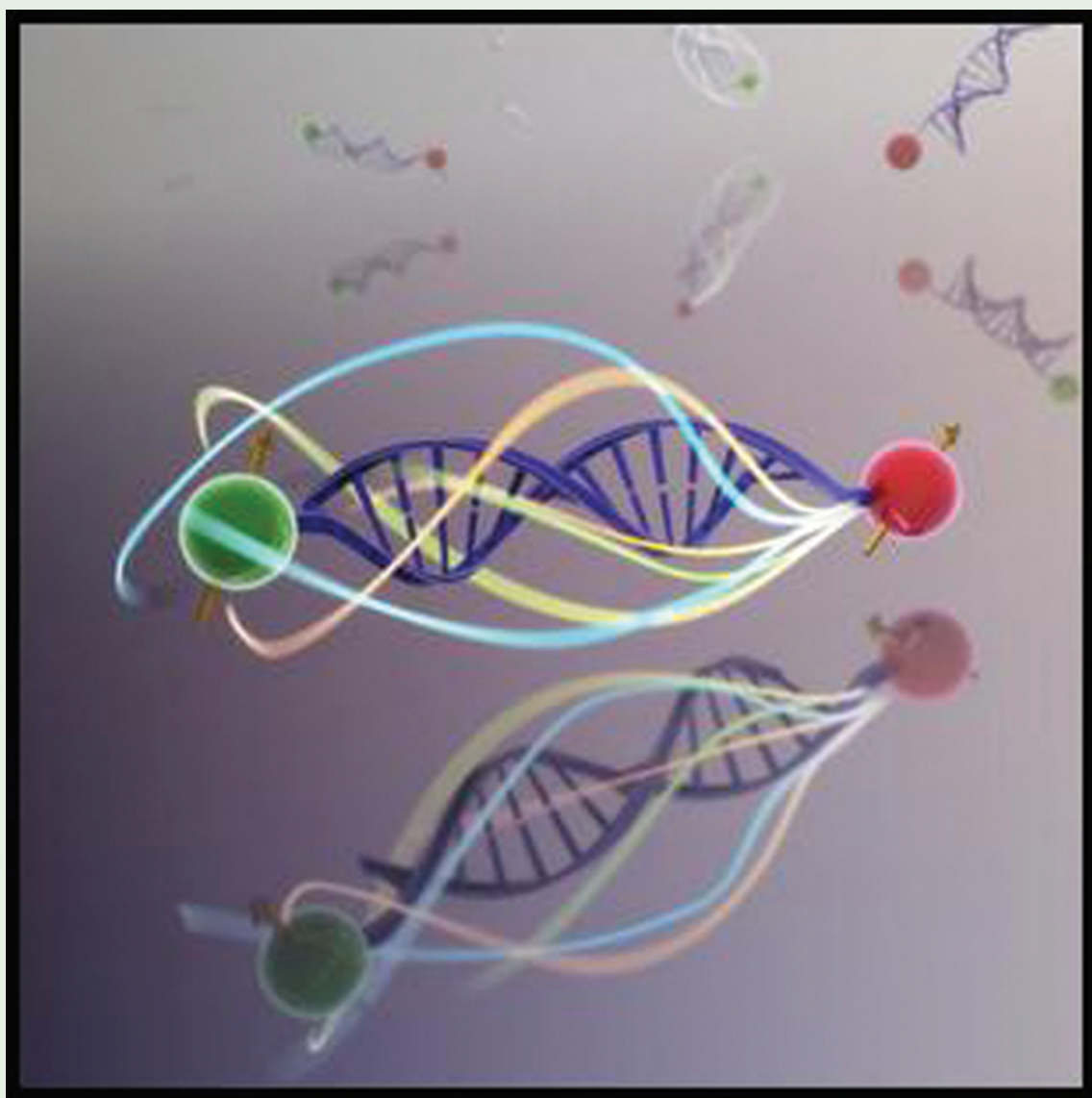


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Nanophotonic Control of the Förster Resonance Energy Transfer Efficiency

Christian Blum,^{1,*} Niels Zijlstra,¹ Ad Lagendijk,^{2,3} Martijn Wubs,⁴ Allard P. Mosk,² Vinod Subramaniam,⁵ and Willem L. Vos²

