Dyes and Pigments 138 (2017) 15–22

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Establishment of highly sensitive and selective fluorescent sensor for Fe^{3+} based on a post-synthetic modification of metal-organic framework

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ARTICLE INFO

Article history:
Received 25 August 2016
Received in revised form
14 November 2016
Accepted 14 November 2016
Available online 16 November 2016

Keywords:
Metal organic frameworks
Post-synthetic modification
Fluorescent sensor
Fe^{3+}

ABSTRACT

A post-synthetic modification method was developed to prepare fluorescent metal organic frameworks by the covalent interaction of ethoxycarbonyl isothiocyanate with amine functionalized UMCM-4. X-ray diffraction spectrometry, X-ray photoelectron spectrometry, elemental analysis, Fourier-transformed infrared spectroscopy, nuclear magnetic resonance spectrometry, thermogravimetric analysis/derivative thermogravimetry analysis, and nitrogen sorption isotherms were employed to characterize the modified metal organic frameworks. With high emission efficiency and excellent fluorescence stability, the sensing properties of Fe^{3+} were studied. Possible mechanisms of energy and electron transfers between the target and the fluorescent probe were demonstrated. Effects of response time, Fe^{3+} concentration, and other metal ions on the fluorescence intensity were also studied.

1. Introduction

Iron ion (Fe^{3+}) plays a significant role in environmental protection, agriculture, and biology, so the design of analytical methodologies for the detection of Fe^{3+} has led to an increasing interest in recent years. Many detection methods have been reported, such as spectrophotometric method [1,2], inductively coupled plasma optical emission spectrometry [3,4], flame atomic absorption spectrometry [5,6], and capillary electrophoresis [7]. Recently, fluorescent methods have consistently attracted much attention due to their simplicity of implementation, real-time monitoring, sensitivity, and specificity. In fluorescent determinations, it is crucial to develop efficient luminescent materials with high emission efficiency and excellent fluorescence stability as fluorescent sensors.

Recently, luminescent porous materials such as conjugate microporous polymers (CMPs), covalent organic frameworks (COF_S), porous aromatic frameworks (PAFs), and metal organic frameworks (MOFs) have attracted a lot of concerns [8–14]. Generally, luminescent porous framework-based sensors possess nanoscale cavities and three-dimensional networks. The nanoscale cavities can be considered as microreactors, which provide abundant space for recognition and selective sensing of guest targets. The three-dimensional networks facilitate exciton migration over the framework and play crucial roles to enhance the sensitivity through signal amplification [10]. Compared with MOFs, the other three have lower emission efficiency, poorer porosity, and fewer active sites. MOFs are more competitive owing to their unique structures, diverse chemical properties, uniform nanoscale cavities, controlled pore sizes, well-tailored molecular structures, and high surface areas [15]. These advantages of MOFs have broadened their range of applications, especially in the field of luminescence including light-emitting device [16], photocatalysis [17], electroluminescence [18], biomedical imaging [19], and fluorescent sensor [20].

Kinds of fluorescent MOFs sensors have been reported in the past years, among which various functionalized MOFs have been developed to increase the specificity of sensing the guests through the introduction of functional groups into MOF [21–25]. However, it remains a challenge to directly achieve functionalized MOFs with conventional solvothermal synthetic methods [26,27]. Under solvothermal conditions, the synthesis of MOFs is often interfered if functional groups are incorporated because they may result in steric, solubility, and metal-coordination problems [28,29]. Post-

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http://dx.doi.org/10.1016/j.dyepig.2016.11.018
0143-7208/

synthetic covalent modification (covalent PSM) provides a valuable alternative for introducing functional groups into MOFs and will not affect their structural integrity, exploiting a wider range of physical and chemical properties than can be achieved by direct synthesis [30,31]. In covalent PSM, functional groups within MOFs usually act as the target to combine with the reaction reagent, among which amine group is a most commonly used target. Based on the covalent interactions with amine groups, isothiocyanate, thiourea, isocyanate, anhydride, and thiol groups have been employed for the post-synthetic modification of MOFs [32–35]. For instance, Volkringer et al. [34] conducted the post-synthesis of MIL-53(Al)-NH_2 with isothiocyanate, thiourea, and thiocarbamate groups. The pore functionalities with these groups resulted in significant changes in the gas sorption isotherms and thus enhanced the selectivity for gas uptake.

Here, a post-synthetic covalent modification strategy was used to modify MOFs (UMCM-4-NH_2) with thoxycarbonyl isothiocyanate (ECIT) as the functional group. ECIT was introduced into cavities of the UMCM-4-NH_2 framework to increase the active sites and interaction interface. Based on the fluorescence quenching phenomenon caused by the interaction of ECIT and Fe^{3+}, the prepared UMCM-4-NH_2-ECIT was applied to fluorescent detection of Fe^{3+}. To the best of our knowledge, this is the first time that post-modified MOFs are utilized as fluorescent probe for sensing Fe^{3+}.

2. Experimental

2.1. Chemical and materials

All the reagents were of analytical grade and used without further purification. Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), ECIT, *N*,*N*-dimethylformamide (DMF), and methanol (MeOH) were purchased from Aladdin Reagent (Shanghai, China). 2-Amino-1,4-benzenedicarboxylic acid (NH_2-H_2BDC) was obtained from Sigma-Aldrich Company (St. Louis, MO, USA). 4,4′,4″-Tricarboxytriphenylamine (TPA) was supplied by Alfa Chemistry Co., Ltd. (Zhengzhou, China). Chloroform ($CHCl_3$) and dichloromethane (CH_2Cl_2) were purchased from Beijing Chemical Works (Beijing, China).

