

# Photo-Luminescence Characteristics of Aligned Organic Fluorescent Dye in Liquid Crystalline Polymer Films for Photosynthesis Promotion

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## ABSTRACT

*For photosynthesis promotion in the field of agriculture, we investigated fluorescence characteristics of solution-processed wavelength conversion films composed of liquid crystalline monomer and fluorescent coumarin dye. As the results, we have succeeded in controlling polarized emission and enhancement of photo-luminescence intensity in their films.*

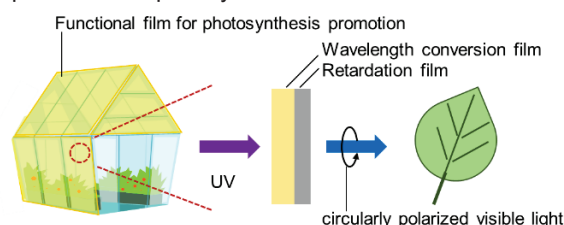
## 1 INTRODUCTION

Large-area wavelength conversion films are expected to contribute the global food crisis. The wavelength of transmitted light to their films can be converted to different wavelength from incident light. This optical feature is useful for utilization efficiency of the incident light. In the field of agriculture, reflected light by plant leaves can be converted to wavelength of photosynthesis [1]. This phenomenon is useful for increasing of crop yields and suppress the global field crisis. Also, it has been reported that there is optical anisotropy in the light absorption of plant leaves [2]. For example, legumes are more likely to absorb left circular polarized light. Therefore, it is necessary to establish a technology for production of large-area wavelength conversion films whose polarization direction can be controlled. Such functional films can be realized by stacking of two layers (see Fig.1). In the first layer (wavelength conversion film), incident light converts a specific wavelength of light to emit linearly polarized fluorescence. The second layer like retardation film converts the fluorescence of linearly polarized light into circularly polarized light. Of these, development of the first layer has been required for photosynthesis promotion because the retardation film is commonly commercialized.

For the development of such large-area wavelength conversion films, solution coating process in order to adapt Roll-to-Roll process is desirable for production of low-cost films in the future. This process can be manufactured continuously while winding the roll-like films. Conventionally, uniaxially-stretched dye-doped resin has been reported so far [3]. In this method, the fluorescent dye is blended into transparent films on the basis of resin material. By stretching method, dye molecules are aligned along stretched direction. However, the conventional stretching method is not suitable for Roll-to-Roll process. And also, variety of fluorescent materials are limited by

concentration quenching effect.

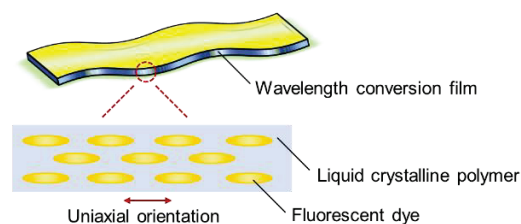
To overcome these issues, we proposed the fluorescent organic dye-doped liquid crystalline polymer films as the solution-processed wavelength conversion films in this paper. Here, we discuss the relationship between dye concentration and fluorescence characteristics in the coating films in which an organic fluorescent dye is dispersed in a liquid crystalline monomer.



**Fig. 1 Application example of large-area polarized photo-luminescent films for photosynthesis promotion.**

## 2 PROPOSAL of COATED FILM THAT EXPECTED TO EMIT POLARIZED LIGHT

The proposed films are composed of photo-polymerized monomer and organic fluorescent dye. This film can be manufactured by solution process because liquid crystalline monomer has liquid state under the room temperature. The molecular interaction between liquid crystalline monomer is expected to control of molecular alignment of fluorescent dye. By aligning the fluorescent dye molecules, the transition moments are aligned along the uniaxial direction. There is a possibility of polarized light emission from alignment-controlled monomer/dye mixture films (see Fig. 2). Furthermore, by combining the proposed film with a retardation film, the fluorescence is expected to be circularly polarized.



