipole moment,  $\boldsymbol{E}_{\rm D}(\mathbf{r}_{\rm D})$  the electric field at the donor location and  $\omega$  is the emission frequency of the donor.  $\Gamma_0 = \frac{\omega^3}{3\pi\varepsilon_0 hc^3} |\boldsymbol{\mu}_{\rm D}|^2$  is the spontaneous emission rate of the donor in free space, and  $P_0 = \frac{\omega^4}{12\pi\varepsilon_0 c^3} |\boldsymbol{\mu}_{\rm D}|^2$  is the power radiated by the donor in free space.



Fig. 3 (a) Calculated emission rate enhancement  $\frac{\Gamma_{\rm D}}{\Gamma_{\rm 0}}$  as a function of the gold particle diameter *D* at the donor wavelength  $\lambda_{\rm D} = 630$  nm (b) The calculated normalised energy transfer rate  $\frac{\Gamma_{\rm ET}}{\Gamma_{\rm 0}}$  as a function of  $\frac{\Gamma_{\rm D}}{\Gamma_{\rm 0}}$  at the donor wavelength  $\lambda_{\rm D} = 630$  nm. (c) Electric field distribution at the donor emission wavelength.

In parallel, the FRET rate  $\Gamma_{\! \! ET}$  can be calculated using the expression^{[3]}

$$\Gamma_{\rm ET} = \Gamma_0 \frac{P_{\rm ET}}{p} \tag{3}$$

where  $P_{\rm ET}$  is the power transferred from the donor to the acceptor and can be written as<sup>[3]</sup>

$$P_{\rm ET} = \frac{\omega}{2} \operatorname{Im}\{\alpha_{\rm A}\} |\mathbf{n}_{\rm A} \cdot \mathbf{E}_{\rm D}(\mathbf{r}_{\rm A})|^2 \qquad (4)$$

where  $\omega$  is the emission/absorption frequency of the donor/acceptor,  $\mathbf{n}_A$  is a unit vector in the direction of the acceptor's dipole moment  $\boldsymbol{\mu}_A$ ,  $\mathbf{E}_D(\mathbf{r}_A)$  the donor field at the location of the acceptor ( $\mathbf{r}_A$ ) and  $\alpha_A$  the acceptor polarizability, which can be related to  $\boldsymbol{\mu}_A$  and  $\mathbf{E}_D(\mathbf{r}_A)$  via  $\boldsymbol{\mu}_A = \alpha_A \mathbf{E}_D(\mathbf{r}_A)$ .

 $P_{\rm D}$  and  $P_{\rm ET}$  are numerically calculated by solving Maxwell's equations using FDTD method<sup>[41]</sup>. In the calculations, we implemented a uniform grid spacing of 1 nm and stretched coordinate perfect matching layer boundary conditions. Calculations were terminated when the fields reached  $10^{-5}$  of their original value. Experimental data from Palik were used to describe the optical constants of silver<sup>[42]</sup> and from Johnson and Christy to describe the optical constants of gold<sup>[43]</sup>. In all cases,  $\Gamma_{\rm D}$  and  $\Gamma_{\rm ET}$  were calculated at the donor emission wavelength  $\lambda_{\rm D} = 630$  nm, corresponding to the emission peak of our experimental molecular donor, Pyridine1 (see Fig. 2), and  $\Gamma_{\rm ET}$  was calculated for an acceptor dipole moment polarised along the z-direction and located laterally 10 nm away from the donor.

First, we study theoretically the relation between the donor spontaneous emission decay rate,  $\Gamma_D$  (thus LDOS), and the gold particle size *D*. In these calculations the donor was placed at the centre of the nanogap (see Fig.1) and  $\frac{\Gamma_D}{\Gamma_0}$  was calculated at  $\lambda_D = 630$  nm using equation (2). The results of these calculations are presented in Fig. 3a. The three investigated antennas provide comparable level of  $\frac{\Gamma_D}{\Gamma_0}$  (thus LDOS), averaging at  $\left\langle \frac{\Gamma_D}{\Gamma_0} \right\rangle = 52$ . These results indicate clearly that the LDOS of our designed plasmonic nanopatch antennas have weak dependence on the gold nanoparticle diameter *D* and provide a similar level of LDOS ( $\frac{\Gamma_D}{\Gamma_0}$ ) at the donor wavelength.

