DNA-mediated excitonic upconversion FRET switching

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Abstract

Excitonics is a rapidly expanding field of nanophotonics in which the harvesting of photons, ensuing creation and transport of excitons via Förster resonant energy transfer (FRET), and subsequent charge separation or photon emission has led to the demonstration of excitonic wires, switches, Boolean logic and light harvesting antennas for many applications. FRET funnels excitons down an energy gradient resulting in energy loss with each step along the pathway. Conversely, excitonic energy upconversion via upconversion nanoparticles (UCNPs), although currently inefficient, serves as an energy ratchet to boost the exciton energy. Although FRET-based upconversion has been demonstrated, it suffers from low FRET efficiency and lacks the ability to modulate the FRET. We have engineered an upconversion FRET-based switch by combining lanthanide-doped UCNPs and fluorophores that demonstrates excitonic energy upconversion by nearly a factor of 2, an excited state donor to acceptor FRET efficiency that is close to unity. These findings offer a promising path for energy upconversion in nanophotonic applications including artificial light harvesting, excitonic circuits, photovoltaics, nanomedicine, and optoelectronics.

1. Introduction

In many nanophotonic systems, excitons are funneled down an energy gradient created by an array of fluorophores possessing successively lower excitation energies. Examples of such excitonic systems include light harvesting antennae in higher plants [1, 2], certain bacteria [3, 4], synthetic waveguides [5, 6], switches, and logic gates [7–9]. The energy is degraded due to losses at each step in the exciton transfer process, limiting the performance of exciton funnels. This degradation raises the question of whether the exciton funnel performance can be improved via an upconversion process in which two excitons combine to form a single exciton of higher energy, thus rejuvenating the exciton energy. Indeed, nature appears to have taken this approach, as energy upconversion has been observed in the energy transfer pathways present within the Fenna–Mathews–Olson complexes of natural photosynthetic systems [10, 11]. Optical upconversion also occurs in lanthanide-doped materials such as NaYF₄:Gd³⁺, Yb³⁺, Er³⁺, both in bulk solid crystals and nanoparticles; however, the upconversion process in these materials differs mechanistically from the natural upconversion phenomenon [12, 13]. Although inherently inefficient, the efficiencies of upconversion nanoparticles (UCNPs) continue to improve [14], which offers an opportunity to pursue energy upconversion in artificial excitonic systems including excitonic wires, switches, and light harvesting antennae. UCNPs are being explored in the biomedical field as alternatives or supplements to current imaging agents, bioassays, and drug delivery modalities because of their narrow bandwidth emission, zero autofluorescence, low toxicity, deep tissue penetrating near infrared (NIR) excitation, and minimal photobleaching [15, 18–24]. Additionally, UCNPs are currently studied as potential components in optoelectronic applications such as light-emitting diodes [25], fluorescent lighting [26], telecommunications [27], security coatings [23, 24], and photovoltaic devices [28, 29]. Further
FRET is excitonic energy transfer on the nanometer scale between donor and acceptor molecules mediated by dipole coupling [35, 36]. The acceptor molecule need not be a fluorophore, and the energy transferred need not be radiated as fluorescence [37–39]. Though there are multiple ways in which combined upconversion and FRET systems can be constructed, here the focus will be on FRET between a UCNP donor and an acceptor fluorophore. During FRET, the fluorescence from the donor UCNP decreases (i.e., a quenching effect) with a simultaneous increase in the acceptor molecule’s fluorescence as the donor–acceptor pair are brought into proximity (i.e., a transfer effect) [40]. A simple schematic of the upconversion to FRET process is provided in figure 1, in which the sensitizer–activator complex provides the two photon absorption pathway within the UCNP [15–17, 33, 41], thereby initiating the FRET cascade from the UCNP to the fluorophore. In this report, we demonstrate the upconversion of incident infrared photons in NaYF4:Gd3+,Yb3+,Er3+ nanoparticles followed by excitonic transfer (i.e., FRET) to fluorophores that emit photons in the visible region, that can be dynamically switched ‘ON’ and ‘OFF’. Switching is accomplished via DNA hybridization and toehold-mediated DNA strand-displacement reactions [42], in which auxiliary DNA oligomers attached to the UCNP’s are used to control subsequent reversible binding of DNA oligomers carrying the fluorophores to the nanoparticle.

