Relationship between Molecular Skeleton and Stimulated-emission Threshold in Dilute Thin Films of Linear-chain-structured Fluorescent Dyes

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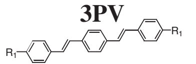
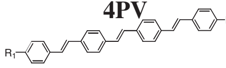
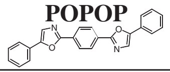
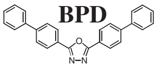
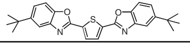
We carried out photopumping measurements for the dilute thin films of linear-chain-structured laser dyes where π-units such as benzene, ethylene, and oxazole are linearly linked via σ-bonds. Among them, 4-4′-bis[4-(di-*p*-tolylamino)styryl]biphenyl recorded the lowest stimulated-emission threshold of $2\,\mu J/cm^2$. It was revealed that the threshold was related to whether the number of constituent π-units was even or odd.

Recent advance in the studies on organic light emitting diodes (OLEDs) has been stimulating the development of organic laser diodes.[1,2] So far, photopumped lasing has been observed in the organic thin films of fluorescent small molecules or conjugated polymers.[1–3] Toward realization of electrically-pumped lasing, however, there remain several problems to be solved.[4–6] One of them is that the current density required for lasing is estimated to be beyond $1\,kA/cm^2$ from photopumping measurements,[1] which is three orders of magnitude higher than that attainable in OLED structure. As a material-based approach to overcome this problem, the design of fluorescent molecules with low lasing threshold is desired. Thus, we have been investigating stimulated-emission phenomena of various fluorescent dyes by photopumping, and considering which of molecular skeletons are favorable for low-threshold lasing in the solid state.[7,8] In this letter, we report on our guideline derived from the results of linear-chain-structured laser dyes where π-units such as benzene, ethylene, and oxazole are linearly linked through σ-bonds.

Fluorescent dyes were dissolved in CH_2Cl_2 with a binder polymer of polycarbonate (PC-BisZ) at the ratio of dye:polymer = 1:20 (w/w). The films with thickness about 300 nm were prepared by spin-coating on glass substrates. As the pumping source, a nitrogen laser with a 500 ps pulse at a 10-Hz reputation rate was used. The laser beam was focused on the film by a cylindrical lens, obtaining a rectangular 1 mm × 5 mm excitation strip. The light emitted from the film was detected at the edge of sample in a direction parallel to film slab. The stimulated-emission threshold of the sample was defined as the excitation energy by which the full-width at half-maximum (FWHM) of the waveguided emission is narrowed in half of that of the spontaneous emission. To compare the thresholds among the samples, the obtained values were corrected by normalizing the differences of absorption intensities at the excitation wavelength of 337 nm.

Most of the linear-chain-structured fluorescent dyes, we investigated, showed spectral narrowing as the pump energy was raised up. Several representatives are summarized in Table 1. The thresholds of these dyes were much lower than those of another structured laser dyes such as coumarin, rhodamine and DCM, which are so high in the film states[3] that we could not observe the spectral narrowing. On the other hand, the dyes listed in Table 1, which all have a two-fold axis of symmetry, showed lower threshold than the unsymmetrical analogs (data not shown); this coincided with our guide reported previously.[8] Therefore, it can be safely said that symmetrical linear-chain-structured laser dyes are promising for lower-threshold amplification in the film states. Among such dyes, styrylbenzene derivatives exhibited in particular better performance compared to the others, and 4-4′-bis[4-(di-*p*-tolylamino)styryl]biphenyl (DSBP) recorded the lowest threshold of $2\,\mu J/cm^2$. Figure 1 shows the change in the emission spectra of DSBP by increasing pump energy. The emission intensities from the edges of the slab waveguide depend exponentially on pumping rate, surely indicating that the spectral narrowing is due to the amplified spontaneous emission (ASE), which is prerequisite for laser radiation.

Table 1. Gain-narrowing perfomance of representative linear-chain-structured dyes in spin-coated film

	Threshold / μJcm^{-2}	FWHM / nm	Intensity /10^4 cnt.
3PV 	4	6.3	60
4PV 	5	13.7	20
DSBP 	2	7.1	40
QP 	10	8.8	7
POPOP 	26	6.8	3
BPD 	14	5.7	5
BBOT 	10	2.6	30

R_1: di-*p*-tolylamino group. R_2: diphenylamino group.

