



Synthesis, photoelectric properties and application of a polymer fluorescent probe with quinoline and benzene groups



Yang Deng^a, Weiping Niu^{a,b}, Zhijun Wang^{c,*}, Liheng Feng^{a,*}

^a School of Chemistry and Chemical Engineering, Shanxi University, Taiyuan 030006, PR China

^b Shanxi Station for Plant Protection and Quarantine, Taiyuan 030001, PR China

^c Department of Chemistry, Changzhi University, Changzhi 046011, PR China

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ABSTRACT

A novel π -conjugated polymer comprised of 8-methoxyquinoline and benzene groups has been successfully synthesized and characterized. The polymer exhibits good photo and thermal stabilities with decomposition temperature (T_d) of 240 °C and glass transition temperature (T_g) of 325 °C. The maximum absorption and emission wavelengths of the polymer are 325 nm and 430 nm with a high fluorescence quantum yield (0.74) in chloroform, respectively. The electrochemical properties of the polymer were investigated with the cyclic voltammetry method, and the results agreed with the data of theoretical calculation by the Gaussian 09 software. Based on the excellent photoelectric properties, the polymer as a fluorescent probe was used to detect metal ions in solution and biological cells. Experimental results indicate that the polymer has a high selectivity and sensitivity for Fe^{3+} with the fluorescence quenched processes. Noticeably, the detection of the polymer for Fe^{3+} can be processed in biological system.

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1. Introduction

As the focus on innovative material researches, conjugated polymers (CPs) have received a significant attention in recent years [1–3]. It is well-known that conjugated polymer possesses a plenty of repeat units, which form the backbone of polymer. Due to their specific structures, the excitation energies of conjugated polymers can transfer along the backbone, and produces the “signal-amplification” effect [4,5]. Compared with small molecules, conjugated polymers have been verified as potential materials in chemical and biological fields because of their excellent properties such as high photostability, good biocompatibility and facile modification further [6,7]. Meanwhile, some conjugated polymers owning excellent electrical and optical properties are also popular in flat-panel displays and solar cells [8,9].

Owing to the excellent optical properties of conjugated polymers, some highly selective and sensitive chemosensors towards cations [10–14], anions [15,16], small molecules [17] and proteases [18] have been reported in recent ten years. For example, Li and co-workers prepared an “off-on” fluorescent probe containing perylene and salen moieties. For the probe, an obvious change of the solution color from red to yellow could be observed by

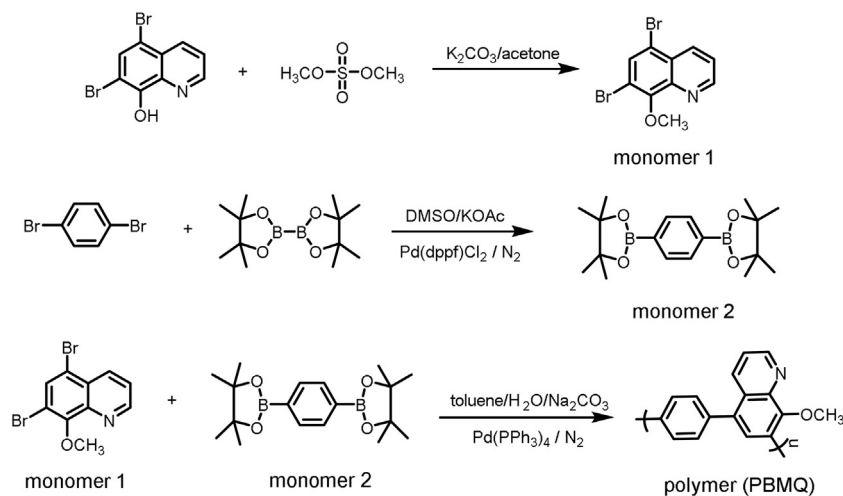
the naked eye when introducing Hg^{2+} [19]. Wu and co-workers designed a conjugated polymer-based chemosensor to CN^- , which successfully realized a “signal-amplification” effect and lower detection limit for CN^- [20]. Based on fluorescence resonance energy transfer (FRET) mechanism, Wang and co-workers reported a conjugated polymer fluorescent probe, which showed potential recognition capacity to H_2O_2 . Furthermore, utilizing this H_2O_2 -sensitive conjugated polymer could detect glucose and trace the choline consumption process in cancer cells [21]. However, conjugated polymers as chemosensors are still scarce in comparison with small molecules.

In recent years, there has been an increasing interest to detect transition metal ions [22,23]. As one of the most abundant elements, iron plays an essential role in biological and environmental systems because it participates these processes of cell metabolic, gene regulation, oxygen transport and enzyme catalysis [24–26]. Maintaining the balance of iron in living systems is vital to ensure the normal physiological activities. Overload of Fe^{3+} in living system may damage nucleic acids and proteins. While the deficiency of Fe^{3+} can also result in anemia, hypotension, decreasing immune function, even inducing Alzheimer and Parkinson [27–30]. So it is imminent to develop highly selective and sensitive chemosensors towards Fe^{3+} .

With the extensive application in organic light-emitting diodes and solar cells, quinoline has drawn much attention from researchers [31,32]. And the excellent chelation to metal ions fur-

* Corresponding authors.

E-mail addresses: czxywzj@163.com (Z. Wang), lhfeng@sxu.edu.cn (L. Feng).



