

## Excited-state quenching of a highly luminescent conjugated polymer

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The optical properties of a luminescent polymer, poly[1,4-phenylene-1,2-di(phenoxyphenyl) vinylene], have been investigated. Its photoluminescence yield increases unusually in the solid-state over solution, 52%–6% respectively. Investigations into the stimulated emission properties of this material were carried out but no amplified spontaneous emission was observed. To investigate the presence of excited-state absorption features, the photoinduced absorption spectrum was measured. An observed polaron absorption band, from 1.5 to 2.25 eV, overlaps the emission spectra and therefore quenches stimulated emission. This highlights the need to consider the effects of excited-state absorption on the emission when synthesizing new materials. © 2001 American Institute of Physics. [DOI: 10.1063/1.1345840]

In recent years there has been a rapid development in the physics of organic electroluminescent devices.<sup>1</sup> Enhanced understanding of material properties, like carrier mobilities and photoluminescence (PL) yield, is significant for realizing an electrically pumped polymeric laser. Optically pumped organic lasing has been observed in numerous polymeric<sup>2</sup> based devices and in many different structures.<sup>3,4</sup> Investigations into electrically pumped lasing have been less successful. Large carrier densities have been observed but no spectral narrowing has been noted.<sup>5</sup> Two explanations are put forward for this: nonbalanced charge transport and excited-state absorption, which inhibits optical gain. In this letter we present a detailed analysis of the emission properties of a highly luminescent polymer, poly[1,4-phenylene-1,2-di(phenoxyphenyl) vinylene, (DPOP-PPV)], as well as results on the quenching of stimulated emission by excited-state absorption. This work emphasizes that during the design of polymers for high luminescence efficiency optical applications, the excited-state absorption must be carefully considered.

The polymer, DPOP-PPV, was synthesized by reductive coupling (de-halogenation polymerization) of appropriately substituted tetrachlorides.<sup>6</sup> DPOP-PPV has phenoxy-phenyl side chains [Fig. 1(a)], which aid both solubility and increase the glass transition temperature ( $T_g \sim 163^\circ\text{C}$ ). The polymer batch used for this work had a molecular weight ( $M_w$ ) of  $\sim 23\,800$ .

Absorption and PL spectra of 0.25 mg/ml solutions of DPOP-PPV in various solvents were measured using a Shimadzu UV-2101PC absorption spectrometer and a Perkin-Elmer LS50B luminance spectrometer, respectively. Solid-

state spectra were taken of a thin film prepared by spin coating from a 75 mg/ml solution in toluene at 700 rpm, giving a film thickness of 690 nm. For PL the samples were excited at 440 nm, the excitation maximum.

The PL yield of DPOP-PPV in: a dioxane solution, a 1% doping of a polystyrene (PS) matrix and a neat film were measured using an integrating sphere connected to a charge coupled device (CCD) grating spectrometer by an optical fiber, with an excitation wavelength of 354 nm from a helium cadmium laser at  $0.1\text{ mW/cm}^2$ . The use of the CCD spectrometer allows us to distinguish between the PL signal and the exciting laser signal without the use of filters.<sup>7</sup> The external PL quantum yield, defined as the ratio of the number of photons emitted to the number of photons absorbed, is calculated from the ratio of the integrated PL signal, with the sample in place, to the increase in the integrated laser intensity when the sample is removed.

Amplified spontaneous emission (ASE) measurements were carried out on a DPOP-PPV waveguide fabricated on  $\text{SiO}_2$ , using the method of Ref. 8. The polymer layer was produced by spin coating from a 75 mg/ml solution in toluene onto the substrate. Waveguide loss of this sample was found to be 5.7 dB/cm, using the method of Ref. 9, at 632.8 nm, by recording the scattered light along the track of a resonant mode using a Nikon digital camera. The emission spectrum from the waveguide used demonstrated no spectral narrowing with increased pump intensity (maximum pump intensity was  $8.5 \times 10^5\text{ W/cm}^2$ ) or pump length dependence.

To investigate the absence of ASE within a material of large PL yield and low scattering losses, the excited-state absorption of DPOP-PPV was investigated. Two complementary techniques were carried out, one was photoinduced absorption (PA) spectroscopy and the other was measuring the absorption of 0.2 mg/ml DPOP-PPV toluene solutions

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doped with a charge transfer species,  $\text{FeCl}_3$  (0.025 M).

PA spectroscopy probes excited-state absorptions (e.g., triplets and polarons) formed by photoexcitation. A 457.9 nm argon-ion laser line is used as the pumps the sample while a monochromated tungsten white light source is used as the probe. An acousto-optical modulator modulated the pump beam, while a photodetector and a lock-in amplifier monitored the changes in the transmission of the probe beam. The lock-in amplifier simultaneously measures the in-phase and quadrature signals with the laser modulation. All measurements were performed on drop cast films under vacuum ( $\sim 2.7 \times 10^{-3}$  Torr) at 80 K.