In general, laser action of molecules is also explained by the four-level laser mechanism,[9] where the I and III levels refer to the equilibriums in the ground (S_0) and excited (S_1) states, respectively, while the II and IV levels are non-equilibrium Frank–Condon vibronic levels of S_1 and S_0, respectively; ASE occurs at the vibronic transition from III to IV. To lower ASE threshold, it is suggested that a net optical gain and a fluorescence quantum efficiency for the ASE wavelength must be enhanced.[10] Since the former that depends upon the excited-

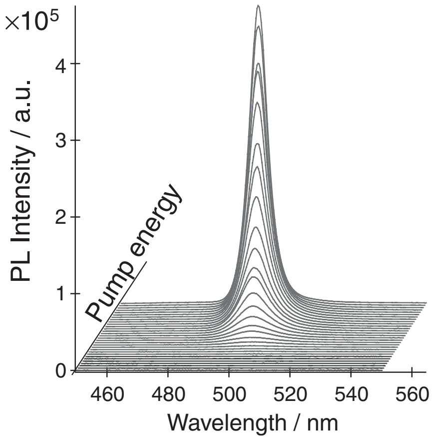


Figure 1. Change in emission spectra of 4-4′-bis[4-(di-*p*-tolylamino)styryl]biphenyl by increasing pump energy.

state lifetime (τ) is not so different among organic laser dyes with almost $\tau \approx$ ns, the latter seems to be rather significant.[11] Namely, it will be preferable to suppress vibronic transitions irrelevant to ASE. From such a viewpoint, we considered the reason why DSBP shows the lowest threshold.

In the case of linear-chain-structured dyes, it is known that the vibronic transition inducible to ASE (i.e., III $\rightarrow$ IV) is closely related to torsional twisting modes around σ-bonds linking π-units.[9,12] The molecular orbital calculations for the dyes listed in Table 1 suggest that their highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are represented by linear combination of the HOMOs and the LUMOs of constituent π-units, respectively, except for the case of 2,5-bis(2-benzoxazolyl)thiophene (BBOT).[13] For all σ-bonds linking π-units, π-antibonding and π-bonding interactions are seen in the HOMOs and the LUMOs, respectively, implying that molecular structures tend to be more planer by the HOMO–LUMO transition. On the other hand, the electronic distributions in both HOMO and LUMO are the largest in the center of a dye, getting smaller to the both sides, which can be readily predicted by simple quantum chemical consideration for a one-dimensional box. Therefore, it is in the center of a dye that the electronic change caused by the HOMO–LUMO transition is the largest. In DSBP, it corresponds to the σ-bond between two benzene rings. The conformational change between S_0 and S_1 in DSBP is thus considered to be similar to that in biphenyl which is assigned to the large-amplitude internal twisting around the σ-bond.[14] Such a situation that the central part of a dye is located on a σ-bond occurs when the number of π-units (N) is even: $N = 6$ in DSBP. Quaterphenylene (QP) with $N = 4$ also belongs to this category. When N is odd, however, the central part is located on a π-unit, so that the torsional twisting is predicted to be caused mainly around the two σ-bonds linked to the central π-unit. Judging from the freedom of σ-bond rotation coupled with the electronic transition, it can be thus said that even systems are more effective than odd ones. In fact, as shown in Figure 2, the occurrence of the side bands that are not involved in ASE is confirmed for odd systems under excitation near the threshold energy. It is therefore suggested that the lower threshold of DSBP than another styrylbenzene derivatives results from such a reason.

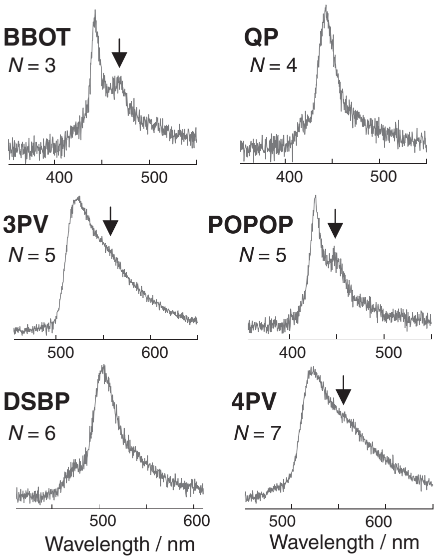


Figure 2. Comparison of emission spectra under excitation near the threshold energies. Arrows indicate the side bands which are not involved in ASE.

With regard to FWHM, BBOT exhibited the smallest value of 2.6 nm. FWHM will depend on whether the molecular geometry of III is rigidly determined to a nuclear coordinate. Since all σ-bonds linking π-units have more or less potential for bond rotation, it is presumed that FWHM is narrower as N is smaller.

In summary, the ASE threshold of linear-chain-structured dyes was found to be dependent upon whether the number of constituent π-units is even or odd. On the basis of this guide, our studies are now in progress.

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