Low Threshold Gain-Narrowing Characteristics of Fluorescent Styrylbenzene Derivatives as a Guest Molecule in an Organic Thin-Film Optical Waveguide

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We demonstrate that fluorescent styrylbenzene derivatives (**SBD**s) as a guest molecule (10 mol%) in an organic thin-film optical waveguide show excellent gain-narrowing performance by optical pumping. In particular, an extremely low threshold for gain narrowing is obtained with 4,4'-bis[4-(di-*p*-tolylamino)styryl]biphenyl (**LD3**). In addition, the incorporation of heterocyclic moieties into the styrylbenzene skeletons results in a higher threshold and also causes no spectral narrowing.

The recent success in organic light emitting diodes (OLEDs) has provided a new challenge for organic laser diodes (OLDs).[1] Electrically pumped OLDs, however, have not been developed yet due to the requirements of high current excitation (typically >10 KA/cm^2), as well as serious propagation loss caused by metal and metal oxide electrodes, which have high attenuation indices.[2] Thus, the development of new device structures and new fluorescent molecules is expected to provide low-threshold electrical pumping.

One of the promising structures for the organic active layer is a guest–host system[3] where efficient Förster energy transfer between host and guest molecules can be allowed, since we can expect high photoluminescence (PL) efficiency even in a solid state, resulting in low laser threshold. In this study, we used eight new styrylbenzene derivatives (**SBD**) as an active guest molecule and we investigated the gain-narrowing performance that is indicative of laser action.[4] Figure 1 shows the seven guest (**LD1**–**LD7**) and host molecules used in this study. All the guest molecules contain a styryl benzene with very strong fluorescence in a dilute solution. We used 4,4'-bis[4-(di-*m*-tolyl)amino]benzidine (**TAD**) as a host molecule due to the wide overlap integral between **SBD** absorption and **TAD** emission in order to achieve efficient Förster energy transfer.

The structure of the optically pumped devices consists of a 100-nm-thick organic layer on a 1.1-mm-thick glass substrate. The organic layers were grown in a vacuum of 1×10^{-6} Torr by the thermal co-deposition of host and dopant molecules at a fixed molar ratio of 10 mol%. The organic film (refractive index n = 1.8) forms a slab optical waveguide with the SiO_2 substrate (n = 1.46) on one side and air (n=1.0) on the other side. After the deposition of organic layers, the substrate was cut at a width of 5 mm. Then, the devices were optically pumped with about 500-ps pulses generated at a 10-Hz repetition rate by a nitrogen laser at λ = 337 nm. The pump beam was focused onto an approximately 500-μm-wide stripe on the surface of the organic films. The light emission was observed from the edge of the film. An optical fiber connected to a spectrometer (Hamamatsu Photonics, PMA-10) was closely faced to the edge.

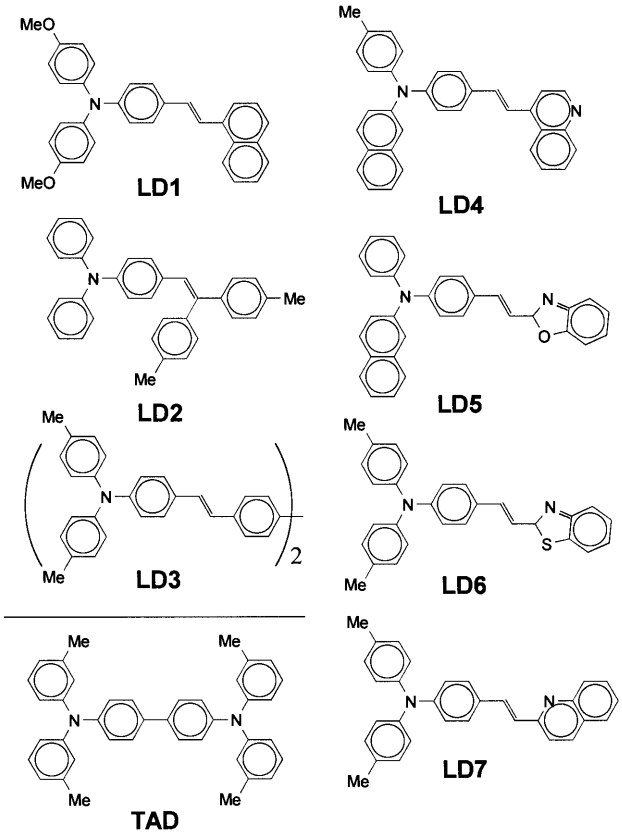

Figure 1. Molecular structures of fluorescent styrylbenzene derivatives (**LD1-LD7**) as a guest and **TAD** as a host.

Figure 2 shows the emission intensity and full width at half maximum (FWHM) as a function of excitation pulse energy using **LD3** as a guest molecule. The significant decrease of FWHM and the increase of emission power, which corresponds to gain narrowing, were observed above the excitation energy of ~0.5 μJ/cm^2. This value is one of the lowest thresholds ever reported,[1,3,4] suggesting that **LD3** is a promising molecule for OLDs. Figure 3 shows the edge emission spectrum of **LD3** operating below and above the threshold. The narrow emission spectrum centered at 498 nm with a 9-nm-FWHM clearly shows gain narrowing above the threshold, while the spectrum is broad (FWHM = 46 nm) below the threshold, similar to the PL spectrum.

