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# Exciton dynamics in pentacene and tetracene studied using optical pump-probe spectroscopy

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**Abstract:** We present room temperature photoinduced reflection and transmission measurements in pentacene and tetracene single crystals using optical pump-probe spectroscopy. Singlet exciton recombination, singlet-triplet fission, excited singlet, and triplet state absorption is observed.

## 1. Introduction

Organic semiconductors are attracting much interest due to their strong potential for use in technological applications [1]. Charge carriers play a key role in such applications, but their nature (molecular excitons or semiconducting band carriers) is still not completely understood and remains controversial [2,3]. In the molecular exciton model the excited states are localized and the primary photoexcitations are excitons, which can dissociate into free polarons, while in the semiconductor band model, they are delocalized, and mobile polarons are created directly from free electron-hole pairs by the absorption of light. Ultrafast optical measurements are important in this regard as the dynamics of the photoexcitations can be temporally resolved, and pump-probe experiments have been widely used to help elucidate the excited state dynamics of singlets and triplets [4,5].

Here we present optical pump-probe measurements of photoinduced (PI) changes in the reflectivity ( $\Delta R/R$ ) and transmissivity ( $\Delta T/T$ ) of tetracene and pentacene single crystals, respectively. Tetracene and pentacene belong to the polyacene series of organic crystals which, in order of increasing molecular size, includes, naphthalene, anthracene, tetracene, and pentacene. The energy difference between the lowest singlet exciton and two lowest triplet excitons  $E(S_1) - 2E(T_1)$  is  $-1.3$  eV in naphthalene,  $-0.55$  eV in anthracene,  $-0.21$  eV in tetracene, and  $0.11$  eV in pentacene [4]. Therefore, in pentacene, the excitonic fission process from the lowest single exciton to a pair of lowest triplet excitons  $S_1 \rightarrow 2T_1$  is energetically allowed, while in tetracene the  $T_1$  level can only be populated by thermally activated fission with a thermal excitation energy greater than  $0.21$  eV. This process is strongly suppressed in naphthalene and anthracene. In these experiments we studied the photoexcited carrier relaxation dynamics in tetracene and pentacene as a function of probe photon energy aiming to elucidate the electronic structure and carrier dynamics in the singlet and triplet manifolds. In

our data we see a strong PI absorption peak in pentacene, which is much weaker in tetracene in agreement with the physics of the excitonic fission process. In addition, we infer from the broadness of the PI absorption band in both pentacene and tetracene that the final state in the triplet manifold is a band-like state.

High quality single crystals were grown in a flow of inert gas. The experiments utilized a commercial-based regeneratively amplified Ti:Al<sub>2</sub>O<sub>3</sub> laser system operating at 250 KHz producing nominally 10  $\mu$ J, sub-50 fs pulses at 1.5 eV. The samples were excited at 3.0 eV with an excitation fluence of  $\sim$ 100  $\mu$ J/cm<sup>2</sup>, and the PI changes in reflectivity (transmissivity) were measured over the range of probe photon energies from 0.6–2.5 eV using an optical parametric amplifier. The photon energy of the pump pulse was above the absorption band of  $\sim$ 1.9 eV in pentacene, and  $\sim$ 2.4 eV in tetracene. The approximate energy level diagrams for tetracene and pentacene are shown as insets to Fig. 1. Negative  $\Delta T/T$  is associated with PI absorption, and positive  $\Delta T/T$  is associated with PI bleaching. The thickness and the lower gap of the pentacene crystals complicated transmission measurements and the pentacene measurements were therefore obtained in reflection. It was however verified that  $\Delta R/R$  had the same sign as  $\Delta T/T$ .

## 2. Results and Discussion

Fig. 1 shows the dynamics of PI changes in the (a) transmissivity of tetracene and (b) reflectivity of pentacene as a function of time for several probe photon energies. In both compounds the dynamics consists of two contributions: an exponential decay component with decay time  $\tau \sim 100 \pm 20$  ps for tetracene and  $\tau \sim 0.7 \pm 0.2$  ps for pentacene, and a much longer lived contribution, manifested as an offset at times  $t \gg \tau$ . In tetracene, as Fig. 1(a) shows, at low and high photon energies the recovery is almost completed on a 100 ps timescale. This PI absorption can be associated with  $S_1 \rightarrow S_n$  transitions and indicates a large

