4 Nanodevice Technologies
– From New Functions of Extreme Substances to Telecommunication Technologies –

4-1 Controlling Intermolecular Interactions using Nano-Structural Molecules

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Controlling intermolecular interactions is one of the key issues for applying optical materials based on isolated electron system (eg. organic molecules and quantum dots) to photonic devices. We describe controlling technique of intermolecular interactions using nanomolecular structure and novel scattering laser emission from nano particle emissive media. We also report laser applications of liquid crystals used as a photonic crystalline framework.

Keywords
Optical functional organic molecule, Intermolecular interaction, Molecular nanophotonics, Dendrimer, Cholesteric liquid crystal, Laser

1 Introduction

Optically functional organic molecules with emissive or nonlinear optical properties, in addition to being inexpensive and versatile, possess fast and efficient optical functions originating from the resonance of isolated electrons in π-conjugated systems. These characteristics make these materials strong candidates for use in optical control devices for ultrahigh-speed communications. However, orbitals of the π electrons, being exposed on the molecular surface, are easily influenced by surrounding media, substrates, adjacent molecules, and other factors, which may result in changes in optical responses. For this reason, control of intermolecular interactions is a significant issue in the incorporation of highly functional molecules into devices. Interaction control in nanoscale spaces has also drawn attention in inorganic materials, including functional applications of isolated electron systems such as quantum dots, and as such is also an important topic of research for materials and devices of the future.

A hyper-branched molecule has a repeated structure consisting of molecules with low molecular weights. As it is possible to produce relatively large and well-defined nanomolecular structures, these structures are suitable for use as frameworks for controlling nanoscale intermolecular interactions. Dendrimers are particularly noteworthy materials as they are controllable spatially three dimensions [1]-[3]. A dendrimer is a type of polymer that has an arboreal structure composed of regular repetitions of branched units (Fig. 1). Dendrimers of sufficient molecular weight take on a spherical form due to extension of the molecular chains. As the branched structure of a dendrimer is constructed step by step during synthesis, it is possible to put various functions in arbitrary positions within the structure, a characteristic that cannot be obtained with linear or sheet oligomers. In this manner, the structure of a dendrimer is suitable for controlling intermolecular interactions spatially.

This report describes an attempt to control intermolecular interactions by introducing optically functional molecules into the dendrimer framework. First, we will discuss improvements in optical functionality conferred by physical and chemical shielding effects gained through utilization of the shell-like structures of dendrimers. Next, we will describe the novel lasing emission caused by weak scattering of molecular particles and offer an example of the explicit application of intermolecular interactions: namely, a new approach in which a dendrimer is treated as a nanoscale reaction chamber. Finally, we will provide an outline of laser oscillation control using liquid crystals, which are typical substances that form higher-order structures due to intermolecular interactions.

2 Functionality improvements gained through shielding effects (molecular capsules)

2.1 Control of intermolecular interactions via physical shielding effects

Fluorescent organic molecules are known to have high quantum yields and wide-gain bandwidths. These characteristics make them suitable for lasing media, and in fact they have found applications in tunable lasers. However, their usability has been decreasing in recent years with the development of solid-state tunable lasers. Nevertheless, their low cost and stability have contributed to increased demand for solid-state dye lasers in industrial and medical applications. Problems with making realistic solid-state dye lasers include quenching due to aggregation of the fluorescent dyes in the medium and loss of their activity due to interactions with the medium, both of which are the result of photophysical interactions involving energy transfer from photoexcited molecules to other molecules or to the medium. These photophysical interactions take place within a space several nanometers in radius. Since high-molecular weight dendrimers tend to become extended spherical molecules of 2 to 4 nm in size due to their treelike structures, placement of a chromophore at the core of a dendrimer sphere would provide several nanometers of space and likely serve to reduce the photophysical interactions.

