Evidence for the Double Excimer State of conjugated polymer in a liquid solution

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In this paper, the spectral properties of a conjugated polymer poly [2-methoxy-5-(2-ethylhexyloxy)-1, 4-phenylenevinylene] (MEH-PPV) in benzene have been studied. The results showed that the fluorescence spectra of MEH-PPV under low concentrations had two peaks; the dominant one due to monomer was around 560 nm, and the shoulder one attributed to the excimer was around 600 nm. Under higher concentrations, it was found that there was only one band around 600 nm due to the excimeric state. By increasing the concentrations of MEH-PPV, it could be seen that there was a new band around 640nm. This band is being attributed to the double excimer. Under high power pulsed laser excitation, we observed amplified spontaneous emission (ASE) at 570 nm, 605 nm and 650 nm. These ASE peaks could arise from the monomer, excimer and double excimer states of the macromolecule respectively. To the best of our knowledge this is perhaps the first report on ASE from double excimer of the conjugated polymer, MEH-PPV in liquid solution.
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Keywords: Conjugated polymer MEH-PPV, fluorescence, double excimer, ASE from double excime

1 INTRODUCTION

Many conjugated polymers are capable of light emission [1]. This can be generated either optically, by shining light onto a sample to give fluorescence, or electrically, by applying a voltage to a polymer light-emitting diode [2].

The excited states that exist in conjugated polymers by charge injection or photo excitation have photo physical characteristics similar to those of small organic chromophores such as laser dyes [3]. There are several reasons why semiconducting polymers could be attractive laser materials [4]–[6]: The first is that there exists a range of polymers that can emit light across the visible spectrum. Secondly, these polymers have broad spectra suitable for tunable lasers. They have very strong absorption and emission cross section, which implies that there is the potential for the strong amplification of light. Thirdly, the absorption and fluorescence spectra are well separated, so that re -absorption of emitted light is weak. Fourthly, in many fluorescent organic molecules (including laser dyes), light emission is severely quenched at high concentrations such as that typically found in solid films. In contrast, conjugated polymers can emit light as neat solid films and, in addition, are capable of charge transport, thereby providing the potential to make electrically pumped lasers in the not too distant future.

The laser action of a semiconducting polymer MEH-PPV in the liquid state, operating in the yellow/ red wavelength region, was achieved for the first time in 1992. The reported lasing performance of this polymer was comparable to that of the most efficient laser dye, Rhodamine 6G [7]. The lasing performance and wavelength tunability of a novel high efficiency copolymer TOP-PPV was achieved for the first time in 1995. The reported lasing of this polymer was comparable to those of Coumarin 120 and Coumarin 47 [8].

The spectral properties of MEH-PPV in different solvents and different concentrations had been described in a preceding paper by us. The results showed that the conjugated conducting polymer MEH-PPV could exist in the excimer state in a few solutions [9]. The amplified spontaneous emission characteristics (ASE) of MEH-PPV in different solvents and at different concentrations were studied under pulsed-laser excitation at 355 nm and 532 nm; the conversion efficiency of MEH-PPV is comparable to other conventional laser dyes Rhodamine B and Rhodamine 6G [10].

In this paper, the spectral properties of a conjugated polymer, MEH-PPV in benzene with different concentrations and temperatures are described. The results showed that under suf-
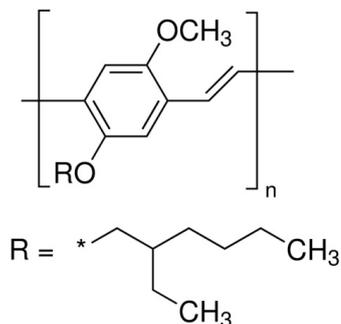
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FIG. 1 Molecular Structures of polymer of MEH-PPV.

FIG. 2 Absorption spectra of MEH-PPV in benzene at different concentrations.

ficient concentration, this conjugated polymer could exhibit double excimer formation with a fluorescence peak at 640 nm. At this concentration, with sufficient pump power, the ASE with a peak at 650 nm with FWHM of 8 nm also could be obtained.

2 EXPERIMENTAL

MEH-PPV was purchased from Sigma-Aldrich. The molecular structure is given in Figure 1. This is a macromolecule with a molecular weight of 70000–100000. The absorption and fluorescence spectra of MEH-PPV in benzene were studied under wide range of concentrations. The spectra for the solutions were measured in a quartz cuvette with the dimensions $1 \times 1 \times 4$ cm with an optical path length of 1 cm.

UV-VIS absorption spectra were taken using a Perkin Elmer spectrophotometer and the fluorescence was measured on a Perkin Elmer LS45 spectrofluorometer.