Spectral overlap between the donor emission and the acceptor absorption and donor–acceptor distance are the two key components required for efficient FRET. In an ideal FRET process, such as that depicted in figure 2(a), complete nonradiative energy transfer between the donor and acceptor occurs (dashed curve). This energy transfer can be maximized by optimizing the spectral overlap and reducing the distance between the donor and acceptor to maximize FRET. More typically, competing parasitic processes such as bleed-through, cross-talk, internal energy loss, and donor emission into free space decrease FRET efficiency (solid curve, figure 2(a)). As defined by Berney and Danuser [43], cross-talk occurs when the donor emission spectrum overlaps that of the acceptor emission, thereby artificially increasing the apparent acceptor emission signal. Cross-talk [21–23] can be virtually eliminated through the careful selection of the fluorophore acceptor such that its emission does not overlap that of the donor. Conversely, bleed-through [43] involves undesired excitation of the acceptor molecule at the donor excitation wavelength. An advantage to UCNP-fluorophore FRET systems, bleed-through is eliminated completely because the excitation wavelength of the UCNP donor

Figure 1. Schematic illustration of optical upconversion followed by FRET for a donor (UCNP)/acceptor (fluorophore) pair. The donor UCNP undergoes a multi-step energy transition upon low energy near infrared (NIR) excitation as detailed in various review publications [15–17, 27, 33, 41]. Upon relaxation to the ground state, the UCNP non-radiatively transfers its energy via dipole–dipole interactions (FRET) to an acceptor molecule (fluorophore). This process results in emission of a photon from the acceptor.
lies in the NIR spectrum, while the acceptor fluorophore excitation is in the visible. As a result, the incident UCNPs excitation photons do not have sufficient energy to directly excite the acceptor fluorophore.

Figure 2(b) shows the relevant absorption and emission spectra of the FRET system components used in this study (i.e., spectral overlap). This system is composed of an upconverting NaYF₄ nanoparticle donor doped with Gd³⁺, Yb³⁺, and Er³⁺ and a 6-carboxy-X-rhodamine (ROX) fluorophore acceptor bound to the UCNPs via a hybridized DNA tether. Nanoparticle information, DNA sequences, and fluorophore details are provided in supplementary material S1. The low wavelength absorbance shoulder of the ROX acceptor coincides well with the emission peaks of the UCNPs in the range of 515–562 nm, which provides adequate spectral overlap for FRET. Furthermore, cross-talk is minimized as the acceptor emission peak lies in a longer wavelength region than the donor emission resulting in virtually no cross-talk at the 608 nm peak ROX acceptor emission wavelength. It should be noted that some attenuation of the UCNPs fluorescence in the range of 515–562 nm occurs when ROX is introduced, which will be discussed later. There is also potential cross-talk between the donor and acceptor in the 645–675 nm range; however, this spectral region falls well outside the spectral overlap region and does not contribute to the FRET. Thus, the unique optical properties of the UCNPs donor and choice of ROX as the acceptor allow clear observation of donor quenching and acceptor emission in the spectral data.

There have been several reports of UCNPs-fluorophore FRET systems [44–49], which have also been referred to as energy transfer [18, 50] or luminescence resonance energy transfer systems [51–56]. To the best of our knowledge, published investigations of UCNPs fluorophore FRET systems have primarily demonstrated one aspect of the FRET process, namely donor quenching [57–60], accompanied by a nominal increase in acceptor molecule emission suggesting an inefficient FRET process. In order for potential optoelectronic applications of UCNPs-fluorophore FRET-based constructs, realization of higher efficiency FRET (figure 2(a)), in which both donor quenching and acceptor emission are significant, is an essential challenge that must be addressed.
2. Materials and methods

To address the primary challenge of hydrophobicity of as-synthesized lanthanide-doped UCNPs, biofunctionalization techniques have been used such as PEGylation, recombinant antibody fragment coating, aminoethyl dihydrogen phosphate, citrate capping, polyacrylic acid, streptavidin coating, and silica shell growth. These UCNP modification methods enable the use of acceptor molecules currently employed in the FRET process; however, these techniques potentially increase the UCNP dimensions resulting in greater donor–acceptor pair separation distances, which decreases the FRET efficiency. Additionally, typical biofunctionalization methods, such as covalent lectin binding, covalent biotinylation, fluorophore incorporation within hydrophilic coatings, amino group conjugation, and stain intercalation, involve multi-step processes.

