Gain-narrowing characteristics of fluorescent organic molecules with symmetrical or asymmetrical structures in a neat thin-film optical waveguide

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Abstract

We investigated gain-narrowing performance of fluorescent styrylbenzene and azomethyne derivatives in a neat thin-film waveguide by optical pumping. In particular, an extremely low-threshold for gain-narrowing was obtained with 4,4′-bis[4-(di-*p*-tolyl-amino)-styryl]biphenyl (LD1), and the obtained threshold was comparable to the threshold of LD1 in the high efficient guest–host system previously reported. High symmetry of the molecular structure was important for the gain-narrowing performance.
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1. Introduction

The recent success in organic light-emitting diodes (OLEDs) has provided a new challenge for organic semiconductor lasers (OSLs) [1–3]. However, electrically pumped OSLs based on OLEDs, which can be called organic laser diodes (OLDs) have not been developed yet due to the requirements of high current excitation (typically $>10\,\text{kA/cm}^2$), as well as serious propagation loss caused by metal and metal oxide electrodes, which have high attenuation indices [4]. Therefore, the development of new fluorescent molecules in solid-state is an important work in order to provide the low-threshold electrical pumping.

Under this circumstance, we have demonstrated that several styrylbenzene derivatives exhibit low-threshold gain-narrowing in guest–host systems in solid-state [5]. Particularly, an extremely low-threshold for gain-narrowing was obtained with 4,4′-bis[4-(di-*p*-tolyl-amino)styryl]biphenyl (LD1). We also demonstrated that the incorporation of heterocyclic moieties into the styrylbenzene skeletons resulted in a higher threshold and also caused no spectral narrowing, although these styryl derivatives with heterocyclic moieties

exhibits strong photoluminescence. In this study, we used LD1 and other five organic materials including two new styrylbenzene derivatives and a new azomethyne derivative as an laser active molecule and we investigated the gain-narrowing performance, which is indicative of laser action [6], of these compounds in neat thin films.

2. Experimental

Fig. 1 shows chemical structures and their notations of fluorescent organic materials used in this study. All the materials contain styrylbenzene or azomethyne and exhibit very strong fluorescence in a dilute solution and even in a neat thin film. 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 thermally deposited on the substrate under a vacuum of $6 \times 10^{-4}\,\text{Pa}$. The organic layer, which exhibits large refractive index compared with the glass substrate ($n = 1.5$), forms a slab optical waveguide with the glass substrate and air as optical cladding layers. After the deposition of organic layers, the substrate was cut at a width of 5 mm. Then, a nitrogen gas laser that generated 500 ps pulses at a 10 Hz repetition rate at 337 nm optically pumped the devices. The pump beam was focused onto an approximately 1 mm wide stripe on the surface of the organic

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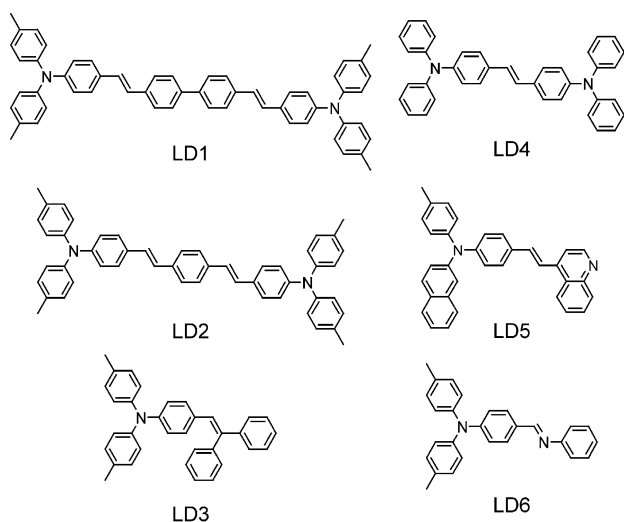musubu@giptc.shinshu-u.ac.jp (M. Ichikawa).

Fig. 1. Structure and its notation of fluorescent organic materials used in this study.
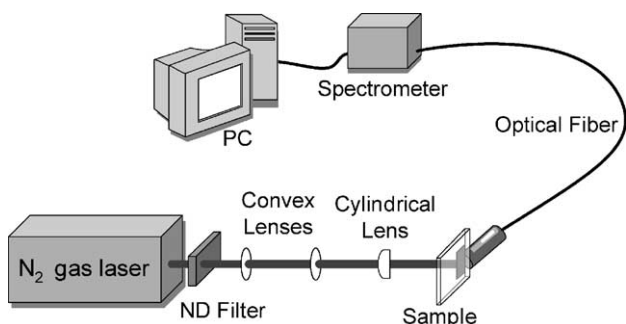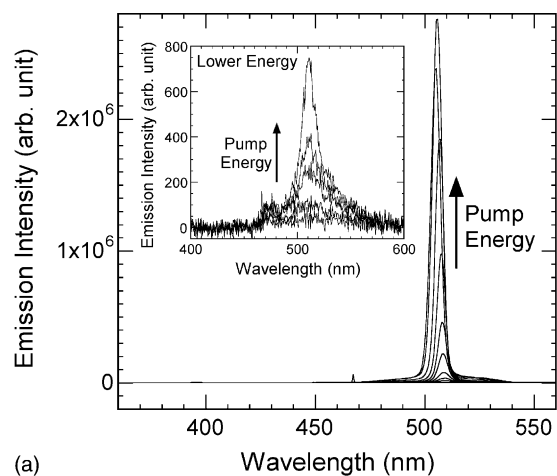

Fig. 2. Schematic illustration of experimental setup for gain-narrowing by photopumping.

