Transient photoluminescence of *para*-hexaphenyl layers

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Para-hexaphenyl layers exhibit dramatic changes in their steady-state optical and transient photoluminescence (PL) responses when they are grown with different orientations. For a film in which molecules stand perpendicular to the substrate, radiative recombination of intramolecular Frenkel singlet excitons occurs in less than 2 ps. If the layer is grown with molecules lying parallel to the substrate, short-lived and long-lived PL decay components are found. The former is best reproduced with an annihilation rate equation, characteristic of mobile excitons relaxing in 1 ns while the latter, spectrally redshifted, confirms intermolecular exciton migration.

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Materials based on the six-phenyl-ring *para*-hexaphenyl molecule (PHP or Φ_6) are of considerable interest for application in blue-light-emitting electroluminescent devices.[1] Nowadays, it has become common practice to grow layers with PHP molecules lying parallel or standing perpendicular to various substrate surfaces.[2–4] The structural properties of these layers are known to strongly influence their optical performances but the relations between layer morphologies and exciton phenomena are still to be explored.[5] In particular, little experimental data are available on their ultrafast emissive properties and most results concerning exciton formation and transport were obtained from transient photoabsorption (PA) experiments.[6] One study focused at the picosecond photoluminescence (PL) of a lying, textured PHP film that was interpreted to arise from localized excitons trapped around radiative defects, but no comparison was made with other layer morphologies.[7] In addition, several PL studies of electroluminescent polymers have clearly demonstrated that effective conjugation length, and chain alignment sharply control the exciton evolution in these systems.[8] It is therefore highly desirable to seek out more clues concerning exciton dynamics in oligomer systems in which chain length is actually fixed.

In this paper we investigate the steady-state optical and transient photoluminescence (PL) responses of a polycrystalline disordered lying PHP film 1 grown at ambient temperature, in which the long *c* axis of the molecules is parallel to the substrate and of a highly oriented, standing PHP film 2 grown at 440 K, in which *c* is almost perpendicular to the support. The respective thicknesses are 300 nm and 170 nm. Our data testify that exciton dynamics depends drastically on film morphologies.

The two samples were probed by x-ray diffraction and both belong to space group $P2_1/a$ with $a=0.808$ nm, $b=0.559$ nm, $c=2.63$ nm, $\beta=98°$. In contrast to samples studied in Ref. 7 film 1 has no preferential orientation in the substrate plane. The average size of the microcrystalline ordered domains was estimated from scanning electron microscopy to be $R\approx 4-12$ μm and $100-300$ nm in the standing and lying film, respectively.[2,3]

UV-visible absorption was obtained at 4 K with a Varian-Cary 2300 spectrophotometer working in transmission mode. Continuous-wave (cw) PL was excited at 3.7 eV at room temperature and recorded with a fluorometer. Time-resolved experiments were carried out at room temperature using a high time resolution (1.5-ps) streak camera and 1 ps frequency-doubled laser pulses at 4.22 eV.[9] The beam diameter onto the samples was about 200 μm. The laser energy E_d was tuned between 0.8- and 35-μJ per pulse.

Optical absorption results are shown in Fig. 1. We attribute the broad absorption envelope of the lying film 1 at about 3.87 eV (320 nm) to noninteracting molecules while the superimposed vibronic structure is indicative of exciton states generated by the crystalline phase. In contrast, the absorption of the standing film 2 blueshifts and monotonously decreases between 6.2 eV (200 nm) and 3.1 eV (400 nm) with two weak structures at 4.4-eV (282-nm) and 3.87-eV (320-nm) signaling exciton bands. For both films, the PL pump wavelengths reach the exciton bands. Note that these absorption spectra confirm the orientational anisotropy of the films.[10] The cw-PL experiments reveal strong blue emission with vibronic structures (Fig. 1, peaks A–D). In film 1, we assign peak B in luminescence to the free-exciton band (0-0 transition) and find a Stokes shift of about 1 eV. The mean

