Performing 2D Electronic Spectroscopy on TIPS-Pn in Toluene to Demonstrate CLS Beating Pattern

Wee Ze Yu Supervised by Assoc Prof Tan Howe Siang

NANYANG TECHNOLOGICAL UNIVERSITY SINGAPORE
Odyssey Research Programme
School of Physical and Mathematical Sciences

Introduction

Semiconductors are an essential component in electronic devices. 6,13-Bis(triisopropylsilylethynyl)pentacene(TIPS-Pn), an Organic Semiconductor (OSC) is found to be a popular choice in optoelectronic devices. TIPS-Pn is also a model system for studying singlet fission, owing to its ability to undergo the spin-allowed process. Despite that, we require a greater grasp at the fundamental processes happening in TIPS-Pn, as such we carried out 2D Electronic Spectroscopy (2DES) in toluene to probe the dynamics involved. Due to the time-dependent evolution of the system, a frequency fluctuation correlation function (FFCF) may be used to describe the spectral diffusion dynamics.

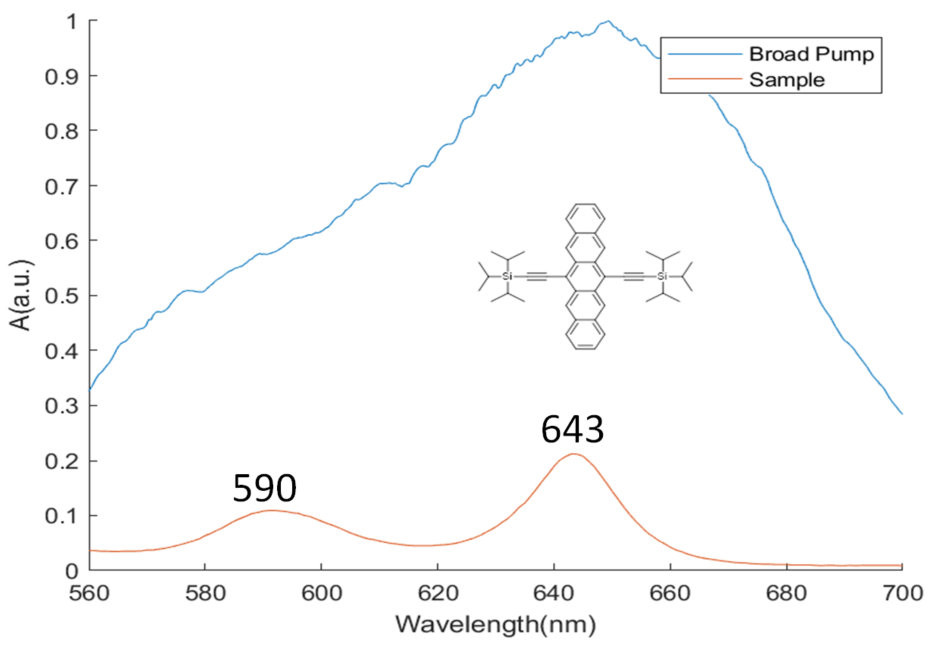

Fig 1: Excitation features of TIPS-Pn overlain with the pump spectrum

Methodology

The TIPS-Pn was dissolved in toluene and diluted until an optical density (OD) of 0.2 was achieved. The 2DES measurement was performed using a partially collinear pump-probe beam geometry setup. A commercial pulse shaper is used to split the single pump pulse, creating a pump-pulse train shown schematically below.

