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Stabilization of facial isomer of tris(8-hydroxyquinolate)aluminum through confinement in silica-surfactant mesostructures

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The self-assembled nanocomposites of tris(8-hydroxyquinolate)aluminum (AlQ_3) confined in the silica-surfactant mesostructures are investigated. In the photoluminescence (PL) spectra, the AlQ_3 molecules confined in the mesostructures exhibit a significant blueshift by 50 nm compared with that of the pristine AlQ_3 . The PL efficiency is enhanced for the nanocomposites prepared at a higher temperature. The spectral analyses reveal that fac- AlQ_3 molecule, which is hard to prepare due to its relatively thermodynamically instability, is obtained with this efficient and simple method. PL decay analysis implies experimentally the lifetimes corresponding to facial and meridional isomers. © 2007 American Institute of Physics. [DOI: 10.1063/1.2746420]

Tris(8-hydroxyquinolate)aluminum (AlQ_3) has been intensively investigated since 1987,¹ due to its important applications in organic light emitting diodes. An unresolved issue exists in respect of the isomerism of the AlQ_3 molecule, and much effort has been devoted to explore the existence and property of facial isomer,²⁻¹² since the facial component is assumed to act as an efficient trap in the electron transport process,² and fac- AlQ_3 is also particularly desirable for its blueshifted fluorescence and high quantum yield.^{5-7,10} However, the wall up against is that the fac- AlQ_3 is commonly prepared in the subgram order by a solid-state phase conversion at a very high temperature, because the synthetic control of a ligand configuration is difficult as a result of the favorable formation of the thermodynamically more stable mer isomer.^{6,10} In this letter, the transformation of blue fluorescent fac- AlQ_3 from commercial mer- AlQ_3 was realized through the nanoscaled confinement in silica-surfactant mesostructures with a solution route. A model for clarifying the underlying correlation between the host mesostructure and the transformation of fac- AlQ_3 was developed.

The self-assembled hybrid nanocomposite was obtained through a modified one-step approach,¹³ in which a solution of AlQ_3 in hydrophobic chloroform was injected into the surfactant micelles before addition of silica source. Due to their hydrophobic nature, AlQ_3 and chloroform were dissolved in the inner hydrophobic core of the micelles, viz., the organic region of the silica-surfactant mesostructures.¹³⁻¹⁵ A typical synthesis procedure is as follows: 1.2 g cetyltrimethylammonium bromide (CTAB) was dissolved in 60 mL H_2O and 4.75 g of concentrated NH_3 (25%) was added. The solution was stirred in a sealed container and heated to 323 K. This mixture was added an appropriate amount of AlQ_3 dissolved in the minimum chloroform via injection. The resulting mixture was stirred rigorously for 20 min at 323 K, followed by the addition of 5 g tetraethoxysilane at once via injection. The mixture was subsequently stirred for another 60 min at the given temperature. Then the product was centrifuged, washed with distilled water, and dried at 333 K overnight.

The incorporated amount of AlQ_3 in the nanocomposites was adjusted by controlling the starting mole ratio of the complex and CTAB.

X-ray diffraction (XRD) studies were carried out on a Rigaku Dmax 2000 x-ray powder diffractometer using $\text{Cu } K\alpha$ ($\lambda = 1.5405 \text{ \AA}$) radiation. High-resolution transmission electron microscopic (TEM) characterization was performed with a Philips Tecnai F30 FEG-TEM operated at 300 kV. The AlQ_3 content of nanocomposites (digested first) was determined on an inductively coupled plasma-optical emission spectrometer (ICP-OES) (Vista Varian). Fluorescence spectra were recorded on a Hitachi F-4500 spectrophotometer at room temperature. Time-resolved fluorescence spectra were recorded on an Edinburgh FLS920 fluorescence spectrophotometer. The instrument was operated with a thyatron-gated flash lamp filled with hydrogen at a pressure of 0.5 atm. The lamp was operated at a frequency of 40 kHz, and the pulse width of the lamp under operating conditions was about 1.2 ns. The lifetimes were estimated with the measured fluorescence decay curves and the lamp profile using a nonlinear least squares iterative fitting procedure.

