

Emission properties of *para*-hexaphenyl polycrystalline films

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The emission properties of *para*-hexaphenyl polycrystalline films are investigated by combining time-resolved photoluminescence and pump-probe measurements with site-selective spectroscopy. Photoinduced absorption, gain, and photoluminescence exhibit the same temporal behavior, showing that the same emitting species are involved. The photoluminescence decay is relatively long, featuring a lifetime of 400 ± 10 ps at 300 K. Absorption and photoluminescence excitation profiles, as well as the relaxation processes and the photoinduced dynamics, can be rationalized assuming that photoexcitations are intramolecular species. Dichroic and site-selective photoluminescence measurements point to an important short-range orientational and energetic disorder. Both kinds of disorder do not favor the molecular exciton coupling (H aggregates), and this agrees with the high external photoluminescence quantum yield 0.3 of *para*-hexaphenyl in the solid state. [S0163-1829(97)09440-X]

I. INTRODUCTION

The six membered oligomer of poly(*para*-phenylene), namely *para*-hexaphenyl (PHP), is a very interesting material which has been successfully used as a highly efficient blue-light emitting layer in electroluminescent devices.¹ A fundamental advantage of the bright PHP blue emission light is the efficient down conversion into green and red, which has permitted the realization of multicolor organic light emitting devices.² Homogeneous thin films can be prepared by evaporation on different substrates and, depending on the evaporation conditions, different degrees of crystallinity and molecular orientation can easily be obtained.³ These properties are very attractive for fabrication of color flat panel displays, so that a complete optical characterization of *para*-hexaphenyl is particularly needed. Furthermore, the well defined conjugation length and chemical structure of *para*-hexaphenyl may allow us to better understand the physical properties of the parent poly(*para*-phenylene), which is nowadays widely investigated together with its derivatives based on copolymers and ladderpolymers.⁴

Intermolecular excited-state interactions can take place in organic materials, leading to different excited species, e.g., Frenkel excitons, dimers, etc. In particular, the molecular organization within polycrystalline films of π -conjugated linear oligomers can favor the formation of nonradiative excitons (H aggregates), as suggested for oligothiophene films.⁵⁻⁷ The existence of such "dark" excitons in phenylene-based materials is then critical for their exploitation in light emitting devices and lasers. In spite of its fundamental character, this issue is not yet understood.

Fundamental optical properties of PHP, such as radiative recombinations, are still unexplored. Measurements of pho-

toluminescence (PL) in conjugated polymers allow us to reach important and direct information on the radiative and nonradiative decay pathways.⁸ In this paper, we report steady-state and picosecond time-resolved PL measurements in *para*-hexaphenyl polycrystalline films to study photoexcitation formation and decay. We compare the transient PL with transient photoinduced absorption (PA) and stimulated emission (SE), and we give a comprehensive picture of the oligomer photophysics.

II. EXPERIMENT

Para-hexaphenyl is up to now the longest oligophenyl synthesized in a very pure state.⁹ Highly purified PHP was evaporated in high vacuum ($< 10^{-6}$ mbar) onto sapphire kept at room temperature, obtaining PHP polycrystalline layers a few 1000 Å thick. X-ray studies indicate that crystallites with arbitrary orientation are grown.

Femtosecond pump and probe experiments were performed using a TiAlO₃ laser system with chirped pulse amplification, delivering pulses of 150-fs duration. The details of the setup are described elsewhere.¹⁰ The samples, kept at room temperature, were pumped by pulses at 3.2 eV with energy ranging from 5 nJ to 130 nJ (excitation density from 3×10^{13} photons/cm² to 8×10^{14} photons/cm²) and 1 kHz repetition rate.

