Quantum Beats in Transient Absorption of Bis(thienyl)diketopyrrolopyrrole Thin Films

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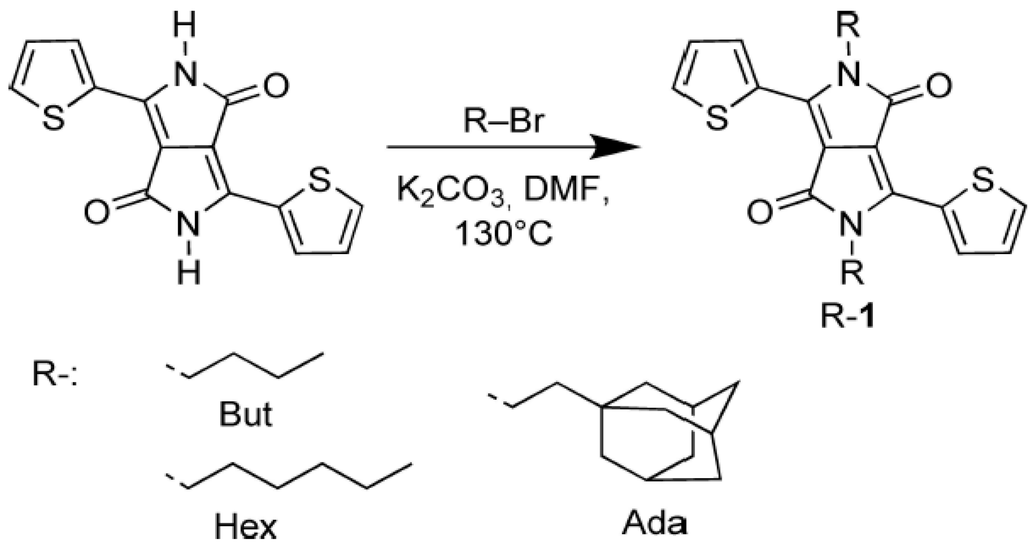
Singlet fission (SF) is a process in which an initially excited singlet state spontaneously splits into a pair of triplet excitons, it provides a promising route for overcoming the Shockley–Queasier limit in solar cells.

Despite SF dynamics having been extensively investigated the important aspects to understand SF mechanism like singlet state delocalization, nature of the ^{1}(TT) triplet pair state and the decoherence of ^{1}(TT) triplet pair state,.. are remain active areas of investigation.

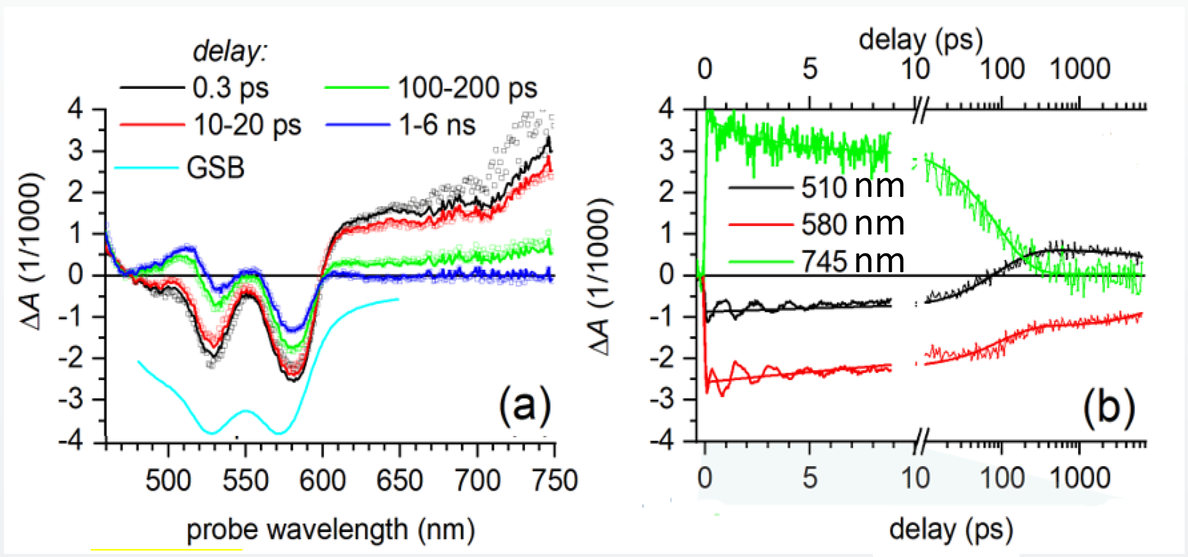
SF fission in Bis(thienyl)diketopyrrolopyrrole Thin Films have been studied in our previous work were we observed oscillatory signals in femtosecond transient absorption spectroscopy measurements.