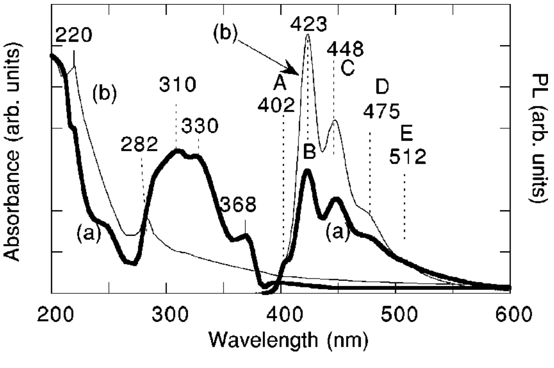

FIG. 1. Optical absorption at 4 K and room-temperature cw-photoluminescence of *para*-hexaphenyl: (a) lying film 1, bold lines; (b) standing film 2, thin lines.

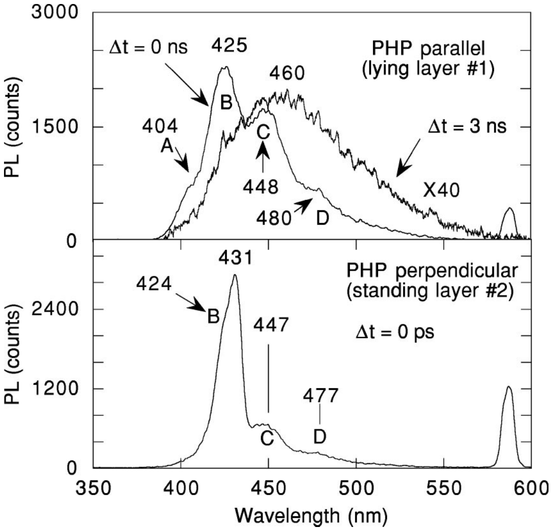

FIG. 2. Time-resolved photoluminescence of *para*-hexaphenyl thin films taken just after the 4.22 eV excitation pulse and at longer time. Upper panel: lying film 1, lower panel: standing film 2. The peak at 588 nm corresponds to the laser signal and the energy is $20-\mu$J per pulse.

vibronic progression of 0.16 eV in absorption and luminescence spectra matches the Raman transition of the symmetric inter-ring $C-C$ stretching mode at about 1280 cm^{-1}. According to previous studies on luminescent polymers and oligomers, this vibronic structure may be ascribed to a strong electron-vibration coupling that favors the formation of polaron-excitons during the optical excitation of the molecules.[11–13]

Time-resolved PL responses of the nonoriented lying film 1 reveal two spectral time-dependent PL components (Fig. 2, upper panel). The short-lived PL profile recorded at time delay $\Delta t \approx 0$ is similar to that obtained in the steady state at room temperature with well-resolved vibronic structure (peaks $A-D$). Interestingly, we find a delayed weak fluorescence exemplified by the slow component taken at $\Delta t = 3$ ns whose broad, featureless emission redshifts by $\Delta E_{em} = 220$ meV. Spectral transients extracted from the luminescence map show that vibronic coupling is indeed suppressed after 1 ns. In the streak image of the oriented-textured standing film 2, the zero-time delay spectrum exhibits also vibronic features (Fig. 2, lower panel). We observe a peak at 2.87 eV (431 nm) of unknown origin perhaps signaling stimulated emission. For $\Delta t > 2$ ps, the PL is entirely suppressed. Therefore, due to a much longer phonon relaxation time in film 1 (of the order of 1 ns) as compared to that of film 2 (less than 2 ps), we probably see here signatures for a coherent motion of intramolecular excitons in film 1. For both PHP films, there is a non-negligible Stokes shift comparatively to luminescent polymers (0.1 eV–0.3 eV) and relatively large subband widths (0.17 eV).[11] The Stokes shift is caused by the different conformations of the phenyl rings in the ground and in the excited state. In the ground state, the rings adopt a tilted geometry with a torsional angle of 20° between them, whereas in the excited state they tend to be more coplanar with a quinoid electronic structure.[14]

