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Amplified spontaneous emission and optical gain spectra from stilbenoid and phenylene vinylene derivative model compounds

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We report single-pass optical gain measurement in poly(styrene) waveguides doped with stilbenoid and phenylene vinylene derivative model compounds under picosecond excitation. Using a wavelength dependent model of amplified spontaneous emission, we produce optical gain spectra for these materials. Net optical gains of $g = 15\text{--}20\text{ cm}^{-1}$ are deduced. The spectra also exhibit features consistent with excited state absorption and fluorescence depletion via stimulated emission. A figure of merit describing the potential of a material for use as a laser medium is presented and comparisons with other recent publications are made. This comparison indicates that organic materials can compete with inorganic semiconductors for optically pumped applications. © 1999 American Institute of Physics. [S0021-8979(99)05320-7]

I. INTRODUCTION

Organic conjugated polymers have become an increasingly important material technology in the last 2 decades, initially due to the possible applications of polymers for nonlinear optics.¹ Following the observation of efficient optically pumped light emission and the semiconducting nature of some of these materials, light emission from an electrically pumped polymer layer was demonstrated.^{2,3} The possibility of an electrically pumped polymeric diode laser is now being actively investigated. Much work is in progress to understand the processes of emission and amplification of light in conjugated polymers and to define structure–property relationships as an aid to molecular engineering. Low molecular weight model compounds are finding use in this regard, allowing us to study the effect of chemical functional groups on optical processes in a controlled and convenient fashion. Thorough optical characterization of these materials is essential to determine their potential for use in active optical devices, whether optically or electrically pumped.

Here we report optical gain studies involving two model compounds; 1,4-bis-(4'-diphenylamino-styryl)-benzene and 1,4-bis-(β -cyanostyryl)-2,5-dimethoxybenzene. For reasons of clarity, the compounds are referred to as SP35 and G33, respectively, which is also in keeping with recent publications involving the same material. Table I lists the optical properties and of these two compounds in poly(styrene) host. Figure 1 shows the chemical structure of the compounds. Synthesis of the compounds is described by Hörhold *et al.*⁴ Lasing characteristics of SP35 in toluene solutions are reported by Henari *et al.*,⁵ and rival those of conventional laser dyes in slope efficiency over the same wavelength range.

Stimulated emission cross sections and excited triplet absorption cross sections for G33 are reported by Henari *et al.*⁶ These compounds exhibit only small changes in optical properties as dopants in solid poly(styrene) when compared to solutions in toluene or *ortho*-xylene. This includes small shifts in absorption and fluorescence maxima and little change in fluorescence quantum yield. The high fluorescence quantum yields ϕ_f bode well for use of these compounds in “active” optical media.

The measurement of optical gain presented here is similar to the method used by Shaklee and Leheny⁷ in semiconductor crystals and by Sorek *et al.*⁸ in organic doped glass waveguides. This technique involves the measurement of spontaneous (fluorescent) emission, amplified via stimulated emission as it passes through the excited volume of a sample. Amplified spontaneous emission is a purely random process relying on chance interactions of fluorescent photons with excited states along the optical path. It does not require a population inversion to be observed, only a sufficient number of excited states along the optical path length. Provided optical losses (e.g., scattering and absorption) are sufficiently low, and the optical path is sufficiently long, amplification and fluorescence narrowing may be observed for arbitrarily small pump intensities. We present a model of amplified spontaneous emission (ASE) that explicitly includes wavelength dependent optical gain. We use this model to produce optical gain spectra for the above model compounds.

II. THEORY

What is now commonly referred to as ASE theory usually starts with a one-dimensional approximation^{7,8} describing the rate of change of fluorescence intensity with length of the pumped region;

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TABLE I. Optical properties of the model compounds under study in solid poly(styrene) host. F is the figure of merit described in this article.

