

Vertical-cavity surface-emitting laser in the long-wavelength (700 nm) region in the visible by energy transfer between organic dyes

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Abstract In this work, organic vertical-cavity surface-emitting lasers (VCSELs) with single-mode laser output in the long-wavelength region (~ 700 nm) of the visible were reported based on the energy transfer between dye pairs consisting of pyrromethene 597 (PM597) and rhodamine 700 (LD700). By co-doping PM597 into the polymeric hosts, the fluorescence intensity of LD700 was enhanced by 30-fold and the photophysical parameters of the donor–acceptor pairs were investigated, indicating the involvement of non-radiative resonance energy transfer processes between PM597 and LD700. Active distributed Bragg reflectors (DBR) were made by alternately spin-coating dye-doped polyvinylcarbazole and cellulose acetate thin films as the high and low refractive index layers, respectively. By sandwiching the active layer with 2 DBR mirrors, VCSEL emission at 698.9 nm in the biological first window (650–950 nm) was observed under the 532-nm laser pulses. The laser slope efficiency and threshold were also measured.

1 Introduction

Since the mid-1980s, intensive research efforts have been devoted to the organic solid-state dye lasers, which brought benefits such as non-toxic and maintenance-free in

comparison with their liquid counterparts due to their charming applications in fields of spectroscopy, biomedical engineering, environment sensing, chemical analysis, etc. [1–6]. Among the extensive configurations of organic tunable lasers, vertical micro-cavity structures were especially attractive because of their advantages such as low threshold energy, single wavelength oscillation, improved spatial beam quality, easy of fabrication, and compatibility with other integratable elements [7–12]. So far, several types of vertical cavities have been demonstrated by using metal mirrors, evaporated inorganic thin films, and spin-coated organic thin films as DBR resonators, which offered one-dimensional optical confinement to the active medium [7, 12]. By the introduction of nanometer-sized silica particles into the active layer and/or utilizing dye-doped organic films as active Bragg reflectors, the laser performances of pyrromethene dyes doped into the organic vertical-cavity surface-emitting laser (VCSEL) have been significantly improved, with the laser threshold reduced to the level of nJ and the laser lifetime extended to the level of 10^5 pulses [10–15]. The laser emission intensity of the organic VCSEL was drastically enhanced with linewidth considerably narrowed by coupling with the stimulated resonant Raman scattering [7]. Multi-color laser emission from the rhodamine-based micro-cavity laser arrays was also demonstrated, which were promising to their broad applications, especially in compact display and biosensors [8]. However, to the best of our knowledge, the spectral coverage of the organic VCSELs was mainly in the yellow and red regions, from 540 to 650 nm, although long-wavelength (>650 nm) lasing in the biological first window (650–950 nm) had some distinct advantages in biomedical and biophotonic applications because of the deeper penetration depth of long-wavelength light [16]. Such absence in the spectral coverage of organic VCSELs could

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be mainly ascribed to the low absorption to the most frequently employed Nd:YAG pump laser sources at 532 nm and the poor photostability of laser dyes in this spectral region. In this concern, it was suggested that Forester-type energy transfer based on donor–acceptor dye pairs might be one of the most feasible technical approaches to overcome the problems for organic VCSELs emitting in the red and near infrared regions.

Herein, for the first time to our knowledge, organic VCSELs with single-mode laser emission at ~ 700 nm were reported based on the energy transfer between dye pairs consisting of a pyromethene dye, PM597, and a rhodamine dye, LD700. The fluorescence intensity of LD700 was enhanced by at least 30-fold with the introduction of PM597, and the main energy transfer mechanisms involved in the PM597–LD700 pair were characterized to be non-radiative resonance energy transfer processes. Active Bragg reflectors were made by alternately spin-coating dye-doped polyvinylcarbazole (PVK) and cellulose acetate (CA) thin films as the high and low refractive index layers, respectively, and by sandwiching the active layer with 2 DBR mirrors, VCSEL emission at 698.9 nm was observed under the 532-nm pulsed laser pumping. Other laser properties such as the slope efficiency, threshold, and laser lifetime were also characterized.

