Research Article

A Simple Incorporation Route of Tris(8-hydroxyquinoline)aluminum(III) into Transparent Mesoporous Silica Films and Their Photofunctions

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The molecular aggregation states of tris(8-hydroxyquinoline)aluminum(III) (Alq) adsorbed in the transparent mesoporous silica (MPS) films with the different pore sizes (3.0 and 5.4 nm) were successfully clarified. The Alq molecules were easily incorporated into the films from the solution without the segregation on the surfaces. The adsorbed amount of Alq was controlled by changing the added amount in the initial solution to resultantly give the transparent and yellow-color films. The photoluminescence spectra significantly revealed that the state of Alq molecules in the mesopore varied depending on the adsorbed amount of Alq as well as the pore size, suggesting the characteristic mobility of the adsorbed Alq molecules in the mesopores as compared with that at the bulk or solution state. Therefore, the guest-guest interactions between Alq molecules as well as the host-guest interactions between Alq and mesopore were elucidated. This finding by the use of the mesoporous film hosts will be utilized for including luminescence species and be applicable for optical devices.

1. Introduction

Studies on the incorporation of functional organic molecules into porous inorganic solids have been extensively conducted to construct the functional inorganic-organic supramolecular nanosystems [1]. The molecular aggregation/dispersion states of functional guest species on the well-defined mesostructures affect the physicochemical properties of the host-guest hybrids. The controlled adsorption properties on the various inorganic supports [2–7] are known to give the merits of the immobilization of functional units. Accordingly, the host-guest and guest-guest interactions are important factors to offer the multiple possibilities, so that the systematic studies on the design and characterization of the hybrids by various compositions and different nanostructures are worth conducting.

After the discovery of mesoporous silica (MPS) prepared by the cooperative organization of surfactant and inorganic

species, the synthesis, characterization, and applications of the mesostructured materials have extensively been investigated. The MPS prepared by supramolecular templating methods [8, 9] possesses attractive features such as well-defined and controllable pore sizes, large surface areas, and reactive surfaces for the guest organization. The effect of the guest confinement into the nanospaces on the photophysical properties has been investigated [10]. In addition to the host-guest interactions, the guest-guest interactions can be controlled. Accordingly, the host-guest complexes based on MPS have been synthesized, and the possible applications for optical materials have been reported [11–13]. Although a wide variety of host-guest complexes have been synthesized, the possible effect of pore size on the photofunctions has hardly been reported. Furthermore, the processing of the photofunctional mesostructures with controlled morphology is a basic prerequisite for the applications. Accordingly, the controlled macroscopic morphologies, such as films [14–18],

particles [19–21], and monoliths [22, 23] with the mesostructures, have been suggested as the host-guest complexes.

In this study, we investigated the adsorption of tris(8-hydroxyquinoline)aluminum(III) (Alq), which has been studied as an organic light-emitting material [24], into the MPS films with different pore sizes (3.0 and 5.4 nm) prepared from cationic and nonionic surfactants to clarify the molecular aggregation/dispersion states of Alq at the film mesopore structures. It is known that the photoluminescence characteristics of bulk state depend on the Alq crystalline phases (α , β , γ , etc.) and molecular packing [25–28], and these parameters have been controlled by synthetic pathways as well as by postsynthetic treatments, indicating that the crystalline phase is associated with the luminescence properties of Alq. Although the effects of the morphologies of neat Alq on the performance of the devices have been intensively investigated [29–31], the effective control of the intermolecular interactions of Alq has not been well-documented. Therefore, the control of the intermolecular interactions of Alq as well as the interactions between Alq and mesopore surfaces is the possible way to understand the correlation between the intermolecular interactions of Alq and the luminescence. We have already found that the Alq was easily occluded into the MPS powders from solutions [32, 33], suggesting the importance of the host-guest interactions between MPS and Alq. In the present study, we conducted the adsorption of Alq into the transparent MPS films with the different pore sizes and investigated the states of the Alq.

