Luminescence of Tris(8-quinolinato)aluminum(III) (Alq_3) Adsorbed into Mesoporous Silica

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The adsorption of tris(8-quinolinato)aluminum(III) (Alq_3) into mesoporous silica was investigated. Alq_3 was easily occluded into the mesoporous silica from Alq_3 solution and the luminescence altered with respect to the amount of adsorbed Alq_3. This is the first report to effectively modify the luminescence properties of Alq_3 by the host–guest and guest–guest interactions.

Studies on the introduction of functional units into porous inorganic solids have been conducted in order to construct functional inorganic–organic supramolecular systems.[1] Among possible porous solids, mesoporous silicas prepared by supramolecular templating methods possess various attractive features such as well-defined and controllable pore size, large surface area, and reactive surfaces for the guest organization. Accordingly, host–guest complexes have been synthesized from mesoporous silicas for such purposes as catalytic and optical applications.[2–4] In the present study, the adsorption of tris(8-quinolinato)aluminum(III) (Alq_3), which has been studied most widely as an organic light-emitting material,[5] into mesoporous silicas was investigated. It is known that the luminescence characteristics of Alq_3 depend on the states of Alq_3 such as crystal structures and molecular packing,[6–8] and these parameters have been controlled by synthetic pathways as well as by post-synthetic treatments. The immobilization of Alq_3 in confined nanospace seems to be an alternative way to control the states as well as optical properties of Alq_3. Here, we report the incorporation of Alq_3 into mesoporous silica with varied loading amounts, in order to investigate the states of the Alq_3 in mesopore.

In order to compare the interactions between the adjacent Alq_3 with the interaction between Alq_3 and mesopore surface, pore size (R) of $2.0 < R < 3.5$ nm is thought to be suitable to accommodate Alq_3 for the investigation of the adsorption behavior of Alq_3.[9] Accordingly, mesoporous silica with the BET surface area of 1090 $m^2 \cdot (g\ silica)^{-1}$ and the BJH[10] pore size of 3.1 nm (designated as MPS-3.1) was selected for the first trial. MPS-3.1 was hydrothermaly synthesized (150 °C and 48 h) and subsequent calcination (550 °C and 8 h), according to the method reported by Mokaya,[11] and used. The formation of the mesoporous silica was confirmed by the analyses of X-ray diffraction (XRD) patterns and nitrogen adsorption/desorption isotherms. The adsorption of Alq_3 onto MPS-3.1 was conducted by the admixture of the dried MPS-3.1 (120 °C, 4 h, and under dry air flow) with absolute ethanol solutions of Alq_3 at room temperature for 1 h under dry N_2 atmosphere. The resulting solids were collected by centrifugation and dried under reduced pressure for 1 day. The adsorbed amount of Alq_3 into the MPS-3.1 was determined by UV–vis absorption spectra.[12] The resulting complexes were evaluated by XRD, photoluminescence and luminescence microscopy.

Alq_3 was adsorbed effectively onto MPS-3.1 to give lightly yellow-colored products. The adsorption isotherm of Alq_3 onto MPS-3.1 (Figure 1) was classified as Langmuir type, showing strong adsorbent–adsorbate interactions. Judging from the adsorption isotherm, the adsorbed amounts of Alq_3 could be controlled by changing the added amount in solution. Generally, on the silica surface, uncondensed hydroxyl groups are present,[13] which induce polar nature on the surface. Thus, it was thought that Alq_3 was captured on the silica surface by hydrogen-bonding interactions with silanol groups. After drying under reduced pressure, the adsorbed Alq_3 molecules adhered to the pore surface firmly enough not to be eluted by sonication in ethanol, using standard ultrasound washing equipment.

The X-ray diffraction pattern of the MPS-3.1 with the adsorbed Alq_3 amount of 304 $\mu mol\ (g\ silica)^{-1}$ is measured, together with that of MPS-3.1. The low-angle diffraction peaks for (100), (110), (200), and (210) were observed, which confirmed the ordered hexagonal mesopore arrangement before and after the adsorption of Alq_3.[14]

Photoluminescence spectra of the Alq_3 adsorbed mesoporous silica (excitation at 365 nm) are shown in Figure 2(I). The scattering from the MPS-3.1 was subtracted to calibrate the luminescence spectra. The luminescence maxima were observed at around 470 and 520 nm. Moreover, the relative contribution of the two bands varied depending on the loading amounts of Alq_3. The variation of the relative luminescence intensity at 520 nm to that at 470 nm (I_{520}/I_{470}) as a function of the adsorbed amount of Alq_3 is shown in Figure 2(II), where I_{520} and I_{470} denote the luminescence intensity at 470 and 520 nm. Spectral variation of the crystalline Alq_3 has been reported and the luminescence red shift was ascribed to the shorter interligand distance and/or the denser molecular packing of Alq_3.[7] In particular, the luminescence near 470 and 520 nm was ascribed to the δ-crystalline phase of Alq_3 arranged in a manner minimizing the overlap of the π orbitals between pairs of quinolinato ligands belonging to neighboring Alq_3 molecules and to the amorphous state formed the favorable overlap between facing ligands, respectively.[7,8] So, we ascribed the two bands at 470 and 520 nm observed

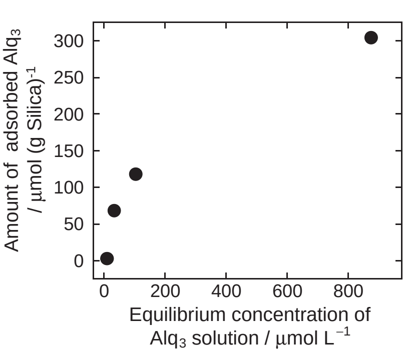

Figure 1. Adsorption isotherm of Alq_3 onto the MPS-3.1 from ethanol.