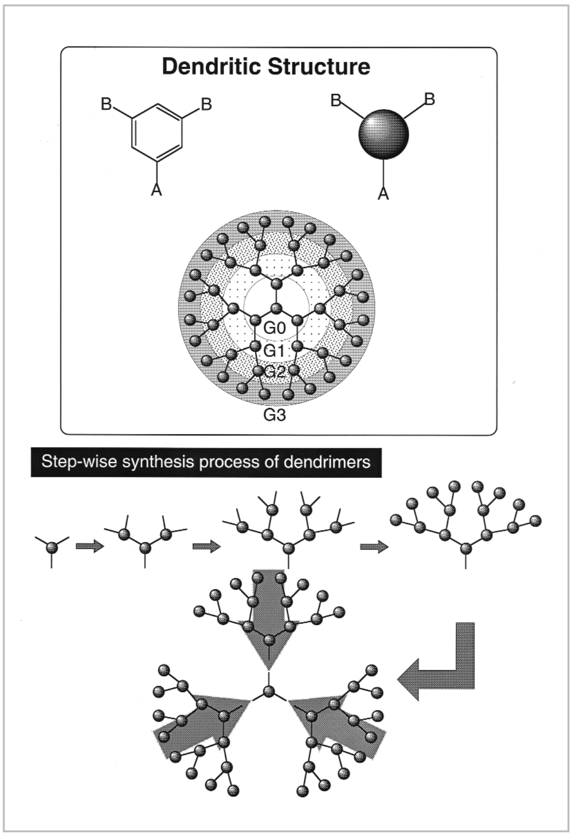


Fig.1 Structure of a dendrimer

A core/shell type dendrimer was synthesized with rhodamine B bonded to its core (Fig. 2) and its intermolecular interactions were studied to determine their controllability depending on the size of the dendrimer [4]. This method produces a certain core-shell structure, ensuring the shielding of the dye molecule. Substrates were coated with dendrimer molecules of different generations and the fluorescence lifetime was measured as a means of determining the controllability of the intermolecular interactions of the dendrimer shell. Figure 3 shows the fluorescence decay characteristics of the dye in dendrimer molecules of different generations and in solution. Interactions caused by Föster energy transfer at intermolecular distances of 5 to 6 nm or less were seen for rhodamine B, which resulted in decreased fluorescence lifetime. With smaller intermolecular distances, at which dimer formation occurred, the activity was lost and the fluorescence was quenched. In other words, the rhodamine B coating itself did not show fluorescence. Nevertheless, the dendrimer coating showed fluorescence due to the shielding effect of the dendrimer shell, which prevents dimer formation. It is also clear from the figure that fluorescence lifetime increases with increasing dendrimer size, indicating that the shell is responsible for the mitigation of the interactions.

The solubility of dendrimers can be controlled via the properties of their peripheral groups. It is also possible to control their solubility in solid media and high-dose doping is likely to produce high-gain media.

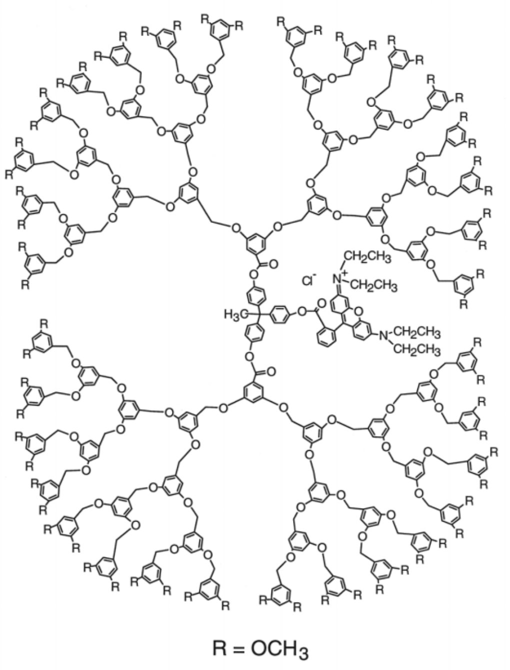


Fig.2 *Structure of rhodamine B core/shell type dendrimer*

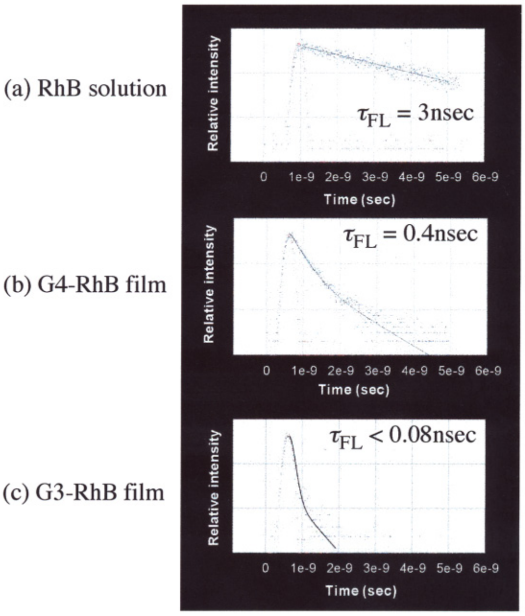


Fig.3 *Variation in physical shielding effects and fluorescence lifetime for different generations*