2. Experimental

2.1. Preparation of Mesoporous Silica Films and Their Alq Complexation. In order to compare the interactions between the adjacent Alq molecules with the interactions between Alq and mesopores, the MPS with Barrett-Joyner-Halenda (BJH) [34] pore sizes of 3.0 and 5.4 nm was prepared using the different template surfactants of octadecyltrimethylammonium chloride (C_{18} TAC, Tokyo Chemical Industry (TCI) Co., Ltd.) and triblock poly(ethylene oxide (EO))-poly(propylene oxide (PO))-poly(ethylene oxide (EO)) copolymer ($EO_{20}PO_{70}EO_{20}$, Aldrich Co., Ltd.) denoted by P123. Here, the MPS with the pore sizes of 3.0 and 5.4 nm was designated as C18MPS-3.0 and P123MPS-5.4, respectively.

C18MPS-3.0 film was synthesized based on the previous report [14, 18]. 1.94 mL of tetramethoxysilane (TMOS, TCI Co., Ltd.), ultrapure water (472 μ L), and hydrochloric acid aqueous solution (0.1 N, 100 μ L) were mixed at 313 K for 1 h. Then, 534 mg of C_{18} TAC was dispersed into ultrapure water (1.4 mL) at 313 K, and the siliceous solution was added to the surfactant solution and immediately 100 μ L of hydrochloric acid aqueous solution (1 N) was added to the mixed solution and stirred at 313 K. In contrast, P123MPS-5.4 film was synthesized based on the modified previous report [35]. 1.12 mL of tetraethoxysilane (TEOS, TCI Co., Ltd.), ultrapure water (130 μ L), ethanol (1121 μ L), and hydrochloric acid aqueous solution (1 N, 29 μ L) were mixed and stirred at 333 K. Then, 252 mg of P123 was dispersed into hydrochloric acid aqueous solution (0.01 N, 415 μ L), and the siliceous solution was added

to the surfactant solution and stirred at room temperature for 2 h.

These resulting solutions were spin-coated on a glass substrate at a rotation speed of 6000 rpm and then dried at 333 K for 18 h. The supramolecular templates were removed by the calcination at 723 K for 6 h, which was confirmed by a Fourier transform infrared (FT-IR) spectroscopy.

2.2. Preparation of Alq Powders. The solvated Alq powders were prepared using a vacuum concentration method from the ethanol or benzene solution, suggesting the recrystallization of the ethanol-Alq and benzene-Alq powders [26]. By the morphological observation of the powders by an optical microscopy, it was confirmed that the crystal shapes and sizes from benzene were more homogeneous and smaller. Accordingly, the benzene solution was used in this study. The Alq crystals recrystallized on the C18MPS-3.0 and P123MPS-5.0 film and glass substrate surfaces were prepared from the higher Alq concentration in benzene at 1.2 mM.

2.3. Adsorption of Alq into MPS Films. The adsorption of Alq (α -phase powder, TCI Co., Ltd.) into the MPS films was conducted by the admixture of the MPS films (dried at 393 K for 4 h under dry air) with benzene solution of Alq with the different concentrations at room temperature for 1 h. The resulting films were physically washed by ultrapure water and dried under reduced pressure for 1 day and were designated as Alq/C18MPS-3.0 and Alq/P123MPS-5.4.

2.4. Characterization. The surface nanostructures were analyzed by an atomic force microscope (AFM: Nanocute, SII Investments, Inc.) in areas of 0.5×0.5 and $5.0 \times 5.0 \mu\text{m}^2$. The surface roughness (R_{rms}) was calculated by the root mean squares in the height images. X-ray diffraction (XRD) patterns were recorded with a powder X-ray diffractometer (Smart Lab, Rigaku, Japan) equipped with monochromatic $\text{CuK}\alpha$ radiation operated at 20 mA and 40 kV. The nitrogen adsorption isotherms of the films were measured at 77 K on an BELSORP-miniII instrument (MicrotracBEL Co., Ltd.) to calculate Brunauer–Emmett–Teller (BET) surface areas [36] and BJH pore size distributions. Prior to the measurement, a number of samples were degassed under vacuum at 393 K for 4 h.

