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CHAPTER 4

Spatial light confinement and laser emission from a gain medium containing dendrimer

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1. Introduction

Since the first reports on organic and polymeric materials that showed high optical gain and stimulated emission properties, there has been growing interest in exploiting laser applications. This growing interest is because of their wide wavelength tunability and processing flexibility in solutions [1–3], films [4–7], and fibers [8,9]. Dendritic macromolecules, called *dendrimers*, are a new category of hyper-structured material [10]. Their long branching chain and the high degree of control over regular molecular weight created a three-dimensional structure that is roughly spherical or globular [11]. In optical applications, radiative action from the high-gain medium, containing small particles such as dendrimers, may be altered significantly under coherent optical excitation [12]. In the study reported here, we found that using a homogeneous gain medium containing dendrimers increases the stimulated emission efficiency and facilitates fine-tuning the laser modes. We also identified an optical input–output threshold behavior above which laser emission with a linewidth of less than 0.1 nm was observed, even though our optical system lacked a real optical cavity. The input threshold energy from the gain medium was much smaller than the energy from the pure dye solution.

Organic laser dyes typically show a large fluorescence yield ranging from about 0.6 to near the optimum 1.0. In spite of this large yield, the dye concentration in the dye

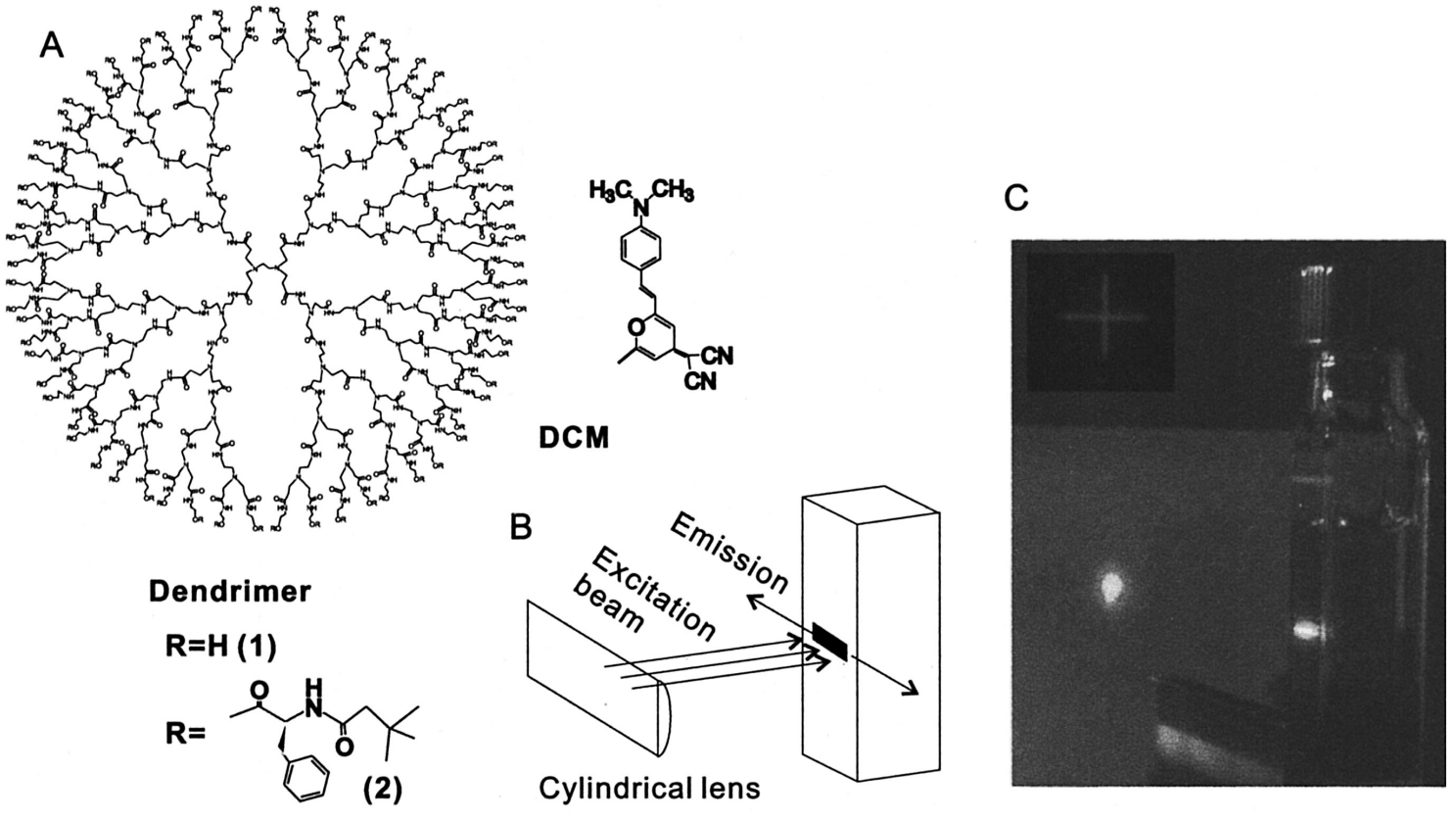

Fig. 1: Details of materials and optical experiment. (A) Chemical structure of dendrimers, **1** and **2**, and DCM. (B) Schematic of stimulated emission experiment setup. (C) Photograph of laser emission from DCM/dendrimer solution showing the red output beam radiating some distance from the cuvette facet. Inset, interference pattern of output beam after passing through cross-diffraction grating.

laser medium must be kept low to achieve highly efficient spontaneous emission. At higher concentrations, molecular aggregation, which forms dimers or higher aggregates, almost completely suppresses the fluorescence [13]. This is in contrast with the general tendency of π-electron-conjugated chromophores, which easily aggregate to form complex structures. Therefore, a dye concentration of less than 10^{-3} mol/l is generally used in laser operations.