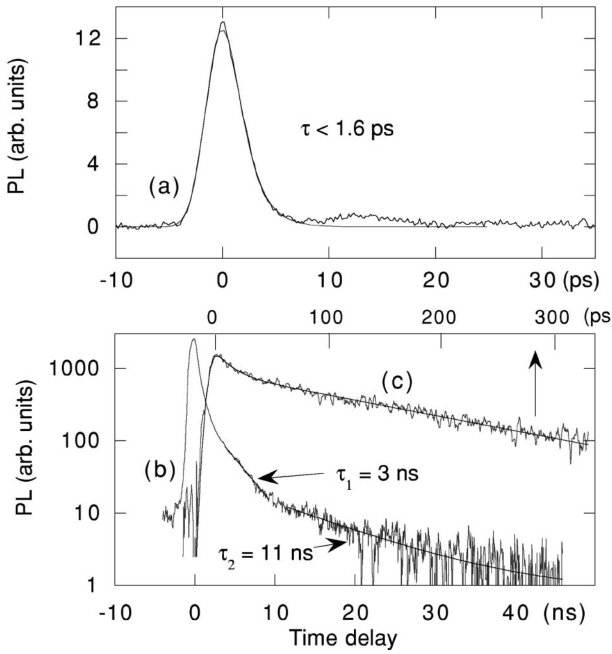

FIG. 3. Kinetics of photoluminescence decays (20-μJ per pulse). (a) Standing layer 2. The solid line is a monoexponential fit. The replica at ≈ 12 ps comes from a reflection on the faces of the film substrate. (b), (c) Lying film 1 against ns (ps) time scales.

The temporal response of 2 is displayed in Fig. 3 (a) against a PL linear scale. This profile can be fitted with a single state decaying exponentially in less than 1.6 ps. This ultrafast luminescence resembles closely that found in poly-paraphenylenevinylene (PPV) polymers.[8] We attribute it to the formation of excitons which relax by phonon interaction onto the lowest vibrational level of the first excited state. The absence of delayed luminescence is explainable if singlet states are involved. We assume these excitons do not migrate in the crystal but rather localize on a limited number of molecules. The quenching of PL after 2 ps might indicate an ultrafast conversion of these singlet excitons into nonradiative triplets excitons via intersystem crossing ($S_1 \rightarrow T_1$) as suggested by femtosecond pump-probe measurements in polycrystalline Φ_6 layers.[6] Singlets may also relax rapidly via nonradiative decay channels involving recombination sites as intramolecular quenching centers. Photo-oxidation of PPV ($C{=}O$ groups) and of oriented PHP films was ascertained by spectroscopy.[7,15] There is no electron paramagnetic resonance evidence for extrinsic impurity quenchers in PHP films but it is possible, however, that hydroperoxide quenching centers could be formed by breaking ring $C-H$ bonds under UV light irradiation followed by air oxidation according to the reaction $C-H \rightarrow C^{\bullet} + H^{\bullet} + O_2 \rightarrow COO^{\bullet} + H^{\bullet} \rightarrow COOH$.

Figures 3(b) and 3(c) and Fig. 4 present the PL decays of film 1 in the 50-ns and 1-ns time domains, respectively, plotted against a logarithmic scale. The kinetics dramatically changes with respect to that of film 2. At long times between 1 ns–50 ns, the system apparently decays biexponentially with two weak components at $\tau_1 = 3$ ns and $\tau_2 = 11$ ns whose spectral weight is between 3% and 0.1% of the zero-

