Research Article

Preparation of Transparent Film of Layered Double Hydroxide with Anionic Pyrene Derivatives and Its Luminous Toluene Detection Ability

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To prepare the transparent solid film of layered double hydroxide, the filtration-film transfer (FFT) method using LDH nanosheet colloidal suspension was investigated. It was found that the homogeneous LDH solid film with enough transparency in the visible light range could be prepared by the FFT method. Moreover, anionic pyrene (Pyr−) molecules could be incorporated into the transparent LDH solid film by immersing in anionic pyrene solution. From both absorption and emission spectra of the transparent Pyr−/LDH solid film, Pyr− incorporated in the LDH solid film formed aggregates and mainly showed the strong excimer emission. Additionally, the luminous response of the transparent Pyr−/LDH solid film was investigated in ethanol-toluene mixed solution with various toluene contents. As results, the ratio of luminescence intensities from static excimer and monomer of incorporated Pyr− molecules depended on the toluene content, and excimer emission decreased with an increase in the toluene content. This luminous response can be caused by an increase of the monomeric Pyr− species, because Pyr− aggregates are broken by adsorption of toluene molecules into the LDH interlayer space. The obtained transparent hybrid film may be useful as a detectable material of toluene in solvent by luminous change.

1. Introduction

Layered double hydroxide (LDH), which has crystal structure stacked brucite-like metal hydroxide layer with positive charges and anion species alternatively, is one of anion exchangeable inorganic layered materials, and its general chemical formula is \[ \frac{\left[ M^{2+} \right]_{1-x} \left[ M^{3+} \right]_{x} \left( \text{OH} \right)_{2} \left( A^{n-} \right)_{x}}{n} \], where \( M^{2+} \) is the divalent cation, \( M^{3+} \) is the trivalent cation, and \( A^{n-} \) is the \( n \)-valent interlayer anion, and \( x \) is the amount of trivalent cation, respectively [1–3]. It is well known that various anions such as anionic functional dyes can be intercalated into the LDH interlayer space by anion-exchange reaction. Then, it can be expected that the anionic functional dyes intercalated in the interlayer space show the unique photophysical and/or photochemical properties, which differ from those properties observed in bulk solutions. Thus, many researchers have reported the intercalation of the functional dyes into the interlayer space of LDH, and then the photophysical and/or photochemical properties of functional dyes in LDH interlayer space have been also reported [4–8]. These reports suggested that the materials hybridizing functional dyes with LDH are one of promising material systems for various functional devices such as sensor, light emitting devices, display, and memory [9–14]. However, it is very difficult to quantitatively characterize the details of photophysical and/or photochemical properties of the most of reported hybrid systems, because the hybrid sample can be prepared as powder in usual case. To understand the nature of the functional dyes intercalated in the interlayer space of LDH and the detailed mechanism of the photofunctionalities, the transparent film sample of these hybrid materials will be required.

Some preparation techniques to obtain the transparent film consisting of layered materials such as casting,
Langmuir-Blodgett (LB), and layer-by-layer (LbL) methods have been already reported [15–18]. The casting method is very easy, but it is difficult to prepare the film with high uniformity and transparency. On the other hand, LB and LbL methods can provide the film with good uniformity and transparency. However, procedures of them are complicated, and several spectrometric analyses will be disturbed by low absorbance and/or emission intensity of the dye/layered material hybrid films prepared by these methods because of the small number of the layers in the film. Kawamata and Takagi et al. succeeded to prepare the uniform transparent thin film consisting of clay mineral and/or dye by transfer of the clay mineral and/or dye residue, which was obtained via filtration of those dispersion, on glass substrate [10, 19, 20]. This method (filtration-film transfer (FFT) method) is easy way, and the hybrid film, which have enough transparency, absorbance, and emission intensity to measure several spectrometric techniques, consisting of dyes and clay minerals can be prepared. We reported that the transparent and uniform α-zirconium phosphate thin film can be also prepared by the FFT method. To prepare the transparent film of layered materials by the FFT method, the nanosheet colloidal dispersion, which can be prepared by delamination of layered compound by delamination reagent, is required [21]. Iyi et al. reported on the preparation of LDH nanosheet colloidal aqueous dispersion. Moreover, Iyi et al. succeeded to prepare the transparent LDH film by simple evaporation of LDH nanosheet aqueous dispersion and demonstrate the ion-exchange reaction of this film [22]. However, it is easily expected that it is hard to control the thickness and/or uniformly of the obtained film.