These multi-step biofunctionalization processes reduce overall yield and add complications to the UCNP preparation. Recently, a simple single-step ligand exchange method was reported by Li et al., in which single stranded DNA (ssDNA) was directly attached to the UCNP in a step process, producing hydrophilic, monodispersed UCNPs for salt concentrations ranging from 5 to 100 mM. Subsequently, they were able to selectively attach a variety of ssDNA functionalized particles such as gold nanoparticles (AuNPs), Cy3 fluorophores, and cell targeting aptamers via Watson–Crick hybridization to the available ssDNA. We believe this ssDNA functionalization method is advantageous for UCNP-based excitonic FRET because not only is it a single-step process, but additionally it reduces the donor–acceptor pair separation distance, thereby enhancing their FRET efficiency. Moreover, ssDNA functionalization enables the modulation of FRET through toehold-mediated strand-displacement reactions when invasion (INV) and restoration (RES) ssDNA strands are introduced to perform UCNP-based FRET excitonic switching.

To explore the possibility of DNA-mediated UCNP-fluorophore FRET switching, four distinct challenges needed to be addressed: (i) rendering the hydrophobic UCNPs hydrophilic, (ii) functionalizing the hydrophilic UCNPs using the ssDNA biofunctionalization method, (iii) devising a FRET system, and (iv) designing a strand displacement sequence. Oleic acid capped, hydrophobic UCNPs were rendered both hydrophilic and functionalized with ssDNA, denoted as UCNP_d via the one step ssDNA biofunctionalization method demonstrated by Li et al., as described in the supplementary material S2. In addition to imparting hydrophilicity, the ssDNA on the UCNP surface serve as tethers to which complementary ROX-functionalized ssDNA oligomers can hybridize. ROX was chosen as the acceptor because it can be readily attached to ssDNA and it provides adequate spectral overlap with the donor as discussed previously.

The scheme that was implemented to control the FRET between ssDNA functionalized UCNP_d and the ROX fluorophore is illustrated in figure 3. The ROX fluorophore is covalently attached to a ssDNA oligomer complementary to a portion of the UCNP_d ssDNA sequence; this ROX-DNA pair is referred to as ROX_d.

Figure 3 (1) shows the UCNP_d in the ‘OFF’ state where no ROX emission is observed. Switching to the ‘ON’ state occurs when the ROX_d hybridizes to the tether on the UCNP_d as shown in (2). Here, the hybridization of the ROX_d strand to a 10 nucleotide (nt) toehold binding region (TH) on the UCNP_d tether holds the ROX_d fluorophore in proximity to the UCNP_d enabling FRET and the consequent ROX emission. Switching to the ‘OFF’ state is accomplished by displacement of the ROX_d from the donor with the introduction of a 22 nt invasion (INV) strand (3). Finally, restoration of the ROX_d strand to the UCNP_d and thus reestablishing the ‘ON’ state, is achieved by addition of a 17 nt restoration (RES) strand displacing ROX_d by preferentially hybridizing with the INV strand (4). The process can be iterated to reversibly switch the system between the ‘ON’ and ‘OFF’ states (5). For the experiments described in this paper, the concentration of available DNA tethers was estimated to be ~4 μM using the procedure described in supplementary material S2.3.

3. Results and discussion

The state of the FRET system was monitored in two ways after each switching event via fluorescence spectroscopy under conditions of continuous 980 nm excitation (instrumentation details provided in supplementary material S3). The emission intensity of the donor and the acceptor were acquired as a function of wavelength and time; the latter was performed at the peak emission wavelength of the ROX acceptor (608 nm). Figure 4 shows the normalized fluorescence spectra obtained for the ‘OFF’ and ‘ON’ states before and after
addition of INV and RES strands to induce one cycle of excitonic switching. The normalization process is described further in supplementary material S4. As a control, the initial emission spectrum of the UCNP in the absence of ROX strand is shown as the black curve in figure 4.