The third harmonic of an Nd: YAG laser (355 nm) Quantel Inc., with a pulse width of 6 ns, was used as the excitation source. The UV laser was focused by a quartz cylindrical lens with a focal length of 5 cm. This was used to do transverse excitation of the MEH-PPV solution taken in a four-side polished quartz cell, which was kept canted to avoid feedback. See reference [10] for more details. At optimum values of the pump power and concentrations of MEH-PPV, we observed an ASE beam coming out as a cone of light. This was collected by a 1 mm entrance slit of an ICCD camera, which displayed the spectra of the ASE.

3 RESULTS AND DISCUSSION

3.1 Excimer State of MEH-PPV

3.1.1 Spectral Properties:

The absorption spectra of MEH-PPV in benzene were recorded for a wide range of concentrations from 1.0 to 8.0 μM. It was found that there were two peaks: one around 333 nm and the other around 500 nm; the shape of the absorption spectra remained the same irrespective of the concentration, although the optical density increased with an increasing concentration of MEH-PPV as shown in Figure 2.

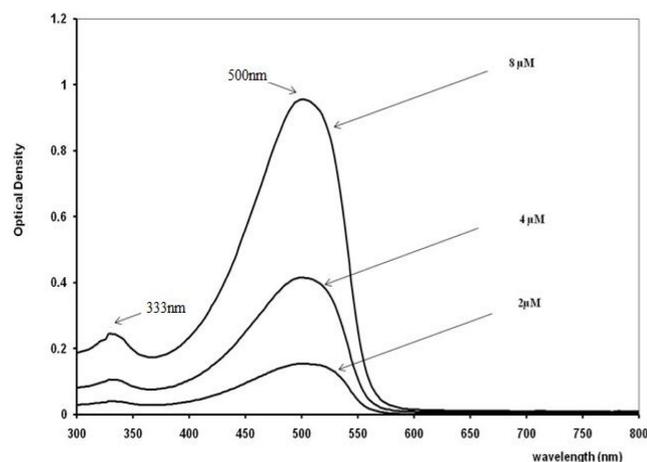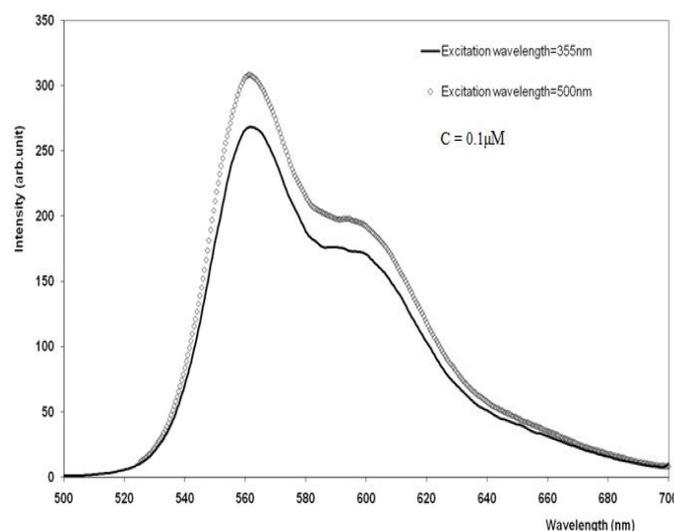The fluorescence spectra of MEH-PPV in benzene at low con-

FIG. 3 Fluorescence spectra of MEH-PPV in benzene at two different wavelengths of excitations (355 & 500 nm).

centration (1 μM) were recorded. The result showed that there were two peaks of the fluorescence: one around 560 nm, and other at 600 nm; the shape of the fluorescence spectra did not change for two different wavelengths of excitation (355 nm and 500 nm), as shown in Figure 3, indicating that there was only one emitting species for MEH-PPV in benzene at low concentrations.

For high concentrations from 0.1 to 10.0 μM of MEH-PPV in benzene, the fluorescence spectra were dramatically different. It can be seen that when the concentration was increased up 1.0 μM, the result showed that the band around 600 nm, which was weaker at 0.1 μM, became comparable to that at 560 nm. At concentrations greater than 1.0 μM, the band around 600 nm became dominating, and the band around 560 nm was almost absent as shown in Figure 4. It means that MEH-PPV in benzene exists in the excimeric state [9].

