Intrinsic Room-Temperature Electrophosphorescence from a π-Conjugated Polymer

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Electrically induced phosphorescence from a poly(para-phenylene) ladder-type polymer is observed for the first time and characterized using time resolved spectroscopy. Short-lived phosphorescence is also observed in gated fluorescence spectra and is found to be quenched reversibly by oxygen. Thermally activated triplet diffusion to covalently bound palladium sites, which are formed at a concentration of about 80 ppm in a side reaction during polymer synthesis, is believed to be the cause of this novel effect, which suggests a new approach to the design of efficient electroluminescent materials.

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Conjugated polymers are a fascinating class of materials with significant potential for optoelectronic applications. A vast research effort over the past decade has yielded impressive improvements in the performance of devices based on conjugated polymers as well as a detailed understanding of the electronic material properties and structure-property correlations [1]. Much effort has been directed to the understanding of the physical principles governing polymer based light-emitting diodes (LEDs). Currently the greatest puzzle relates to the role of triplet excitons in conjugated polymers [2–13]. Charge carriers injected at opposite electrodes of an LED can combine to form excitons either in the singlet or in the triplet state, but only the singlet excitons are generally considered to contribute to visible luminescence in the absence of triplet harvesting dyes [12]. Although the precise ratio of singlet to triplet excitons is currently debated, it has been established that approximately half the excitations formed are in the triplet state, which is substantially lower in energy than the singlet state [5,8]. Remarkably, these triplets appear to be rather elusive, and the confirmation of their presence in diode structures has relied mainly on external probe measurements such as optical absorption and magnetic resonance [14–17]. The way to observe triplets directly in conjugated polymers is to study their phosphorescence spectra using time gated spectroscopy. This has been done for a number of conjugated polymers in films and solutions, yielding long-lived emission spectra typically redshifted by 0.6 to 1 eV from the prompt and delayed fluorescence [3,8]. As the quantum yield of this emission is low and triplets may be quenched by carriers, it has been proposed that it should not be possible to observe triplet emission in LEDs [3]. In this Letter, we present evidence for electrophosphorescence from a commonly used conjugated polymer for the first time. In contrast to previously reported electrophosphorescent platinum containing polyynes [11,18,19] we show that only a trace concentration of covalently bound metal atoms is necessary to allow efficient triplet emission due to triplet diffusion without the need of modification of the electronic and structural material properties such as electronic delocalization and intersystem crossing (ISC). Our system provides a tool to study the intrinsic properties of triplet excitons in conjugated polymers, demonstrating the correctness of the previous assumption that metal-organic polymers can be used as model systems for conjugated polymers to gain information on exciton formation cross sections [11].

The system studied is a novel derivative of the well characterized ladder-type poly(para-phenylene) (LPPP), a diaryl (diphenyl)-substituted LPPP derivative (PhLPPP), the structure of which is shown in the inset of Fig. 1. Ladder-type polyphenylenes are a particularly interesting class of materials due to their high degree of purity and the low level of structural disorder [20]. They

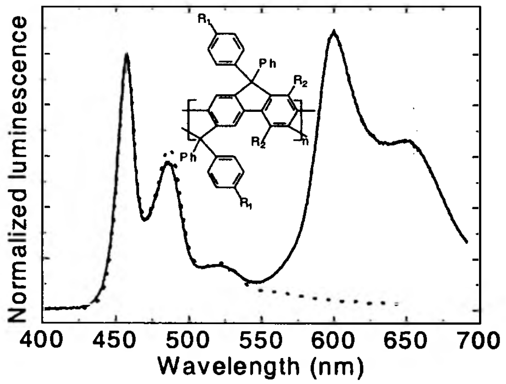

FIG. 1. Cw electroluminescence (solid line) (8 V, 10 mA cm^{-2}) and photoluminescence (dotted line) spectra of the phenyl substituted poly(para-phenylene) ladder polymer PhLPPP at 295 K. The inset shows the structure of the polymer (R_1: decyl; R_2: hexyl).

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have been used in a variety of optoelectronic applications and were also the first conjugated polymers to exhibit intrinsic phosphorescence at low temperatures [3]. Single layer LEDs were fabricated from this material on solution etched indium tin oxide (ITO) substrates ultrasonicated in isopropanol and optionally treated in an O_2 plasma. A charge transport layer (50 nm) of poly(3,4-ethylenedioxythiophene)/poly(styrene)-sulfonate (PEDOT/PSS) was deposited on the ITO layers and dried on a hot plate. The solutions were spin coated onto the substrates to yield films typically 100 nm thick, which were then contacted with aluminum electrodes, 150 nm thick and 4 mm^2 in area. All measurements were performed under a dynamic vacuum of 10^{-4} mbar at room temperature. Electroluminescence (EL) spectra were recorded using an Oriel spectrometer with an attached CCD camera. Photoluminescence (PL) emission spectra were recorded using a Shimadzu RF5301 spectrofluorometer under excitation at 380 nm. Figure 1 shows a comparison of EL and PL spectra. Both spectra exhibit a narrow vibronic progression characteristic of LPPPs. In the EL spectra two further features are observed at 600 and at 650 nm. Whereas the high energy band at 460 nm coincides with the known emission spectrum of the LPPP singlet exciton [20], we note that the lower energy feature observed only in EL corresponds to the previously observed triplet emission reported under gated detection at low temperatures [3]. We found that the ratio between the 600 nm band and the 460 nm band depends sensitively on the operating voltage/current and on the sample temperature. The 600 nm band was found to decrease substantially with increasing driving voltage and decreasing temperature.

