Excitonic coupling in covalently-bound Perylene Bisimide dimers revealed by two-dimensional electronic spectroscopy

Giovanni Bressan, Dale Green, Yohan Chan, Philip Bulman Page, Garth Jones, Stephen R. Meech and Ismael A. Heisler

School of Chemistry, University of East Anglia, Norwich, Norfolk, UK

UEA University of East Anglia

EPSRC

Introduction

Supramolecular structures based on Perylene Bisimides (PBIs) have been extensively studied because of their fundamental photophysical properties and for their application in a range of different optoelectronic devices [1].

Two-dimensional electronic spectroscopy (2D-ES) is the most complete third order ($\chi^{(3)}$) technique. It has been shown to be particularly useful in disentangling close-lying energy levels and revealing dynamics in coupled molecular systems.

Two different PBI covalently bound "head-to-tail" dimers (D0 and D1) with increasing interchromophoric separation were synthesised, shown in **Figure 1**. They were studied by means of 2D-ES and compared to a reference monomer (M) in order to characterise the 1 to 2-exciton state transition as a function of the PBI-PBI distance.
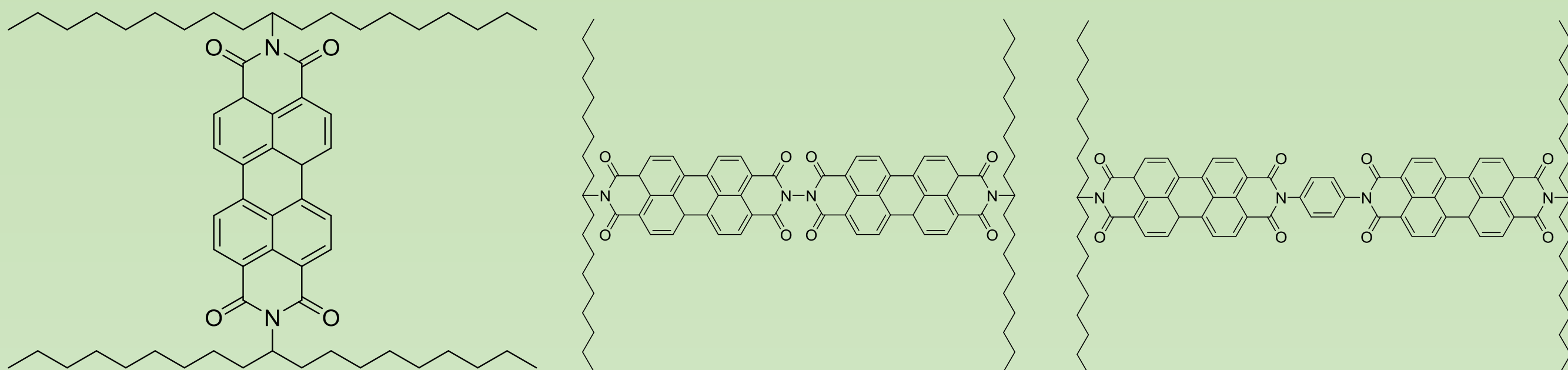

Figure 1: Molecular structures of the three compounds studied in this work. PBI monomer M (left), dimer D0 (centre) and dimer D1 (right)

Two-dimensional Electronic Spectroscopy [2]

2D-ES is a third order nonlinear technique involving three electromagnetic field-matter interactions, two time delays and the generation of a (heterodyned) signal, which is characterized in terms of phase and amplitude. Our experiments were done using a commercial Non-collinear Optical Parametric Amplifier (NOPA), producing ~20 fs pulses in the 490-750 nm range, seeded by a commercial Ti:Sa amplified laser system.