Figure 5 shows the variation in the fluorescence intensities for MEH-PPV in benzene at 0.4 μM for different temperatures. The results show that the fluorescence due to the excimer is 75% of the fluorescence due to the monomer at room temper-

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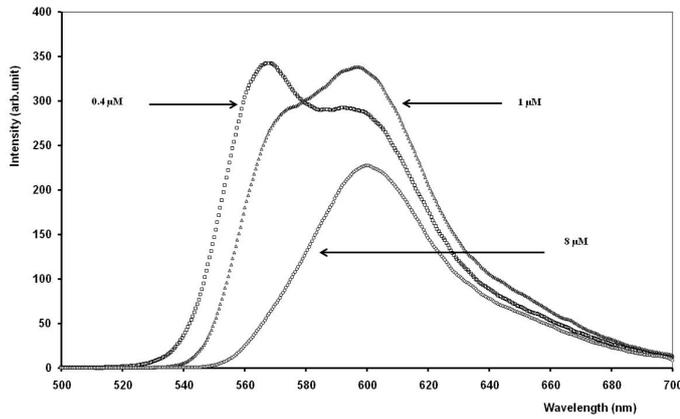
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FIG. 4 Fluorescence spectra of MEH-PPV in benzene at different concentrations.
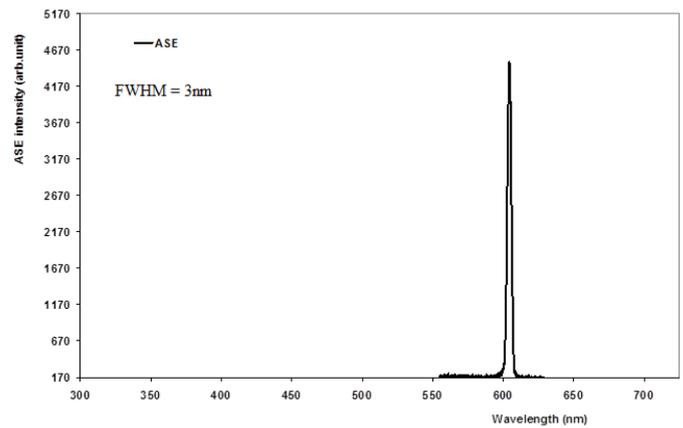

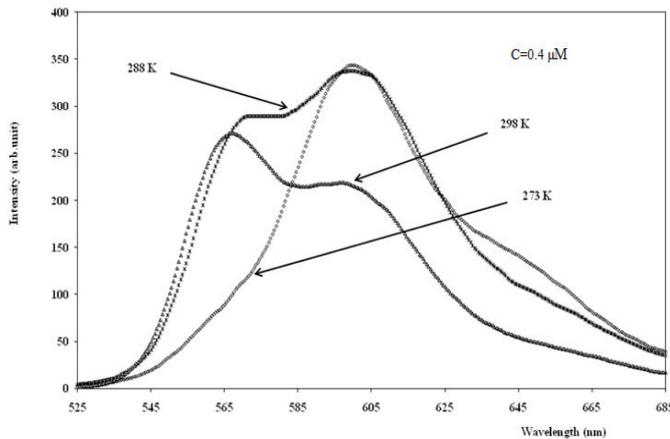FIG. 6 ASE spectra of MEH-PPV in benzene at 10 μM.

FIG. 5 Fluorescence of MEH-PPV in benzene at 0.4 μM for different temperatures.
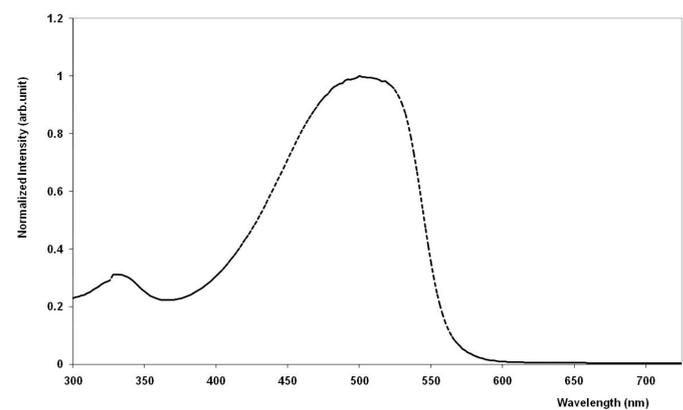

FIG. 7 Absorption spectra of MEH-PPV in benzene at 300 μM.

ature (25°C); but, as the temperature was increased, the intensities of both bands decreased, although the band around 600 nm fell faster. On the other hand, when the temperature was decreased, the intensities of both bands increased, although the band around 600 nm grew much faster, and at 0°C, there was just only one band, which was around 600 nm; the band around 560 nm was almost absent. This is the general trend for any excimer [9].

