



## Regular Article

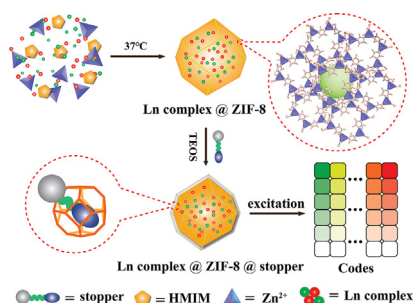
## Stable photoluminescence of lanthanide complexes in aqueous media through Metal-Organic Frameworks Nanoparticles with plugged surface



Feng Chen, Liucan Wang, Yuxin Xing, Jixi Zhang\*

Key Laboratory of Biorheological Science and Technology, Ministry of Education, College of Bioengineering, Chongqing University, No. 174 Shazheng Road, Chongqing 400044, China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## Article history:

Received 20 March 2018

Revised 11 May 2018

Accepted 11 May 2018

## Keywords:

Lanthanide complex

ZIF-8

Ionic liquid

Stopper

Stable photoluminescence

Aqueous media

## ABSTRACT

The photoluminescence stability of lanthanide complex in aqueous media is a prerequisite for diagnostics probes. The combination of building blocks working in concert to facilitate host–guest structures is now considered state of the art in surpassing this roadblock, yet there still remains a tremendous challenge. Here, a stable, highly-luminescent system was developed through trapping anionic complexes sensitized by tridentate pyridine-tetrazolate (pytz) ligands within the rigid framework of ZIF-8 (zeolitic imidazolate framework-8) particles (~60 nm in size). The key to maintaining the stable luminescence of lanthanide complexes inside ZIF-8 frameworks is a stopcock design, i.e. stopper molecules (an imidazolium based ionic liquid) selectively plugged on the pore entrances located at the exterior surface of the ZIF-8 host, which protect both the host and the guests from deteriorations by surrounding ions/water molecules. Remarkably, the obtained Ln complex encapsulated ZIF-8 particles (Ln = terbium, europium) particles possessed high quantum yields (23.2% and 8.5%), large absorption cross-section (~10<sup>-12</sup> cm<sup>2</sup>), and long luminescence lifetimes (1.9 and 3.0 ms) in PBS buffer. In addition, the system can realize single/multi-color encoding by altering the loading amounts and the weight ratios of complexes emitting at different wavelengths.

© 2018 Published by Elsevier Inc.

## 1. Introduction

Lanthanide-based complexes are very promising for efficient light conversion molecular devices, on account of their excellent luminescence features such as long lifetimes, large Stokes shifts

and narrow-band emissions, which are suitable for varying photoluminescence applications [1,2]. Notwithstanding these advantages, the luminescent intensity of lanthanide ions (Ln<sup>3+</sup>) is very sensitive to structural details of the coordination environment [3]. Notably, the luminescence of lanthanide complexes can significantly deteriorate through the quenching by water molecules or ions [4]. This is, however, the design rationale of the biosensors, bioanalytics on the basis of lanthanide doped/encapsulated

\* Corresponding author.

E-mail address: [jixizhang@cqu.edu.cn](mailto:jixizhang@cqu.edu.cn) (J. Zhang).

host-guest hybrid materials [1,5]. It has now become increasingly evident that the encapsulation of lanthanide complexes inside a host is typically preferred to develop imaging or diagnostics probes with stable luminescence [6,7]. Barcoded particle-based suspension biochips, for instance, require high photostability in biological media for precise recognition of different target biomarkers [8–10]. Unfortunately, work on enhancing aqueous luminescence properties of lanthanide complexes for the application in aqueous solutions, especially in biological media containing high concentrations of ions, is scanty and lacks, in most cases, generality.

For stable structure and controllable size, a lot of research has focused on the application of nanoparticles (NPs) incorporating lanthanide complex in optical materials such as polymer [11–13] and silica [14]. As multi-chromophore systems, these NPs are often brighter, resulting from the high number density of luminescent units per NP. To further enhance the loading capacity and realize homogeneous distribution, lanthanide complexes could be incorporated into various porous particles [15,16]. In the past decade, an intriguing type of supramolecular soft matter, i.e. metal-organic frameworks (MOFs) synthesized by assembling inorganic ions or clusters with organic ligands [17], is emerging as a promising porous material for constructing fluorescent/luminescent nanoparticles. A veritable explosion of research effort has occurred in the area of immobilizing organic fluorophores into the pore spaces and frameworks of MOFs [18], stemming from the minimized aggregation-caused quenching, strong host-guest interactions (such as  $\pi$ - $\pi$ , electrostatic, and van der Waals interactions) between ligands in MOFs and guest dyes, as well as high dye contents in the host [19].

