The Magnet: With More Power Comes More Annihilation

*Colette M. Sullivan and Lea Nienhaus**

[1] Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306, USA

*Corresponding Author: lnienhaus@fsu.edu

Summary

Probing the underlying attributes of triplet-triplet annihilation-based upconversion systems is necessary to enable future practical applications. Through a combination of excitation power-dependent upconversion measurements under applied magnetic fields and molecular dynamics simulations, Schmidt and coworkers have recently demonstrated a quantitative approach for extracting critical parameters detailing the intricate upconversion process.

Main Text

Since its initial discovery by Parker and Hatchard in 1962,[1] triplet-triplet annihilation upconversion (TTA-UC), also known as triplet fusion, has become an exciting area of research.[2–4] The UC process combines multiple low energy photons into a single photon of higher energy, effectively shortening the wavelength of light emitted after illumination. In TTA-UC systems, the interaction between two spin-triplet states creates an excited spin-singlet state, producing an apparent anti-Stokes shifted upconverted photon upon radiative relaxation. Due to the selection rules governing optical transitions, population of the triplet state is commonly achieved by means of triplet energy transfer from triplet sensitizers, as direct excitation from the ground state to the triplet excited state is spin-forbidden and only exhibits weak oscillator strength. This results in long triplet state lifetimes since the relaxation process to the ground state is also spin-forbidden, allowing spin-triplet states to be used as a form of long-lived energy storage. Therefore, TTA-UC can already become efficient at low, solar-relevant fluences. As a result, (solid-state) TTA-UC has the potential to improve solar-powered technologies by utilizing sub-bandgap infrared photons to generate usable produce photons across the visible spectrum.[4]

In solution-based TTA-UC systems, the visible solar spectrum can be unlocked and interconverted using appropriate annihilator and triplet sensitizer pairs, most commonly polyacene-based annihilators coupled with nanocrystals or metal-organic complexes. High TTA-UC efficiencies have been reported in solution, however, translating the success of these solution-based systems into the solid state has been less straightforward. Energetic shifts that accompany molecular aggregation, quantum yield differences due to additional relaxation pathways such as singlet fission or enhanced non-radiative pathways, and limited exciton diffusion in certain solids are just a few of the additional factors that must be taken into consideration.[4] To understand critical loss pathways during the UC process, experimental methods that can probe the different states involved in TTA-UC directly are required.

One popular approach to unraveling the underlying TTA-UC mechanism utilizes magnetic fields to manipulate the triplet states, which influences the rate of TTA-UC. This effect can be explained by Merrifield theory:[5] upon introduction of a magnetic field, the number of triplet pair states that exhibit singlet character reduces from three to two (of nine total), thus the probability of successful TTA-UC is reduced. The nonmonotonic positive magnetic field effect has been used to distinguish singlet fission, while the characteristic negative magnetic field effect of TTA-UC has been used to determine that TTA-UC is indeed the underlying cause of (apparent) anti-Stokes emission.[6] Despite the fairly widespread use of the characteristic magnetic field effect of singlet fission or TTA-UC to prove their respective roles in the experimental observations, to date, the information gained has been qualitative. For example, a change in the magnetic field effect based on excitation density, i.e., triplet density has been reported;[7,8] however, this observation was not further discussed or modeled, hence the underlying cause was not determined.

