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Single-shot transient absorption spectroscopy of an organic film

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ABSTRACT

We report single-shot transient absorption (SSTA) measurements of an organic film of 3,3'-Diethyloxatricarbocyanine iodide (DOTCI). In SSTA, the pump-probe time delay is spatially encoded by using a tilted pump pulse. Translation of the sample during SSTA measurements averages over any spatial heterogeneity in the film. We demonstrate that exciton dynamics measured with the single-shot technique agrees with traditional transient absorption measurements of the same film. A signal-to-noise ratio of ~40 is achieved in 10 s. The ability to measure exciton dynamics in organic films will enable future SSTA measurements of exciton dynamics during the molecular aggregation events that result in film formation.

INTRODUCTION

The utility of an organic semiconducting material for photovoltaic [1], light emitting [2], or transistor [3] applications depends on the behavior of excitons. The rates of the physical processes that an exciton can undergo after photoexcitation can be determined using transient absorption (TA) spectroscopy, whereby a pump pulse photogenerates excitons before a probe pulse measures the differential transmission. The exciton dynamics is revealed by varying the delay between photogeneration and the differential measurement. Typically, the delay between the pump and probe pulses is controlled by changing the length of the path travelled by one of the pulses using a retroreflector mounted to a motorized translation stage. Differential transmission is measured at each retroreflector position in series, and the measurements are repeated as

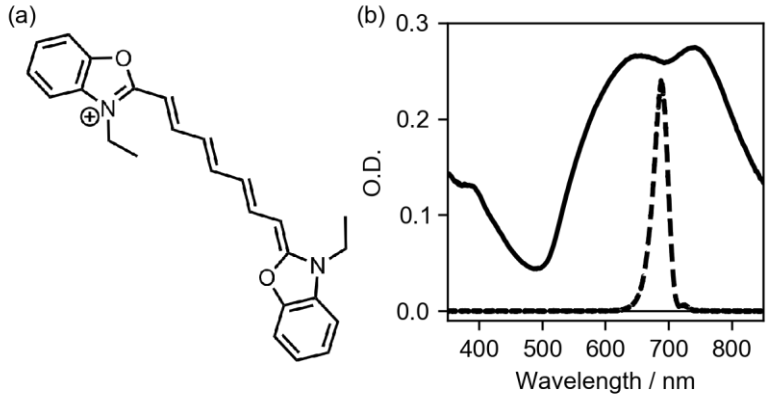

Figure 1. (a) Structure of DOTCI. (b) UV-Vis spectrum of a DOTCI film (solid) overlaid with the laser spectrum (dashed) centered at 690 nm.

needed to increase the signal-to-noise ratio, a process that takes many minutes to multiple hours. The accurate measurement of exciton dynamics requires that the sample does not change during data collection, so the differential transmission measured at short and long pump-probe time delays is indicative of the photophysics of the same sample. As a result of this limitation, TA spectroscopy has been largely limited to materials systems that are at structural equilibrium. We have implemented single-shot transient absorption (SSTA) spectroscopy, which uses tilted pulses to spatially encode the pump-probe time delay, enabling the measurement of 45 ps of dynamics in a single laser shot. Multiple shots are averaged to increase the signal-to-noise ratio. In our previous work [4], we demonstrated that this technique can accurately measure exciton dynamics in solutions of organic semiconductors. In this work, we show that a spatially encoded delay can also be used to measure exciton dynamics in an organic film of 3,3'-diethyloxatricarbocyanine iodide (DOTCI), shown in Figure 1(a), with a signal-to-noise ratio (SNR) of ~40 in 10 s. The ability to perform TA spectroscopy with sub-10 s data collection times in solutions and in films will enable the measurement of exciton dynamics during the process of molecular aggregation and film formation from solution.

EXPERIMENTAL DETAILS

Glass substrates (75 mm x 25 mm x 1 mm) were cleaned by sonication in methanol for 10 min. Films with an optical density of ~0.3 were produced by dropcasting a solution of DOTCI (Kodak) in acetone on the cleaned substrates. During deposition the substrate temperature was 19 °C.

