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Dual-emitting fluorescent chemosensor based on resonance energy transfer from poly(arylene ether nitrile) to gold nanoclusters for mercury detection

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ABSTRACT

A dual-emitting fluorescent chemosensor has been designed for sensitive and specific detection of Hg^{2+}. The principle of this chemosensor is based on the fluorescence resonance energy transfer (FRET) which employs blue intrinsically fluorescent poly(arylene ether nitrile) (FPEN) and red-emitting gold nanoclusters (Au NCs) as energy donor and acceptor, respectively. Firstly, two FPENs with different repeating units (*homo*-FPEN and *co*-FPEN) in backbone were synthesized to optimize the FRET efficiency. Specifically, *homo*-FPEN was polymerized to contain twofold carboxyl moieties in main chain than that of *co*-FPEN. The steady state and transient fluorescent spectroscopy indicated that FRET with higher efficiency could be obtained by using *homo*-FPEN as an optimized energy donor. Furthermore, the optimized sensor platform (*homo*-FPEN/Au NCs) displayed a dramatic emitting color changing from pink to blue upon Hg^{2+} exposure, leading to specific determination of 10 nM Hg^{2+} by fluorometric detection. The performance of proposed chemosensor was validated by its competitive responses to several common metal ions and efficient application in real environmental samples (tap water and lake water spiked with Hg^{2+}). More interestingly, the fluorescent nanofiber mat was fabricated by electron spinning of FPEN solution, which exhibited naked-eye discrimination of 10 μM Hg^{2+} aqueous solution after adsorption of Au NCs. Therefore, the easily regenerated fluorescent nanofibers based on FPEN and Au NCs with fast, sensitive and specific responses open a new way for the development of robust chemosensor for Hg^{2+} detection.

1. Introduction

Excessive heavy metals pollutions have been considered as an important issue in environmental monitoring. Among them, the mercury ions (Hg^{2+}) are widely distributed and causing many serious problems around the globe [1]. The hazardous effects of mercury derive from its bioaccumulation and neurotoxicity, which leads to chronic poisoning in human's physiological system [1,2], the severe damage in brain, heart, kidney, immune system and Minamata disease [3–6]. Therefore, the United States Environmental Protection Agency (EPA) restricts the level of mercury ions under 10 nM in drinking water strictly [7]. So far, a variety of methods have been developed toward Hg^{2+} detection, such as inductively coupled plasma–mass spectrometry (ICP–MS) [8], inductively coupled plasma–atomic emission spectrometry (ICP–AES) [9], surface enhanced Raman scattering (SERS) [10], spectrofluorometry [11,12], cold vapor atomic absorption spectrophotometry (CV-AAS) [13], etc. Although these methods exhibit many advantages (e.g., good specificity, high sensitivity), the requirements of bulky instruments, high cost, long detection period and laborious sample pretreatment obviously limit their wide applications [14]. Therefore, the more economical and robust methodologies which can provide faster and sensitive responses are still highly demanded.

In recent decades, fluorescent chemosensors have attracted a wide attention because of their simplicity, low cost and high sensitivity [15–18]. In addition, both the fluorescent intensity and emission wavelength shift (i.e., the color changing) can be employed as the optical responses for analyte detection. Common mechanisms of fluorescent chemosensors are paramagnetic fluorescence quenching, photoinduced electron transfer (PET), photoinduced charge transfer (PCT), fluorescence resonance energy transfer (FRET), excimer or exciplex formation and irreversible reaction-based sensors [19,20]. Especially, FRET based chemosensor is constructed via the dipole–dipole interactions of two fluorophores, namely a donor and an acceptor [21]. Since efficient FRET pair needs a substantial spectrum overlap between donor

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emission and acceptor absorption, large pseudo-stokes shift is usually observed in this kind of sensing platform [22], and the relative intensity of the two fluorescent peaks can be employed as optical responses as well [23]. Therefore, FRET-based sensors have already been widely used as multi-fluorophores systems showing rapid response, good specificity as well as low detection limit in various applications [23–25].