2.2 Reduction of photochemical bleaching via chemical shielding effects

The problem of photobleaching poses a large barrier to the practical use of high-performance organic dyes in photonic devices. Photobleaching is caused by reactions occurring through photochemical or photothermal processes. Here, an attempt was made at reducing photochemical bleaching using the chemical shielding effects of the molecules on the outermost shell of a dendrimer. The tree-like structures of dendrimers, with their many outward-extending branches, permit the easy encapsulation of small molecules. Consequently, a dye can be easily encapsulated by simply mixing a dendrimer and the dye in a solution. After encapsulation, modification of the outermost shell with molecules that prohibit chemical reactions makes it possible to suppress chemical reactions occurring between the molecules inside and outside of the dendrimer molecule.

This experiment was performed to evaluate the effects of the molecular capsule on reactions involving singlet oxygen, which are the most common photochemical bleaching reactions [5]. Singlet oxygen is generally autogenerated by photoexcited dyes. In this experiment, however, another dye was added to generate singlet oxygen outside of the molecular capsule. The encapsulated fluorochrome is rubrene, which is typically used for detecting singlet oxygen. For comparison purposes, two types of molecules were separately attached to the outermost shell: one that quenches singlet oxygen and one that does not (Fig. 4).

When molecules that do not quench singlet oxygen are attached to the outermost shell, the reaction with the encapsulated dye was suppressed to approximately 1/50. With this type of molecule, the only factor that prohibits the reaction is obstruction of the diffusion of singlet oxygen. This fact serves to confirm that the dendrimer shell structure functions effectively as a molecular capsule. When the outermost shell was covered with molecules capable of quenching singlet oxygen, further suppression of the reaction was observed, to approximately 1/60. Considering that the molecules used in this experiment are smaller and cause a lesser diffusion resistance effect than those used in the previous experiment, the effect of the quenching ability was expected to be larger than that observed here. In summary, it is effective to use larger outermost shell molecules with quenching ability in order to provide the molecules (as molecular capsules) with chemical shielding effects.

