

Triplet-Triplet Annihilation Upconversion in Solid Materials

Ryan Rooney

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Upconversion is the observation of high energy photon emission from low energy photon absorption.¹ Among the multiple upconversion mechanisms, one that has drawn recent interest is triplet-triplet annihilation (TTA). TTA holds significant advantages over its upconversion counterparts including its use of simple, tunable molecules and its ability to operate under low intensity, non-coherent light.^{1,2} Thus, TTA provides a practical option to implement upconversion into light-harvesting technologies that cannot utilize a large portion of the solar spectrum, mainly the IR region. Accessing these photons would allow for improved efficiencies for photovoltaic, photocatalytic and optoelectronic devices.³

TTA Upconversion is achieved by the interaction of a sensitizer and emitter. As seen in Figure 1, the sensitizer molecule absorbs a photon populating the singlet excited state ($^1S^*$) which in turn decays via intersystem crossing to the triplet excited state ($^3S^*$).⁴ Next, a Dexter type triplet-triplet energy transfer (TTET) occurs when the sensitizer comes in contact with the emitter.

It is believed that this interaction occurs when the two different components come within nanometers of each other so that their wavefunctions overlap.⁵ The electron in the excited triplet state of the sensitizer exchanges with an electron in the singlet ground state of the emitter, creating a sensitizer singlet and an emitter triplet ($^3E^*$). This emitter triplet then interacts with another emitter triplet to undergo the TTA process, producing a ground state emitter and an excited singlet state emitter ($^1E^*$). The excited emitter singlet state undergoes conventional fluorescence, yielding Anti-stokes emission of a photon with higher energy than the one originally absorbed.⁴

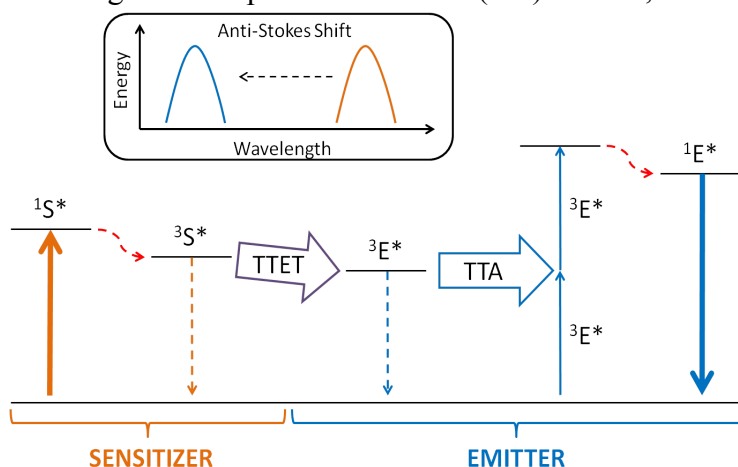


Figure 1. Simplified TTA mechanism resulting in Anti-stokes shift

TTA was first achieved by Parker and Hatchard in 1962 using solutions of phenanthrene and anthracene as the sensitizer and emitter, respectively.⁶ Transition metal complexes such as Ru(II) polyimines and Pt(II)/Pd(II) porphyrins have become the workhorse absorbers because of their favorable absorption spectrums, high population of the triplet state via intersystem crossing, and long-lived triplet lifetimes. On the other hand, the anthracene based 9,10-diphenylanthracene (DPA) has maintained the most popular emitter choice for its strong blue emission.¹ Due to a number of sequential processes that must occur the overall TTA quantum yield is inherently low. Even before other considerations, the fact that two photons absorbed result in one photon emitted limits the maximum quantum yield to 50%.² Other parameters such as the molar absorptivity, TTET efficiency and TTA efficiency also contribute to the overall quantum yield. To date, the highest triplet-triplet annihilation quantum yield is 26% reported by Monguzzi and coworkers using a solution of platinum (II) octaethylporphyrin (PtOEP) and DPA in tetrahydrofuran solvent.⁷ These efficiencies are only further complicated by incorporation into solid materials. Despite these challenges, achieving TTA in solid materials offers additional

advantages such as easier implementation, enhanced protection against oxygen quenching, as well as superior architectural control of chromophores to study and improve the multiple processes that must occur.¹

TTA has been extensively studied in polymer systems beginning with the work of Castellano and coworkers, who first achieved the feat in 2007.⁸ PtOEP and DPA were incorporated into a poly(ethylene oxide/epichlorohydrin) host copolymer and cast into a film. Upconversion was readily detected at 430 nm upon illumination with 544 ± 18 nm light. TTA was achieved at light intensities comparable to solar irradiance (~ 100 mW/cm²), as well as under ambient aerated conditions. Variant temperature studies determined that the upconversion fluorescence diminished as the temperature decreased below 77 K, suggesting that translational or rotational mobility of the rubbery host copolymer allows for the bimolecular energy transfer and subsequent TTA process to occur.⁹

