Correlation between Molecular Arrangement and Emission Mechanism of Melem in Langmuir-Blodgett Films of Lanthanide(III) Complex with Stearic Acid

Control of molecular arrangements, which have been extended to 2 and 3 dimensions, is one of the key approaches to functional progress on molecular devices at the nanoscale. Research has been concentrated on metal-organic coordination compounds because their various coordination modes lead to multi-functional properties. However, in the case of the solid state or in solution, it is difficult to control their proper arrangements. For these molecular systems, we have proposed an innovative application of an existing film technology to make a molecular base functional control. A technique using Langmuir-Blodgett (LB) films [1] that consist of layers of organic molecules is susceptible to controlling the orientation and density of the molecules. The films are built-up one layer at a time until the desired number of layers is obtained. For this system, we used two different layers. One layer contains the organic compound melem, which is capable of emitting light at specific wavelengths. The other layer contains a metal ion of the lanthanide series, namely praseodymium (Pr(III)), complexed with long-chain fatty acids [2]. Since the first application of LB film techniques in the 1930s, our investigation into metal complexes and molecular interactions will uncover new optical properties for the first time. Consequently, a new possibility has been found by combing an established method and coordination chemistry [3].

Knowing the exact position of these molecules is essential to understanding a profound effect on their optical behavior, that is, a basic structural model of the LB film is important for the description of emission phenomena. In order to get structural information about the thin-films, we have carried out X-ray diffraction measurements on beamline **BL02B2** [4]. Because of the low emittance and high brilliance of SPring-8, we succeeded in reliable and precise data collection even at lower angle diffraction from LB films approx. 25 nm thick. The XRD data were interpreted to indicate that the lanthanides (Ln(III)) are arranged in a plane coordinated to stearic acid (SA, $CH_3(CH_2)_{16}COOH$), whereas melem is intercalated into the film without complexation to Pr(III) (Fig. 1(a)). In the PrSA film, melem is located between alkyl chains of SA at intervals of 54.4 Å, which is different from melem in the SA film without Pr(III). From the Bragg peaks the metal-metal interlayer distance was calculated as 48.6 Å, regardless of the presence of melem. However, EXAFS spectroscopy at the Pr(III) L_3-edge, carried out at beamline **BL01B1** [5], which provides information about the coordination number, showed that the coordination structure around Pr(III) is changed by the presence of melem in the film (Fig. 1(b)). In the case of the film with melem, the coordination structure around Pr(III) is almost the same as that of the Pr(III) coordinated to SA in the solid state.

The emission spectra of the films were also studied in detail. In the PrSA film, two distinct fluorescence bands of melem with different polarity were observed