The adsorbed amount of Alq in the MPS was determined by the change in the concentration of Alq in the solution before and after the reaction, which was determined by the changes of absorbance of Alq in benzene at 377 nm using a UV-visible absorption spectroscopy (V-750, JASCO Co., Ltd.). The adsorption amount at the equilibrium state (W) was calculated by (1) based on the adsorption isotherms. On the basis of the Langmuir adsorption isotherm formula, the equation of state for the one-component adsorption can be represented as follows:

$$\frac{C}{W} = \frac{1}{(K_{\text{eq}} \cdot W_{\text{max}})} + \left(\frac{1}{W_{\text{max}}} \right) C, \quad (1)$$

where C , K_{eq} , and W_{max} are the Alq concentration in the equilibrium state, the adsorption equilibrium constant, and

the maximum adsorption amount, respectively. K_{eq} and W_{max} were determined from the slope of a C/W versus C plot. The Alq adsorption based on the correlation coefficient was found to be Langmuir type monolayer adsorption.

The photoluminescence spectra were recorded on a FP-8500 spectrophotometer (JASCO Co., Ltd.) with the excitation wavelength at 365 nm (atmosphere: air, excitation-slit/detection-slit: 2 nm/2 nm, measure time: 0.1 s, step width: 1.0 nm, sample weight: 150 mg, and shape: pellet), and the detection was used by photomultiplier tube. A cryostat was used to obtain the temperature-dependent photoluminescence spectra between 80 and 300 K. The inside temperature was controlled using a heater in conjunction with the cryostat. All the photoluminescence spectra were measured through a quartz window. From the spectra, the integrated luminescence intensity (I) was calculated by the areas in the range between 420 and 670 nm, and I per 1 mol of Alq was calculated by dividing I by the adsorbed molar amount of Alq on the MPS films. The intensity maxima among the MPS with the different adsorbed amount of Alq were fixed to be 1.0. The integrated luminescence intensities centered at the peak tops of 462 and 525 nm, which are abbreviated as I_{462} and I_{525} , were calculated based on the Gaussian-function deconvolution and fitting to obtain the I_{525}/I_{462} values. In the deconvolution, the components and peak positions were initially fixed and then were refined only for the peak heights. During the final optimization, only the components and peak widths were refined again to reduce the residual values. The luminescence microscope image of the MPS adsorbed Alq was obtained by a CKX41N-FL photoluminescence microscope (OLYMPUS Co., Ltd., excitation wavelength: 360–400 nm, exposure time: 100 ms) through the emission source (OLYMPUS Co., Ltd., U-RFLT50).

3. Results and Discussion

Figure 1 shows the AFM images of the MPS film surfaces and their nitrogen adsorption and desorption isotherms and BJH pore size distributions. The surface structures are particulate and the domain size of P123MPS-5.4 was larger than that of C18MPS-3.0, which were also seen in the phase-shift images (see Figure S1 in Supplementary Material available online at <https://doi.org/10.1155/2017/7351263>), and R_{rms} of the C18MPS-3.0 and P123MPS-5.4 films were 1.6 and 2.6 nm, respectively. In the nitrogen adsorption and desorption isotherms, the hysteresis loops between the adsorption and desorption processes were observed. According to the IUPAC classification [37], the isotherm and hysteresis classifications were indexed as type IV and H4 for C18MPS-3.0 and type IV and H1 for P123MPS-5.4, indicating the existence of mesopores. The BET surface area of C18MPS-3.0 was higher than that of P123MPS-5.4 as shown in Table 1. The BJH pore size distributions indicate the mesopore range up to approximately 15 nm. Therefore, the different surface structures were successfully prepared. It was suggested that the BJH pore sizes of 3.0 and 5.4 nm are large enough to accommodate Alq when the hydrodynamic space by molecular diffusion in addition of the distance between Alq and silanol group in the mesopore is considered.

