STRUCTURE-PROPERTY RELATIONSHIPS IN ANTHRACENE ANNIHILATORS FOR TRIPLET-TRIPLET ANNIHILATION PHOTON UPCONVERSION

Džiugas Krencius[1], Justas Lekavičius[1], Manvydas Dapkevičius[1], Steponas Raišys[1], Edvinas Orentas[2], Karolis Kazlauskas[1]

[1]Vilnius University, Faculty of Physics, Institute of Photonics and Nanotechnology, Lithuania
[2]Vilnius University, Faculty of Chemistry and Geosciences, Institute of Chemistry, Lithuania
dziugas.krencius@vu.ff.lt

Triplet–triplet annihilation photon upconversion (TTA-UC) enables conversion of two low-energy photons into one higher-energy photon using a sensitizer/annihilator pair, offering routes to improved photocatalysis [1], bio-optical applications [2], and solar utilization [3].

Anthracene derivatives are among the most widely investigated TTA-UC annihilators, yet predictive design rules connecting substitution patterns to UC efficiency remain incomplete. This study aims to investigate how systematic structural modifications of anthracene annihilators (Fig. 1) affect the photophysical properties governing TTA-UC. A commonly used PtOEP was selected as the triplet sensitizer, with its relatively high triplet energy (1.94 eV), while explicitly accounting for sensitizer-related losses such as reabsorption/inner-filter effects. Steady-state spectroscopy and time-resolved upconversion/phosphorescence measurements reveal that increasing linker rigidity from a vinyl (C=C) to an ethynyl (C≡C) motif sharpens vibronic structure and narrows emission spectra, consistent with reduced conformational disorder. This substantially increases UC quantum yield from 3.9% for bTPhS(DB)-Anc to 15.6% for bTPhS(TB)-Anc. In general, symmetric 9,10-disubstituted anthracenes show higher fluorescence quantum yields and larger spin-statistical factors f (≥ 0.40), supporting reduced non-radiative losses and more productive triplet-pair pathways.

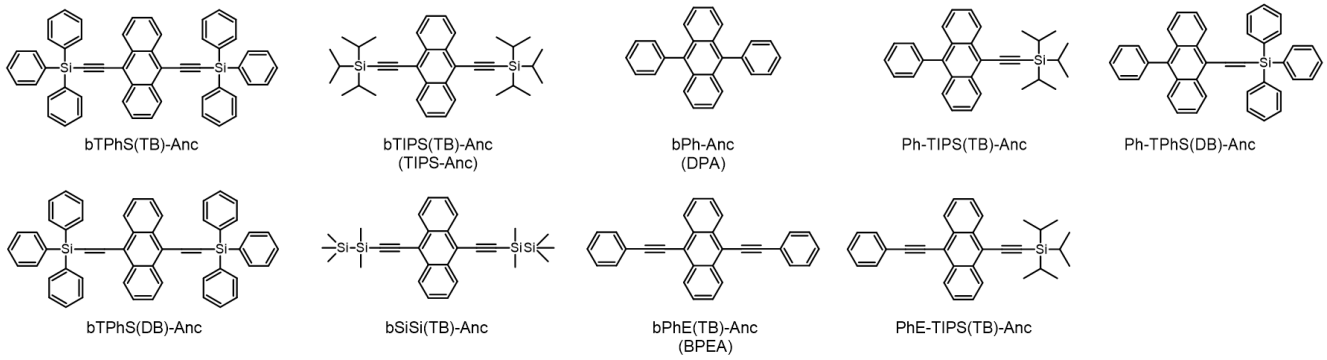

Fig. 1. Molecular structures of anthracene compounds.

These findings demonstrate that modest structural changes have a strong influence on TTA-UC performance, enabling rational design of annihilators beyond trial-and-error screening.

[1] S.-Y. Hwang, D. Song, E.-J. Seo, F. Hollmann, Y. You, and J.-B. Park, "Triplet–triplet annihilation-based photon-upconversion to broaden the wavelength spectrum for photobiocatalysis," Scientific Reports, vol. 12, no. 1, p. 9397, Jun. 2022, doi: 10.1038/s41598-022-13406-8.

[2] Y. Sasaki et al., "Near-Infrared Optogenetic Genome Engineering Based on Photon-Upconversion Hydrogels," Angewandte Chemie, vol. 131, no. 49, pp. 17991–17997, doi: 10.1002/ange.201911025.

[3] L. Naimovičius, P. Bharmoria, and K. Moth-Poulsen, "Triplet–triplet annihilation mediated photon upconversion solar energy systems," Materials Chemistry Frontiers, vol. 7, no. 12, pp. 2297–2315, Jan. 2023, doi: 10.1039/d3qm00069a.