Our setup is based on conventional optics (the four phase coherent beams are generated with 2 beamsplitters); it is depicted in **Figure 2** [2].
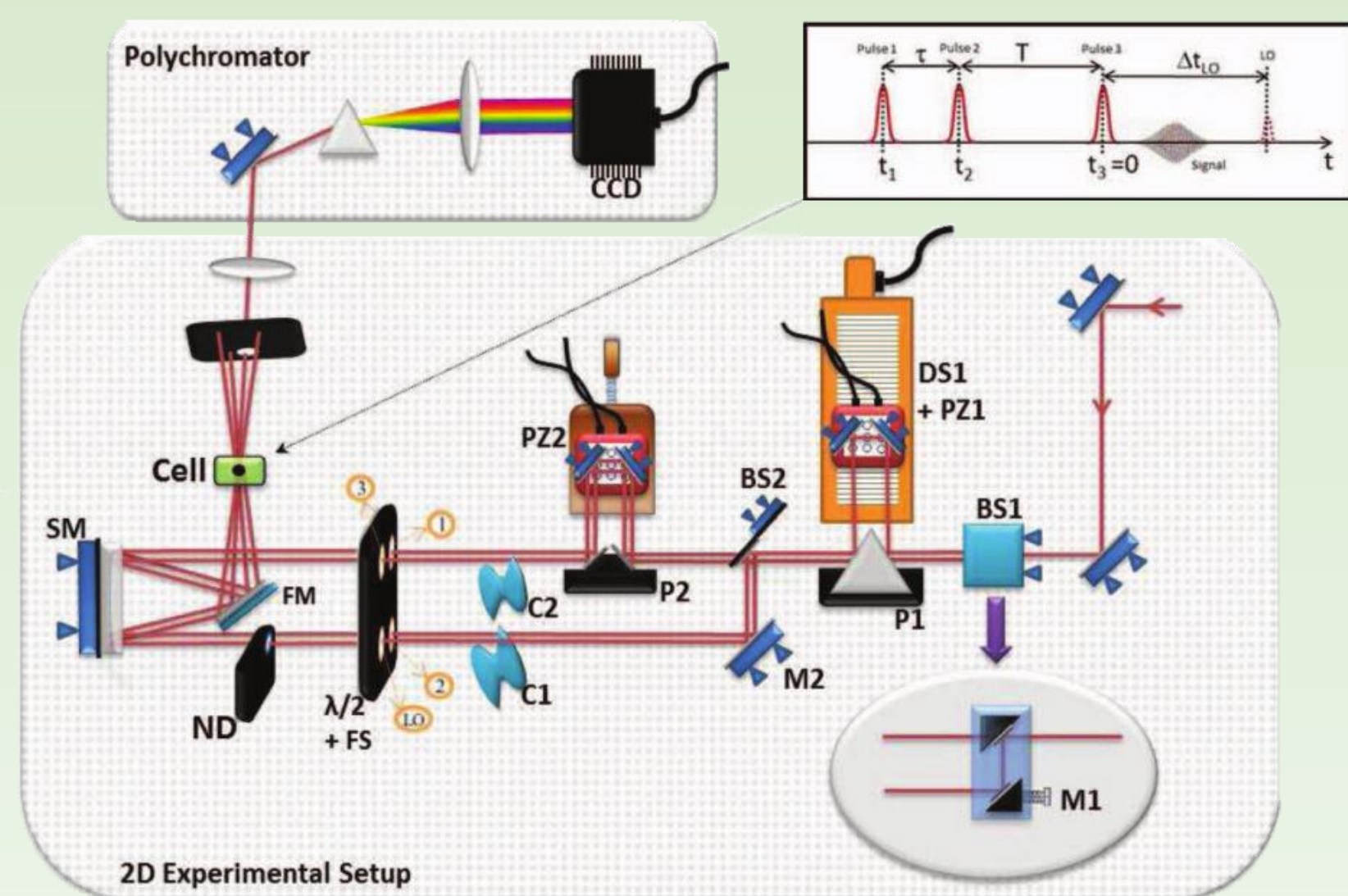

Figure 2: 2D-ES setup where: BS1,2 beamsplitters; P1,2 aluminium coated knife-edge right angle prisms; DS1 and PZ1,2 mechanical delay stages; C1,2 optical choppers; λ/2+FS half-wave plates plus fused silica windows; ND neutral density filter; SM spherical mirror; FM folding mirror.