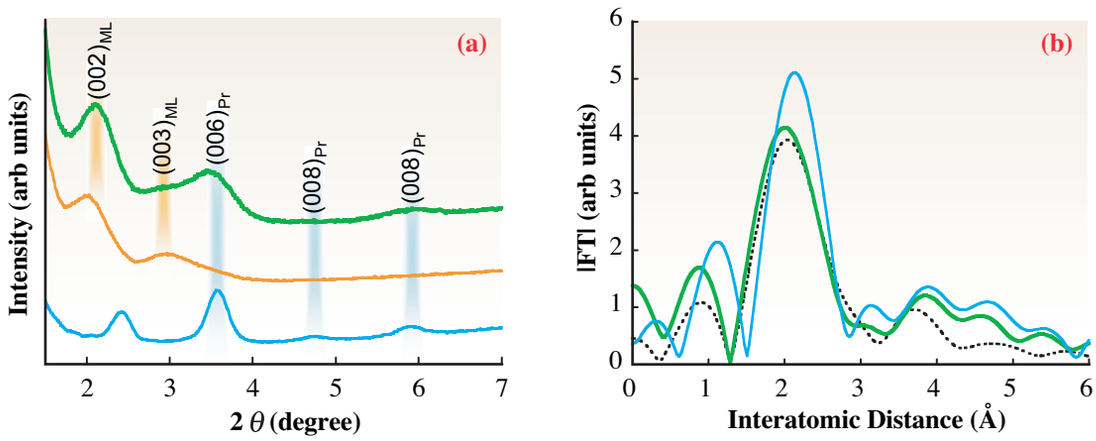

Fig. 1. **(a)** Synchrotron X-ray diffraction patterns of the PrSA-melem film (green), the SA-melem film (red), and the PrSA film (blue), together with assignments of the Bragg reflections. **(b)** Fourier transforms of EXAFS spectra of Pr L_3-edge for the PrSA-melem film (green) and the PrSA film (blue) compared with that for $[Pr(SA)_3(H_2O)]$ in the solid state (dotted line).

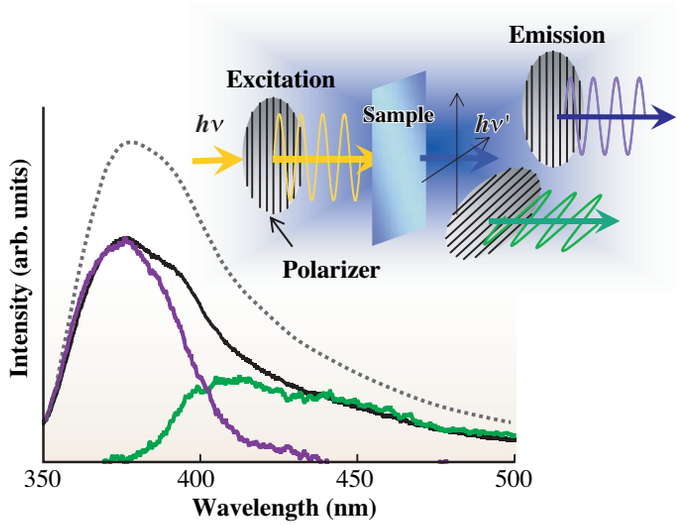

Fig. 2. Fluorescence (dotted line) and the polarized fluorescence spectra of melem in the PrSA film (λ_{ex} = 280 nm) with the vertical or the horizontal emission polarizer, which can be resolved into two components (blue and green).

at 375 nm and 405 nm (Fig. 2 and Fig. 3), polarized at an angle of 0° and 30°, respectively. Interestingly, the dual polarized emissions of melem obtained from the thin film have not been observed in a mixture of the two compounds in the solid state nor in solution. That is, the arrangement and orientation of the molecules using the LB film technique has led to novel emission properties. The present finding may lead to the application of the development of duplex fiber-optic communication systems using this film.

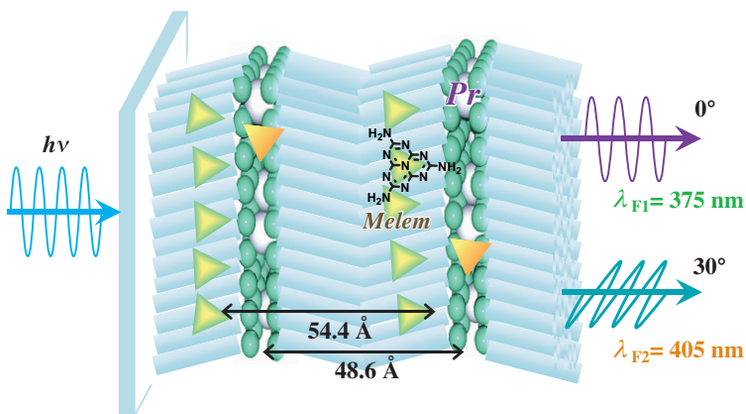

Fig. 3. Illustration of dual polarized emissions of melem arranged in the PrSA film.

Ayumi Ishii [a] and Miki Hasegawa [a,b,*]

[a] College of Science and Engineering, Aoyama-Gakuin University
[b] Research Center for Advanced Science and Technology, The University of Tokyo

*E-mail: hasemiki@chem.aoyama.ac.jp

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