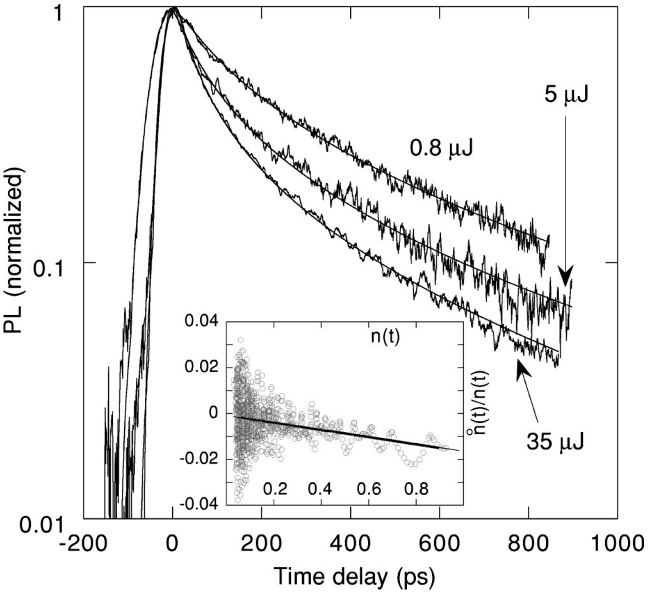

FIG. 4. Normalized kinetics vs different energy densities for the lying film 1 fitted with the annihilation model described in the text. In inset, logarithmic derivative of the decay at 35 μJ per pulse in film 1. The linear regression fits the data with $\gamma n_0 = 0.015$ ps^{-1} and $\beta = 9.7\times 10^{-4}$ ps^{-1}.

time delay response. However, for shorter times ($\Delta t < 1$ ns), one gets clearly *nonlinear* decays exemplified in Fig. 4, where the logarithmic temporal PL response of 1 is displayed vs different laser energies E_d in the 1-ns window. When the pump power increases, the relative spectral weight gradually diminishes at a given time.

A close examination of the experimental data at low-energy density ($\Delta t < 1$ ns) suggests that the dynamics follows a second-order rate equation accounting for simultaneous monomolecular and bimolecular processes. Numerical integration of the following rate equation:

$$\frac{dn(t)}{dt} = \frac{I}{\tau_0\sqrt{2\pi}}\exp\left[-\frac{(t-t_0)^2}{2\tau_0^2}\right] - \beta n(t) - \gamma n(t)^2 \quad (1)$$

reproduces satisfactorily our data (Fig. 4). Here, we have included the Gaussian time dependence of the laser pulse. β and γ are the monomolecular and annihilation decay rates, respectively, t_0 the maximum position of the pulse (origin of decay times), I its integrated intensity, and τ_0 its width. Note that the responses are normalized to the maximum concentration of emitting excitations n_0. The model yields values of γn_0 lying between 4.7×10^9 s^{-1} at 0.8 μJ per pulse and 1.3×10^{10} s^{-1} at 35 μJ per pulse. The bimolecular decay rate γn_0 increases with the increase of light intensity in the same manner as in a polythienylene vinylene film.[16] The monomolecular constants $\tau = 1/\beta$ are physically realistic and range between $\tau = 1148$ ps at low E_d and 925 ps at high E_d ($\beta = 10.8\times 10^8$ s^{-1}). With a penetration depth of the beam of about 300 nm in this film, γ amounts 2.36×10^{-12} cm^3 s^{-1} at 35 μJ per pulse. It is comparable to that found in stilbene (2.0×10^{-12} cm^3 s^{-1}) and of the same order that of α-sexithienyl ($T6$) thin films (3×10^{-13} cm^3 s$^{-1/2}$).[17,18]

In C_{60} and $T6$ thin films, PA data have been interpreted over a time range excluding the laser-pulse duration with a non-Markovian Förster rate equation,[18,19]

$$\frac{dn(t)}{dt} = -\beta n(t) - \gamma(t) n(t)^2, \quad (2)$$

where $\gamma(t) = \gamma t^{-1/2}$. When the pulse shape is a δ function, Eqs. (1) and (2) are similar, but the latter involves a $t^{-1/2}$ time-dependent annihilation rate meaning that annihilation of excitons depends on their spatial separation. This process is explained by a long-range resonance interaction involving *spatially fixed*, Frenkel excitons. Such peculiar dynamics deserves inspection in our system. We assert that a sufficient condition for checking the time dependence of $\gamma(t)$ in our film and thus the mobility of the excitons, consists in plotting the logarithmic derivative of the experimental luminescence data $n(t)$ (Fig. 4, inset),

