Supporting Information

Sub-10 Femtosecond Time-Resolved Vibronic Optical Microscopy

Christoph Schnedermann†, Jong Min Lim‡, Torsten Wende†, Alex S. Duarte†,§, Limeng Ni‡,
Qifei Gu‡, Aditya Sadhanala‡, Akshay Rao‡, Philipp Kukura†,*

† Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, United Kingdom
‡ Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, Cambridge CB3 0HE, United Kingdom
§ Present address: ICFO - Institut de Ciencies Fotoniques, The Barcelona Institute of Science & Technology, 08860 Castelldefels (Barcelona), Spain

Corresponding Author

*philipp.kukura@chem.ox.ac.uk
Methods

**Femtosecond Transient Absorption Microscopy (fs-TAM).** Our fs-TAM setup is schematically depicted in Figure 1b. Pulses were delivered by a Yb:KGW amplifier (Pharos, LightConversion) that seeded two broadband white light (WL) stages at a repetition rate of 200 kHz. The probe WL was generated in a 3 mm YAG crystal and adjusted to cover the wavelength range from 650-950 nm by a fused-silica prism-based spectral filter. In contrast, the pump WL was generated in a 3 mm sapphire crystal to extend the WL in the high-frequency to 500 nm, and short-pass filtered at 650 nm (Thorlabs). A set of chirped mirrors (pump – Layertec, probe – Venteon) and a pair of fused silica wedges (Layertec) compressed the pulses to sub-10 fs, as verified by second-harmonic generation frequency-resolved optical gating.\(^1\) Pump and probe pulses were subsequently focused onto the sample under a small angle to \(\sim 25 \times 25 \, \mu m^2\) ensuring sub-15 fs temporal resolution. In addition, we took special care to avoid any spatial inhomogeneity and spatial chirp across the pulses.

The transmitted light was collected by a 1.42 NA oil immersion objective (60x, Olympus) and sent to an imaging system featuring a 1:2 telescope with a slit in the intermediate image plane. Addition of a tube lens after the telescope enabled the non-dispersed imaging modality. Upon closing the slit to a diffraction-limited line of the image and inserting an F2 prism to disperse the light perpendicular to the slit, we could access spectrally-dispersed images over the selected region. Both channels were recorded with a CMOS camera (Grasshopper 3, Point Grey Research) and pump light was suppressed by a 650 nm long-pass filter (Thorlabs) inserted in front of both cameras. The magnification of the imaging system was 333x and 200x for non-dispersed and dispersed detection channels, respectively. A different magnification for dispersed detection was chosen to enable full detection of the probe light with a spectral resolution of \(\sim 5 \, cm^{-1}/pixel\). Using the full bandwidth of the probe
pulse centered at 800 nm, we achieved a diffraction-limited spatial resolution of ~280 nm. Differential imaging was achieved by modulating the pump beam at 50 Hz by a mechanical chopper. We remark, that this setup can also be used in controlled or inert atmospheres, provided the additional dispersion on the pulse can be compensated for by the employed third-order compensated chirped mirror pairs.

Sample Preparation of TIPS Pentacene Films.

TIPS pentacene was obtained commercially from Ossila. Thin films (thickness = 100 nm) of TIPS pentacene were spin-coated from 30 mg/ml chloroform solutions on pre-cleaned microscope cover slides (thickness = 0.16 mm). All samples were prepared in an inert environment, and encapsulated with a second microscope cover slide and epoxy glue to avoid exposure to air.

Sample Preparation of Perovskite Films.

MAPbI$_{3-x}$Cl$_x$ perovskite films (thickness = 200 nm) were fabricated by the hot-casting approach as described previously.$^2$ Briefly, a solution of lead iodide (PbI$_2$) and methylamine hydrochloride (MACl) was heated to 70 ºC and spin-coated on a microscope cover glass slide (thickness = 0.16 mm) pre-heated to 180 ºC. All samples were subsequently encapsulated.

Data Acquisition and Analysis.