2 Experiment

The pyromethene family dye PM597, rhodamine family dye LD700 (laser grade from Exciton), the commercially available polymers for the high and low refractive index layers, PVK (TCI), and CA (Sigma Aldrich, M.W. $\sim 30,000$) together with their solvents were used as received without further purification.

For the fabrication of high and low refractive index layers of DBR mirrors, chlorobenzene and diacetone alcohol were adopted as the solvents for PCK and CA, respectively. First, PVK and CA were dissolved into their solvents at the concentration of 22.2 and 28.6 mg/ml, respectively, under continuously vigorous magnetic stirring. Laser dyes were also dissolved into the solutions at various concentrations, which would be mentioned specifically later. After the ultrasonic treatment and filtering (Whatman, PTFE 0.2 μm), the PVK/chlorobenzene or CA/diacetone alcohol solutions were spin-coated alternately onto the quartz substrates ($\varnothing = 35$ mm, 1 mm thickness). The spin-coated films were then cured in a 130 $^{\circ}\text{C}$ oven for 5 min to remove the solvents before the deposition of next layers, and the optical thickness of each layer was precisely controlled to be a quarter of the designed wavelength at 700 nm. After the fabrication of DRB resonators

comprising 17.5 pairs of PVK/CA layers, a dye-doped CA films as the active layer with the thickness of 2.0 μm were deposited onto one of the DBR mirrors, which were then sandwiched for laser characterization. And thus the micro-cavity lasers were made.

The UV–vis absorption and photoluminescence (PL) spectra of the dye-doped PVK and CA films were measured by a Perkin-Elmer Lambda 20 and a Hitachi 850 fluorescence spectrophotometer, respectively. The scan speed and the slit width were kept at 60 nm/min and 1.0 nm, respectively. The radiative decay curves of the dyes doped into PVK and CA films were recorded by the time-correlated single-photon counting technique (Edinburgh Instrument, ηF900). The excitation and emission slits were kept at 0.1 nm, and a hydrogen flash lamp with pulse duration of ~ 1.0 ns (full-width at half-maximum, FWHM) at the repetition rate of 40 kHz was used as the excitation source. The excitation wavelength was fixed at 355 nm as concerning the spectra of hydrogen flash lamp, and the monitoring wavelengths were determined according to the steady-state fluorescence peaks. Fluorescence decay curves were analyzed as a one-exponential decay ($\chi^2 < 1.2$), and the fluorescence decay time (τ) was obtained from the slope. The refractive indexes of the PVK and CA films were measured by a commercial prism coupler (Metriton Model 2010) at 633 nm. The refractive index and thickness of the dye-doped PVK and CA films were also measured by a scanning ellipsometer (Semilab, GES 5E). The morphology of the films was observed by atomic force microscopy (Bruker, Dimension Edge).

For the characterization of laser properties, the second harmonic output from a Q-switched Nd:YAG laser with pulse width of 3–5 ns (FWHM) was used as the pump source and the pumping beam was focused by a spherical focal lens ($f = 300$ mm) to form the pumping spot of ~ 80 μm in diameter on the sample surface. The dye-doped micro-cavity lasers were pumped longitudinally, and the output lasers were monitored perpendicular to the sample surface by an optical fiber spectrometer (Ideaoptics, FX4000) with a spectral resolution of 0.35 nm. The laser output energy was measured by a laser energy meter (Ophir, Nova II, and PD10).

3 Results and discussion

The typical absorption and fluorescence spectra of PM597 and LD700 solely doped into CA films are presented in Fig. 1, respectively. The absorption and fluorescence peaks of PM597 doped into CA films were 530 and 568 nm, respectively, while those of LD700 doped into CA films were 652 and 674 nm, respectively. Given the dye concentration and the film thickness, the absorption

