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Laser emission from solutions and films containing semiconducting polymer and titanium dioxide nanocrystals

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Abstract

We report laser emission from solutions and dilute blend films containing a semiconducting polymer, poly(2-methoxy,5-(2′-ethyl-hexyloxy)-1,4-phenylene-vinylene) (MEH-PPV), and titanium dioxide (TiO_2) nanocrystals under pulsed optical excitation at 532 and 435 nm. The TiO_2 nanoparticles multiply scatter photons in the active polymer medium such that gain exceeds loss above a critical excitation threshold. Above threshold, the emission spectrum narrows significantly. Solid state lasing is observed from free standing films of MEH-PPV and TiO_2 in polystyrene. This is the first demonstration of lasing with a semiconducting polymer in the solid state as the active medium.

1. Introduction

The discovery that semiconducting conjugated polymers can be used as the active medium in diodes [1] and light emitting diodes [2,3] stimulated research aimed at realizing a variety of optoelectronic devices including large area flexible LEDs [4], photodiodes [5–8], polymer grid triodes [9], and light emitting electrochemical cells (LECs) [10]. These thin film devices benefit from the processability of semiconducting polymers; optical quality films can be cast from solution using common organic solvents. Polymer electroluminescence (EL) has been demonstrated with colors throughout the visible spectrum, including white light emission [11,12]. Typically, the EL spectrum closely resembles the photoluminescence (PL) spectrum; both consist of a vibronic series that is red-shifted from the absorption.

The achievement of spectrally narrow polymer laser diodes is an important goal for polymer optoelectronic devices. By restricting the allowed modes of the radiation field, microcavities redistribute emission, increasing the intensity at some wavelengths at the expense of others [13–15]. This control, however, comes at the expense of requiring high-Q resonant cavities for each desired wavelength. Moreover, the color of light emitted from microcavity LEDs depends on viewing angle, making such devices unsuitable for some applications. To date, laser action has not been observed from polymers in microcavities.

We report laser action from solutions and from solid films of poly(2-methoxy,5-(2′-ethyl-hexyloxy)-1,4-phenylene-vinylene) (MEH-PPV), in polystyrene. Our approach exploits the work of Lawandy et al. [16,17], who demonstrated isotropic laser emission

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from optically pumped dye solutions containing colloidally suspended titanium dioxide (TiO_2) particles. In the solutions and films containing MEH-PPV, the titania particles multiply scatter emitted photons in the active polymer medium such that gain exceeds loss above a critical excitation threshold. This is the first demonstration of lasing with a semiconducting polymer in the solid state as the active medium. We discuss the advantages of this approach and the hurdles that remain for the eventual production of solid-state polymer laser diodes.

The idea underlying this approach is straightforward. Scattering off the randomly distributed high-index of refraction titania nanocrystals greatly increases the path length traversed by the emitted light [16]. This allows stimulated emission gain to occur if the medium is pumped above threshold and the scattering length exceeds the gain length [18]. In essence, the colloidal particles function as an isotropic, random microcavity which provides the feedback necessary for laser action. Subsequent studies explored the concentration dependences of the active gain medium and the scatterers [19,20], the effect of scattering on energy transfer in binary dye solutions [21], and the radiative coupling between sheets of dye and scatterers dispersed in host polymers [22]. Potential applications for titania–dye mixtures have been proposed, including lasing textile fibers [23] and photonic paint [24].

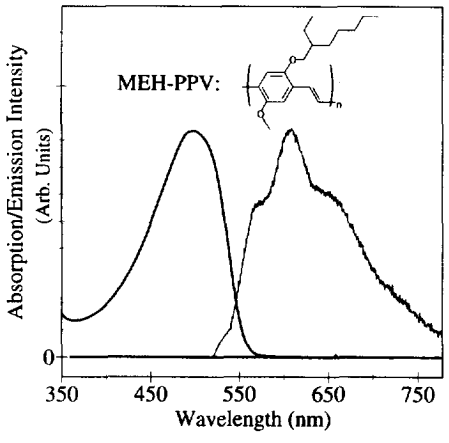


Fig. 1. Absorption (heavy smooth curve) and PL (thin, slightly noisy curve) spectra of dilute solutions of MEH-PPV in cyclohexanone in a 1 mm cuvette. The absorption was measured with a 0.01% w/v solution, and the PL measurements were performed with low energy 532 nm excitation in a 0.1% w/v solution. Inset: chemical structure of MEH-PPV.

