Sensors and Actuators B 207 (2015) 281–290

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

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

A colorimetric and fluorescence "turn-off" chemosensor for the detection of silver ion based on a conjugated polymer containing 2,3-di(pyridin-2-yl)quinoxaline

Wei Cui [a], Lingyun Wang [a,*], Gang Xiang [a], Lixia Zhou [b], Xiaoning An [a], Derong Cao [a,**]

[a] School of Chemistry and Chemical Engineering, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510641, China
[b] South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China

ARTICLE INFO

Article history:
Received 14 July 2014
Received in revised form 11 October 2014
Accepted 16 October 2014
Available online 27 October 2014

Keywords:
Conjugated polymer
Silver ion detection
Colorimetric and fluorescent chemosensor
Quinoxaline

ABSTRACT

Two novel conjugated polymers containing 2,3-di(pyridin-2-yl)quinoxaline (DPQ) unit (**P1**) and 2,3-di(thiophen-2-yl)quinoxaline (DTQ) unit (**P2**) were designed and synthesized through Sonogashira coupling reaction. **P1** provided high sensitivity and selectivity to silver ions: color change from green to brown red and fluorescent emission quenching, which can be observed by naked eye, even in the presence of interference cations. However, **P2** with the similar polymer backbone to **P1** showed no absorption and fluorescence changes toward any cations. Therefore, the DPQ units in **P1** exhibited a key role for the selective recognition of Ag^+, which was further confirmed by the ^1H NMR titration, density functional theory (DFT) calculations and electrochemical studies. These results not only imply that DPQ based conjugated polymer is a promising probe of Ag^+ ions but also afford a good guidance to design effective polymer sensors in future.

1. Introduction

Silver ion (Ag^+) as one of the precious metal ions has attracted enormous attention due to its rarity, valuableness, and importance in many industrial processes and products [1]. Meanwhile, it has been assigned to the highest toxicity class [2]. In addition, silver ion also plays a crucial role in biological system for instance as microelements existing in the human tissue, having antimicrobial activity [3]. Owing to the fact that Ag^+ has moderate coordination ability, it is quite difficult to be discriminated from other similar heavy metal ions. The instrumental techniques are the traditional analytical methods used for its detection. Nevertheless, these techniques are restricted owing to expensive facilities and sometimes need tedious sample-pretreatment procedures [4]. Several advantages such as high sensitivity, quickness, convenience and cheapness make colorimetric and fluorimetric methods more desirable. The mechanisms of these methods are mostly based on the complexation between Ag^+ and ligands [5].

Over the past decades, conjugated polymers (CPs) as sensing probes have been a focal point in many detecting fields such as metal ions, toxic chemicals and biomolecules due to their particular sensing ability [6]. Compared to the small organic compounds, the delocalized π-electronic conjugated "molecular wires" can greatly amplify the fluorescence signal by the facile energy migration along the polymer backbone upon light excitation [7]. Additionally, polymers are easily fabricated into film sensors and matrix [8]. A number of CP sensors for various metal ions have been investigated [9]. Nevertheless, there are only few papers for detecting Ag^+ [10]. Qin et al. reported selective detection of Ag^+ with an organometallic conjugated polyelectrolyte [10a]. Hu et al. constructed a meta-substituted monopyridyl conjugated polymer for Ag^+ detection [10b]. Tong et al. utilized conjugated polyquinoline as a selective sensor for Ag^+ detection [10c]. Bao et al. developed a conjugated polymer sensor for the detection of amino acid through the second complexes of conjugated polymer with Ag^+ [10e]. In these literatures, less works are regard to the colorimetric and fluorescent probes of silver ions [10a].

