



A novel solution-processable amino-group-substituted oligopyrene: Synthesis, electropolymerization, properties, and application in fluorescent chemosensor



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ABSTRACT

Novel solution-processable fluorescent oligo(1-aminopyrene) was readily electrosynthesized by direct anodic oxidation of its monomer 1-aminopyrene in neutral medium CH_2Cl_2 - Bu_4NPF_6 (0.1 mol L^{-1}). FT-IR spectrum demonstrated that the polymerization of 1-aminopyrene probably occurred at C_3 and C_8 positions. In addition, the resulting oligo(1-aminopyrene) film showed good redox activity, water-solubility and enhanced fluorescence property in comparison with its monomer, indicating potential application as fluorescent materials. Oligo(1-aminopyrene) was also employed as fluorescent chemosensor to sense Fe(III) and Pd(II) in aqueous solution, and it showed pronounced sensitivity and fast response.

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1. Introduction

Fluorescent chemosensors based on conjugated polymers (CPs) have attracted a great deal of attention owing to their simplicity of use, signal amplification, easy fabrication into devices, combination of different outputs [1–5] and other advantages of conjugated polymers, such as charge transport, conductivity, emission intensity, and exciton migrations. Many exciting results reported by various groups prove that fluorescent chemosensors based on polymers are useful tools for sensing various analytes [6–8].

Generally, fluorescent conjugated polymers were synthesized by both chemical and electrochemical methods. Electro-oxidative polymerization of aromatic compounds with concurrent polymer films deposition has been proved to be an especially useful method for the preparation of conducting polymer films. As an important synthetic method, it shows some unique advantages in comparison with chemical method, such as (1) only small amounts of monomer and no catalyst are required; (2) the polymer is obtained directly as a thin film, the shape of which may be tailored as required by tailoring the electrode shape; (3) the thickness and morphology of polymer obtained may be

controlled instrumentally *via* the electrochemical parameters; (4) the thermodynamics of the system may be controlled by the potential applied to the working electrode; (5) the rate of reaction may be controlled *via* the current at the working electrode; (6) different electrochemical polymerization may be performed under identical conditions, allowing comparison between different systems and assisting in property screening; (7) electrochemical polymerization studies give fast information on the characteristics and properties of electropolymerized materials [9]. However, the resulting polymers obtained by electropolymerization are always not dissolved in common organic solvents, severely restricting their application in fluorescent chemosensors. Up to date, rare attention has been concentrated on fabricating fluorescent chemosensors using the electrosynthesized conducting polymers [10]. Therefore, it is very necessary and also a considerable challenge to electrosynthesize novel fluorescent conjugated polymers with favorable solubility.

Our continuing interest in electrosynthesized heterocyclic/fused-ring conducting polymers prompted us to explore and develop their applications in various fields [11–14]. Most recently, we prepared several oligo/polymers with good solubility in common solvents, such as poly(9-aminofluorene) [7,15] and polybenzanthrone [16], and successfully fabricated their based fluorescent chemosensors to detect metal ions, inorganic phosphates, and carboxylates. These low-cost sensors displayed high selectivity and sensitivity to analytes even in real practice, such as

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in living cells, real water samples, agricultural crops, and environment, etc. These interesting results are receiving more and more attention and also pave the way for further practical use in biological science and plant physiology.

On the other hand, among fluorescent conjugated polymers, oligo-/polypyrene and their derivatives have various applications in fluorescence sensing [17] due to their unique properties including high crystallinity and blue/multicolored fluorescence with high quantum yields [18]. However, due to their rigid chain backbones and the lack of graft chains, only very few oligo-/polypyrenes are soluble [17]. Therefore, several soluble derivatives of oligopyrene, such as oligo(1-pyrenebutyric acid) and its ester, were synthesized most recently [17,19–21]. These oligomers are soluble in water because of their negatively or positively charged side groups [19,22]. Nitryl and phenyl substituted oligopyrene have also been synthesized *via* electrochemical and chemical polymerization [23]. Compared with other fluorescence sensing materials, oligo/polypyrene and its derivatives have been widely used as a fluorescence probing molecule for detecting nitroaromatic compounds both in atmosphere and aqueous media mainly because of the large conjugated pyrenyl rings of oligopyrene chain backbones that have strong affinity with aromatic molecules.

Amino group, an important substituent usually employed to adjust the band gaps and solubility of CPs [24], has not yet been introduced into oligopyrene. As an electron-rich functional group, amino can increase the electron densities of the corresponding polymers. Furthermore, amino can also promote the process of electropolymerization and increase the solubility of resulting polymers.

In this study, 1-aminopyrene was successfully synthesized and its corresponding oligomer films was prepared by direct anodic oxidation in $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) for the first time. Structure characterization and properties of the resulting oligomer films, including FT-IR, UV-vis, redox activity, and polymerization mechanism, were comparatively discussed. Further, its based fluorescent chemosensors were also fabricated to detect metal ions and they displayed high selectivity, pronounced sensitivity, and fast response.

