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## Luminescent hybrid materials based on zeolite L crystals and lanthanide complexes: Host–guest assembly and ultraviolet–visible excitation



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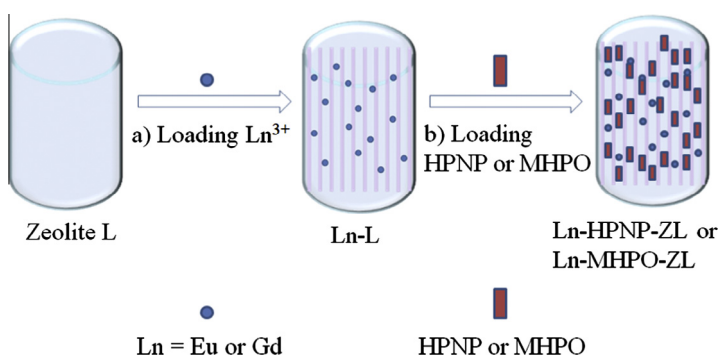
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### HIGHLIGHTS

- Novel kinds of lanthanide complexes are assembled with zeolite L.
- Wide excitation covering ultraviolet and visible region.
- Luminescence color integration.

### GRAPHICAL ABSTRACT

Host–guest hybrids are assembled with a ship in a bottle method by loading 9-hydroxy-2-methylphenalenone (MHPO) or 9-hydroxyphenalen (HPNP) from gas phase into the nanochannels of  $\text{Ln}^{3+}$ -exchanged zeolite L crystals.



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### ABSTRACT

Several kinds of host–guest hybrid materials have been synthesized employing a ship in a bottle method by loading 9-hydroxy-2-methylphenalenone (MHPO) or 9-hydroxyphenalen (HPNP) from gas phase into the nanochannels of  $\text{Ln}^{3+}$ -exchanged zeolite L (ZL) crystals ( $\text{Ln} = \text{Gd}$  or  $\text{Eu}$ ). The resulting hybrids without lanthanide ions, MHPO–ZL, HPNP–ZL and the hybrids with lanthanide ions  $\text{Ln}$ –MHPO–ZL and  $\text{Ln}$ –HPNP–ZL are characterized with FT-IR, UV–vis DRS and photoluminescence spectroscopy. The photoluminescence properties of these hybrid materials have been analyzed and discussed, exhibiting the luminescence of  $\text{Eu}^{3+}$  and ligands under the excitation at ultraviolet–visible region. These results provide useful data and can be expected to have potential application in the practical fields.

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### Introduction

Because of the protection and isolation effect of the zeolite framework and space restriction effect of the zeolite nanopores, it is possible to load the nanoclusters, dye and complexes guest

species to nanopores to assemble new host–guest materials, where functional species show superior performance in the zeolite pores [1–4]. Zeolite microporous crystalline materials play an increasingly important role in the host–guest assembly chemistry, which has shown great potential for practical application fields [5,6]. Recently, lanthanide complexes are assembled in zeolite L (ZL) nanopores, which are of particular interest in the area of novel materials due to the fascinating luminescence properties of

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lanthanide ions. This has been regarded as novel kind of photo-functional materials toward specific goals for some applications such as optoelectronic devices and sensors [7–12].

ZL is a crystalline hexagonal aluminosilicate with a rigid three-dimensional framework of tetrahedral  $[\text{AlO}_4]^{5-}$  and  $[\text{SiO}_4]^{5-}$  primary building units, which are connected by oxygen bridges and thus give rise to 12-membered rings. These units consist of cancrinite cages ( $\epsilon$ -cage) linked by double 6-rings (D6R). As a consequence, ZL contains of one-dimensional channels running along the  $c$ -axis of the hexagonal crystals [13]. Zeolite has a high thermal stability, and its skeleton's vibration frequency is low [14,15]. So it is a good host to load organic dye molecules to assemble dye–zeolite hybrids. There is free Si–OH groups on the ZL surface, as a result, ZL is easily functionalized with targeting groups. Besides, the surfaces of ZL can also be easily chemically modified and the zeolite channels can be conveniently entrapped inside [16,17].

Recently, lanthanide organic complexes have successfully been inserted into the perfect one-dimensional channels of ZL crystals, which has been known as “ship in a bottle” method [18,19]. A marked enhancement of the thermal stability, photo stability and mechanical properties of the incorporated complexes has been achieved. Thus, the assembly of uniformly oriented monolayers of zeolite microcrystals have been prepared, which can be also fabricated into monolayers with tunable luminescence by a functional linker [20,21]. Moreover, lanthanide organic complexes of lanthanide ions and organic ligand incorporated into the channels of ZL are recently reported [22,23]. Less attention, however, has been paid to the insertion of lanthanide organic complexes into the channels of ZL with currently to be only nanopores material adjustable in a large range.

In this work, FT-IR, UV–vis DRS and photoluminescence spectroscopy are used to characterize the properties of ZL and lanthanide ion exchanged zeolite L etc. Four novel hybrid materials Ln–MHPO–ZL and Ln–HPNP–ZL (Ln = Gd, Eu) equipped with special luminescent properties have been assembled firstly. Full physical characterization and detailed luminescence properties of all these materials are analyzed and compared in detail.