Extending this idea to solid-state polymer lasers places stringent requirements on the conjugated polymer; the polymer must exhibit stimulated emission. MEH-PPV has proven to be a versatile semiconducting polymer for use in optoelectronic devices [3–10]. We have chosen MEH-PPV (Fig. 1) for our initial studies, because of its solubility in conjugated form in common organic solvents and the relatively high brightness and efficiency of LEDs and LECs made with MEH-PPV. Ultrafast spectroscopy [25] showed stimulated emission from MEH-PPV in solutions and in dilute host polymer films, consistent with photopumped lasing in concentrated MEH-PPV solutions [26]. These studies indicate, however, that stimulated emission in pure MEH-PPV is inhibited in the solid state [25], presumably because of interchain interactions. Thus, gain narrowing by scattering from titania particles should be possible with MEH-PPV only in solutions and in dilute solid films.

2. Experimental methods

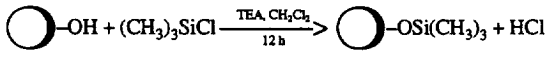
Solutions and dilute films of MEH-PPV with suspended titania particles must be made with care as a result of potential material incompatibilities. Hydroxy-terminated TiO_2 nanocrystals do not disperse well in the solvents of choice for MEH-PPV. Dilute solid films of MEH-PPV in host polymer matrices must be molecularly dispersed, since phase segregation results in MEH-PPV interchain interactions which quench stimulated emission. By appropriate choice of solvents and host polymer and a simple modification of the titania particle surface, we have successfully produced both solutions and dilute film blends of MEH-PPV and titania particles that demonstrate laser action.

MEH-PPV was obtained from UNIAX Corp. and used as received. Solutions of MEH-PPV in cyclohexanone, at concentrations ranging from 0.1 to 1.0% w/v, were prepared by stirring at room temperature in a nitrogen environment. The titania particles were obtained from DuPont Chemicals (Ti-Pure R900) and had an average diameter of 270 nm. The desired amount of titania was added to the solutions and dispersed by additional stirring. For lumines-

cence measurements, the solutions were transferred to 1 mm sealed glass cuvettes.

Dilute solid films of MEH-PPV were prepared using polystyrene (PS) (MW 125000–250000, from Polysciences, Inc.) as the inert matrix. Polystyrene is an excellent host: it is optically clear and soluble in many of the same solvents as MEH-PPV.

Our initial attempts to produce blended films of MEH-PPV:TiO_2 were hampered by aggregation of TiO_2 particles in the MEH-PPV/PS blend. Thus, we modified the polar surface of TiO_2 nanoparticles by silation:



where the large circles in Eq. (1) represent the titania nanocrystals. The reaction is run in freshly distilled methylene chloride (CH_2Cl_2) in the presence of catalytic amounts of the base, triethylamine (TEA), in inert atmosphere. The precipitate was rinsed and allowed to dry.

Films were cast from a solution containing 0.5 g of PS and the desired amount of modified titania particles and MEH-PPV, all in tetrahydrofuran (THF). Concentrated solutions of PS (20% w/v) were used, making the mixture sufficiently viscous to prevent sedimentation of the titania particles during processing. The resulting mixture was stirred vigorously at 35°C for 12 h, and then degassed under vacuum to prevent bubble formation during film fabrication. The mixture was spread in a small Petri dish and dried at 35°C, yielding homogeneous free-standing films with typical thicknesses of 150–250 μm. Reference films containing no titania particles were prepared by a similar procedure.

