Phosphorescence of π-Conjugated Oligomers and Polymers

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We observed phosphorescence from a ladder-type poly-(para-phenylene) and an analogous oligomer containing five phenylene rings. The spectra are similar to the intrinsic fluorescence spectra and bear out a singlet-triplet splitting of 5000 cm^{-1} (polymer) and 6800 cm^{-1} (oligomer). Phosphorescence decay of the polymer occurs on a 10−100-μs scale obeying a power law and suggestive of nonradiative quenching, while that of the oligomer is asymptotically exponential with an intrinsic decay time of $\simeq$250 ms. The polymer also exhibits delayed fluorescence. It originates from delayed recombination of geminate electron-hole pairs rather than from triplet-triplet annihilation.

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Long-lived phosphorescence is a ubiquitous property of organic molecules. It is caused by spin-forbidden decay from the first triplet state (T_1), usually populated via intersystem crossing from the first singlet (S_1) state. The energy gap between the S_1 and T_1 levels is typically on the order of 1 eV (8000 cm^{-1}) and is a signature of strong electron-electron correlation. It is an unresolved question why no intrinsic phosphorescence from π-conjugated polymers has been observed, although transient absorption [1,2], delayed luminescence [3], electroluminescence [4], and optically detected magnetic resonance [5−7] have been considered as indirect evidence for the existence of triplet excitations. In our opinion the claimed first observation of phosphorescence from poly(3-hexylthiophene) [8] is questionable because (i) the spectrum of this emission is unrelated to that of fluorescence, (ii) it does not originate from intersystem crossing from the S_1 state, and (iii) the emission is independent of the polymer chain length. In the context of organic electroluminescence the absence of phosphorescence is particularly astonishing since, due to spin statistics, recombination of electrons and holes, for instance, injected from the electrodes in light-emitting diodes (LEDs), should generate three triplets per one (emissive) singlet excitation. In order to resolve the puzzle it has been conjectured that π-conjugated polymers behave like inorganic semiconductors rather than organic molecules implying negligible electron-electron correlation [9]. If true there should be no S-T gap and no redshifted phosphorescence should be observable either.

Another reason for the so far not observed phosphorescence might lie in the polymeric material itself as there are topological disorder and traps which might reduce the strong electron-electron correlation. In view of the importance of triplet states in LEDs and of the fundamental understanding of conjugated polymers, we attempted to delineate their intrinsic phosphorescence.

The test systems are the ladder-type methyl-substituted poly-phenylene (MeLPPP) and the corresponding unsubstituted dimer (LDPP) containing 5 phenylene rings. Both molecular structures are depicted in the insets of Figs. 1 and 3, respectively. The presumed advantages of MeLPPP are its chemical purity, the low degree of structural disorder as evidenced from the rather narrow bands of the absorption and fluorescence spectra, and a low content of physical aggregates which might act as traps [10]. MeLPPP samples were spun cast from a solution of chloroform. LDPP was dissolved in methyltetrahydofurane (MTHF) at a concentration of 10^{-5} mol/liter, which forms a glassy matrix at 77 K. Luminescence was excited by a tunable parametric oscillator pumped by the third harmonic of a Q-switched Nd:YAG laser with a pulse duration of 7 ns and a maximum pulse energy of 0.1 mJ operated at 10 Hz. Both materials were excited into the first vibronic transition of their $S_1 \leftarrow S_0$ absorption band. The emission was dispersed by a monochromator with a resolution of 2 nm ($\simeq$100 cm^{-1}) and recorded by an optical multichannel analyzer (PAR model 1460) with a gated intensified diode array detector allowing for an integration time (gate width) of detection from 100 ns to 10 ms and a variable delay after excitation. Each measurement was recorded by averaging over 100 laser pulses.

Figure 1 shows existence of delayed luminescence from a MeLPPP film at 77 K recorded with a delay time of 500 ns, i.e., after the complete decay of the prompt fluorescence signal. The spectra consist of three contributions. The high energy portion (I) is identical to the prompt fluorescence with a maximum near 21 500 cm^{-1} followed by a vibronic replica with a dominant vibrational mode of $\simeq$1500 cm^{-1}. The second vibrational overtone overlaps with a broad excimerlike band (II) centered at 19 000 cm^{-1}. The third spectral contribution (III) is resolved only at lower temperature (bottom spectrum in Fig. 1), and upon raising the temperature to 295 K it rapidly decreases and is masked by the relatively strong spectral contribution II. This contribution has a similar vibronic structure to the fluorescence, but is offset from