Excitonic coupling in PBI dimers

According to Kasha's early works on excitonic coupled dimers, the coupling in D0 will be stronger than in D1, which has a bigger interchromophoric separation (1.27 nm for D0 and 1.70 nm for D1). The changes in the steady-state absorption spectra (red shift and enhancement of the 0-0/0-1 intensity ratio) and single molecule fluorescence studies [3] confirm this hypothesis.

Nevertheless, fluorescence cannot yield information about higher excited (two-exciton) states, which can provide further evidence for coupling in the dimers. 2D-ES absorptive data at early population times (T = 100 fs) for the PBI monomer M and D0 and D1 dimers are shown in **Figure 3**.
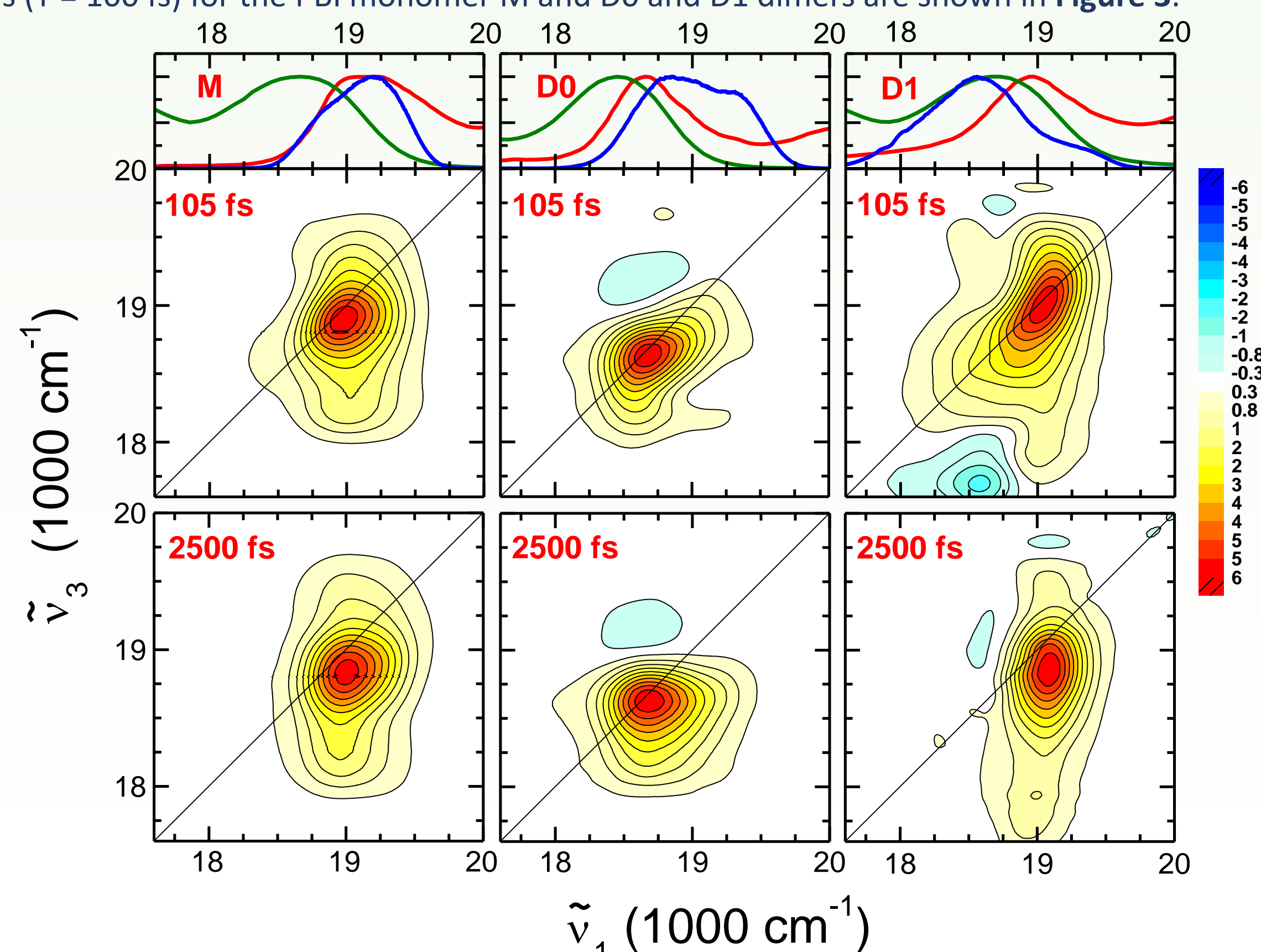