**Fig. 2 Proposal the novel wavelength conversion films with aligned fluorescent dye**

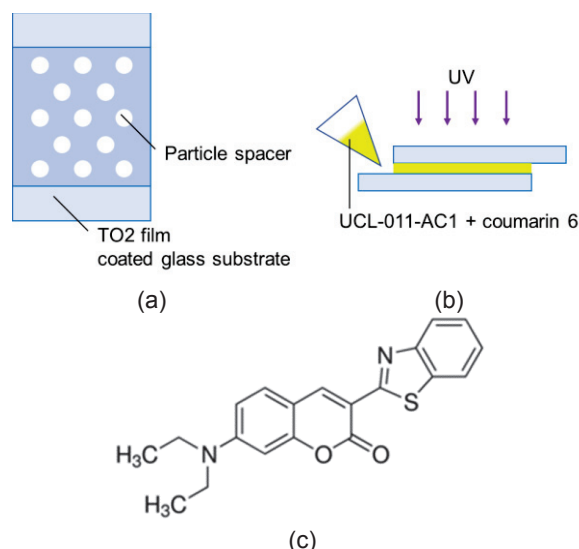
### 3 INVESTIGATION OF THE OPTIMAL FILM THICKNESS

Before solution coating, we examined thickness of dye/monomer mixture films to absorb excitation light sufficiently. Here, we investigated the optimal thickness using a cell structure (defined as sandwiched spacer material with two substrates). The particle spacer was used in order to control the film thickness accurately. The fabrication procedure of the cell is as follows.

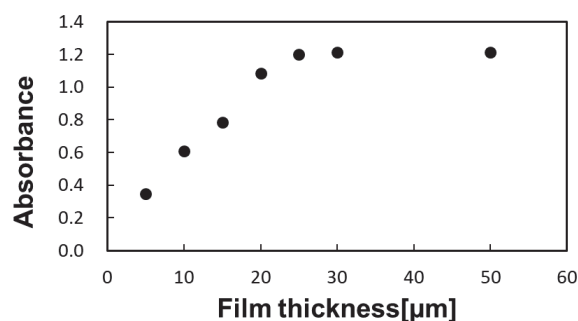
First, as shown in Fig. 3, a mixture solution was prepared by 99.5 wt% of UV-curable liquid crystalline monomer (UCL-011-AC1, DIC Corp.) and 0.5 wt% of the typical rod-shaped organic fluorescent dye. Next, we prepared ultrasonically-cleaned two glass substrates coated with a photo-alignment film (TO2, Nissan Chemical). This photo-alignment film is for parallel alignment of liquid crystal. A cell structure was constructed by these substrates and dispersed particle spacer on a substrate. Finally, the mixture solution composed of liquid crystalline monomer and dye was injected into the cell and cured by irradiation of ultraviolet (UV) light (see Fig. 3(b)). As a model case, we used rod-shaped fluorescent dye Coumarin 6 (Fig.3(c)). The absorbance of the UV-cured films was evaluated at the maximum absorption wavelength of Coumarin 6 using ultraviolet-visible near-infrared spectrophotometer (V-770, JASCO Corp.).

Fig. 4 shows thickness dependence of absorbance at maximum absorption wavelength composed of liquid crystalline polymer and Coumarin 6. At thickness from 5  $\mu\text{m}$  to 25  $\mu\text{m}$ , absorbance increased in proportion to the film thickness. The absorbance over 25 $\mu\text{m}$  thickness saturated at a constant absorbance. From this result, we confirmed that the light having excitation wavelength can be sufficiently absorbed over 25 $\mu\text{m}$  thickness when the dye concentration is 0.5 wt%.