¹*Nanobiophysics (NBP), MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands*

²*Complex Photonic Systems (COPS), MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands*

³*FOM-Institute AMOLF, Science Park, 1098 XG Amsterdam, The Netherlands*

⁴*Department of Photonics Engineering, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark*

⁵*Nanobiophysics (NBP), MIRA Institute for Biomedical Engineering and Technical Medicine*

and MESA+ Institute for Nanotechnology, University of Twente, 7500 AE Enschede, The Netherlands

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We have studied the influence of the local density of optical states (LDOS) on the rate and efficiency of Förster resonance energy transfer (FRET) from a donor to an acceptor. The donors and acceptors are dye molecules that are separated by a short strand of double-stranded DNA. The LDOS is controlled by carefully positioning the FRET pairs near a mirror. We find that the energy transfer efficiency changes with LDOS, and that, in agreement with theory, the energy transfer rate is independent of the LDOS, which allows one to quantitatively control FRET systems in a new way. Our results imply a change in the characteristic Förster distance, in contrast to common lore that this distance is fixed for a given FRET pair.

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In the field of cavity quantum electrodynamics, it is recognized that the fundamental interactions between a single two-level quantum emitter—such as an atom, molecule, or quantum dot—and the light field can be exquisitely controlled by the photonic nano-environment of the emitter [1–5]. In comparison, reports on the control of multiple interacting emitters, even in case of only two emitters, are scarce. A particularly interesting and well-known optical emitter-emitter interaction is Förster resonance energy transfer (FRET), which is a near-field nonradiative energy transfer between pairs of dipoles where the quantum of excitation energy is transferred from one emitter, called donor, to a second emitter, called acceptor [6]. FRET is the dominant energy transfer mechanism between emitters in nanometer proximity and plays a pivotal role in the photosynthetic apparatus of plants and bacteria [7,8]. Many applications are based on FRET, ranging from photovoltaics [9,10] and lighting [11,12], to sensing [13] where molecular distances [14,15] and interactions are probed [16,17]. The dipole-dipole interactions in FRET are also relevant to the storage and transfer of quantum information [18–22].

The properties of a FRET system are traditionally controlled by the spectral properties of the coupled emitters, by their distance R with a typical $(R_0/R)^6$ dependence (where R_0 is the Förster distance), or by the relative orientations of the dipole moments [6,23]. It is an open question, however, whether Förster transfer can be controlled purely by means of the photonic environment while leaving the FRET pair geometrically and chemically unchanged. The photonic environment is characterized by the local density of optical states (LDOS) that counts the

number of photon modes available for emission, and is interpreted as the density of vacuum fluctuations [24,25]. While qualitative photonic effects on FRET have been reported [26,27], there is an unresolved debate on how the Förster energy transfer rate depends on the LDOS. Pioneering work by Andrew and Barnes suggested that the transfer rate depends linearly on the donor decay rate and thus, the LDOS at the donor emission frequency [28], as was confirmed elsewhere [29]. While this result was supported by theory [30], it was also stated that the transfer rate is differently affected by the LDOS. Subsequent work suggested a dependence on the LDOS squared [31], or a transfer rate *independent* of the LDOS [32]. Possible reasons for the disparity in these observations include lack of control on the donor-acceptor distance and on exact pairing of every donor to one acceptor, or cross talk between neighboring FRET pairs. Therefore, we have decided to embark on a study of the relation between Förster transfer and the LDOS, using precisely defined, isolated, and efficient donor-acceptor pairs. A precise control over the LDOS is realized by positioning the FRET pairs at well-defined distances to a metallic mirror [1,25,33].

