Title:

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Citation:

"Naitik A. Panjwani & Jan Behrends, 2Nature Materials volume 21, pages1221–1222 (2022) ; https://doi.org/10.1038/s41563-022-01387-y"
Archiviert unter http://dx.doi.org/10.17169/refubium-38225

Framing Fusion and Fission

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Engineering inter-triplet exchange coupling allows spin mixing between singlet and quintet manifolds in triplet-triplet pair states in metal organic frameworks, demonstrating increased room-temperature triplet-fusion rates under relatively small applied magnetic fields

Absorption of light in organic molecules can result in the formation of strongly coupled electron-hole pairs referred to as excitons. They play a key role in all types of optoelectronic devices that either produce light (such as light-emitting diodes) or absorb light (such as solar cells or photodetectors). Excitons can have singlet (spin 0) or triplet (spin 1) character, and the probability for their radiative decay strongly depends on the spin state. In most organic molecules with a singlet ground state the decay of triplet excitons is spin-forbidden, resulting in long lifetimes of triplet excitons, which are therefore also called 'dark states'. Harvesting these non-emissive triplet states by converting them, through reverse intersystem crossing, to emissive singlet excitons, for which radiative decay is spin-allowed, was the key achievement that led to the success of organic light-emitting diodes.[1]

A particularly promising strategy for utilising dark triplet states for optoelectronic applications is based on the conversion of a pair of triplet excitons into one singlet exciton via triplet fusion as well as the reverse process, singlet fission. As the energy of the singlet exciton is higher than the energy of the individual triplet states, triplet fusion is referred to as upconversion. The probability for the upconversion process strongly depends on the electronic coupling between both triplet states. In molecular solids, both triplet-triplet (TT) pair constituents can be very close, resulting in strong inter-triplet exchange coupling. The strongly-coupled TT pair can be in a singlet (spin 0), triplet (spin 1) or quintet (spin 2) state. Quintet TT states have been shown to be relevant for the efficiency of triplet fusion as well as singlet fission.

In cases where the two constituent triplets that form the TT pair are in close proximity such that orbital overlap and therefore inter-triplet exchange coupling is large, the quintet TT state is energetically not accessible, and efficient conversion into the emissive singlet state is not possible. However, increasing the probability for the upconversion process is highly desirable for a number of applications. This requires singlet-quintet (SQ) spin mixing, which is most efficient when the energies of the states involved in this process are equal (close to avoided level crossings). This situation can be achieved by applying a magnetic field which affects the energies of the states involved in the conversion process. The field-induced energy changes have to be on the order of the exchange coupling between the TT pair constituents, which usually requires strong magnetic fields (several T), far beyond what would be realised in practical applications.[2]

Ha and colleagues[3] came up with a clever strategy to increase the SQ mixing at moderate magnetic fields. They achieved this by engineering the inter-triplet exchange coupling by placing the exciton-accommodating molecules far away from each other in a well-defined distance using metal-organic frameworks (MOFs). The spatial separation results in weak exchange coupling and concomitantly effective mixing between singlet and quintet TT pair states at moderate magnetic field well below 1 T. Further, the fixed arrangement in the MOF prevents the triplet excitons from separating through diffusion, thereby increasing the TT pair lifetime and thus the time available for spin mixing.

The weak inter-triplet exchange coupling is quantified in magnetic field effect (MFE) experiments, in which the light emitted by the sample through radiative decay of singlet excitons is measured as a function of the magnetic field strength. The anomalous MFE curves can, in combination with simulations, be considered as smoking-gun evidence for the existence of weak electronic coupling between the triplet states.

The distance between neighbouring triplet excitons can also be adjusted in dimers formed by two covalently linked molecules. This has previously been used in molecules undergoing singlet fission.[4] However, the possibility to engineer the distance between the chromophores, and thus the exchange-coupling strength, is limited by the flexibility of the dimers, in particular for large distances. In contrast, the rather rigid and tunable structure of MOFs holds particular promise for applications which require precise control of electronic couplings. Furthermore, MOFs reduce molecular vibrations which are known to modulate

the exchange interaction during SQ mixing, which is more difficult to realise in dimer structures.