Next, we study the energy transfer rate in these nanopatch antennas. Along with the FDTD simulations results, we used equations (3) and (4) to calculate  $\Gamma_{\rm ET}$  as a function of  $\Gamma_D$ . The calculated values are presented in Fig. 3b. Despite the fact that the antennas are constructed using different particle sizes, they provide a similar level of  $\Gamma_{\rm ET}$ . These results clearly demonstrate that the FRET rate,  $\Gamma_{\rm ET}$  stays constant in nanopatch antennas of similar level of LDOS regardless of the antenna's particle size. To support this observation further, we plot in Fig 3c the electric field distribution associated with the investigated antennas at the donor emission wavelength. In all cases, the antennas exhibit comparable electric field intensity within the nanogap.

To confirm our theoretical predictions, we investigated experimentally the relation between the FRET rate,  $\Gamma_{ET}$ , and the spontaneous emission rate of the donor,  $\Gamma_D$  (thus LDOS) in equivalent nanopatch antennas formed between a gold nanoparticle of diameter 100 nm, 250 nm and 400 nm, and a 100 nm thick extended sliver film separated by a 30 nm gap, hosting the donor-acceptor pair (Pyridine1-Rhodamine800) (see Fig. 1).

To quantify the LDOS in the fabricated nanopatch antennas, we measured the fluorescence lifetime of the Pyridine1 molecule (the donor molecule in the FRET experiment) in those systems. In Fig. 4a we plot the fluorescence decay traces of the Pyridine1 samples as a function of the gold nanoparticle diameter *D*. The dependence of the Pyridine1 emission rate,  $\Gamma_D$ , on the gold particle diameter is summarised in Fig. 4b. These results clearly show that in our nanopatch antennas the LDOS is independent of the gold particle size, in agreement with our theoretical calculations in Fig. 3a.



Fig. 4 (a) Emission decay traces of donor Pyridine1 measured from nanopatch antennas with gold particle of diameter 100 nm, 250 nm and 400 nm and on glass. (b) Measured emission decay rate enhancement  $\frac{\Gamma_{\rm D}}{\Gamma_0}$  as a function of the gold nanoparticle diameter *D*.

Fig. 5a shows the intensity decay traces from the donor-acceptor (Pyridine1-Rhodamine800) measured at the donor pair wavelength  $\lambda_{\rm D} = 630 \text{ nm}$  as a function of the gold nanoparticle size. The presence of the acceptor decreases the donor emission lifetime, clearly illustrating the occurrence of FRET in the nanoantenna. The FRET rate,  $\Gamma_{ET}$ , can be calculated using  $\Gamma_{ET}$  =  $\Gamma_{Total}-\Gamma_{D}\,,$  where  $\Gamma_{Total}$  is the total decay rate of the donoracceptor pair. The results from Fig. 4b and Fig. 5a allow us to investigate the relation between the FRET rate  $\Gamma_{\! \rm ET}$  and spontaneous emission rate  $\Gamma_D$  (thus the LDOS) in our nanopatch antennas. The results of this analysis are depicted in Fig. 5b. The data show that the fabricated antennas provide a similar level of FRET rate with  $\langle \Gamma_{ET} \rangle = 0.67 \text{ ns}^{-1}$  and clearly indicate that antennas of comparable level of LDOS result in the similar FRET rate modifications, in an excellent agreement with our theoretical modelling in Fig. 3b. To support this argument further we also measured the spontaneous emission rate  $\Gamma_{\! D}\,$  and the FRET rate  $\Gamma_{ET}$  from areas off the nanopatch antenna but still on the silver metallic film. The measured donor spontaneous emission rate was  $\Gamma_{\! D_{\rm off}} = 0.87 \ \rm ns^{-1}$  , much lower than the emission rate associated with the antenna  $\sim 1.6 \text{ ns}^{-1}$ . The corresponding measured FRET rate off the nanopatch antenna was  $\Gamma_{ET_{off}} =$  $0.25 \ \mathrm{ns^{-1}}$  while the FRET rate associated with the antenna  ${\sim}0.7~{\rm ns}^{-1}.$  These results indicate clearly that LDOS plays an important part in controlling the FRET rate, also in agreement with our previous work<sup>[16]</sup>.