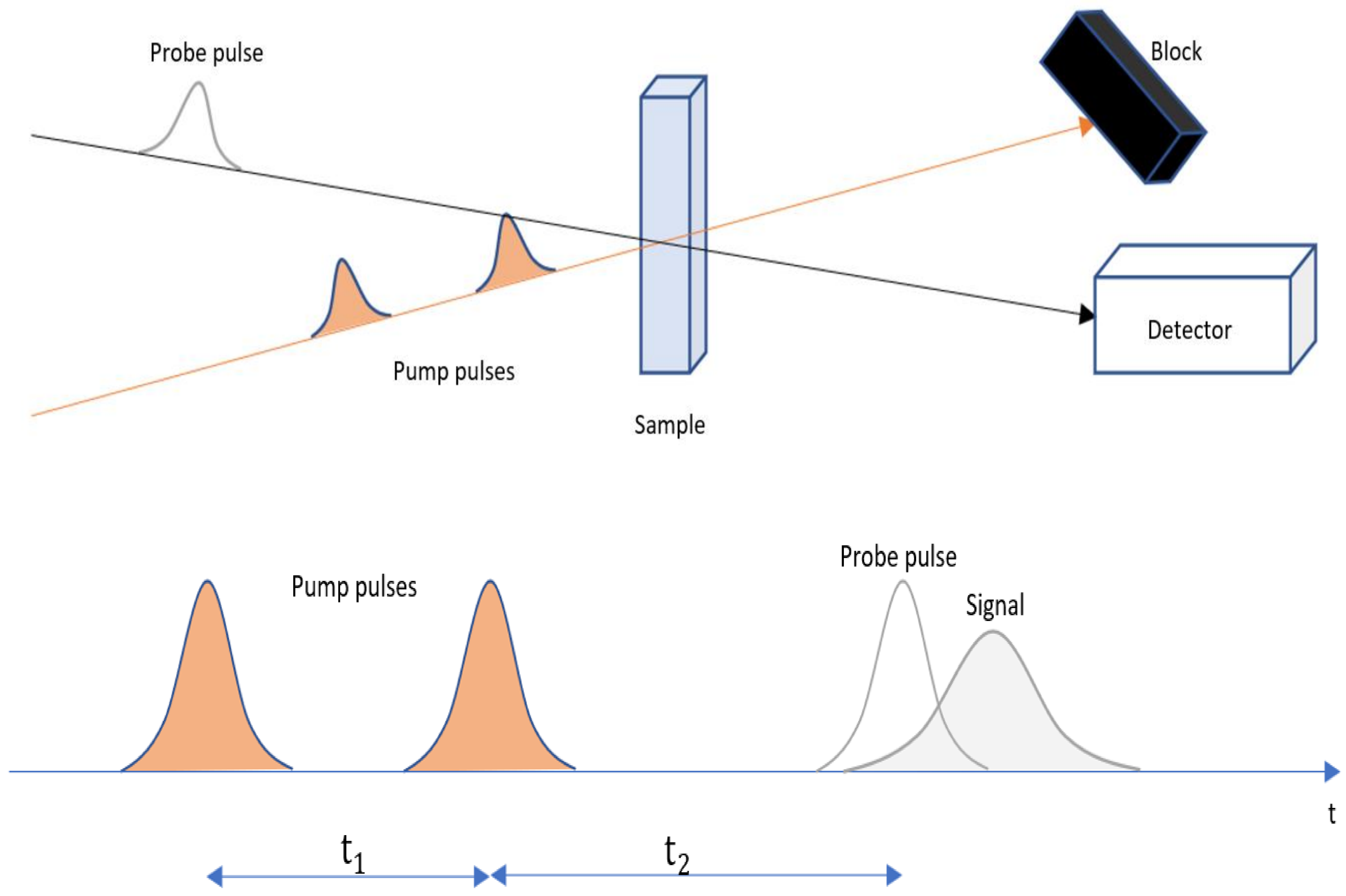

Fig 2: Spatial (top) and temporal (bottom) arrangement of our 2DES setup

Results

To characterise the spectral diffusion dynamics of TIPS-Pn in toluene, we used the Center Line Slope (CLS) analysis to study the peak shape. To obtain the CLS, the center points must first be determined by taking horizontal and vertical slices of the 2D spectrum at different waiting times, t_2, to visualise the maxima. A linear fit is then applied to the center points. By studying the change of the CLS over t_2, we arrive at an oscillatory plot that can be modelled by a sum-of-sines **(Fig 3)**.

We obtain the aforementioned FFCF, which represents an ensemble average, quantifying how a change in the environment influences the transition frequency. **Fig 3** demonstrates the FFCF having a strong oscillatory beating pattern across t_2 and reveals a decay in amplitude as the waiting time approaches 1 ps. By implementing a fast Fourier transform (FFT), **Fig 4** shows that the CLS oscillates with 1 distinct frequency.

