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Photofunctional hybrids of lanthanide functionalized bio-MOF-1 for fluorescence tuning and sensing

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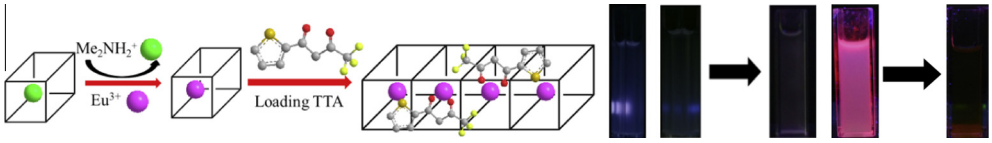
GRAPHICAL ABSTRACT



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ABSTRACT

A series of luminescent Ln^{3+}@bio-MOF-1 (Ln = Eu, Tb, bio-MOF-1 = $Zn_8(ad)_4(BPDC)_6O{\cdot}2Me_2NH_2$ (ad = adeninate, BPDC = biphenyldicarboxylate)) are synthesized via postsynthetic cation exchange by encapsulating lanthanide ions into an anionic metal–organic framework (MOF), and their photophysical properties are studied. After loading 2-thenoyltrifluroacetone (TTA) as sensitized ligand by a gas diffusion ("ship-in-bottle") method, it is found that the luminescent intensity of Eu^{3+} is enhanced. Especially, when loading two different lanthanide cations into bio-MOF-1, the luminescent color can be tuned to close white (light pink) light output. Additionally, bio-MOF-1 and Eu^{3+}@bio-MOF-1 are selected as representative samples for sensing metal ions. When bio-MOF-1 is immersed in the aqueous solutions of different metal ions, it shows highly sensitive sensing for Fe^{3+} as well as Eu^{3+}@bio-MOF-1 immersed in the DMF solutions of different metal ion. The results are benefit for the further application of functionalized bio-MOFs in practical fields.

1. Introduction

Trivalent lanthanide ions have special photoactive properties such as sharp emission spectra for high color purity, broad emission bands covering ultraviolet–visible–near infrared region, a wide range of lifetimes from microsecond to second, and high luminescence quantum efficiencies. These advantages make them to have practical applications such as lighting devices and biomedical analysis [1–3]. However, the f–f transitions of lanthanide ions are spin forbidden so that it is difficult to generate efficient luminescence emission by direct excitation. In order to solve this trouble, the common method is to dope lanthanide ions into special matrices [4,5] or coordinate to organic ligands [6,7]. For the latter, luminescent lanthanide complexes possess the poor stability, which limits their practical application [6,7].

Inorganic–organic hybrid materials combine inorganic and organic components at a molecular or nanometer scale, which provides certain strong points of organic compounds with the advantages of inorganic components [8–11]. Moreover, the composition of hybrids may realize the functional integration to produce new property for application, which is particularly benefit for photofunctional fields [12]. To presence, the chemically bonded hybrids have attracted great interest for their advantage for strong interactions such as covalent, ion–covalent, coordination and Lewis acid/base bonds [13–16]. And the focus has shifted to the introduction of crystalline building blocks into hybrid systems to combine inorganic–organic hybrids and nanocomposites, which can show the luminescence behaviors of both inorganic phosphors and molecular materials [17–20]. So far, two important applications

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have been developed: one is as sensors or labels in biomedicine [21], which depends on controlling the scale and structure of the hybrids; the other is luminescent devices, depending on the preparation technology and functional integration [22].

Metal–organic frameworks (MOFs) are an important class of hybrid inorganic–organic materials [23,24], which have emerged as promising hybrids in many areas of gas sorption, catalysis, separation, drug delivery, luminescence sensor and biological-imaging [25–27]. MOFs belong to inorganic–organic hybrid solids with porous crystalline structures and can be synthesized with a wide range of metal ions and organic ligands [28]. The versatile choice of metal ions and organic ligands as building blocks provides the great potential to embody unique performance for their host–guest interactions within the framework [29]. Besides, MOFs display a wide range of luminescent performance resulting from the multifaceted nature of their structure [30]. The hybrid nature of MOF materials involves both an organic ligand and a metal ion within the special porous structure [31,32]. This enables a wide range of emissive phenomena to be found, which is classified by Allendorf and Bauerin according to the luminescence origin: linker-based luminescence, the coordinated metal ions based luminescence, antenna effects for energy transfer and sensitization luminescence, excimer and exciplex formation emission, and so on [33].

It is worthy pointing out that luminescent lanthanide ions are emphasized in MOF based hybrid materials. Lanthanide ions themselves behave as the central metal ions to form all kinds of luminescent MOFs [34,35]. On the other hand, lanthanide ions also can be fabricated to MOFs as an active species to form luminescent lanthanide functionalized MOFs [36–39]. In both of the two kinds of MOFs based hybrid materials, the introduction or existence of lanthanide ions make the whole hybrid system possess complicated, possibly involving inker-based, metal-based luminescence, antenna effects luminescence or guest molecule luminescence [34–39]. Besides, lanthanide species can compensate with MOFs or ligands as the luminescent species for their different luminescent region, which is favorable for tuning multi-color and integrating white color emission [40–43].

