Singlet fission is a spin allowed process allowing to convert a singlet excitation into two triplets.\(^1\) This process is a major interest as it can double the charge generation quantum efficiency of solar cells in the UV region, where the excess energy is otherwise lost into phonons.

The process of singlet fission as shown to be efficient and fast through the formation of a triplet pair (TT) from the singlet excitation, which is overall a spin conserving process. Amongst singlet fission materials, acenes offers a wide range of molecules with different singlet and triplet energies, ranging from endothermic to exothermic singlet fission systems. The energy favorable exothermic fission is efficient, but surprisingly endothermic fission can be very efficient, as seen in tetracene.\(^2\)

TIPS-tetracene (TIPS-Tc) is a derivative of tetracene made solution processable by the addition of TIPS side groups. We study here this derivative so as to study singlet fission process in an endothermic singlet fission material.

We aim at getting more insight on the timescales and processes leading to the formation of the TT excimer\(^3\) from singlet excitations, by using ultrafast transient absorption spectroscopy with 15fs time resolution and vibrational spectroscopy analysis.
The ultrafast pump pulses of our setup allows for excitation of vibrational modes in both the ground and excited states of the system. The analysis of these modes allows to obtain valuable information on the nature of singlet fission in TIPS-Tce, in addition to unraveling the electronics photophysics of the system.

The vibrational modes created by the pump are clearly visible from the TA data (fig.1,a). The pure vibrational contributions can be extracted from the electronic response by fitting the latter with exponential decays.

The electronic response shows that the TT formation from singlet happens in two timescales of 500fs and 15ps, the second being confirmed by photoluminescence studies.

The residuals, containing only the vibrational response, can then be Fourier transformed to obtain the data shown in fig.1,b, showing the amplitudes of the vibrational modes for different probe wavelengths. The vibrational modes are then identified and allows to attribute them to the different states present in the photochemistry of the film. A sliding window Fourier transform applied on the 316cm⁻¹ and 760cm⁻¹ modes, associated with singlet (conjugated backbone deformation) and TT respectively, indicate that the former is damped while the latter is formed on a 200fs timescale (fig.1,c).

These results shows that the singlet to TT transformation preserved the coherence of nuclear wavepackets and therefore that singlet fission in TIPS-Tce happens via vibronically coupled potential energy surfaces (PES). This shows that endothermicity of singlet fission systems is not hindering singlet fission as the vibronic degrees of freedom can allow for the two PES to get similar energies on ultrafast timescales, allowing for ultrafast singlet fission.

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