In our previous work, a conjugated polymer containing ethyl 2-(2-(pyridin-2-yl)-1*H*-benzo[d]imidazol-1-yl) acetate (PBMA) unit was synthesized to selectively detect trace amounts of Ag^+ through fluorescence quenching mechanism [10d]. In the detecting process, three groups (pyridine, benzimidazole and ester) in PBMA

* Corresponding author. Tel.: +86 2087110245.
** Corresponding author.
E-mail addresses: lingyun@scut.edu.cn (L. Wang), drcao@scut.edu.cn (D. Cao).

http://dx.doi.org/10.1016/j.snb.2014.10.072
0925-4005/

unit synergistically bound silver ions. Yet, it failed to realize neither colorimetric detection nor remarkable fluorescence change. Thus, it is urgent to explore a colorimetric and fluorescent chemosensor for detecting Ag^+. As a common sense, the quinoxaline unit has similar structure of nitrogen atom to benzoimidazole unit; the pyridine and thiophene units have strong complexing ability with Ag^+. DPQ and DTQ units are often employed as optical materials [11] but are rarely used in the field of sensors [12]. Electron-rich fluorene acetylene triple bonds as bridges are often introduced to form a convenient electrons transfer channel. Inspired by these considerations, two novel conjugated polymers (**P1** and **P2**) were designed and synthesized. The optical properties of **P1** and **P2** toward metal ions in THF solution were studied through absorption and fluorescence emission spectroscopy. **P1** as a colorimetric and fluorescent probe could selectively and sensitively detect silver ions. To the best of our knowledge, DPQ unit is utilized for the first time in the field of the CP fluorescent probes for the detection of Ag^+. However, **P2** shows no response to any cations. Density functional theory (DFT) calculations were carried out to understand the geometrical configuration and electron distributions of **P1** and **P2.** The interaction mechanism between the polymer and metal ions was studied by ^{1}H NMR titration and electrochemical measurements.

2. Experimental

2.1. Materials and metal ion titration

All of metal salts in analytical grade were purchased from Guangzhou Chemical Co. and used without further purification. Toluene was dried and freshly distilled over before use. 3,6-Dibromobenzene-1,2-diamine (**1**) [10d], compounds **4** [10d] and **6** [13] were prepared according to the literature. All other organic reagents were purchased from Aladdin Corporation and used without further purification.

Polymers were dissolved in 100 mL tetrahydrofuran (THF) to afford a solution of 2×10^{-5} mol L^{-1}. This stock solution was diluted to 5×10^{-6} mol L^{-1}. Inorganic salt (0.1 mmol) was dissolved in ultrapure water (10 mL) to afford a 1×10^{-2} mol L^{-1} aqueous solution. The stock solution was diluted to the desired concentrations with ultrapure water when needed.

Metal ion titration experiment was performed with 2.0 mL of polymer solution in THF with a known concentration. The solutions of chlorate or nitrate metal salts were used for the titration. Both of absorption and fluorescence titrations were carried out by adding aliquots of a solution of the selected metal salts to the THF solution of **P1** or **P2** (2.0 mL) in a quartz cuvette.

2.2. Measurements

NMR (^{1}H and ^{13}C) spectra were collected on a Bruker DRX 400 spectrometer (Bruker, Germany) in $CDCl_3$ with tetramethylsilane as internal reference. UV–vis absorption spectra were recorded on a HP 4803 instrument (HP, Japan). The fluorescence measurements (FL) were recorded on a Hitachi F4500 spectrofluorometer (Hitachi, Japan) equipped with a Xenon lamp excitation source (Ex Slit: 5.0 nm; Em Slit: 5.0 nm; PMT Voltage: 700 V) at room temperature. Molecular weights and molecular weight distributions were determined by waters GPC 515-410 (Waters, USA) in THF using a calibration curve of polystyrene standards. Mass spectra were performed on a Bruker maXis impact (Bruker, Germany). All spectra were measured at room temperature. The cyclic voltammograms were recorded with a CH Instruments Model 600D Series electrochemical workstation (CH Instruments, USA) with Pt plate as the working electrode, Pt wire as the counter electrode and Hg/Hg^{2+} (0.1 M) as the reference electrode. All spectra were measured at room temperature.

