A new covalent organic polymer used to highly selective detection of Fe³⁺ ions

Han Zhang¹, Xin-Long Wang^{1,2,*}, Chun-Yi Sun^{1,2}, and Zhong-Min Su^{1,2}

¹School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun 130022, China.

²National & Local United Engineering Laboratory for Power Batteries, Key Laboratory of Polyoxometalate Science of Ministry of Education Department of Chemistry, Northeast Normal University, Changchun 130024, China.

Abstract. Covalent organic polymers (COPs) received much attention due to their application in diverse fields, especially in sensing. A highly efficient fluorescence sensor in selective detection of Fe³⁺ ions is necessary to develop. In this work, we successfully synthesized a new covalent organic polymers named COP-TP, with the excellent performance in selective detection of Fe³⁺ ions, the quenching mechanism mainly due to the energy transfer process. The above results show COP-TP has the possibility to be a new candidate in selective detection as Fe³⁺ ions sensor.

1.Introduction

Covalent organic polymers (COPs) [1-2], as a new class of organic materials have drawn lots of attention due to their attractive properties with pre-designed structure [3], stable-band [4], and good dispersion[5] as well as the chemical and physical stability. And the selected monomers or building units make the COPs have the possible applications in sensing, gas storage, chemical separation, drug delivery, and catalysis[6-10]. Fe³⁺ ions are the important trace elements in the body, which influence the oxygen-uptake and electron transfer[11-12]. Moreover, the concentration of Fe³⁺ ions should be moderated at a suitable range, the deficiency and the overload would cause the diverse diseases. Different ions will cause different environmental and health problems, and the materials with specific and selective selection of Fe³⁺ ions are worthy to attention. To date, there are many materials used to act as sensors to detect metal ions, such as metal-organic polymers (MOPs) [13-16] and small organic molecules [17-20]. However, covalent organic polymers act as sensors to detect Fe³⁺ ions are rarely reported, a COP with excellent selective ability to Fe³⁺ ions is promising to design.

In this work, we successful designed and synthesized a new covalent organic polymer named COP-TP through the simple-green Suzuki-coupling reaction, characterized by FT-IR, PXRD, fluorescence spectrum and SEM. The COP has the great performance as sensor to selective detection of Fe³⁺ ions among the other trace elements ions and Mg²⁺ ions. The COP may provide a new fast method to selectively detect and monitor the Fe³⁺ in practice.

2.EXPERIMENTAL SECTION

2.1.Materials and measurements

All reagents and solvents for the synthesis were purchased from commercial sources and used as received, unless otherwise indicated. Infrared spectra were obtained from KBr pellets in a wavelength ranging from 3300-400 cm⁻¹ on a Nicolet 380 FT-IR spectrophotometer. PXRD pattern was recorded on a Siemens D5005 diffractometer with Cu K α (λ = 1.5418 Å) radiation in the range of 2 – 15°. SEM images were recorded on XL-30 ESEM-FEG Scanning Electron Microscope. Photoluminescence spectra were recorded on a FL-4600 FL spectrophotometer.

2.2.Synthesis of COP-TP

The COP-TP was synthesized through the Suzuki-coupling reaction according the literature (Scheme 1) [21], a mixture of Pyrene-2,7-diboronic acid, pinacol ester (PDABE) and 1,3,5-Tribromobenzene (TBB) (molar

* Corresponding author: wangxl824@nenu.edu.cn

Scheme 1. Synthesis route of the COP-TP.

ratio: 3:2), tetrakis(triphenylphosphine) palladium (0.01 mmol) and K_2CO_3 (3.2 mmol) was dissolved in DMF / H_2O (16 mL / 2 mL), the mixture was degassed by three freeze-pump-thaw cycles and purged with N_2 . The mixture was stirred at 150 °C for 72 h and then cooled to room temperature and poured into water. The precipitate was collected by filtration, repeatedly washed by Soxhlet extraction for 24 h, and finally dried in vacuum to give COP-TP as powder.

Fig. 1 FT-IR of COP-TP

2.3. Chemical sensing of metal ions

Titration experiments of metal ions were carried out by adding same concentration of metal salt solutions (20 μ L) into the dimethylacetamide (DMA) suspension (1 mL) containing COP-TP (0.1 mg/mL) at intervals of 5 min. Fluorescence spectra were recorded after the addition of metal salt solutions.

Fluorescence quenching % = $(1 - I/I_0) \times 100$ %, where I_0 is the initial fluorescence intensity in the absence of metal ions, I is the fluorescence intensity in the presence of corresponding analyte [22].