In this paper, we attempted to utilize the FFT method to obtain the transparent LDH film. Then, anionic pyrene derivative (pyrene-1-sulfonate, abbreviated as Pyr−), which was used as photofunctional dye in this study, [23–25] was intercalated into the interlayer space of the LDH film to investigate the photophysical behavior of the anionic pyrene in LDH. Furthermore, we investigated the luminous response of the present film in ethanol-toluene mixed solution to explore the possibility of the present transparent hybrid film as a detectable material of toluene in solvent by luminous change.

2. Materials and Methods

2.1. Materials. 1-Pyrenesulfonic acid sodium salt (Merck) and layered double hydroxide (acquired from Kyowa chemical Industry, co., LTD.) were used as received. Stoichiometric formula of carbonate type LDH is [MgAl (OH)₆] [CO₃]·[H₂O]. Sodium chloride, acetic acid (AcOH), ethanol, sulfuric acid, propionic acid (PrOH), and toluene were purchased from Fujifilm Wako Pure Chemical Corporation and used as received without purification. The glass substrate (cover glass) was purchased from Matsunami Glass Ind., Ltd. The glass substrate was sonicated with water for 30 min and then treated in sulfuric acid overnight at room temperature. After that, glass substrate was washed with enough water. All water used within this work is Milli-Q water prepared by a Direct-Q UV system (Merck Millipore).

2.2. Preparation of the Transparent LDH Only Film. Flow chart of the experimental procedure to prepare the Pyr−/LDH film was shown in Figure 1. PrO− type LDH was prepared via decarbonation and ion-exchange reaction according to literatures [22]. Obtained PrO− type LDH (40 mg) was dispersed in 20 mL of water to obtain LDH nanosheet dispersion. 600 μL of obtained dispersion was filtered through a PTFE membrane filter (pore size = 0.1 μm), and the residue was transferred upon the glass substrate. The obtained thin film was dried up under reduced pressure condition overnight.

2.3. Preparation of the Pyr−/LDH Film. Two pieces of the LDH only film were immersed in EtOH (300 mL) in three-neck separable flask, and solution was purged with nitrogen gas to remove the CO₂. The concentration of CO₂ in exhausted N₂ gas was monitored with CO₂ meter (Testo 535). 0.17 mL of AcOH was added in the flask, and solution was stirred overnight under N₂ flow. The film was washed with EtOH and then dried under reduced pressure condition, and the AcO− type LDH film was obtained. The AcO− type LDH film was immersed in Pyr−/EtOH solution (500 mL, 5.1 × 10⁻⁴ M, corresponding to 2.5% versus anion-exchange capacity of the LDH film) for 24 hours under N₂ flow. The obtained hybrid film was washed with EtOH and dried under reduced pressure condition. Amount of intercalated Pyr− was estimated from the decreased absorbance of Pyr− in immersion solution.

2.4. The Effect of the Toluene on Fluorescence Spectra of the Pyr−/LDH Film. The Pyr−/LDH film was immersed in mixture of EtOH and toluene (concentrations of the toluene are 0, 10, 30, 50, 70, 90, and 100%(v/v)) in quartz cuvette, and then the film was set at 45° against the direction of the excitation light source and the detector of emission to reduce the incident light, which is reflected excitation light by the film and substrate, to the detector. The top view of the setup for emission measurement was shown in Figure 2.

2.5. Characterization. The absorption spectra, XRD patterns, and FT-IR spectra were measured with V-750 (JASCO), Mini-Flex II (RIGAKU), and FT-IR 6100 (JASCO), respectively. The fluorescence and excitation spectra were examined through a fluorescence spectrophotometer (FP-6600, JASCO).
3. Results and Discussion

3.1. Preparation of the LDH Only Film. In Figures 3(a) and 3(b), photograph and transmittance spectrum of the LDH film prepared by the FFT method were shown, respectively. From the photograph (see Figure 3(a)), the enough transparency of the obtained LDH solid film was visible. The transmittance of the LDH film was higher than 55% in the range of 350 to 800 nm as shown in Figure 3(b). These results indicate that the transparent LDH solid film can be prepared by the FFT method. Therefore, it is found that the FFT method is one of useful and applicable techniques for preparing the transparent solid film from LDH nanosheet suspension.