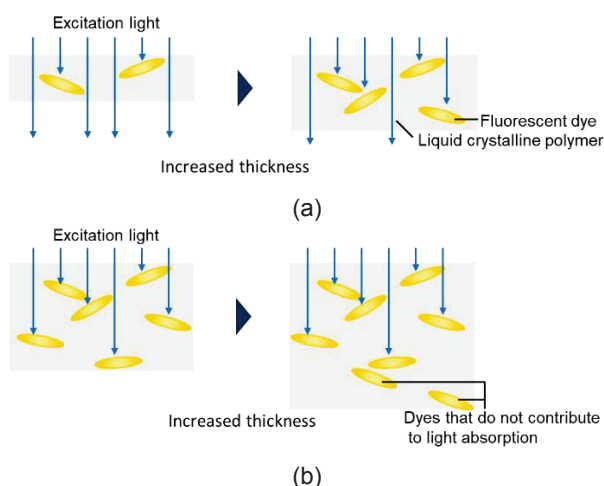
Here, we discuss the relation between film thickness and absorbance. When the film thickness is smaller than 20 $\mu\text{m}$ , the absorbance is proportional to the film thickness. This phenomenon is based on Lambert-Beer's law. The absorbance increased with increasing of dye concentration. (see Fig. 5(a)). On the other hand, when the film thickness is larger than 25 $\mu\text{m}$ , the absorbance was not changed regardless of the film thickness. This is attributed to only increases the number of fluorescent dye molecules that are not used for absorption (see Fig. 5(b)).



**Fig. 3** Fluorescent thin film produced in the cell (a) Top view of the cell (b) Method of preparing the fluorescent thin film (c) Coumarin 6 molecule



**Fig. 4** Relation between film thickness and its maximum absorbance at excitation wavelength.



**Fig. 5** Schematic illustration of relation between absorbance and dye concentration in UV-cured polymer (a) less than 20  $\mu\text{m}$  thickness (b) over 25 $\mu\text{m}$  thickness

## 4 INVESTIGATION OF THE OPTIMAL CONCENTRATION

### 4.1 Evaluation of fluorescence characteristics

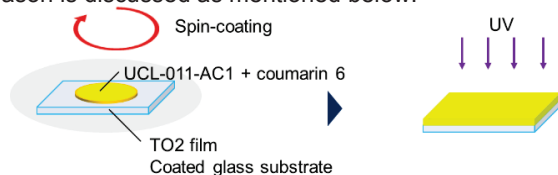
We investigated the optimal concentration of polymer/dye film based on the data in Section 3. The procedure from solution coating to evaluation of fluorescent characteristics is as follows.

First, a solution was prepared by mixing UV-curable liquid crystalline monomer and Coumarin 6. We investigated the concentration of 0.9 wt% in Coumarin 6 with respect to monomer because dye concentration over 1.0 wt% cannot be solved in liquid crystalline monomer. As shown in Fig. 6, photo-alignment films coated on glass substrates, and the mixture solutions were coated onto the substrates by means of spin coating method. the coating films were cured by ultraviolet irradiation. Here, the rotation speed and coating time were 400 rpm and 60 sec, respectively.

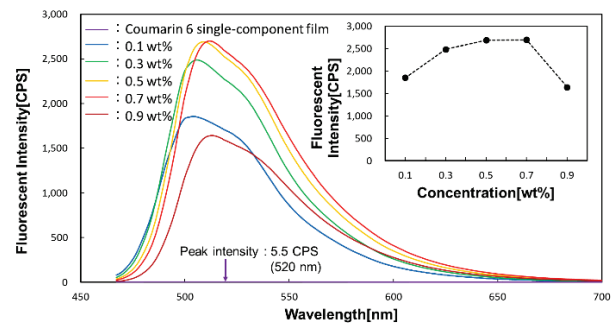
In the evaluation of fluorescent spectra, maximum excitation wavelength and maximum fluorescence wavelength of each sample were investigated in advance. The fluorescence intensity at the maximum fluorescence wavelength were measured by irradiation of the maximum excitation wavelength into the sample.