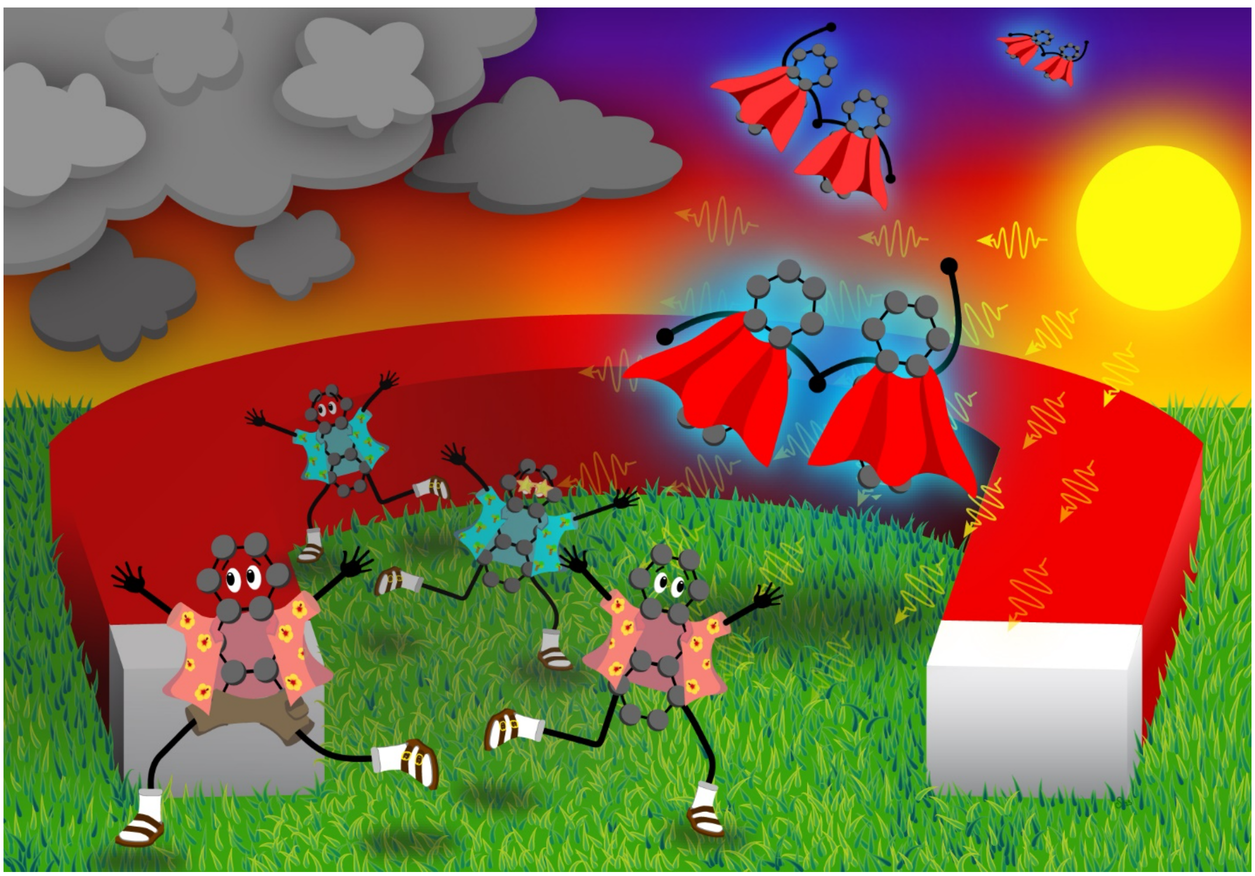

Figure 1: Illustration of the excitation power dependence of the magnetic field effect on TTA-UC. On the left, low excitation fluences cause a prominent magnetic field effect due to the low triplet population, while on the right, at high powers, a large population of triplet states results in a smaller magnetic field effect.

Enter Schmidt and co-workers, who aspired to understand the loss pathways occurring during TTA-UC and the critical parameters of TTA-UC with the help of applied magnetic fields. Their recent work gives important insight into the underlying cause of the power dependence of the magnetic field effect.[9] The triplet annihilation quantum yield, Φ_{TTA}, is dependent upon B, the applied magnetic field, the triplet concentration [T], and the first- and second-order rate constants k_1 and k_2 for the annihilator triplet states, shown in equation 1.

$$\Phi_{TTA}(B, [\mathrm{T}]) = \frac{k_2(B)[\mathrm{T}]}{2*k_2(B)[\mathrm{T}]+k_1} \tag{1}$$

This equation indicates that the magnetic field effect will be greatly influenced by the relative magnitude of the first- and second-order decay constants k_1 and k_2 and population [T] of the triplet state: for low triplet concentration, Φ_{TTA} will mirror the magnetic field dependence of $k_2(B)$. At high triplet concentrations, the magnetic field effect will be reduced since Φ_{TTA} is dictated by k_2[T].

Recent work by Forecast *et al.*[9] used a combination of optical excitation power dependent magnetic field effect measurements paired with molecular dynamics simulations to build a quantitative approach to understand the TTA-UC characteristics for a perylene/octaethylporphyrin platinum (II) (PtOEP) model UC system. Figure 1 illustrates the power dependent effect of TTA-UC within applied magnetic fields: on the left-hand side, low incident powers (low triplet population) result in a large magnetic field effect due to strongly reduced annihilation quantum yields. On the right-hand side, high incident powers result in a high triplet population and a diminished magnetic field effect, allowing for efficient TTA-UC despite the applied magnetic field. The authors directly influenced the triplet population by varying the incident excitation power, where the lowest triplet population was achieved through a low incident excitation power. Importantly, computational studies using their modified Atkins and Evans model (an extension of the Merrifield theory) matched the experimental observations,[10] and enabled the determination of three key fitting parameters, a, τ_a, and λ, corresponding to the power dependence, the translational correlation time or time scale for triplet collision, and the fraction of triplet collisions resulting in successful TTA-UC for the perylene system, respectively.