In Figure 4, the XRD patterns of the carbonate type LDH powder, PrO\(^-\) type LDH powder and LDH only film were shown.

In the XRD pattern of the LDH only film, the diffraction lines from 00l plane could be observed at 11.2° (003) and 22.7° (006), respectively. This diffraction pattern of the LDH solid film was almost the same as that of carbonate type LDH powder, but not as PrO\(^-\) type LDH powder, in which the lots of diffraction peaks were observed because of the mixed hydration and dehydration phase [22]. These results suggest that counter anion incorporated in LDH would be an exchange from PrO\(^-\) to carbonate anions during the FFT process. This consideration can be supported by the previous report by Iyi et al., which reported that carboxylate type LDH was not stable in air, and then incorporated carboxylate ion was replaced by carbonate ion. Thus, we can succeed in preparing the transparent LDH solid film with carbonate anion as exchangeable anion species by the FFT method.

3.2. Preparation of the Pyr\(^-\)/LDH Hybrid Film and Its Luminous Behavior. To hybridize Pyr\(^-\) with the LDH solid film, counter anion species in the LDH only film had to be exchanged from carbonate to AcO\(^-\) anion, because the prepared LDH solid film had carbonate anion, which is hardly exchanged into other anion species [3, 26]. The XRD patterns
of the LDH solid film obtained after decarbonation treatment using ethanol-acetic acid mixed solution (see Figure 5(b)) agreed with that of AcO$^-$ type LDH powder reported in the literature [22]. This result indicates that the effective decarbonation treatment for carbonate type LDH powder is also effective for the present LDH solid film. Figure 5(c) shows the XRD pattern of the LDH solid film obtained after immersing the AcO$^-$ type LDH solid film into Pyr$^-$ ethanol solution. In this XRD pattern, the new diffraction peak could be observed without that from carbonate type and/or AcO$^-$ type LDHs. This result indicates that the Pyr$^-$ anions can be incorporated in the LDH solid film via anion-exchange reaction. However, the interlayer space (0.34 nm) calculated from this peak was larger than the interlayer space (0.31 nm) of carbonate type LDH film and smaller than the thickness of Pyr$^-$ considering the diameter of sulfonate and thickness of aromatic ring (ca. 0.5 nm) [27, 28]. Thus, there are both Pyr$^-$ and carbonate anions in the present Pyr$^-$/LDH solid film. This can be supported by small amount of incorporated Pyr$^-$ anions in the Pyr$^-$/LDH solid film (0.14%vsAEC), which was calculated from absorbance of residual Pyr$^-$ anion in filtrate obtained after the immersing process.

In Figure 6, photographs of Pyr$^-$/LDH solid films under (a) room light, (b) UV irradiation (365 nm), and (c) absorption spectra of the Pyr$^-$/LDH film (black line) and Pyr$^-$ aqueous solution (1.0 × 10$^{-5}$ mol/L, red line).
hybridization of Pyr$^-$ anions, and then strong sky-blue color emission, which is known as typical excimer emission of pyrene derivatives, could be observed by UV irradiation (365 nm) as shown in Figure 6(b). This result also indicates that Pyr$^-$ anions were incorporated in the LDH solid film. In Figure 6(c), the new absorption band appeared around 350-390 nm in the Pyr$^-$/LDH film. Similar spectral change was observed in the diffuse reflectance spectra of LDH powder incorporating anionic pyrene and heptanesulfonate [7]. This result indicates the incorporation of Pyr$^-$ in LDH although absorption spectra of the hybrid film were different from that of Pyr$^-$ aqueous solution. As discussed later, this spectral change suggests that Pyr$^-$ formed the aggregate in the interlayer space of LDH. The emission spectra of the Pyr$^-$/LDH film in air and Pyr$^-$ aqueous solution were shown in Figure 7.