In order to clarify the optimal concentration of fluorescent dye, we investigated the relationship between the dye wavelength and the fluorescence intensity in the coated fluorescent dye-doped liquid crystalline polymer films on glass substrate. Here, thickness of the coating films under each condition were set to 30  $\mu\text{m}$  based on the results in section 3.

Fig. 7 shows the wavelength-fluorescence characteristics at each dye concentration. For comparison, the fluorescence characteristic of Coumarin 6 single film (without monomer) is included in Fig. 7. The maximum fluorescent wavelength of polymer/dye films was around 510 nm. The fluorescence intensity of the films with the liquid crystalline monomer was drastically improved, compared to Coumarin 6 single-component film. The plotted data in inset of Fig. 7 shows extracted maximum fluorescent intensity from fluorescent spectra. From dye concentration of 0.1 wt% to that of 0.7 wt%, the fluorescence intensity increases with increasing of concentration. However, fluorescent intensity in dye concentration of 0.9 wt% was decreased significantly. These results indicate that there is the optimal concentration which maximize fluorescence intensity. This reason is discussed as mentioned below.



**Fig. 6 Fabrication method of coated liquid crystalline polymer/dye film**



**Fig. 7 Fluorescent spectra at various dye concentrations (Inset: extracted maximum fluorescent intensity vs. dye concentration)**

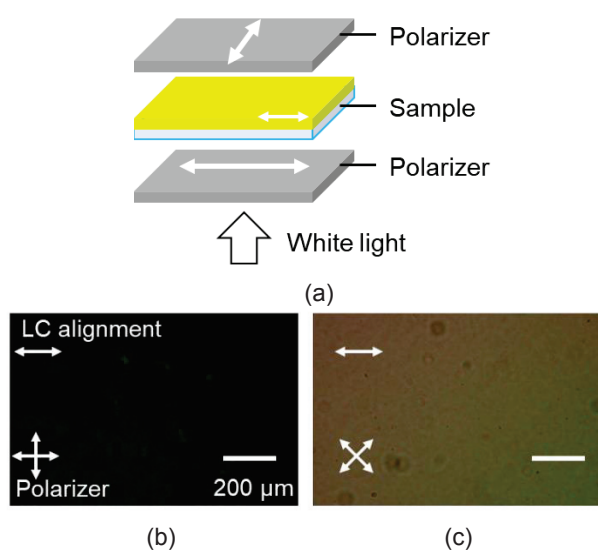
### 4.2 Optical investigation of molecular alignment

In this section, we discuss the reason why the optimal concentration of the dye exists. To clarify the molecular alignment state of the liquid crystalline polymer and the fluorescent dye, we attempted optical evaluation to their films using polarizers. Fig. 8(a) shows crossed-Nicols polarizing microscope images of coated fluorescent dye-doped liquid crystalline polymer films. Fig. 8(b, c) shows the observation results of the coating film with a polarizing microscope. When the transmission axis of the polarizer and the photo-alignment direction on the coating film were parallel, black-colored image was observed. When the direction was 45 degrees, coloration based on retardation was observed. Therefore, the mesogenic group of liquid crystalline polymer is aligned to photo-alignment direction on alignment film surface.

