Upconverting Nanoparticle Based Resonance Energy Transfer Relays

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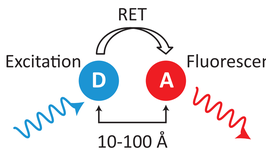
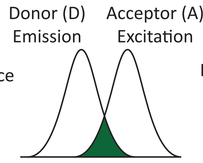
Abstract

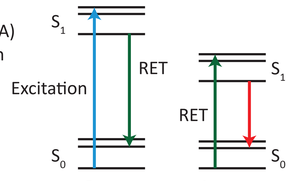
Resonance energy transfer (RET) logic offers molecular scale computation in a variety of unique environments. Chromophores are arranged into nanophotonic networks which are excited by input photons and perform logical operations on the generated excitons. The spectral overlap requirements of RET which enable this computation, however, also force excitons in the network to lose energy as they travel downstream from input to output. This inherent energy loss prohibits RET logic from being cascaded to create more complex circuits. To restore this energy, we propose an upconverting nanoparticle (UCNP) based RET relay which converts multiple low energy excitons to a single high energy exciton. The higher energy output of this relay can then act as the input to a cascaded network.

Resonance Energy Transfer (RET) Logic

Resonance energy transfer (RET) is a weak dipole-dipole coupling that allows an excited chromophore to non-radiatively donate its energy to a neighboring chromophore. In order for RET to occur, the donor's emission spectrum must overlap the acceptor's excitation spectrum and the molecules must be roughly 10-100 Å apart.

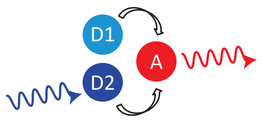




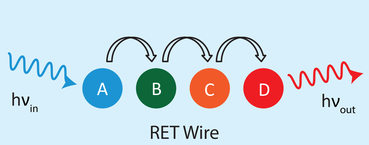


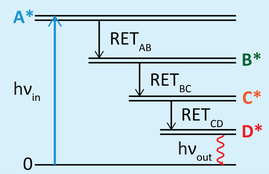
Chromophores can be spatially arranged into networks which perform logical operations using RET (RET Logic) [1]. Input chromophores are excited by a far field source and output chromophores are monitored for fluorescence. For example, an OR gate is composed of two distinctly addressable donors (D1 and D2) that can transfer to a single acceptor (A).

OR gate: two donors, one acceptor



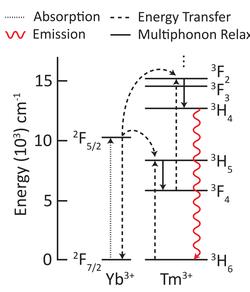
Problem: As excitons traverse a RET network, they inevitably lose energy due to the spectral overlap requirements of RET. For example, excitons in the RET wire below lose energy with every transfer event. This loss prohibits the cascading of networks since output excitons (at D) are too low in energy to excite another network's input (such as A).

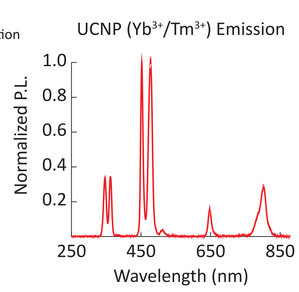




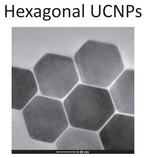
Upconverting Nanoparticles (UCNPs)

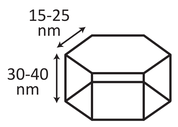
Upconverting nanoparticles consisting of a $NaYF_4$ host lattice co-doped with two different lanthanide elements undergo energy transfer upconversion. Yb^{3+} sensitizer ions are excited at 980 nm and transfer their energy non-radiatively to neighboring activator ions (Tm/Er/Ho), illustrated by the partial energy diagram shown below. After multiple transfer events (dashed lines), the highly excited activator ions can return to their ground state and release a visible photon (red line) [2].





