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Molecular luminescence spectroscopy of decatungstoeuropate Langmuir–Blodgett monolayers

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Abstract

Fabrication condition and photoluminescence behavior of decatungstoeuropate/dimethyldioctadecylammonium (EuW10/DODA) Langmuir–Blodgett (LB) monolayers were investigated. Stable Langmuir monolayer were formed on the EuW10 aqueous solution within the concentration range of 0.84–3.1 μmol dm^{-3}. The monolayer formed on the solution was successfully deposited onto quartz substrates with nearly ideal transfer ratio. The presence of EuW10 anion was confirmed by UV–vis spectroscopy. Strong red emission derived from Eu^{3+} was clearly observed even for the EuW10/DODA LB monolayers when excited by 266 nm laser light. The intensity of $^5D_0 \rightarrow {}^7F_4$ emission was unusually high, suggesting the effect of two-dimensional organization of EuW10 anions in the monolayer.

Keywords: Thin films; Langmuir–Blodgett; Luminescence; Polyoxometalate

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1. Introduction

In order to organize molecules on the solids, Langmuir–Blodgett (LB) technique is one of the promising methods due to its controllability of nanometer-ordered molecular films [1]. Cationic surfactants enable us to fabricate LB films composed of anionic polyoxometalates (POMs), and several kinds of POM multilayer have recently been prepared by LB technique [2–11]. There is only one report on surfactant-encapsulated POM monolayer [8] and none on the POM LB monolayer, although the structural characterization of POM monolayer on solid/solid or liquid interfaces is essential for constructing molecular devices based on POMs.

Strongly photoluminescent lanthanide–POM (Ln–POM) [12–18] LB monolayers has been chosen to investigate the self-organization of Ln–POM in the LB monolayer by measuring the emission behavior sensitive to the coordination geometry of lanthanide atom. $Na_9[Eu(W_5O_{18})_2]\cdot 32H_2O$ (denoted as Na·EuW10) is known to be highly photoluminescent (the quantum yield of the energy transfer from the $W_5O_{18}{}^{6-}$ ligand to Eu^{3+} is nearly unity) [13–18].

In this report, the fabrication and photoluminescence of LB monolayers consisting of EuW10 and dimethyldioctadecylammonium (denoted as DODA) is described for the first time, which will provide advanced understanding of POM LB monolayers.

2. Experimental

Na·EuW10 was synthesized according to the literature [16]. LB layer fabrication was carried out by spreading chloroform solution of DODA·Br (1 mmol dm^{-3}) onto Na·EuW10 aqueous solution (0.84–8.7 μmol dm^{-3}) on a KSV3000 apparatus. A compression rate and subphase temperature were 15 cm^2 min^{-1} and $20.5 \pm 0.5\,^{\circ}C$, respectively. After the surface pressure reached 30 mN m^{-1}, LB monolayers were stabilized for at least 30 min, and subsequently deposited on quartz substrates by vertical dipping method with a rate of 10 mm min^{-1}. LB multilayers (seven layers) were deposited by the same procedure as above.

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UV–vis spectra of EuW10/DODA LB monolayers deposited on quartz substrates were measured on a JASCO V-570 spectrometer. Photoluminescence emission spectra were recorded at room temperature with a Spex 750 M coupled to a Hamamatsu Photonix R636 photomultiplier tube, and the light source was a Rature Systems CPY20-10FHG laser (266 nm, 30 Hz). Time profiles of the luminescence were measured on a LeCloy 9361 digital storage oscilloscope. Excitation spectra were recorded on a Hitachi F-4500 fluorescence spectrometer equipped with a Xe lamp.

3. Results and discussion

Fig. 1 shows surface pressure–area (π–A) isotherms of DODA·Br on pure water (Fig. 1a) and Na·EuW10 solutions (Fig. 1b–d). Isotherms on the Na·EuW10 solutions of 0.84, 2.0, and 3.1 μmol dm^{-3} (data not shown) were nearly the same as in Fig. 1b (1.0 μmol dm^{-3}). The decrease in the molecular area and the increase in the surface pressure on the Na·EuW10 solutions are probably due to the dense formation of Langmuir monolayer of DODA, which was induced by the charge compensation by EuW10 anions and the decrease in the strong repulsion between polar heads of DODA [2–6].