Figure 1(a) depicts the small-angle XRD patterns of the resulting nanocomposites which contain the same AlQ_3 content ($4.2 \mu\text{mol/g}$) prepared at different temperatures. For the sample MS1 prepared at 323 K, a very sharp diffraction peak appears around 1.9° and two weak peaks are observed at relative higher angles. The three well-resolved peaks can be indexed as (100), (110), and (200), the typical diffractions of a long-range ordered hexagonal ($p6mm$) mesoporous solid, and corresponding to a d_{100} distance of 4.64 nm. With the preparation temperature of the nanocomposites increasing, only one broad peak is observed at low angles, characteristic of a wormlike pore structure.^{16,17} The TEM images of the nanocomposite MS1 exhibit highly ordered hexagonal arrays [Fig. 1(c)] of mesopores with one-dimensional channels [Fig. 1(b)] throughout the sample. The TEM image of the sample MS2 shown in Fig. 1(d) clearly exhibits the disordered wormlike pores. The changes of the TEM images are consistent with the XRD results.

The photoluminescence (PL) spectra of the nanocomposites and pristine AlQ_3 are shown in Fig. 2. All of the solid-

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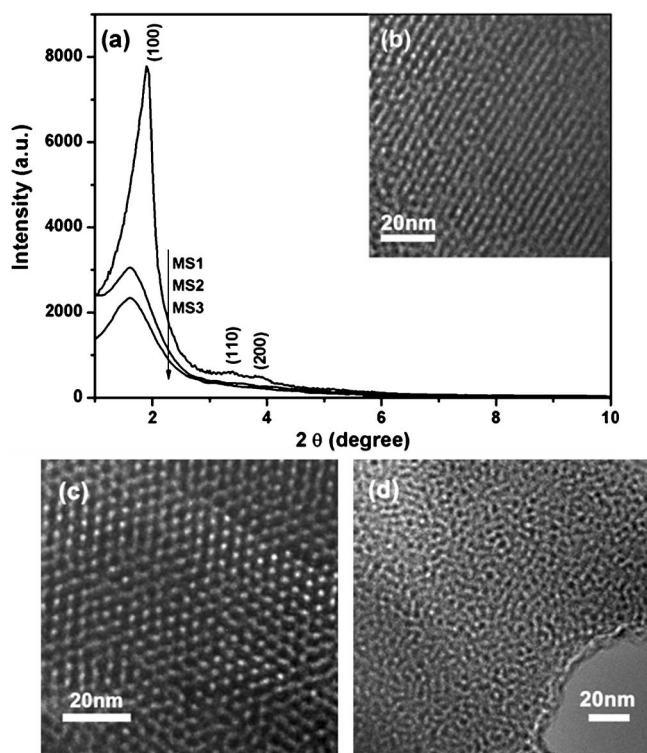


FIG. 1. XRD patterns of the nanocomposites prepared at different temperature (MS1: 323 K, MS2: 333 K, and MS3: 348 K) (a). The TEM images of the nanocomposite MS1 recorded in the direction perpendicular to the pore axis (b) and in the direction of the pore axis (c) and of the nanocomposite MS2 (d).

state samples exhibit a blue emission at approximately 460 nm, an obvious blueshift by 50 nm (0.25 eV) in comparison with that of the pristine Alq₃ (510 nm). Most studies have proven that such an extremely blueshifted luminescence (approximately 0.2 eV) is the characteristic of the fac-Alq₃ molecules.^{5,6,10,11} It is noted that the large blueshift of 0.25 eV exhibited in this work is close to the difference of highest occupied molecular orbital–lowest unoccupied molecular orbital gaps, around 0.3 eV calculated by density functional theory, between the mer- and fac-Alq₃ molecules.² Meanwhile, it has been proven that interconversion between the two species under certain conditions is possible.^{6,10,12} Therefore, the blueshift of 50 nm (0.25 eV) in this work is

