Using proton-transfer laser dyes for organic laser diodes

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Photopumping measurements for the dilute thin films of the representative proton-transfer laser dye, 2-(2-hydroxyphenyl)benzothiazole (HBT) revealed that it exhibited better stimulated-emission performance, especially at the high doping level of 26 wt %. This suggests that HBT has an ability to form high gain media, in addition to an inherent potential for widely tuning gain wavelength. Both are advantageous for overcoming the polaron-absorption problem that is a major obstacle to making organic laser diodes. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1868885]

Since the reports that the possibility of organic laser diodes (OLDs) was referred,[1,2] a considerable number of attempts have been made to date.[3–6] Although photopumped lasing has been observed in the slab waveguides made of small molecules or conjugated polymers, there has yet been no report on electrically pumped lasing from organic light-emitting diode (OLED) structures. The primary requirement for the achievement of laser radiation is that the optical gain of emissive medium must be predominant over the sum of all the losses, such as scattering and absorption; namely, the net gain must become positive. Within the OLED devices, however, inherent low carrier mobility of organics brings about the situation that the density of charge carriers (i.e., polarons) is much higher than that of emissive excitons, thereby causing a large absorption loss of stimulated emission by polarons.[7,8] Actually, in a thin film of tris-(8-hydroxyquinoline) aluminum (Alq)-doped with a DCM2 laser dye, which is a host-guest type of emitting layer enabling an efficient Förster energy transfer, it is shown that the optical gain of DCM2 cannot be obtained due to the absorption loss by large amounts of anionic Alq hosts.[7] The drastic raising of mobility enough to change such a situation could hardly be expected under the carrier-transport mechanism of organics described by hopping, so that the polaron-absorption problem is a serious obstacle to the realization of OLDs.

One of the strategies for circumventing this problem is to design the device such that the gain spectrum of a laser dye has little overlap with the absorption spectra of charge carriers.[5] For this purpose, the use of the cascade Förster energy-transfer system that is formed by simultaneous doping of two or more guests into a host matrix[9] might be an effective way, since the gain wavelength can be widely changed by the combination of guests suitably matched in their absorption and emission spectra. Thus, for example, a further addition of adequate laser dyes into the Alq:DCM2 system might enable one to shift the gain wavelength to the region where absorption of Alq anions is relatively weak; however, it also might require a high technique for vapor codeposition of several materials with their concentration ratio exactly controlled.

On the other hand, as another gain-wavelength shifting method, we have been focusing on the use of proton-transfer (PT) laser dyes. A characteristic property of PT dyes is that the four-level laser scheme for forming a population inversion state is constructed on the basis of tautomerization by excited-state intramolecular proton transfer (ESIPT).[10–12] The absorptive and emissive tautomers with different geometries give rise to Storks shift ranging from 6000 to 10 000 cm^{-1}, which are much larger than those of conventional laser dyes: e.g., $\sim$4000 cm^{-1} in DCM2. Thus, it can be said that the PT dyes themselves potentially have a wider shiftable range of emission wavelength. In fact, the emission wavelength of a certain PT dye is largely changed depending on the surrounding solvents.[13] Moreover, from the viewpoint of organic synthesis, the chemical modification design for the control of Storks shift should be possible by quantum chemical consideration that can provide a reasonable explanation for ESIPT reactions.[14]

With such characteristics, the PT dyes have been taken up as a promising dopant molecule for finely tuning gain wavelength so as not to overlap with polaron-absorption regions. In the first step of the study, we investigated the stimulated-emission properties for dilute thin films of a representatives PT dye, 2-(2-hydroxyphenyl)benzothiazole (HBT) (inset of Fig. 1). From the results, we insist that for the development of OLDs, the PT dyes, such as HBT, are advantageous in terms of not only potentially having a tuning ability of gain wavelength, but also forming high gain media.

The HBT dye was dissolved in dichloromethane with a binder polymer of polycarbonate (PC-BisZ), and the films
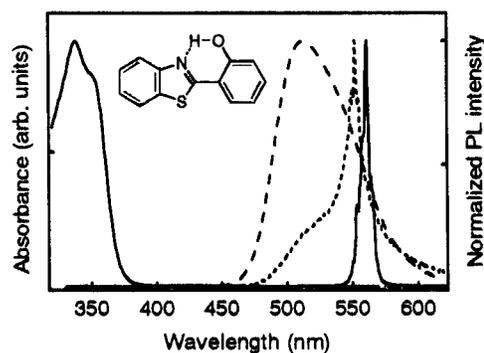

FIG. 1. Absorption and emission spectra of PC-bisZ films doped with 26 wt % HBT: Absorption (solid line, left-hand side), spontaneous emission (dashed line), ASE at pump intensites of 14 μJ/cm^2 (dotted line) and at 445 μJ/cm^2 (solid line, right-hand side). The inset shows chemical structure of HBT.

