Dye-doped polymers for blue organic diode lasers

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Amplified spontaneous emission (ASE) in optically pumped polymeric films containing the luminescent and hole-transporting organic molecule N,N' -Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) is demonstrated. ASE is observed in polymer films of polystyrene and poly(N-vinylcarbazole) doped up to 20% with TPD. From these results, we conclude that TPD-based films are candidates for blue-emitting organic diode lasers. © 2002 American Institute of Physics. [DOI: 10.1063/1.1485303]

Since the discovery of conductivity in polymers and certain organic molecules and crystals, remarkable progress has been made in synthesizing organic materials, in understanding their properties, and in developing them for use in electronic and optical devices.\(^1\) Most of the photonic and electronic phenomena known in conventional inorganic semiconductors have been observed in semiconducting polymers\(^2\) and organic molecules.\(^3\) Currently, polymer and organic diodes, light emitting diodes (LEDs), photodiodes, field-effect transistors, and photovoltaic cells are all being pushed towards commercialization. These devices are important because they can be fabricated by inexpensive techniques, such as spin coating, photolithography, ink-jet printing, low temperature fiber drawing, screen printing, and micromolding onto almost any type of substrate, including flexible ones. This constitutes a real advantage as compared to the sophisticated technology used with inorganic materials in the traditional semiconductor industry.

In spite of this huge advance in the development of organic photonic and electronic devices, one of the most important devices is still missing in the market—the laser diode. Since the demonstration in 1996 of photopumped lasing from semiconducting polymers,\(^4\)–\(^6\) much effort has been devoted to the development of organic diode lasers.\(^2,3\) However, due to the presence of strong charge-induced absorption and electrode-induced absorption, past efforts to make polymer diode lasers from organic and polymeric films have been unsuccessful. Recently, an electrically driven organic laser that uses a high-quality single crystal of tetracene has been demonstrated.\(^7\) This important discovery has motivated to continue searching for lasing materials. However, in order to exploit the previously mentioned inexpensive preparation techniques, the most interesting materials are those that are soluble and can be prepared in the form of thin films.

In this letter we investigate the possibility of using different kinds of luminescent and semiconducting organic molecules and polymers, in the form of thin films, as active lasing materials for the construction of organic diode lasers. They are prepared as follows.

The samples are made by spin coating onto glass substrates 300–1000-nm-thick films from a solution containing a polymer doped with one or several organic molecules. Three types of films are investigated: (1) films based on polystyrene (PS) (inert polymer) doped with the diamine derivative N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD) (5%, 10%, 15%, and 20%); (2) films based on the widely used polymer poly(N-vinylcarbazole) (PVK), doped with TPD (5%, 10%, 15%, and 20%), and (3) PS-based films doped with TPD (15%) and the oxidiazole derivative 2-(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD) (2%, 5%, and 10%). All three compounds (TPD, PVK, and PBD) absorb in the 300–350 nm spectral regime and are luminescent with emissions close to 400 nm.\(^8\) In addition, TPD and PBD are organic molecules widely used in light-emitting diodes as good hole- and electron-transporting materials,\(^9\) respectively. PVK is a polymer used in many applications for its hole-transporting properties. All three compounds are obtained from Aldrich and used as received. The solvents used for the preparation process are toluene and tetrahydrofuran for the PS and PVK films, respectively. These films constitute planar waveguides, since the refractive index of both, PS (n = 1.59) and PVK (n = 1.64) are larger than the refractive index of the substrate (n = 1.54).

The experimental setup to investigate the lasing properties of these materials has been described previously.\(^10\) The samples are photopumped at 355 nm, which is close to the absorption maximum of TPD, PVK, and PBD, using 10 ns pulses from a frequency tripled Nd:Yttrium–aluminum–garnet laser (10 Hz repetition rate). The energy of the pulses was controlled with calibrated neutral density filters. An adjustable slit and a cylindrical lens are used to shape the beam into a 0.5 mm × 10 mm stripe. Samples are pumped at normal incidence with the pump stripe straddling the edge of the film. The light emitted from the edge is collected with a fiber spectrometer. The use of a variable length stripe allows us to

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demonstrate that the mechanism responsible for spectral narrowing is amplified spontaneous emission (ASE), as opposed to other mechanisms such as superfluorescence or superradiance.

We first study films of PS doped with TPD. Since PS is an inert polymer, optical studies give information about the neat dopant, TPD. The emission spectra of films containing 5%, 10%, 15%, and 20% of TPD are collected at various pump intensities, keeping a constant pump stripe length of 10 mm. As an example, Fig. 1 shows the results for a 15% doped film. When the pump pulse intensity is less than about 30 μJ the emission has the broad spectrum characteristic of spontaneous emission. Above threshold the emission at the peak of the spectrum (at around 420 nm) grows much more strongly with pump intensity than it does at other wavelengths, resulting in a spectrum with a full width at half of the maximum (FWHM) of only 7.5 nm. This collapse of the optical spectrum is one of the signatures of the presence of stimulated emission. Figure 2 shows the FWHM as a function of the pump energy, for different concentrations of TPD. The gain-narrowing threshold decreases with increasing concentration, until it reaches saturation at about 20%.