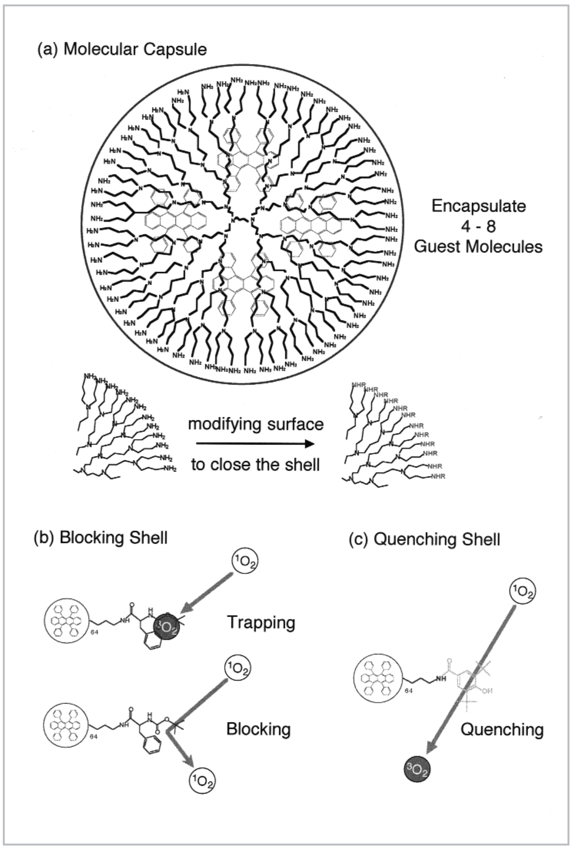


Fig.4 Configuration of molecular capsule and chemical shielding effects

3 Random laser oscillations caused by weak scattering

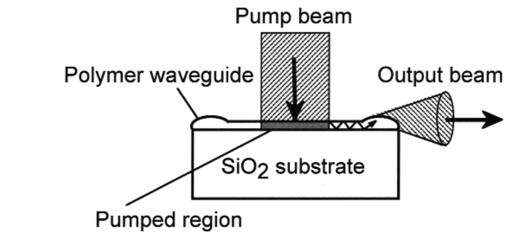
In the previous section, we demonstrated that it is possible to produce a high-concentration medium and to increase fluorescence lifetime by doping and encapsulating dyes in dendrimers and utilizing the physical and chemical shielding effects thereof. In this section, we will demonstrate that it is possible to obtain laser beams without external oscillator structures by using the properties of dendrimers as molecular particles. In a strong light-scattering medium, photons can be localized due to the interference of the scattered light. Confinement of light by interference such as in the example described here can be viewed as a kind of oscillator structure. A light source implemented with light amplification factors is specifically called a “random laser” [6] and a random laser with a semiconductor nanoparticle scattering (amplifying) medium is known to produce single-mode oscillation [7].

When introducing a dendrimer into a solid film or solvent as a guest molecule, the solubility in the host material depends mainly on the chemical structure of the dendrimer. In other words, it is possible to change the solubility of the encapsulated dye in a solid or solution freely by selecting the type of peripheral molecule of the dendrimer. For example, the dendrimer shown in Fig. 2 forms phase separation clusters in polymethylmethacrylate

(PMMA), a polymer host, and scatters light. As the indices of refraction for PMMA and the dendrimer differ only by 0.04, the induced scattering is extremely weak and the propagation loss is only approximately 3 dB/cm even though the cluster concentration may be as high as 10^{15} cm^{-3}. Introduction of weak and dense scattering such as this into a photoamplification medium causes an interesting phenomenon to occur. Figure 5 shows the excitation light intensity dependence of the output peak power of the propagation light from a film containing dendrimers in 10 wt% PMMA. The DCM dye (4-(dicyanomethylene)-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran) is mixed in as light-emitting molecules at 0.5 wt%. The output lasing characteristics obtained shows a distinct threshold at 1 mJ/cm^2 [8]. For the laser light, the spectral full width at half maximum is 0.04 nm (the same as the resolution of the spectrometer), which indicates that the emission is not amplified spontaneous emission (ASE) but is rather caused by oscillation (Fig. 6). The thin film in this case had been spin-coated and thus the end faces of the film did not form an oscillatory structure. This laser oscillation was obtained from multiple scattering oscillators inside of the film. The threshold of the oscillation can be lowered further by increasing the dye concentration.

The phenomenon of generation of laser light by an organic scattering medium is known in systems comprised of dispersed submicron inorganic particles such as TiO_2 in dye solutions. However, in these systems, the scattering cross section of each particle is too large to permit the extraction of light as a single oscillation and the spectral variation of the laser light shows typical ASE characteristics [10]. As the organic system used in this study involves even weaker scattering and higher gain, it is possible to increase the oscillation output power in single mode with an increased coherence region and thus produce laser light with small beam spread without the use of oscillator mirrors (Fig. 7).