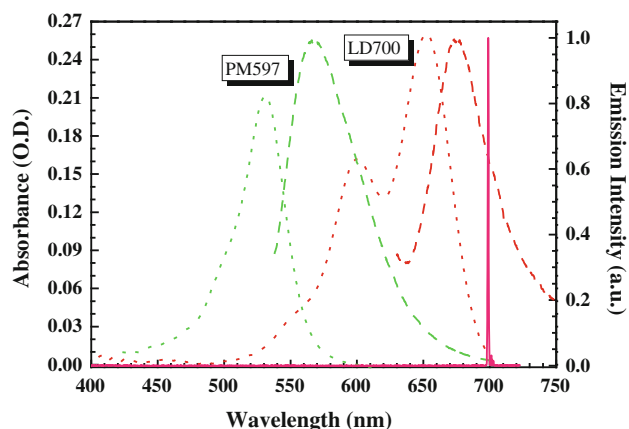


Fig. 1 UV-vis absorption (dotted line) and fluorescence (dash line) spectra of PM597 and LD700 solely doped into CA films, respectively, together with the laser emission spectrum (solid line) PM597 + LD700 co-doped micro-cavity lasers

cross-section of LD700 doped into the CA films at 532 nm was $1.1 \times 10^{-17} \text{ cm}^2$, which was somewhat too low to be pumped efficiently by the second harmonic of Nd:YAG lasers as considering the limited active region of the vertical-cavity structures. In this concern, the technical pathways of increasing the absorption cross-section of LD700 at 532 nm via energy transfer from donor dyes were proposed. As shown in Fig. 1, the possibility of energy transfer process between PM597 and LD700 could be ascertained with the overlaps of the absorption and emission spectra of the donor and acceptor, respectively [17, 18]. From the overlap between the emission spectrum of PM597 and the absorption spectrum of LD700, it was obvious that the excited state PM597 could be quenched by the ground state LD700. In this work, the dye concentration of LD700 in organic films was decided firstly for designing the proper concentration ratio between PM597 and LD700 of the micro-cavity lasers. At various concentrations of 1.0, 2.0, 3.0, 4.0, 5.0, and 6.0 wt%, the fluorescence lifetime of LD700 in CA films were measured to be 6.43, 6.07, 5.82, 5.66, 5.10, and 4.47 ns, respectively. It should be mentioned that with the increase in dye concentrations, the fluorescence yields and radiative lifetime might be decreased due to the formation of aggregates such as dimers and the presence of re-absorption re-emission processes [17]. Thus, in this concern, the concentrations of LD700 in both PVK and CA films were fixed at 1.0 wt% in the following discussions of this work.

The fluorescence spectra of LD700 doped in CA films in the absence and presence of PM597 are presented in Fig. 2, and the variation in the peak fluorescence intensity of the acceptor with donor concentration was shown. The maximum peak fluorescence intensity was observed at the donor concentration of 3.5 wt%. At lower donor concentration,

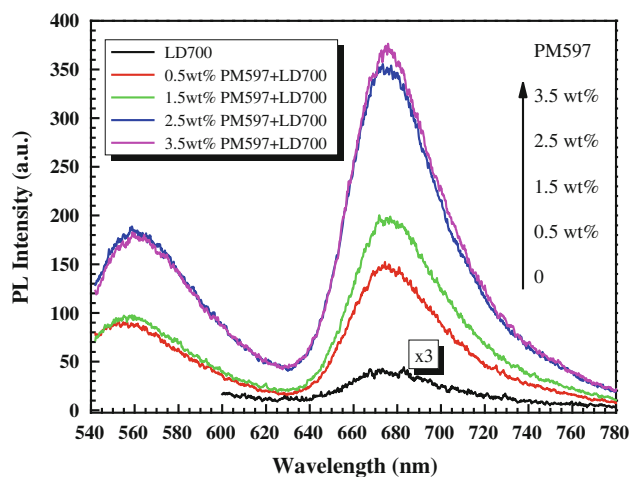


Fig. 2 Fluorescence spectra of LD700 doped into CA films in and without the presence of PM597 (excitation wavelength 470 nm)

the peak fluorescence intensity of the acceptor dye increased with the increase in the donor concentration because the intermolecular distance between the donor and acceptor molecules was large and reduced continuously with the addition of the donor dye. Above a certain concentration, for instance, when the concentration of PM597 increased from 2.5 to 3.5 wt%, there was only marginal enhancement on the peak fluorescence intensity of LD700. Further increase in the donor dye concentration would even lead to decrease in the fluorescence intensity of LD700, which might be attributed to the effect of non-radiative fluorescence quenching interactions between donor molecules as the results of decrease in the effective distance between donor molecules with the increase in the donor concentration, and thereby caused energy transfer within the donor system itself [17, 18]. At the donor-acceptor ratio of 3.5:1, i.e., the PM597 concentration of 3.5 wt%, the fluorescence intensity of LD700 reached its maximum, which was about 30-fold of that in the absence of PM597. Thus, in the following discussions, the concentrations of 3.5 and 1.0 wt% for PM597 and LD700 were selected as the optimized donor-acceptor ratio for the micro-cavity lasers.

