



Layer-by-layer assembly of ordered organic–inorganic luminescent film toward sensing nitrobenzene compound



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ABSTRACT

Luminescent film materials sensitive to pollutions are important to develop new types of optical sensors toward environmental detection. Herein we report organic–inorganic hybrid thin films (TFs) with reversible luminescence response to the volatile nitrobenzene (NB) using layer-by-layer (LBL) assembly of fluorescent brightener CXT and Mg–Al-layered double hydroxide (LDH) nanoparticles. The structural and surface morphology studies show that the TFs are continuous and uniform with stacking order in the normal direction of the substrate. AFM and SEM measurements indicated that the films feature periodic structure with a period of *ca.* 25 nm as well as uniform surface morphology. Moreover, the CXT/LDH TF displays a high luminescent response as a fast colorimetric chemosensor for NB vapor with a low detection limit (4.02 ppb), good regeneration and high selectivity. In addition, by combining suitable luminescent building blocks, the films can also be extended to other two-color luminescence systems, which exhibit changes in both luminescence intensity and ratiometric fluorescence upon interaction with NB vapor, suggesting that these films can serve as new types of selective solid luminescent sensor. Therefore, this work supplies a facile LBL strategy for the fabrication of TFs as selective luminescent sensor for the trace detection of NB.

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1. Introduction

Recently, the pollutions existing in the air, water and soil have a serious influence on the environment and the survival of human race. For example, the organic pollutions (such as polycyclic aromatic hydrocarbons) in wastewaters can cause serious environmental problems [1]. In addition, these globally distributed environmental contaminants pose a severe threat to the human health and animals' exist even at a trace level, because they are non-biodegradable and can accumulate in the food chain [2,3]. Therefore, from both academic and engineering perspectives, it is still a challenge to achieve the timely and fast trace detection of the pollutions in the environment. The volatile organic compounds (VOCs) can be one of the most serious pollutants in the air and water, and the development of efficient sensors and methods for the detection of VOCs has received much attention [4–6].

Nitrobenzene (NB) is a highly toxic VOC and chemical intermediate, which is widely used in many fields, such as the pharmaceutical, pesticide, explosive and dye industry. At the same time, NB has a serious impact on the environment and the people's health. To meet the needs of environment protection and public health, it is highly desirable to develop a simple and rapid method for highly sensitive and selective determining NB in the environment. Several analytical methods have been developed for the sensitive detection of nitroaromatic compounds, for instance, chromatography, amperometry, surface-enhanced Raman spectroscopy, energy dispersive X-ray analysis, *etc.* [7–10]. However, the expensive and complicated manipulation is the main bottle-neck for the popularization of these methods. As an alternative detection approach, fluorescence-based sensor has also been paid increasing attention, because it is a highly sensitive, convenient, and cost-effective method. In this sense, molecule-based luminescent materials have recently become good candidates to achieve effective detection, based on the selective quenching effects of luminescence induced by the nitroaromatic compounds.

Fluorescent chemosensors have experienced a great development during the last one decade because of their important applications in many areas, particularly in medical diagnostics,

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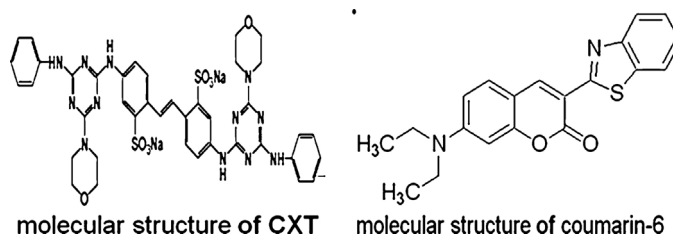
environmental control, and material science [11–13]. Recently, several studies have moved toward complex and sophisticated structures, with the aim to exceed their limits of sensitivity and selectivity. As well, many solution or powdered systems have been proposed, while this is unfavorable for their facile manipulation and cycling utility. Moreover, most of the luminescent solution systems can also result in environmental pollution and even operational risk, which is detrimental to human health. Therefore, the development of promising sensing systems based on new types of solid luminescence is required to integrate high selectivity and easy operation.