PL experiments were performed at room temperature following Lawandy et al. [16]. The frequency doubled output (532 nm) of a 10 Hz, Q-switched Nd:YAG laser (Spectra Physics Quanta-Ray DCR-3) served as the excitation source (additional experiments used 435 nm light produced as the first anti-Stokes Raman line from the 532 nm light passed through a high pressure H_2 cell). The ~10 ns pulses, focused to a spot size of ~1.5 mm, were incident on the samples at a 30° angle to avoid the possibility of lasing off the cell walls or film edges. The emission that passed through a ~2 mm aperture placed normal to the front face of the sample was collected, frequency dispersed in a single monochromator (Spex), and detected by a Peltier-cooled CCD array (Photometrics). A typical experimental run recorded changes in the PL spectrum as a function of the excitation energy per pulse. We note that the width of the observed emission spectrum is dependent on the geometry used for collection. For example, light collected parallel to the front face of the sample can undergo amplified spontaneous emission (ASE), leading to some line narrowing even in the absence of colloidal TiO_2. The geometry we employed enabled us to reproduce the emission results of Lawandy et al. on TiO_2 particles suspended in Rhodamine 640/methanol solutions [16].

3. Results and discussion

Initial experiments examined the effects of titania particles on the PL of MEH-PPV in solutions. The spectrum (see Fig. 1), characterized by a vibronic series with the 0–0 transition at ≈ 570 nm, remains essentially constant with increasing pump energy, as indicated by the solid curve in Fig. 2a. In the presence of ~10^{10} cm^{-3} titania particles, however, dramatic gain narrowing is observed (Fig. 2a, dashed curve) [2] when pumped above the threshold for stimulated emission, indicative of laser action.

The effect of pump energy on the PL of MEH-PPV:TiO_2 solutions is presented in Fig. 2b, which shows the spectra obtained from a 1.0% w/v solution of MEH-PPV in cyclohexanone with ~10^{11} cm^{-3} suspended TiO_2 nanocrystals pumped at two energies: 0.12 mJ (solid curve) and 3.6 mJ (dashed curve). The solid curve is the typical broad emission from MEH-PPV. The dashed curve shows emission from the same solution pumped well above the lasing threshold. Again, striking gain narrowing is observed, as well as a blue-shift of the narrowed emis-

[2] Although the average particle size is 270 nm, the solutions and films appear milky to the eye. This indicates some association of the particles into scattering aggregates that have sizes comparable to visible wavelengths. Thus, the particle densities quoted here likely overestimate the number density of scattering entities.

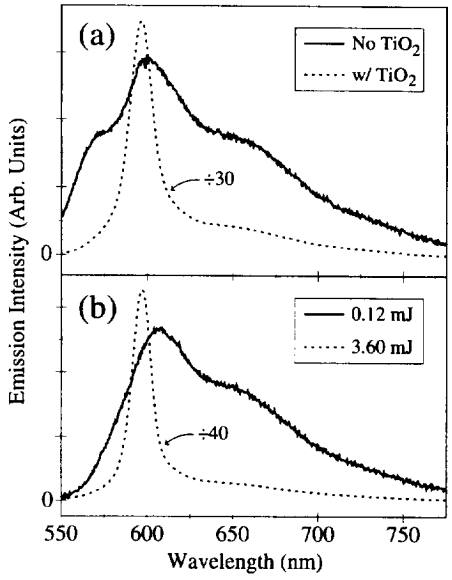


Fig. 2. (a) Effect of TiO_2 nanoparticles on the luminescence of MEH-PPV/cyclohexanone solutions: Solid curve: PL of 0.6% w/v MEH-PPV solution pumped with 4.5 mJ of 532 nm light; dashed curve: PL of the same solution under identical excitation conditions after addition of $\sim 10^{10}$ cm^{-3} titania particles. (b) Effect of excitation energy on the luminescence of MEH-PPV/cyclohexanone solution (1.0% w/v) with $\sim 10^{11}$ cm^{-3} titania particles.