Spontaneous emission was excited by the fourth harmonic of a pulse-compressed Nd:Yag laser delivering 4-ps-long pulses, or by the second harmonic of a synchronously pumped dye-laser delivering 0.5-ps-long pulses. The excitation density was 10^{10} photons/cm². Spectral resolution was obtained by means of spectral filters or through a monochromator. Temporal dispersion of the signal was achieved

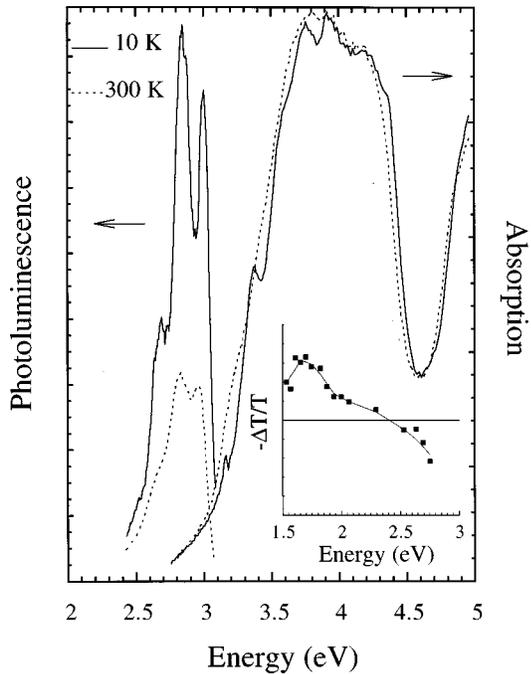


FIG. 1. Room (dashed lines) and low-temperature (continuous lines) absorption and photoluminescence emission spectra of *para*-hexaphenyl film. Inset: change of the probe beam transmission at delay of 200 fs after photoexcitation.

through a Hamamatsu optical sampling oscilloscope, which combines a high time resolution (≈ 20 ps) with a high dynamical range. For the low-temperature measurements, the sample was mounted in a cold finger cryostat.

The steady-state PL spectra were recorded upon excitation with the second harmonic of the dye laser. Excitation energies ranging from 3.01 to 3.3 eV were used.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Steady-state measurements

In Fig. 1, we report the absorption spectrum and the steady-state photoluminescence at 300 and 10 K. The absorption curves show a broad absorption band centered near 3.8 eV. The bandwidth is about 1 eV and no vibronic fine structure is resolvable at room temperature. At $T=10$ K some weak features are superimposed on the large absorption band.

While the absorption spectrum is poorly structured even at low temperature, the PL spectra shown in Fig. 1 consists of a main band followed by a vibronic progression which becomes much more evident when temperature is lowered. At 10 K there are three structures centered at 2.67, 2.84, and 3 eV, which are redshifted by about 30 meV at 300 K. The absorption maximum and the highest-energy luminescence peak are separated by about 0.8 eV.

In conjugated polymers, most of the inhomogeneous broadening of the optical absorption comes from the conjugation length distribution.^{11–13} On the other hand, molecular crystals such as PHP films possess well defined oligomer lengths. The large broadening of the absorption spectrum may be mainly ascribed to conformational disorder, i.e., variety of oligomer geometrical arrangements due to the tor-

sional degree of freedom of adjacent rings. In the case of shorter oligomers biphenyl and *p*-terphenyl, oligothiophenes, and oligophenylenevinyls in solution, conformational disorder is responsible for the large absorption bandwidth (up to 0.7 eV). Dynamical effects like conformational mobility (ring libration) and planarization of the excited state lead to the observed deviation from the mirror image rule between absorption and luminescence spectra at room temperature.^{6,14–16} By cooling slowly the solution, well resolved vibrational progressions have been shown to appear both in the absorption and fluorescence spectra, revealing mirror image, and vanishing Stokes shift.^{5,6,17} In polycrystalline films, such as PHP, conformational disorder persists even at low temperature. This points to the minor role of dynamical effects, such as conformational mobility which would be quenched at low temperature, and supports the presence of important static disorder. Different geometrical arrangements of the molecules could be caused by different local environments. Finally, a further contribution to the PHP broad absorption band could come from short-axis polarized transitions,¹⁸ which are expected at energies higher than the ones polarized along the long axis.