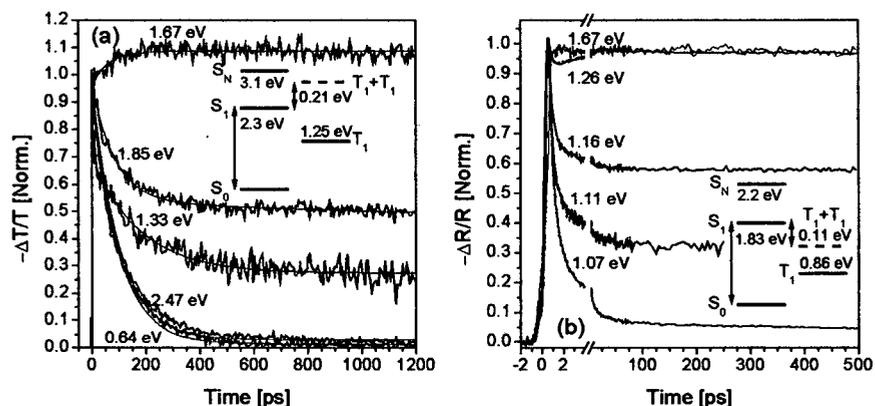


Fig. 1. Time-resolved PI change in tetracene single crystals versus pump-probe delay time at varies probe photon energies for (a) tetracene in transmission and (b) pentacene in reflection. The thickness and the lower gap of the pentacene crystals complicated transmission measurements.

singlet exciton population that recombines to the ground state. However, the long offset that is observed in the 1.33, 1.67, and 1.85 eV probe scans shows that some of the population is transferred to the triplet state. As Fig. 1(b) shows, in pentacene the dynamics are substantially different. In this case the  $S_1 \rightarrow 2T_1$  fission process occurs on a 1 ps timescale, and the majority of the  $S_1$  exciton population is rapidly transferred to the triplet manifold consistent with  $2E(T_1) < E(S_1)$ .

Fig. 2 shows the PI spectrum of the (a) transmissivity of tetracene and (b) reflectivity of pentacene at different time delays after photoexcitation. Both compounds display a broad long-lived ( $\gg 1$  ns) photoinduced absorption. In tetracene this feature is centered at approximately  $\sim 1.7$  eV, while in pentacene it is centered around  $\sim 1.4$  eV and is very pronounced. The long relaxation time suggest that the state being probed is the triplet state  $T_1$  (i.e.  $T_1 \rightarrow T_n$ ). The width of the PI absorption band suggests that the final state is a band-like state at 1.7

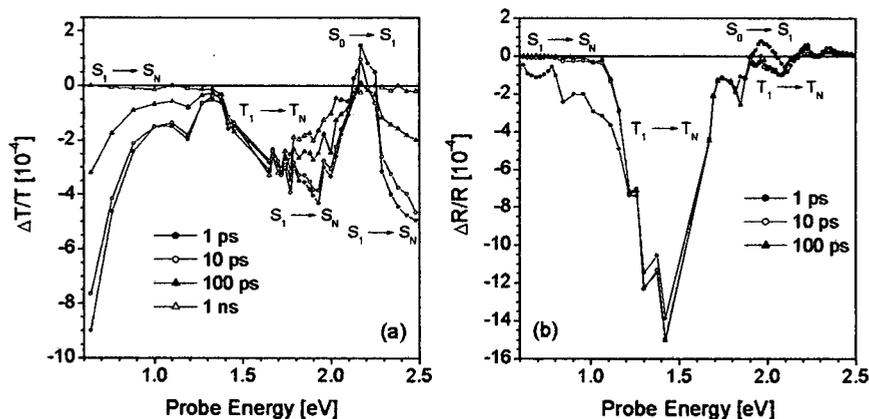


Fig. 2. (a) Transient  $\Delta T/T$  spectra at 1 ps, 10 ps, 100 ps, and 1 ns delay in tetracene. (b) Transient  $\Delta R/R$  spectra at 1 ps, 10 ps, and 100 ps delay in pentacene.

eV (1.4 eV) above the triplet state in tetracene (pentacene). This observation is consistent with the semiconductor band model [2,3]. Interestingly, we also note that the 1.7 eV (1.4 eV) PI absorption is very close to the energy difference between the  $T_1$  energy level and  $S_n$  of 1.85 eV (1.34 eV) for tetracene and (pentacene) as shown in the approximate energy level diagrams in Fig. 1. Further investigations into the origin of the observed features are currently being pursued.

## References

- 1 M.A. Baldo, M.E. Thompson, and S.R. Forrest, *Nature* **403**, 750 (2000).
- 2 F.A. Hegmann, *Physics in Canada* **59**, 127 (2003).
- 3 V.K. Thorsmølle, R.D. Averitt, X. Chi, D.J. Hilton, D.L. Smith, A.P. Ramirez, and A.J. Taylor, *Appl. Phys. Lett.* **84**, 891 (2004).

- 4 C. Jundt, G. Klein, B. Sipp, J. Le Moigne, M. Joucla, and A.A. Villaeys, Chem. Phys. Lett. **241**, 84 (1995).
- 5 C. Frolov, Ch. Klog, J.H. Schön, and B. Batlogg, Chem. Phys. Lett. **334**, 65 (2001).