2.2. Instruments

Powder X-ray diffraction (PXRD) patterns were collected using a D/Max-IIIC (Rigaku, Japan) with Cu *Kα* radiation and the recorded range of 2θ was 4–40°. XPS data were recorded with an X-ray photoelectron spectrometer (Thermo Electron, USA). Elemental analysis was conducted with a vario MICRO cube (Elementar Analysensysteme GmbH, Germany). Fourier-transform infrared (FT-IR) spectra were recorded using KBr pallets in the range of 4000–450 cm^{-1} on a Spectrum One FT-IR spectrometer (Perkin-Elmer, USA). ^1H NMR spectra were recorded on a Bruker Advance III 500 spectrometer. Thermogravimetric analysis/derivative thermogravimetry analysis (TGA-DTG) determinations were performed with an STA-449C thermal gravimetric analyzer (Netzsch Company, Germany). Surface area measurements were obtained on an ASAP 2420 gas adsorption instrument (Micromeritics, Atlanta, USA). All fluorescence measurements were performed on an FL5301 fluorescence spectrophotometer (Shimadzu Company, Japan) with the emission and excitation slit widths both set at 3 nm. The fluorescence lifetime and absolute fluorescence quantum yield were carried out with an FLS920 fluorescence spectrophotometer (Edinburgh Instruments, England).

2.3. Synthesis of UMCM-4-NH_2

The synthesis of UMCM-4-NH_2 was performed according to a modified procedure as reported in previous literature [36]. Briefly, TPA (0.343 mmol) and NH_2-BDC (0.575 mmol) were dissolved in dehydrated DMF (150 mL) and then $Zn(NO_3)_2 \cdot 6H_2O$ (2.27 mmol) was added, after which the yellow solution was sonicated for 15 min. The solution was divided into 10 mL portion and transferred to 15 scintillation vials. The vials were then placed in an oven at 85 °C for 3 days. After cooling overnight, the mother liquor from each vial was decanted, and the product was rinsed with DMF (3 × 10 mL) to remove the unreacted reagents. Thereafter, the product was soaked in CH_2Cl_2 for 3 days and then dried at 120 °C in vacuum for 24 h.

2.4. Procedure for post-synthetic covalent modification of UMCM-4-NH_2-ECIT

UMCM-4-NH_2 was modified with ECIT according to a previously reported method [34,37]. 100 mg obtained UMCM-4-NH_2 was suspended in 10 mL $CHCl_3$ containing 10% MeOH and then 100 μL ECIT was added, after which the suspension was refluxed at 55 °C for 3 days and then centrifuged. The obtained product was washed with $CHCl_3$ to remove unreactive substrates and soaked in 10 mL CH_2Cl_2 for 3 days with fresh CH_2Cl_2 added every day. It was then dried under vacuum at 120 °C to obtain UMCM-4-NH_2-ECIT.

2.5. Fluorescence assay of Fe^{3+}

All fluorescence determinations of Fe^{3+} were conducted at room temperature. In a typical run, UMCM-4-NH_2-ECIT was dispersed in DMF for 5 min, after which Fe^{3+} solutions with different concentrations were added. A 1 cm × 1 cm quartz cell was employed and the excitation wavelength was set at 387 nm. The fluorescence spectra of other metal ions (Na^+, K^+, Ca^{2+}, Cd^{2+}, Ni^{2+}, Mg^{2+}, Co^{2+}, Fe^{2+}, Ag^+, Cu^{2+}, and Cr^{3+}) were also carried out in the same way.

3. Results and discussion

3.1. Synthesis and characterization of UMCM-4-NH_2-ECIT

In the present work, UMCM-4-NH_2 was used as the starting point. UMCM-4-NH_2 was isostructural to UMCM-4, which consisted of $Zn_4O(CO_2)_6$ clusters and organic linkers (BDC and TPA) in DMF [36]. In order to introduce amine groups into the framework, BDC was replaced by NH_2-BDC to be used as the organic linkers together with TPA. A brief procedure was illustrated in Scheme 1. After UMCM-4-NH_2 was prepared, ECIT was introduced into cavities of the UMCM-4-NH_2 framework in the step of post-synthesis modification.

The crystal structures of both UMCM-4-NH_2 and UMCM-4-NH_2-ECIT were verified by PXRD patterns, which were shown in Fig. 1A. The PXRD pattern of UMCM-4-NH_2 corresponded to that of a crystalline material with the simulated structure. In addition, a comparison of UMCM-4-NH_2 and UMCM-4-NH_2-ECIT illustrated that the diffraction peaks changed little, implying that good crystallinity of UMCM-4-NH_2 was preserved for UMCM-4-NH_2-ECIT. UMCM-4-NH_2-ECIT was also characterized by XPS in order to explore elemental compositions. Results were shown in Fig. 1B. Typically, the spectra at 163.4, 284.5, 399.9, and 531.6 eV corresponded to S2p, C1s, N1s, and O1s, respectively. As a comparison, the XPS spectrum of UMCM-4-NH_2 was illustrated in the inset of Fig. 1B, indicating that S element was introduced into the modified framework. CNHS elemental analysis of the prepared UMCM-4-NH_2-ECIT was carried out, demonstrating that the contents of C,