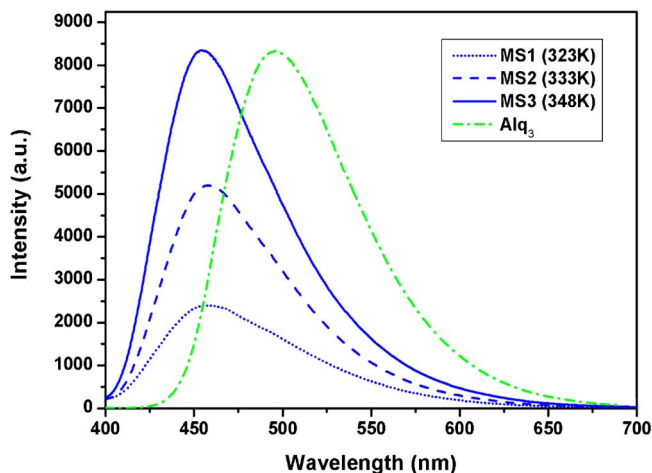


FIG. 2. Photoluminescence spectra of the nanocomposites and the pristine Alq₃, excitation wavelength of 370 nm. The PL intensities of the pristine Alq₃ were normalized for comparison.

supposed to be mainly determined by the formation of fac-Alq₃ molecules. Furthermore, Fig. 2 also indicates that the PL intensity at approximately 460 nm increases with elevating the preparation temperature. Since the conversion from mer- to fac-Alq₃ is a thermally activated process,^{6,10} a higher preparation temperature is beneficial to the isomerization from mer- to fac-Alq₃. Thus, it is possible to obtain a self-assembled nanocomposite with more transformed fac-Alq₃ molecules and thus higher PL intensity through elevating the preparation temperature, as the blue luminescent fac-Alq₃ has higher PL quantum efficiency.⁶

The preparation temperature dependence of the PL intensity of the nanocomposites discloses that both mer- and fac-Alq₃ exist in the nanocomposites. The site selective PL measurements give more insight into this result. As the wavelength of 450 nm is located in the tail of the absorption of *a*-Alq₃ (composed only of meridional isomers) and, in particular, below the absorption edge of δ -Alq₃ (consisted only of facial isomers) (Ref. 5) it is chosen as an excitation wavelength. The peak position of the nanocomposites depends obviously on the excitation wavelength. A shift of the PL maximum from 460 nm upon 370 nm excitation to 510 nm upon 450 nm excitation is observed, indicating the presence of both two isomers in the hybrid nanocomposites.^{12,18} Gaussian fits used to evaluate the contribution of the two components on the overall luminescence of the nanocomposite MS2 [Fig. 3(a)] disclose two peak positions at 2.49 and 2.73 eV, corresponding to the green luminescent and blue luminescent Alq₃ molecules, respectively. The described approach is applied to the emission spectra of the samples prepared at different temperatures. From the fits, the PL integral intensities I_{gr} and I_{bl} corresponding to green luminescent mer- and blue luminescent fac-Alq₃, respectively, were inferred. Ratio of I_{bl}/I_{gr} gradually increases with the increase in the preparation temperature [Fig. 3(b)], which is in agreement with the above results. Higher preparation temperature enhances the probability and efficiency of the isomer transformation.

Both PL decays ($\lambda_{ex}=370$ nm and $\lambda_{em}=460$ nm) of pristine Alq₃ and the nanocomposites were measured at room temperature. The PL decay of the pristine Alq₃ (composed dominantly of meridional isomers^{6,11}) was fitted to a single-exponential function with a lifetime $\tau=18.7$ ns, which compares well with the reported values.¹⁹ However, the Alq₃ relaxation dynamics becomes biexponential upon confinement in silica-surfactant mesostructures. Although it is claimed that the short and longer lifetimes correspond to the photoluminescence from facial and meridional isomers of Alq₃, respectively,²⁰ more detailed experiments are necessary to conclude the correlation between the isomeric states and two lifetimes in the biexponential decay, and the possibility might not be excluded thoroughly in this case. The lifetime, relative weights, and χ^2 of decay analyses of pristine Alq₃ and the nanocomposites are given in Table I. Both the lifetimes, τ_1 and τ_2 , increase slightly as a function of preparation temperature, which may be attributed to the increased activation energies for the nonradiative process of Alq₃, due to the larger geometric confinement effect and site-isolation effect of the wormlike mesoporous nanocomposites formed at higher temperature compared with the ordered channels.²¹