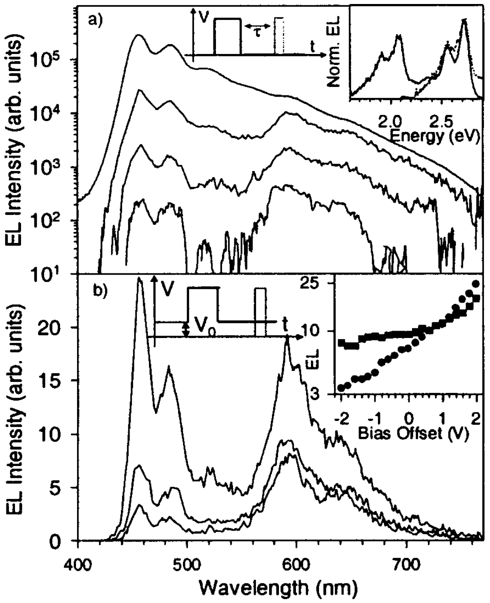

FIG. 2. Gated EL spectra of PhLPPP at 295 K. (a) EL spectra measured in a 1 μs gate at different delays after a 40 μs long voltage pulse of 6 V amplitude. From top to bottom: -10 μs (“cw”), 0 μs (at voltage turn-off), 2 μs, and 10 μs. Note that the detector sensitivity was increased between the cw and the delayed spectra. The inset shows the 0 μs spectrum (solid line) with the low energy feature shifted to coincide with the high energy feature (dotted line). (b) Gated EL spectra measured in a 10 μs gate 10 μs after turn-off for different bias offsets (from top to bottom): 2.0, 0, and -2.0 V. The inset shows the bias offset dependence of the delayed emission bands at 460 nm (solid circles) and 600 nm (solid squares). The sketches show the detection schemes employed.

It was recently demonstrated that gated EL provides an extremely sensitive technique to distinguish between different emitting species and recombination pathways present in LEDs [21]. Figure 2 shows gated EL spectra recorded upon electrical excitation by a 6 V pulse of 40 μs duration and 0.5 ms period. Immediately after the end of the voltage pulse (0 μs delay) the 600 to 460 nm peak ratio increases from 0.03 during the pulse by an order of magnitude to 0.38 and rises further to 1.8 at 10 μs delay. A bias offset applied to the LED dramatically modifies the delayed recombination and EL spectra, but not the delayed emission originating from long-lived phosphorescent dopants [21]. We varied the offset of the voltage pulse below the turn-on bias of the LED (2.1 V), keeping the pulse amplitude (6 V) and therefore the injected current constant. As can be seen in Fig. 2(b) the delayed emission from the singlet excitons depends strongly on the bias offset. This can be explained in terms of delayed recombination of diffusing charge carriers, whereby the carrier diffusion post turn-off is modified by the external field [21]. In contrast, the delayed 600 nm emission is not modified by a negative bias offset and increases only slightly for large positive offsets, as shown in the inset of Fig. 2(b). The two spectral components at 460 and 600 nm are overlaid in the inset of Fig. 2(a) by shifting the lower energy component by 0.64 eV to higher energy. Remarkably, the two spectral features are identical, as was previously observed in low temperature measurements of the delayed fluorescence and phosphorescence of a similar material [3].

