

## Charge-transfer excitons in lamellar organic semiconductors

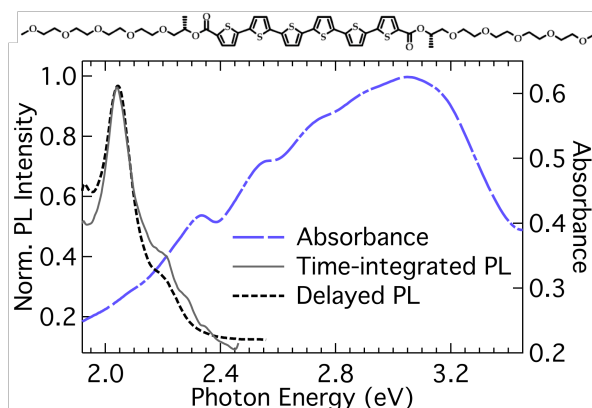
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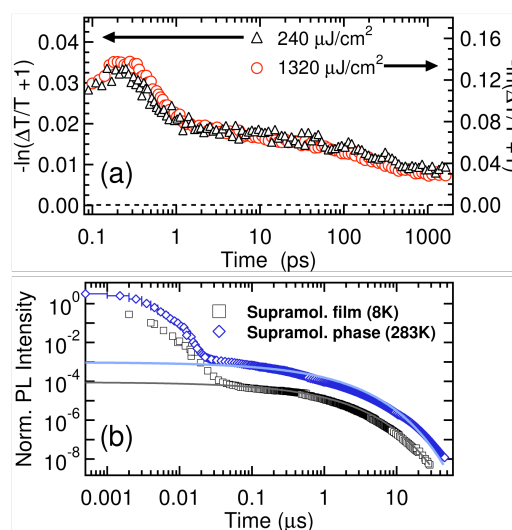
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**Abstract** – Time-resolved and temperature-dependent photoluminescence measurements on one-dimensional sexithiophene lattices reveal intrinsic branching of photoexcitations to two distinct species: self-trapped excitons and dark charge-transfer excitons (CTX; >5% yield), with radii spanning 2–3 sites. The significant CTX yield results from the strong charge-transfer character of the Frenkel exciton band due to the large free exciton bandwidth (~400 meV) in these supramolecular nanostructures.

In organic semiconductors, molecules or polymers are the building blocks of desired architectures, instead of atoms as in traditional semiconductors. This has the advantage that individual motifs can be tailored synthetically for specific electronic properties. However, electronic interactions between building blocks are often complex due to energetic disorder. Here, we address the nature of photoexcitations in chiral, near-cofacial stacks of a sexithiophene derivative that exhibits strong supramolecular  $\pi$  electronic coupling [1]. Time-resolved, temperature-dependent photoluminescence measurements on these one-dimensional lattices reveal intrinsic branching of photoexcitations to two distinct species: self-trapped excitons and dark charge-transfer excitons (CTX; >5% yield), with radii spanning 2–3 sites. The significant CTX yield results from the strong charge-transfer character of the Frenkel exciton due to the large free-exciton bandwidth (~400 meV) in these supramolecular nanostructures. We have demonstrated that in organic semiconductors, the supramolecular coupling energy dominates the nature of the primary photoexcitations. The large free-exciton bandwidth is significantly larger than attainable in the most highly organised semiconductor polymer microstructures, but the primary photoexcitations are highly localised. The Frenkel exciton band mixes with CT states, which play an important role in the primary photophysics.



**Figure 1:** Molecular structure of OT6. Absorbance, time-integrated PL spectrum, and delayed PL spectrum from 6.5  $\mu$ s after excitation and a gate width of 500  $\mu$ s. The solution temperature was 283 K.



**Figure 2:** (a) Femtosecond absorption transients probing at 1.42 eV with two pump fluences indicated in the caption. (b) Time-resolved PL intensity in the supramolecular phase (blue diamonds), and in a drop-cast film of the stacks at 8 K (black squares). The data are offset vertically for clarity.

## References

[1] S. Westenhoff, A. Abrusci, W.J. Feast, O. Henze, A.F.M. Kilbinger, A.P.H.J. Schenning, and C. Silva. *Advanced Materials* 18 (2006) 1281 – 1285.