Contrary to the common method that fac-Alq₃ is formed by the solid-state phase conversion at temperatures above 653 K,^{5,6,10} the present formation method of fac-Alq₃ is in-

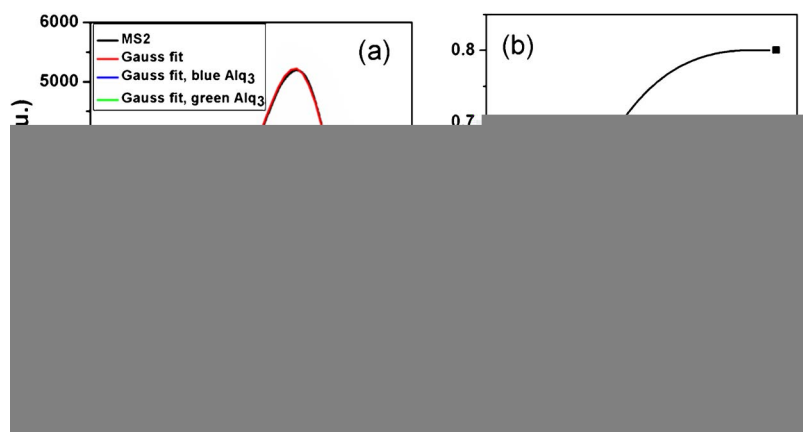


FIG. 3. Gaussian fits of the PL spectra of the nanocomposite MS2 (a). Variation of the relative PL integral intensity proportion I_{bi}/I_{gr} vs the preparation temperature (b).

triguing that it works from the solution and the samples are never treated at such high temperatures. It has been reported that the energy needed for this isomerization was small in solution based on NMR studies, which indicates that the fac-to-mer-Alq₃ isomerization can occur rapidly at the temperature below 373 K.^{22,23} In addition, this isomerization in solution is temperature dependent, and an interval temperature of 10 K improves significantly the isomerization efficiency.²³ Hence, it is reasonable to assume that the fac-Alq₃ molecules existed in the inner hydrophobic cores of the micelles can become the preferred form during the self-assembly process because of the thermal energy transfer. A simple idea developed here is to stabilize this already transformed fac-Alq₃, in which the mesoporous silica with well-defined nanopores and rigid frameworks is selected as a promising candidate for such application, since it generally shows better quantum and spatial confinement effects.²⁴ This inorganic host can provide a physically confined microenvironment to stabilize the transformed fac-Alq₃ molecules, which also matches the features highlighted by Levichkova *et al.*, who recently demonstrated that the fac-Alq₃ transformed through a local overheating in vacuum processes can be maintained in a SiO₂ matrix.¹² Therefore, the more transformed fac-Alq₃ molecules in the nanocomposites at higher preparation temperature could be attributed to the higher isomerization efficiency and better physical confinement effects of the formed host mesostructures.

The functional materials formed here combine the interesting change of physicochemical property and guest-structuring mechanisms produced by confinement in well-defined mesopore structures. For a control experimental, we dispersed Alq₃ among 50 nm SiO₂ nanoparticles with the same Alq₃ content as the nanocomposites through an evaporation-induced method at various temperatures. Both

the obvious maximum luminescence blueshift and the pronounced temperature-dependent PL efficiency enhancement were not observed in this Alq₃/SiO₂ dispersion, which further confirm the importance of the confinement effects of the host mesostructure.

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TABLE I. PL decay analysis data of the pristine Alq₃ and the nanocomposites.

Sample	Lifetimes (ns)		Relative weights (%)	
	τ_1	τ_2	$\tau_1 : \tau_2$	χ^2
Alq ₃	18.4			1.21
MS1	11.3	3.0	83:17	1.19
MS2	12.3	3.8	77:23	1.25
MS3	13.5	4.4	75:25	1.29