(a) Schematic illustration of the experimental set-up



(b) Laser output power as a function of pumping fluence

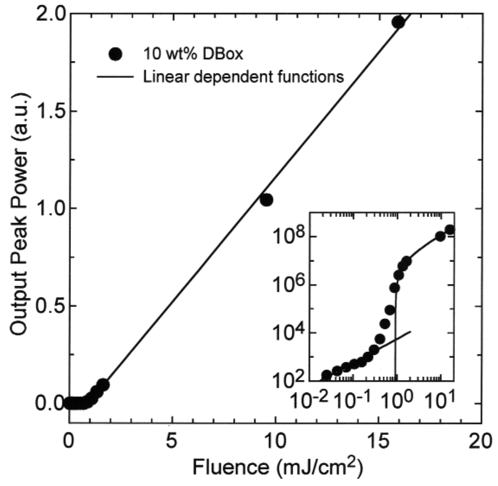


Fig.5 *Laser output characteristics of dendrimer/PMMA thin film*

4 Triplet-sensitized photochemical reactions in localized nanospace

As previously discussed, dendrimer molecules are 2 to 4 nm in size and have the ability to encapsulate small molecules. It is possible to induce highly efficient photochemical reactions based on effective photoexcited energy transfer by using this local nanospace as a reaction chamber. This photoinduced triplet-triplet energy transfer (i.e., the “Dexter mechanism”) is involved in reactions such as the polymerization of molecules and thus with proper control this intermolecular interaction can be utilized as a molecular device construction technique. Excited triplet states are also utilized as the source of the highly efficient luminescence for organic electroluminescence (EL) devices and control of excited triplet states is significant within the field of molecu-

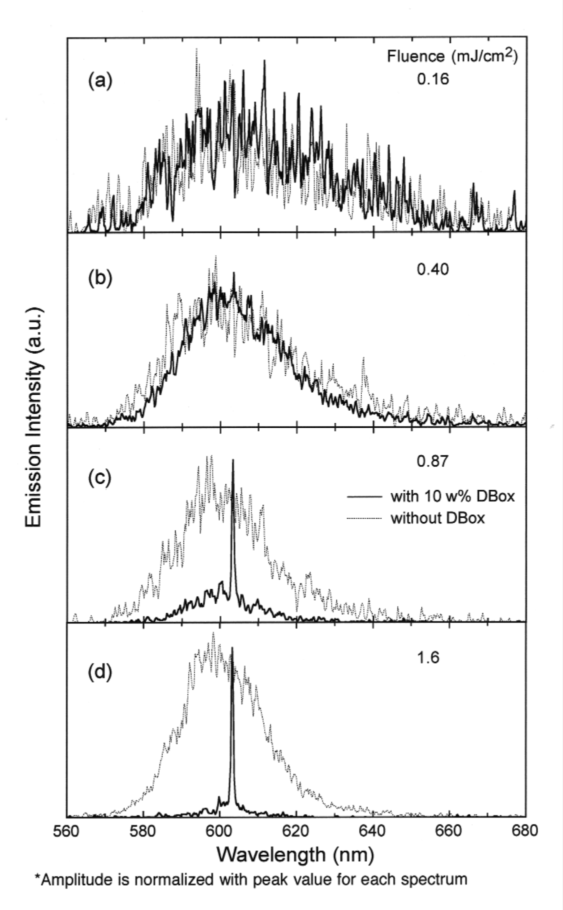


Fig.6 Laser oscillation spectra of dendrimer/PMMA thin film

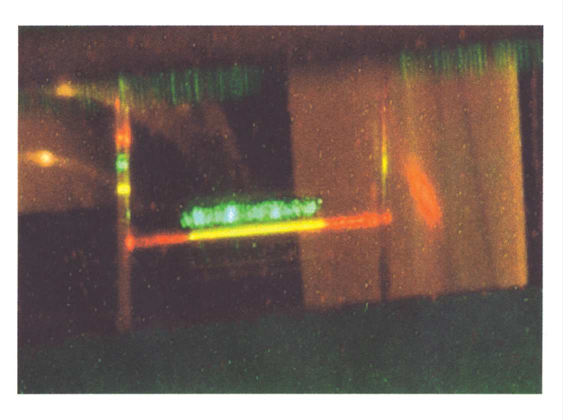


Fig.7 Laser light from dendrimer/PMMA thin film

lar photonics as well. The Dexter mechanism works on the principle of electron orbital exchange between a donor and an acceptor, and consequently the distance between the molecules must be approximately 1 nm or less. For this reason, excess donor doping is required to facilitate effective transfer energy in an ordinary dispersed system. However, this excess doping inhibits the functions of optically functional molecules. The present study targets the realization of efficient triplet-sensitized photochemical reactions with molecular-level reaction control through the encapsulation of excited triplet donor molecules within the nanospace of a dendrimer, permitting the utilization of efficient photoinduced triplet-triplet energy transfer to photocrosslinkable moieties on the outer shell of the dendrimer.

As shown in Fig. 8, a photocrosslinkable dendrimer bearing cinnamoyl residues on its outermost shell was synthesized and Michler's ketone (MK) was encapsulated as a triplet sensitizer within the dendrimer. The number of encapsulated molecules is three for the third generation (G3) and eight for the fifth generation (G5). The dendrimers encapsulating the MK molecules were dispersed in a PMMA solution, which was then spin-coated to form a film.