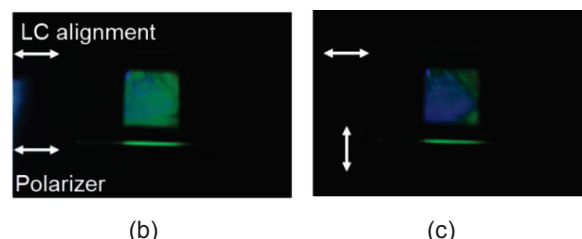
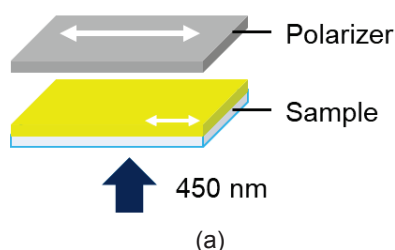
To clarify the alignment state of Coumarin 6 molecules in liquid crystalline polymer, as shown in Fig. 9(a), a polarizing plate was placed on the coating film, and light of 450 nm, which corresponds to the excitation wavelength of Coumarin 6, was incident and fluorescence was observed. Fig. 9(b, c) shows the fluorescent behavior of the entire coating film. When mesogenic group of the liquid crystalline polymer and the transmission axis of the polarizer were parallel, we confirmed that fluorescence transmitted through the polarizer. When alignment direction of polymer and the transmission axis of polarizer were orthogonal relation, fluorescent could not be observed. Therefore, we clarified that the fluorescent dye molecules are aligned toward parallel to the polymer and emitted linearly polarized fluorescence. These results mean that the liquid crystalline polymer and Coumarin 6 are aligned by guest-host interaction, as well known [4].

Based on the molecular aligned structure, we discuss the reason of the optimal concentration to maximize fluorescent intensity. When the fluorescent dye was doped into the monomer, the fluorescence intensity increased as the concentration of the dye increased. The

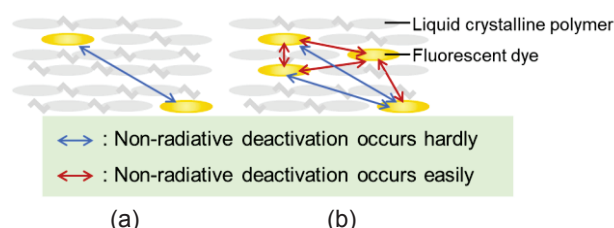
decreasing of fluorescence intensity at dye concentration over 0.7 wt% is attributed to concentration quenching effect. The concentration quenching is known as energy transfer among neighbor dye molecules. The energy of excitation light absorbed by fluorescent dye is used for molecular thermal vibration and not converted to fluorescence light emission. This conversion of the excitation energy into thermal vibration is called as non-radiative deactivation. Non-radiative deactivation is more likely to occur as the distance between fluorescent dye molecules is smaller. For this reason, when the concentration of the dye is low, a large amount of polymer enters between the fluorescent-dye molecules and the distance between the fluorescent dyes is sufficiently maintained, so that non-radiative deactivation due to energy transfer is unlikely to occur (see fig. 10(a)). On the other hand, when the dye concentration is high, fluorescent dyes are adjacent to each other and dimerization is likely to occur, so that non-radiative deactivation becomes dominant (see fig. 10(b)). As this evidence, fluorescent intensity in single-component coumarin 6 film was extremely small value, as mentioned in Fig.7. The proposed technique in this paper will be useful for improvement of quenching effect in organic fluorescent materials.



**Fig. 8 Optical observation of the coating films with a polarizing microscope (a) Observation system (b) polarizer 0deg. (c) polarizer 45deg.**



**Fig. 9 Optical observation of fluorescent behavior in the dye-doped liquid crystalline polymer films (a) Observation system (b) polarizer 0 deg. (c) polarizer 90 deg.**



**Fig. 10 Schematic illustration of suppression effect of concentration quenching among fluorescent dye (a) low concentration (b) high concentration**

## 5 CONCLUSIONS

In this paper, we have proposed the fluorescent dye-doped liquid crystalline polymer films for realization of polarization control of emitted light and improvement of fluorescent intensity in solid state. We found that there is an optimal dye concentration that maximizes the fluorescence intensity. In addition, we demonstrated that the rod-shaped fluorescent dye is aligned with the liquid crystalline polymer by guest-host interaction and exhibits polarized light emission. In the future, we will fabricate a polarization-controllable wavelength conversion film based on the proposed films and wavelength plate for photosynthesis.

## ACKNOWLEDGEMENT

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