Poly(arylene ether nitrile) (PEN), a high performance thermoplastic polymer with high thermostability, good mechanical strength, excellent film-forming ability and spinning property, has been systematically investigated in decades [26–28]. Recently, a series new kind of PEN, which contains carboxyl-functionalized moieties, have been synthesized as a blue emitting intrinsically fluorescent polymer (FPEN) in our group [28]. Due to the reactivity of carboxyl group, FPEN shows an outstanding chemical and physical interaction to combine with other chemical substance. For instance, FPEN doped with rare-earth compounds, such as $EuCl_3{\cdot}6H_2O$ and $TbCl_3{\cdot}6H_2O$ [29], have been fabricated into transparent nanocomposites films showing red, green and blue fluorescence under UV light exposure. On the other hand, silver nanoparticles (Ag NPs) [30] and gold nanoclusters (Au NCs) [31] have been employed to finely modulate the fluorescent properties of FPEN.

Considering that Au NCs have been used as a highly sensitive, rapid and low toxicity noble metal nanomaterial in mercury sensing [32–35], and the fluorescent emission of FPEN is rather stable in the presence of mercury ion, herein we expect to obtain a FRET-based dual-emitting chemosensor for mercury detection. Specifically, the FPEN-Au NCs hybrid complex manifests pink emission under UV excitation, but a color changing from pink to blue was observed upon addition of mercury ions due to the fact that red emission of Au NCs can be easily quenched by Hg^{2+}. Additionally, different from many fluorescent sensors based on small molecules that only work in solution phase [33,36], FPEN can be fabricated as a solid sensor substrate (nanofiber or membrane) due to its good processability. For instance, PEN nanofiber mats with controlled morphology have been revealed recently in some reports using electrospinning technique, and PEN nanofiber's morphology can be controlled by the polymer's molecular weight, concentration and solvent polarity [27,37]. Thus, FPEN nanofiber mat could act as suitable substrates to adsorb Au NCs for fluorescent sensing. On the other hand, we have discovered that carboxyl group in backbone of FPEN played an impotent role in modulating the energy transfer process from FPEN to Au NCs in the previous work [31].

In this work, two FPEN samples (*homo*-FPEN and *co*-FPEN) with different relative quantity of carboxyl groups in main chain have been synthesized to further optimize the FRET efficiency. Subsequently, the fluorescent sensing platform based on FPEN/Au NCs pair can be established directly in solution or electrospun nanofiber mats. Finally, the specific and sensitive detection of trace concentration of Hg^{2+} down to 10 nM can be obtained under optimized condition.

2. Experimental

2.1. Materials

N,*N*-Dimethylformamide (DMF, AR), *N*-methyl-2-pyrrolidone (NMP, AR), toluene (AR), HCl (AR), K_2CO_3 (AR), bovine serum albumin (BSA, AR), $HAuCl_4$ (AR) and all the metal salts ($HgCl_2$, $AgNO_3$, $Ba(Ac)_2$, $Cd(Ac)_2$, $Co(Ac)_2$, $Cu(Ac)_2$, $Mg(Ac)_2$, $Pb(Ac)_2$, $Zn(Ac)_2$, $AlCl_3$, $FeCl_3$) were purchased from Tianjin Bodi chemicals. 2,6-Dichlorobenzonitrile (DCBN, AR) and bisphenol A (BPA, AR) were obtained from Yangzhou Tianchen chemicals, Jiangsu, China. Phenolphthalin (PPL) was synthesized according to our previously published procedure [28]. For real environmental samples tests, the lake water was obtained from the Shahe Lake in Chengdu, and the tap water was acquired from our laboratory.