Nowadays, the fabrication of supramolecular inorganic–organic hybrid materials with ordered nanostructure has attracted much attention because their new functionalities generally differ from those of the pristine components, as the results of host–guest interactions [14]. Layered double hydroxides (LDHs) are a large class of two-dimensional (2D) host materials, which can be described by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{2+}A^{n-}_{z/n} \cdot yH_2O$ (M^{II} and M^{III} are divalent and trivalent metals respectively; A^{n-} is the anion) [15–17]. Recently, the LDH nanoparticles can serve as promising building blocks for the preparation of functional organic–inorganic thin films (TFs) through layer-by-layer (LBL) assembly [18–20]. Several examples show that the immobilization of luminescent molecules within a confined LDH film exhibited enhanced photoluminescent performance, which is absent in solution and favorable for their application as solid luminescent materials [21–23]. The previous works have mainly studied on the structures and static photophysical properties of LDH films, whereas little attention has been paid on the dynamic and reversible fluorescence response of the films to the analytes, especially for VOCs. In addition, from the perspective of the molecule species, the LBL assembly of LDH nanoparticle with neutral molecule has little been reported due to the absence of electrostatic interaction. In this work, we chose anionic benzenesulfonate, 2,2'-(1,2-ethenediyl)bis[5-[[4-(4-morpholinyl)-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt (named as fluorescent brightener CXT, shown in Scheme 1) and neutral molecule (coumarin-6, shown in Scheme 1) as guests to fabricate new type of organic–inorganic hybrid TF systems via LBL method. The resulting CXT/LDH TFs show long range ordered structures. Furthermore, it was also found that the luminescence of the TFs is selectively sensitive to the volatile NB with different concentrations. Moreover, the CXT@coumarin-6/LDH TF systems with dual-color emission have also been fabricated, which show changes in ratiometric fluorescence upon interaction with NB. Therefore, this work provides a facile method for the fabrication of TFs with one-/two-color luminescence by the incorporation of photoactive chromophores within a 2D LDH host matrix, which can also be applied as a luminescent sensor for the selective detection of NB.

2. Experimental

2.1. Materials

3-(2'-Benzothiazolyl)-7-diethylaminocoumarin (coumarin-6, 98%) were purchased from J&K Chemical Co. Ltd. Benzenesulfonate, 2,2'-(1,2-ethenediyl) bis 5-[[4-(4-morpholinyl)-6-(phenylamino)-1,3,5-triazin-2-yl]amino]-, disodium salt (CXT, 99%) was purchased from Hebei Sanchuan Chemical Co. Ltd. Analytical grade chemicals including $Mg(NO_3)_2 \cdot 6H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, NaOH, nitrobenzene, *N,N*-dimethyl formamide (DMF), aether, ethanol, chloroform, cyclohexane, and trichloromethane were used without further purification. The deionized and decarbonated water was used in all the experimental processes.



Scheme 1. The molecular structures of the CXT and coumarin-6.

2.2. Synthesis of LDH colloidal nanoparticles

A colloidal LDH suspension was prepared according to the separate nucleation and aging steps (SNAS) method reported previously [24]. Typically, 70 mL of solution A (0.06 M of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.03 M of $Al(NO_3)_3 \cdot 9H_2O$) and 80 mL of solution B (0.18 M of NaOH) were simultaneously added to a colloid mill with a rotor speed of 3000 rpm and mixed for 1 min. The resulting LDH slurry was obtained via centrifugation and washed with water and then dispersed in 400 mL of deionized water. The aqueous suspension was transferred into a stainless steel autoclave with a Teflon lining. After hydrothermal treatment at 110 °C for 24 h, a stable homogeneous MgAl–LDH suspension with a narrow size distribution can be obtained. The concentration of LDH colloidal particles used for the fabrication of the thin film materials was 0.10% (wt%). The XRD pattern of the resulting suspension is shown in Fig. S1 (Supporting information), which presents the characteristic diffraction peaks of Mg_2Al-NO_3 LDH.

2.3. Fabrication of (CXT/LDH)_n and (CXT@coumarin-6/LDH)_n TFs

A quartz glass substrate was first cleaned in concentrated $NH_3/30\% H_2O_2$ (7:3) solution and then concentrated H_2SO_4 for 30 min in each case. After each step, the quartz substrate was rinsed and washed thoroughly with deionized water. The substrate was dipped in a colloidal suspension (1 g/L) of LDH nanoparticles for 10 min followed by thorough washing, and then the substrate was immersed into 100 mL of aqueous CXT solution (1 g/L) for 10 min. Multilayer films of (CXT/LDH)_n were fabricated by alternate deposition of the suspension of LDH colloidal particles and the CXT solution for *n* cycles. The resulting films were dried under a nitrogen gas flow for 2 min at 25 °C. (CXT@coumarin-6/LDH)_n was prepared with the same process by the alternate assembly of LDH colloidal suspension (1 g/L) and the aqueous solution (100 mL) containing the mixed CXT (0.1 g) and coumarin-6 (0.001 g).

2.4. The response of the CXT/LDH and CXT@coumarin-6/LDH TFs toward the volatile NB and other VOCs

The VOCs (such as NB, DMF, aether, ethanol, chloroform, cyclohexane, and trichloromethane) with different concentrations were prepared by putting different quantities of VOC solutions into the hermetic gas bottles for a certain time to achieve liquid–gas equilibrium. The colorimetric chemosensor fixed into a standard quartz cell was immersed into the gas bottle filled with various VOCs for enough time, and then was observed under the irradiation of 365 nm with a UV lamp for the detection of the fluorescent color change. The fluorescence measurement was also performed.

2.5. Sample characterization

UV–vis absorption spectra were collected in the range from 200 to 700 nm on a Shimadzu U-3000 spectrophotometer, with a slit width of 1.0 nm. The fluorescence spectra were recorded on a RF-5301PC spectrofluorophotometer with an excitation

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