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Efficient interchain photoluminescence in a high-electron-affinity conjugated polymer

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We report measurements of photoluminescence efficiency and time dependence in a high-electron-affinity cyano-substituted derivative of poly(*p*-phenylenevinylene). We find that the luminescence is much longer lived in solid films than in solutions and interpret this result as emission in the film being from an interchain excitation. These results suggest that intermolecular interactions are an important consideration in the design of highly luminescent conjugated polymers.

Measurements of luminescence in conjugated polymers[1–13] are important both for understanding the nature of their excited states, and the operation of electroluminescent devices. Conjugated polymers combine semiconducting electronic properties with favorable processing characteristics. The possibility of chemical tailoring to realize desired properties is a particular advantage of these materials. For example, the energy gap of conjugated polymers may be tuned by chemical substitution or making copolymers.[14,15] A recent molecular engineering innovation has been the development of high-electron-affinity polymers, made by cyano-substitution of members of the poly(arylene vinylene) family.[7] The particular polymer studied here is a cyano-substituted poly(*p*-phenylenevinylene), referred to as CN-PPV and shown in Fig. 1. The increased electron affinity facilitates electron injection from stable electrodes such as aluminum in light-emitting diodes, thereby improving device performance.[7] The alkoxy sidegroups confer solubility in solvents such as toluene and chloroform. In this paper we report measurements of luminescence efficiency and time dependence in CN-PPV.

The operation of an electroluminescent device involves several steps: charge injection at the contacts; charge transport through the device; charge capture to form an exciton, which (if singlet) then decays by a combination of radiative and nonradiative decay channels. Photoluminescence measurements enable the last step to be studied directly, and therefore help us to understand the photophysics of luminescent polymers.

The picture that has emerged in PPV is that photoexcitation leads to the generation of singlet excitons which then decay by a combination of radiative and nonradiative pathways. The relative rate of the radiative and nonradiative decay processes determines the quantum efficiency of luminescence. For example, if nonradiative decay is very rapid then most of the excitons will decay by this route before they have time to emit so that luminescence will be weak.

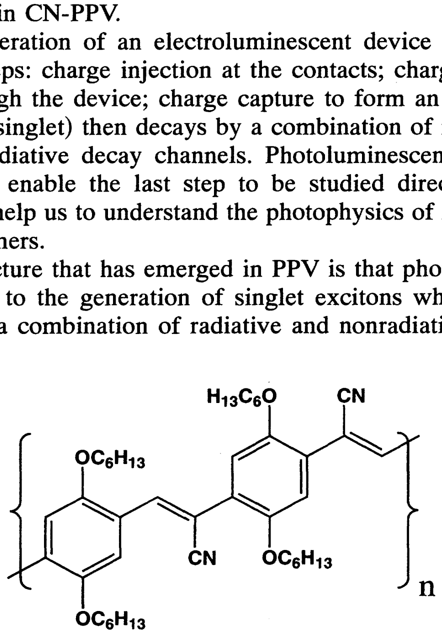

FIG. 1. The CN-PPV molecule—a high-electron-affinity conjugated polymer.

The measured lifetime of the luminescence τ is shorter than the natural radiative lifetime τ_R, and can be related to the rate constants for radiative and nonradiative decay k_R and k_{NR} by

$$1/\tau = k_R + k_{\mathrm{NR}} \tag{1}$$

and the efficiency is then given by

$$\Phi = bk_R/(k_R + k_{\mathrm{NR}}) = b\tau/\tau_R\,, \tag{2}$$

where $\tau_R = 1/k_R$ is the natural radiative lifetime, i.e., the lifetime the luminescence would have in the absence of nonradiative decay processes. b is the fraction of absorbed photons leading to the generation of singlet excitons. We believe that b is close to 1, and have recently shown that this is the case in PPV prepared in Cambridge.[10]

τ_R can be estimated from measurements of Φ and τ, assuming that the emitting species is formed with unit quantum efficiency. There is some sample to sample variation of Φ and τ and so in order to deduce a meaningful value of τ_R it is essential that they are measured on identical samples. In films of PPV prepared in Cambridge, the quantum yield was measured to be 0.27 ± 0.03 and the luminescence lifetime was 320 ± 30 ps, implying $\tau_R = 1.2 \pm 0.1$ ns.[10] The natural radiative lifetime of the model oligomer *trans,trans*-distyrylbenzene in solution is also close to a nanosecond.[16] In solutions of poly(2-methoxy,5-(2′ethyl-hexyloxy)-*p*-phenylenevinylene) (MEH-PPV) the measured quantum yield of 0.35 ± 0.05 and the luminescence decay time of 330 ± 30 ps imply a natural radiative lifetime of approximately a nanosecond.[4] These results on PPV and MEH-PPV are summarized in Table I.