## Experimental section

### Materials

Zeolite L crystals were synthesized with sodium hydroxide (Aladdin), potassium hydroxide (Aladdin), sodium metaaluminate (Aladdin), colloidal silica (Ludox HS-40, Aladdin) and deionized water.  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  (Ln = Eu, Gd) were obtained by dissolving their oxides ( $\text{Eu}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$ ) in concentrated nitric acid. The synthesis of 9-hydroxy-2-methylphenalenone (MHPO) was prepared with the method in Ref. [24] and 9-hydroxyphenalen (HPNP) was synthesized with the procedure in Ref. [25].

### The synthesis of ZL

ZL crystals were synthesized hydrothermally from aqueous mixtures of materials above-mentioned. The molar compositional ratio of the resulting gel was 5.7  $\text{Na}_2\text{O}$ :5.4  $\text{K}_2\text{O}$ :1  $\text{Al}_2\text{O}_3$ :30  $\text{SiO}_2$ :500  $\text{H}_2\text{O}$ . Calculated amounts of sodium hydroxide, potassium hydroxide and sodium metaaluminate were added to a certain amount of deionized water being stirred vigorously for 0.25–1 h at room temperature to prepare sodium and potassium aluminate solution. Afterwards, milk-like mixture was further aging for 2 h at room temperature in the reactor. The mixture was then transferred into a PTFE-lined autoclave and placed in an air-heated oven at 443 K for 24 h. Before opening, PTFE-lined autoclave was cooling

with ice water for 1 h. The white product was separated by centrifugation, and washed with boiling deionized water to pH = 7. After being dried in oven at 373 K for 16 h, the final ZL crystals was obtained.

### The synthesis of HPNP

2-Methoxynaphthalene (1.58 g, 0.01 mol) and cinnamoyl chloride (1.66 g, 0.01 mol) were dissolved in 100 mL dichloromethane. After the reactant was dissolved and the reaction flask was cooled in an ice bath, aluminum chloride (1.35 g, 0.052 mol) was slowly added to the flask with mechanically stirring. After about 0.5 h when the reaction had come to room temperature, a further 7.3 g (0.055 mol) of aluminum chloride was added to the solution, and the reaction mixture was heated to reflux for 3 h. Ice hydrochloric acid was added to the mixture, and the mixture was filtered. The solid was repeatedly boiled with hot methylene chloride and filtered till the filtrate became colorless. The total organic extracts were combined, dried over anhydrous sodium sulfate, and taken down on a rotary evaporator to obtain a yellow solid. The product was purified by two sublimations followed by a recrystallization from ethanol to yield yellow needles. The yield was 58%. For HPNP:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ):  $\delta$  16.06 (H, s, OH),  $\delta$  8.15 (H, d),  $\delta$  8.13 (H, d),  $\delta$  8.07 (H, d),  $\delta$  8.05 (H, d),  $\delta$  7.64 (H, t),  $\delta$  7.23 (H, d),  $\delta$  7.21 (H, d).

### The synthesis of MHPO

2-Methoxynaphthalene (10.00 g, 0.063 mol) and  $\alpha$ -methylcinnamic acid (10.25 g, 0.063 mol) were dissolved in 100 mL of dichloromethane, after the reactant was dissolved, phosphorus pentachloride (13.12 g, 0.063 mol) was added, and the mixture was taken to reflux for 5 min. Aluminum chloride (8.40 g, 0.063 mol) was slowly added to the reaction flask with mechanically stirring after the flask was cooled in an ice bath, after which the mixture was heated to reflux for 10 min. A further aluminum chloride (8.40 g, 0.063 mol) chloride was added to the solution, which was taken to reflux for 12 h. Then the mixture was quenched with ice hydrochloric acid, and the organic layer was washed with water and dried with sodium sulfate. The solvent was removed and the residue was mixed with aluminum chloride (25.20 g, 0.189 mol), and then the flask was immersed in an oil bath for 1 h with stirring, which had been preheated to 180 °C. The reaction mixture was poured into iced hydrochloric acid, and then 80 mL dichloromethane was added, the organic layer was washed with water and dried with sodium sulfate. The mixture was handled by rotary evaporation to give black oil. The final product was purified by sublimations to obtain yellow needles, yield 64%. For MHPO:  $^1\text{H NMR}$  ( $\text{CDCl}_3$ ,  $\text{Me}_4\text{Si}$ ):  $\delta$  16.27 (H, s, OH),  $\delta$  8.01 (H, d),  $\delta$  7.90 (H, d),  $\delta$  7.85 (H, d),  $\delta$  7.82 (H, s),  $\delta$  7.51 (H, t),  $\delta$  7.13 (H, d),  $\delta$  2.36 (3H, s,  $\text{CH}_3$ ).

### The preparation of HPNP–ZL and MHPO–ZL

HPNP–ZL and MHPO–ZL were synthesized by the method of “ship in a bottle”. ZL was dried and degassed for 1 h at 423 K, and then it was exposed to the HPNP or MHPO vapor at 453 K for 18 h. The product was washed with dichloromethane until the filtrate became colorless, and then dried at 313 K under vacuum (see the scheme in Fig. 1).

### The preparation of Ln–ZL, Ln–HPNP–ZL and Ln–MHPO–ZL

The ZL– $\text{Ln}^{3+}$  samples were prepared by ion-exchange. 100 mg of ZL was stirred in 20 mL of a 0.05 or 0.10 mol/L aqueous solution of  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  (Ln = Gd, Eu) for 12 h at 353 K. The products were collected by three times of centrifugation, and then washed with

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