Consecutive pump-ON and pump-OFF images for each time delay were corrected for camera background and converted to a single $\Delta T/T$ image. To increase the signal-to-noise ratio (SNR), we repeated the experiments several times and averaged corresponding images, which we subsequently binned in space. We carried out 100 runs for the perovskite experiment (Fig. 2) resulting in a noise-floor of $\Delta T/T = 1.5 \times 10^{-4}$ for a diffraction-limited pixel (SNR = 100), while 150 runs were averaged for TIPS pentacene resulting in a noise level of $\Delta T/T = 5 \times 10^{-5}$.
Figure S1. iSCAT images of different regions in perovskite blends. Images were recorded with continuous-wave illumination at 638 nm and normalized to the maximum scattering intensity. The superimposed photoluminescence signal was filtered by means of a 650 nm short-pass filter. The scale bar corresponds to 5 µm with 60.8 nm/px.

(SNR(dynamics) = 800, SNR(FFT) = 81). We remark that the two experiments in the main text were carried out at different camera saturation levels due to sample constraints. All experimental data was sampled with a time step of 3.5 fs, resulting in a total acquisition time of ~30 s for a single run covering 1.2 ps. We independently verified that our setup remains shot-noise limited down to at least $\Delta T/T = 5\times10^{-5}$. Mechanical focus drift was removed during the measurement by implementing an autofocus routine as described elsewhere.3

Interferometric Scattering Microscopy (iSCAT) of Perovskite Grain Boundaries

To quantify the scattering behavior of perovskite grains we carried out iSCAT microscopy at 638 nm, known to be highly sensitive to local changes in the refractive index of a material (Figure S1).3,4 Apart from local intensity differences in the grain boundaries, all regions show an enhanced signal at the grain boundary compared to the grain, suggesting that grain boundaries act as strong light scatterers. This enhanced scattering effect will interfere with the
Figure S2. Normalized transmission images of TIPS pentacene films. (a) Aged TIPS pentacene film as shown in the main text. (b) Freshly prepared TIPS pentacene film. The scale bar corresponds to 5 µm with 175.9 nm/px. Both images were normalized to the underlying probe illumination profile.

purely absorptive response of the grain boundary observed in a transmission image, resulting in a lower transmission intensity, as shown in Figure 2a.

Morphological Differences Between Aged and Freshly Prepared TIPS Pentacene Films

Keeping TIPS pentacene films under ambient light conditions changes their morphology due to degradation, as we propose in the main text (Figure 3a and Figure S2a). To validate this aspect, we freshly prepared a TIPS pentacene film for comparison of the transmission properties. As shown in Figure S2b, the freshly prepared film shows significantly less spatial inhomogeneity, making a degradation by ambient light over the course of one month the most likely explanation for the observed structural inhomogeneity in aged films.

To ensure that the transient dynamics are spatially uniform for freshly prepared TIPS pentacene samples, we applied dispersed fs-TAM (Figure S3). The dispersed imaging modality allows us to monitor the spatial and spectral behavior of the sample simultaneously,
Figure S3. Dispersed fs-TAM images for a freshly prepared TIPS film at different time delays illustrating the homogeneity of the sample. The vertical scale bar corresponds a spatial dimension of 10 μm. The original data was binned to 175.8 nm/px in space and 3.48 nm/px in wavelength, making it particularly powerful to investigate spectral shifts as a function of space, as observed for the aged film. Apart from two regions along the spatial dimension, which show enhanced signals, the overall response of the film is homogenous in space and spectrum over the entire image. Relative intensity differences stem from wide-field pump illumination, which can be readily corrected for.
Figure S4. Spatially-resolved Fourier power map for a freshly prepared film. The data was derived from the dispersed fs-TAM results presented in Figure S3 by averaging from 720-760 nm. The scale bar corresponds to 10 μm.