The red curve in figure 4 shows that once the ROX strand attaches to the UCNP, a clear decrease in the donor emission peaks in the range of 515–562 nm and a concomitant increase in the acceptor emission in the range of 580–630 nm, indicating FRET from the donor (upper inset) to the acceptor (lower inset). To our knowledge, such a significant and pronounced increase in acceptor fluorescence has not been previously observed in the published studies of lanthanide-doped UCNPs [44, 45, 50, 60, 61]. In these prior works, acceptor emission was either not observed or was nominal. We attribute the clear acceptor emission increase demonstrated in figure 4 to the shorter donor–acceptor (i.e., UCNP to ROX) distance arising from the direct

**Figure 3.** Diagram of the DNA-mediated excitonic upconversion FRET-based switching scheme. The initial state of the functionalized UCNP is shown at (1). The red ROX strand hybridizes to a TH region of the black ssDNA attached to the UCNP, resulting in ‘ON’ state FRET emission (2). The green invasion strand (INV) interacts with a toehold region on the red ROX strand, removing the acceptor from the donor (3), returning the donor to its original ‘OFF’ state. The blue restoration strand (RES) associates with a toehold region of the INV strand (4), freeing the red ROX strand to reattach to the UCNP and returning the system to its ‘ON’ state. Reversible switching is thus accomplished by repeatedly introducing the INV and RES strands (5).

**Figure 4.** Normalized emission spectra of functionalized UCNPs under continuous 980 nm excitation. Hybridization of the ROX acceptor strand (step 2, figure 3) produced a decrease in the UCNP emission peaks in the range of 515–562 nm coupled with a simultaneous increase in the ROX emission (red trace) in the range of 580–630 nm. Introduction of the ROX invasion strand (step 3, figure 3) induced a reduction of FRET (blue trace). Subsequent addition of the ROX restoration strand (step 4, figure 3) increased ROX emission (green trace), a signature of increased FRET and a demonstration of excitonic upconversion FRET switching. Spectra were collected approximately 30 min post interaction with the indicated strand. Interaction time is well beyond the calculated time to half completion of 120 ± 40 and 500 ± 120 s for the ‘ON’ and ‘OFF’ states, respectively, as described in the supplementary material S6.

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DNA functionalization method [70]. Although removal of the ROXₐ (step 3, figure 3) by addition of INV strand only resulted in partial recovery of the donor emission peaks in the range of 515–562 nm to their original values, a simultaneous significant reduction (i.e., quenching) in the 608 nm acceptor emission peak was noted (lower inset blue curve). The partial recovery of the donor emission peaks in the range of 515–562 nm is most likely due to the incomplete removal of ROXₐ from the UCNPₐ as evidenced by the incomplete quenching of the 608 nm acceptor emission. Analysis of the area containing the donor emission peaks was performed by integrating from 500 to 562 nm and revealed values consistent with expected changes (supplementary material S13). The subsequent addition of the ROX restoration strand (step 4, figure 3) returns the ROXₐ emission to the values of the green curve indicated in figure 4. To demonstrate the repeatability of this switching, the ‘OFF–ON’ cycle was iterated again resulting in spectra similar to the blue and green curves in figure 4 (raw emission spectra of all three cycles are provided in supplementary material S5).

Isothermal dynamic switching of FRET between UCNPₐ and ROXₐ (i.e., induced acceptor emission changes at 608 nm as a function of time) is further highlighted in figures 5(a) and (b), which shows a series of successive switching events. Sequential and reversible switching between ‘ON’ and ‘OFF’ states is clearly demonstrated as evident by the saw-tooth pattern of figure 5(a), which is averaged over three trials. Stoichiometric dynamic switching was performed on 30 min intervals, figure 5(b). The average time to half-completion, as modeled by second-order kinetics for attachment (‘ON’ state) and removal (‘OFF’ state) of the ROXₐ to the UCNPₐ, were calculated to be 120 ± 40 s and 500 ± 120 s, respectively, at ~80 µM concentrations (data provided in supplementary material S6). As noted in figure 4 and observed in figures 5(a) and (b), the ROXₐ emission at 608 nm does not return to zero in the ‘OFF’ state, which can most likely be attributed to the incomplete removal of the ROXₐ strand from the UCNPₐ as discussed earlier. Except for the acceptor emission data (figures 4 and 5) in which the INV and RES strands were added in 1:1 stoichiometry, the acceptor emission does not noticeably decrease further upon application of INV strand in excess ratios (data not shown). Hence, it can be inferred that a substantial fraction of the initially supplied ROXₐ is bound to the UCNPₐ in such a manner that it cannot be removed by strand invasion. Incomplete invasion due to oligomer crowding and direct adsorption of the ROX fluorophore to the surface of the UCNPₐ may explain why the 608 nm acceptor fluorescence does not return to zero in the switched ‘OFF’ state. Relative to the latter, we have found evidence of direct adsorption of the ROX fluorophore, or unspecified binding, when a control experiment was performed in which a mismatched sequence of the ssDNA ROX strand was used and added to a solution of UCNPₐ while monitoring the 608 nm acceptor emission (supplementary material S13). Nonetheless, the switching results demonstrated in figures 5(a) and (b) indicate that the toehold domains at least moderately retain their ability to perform the toehold-mediated strand-displacement reactions necessary for excitonic switching.

