

# Variable self-assembled micronanostructures of Bis(8-hydroxyquinolato)-urushiolato Aluminum (III) by the reverse breath figure method

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A novel urushiol-based complex bis(8-hydroxyquinolato)-urushiolato Aluminum (III) (AIUQ<sub>2</sub>) has been successfully synthesized and characterized by FT-IR and Elemental analysis. The optical properties are investigated by UV-Vis and fluorescent spectra, and the result shows it emits green light with the wavelength at about 520 nm. The self-assembled ordered structures formed by layered nano-rods with the diameter of approximate 100 nm and the length of 300 nm via the reverse breath figure method, can be observed by SEM. By changing different solvents and vapor atmosphere, the micronanostructures of AIUQ<sub>2</sub> with variable morphology can self-assemble, obtaining dispersed nano-plates and aggregated nano-rods.

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## 1. Introduction

On the basis of different noncovalent interactions such as van der Waals, electrostatic interactions, hydrogen bonds, stacking interactions and metal-ligand coordination, a wide variety of micronanostructures like fibers, rods, sheets, cubes and tubes, have been fabricated with functional organic molecules by self-assembly process [1-5]. It is relatively significant for developing advanced functional molecular materials as well as nanoscale optoelectronic and biological devices [6]. The number of carbon atoms is a key parameter in obtaining highly ordered structures [7]. However, the yields of compounds with long-chain alkyl groups are usually relatively poor with most of the precursors from petroleum derivatives wasted. As abundant, renewable biomass derivatives, urushiol is a mixture of several closely-related organic compounds, consisting of catechols substituted with a saturated or unsaturated alkyl chain that has about 15 carbon atoms. And urushiol could be an alternative raw material to self-assemble micronanostructure [8]. Recently, the formation of self-assembled monolayer and multilayer using urushiol as material has been examined [7,9]. Because of the excellent luminescent property, the aluminum complexes based on the quinoline ligands have been developed useful emissive materials [10]. 8-hydroxyquinoline introduced as the second ligand, the aluminum complex based on the active phenolic hydroxyls of urushiol not only has luminescent property, but also can self-assemble micronanostructures. Herein, we have designed and synthesized a novel urushiol-based complex: bis(8-hydroxyquinolato)-urushiolato-Al(III)

(AIUQ<sub>2</sub>, shown in Fig. 1), which has the optical properties of green light emitting in the fluorescence spectra. With the reverse breath figure method [11], the AIUQ<sub>2</sub> micronanostructures of variable morphology can self-assemble in different solvents and vapor atmosphere.

## 2. Experimental

### 2.1. Materials

Urushiol was extracted by acetone method [12] from the lacquer (Maoba, China); anhydrous ethanol was prepared by refluxing and then distilling ethanol over magnesium with iodine as catalyst; aluminum iso-propoxide, 8-hydroxyquinoline, methanol, dichloromethane and chloroform were purchased from commercial sources (C.P.) without further purification.

### 2.2 Preparation

AIUQ<sub>2</sub> was synthesized based on literature [13,14] as shown in Fig. 1. A mixture of aluminum iso-propoxide (0.204 g, 1.0 mmol) and anhydrous ethanol (40 ml) was added into a 150 mL 3-necked flask equipped with a reflux condenser and a gas inlet tube. Under nitrogen atmosphere, the solution of anhydrous ethanol containing 8-hydroxyquinoline (0.145g, 1.0 mmol) was added dropwise from a constant-pressure dropping funnel with stirred rapidly over 1h under the reflux condition. Then the mixture of 8-hydroxyquinoline (0.145g, 1.0 mmol) and urushiol (0.345 g, 1.1 mmol) was dropped slowly. After vigorous stirring for 6 h under the reflux condition, the

reaction mixture was allowed to cool down and separated by centrifugation. Washed by water and ethanol, the brown-green powders were obtained (0.473g, 75.3% yield).

