Molecular sensors for calcium ion detection via triplet-triplet annihilation upconversion

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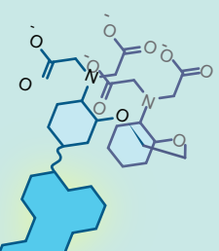
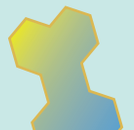
The work described in the present thesis serves as a foundation for the advancement of metal-cation sensing via TTA-UC in aqueous solution. The Ca^{2+}-chelating moiety that was used throughout this thesis, BAPTA, may in principle be replaced by a chelating moiety that is either specific to other metal cations, or still specific to Ca^{2+}, but with different affinity.
This work introduces two innovative approaches. First, liposomes address the low water solubility of the molecular components involved in TTA-UC. Second, unfunctionalized perylene was added to the liposome formulation to address the low probability of photosensitizer and annihilator to collide due to their different hydrophobicity and low mobility in lipid membranes.

Ultimately, the two approaches might be combined to allow for imaging calcium ions in living cells, thus avoiding problems related to autofluorescence, although this still needs to be demonstrated.

The structure-properties relationship discussed in this thesis improves our understanding of these systems. The association constants of the sensor molecule as well as its contrast, represented by the difference in emission between the OFF and ON states, appear to depend strongly on the environment. The formulas describing the kinetics and performances of TTA-UC generally consider a bimolecular process, and cannot be applied to our Ca^{2+} sensitive upconversion systems, which require the involvement of three molecules instead of two.

A critical challenge in implementing TTA-UC-based sensing lies in its sensitivity to dioxygen. Use of antioxidants is undesirable for *in vivo* application of calcium-sensing TTA-upconverting nanovesicles, and alternative methods to mitigate dioxygen sensitivity will need to be found. Once resolved, this kind of approaches holds the potential to become a useful tool in bioimaging due to the absence of upconversion in natural systems.

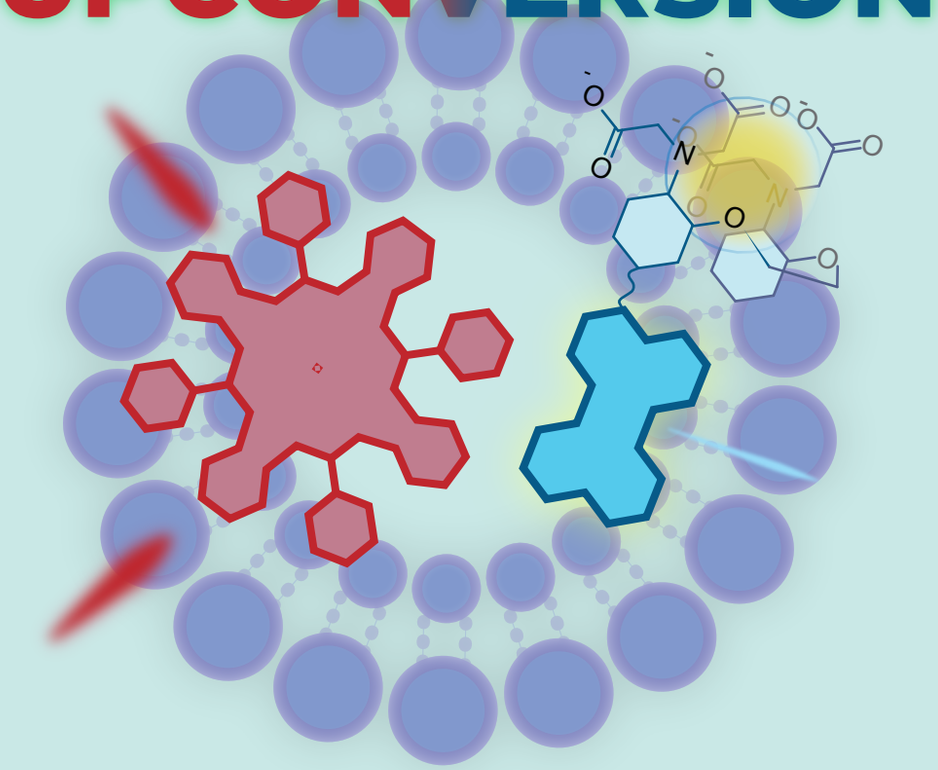




MOLECULAR SENSORS FOR CALCIUM ION DETECTION VIA TRIPLET-TRIPLET ANNIHILATION **UPCONVERSION**

Valeriia D. Andreeva

MOLECULAR SENSORS FOR CALCIUM ION DETECTION VIA TRIPLET-TRIPLET ANNIHILATION UPCONVERSION



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