The absorption and PL spectra for DPOP-PPV in various solvents and the solid state are shown in Fig. 1(a). An absorption edge is observed at  $\lambda = 440$  nm with an absorption maximum at  $\lambda = 368$  nm. In solid state this absorption peak is less well resolved than in solution, and no spectral shift is observed. The PL in both solution and the solid-state peaks at  $\lambda = 520$  nm, with no other strong vibrational features notable. The peak emission wavelength and the full width at half maximum were found to be largely independent of the solvent used. A Stokes shift of  $\sim 150$  nm is observed in solution and solid state. The peak PL intensity and hence PL yield was found to be highly solvent dependent. Significant decreases in emission were noted with toluene, tetra-hydrofuran and chloroform when compared to dioxane.

The PL yield for a dioxane solution of DPOP-PPV was measured to be  $\sim 6\%$ . In the solid state a PL yield of 52% is measured for a neat film, while the PL yield drops to 22% for the DPOP-PPV doped PS matrix.

Solvent choice has strong influences on the PL of organic materials through dipole interactions, rotational effects, conformational changes<sup>10,11</sup> and vibrational interactions.<sup>12</sup> The unusual PL yield relationship in solution and the solid state can be addressed by considering the large side groups attached to DPOP-PPV. There is a steric hindrance between the two substituted phenoxyphenyl side groups and the phenyl ring on the polymer backbone resulting in a nonplanar, conformation of the polymer. X-ray diffraction experiments<sup>13</sup> have shown that in the solid state the polymer packs rigidly in a highly amorphous manner, producing severe torsional hindrances along the polymer backbone. This results in large energy barriers to exciton hopping along the chain, which prevents exciton diffusion to quenching sites, and raises the PL yield. Similar improvements in PL yield have been observed in meta-substituted copolymers of PPV where the conjugation along the polymer backbone has been broken.<sup>14</sup> Further evidence for this interpretation arises from the luminescence emission maxima in solution and thin film occurring at the same wavelength, which indicates an equivalent polymer chain orientation in both solution and solid state. This is further supported by the strong relationship between PL yields and solvent choice. In solution the polymer chains have greater spatial freedom to explore more planar conformations. This reduces the energy barriers for exciton diffusion along the polymer backbone, increasing the number of nonradiative routes and decreasing the PL yield. The conformational freedom that the polymer has in solution depends on the viscosity of the solvent environment. We find that the photoluminescence is inversely

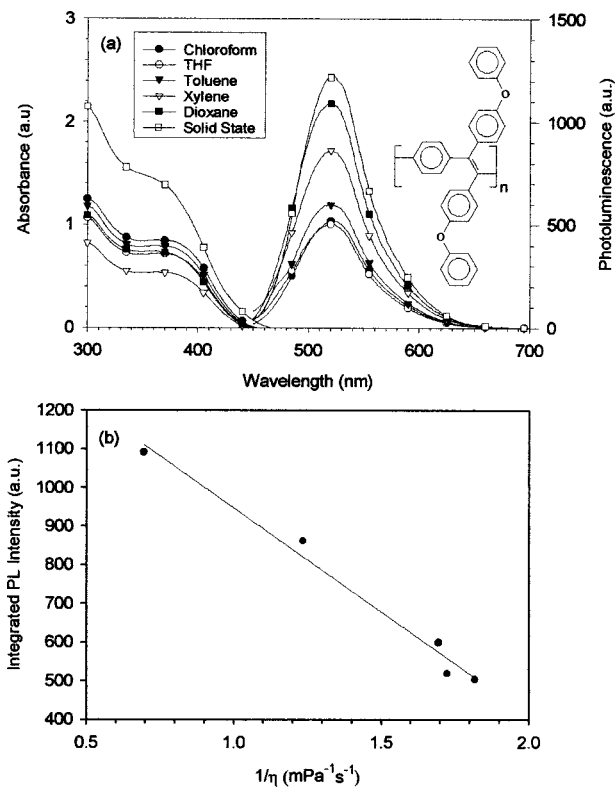


FIG. 1. (a) Absorption and PL spectra of DPOP-PPV in various solutions and solid state with structure of DPOP-PPV inset. (b) The relationship between integrated PL Intensity and viscosity of solvent for DPOP-PPV in various solvents (see Ref. 15).

proportional to the solvent viscosity<sup>15</sup> from Fig. 1(b). The quantum yield of DPOP-PPV in polystyrene, at 22%, indicates that the side chains have less freedom in the solid state than in solution. The decrease in PL yield from neat solid state to polystyrene is related to the fact that the side chains are not subject to close packing in the polystyrene matrix that they suffer in a DPOP-PPV environment.

The absence of ASE within this material cannot be explained by scattering loss within the material. The waveguide loss of 5.7 dB/cm indicates a low degree of polymer crystallinity, and compares well with other highly emissive materials exhibiting ASE, e.g., mLPPP which has a waveguide loss of  $\sim 54$  dB/cm.<sup>16</sup> We therefore consider the excited state absorption of DPOP-PPV at high excitation intensities.

