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Nanoscaled lanthanide/nucleotide coordination polymer for detection of an anthrax biomarker

Hongliang Tan*, Chanjiao Ma, Lili Chen, Fugang Xu, Shouhui Chen, Li Wang*

Key Laboratory of Functional Small Organic Molecule, Ministry of Education, College of Chemistry and Chemical Engineering, Jiangxi Normal University, Nanchang 330022, PR China

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ABSTRACT

The metal-organic coordination polymers as attractive functional nanomaterials have shown a promising potential in a variety of important applications. In this work, we employed a hydrophilic lanthanide/nucleotide coordination polymer constructed by spontaneous self-assembling of terbium ion (Tb^{3+}) and adenosine monophosphate (AMP) as a receptor platform for direct detection of anthrax biomarker (dipicolinic acid, DPA) in aqueous solution. Due to the coordination of DPA with Tb^{3+} on the surface of the AMP/Tb, significant enhancement in the fluorescent intensity of the coordination polymer (AMP/Tb) was obtained. The enhanced fluorescence intensity of AMP/Tb displayed a good linear response to DPA concentrations in the range from 20 nM to 20 μM with a detection limit of 10 nM. As a kind of DPA sensor, the AMP/Tb also showed excellent selectivity. Compared with conventional receptor platforms based on molecular lanthanide compounds, the presented receptor platform has an advantage of allowing simple, direct analysis for DPA without requiring complicated preparation processes and any extra steps of surface modification. This presented straightforward strategy may be extended to the construction of other coordination polymer-based lanthanide receptor reagent and hence a wider application field of coordination polymer as fluorescent sensor is expected.

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1. Introduction

Coordination polymers, as a class of hybrid materials built from metal ions and organic bridging ligands, have aroused tremendous interest because of their tunable structure and properties. Compared to conventional organic or inorganic nanomaterials, nanoscaled coordination polymers (NCPs) are innumerable owing to the choice of a vast range of metal ions and organic linkers, and can offer the advantages of structural and chemical diversity, high loading capacity, and intrinsic biodegradability [1]. Luminescent properties are one of the most interesting behaviors of the NCPs [2]. Up to now, many luminescent NCPs have been reported. Particularly, lanthanide based luminescent NCPs attracted considerable interest due to the unique optical properties of lanthanide ions. Some lanthanide NCPs have been used as luminescent probes for sensing metal ions, anions and small molecules [3–9]. However, most of the lanthanide NCPs are constructed by using hydrophobic organic ligands and consequently their sensing reactions are mainly performed in organic media. This limits their further applications, especially in biomedical field. Therefore, it is desirable for the construction of luminescent coordination polymers using benign building blocks that are biologically and environmentally compatible to meet the requirement for bioanalysis.

Nucleotides are often water-soluble and their multiple functional groups – nucleobases and phosphate groups – make them ideal for constructing metal-organic coordination polymers as bidentate ligands. Recently, Kimizuka group prepared a series of nucleotide-based NCPs by employing lanthanide ions as metal nodes [10–12]. These NCPs not only can function as a potent magnetic resonance imaging (MRI) contrast agents, but also exhibited surprising properties of adaptive encapsulation for guest molecules in the course of self-assembly. However, the most of nucleotide-based NCPs displayed weak fluorescence due to the radiativeness deactivation of coordinated water molecules. It is well known that replacement of coordinated water molecules by introducing of ancillary ligands can switch on the fluorescence of lanthanide complex. This principle has been probed extensively for potential applications of lanthanide complex as optical sensors. But, most of the optical sensors were constructed by using conventional lanthanide chelates as receptor reagent; very few examples of lanthanide NCPs were reported despite the potential sensing properties of fluorescent coordination polymers having been reported a decade ago.

Dipicolinic acid (DPA, pyridine-2, 6-dicarboxylic acid) is a unique and major constituent for bacterial spores, including those

* Corresponding authors. Tel.: +86 791 88120861; fax: +86 791 88120861.
E-mail addresses: hltan@jxnu.edu.cn (H. Tan), lwanggroup@yahoo.com.cn (L. Wang).

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of *Bacillus anthracis* (anthrax). Inhalation of more than 10^4 *B. anthracis* spores can result in death [13]. DPA represents 5–15% of dry mass of the spores and not found in other commonly occurring natural or man-made materials [14]. Therefore, DPA is a useful biomarker for anthrax. Many methods have been developed for the detection of DPA, including polymerase chain reactions (PCR) [15], surface enhanced Raman spectroscopy (SERS) [16], high-pressure liquid chromatography [17], electrochemical detection [18], and fluorescent detection [19–22] and so on. Among these methods, lanthanide ion based fluorescent detection system for DPA is a promising one owing to its simple and fast detection procedure, high detection sensitivity and low cost. These fluorescent detection systems were mostly built either in the form of molecular lanthanide compounds solutions or solid supports-based suspensions. Compared with solutions-based detections, the solid supports-based detections exhibit some unique properties, including miniaturization of the sensor, good portability, and real-space measurements. To date, various organic or inorganic materials have been used as solid supports to immobilize lanthanide ion to construct lanthanide receptor platform for DPA detection, such as PVA film [23], polymer nanoparticles [13], SiO_2 nanoparticles [24], single-walled carbon nanotubes [18], and zeolite [25]. However, complicated preparation procedures and extra steps of surface modification are often required for the construction of these lanthanide receptor platforms. Very recently, nanoscaled metal-organic frameworks (NMOFs) have been employed as lanthanide receptor platform to detect DPA [26,27], and showed great potential in the development of nanoscale functional materials. Nevertheless, the NMOFs have to be coated with silica shell to enhance the stability and bio-compatibility of the core particles or the detection reaction was carried out in organic media because of their very limited solution-based behavior. Thus, this makes it very challenging to use directly the NMOFs as sensing material in bioanalysis at real-time.