Bio-MOFs, metal-adeninate organic frameworks reported by Rosi's group are appealing candidates for practical applications because of their permanent microporosity, high surface areas and chemical stability due to the presence of basic bio-molecule building units [44]. In particular, $Zn_8(ad)_4(BPDC)_6O{\cdot}2Me_2NH_2$ (where ad = adeninate, BPDC = biphenyldicarboxylate, denoted as bio-MOF-1), which are interconnected via biphenyl-dicarboxylate linkers [45], which can be further functionalized via post-synthetic cation exchange of luminescent lanthanide ions [46].

In this paper, considering the possibility of the functionalization of bio-MOF-1 exchanged by lanthanide ions, we want to prepare the lanthanide ion modified bio-MOF-1 by ionic exchange and further introduce some ligands (TTA) by gas diffusion ("ship-in bottle") to improve the luminescence firstly. Then we try to tune the luminescence color and even integrate the close white luminescence. Moreover, we study the application of lanthanide functionalized bio-MOF-1 in the sensing of metal ions

2. Experimental section

2.1. Staring materials

Bio-MOF-1 was synthesized according to the reported procedure [45]. Solutions of $Tb(NO_3)_3{\cdot}6H_2O$ and $Eu(NO_3)_3{\cdot}6H_2O$ in acetonitrile were obtained by dissolving their oxides Tb_4O_7 and Eu_2O_3 in nitric acid, followed by evaporation and solvation in acetonitrile solvents. 2-Thenoyltrifluroacetone (99%, TTA, Adamas), N, N′-dimethylformamide (DMF, 99.9%, Aladdin) were used as received. All the other reagents are analytical pure and purchased from China National Medicines Group.

2.2. Preparation of Ln^{3+}@bio-MOF-1 and TTA-Eu^{3+}@bio-MOF-1

The loading of lanthanide ions onto bio-MOF-1 was performed by cation exchange [46]. The as-synthesized bio-MOF-1 was soaked in the acetonitrile solutions of Ln^{3+} nitrate: Eu^{3+} (1.8 mmol L^{-1}) and Tb^{3+} (5.0 mmol L^{-1}), respectively at 65 °C for 24 h. Then the resulting products were washed with ethanol three times and dried at 353 K under normal atmospheric conditions. In order to introduce TTA into Eu^{3+}@bio-MOF-1, we used an encapsulation method called "ship-in-bottle" by TTA gas diffusion, similar to modified zeolite. Eu^{3+}@bio-MOF-1 was kept in the vapor of TTA at 313 K for 12 h, whose choice of temperature depends on the sublimation of TTA. The resulting product was washed with acetonitrile, centrifuged twice and finally dried at 353 K under normal atmospheric conditions. The elemental analyses data were shown in supporting information.

Fig. 1 shows the selected scheme for the synthesis procedure of Eu^{3+}@bio-MOF-1 and the encapsulation of TTA with "ship-in-bottle" method. Through the cation exchange to functionalize bio-MOF-1, three kinds of visible light emissive lanthanide ions can be incorporated into bio-MOF-1 host [46]. Here the formation of $Me_2NH_2^+$ in bio-MOF system provide the possibility to realize the cation exchange reaction. After that, TTA ligand can be further introduced with a "ship-in-bottle' method used in the functionalization of Eu^{3+}@bio-MOF-1 [47]. The vapor diffusion of TTA ligand will coordinates to lanthanide ions in the pore of bio-MOF-1. Similarly to the method to synthesize Eu^{3+}-bio-MOF-1 hybrids, some metal ions can be introduced into solution of Eu^{3+} -bio-MOF-1, whose sensing property can be checked from the luminescent spectra of the mixed solution system.

2.3. Physical characterization

Fourier transform infrared spectra (FTIR) were measured with KBr slices from 4000 to 400 cm^{-1} using a Nexus 912AO446 infrared spectrum radiometer. The contents of Ln^{3+} ions (Ln = Eu, Tb) and Zn^{2+} in the hybrids were determined with ICP-AES. The elemental analyses of nitrogen element the hybrids are measured with a CARIO-ERBA 1106 elemental analyzer. X-ray powder diffraction patterns (XRD) were acquired on a D8 Foucs (Bruker) with Cu Kα radiation Field-emission; the data were collected within 2θ range

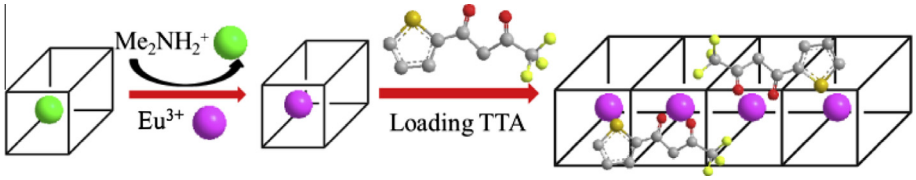

Fig. 1. The selected scheme for the synthesis procedures of Eu^{3+} functionalized bio-MOF-1 (Eu^{3+}@bio-MOF-1)) via cation exchange and the encapsulation of TTA with "ship-in-bottle" method.