Studies of photoluminescence in PPV and MEH-PPV suggest that the sample consists of regions with a range of conjugation lengths and environments, and that excitations tend to migrate to lower-energy regions before emitting photons.[3,4,6,11,17] Evidence for this comes from the photoluminescence spectrum being much narrower than the absorption spectrum, the observation of a redshift of the emission

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TABLE I. The table summarizes measurements on CN-PPV and compares them with other polymers. Φ is the quantum yield for luminescence, τ is the luminescence lifetime, and k is the corresponding rate constant. k_R and k_{NR} are rate constants for radiative and nonradiative decay, and τ_R and τ_{NR} are their reciprocals.

	Φ	τ/ns	$k/10^8\ \mathrm{s}^{-1}$	τ_R/ns	$k_R/10^8\ \mathrm{s}^{-1}$	τ_{NR}/ns	$k_{\mathrm{NR}}/10^8\ \mathrm{s}^{-1}$
CN-PPV solution	0.52±0.05	0.9 ±0.1	11.1±1	1.7±0.2	5.8±0.5	1.9±0.2	5.3±0.5
CN-PPV film	0.35±0.03	5.6 ±0.2	1.8±0.1	16±2	0.6±0.06	8.6±0.8	1.2±0.1
PPV film[a]	0.27±0.03	0.32±0.03	30±3	1.2±0.2	8.2±1	0.5±0.05	21.8±2
MEH-PPV solution[b]	0.35±0.05	0.33±0.03	30±3	0.9±0.2	11±2	0.5±0.05	19±2

[a] Reference 10.

[b] Reference 4.

with time, simpler decay kinetics when the polymer is excited in the low energy tail of its absorption, and site selective fluorescence spectroscopy. The decay of the luminescence has been observed to be faster in solid films than in fluid or solid solution, and this is interpreted as being due to easier migration of excitons to quenching sites.[4,5]

The CN-PPV was synthesized as previously described,[7] and thin film samples for optical measurements were prepared by spin coating from chloroform solution onto spectrosil substrates. Luminescence quantum yield measurements of CN-PPV in toluene solution were performed using the referencing method of Williams *et al.*[18] Rhodamine 101 in ethanol, which is known to have a quantum yield close to 1,[19] was used as the reference standard, and all solutions were degassed by bubbling with nitrogen for ten minutes. The luminescence quantum yield of the CN-PPV film was measured following excitation at 488 nm using an integrating sphere, and further details are given elsewhere.[10]

Time-resolved luminescence measurements were made by time-correlated single photon counting. Excitation was provided by a cavity-dumped mode-locked dye laser synchronously pumped by the second or third harmonic of a continuous-wave mode-locked Nd:YAG (yttrium aluminum garnet) laser. This system produced pump pulses of 10–15 picoseconds duration, at a repetition rate of 4 MHz, and typical excitation intensities at the sample were of order 0.4 kW/cm^2. Thin-film samples were measured in a cryostat which was maintained at a pressure of 10^{-5} torr, and all measurements were made at room temperature. Solution measurements were made on dilute solutions of approximately 1 mg/l concentration in toluene with peak absorbance no greater than 0.1 cm^{-1}. Toluene is a good solvent for this polymer, and at these low concentrations we believe that the polymer chains are well separated. The luminescence passed through a polarizer and a subtractive-dispersion monochromator to a microchannel plate photomultiplier tube detector. The temporal instrument response function of the system was 50 ps. Data analysis was performed by a nonlinear least-squares iterative fitting of the luminescence decay to a sum of exponentials convolved with the measured instrument response function.