2. Experiment

In order to obtain a higher gain medium for stimulated emission, we used a dendrimer, which encapsulates the laser dye inside and increases the dye concentration with little fluorescence quenching. The dendrimer used in this study was poly(amidoamine) with 64 hydroxyl-terminated groups (*Starburst*® PAMAM-OH dendrimer, Dendritech, Inc.) **1** [14], and the laser dye used was 4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyril)-4H-pyrane (DCM) (Fig. 1A). The DCM-doped dendrimer was obtained by mixing DCM and a dendrimer in a methanol solution. The DCM concentration was varied between 2.0 and 12.0 mM, whereas the DCM/dendrimer ratio was kept constant. As long as the DCM/dendrimer ratio was kept at 2.0, the fluorescence intensity increased as the level of the DCM concentration increased. However, the saturation concentration of DCM in methanol was less than 1.0 mM. The dendrimer was thus a good host for the DCM, increasing its solubility and yielding high emission efficiency.

We used a nitrogen laser (337 nm, pulse duration 4.0 ns, repetition rate 10 Hz) as the excitation source for stimulated emission experiments. The excitation intensities were varied between 0 and 20 μJ/pulse. A cylindrical lens focused the excitation beam into a stripe, 200 μm × 5 mm on a quartz cuvette, which contained either the DCM and dendrimer mixture or a pure DCM solution in methanol (Fig. 1B). The emissions guided along the excitation stripe were collected from the side of the cuvette using a round lens, and were then spectrally analyzed using a spectrometer and a charge coupling device (CCD).

3. Results

The emission spectra from the DCM/dendrimer ([DCM] = 2.0 mM) solution as a function of the excitation intensity gradually narrowed from relatively low excitation intensities up to 15 μJ/pulse (Fig. 2). The emission intensity, I_{se}, grew exponentially with I (Fig. 2, inset), which is consistent with amplified spontaneous emission (ASE) [15]. The gain guiding ASE process in an excitation-stripe is characterized by $I_{se} = \beta(e^{(\gamma-\alpha)L} - 1)$, where β is a constant that depends on the excitation geometry, L is the excitation-stripe length, and γ and α are the optical gain and loss coefficients, respectively. Because γ is linear with excitation intensity in the simple approximation, $\ln(I_{se}) \propto I$ for the ASE process is in agreement with the experimental results fitted in Fig. 2, inset. When the excitation intensity became high, the emission spectrum