Fig. 3. (a) Emission spectra of LD1 at various pumping pulse energies; (b) emission intensities and FWHM as a function of pumping pulse energy.
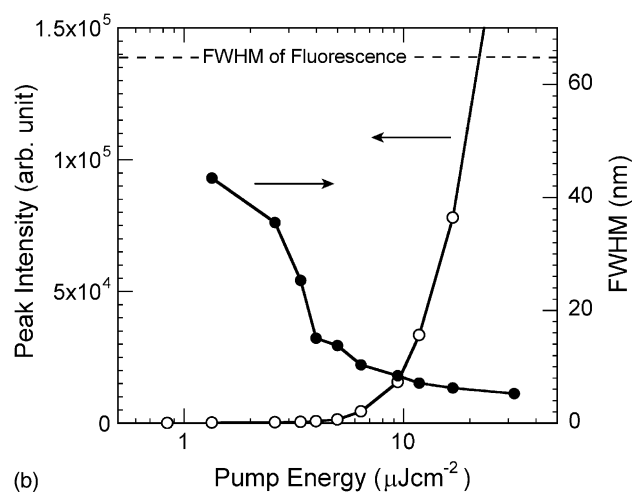
films. The light emission was observed from the edge of the layer through a UV-cut filter. An optical fiber connected to a spectrometer with an image intensified charge couple device camera (Andor, InstaSpecV) was closely faced to the edge. Fig. 2 shows the schematic illustration of experimental setup used in this study.

3. Results and discussion

Fig. 3(a) shows emission spectra of LD1 at various pumping pulse energy, and (b) shows their emission intensities and full widths at half maximum (FWHM) as a function of pumping pulse energy. The significant increase of emission intensity and the decrease of FWHM, which corresponds to gain-narrowing, were observed above the excitation energy of $3\,\mu J/cm^2$. This value is large compared with our previously reported value of $0.5\,\mu J/cm^2$, which was obtained in the LD1/4,4′-bis[4-(di-*m*-tolyl)amino]benzidine guest–host system. Guest–host systems where the efficient Förster energy transfer between host and guest molecules can be

allowed is one of the promising systems for laser oscillation [7]. This is because reabsorption by the active material itself can be negligible due to the large effective Stokes shift that consists of host-absorption and guest-luminescence. In this study, since we employed the neat system, the threshold was enlarged. However, this threshold is small compared with previously reported value [1,6,7]. Thus, LD1 is a promising molecule for OLDs.

Table 1 summarizes the threshold for gain-narrowing, FWHM, PL peak wavelength, relative PL intensity, and Stokes shift of the prepared samples. LD1–LD4 showed significant gain-narrowing with low-threshold. However, LD5, a styrylbenzene derivative with heterocyclic moieties (quinoline), resulted in a broad PL spectrum even at a high pumping power above $100\,\mu J/cm^2$. LD6, an azomethyne derivative of LD3, also resulted in the same. Thus, previously proposed our empirical guide for low-threshold gain-narrowing [5], which was that incorporation of heterocyclic moieties into styryl structure resulted in inferior gain-narrowing performance, and therefore should be excluded, was confirmed in the neat system. As in Table 1,

Table 1
Gain-narrowing performance and spectroscopic properties of the prepared samples

Material	Threshold (mJ/cm^2)	FWHM (nm)	PL peak wavelength (nm)	Relative PL intensity	Stokes shift (nm)
LD1	3.0	4.8	477, 505	405	76
LD2	13.2	4.0	482, 515	200	71
LD3	21.5	6.3	476	208	101
LD4	10.7	3.0	440, 469	93	76
LD5	–	–	520	246	108
LD6	–	–	468	24	99

no significant correlation in the PL intensity was observed for the threshold for gain-narrowing. Reabsorption by the active material itself should be excluded, since the thresholds have no correlation with the Stokes shifts. In other words, the Stokes shift for each compound is large enough for gain-narrowing. In addition, while it is well known that triplet–triplet (T–T) absorption is an important dissipation process of electronic excitation energy [8], the use of about 500 ps pulse excitation should exclude this possibility. Thus, T–T absorption is minor problem during such short pulse excitation.

Finally, we should point out the correlation between the thresholds for gain-narrowing and chemical structures. Three materials exhibiting lower threshold, LD1, LD2, and LD4, have symmetrical chemical structures. Since such symmetrical structures reduce a dipolar moment of the molecule, intermolecular interactions become small compared with asymmetrical polarized molecules. Therefore, the threshold of these three materials becomes lower than LD3. This reason is supported by the small difference of the threshold between in the neat system and in the guest–host system [5]. We believe at the present stage that because heterocyclic moieties and azomethyne skeletons enhance intermolecular interactions, LD5 and LD6 exhibits no gain-narrowing characteristics.

4. Conclusion

In conclusion, we found that LD1–LD4 exhibit excellent low-threshold gain-narrowing characteristics in the neat system. Particularly, LD1 shows remarkably very low-threshold even in the neat system. High symmetric styrylbenzene skeletons without heterocyclic moieties are advantageous for low-threshold gain-narrowing.

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