

Dynamics of Exciton Delocalization in Small Molecule Semiconductors

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Exciton coherence in molecular systems is a prerequisite for achieving efficient and robust energy transfer in potential quantum information applications. The onset of coherence is a complex many-body problem that requires an intermediate exciton-phonon coupling regime where the short-range π -stacking and long-range intermolecular Coulomb interaction are on equal footing with the reorganization energy. Delocalization and coherence happen where the excitonic states couple with low-energy vibrational modes (phonons) while coupling to high-energy localized molecular vibrations destroys coherence. The small molecule families are ideal platforms for molecular and crystalline architecture design that potentially leads to robust room temperature coherence.

Here we report on experimental ultrafast spectroscopy studies of coherent exciton formation in a series of different soluble derivatives of small molecules including a species of phthalocyanine (H_2Pc) (Fig. 1), quinacridone, charge-transfer co-crystals and a merocyanine dye, where the bandgap, the π -stacking and the crystalline packing can be changed through the addition of alkyl chains that also makes the molecules soluble in volatile organic solvents. Crystalline thin films with macroscopic ordering are deposited using a meniscus-guided technique, resulting in mm-sized crystalline grains oriented along the pen-writing direction (Fig. 1a). [1] Atomic force microscopy (Fig 1b) show the presence of molecular terraces that confirm the superior ordering originally reveal by grazing incidence X-ray diffraction. [2] Comprehensive polarization, temperature, and time-dependent photoluminescence (PL) microscopy experiments that revealed some π -stacking configurations favor the formation of delocalized excitons and strong radiative recombination (Fig. 1c) [4]

Most importantly, the formation of a delocalized exciton state (photoinduced absorption at $\lambda \sim 930\text{nm}$) is observed, in addition to the expected Frenkel exciton (bleaching at $\lambda \sim 890\text{nm}$). These were revealed with room-temperature femtosecond transient-absorption measurements using the NIR portion of a white light continuum. Approximately 30 ps later, we observe the onset of a long-lived photoinduced absorption feature which appears as a result of exciton localization by dynamic disorder present at elevated temperatures.

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References

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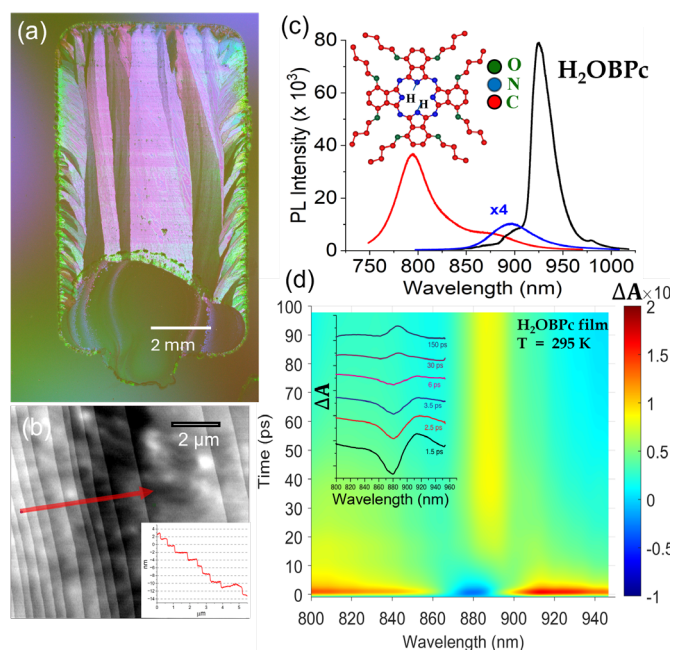


Fig. 1. (a) Polarized microscope image of crystalline small molecule thin films deposited from solution using a meniscus guided technique. (b) Atomic force microscope (AFM) image of molecular terraces in the same film confirms the superior long range ordering in these films. (c) Long range ordering results in the formation of a strongly emitting delocalized exciton. (d) Transient absorption reveals the formation and dynamics of delocalization at room temperature