	SP35	G33
Absorption $\lambda_{\max}$ (nm)	390	410
Fluorescence $\lambda_{\max}$ (nm)	470, 490	505
Fluorescence yield, ϕ_f	0.85	0.65
Gain $\lambda_{\max}$ (nm)	487	510
Gain $g_{\max}$ (cm^{-1})	19.8	15.5
$g(\lambda)$ FWHM (nm)	12	15
F (nm cm J^{-1})	4.2×10^8	4.1×10^8

$$\frac{dI}{dx} = AP_0 + gI, \quad (1)$$

where I is the fluorescence intensity propagating along the x axis, $g = g' - \alpha$ is the net optical gain, α accounts for all loss mechanisms, and AP_0 describes spontaneous emission proportional to pump intensity. The solution of this equation with respect to pump length is

$$I = \frac{AP_0}{g} \{\exp(gl) - 1\}, \quad (2)$$

where l is the length of the pumped strip. To explicitly include wavelength dependence of the fluorescence amplification, we first start by expressing fluorescence quantum yield, ϕ_F in a wavelength dependent manner as⁹

$$\phi_F = \int_{\lambda_a}^{\lambda_b} E_F(\lambda) d\lambda, \quad (3)$$

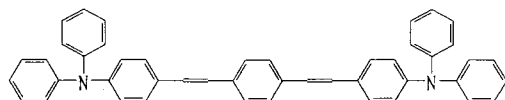
where $E_F(\lambda)$ is the fluorescence quantum distribution, and λ_a and λ_b are the limit of the fluorescence spectrum. When considering the AP_0 term in Eqs. (1) and (2), it is apparent that A must be proportional to the fluorescence quantum yield ϕ_F if AP_0 is to describe spontaneous emission proportional to pump intensity. Expressing A directly proportional to ϕ_F as

$$A = C\phi_F, \quad (4a)$$

where C is a constant of proportionality, we can also write

$$A(\lambda) = c(\lambda) \cdot E_F(\lambda), \quad (4b)$$

SP35



G33

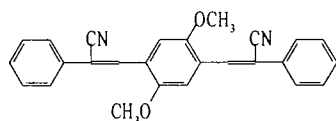


FIG. 1. Chemical structure of the model compounds under study. 1,4-bis-(4'-diphenylamino-styryl)-benzene, referred to as SP35, 1,4-bis-(β -cyanostyryl)-2,5-dimethoxybenzene referred to as G33.

where $c(\lambda)$ is a wavelength dependent expression of C . By substitution of Eq. (4) into Eq. (2) we can now write an equation describing amplified spontaneous emission which explicitly includes wavelength dependence

$$I(\lambda) = \frac{c(\lambda) \cdot E_F(\lambda) \cdot P_0}{g(\lambda)} \{\exp(g(\lambda) \cdot l) - 1\}, \quad (5)$$

where $g(\lambda)$ is the net gain per length at wavelength λ . Positive values of $g(\lambda)$ will produce an exponential increase in output intensity. The exponential term indicates that small changes in $g(\lambda)$ can produce appreciable changes in output intensity over sufficient path lengths. This produces a narrowing of the fluorescence output as some wavelengths are amplified to a greater extent than others. Equations (2) and (5) can be related as follows: the total fluorescence intensity I is equal to the integrated intensity of the fluorescence spectrum, i.e.,

$$I = \int_{\lambda_a}^{\lambda_b} I(\lambda) d\lambda = \lim_{d\lambda \rightarrow 0} \sum_{\lambda} I(\lambda) \quad (6)$$

and as $I(\lambda) \propto \exp(g(\lambda) \cdot l)$, we can also write

$$I \propto \sum_{\lambda} \exp[g(\lambda) \cdot l]. \quad (7)$$

For $g(\lambda) \cdot l \ll 1$ the sum in Eq. (7) is close in value to $\exp[g_{\max}(\lambda) \cdot l]$. Assuming that optical gain spectra exhibit a reasonably well defined peak, then the net gain, g for the integrated intensity, as expressed in Eq. (2), is very close to the maximum value of $g(\lambda)$. With this in mind, we are in a position to compare similar single-pass fluorescence amplification experiments, irrespective of whether the amplification is measured at a single wavelength, across the fluorescence spectrum, or for the total fluorescence intensity.