In this work, we attempt to utilize hydrophilic lanthanide/nucleotide coordination polymer as a receptor platform for the direct detection of anthrax biomarker in aqueous solution (Scheme 1). Water-soluble adenosine monophosphate (AMP) and terbium ions (Tb^{3+}) were selected to construct coordination polymer (AMP/Tb). Due to the low coordination ability of adenine units to Tb^{3+} and quench effect caused by O—H vibrational of the coordinated water molecules, no fluorescence can be observed for the coordination polymer AMP/Tb. As stated above, DPA is an ideal tridentate ligand for Tb^{3+}. It not only can offer its O atoms of carboxylic acid groups and N atom of aromatic ring for the coordination of Tb^{3+} and form AMP/Tb-DPA complex, but also transfer its absorbed energy to Tb^{3+} to sensitize the fluorescence of Tb^{3+} (antenna effect). Moreover, the coordination of DPA with Tb^{3+} leads to the removal of the coordinated water molecules. Therefore, the AMP/Tb-DPA complex is expected to emit strong fluorescence.

2. Experimental

2.1. Chemicals and solutions

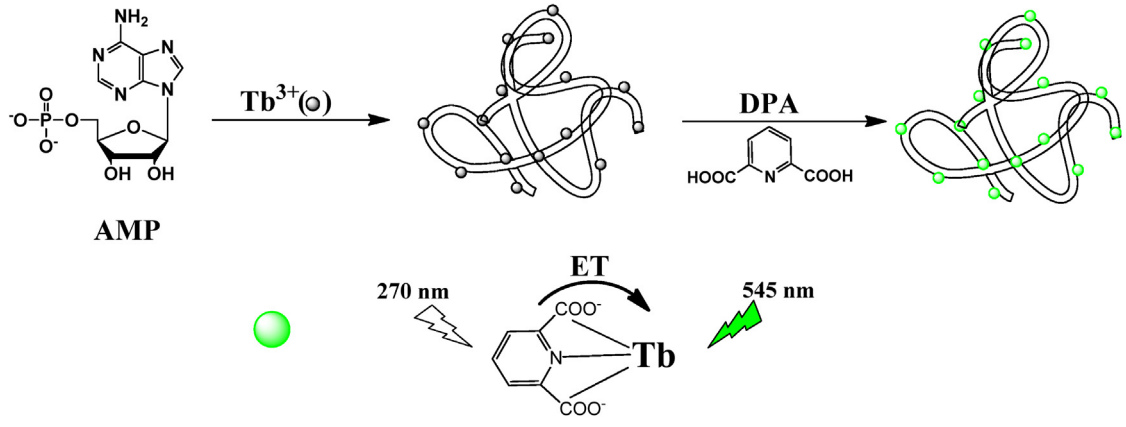
Terbium nitrate (99.99%) was purchased from Rewin Rare Earth Metal Materials Co., Ltd.; Adenosine-5′-monophosphate disodium, N-2-hydroxyethylpiperazine-N′-2-ethanesulfonic acid (HEPES) were obtained from Sangon Biotech (Shanghai) Co., Ltd.; dipicolinic acid (99%, DPA, 2, 6-pyridinedicarboxylic acid) was purchased from Sigma-Aldrich; interference substances (nicotinic acid, *o*-phthalic acid, 1,3 *m*-phthalic acid, nicotinamide adenine dinucleotide, benzoic acid, 2,4-dichlorophenoxy acetic acid, and pyridine) were purchased from Sinopharm Chemical Reagent Company. HEPES buffer (100 mM, pH 7.5) was prepared by dissolving HEPES in ultrapure water; 10 M NaOH was used to adjust pH to 7.5. The pH value was calibrated with a pH meter (Sartorius). Ultrapure water (18 MΩ cm) was used for the preparation of all aqueous solutions. Unless otherwise stated, all chemicals are of analytical reagent grade and used without further purification.

2.2. Instruments and determinations

The morphology of coordination polymer was examined by transmission electron microscopy (TEM, JEM-2100, Japan). Fluorescence spectra and emission intensity were recorded on an LS 55 luminescence spectrometer (PerkinElmer, UK), with a xenon lamp as excitation source. The detection solution was placed in a quartz micro cuvette with 100 μL capacity. The light path of the quartz cuvette is 2 mm. The 270-nm excitation wavelength was used for the emission spectra. A delay time of 0.05 ms and a gate time of 2 ms were used. Excitation spectra were recorded by observing the emission intensity of Tb^{3+} at 545 nm. For the emission lifetime, the fluorescent intensities at 545 nm were recorded under different delay times and fitted with an exponential function. UV–visible absorption spectra were recorded with a UV-3150 spectrophotometer (Shimadzu, Japan) at room temperature. All the experiments were performed at room temperature.

2.3. Preparation of nucleotide/lanthanide coordination polymer

The coordination polymer AMP/Tb was prepared according to the reported method [10]. Typically, 1 mL of $Tb(NO_3)_3$ aqueous solution (10 mM) was added to 1 mL of AMP disodium salt solution (10 mM) dissolved in HEPES buffer (100 mM, pH 7.4) under



Scheme 1. Illustration of coordination polymer AMP/Tb for detection of DPA.

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