Irradiation of the G5/PMMA thin film containing encapsulated MK molecules with 365-nm light resulted in the spectral change shown in Fig. 9. The absorption band of the MK molecule is near 370 nm and that of cinnamamide is near 270 nm. As shown in Fig. 9b, cinnamamide does not show absorption at 365 nm. These results demonstrate that the

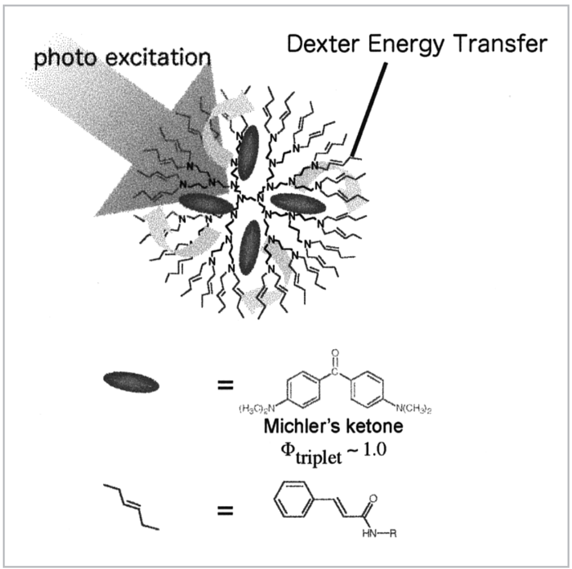


Fig.8 Photocrosslinkable dendrimer

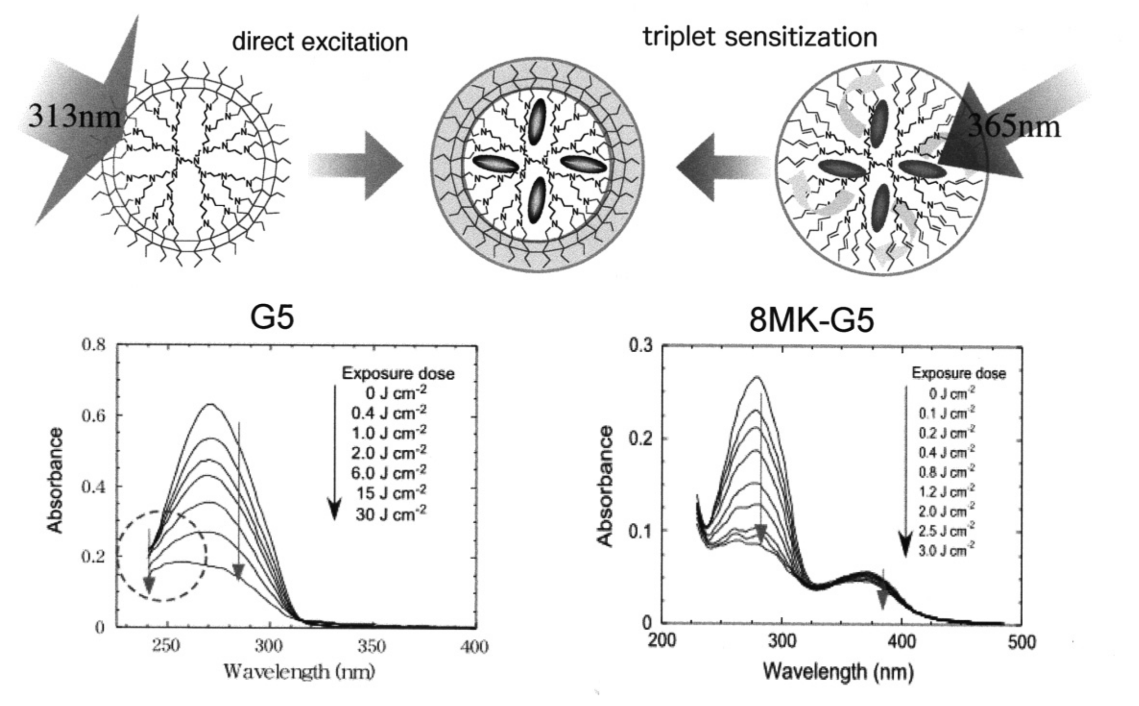


Fig.9 *Triplet-sensitized photochemical reaction of a photocrosslinkable dendrimer*

dimerization reaction of cinnamamide is induced by the energy transfer from the MK molecules. This reaction is also more efficient and requires a lesser exposure as compared with direct excitation by 313 nm light.