3.1.2 ASE Spectrum:

The ASE spectrum of MEH-PPV in benzene at a concentration of 10 μM was studied. This solution was excited using the third harmonic of Nd: YAG laser ($\lambda = 355$ nm). The results showed that the ASE peak was found around 600 nm with a narrow spectral bandwidth of 3 nm (FWHM). This peak coincided with the maximum of the fluorescence emission spectrum at this concentration, as shown in Figure 6. One can immediately see that the ASE with high degree of optical gain and hence the laser action had been produced from the excimeric state [10].

3.2 Double Excimer State (MEH-PPV)

3.2.1 Spectral Properties:

To study the spectral properties of MEH-PPV at still higher concentrations, MEH-PPV was dissolved for different con-

centrations from 10 to 300 μM. The absorption spectra of MEH-PPV in benzene under all of these concentrations were recorded using a thin film of solution in the cuvette. The experimental results showed the presence of two peaks of absorption spectra as reported earlier [9] and one around 333 nm and the other around 500 nm. The shape of the absorption spectra did not change for all these concentrations indicating the absence of ground state aggregation. It was observed that the optical density increased with an increasing concentration of MEH-PPV as shown in Figure 7. Note the ordinates are displayed only as normalized intensity in arbitrary units.

The fluorescence spectra also were recorded for the above set of solutions. At concentration 10 μM; there was only one band around 600nm which was due to the excimer and the peak around 560 nm almost disappeared, as mentioned earlier, (see Figure 4). When the concentration increased up to 100 μM, it was found that the peak due to the excimer was red shifted to 610 nm; this red shift may be due to the re-absorption process, and at the long wavelength end of the spectrum there was a small hump around 640 nm (as shown in Figure 8). This peak around 640 nm is a new peak and did not exist for low concentrations. This is attributed the double excimeric state of MEH-PPV.

By increasing the concentration to 200 μM, the peak around 610 nm (which due to the excimer) was shifted to be around 615 nm and the intensity decreased, while the intensity of the peak at 640 nm, attributed to the double excimer, increased
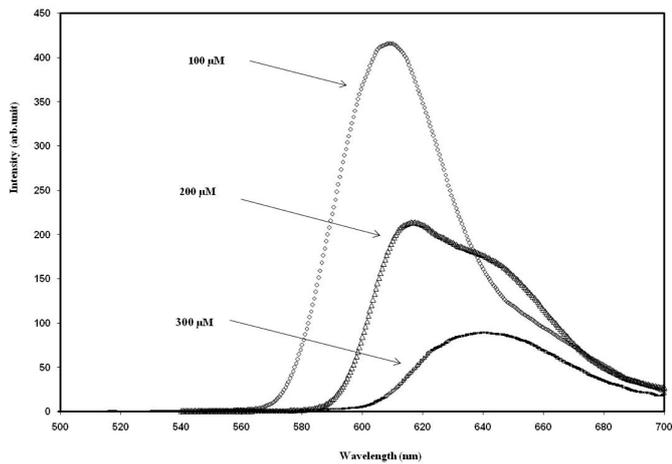
FIG. 8 Fluorescence spectra of MEH-PPV in benzene at different higher concentrations.
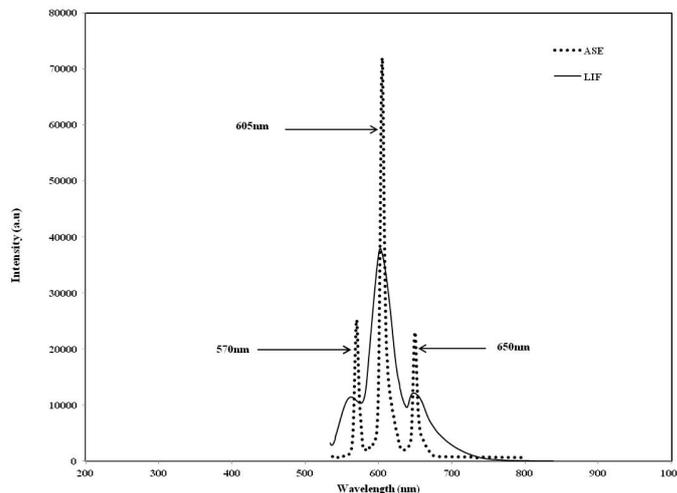