We obtain the energy transfer rate γ_{FRET} and concomitant efficiency η_{FRET} from measurements of the donor emission rate γ_{DA} in presence of the acceptor and the rate γ_{D} in absence of the acceptor [23]. Adding a FRET acceptor to a donor introduces the energy transfer as an additional decay channel; hence, the total decay rate γ_{DA} of a FRET-coupled donor equals $\gamma_{\text{DA}} = \gamma_{\text{D}} + \gamma_{\text{FRET}}$. Therefore, we obtain the energy transfer rate γ_{FRET} from

$$\gamma_{\text{FRET}} = \gamma_{\text{DA}} - \gamma_{\text{D}}. \quad (1)$$

Since the decay rate γ_D of an isolated donor is equal to the sum of the radiative rate γ_{rad} and the nonradiative rate γ_{nr} ($\gamma_D = \gamma_{\text{rad}} + \gamma_{\text{nr}}$), the energy transfer efficiency η_{FRET} is equal to

$$\eta_{\text{FRET}} = \frac{\gamma_{\text{FRET}}}{\gamma_{\text{FRET}} + \gamma_{\text{rad}} + \gamma_{\text{nr}}} = 1 - \frac{\gamma_D}{\gamma_{\text{DA}}}. \quad (2)$$

The FRET pair we used consists of the efficient fluorescent dye molecules Atto488 as donor and Atto565 as acceptor emitters. The dye molecules are covalently bound via short linkers to the opposite ends of a 15 basepair long double-stranded DNA. The DNA forms a rigid helix that separates the donor and the acceptor by a precisely defined distance [34] of 6.8 nm, see Fig. 1(a). The FRET system was synthesized with high purity to ensure that each donor was accompanied by an acceptor, since uncoupled FRET donor emitters would disturb the measurements. For intentional donor-only samples, we used Atto488 covalently attached to an identical double strand of DNA (Atto488-DNA). The absorbance and emission spectra of the FRET system in solution show the relevant peaks of both molecules, see Fig. 1(b). The spectral overlap and separation between the two dyes ensures Förster transfer [6]. Indeed,

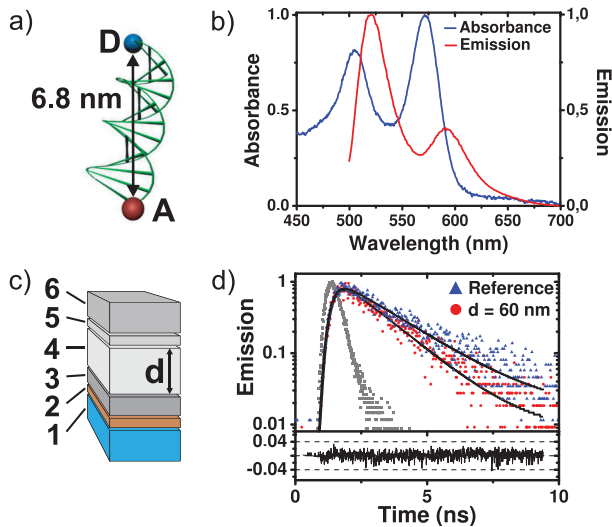


FIG. 1 (color). (a) Our FRET system consists of fluorescent dyes as donor (D, Atto488) and acceptor (A, Atto565) spaced by 6.8 nm by a short DNA strand. (b) Normalized absorbance (blue) and emission spectra (red) of the FRET system in solution. (c) Scheme of the sample to control the LDOS. 1: Si-wafer; 2: adhesive layer; 3: Ag mirror; 4: SiO_2 spacer layer of precisely defined thickness d ($60 < d < 270$ nm); 5: thin < 20 nm polyvinyl alcohol film containing the FRET pairs; 6: thick poly(methyl methacrylate) cover layer; (d) Typical normalized donor decay curves for the reference FRET sample ($d = \infty$, blue triangles) with $\gamma_{\text{DA}}^0 = 0.555 \pm 0.009 \text{ ns}^{-1}$ and near a mirror $d = 60$ nm (red circles) with $\gamma_{\text{DA}} = 0.704 \pm 0.008 \text{ ns}^{-1}$. Light grey squares: instrument response function, solid curves: single exponential fits plus background. The residuals for the reference decay are random (bottom).

excitation of Atto488 yields emission from both Atto488 around $\lambda = 525$ nm and Atto565 around $\lambda = 590$ nm.