The 600 nm emission feature is long lived in comparison to the short-lived singlet exciton. The bias offset dependence shows that excitations resulting in 600 nm emission are generated during the voltage pulse and not post turn-off, as in the case of delayed singlet emission. A negative bias offset results in a rapid depletion of the device of charge carriers and a reduction of delayed recombination. Whereas this has a strong effect on the delayed 460 nm emission, the delayed 600 nm emission is not affected. For large positive bias offsets a small increase in delayed 600 nm emission is observed. However, as the built-in field of the device is small (approximately 0.5 V), a positive bias offset will result in continued injection and therefore an increase in the number of excitations formed during the pulse. A positive external field will also counteract the built-in carrier sweep-out post turn-off, leading to increased delayed recombination. The above evidence leads us to the conclusion that the 600 nm emission band results from triplet emission due to phosphorescence. Clearly, however, there should be evidence for phosphorescence at room temperature in PL, so we performed time resolved PL spectroscopy on films of PhLPPP. Figure 3 shows normalized PL spectra detected at different delay times, which were recorded on thin films of PhLPPP using a frequency-doubled mode-locked titanium-sapphire laser operating at 380 nm and a repetition rate of 80 MHz, as well as a Hamamatsu streak camera coupled to a 0.5 m monochromator with a 50 lines/mm grating. The spectrum is found to broaden rapidly within the first 40 ps. After 1 ns delay all of the singlet emission has decayed and a broad band centered at 560 nm with shoulders at 530 and 600 nm is observed. After 3 ns delay the broad 560 nm band is overlaid by a narrow band centered at 600 nm, with a vibronic shoulder at 650 nm. We note that the spectral broadening of the polymer emission spans the entire visible spectrum within 3 ns.

In order to clarify whether the narrow peak observed at 600 nm in the delayed PL spectra is due to phosphorescence, we probed the sensitivity to ambient oxygen [6]. Figure 4 depicts the change in delayed emission 3 ns after excitation upon purging the vacuum chamber with air and reevacuating. For an increase in base pressure from 10^{-4} to 1 mbar the 600 nm feature almost vanishes, as seen in Fig. 4(a). As the chamber pressure is increased further, the broad 560 nm feature increases. Note that the spectra are not normalized but depict the absolute spectral change. Upon evacuation the 560 nm feature is found to decrease again, as seen in Fig. 4(b). Below a pressure of 10^{-3} mbar the phosphorescence band reappears and increases further in intensity as the pressure is lowered. The insets depict the same spectra on a logarithmic scale normalized to the 560 nm emission. We note that the broad band at 560 nm is also observed in the delayed PL spectra of dilute solutions, albeit at substantially weaker intensity. It is therefore most likely related to emissive oxidative defects as in the case of polyfluorenes [22,23], rather than aggregates or excimers [3].

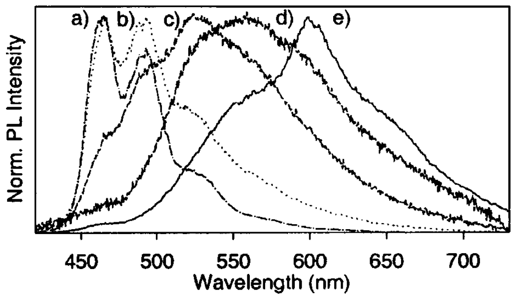

FIG. 3. Delayed PL spectra at 295 K excited at 380 nm and detected at (a) 0–40 ps, (b) 100–140 ps, (c) 300–400 ps, (d) 1–2 ns, and (e) 3–4 ns.

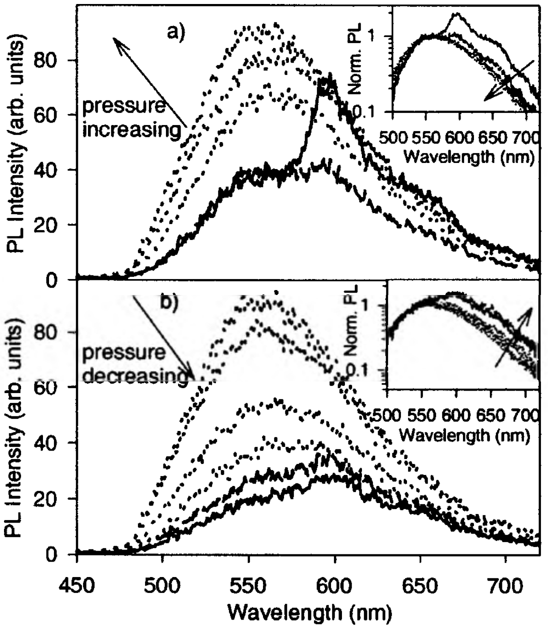

FIG. 4. Delayed PL spectra detected in a 1 ns window at 3 ns after excitation in dependence of vacuum pressure. (a) Pressure increasing from bottom to top from 10^{-4} mbar (solid line), 1 mbar (dashed line), to atmospheric pressure (dotted line). (b) Decreasing pressure on the same sample spot from top to bottom from atmospheric pressure (dotted line) to 10^{-3} mbar (dashed line) to 10^{-4} mbar (solid line). The insets show the same spectra normalized to the band at 540 nm.