$$\frac{\dot{n}(t)}{n(t)} = -\beta - \gamma(t) n(t). \quad (3)$$

It is clear that linearity of $\dot{n}(t)/n(t)$ should imply a Markovian process with constant $\gamma(t)$. Indeed, when $\Delta t > 0$, we find a striking linear regression fitting well the logarithmic-derivative data of PHP for $E_d = 35$ μJ per pulse. Further, the values of β and γ extracted from fitting Eq. (3) to the data coincide with those obtained numerically from Eq. (1): we find $\beta = 9.7\times 10^8$ s^{-1} and $\gamma n_0 = 1.5\times 10^{10}$ s^{-1}. We conclude that γ is time independent at high energy density. This supports the conjecture that exciton annihilation at relatively short-time delay in the PHP sample 1 is a Markovian process typical of *mobile* S_1 singlet excitons. In this context, bimolecular annihilation processes will predominate over monomolecular ones if the distance between two excitons is less than the critical radius[20]

$$R_c = \left(\frac{3\gamma}{4\pi\beta}\right)^{1/3} \quad (4)$$

From our fits and Eq. 4, we find $R_c = 0.805$ nm. This value, comparatively larger than the b-cell parameter and of the same order that of the a-cell parameter, hints at short-range exciton-exciton interaction in this film for $\Delta t < 1$ ns.[18] Accordingly, propagation of excitations through the crystal is best depicted by hopping of S_1 singlet excitons between first-neighbor PHP molecules, possibly in a direction nearly orthogonal to their long axis, before radiative recombination happens.

Further indication of exciton migration in film 1 is given by the redshifted luminescence tail (Fig. 2) associated with the *slow* decay channel ($\Delta t > 1$ ns). Literature survey indicates that emission in polyparaphenylene (PPP), its oligomers (from Φ_2 to Φ_8), and in PPV is shifted to red energy ranges as the chain length increases. In PPV, the redshifted luminescence is also delayed. Triplet-triplet annihilation into singlets and exciton migration were proposed as possible mechanisms.[8,21,22] To test this fusion process, we have reproduced the *long-lived luminescence* data of 1 between 2 ns and 50 ns using bimolecular recombination with rate parameters $\tau = 8.7$ ns and $\gamma \approx 10^{-15}$ cm^3 s^{-1}. Our conclusion is that annihilation of triplets accounts well for the delayed component. Since the initial luminescence intensity of the slow component ($\Delta t > 1$ ns) is very weak (3% for $\tau_1 = 3$ ns) the probability of triplet collisions is therefore low: the γ value is three and two orders of magnitude lesser than in anthracene and in $T6$. The natural lifetime of the triplets is long and their diffusion lengths is one or two order of magnitude greater than those of singlet excitons which means that in six-ring chains as PHP, long-range transfer of triplet excitons requires intermolecular hopping. A broad estimate of the intermolecular diffusion constant $D_c = R^2/\tau$ is 1.1×10^{-2} cm^2/s, equivalent to that found in $T6$ thin films from picosecond PA ($D_c = 0.6 \times 10^{-2}$ cm^2/s), and taking into account that the average domain size in these layers was three times smaller than in our material.[23]

In summary, our time-resolved PL experiments corroborate that orientational texture of PHP films affects drastically their emission properties. Films with lying molecules are the best candidates for electroluminescent devices because of longer survival of excitations and triplet generation. In both films, ultrashort transients display a well-resolved vibronic structure indicative of intramolecular excitons strongly coupled to the intramolecular phonons. The ultrafast kinetics of the standing film should proceed from intramolecular Frenkel excitons that radiatively recombine in a subpicosecond time range by vibrational interaction. The fast response ($\Delta t < 1$ ns) of the lying film can be modelized with a time-independent annihilation rate equation indicating mobile, short-range interacting singlet excitons. The long redshifted luminescence ($\Delta t > 1$ ns) is ascribed to triplet fusion followed by radiative desexcitation of S_1 singlet excitons. The observed transients are in accord with exciton migration in this film.

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