Figure 2 shows the fluorescent microscope images and photoluminescence spectra of the solvated Alq powders before and after the recrystallization. The morphologies of α -Alq, ethanol-Alq, and benzene-Alq crystals were needle, cuboid, and plate-like shapes, respectively, and the crystal shape and size from benzene were more homogeneous and smaller. Moreover, the luminescence maximum of benzene-Alq was longer region as compared with those of the other crystals, indicating the strong Alq-benzene packing interactions. These results would be attributed to the solvent polarity. In the case of benzene, the π - π interactions were thought to be enhanced through the intervention of the solvent molecules [26]. Thus, benzene was used as the adsorption solvent in the following experiments.

Figure 3(a) shows the adsorption isotherms of Alq into the MPS films. The adsorbed amounts were controlled by changing the added amount of Alq in solution. The adsorption isotherm of the Alq into C18MPS-3.0 could be classified as a Langmuir type [38], indicating the strong adsorbent-adsorbate interaction. When P123MPS-5.4 was used, the adsorption isotherm was S type, indicating the weaker adsorbent-adsorbate interaction. As shown in Table 1, the adsorption properties were different between the MPS host and the W_{max}/S_{BET} , which denotes the amount of adsorbed Alq per the experimentally determined BET surface area. W_{max}/S_{BET} observed for P123MPS-5.4 was smaller as compared with that for C18MPS-3.0, suggesting that the host-guest interactions are clearly different depending on the pore size and templating surfactant. Generally, the uncondensed hydroxyl groups on the silica surface induce polar nature on the surface. Thus, Alq was electrostatically captured on the silica surface by hydrogen-bonding interactions with silanol groups. After drying, the Alq molecules adhered to the pore surface firmly enough not to be eluted. Therefore, one could argue that the “host-guest interactions” were successfully formed at the mesopores.

In the adsorption process at the higher Alq solution (1.2 mM), the segregation of the Alq crystals grown on the C18MPS-3.0 and P123MPS-5.4 films was observed (Figures 3(b) and 3(c)), suggesting that the adsorption behavior dominantly occurs at the concentration less than 1.2 mM. The morphologies of crystals depend on the MPS, and that on P123MPS-5.4 (Figure 3(c)) was clearly different from those on the C18MPS-3.0 (Figure 3(b)) and glass (Supplementary Material, Figure S2). These results indicate that the molecular stacking structures were dominantly originated from the inside and/or outside mesopore surface properties.

Figures 4(a) and 4(b) show the XRD patterns of C18MPS-3.0, Alq/C18MPS-3.0, P123MPS-5.4, and Alq/P123MPS-5.4 films. The X-ray diffraction patterns suggested that the ordered hexagonal mesopore arrangements are preserved with the adsorption of Alq. Alq was adsorbed effectively into the films to apparently give transparently yellow-color, and the photographs of the films with the maximum adsorbed amounts of Alq in Figures 4(c) and 4(d) indicate the preservation of transparency with the adsorption. The AFM topographic images in Figures 4(e) and 4(f) clearly exhibited no segregation on the films, which were also seen in the phase-shift images (Supplementary Material, Figure S3), and

FIGURE 1: (a, b) AFM topographic images (observation area: 500 nm²), (c, d) nitrogen adsorption (open symbols) and desorption (closed symbols) isotherms, and (e, f) BJH pore size distributions of (a, c, e) C18MPS-3.0 and (b, d, f) P123MPS-5.4 films.

FIGURE 2: (a–c) Fluorescent microscope images and (d–f) photoluminescence spectra of (a, d) neat Alq powder and solvated Alq powders recrystallized from (b, e) ethanol and (c, f) benzene.

TABLE 1: S_{BET} and r_{BJH} of the C18MPS-3.0 and P123MPS-5.4 films and the adsorption properties of Alq (W_{max} , $W_{\text{max}}/S_{\text{BET}}$, K_{eq}) from the adsorption isotherms by the saturation method based on Langmuir equation.

	Mesopore properties		Adsorption properties of Alq into MPS		
	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	r_{BJH} (nm)	W_{max} ($\mu\text{mol} \cdot (\text{g of MPS})^{-1}$)	$W_{\text{max}}/S_{\text{BET}}$ (Molecules $\cdot (\text{nm}^2 \text{ of MPS})^{-1}$)	K_{eq} (10^{-3}M^{-1})
C18MPS-3.0	1089	3.0	300	0.16	18.1
P123MPS-5.4	742	5.4	150	0.12	6.7

R_{rms} values of the Alq/C18MPS-3.0 and Alq/P123MPS-5.4 films were 5.2 and 4.6 nm, respectively.

