Dyes and Pigments 156 (2018) 1–7

Contents lists available at ScienceDirect

Dyes and Pigments

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

Reaction-based AIEE-active conjugated polymer as fluorescent turn on probe for mercury ions with good sensing performance

Yuanrong Shan[1], Wenjie Yao[1], Ziqin Liang, Lihong Zhu, Shuibin Yang, Zhijun Ruan*

Hubei Key Laboratory of Processing and Application of Catalytic Materials, College of Chemistry and Chemical Engineering, Huanggang Normal University, Huanggang 438000, China

ARTICLE INFO

Keywords:
Aggregation induced emission enhancement
Conjugated polymer
Chemodosimeter
Mercury ions
Fluorescence probe

ABSTRACT

Based on Hg^{2+}-promoted deprotection reaction of thioketal, a type of thioketal decorated conjugated polymer (**PTS**) with the feature of aggregation induced emission enhancement (AIEE) was successfully synthesized as fluorescent turn on probe for Hg^{2+}. With the introduction of trace aqueous Hg^{2+}, fluorescence of **PTS** in THF-H_2O mixture (water fraction of 98%) exhibited significant enhancement. The response was very fast with good selectivity towards Hg^{2+} due to the specific chemical reaction. Other common metal ions (Ag^+, Cr^{3+}, Al^{3+}, Fe^{3+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Ba^{2+}, Li^+, Na^+ and K^+) gave nearly no disturbance to the sensing process. Furthermore, the detection limit of Hg^{2+} reached 2.3×10^{-7} mol L^{-1} for this sensing system.

1. Introduction

Mercury ions are one of the most toxic heavy metal ions, have many adverse effects on the endocrine system, immune system and nervous system of organisms [1–3]. Even more seriously, some lower organisms can transform inorganic mercury into methylmercury, a potent neurotoxin for central nervous system, the harmful influence will dramatically increase [4–6]. Moreover, the mercury pollutant will be stored in animal tissues rather than excreted, the concentration may be very high in animals that at the top of the food chain. Thus, global mercury pollution from human activities and nature has become a serious threat to living beings and environment [7,8]. It is urgent to develop convenient methods for selective and sensitive detection of mercury ions. Traditional analytical methods include atomic absorption spectrometry, inductively coupled plasma mass spectroscopy, and chromatography. Whereas, most of them are incapable to meet the requirement of easy-to-use detection due to complicated sample pretreatment and expensive instruments. Great efforts have been invested in developing straightforward methods, such as colorimetric, fluorescent and electrochemical probes. Among these methods, fluorescence-based probe has appeared as a powerful tool to detect mercury ions, due to its simple operation, high sensitivity and low-cost [9–13]. In the past several years, various fluorescent mercury ions probes based on polymers [14–18] or small organic molecules [19–28] have been developed. Compared to small molecular probes, probes based on fluorescent conjugated polymers (CPs) have displayed huge superiority in detection sensitivity owing to their large delocalized molecular structures with unique signal amplification effect [29–31].

Recently, Tang and coworkers have found that some organic molecule was weak emissive in solution but strongly emissive in aggregated state [32,33]. These aggregation induced emission enhancement (AIEE) luminogens exhibited many advantages, such as intrinsic strong emission in aggregated state, good photobleaching-resistance and high sensitivity when used as fluorescent probes [34–40]. Since then, lots of turn on fluorescent Hg^{2+} chemosensors based on AIEE small molecules have been successfully constructed [41–46].

To achieve high selectivity, fluorescent mercury ions probes based on specific chemical reactions have been developed [47–54]. In previous work, we have designed a novel AIEE-active fluorescent small molecular probe **TPE-S** towards mercury ions based on the Hg^{2+}-promoted deprotection reaction of mercaptal (Chart S1 and S2) [55]. The nitrobenzene moieties in **TPE-S** was highly twisted, so the nitro group was close to the fluorophore (tetraphenylethylene, TPE), quenching its fluorescence emission. While the nitro group in **TPE-O** was far from the TPE moiety, weakening the quenching effect (the crystal structures seen Chart S1). Thus, once triggered by Hg^{2+}, the conversion of **TPE-S** to **TPE-O** could give a turn on signal output. However, the fluorescence intensity and fluorescence enhancement value of this sensor were very limited, regardless of its high selectivity (Inset photos in Chart S1).

