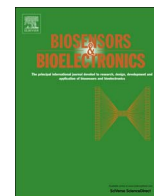




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Charge-transfer-based terbium MOF nanoparticles as fluorescent pH sensor for extreme acidity

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ABSTRACT

Newly emerged metal organic frameworks (MOFs) have aroused the great interest in designing functional materials by means of its flexible structure and component. In this study, we used lanthanide Tb^{3+} ions and small molecular ligands to design and assemble a kind of pH-sensitive MOF nanoparticle based on intramolecular-charge-transfer effect. This kind of made-to-order MOF nanoparticle for H^+ is highly specific and sensitive and could be used to fluorescently indicate pH value of strong acidic solution via preset mechanism through luminescence of Tb^{3+} . The long luminescence lifetime of Tb^{3+} allows eliminating concomitant non-specific fluorescence by time-revised fluorescence techniques, processing an advantage in sensing H^+ in biological media with strong autofluorescence. Our method showed a great potential of MOF structures in designing and constructing sensitive sensing materials for specific analytes directly via the assembly of functional ions/ligands.

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1. Introduction

pH homeostasis is fundamental and important for all living organisms because most proteins have distinct ranges of pH for their functions (Swietach et al., 2014; Krulwich et al., 2011). Intracellular pH plays a critical role in cell, enzyme, and tissue activities including proliferation and apoptosis, multidrug resistance, endocytosis, and neuronal excitability, signal cascades (Han et al., 2010; Lee et al., 2013). Abnormal pH values are related to inappropriate cell function and growth. For example, malignant tumors (cancers) often have a more acidic extracellular pH and a more alkaline intracellular pH than normal tissue because of H^+ production and excretion from increased glucose metabolism (Webb et al., 2011). Therefore the precise measurement of pH values in biosystems is very important.

Compared to other pH measurement methods such as micro-electrodes, absorbance spectroscopy and NMR (Wencel et al., 2014; Kim et al., 2016; Dengler et al., 2015; Mori et al., 1998; Yu et al., 2014), fluorescence methods not only have advantages with respect to spatial and temporal observation of pH changes but also have higher sensitivities and are in most cases nondestructive to cells. The pH-sensitive fluorescent proteins have been used to measure the intracellular pH 5–9 (Tantama et al., 2011; Berbasova et al., 2013). However, they are not suitable for measuring pH levels below 5 due to acid-induced denaturation of proteins. Some

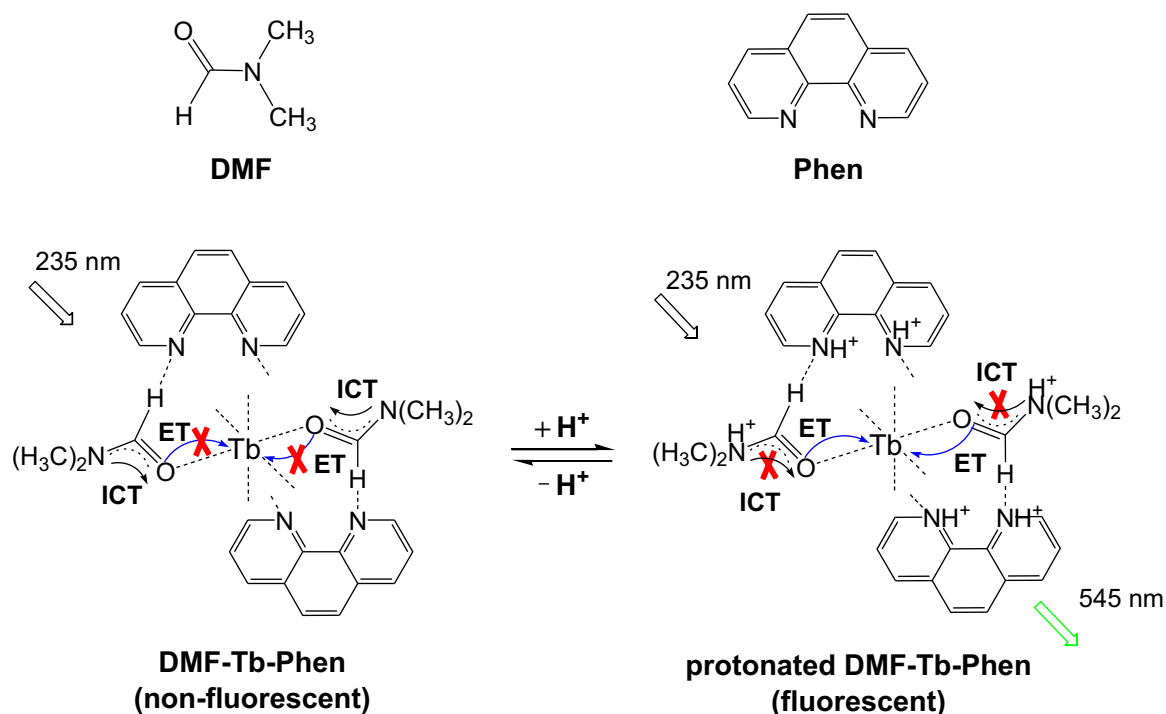
pH-sensitive fluorescent dyes are also used for measuring the acidity of organelles (Saha et al., 2011; Yang et al., 2012; Yuan et al., 2012; Ma et al., 2012). They typically have a narrow pH working range determined by their pKa values. New fluorescent nanomaterials such as carbon-dots have been used as pH sensors (Shi et al., 2016; Aguilera-Sigalat et al., 2014). The measurement of pH using common fluorophores has another drawback that is easily suffered from the interference of strong intrinsic autofluorescence of biosamples/biological media. An accurate fluorescent measuring for low pH values of less than 5 is still a challenging and lacks simple effective methods.