The approach by Ha and colleagues provides a very interesting and exciting pathway for future research. The reported upconversion efficiency of <1% in this proof-of-principle study is nevertheless relatively low and not yet sufficient for real-world optoelectronic applications. However, given the fact that MOFs are highly designable in structure and functionality,[5] it seems likely that the SQ conversion efficiency can be improved substantially in the near future. The authors point out some of the key parameters that could lead to improved upconversion efficiencies, such as the fusion rate, exciton hopping rate and decoherence time. This could also involve engineering the relative orientation of constituent molecules which are involved in fusion, since the inter-triplet coupling and hopping rates are orientation dependent.

Control over SQ mixing can help harvesting low-energy photons in solar cells via triplet fusion[6] and high-energy photons via singlet fission.[7] It can also improve the performance of organic light-emitting diodes.[8] Furthermore, it is conceivable that MOFs with optimised triplet-fusion capabilities may be used as drug-delivery systems for the transport of therapeutic agents that can be activated by upconverted skin-penetrating near-infrared light.[9]

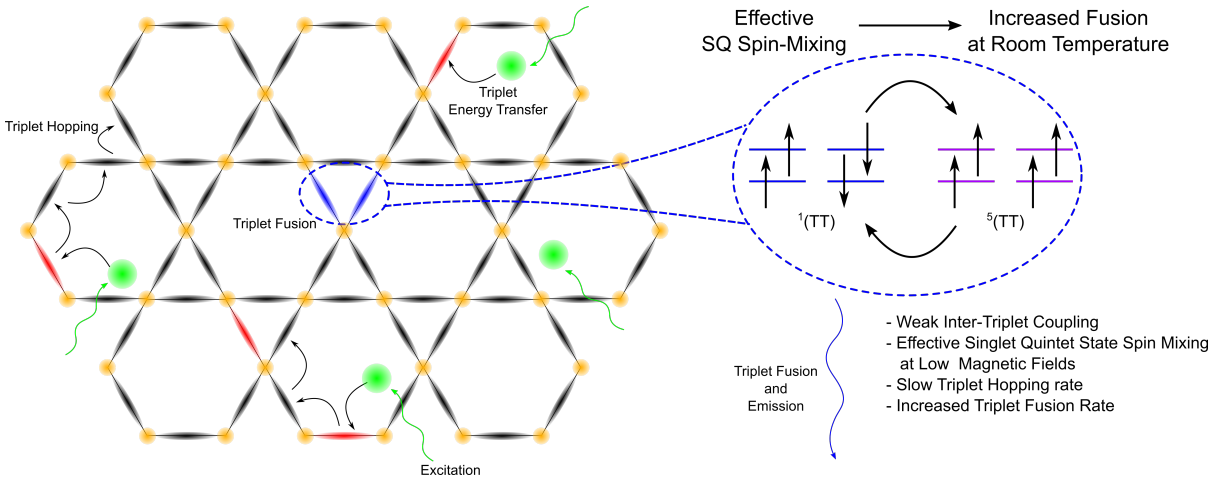

Figure 1: Schematic structure of MOF NU-1000 as well as photo- and spin- physics involved in triplet fusion.

The left schematic depicts the MOF NU-1000 structure. Orange circles represent oxo-Zr_6 SBU (MOF node), green circles PtOEP (sensitizer molecules located in the pores of the MOF), black ellipses H_4TBAPy (MOF linker). Excitation of PtOEP (green curly arrow) results in, after intersystem crossing, a triplet state. Dexter triplet energy transfer results in the triplet energy migrating from the PtOEP to a nearby H_4TBAPy molecule (red ellipse). Subsequently triplet exciton hopping occurs until two triplet on nearby H_4TBAPy molecule meet, allowing for triplet fusion (blue ellipses). The singlet-quintet spin mixing occurring in NU-1000 under low magnetic fields due to weak inter-triplet coupling is shown on the right. This leads to increased room-temperature triplet fusion and light emission.

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