3. Results and discussion

Fig. 2 PXRD of COP-TP

Fig. 3 (a) Fluorescence spectrum of COP-TP; (b) SEM image of COP-TP.

Fig. 1 shows the FT-IR spectra of the COP-TP, DBTPA and TBB monomers as the reference units. The direct evidence of the Suzuki coupling reaction has already occurred is that the disappearance of characteristic peaks at 615 cm^{-1} , belonging to the C-Br vibration of the building monomers (TBB). And peaks at 1180 cm^{-1} is also disappearance which belongs to the C-O vibration of the building monomers (PDABE). The B-O vibration peaks around 1350 cm^{-1} is a lot lower compare to the PDABE, suggesting the PDABE was excessive before the reaction and the TBB was completed reacted. The spectra of FT-IR proved that the COP-TP was successful synthesized.

There is no obvious diffraction peak in the powder X-ray diffraction (PXRD) patterns (Fig. 2), indicating the amorphous nature of the COP-TP. The amorphous nature is similar to the reported materials that constructed by C-C coupling reaction [23]. The fluorescence spectrum (Fig. 3a) shows the COP-TP would emit the indigo color under the excitation wavelength at 300 nm, and the photographs of COP-TP dispersed in DMA have a obvious change under the 365 nm UV-lamp. The SEM image (Fig. 3b) exhibits the COP-TP is a irregularly layered structure.

Fe^{3+} ions play the very important roles in oxygen uptake,

Fig. 4 Fluorescence intensity change of COP-TP after added different metal ions.

biological mechanisms and electronic transmission, and the moderate concentration is important to the life activity. The selective detection of Fe^{3+} ions among the other cation ions is very challenge and urgent. So we used the COP to act as a fluorescence sensor to detect Fe^{3+} ions. In order to get more insights into the metal ions sensing behavior of COP-TP, we tested the capability of them in the chemical sensing of metal ions include Fe^{3+} , Co^{2+} , Zn^{2+} , Cr^{3+} , Cu^{2+} , Mg^{2+} ions. As shown in Fig. 4, the fluorescence intensity of COP-TP suspension has barely change after added Co^{2+} , Zn^{2+} , Cr^{3+} , Cu^{2+} , Mg^{2+} ions, and with the concentration up to 100 μL , the fluorescence intensity still not changed. The results showed the COP-TP will not be affected by the Co^{2+} , Zn^{2+} , Cr^{3+} , Cu^{2+} , Mg^{2+} ions. As for Fe^{3+} ions, when added 20 μL Fe^{3+} ions to the suspension of COP-TP, the quenching effect is very obvious. And with the increase of the Fe^{3+} ions concentration, the fluorescence intensity of COP-TP decreased gradually, the phenomenon exhibits the COP-TP has the excellent performance to selective detection of Fe^{3+} ions.

The quenching percentage can directly express the selective expression of Fe^{3+} ions. As shown in Fig. 5, the quenching percentage of COP-TP is up to the 95.41% after added 100 μL Fe^{3+} ions, whereas the fluorescence quenching percentage after added Co^{2+} , Zn^{2+} , Cr^{3+} , Cu^{2+} , Mg^{2+} ions are 12.76 %, 12.76 %, 6.00 %, 8.05 %, 5.44 %, respectively. The results show the COP-TP has the great selective ability to detect Fe^{3+} ions in aqueous.

The quenching process of COP-TP after add Fe^{3+} ions mainly due to the energy transfer mechanism. As previous reported [24-26], the Fe^{3+} ions has the empty d orbital, which is the perfect receptor to electrons. And the fluorescence COP is a electrons donor material, when the UV-lamp excites the electrons from COP-TP, the electrons would transfer to the d orbital with the energy transfer, leading to the fluorescence quenching. This clear mechanism could provide a theoretical basis for the successful application of material.

Fig. 5 Quenching percentage of COP-TP after added 100 μL metal ions.

4. Conclusion

We successful synthesized a new covalent organic polymers named COP-TP by Suzuki reaction, and confirmed by FR-IR, PXRD, Fluorescence spectrum, and SEM. The emission color change under the UV-Lamp shows the potential application in sensing, and the selective tests show the COP-TP has the great performance in selective detection of Fe^{3+} ions. And The clear mechanism provides a theoretical basis for its application. The COP-TP may provide a new method to selective detection of Fe^{3+} ions in aqueous.

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