Asymmetric Energy Exchange Observed in Two-beam Coupling Experiment on Immobilized Films of Bilayer Amphiphiles Possessing Carbazole and Nonlinear Optical Chromophores

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Amphiphilic compounds containing carbazole and a nonlinear optical (NLO) chromophore were synthesized and a two-beam coupling experiment was performed on a multilayered film of a mixture of these amphiphiles. Asymmetric energy exchange was observed in a multilayered film while no exchange was observed in an amorphous one.

Multilayered films made of bilayer-forming amphiphiles are stacked two-dimensional arrays of molecules and are widely used for preparing ordered functional units.[1] Regular multilayered films are obtained by the casting of aqueous bilayer dispersions of amphiphiles onto a solid substrate. This method can be exploited for the optimization of molecular arrangement in several functional materials. Recently, the photorefractive effect of organic materials has been attracting great interest.[2] Especially, many studies on the photorefractive effect of glassy materials have been reported.[3-7] The photorefractive effect is a change in refractive index induced by the absorption of light. It can be utilized for a wide variety of photonic applications. Since the photorefractive effect is a combined phenomenon of photoconductivity and the second order NLO effect, its performance can be optimized by choosing the appropriate combination of functional molecules. Furthermore, both photoconductivity and NLO effects are strongly affected by the spacial chromophoric orientation. Should both chromophores be designed to spontaneously align into an appropriate structure, the material showing high photorefractivity could be produced.[8] Here we prepared a multilayered material composed of the amphiphiles that contain photoconductive and NLO moieties based on amphiphilic self-assembly. In a multilayered film of amphiphiles, the chromophores are to be highly ordered, hence photorefractivity is expected to effectively appear. In this report, energy exchange in a two-beam coupling experiment on a multilayered film of amphiphiles is presented.

The structures of the compounds used in this study are shown in Figure 1. These amphiphiles were synthesized according to the literature.[9,10] Cz-N^+ was dispersed in an aqueous solution by ultrasonication. In the UV-vis absorption spectra of the aqueous solution of Cz-N^+, all transition bands were found to be broadened and shifted to longer wavelength. It was confirmed from the UV-vis spectra that Cz-N^+ molecules aggregate in an aqueous solution even at a dilute concentration (~10^{-6} mol/L). The aqueous solution was cast on a glass plate and dried at room temperature under a vacuum. Prior to the experiments, the film was annealed at 40 ℃ for 12 h. Birefringence was observed all over the film under a polarizing microscope. XRD measurement provided sharp signals from 2.20 to 17.90 degrees as 2θ with which the layer spacing was estimated to be 39 Å. It was supposed that Cz-N^+ molecules probably constructed an interdigitated structure in each layer by taking into account the length of the molecule (27.2 Å). On the other hand, the cast film prepared from a chloroform solution of Cz-N^+ did not exhibit birefringence. Mixed films of Cz-N^+ and Cz-NLO were prepared in several mixing ratios. A uniform film was obtained as long as the Cz-NLO concentration is lower than 30 mol%. For the two-beam coupling experiment, a small amount of sensitizer (trinitrofluorenon, TNF) was added to the sample.[11]

The photorefractive property was investigated using a two-beam coupling experiment. The experimental setup is shown in Figure 2. A P-polarized beam from a He-Ne laser (633 nm, 7 mW output) was separated by a half-mirror and refocused at the sample film. The sample was tilted 30° and the angle between the two incident beams was 40° which gave a grating spacing of 0.17 μm. The change in transmitted beam intensity

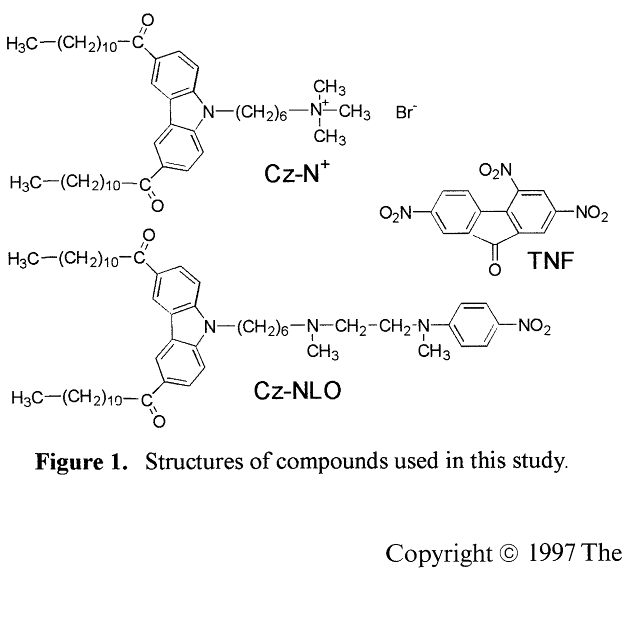

Figure 1. Structures of compounds used in this study.