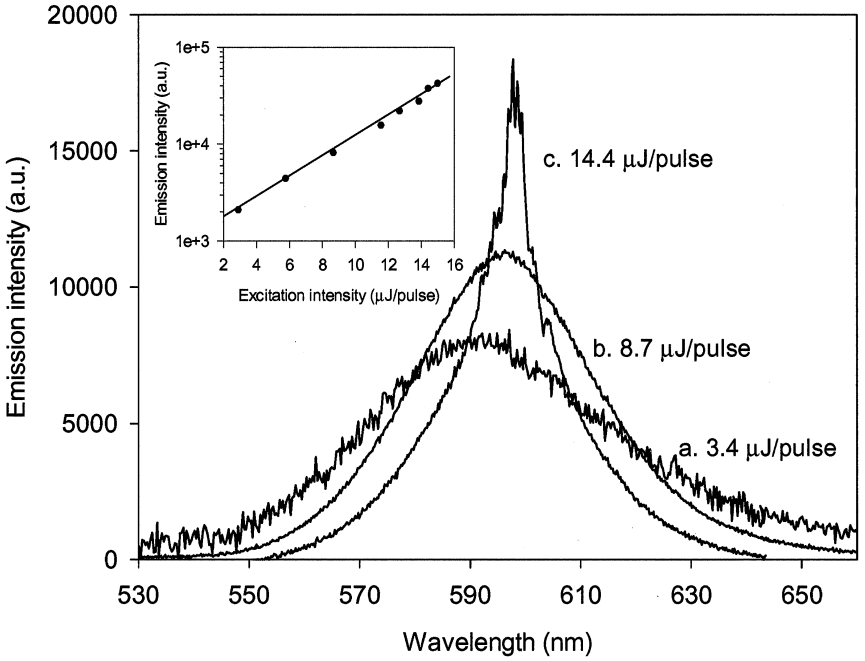

Fig. 2: Emission spectra from DCM/dendrimer (= 2/1, [DCM] = 2.0 mM) solution in methanol at increasing excitation intensities. Spectrum *a* was magnified by 20. Spectrum *b* was magnified by 3. Inset: the line through emission intensities against excitation intensities was fit using ASE.

collapsed into multiple narrow peaks (Fig. 3), and the emission intensity increased linearly as the excitation intensity increased.

A clear threshold behavior in the I_{se} vs. I plot (Fig. 4A) and a second decrease in the linewidth at higher excitation intensity (Fig. 4B) indicated the onset of laser action. The strongly modulated spectrum, with numerous peaks that were evenly spaced, clearly indicated the resonant cavity modes. The resonant peaks had a linewidth that was less than 0.1 nm. The laser beam was highly polarized in a longitudinal direction. The polarization ratio $P = I_{se,\perp}/I_{se,\parallel}$ was about 150, where $I_{se,\perp}$ and $I_{se,\parallel}$ are emission intensities with polarization in longitudinal and lateral directions. The output beam was easily visible, as shown in Fig. 1C. The interference pattern is clearly projected after passing through a diffraction grating. This indicates that the output beam was coherent, though our optical setup lacked a real optical cavity.

The distance between the resonance peaks can be given by $\Delta\lambda = \lambda^2/(2nL)$, where n is the refractive index and L is the optical length of the resonator or cavity [16]. Using the measured peak separation of $\Delta\lambda = 0.85$ nm in Fig. 3, we estimated L to be 142 μm. Laser emission requires optical feedback, e.g., reflections from the cavity edges, and the cuvette sides may have become a reflecting mirror. However, such a reflection (10 mm separation) was inconsistent with the optical length estimated from the emission spectrum. We attributed the resonant mode of the output beam to the spatial confinement of the emitted light in the slab laser. To clarify this spatial confinement, the near-field

