

Two In, One Out: Molecular Architectures for Efficient Photon Upconversion

Soumitra MANNA¹, Francesca S. FREYRIA², Barbara BONELLI², <u>Jenny G. VITILLO^{*,1}</u> ¹ Department of Science and High Technology and INSTM, Università degli Studi dell'Insubria, Via Valleggio 9, I-22100 Como, Italy. ² Department of Applied Science and Technology and INSTM-Unit of Torino Politecnico, Corso Duca degli Abruzzi 24, Politecnico di Torino,10129 Torino, Italy. * jenny.vitillo@uninsubria.it

Significance and Relevance

Triplet-triplet Annihilation Up Conversion (TTA-UC) converts two photons into one having almost double the energy, allowing the exploitation of visible or NIR photons in devices having larger band gaps. Unlike other UCs, it works also with non-coherent and relatively low-intensity incident light, so being particularly promising for solar applications. Several molecules have been reported as TTA annihilators, but comprehensive analysis of their geometry is scarce in the literature. While most of the annihilators are known to be planar, some well-known emitters show twisted geometries. Because of the difficulties in simulating these systems in their working conditions, an empirical analysis of the criteria of a good annihilator can be very useful for the research field. Here we use Kohn-Sham Density Functional methods with the aim to find common geometrical and electronic properties among the different TTA families reported so far in the literature.

Preferred and 2nd choice for the topic: 1) Photocatalysis and photoelectrocatalytic approaches, solar energy utilization; 2) Sustainable and clean energy production and transport. Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

TTA-UC is a powerful process, because it allows to get what is perceived to be impossible in a normal absorption process, that is to have absorption although the frequency of the incident photons is lower than the band gap. This is possible because of the presence of molecules, the TTA-UC annihilators, that after excitation can form dimers involved in an entangled triplet state. Each dimer can decay with one of the monomers in the ground state (S_0) while the other being in a singlet excited state (S_1). This latter molecule can then relax by emitting a photon through the $S_1 \rightarrow S_0$ fluorescence that has twice the energy of the $S_0 \rightarrow T_1$ transition.¹

The simulation of the dimer in the entangled triplet state is not easily achievable through time dependent density functional methods (TD-DFT) while its simulation using advanced multireference wave function-based methods is limited by the dimension of the dimeric systems and the corresponding active spaces, besides presenting significant difficulties in identifying the correct electronic configuration associated with it.¹

In this work,² we have considered a novel approach to determine the characteristics of good TTA emitters. We have collected the different families of TTA-UC emitters reported so far in the literature and modeled them using DFT to find the common points that are shared among the molecules that are good TTA-UC annihilators.

Methods

All DFT calculations were performed using the *Gaussian 16* program. Geometry optimization was carried out by means of the Berny optimization algorithm with analytical gradient and default convergence thresholds. Unscaled, harmonic vibrational frequencies were computed analytically.



Results and Discussion

A collection of > 50 molecules reported as TTA-UC annihilators has been obtained through extensive review of the literature. Each of these molecules has been optimized by means of DFT and it has been verified to be a minimum of potential energy. The UV-Vis absorption spectrum has also been simulated using TD-DFT.



Figure 1 Structures of the most common TTA-UC annihilators in the literature: (a) tetracene, (b) rubrene, (c) pyrene, and (d) benzothiazole. Structures as optimized at the B3LYP/def2-TZVP level in their ground state. Color code: grey (carbon), yellow (sulfur), blue (nitrogen), white (hydrogen).

The key finding of this work is that most of the reported TTA-UC annihilators exhibit a planar structure in regions where the primary changes in electron density occur during $S_0 \rightarrow T_1$ and $S_0 \rightarrow S_1$ electronic transitions. This implies that the functional groups linked to these emitting cores should be carefully chosen to prevent structural distortions that can limit quantum yields. We also verified that geometrical distortions decrease the oscillator strengths for the $S_0 \rightarrow T_1$ and the $S_0 \rightarrow S_1$ transitions due to reduced aromaticity, as shown in electronic density maps. The condition of planarity for the observed TTA emitters applies to molecules undergoing TTA through the favourable S_1 pathway. However, few emitters exist with distorted core undergoing TTA through the less favourable T_2 pathway. The distortions in the molecular core occur to accommodate the bulky substituents to the core. Electron density maps of these molecules suggest that the distortion in molecular geometry facilitates the T_2 - S_1 intersystem crossing leading to conversion of T_2 excitons to up-converted S_1 photons. Overall, the functional groups attached to the molecular core of annihilators play significant role in deciding the molecular geometry which in turn is associated with the observed TTA efficiency. These results linking a structural property with TTA-UC quantum yield represent an advancement in the field and they provide easy directions for more efficient design of new TTA-UC annihilators.²

References

- 1. X. Wang et al., J. Mater. Chem. C, 2020, 8, 10816.
- 2. S. Manna, J.G. Vitillo, in preparation.

Acknowledgements

This study was carried out within the « GREEN UP: GREENER NANOMATERIALS FOR UPCONVERSION IN PHOTOCATALYTIC APPLICATIONS» project –funded by the Ministero dell'Università e della Ricerca –within the PRIN 2022 program (D.D.104 -02/02/2022) funded by the European Union - Next Generation EU.

This manuscript reflects only the authors' views and opinions and the Ministry cannot be considered responsible for them.