The steady state absorption and luminescence spectra of CN-PPV in solution and thin-film form are shown in Fig. 2. In solution the peak of the absorption is at 450 nm and the peak of the luminescence is at 555 nm. The thin-film spectra are redshifted with respect to the solution spectra, and this difference is particularly pronounced in the case of luminescence—the peak of the absorption is at 490 nm, and the peak of the luminescence is at 690 nm. In addition the thin film luminescence spectrum is relatively broad and structureless. The luminescence quantum yield in solution was 0.52± 0.05, which is one of the higher values observed for a conjugated polymer.

We have made time-resolved measurements of luminescence in CN-PPV solutions under a range of conditions of excitation wavelength, emission wavelength, and polarization. The main feature of all of these measurements is that the decay of the luminescence is dominated by a component of time constant 900± 100 ps. Figure 3(a) shows the decay of the luminescence measured at three different emission wavelengths following excitation at 432 nm. Figure 3(b) shows the decay of the luminescence measured at 580 nm following excitation at three different wavelengths. The data shown are for so-called magic-angle polarization. The results are relatively insensitive to the excitation and emission wavelengths:

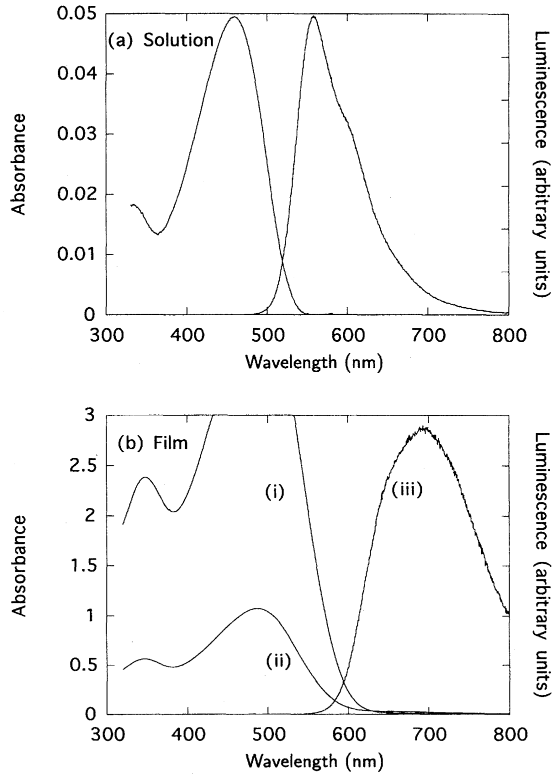
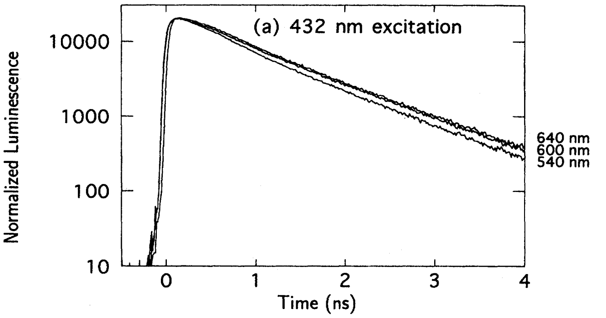


FIG. 2. (a) Absorption and steady-state photoluminescence (excited at 488 nm) spectra of CN-PPV in toluene solution. (b) Absorption and steady-state photoluminescence (excited at 488 nm) spectra of CN-PPV thin film. Curves (i) and (iii) are the absorption and luminescence spectra of the film used for time-resolved luminescence measurements. Curve (ii) is the absorption spectrum of a thinner film.



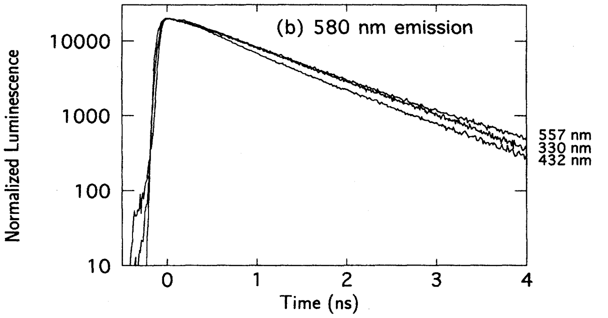


FIG. 3. (a) Time-resolved luminescence of CN-PPV in toluene solution following excitation at 432 nm. The three graphs are marked with the emission wavelength. (b) Time-resolved luminescence of CN-PPV in toluene solution measured for emission at 580 nm. The three graphs are marked with the excitation wavelength.

in all cases the decay of the luminescence is approximately monoexponential with a time constant of 900± 100 ps. There are some small differences in detail—for example, the luminescence is slightly shorter lived at shorter emission wavelengths. This could arise from migration of excitations along the polymer chain to more-conjugated regions or from rearrangement of the polymer chain around an excitation to give improved conjugation and therefore lower-energy emission.