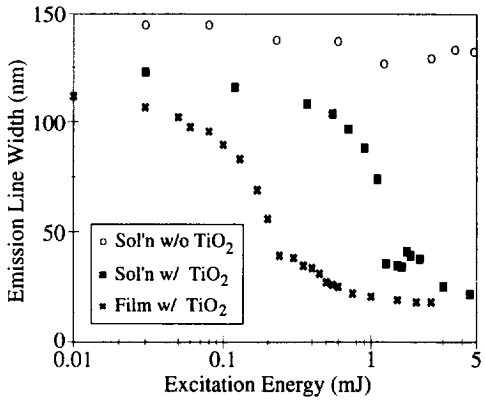


Fig. 3. Emission line width (full width at 1/e height) as a function of energy for scattering MEH-PPV/cyclohexanone solutions and PS dilute blend films. Open circles: 0.6% w/v MEH-PPV solution with no titania particles (same as solid curve in Fig. 2a); solid squares: identical solution after addition of $\sim 10^{10}$ cm^{-3} TiO_2 nanocrystals (same as dashed curve in Fig. 2a); crosses: 0.9% w/w MEH-PPV in PS free-standing film with $\sim 10^{11}$ cm^{-3} titania particles; cf. Fig. 5.

sion with respect to the low-energy luminescence (cf. Fig. 4, below). The high energy vibronic shoulder, corresponding to the 0-0 transition observed at lower MEH-PPV concentrations (Fig. 1), is suppressed in this concentrated solution. The amplitude of this feature decreases with increasing MEH-PPV or particle concentrations, consistent with self-absorption.

Fig. 3 displays the dependence of the emission line width (full width at 1/e height) [3] as a function of pump energy for the solution of Fig. 2a (0.6% w/v MEH-PPV in cyclohexanone, $\sim 10^{10}$ cm^{-3} titania particles). The solid squares show a factor of ~ 5 decrease in line width, and indicate that the threshold for laser action occurs ~ 1 mJ. The open circles represent the line width for an identical MEH-PPV solution without titania particles. Clearly, the scattering particles are crucial to the achievement of gain narrowing [4]. The MEH-PPV solution results (Figs. 2 and 3) are in good qualitative agreement with those obtained earlier from dye solutions [16].

We have investigated line narrowing in solutions with four different concentrations of MEH-PPV (0.1, 0.3, 0.6, and 1.0% w/v) and two different concentrations of scattering particles ($\sim 10^{10}$ and $\sim 10^{11}$ cm^{-3}). At the lowest MEH-PPV concentration (0.1% w/v), we find no significant gain narrowing up to 5 mJ for either of the 2 particle concentrations; the amplification length in the dilute gain medium is too large for laser action to occur. When the concentration of MEH-PPV is increased to 0.3% w/v, gain narrowing occurs above ~ 1.5 mJ, but the line width

[3] We have chosen the full width at 1/e height to represent the line width of the emission spectra since this is more suitable (compared to other definitions such as FWHM) for comparison of disparate emission spectra with varying magnitudes of vibronic features.

[4] In the most concentrated solutions and films, we observe some narrowing of the emission even without the addition of titania particles. This is likely due to ASE that is reaching the detector. Unlike the data presented in Fig. 3, there is no sudden drop in line width with increasing energy for these concentrated solutions, and the final line width is broader than in the corresponding samples with TiO_2 particles.

decreases by only a factor of ~ 2. With continued increases in the MEH-PPV concentration, the threshold for lasing moves to lower energies, and the gain-narrowed line width decreases. At the highest concentration studied (1.0% w/v), the threshold for lasing action is ~ 0.7 mJ, and the line width decreases by over a factor of 6 between 0.2 and 2.0 mJ pump energy. There was little effect of changing the concentration of scatterers from ~ 10^{10} to ~ 10^{11} cm^{-3} at any concentration of MEH-PPV. The dependence of gain-narrowing on MEH-PPV concentration and lack thereof on titania particle concentration in this range are consistent with results obtained from dye molecule solutions [19,20].

