



Selective detection of metal ions based on nanocrystalline ionochromic polydiacetylene

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ABSTRACT

Metal ion detection using commercially available ionochromic polydiacetylenes has not been selective. In this work, we report selective detection of metal ions in small organic compound (SOC)-stabilized poly(10,12-pentacosadiynoic acid) (PDA) nanocrystals suspended in an aqueous solution. These PDA nanocrystals were topochemically polymerized using a 254-nm UV light from the corresponding SOC-stabilized DA nanocrystals prepared by a solvent/nonsolvent micellization method. In this detection, the stabilizing SOC could selectively regulate the intercalation of specific metal ions into the galleries of PDA nanocrystals. Whenever the specific metal ions were intercalated, a fast (<1 min) ionochromic transition was observed. In addition, different metal ion selectivity could be achieved by utilization of different SOCs. For example, selective detections of Pb^{2+} and Ag^+ with different detection sensitivities were achieved for a PDA/glycine (Gly) nanocrystal suspension and selective detection of Zn^{2+} was found for a PDA/boric acid nanocrystal suspension. X-ray diffraction and Fourier transform infrared studies revealed that Pb^{2+} and Ag^+ intercalated into the galleries of PDA nanocrystals and deprotonated most $-\text{COOH}$ groups in the side chains of PDA, forming a strong ionic interaction. This strong ionic interaction effectively reduced the conjugation length in the PDA main chain, and therefore selectively induced a blue-to-red ionochromic transition.

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1. Introduction

Detection of metal ions, especially heavy metal ions, is of great importance, because they play an important role in the survival and development of organisms and the environment. Among numerous analytical methods available for the detection of metal ions, fluorescence detection attracted the most attention because of its high sensitivity and local observation by fluorescence imaging spectroscopy [1–4]. However, precise fluorophore design and complicated organic synthesis largely restrict the development of cheap fluorescence chemosensors for metal ions. Compared with fluorescence sensors, metal ion sensors based on polydiacetylenes have demonstrated some merits: 1) Polydiacetylenes demonstrate obvious changes in color and “turn-on” fluorescence in response to the complexation with metal ions; 2) Precise design of the photo-physics involved in traditional fluorescence sensors is unnecessary for sensors based on polydiacetylenes, since their chromatic change

in the main chain is resulted from the perturbation of side chains [5–9].

Successful attempts to fabricate metal ion sensors based on polydiacetylenes can be divided into three categories: 1) Chemical modification of polydiacetylenes to introduce a receptor unit for metal ions [10,11], 2) synthesis of receptor modified amphiphilic diacetylene monomers, followed by self-assembly and subsequent photo-topochemical polymerization [12–16], and 3) embedding of ionophores in the self-assembled polydiacetylene lipids [17]. Nonetheless, in the first and third strategies, there is a risk of inducing chromatic transition by chemical modification of polydiacetylenes and by embedding ionophores in the self-assembled lipids of polydiacetylenes. In the second strategy, the difficulty lies in the self-assembly of chemically modified diacetylenes into properly packed crystals to meet the strict requirements for topochemical polymerization. Therefore, it is highly desirable to develop polydiacetylene-based metal ion sensors without any introduction of receptor units for metal ions by chemical modifications.

To tackle this challenge, for the first time we report a novel strategy towards selective and sensitive detection of metal ions using commercially available 10,12-pentacosadiynoic acid (DA) and

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regulating small organic compounds (SOCs), without any chemical modification of the DA or PDA molecules. First, a water-soluble SOC will be used to stabilize DA/SOC nanocrystals by the solvent/non-solvent method for preparing noncovalently connected micelles (denoted as the NCCM method) [18]. Second, UV-induced topochemical polymerization will convert the DA/SOC nanocrystals to PDA/SOC nanocrystals. Third, the SOC will interact with (or “capture”) non-targeted metal ions in solution and only allow targeted metal ions to intercalate into PDA in order to induce ionochromic transition. Therefore, a small PDA crystal size is critical for the fast intercalation of ions into PDA galleries, and the specific regulating ability of the SOC is critical for the detection selectivity.

2. Experimental

2.1. Materials

10,12-pentacosadiynoic acid (DA), $\text{CH}_3(\text{CH}_2)_{11}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{C}(\text{CH}_2)_8-\text{COOH}$, was purchased from GFS chemicals, Inc. (Powell, OH). Glycine (Gly), boric acid (BA), and anhydrous ethanol were purchased from Sinopham Chemical Reagent Co., Ltd, China, and were used without further purification.

2.2. Preparation of PDA/SOC nanoaggregate suspension

DA was dissolved in anhydrous ethanol at a concentration of 1.25 mg/mL, followed by filtration through a 0.45 μm PTFE filter to remove any pre-polymerized PDA impurity prior to use. DA/Gly nanoaggregate suspension was prepared by dropwise addition of 0.4 mL DA ethanol solution into 5.0 mL Gly aqueous solution (5.0 mg/mL) under mechanical stirring at 25 °C. Then, the DA/Gly nanoaggregate suspension in a sealed vial was annealed in a gravity oven at 50 °C for 4 h in the dark. After cooling to room temperature, the DA/Gly nanoaggregates in solution were polymerized by a 254-nm UV irradiation (ZF-1 UV lamp, Shanghai Baoshan Gucu Electro-optic Instrument Factory, Shanghai, China) for 10 min at room temperature. Similarly, DA/BA nanoaggregate suspension was prepared by dropwise addition of 0.4 mL DA solution into 5.0 mL BA aqueous solution (0.5 mg/mL) under stirring at 25 °C. Then, the DA/BA nanoaggregate suspension was stored in a refrigerator (4 °C) overnight. Finally, PDA/BA nanoaggregates were prepared by a 254-nm UV irradiation for 30 min at room temperature.