For further insight into the energy transfer mechanisms between PM597 and LD700, the radiative decay curves of PM597 doped into CA films in the absence and presence of LD700 at various concentrations were also investigated, as shown in Fig. 3. The fluorescence lifetime of PM597 in the absence of LD700 were 7.30, 7.23, and 6.82 ns, at the concentration of 0.5, 1.5, and 2.5 wt%, respectively. With the addition of acceptor molecules, the fluorescence lifetime of PM597 decreased sharply to 1.24, 1.15, and 1.14 ns at the above concentrations accordingly. Given the fluorescence intensities and lifetime of PM597 in the absence and presence of LD700, the efficiency of the energy

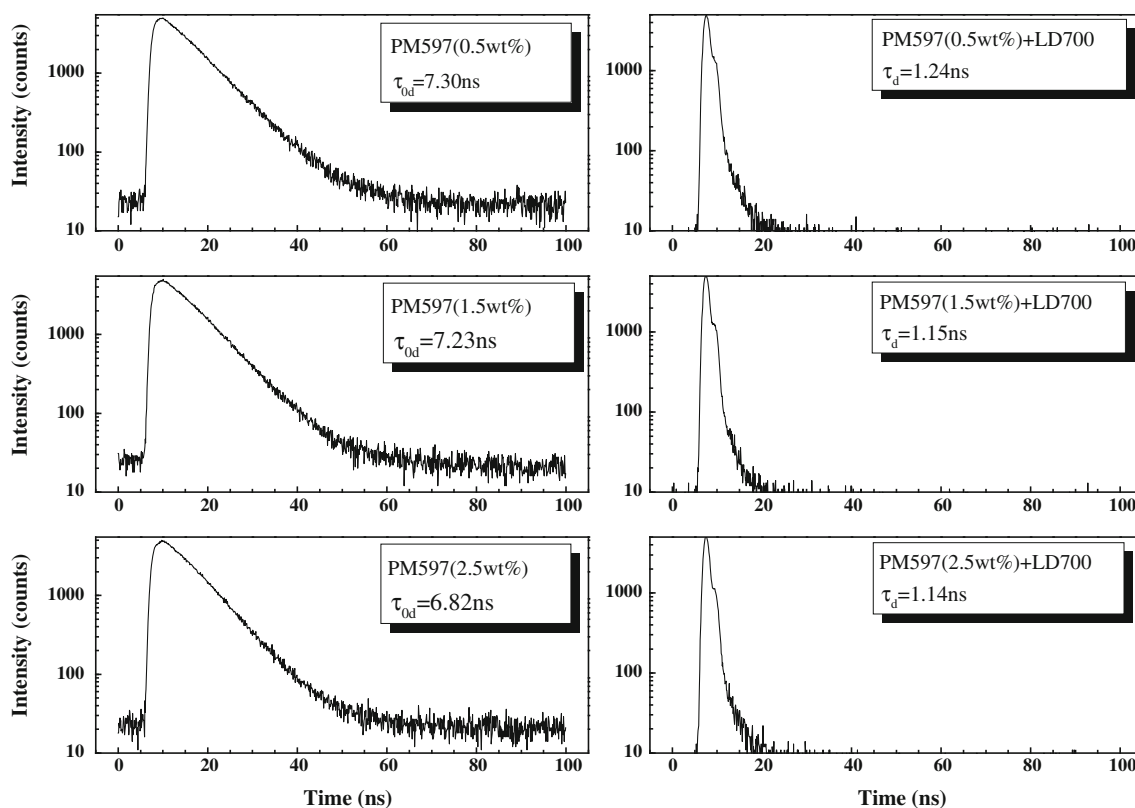


Fig. 3 Radiative decay curves of PM597 doped into CA films in and without the presence of LD700 (excitation wavelength 355 nm; monitored at the fluorescence peaks of each dye)

transfer processes (η) and non-radiative energy transfer processes (η_{non}) could be calculated by the formulas shown below

$$\eta = 1 - \frac{I_D}{I_{0D}} \quad (1)$$

$$\eta_{\text{non}} = 1 - \frac{\tau_D}{\tau_{0D}} \quad (2)$$

where I_{0D} , I_D , τ_{0D} , and τ_D were the fluorescence intensity and lifetime of the donor in the absence and presence of the acceptor, respectively [19].