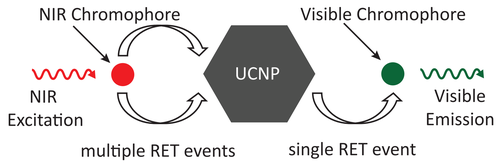
Hexagonal UCNPs





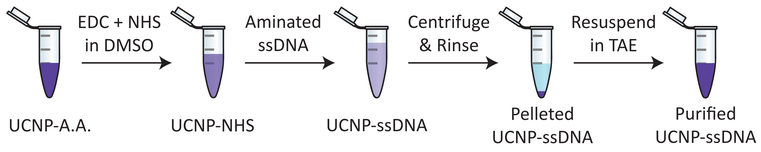
UCNP Based RET Relay Schematic

UCNPs offer a solution to the energy loss inherent to RET logic. NIR emitting chromophores with significant emission overlap at 980 nm can donate multiple low energy excitons via RET to the UCNP [3], resulting in highly excited activator ions. Once in this state, the UCNP acts as a RET donor, transferring a single high energy exciton to a visible chromophore whose excitation spectrum overlaps with the UCNP's emission [4]. In the future, the NIR chromophore will be replaced with the output of a RET network.

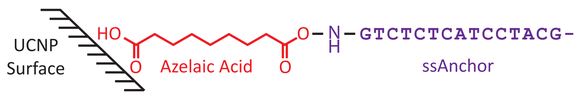


UCNP ssDNA Functionalization

To build the RET relay, we first need a strategy for attaching chromophores to the UCNPs. Ultimately, ssDNA functionalization offers the highest compatibility with RET logic since many RET networks are self-assembled on DNA nanostructures. To functionalize the particles with ssDNA, UCNPs capped with a mixture of azelaic acid (A.A.) and oleic acid undergo the coupling procedure shown below:

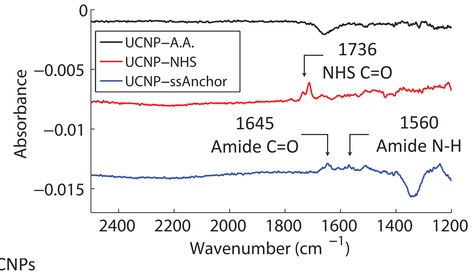


The final product contains ssDNA, called ssAnchor, bound to the UCNP surface.

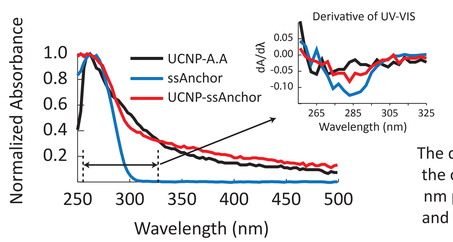


DNA conjugation can be confirmed via FTIR spectroscopy. Introducing EDC and NHS to the UCNP-A.A. stock results in a clear 1736 cm^{-1} peak due to the C=O stretch of the NHS ester. By adding aminated ssAnchor to the UCNP-NHS sample, the NHS peaks disappear and the characteristic C=O stretch and N-H bend of an amide bond form at 1645 cm^{-1} and 1560 cm^{-1}.

UCNP ssAnchor Conjugation FTIR Results



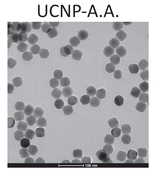
UV-VIS of Functionalized UCNPs



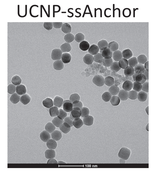
UV-VIS of UCNP-ssAnchor is roughly the superposition of ssAnchor and UCNP-A.A. The derivative shows the onset of the 260 nm peak in the DNA and UCNP-ssAnchor.

TEM images before and after show no changes in morphology.

UCNP-A.A.