2.3. Characterization and instrumentation

Dynamic light scattering (DLS) measurements were conducted at a fixed scattering angle of 90 °C at 25 °C using an ALV-5000 laser light scattering spectrometer equipped with a multi- τ digital time correlation (ALV5000) and a He–Ne laser ($\lambda_0 = 632.8 \text{ nm}$) light source. The $\langle R_h \rangle$ and polydispersity index (PDI) were obtained by the CONTIN program. A Shimadzu UV-2550 apparatus was used for UV–Vis measurements. Colorimetric response (CR) describes the relative change in “percent blue” (PB). The initial percent blue, PB_0 , is defined as: $\text{PB}_0 = A_{\text{blue}}/[A_{\text{red}} + A_{\text{blue}}] \times 100\%$, where A_{blue} and A_{red} are the absorbance at the “blue” (648 nm) and “red” (552 nm for PDA/Gly and 548 nm for PDA/BA nanoaggregates) wavelengths in a UV–Vis spectrum. The CR characterizes the percent conversions to the red phase: $\text{CR} = [\text{PB}_0 - \text{PB}_1]/\text{PB}_0 \times 100\%$, where PB_1 is the final percent blue after addition of metal ions. All Fourier transform infrared (FTIR) spectra were recorded with 64 scans in the range 4000–400 cm^{-1} on a Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1} . The fluorescence spectra were measured by using an Edinburgh Photonics FLS 920 luminescence spectrometer at 20 °C. PDA/Gly nanoaggregate suspension was excited by 483 nm as determined by the excitation spectrum. Inductively coupled

plasma atomic emission spectroscopy (ICP-AES) was conducted on a Hitachi P-4010 spectrometer. In detail, metal ions were added to the PDA/Gly nanoaggregate suspension. The mixture was stored at ambient temperature for several hours and then measured by ICP-AES. The PDA/Gly nanoaggregates were collected by centrifugation at 12,000 rpm for 1.5 h and purified by washing with deionized water for three times. The content of metal ions in the PDA/Gly nanoaggregates and supernatant (including the washing solution) was tested, respectively. TEM observation was carried out on a Philips CM120 electron microscope at an accelerating voltage of 80 kV. The sample was drop-cast onto a 400-mesh carbon-coated copper grid. Extra solution was blotted away using a filter paper and the remainder solution was allowed to dry at room temperature.

3. Results and discussion

3.1. Selective detection of Pb^{2+} and Ag^+ based on PDA/Gly nanocrystal suspension

PDA is known to have an ionochromic property due to the metal ion–carboxylic acid (in the side chains) interaction, which disturbs the main chain conjugation length [13]. However, this ionochromic detection is not selective at all. To improve the detection selectivity and avoid complicated chemical modification, here we propose a novel strategy. Because PDA has no selectivity to metal ions, we will use a regulating SOC or polymer for two purposes. First, the SOC or polymer will interact with DA via non-covalent bonding and stabilize DA nanocrystals (or prevent DA crystals from growing into large ones). The nanosized PDA crystals can facilitate fast intercalation of metal ions into PDA galleries. Second, the stabilizing SOC or polymer will interact with metal ions and regulate their intercalation into PDA galleries for selective detection.

On the basis of our recent reports [19,20], water soluble poly(vinyl pyrrolidone) (PVPy) and poly(vinyl alcohol) (PVA) could stabilize nanosized (a few tens to a hundred nanometers) DA crystals in aqueous solutions, and intercalate into their galleries via intermolecular hydrogen bonding. After UV-initiated topochemical polymerization, reversible thermochromic transitions were observed. However, no ionochromic transition was studied for these polymer/PDA nanocrystals.

In this work, we focus on water soluble SOC that could regulate the interaction with metal ions in the aqueous solution. Hydrophilic amino acids were known to have specific interactions with metal ions. Among a number of water soluble amino acids, glycine (Gly) was identified to be able to stabilize DA nanocrystals in an aqueous solution without destroying the capability of topochemical polymerization. In a typical NCCM method, 0.4 mL of DA solution in ethanol was dropwise added into 5.0 mL of an aqueous Gly solution (5.0 mg/mL) under stirring. Due to the insolubility in the mixed solvent (water/ethanol = 12.5/1 vol./vol.), DA aggregated into nanosized particles (see Fig. 1A and B). However, further aggregation of these nanoparticles was stopped by the stabilization effect from the DA–Gly interaction.

The DLS result in Fig. 1A shows that the Z-average hydrodynamic radius ($\langle R_h \rangle$) of DA/Gly NCCM particles is ca. 60 nm. TEM observation in Fig. 1B reveals spherical DA/Gly NCCM particles with the particle size ranging from 25 to 72 nm, nearly consistent with the DLS result. Direct UV irradiation of the DA/Gly NCCM suspension at 254 nm for 10 min only resulted in a very faint blue color. This faint blue color did not deepen even after a prolonging UV irradiation time. We consider that this was probably resulted from the less proper packing of DA molecules in the nanocrystals. Therefore, the DA/Gly NCCM suspension was thermally annealed at 50 °C (below the melting temperature of DA crystals at 62 °C) for

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