Directional charge–phonon coupling in mixed exciton–charge-transfer states in DNTT single crystals

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We investigate exciton–phonon coupling in single-crystal DNTT, high-mobility organic semiconductor widely used in Organic Field-Effect Transistors (OFETs) [1]. Previous studies on OFETs have shown that hole mobility is significantly higher along the axis of parallel-aligned molecules (a-axis) compared to the perpendicular direction [2]. However, charge transport in these soft molecular materials is strongly influenced by low-frequency lattice vibrations. In particular, a low-frequency sliding phonon mode at ~0.5 THz has been proposed as a key factor limiting charge transport [3]. While previous optical pump THz probe (OPTP) measurements revealed that charges transiently delocalize in polycrystalline DNTT mediated by low-frequency THz vibrations [4], direct experimental evidence of coupling between this sliding motion and the photoexcited charges has been lacking.

Using a combination of optical pump–THz probe (OPTP) spectroscopy and polarization-resolved optical pump–visible probe microscopy, we directly probe the interplay between electronic excitations and lattice dynamics in DNTT single crystal.

Polarization-resolved linear absorption spectra, together with theoretical analysis, reveal that a mixture of free charges and localized Frenkel excitons is generated upon photoexcitation. To further investigate the composition of this mixture, we performed transient absorption (TA) measurements (see Fig. 1a). Along the a-axis, charges behave predominantly as free carriers, whereas along the perpendicular b-axis, they remain largely Frenkel excitons. This distinction is evidenced by analysis of the first and second derivatives of the polarization-resolved static absorption spectra. TA signals show pronounced polarization-dependent energy shifts arising from the electric field of photoexcited charges (Stark effect). Along the a-axis the Stark shift is

mainly attributed to the linear contribution arising from free holes, whereas along the b-axis the second order Stark shift reflects the polarizability of exciton states (see Fig. 1b) .

Moreover, we observe a modulation of the transient absorption signal within the first 15 ps due to the 0.5 THz mode, providing direct evidence of its coupling to the photoinduced states (Fig. 1c). By dispacing the molecules along this 0.5 THz lattice vibration, our theoretical model demonstrates that this sliding motion modulates the interaction between excitons and charge transfer states. Following charge–lattice relaxation, transient absorption microscopy further reveals strongly anisotropic diffusion, with enhanced delocalization along the a-axis. Our results establish a direct connection between low-frequency lattice dynamics and anisotropic charge delocalization, identifying the sliding phonon mode (0.5 THz) as an active mediator of exciton–charge coupling in an organic single crystal.

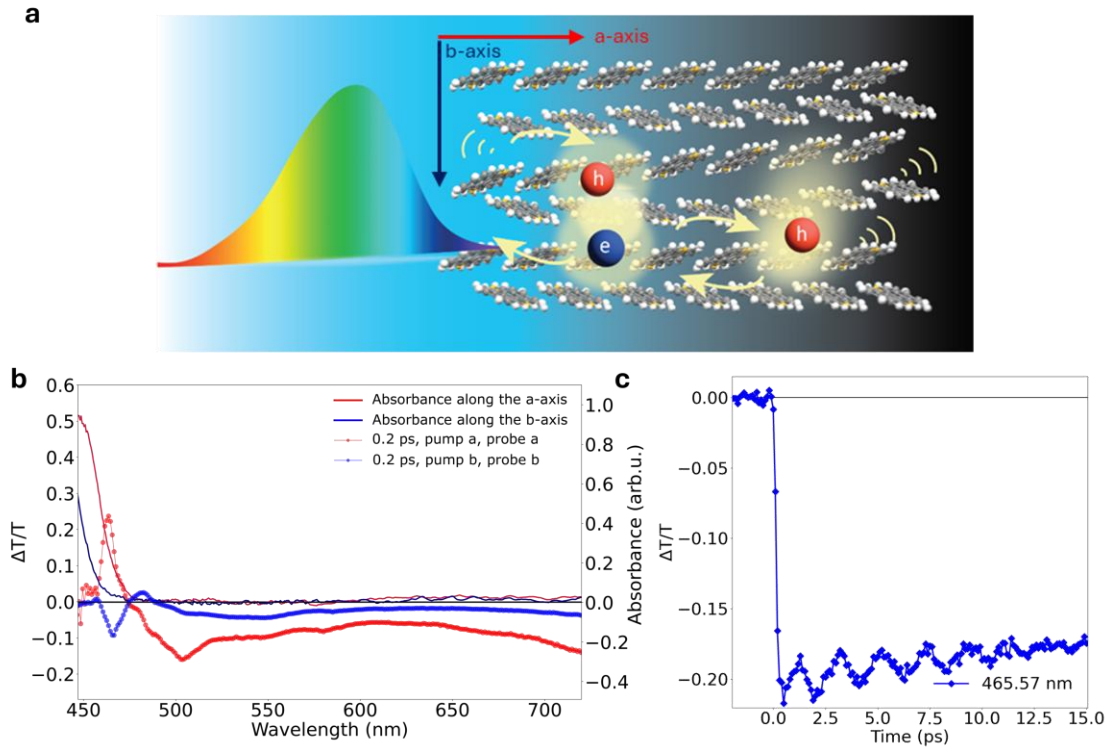

Figure 1: a Schematic of the DNTT single crystal with arrows indicating the crystallographic a (red arrow) and b (blue arrow) axes probed by the white-light supercontinuum. Exciton (e-h) and free hole (h) excitations interact with the lattice vibrations. **b**. The dark red (dark blue) line shows the static absorbance measured with light polarized along the a- (b-) axis, plotted on the right y-axis. Points represent the transient absorption signal at 0.2 ps after pump arrival. The displayed pump–probe configurations are: red pump along a and probe along a, and blue pump–probe along b. **c.** Charge dynamics are shown around 465.57 nm, corresponding to the dip in the blue TA trace of panel b. Oscillations with a period of ~2 ps, corresponding to the 0.5 THz lattice vibration, are observed.

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