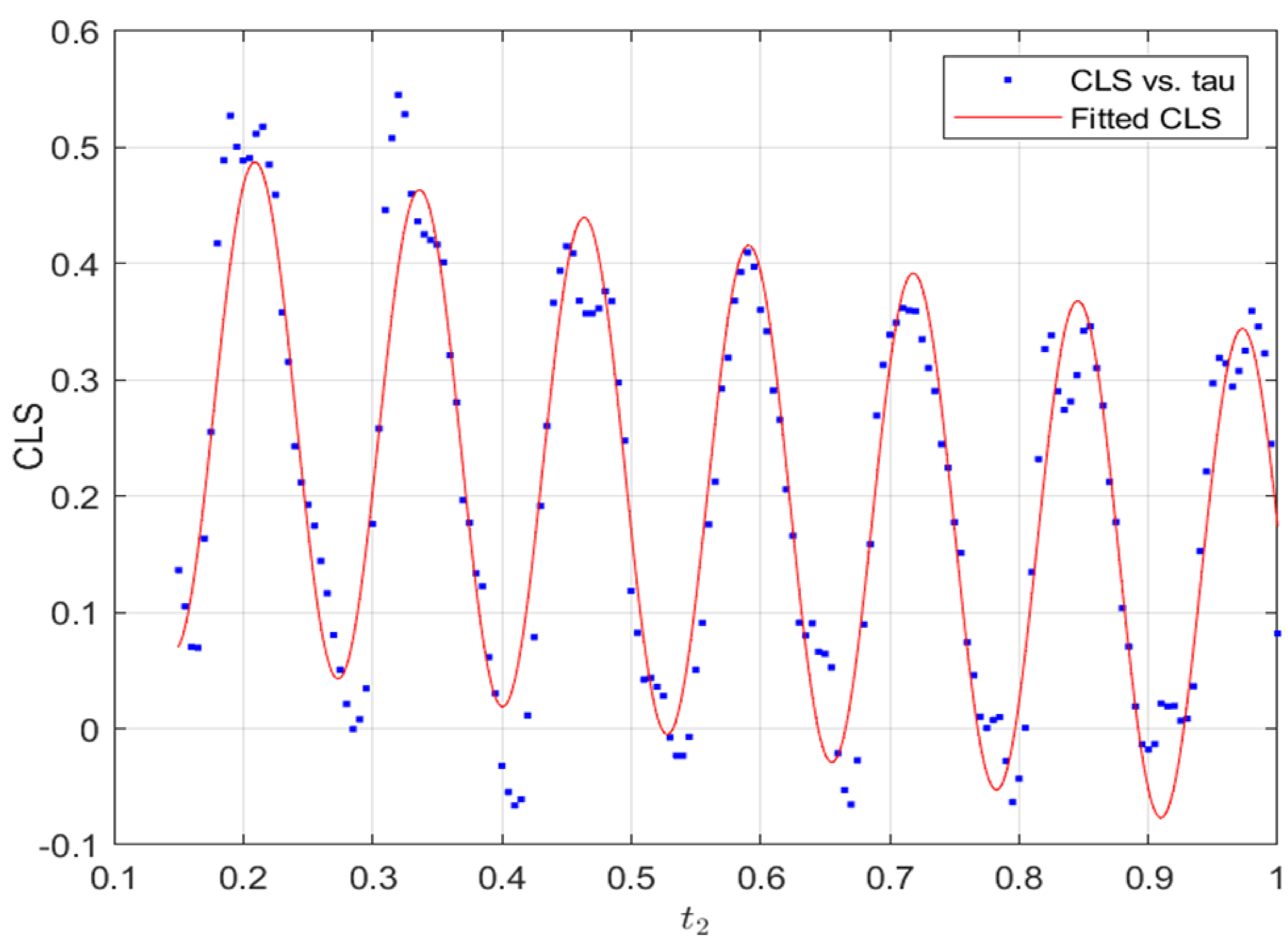

Fig 3: Plot of fitted CLS vs t_2 showing strong oscillatory pattern

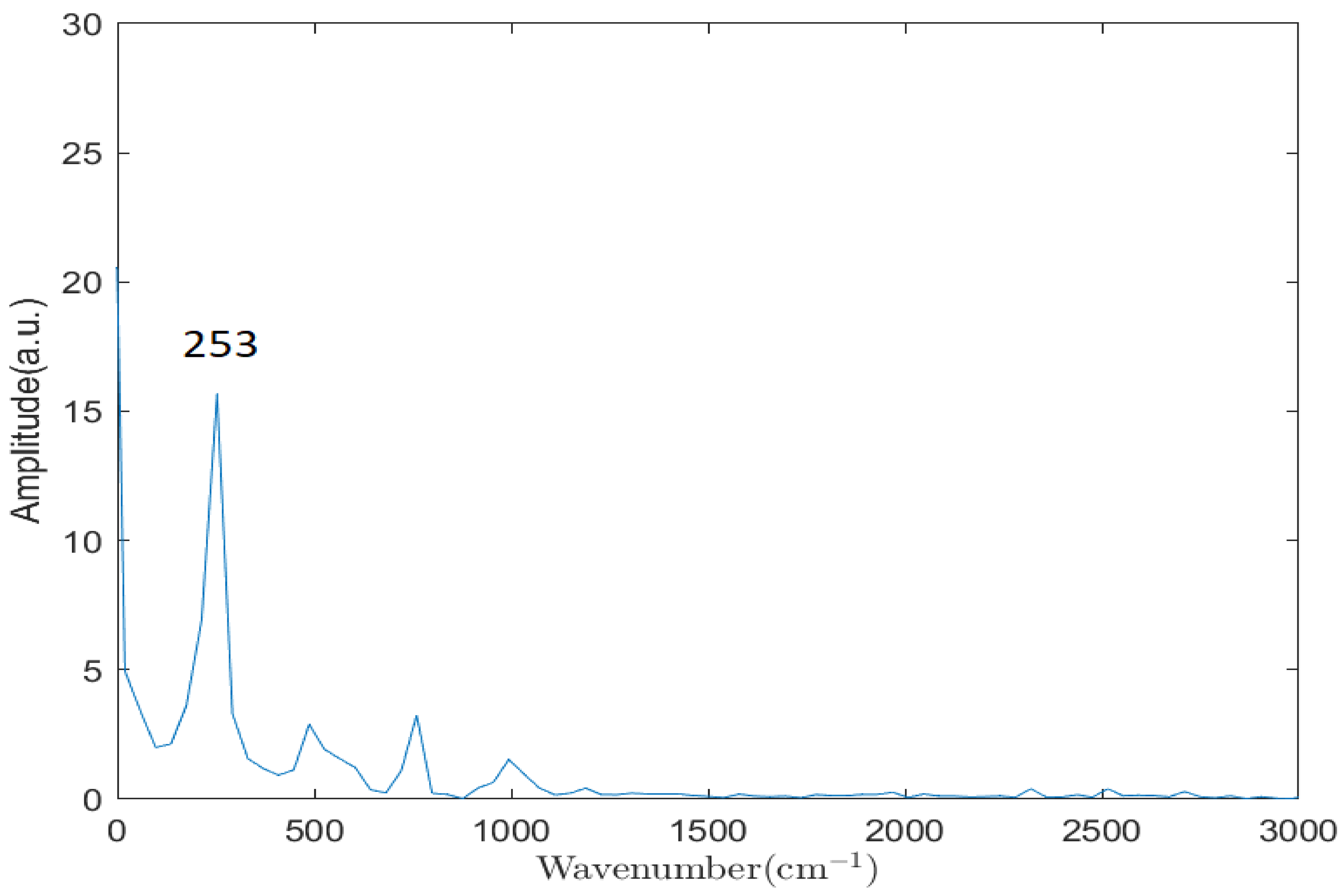

Fig 4: Fourier transform of the CLS beating using a Fast-Fourier Transform (FFT) algorithm.

References

[1] Mukamel, S. (2000). Multidimensional femtosecond correlation spectroscopies of electronic and vibrational excitations. *Annual Review of Physical Chemistry*, *51*, 691–729.
[2] Le, D. V., de la Perrelle, J. M., Do, T. N., Leng, X., Tapping, P. C., Scholes, G. D., Kee, T. W., & Tan, H.-S. (2021). Characterization of the ultrafast spectral diffusion and vibronic coherence of TIPS-pentacene using 2D electronic spectroscopy. *The Journal of Chemical Physics*, *155*(1), 14302–014302.
[3] Le, D. V., Leng, X., & Tan, H.-S. (2021). Regarding expressions of the oscillatory patterns in the 2D spectra of a displaced oscillator model. *Chemical Physics*, *546*, 111142–.