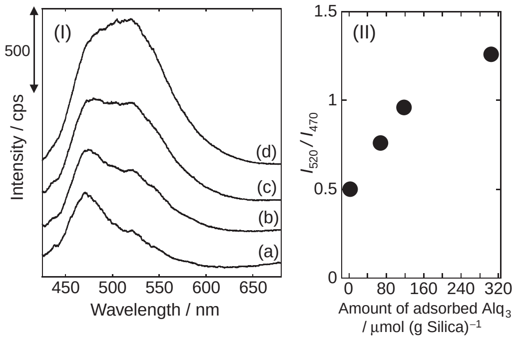

Figure 2. (I): Changes in the luminescence spectra of MPS-3.1 adsorbed Alq_3 upon the variation of the adsorbed amounts (the amount of (a) 3, (b) 68, (c) 118, and (d) 304 μmol (g Silica)$^{-1}$. (II): Variation of the relative luminescence intensity at 520 nm to that at 470 nm as a function of the amount of Alq_3 adsorbed onto MPS-3.1.

in the present material to isolated and aggregated Alq_3 in the mesopore, respectively. It is thought that the strong interactions between Alq_3 and mesopore surface led the adsorption of Alq_3 as isolated molecule at low loadings in Figure 3. In addition, the increased loading resulted in the enhancement of the intermolecular interactions between the adjacent Alq_3 in the mesopore, so that the I_{520}/I_{470} gradually increased with the increase in the amount of adsorbed Alq_3. Considering the luminescence maxima of Alq_3 at 515 nm in ethanol (at 514 nm in methanol[7]), the state of Alq_3 in the mesopore was clearly different from these solution state and further varied with respect to the amount of adsorbed Alq_3.

Introduction of Alq_3 into the mesoporous silica was imaged during the immersion of MPS-3.1 in an Alq_3/ethanol solution. The changes in the image were monitored in situ by a luminescence microscope.[15] Figure 3a shows the luminescence microscope image of MPS-3.1 in the Alq_3/ethanol solution, which consisted of 1.0 mg of MPS-3.1 immersed in ca. 0.25 mL of 1.5 mM-Alq_3/ethanol. The luminescence color of the Alq_3/ethanol solution was green and that of MPS-3.1 was colorless (not luminescent), originally. The solution became no luminescent after 5 min and MPS-3.1 showed the blue luminescence (Figure 3b). In this case, it is thought that the state of Alq_3 in the mesopore was isolated among the Alq_3 molecules by the interactions with the mesopore surface as described above. After 10 min, MPS-3.1 showed green luminescence (Figure 3c). Surprisingly, after 35 min, MPS-3.1 part showed brightly greenish-yellow luminescence without Alq_3 separating out around the MPS-3.1 (Figure 3d). The luminescence was clearly red-shifted as compared to the Alq_3/ethanol solution. With regard to the foregoing prospects for Figure 3, it is thought that the intermolecular interactions among the Alq_3 molecules were strongly affected after the evaporation of ethanol in the mesopore especially when the loading amount of Alq_3 was high. In consequence, the luminescence red shift was observed in the range of the reaction time between 5 and 35 min. The adsorption of Alq_3 onto mesoporous silicas with different pore sizes and from different solvents are in progress in our laboratory and the results will be reported subsequently.

In summary, Alq_3 was successfully occluded into the mesoporous silica with the pore size of 3.1 nm by admixing an ethanolic solution of Alq_3 at room temperature. The behavior was imaged in situ by a photoluminescence microscope. The luminescence altered with respect to the amount of adsorbed Alq_3. This is a new method for modifying the photophysical properties of Alq_3 by controlling the state of Alq_3 by means of host–guest interactions between Alq_3 and mesoporous silica.

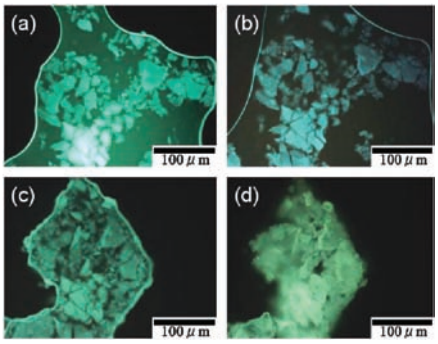

Figure 3. Luminescence microscope images of MPS-3.1 in the Alq_3/ethanol solution at (a) 0, (b) 5, (c) 10, and (d) 35 min after immersion.

References and Notes

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