Equation (5) implies that spectral narrowing is influenced by the low intensity fluorescence spectrum, which is proportional to $E_F(\lambda)$, unless there is significant overlap between absorption and emission spectra. However, $E_F(\lambda)$ is not constant under conditions where stimulated emission is significant, increasing for strongly amplified wavelengths and decreasing for others. Similarly, if one considers the number of emitted photons detected per pump photon absorbed, $c(\lambda)$ must include a term accounting for the geometric distribution of the emitted photons, often assumed isotropic. But $c(\lambda)$ is not constant due to the directional nature of stimulated emission. As fluorescence amplification becomes observable, this produces an increase in the apparent emission efficiency along the desired propagation direction for the range of amplified wavelengths, but a decrease in efficiency at all wavelengths in all other emission directions.

The changes in $c(\lambda)$ can account for the decrease in emission efficiency seen by Gelinck *et al.*¹⁰ when detecting at 45° to the plane of the film, as also suggested by McGehee *et al.*¹¹ Urbach and Rikken¹² recently report that the spontaneous emission rate in a dielectric slab is modified by the presence of waveguide modes. As a result assumptions to the effect that emission is isotropic from a fluorescent waveguide, even under low pump intensities, may not be valid. In addition, $c(\lambda)$ may change strongly across the fluorescence

spectrum, particularly at wavelengths close to waveguide mode cutoff conditions. The use of bulk values for $E_f(\lambda)$, and hence for ϕ_f , may be similarly limited.

For our purposes, we note the linear dependence of output intensity on $E_f(\lambda)$ and $c(\lambda)$ and assume for large values of $g(\lambda)$ that the exponential term in Eq. (5) will dominate over changes in $E_f(\lambda)$ or $c(\lambda)$. No sudden changes in $c(\lambda)$ due to waveguide cutoff conditions are expected across the fluorescence region. No further consideration is given to changes in $E_f(\lambda)$ and $c(\lambda)$, as general features in optical gain spectra will not be affected. To obtain an optical gain spectrum from a sample, we measure emission spectra from the sample as a function of pump length. For each wavelength in the spectra we apply a nonlinear least squares fitting routine, adjusting $g(\lambda)$ and AP_0 to obtain the best fit to Eq. (5).

III. EXPERIMENT

The samples are produced by spin coating from a 75 g/l poly(styrene) solution in *ortho*-xylene doped with 1.5 g/l of the model compounds. The substrates used were silicon wafers with a 1.5 μm thick thermal oxide overlayer, cleaved along the $\langle 100 \rangle$ plane after the polymer film was deposited. Refractive index and film thickness were measured using mode-line spectroscopy¹³ with a prism film coupler. Waveguide propagation losses are estimated at $\lambda=632.8$ nm to be between 2.2 and 3.0 dB cm^{-1} , and no higher than 4 dB cm^{-1} at $\lambda=514.5$ nm, measured during prism coupling experiments (3 dB $\text{cm}^{-1}=0.69$ cm^{-1}). We note that fluorescent intensity continues to increase for pump lengths in excess of 9 mm, despite the drop in pump intensity (due to beam profile) and available excited states (depleted via stimulated emission of photons emitted at shorter pump lengths). This suggests that ground state reabsorption and scattering losses can be neglected for the short pump lengths used, across the fluorescence band.

The thicknesses of the polymer films were chosen to support two guided modes: TE_0 and TM_0 at the fluorescence maximum of the samples. This results in a desired thickness of 0.45 μm for G33 doped films ($\lambda_{\text{max}}=510$ nm) and 0.4 μm for SP35 doped films ($\lambda_{\text{max}}=490$ nm). All films were fabricated to within 10% of the required thickness. Solution and waveguide preparation, and all optical measurements were performed in air at room temperature.

The sample is pumped using a frequency tripled beam from a Nd:YAG laser, producing 0.9 μJ pulses of 35 ps duration at 355 nm. The beam is spatially filtered and expanded, producing a thin pumped stripe 30 mm long by 0.1 mm wide. The pump beam is aligned so that the center of the beam and the edge of the sample are coincident. The pump length is adjusted by means of the shutter mounted on a translation stage. Maximum pulse intensity incident on the sample is 8.7×10^5 W cm^{-2} . The waveguided output fluorescence is detected using a peltier cooled charge coupled device spectrometer. The maximum pump length used for the calculation was 3 mm. The pump intensity is assumed to be constant across this region.