With the concentration of 0.84–3.1 μmol dm^{-3} of EuW10, LB monolayers of EuW10/DODA were successfully deposited on quartz substrates. The transfer ratio was nil for the down-stroke and unity for the up-stroke, which is typical of the deposition of Langmuir monolayer on hydrophilic substrates such as quartz. In the case of more than 4 μmol dm^{-3} of EuW10, a stable Langmuir monolayer was not formed, since insoluble fine particles composed of EuW10 and DODA may have been produced at the air/solution interface.

As shown in Fig. 2a, UV–vis spectrum of EuW10/DODA LB monolayer deposited by using Na·EuW10 solution of 2.0 μmol dm^{-3} exhibited a broad peak around 270 nm and characteristic absorption in the ultraviolet region below 250 nm. These absorption bands can be assigned to O → W ligand-to-metal charge-transfer (LMCT) bands. This spectroscopic feature coincided with that of Na·EuW10 aqueous solution (Fig. 2b), demonstrating that EuW10 anions were successfully organized onto the quartz substrate. For the EuW10/DODA LB monolayer (Fig. 2a), no peak was observed below 250 nm, indicating that the peak at 192 nm for Na·EuW10 solution slightly shifted to lower wavelength region. This may be because EuW10 anions were organized two-dimensionally in the EuW10/DODA LB monolayer.

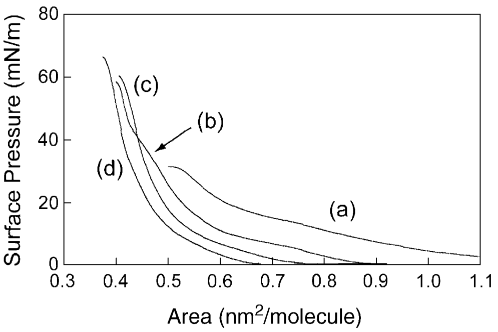

Fig. 1. Surface pressure–area (π–A) isotherms of DODA·Br on pure water (a) and on Na·EuW10 solution with a concentration of (b) 1.0 μmol dm^{-3}, (c) 4.1 μmol dm^{-3}, and (d) 8.7 μmol dm^{-3}.

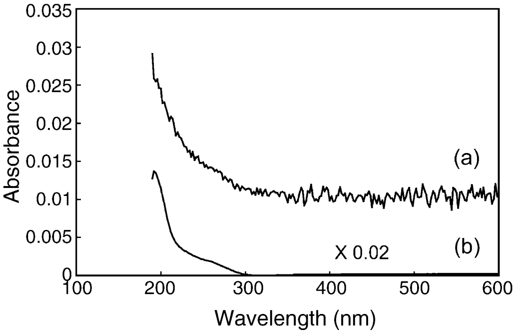

Fig. 2. UV–vis spectra of: (a) EuW10/DODA LB monolayer deposited on quartz by using Na·EuW10 solution with a concentration of 2.0 μmol dm^{-3} and (b) Na·EuW10 aqueous solution with a concentration of 14 μmol dm^{-3}.

Photoluminescence was clearly observed for the EuW10/DODA LB monolayers. Excitation spectra (not shown) of the EuW10/DODA monolayers fabricated above showed a broad peak around 230–300 nm and weak f–f transitions. This behavior has been misunderstood as effective energy transfer from the $W_5O_{18}{}^{6-}$ ligands to the Eu^{3+} in literatures [6,7], which leads to the contradiction of the quantum yield of the energy transfer with more than unity. The observable dominance of the $W_5O_{18}{}^{6-}$ ligands in the excitation spectra suggests the importance of the optical property due to the multiple reflections of the UV light inside the LB monolayer derived from different dielectric constants of EuW10 and DODA.