The PL quantum yield of our *para*-hexaphenyl films is 0.30 ± 0.03 at room temperature,¹⁹ much higher than for oligothiophene and oligophenylenevinylene films (10^{-3} – 10^{-2} and <0.1 , respectively^{6,20}). This indicates that the H-aggregate exciton model, successfully invoked for oligothiophene and oligophenylenevinylene films to account for the absorption line shape and the low luminescence quantum yield,^{5–7} does not hold in PHP. In order to investigate the intermolecular organization, we have performed steady-state polarized luminescence measurements by detecting the PL intensity emitted with polarization parallel to the incoming laser, I_{\parallel} , and with polarization perpendicular to the laser, I_{\perp} . We have found that the cw-photoluminescence depolarization ratio $\rho = I_{\parallel}/I_{\perp}$ is 1.3 ± 0.1 for all the emission energies (for a film constituted by randomly oriented domains, the upper limit is $\rho=3$). The low luminescence anisotropy implies that absorbing and emitting molecules are differently aligned.

The influence of disorder on the emission and relaxation processes has been explored by site-selective photoluminescence spectroscopy. Measurements have been performed by detecting the photoluminescence spectra at 10 K with the excitation energy ranging from 3.3 eV down to the tail of the absorption band. A number of these PL curves, vertically displaced for clarity, are shown in Fig. 2 (for some spectra the excitation beam partially overlaps the PL in the high-energy side). Two features are evident: (i) the spectra shift to lower energies and become much better resolved as the excitation energy moves into the absorption tail; (ii) the spectra do not change when the excitation energy is sufficiently high. These results are summarized in the inset of Fig. 2, which reports the spectral position of the three PL peaks as a function of the excitation energy. A “localization energy” $E_m \approx 3.1$ eV in the tail of the absorption band can be defined, below which the emission is quasisonant with the laser energy. For excitation energies greater than E_m the emission spectrum is independent of excitation.

Our findings on the localization threshold E_m are similar to those reported for conjugated polymer films,^{11,21,22} and

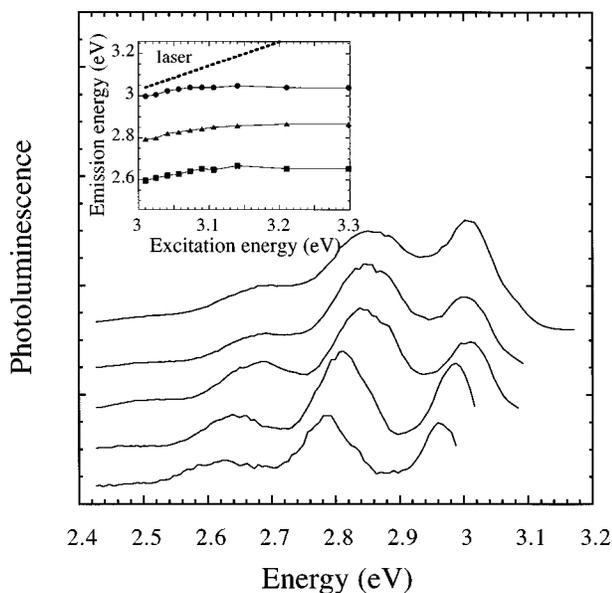


FIG. 2. Photoluminescence spectra excited at different energies ($T=10$ K). From the top to the bottom, the excitation energy is 3.3, 3.21, 3.14, 3.04, and 3.01 eV. Spectra are vertically displaced for clarity. The inset shows the peak energies of the 0-0, 0-1, and 0-2 vibronic emissions versus excitation energy.

can be rationalized assuming that photoexcitations undergo an incoherent motion (spectral diffusion) within an inhomogeneously broadened density of energy states introduced by disorder. If excited above E_m , they release part of their energy by relaxation to the lowest-energy vibrational level and by spectral diffusion. If excited below E_m , spectral diffusion is considerably inhibited, because adjacent sites with lower energies are no more available within the lifetime of the excited species. Intramolecular geometrical relaxation of the emitting chromophores causes the small shift (<40 meV) between excitation and emission.