Scheme 1. The synthesis route of monomers and polymer PBMQ.

ther has made it to be the focus on chemical and biological sensors [33–35]. Hence, in this work, we report a novel conjugated polymer containing benzene and quinoline units for using as a fluorescent chemosensor (Scheme 1). The experiments for performance tests indicate that the conjugated polymer has excellent photoelectric properties, thermal stability and electron transfer capacity. Based on the UV–vis absorption and fluorescence emission spectra, we find that the conjugated polymer possesses high selectivity and sensitivity for Fe^{3+} with fluorescence “On-Off” response. Additionally, the interaction of the conjugated polymer to Fe^{3+} in vitro cells has been investigated.

2. Experimental

2.1. Materials and instruments

Unless otherwise stated, all chemical reagents were obtained from commercial suppliers and used without further purification. Solvents used were purified and dried by standard methods prior to use. 1,4-Dibromobenzene, bis(pinacolato)diboron, dimethyl sulfate, $\text{Pd}(\text{dppf})\text{Cl}_2$, $\text{Pd}(\text{PPh}_3)_4$, and 5,7-dibromo-8-hydroxyquinoline were purchased from Aldrich (Steinheim, Germany). Other routine solvents were purchased from Beijing Chemical Plant (Beijing, China). Metal ions were all nitrates and provided from Alfa Aesar (Tianjin, China). ^1H NMR and ^{13}C NMR spectra were measured on a Bruker ARX400 spectrometer with chemical shifts reported as ppm (TMS as an internal standard). Gel permeation chromatography (GPC) measurements were performed on a Waters-410 system against polystyrene standard with tetrahydrofuran (THF) as eluent. UV–vis spectra were measured with a Hitachi 5300 absorption spectrophotometer. Fluorescence spectra were acquired with a Hitachi F-4600 fluorescence spectrophotometer, the excitation and emission slit widths both were 5.0 nm. Confocal laser scanning microscopy (CLSM) imaging was taken on a confocal laser scanning biological microscope (FV1000-IX81, Olympus, Japan). Viability of cells assay was reported by a microplate reader (BIO-TEK Synergy HT USA) with 490 nm wavelength. The fluorescence intensity of photostability assay was recorded by the fluorescence microscopy (Olympus 1×71). The glass transition temperature of the polymer was determined by DSC using a DSC-Q10 instrument under a nitrogen atmosphere. The decomposition temperature corresponding to 5% weight loss was detected using a Perkin-Elmer Pyris 1 TGA thermal analyzer. Cyclic voltammetry (CV) measurement was determined on a three-electrode AUTOLAB (model PGSTAT30)

workstation in a solution of Bu_4NClO_4 (0.10 M) in acetonitrile at a scan rate of 50.0 mV/s at room temperature.

2.2. Synthesis of monomer 1, monomer 2 and polymer (PBMQ)

The monomers and polymer were prepared according to our reported work [31].

A mixture with 0.317 g monomer 1 (1.0 mmol) and 0.33 g monomer 2 (1.0 mmol) in toluene (10.0 mL), 2.0 mol/L Na_2CO_3 (5.0 mL) was added and stirred for 30 min at room temperature under nitrogen atmosphere. Then, 50 mg $\text{Pd}(\text{PPh}_3)_4$ catalyst was quickly added to the suspension and heated the mixture to 110°C for 48 h under nitrogen atmosphere. After the suspension was concentrated to 2–3 mL, 50 mL chloroform was added to the suspension. The obtained mixture was washed with water for three times. The organic layer was dried over anhydrous MgSO_4 . After removal of a mass of chloroform, the residue was precipitated with methanol and the precipitate was collected by centrifugation. The crude polymer was purified by precipitation for twice from chloroform into methanol. The final grey white solid product was obtained through centrifugation and drying under vacuum in 33.3%. ^1H NMR ($d\text{-CHCl}_3$, 400 MHz) δ 9.08 (s, 1H), 8.43 (broad, 1H), 7.97 (broad, 1H), 7.79 (broad, 1H), 7.71 (d, $J = 10.8$ Hz, 2H), 7.53 (d, $J = 22.8$ Hz, 2H), 4.04 (s, 3H); ^{13}C NMR ($d\text{-CHCl}_3$, 100 MHz) 62.34, 121.32, 127.46, 128.40, 128.91, 129.78, 130.16, 130.31, 132.59, 134.63, 135.42, 137.26, 143.52, 149.95, 152.87; $M_n = 19316$, $M_w = 28826$, PDI = 1.49.

2.3. UV–vis and fluorescence measurements for PBMQ

All used water was the redistilled water. The polymer PBMQ was dissolved in DMSO or chloroform as the stock solutions (1.0×10^{-2} mg/mL), respectively. The working solutions were prepared by a diluting method with mixed media ($\text{H}_2\text{O}/\text{DMSO} = 1/9$). The working solution was placed in a quartz cuvette with 1 cm path. The total volume of working solution was 2.0 mL. The UV–vis and fluorescence measurements were carried out by the titration method and the added volume did not exceed 3% of the total. After the mixed solutions were shaken for 30 s, the new spectra were measured. All of the experiments were performed at barometric pressure and room temperature.

2.4. Cells culture and imaging

Human cervical cancer cells (HeLa) were cultured in DMEM medium containing 10% FBS routinely under a humidified atmo-

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