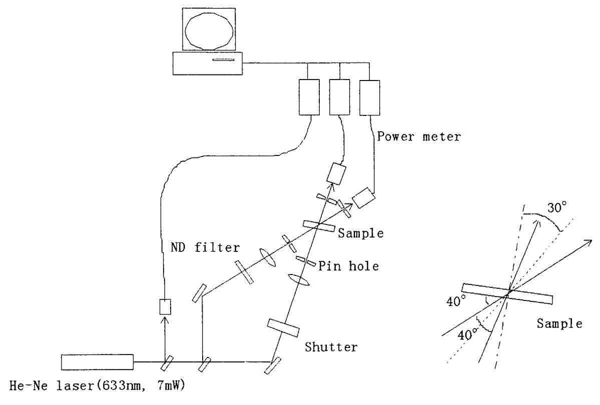

Figure 2. Experimental setup for the two-beam coupling.

was monitored by power meter and recorded by a computer. Two-beam coupling experiment on an organic material is generally performed with applying a strong electric field (30~50 V/μm) across the sample film.[2] However, we could not apply an electric field to the sample because the compound used in this study possessed an ionic structure. Thus the two-beam coupling experiment was conducted without the application of an electric field. When two beams were interfered in the sample, the transmitted intensity of one beam increased while that of the other beam decreased (Figure 3 inset). An energy exchange of ca. 0.1% was observed under these conditions. The gain coefficient was estimated to be 0.3 cm^{-1}. When the irradiation of one beam was turned off, the transmitted intensity of another beam gradually returned to its original value. The dependence of the film composition on diffraction efficiency is shown in Figure 3. An asymmetric energy exchange was

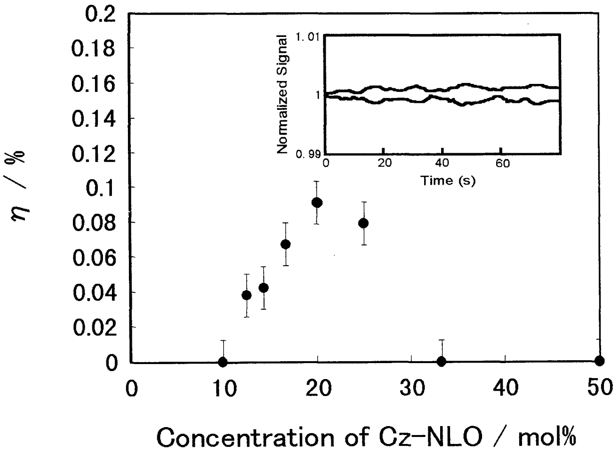

Figure 3. Concentration dependence of Cz-NLO on diffraction efficiency. (inset) Typical example of the asymmetric energy exchange observed during two-beam coupling experiment.

observed only in films of Cz-NLO concentrations between 15 mol% and 20 mol%. Below the Cz-NLO concentration of 15 mol%, the Pockels effect would not be strong enough to promote the asymmetric energy exchange. In addition to the photorefractive effect, the thermal effect is a plausible candidate for the energy exchange phenomenon in Figure 3. Since the energy exchange disappeared when the concentration of Cz-NLO is higher than 30 mol%, where the film did not maintain a regular multilayered structure any more, ordered chromophore alignment is likely to be necessary for the emergence of the asymmetric energy exchange. In fact, the cast film prepared from chloroform solution did not exhibited energy exchange.

In order to clarify whether the result obtained here is attributed to the photorefractive effect or thermal effect, the same experiment using a non-aqueous bilayer membrane with fluorocarbon amphiphiles is now in progress. Using the fluorocarbon amphiphiles allows us to apply an electric field on the film because they do not possess an ionic moiety at all.[12] The effect of an electric field on the asymmetric energy exchange is examined, and the influence of the amphiphilic multilayer on the photorefractive effect will soon be clearly discussed.

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References and Notes

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10 Cz-NLO was synthesized by the reaction of N-(6-bromohexyl)-3,6-didodecanoylcarbazole with the NLO moiety (p-nitro-N,N'-dimethylethylenediaminobenzene). N-(6-bromohexyl)-3,6-didodecanoylcarbazole was synthesized via the Friedel-Crafts acylation of N-(6-bromohexyl)carbazole. The NLO moiety was synthesized by the reaction of 4-nitrofluorobenzene with N,N'-dimethylethylenediamine.
11 The concentration of TNF is uncertain because TNF could not be completely dispersed in water. One mol% of TNF was added to the dispersion of $Cz\text{-}N^+$ and CZ-NLO, and the solution was filtered using a membrane filter after sonication.
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