The molecular nature of the emission processes satisfactorily describes the PL blueshift at low temperatures found in Fig. 1. It has been shown that in *p*-terphenyl and quaterphenyl crystals the central phenyl rings of the molecules librate in a double-well potential whose barrier is very low (about 0.025 eV in terphenyl).²³ At room temperature molecules are statistically planar.^{23–25} On cooling the crystals, the central rings are stabilized in one of the two valleys, showing a torsion angle of about 20°. Results in Fig. 1 therefore suggest a similar behavior in hexaphenyl, since a defined nonplanar geometry at low temperature agrees with an increase of the $\pi-\pi^*$ gap. Due to a large inhomogeneous broadening, this blueshift is not evident in the absorption spectrum.

B. Time-resolved measurements

In the inset of Fig. 1, the relative change of the probe beam transmission, $-\Delta T/T$ at delay time of 200 fs upon photoexcitation is shown. The spectrum presents a positive sign (i.e., an increase of the transmitted probe intensity) for probe beam quantum energies greater than 2.5 eV. In cw-photoluminescence measurements we detect emission in this spectral region, while no significant ground-state absorption is measured, indicating that positive $\Delta T/T$ is not due to photobleaching of absorptive transitions but to optical gain.

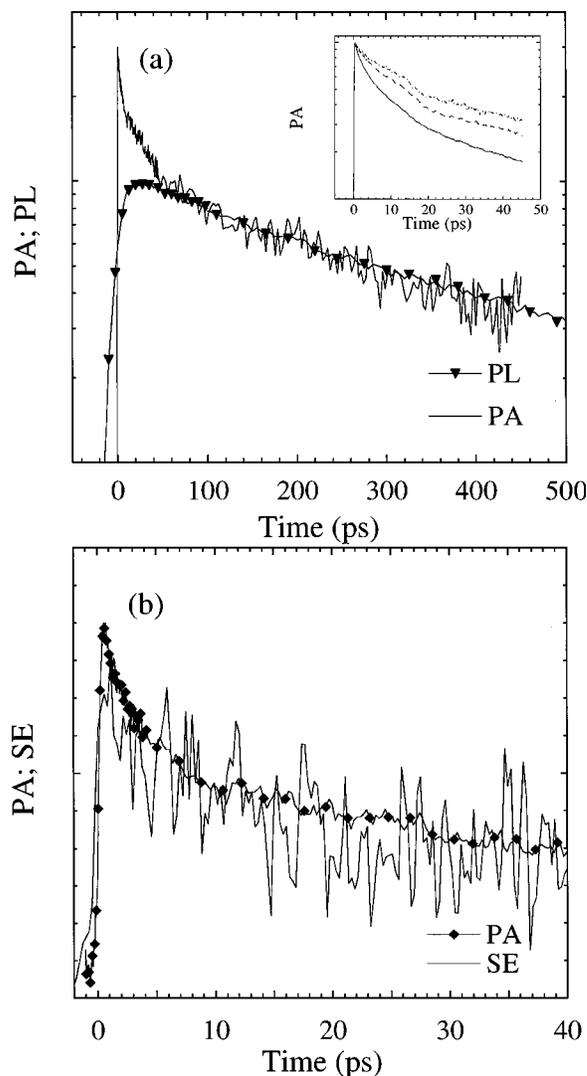


FIG. 3. (a) Room temperature transient dynamics of the spectrally integrated PL compared with PA detected at 1.65 eV. Inset: PA decay detected at 1.65 eV for different excitation density. From the top to the bottom: 3×10^{13} photons/cm², and 8×10^{13} photons/cm², and 8×10^{14} photons/cm². (b) Room temperature stimulated emission dynamics at 2.7 eV compared with PA at 1.65 eV.