In this work, taking advantage of the excellent fluorescence

* Corresponding author.
E-mail address: ruanzhijun87@126.com (Z. Ruan).
[1] Contributed equally.

https://doi.org/10.1016/j.dyepig.2018.03.060
Received 17 February 2018; Received in revised form 25 March 2018; Accepted 25 March 2018
Available online 30 March 2018
0143-7208/

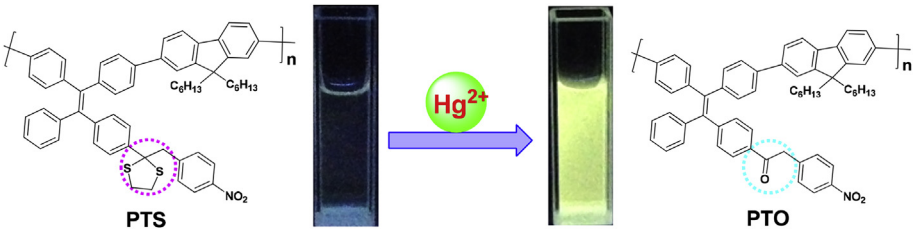

Fig. 1. Chemical structure and the Hg^{2+} sensing process of **PTS**.

amplification effect of CPs, **TPE-S** was copolymerized with fluorene moieties to construct a new conjugated polymer of **PTS** with the aim of obtaining better sensing performance. So far, the AIEE-active conjugated polymers as fluorescence turn on probes for Hg^{2+} are very rare [56–59]. The chemical structure and the sensing process of **PTS** are shown in Fig. 1. In fact, **PTS** emits very weak fluorescence in THF-H_2O mixtures with the water fraction of 98%. After the addition of trace Hg^{2+} ions to **PTS**, the deprotection reaction happened immediately, accompanying with the emission becomes dramatically strong. Other metal ions (Ag^+, Cr^{3+}, Al^{3+}, Fe^{3+}, Ca^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Cu^{2+}, Zn^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+}, Cd^{2+}, Ba^{2+}, Li^+, Na^+ and K^+) gave nearly no disturbance to the sensing process. Herein, we present the synthesis, characterization, sensing behavior of **PTS** in detail.

2. Experimental

2.1. Material

Tetrahydrofuran (THF) was dried over and distilled from K-Na alloy under an atmosphere of dry nitrogen. Dichloromethane (DCM) was dried over and distilled from CaH_2. The solutions of various metal ions were prepared by double distilled water. Compounds **1** and **3** were synthesized according to previous literatures [60,61]. All other reagents were used as received without further purification.

2.2. Synthesis of 1-(4-(2,2-bis(4-bromophenyl)-1-phenylvinyl)phenyl)-2-(4-nitrophenyl)ethanone (2)

$SOCl_2$ (1 mL) was added to a solution of 2-(4-nitrophenyl)acetic acid (0.181 g, 1 mmol) in nitrobenzene (10 mL) and stirred at 60 °C overnight. Excess $SOCl_2$ was stripped off under vacuum at room temperature. Compound **1** (0.490 g, 1 mmol) was added to the resultant solution with an ice bath under nitrogen atmosphere, then $AlCl_3$ (0.133 g, 1 mmol) was added. After 4 h, the reaction mixture was extracted with DCM for several times, the organic layer was combined and dried over anhydrous Na_2SO_4. After evaporation of the DCM solvent, the crude product was purified by column chromatography using PE (petroleum ether)-EA (ethyl acetate) (10:1, V/V) as eluent to afford a pale-yellow solid (0.451 g, 69%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.22 (d, J = 8.7, 2H, ArH), 7.79 (d, J = 8.7, 2H, ArH), 7.42 (d, J = 8.7, 3H, ArH), 7.24 (m, 2H, ArH), 7.16 (m, 6H, ArH), 6.98 (br, 2H, ArH), 6.88 (d, J = 7.2, 4H, ArH), 4.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.3, 148.8, 147.0, 142.1, 142.0, 141.4, 140.8, 140.2, 134.2, 133.0, 132.8, 132.8, 131.6, 131.4, 131.2, 131.0, 130.6, 128.1, 128.0, 127.3, 123.6, 121.3, 121.1, 44.8. MS (EI), m/z [M^+]: 653.4, calcd: 653.1. Anal. calcd for $C_{34}H_{23}Br_2NO_3$: C 62.50, H 3.55, N 2.14; found: C 62.81, H 3.66, N 2.08.