Fig. 5 (a) Emission decay traces of donor-acceptor pair (Pyridine1-Rhodamine 800) measured from nanopatch antennas with gold nanoparticles of diameter 100 nm, 250 nm and 400 nm and on glass. (b) Measured FRET rate  $\Gamma_{ET}$  as a function of the spontaneous emission rate of the donor  $\Gamma_D/LDOS$ .

In Figure 6 we plot the FRET efficiency  $\eta = \frac{\Gamma_{ET}}{\Gamma_{ET} + \Gamma_D}$  as a function of the donor emission rate  $\Gamma_D$ . The FRET efficiency varies between 0.27-0.3 compared to 0.33 on glass. Despite the differences in the particle size of the fabricated nanopatch antennas, our results show that in nanopatch antennas of comparable LDOS level, the FRET efficiency stays stationary.



Fig. 6 Energy transfer efficency as a function of the donor emission rate  $\Gamma_{\! D}/LDOS.$ 

Conclusion

In conclusion, we investigated both theoretically and experimentally the dependence of the FRET rate and efficiency on the LDOS in plasmonic nanopatch antennas formed between a gold nanoparticle and an extended silver film. Our results reveal that despite the fact that the investigated nanopatch antennas have different particle sizes, antennas with comparable level of LDOS provide similar level of FRET rate and FRET efficiency. Our findings indicate that LDOS plays an important part in controlling both FRET rate and efficiency and will help guide and design novel FRET based optoelectronics devices, light harvesting and sensing systems.

## **Experimental Section**

The nanopatch antennas composed of a glass substrate coated with a 100 nm thick layer of silver, a 10 nm spacing layer of Zeonex (Zeon Chemicals Europe Ltd) deposited by spin-coating a 3 mg · ml<sup>-1</sup> solution of Zeonex in toluene at a speed of 2000 rpm for 30 s, a 10 nm active layer consists of PMA (Poly(methacrylic acid), Scientific Polymer Products Inc.) layer doped with Pyridine1-Rhodamine800 as the donor-acceptor pair in 5% and 0.5% concentrations by weight respectively. The 10 nm PMA film was achieved by spin-coating a  $3 \text{ mg} \cdot \text{ml}^{-1}$  solution of PMA in ethanol at a speed of 2000 rpm for 30 s. This step was followed by another 10 nm spacing layer of Zeonex. The antenna was then finished by spin-coating gold nanoparticles (Cytodiagnostics Inc.) from concentrations less than  $10^{-3} \text{ g} \cdot \text{L}^{-1}$  in ethanol at a speed of 2000 rpm for 30 seconds. These concentrations were used to obtain particle spacing  $>5\,\mu m\,.$  The Pyridine1-Rhodamine800 pair were chosen because of the large spectral overlap between the Pyridine1 emission spectrum and the Rhodamine800 absorption spectrum (see Fig. 2). The time-resolved emission measurements were performed using a pulsed 405 nm picosecond laser diode with a pulse width of 40 ps and a repetition rate of 80 MHz for excitation and a Becker & Hickl HPM-100 timecorrelated single-photon-counter of 100 ps time resolution. The excitation laser was focused on the sample using a  $100 \times$ magnification Mitutoyo infinity corrected objective lens of numerical aperture NA = 0.7. The same objective was used to collect the donor emission signal, which was then directed toward an iHR320 Horiba spectrometer where it was dispersed using a 150 line/mm grating onto the HPM-100 time-correlated singlephoton-counter. The donor emission lifetime was extracted via the deconvolution of the instrument response function (IRF). The approach is based on defining a fluorescence decay function then the convolution integral of the flurescence decay function and the IRF was calculated. The model function was then compared with the measured data with its paprameters varied until a best fit was achieved<sup>[44]</sup>.