2.3. Synthesis

2.3.1. Synthesis of Compound 3

Compound **2** was synthesized by the literature method [14]. To a solution of **1** (0.30 g, 1.13 mmol) in HAc (15 mL), **2** (0.26 g, 1.24 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature, water (20 mL) was added. The mixture was extracted by CH_2Cl_2. The combined organic phase was washed repeatedly with brine, dried over Na_2SO_4, and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel, ethyl acetate/petroleum ether (b.p. 60–90 °C): 1/3) to give **3** as a yellow solid (mp 253–255 °C) (0.40 g, 0.90 mmol) in 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.30–8.27 (m, 4H), 7.96 (s, 2H), 7.92–7.88 (m, 2H), 7.27–7.24 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz, ppm): δ 156.6, 153.5, 148.2, 139.4, 137.0, 133.7, 124.6, 123.8, 123.5. HRMS (ESI, m/z): $[M+H]^+$ calcd. for $C_{18}H_{11}{}^{79}Br^{79}BrN_4$: 440.9345, found 440.9346. $[M+H]^+$ calcd. for $C_{18}H_{11}{}^{79}Br^{81}BrN_4$: 442.9325, found 442.9326.

2.3.2. Synthesis of 6

Compound **6** was prepared as yellow solid using the reported method [13]. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 2H), 7.57–7.56 (m, 2H), 7.48 (s, 2H), 7.06 (m, 2H).

2.3.3. Synthesis of P1 and P2

A solution of toluene and NEt_3 was degassed 30 min with N_2, and then injected under Ar into a mixture of compound **3** (100 mg, 0.23 mmol), compound **4** (131 mg, 0.24 mmol), CuI (10 mg, 0.053 mmol) and $Pd(PPh_3)_4$ (26 mg, 0.023 mmol). The mixture was stirred at 60 °C for 36 h. After cooling to room temperature, the reaction mixture was subjected to a water/CH_2Cl_2 workup. The organic phase was washed with water three times and then dried over anhydrous Na_2SO_4. After the solution was concentrated, it was dropped into MeOH (100 mL) to give **P1** as a black solid (111 mg) in 60% yield. M_w = 16,879 g mol^{-1}, M_n = 8511 g mol^{-1}, M_w/M_n = 1.98. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 8.41–8.29 (br, PyH), 8.13–8.06 (br, PyH), 7.96–7.90 (br, PyH), 7.78–7.65 (br, PyH, ArH), 7.56–7.52 (br, ArH), 7.31–7.28 (br, PyH), 2.03 (br, —CH_2—), 1.56 (br, —CH_2—), 1.25–1.07 (br, —CH_2—), 0.87–0.81 (br, —CH_3).

P2 was prepared as black solid (yield 80%) from compounds **6** and **7** by using the similar procedure of **P1**. M_w = 20,308 g mol^{-1}, M_n = 9878 g mol^{-1}, M_w/M_n = 2.06. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.90 (br, ThH), 7.78–7.68 (br, ThH, ArH), 7.58–7.46 (br, ThH, ArH), 7.08 (br, ThH), 2.03 (br, —CH_2—), 1.56 (br, —CH_2—), 1.25–1.07 (br, —CH_2—), 0.87–0.81 (br, —CH_3).

3. Results and discussion

3.1. Synthesis and characterization of P1 and P2

The synthetic route of **P1** and **P2** is shown in Scheme 1. **P1** and **P2** were synthesized by Sonogashira reaction from **4** and **3**, and **6** and **7**, respectively, and characterized by spectroscopic methods (^{1}H NMR and GPC). The ^{1}H NMR spectrum of **P1** (Fig. 1a) shows that the chemical shifts and the ratio of the hydrogen atoms are in accordance with the proposed structure: the signals between δ 8.41–8.29 and 8.13–8.06 ppm are assigned to the protons of pyridine; the signal at δ 2.03 ppm is for the protons of the methylene linked to fluorene. The ^{1}H NMR spectrum of **P2** also displays the proposed structure (Fig. 1b): the signal at 7.09 ppm is assigned to the protons of thiophene; the signal at δ 2.03 ppm is assigned to the protons of methylene adjacent to the fluorene. In the two polymers'