5 Laser oscillation control by chiral photonic band liquid crystals

Cholesteric (chiral nematic) liquid crystals have supramolecular helical structures (Fig. 10) consisting of chiral molecules. When a cholesteric liquid crystal is placed between substrates prepared through the rubbing process, the helical axis of each of the molecules self-organizes and aligns perpendicular to the substrates to form a Grandjean texture. In this case, light of a specific wavelength is selectively reflected; the reflection band (λ_{ref}) is determined by the average index of refraction (n) and the pitch of the helix (p) according to the following expression: $\lambda_{ref} = np$. As the index of refraction, and thus the dielectric constant, modulates along the helical axis of a liquid crystal molecule, such molecules can be treated as one-dimensional photonic crystal structures. Recently, a great deal of interest has been directed toward studies on laser oscillation using cholesteric liquid crystals.

In this study, we successfully achieved electric field control and optical control of laser oscillation by utilizing the self-organized photonic band structure of a cholesteric liquid crystal. Photoexcitation of a cholesteric liquid crystal containing chromophores with a linearly polarized pulse laser induced laser emission at the reflection band edge of the cholesteric liquid crystal due to the distributed feedback effect of the cholesteric liquid crystal cells. Moreover, application of an alternating electric field to the cholesteric liquid crystal cells during the photoexcitation permitted successful reversible control of the laser oscillation as the arrangement and orientation of the cholesteric liquid crystal molecules changed [9]. We further attempted to gain optical control of the laser oscillation wavelength using a photoreactive cholesteric liquid crystal; emission of deep ultraviolet light on liquid crystal cells containing cholesteryl iodide enabled optical control of the laser oscillation wavelength in the wide range of 560 to 620 nm in correspondence with the continuous change of the reflection band [10].