Figure 3 shows the dependence of the wavelength-integrated light intensity emitted from the edge as a function of the pump intensity. It can be determined from the change in slope at around 45 μJ/pulse that the measured relative efficiency increases by a factor of 10 when spectral narrowing occurs. This is additional support for amplification. TPD-based films therefore show potential for the fabrication of organic lasers.

The gain narrowing mechanism is observed only when the films are waveguiding. Films prepared under the same conditions, but using poly-methyl-metacrilate (PMMA) instead of PS did not show gain narrowing, due to the fact the refractive index of PMMA (n = 1.48) is lower than the refractive index of the substrate. Although this observation together with the previous results is fully consistent with ASE, this does not constitute proof that ASE is responsible for spectral collapse. Measurements of the dependence of signal on the length of the pump stripe were performed to study the mechanism of spectral collapse. As expected from ASE, we observed that the spectra were broad for short pump stripe lengths and they narrow as the excitation length increases. Moreover, the dependence of the emission intensity at λ = 420 nm on the excitation length was in good agreement with ASE. By fitting these data to the mathematical expression for ASE, the net gain of the waveguides for several pump intensities was determined. Gain coefficients ranging from 3.5 to 10 cm⁻¹ were obtained for pump intensities between 66.5 and 140 μJ/pulse. These values are lower that those obtained for neat films of semiconducting polymers, which is reasonable since in our case the concentration of active material is much smaller. All these data, together with the fittings for determining the gain coefficients will be published elsewhere.

Next, we performed similar experiments to investigate the optical properties of first, PBD as a dopant in PS, and second PVK as a neat film and also as a dopant in PS. Since their absorption and luminescence spectra are similar to those of TPD, one could expect the possibility of observing ASE also in these systems. Although the films emitted blue luminescence, line narrowing at high pump intensities was not observed. This indicates that neither PVK nor PBD show ASE.

Subsequent experiments focused on using TPD as the active laser component by inserting it in different polymer matrices. First, we studied films containing PVK doped with TPD (5%, 10%, 15%, and 20%). The interest of this system is based on the fact that PVK (that acts as the host matrix) and TPD are both good hole-transporting materials, thus the
system is expected to have better conducting properties than PS films. [The problem of having only one carrier (holes) could be compensated in a device by introducing an electron-transport layer]. As for the TBD-doped PS films, it also displays a collapse of the spectrum when the pump intensity is increased. The photoluminescence (PL) spectrum, both below and above threshold, has almost the identical shape as for TPD in PS (Fig. 1). This means that, although PVK is also luminescent, the emitted light comes mostly from the TPD. We conclude then, that in this type of system, PVK acts simply as a matrix while from the point of view of the luminescence, it is dominated by the TPD. Although these results show that these materials have potential for the fabrication of diode lasers, there is an important problem that needs to be addressed: stability. Contrary to the results obtained with the PS:TPD films that show stable ASE, the PVK:TPD films showed a broadening of the spectral width over time, as well as a decrease in the PL intensity. This implies a degradation mechanism or interaction between PVK and TPD that inhibits the ASE. It is well-known \(^9\) that although TPD has high charge carrier mobility and great amorphous film forming capabilities, it shows problems of crystallization under continuous operation or storage due to its low glass transition temperatures \((T_g)\). This might be one of the reasons for the observed degradation of the ASE. Nevertheless, a detailed understanding of these processes requires further studies that are beyond the scope of this paper.

Finally, we investigated films of PS doped with PBD and TPD. The PS constitutes the matrix while TPD is the active laser molecule. Although PBD is also a luminescent molecule, it is used for its electron-transporting properties; in contrast to TPD, which is a hole-transporting material. This strategy might improve the conducting properties of the system, since carriers are compensated. Moreover, it would not be necessary to include additional transporting layers in the devices. We studied films containing a fixed concentration of TPD (15\%) and varying concentrations of PBD (2\%, 5\%, and 10\%). Figure 4 shows that when the films are pumped at high intensities, the PL spectra develops two broad peaks, corresponding to luminescence from TPD and PBD. Even at low concentrations of PBD, ASE was not observed. When the PBD concentration increases, the peak corresponding to PBD gets larger. Therefore, in this case the presence of the two compounds prevents ASE. We can conclude then, that this system is not appropriate for lasing applications.

In conclusion, we have observed blue ASE in polymer films containing the luminescent and hole-transporting molecule TPD by optical excitation. Since the films have semiconducting properties, they can be considered as candidates for blue-emitting organic diode lasers.

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