Vibronic Effects in Singlet Fission Observed by Coherent Electronic 2D Spectroscopy

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We use electronic 2D spectroscopy to study the intermediate states responsible for ultrafast singlet exciton fission in pentacene-/tetracene- based molecular crystals and in pentacene dimers. Our results show the vibrational coupling enhances interaction between the singlet and multiexcitonic double-triplet states, which greatly facilitates fission process.

Singlet fission is the spin-allowed conversion of a spin-singlet exciton into a pair of spin-triplet excitons residing on neighbouring molecules.[1] To rationalise this phenomenon, a multiexcitonic spin-zero triplet-pair state has been hypothesised as an intermediate in singlet fission. However, the nature of the intermediate states and the underlying mechanism of ultrafast fission have not been elucidated experimentally.

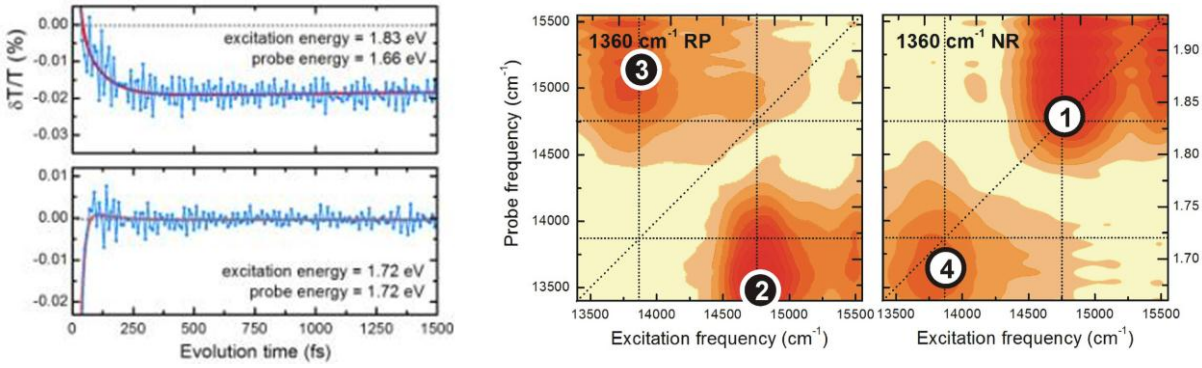

Fig.1. (left) The oscillatory components in the 2D data for pentacene crystal. Blue curves are evolution-time transients corresponding to the different locations in the 2D spectrum. Red curves are population dynamics. (right) The rephasing (RP) and non-rephasing (NR) part of 2D beating maps corresponding to observed high frequency vibrational mode of pentacene. Peaks 3-4 are associated with the 'dark' multiexcitonic state.

Here, we study a series of pentacene and tetracene derivatives using ultrafast 2D electronic spectroscopy and unravel the origin of the states involved in fission. Our data reveal vibronic beating signals associated with both singlet and multiexciton-intermediate excited states (fig.1). The beating analysis and theoretical modelling point towards the crucial role of vibrational degrees of freedom coupled to electronic excitations that facilitate the mixing of multiexcitonic states with singlet excitons. For pentacene-based molecular crystals,[2] the resulting manifold of vibronic states drives sub-100-fs fission with unity efficiency. For tetracene derivatives and pentacene dimer vibronic coupling forms new emissive intermediate states which are responsible for the irreversibility of fission dynamics. Our results provide a framework for understanding singlet fission and show how the formation of vibronic manifolds with a high density of states facilitates fast and efficient electronic processes in molecular systems.

[1] A. Rao *et al*., JACS, **132**, 12698, (2010).
[2] A. Bakulin *et al*., Nature Chem. **8,** 16 (2016).