One interesting feature of the scattering polymer solutions not observed in dye solutions is a definite blue-shift of the emitted light with increasing excitation energy. Fig. 4 presents the wavelength of the emission maximum as a function of pump energy for the same solution used for obtaining the data in Figs. 2a and 3 (solid squares). The emission peak blue-shifts precipitously at approximately the same energy as the collapse of the emission line width, providing further evidence of laser action. We believe that this blue-shift is a result of temporal narrowing of the emitted laser light. Ultrafast spectroscopy of MEH-PPV [27] shows an initially blue-shifted PL spectrum which evolves to the steady-state emission spectrum over the first tens of ps following photoexcitation. This spectral evolution has been assigned to energy transfer from excited polymer segments with shorter

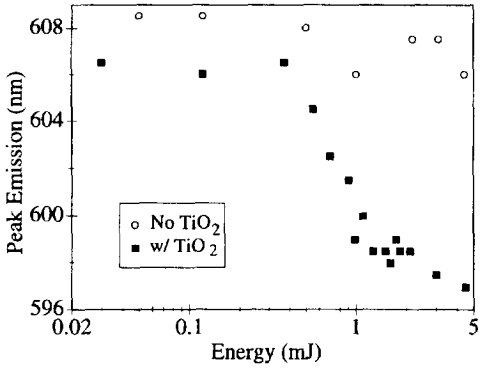


Fig. 4. Emission peak position as a function of energy for the same MEH-PPV and MEH-PPV:TiO_2 solutions used for Fig. 3; symbols are the same as in Fig. 3.

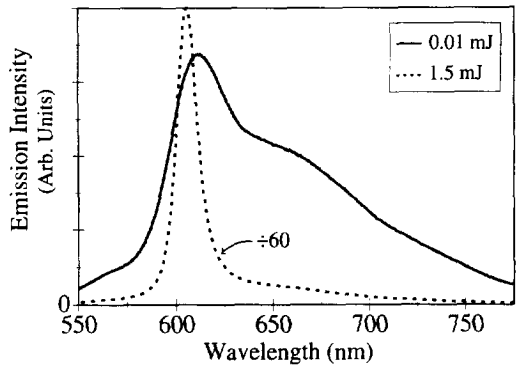


Fig. 5. Effect of excitation energy on the luminescence of dilute free-standing films of MEH-PPV (0.9% w/w) in PS with ~ 10^{11} cm^{-3} titania particles.

conjugation lengths to more ordered segments with longer conjugation lengths. Streak camera measurements indicate that the gain-narrowed emission in scattering dye solutions also occurs on the tens of ps time scale [20]. Thus, above the lasing threshold, stimulated emission in scattering polymer solutions largely occurs before energy transfer can take place, resulting in enhanced gain from the early time blue-shifted emission. Photoinduced absorption, which overlaps the red edge of the PL [25], may play a significant role at high excitation densities. Of course, both photoinduced absorption and temporal narrowing may be involved.

The observation of laser action in solutions provides the necessary insight for the achievement of lasing in solid polymer films. The emission spectra from a dilute (0.9% w/w) blend of MEH-PPV in PS with ~ 10^{11} cm^{-3} titania nanoparticles above and below the lasing threshold are shown in Fig. 5. Clearly, gain narrowing occurs in the solid film: the final line width is slightly narrower and the long wavelength luminescence tail is better suppressed in the film than in the comparably concentrated solution. The gain narrowing as a function of energy for this film is shown as the crosses in Fig. 3. The collapse of the line width and the blue-shift of the emission peak for the solid polymer film occur at nearly an order of magnitude lower energy than in the comparably concentrated solution. The enhanced narrowing and lower threshold in polymer films compared to solutions was general to 3 concentra-

tions of MEH-PPV in PS (0.2, 0.9, and 1.5% w/w) and 2 titania particle densities ($\sim 10^{10}$ and $\sim 10^{11}$ cm^{-3}) that we studied.