Figure 3: 2D-ES absorptive (R + NR) real correlation maps for PBI monomer M, D0 and D1 dimers at T = 105 fs (top row) and T = 2500 fs (bottom row). In the top plots the red line is the steady state absorption, the green line is the steady-state fluorescence and the blue line is the NOPA spectrum.

- All samples present a positive mixed Ground State Bleach (GSB) + Stimulated Emission (SE);
- The positive monomer signal is rounded while the dimers are more elongated on the diagonal, indicating a higher degree of static disorder (inhomogeneous broadening). The spectral diffusion and dynamic Stokes Shift observed are not the main focus of the current work, but occur within the first 10 ps for both D0 and D1;
- A negative Excited State Absorption (ESA) peak appears above the diagonal in the D0 map only, this is predicted for pure excitonically coupled dimers [4] and originates from a 1 to 2-exciton state transition. An increased interchromophoric separation results in a smaller value for *J*, making the positive and negative peak too close to be resolved in the D1 spectrum.
- The splitting between the positive and negative maxima corresponds to twice the coupling strength *J*, as shown in the level diagram sketched in **Figure 4**.
- **Figure 5** shows the average over 600 ps of population times **T** of vertical cuts on the 2D map of D0, and its fit, which allows to estimate *J*. The experimental value we measured *is J = 190 cm⁻¹*.
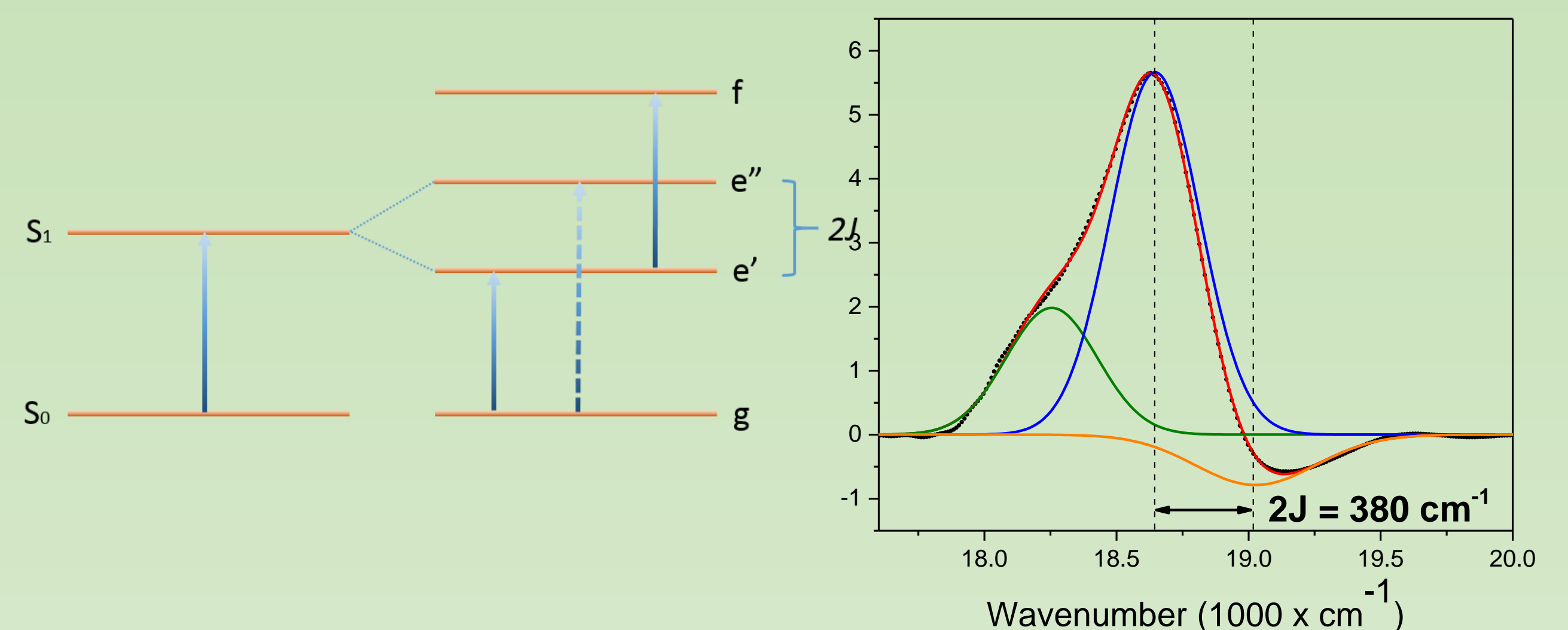
Figures 4 and 5: Energy level diagram for a PBI monomer and an excitonically coupled dimer (left). Average of the cuts along a vertical line of the D0 2D correlation map showing the fitted positive SE (blue and green lines of the fit) and the negative ESA (orange line) bands and their distance (right).

