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A novel fluorescent multi-functional monomer for preparation of silver ion-imprinted fluorescent on–off chemosensor

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ABSTRACT

A new fluorescent multi-functional monomer (E)-3′,6′-bis (allyloxy)-2-((thiazol-2-ylmethylene)amino)-4a′,9a′-dihydrospiro[isoindoline-1,9′-xanthen]-3-one (ATMIX) was successfully synthesized for the first time. The obtained ATMIX not only exhibited fluorescence on–off characteristics toward Ag(I), but also could produce radical polymerization with cross-linkers. Based on ATMIX, a novel ion-imprinted fluorescent on–off sensor (IIFOS) was fabricated successfully for selective recognition of Ag(I). The morphology, structure and fluorescent property of IIFOS was characterized by infrared spectroscopy, scanning electron microscopy (SEM) and fluorescent spectrometry. The results indicated that the obtained IIFOS exhibited high selective fluorescence on–off characteristics toward Ag(I) based on the mechanism of photoinduced electron transfer. What is more, the IIFOS is reusable and has been applied to detect Ag(I) in water sample with satisfactory recoveries.

1. Introduction

In recent decades, various fluorescent probes such as quantum dots [1–5], fluorescein derivatives [6–10] and so on have been reported on the detection of metal ions. Undoubtedly, those fluorescent probes can exhibit high sensitivity and selectivity for target metal ions. However, a lot of those probes shall undergo strong reactions with target ions, and difficult to be reused for continuous detection, thus the signal changes are usually unidirectional. Strictly, these kinds of probe should not be referred to as sensor [11]. An important property for a sensor is that it can be regenerated fast and be reused continually. Chemosensors based on fluorescence signal changes are commonly referred to as fluorescent sensors. Usually, fluorescent sensors are made up of three components: a receptor, a fluorophore and a spacer moiety that links the receptor and fluorophore together [12]. Fluorescent sensors have gained increasing attentions due to their advantages of convenient use, fast response and high sensitivity [12–14].

On the other hand, molecularly imprinted polymers (MIPs) have the advantages of high selectivity and resistance to harsh environment, and can be regenerated easily, thus MIPs have been widely used in biomimetic sensor [15,16], enzymatic catalysis [17,18], chromatographic separation [19], solid phase extraction (SPE) [20–22] and so on. In recent years, more and more researchers have begun to study molecularly imprinted fluorescent sensor (MIFS) by coupling the advantages of MIPs and fluorescent sensor [23].

However, most of the MIFS themselves have no fluorescence properties, thus the fluorescence signals can only be induced through binding with those fluorescent organic substances. For a long time, the previous reports about MIFS have been mainly limited to the detection of fluorescent organic substances, such as caffeine [24], cocaine [25], bisphenol A [26], proteins [27,28], herbicides [29] and other fluorescent substances [30,31]. Up to now, fabricating stable ion-imprinted fluorescent sensor (IIFS) for metal ions is still a challenging work, since most metal ions have no fluorescent characteristics. Although the classic methods such as atomic absorption spectrophotometry (AAS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) have been applied widely for the determination of metal ions, these methods are laboratory-based, and very difficult to satisfy on-site and remote monitoring. Due to the unique advantages of IIFS for conjugating with fiber-optic sensor [24,30] to realize on-line and/or remote monitoring metal ions, IIFS has been causing the increasing attentions of researchers recently.

Narayanaswamy et al. developed a MIP fluorescence sensor for the detection of aluminum ions in aqueous media. In the work 8-hydroxyquinoline sulfonic acid ligand was used as the fluorescence tag for aluminum ions by entrapping physically in the

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polymer network [32]. However, the leaching problems associated to the physical entrapment may cause sample contamination and a reduction of the analytical signal over time. Therefore, fabricating a suitable fluorescent multi-functions monomer shall be the key to obtain a stable IIFS. The ideal fluorescent monomer should be of such properties: firstly, it should possess selective ligands to chelate with target metal ions; secondly, it should contain several terminal double-bonds to produce radical polymerization with cross-linkers, and result in quantities of recognition sites chemically bound in the polymer network; thirdly, it should conjugate a fluorophore responsive to the binding interaction between metal ions and the recognition sites. So far, seldom literatures have been found on fabricating IIFS based on such kind of fluorescent multi-functional monomer. With a fluorescent monomer, Pinheiro et al. have prepared a fluorescent ion-imprinted monolith. Prior to the fluorescence quenching measurements for Cu(II), the ion-imprinted monolith must be broken into small fragments before packing into a silica cell [33].

Since the sensing membrane based on fluorescence enhancing effect is more suitable to be used as the signal transducer on optical fiber to realize the remote or in vivo monitor of metal contamination. In this study, a novel fluorescent polymerizable multi-functional monomer has been synthesized successfully for the first time [34–36]. By using that, a stable ion-imprinted fluorescent on–off sensor (IIFOS) based on imprinting membrane was further fabricated for responding to Ag(I) through fluorescence enhancing. The morphology, spectroscopic features, as well as the selective recognition ability of IIFOS for Ag(I) in water sample have been characterized and investigated in detail.