2.2. Instrumentations

The fluorescent excitation and emission spectra were recorded on fluorospectrometer F-4600, Hitachi. The time-correlated photoluminescence decay and fluorescence lifetime were determined by using a Horiba Jobin Yvon Tempro-01 instrument. All the fluorescent microscopic images of nanofiber mat were captured using a fluorescent microscope (TE-2000U, Nikon, Japan). Morphology of Au NCs was characterized by a transmission electron microscope (TEM, JEOL, JEM-2100F) operating at 200 kV. The other images of samples were taken under UV light (365 nm) and white light illumination by a digital camera (Nikon D7000 DSLR). Gel permeation chromatography (GPC) analysis was measured on PL-GPC220 system using polystyrene as standard. The thermal stability analysis (TGA) of polymer was recorded by TA Instruments TGA-Q50 under nitrogen flowing and heating at rate of 20 °C min^{-1}. The ^1H NMR (400 MHz) chemical shifts were measured relative to DMSO-d_6 (H: δ = 2.50 ppm) as the internal references.

2.3. Synthesis

2.3.1. Synthesis of homo-FPEN

The chemical structure of *homo*-FPEN repeating unit is shown in Fig. 1a. *Homo*-FPEN was synthesized from DCBN and PPL via nucleophilic aromatic substitution polymerization as previously reported [38]. In a typical synthesis, PPL (20.00 mg, 0.06 mmol), DCBN (11.00 mg, 0.06 mmol), K_2CO_3 (26.00 mg, 0.19 mmol), NMP (30 mL) and toluene (10 mL) were added into a 100 mL three-necked round bottom flask equipped with a condenser, a Dean–Stark trap and an overhead mechanical stirrer. Then, the system was heated up to 150 °C to promote the formation of phenolate and kept for 2 h. Afterwards, the water–toluene azeotrope was removed and heated up to 200 °C for 3 h to complete the polymerization. The crude products were purified with dilute hydrochloric acid firstly, and boiled with water three times to remove K_2CO_3, DCBN and solvent. Finally, the precipitate was collected and dried at 80 °C for 48 h in a vacuum oven. The weight average molecular weight (M_n), number average molecular weight (M_w) and polydispersity index (M_w/M_n) of synthesized *homo*-FPEN were 21641 g mol^{-1}, 12005 g mol^{-1} and 1.80, respectively. TGA result showed its 5% weight loss temperature ($T_{5\%}$) was at 324 °C. ^1H NMR (400 MHz, DMSO-d_6, δ): 6.60 (*d*, *J* = 8 Hz, 2H; ArH); 6.70 (s, 1H; —CH—); 7.06 (*d*, *J* = 8 Hz, 1H; ArH); 7.15 (dd, *J* = 8 Hz, 12 Hz, 8H; ArH); 7.35 (*t*, *J* = 8 Hz, 1H; ArH); 7.52 (*q*, *J* = 8 Hz, 2H; ArH); 7.82 (*d*, *J* = 8 Hz, 1H; ArH), 12.98 (s, 1H; —COOH).

2.3.2. Synthesis of co-FPEN

Co-FPEN was synthesized by using equal molar concentration of bisphenol A (BPA) and phenolphthalin (PPL) and the repeating unit structure is shown in Fig. 1a as well. Specifically, PPL (41.60 mg, 0.13 mmol), BPA (30.00 mg, 0.13 mmol), DCBN (44.70 mg, 0.26 mmol), K_2CO_3 (70.00 mg, 0.50 mmol), NMP (100 mL) and toluene (35 mL) were used in synthesis process. And the other procedure of the synthesis was the same with *homo*-FPEN. The GPC, TGA and NMR results of *co*-FPEN were displayed as follows: M_w = 28337 g mol^{-1}, M_n = 11904 g mol^{-1}, M_w/M_n = 2.38. $T_{5\%}$ = 512 °C. ^1H NMR (400 MHz, DMSO-d_6, δ): 1.67 (s, 6H, —CH_3—); 6.58 (*t*, *J* = 8 Hz, 4H); 6.74 (s, 1H, —CH—); 7.05 (*d*, *J* = 8 Hz, 2H; ArH); 7.12 (*d*, *J* = 12 Hz, 12 H; ArH); 7.33 (*d*, *J* = 8 Hz, 4H, ArH); 7.50 (*q*, *J* = 8 Hz, 2H, ArH); 7.80 (*d*, *J* = 8 Hz, 1H, ArH).