Calculated 2D-ES spectra

Following Kasha theory, each PBI monomer is modelled by a two-state electronic Hamiltonian, with the coupling of transition dipole moments given by the Förster equation. Numerical diagonalization produces the state diagram shown above. 2D spectra are calculated in the impulsive limit (temporal envelopes assumed to be delta functions) as the double Fourier transform of the third order molecular response function. The Hierarchical Equations of Motion (HEOM) are used to propagate the reduced density matrix between instantaneous optical interactions [5]. The solvent environment is modelled by an overdamped Debye spectral density.
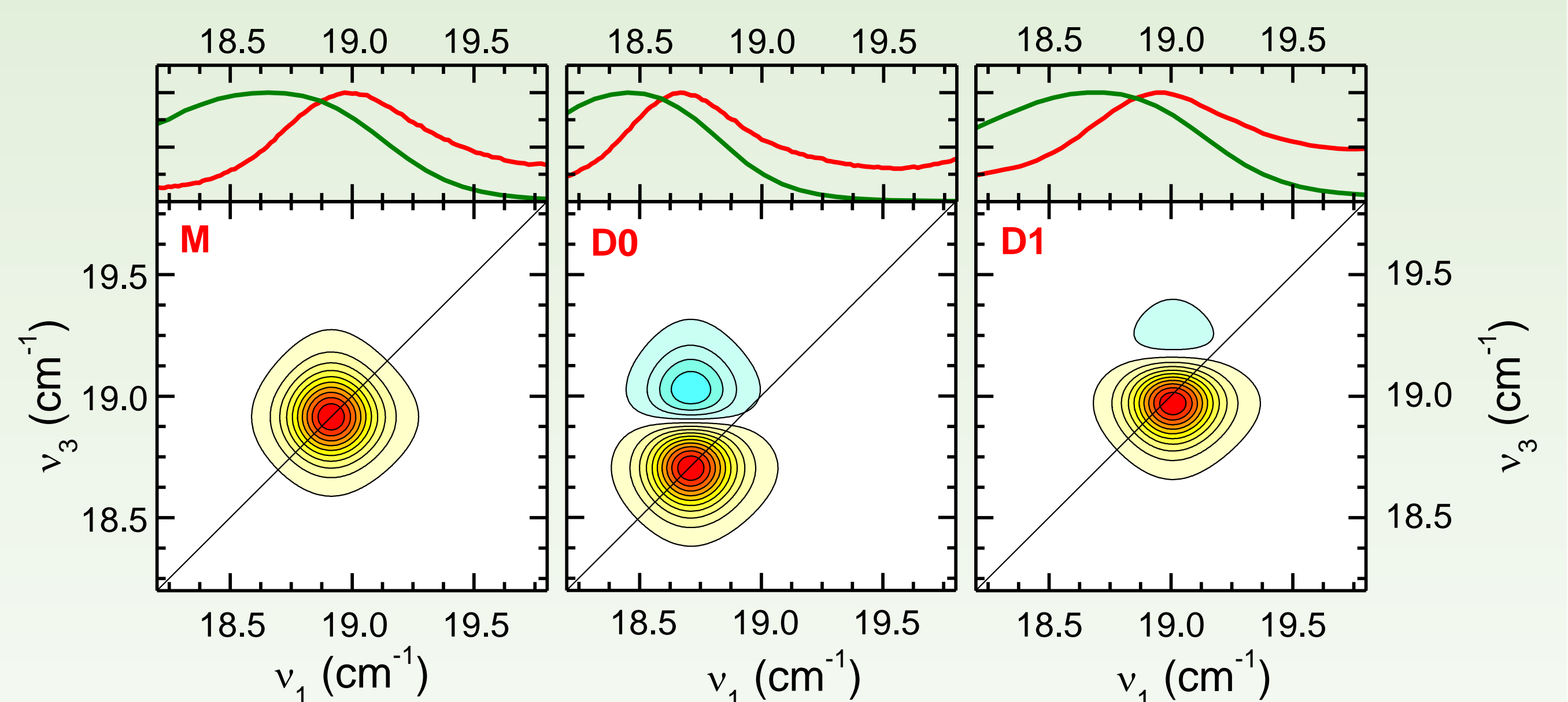