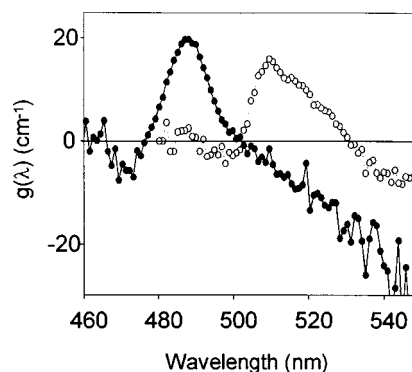


FIG. 2. Optical gain spectra produced using a nonlinear least squares fit to Eq. (5) at incident pump power of 8.7×10^5 W cm^{-2} . Solid circles are for SP35 doped waveguides, open circles are for G33 doped waveguides.

IV. RESULTS AND DISCUSSION

Figure 2 shows the optical gain spectra obtained for the doped poly(styrene) waveguides at the maximum incident pump intensity 8.7×10^5 W cm^{-2} . Results obtained from these spectra are included in Table I. Figure 3 shows a typical length dependence of the amplified fluorescence at the gain maxima for both samples. Both SP35 and G33 doped samples exhibit a single well defined peak in $g(\lambda)$, at $\lambda=487$ and 510 nm, respectively, with G33 also exhibiting a weak shoulder near 520 nm. The maximum net gains obtained are $g=19.8$ cm^{-1} for SP35 and $g=15.5$ cm^{-1} for G33. Full width at half maximum (FWHM) for the gain spectra are 12 and 15 nm, respectively. Minimum FWHM for the narrowed fluorescence spectra approached 8 nm for SP35 doped samples and 12 nm for G33 doped samples.

By estimating the density of dopant molecules in the poly(styrene) matrix we can set a lower limit on the value of the effective stimulated emission cross section, $\sigma_{\text{S.E.,eff}} = \sigma_{\text{S.E.}} - \sigma_{\text{abs}}$ by using the relation

$$g = N_{\text{chr}} \sigma_{\text{S.E.,eff}}, \quad (8)$$

where g is the net optical gain and N_{chr} is the chromophore number density. This assumes that all dopant molecules are excited by the pump pulse and that stimulated emission dominates over spontaneous emission for all wavelengths. We estimate N_{chr} to be approximately 10^{18} cm^{-3} for SP35

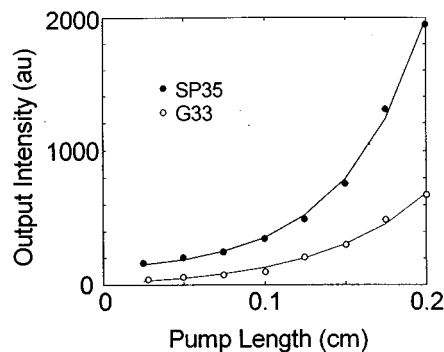


FIG. 3. Length dependence of the amplified fluorescence at the maximum gain wavelength for SP35 (solid circle) and G33 (open circle) doped waveguides. The solid line is a least-squares fit to Eq. (5). SP35 samples yield a net gain $g=19.8$ cm^{-1} at $\lambda=488$ nm, G33 samples yield $g=15.5$ cm^{-1} at $\lambda=510$ nm.

and G33 in the poly(styrene) waveguides, which implies a minimum value for $\sigma_{\text{S.E.,eff}} = 2 \times 10^{-17} \text{ cm}^2$, in good agreement with the value reported by Henari *et al.*⁶ of $\sigma_{\text{S.E.,eff}} = 5.5 \times 10^{-17} \text{ cm}^2$ ($\lambda = 514.5 \text{ nm}$) for G33 in toluene solution.