In order to discuss the state of the Alq molecules in the mesopore, the photoluminescence spectra of the Alq adsorbed in the MPS films were investigated as a function of the adsorbed amount of Alq. Figures 5(a) and 5(b) show the luminescence spectra of the Alq/C18MPS-3.0 and Alq/P123MPS-5.4 films with the different adsorbed amount. When the adsorbed amount of Alq was smaller, the luminescence bands split into 462 and 525 nm. At the maximum adsorbed amounts, the luminescence maxima were observed at 510 nm for C18MPS-3.0 and 513 nm for P123MPS-5.4 without the spectral split. I increased with increasing the

adsorbed amount of Alq (Figure 5(c)). The changes in I per 1 mol of Alq exhibited the minimal luminescence intensity regions (Figure 5(d)). Considering the increase in the intensity at around 525 nm region (Figure 5(e)), it was thought that the guest-guest interactions (e.g., long-period π - π interactions [26]) were changed to be dominated above the threshold amount of adsorbed Alq. I per 1 mol of Alq in the P123MPS-5.4 film was higher at the maximum adsorption amount of Alq. When P123MPS-5.4 was used as the host, the luminescence was observed at the longer wavelength, suggesting that the larger pore size enabled the adsorbed Alq to aggregate even at the low Alq concentration. As shown in inset fluorescent microscope images, the Alq/C18-MPS and

(a)

(b)

(c)

FIGURE 3: (a) Adsorption isotherms of Alq into C18MPS-3.0 and P123MPS-5.4 from benzene solution. Fluorescent microscope images of the segregation Alq crystals grown on (b) C18-MPS and (c) P123-MPS films, which were precipitated under the higher Alq concentration in benzene at 1.2 mM.

Alq/P123-MPS films with the maximum adsorption amount of Alq homogeneously exhibited the green luminescence. This is the first time to successfully prepare the Alq-silica complex films.

Considering the luminescence maxima of Alq in benzene at 517 nm, ethanol at 515 nm, and methanol at 514 nm [26] and their monomodal spectral shapes, it is suggested that the state of Alq molecules in the mesopores was different from that in the solution state. From the spectral variation of the crystalline Alq, the luminescence red-shift was ascribed to the shorter interligand distance and/or the denser molecular packing of Alq [26]. Based on the other reports [27, 28], the luminescence at around 470 and 520 nm was ascribed to the delta or gamma crystalline phase of Alq arranged in a manner minimizing the overlap of the π -orbitals between pairs of hydroxyquinoline ligands belonging to neighboring Alq molecules and to the amorphous state which formed the favorable overlap of facing the ligands, respectively [32]. Accordingly, we have ascribed the two bands at 462 and 525 nm to isolated and aggregated Alq in

the mesopore, respectively [21]. The bimodal peak variations of the relative luminescence intensity (I_{525}/I_{462}) as a function of the adsorbed amount of Alq are shown in Figure 5(e). I_{525}/I_{462} varied depending on the adsorbed amounts of Alq and increased gradually for C18MPS-3.0 and dramatically for P123MPS-5.4, suggesting that the intermolecular interactions among Alq molecules were enhanced by the P123MPS-5.4 host. It is thought that the strong interactions between Alq and mesopore surface led to the adsorption of Alq as isolated molecular states at the lower adsorbed amounts and then the intermolecular interactions enhanced upon crowding as suggested in Figure 6. It was supposed that nonionic P123-templated mesopore surfaces with the smaller amount of silanol groups affected the crowding of Alq (i.e., guest-guest interactions) at the lower concentrations. Therefore, the state of Alq in the mesopore with the amount of adsorbed Alq apparently varied depending on the pore size as well as the surface properties based on templating surfactants.