We have also pumped the PL of blend films and solutions at 435 nm. The thresholds for spectral narrowing are somewhat higher, consistent with the lower absorption at 435 nm compared to 532 nm (cf. Fig. 1). As a result, pumping is less effective.

The observation of polymer lasing in the solid state is encouraging in another respect: laser action occurs at energies well below the onset of optical damage. For all films, there is an energy threshold above which dark spots appear, accompanied by an increase in the emission line width. In our standard geometry, the damage threshold occurs near 2.5 mJ, nearly an order of magnitude higher in energy than the threshold for gain narrowing. As expected, both the lasing and damage thresholds are sensitive to the excitation spot size.

Efforts are underway to investigate the feasibility of making an electrically pumped solid state laser with a semiconducting polymer as the active gain medium. Our approach of using scattering to produce lasing has several advantages. Lasing action provides an increase in the luminescence quantum yield, offering the possibility for more efficient EL devices. The isotropic nature of the scattered laser light should fit well with the requirements of many applications. Titania nanoparticles are inexpensive and readily available in industrial quantities. Moreover, TiO_2 can be incorporated into existing polymer processing technologies with minimal disruption. Finally, TiO_2 scatters over the entire visible spectrum, making this approach applicable to conducting polymers that emit in any spectral region.

Despite these advantages, realization of solid-state polymer laser diodes will require progress in two areas: First, the role of the thickness of the polymer film in producing lasing by scattering must be understood; and second, current densities sufficient to surpass the laser threshold by electrical pumping must be achieved.

The thickness is important because typical films in LEDs (0.1–0.2 μm) are much thinner than those used to demonstrate solid state lasing ($\sim$ 100 μm). Balachandran et al. [28] (see also Refs. [16,17]) observed gain narrowing in scattering dye solutions in thin cells (100 μm), but the minimum thickness for lasing in films is unknown [5]. Clearly, the effects of sample thickness on gain narrowing in scattering media need to be explored for films with micron and submicron thicknesses. While thicker films of conducting polymers are readily achievable, such films produce electrically pumped devices with higher turn-on voltages. An alternative approach would be to incorporate the titania particles into the light-emitting electrochemical cell (LEC) [10] since the performance of the LEC is insensitive to film thickness.

Achieving sufficient carrier concentrations to produce laser action in dilute blend films with electrical pumping involves serious technical challenges. In order to achieve the same photon densities as in the optically pumped films, transient current densities of the order of 10^5–10^6 A/cm^2 will likely be necessary to reach the threshold for gain narrowing. Current densities of 25 A/cm^2 were reported in electrically pulsed MEH -PPV diodes (4×10^{-3} cm^2 area) when operated with 3 μs pulses at a low duty cycle [29]. With improved thermal management, smaller active areas, and shorter current pulses, sufficiently high current densities should be possible. Conjugated polymers that show high PL efficiency and long-lived stimulated emission in the pure form (rather than in dilute blends) could provide both sufficiently good transport and a somewhat lower gain threshold.

4. Conclusions

In summary, we have used scattering from titanium dioxide nanocrystals to produce laser action from optically pumped solutions and free-standing dilute blend films of the conducting polymer MEH-PPV. Gain narrowing was observed above a critical pump threshold at two different pump wavelengths for several polymer and particle concentrations. The polymer emission exhibits a blue shift at approximately the same threshold pump energy. We believe this constitutes the first observation of lasing from a conjugated polymer in the solid state. The isotropic nature of the narrowed emission and the straightfor-

[5] Lasing action has been observed even though the gain medium thickness is shorter than the photon scattering length, see Refs. [16,17].

ward extension of adding titania particles to polymer EL devices are promising for the eventual production of scattering solid state polymer laser diodes.

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