We have used Fast Fourier Transform(FFT) and Raman spectroscopy to understand the observed quantum beats.



Transient absorption (TA) spectroscopy

TA characteristics of Bu-TDPP SC thin films after photoexcitation by laser pulses with central wavelength 450 nm: representative TA spectra and the kinetics traces (b). Symbols denote the experimental data and full lines show the best fits using a sequential EADS model at various delay times (a) and probe wavelengths (b), respectively.



At early delay time (first observed transient) positive TA signal above 610 nm assigned to excited state absorption (ESA), identified as spectral profile of the singlet excitons. The spectral profile found at long delay time (> 1 ns) assigned to triplet excitons. Negative peaks (530,580 nm) at short delay (10-20 ps) represent the ground state bleach (GSB).

ESA at probe wavelength 745 nm (singlet absorption peak) decays to zero with a time constant 90 ps. In early delay times, the signal at 510 nm is dominated by the GSB, but in longer delays the positive triplet-triplet ESA prevails, resulting in positive overall signal. This transition follows first-order kinetics with a time constant that agrees with the 90 ps time constant of the singlet ESA decay.

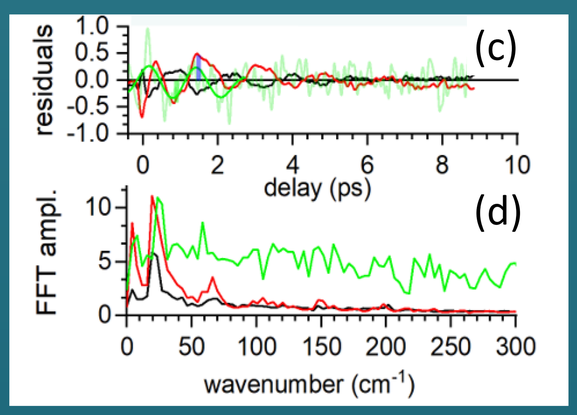
The negative signal at 580 nm is dominated by negative GSB, we can expect contribution from positive ESA of both singlet and triplet excitons due to spectral overlap. One would expect an increase of the TA signal at this probe wavelength, due to reduced occupation of the ground-state caused by the SF process. Instead, we observed the reduction, which happened due to the spectral overlap between ESA signals and the GSB signal.

The lifetime of the triplet spectral component shows rather slow decay, that could be fitted with two exponential time constants 50 ns and 1 µs.

Quantum beatings

Moreover an ultrafast oscillatory modulation of the TA signal within the delay range up to ca. 10 ps was observed in GSB recovery at probe wavelength 510 and 580 nm.

After subtracting the fitted exponential kinetics from the experimental time-traces, we obtained the evolutions of the residual oscillatory TA signal (c). Corresponding FFT amplitudes of the residual signals is shown in Figure (d). The samples show oscillations at the same main frequency about 21 cm^{-1} in all cases.