Two sharpen peaks (at 378 and 399 nm) and broaden peak (around 465 nm) were observed in emission spectra of the Pyr$^-$/LDH hybrid film. The maximum emission wavelength of sharpen peaks is almost the same as the emission maximum wavelength of Pyr$^-$ in aqueous medium (377 and 396 nm), indicating that these sharpen peaks at 378 and 399 nm were emission from excited Pyr$^-$ monomer in LDH. Emission band around 465 nm will be emission from excimer of Pyr$^-$, judging from large red shift and peak broadening. This result indicated that emission from excimer and monomer can be observed in this system. Excitation spectra of the hybrid film monitored at 400 and 460 nm were shown in Figure 8.

Excitation spectrum observed from emission at 400 nm was almost the same as absorption spectrum of Pyr$^-$ monomer in aqueous medium. This result indicates that the emission at 400 nm originates from the monomeric state of Pyr$^-$ anions in the LDH solid film. On the other hand, excitation spectra observed from emission at 460 nm did not correspond to the excitation spectra observed at 400 nm, although excitation spectra of typical excimer, which is a dimer associated in an excited state, correspond to the excitation spectra monitored at monomer emission. This result indicates that the Pyr$^-$ species with 460 nm emission have a different grand state from the monomeric Pyr$^-$ species with 400 nm emission. This fact indicates that there will be intermolecular interaction among Pyr$^-$ species in the grand state; that is, Pyr$^-$ dimer will be associated in the LDH solid film. Thus, the strong excimer-like emission at around 460 nm can be explained as emission from Pyr$^-$ dimer associated in the grand state under UV irradiation, so-called as “static excimer” [29–32]. Additionally, peaks originated from monomeric Pyr$^-$ was not observed in excitation spectra monitored at 460 nm, indicating the absence of typical excimer, which was called as “dynamic excimer” and which is formed by the encounter between excited pyrene and second pyrene in the grand state.

In Figure 9, the emission spectra of the Pyr$^-$/LDH solid film normalized by emission intensity at 400 nm after immersed in the ethanol-toluene mixed solution with various toluene content (v/v%) are shown.

The normalized intensity of emission from excimer (460 nm) decreased with an increase in the toluene content, but the peak wavelength of excimer emission did not change, even when the toluene content was varied. These results indicate that the decrease of the normalized emission intensity from excimer is caused by the decrease of abundance amount of “static excimer,” but not the change of the chemical state of incorporated Pyr$^-$ anions.

It is known that aggregates and emission behavior of pyrene derivatives depend on their medium [33, 34]. Judging from the observed emission spectral change and this dependency, the mechanism of the decrease of emission originated from static excimer will be ascribed to the dissociation of Pyr$^-$ aggregate by adsorption of toluene in the interlayer spaces as follows. Pyr$^-$ associated the aggregates in ethanol or the mixed solution containing small amount of toluene because of strong hydrophobic interaction, thus static excimer can be observed (Figure 10(a)). On the other hand, when concentration of toluene was increased, toluene will be adsorbed in the interlayer space of LDH, and Pyr$^-$ aggregates were dissociated because hydrophobic interaction is weakened by toluene adsorption (Figure 10(b)).

4. Conclusions

The LDH thin film was prepared by the FFT method, and transparency of the obtained film was enough to measure transmission spectra. It was succeeded to prepare the transparent Pyr$^-$/LDH hybrid film via decarbonation and anion-exchange processes, and it was revealed that intercalated Pyr$^-$ formed emissive aggregate, which is called as static excimer. The luminous response of the transparent Pyr$^-$/LDH solid film was investigated in ethanol-toluene mixed solution with various toluene contents. The ratio of luminescence intensities from static excimer of incorporated Pyr$^-$ molecules depended on the toluene content and decreased with an increase of the toluene content because of the dissociation.
of Pyr− aggregate by adsorption of toluene. Obtained results suggested that the present transparent hybrid film may be useful as a detectable material of toluene in solvent by luminous change.

**Data Availability**

The data used to support the findings of this study are available from the corresponding author upon request.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest.

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