

Charged photoexcitations in thiophene-based molecular semiconductors

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We applied the steady-state photomodulation spectroscopy to vacuum-deposited films of thiophene oligomers with controlled mesoscopic organization in order to understand the relation between structural order and charge photogeneration. We studied α,ω -dihexylsexithiophene films, which are highly ordered, and β,β' -dihexylsexithiophene films, which are amorphous. We observed pairlike excitations in the former (bipolarons and π -dimers), triplets and polarons in the latter. To explain the results we propose a topological dependent charge separation model in which both dimensionality and carrier mobility play a role. [S0163-1829(98)01035-2]

π -conjugated molecular semiconductors are very interesting materials that exhibit a wealth of quantum phenomena. In particular, thiophene oligomers (T_n) have attracted much attention because they are well-defined chemical systems and their conjugation length can be exactly controlled. Moreover, they can be easily functionalized, with different pendant groups to obtain soluble materials and have been used as active layers in FET (Ref. 1) and in LED.² While the photo-physics of oligothiophenes in solution is well understood,^{3,4} little is known regarding the electronic properties in the solid state. This is a serious obstacle to the improvement of organic thin-film devices based on these materials.

The properties of thin films are related both to the chemical structure of the single molecule, which forms the system, and to the way these molecules interact between each other. This opens attractive perspectives for controlling the material properties by molecular engineering. One way to control the structural organization of films is based on self-recognition created by a proper chemical modification of the molecular unit. In the case of sexithiophene (T_6), this approach has been used to produce materials that form films with different structural characteristics.

We have studied two dihexyl substituted sexithiophenes, namely, α,ω -dihexylsexithiophene (α,ω DHT₆), which forms highly ordered films, and nonregioregular substituted β,β' -dihexylsexithiophene (β DHT₆), which forms amorphous films.⁵ X-ray measurements by the θ - 2θ diffraction technique were carried out on thick α,ω DHT₆ films grown under exactly the same conditions used to produce our samples, and were reported in Ref. 5. α,ω DHT₆ films show that an important degree of crystallinity has been obtained as confirmed by the numerous high-order 00*l* (with even *l*) reflections, up to the 34th order.⁵ The data are consistent with a monoclinic arrangement comparable to the one attributed to unsubstituted T_6 , with β angle value of 11 1.3° and unit-

cell parameters $a=5.88$ Å, $b=7.88$ Å, and $c=71.2$ Å. α,ω DHT₆ molecules are closely packed in the herringbone geometry, with an average intermolecular distance of 5 Å. From the sharply resolved diffraction peaks the monolayer thickness could be estimated to be 35.5 Å. The different mechanical properties of the core conjugated system and its external pendants lead to segregation of the alkyl subunits, which form a buffer in between T_6 layers, giving the characteristic two-dimensional (2D) topology. The structural organization of the films, obtained by x-ray pole figure characterization, shows that only one spatial orientation is obtained: microcrystals stand on the substrate with their long axis perpendicular to the substrate plane.

The effect of substitution at the β position is to increase the intermolecular distances in one direction within the layer, leaving the possibility of a one-dimensional stacking. In our case, however, no clear structural organization could be deduced from x-ray analysis as a consequence of the nonregioregular substitution.

Both optical⁵ and transport properties⁶ are affected by the molecular organization. The absorption spectrum of β DHT₆ films shows a molecularlike Franck-Condon vibrational progression, with the 0-0 transition at 2.4 eV. By contrast the absorption spectrum of α,ω DHT₆ films shows a sharp and structureless peak at 3.6 eV which have been assigned to a molecular exciton. We note that the unsubstituted T_6 shows an absorption spectrum that is the combination of these two and it is understood as intermediate case. Conductivity and field effect mobility of α,ω DHT₆ are enhanced by almost two orders of magnitude with respect to T_6 and a substantial anisotropy is observed in favor of the in-plane direction because of the 2D topology. In β DHT₆ a strong decrease of conductivity is observed, confirming that there is a very little intermolecular coupling. The photoluminescence (PL) quantum efficiency remain high in β DHT₆ films, whereas it is