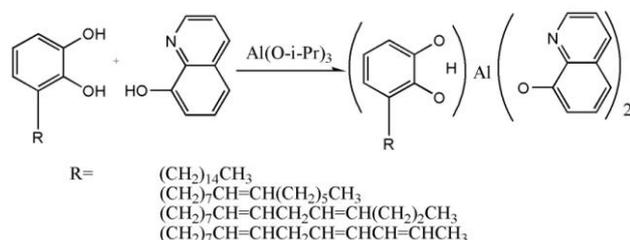


Fig. 1. Synthetic route of AlUQ<sub>2</sub>.

Through the reverse breath figure process [11], the self-assembled structures were formed as follows. AlUQ<sub>2</sub> was dissolved in solvents such as CHCl<sub>3</sub> and CH<sub>2</sub>Cl<sub>2</sub> with the concentration of 10 mg/mL. With a microsyringe, a drop of the solution was cast onto a glass slide in a static nonsolvent vapor atmosphere such as distilled H<sub>2</sub>O and MeOH. A thin layer was obtained on the substrate after the complete evaporation of solvent at room temperature.

### 2.3 Characterization

IR spectrum was recorded on a Nicolet 5700 FT-IR with KBr pellet. Elemental analysis was taken on a vario EL-III elemental analyzer. The content of Al was determined by ultraviolet spectrophotometry while the aluminum ion was obtained by the ash method [15]. The absorption spectra were recorded on a Varian Cary 50 Bio UV-Vis Spectrophotometer and the fluorescence spectra were obtained on a Hitachi F-7000 fluorescence spectrophotometer with CH<sub>2</sub>Cl<sub>2</sub> as the solvent. The morphology of samples was characterized by Scanning electron microscope (SEM) with a JSM-7500F instrument operating at 15 kV.

### 3. Results and discussion

There are bands around 3377, 2966, 2924 and 2853 cm<sup>-1</sup> corresponding to the O–H vibration and saturated C–H vibration, which belongs to the groups of urushiol in the FT-IR spectrum of AlUQ<sub>2</sub>. The bands at 1603, 1580, 1500, 1468 and 1428 cm<sup>-1</sup> are assigned to the aromatic rings of urushiol and quinoline rings. The IR peak at 419 cm<sup>-1</sup> can be assigned to the Al–N stretching vibration, while the peaks at 458, 558 and 751 cm<sup>-1</sup> can be assigned to Al–O stretching vibrations.

As urushiol is a mixture of 3-substituted catechols with saturated and unsaturated side chains as scheme 1 shown, the average of side chains is –C<sub>15</sub>H<sub>27</sub>. The molecular formula of AlUQ<sub>2</sub> could be written as C<sub>39</sub>H<sub>43</sub>O<sub>4</sub>N<sub>2</sub>Al. By the elemental analysis, C was found 75.02 (calc. 74.55%) with H, 6.51% (calc. 6.89%) and N,

4.50% (calc. 4.46%). By the ash method, the content of Al was determined to be 3.10% (calc. 3.23%). The structure of AlUQ<sub>2</sub> can be confirmed.

The UV-Vis absorption spectrum of AlUQ<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> exhibits two main bands (the left line) in Fig. 2, the maximum of which is located in 260 nm attributed to the π–π\* transitions of aromatic ring, and the long wavelength band of 380 nm attributed to the absorption of the ligand-centered π–π\* transitions. The fluorescence spectrum of AlUQ<sub>2</sub> is shown in Fig. 2 (the right line). When excited at 379 nm, AlUQ<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution exhibits green luminescence with the fluorescence emission maximum at about 520 nm.

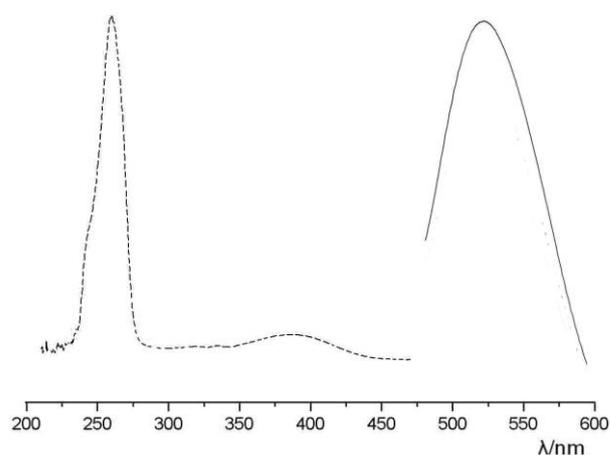


Fig. 2. UV-Vis absorption and fluorescence emission spectra of AlUQ<sub>2</sub>.