To control the distance d between the emitters and the silver mirror, and thus, the LDOS the emitters experience, we fabricated SiO_2 spacer layers with thicknesses between 60 nm and 270 nm on the mirror, see Fig. 1(c). The emitters were deposited in a thin film (< 20 nm) of polyvinyl alcohol on top of the spacer layer, resulting in a random orientation of the donor-only or coupled donor-acceptor FRET systems with respect to the mirror. The emitter layer was covered with a thick layer of refractive-index matching poly(methyl methacrylate) to suppress interference effects from the sample-air interface. In addition, we fabricated reference samples without mirror, corresponding to a mirror at infinite distance ($d \rightarrow \infty$) [35].

Decay curves were measured using a time-correlated single-photoncounting based lifetime imaging system [36]. The detection was limited to a spectral band around the donor emission peak ($\lambda = 525 \pm 8$ nm) where only the donor emits. Typical decay curves of the FRET donor are shown in Fig. 1(d). All curves could be well modeled using single exponential decays. The presence of unwanted donor fluorophores not coupled to a FRET acceptor fluorophore would result in a second decay component. Nonuniform distances and orientations between the FRET fluorophores would also lead to nonsingle exponential decay. Therefore, we conclude from the absence of additional decay components that our samples consist of the intended one donor on one acceptor FRET-pairs placed at a well-defined distance from the mirror.

We have recorded many decay curves from different areas of the sample, yielding an average of 1200 decay rates at each sampled emitter-mirror distance. From all decay rates, we determined the decay rate distribution at each LDOS value, from which we extracted the most frequent decay rate and the width of the distribution. In Fig. 2, we present the resulting donor decay rates for the different emitter-mirror distances. For the donor-only samples, we observe the well-known oscillation of the decay rate γ_D that originates from the modification of the LDOS by the metallic mirror, see Fig. 2(b) [1]. The measured decay rates γ_D generally agree very well with the expected values based on the quantum efficiency determined for Atto488-DNA (see Ref. [36]), the peak emission wavelength of 525 nm for Atto488 and an isotropic distribution of emitter orientations. We consider the rate obtained for $d = 270$ nm to be an outlier, probably originating from an unknown error in the spacer layer fabrication that may have resulted in deviations of the refractive index of the spacer layer or in the introduction of a contaminant that quenched the emitters. The reference decay rate in the limit $d \rightarrow \infty$ was obtained from the samples without mirror [37]. The good agreement between the modeled and the measured donor-only decay rates γ_D confirms that we achieve a precise control over the LDOS [35].

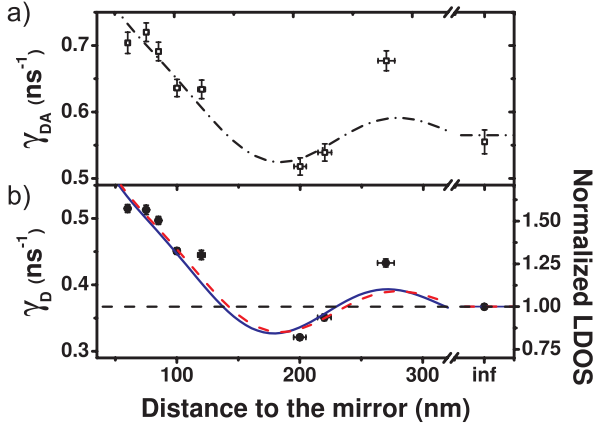


FIG. 2 (color). (a) Total donor decay rate γ_{DA} of the FRET samples oscillates with distance to the mirror. Dash-dotted curve: model consisting of the calculated LDOS, averaged over the whole donor emission band, plus a constant FRET rate $\gamma_{\text{FRET}} = 0.197 \pm 0.006 \text{ ns}^{-1}$. (b) The total decay rate γ_D of the donor-only samples shows the well-known oscillation as a function of distance d to the mirror. Solid blue curve: calculated LDOS for the center of the detection band at 525 nm; dashed red: calculated LDOS, averaged over the whole donor emission band.

For the FRET samples, we find a similar oscillation of decay rates γ_{DA} with distance to the mirror, as depicted in Fig. 2(a). The decay rates γ_{DA} are always higher than the corresponding rates γ_D for the donor-only samples, which confirms that the additional decay rate γ_{FRET} due to energy transfer is positive (cf. Eq. (1)), as is physically expected.