In order to compare this exciton upconversion FRET system with other published work [44, 45, 50, 50, 60, 61], the energy conversion efficiency (E_conv) was determined. The E_conv is defined as the ratio of the number of photons emitted by the acceptor in the presence of the donor to the number of photons emitted by the donor (UCNP) in the absence of the acceptor (fluorophore). This quantity is conveniently computed using the simple relationship:

**Figure 5.** (a) Dynamic 608 nm emission of the DNA functionalized donor UCNP (UCNPₐ) upon 980 nm excitation via hybridization of the fluorophore acceptor (ROXₐ) labeled ssDNA. Cycling of the emission intensity by switching between ‘ON’ (blue circle) and ‘OFF’ (black square) states was achieved through toehold-mediated strand-displacement of the ROXₐ strand. The lines between data points are provided for clarity and error bars represent three switching trials. (b) Dilution corrected reactions kinetics fluorescence data recorded at 608 nm. The excitation wavelength was 980 nm.
was applied to our data prior to computing UCNP emission, producing by the attachment chemistry increases nonradiative energy losses of either the donor or acceptor within experimental uncertainty and falls within the range of the literature values for the quantum efficiency of those quantities: the energy transfer efficiency (eff), indicating ROX is also occasionally referred to as the quenching efficiency [44, 74]. Assuming the decrease in the fluorescence of the donor in the presence of the acceptor is entirely due to the transfer of those photons to the acceptor, Qeff is then given by

\[ Q_{\text{eff}} = \frac{f_{\text{AD}} - f_A}{f_D - f_{\text{DA}}} \]  

(3)

Qeff is a measure of the efficiency with which excitonic quanta transferred to the donor are converted into acceptor fluorescence photons and is thus a measure of the FRET acceptor’s fluorescence quantum yield. For the UCNP–ROX system, direct excitation of the ROX by the infrared laser used to pump the UCNP did not result in significant measurable ROX fluorescence, thus we can reasonably assume that \(f_A = 0\) for this system (see supplementary material S9). Under these conditions, equations (1)–(3) yield:

\[ E_{\text{con}} = Q_{\text{eff}} E_{\text{trans}}. \]  

(4)

This decomposition of \(E_{\text{con}}\) provides a means of assessing the relative contributions to the conversion efficiency of two separate physical effects: exciton transfer from the donor to the acceptor and fluorescence emission of the acceptor.

A number of studies have been conducted to determine the Qeff of ROX [75–78], all of which report values within the range of 1.0 ± 0.05 (i.e., unity quantum yield, within experimental uncertainty), indicating ROX is highly efficient at re-emission of absorbed photons. To calculate Qeff of the UCNP–ROX system using equation (3), the donor emission peak areas from the spectra shown in figure 4 (black and red curves) were integrated from 514 to 562 nm, and the acceptor emission peak areas were integrated from 565 to 645 nm. Although minimal, it was necessary to consider the attenuation of the UCNP in the presence of ROX. An attenuation correction factor \(\left(\frac{f_D}{f_{\text{DA}}}\right)\) was applied to our data prior to computing Qeff and \(E_{\text{trans}}\) for our system to account for free ROX absorption, however, this could not be performed for the comparison to other published work (supplementary material S10). The Qeff of this system calculated via equation (3) (1.08 ± 0.11) is unity within experimental uncertainty and falls within the range of the literature values for the quantum efficiency of