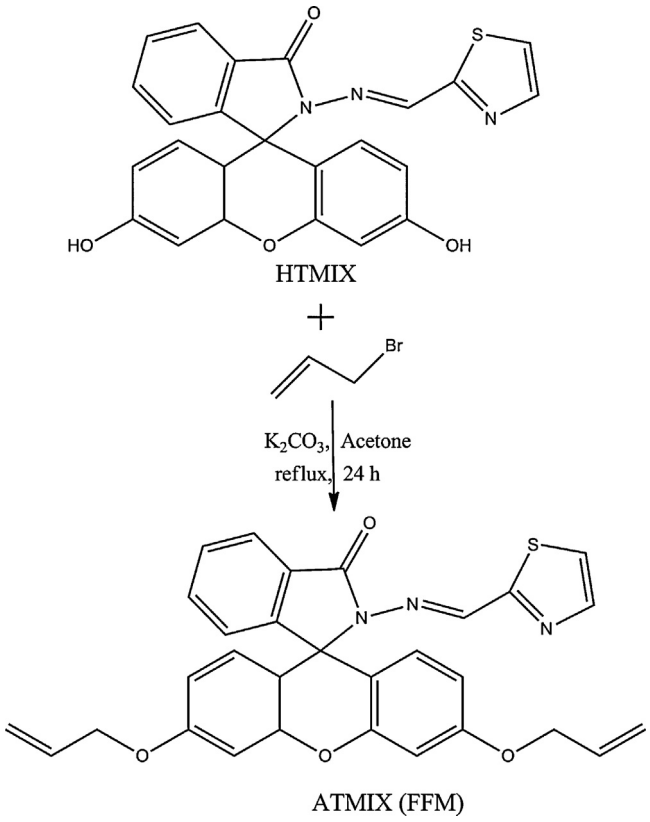

Fig. 1. The synthetic route of ATMIX.

2. Materials and methods

2.1. Chemicals and reagents

The materials for synthesis were purchased from commercial suppliers and used without further purification. Fluorescein and hydrazine hydrate were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). 2-Thiazolecarboxaldehyde was purchased from Beijing Ouhe Chemical Technology Co., Ltd. (Beijing, China). Potassium carbonate was purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Allyl bromide was purchased from J&K Scientific Ltd. (Beijing, China). Methacrylic acid (MAA) and azobisisobutyronitrile (AIBN) were purchased from Tianjin Damao Chemical Reagent Company (Tianjin, China). Ethylene glycol dimethacrylate (EGDMA) was purchased from Tokyo Chemistry Industry. Polyvinylidene fluoride (PVDF) film was purchased from Tianjin Jinteng Experimental Equipment Co., Ltd. (Tianjin, China). Acetonitrile, acetic acid, ethanol and methanol were from Kermel (Tianjin, China). Aqueous solutions of metal ions were prepared from their nitrate or chloride salts which were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). Unless otherwise specified, all reagents used were HPLC or analytical grade, and distilled water was used throughout the experiment.

2.2. Synthesis of fluorescent multi-functional monomer

The synthetic route of the new fluorescent multi-functional monomer, (E)-3′,6′-bis(allyloxy)-2-((thiazol-2-ylmethylene)-amino)-4a′,9a′-dihydrospiro[isoindoline-1,9′-xanthen]-3-one (ATMIX) is shown in Fig. 1.

In summary, 940 mg of K_2CO_3, 60 mL of acetone, 1.2 g of (E)-3′,6′-dihydroxy-2-((thiazol-2-ylmethylene)amino)spiro-(isoindoline-1,9′-xanthen)-3-one (HTMIX) (HTMIX was prepared based on our previous report [10]) and 0.59 mL of allyl bromide were added into 100-mL flask. The mixture was stirred and refluxed at 50 °C for 24 h. Following reaction, the solvent in the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate:petroleum ether = 1:3). The eluate was evaporated to dry under reduced pressure to give 1.0671 g of yellow powder with the yield of 75.30%. The structure of ATMIX was confirmed by ^1H, ^{13}C NMR and mass spectrometry. NMR was performed with a Varian NMR System 400 MHz Spectrometer (Varian, USA) using tetramethylsilane as internal standard and dimethyl sulfoxide-d6 (DMSO-d6) as solvent. Mass spectra were obtained on a Finnigan LCQ Deca XP MAX spectrometry (Finnigan, USA).

2.3. Fabricating ion-imprinted fluorescent on–off sensor

The ion-imprinted fluorescent on–off sensor (IIFOS) was synthesized as following: 0.1042 g (0.2 mmol) of fluorescent multi-functional monomer (ATMIX) was dissolved in the mixture of 10 mL of acetone and 10 mL of acetonitrile in a glass bottle. Then 0.5 mL of 0.1 M $AgNO_3$ (0.05 mmol) solution was added to above mixture and stirred for 30 min. After that, 0.1 mmol of MAA, 1.5 mmol of EGDMA and 0.05 g of AIBN were added to the mixture and sonicated for 30 min. A PVDF film was soaked in 0.15 M AIBN solution (in acetonitrile) for 10 min, and then soaked in the prepared polymerizable organic mixture for 30 min. Then the PVDF film was clamped between two quartz plates and sealed with palm film and polymerized for 48 h under a UV lamp (18 W, 365 nm). The IIFOS produced was washed with 0.1 M $Na_2S_2O_3$ solution and methanol successively for removal of Ag(I) and the unreacted reagents. The non-imprinted membrane (NIM) was synthesized with the same procedure as the IIFOS without adding Ag(I) ion during the polymerization.