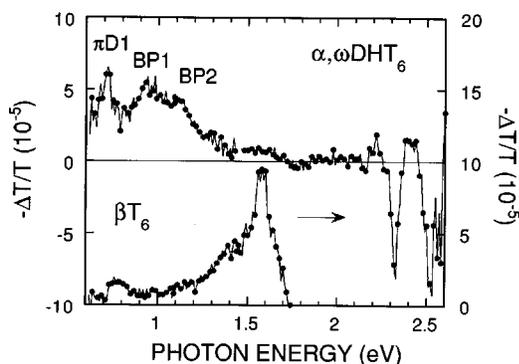


FIG. 1. PA spectra of $\alpha,\omega\text{DHT}_6$ ($\lambda_{\text{exc}}=363$ nm, laser intensity = 650 mW/cm^2) and βDHT_6 ($\lambda_{\text{exc}}=488$ nm, laser intensity = 80 mW/cm^2) measured at $T=77$ K and with $f_{\text{ch}}=20$ Hz.

strongly reduced in $\alpha,\omega\text{DHT}_6$ films. All of these observations show that $\alpha,\omega\text{DHT}_6$ and βDHT_6 are paradigmatic experimental systems: $\alpha,\omega\text{DHT}_6$ is a prototype 2D molecular semiconductor with large exciton bandwidth while βDHT_6 is a prototype of amorphous molecular materials.

The aim of this report is to investigate the effect of structural parameters, e.g., order, dimensionality, and intermolecular coupling, on charge photogeneration by applying the steady state photomodulation (PM) spectroscopy to βDHT_6 and $\alpha,\omega\text{DHT}_6$ films. Our results, compared to those of T_6 , show that charge photogeneration is enhanced in the ordered structure and that the double charged excitations are favored by the 2D topology and the high mobility.

The thiophene oligomers were synthesized according to a previously described procedure.⁶ Thin films were prepared by evaporation under reduced pressure of the powdered compound on glass substrates from highly purified materials that contained, after several sublimation cycles, a concentration of impurities $<10^{16}$ cm^{-3} . PM spectra were recorded using a homemade apparatus described in details elsewhere.⁷ Resonant photoexcitation (pump) was obtained from an Ar^+ laser at 363 and 488 nm for $\alpha,\omega\text{DHT}_6$ and βDHT_6 films, respectively. Mechanical modulation frequency of the pump beam (f_{ch}) was changed from 10 to 3 kHz and the sample temperature from 20 to 300 K. Photoinduced absorption (PA) spectra are obtained as normalized change in transmission, i.e., $\Delta T/T$, where ΔT and T are measured separately using the standard phase-sensitive lock-in technique. In spectral regions where photoinduced absorption and PL overlap, the PL spectrum is measured separately, blocking the probe, and a simple numerical subtraction of obtained data yields true ΔT changes.

The PA spectrum of $\alpha,\omega\text{DHT}_6$ films measured at 77 K, with a modulation frequency of 20 Hz and shown in Fig. 1, consists of a sharp band, πD1 at 0.7 eV, two broad PA bands at 0.95 eV (BP1) and at 1.1 eV (BP2) (where BP is bipolaron) and a strong oscillating pattern between 2 and 2.6 eV. The PA spectrum for βDHT_6 films, also shown in Fig. 1, is completely different: there is a prominent PA band peaked at 1.58 eV, which survives at room temperature; moreover, there is a shoulder apparently peaking at 1.4 eV and a weak PA band peaked at ~ 0.8 eV (the laser intensity was kept very low to reduce the spurious PL contribution). None of these structures survive in the out-of-phase measurements,