Emission spectrum of EuW10/DODA LB monolayer deposited by using Na·EuW10 solution of 2.0 μmol dm^{-3} is described in Fig. 3. The intensity ratio of the $^5D_0 \rightarrow {}^7F_1$ to the $^5D_0 \rightarrow {}^7F_2$ emission was below unity and the symmetrically forbidden emission of $^5D_0 \rightarrow {}^7F_0$ was observed, indicating the decrease in the symmetry of coordination environment

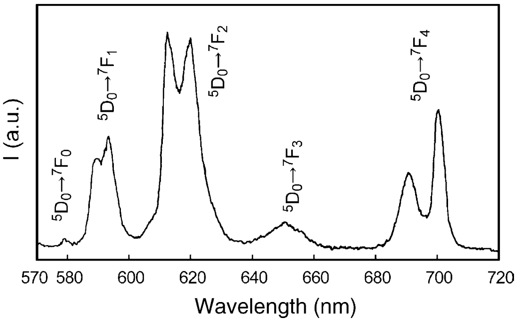

Fig. 3. Emission spectrum of EuW10/DODA LB monolayer deposited on quartz by using Na·EuW10 solution with a concentration of 2.0 μmol dm^{-3}. Excitation wavelength is 266 nm at room temperature. Assignments of the emission are in the Figure.

of Eu^{3+}. Notable characteristic in Fig. 3 is unusually higher intensity of $^5D_0 \rightarrow {}^7F_4$ emission than in the case of other Eu–POM multilayers [5–9]: the relative intensities of the $^5D_0 \rightarrow {}^7F_J$ emission of Eu^{3+} were 1:17:53:5:25 with respect to the total intensity of the $^5D_0 \rightarrow {}^7F_J$ ($J = 0$–4). The same feature as above was observed for the EuW10/DODA LB multilayers, which may be due to two-dimensional organization of EuW10 anions on the substrate.

Emission lifetime of EuW10/DODA LB monolayer deposited by using Na·EuW10 solution of 2.0 μmol dm^{-3} was 0.84 ms, while that of Na·EuW10 solid was 2.6 ms. According to the relationship of n (number of aqua ligands in the first coordination spheres of Eu^{3+}) = $1.05\Delta\tau^{-1}$ (τ in ms unit) [18,19], n value for EuW10 molecules in the EuW10/DODA LB monolayer was estimated to be 0.8 (=$1.05 \times (1/0.84–1/2.6)$). The kinetic constants of energy transfer also can be estimated by using the $^5D_0 \rightarrow {}^7F_1$ as a standard [18]. The $^5D_0 \rightarrow {}^7F_1$ transition contained 0.17 of the total emission (described above) with the rate of 1.35×10^2 s^{-1} [18]. Therefore, the radiative rate (k_{rad}) for EuW10/DODA LB monolayer was 7.9×10^2 (=$1.35 \times 10^2/0.17$) s^{-1}. The experimental decay rate for EuW10/DODA LB monolayer was 1.2×10^3 (=$1/(0.84 \times 10^{-3})$) s^{-1}, and then the nonradiative rate (k_{nr}) was estimated to be 4.1×10^2 (=$1.2 \times 10^3 - 7.9 \times 10^2$) s^{-1}.

The relative intensities of $^5D_0 \rightarrow {}^7F_J$ emission ($J = 0$–4) and emission lifetimes for EuW10/DODA LB monolayers tended to change depending on the concentration of Na·EuW10 solution in the subphase. Detailed measurements are in progress and the results will be discussed elsewhere.

4. Conclusions

We successfully fabricated EuW10/DODA LB monolayers on quartz substrates. The fabrication strongly depended on the concentration of Na·EuW10 in the subphase, and the organization of EuW10 anions on the substrates was confirmed by UV–vis and photoluminescence spectroscopy. Unusually high intensity of $^5D_0 \rightarrow {}^7F_4$ emission in the emission spectra of EuW10/DODA LB monolayers suggests the effect of two-dimensional organization of EuW10 anion in the LB monolayer. The fabrication method of EuW10/DODA monolayer described here will contribute to the construction of POM-based molecular devices, which could be nicely characterized by the photoluminescence spectroscopy.

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