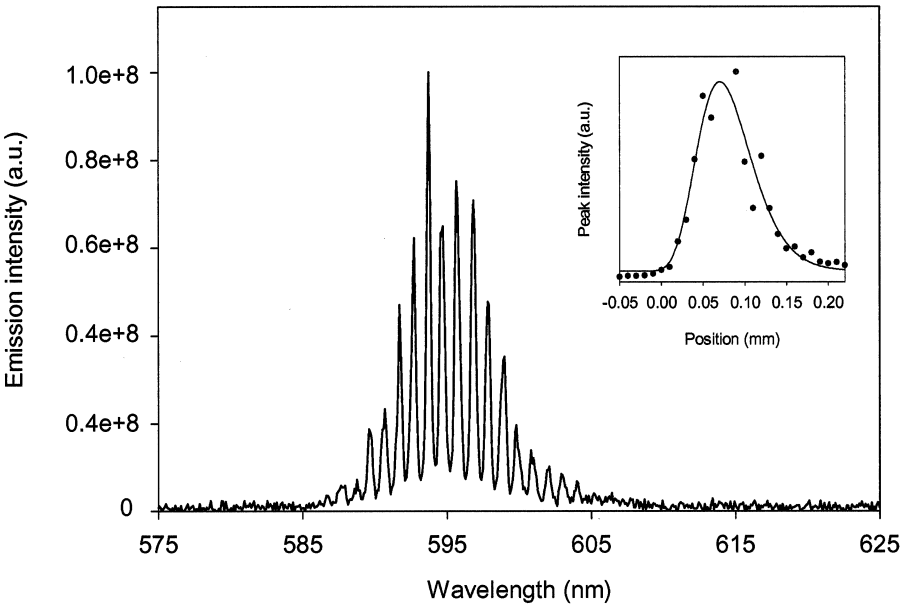

Fig. 3: Spectrum of output laser beam from DCM/dendrimer (= 2/1, [DCM] = 2.0 mM) solution in methanol at excitation intensity above the threshold. Inset: beam-intensity dependence of near-field pattern measured at facet of cuvette in lateral a direction.

pattern of the laser beam was measured using side-imaging spectroscopy. We placed a 10 μm pinhole near the face of the cuvette to monitor the emission intensity at a given position (Fig. 3, inset). The laser intensities were concentrated on the face of the cuvette approximately 140 μm in the lateral section. Assuming that the excitation stripe can act as a waveguide on the cuvette, forming a 140 μm-long slab laser, this optical length is in excellent agreement with the resonant mode separation of $L = 142$ μm estimated from the spectrum. This indicates that the emitted light was confined by gain guiding within the stripe, resulting in laser feedback.

The dendrimer is a good host to encapsulate DCM; its concentration is increased up to 12 mmol/l. Since the DCM/dendrimer has a high emission efficiency at various concentrations, laser emission intensities increased as the DCM/dendrimer concentration was increased as shown in Fig. 4. More importantly, the lasing threshold intensity became much lower as the concentration of the DCM/dendrimer was increased.

DCM/dendrimer was found to be a high-gain medium for laser emission. The explanation of how the dendrimer acts as a small particle for the laser feedback is not obvious. However, optical gain in the homogeneous medium may, in part, have occurred when dendrimer behaves as a small particle. The surface unit of dendrimer **2** was modified with a *hydrogen-bonding* unit, such as a *N-tert*-butoxycarbonyl-L-phenylalanine. Because of this modification, dendrimer **2** achieved a highly dense hydrogen-bond shell with solid-state characteristics [17], becoming a molecular particle with a diameter of about 5 nm. Lasing actions from the DCM solution with or without