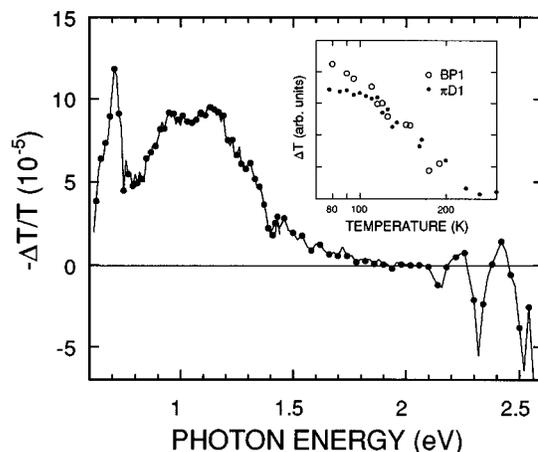


FIG. 2. PA spectrum of $\alpha,\omega\text{DHT}_6$ at $T=20$ K ($\lambda_{\text{exc}}=363$ nm, laser intensity = 650 mW/cm^2 , $f_{\text{ch}}=20$ Hz). Inset: temperature dependence of the PA signal measured at 0.75 eV (πD1) and at 0.95 eV (BP1).

indicating a rather short lifetime of the photoexcited species. Upon further cooling the $\alpha,\omega\text{DHT}_6$ film down to 20 K, the πD1 intensity increases by a factor of 2, and a shoulder at 1.3 eV and a small hump around 1.4 eV become apparent (Fig. 2). The full width at half maximum of πD1 is about 50 meV, the smallest value ever observed in π -conjugated linear systems. The inset of Fig. 2 shows the behavior of πD1 and BP1 versus temperature, pointing to a larger activation energy for πD1 . Raising the modulation frequency to 1 kHz at 77 K, the πD1 intensity is reduced by one order of magnitude, while BP1 and BP2 become one-third of the value at 20 Hz and dominate the spectrum (Fig. 3). The inset in Fig. 3 reports the frequency-dependent measurements for characteristic probe energies, providing information on the lifetime of the photoexcitations. It is clear that πD1 never reaches a plateau in the measured frequency range, and thus has a lifetime longer than 0.1 s, whereas BP1 is frequency independent below 0.8 kHz, suggesting a lifetime of about 1 ms.⁸ Figure 4 shows PA versus excitation intensity at 0.7 and 1.15 eV in the range 40 mW/cm^2 – 1 W/cm^2 . The observed depen-

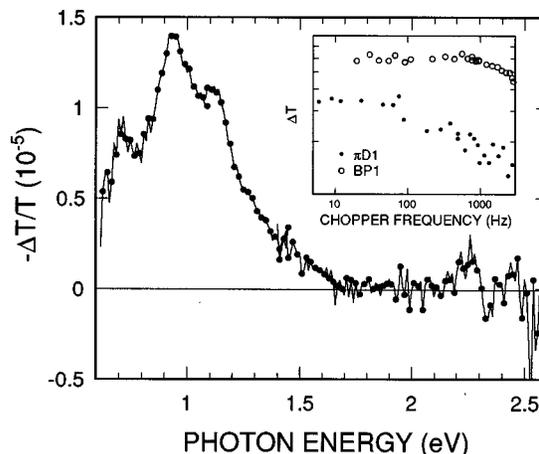


FIG. 3. PA spectrum of $\alpha,\omega\text{DHT}_6$ measured with $f_{\text{ch}}=1$ kHz ($T=77$ K, $\lambda_{\text{exc}}=363$ nm, laser intensity = 650 mW/cm^2). Inset: frequency dependence of the PA signal measured at 0.75 eV (πD1) and at 0.95 eV (BP1).