In thin films of CN-PPV, the luminescence quantum yield was measured to be 0.35±0.05, which is larger than the quantum yield of 0.27±0.03 for PPV and 0.10–0.15 for MEH-PPV.[10] Figure 4 shows the results of time-resolved luminescence measurements on a CN-PPV film, measured for excitation and detection polarizations parallel. The decay of the luminescence at 780 nm is described well by single exponential decay of time constant 5.6 ns, which we take to be the lifetime of the emitting species. At other wavelengths, the decay of the luminescence is dominated by a component with a time constant of 5.6±0.2 ns. The luminescence is much longer lived in the solid film than in solution, as shown in Fig. 5. This is a surprising result, as the opposite has been observed in other comparisons of solution and solid state luminescence kinetics in related polymers such as MEH-PPV and phenyl-substituted PPV, PPPV.[4,5]

The most striking result is that the decay of the luminescence is slower in the film than in solution. The 5.6±0.2 ns lifetime seen in the film here is approximately twenty times longer than the lifetime in the related polymers PPV and PPPV.[3,5,11] We can estimate τ_R from Φ and τ, assuming that the emitting species is formed with unit quantum efficiency. In the case of the CN-PPV solution, taking $\Phi=0.52\pm0.05$ and $\tau=0.9\pm0.1$ ns we obtain $\tau_R=1.7\pm0.2$ ns, whilst in the film $\Phi=0.35\pm0.03$ and $\tau=5.6\pm0.2$ ns so that $\tau_R=16\pm2$ ns. These values are summarized in Table I, and should be compared with MEH-PPV in solution,[4] PPV films,[11] and the oligomer *trans,trans*-distyrylbenzene[16] in solution which all have τ_R close to a nanosecond. We consider that the emission from solutions of CN-PPV is from intrachain singlet excitons. We note that although according to the Strickler-Berg relationship[20] the transition rate depends on factors such as the refractive index and frequency of the transition, these factors cannot account for the much longer τ_R in the film than in the solution.

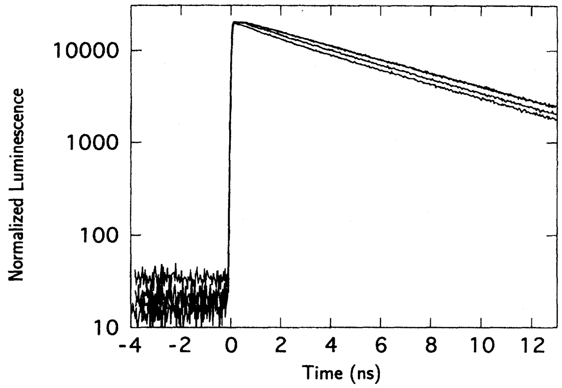


FIG. 4. Time-resolved luminescence of CN-PPV in toluene solution following excitation at 600 nm. The graphs (from bottom to top) are for 720 nm, 800 nm, 820 nm, and 780 nm emission. The decay curves for 820 and 780 nm are almost identical (and appear as one curve on the graph).

We consider that the nature of the emitting species in the film is different from that in the solution. The emitting species is far less strongly radiatively coupled to the ground state in films than in solution. The radiative coupling to the ground state is also far less strong than in films of other conjugated polymers such as PPV and PPPV. The difference between solution and film results implies that the emission in the film is from an interchain excitation, and we propose that it is either from a (physical) dimer or an excimer.