To visualize the effect of the LDOS on Förster transfer, we show in Fig. 3, as our main result, the energy transfer rate γ_{FRET} and the concomitant efficiency η_{FRET} versus the donor-only decay rate γ_D . According to Fermi's golden rule, γ_D depends linearly on the LDOS at the donor emission frequency [4]. We determined γ_{FRET} and η_{FRET} from the measured rates γ_{DA} and γ_D using Eqs. (1) and (2), respectively. Apart from the point at normalized LDOS = 1.25 that originates from the anomalous $d = 270 \text{ nm}$ sample identified above, our data in Fig. 3(a) show that the FRET rate γ_{FRET} is independent of the LDOS at the emission frequency of the donor, in agreement with De Dood *et al.* [32]. The independence is confirmed by the observation that the average of the rates is $\gamma_{\text{FRET}} = 0.197 \pm 0.006 \text{ ns}^{-1}$, which agrees very well with the separate measurement $\gamma_{\text{FRET}}^0 = 0.188 \pm 0.010 \text{ ns}^{-1}$ on the reference sample. We have also verified that γ_{FRET} is independent of the LDOS averaged over the emission band of the donor (cf. Fig. 2). Our data are not in agreement with a linear or quadratic dependence of the Förster energy transfer rate on the LDOS proposed earlier [28,31]. Our observations are consistent with theoretical quantum-optical considerations, wherein the properties of the Green function are analyzed [30,36]. The Green function that describes the FRET mechanism can be expressed as an integral of the LDOS over a very broad frequency interval,

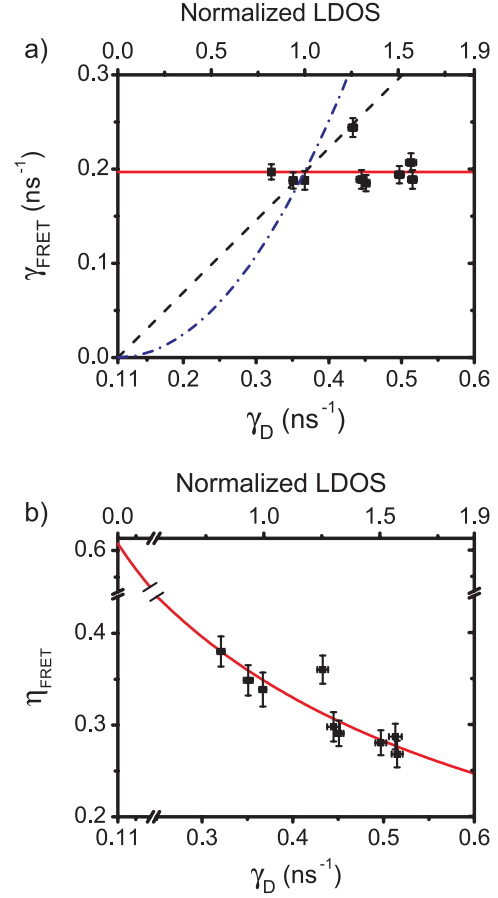


FIG. 3 (color). (a) Förster energy transfer rate γ_{FRET} as a function of the donor-only decay rate γ_D that is proportional to the normalized LDOS at the donor emission frequency. The curves show the calculated FRET rates γ_{FRET} for proposed models: independent from LDOS (red, solid lines), linear (black, dashed), and quadratic (blue, dash-dotted) dependence on LDOS. The curves coincide for the reference case, at normalized LDOS = 1 ($d \rightarrow \infty$). (b) Förster energy transfer efficiency η_{FRET} as a function of donor-only decay rate γ_D and LDOS. The energy transfer efficiency agrees well with the model (red line), calculated from the rates γ_{rad} , γ_{nr} , and γ_{FRET} and the dependence of γ_{rad} on LDOS. The maximum energy transfer efficiency occurs when the LDOS and γ_{rad} vanish, i.e., in a 3D photonic band gap. Then, γ_D equals γ_{nr} (here, $0.109 \pm 0.029 \text{ ns}^{-1}$).

from zero to about ten optical frequencies, plus an integral over all even higher frequencies [36]. In the former integral, LDOS enhancements in certain frequency bands will be canceled by LDOS reductions in other frequency ranges; moreover, the latter integral is the dominant contribution. Thus, controlling the LDOS at optical frequencies does not significantly affect the Förster energy transfer rate.