Metal organic frameworks (MOFs) composed of metal ions and organic molecules have received great attention in designing new functional materials due to their diversity of structure and composition. MOF's flexible structure and composition allows it to be designed to be specific functional materials. We have used MOF frameworks as a scaffold to make tailored sensing fluorescent materials for specific analytes (Qi et al., 2016; Liu et al., 2013; Tan et al., 2012).

In this paper, we showed how lanthanide ions and small molecular ligands, through MOF structure, could be used to design and assemble to be a sensitive material for H^+ (pH value). This sensitive material was consisted of N,N-dimethylformamide (DMF), Tb^{3+} and 1, 10-phenanthroline (Phen). We chose DMF molecule because it includes both an electron-donor part and an electron-acceptor part which is peculiarly prone to generate an intramolecular charge transfer (ICT) (Dimitriev and Kislyuk, 2007; Fraenkel and Franconi, 1960); besides, it is also has an antenna effect for the luminescence of Tb^{3+} . Therefore, the protonation of

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Scheme 1. Schematic diagram of intramolecular-charge-transfer-based fluorescent pH sensor.

H^+ could change the charge transfer of DMF, and then change the antenna effect for Tb^{3+} , leading to a change in the luminescence of Tb^{3+} . The introduction of Phen molecule may enhance such a change and reduce the fluorescence quenching of Tb^{3+} by replacing the coordination of water molecules. We expect a process sensing H^+ could occur as [Scheme 1](#).

2. Experimental section

2.1. Chemicals and solutions

Terbium nitrate (99.99%) was purchased from Baotou Rewin Rare Earth Metal Materials Co., Ltd.; N,N-Dimethylformamide (99.5%, DMF) was purchased from Sangon Biotech; 1, 10-Phenanthroline Monohydrate (98%, Phen) was purchased from Aladdin. Metal salts (KNO_3 , NaCl, $AgNO_3$, $Zn(NO_3)_2$, $MgCl_2$, $CaCl_2$, $CuCl_2$, $Pb(NO_3)_2$, $Co(NO_3)_2$, $MnCl_2$, $CrCl_3$, $FeCl_2$, $FeCl_3$, $Hg(NO_3)_2$, NaF, NaBr, $NaIO_3$, CH_3COONa , Na_2SO_4 , Na_2SO_3 , Na_2CO_3 and Na_3PO_4) were purchased from Sinopharm Chemical Reagent Company. Ultrapure water (18 $M\Omega$ cm; Milli-Q, Millipore) was used for the preparation of all aqueous solution. PBS buffer (100 mM) was prepared by dissolving 1.79 g $Na_2HPO_4 \cdot 12H_2O$ and 0.68 g KH_2PO_4 in 100 mL water. The different pH of PBS buffer was adjusted by concentrated HCl and NaOH. The stock solutions of metal ions and anions (100 mM) were prepared by dissolving appropriate amounts of above salts in water. Unless otherwise stated, all chemicals are of analytical reagent grade and were used without further purification.

2.2. Instruments and determinations

The morphology and size of nanoparticles were observed by transmission electron microscopy (TEM) (JEM-2100, Japan). The selected area electron diffraction (SAED) analysis was performed by TEM with an XD-3AX X-ray diffractometer (Shimadzu, Japan). Fluorescence spectra and emission intensity were recorded on an LS55 luminescence spectrometer (PerkinElmer, UK). The detection

solution was placed in a quartz microcuvette with 10 mm light path. The 235-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 emission lifetime, the fluorescence intensities at 545 nm were recorded under different delay times and fitted with an exponential function. Fourier transform infrared (FT-IR) spectra were recorded with an Avatar 360 FT-IR spectrometer (Nicolet, U.S.A.). UV-visible absorption spectra were recorded with a UV-1800 spectrophotometer (Shimadzu, Japan). The pH values were recorded using a pH meter (PB-10, Sartorius). All the experiments were performed at room temperature.

2.3. Preparation of DMF-Tb-Phen MOF nanoparticles

The DMF-Tb-Phen MOF nanoparticles (NPs) were prepared on the basis of the previous method ([Qi et al., 2016](#); [Tan et al., 2012](#)). Typically, 400 μ L of DMF solution of Phen (100 mM) was added to 8 mL of N,N-Dimethylformamide (DMF) and mixed well. Then 800 μ L of $Tb(NO_3)_3$ aqueous solution (100 mM) was added to the mixture under stirring. After stirring 20 min, the mixture was sealed in a Teflon-lined autoclave, heated at 160 $^{\circ}C$ for 2 h, and then cooled to room temperature naturally. The white precipitate was collected by centrifugation at 13,000 rpm for 10 min. To remove unreacted reactants, we washed the precipitates several times with absolute ethanol. Finally, the precipitate (approximately 0.0284 g after drying) was dispersed in 1 mL of ultrapure water to form a DMF-Tb-Phen NPs suspension of 284 mg/mL for the subsequent experiments. As a control experiment, DMF-Tb was synthesized by the same experimental steps and conditions mentioned above except replacing Phen by 400 μ L of DMF. The obtained precipitate (approximately 0.0227 g after drying) was dispersed in 1 mL of ultrapure water to form a DMF-Tb suspension of 22.7 mg/mL. DMF-Tb-Phen and DMF-Tb suspensions were further diluted 4-fold for the use of determinations.

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