#### Acknowledgements

This work was supported by the UK EPSRC through Grant EP/L025078/1 and the EU Horizon 2020 research and innovation programme under grant number 861950, project POSEIDON. We also acknowledge the Viper High Performance Computing facility of the University of Hull and its support team. We thank Stuart Harris at Zeon Chemicals Europe Ltd for the gift of the Zeonex polymer.

**Keywords:** Förster resonance energy transfer • plasmonic nanogap • nanopatch antennas • local density of optical states • FDTD modelling • time resolved spectroscopy

- [1] T. Forster, Ann. Phys. 1948, 437, 55.
- [2] B. Weib van der Meer, FRET Förster Resonance Energy Transfer, Wiley-VCH, 2013.
- [3] B. Novotny, L. Hecht, *Principles of Nano-Optics*, Cambridge University Press, Cambridge, **2012**.
- [4] H. T. Dung, L. Knöll, D. G. Welsch, *Phys. Rev. A* 2002, 65, 438131–4381313.
- [5] C. Wu, Y. Zheng, C. Szymanski, J. McNeill, J. Phys. Chem. C 2008, 112, 1772–1781.
- [6] L. Gartzia-Rivero, L. Cerdán, J. Bañuelos, E. Enciso, Í. López Arbeloa, Á. Costela, I. García-Moreno, *J. Phys. Chem. C* 2014, *118*, 13107–13117.
- [7] S. Ghataora, R. M. Smith, M. Athanasiou, T. Wang, ACS Photonics 2018, 5, 642–647.
- [8] R. D. Mehlenbacher, T. J. McDonough, M. Grechko, M. Y. Wu, M. S. Arnold, M. T. Zanni, *Nat. Commun.* 2015, *6*, 6732.
- [9] H. S. Peng, J. A. Stolwijk, L. N. Sun, J. Wegener, O. S. Wolfbeis, *Angew.Chem.* **2010**, *49*, 4246–4249.
- [10] M. Baibakov, S. Patra, J. B. Claude, A. Moreau, J. Lumeau, J. Wenger, ACS Nano 2019, 13, 8469–8480.
- [11] K. H. Drexhage, J. Lumin. 1970, 1–2, 693–701.
- [12] M. Wubs, W. L. Vos, New J. Phys. 2016, 18, 053037.
- [13] J. Ren, T. Wu, B. Yang, X. Zhang, *Phys. Rev. B* 2016, 94, 125416.
- [14] F. T. Rabouw, S. A. Den Hartog, T. Senden, A. Meijerink, *Nat. Commun.* 2014, 5, 3610.
- [15] J. A. Gonzaga-Galeana, J. R. Zurita-Sánchez, J. Chem. Phys. 2013, 139, 244302.
- [16] A. O. Hamza, F. N. Viscomi, J. S. G. Bouillard, A. M. Adawi, J. Phys. Chem. Lett. 2021, 12, 1507–1513.
- [17] P. Ghenuche, M. Mivelle, J. De Torres, S. B. Moparthi, H. Rigneault, N. F. Van Hulst, M. F. García-Parajó, J. Wenger, *Nano Lett.* **2015**, *15*, 6193–6201.
- [18] S. Hou, Y. Chen, D. Lu, Q. Xiong, Y. Lim, H. Duan, Adv. Mater. 2020, 32, 1906475.
- [19] X. Zambrana-Puyalto, P. Ponzellini, N. MacCaferri, D. Garoli, *Phys. Rev. Appl.* **2020**, *14*, 054065.
- [20] A. Konrad, M. Metzger, A. M. Kern, M. Brecht, A. J. Meixner, *Nanoscale* **2015**, *7*, 10204–10209.
- [21] M. J. A. De Dood, J. Knoester, A. Tip, A. Polman, *Phys. Rev. B* 2005, 71, 115102.
- [22] C. Blum, N. Zijlstra, A. Lagendijk, M. Wubs, A. P. Mosk, V. Subramaniam, W. L. Vos, *Phys. Rev. Lett.* **2012**, *109*, 203601.
- [23] S. Bidault, A. Devilez, P. Ghenuche, B. Stout, N. Bonod, J. Wenger, ACS Photonics 2016, 3, 895–903.
- [24] J. Bohlen, A. Cuartero-González, E. Pibiri, D. Ruhlandt, A.
  I. Fernández-Domínguez, P. Tinnefeld, G. P. Acuna, Nanoscale 2019, 11, 7674–7681.
- [25] N. Aissaoui, K. Moth-Poulsen, M. Käll, P. Johansson, L. M. Wilhelmsson, B. Albinsson, *Nanoscale* **2017**, *9*, 673–683.
- [26] P. Andrew, W. L. Barnes, Science 2004, 306, 1002-1005.
- [27] T. Nakamura, M. Fujii, S. Miura, M. Inui, S. Hayashi, *Phys. Rev. B* 2006, 74, 045302.
- [28] P. Ghenuche, J. de Torres, S. B. Moparthi, V. Grigoriev, J. Wenger, *Nano Lett.* **2014**, *14*, 4707–4714.