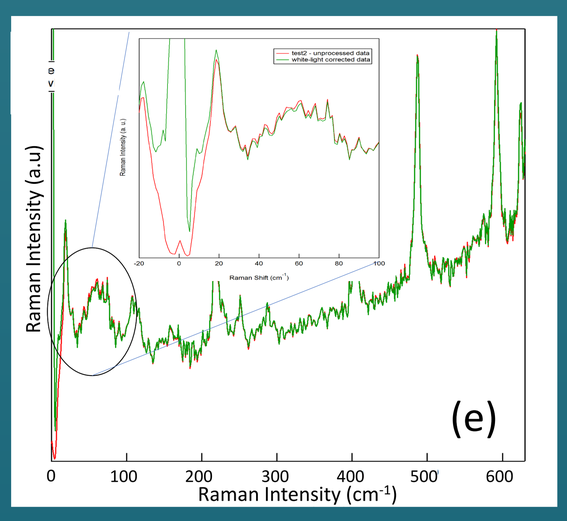


Figure (e) shows the Raman spectra in a spectral range of 0–600 cm^{-1} at room temperature and excitation at 532 nm. Red curve shows the experimental data and green curve represents the corrected spectrum. We observed a vibration peak at 21 cm^{-1}, similar to our FFT peak from TA analysis.

Interpretation: We assigned these oscillations to the lattice phonons modulation of the coupling of the $|S_0,S_1\rangle$ and $|S_1,S_0\rangle$ states of adjacent, dimer-forming molecules, with their biexciton state $|T_1,T_1\rangle$.

$$\mathcal{H}_{int} = \mathcal{H}_{el} + \mathcal{H}_{sp}$$

In general, SF is represented by an interaction Hamiltonian ($\mathcal{H}_{int}$) with a spin free electronic part ($\mathcal{H}_{el}$) and spin dependent part ($\mathcal{H}_{sp}$) with a spin-conserving splitting of one singlet exciton into two triplet excited states. In the generally accepted mechanism of SF

$$|S_0S_0\rangle \xrightarrow{h\nu} |S_0S_1 \rightarrow |^1(T_1T_1) \rightarrow |T_1\rangle + |T_1\rangle$$

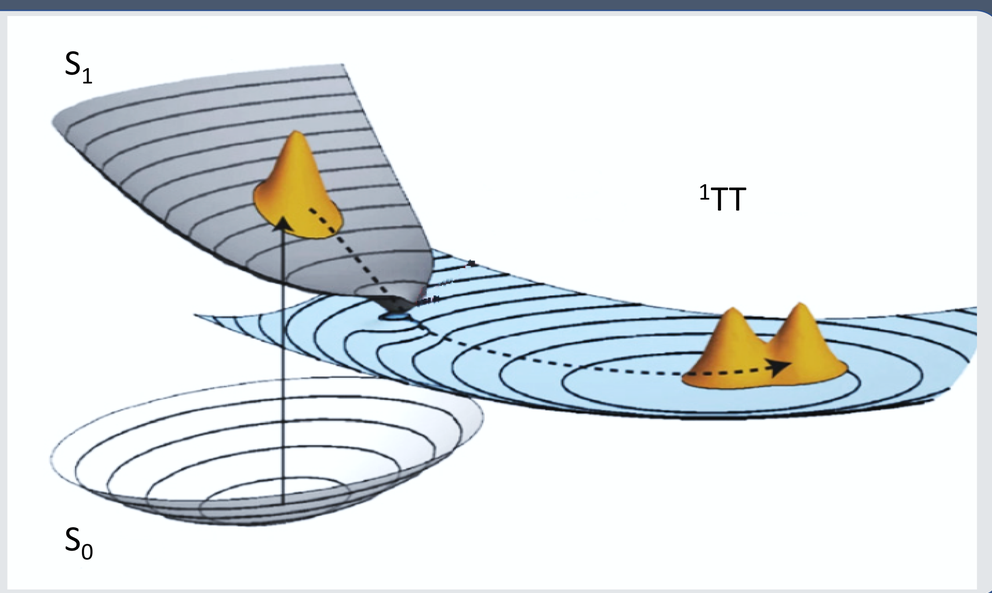
The transition between localized electronic states can be controlled and modulated by delocalized lattice phonons.

We observed quantum beatings in early GSB recovery TA signals at probe wavelengths 510 and 580 nm.

We observed a peak at 21 cm^{-1} in FFT analysis.

A similar peak was found by Raman spectroscopy.

Observed peak was assigned to lattice phonons modulation of the coupling between the $|S_0,S_1\rangle$ and $|S_1,S_0\rangle$ statesof adjacent, dimer-forming molecules, with their biexciton state $|T_1,T_1\rangle$.



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