It was later hypothesized that the energy transfer and annihilation process could occur as a result of exciton diffusion rather than miniscule molecular mobility in the polymer host.¹⁰ Therefore, the spatial proximity of chromophores to one another becomes an important aspect to control in order to achieve effective triplet migration throughout the material. For bulk, polymeric materials, this concept of spatial distribution translated into controlling the chromophore concentration; higher concentration theoretically results in faster exciton diffusion. However, a large obstacle for increasing the concentration of TTA components is phase separation between the polymer host and the chromophores.⁸ To overcome this, glassy polymers were used as the host and increased chromophore concentration achieved by casting hot polymer/chromophore mixtures to kinetically trap chromophores in the matrix.¹¹ The sensitizer and emitter components have also been attached as pendants to the backbone of polymers with methacrylate spacers to adjust chromophore distances.¹² While higher concentrations of chromophores was accomplished, efficiency actually decreased. This was attributed to undesired interactions of chromophores resulting in back-transfer of triplet states and undesired decay pathways. It suggested that concentration enhancement alone is not enough to achieve efficient upconversion.¹²

The morphology and spatial architecture of the chromophores in solid materials must be controlled in order to optimize the exciton diffusion. Assembling the sensitizer and emitter in an ordered fashion will allow for improved transfer efficiencies. One such novel approach is the self-assembly of modified anthracene units into an amphiphilic nano-ribbons, dispersed in chloroform as seen in Figure 2.¹³ The anthracene emitter units align due to the solvophilic and solvophobic interactions of the modified alkyl tail ends and DPA units, respectively. PtOEP

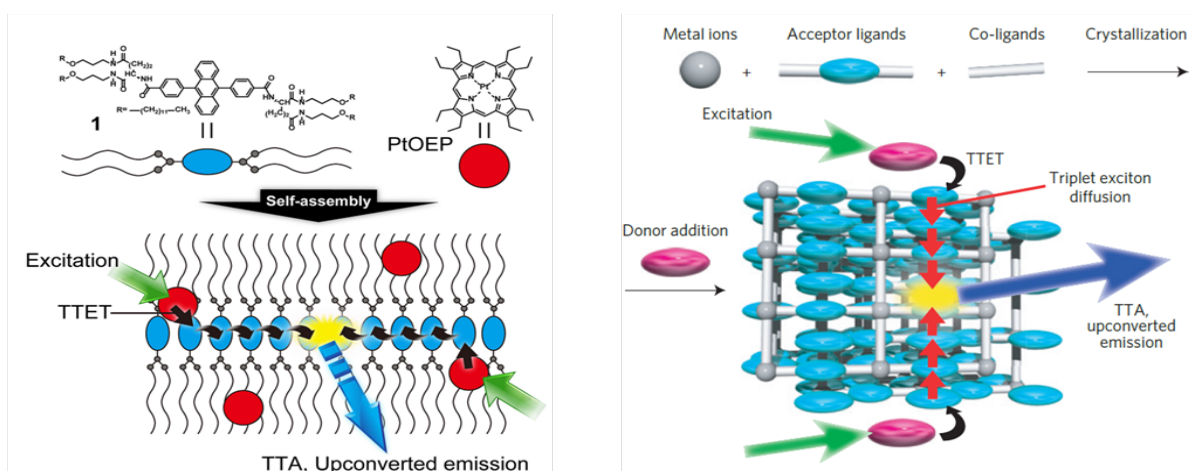


Figure 2. Schematics of self-assembly (left) and MOF (right) upconversion

sensitizer is then introduced and embeds itself into the long alkyl chains of the self-assembly. This design allows for high TTET as well as extensive triplet diffusion along the assembly backbone. This motif resulted in an incredibly high quantum yield of 30% and diffusion constants similar to that of just DPA units in solution. The assemblies were further modified into organogels as well as casted into films, which also demonstrated successful upconversion. All variations of the self assemblies displayed upconversion under aerated conditions.

The success of the self assembly lead to the investigation of an even more ordered array of emitter units. A series of metal-organic framework (MOF) with zinc metal centers and modified anthracene emitter units as organic linkers was successfully synthesized and studied for TTA upconversion, as depicted in Figure 2.¹⁴ The MOF crystals exhibited upconversion when dispersed in solution with PtOEP sensitizer. To increase the efficiency of the TTET process, the PtOEP was attached directly to the MOF surface via carboxylate functional groups. These surface modified MOFs were incorporated into poly(methylmethacrylate) films which also generated upconversion upon irradiation. While the overall quantum yield is not particularly high at ~2%, the triplet diffusion constants calculated were comparable to the self-assembly motif, corresponding to diffusion lengths on the order of microns. The MOF system also showed incredibly low excitation power necessary to achieve maximum quantum yield.

TTA upconversion holds much potential for light-harvesting applications. Development of TTA in solid materials not only provides significant advantages such as improved exciton diffusion and practical implementation, but also offers a new platform to study the many intricate energy transfer processes that must occur in order to achieve upconversion.

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