The PA spectrum of the DPOP-PPV film is shown in Fig. 2(a). The PA spectrum is represented as the measured change in transmission normalized to the transmission for the probe beam. A strongly defined absorption feature appears at 1.9 eV in the PA spectrum. Figure 2(a) also shows an example absorption spectrum of DPOP-PPV solution after  $\text{FeCl}_3$  doping. Successive amounts of  $\text{FeCl}_3$  were added to the DPOP-PPV solution. The doping induced absorption was found to increase linearly and without change in line shape with increased doping. There is a broad absorption band at 1.8 eV, which overlaps the PL spectrum of DPOP-PPV. This absorption may be attributed to positive polarons, which are formed by oxidation of the polymer chains, stabilized by a  $\text{FeCl}_4^-$  anion.<sup>17</sup> This corresponds with the energy of the PA absorption feature, within the limits of a possible solvatochromic redshift,<sup>18</sup> and we assign this feature to photogenerated polarons. The presence of polarons is known to quench

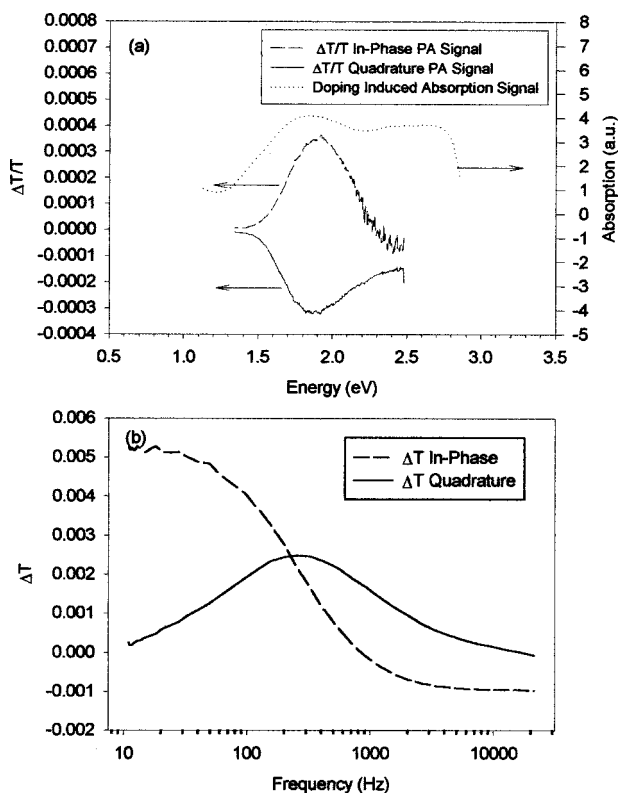


FIG. 2. (a) Photoinduced absorption signal for in-phase and quadrature of a DPOP-PPV film. Also shown is the induced absorption when a solution of DPOP-PPV in toluene is doped with  $\text{FeCl}_3$ . (b) The frequency response of the PA signal which is used to calculate the lifetime.

singlet excitons<sup>19</sup> and hence strongly reduce stimulated emission processes. The spectral width of this feature is narrower, 0.48 eV, than the doping induced absorption feature, 0.9 eV. We propose this is due to the difference in temperature between the two measurements.

Figure 2(b) shows the PA dependence on the pump beam modulation frequency. For polaron species, the frequency response of the in-phase and quadrature signals is well known.<sup>20</sup> The polaron lifetime measured from the frequency response of the PA signal is 0.7 and 0.6 ms for the in-phase and quadrature signals, respectively. The long lifetime indicates an energetically stable state that outlives the fluorescence ( $\sim 1.44$  ns)<sup>21</sup> of the material. This indicates that the polaron will strongly quench the singlet fluorescence and hence quench stimulated emission.

The phenoxyphenyl side chains provide the high  $T_g$  and PL yield for DPOP-PPV. However, they also have adverse effects by causing the high polaron population. Studies on families of di-phenyl substituted polymers have shown that none are suitable for optically pumped lasing.<sup>6</sup> This is most likely due to a very stable excited state, the quinoid structure, which is formed when the phenoxyphenyl groups become charged. This state is energetically stable and does not reduce quickly back to the ground state. The state is also localized over short chain lengths, which is consistent with the blueshift of the polaron absorption feature when compared to other PPV derivatives of similar emission wavelength.<sup>22</sup> It is this polaron absorption feature which is preventing lasing from materials of this type by inhibiting emission from singlet excitons.

This work provides an interesting study of how the

chemical structure of DPOP-PPV strongly affects its optical properties in a conflicting manner that was not foreseen. Initial results indicated excellent luminescent properties through exciton confinement along the polymer backbone. PA and doping induced absorption measurements have shown that the same structural feature that enhances luminescence destroys the stimulated emission properties. The broad polaron absorption band centred on 1.9 eV suggests DPOP-PPV is limited optically as a candidate for further electroluminescence studies only. To conclude, this work clearly demonstrates that in the design of highly luminescent polymers the alteration of excited-state absorption is valuable to complete the information of the ground state absorption and luminescence properties.

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