



Oxidative deoxygenation reaction induced recognition of hypochlorite based on a new fluorescent lanthanide-organic framework

Zhan Zhou^{a,1}, Xiangqian Li^{b,1}, Yiping Tang^c, Cheng Cheng Zhang^d, Hongru Fu^a, Naiteng Wu^a, Lufang Ma^{a,*}, Jinwei Gao^e, Qianming Wang^{b,*}

^a College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang 471934, China

^b Key Laboratory of Theoretical Chemistry of Environment, Ministry of Education, School of Chemistry & Environment, South China Normal University, Guangzhou 510006, China

^c College of Material Science and Engineering, Zhejiang University of Technology, Hangzhou, Zhejiang 310014, China

^d Departments of Physiology and Developmental Biology, University of Texas, Southwestern Medical Center, Dallas, TX 75390-9133, USA

^e Guangdong Provincial Engineering Technology Research Center For Transparent Conductive Materials, South China Normal University, Guangzhou 510006, China

HIGHLIGHTS

- “off-on” signal changes can be realized by oxidative deoxygenation reaction.
- Dual luminescence modes were explored.
- Detection limit is calculated to be as low as 16 nM.

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ABSTRACT

Assembly of a new functional organic linker, (dimethyl 4-(carbaldehyde oxime) pyridine-2,6-dicarboxylate, L1), with europium ions modified Uio-67 leads to Uio-Eu-L1, which is shown to be a new molecular-based probe with high sensitivity and selectivity for ClO^- . The detection limit is calculated to be as low as 16 nM. To our knowledge, this is the first report of a sensitive europium sensor for ClO^- established on the oxime isomerization reaction. The nature of organic L1 sensitizer within the complex has been demonstrated to control the photoluminescence effectively. The “off-on” signal changes can be realized by oxidative deoxygenation reaction induced recognition of hypochlorite. More strikingly, both continuous-mode lanthanide emission (steady-state photoluminescence measurement) and time-gated luminescence detection are collected in the presence of several interference organic dyes. This remarkable optical feature will allow easy spectral and discrimination of their emission bands from separation of noisy signals.

1. Introduction

Hypochlorite or hypochlorous acid is an important small molecule of reactive oxygen species. As an unstable weak acid, it is widely used in life and industry for wastewater treatment, hospital laundry and disinfection, and bleaching of paper and textile industries. In addition, it plays an important role in intracellular redox balance. Excess amounts of hypochlorite can cause tissue damage and some various diseases, such as Alzheimer's disease, cardiovascular disease and so on [1–3]. Therefore, it is very necessary to develop some effective techniques for highly sensitive and selective detection of hypochlorite. Among the many methods for detecting hypochlorite, fluorescent probe technology

has drawn more attention for its advantages including simple equipment, easy operation, real-time monitoring, high sensitivity and good selectivity [4–6].

In recent years, the geometrically well-defined structures such as metal-organic frameworks (MOFs) have aroused considerable attention in the field of supramolecular solids [7–20]. At first, the inherent porosity in these molecular-based materials will allow effective adsorption of guest species adjacent to the luminescent centers. Additionally, their rigid scaffolds may restrict the free movement of linker units and the crystalline lattice will protect lanthanide ions from attacking by solvent molecules. During the interaction with an analyte, changes in the coordination structure could trigger delicate responses in the

* Corresponding authors.

E-mail addresses: mazhuxp@126.com (L. Ma), qmwang@snu.edu.cn (Q. Wang).

¹ The two authors contributed equally to this work.

luminescence signals and a variety of synthetic strategies were explored for the molecular recognition [21–30]. Following this idea, a few lanthanide-containing functional frameworks have been developed for guest detection purpose [31–41]. However, the coordination sphere of trivalent lanthanide ions is usually quite large (coordination number 9–12) and their complexation modes are flexible. Their remaining coordination sites may offer the opportunity for providing new opportunities to modulate the MOFs luminescence.

Therefore, at the first stage, the typical Uio type platform with chemical stability was employed as the suitable host to anchor europium ions in this study and the bipyridine units in the complex could participate into the coordination reaction. Secondly, a functional building block named as dimethyl 4-(carbaldehyde oxime) pyridine-2,6-dicarboxylate was incorporated and the red emission derived from europium ions was significantly suppressed due to the influence of isomerization of unbridged C=N bond. Since oxime can be easily deprotected by hypochlorite, a highly selective probe for ClO^- was assembled and the striking red luminescence was recovered. Thirdly, the conventional analytical methodologies that focus on ClO^- determination are mainly based on steady-state detection mode. In this case, the negative effects from autofluorescence and scattering lights will be difficult to eliminate and the collected results may lead to low signal-to-noise ratio. But the lifetime of lanthanide excited state is between microseconds to milliseconds. The long-lived red emission will be beneficial in view of chemical analysis and this fact will allow time-gated measurements to achieve the lanthanide luminescence that will address the challenges of background signals. To our knowledge, it is the first example that time-resolved emission spectra have been used to explore hypochlorite detection. The chemical process has been established on oxidative deoximation reaction of a new lanthanide MOF structure.

2. Experimental section

2.1. Materials

Europium (III) chloride hexahydrate ($\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$), 2,2'-Bipyridine-5, 5'-dicarboxylic acid (bpd, 98%), 2,4-Dihydroxy-5,6-dimethylpyrimidine (PCC, 98%) and Zirconium tetrachloride (98%) were purchased from HWRK Chem. Co., Ltd., Beijing, China. 2,6-Pyridinedicarboxylic acid (DPA, 99%), hydroxylammonium chloride (99%), L-proline (99%), Iron sulfate heptahydrate (99%) and hydrogen peroxide solution (30% in H_2O) were purchased from Aldrich.