Transients were collected using a homebuilt SSTA instrument, described elsewhere [4] and shown in Figure 2. Briefly, a 1 kHz Ti:sapphire laser (Coherent Astrella) and optical parametric amplifier (OPA) produce pulses at 690 nm. This is resonant with the absorption of DOTCI, Figure 1(b), and can photogenerate excitons in the sample. A beam splitter divides each pulse into pump and probe pulses. The energy of the pump pulse is set to 1.3 μJ using a waveplate and polarizer, with a pump:probe energy ratio of 11:1. A flat pump spatial profile is generated by geometric beam shaping using a phase-only spatial light modulator (SLM, Meadowlark). An optical chopper blocks alternate pump pulses. The probe pulse is directed into a retroreflector, which is mounted on a motorized translation stage. After expanding both beams, they are focused to a 18.6 mm x 25 μm line on the sample plane using cylindrical lenses. A CMOS camera (Andor Zyla 5.5) is used with an exposure time of 1 ms to image the probe beam.

The angle of the pump pulse relative to the sample plane (θ), the speed of light (c), and length (d) of the overlap region between the pump and probe on the sample determine the time delay range, $t_{range} = d \sin(\theta) / c$. To spatially encode a pump-probe delay range of 45 ps, the probe beam is incident normal to the sample plane while the pump pulse is angled at $\theta = 42.5°$. The time resolution of the measurement is governed by the laser source, angle between the pump and the probe, the resolution of the array detector, and the thickness of the sample. In this work, the time resolution of the measurement was limited by the duration of the laser pulse. Optical Kerr effect measurements determined that the pulse duration at the sample is ~50 fs.

During signal acquisition, the sample was repeatedly translated over 8 mm at a speed of 0.3 mm/s by a linear actuator, as shown in Figure 2. This averaged over any heterogeneity in the film. Taking an average of multiple laser shots also improved the SNR. The probe illuminated 20 x 2560 pixels on the detector, and each of the 20 rows of pixels was summed together to provide a 1 x 2560 probe image. The camera collected images of the probe beam with the pump beam blocked (T_{off}) and unblocked (T_{on}) by the optical chopper before the sample plane. Raw transmission values more than four standard deviations from the mean, arising from dust particles or defects in the film, were removed. Normalized differential transmission is calculated by $\Delta T / T = (T_{on} - T_{off}) / T_{off}$. This measurement represents the change in transmission due to the presence of excitons.

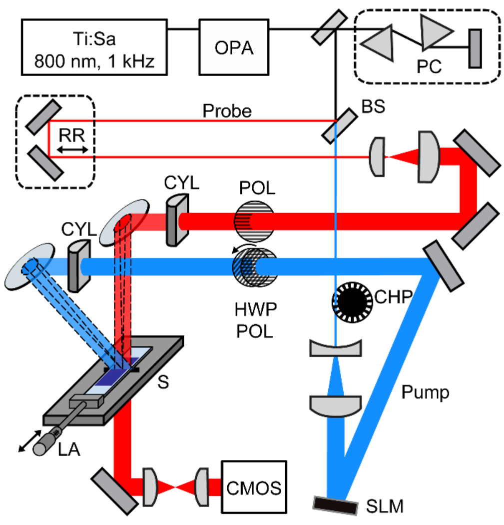

Figure 2. Schematic of SSTA instrument. BS, beam splitter; CHP, optical chopper; CMOS camera; CYL, cylindrical lens; HWP, half-wave plate; LA, linear actuator; OPA, optical parametric amplifier; PC, prism compressor; POL, polarizer; RR, retroreflector; SLM, spatial light modulator; S, sample.

RESULTS AND DISCUSSION

Figure 3 shows $\Delta T / T$ of a DOTCI film as a function of retroreflector position. A sharp increase in the $\Delta T / T$ signal is observed at "time zero" due to the creation of excitons. The time zero for each pixel occurs at the retroreflector location that results in spatial and temporal overlap of the pump and probe pulses within the sample. Time zero is unique for each pixel because of the tilt of the pump pulse. The pixel location and retroreflector position at each time zero exhibit a linear relationship, as shown in Figure 3(a), demonstrating that the wavefront is flat as it passes through the sample plane [5]. The slope of this line can be used to calibrate the spatially encoded pump-probe time delay. In this work, the time delay is determined to be 22.6 fs/pixel. SSTA measurements are then collected while holding the retroreflector at a static location.