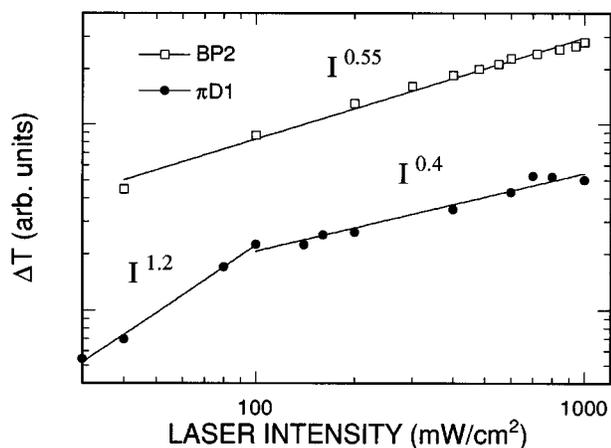


FIG. 4. Laser intensity dependence of the PA signal measured at 0.75 eV (π D1) and at 1.15 eV (BP2) ($T=77$ K, $\lambda_{\text{exc}}=488$ nm, $f_{\text{ch}}=230$ Hz).

dence is, in principle, related to the kinetics of formation and recombination of the photoexcited species. Since long-lived excited states are stabilized by trapping to defects, even when intrinsic in origin, saturation of PA has to be taken into account. For π D1, we consider that the sublinear behavior for excitation power above 120 mW/cm² is due to this latter effect, while the superlinear ($I^{1.2}$) dependence observed for lower excitation reflects the true dynamics. On the contrary both BP1 and BP2 show a sublinear dependence in the whole measured range, close to the square root ($I^{0.55}$), which probably describes the real population kinetics.

In order to discuss our results it is useful to briefly summarize which kind of photoexcitations can be generated in T_6 polycrystalline films and which are their spectroscopic features. Single (polaron or radical cation) and double (bipolaron or radical dication) charged excited states show subgap transition energies, at 0.75 eV (P_1) and 1.58 eV (P_2) for polarons and 1.05 eV (BP) for bipolarons respectively.⁹ The PA bands display vibronic replicas of the main backbone modes (about 1200 cm⁻¹) indicating the tightly bound intramolecular character of the states. The two species are usually observed simultaneously in the photoexcited films.¹⁰ Furthermore, another excitation can occur, namely, π -dimers.¹¹ These are diamagnetic excitations consisting of like-charged interacting ions located on neighboring sites. In π -dimers the optical transitions of the composing polarons (P_1 and P_2) are shifted to higher energies (π D2 and π D3), while a new prominent absorption band (π D1), namely, the charge-transfer transition, appears at lower energy¹² (see the energetic level scheme shown in Fig. 5). Finally triplet-

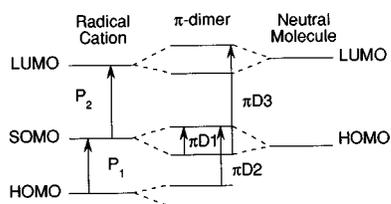


FIG. 5. Energetic level scheme of molecular, radical cations, and π -dimer states.

triplet PA transitions have also been identified in T_6 films at very low temperature,⁴ associated with a subgap PA band at about 1.5 eV.

The first remark relevant to our discussion is that the chemical substitution to the T_6 molecule does not affect directly the main π -electron system. This is demonstrated by the fact that differently substituted molecules dissolved in solution display the same behavior except for the effective conjugation length, which is, however, controlled by the molecular conformation.¹³ Due to the steric hindrance of the substituents a deviation from planarity may take place, reducing the π -electron delocalization. It is this conformational effect that modulates the optical gap and affects the relaxation process. Generally speaking, however, both α,ω DHT₆ and β DHT₆ in solution have similar properties: they act as strong chromophores, they show a rather large PL quantum yield and the main excited state deactivation channel is intersystem crossing to the triplet manifold.⁵ Based on these observations we conclude that the striking difference between PA spectra of α,ω DHT₆ and β DHT₆ have to be ascribed to solid-state effects.