### Table 1. Comparison of UCNP-fluorophore systems.

<table>
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<tr>
<th>Fluorophore</th>
<th>(f_D)</th>
<th>(f_{\text{AD}})</th>
<th>(E_{\text{con}})</th>
<th>Reference</th>
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<tr>
<td>TAMRA</td>
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<td>1.23</td>
<td>0.08</td>
<td>[49]</td>
</tr>
<tr>
<td>BOBO3</td>
<td>20.9</td>
<td>0.84</td>
<td>0.04</td>
<td>[44]</td>
</tr>
<tr>
<td>RhB</td>
<td>19.4</td>
<td>2.35</td>
<td>0.12</td>
<td>[60]</td>
</tr>
<tr>
<td>TAMRA</td>
<td>20.0</td>
<td>2.80</td>
<td>0.14</td>
<td>[59]</td>
</tr>
<tr>
<td>RhB</td>
<td>18.2</td>
<td>1.44</td>
<td>0.08</td>
<td>[43]</td>
</tr>
<tr>
<td>ROX</td>
<td>13.5</td>
<td>3.07</td>
<td>0.23</td>
<td>this work</td>
</tr>
</tbody>
</table>
ROX. This result indicates that the excitonic coupling to the UCNP and attachment scheme adopted for ROXₐ have no observable detrimental effect on the $Q_{\text{eff}}$ of ROX.

The energy transfer efficiency ($E_{\text{trans}}$) for the UCNPₐ–ROXₐ system was evaluated using equation (2), where again peak areas from 514 nm to 562 nm and 565 nm to 645 nm were used to calculate the donor and acceptor emission, respectively. Black bars in figure 6 represent $E_{\text{trans}}$ for the first ‘OFF–ON’ cycle evaluated for three separate trials.

The average value of $E_{\text{trans}}$ for these three trials was 0.23 ± 0.03 (see supplementary material S11); note that since in our system $Q_{\text{eff}}$ is close to unity, $E_{\text{trans}}$ is essentially equal to $E_{\text{ON}}$ as shown in table 1. The nearly 25% energy transfer conversion efficiency is comparable to that of other UCNP FRET systems reported in the literature [44, 45, 50, 60, 61]. Figure 6 also displays $E_{\text{trans}}$ evaluated for the second and third ‘OFF–ON’ cycles (red and blue bars) for each of the three trials. The combined average value of $E_{\text{trans}}$ for all of the second and third ‘OFF–ON’ cycles is 0.07 ± 0.03. As already indicated, not all the ROXₐ is removed from the UCNPₐ by the INV oligomers used to transition the system from the ‘ON’ state to the ‘OFF’ state (see figure S3, supplementary material). Hence, after the first ‘OFF–ON’ cycle, there are fewer attachment sites to which ROXₐ (supplementary material S12) can bind; however these sites remain active on successive cycles as indicated by the similar $E_{\text{trans}}$ values for the two additional switching cycles (cycles 2 and 3). An estimate of the fraction of ROXₐ binding sites that remain active ($Rₐ$) for FRET switching is given by:

$$Rₐ = 1 - \frac{F_{\text{ADoff}}}{F_{\text{ADon}}}$$  \hspace{1cm} (5)

where $F_{\text{ADon}}$ and $F_{\text{ADoff}}$ are $f_{\text{AD}}$ evaluated for the system in the ‘ON’ state, and $F_{\text{ADoff}}$ is $f_{\text{AD}}$ evaluated for the system in the ‘OFF’ state. The averaged $Rₐ$ value for successive ‘OFF–ON’ cycles is 0.45 ± 0.11. Hence, 45% of the ROXₐ binding sites remain active, which is one area that can be improved upon in future work.

4. Conclusion

We have demonstrated efficient and switchable DNA-mediated upconversion FRET by engineering an UCNP–ROX donor/acceptor excitonic system through implementing (1) a simple, one-step direct attachment of ssDNA to hydrophobic UCNPs, and (2) a ROX acceptor–DNA strand design that exploits the ability to both hybridize with the ssDNA biofunctionalized UCNPs and undergo toehold-mediated strand-displacement. Decreased donor–acceptor distance from the direct attachment resulted in a quantum efficiency indistinguishable from unity and superior FRET that produced energy conversion and energy transfer efficiencies of nearly 25%. Successive switching events were performed using toehold-mediated strand-displacement that, although only 45% of sites were actually switching, allowed cycling of the excitonic FRET switch’s state to be performed through three complete ‘OFF–ON’ cycles. The FRET produced a clear quenching of the donor emission with a significant simultaneous increase in acceptor emission that has yet to be fully demonstrated in other work. In principle, the upconversion FRET scheme reported here can lead to more efficient artificial light harvesting systems and excitonic devices, be incorporated to enhance photovoltaic devices, and be utilized to produce novel nanomedical assays.
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