Figure 3 compares transient photoinduced absorption, gain, and spectrally integrated photoluminescence at room temperature. The excitation energies are 3.2 eV for PA and gain, and 3.3 eV for PL. The PL decay shown in Fig. 3(a) has lifetime $\tau_{PL}=400 \pm 10$ ps, whereas a biexponential decay with time constants of 29 ± 5 and 400 ± 30 ps describes the PA detected at 1.65 eV. PA is faster than PL below 40 ps, while from 40 to 400 ps PL and PA dynamics coincide. While affected by relevant noise, the gain curve in Fig. 3(b) approximately follows the PA.

The initial faster decay of PA and gain with respect to PL, as measured by the fs system, is accounted for by bimolecular singlet annihilation caused by the high excitation intensity, which is 3–4 orders of magnitude greater than in PL measurements. This is demonstrated in the inset of Fig. 3(a), where the dependence of the recombination rate on excitation density is clearly observed.

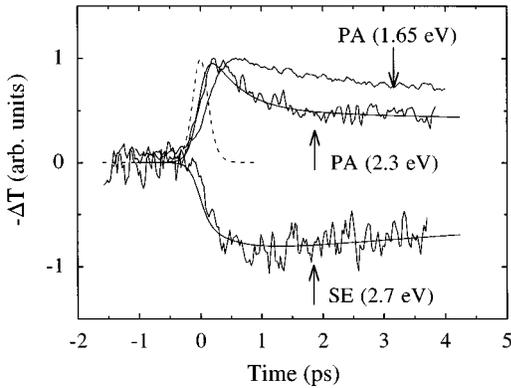


FIG. 4. ΔT dynamics excited at 3.2 eV and detected at different energies ($T=300$ K). The cross-correlation of the pump-probe setup is also shown (dashed curve). Smooth curves are calculated as explained in the text.

The results reported in Fig. 3 support the hypothesis that at early times following the photoexcitation the same species, with *intrachain* character, are involved in emission and absorption. The gain at 2.7 eV can be ascribed to probe amplification by stimulated emission (SE) of the excitations which are also responsible for PA and PL. The photoinduced absorption being related to emissive species, we conclude that even if chain aggregation could be envisaged in our films, mechanisms yielding nonradiative *interchain* excitations²⁶ are not efficient.

We have investigated the PL dynamics both at 10 and 300 K as a function of the detection energy. Scanning the emission energy from 2.4 to 3 eV results in similar PL traces. τ_{PL} does not change for all the emission energies. Energy migration of the photoexcitations should lead to a transient spectral shift of the emission which is not evident in the time domain of our PL data, suggesting that spectral diffusion occurs at shorter times.

Figure 4 shows that PA decay at 2.3 eV, i.e., close to the energy where the $-\Delta T/T$ spectrum at delay of 200 fs changes from negative to positive, is faster than the typical decays observed throughout the entire investigated range. Contributions of both photoabsorption and emission processes are expected in proximity of this spectral position, so the PA ultrafast decay could be attributed to the formation time of the stimulated emission. By fitting the curve at 2.3 eV, we find that this decay time is ≈ 500 fs. We have calculated the stimulated emission trace using this formation time and taking into account for the cross-correlation function between pump and probe beams. The results are consistent with the experimental data. We assign the fast component to intramolecular vibrational redistribution of the excited state, and we believe that the true spectral diffusion time is masked in the gain data by the bimolecular recombination.