Figure 6: 2D-ES calculated absorptive (R + NR) real correlation maps for PBI monomer M, D0 and D1 dimers at T = 105 fs. In the top plots the red line is the measured steady state absorption and the green line is the steady-state fluorescence.

Summary

2D-ES measurements were performed on two PBI dimers with different coupling strengths (D0 and D1) and a reference monomer (M). We observed a long lived ESA band in the D0 2D map which can be assigned to a 1 to 2-exciton transition, which gives information about the value of *J* even in absence of coherent oscillations between the excitonic states, difficult to observe in pure "head-to-tail" dimers due to symmetry constraints. Theoretical modeling and simulated 2D spectra using the HEOM approach are consistent with this hypothesis.

Bibliography

[1] Würthner, F.; Saha-Möller, C. R.; Fimmel, B.; Ogi, S.; Leowanawat, P.; Schmidt, D (2016). Perylene Bisimide Dye Assemblies as Archetype Functional Supramolecular Materials. *Chem. Rev. 116* (3), 962–1052.

[2] Heisler, I. A., Moca, R., Camargo, F. V. A., & Meech, S. R. (2014). Two-dimensional electronic spectroscopy based on conventional optics and fast dual chopper data acquisition. *Review of Scientific Instruments*, *85*(6).

[3] Diehl, F. P., Roos, C., Duymaz, A., Lunkenheimer, B., Köhn, A., & Basché, T. (2014). Emergence of coherence through variation of intermolecular distances in a series of molecular dimers. *J. Phys. Chem. Lett.*, *5*(2), 262–269.

[4] Kjellberg, P., Brüggemann, B., & Pullerits, T. (2006). Two-dimensional electronic spectroscopy of an excitonically coupled dimer. *Phys. Rev. B.*, *74*(2), 1–9.

[5] Dijkstra, A. G.; Prokhorenko, V. I. (2017). Simulation of Photo-Excited Adenine in Water with a Hierarchy of Equations of Motion Approach. *J. Chem. Phys.*, *147* (6), 064102.