This relatively straightforward technique demonstrates the power of combining experimental and computational approaches for understanding the intricate mechanisms underlying TTA-UC systems and fully characterizing them. In addition to the previously mentioned fitting parameters, this approach can yield critical figures of merit for TTA-UC, such as the intensity threshold I_{th} at which TTA-UC becomes efficient:

$$I_{\mathrm{th}} = \frac{8}{aA} \tag{2}$$

where a is the power dependent fitting parameter obtained above and A the illumination area, corresponding to the excitation spot size.

In addition, the triplet radius r_T, half the distance at which TTA-UC can occur, can be determined following the fit using the modified Atkins and Evans model:

$$r_T = \sqrt{\frac{D_T \tau_a}{2}} \tag{3}$$

where D_T is the translational diffusion coefficient and τ_a the fitting parameter for the time scale of triplet collision.

The characteristic parameters of TTA-UC in perylene obtained from this fitting procedure are in excellent agreement with the experimental values and the molecular dynamics simulations, highlighting the immense value of this approach to gain a deeper knowledge of the TTA-UC process.

In summary, the detailed analysis of the magnetic field effect of TTA-UC can facilitate the determination of critical parameters directly without the need for multiple spectroscopic methods. The continued advancement of this approach from the current solution phase to applications in solid-state systems promises to facilitate the expansion of currently feasible annihilators by yielding insight into their TTA-UC characteristics, possibly enabling a more rapid breakthrough in the barriers of efficient solid-state TTA-UC.[4]

Acknowledgements

We acknowledge funding by the National Science Foundation under Grant No. DMR-2237977 and the Camille and Henry Dreyfus Foundation (TC-23-050).

Declaration of Interests

Lea Nienhaus is a member of the Editorial Advisory Board of Matter.

References

1. Parker, C.A., Hatchard, C.G., and Bowen, E.J. (1997). Delayed fluorescence from solutions of anthracene and phenanthrene. Proc. R. Soc. Lond. Ser. Math. Phys. Sci. *269*, 574–584. 10.1098/rspa.1962.0197.

2. Sullivan, C.M., and Nienhaus, L. (2023). Generating spin-triplet states at the bulk perovskite/organic interface for photon upconversion. Nanoscale *15*, 998–1013. 10.1039/D2NR05767K.

3. Singh-Rachford, T.N., and Castellano, F.N. (2010). Photon upconversion based on sensitized triplet–triplet annihilation. Coord. Chem. Rev. *254*, 2560–2573. 10.1016/j.ccr.2010.01.003.

4. Alves, J., Feng, J., Nienhaus, L., and Schmidt, T.W. (2022). Challenges, progress and prospects in solid state triplet fusion upconversion. J. Mater. Chem. C *10*, 7783–7798. 10.1039/D1TC05659J.

5. Merrifield, R.E. (1968). Theory of Magnetic Field Effects on the Mutual Annihilation of Triplet Excitons. J. Chem. Phys. *48*, 4318–4319. 10.1063/1.1669777.

6. Mani, T., and Vinogradov, S.A. (2013). Magnetic Field Effects on Triplet–Triplet Annihilation in Solutions: Modulation of Visible/NIR Luminescence. J. Phys. Chem. Lett. *4*, 2799–2804. 10.1021/jz401342b.

7. Yonemura, H., Naka, Y., Nishino, M., Sakaguchi, H., and Yamada, S. (2016). Switch of the magnetic field effect on photon upconversion based on sensitized triplet-triplet annihilation. Photochem. Photobiol. Sci. *15*, 1462–1467. 10.1039/c6pp00264a.

8. Sullivan, C.M., Bieber, A.S., Drozdick, H.K., Moller, G., Kuszynski, J.E., VanOrman, Z.A., Wieghold, S., Strouse, G.F., and Nienhaus, L. (2023). Surface Doping Boosts Triplet Generation Yield in Perovskite-Sensitized Upconversion. Adv. Opt. Mater. *11*, 2201921. 10.1002/adom.202201921.

9. Forecast, R., Gholizadeh, E.M., Prasad, S.K.K., Blacket, S., Tapping, P.C., McCamey, D.R., Tayebjee, M.J.Y., Huang, D.M., Cole, J.H., and Schmidt, T.W. (2023). Power Dependence of the Magnetic Field Effect on Triplet Fusion: A Quantitative Model. J. Phys. Chem. Lett. *14*, 4742–4747. 10.1021/acs.jpclett.3c00919.

10. Atkins, P.W., and Evans, G.T. (1975). Magnetic field effects on chemiluminescent fluid solutions. Mol. Phys. *29*, 921–935. 10.1080/00268977500100801.