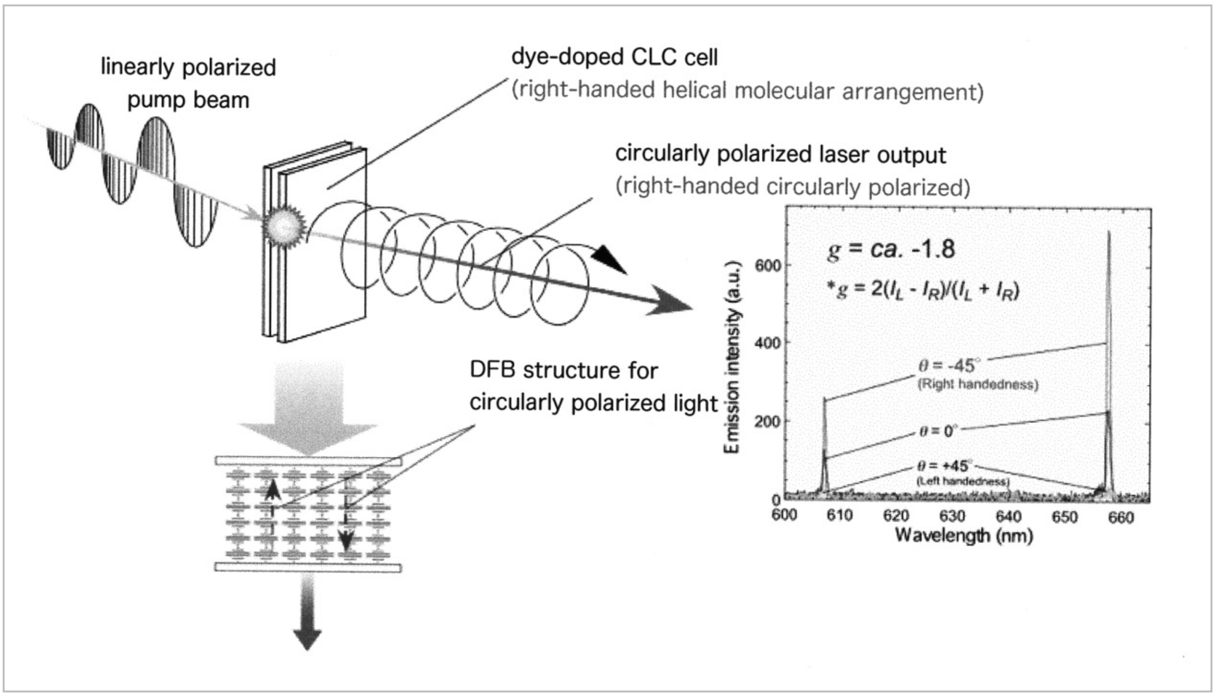


Fig.10 *Supramolecular helical structure of cholesteric liquid crystals and photonic band-gap laser oscillation*

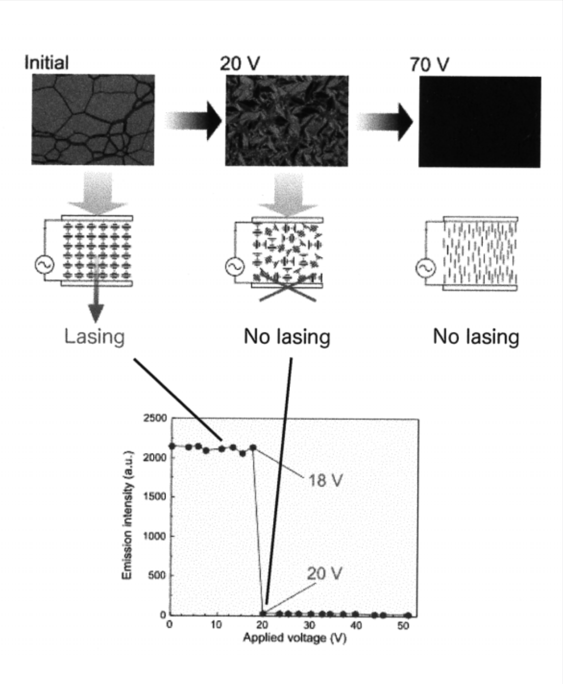


Fig.11 *Electric field control of photonic band-gap laser oscillation*

6 Conclusion

This paper summarizes various techniques for controlling intermolecular interactions. The discussion describes improvements in the functionality of optical functional molecules, laser oscillation, and enhancement in the efficiency of molecular reactions obtained through the use of these techniques. Minimization of quantum dots and semiconductor devices are considered as a means of increasing the degree of intermolecular interaction control in nanospace. The degree of freedom in the nanoscale design of organic materials can also be applied to interaction control in semiconductor devices, and this application will be an important technology in the future.

References

1 D. A. Tomalia, A. M. Naylor, W. A. Goddard III, and Angew. Chem. Int. Ed. Engl. 29,138, 1990.

2 G. R. Newkome (Ed.), “Advances in Dendrite Macromolecules”, JAI Press, Greenwich, CT, Vol. 1, p. 1, 1994.

3 J. M. J.Fréchet, Science, 263, 1710, 1994.

4 S. Yokoyama, A. Otomo, T. Nakahama, and S. Mashiko, Coll., Surf. A.

5 A. Otomo, S. Otomo, S. Yokoyama, and S. Mashiko, Opt. Lett. 27, 891, 2002.

6 N. M. Lawandy, R. M. Balachandran, A. S. L. Gomes, and E. Sauvain, Nature (London), 368, 436, 1994.

7 H. Cao, J. Y. Xu, S. -H. Chang, and S. T. Ho, Phys. Rev. E 61, 1985, 2000.

8 A. Otomo, S. Yokoyama, T. Nakahama, and S. Mashiko, Appl. Phys. Lett. 77, 3881, 2000: Thin Solid Films 393, 278, 2001.

9 S. Furumi, S. Yokoyama, A. Otomo, and S. Mashiko, Appl. Phys. Lett. 82, 16, 2003.

10 S. Furumi, S. Yokoyama, A. Otomo, and S. Mashiko, Appl. Phys. Lett. 84, 2491, 2004.

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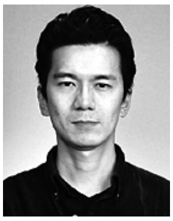
Nanophotonics, Nonlinear Optics



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