Horizontal cross sections of the plot in Figure 3(a) represent SSTA measurements, while traditional TA is represented by vertical slices of the plot. The exciton dynamics measured using the spatially encoded SSTA time delay should be identical to those measured traditionally using a translating retroreflector, and the measurements of the DOTCI film confirm this agreement. As shown by Figure 3(b), vertical cross sections of the plot have near-identical transients. Each vertical slice is a traditional TA measurement detected by a particular pixel, onto which is imaged a particular spatial location of the film. If the pump pulse photogenerated interacting excitons in one region of the film but not in another, the dynamics measured at these regions would be different. The identical exciton dynamics measured by each pixel indicates that the measured volume is absent of exciton-exciton interactions and that measured exciton dynamics is in the linear regime. Similitude between horizontal slices

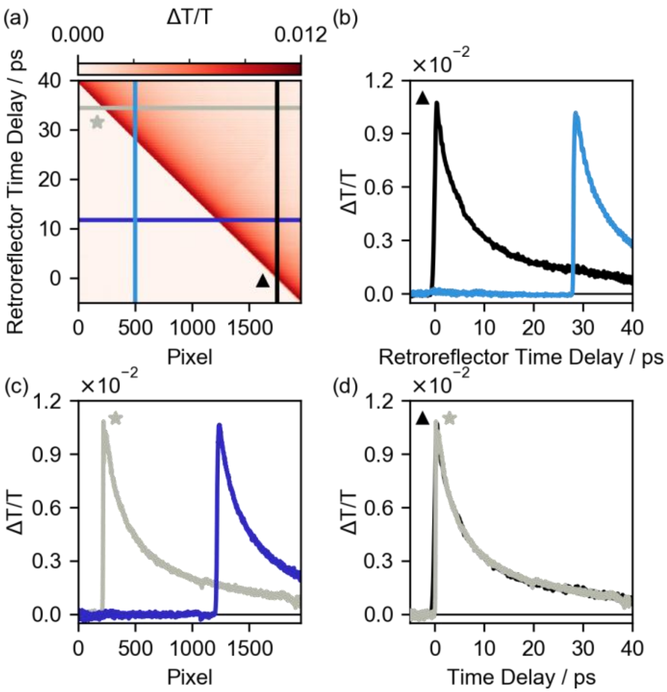

Figure 3. Traditional TA and SSTA measurements of DOTCI at 690 nm. (a) SSTA measurements collected using a range of time delays generated by translating a retroreflector. Equivalence of dynamics measured using traditional TA and SSTA is confirmed by comparing a vertical slice (black triangle) and horizontal slice (grey star), respectively. (b) Comparing vertical slices from (a) at different pixels demonstrates that time zero occurs at different retroreflector locations. (c) Comparing two horizontal slices at different retroreflector positions from (a) demonstrates relative time delays between pixels. (d) Overlay of transients collected by traditional TA (black) and SSTA (grey).

of the data, which represent SSTA measurements at different retroreflector positions, further supports this conclusion, Figure 3(c). Comparing horizontal slices of the plot to vertical slices, Figure 3(d), shows that the dynamics collected by SSTA measurements match those of traditional TA. Transients are collected in 10 s by SSTA, compared to 90 min. by traditional TA. The SNR of SSTA measurements is ~40, attained in 10 s. Comparison with traditional TA measurements indicates that SSTA reveals the same exciton dynamics and can achieve a similar SNR with a significantly shorter measurement time. Therefore, SSTA can be used to reliably measure the electronic dynamics of organic films faster than using traditional TA.

In summary, we have performed TA measurements of a DOTCI film using a homebuilt SSTA spectrometer. To our knowledge, this is the first demonstration of the use of a spatially encoded time delay to measure the exciton dynamics of an organic film. A tilted pump pulse spatially encodes the pump-probe delay times on the sample plane. SSTA measurements as a function of retroreflector position demonstrate that the dynamics measured using SSTA agree with those measured using traditional TA. In SSTA measurements, a signal-to-noise ratio of ~40 was achieved in 10 s, made possible by translating the sample to average over heterogeneity in the film. Further experiments are currently being performed to quantify the degree of heterogeneity that can exist in a film measured using this spatially encoded technique.

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