It may then appear a bit surprising that very few studies, which aimed at utilizing MOFs as host matrices to stabilize and confine luminescent lanthanide complexes, have been performed up to now [20]. A critical obstacle for addressing the challenge concerns the diffusion of ions/water molecules in the porous network of MOFs, which was recently explored to show detrimental/damaging effects on the crystallinity and permanent porosity [21]. Despite smaller pore sizes (<2 nm) as compared with their mesoporous counterparts [15,16], the interwoven porous frameworks of MOFs are still permeable to small species, which makes the porosity become a double-edged sword for incorporating lanthanide complexes. Therefore, it is desirable to enhance the structural stability of MOFs in aqueous solutions, but at the same time, the excellent encapsulation capability of MOFs should remain unaffected.

Inspired by the stopcock designs in porous silica materials [22,23], and motivated by recent breakthroughs in the inclusion of ionic liquid (IL) in MOF [24–26], we herein present a system of host-guest composite nanoparticles with stably strong photoluminescence on the basis of zeolitic imidazolate framework-8 (ZIF-8). As illustrated in Fig. 1, anionic lanthanide (Ln) complexes sensitized by tridentate pyridine-tetrazolate (pytz) ligands, i.e. Ln (pytz)<sub>3</sub>, were encapsulated inside host ZIF-8 nanoparticles *in situ* during the particle formation. Subsequently, the pore entrances of the Ln complex encapsulated ZIF-8 nanoparticles (Ln complex@ZIF-8) were selectively plugged by modification of a stopper, i.e. an imidazolium based IL. The stopper possesses a silane head which can be crosslinked by an additional silica source (TEOS, tetraethyl orthosilicate) in alkaline ethanol.

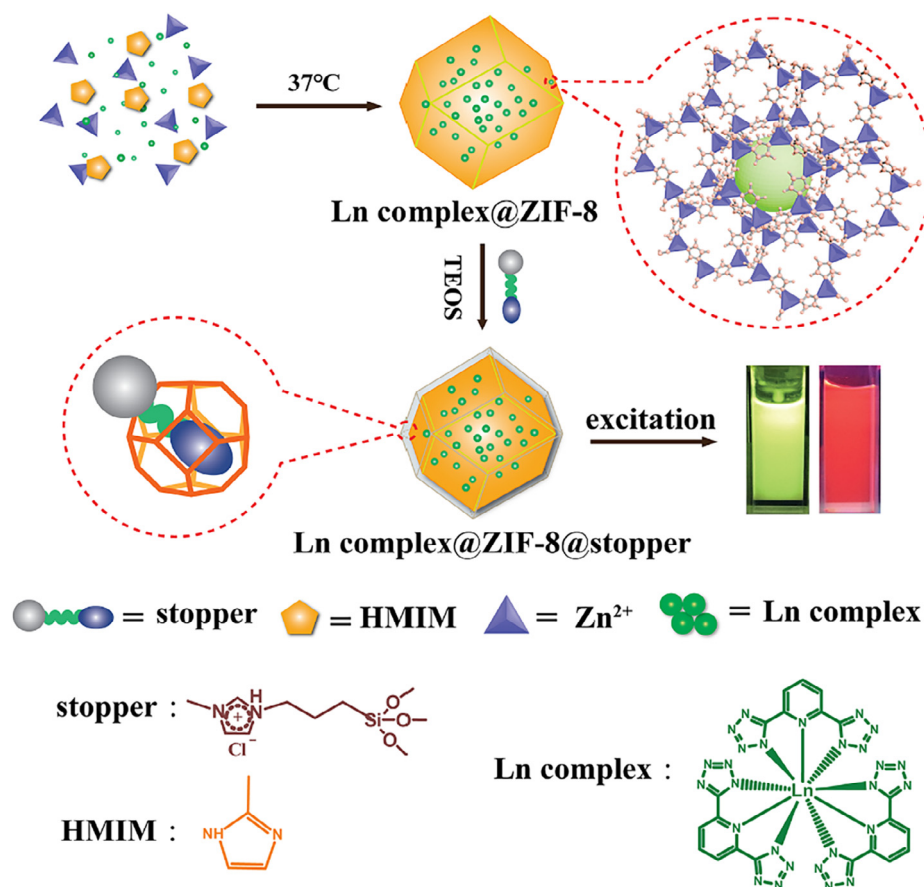


Fig. 1. Schematic illustration for the preparation of Ln complex@ZIF-8@stopper NPs.

Download English Version:

<https://daneshyari.com/en/article/6990133>

Download Persian Version:

<https://daneshyari.com/article/6990133>

[Daneshyari.com](https://daneshyari.com)