2.3. Synthesis of poly[1-(4-(2-(4-(9,9-dihexyl-7-methyl-9H-fluoren-2-yl)phenyl)-1-phenyl-2-p-tolylvinyl)phenyl)-2-(4-nitrophenyl)ethanone] (PTO)

A mixture of compound **2** and compound **3** (1.00 equiv), K_2CO_3 (20.00 equiv), tetrakis (triphenylphosphine) palladium ($Pd(PPh_3)_4$) (5 mol %) and THF/H_2O (2:1 in volume), was charged with argon. The reaction was stirred under reflux for 2 days. Then, the reaction mixture was filtered through a cotton filter, the filtrate was collected. After the solvent was removed under vacuum, the residue was dissolved in a bit of chloroform, added dropwise into 200 mL of methanol through a cotton filter, the precipitates were collected by filtration. Then, the polymer was washed with methanol and dried to a constant weight. Yellow solid was obtained in 75% yield. M_w = 11240; M_w/M_n = 1.74. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.20 (d, J = 7.2, 2H, ArH), 7.82 (m, 4H, ArH), 7.55 (m, 11H, ArH), 7.19 (br, 10H, ArH), 4.35 (s, 2H), 2.00 (br, 4H), 1.03 (br, 12H), 0.74 (br, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 195.4, 151.6, 149.9, 146.9, 143.3, 142.1, 142.0, 139.8, 139.1, 133.8, 131.8, 131.7, 131.3, 130.6, 129.0, 128.0, 126.5, 126.3, 125.8, 123.6, 121.0, 120.0, 55.2, 44.7, 40.4, 32.0, 29.6, 23.7, 22.5, 14.0.

2.4. Synthesis of poly[2-(4-(2-(4-(9,9-dihexyl-9H-fluoren-2-yl)phenyl)-1,2-diphenylvinyl)phenyl)-2-(4-nitrobenzyl)-1,3-dithiolane] (PTS)

PTO (1.00 equiv) and 1, 2-ethanedithiol (3.00 equiv) were dissolved in dry dichloromethane (10 mL), then $BF_3{\cdot}Et_2O$ (6.00 equiv) as the Lewis acid was added, stirring at room temperature for 2 days. Then, the reaction mixture was filtered through a cotton filter, the filtrate was collected. After the solvent was removed, the residue was dissolved in a bit of chloroform, added dropwise into 300 mL of methanol through a cotton filter, the precipitates were collected by filtration. Then, the polymer was washed with methanol and dried to a constant weight. Yellow solid was obtained in 62% yield. M_w = 12835; M_w/M_n = 1.69. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.00 (d, J = 7.2, 2H, ArH), 7.70 (br, 2H, ArH), 7.55 (m, 8H, ArH), 7.24 (m, 15H, ArH), 3.58 (s, 2H), 3.30 (m, 4H), 1.97 (br, 4H), 1.03 (br, 12H), 0.74 (br, 10H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 151.6, 151.5, 146.8, 144.6, 143.5, 143.2, 142.7, 142.4, 141.7, 140.5, 140.3, 140.1, 140.0, 139.5, 139.4, 139.3, 139.1, 132.0, 131.89, 131.8, 131.4, 130.9, 128.7, 128.4, 127.8, 127.1, 126.7, 126.6, 126.2, 125.9, 125.8, 122.4, 120.9, 120.0, 119.9, 55.1, 52.4, 40.4, 39.2, 31.4, 29.6, 23.7, 22.5, 13.9.

2.5. Preparation of the solutions of various metal ions

One millimole of inorganic salt: $Hg(ClO_4)_2{\cdot}3H_2O$, $AgNO_3$, $Cr(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3$ $9H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $CoCl_2{\cdot}6H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Ba(NO_3)_2$, $Pb(NO_3)_2$, $Ni(NO_3)_2{\cdot}6H_2O$, $Zn(NO_3)_2{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $MnSO_4{\cdot}H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Mg(ClO_4)_2$, $Fe(SO_4)_2{\cdot}7H_2O$, KNO_3, $NaNO_3$ and $LiNO_3$ was dissolved in double distilled water (10 mL) to afford 1×10^{-1} mol/L aqueous solution, respectively. The stock solutions were diluted to desired concentrations with double distilled water when needed.

2.6. Fluorescence intensity changes of PTS with different metal ions

A solution of **PTS** (1×10^{-3} mol/L) in THF was prepared. Different metal ions (1×10^{-1} mol/L, 4.5 μL) were added to the solution of **PTS** (60 μL) in a quartz tube respectively, then distilled water was added to help the formation of aggregation state (with water fraction of 98%). The resultant solutions (3 mL) were placed in a quartz cell (10.0 mm width), and the changes of the fluorescence intensity were recorded at room temperature each time (excitation wavelength 368 nm).