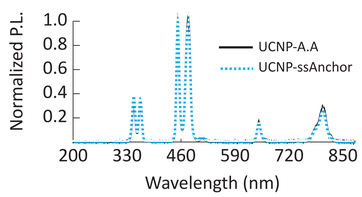


UCNP-ssAnchor



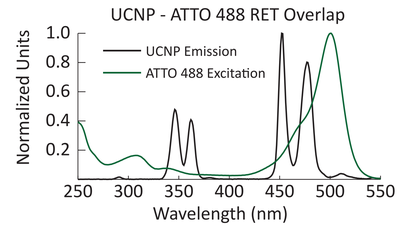
P.L. of Functionalized UCNPs

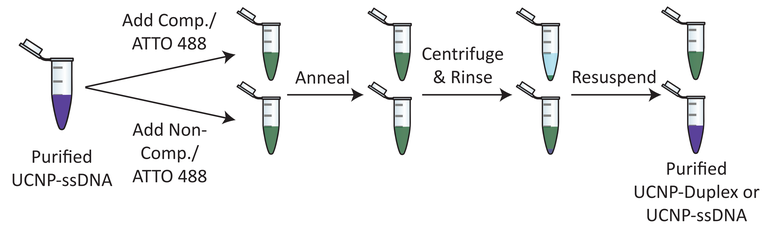
DNA functionalization and resuspension in TAE does not significantly change the UCNP emission spectrum.



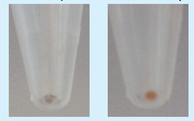
UCNP-Visible Chromophore RET Results

For the visible chromophore of the RET relay, we have chosen ATTO 488 due to the significant overlap of its excitation spectrum with the UCNP emission spectrum. Assuming a quantum yield of 0.1% for the UCNPs [3], the R_0 for RET from the UCNP to ATTO 488 is roughly 1.6 nm. To test both the ssAnchor's ability to hybridize with its complement and RET from the UCNP to ATTO 488, we run the experiment below in which we add ATTO 488 labeled complementary and non-complementary DNA to UCNP-ssAnchor. We then excite both samples at 980 nm.





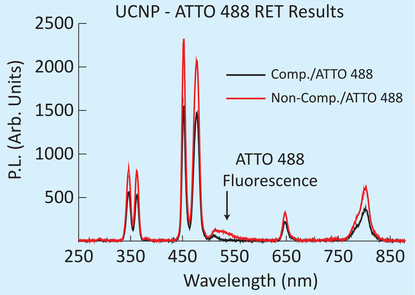
Comp. Non-Comp.



Images of the pelleted and rinsed particles are shown to the left. Contrary to our expectations, the pellet in the non-complementary control sample has a red tint (the color of ATTO 488) indicating that the particles have labeled DNA on the surface. Furthermore, the sample containing complementary DNA does not have a red tint. Instead, it has a gray tint similar to the color of unlabeled, pelleted UCNP-ssAnchor.

Photoluminescence measurements of the resuspended pellets show a strong fluorescent shoulder at 523 nm due to UCNP-ATTO 488 RET in the non-complementary control, but **not** in the sample with the complementary strand. This indicates that the anchor strand is either unavailable for hybridization or weakly available at best. It also indicates that ssDNA may adhere to this UCNP-ssAnchor complex and that these interactions are sequence dependent.

UCNP - ATTO 488 RET Results



Conclusions and Future Work

In the future, we will investigate the cause of the anomalous results shown above and, if possible, use this to our advantage to better label UCNPs with the RET relay chromophores. Despite this peculiar result, we have still shown that the latter half of the RET relay works as expected, with the UCNP donating excitons to a visible dye, ATTO 488. Once fabricated in its entirety, the UCNP based RET relay will serve as a fundamental motif in RET logic. It offers a form of signal restoration necessary for the future development of this technology. By enabling the cascading of circuits, the relay opens doors to previously unachievable circuit complexity in RET logic.

References

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3. Zou, W.; Visser, C.; Maduro, J. A.; Pshenichnikov, M. S.; Hummelen, J. C. Broadband dye-sensitized upconversion of near-infrared light. Nature Photonics, 2012, 6, 560-564.
4. Li, Z.; Zhang, Y.; Jiang, S. Multicolor Core/Shell-Structured Upconversion Fluorescent Nanoparticles. Advanced Materials, 2008, 20, 4765-4769.