Both PL and EL show clear evidence for phosphorescence from PhLPPP at room temperature. As the signal is substantially weaker in PL than in EL, we conclude that phosphorescence arises due to a small number of sites which enable triplet emission rather than due to enhanced ISC as in metal containing polymers [11]. Whereas ISC is close to unity in these materials, in conventional polymers it is in the range of 10^{-3} and thus hard to detect. In the case of EL, triplets are generated at a rate of approximately 2 orders of magnitude greater than in PL [10]. Photoinduced absorption measurements revealed a narrow band associated with the $T_1 \rightarrow T_n$ transition, centered at 1.26 eV A triplet lifetime of 159 ms was determined at 80 K. During this time, triplet excitons can diffuse through the polymer by a thermally activated electron transfer process described by Marcus theory [24]. If a site is reached during this lifetime at which radiative relaxation to the ground state is enabled by spin coupling to a heavy atom, rapid photon emission occurs, resulting in short-lived phosphorescence. The mobility of triplet excitons depends on their energy with respect to the energetic landscape. Lower energy triplet excitons may therefore be trapped and hindered from reaching a recombination site. These contribute to the measured long triplet lifetime in photoinduced absorption. Alternatively, the triplet relaxes nonradiatively through interactions with phonon modes [18]. As the temperature is decreased, triplet diffusion is inhibited and the phosphorescence is reduced. Increasing the operating voltage results in an increase in excitation density, which gives rise to enhanced annihilation of triplets [9,12]. To clarify the origin of the anomalously high rate of triplet emission, we performed a detailed elemental analysis on our polymers in order to identify heavy metal impurities, which may lead to a radiative decay route for triplet excitons. Whereas the palladium concentration in methyl substituted MeLPPP [20] was <2 ppm, a distinctly higher concentration of 79.1 ppm was found in PhLPPP, corresponding to approximately 1700 monomers per Pd atom. The increased incorporation of Pd in PhLPPP is thought to result from the high affinity of Pd to phenyllithium, which is used in the reaction sequence to PhLPPP. Transmetallation to phenylpalladium species and their subsequent reaction with the polymeric intermediates can lead to a covalent incorporation of palladium centers into the polyphenylene backbone [25]. In contrast, the methyllithium used in the synthetic sequence towards MeLPPP possesses a much lower affinity to palladium species.

As our results show, the covalent binding of trace amounts of a heavy metal atom to the polymer backbone leads to efficient phosphorescence at room temperature. Triplets migrate through the host during their lifetime and either relax nonradiatively or recombine radiatively on a Pd atom containing site. We note that in the previous report of optically generated phosphorescence in MeLPPP a power law decay of the phosphorescence with an exponent of $-\frac{1}{2}$ was observed rather than an exponential decay [3]. This was attributed to the diffusion of triplets to quenching sites. As mentioned above, MeLPPP contains a very small, residual concentration of heavy metal Pd atoms (< 2 ppm), which could lead to a deviation from a single exponential decay, or, as in the present case for higher Pd concentrations (PhLPPP), to an enhancement of (electro)phosphorescence. In contrast to previously reported heavy metal containing metal-organic polymers, which have only limited applicability in optoelectronic devices due to problems with stability and purity, we do not modify the chemistry or lose the very favorable electronic properties of the system by activating the phosphorescence channel [11,18,19]. We are therefore able to optically study the *intrinsic* properties of triplet excitons in conjugated polymers, rather than the extrinsic properties enforced by chemical design. We thus demonstrate experimentally that the underlying assumption made by Wilson *et al.* [11], that the properties of triplet excitons derived from a polymer system strongly perturbed by the presence of metal atoms in each repeat unit are comparable to those of metal free polymers, is actually valid. The present system provides the energetically most efficient way of harvesting triplet excitons, which has previously been demonstrated by the incorporation of phosphorescent dyes into a polymeric or molecular host [10,12]. We are able to image the dynamics of triplet excitons and expect also to be able to gain information on the triplet exciton binding energy. In particular, the present results provide an important solution to dealing with triplet excitations in high excitation density applications such as polymer lasers. Triplet accumulation can often lead to a reduction in gain and undesirable thermal heating. A deactivation of the triplet by radiative means bypasses these parasitic effects and could help in the development of electrically driven polymer lasers or optically pumped steady state polymer lasers. It has recently been proposed that the ratio of singlet to triplet emission in EL and PL may be used to derive the exciton formation cross section. We note that in our present system exciton diffusion strongly influences the singlet to triplet emission ratio as well as the apparent difference in triplet exciton formation cross section between EL and PL. As intrachain charge transfer is more efficient than interchain hopping [26], triplet exciton diffusion is expected to depend strongly on chain length. This could influence triplet exciton formation cross sections deduced from a comparison of fluorescence and phosphorescence [11].

In summary, we have demonstrated a novel route for triplet harvesting from conjugated polymers by inclusion of a small amount of covalently bound heavy metal atoms in the polymer backbone. The electronic properties of the polymer and the bulk are not affected by the isolated metal sites. The enhanced rate of radiative triplet decay provides a novel tool to study the energetic structure and dynamics of triplet excitations in conjugated polymers as well as their interaction with charge carriers [27].

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