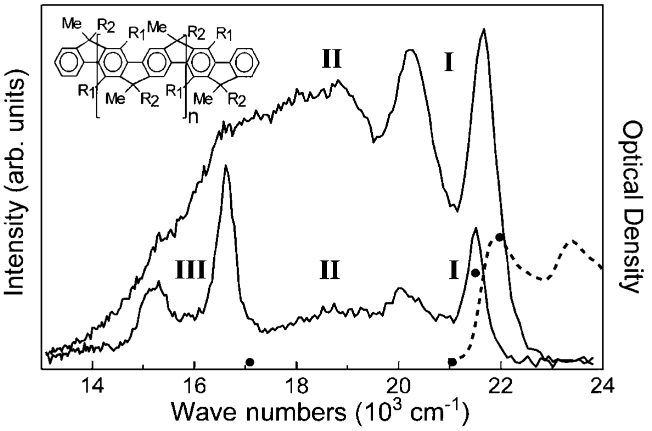

FIG. 1. Delayed fluorescence (I + II) and phosphorescence (III) spectra of MeLPPP ($R_1 = n\text{-}C_6H_{13}$ and $R_2 = 1,4\text{-}(C_6H_4)\text{-}nC_{10}H_{21}$) film at 77 K ($\nu_{\text{exc}} = 23\,000$ cm^{-1}, integration time 100 ns (upper curve) and 10 ms (lower curve), delay 500 ns). Dashed line: absorption spectrum; ●: excitation spectrum of band system III.

the latter by about 5000 cm^{-1}. It can be observed only at integration times larger than 100 μs and between 10 μs and 100 μs it decays in a power law fashion (Fig. 2, solid circles). Here it is important to note that decay of the phosphorescence intensity of the polymer was measured with a gate width at least comparable to if not greater than the delay time, and thus the measured decay corresponds to the so-called "integral" kinetics. In this case the true decay profile is a derivative of the integral kinetics. Differentiating the observed $t^{-0.5}$ decay curve yields the power law $\sim t^{-1.5}$ for the decrease of the momentary concentration of triplets in MeLPPP.

The low temperature (77 K) delayed luminescence spectra of LDPP in MTHF are shown in Fig. 3. The room temperature absorption spectrum (a) is shown for comparison. At 30 ns after excitation and with an integration time of 100 ns LDPP shows delayed fluorescence [DF, curve (b)] and resembles the spectral contribution I in MeLPPP. The delayed fluorescence spectrum is mirror symmetric to the absorption spectrum, except that the intensity of the $S_1 \rightarrow S_0$ 0-0 transition is reduced due to reabsorption. At longer integration and delay times (10 and 3 ms, respectively) a long lasting luminescence appears at 18 500 cm^{-1} [curve (c) in Fig. 3], i.e., 6800 cm^{-1} below the $S_1 \leftarrow S_0$ 0-0 transition, which is a counterpart of the band system III of the polymer. It is superimposed on a broad background which is probably due to photooxidation products of the solvent (MTHF). After a fast initial decrease ($\leq$10 ms) band system (c) features a long lasting exponential decay whose decay time is about 250 ± 100 ms and exceeds the reciprocal repetition rate of the pump laser (Fig. 4).

It is well established that in condensed molecular systems charge recombination and bimolecular annihilation of excitation [11] can contribute to DF. In the case of MeLPPP we have firm evidence that DF, associated with band system I and the excimerlike band II, is mainly due to singlet excitons resulting from the recombination of geminate electron-hole pairs rather than due to T-T annihilation. It comes from an experiment on electric-field mediated DF [12,13], which is to be reported in greater detail elsewhere. On the contrary, in LDPP frozen solutions DF [curve (b)] is caused by annihilation of triplets. In this respect a frozen LDPP solution does not behave differently from many organic compounds [14].