2.2. Characterizations

^1H NMR spectra were recorded on a Bruker Avance 400 MHz NMR Spectrometer. Fluorescence and excitation spectra were measured using a Hitachi F-7000 fluorescence spectrophotometer with a 450 W xenon lamp as a light source. Infrared spectra were recorded by a Nicolet-Magna 550 FT-IR instrument (resolution: 1 cm^{-1} ; range $4000\text{--}400\text{ cm}^{-1}$) with the KBr pellet technique. SEM images were acquired by a scanning electron microscope (FEI Quanta 250 FEG). X-ray diffraction measurements were carried out on powder samples through a Bruker D8 diffractometer using $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.54\text{ \AA}$). Inductively coupled plasma-mass spectrometry (ICP-MS) data were collected on a Thermo Scientific XSERIES 2 ICP-MS system. Thermogravimetric analysis was explored by a STA409PC system under air at a rate of $10\text{ }^\circ\text{C}/\text{min}$. The adsorption-desorption isotherms of nitrogen were measured at 77 K using an ASAP2020M system. The specific surface area was calculated by the Brunauer-Emmett-Teller (BET) method.

2.3. Synthesis of Uio-67

Uio-67 was synthesized by a simple solvothermal method [42]. Mixture of L-proline (0.7 mmol, 80.6 mg), 2, 2'-Bipyridine-5, 5'-

dicarboxylic acid (0.1 mmol, 24.3 mg) and zirconium tetrachloride (0.1 mmol, 23.3 mg) were vigorously stirred in DMF (8 mL) solution. After 30 min, the mixed solution was transferred into a Teflon vessel in a stainless steel autoclave, and heated at $120\text{ }^\circ\text{C}$ for another 3 days. The mixture was cooled to room temperature and the crude product was obtained by centrifugation. Then, the product was subject to centrifugation with fresh DMF, twice with methanol, and the purified product was dried in a vacuum oven at $40\text{ }^\circ\text{C}$ for 8 h (yield: 53% for Zr).

2.4. Synthesis of the ligand (L1)

Pyridine-2,6-dicarboxylate (PDA Ester) and 4-(hydroxymethyl) pyridine-2,6-dicarboxylate (PDA-OH Ester) were synthesized by the previous literature [43]. A mixture of PDA-OH Ester (180 mg, 0.8 mmol), pyridinium chlorochromate (PCC, 260 mg, 1.2 mmol), and dry dichloromethane (30 mL) was stirred at room temperature for 8 h. Ethyl acetate (50 mL) was added before removing the 50% solvent. The mixture was washed with H_2O (once), NaHCO_3 (5%, twice), and NaCl (saturated, once) sequentially. The organic layer was concentrated under reduced pressure before drying by anhydrous sodium sulfate. The crude product was dissolved in methanol (20 mL), then hydroxylamine hydrochloride (194.6 mg, 2.8 mmol), K_2CO_3 (408.1 mg, 3.85 mmol) and water (20 mL) were added into the solution. The mixture was stirred at $80\text{ }^\circ\text{C}$ for 5 h. Ethyl acetate was used to extract the mixture. It was dried by anhydrous sodium sulfate. The solvent was evaporated, and the crude product was purified over a silica gel column (ethyl acetate / dichloromethane, 5:1, v/v) to obtain the target ligand (L1) as a white solid (yield: 65%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$) δ ppm: 12.25 (s, 1H), 8.40 (s, 2H), 5.75 (s, 1H), 3.92 (s, 6H). TOF MS found: m/z 239.0660 [M + H].

2.5. Synthesis of the Uio-Eu-L1

Firstly, Uio-Eu was prepared by dispersing 100 mg of Uio-67 solid in a methanol solution (20 mL) which contained 0.1 mM of europium chloride. The reaction was carried out at $50\text{ }^\circ\text{C}$ for one day. The solid was collected by centrifugation at 5000 rpm for 10 min, and washed five times with methanol to remove the physically adsorbed europium ions. Then, Uio-Eu was obtained by drying at $50\text{ }^\circ\text{C}$ in vacuum. Secondly, 50 mg of Uio-Eu was dispersed into the methanol solution of L1 (0.1 mM) at $60\text{ }^\circ\text{C}$ for one day. In the next step, the solution was changed once and held for another one day. Finally, the target material Uio-Eu-L1 was obtained by centrifugation and drying at $50\text{ }^\circ\text{C}$ in vacuum.

2.6. Synthesis of the europium binary complex (EuL1):

To prepare the EuL1, L1 (25 mg, 1.05 mmol) was dissolved in 10 mL of EtOH in a 25-mL round-bottom flask, and one equivalent of EuCl_3 was added with magnetic stirring. The mixture was refluxed for 3 h at $90\text{ }^\circ\text{C}$. The crude product was washed with water, and dried in a vacuum overnight to give the target EuL1 as a white powder

3. Results and discussion

3.1. Synthesis of Uio-Eu-L1

In this research, an effective strategy for constructing responsive europium complex modified MOF that will be stable in aqueous environment has been provided. The combination of 2,2'-bipyridine-5,5'-dicarboxylic acid and zirconium tetrachloride under solvothermal conditions (DMF, $120\text{ }^\circ\text{C}$, three days) gave the bulk crystals (Uio-67) in 53% yield. In order to incorporate europium ions into the internal structure of Uio-67, the crystal material was immersed into methanol solution of europium chloride and Uio-Eu with red emission was achieved. As for the synthesis of L1, this robust organic linker was

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