In this experiment we also observe coherent oscillations in particular in the region of 740 ± 20 nm (see also Figure S5a). To investigate their spatial dependence, we carried out a Fourier transformation along each spatial pixel and averaged the resulting Fourier power map from 720-760 nm to generate a single Fourier power spectrum for each spatial position (Figure S4). In analogy to the transient kinetics described in Figure S5, the Fourier spectrum is homogeneous and only varies in relative intensity due to the non-uniform pump illumination. This behavior for the freshly prepared film is in stark contrast to the spatially inhomogeneous appearance encountered for the aged TIPS pentacene film (Figure 3).

Transient Signals in Aged TIPS Pentacene Films

We now turn to a comparison between the transient dynamics observed for aged and freshly prepared films. The dispersed transient absorption map recorded for a diffraction-limited spot of the freshly prepared sample shows the common features known from TIPS pentacene
films, i.e. a ground-state bleach at 725 nm superimposed on a broad photoinduced absorption band at 875 nm (Figure S5a).\textsuperscript{5,6}

Aging results in considerable degradation of the film as discussed above. To partially assess the nature of this degradation, we investigated the transient dynamics of the aged film (Figure S5b) and compare it to the same film prior to aging, which were recorded in non-dispersed mode upon insertion of a 740 nm band-pass filter, as outlined in the main text. At 740 nm, a freshly prepared TIPS pentacene film displays an initial fast signal rise followed by a slower decay and sign-inversion at a time delay of \(~1\) ps (black). Conversely, the all-space averaged transient response of the aged film shows a different behavior with a fast rise of a negative signal followed by a much slower decay of the signal (blue). This indicates that the film must have degraded during the aging process. Recent studies on TIPS pentacene suggest that TIPS pentacene films show an almost 100 nm red-shifted band edge (~750 nm), compared to the same molecules in solution (~650 nm).\textsuperscript{5} Upon scanning our transient absorption map across the probe wavelength (Figure S5a), we were able to match the transient response of our aged film at 740 nm to the transient response of a freshly prepared film at 860 nm (Figure S5b, orange). This further suggests that degradation indeed results in (most likely sub-diffraction) inhomogeneity, leading to a breakdown of the molecular structure and hence modifying the coupling between adjacent TIPS pentacene molecules in the aged film. Furthermore, we investigated the dynamics of a Raman active bleach region (green), which exhibits a fast signal rise followed by very slow signal decay, superimposed by coherent nuclear motion. This suggests that even regions that we attribute to be formed of tightly coupled molecules are affected by the macroscopic degradation process.
Figure S5. fs-TAM on TIPS pentacene films. (a) Transient absorption map of a freshly prepared TIPS pentacene film averaged over a diffraction-limited spot. The dashed horizontal line serves as guide to the eye marking a probe wavelength of 740 nm. (b) Transient dynamics at 740 nm and 860 nm derived from (a) compared to the all-space averaged non-dispersed response of aged TIPS pentacene and the dynamics observed at a Raman-active bleach region (center Figure 2b) recorded with a 740 nm band-pass filter in detection.

Comparison of Impulsive Raman Bands for TIPS Pentacene Films

Despite the shifted transient dynamic responses, we can use the observation of vibrational coherences superimposed on the dynamics to assign which structures are underlying the dynamics. To this end, we compare our results for the Raman-active regions of the aged film (see Figure 3c) with the results derived from a dispersed fs-TAM measurement on a freshly prepared film (see Figure S5a) and the ground-state Raman spectra derived from a previously reported time-domain measurement (Figure S6). Apart from minor relative intensity differences, which we attribute to slightly different effective time resolutions of the respective experiments, all spectra exhibit the same band positions, strongly supporting the
Figure S6. Comparison of Fourier spectra for TIPS pentacene films. (a) aged film averaged over the Raman-active bleach region. (b) Freshly prepared film derived from the data shown in Figure S5a recorded at 740 nm. (c) Previously published ground-state Fourier power spectrum using broadband impulsive vibrational spectroscopy (BB-IVS) of a similar TIPS pentacene film. 

notion that the Raman-active ground-state bleach regions in Figure 3 are indeed regions of tightly coupled TIPS pentacene molecules albeit with slightly different absorption characteristics imposed by the surrounding degradation upon aging.
References

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