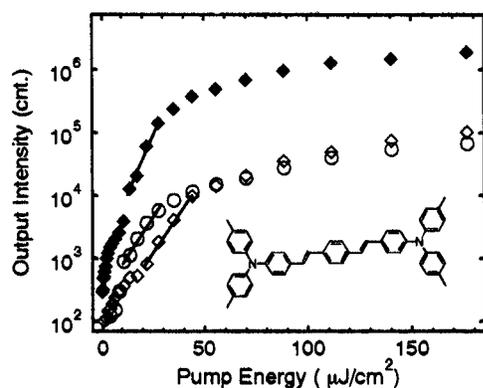
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FIG. 2. The dependence of the output intensity on pumping energy for HBT-doped [5 wt % ($\diamond$) and 26 wt % ($\blacklozenge$)] and DSB-doped [5 wt % ($\bigcirc$)] PC-bisZ films. The lines in low pumping energy region are guides for the eyes. The inset shows the chemical structure of DSB.
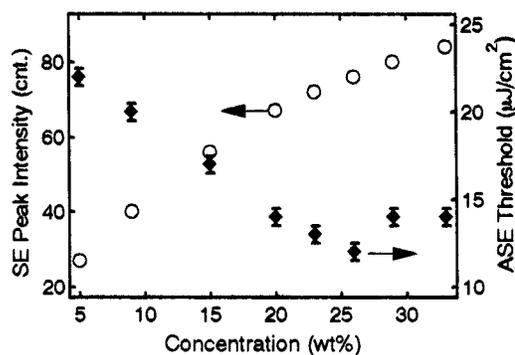

FIG. 3. The dependences of SE peak intensity ($\bigcirc$) and ASE threshold ($\blacklozenge$) on HBT doping concentrations.

with thickness about 300 nm were prepared by spin coating on quartz substrates. The ratio of dye:polymer was varied to determine the optimal concentration for causing stimulated emission. 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 $\times$ 5 mm excitation strip. The light emitted from the film was detected at the edge of sample in a direction parallel to the film slab. As a tentative attempt to dope into the carrier-transporting host matrix, HBT was dispersed in a hole-transporting polymer of poly(N-vinylcarbazole) (PVK). In a similar manner described above, the spin-coated films were fabricated and their stimulated-emission properties were investigated. Moreover, taking the enhancement of bipolarity into account,[15] the measurements were also carried out for the PVK films simultaneously doped with HBT and the electron-transporting material, 2-(4-biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxiadiazole (PBD).

In the case of using PC-bisZ as a binder, we could fabricate homogeneous films at the doping level of under $\sim$33 wt %, which all showed amplified spontaneous emission (ASE) as the pumping power was raised up; namely, for all the samples, it was confirmed that output intensity of edge emission was exponentially dependent on pumping rate. Generally, laser dyes are used in the concentration diluted below several wt % to avoid losses such as a self-absorption and a concentration quenching by bimolecular annihilation and excimer formation. However, HBT rather exhibited better performance at the relatively high doping levels; the lowest ASE threshold and the strongest output intensity were obtained for a 26 wt % doped film. Figures 1 and 2 show the emission spectra and the pumping power dependence of ASE intensity for a 26 wt % doped film, respectively. The spectral narrowing begins to be observed at the pumping energy exceeding 10 μJ/cm^2 (dotted line in Fig. 1). In the ASE spectra, the following two points are characteristic: (1) The ASE peak positions (i.e., gain wavelength) are not in agreement with the spontaneous emission (SE) maximum at 514 nm, which is also seen for PT dyes in solution,[16] and (2) the ASE spectra have a clear vibrational progression that will be ascribed to torsional twisting modes around the σ-bond between benzene and oxathiazole rings.[17] Above the threshold, the output intensity exponentially increases up to $\sim$30 μJ/cm^2, and then gradually approaches saturation (Fig.

2). The full width at half maximum of the spectrum finally becomes narrowed to about 6 nm (dashed line in Fig. 1). An additional note in the ASE spectra is that their centers are gradually shifted from 551 nm to 561 nm with increasing pumping energy. This seems to be related to the fact that the gain wavelength of PT dye is sensitive to its surrounding conditions;[13] environmental change caused by altering pumping power, such as e.g. exciton population, might affect the energetic stability of PT state, resulting in the ASE peak shift.