First we will discuss β DHT₆. The PA spectrum is similar to that observed for unsubstituted T_n in solution. The main PA band at 1.58 eV can be assigned to triplet-triplet transitions.⁴ The only signature of solid-state effects are the weak PA bands at 0.8 and 1.43 eV, which correlate with P_1 and P_2 of T_6 , and could be assigned to polarons. The coexistence of charged and neutral species and the high intensity of the triplet-triplet transition peak is a common feature of quasi-isolated molecules in the solid state and have been also detected in polydiacetylene samples.¹⁴ So PA spectra confirm that β DHT₆ films are basically made of noninteracting units. In this case the initial excited state is a completely local excitation (on one molecule) and the probability of charge separation is reduced.

In the case of α,ω DHT₆ the photoexcitations scenario is somewhat more involved. The PA transitions at 0.95 and 1.1 eV can be attributed to bipolarons, the latter being a vibronic replica of the former, but we have not detected any features that could be unambiguously related to the presence of polarons. As a matter of fact, the very sharp PA band at 0.7 eV does not correspond to a similar feature at 1.5 eV and cannot be associated with P_1 . One possibility is that this band is due to the charge resonance transition in photoinduced π -dimers with a very large hybridization energy. The formation of π -dimers requires a strong π overlap and then a good intermolecular order in which the molecules may face each other. Two more PA transitions are expected for π -dimers: π D2 and π D3. With reference to the energy level scheme in Fig. 5 we can estimate $\hbar\omega_{\pi D1}=0.7$ eV, $1\text{ eV}\leq\hbar\omega_{\pi D2}\leq 1.4$ eV and $\hbar\omega_{\pi D3}\leq 2.3$ eV. So π D2 can be identified with the shoulder at 1.3 eV evident at low T , when π D1 actually dominates the PA spectrum. π D2 overlaps with the transition at 1.1 eV, causing a different behavior of the two bands (BP1 and BP2) that we attribute to bipolarons. In the high-energy region things are more involved, due to the rather strong oscillating pattern probably superimposed on π D3. The oscillations intensity dependence on the chopper frequency f_{ch} can be fitted using the decay law, $1/f_{\text{ch}}$, while the dependence on the pump intensity is linear and does not show any saturation effect, which is consistent with an assignment to

thermal modulation of the optical gap. Then a clue of π D3 presence comes from the comparison of the PA spectra at 77 and 20 K. At low temperature the PA intensity is almost doubled in the whole spectral region, except above 2 eV, where it is reduced. This maybe due to the competition with π D3, because, in principle, thermal effects should not decrease with temperature. Based on the previous discussion we propose to interpret the PA spectrum of α,ω DHT₆ in terms of *paired* excitations: bipolarons and π -dimers.

Our results can be further analyzed within a topological dependent charge separation and recombination model in which both dimensionality and mobility play a role. It has been proposed that charge photogeneration in thiophenes occurs via an intermediate charge-transfer (CT) state which is formed at early times.¹⁵ The CT excitons get then ionized at defects or impurities (e.g., oxygen) injecting a positive charge carrier.¹⁶ In α,ω DHT₆ the generated radicals propagate in the 2D layer. The two main decay channels for the highly mobile radical cations should be (1) collision with another cation forming a doubly charged state (either bipo-

larons or π -dimers), or (2) backtransfer at a negative impurity and then recombination to the ground state. In the pure 2D case the lack of interlayer coupling hampers the generation of single charge species. In T_6 disorder induced trapping and non-negligible interlayer coupling allow us to generate long-lived polarons that can escape geminate recombination. In competition with this mechanism collisions of likely charged radicals lead to the formation of bipolarons. Finally, in the case of β DHT₆ the initial radicals can only diffuse along the one-dimensional stack and then they cannot escape geminate recombination. Weak intermolecular hopping across the side chain or to the adjacent layer is responsible for the small fraction of photoinduced polarons. The fate of most of the excitations is that of localized molecular states: decay by radiative recombination or intersystem crossing to the triplet.

The reported data show that the photogeneration of charged states in substituted thiophene oligomers is related to the degree of order of the sample, more than to the type of the side group.

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