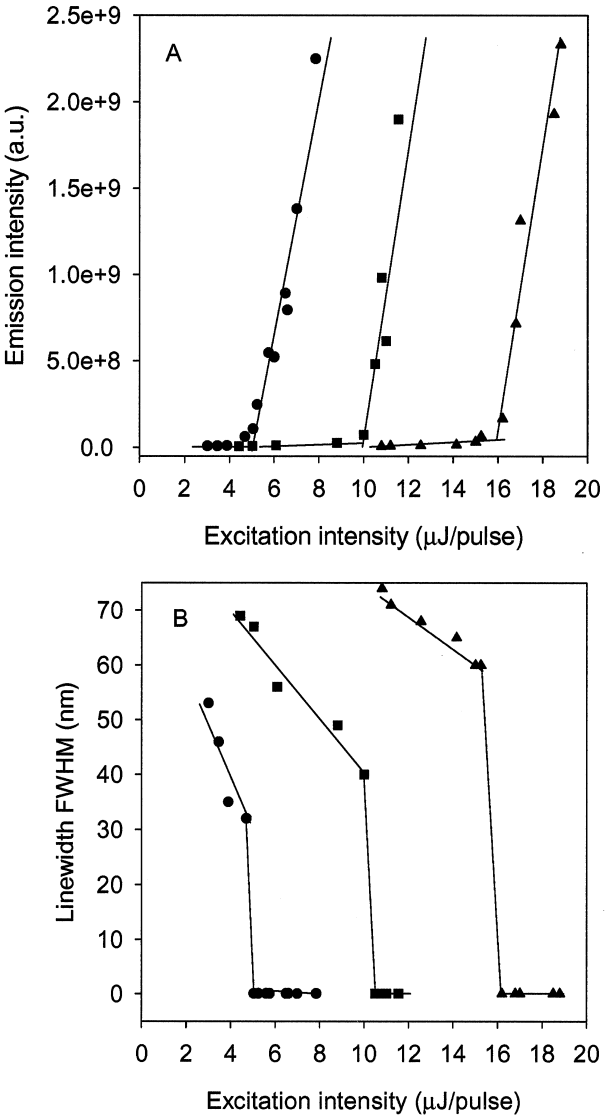

Fig. 4: (A) Dependence of emission intensity on excitation intensity for DCM/dendrimer (= 2/1) solutions at various concentrations. Concentrations of DCM: 2.2 mM (▲), 4.4 mM (■), and 13 mM (●). (B) Dependence of emission linewidth on excitation intensity.

dendrimer were compared in Fig. 5. In this case, dendrimer does not encapsulate DCM inside because of its hard shell structure. The threshold intensity of lasing became very small when the DCM solution contained dendrimer. It seems that dendrimer behaves as a scattering center, increasing the optical gain. In fact, a demonstration of stimulated emission from an inhomogeneous scattering medium, such as a microcavity

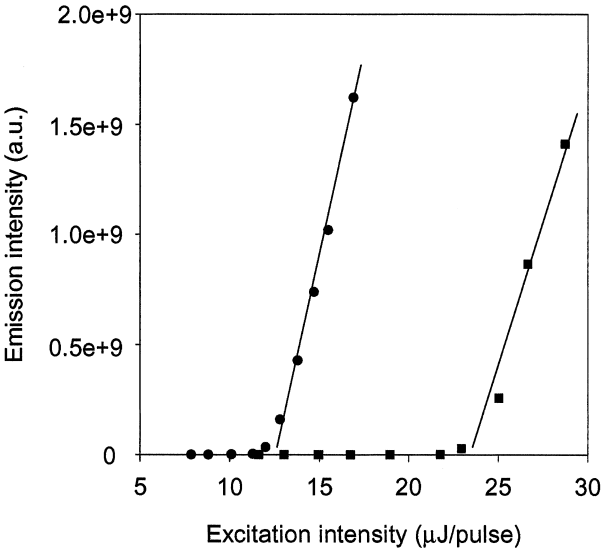

Fig. 5: Dependence of emission intensity on excitation intensity for (•) DCM (1.0 mM) and dendrimer (**2**) mixture and (■) pure DCM (1.0 mM) solution.

or mirrorless laser [18], is an excellent example of how photochemical and optical technologies can be used for emitting materials to make the optical devices simple and small [2,19]. These systems focused on the *random laser*, where the feedback mechanism of the laser emission is attributed to multiple scattering by the particles which keeps the light inside the scattering media for an extended period [19]. In these studies, though a submicrometer particle became a strong optical scattering center, it may also have induced a large optical loss. Since, in our experiment, the diameter of the dendrimer was much smaller than the optical wavelength, the optical gain was large in the DCM/dendrimer media, while the optical loss due to the passive scattering was inhibited by gain guiding. The significantly lower threshold of the laser action from the DCM and dendrimer mixture, compared with that from the pure DCM solution, provides clear evidence that emitted light can spend a great amount of time inside the gain medium. It is obvious that dendrimer produced multiple light scattering in the homogeneous gain medium. We are tempted to attribute the phenomena to photon localization providing an optical feedback for the high-gain laser dye.

4. Conclusion

In conclusion, we have described the spatial light confinement in DCM/dendrimer media, which generated a resonant mode in lasing action. The laser emission was characterized by (i) the appearance of resonance peaks with lines less than 0.1 nm; (ii) a clear threshold excitation intensity for lasing; (iii) a high degree of polarization above the threshold; and (iv) increased coherency. Encapsulating the laser dye into

the dendrimer increased the optical gain of the emitting media. More importantly, the emission process by the resonant modes is applicable to laser-like emission. The results showed that a random optical system consisting of emitting materials, optical excitation, and cavity modes, can be used to fine-tune mirrorless optical devices, even in small-device applications.

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