It was found that at the donor concentration of 0.5, 1.5, and 2.5 wt%, the η for the energy transfer efficiencies were 93.7, 98.2, and 97.3 %, respectively, while the η_{non} for non-radiative energy transfer efficiencies were 83.1, 84.1, and 83.3 %, respectively. Thus, from the high accordance between η_{non} and η , it could be concluded that the energy transfer mechanism between PM597 and LD700 could be mainly ascribed to the resonance non-radiative energy transfer due to the long-range dipole–dipole interaction while radiative energy transfer processes, i.e., the excitation of LD700 molecules by the photons emitted by PM597, still presented as a marginal contribution to the energy transfer processes due to the high quantum yields of pyrromethene dyes [17–19].

By alternately spin coating of PVK and CA films with optical thickness of each layer precisely controlled as a quarter of the designed wavelength at 700 nm, both passive and active DRB resonators in the near infrared region were obtained. The refractive index of the dye-doped PVK and CA films were ~ 1.675 and ~ 1.483 , respectively. As shown in Fig. 4, composed by 18.5 pairs of PVK/CA quarter-wave layers, the DBR mirrors with a stop band centered at 695–700 nm from 670 to 730 nm were fabricated. The morphology of the PVK and CA films was monitored by the AFM, which showed smooth film quality with surface roughness less than 0.6 nm. At the center wavelength of the stopband, the reflectance of the Bragg reflector was ~ 95 %. By co-doping PM597 and LD700 into the PVK and CA films, active DBR mirrors with absorption bands at ~ 530 and 650 nm were also obtained, providing more efficient absorption on the pumping beams at 532 nm, which might reduce the laser threshold of LD700 as a result.

Thus, by sandwiching two active DBR mirrors shown in Fig. 4 and on one of which a 2.4- μm -thick PM597–LD700 co-doped CA film as the active layer was deposited, the micro-cavity lasers emitting in the long-wavelength region in the visible were built. With the pulsed 532-nm laser beam as the pump source and a pumping spot of ~ 80 μm

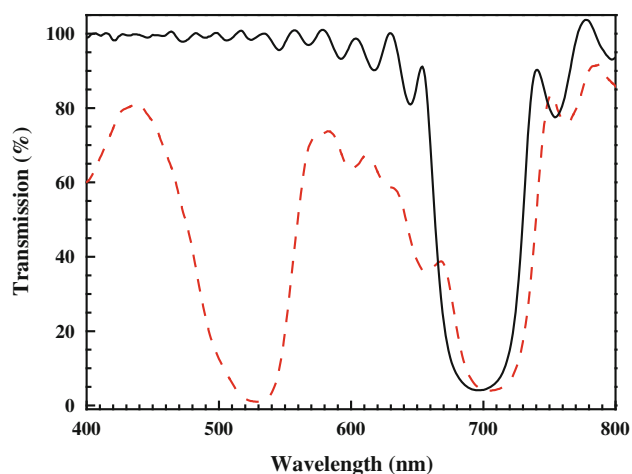


Fig. 4 Transmission spectra of the micro-cavity dye lasers consisting of 18.5 pairs of CA/PVK quarter-wave layers with (*dash line*) and without (*solid line*) the presence of PM597 + LD700 dye pairs