2. Experimental

2.1. Chemicals

Pyrene (95%, Sahn Chemical Technology Co., Ltd.), nitric acid (65%), pure acetic acid (99.5%), anhydrous ethyl alcohol (99.7%), cyclohexane (99.5%), Zn powder (90%), and NH_4Cl (99.5%, Beijing Chemical Plant, China) were stored at 4°C and used directly without further purification. Tetrabutyl ammonium hexafluorophosphate (Bu_4NPF_6 , 99%; Energy Chemical) was dried under vacuum at 100°C for 24 h before use. Dichloromethane (CH_2Cl_2 , >99%, Beijing East Longshun Chemical Plant) was purified by distillation with calcium hydride under a nitrogen atmosphere before use. Aqueous solutions of cations such as Pb(II) , Ca(II) , Al(III) , Co(II) , Sr(II) , Ni(II) , Fe(III) , Cr(III) , Zn(II) , Cu(II) , Mg(II) , and Cd(II) were prepared from their nitrate salts; and aqueous solutions like Hg(II) , Mn(II) , Ba(II) , Sn(II) , and K(I) were prepared from their chloride salts. Other chemicals and reagents (analytical grade, >98%) were all purchased commercially from Beijing East Longshun Chemical Plant (Beijing, China) and were used directly without any further treatment.

2.2. Synthesis

2.2.1. 1-Nitropyrene

Pyrene (5 mmol, 1.01 g) was dissolved in pure acetic acid (30 mL) in a round-bottom flask (50 mL) and the mixture was

stirred magnetically at room temperature for 2 h. Then, 1.15 g nitric acid (65%) was added into the reaction mixture. The crude product was purified by filtration and recrystallization with ethanol to obtain 1.01 g brown-yellow microcrystals in 82% yield.

2.2.2. 1-Aminopyrene

1-Nitropyrene (0.25 g, 1 mmol), NH_4Cl (0.11 g, 2 mmol), and Zn powder (0.33 g, 5 mmol) were added into concentrated methanol (20 mL) and deionized water (10 mL). The reaction was stirred at 75°C for 10 h. After filtration with methanol and evaporation of solvent, the product was purified by recrystallization with cyclohexane to give 1-aminopyrene as greenish yellow farinose solid (1.22 g, 68%). $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.05 (t, $J_{\text{H-H}} = 12$, 2H), 7.98 (t, $J_{\text{H-H}} = 16$, 2H), 7.94 (q, $J_{\text{H-H}} = 8$, 2H), 7.91 (s, 1H), 7.83 (d, $J_{\text{H-H}} = 8$, 1H), 7.83 (d, $J_{\text{H-H}} = 8$, 1H), 4.49 (s, 2H).

2.3. Electrosynthesis and electrochemical tests

All electrochemical tests and polymerization were performed in a one-compartment cell with the use of a model 263A potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control. For electrochemical tests, the working and counter electrodes were typically both Pt wires with a diameter of 1 mm, respectively. To obtain a sufficient amount of the oligomer films for characterization, Pt sheet or ITO-coated glass were employed as the working electrode and another Pt sheet was used as the counter electrode. These aforementioned electrodes were polished carefully with 1500 mesh abrasive paper (for ITO: immersed in ethanol for 6 h and then cleaned by ultrasonic wave for 15 min), cleaned by water and acetone successively, and then dried in air before each experiment. An Ag/AgCl electrode directly immersed in the solution served as the reference electrode, and it revealed sufficient stability during the experiments. The typical electrolytic solution was anhydrous $\text{CH}_2\text{Cl}_2\text{-Bu}_4\text{NPF}_6$ (0.1 mol L^{-1}) containing 0.01 mol L^{-1} monomer. All the solutions were deaerated by a dry nitrogen stream (more than 20 min) and maintained under a slight overpressure through all the experiments to avoid the effect of oxygen.

2.4. Characterization

$^1\text{H NMR}$ spectrum was recorded on a Bruker AV 400 NMR spectrometer with CDCl_3 as the solvent and tetramethylsilane as an internal standard (TMS, singlet, chemical shift: 0.0 ppm). UV-vis spectra of the monomer and oligomer dissolved in acetonitrile were taken by using PerkinElmer Lambda 900 UV-vis near-infrared spectrophotometer. All fluorescence experiments were carried out using a Hitachi F-4500 spectrophotometer. Infrared spectra were recorded using a Bruker Vertex 70 Fourier transform infrared (FT-IR) spectrometer with samples in KBr pellets. Thermogravimetric analysis (TGA) was performed with a Pyris Diamond TG/DTA thermal analyzer (PerkinElmer).

2.5. Detection of metallic ions

A certain amount of oligo(1-aminopyrene) was prepared by electropolymerization and dissolved in a mixed solution of ethyl alcohol and deionized water. Aqueous solutions of a series of cations, such as Pb(II) , Ca(II) , Al(III) , Co(II) , Sr(II) , Ni(II) , Fe(III) , Cr(III) , Zn(II) , Cu(II) , Mg(II) , and Cd(II) , were prepared from their nitrate salts, and aqueous solutions of Hg(II) , Mn(II) , Ba(II) , Sn(II) , and K(I) were prepared from their chloride salts. Besides, a stock standard solution of 0.1 mol L^{-1} Fe(III) was prepared by dissolving an appropriate amount of $\text{Fe(NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in deionized water, then further diluting to 1×10^{-2} to $1 \times 10^{-9} \text{ mol L}^{-1}$ stepwise. Analogously, a stock standard solution of inorganic phosphate (0.1 mol L^{-1}) was prepared by mingling 1.95 mL of NaH_2PO_4 (0.1 mol L^{-1})

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