In this Letter the main emphasis is put on the long-lived parts III and (c) in the delayed luminescence spectra of MeLPPP and LDPP as a direct manifestation of the presence of the triplet excitations. It is straightforward to

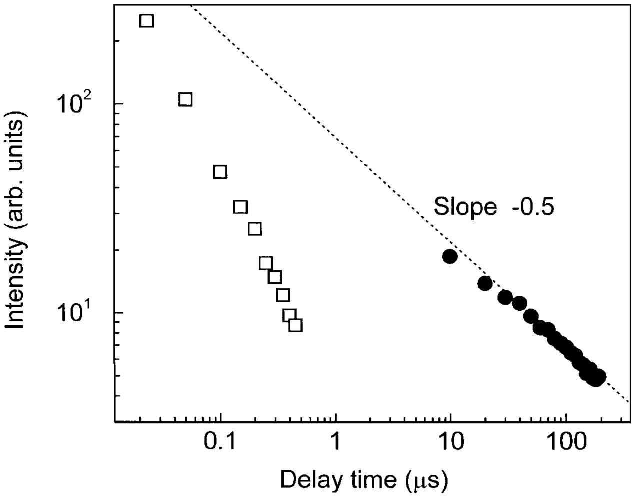

FIG. 2. MeLPPP phosphorescence (●, integration time 10 ms) and delayed fluorescence (□, integration time 100 ns) decay curves on a double logarithmic scale.

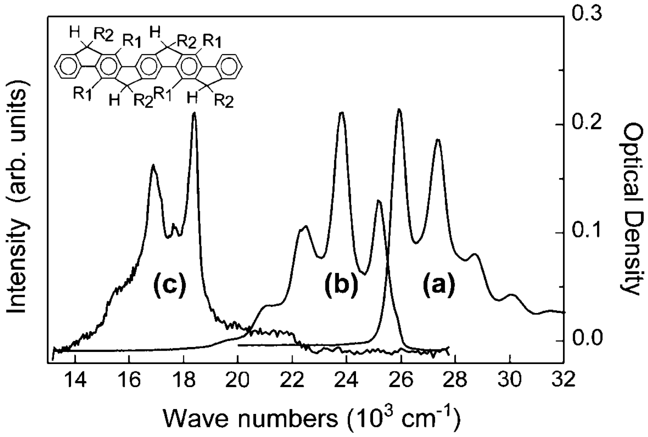

FIG. 3. Spectra of LDPP [$R_1 = n\text{-}C_6H_{13}$ and $R_2 = 1,4\text{-}(C_6H_4)\text{-}C_4H_9$] in MTHF solution (a) absorption spectrum (295 K), (b) delayed fluorescence spectrum (integration time 100 ns, delay 30 ns) at 77 K, and (c) phosphorescence spectrum (integration time 10 ms, delay 3 ms) at 77 K. The excitation energy was $\nu_{\text{exc}} = 25\,975$ cm^{-1}.

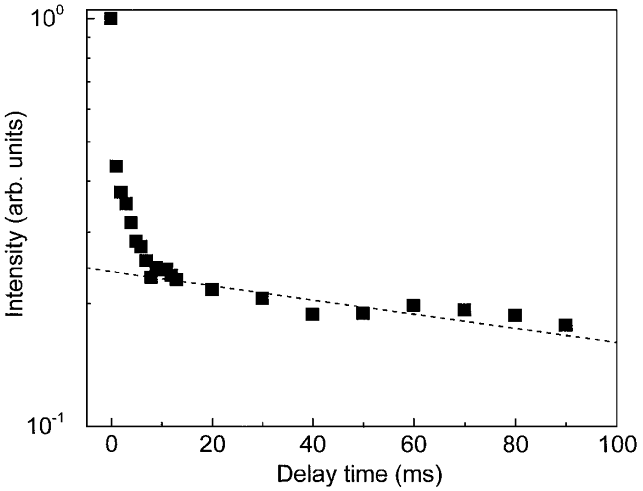

FIG. 4. LDPP phosphorescence decay curve on a semilogarithmic scale ($\nu_{\mathrm{exc}} = 25\,975$ cm^{-1}, integration time 1 ms).

assign these spectral parts of the long-lived emission to phosphorescence with the $T_1 \rightarrow S_0$ transition at 16 500 and 18 000 cm^{-1}, respectively. This assignment is supported by the following facts: (i) The bands (c) in the oligomer and the band system III in the polymer are virtually identical, the bathochromic shift of bands III with respect to the LDPP phosphorescence being a consequence of the extended conjugation length of the polymer, (ii) the vibronic splitting is characteristic of the MeLPPP/LDPP fluorescence spectra, (iii) the measured long wavelength part of the excitation spectrum of the delayed emission coincides with the onset of the absorption spectrum, and (iv) the intensity of the low energy emission from LDPP and the polymer decreases at higher temperature. This represents strong evidence in favor of intrinsic, i.e., not trap-mediated phosphorescence.