- [29] M. F. Garcia-Parajo, M. Mivelle, M. Sanz-Paz, J. Wenger, N. F. van Hulst, *Nanophotonics* **2020**, *9*, 4021–4031.
- [30] H. Asgar, L. Jacob, T. B. Hoang, J. Appl. Phys. 2018, 124, 103105.
- [31] J. De Torres, M. Mivelle, S. B. Moparthi, H. Rigneault, N. F. Van Hulst, M. F. García-Parajó, E. Margeat, J. Wenger, *Nano Lett.* **2016**, *16*, 6222–6230.
- [32] M. Lunz, V. A. Gerard, Y. K. Gun'Ko, V. Lesnyak, N. Gaponik, A. S. Susha, A. L. Rogach, A. L. Bradley, *Nano Lett.* **2011**, *11*, 3341–3345.
- [33] X. Zambrana-Puyalto, N. Maccaferri, P. Ponzellini, G. Giovannini, F. De Angelis, D. Garoli, *Nanoscale Adv.* 2019, 1, 2454–2461.
- [34] R. Collison, J. B. Pérez-Sánchez, M. Du, J. Trevino, J. Yuen-Zhou, S. O'Brien, V. M. Menon, ACS Photonics 2021, 8, 2211–2219.
- [35] H. Szmacinski, K. Ray, J. R. Lakowicz, J. Biophotonics 2009, 2, 243–252.
- [36] L. Cui, L. Zhang, H. Zeng, Nanomaterials 2021, 11, 2927.
- [37] S. T. Kochuveedu, T. Son, Y. Lee, M. Lee, D. Kim, D. H. Kim, *Sci. Rep.* **2014**, *4*, 4735.
- [38] R. Esteban, T. V Teperik, J. J. Greffet, *Phys. Rev. Lett.* **2010**, 026802.
- [39] A. P. Edwards, A. M. Adawi, J. Appl. Phys. 2014, 115, 053101.
- [40] G. M. Akselrod, C. Argyropoulos, T. B. Hoang, C. Ciracì, C. Fang, J. Huang, D. R. Smith, M. H. Mikkelsen, *Nat. Photonics* **2014**, *8*, 835.
- [41] https://www.lumerical.com/tcad-products/fdtd, n.d.
- [42] E. D. Palik, Handbook of Optical Constants of Solids, Elsevier Science, 1998.
- [43] P. B. Johnson, R. W. Christy, *Phys. Rev. B* 1972, 6, 4370– 4379.
- [44] "SPCimage software," can be found under https://www.becker-hickl.com/wpcontent/uploads/2018/12/opm-SPCImage-brochurev07.pdf, n.d.

## **Entry for the Table of Contents**



**FRET and LDOS**: Plasmonic nanopatch antenna to study the dependence of Förster resonance energy transfer (FRET) rate and efficiencity between Pyridine1-Rhodamine800 donor-acceptor pair on the on the local density of optical states (LDOS).

Institute and/or researcher Twitter usernames: @AliAdawi34001598