The morphology of the self-assembled structures by the reverse breath figure method was characterized by SEM. Fig. 3a shows the image of the self-assembled structures formed by the AlUQ<sub>2</sub> in CHCl<sub>3</sub> dropped in the H<sub>2</sub>O vapor atmosphere. The ordered layered structure can be observed clearly and each layer is made up of the nano-rods with the diameter of 100 nm and the length of 300nm approximately. The self-assembly of the nano-rods may be attributed to these reasons: 1) the bipolar structure of AlUQ<sub>2</sub> in the condition of the H<sub>2</sub>O vapor atmosphere, 2) the entanglement of the hydrophobic long side chain of the urushiol, 3) the hydrogen bonding interaction between the uncoordinated phenolic hydroxyl of the urushiol and H<sub>2</sub>O, 4) π–π interaction between the aromatic rings of hydroxyquinoline and urushiol, 5) the interaction between CHCl<sub>3</sub> solvent and AlUQ<sub>2</sub> [16]. Whereas the adhesions of spherical structure in Fig. 3b could be observed with the AlUQ<sub>2</sub> in CHCl<sub>3</sub> dropped in the MeOH vapor atmosphere, which could be the result of a solvation of the side chains of urushiol with MeOH atmosphere. When the solvent is replaced by CH<sub>2</sub>Cl<sub>2</sub>, the dispersed nano-plated structures with the diameter of 100-200 nm can be formed in the H<sub>2</sub>O vapor atmosphere as shown in Fig. 3c. While dropped in the MeOH atmosphere, the adhesions of plated

structures could be formed again as shown in Fig. 3d for the solvation as shown in Fig. 3b. These results show that in addition to the hydrogen bonding interaction and  $\pi$ - $\pi$  stacking between molecules, the influences of the solvent and the vapor atmosphere play an important role in controlling and tuning the morphology of aggregated micronanostructures in the self-assembly process.

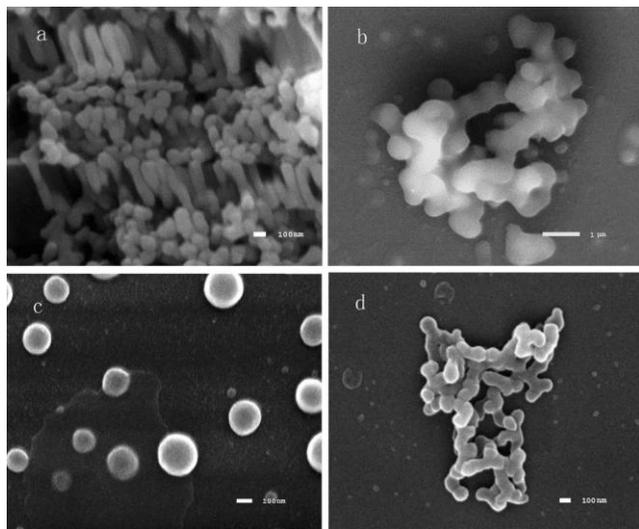


Fig. 3. SEM images of micronanostructures of AlUQ<sub>2</sub>.

#### 4. Conclusions

We have successfully synthesized urushiol-based complex AlUQ<sub>2</sub>. The optical properties are investigated with the result that the emission wavelength is about 520 nm. By changing the solvents and the vapor atmosphere, the micronanostructures of AlUQ<sub>2</sub> with variable morphology can be self-assembled via the reverse breath figure method. The ordered structure can be formed as layered nano-rods and dispersed nano-plates.

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