

Bodipy Derivatives Sensitized Triplet Triplet Annihilation Upconversion in Solution and Liposomes

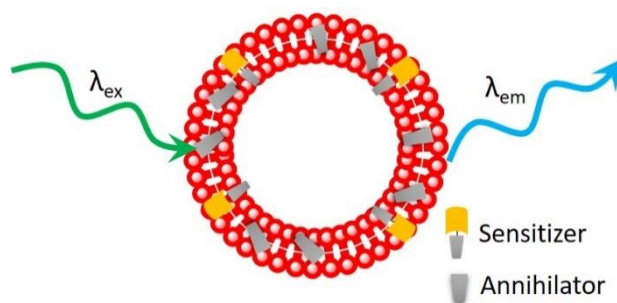
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Abstract

Triplet-triplet annihilation upconversion (TTA-UC) is a photophysical phenomenon in which two low energy photons from triplet excited states are converted to a high energy photon. This process results in the emission of light at shorter wavelength than the associated excitation wavelength used to excite the process. Unlike other UC schemes, TTA-UC does not require high energy or coherent excitation sources so offers exciting opportunities in healthcare applications including photodynamic therapy (PDT) and biological imaging. However, it does make require careful tuning of sensitizer to optimise process efficiency and designing efficient photosensitizer for TTA-UC is challenging with many constraints due to the thermodynamics and multiplicity requirements of the system. BODIPY derivatives, due to their attractive tuneable photophysical characteristics and versatile, synthetic chemistry are proving useful as TTA sensitizers .¹

Herein, we have designed and compared two BODIPY-erythrin based sensitizers for TTA-UC. The first sensitizer is functionalised with a heavy Iodine atom, to promote inter-system crossing through spin-orbit coupling, and the second molecule is a heavy-atom-free sensitizer. We demonstrate that both conjugates are suitable for TTA-UC and also for fluorescence imaging to different degrees. In addition, their long-lived triplet state lifetimes and lipophilic character makes them suitable for liposomal encapsulation. We observe intense oxygen sensitive blue emission with the annihilator under green excitation in solution as well as in cell membrane models.² The biodelivery of the TTA-UC system was further investigated at varied membrane compositions ranging from different alkyl chain length to different melting transition temperature. We observed the most efficient upconversion in the case of highly fluidic zwitterionic membrane.³



Scheme 1: TTA-UC in liposome containing sensitizer and annihilator under 532 nm excitation.

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References

1. S. Dartar, M. Ucuncu, E. Karakus, Y. Hou, J. Zhao, and M. Emrullahoglu. Chem. Commun., 2021, 57,6039.
2. S. H. C. Askes, A. Bahreman, S. Bonnet, Angew. Chem.Int. Ed., 2014, 53, 1029.
3. G. B. Berselli, N. K. Sarangi, P. V. Murphy, T. E. Keyes, ACS Appl. Bio. Mater., 2019, 2, 3404.