Physical dimers are well known in organic molecules and the dimerization leads to a splitting of the exciton level into a higher and a lower lying level.[21] The allowed optical transitions depend on the orientation of the transition dipoles of

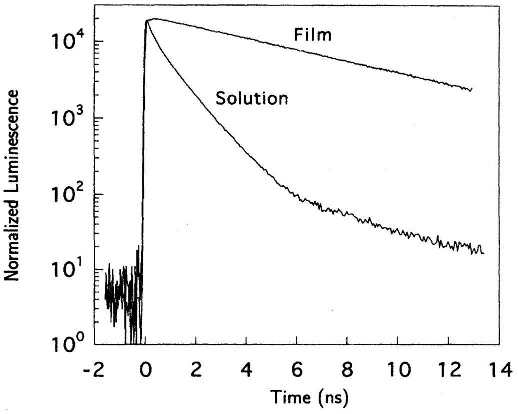


FIG. 5. Comparison of time-resolved luminescence in CN-PPV solution (excited at 330 nm) and film (excited at 600 nm).

the constituent molecules. If the dipoles are parallel then transition to one of the levels will be forbidden. If the dipoles are not parallel then transitions to both levels are allowed. Knox has shown that for transition dipoles which are randomly oriented, on average the lower-lying level will have lower oscillator strength.[22] Physical dimers generally have a broad emission spectrum. They have recently been reported in the conjugated oligomer sexithiophene.[23]

It is also possible for a dimer to form between an excited molecule and its unexcited neighbor, even though there would be a repulsion between them in the ground state. Such a dimer, which does not exist in the ground state, is known as an excimer. Like a physical dimer, it is expected to have reduced oscillator strength.[24] The repulsive ground state potential leads to a broad emission spectrum without vibronic structure, and it also contributes to the apparent Stokes shift between absorption and luminescence.

The formation of an interchain excitation in CN-PPV may be favored by the symmetrical substitution of hexyloxy sidechains on both sides of the phenylene ring. These may have a tendency to crystallize, giving cofacial chain packing of the aromatic part of the molecules. Similar behavior is believed to occur in the poly(3-alkyl thiophene)s.[25] Excimers and exciplexes have been reported in some conjugated polymers,[12,26] but our results are evidence for interchain excitations in a member of the poly(arylenevinylene) family, which is an important class of materials for electroluminescence. It is not easy to determine whether the emission which we observe is from a dimer, an excimer, or an interchain exciton. In principle a dimer will have an associated absorption, but this could easily be hidden under the wide inhomogeneously broadened absorption spectrum of conjugated polymers. The absence of vibronic structure in the emission spectrum is fully consistent with excimer emission, but could also arise from emission from a dimer or an interchain exciton. We note that dimers and excimers are concepts usually applied to small molecules with well-defined chromophores. In conjugated polymers there is extensive electron delocalization which may modify the character of the excitations, making them more like an interchain exciton.

We suggest that the main product of photoexcitation is the generation of intrachain singlet excitons which then migrate either to pre-existing dimers or to regions where excimers form. Studies of electron transfer from conjugated polymers to fullerene,[27] and of ultrafast photoluminescence,[6,11] show that migration of excitations to lower energy regions of the sample can occur in a few picoseconds, which is shorter than the 50 ps time resolution of our measurements. Once formed the excimers or dimers will decay by a combination of radiative and nonradiative channels. One important nonradiative decay process is believed to be migration of excitations to quenching sites. In PPV and PPPV this happens in around 200–300 ps,[3,5,11] and so it is surprising to find that the emission in CN-PPV lasts 5.4–5.7 ns, and furthermore that the luminescence is efficient. Interchain excitations would be less mobile than intrachain excitons and this may explain why nonradiative decay rates are much lower in CN-PPV than in other conjugated polymers such as PPV.

In conclusion, we have performed luminescence efficiency and time-dependence measurements on a high electron affinity electroluminescent polymer, CN-PPV. We find that the luminescence lifetime in the films of 5.6 ns is much longer than in the solution, and much longer than in other conjugated polymers. The corresponding natural radiative lifetime of 16±2 ns is an order of magnitude larger than in related materials. These results suggest that the emission is from a different species from that in related polymers such as PPV, and we propose that it is from an interchain excitation. This would explain the long lifetime, broad structureless emission, and large apparent Stokes shift of CN-PPV films.

The luminescence does not originate from an excitation localized on a single chain, but arises from an excitation that requires chain interactions. This finding has a major influence on the molecular engineering strategy for the synthesis of highly luminescent conjugated polymers. The strategy must now take into account the possibility of enhancing the luminescence efficiency by altering the chain packing properties.

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