The photoluminescence spectral changes, the integrated intensity, and maxima plots with the temperature range

FIGURE 4: XRD patterns of (a) C18MPS-3.0 and Alq/C18MPS-3.0 and (b) P123MPS-5.4 and Alq/P123MPS-5.4 films (insets: the magnified patterns at $2\theta = 3.25-8.25^\circ$ regions). The Alq/C18MPS-3.0 and Alq/P123MPS-5.4 films with the adsorbed amounts of Alq at 267 and 117 $\mu\text{mol}/(\text{g}$ of MPS) were evaluated by (c, d) photographs and (e, f) AFM topographic images (observation area: $5.0 \mu\text{m}^2$).

between 80 and 300 K of α -Alq powder, Alq/C18MPS-3.0, and Alq/P123MPS with the adsorbed amount of Alq at 131 and 91 $\mu\text{mol}/\text{g}$, respectively, were shown in Figure S4 (Supplementary Material). In Figure S4(d-f), the y -axis was the relative luminescence intensity normalized to that at 300 K. For α -Alq powder (Figure S4(a, d)), the increase in the luminescence intensity as the temperature decreases from 300 to 80 K was observed, and these changes were reversible. Similar changes have also been reported previously for the neat Alq powders and films, which were attributed to only the reduction of the temperature quenching [39, 40]. No vibronic structures in the spectra appeared below 150 K, suggesting that the ordering structures of the Alq molecules were preserved by the temperature changes. For the Alq adsorbed in the MPS films, the integrated luminescence intensity increased and the spectral red and blue shifts by C18MPS-3.0 and P123MPS-5.4 were observed with

decreasing temperature from 300 to 80 K, and these changes were reversible. The intensity increased with the temperature variation (the maximum intensity at 80 K) which was observed without exhibiting vibronic structure in the spectra. The luminescence changes of the Alq adsorbed in the MPS films were different from α -Alq and depended on the host. It has been reported that the δ - and γ -crystalline phases showed the blue-shifted luminescence maximum at near 470 nm and have the well-defined molecular arrangements in comparison with those of other phases (α - and β -phases, amorphous state) [27, 28]. The rearrangement of Alq molecules in the mesopore altered from the disorder with the enhanced intermolecular interactions to the δ - and γ -crystal-like states using the P123MPS-5.4 host, and the reverse alternation occurred using the C18MPS-3.0 host. Judging from the results, the states of the adsorbed Alq in the MPS films altered in the temperature variations, which depended on the pore size as

FIGURE 5: Photoluminescence spectra of (a) Alq/C18MPS-3.0, (b) Alq/P123MPS-5.4 films with the different adsorbed amounts of Alq (insets: fluorescent microscope images of the Alq/C18MPS-3.0 and Alq/P123MPS-5.4 films with the adsorbed amount of Alq at 267 and 117 $\mu\text{mol}/(\text{g of MPS})$, resp.), (c) I , (d) I per 1 mol, and (e) I_{525}/I_{462} changes with the adsorbed amount.

FIGURE 6: Possible host-guest and guest-guest interaction changes with increasing the adsorbed amount of Alq in the mesopores.

well as the adsorbed amount of Alq. In particular, P123MPS-5.4 exhibited the characteristic luminescence behavior with the temperature variation if compared with the case in the C18MPS-3.0. Therefore, the effective nanospace confinement of Alq was clarified by controlling the molecular states in the mesopores.

4. Conclusion

Alq was successfully adsorbed without segregation into the MPS films with the different pore sizes. The adsorbed amount was controlled by changing the added amount in the initial solution to resultantly exhibit the transparent and yellow-color films. The molecular states of Alq in the mesopore varied upon the adsorbed amount of Alq as well as the surface properties of the mesopores. The luminescence of the adsorbed Alq revealed that the rearrangements of the molecules in the mesopore occurred to exhibit the significant aggregation/disaggregation between the molecules. Therefore, the MPS surfaces effectively controlled the guest-guest interactions between the Alq molecules as well as the host-guest interactions between the Alq and mesopore. This finding by the use of the mesoporous hosts will be utilized for including luminescence species and be applicable for optical devices.

Conflicts of Interest

There are no conflicts of interest regarding the publication of this paper.

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