on the sample surface, laser output vertically from the PM597–LD700 co-doped micro-cavity lasers could be observed. The laser output spectrum of the micro-cavity laser is shown in Fig. 1 with the single-mode laser output at 698.9 nm and the linewidth of 0.8 nm. The laser output energy of the micro-cavity lasers as a function of input energy is also plotted in Fig. 5. The laser slope efficiency and the laser threshold of the PM597–LD700 co-doped VCSELs were estimated to be 9.0 % and 14.4 μJ , respectively. In comparison with the VCSELs reported by other researchers emitting in the green and yellow regions, the laser threshold of the micro-cavity lasers based on PM597–LD700 dye pairs was relatively higher [10–15]. However, it should also be mentioned that without the co-doping of PM597 and the active DBR resonators, no laser output from LD700 had ever been observed with the increase in pump energy until the damage threshold of PVK/CA films. For further reduction in the laser threshold of VCSELs at 700 nm, it was suggested that by replacing the bottom organic active DBR mirror as inorganic DBR mirrors such as $\text{SiO}_2/\text{TiO}_2$ resonators, which might increase the reflectance of the stopband [13], and/or by adopting the pyrromethene family dyes emitting in the near infrared which have demonstrated much higher quantum yields than rhodamine family dye and efficient lasing under 532 nm pumping [20], the laser threshold of the VCSELs might be further decreased.

Under the pump intensity of 1.3 J/cm^2 and the repetition rate of 2 Hz, the durability of the VCSELs emitting at 698.9 nm was also estimated preliminarily. It was found that under the relatively tough pump intensity, which was fivefold higher than the threshold intensity, the laser output from the LD700-based VCSEL was kept almost unchanged after 2.0×10^3 pulses and dropped gradually to 50 % of its

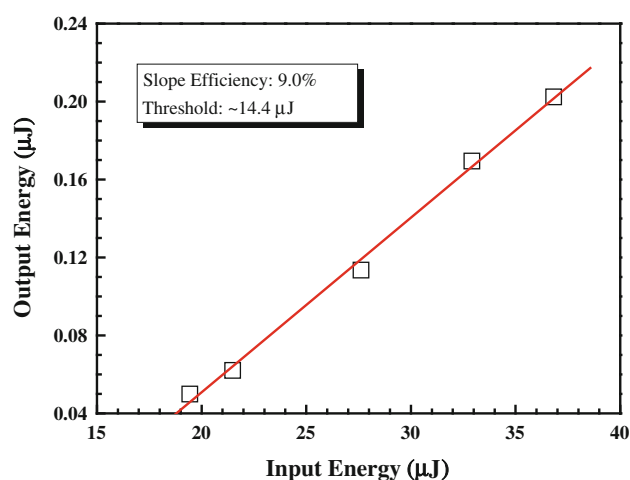


Fig. 5 Laser output energy of PM597 and LD700 co-doped VCSELs as a function of input energy

initial value after 1.0×10^4 pulses. The relatively rapid deterioration could be ascribed to the photodegradation of LD700 molecules via photochemical reactions and other pathways under such a high pumping intensity, which was confirmed by the absorption spectrum of the active layer after the laser lifetime measurement. As considering the demands for long-wavelength organic VCSELs in employments such as biomedical and biophotonic applications, the durability of the micro-cavity lasers should be significantly improved. As mentioned above, it was suggested that by adopting the pyrromethene dyes emitting in the near infrared that were more stable and efficient than rhodamine dyes [20], and introducing photostable additives that might inhibit the photochemical reactions responsible for photobleaching [21] or nanoparticles for random lasing to reduce the threshold energy [14], the laser lifetime of organic VCSELs emitting in the near infrared region would be further enhanced. And this work is currently underway.

4 Conclusion

In this work, organic VCSELs with single-mode laser output in the long-wavelength region in the visible were reported based on the energy transfer between laser dye pairs consisting of PM597 and LD700. With the presence of PM597, the fluorescence intensity of LD700 was enhanced by at least 30-fold and the photophysical parameters of the donor–acceptor system were investigated, indicating the non-radiative resonance energy transfer processes between the PM597 and LD700. Active DBR mirrors were made by alternately spin-coating dye-doped PVK and CA thin films as the high and low refractive index layers, respectively. By sandwiching the active layer with 2 Bragg reflectors, single-mode laser

emission at 698.9 nm was observed under the 532-nm laser pulses. The laser slope efficiency and threshold were measured to be 9.0 % and 14.4 μJ , respectively.

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