In time-resolved polarized photoluminescence, the depolarization ratio reaches 1.3 within the time resolution of our apparatus (≈ 20 ps) and does not change for longer times. Transient PA measurements at 1.65 eV with pump and probe parallel and pump and probe perpendicular are shown up to 40 ps in Figure 5. The inset reports the decay of the photoinduced absorption depolarization ratio $\rho = \Delta T_{\parallel} / \Delta T_{\perp}$. Theoretically, the depolarization ratio in a randomly oriented ensemble of emitters should be 3 initially. On the other hand,

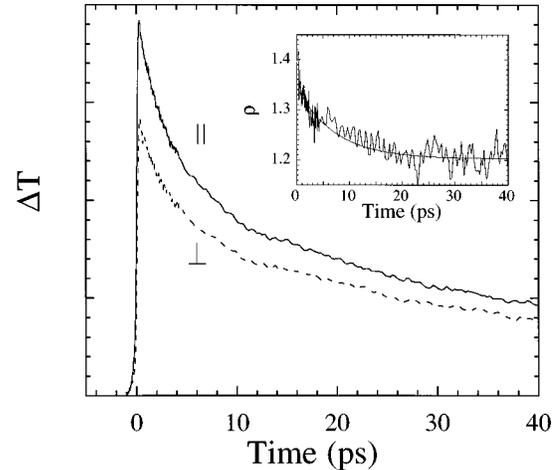


FIG. 5. Decay of ΔT at 1.65 eV measured with probe parallel and perpendicular to pump, respectively. Inset: dynamics of the photoinduced absorption anisotropy $\rho = \Delta T_{\parallel} / \Delta T_{\perp}$. The continuous line represents the best fit to the experimental data as explained in the text.

we find 1.36 ± 0.02 within the temporal resolution (≈ 200 fs). We detect a slower decay (≈ 7 ps), followed by a plateau where $\rho \approx 1.2$, i.e., very close to the value found in PL experiments. The dichroic measurements show that the correlation length of orientational disorder is short, for instance in comparison with hexathiophene polycrystalline films, where $\rho \approx 2$ at 500 ps and 1.5 ns is needed to lose completely polarization memory.²⁷

Further remarks can be made on the basis of the time-resolved results. If radiative and nonradiative decays are monomolecular processes, the quantum yield for emissive species formation, η , is related to the PL efficiency, ϕ , by $\phi = \eta \tau_{\text{PL}} / \tau_r$.²⁸ Here τ_{PL} and τ_r are the measured lifetime of the luminescence and the natural radiative lifetime, respectively. The measured PL efficiency $\phi = 0.30$ therefore provides the lower limit on η . Radiative lifetimes of phenylene-based oligomers are reported in Refs. 6 and 29 for oligophenylenevinylens (τ_r ranges from 1.28 ns to 0.92 ns by passing from the one-unit to the five-units oligomer), and terphenyl ($\tau_r = 1$ ns), respectively. Similarly, low defect poly(*para*-phenylene)-ladderpolymers in solution have $\tau_r = 1$ ns.³⁰ As a first approximation it seems then reasonable to take τ_r about 1 ns for PHP, obtaining $\eta = 0.7$. This rough estimate suggests that in PHP films generation of intrachain photoexcitations is strongly favored.

IV. CONCLUSIONS

The obtained results can be understood based on the following picture. *Para*-hexaphenyl polycrystalline films are an ensemble of weakly interacting molecules and display mainly intramolecular optical properties. The features typical of the exciton coupling have not been observed. In particular, the lowest-energy emission, which is completely forbidden in H aggregates, is permitted, giving rise to the high photoluminescence quantum yield 0.3 of PHP in the solid state. Moreover, site-selective photoluminescence measurements indicate spectral relaxation of the photoexcitations within an inhomogeneously broadened density of states.

The characteristic time scales of the main photophysical

processes have been determined. After photoexcitation, thermalization via vibrational intramolecular redistribution occurs in about 500 fs. The depolarization ratio ρ exhibits a very fast decay (200 fs) and a longer one of about 7 ps. Since polarization-memory loss in condensed systems is due to excited state migration to differently oriented molecules, the temporal behavior of ρ implies that the orientational disorder in PHP has a short correlation length, suggesting the existence of small quasicrystalline domains with different orientations. Once the excited state is fully depolarized, further migration would not lead to a change of ρ . However, the

observation of the negligible spectral shift of the PL indicates that diffusion is indeed extremely slow at times longer than 40 ps.

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