On either side of the gain peak, there are regions exhibiting negative values of $g(\lambda)$. As excited state absorption is normally redshifted from the fluorescence maximum in organic materials, we assume excited singlet absorption to be principally responsible for the long wavelength negative values of $g(\lambda)$. The short duration (35 ps) pump pulse allows us to neglect triplet-triplet absorption, which was reported by Henari *et al.*⁶ in G33 with a characteristic lifetime for T_1 of 11 ms. Similar spectral features are present in femtosecond pump-probe measurements on ladder type poly(*para*-phenylene) (LPPP),^{14,15} in picosecond Kerr ellipsometry measurements on poly(aryleneethynylene) derivatives,¹⁶ and in nanosecond ASE measurements on GaInN/GaN.¹⁷ The short wavelength negative $g(\lambda)$ values are attributed primarily to fluorescence output saturation via stimulated emission.

To enable a comparison between different materials for use in laser devices, a figure of merit may find use. If organic materials are to be successful as solid-state laser materials, tunability must be considered. Therefore, in comparing candidate materials, we must favor not only large net gains, but large gain bandwidths, which we characterize by the FWHM of the gain spectrum and denote as f . We therefore arrive at a figure of merit, F , of the form

$$F = \frac{g_{\text{max}} \cdot f}{P_{\text{abs}}}, \quad (9)$$

where P_{abs} is the absorbed pump pulse energy density to produce g_{max} , the maximum value of $g(\lambda)$. We choose pulse energy density (J cm^{-2}) in lieu of pump intensity (W cm^{-2}) to enable comparisons of measurements using different pump pulse widths.

We estimate that approximately 20% of the incident pump pulse is absorbed by the waveguides studied, including reflection from the Si substrate, suggesting $P_{\text{abs}} = 5.6 \times 10^{-7} \text{ J cm}^{-2}$. This implies values of $F = 4.2 \times 10^8 \text{ nm cm J}^{-1}$ and $F = 4.1 \times 10^8 \text{ nm cm J}^{-1}$ for SP35 and G33 doped films, respectively. Solution lasing measurements of SP35 by Henari *et al.*⁵ indicate that SP35 is at comparable to coumarin dyes in slope efficiency and output. The lasing tuning range and limits of positive $g(\lambda)$ are also similar. As the toluene solution and poly(styrene) host properties of SP35 are similar, this suggests that a material under test using this technique with F significantly larger than $10^8 \text{ nm cm J}^{-1}$ may be reasonably expected to have some use as a solid-state laser medium.

It is instructive to compare the figures of merit of our polymer waveguides with those we obtain using data from previous optical gain studies. We estimate a figure of merit for ladder type LPPP¹⁸ to be $F = 8.3 \times 10^7 \text{ nm cm J}^{-1}$. For LPPP we use $g = 50 \text{ cm}^{-1}$ at 22 kW/cm^{-2} @10 Hz, 6 ns pulse width from Ref. 17, $f \approx 20 \text{ nm}$ from Fig. 2 of Ref. 13. We estimate 90% of the pump pulse is absorbed from Ref. 17. The gain bandwidth may be an overestimate. For

BuEH-PPV¹¹ we estimate $F = 3.3 \times 10^8 \text{ nm cm J}^{-1}$, despite the enormous optical losses. For GaInN/GaN double heterostructures,¹⁷ we estimate $F = 4.7 \times 10^7 \text{ nm cm J}^{-1}$, and for AlGaIn/GaN DHs,¹⁹ $F = 2.7 \times 10^7 \text{ nm cm J}^{-1}$. These figures indicate that G33 and SP35 doped poly(styrene) waveguides may be suitable candidates for optically pumped laser media. This also suggests that organic materials can exceed traditional semiconductor materials for optically pumped laser applications.

V. CONCLUSION

In conclusion, we have presented a wavelength dependent model of amplified spontaneous emission and applied the model to measurements of poly(styrene) waveguides doped with stilbenoid (SP35) and PPV (G33) derivative model compounds. Both dopant molecules exhibit large optical gains for small input pulse energies. We present a figure of merit to enable a comparison of materials for use in optically pumped laser applications. Our figure of merit suggests that organic materials can outperform semiconductors under optically pumped conditions. The model presented may extend the use of single-pass fluorescence amplification experiments in determining the potential of a material as a laser medium.

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