For the sake of comparison to another laser dye, Fig. 2 also shows the result for a PC-BisZ film 5 wt % doped with 1,4-bis(4-di-p-tolylaminostyryl)benzene (DSB), which is one of the conventional laser dyes exhibiting good ASE performance even in the film state;[18,19] the optimal concentration of DSB for causing ASE was surely obtained at 5 wt %. It should be noticed that in the energy region where ASE is given off, the output intensity of HBT is more than one order of magnitude higher than that of DSB, resulting from the higher number density of HBT dyes. With regard to ASE threshold, HBT is somewhat inferior to DSB with the threshold of 9 μJ/cm^2. However, in the pump-energy region of 10–30 μJ/cm^2 where the maximal gain is expected, the gradient of the slope for HBT is much larger than that for DSB. This suggests that, in this energy region, the HBT-doped (26 wt %) film has a higher optical gain. The gain coefficient is given by $g = \sigma \cdot \Delta N$, where σ is the stimulated emission cross section that depends on the excited-state lifetime (τ), especially in the case of small molecules, and ΔN is the population inversion density that depends on the number density of dyes. Since σ is not so different among organic laser dyes with almost $\tau \approx$ ns, the enhancement of ΔN should be more effective to obtain a higher optical gain. In fact, as shown in Fig. 2, the amplification gradient for HBT thin films becomes larger by raising doping concentration from 5 wt % to 26 wt %. Therefore, it is suggested that the PT dyes, such as HBT, are a more promising dopant than the other conventional laser dyes for forming higher gain media.

One of the factors why HBT exhibited good ASE performance in spite of high doping level lies in the fact that self-absorption loss does not occur completely due to the large Storks shift (9000 cm^{-1}). In practice, the SE spectrum with maximum at 514 nm (Fig. 1) is far apart from the absorption band edge around 380 nm, which causes no overlap between the absorption and the emission spectrum. It also means that the doping concentration does not influence the refractivity at the ASE wavelength. As another factor, loss by concentra-
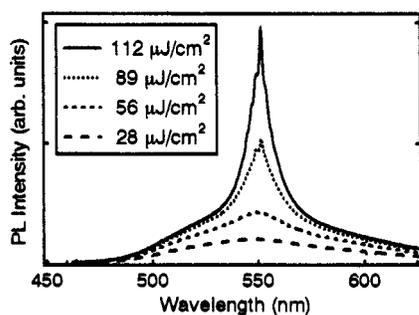
FIG. 4. Emission spectra of PVK films doped with 26 wt % HBT.

tion quenching rarely occurs, although HBT has no bulky groups, such as di-*p*-tolylamine of DSB that are effective to prevent the intermolecular annihilation process. Figure 3 shows the concentration dependence of the SE intensity and the ASE threshold. It should be noted that the SE quenching is not observed up to 33 wt %, although the slope of the intensity becomes smaller around beyond 20 wt %. Both the spectral profile and the location of SE are unchanged by increasing doping concentration, indicating no excimer formation. From these results, it is implied that bimolecular annihilation begins to occur at about 20 wt %, and to cancel out with the SE intensity enhancement by increasing of the HBT number density. The optimal concentration for ASE was not necessarily consistent with the concentration where the SE intensity is maximal.

Also, when HBT was doped into the hole-transporting polymer of PVK, ASE could be observed (Fig. 4). As in the case of PC-bisZ films, the best ASE performance was obtained at the high doping level of 26 wt %; however, the threshold is estimated to be 50 μJ/cm^2, being five times higher than that in a PC-bisZ film. On the contrary, the peak positions of the ASE spectra are at 551 nm, not shifted by a change in the pumping energy; thus, the gain-narrowing characteristics of HBT are sensitive to host matrices. Although a nondoped PVK film shows emission in the range 350–500 nm, only observed for the HBT-doped PVK film is the emission from HBT, indicating that the radiative decay process of PVK is suppressed by interacting with HBT. The energy transfer from PVK to HBT is not really expected due to the poor overlap between PVK emission and HBT absorption spectra. Therefore, intermolecular interaction between the HBT and PVK is suggested to give rise to irrelevant inradiative decay processes, resulting in the higher ASE threshold compared with that in PC-bisZ film. The ASE char-

acteristics of HBT observed for PVK films were, however, not affected by codoping with an electron-transport material of PBD. This result might provide a simple model system to investigate laser emission mechanism under electrically pumped conditons.[20]

In conclusion, one of the representative PT dye, HBT was found to exhibit good ASE performance in the dilute thin-film state, especially at the high doping level of 26 wt %. It is thus suggested that HBT has potentials not only for widely tuning gain wavelength, but also for forming high gain media. These are advantageous for overcoming the polaron-absorption problem that is a major obstacle to making OLDs.

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