The establishment of phosphorescence and a significant singlet-triplet gap of $\simeq 5000$ cm^{-1} in MeLPPP represents another important evidence that the spectroscopic properties of conjugated polymers are those of large π-conjugated molecules rather than semiconductors [15]. From absorption and fluorescence spectra of linear π-conjugated oligomers and polymers it is known that the chain length dependence of the energy $\Delta E(n)$ of the lowest signet ($S_1 \rightarrow S_0$) transition follows a $\Delta E_\infty(n) = \Delta E_\infty + (A_S/n)$ law, where n is the number of the chain repeat units [16]. For ladder-type oligo-PPs, $A_S = \partial \Delta E(n)/\partial(n^{-1}) = 35\,600$ cm^{-1} if n is identified with the number of phenylene rings [16]. Based upon this estimate one would expect the $T_1 \rightarrow S_0$ 0-0 transition of the polymer at 14 900 cm^{-1} while the observed transition occurs at 16 500 cm^{-1}. This implies that the S-T gap decreases as the length of the π-electron system decreases and, simultaneously, that the proportionality constant A_T for the triplet transitions is less than A_S for the singlet transitions. It indicates that the S_1 state becomes less expanded compared to the T_1 state as the conjugation length increases. This is in accordance with theoretical prediction [17].

In a recent publication by Wohlgenannt *et al.* [18] for the same polymer MeLPPP the energy of the triplet state T_1 has been inferred from the additional onset above 25 900 cm^{-1} of the photoinduced absorption from the triplet state T_1. It has been attributed to fission of a singlet excitation into a pair of triplets. If so, the triplet energy should be 12 950 cm^{-1} implying a S-T gap of almost 8000 cm^{-1}. This is in contradiction with our directly measured triplet energy of 16 500 cm^{-1}. Therefore we conclude that the singlet fission cannot be the reason for the increase of the $T_2 \leftarrow T_1$ feature.

The observed decay pattern of the phosphorescence in the polymer as compared with that of the oligomer is not at all surprising. In a conjugated polymer an excitation is delocalized within a conjugated length and is able to migrate incoherently among different segments of either the same or neighboring chains. In this motion it can encounter nonradiative quenching sites, such as oxygen or other structural defects occurring in the course of film formation. In a random hopping system such as conjugated polymers composed of segments of statistically varying chain lengths the excitation motion and their quenching is a stochastic process with a broad distribution of rate constants. Therefore the depletion of the reservoir of triplet excitations will not follow an exponential decay law. On the other hand, in frozen LDPP solution the triplet excitations are localized on particular molecules and are immobile. The initial fast nonexponential decay at $t < 10$ ms (Fig. 4) is presumably due to bimolecular long-ranged triplet-triplet annihilation. Upon lowering the triplet concentration the kinetics becomes monomolecular exponential. For an experimentally observed singlet-triplet splitting of 6800 cm^{-1} according to the singlet-triplet gap law for linear acene molecules [19] one should expect an intrinsic decay time of the order of several 100 ms, consistent with the observed asymptotic behavior with the time constant 250 ms (dashed curve in Fig. 4.

From the kinetic data one can estimate the phosphorescence quantum yield for the polymer. If the initial $1/e$ drop of the phosphorescence due to nonradiative quenching of triplet excitations corresponds to a decay time of the order of 10^{-5} s while the estimated radiative lifetime is of the order of $\sim 10^{-1}$ s the actual phosphorescence yield of the polymer had to be $\simeq 10^{-4}$. This estimate for the phosphorescence yield in conjugated polymers explains why it escapes detection so easily. Another reason for the failure to detect phosphorescence is the presence of the relative strong delayed fluorescence. It can overlap spectrally and mask the phosphorescence as is obvious from the top curve in Fig. 1, notably at short delay/integration time.

In conclusion, we present direct spectroscopic evidence for radiative decay of triplet excitations in a conjugated polymer. The phosphorescence yield is weak because of diffusion-controlled nonradiative quenching by inadvertent impurities. As far as triplet excitations generated by electron-hole recombination in light emitting diodes are concerned, this quenching is crucial. Even if one could eliminate quenching due to impurities such as oxygen, charge carriers, present on a concentration of $\simeq 10^{18}$ cm^{-3}, would act as inevitable quenchers. Therefore the only way for "phosphorescence harvesting" [20] seems to be to add dopants with a short radiative triplet lifetime.

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