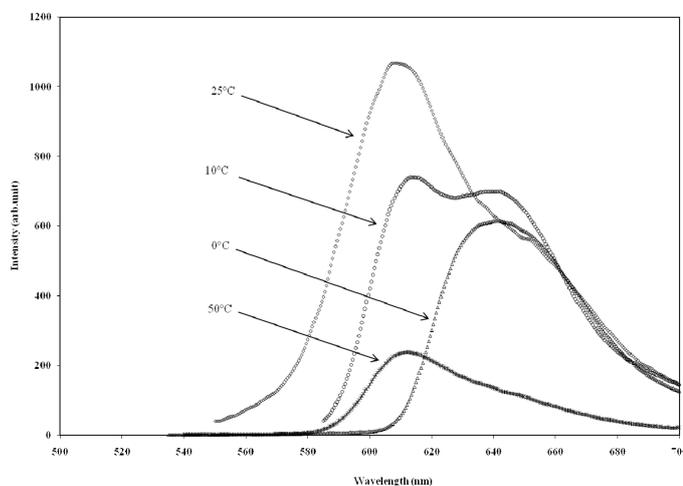FIG. 10 ASE spectra of MEH-PPV in benzene at 300 μM.

FIG. 9 Fluorescence of MEH-PPV in benzene at 100 μM for different temperatures.

a little bit. The fluorescence due to the double excimer was 75% of the fluorescence due to the excimer at room temperature (25°C), see Figure 8. At concentration 300 μM, the peak around 615 nm disappeared and there was only one dominant peak around 640 nm as shown in Figure 8 indicating the double excimeric state of MEH-PPV.

The effect of temperature on the fluorescence intensities of MEH-PPV in benzene at 100 μM was also studied. It could be seen that the intensity at 640 nm (due to double excimer state) was only 50% of the intensity at 615 nm (due to single excimer) at the room temperature (25°C); but, when the temperature was increased, the intensities of both bands decreased, although the band around 640 nm was about to vanish. On the other hand, when the temperature was decreased, the intensities of both bands increased, although the band around 640 nm grew much faster, and at 10°C, the peak at 640 nm became comparable to that at 615 nm; at 0°C, there was only one band around 640 nm and the band around 615 nm almost disappeared as shown in Figure 9. This is the confirmation that MEH-PPV could exist in double excimeric state. There is a one-to-one correspondence between the dynamics of monomer excimer (as in Figure 4 and 5) and double excimer

(as in Figure 8 and 9). These trends give strong evidence to our hypothesis of double excimer of MEH-PPV.

3.2.2 ASEs Spectra:

The MEH-PPV solution (300 μM) in benzene was transversely excited with a UV laser at 355 nm (1 mJ) and the laser induced fluorescence (LIF) was recorded. It could be seen that there were three bands at 570 nm, 605 nm and 650 nm with FWHM of 30 nm (see Figure 10).

As shown in Figure 10, the ASE occurred primarily at 600 nm due to the excimeric state; but there were two peaks one at 570 nm and other at 650 nm with FWHM of each 8 nm which were due to the monomer and the double excimer respectively at a pump power of 50 mJ. Note the one-to-one correspondence between the steady state fluorescence shown in Figure 8, the LIF and the ASE shown in Figure 10.

It is important to mention that any molecule, under higher concentration undergoes a high level of quenching and fluorescence from excimer is rather weak compared to the monomer. The situation gets even worse for the double excimer as shown in Figure 8 and 9. In the concentration range of 100 μM - 300 μM, the excimer and double excimer are in competition as much as the monomer and the excimer in the range 0.5 - 5.0 μM. However, this particular molecule exhibits easier tendency to form excimer [10] but not double excimer. Because of these two reasons, the number of molecule existing in the double excimer state and stimulated emission cross section of both could be far smaller than the (single) excimeric state. This could be the reason why we got ASE at 600 nm mostly due to the (single) excimer and only as a small peak at 650 nm due to double excimer. Also note another shoulder at 570 nm due to the monomer. We had shown earlier that though monomer emission was easier and stronger in steady state fluorescence, it was the excimer overwhelming in optical gain spectra, something parallel to laser Raman and Raman laser dynamics.

At this point we could rather draw attention to the report of Samuel et al [11] of laser action at 640 nm from the same ma-

terial with a distributed feedback configuration achieved by a corrugation embedded on a thin film. This also could be due to the double excimer of MEH-PPV.

4 CONCLUSION

Excimer is generally rare, either in gaseous or liquid states. The laser action from such excimer is still very rare. Under these circumstances, we have been able to show evidence for the existence of double excimer from the steady state fluorescence and laser induced florescence (LIF) of this new molecular species. This paper also shows the newly hypothesized double excimer (from MEH-PPV in benzene solution).has adequate optical gain, capable of producing ASE under pulsed laser excitation.

5 ACKNOWLEDGEMENT

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