Turning from rates to efficiencies, we show in Fig. 3(b) the FRET efficiency η_{FRET} as a function of LDOS in the donor emission band. We observe clear changes of the FRET efficiency: for the range of LDOS sampled (0.86 to

1.65), the FRET efficiency is manipulated from 0.27 to 0.38, a relative change of over 30% by purely nanophotonic means. The role of the LDOS on η_{FRET} can be perceived with the aid of Eq. (2): since the LDOS controls the radiative rate γ_{rad} , it alters the competition between the different decay processes. The FRET efficiency η_{FRET} can be reduced to effectively zero by greatly enhancing γ_{rad} to the point that it dominates the FRET and nonradiative rates. On the other hand, the energy transfer efficiency can be increased by reducing the LDOS and thus, γ_{rad} . The maximum achievable transfer efficiency is reached in the limit of vanishing LDOS and γ_{rad} , which corresponds experimentally to a photonic crystal with a complete 3D photonic band gap [2,5]. The maximum achievable transfer efficiency is limited by the nonradiative rate to $\eta_{\text{FRET}}^{\text{max}} = \gamma_{\text{FRET}}/(\gamma_{\text{nr}} + \gamma_{\text{FRET}})$. For the FRET system studied here, the maximum energy transfer efficiency is 64%, see Fig. 3(b). In the intriguing situation of a FRET donor with unit quantum efficiency placed in a 3D photonic band gap, the energy transfer efficiency will approach 100%, independent of the acceptor properties, and the distances and orientations between the FRET partners. Thus, a 3D photonic band gap is a promising platform to shield dipole-dipole interactions for quantum information applications.

In summary, our observation that the Förster energy transfer rate between donors and acceptors with a fixed separation and in a well-defined geometry is independent of the LDOS settles a debate in the literature. As a consequence, the energy transfer efficiency η_{FRET} in a FRET system can be nanophotonically modified without changing the FRET system itself. The change in η_{FRET} implies a change in the characteristic Förster distance R_0 , which is defined as the distance at which $\eta_{\text{FRET}} = 50\%$ for a given donor-acceptor pair [23]. Using the known distance between the FRET donor and acceptor together with the values determined for η_{FRET} in our experiment, we calculate R_0 to change from 6.1 nm for the reference sample to values between 5.7 nm and 6.3 nm by changing the LDOS. Our result that the characteristic Förster distance R_0 can be changed via the LDOS is counterintuitive for the biochemical literature, where R_0 is taken to be fixed by the molecular properties of the FRET system [23]. In this sense, control over the LDOS allows one to change the scale of the molecular ruler when FRET is used to probe nanometer distances or molecular interactions. Moreover, the basic understanding of nanophotonic control of the FRET efficiency can be also exploited in areas such as lighting technology, where FRET may form an unwanted loss channel, and in advanced photovoltaic technology, where FRET is an important mechanism to transport energy away from the capture site, in analogy to biological photosynthesis.

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*c.blum@utwente.nl; <http://www.utwente.nl/tnw/nbp>;
<http://www.photonicbandgaps.com>

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- [37] In the reference sample, the donor-only fluorescence decay rate is found to be $\gamma_D^0 = 0.367 \pm 0.004 \text{ ns}^{-1}$. Adding the FRET acceptor results in the increase of the donor decay to $\gamma_{DA}^0 = 0.555 \pm 0.009 \text{ ns}^{-1}$. Using Eq. (1), we find a reference FRET rate $\gamma_{\text{FRET}}^0 = 0.188 \pm 0.010 \text{ ns}^{-1}$. Using Eq. (2), we find a reference energy transfer efficiency $\eta_{\text{FRET}}^0 = 34 \pm 3\%$, in reasonable agreement with the value of 28% estimated from emitter spectral properties, distances and orientations [34,36,38]. From the efficiency, we also conclude that the distance between donor and acceptor as set by the DNA-strand is close to the Förster distance R_0 .
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