Table 1 summarizes the threshold for gain narrowing, FWHM, PL peak wavelength, relative PL intensity, and Stokes shift of the composite films. While **LD1**–**LD3** showed signifi-

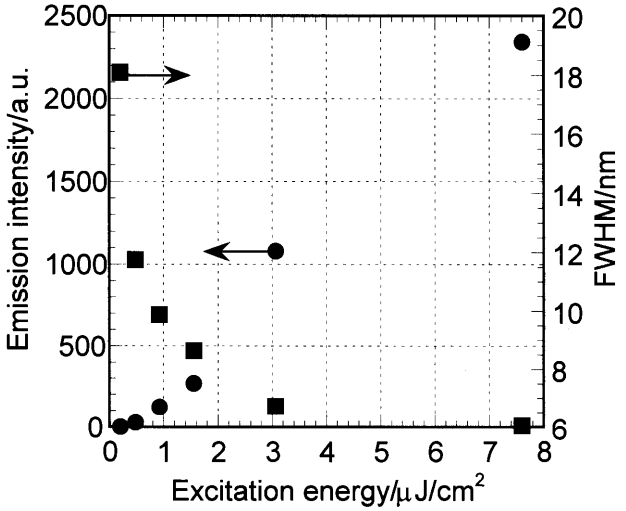

Figure 2. Emission intensity and full width at half maximum (FWHM) as a function of excitation pulse energy with **LD3** as a guest molecule.

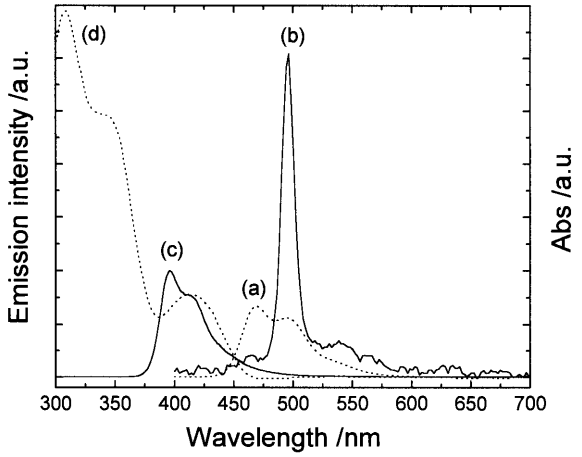

Figure 3. Edge emission spectra of **LD3** as a guest molecule operating below threshold (0.2 μJ/cm^2) (a) and above threshold of (1 μJ/cm^2) (b). Also, a photoluminescent spectrum of a TAD film (c) and an absorption spectrum of **LD3** in CH_2Cl_2 (d) are shown.

cant gain narrowing with low threshold, **LD4**–**LD7**, with the heterocyclic moieties (quinoline, benzoxazole, and benzothiazole) resulted in a broad PL spectrum even at a high excitation power above 100 μJ/cm^2. As in Table 1, no significant difference in the PL intensity was observed in their films. Also, reabsorption by the dopant itself should be excluded, since no correlation between the Stokes shifts and the threshold is observed. Furthermore, while it is well established that triplet–triplet (T–T) absorption is assigned as significant dissipation of excited energy,[5] the use of about 500-ps pulse excitation should exclude this possibility. Thus, T–T absorption does not become serious problem during such short pulse excitation.

Table 1. Optical properties of 10 mol%-SBD:TAD films

Materials	Threshold (μJ/cm^2)	FWHM (nm)	PL peak (nm)	Relative PL Intensity (a.u.)	Stokes shift (nm)
LD1	1.6	5.3	476	357	76
LD2	1.6	6.0	471	253	86
LD3	0.5	6.1	469	403	56
LD4	---	---	488	217	71
LD5	---	---	480	325	66
LD6	---	---	484	333	62
LD7	---	---	478	324	62

In summary, we found that the **LD1**–**3** shows excellent low-threshold characteristics for gain narrowing in a guest–host optical waveguide. In particular, **LD3** was found to show an extremely low threshold of 0.5 μJ/cm^2. Our empirical guideline shows that the incorporation of heterocyclic moieties into a styryl structure resulted in inferior gain-narrowing performance, and therefore should be excluded. Further optical investigation on the heterocyclic dissipation process is now in progress.

References

1 V. G. Kozlov, G. Parthasarathy, P. E. Burrows, and S. R. Forrest, *Nature*, **389**, 362 (1997).
2 M. Nagawa, C. Adachi, T. Koyama, and Y. Taniguchi, *Polymer Preprints Japan*, **47(3)**, 446 (1998).
3 M. Berggren, A. Dodabalapur, R. E. Slusher, and Z. Bao, *Nature*, **389**, 466 (1997).
4 M. A. Diaz-Garcia, F. Hide, B. J. Schwartz, M. D. McGehee, M. R. Andersson, and A. J. Heeger, *Appl. Phys. Lett.*, **70**, 3191 (1979).
5 P. P. Sorokin, J. R. Landkard, V. L. Moruzzi and E. C. Hammond, *J. Chem. Phys.*, **48**, 4726 (1968).