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Visual detection of Al^{3+} ions using conjugated copolymer-ATP supramolecular complex

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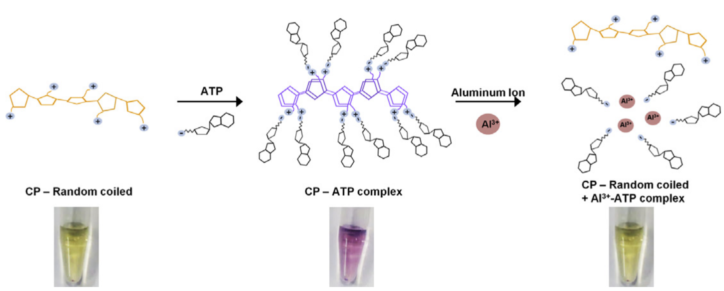
HIGHLIGHTS

- A novel water soluble polythiophene copolymer that demonstrates colorimetric response for Al^{3+} is proposed.
- Optimized ratio of two polythiophene monomers is utilized for selective detection of Al^{3+}.
- Naked eye detection of Al^{3+} is demonstrated without involving sophisticated instrumentation.
- Lowest concentration of Al^{3+} for naked eye detection is ~4 μM, which is below the threshold levels.

GRAPHICAL ABSTRACT



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ABSTRACT

A colorimetric Al^{3+} sensor based on fluorescence recovery of a conjugated copolymer-ATP complex is proposed. An optimized ratio of two polythiophene (PT) monomers is utilized to synthesize copolymer (CP) that yielded maximized colorimetric response for Al^{3+} in deionized (DI) and tap water. The electrostatic disassembly of CP-ATP upon addition of Al^{3+} led to an evident visual color change. The lowest concentration of Al^{3+} for naked eye observation is around 4 μM, which is below the threshold levels in drinking water according to European Economic Community (EEC) standard. Besides, the proposed assay showed a similar response to Al^{3+} in tap water. The proposed methodology showed selective and sensitive detection for Al^{3+} in analytically relevant concentration ranges without involving sophisticated instrumentation, illustrating the applicability for on-site drinking water monitoring.

1. Introduction

Metal ions play an important role in living organisms since they are involved in many biological processes such as osmotic regulation, catalysis, metabolism, biomineralization and signaling [1]. However, abnormal concentration levels of metal ions might cause detrimental effects, for example, trivalent aluminum (Al^{3+}) in

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aqueous solution has been reported to be highly toxic; main source of which is from food and drinking water. The maximum acceptable Al^{3+} concentration in drinking water is 200 $\mu g\ L^{-1}$ (7 μM) according to European Economic Community (EEC) standards [2]. Excess amount of Al^{3+} is believed to cause brain diseases such as dementia dialitica, Parkinson's disease and Alzheimer's disease [3,4]. The poisoning risk could also exist with the accumulation of lower level Al^{3+} in the brain [5]. Therefore developing a method to sensitively and selectively detect Al^{3+} is crucial. In the recent years, various methodologies for metal ion detection have been reported based on potentiometric [6–8], colorimetric [9–11], fluorescence [12–14], liquid chromatography [15], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [16], atomic absorption spectrometry (AAS) [17], etc. Among the reported methodologies, colorimetric sensors have attracted great attention since they are facile and do not involve sophisticated instrumentation. Colorimetric sensors therefore have been investigated for Al^{3+} detection [18–23]. Most reported methodologies demonstrated an evident visual difference only under UV light and their inability to detect the Al^{3+} in aqueous solution limited their practical applications. Herein, we propose a colorimetric Al^{3+} sensor for both naked eye and fluorescence detection based on water-soluble conjugated copolymers.

Conjugated polymers are macromolecules consisting of alternating single/double bonds and delocalized π electrons throughout their backbones. This unique molecular structure of conjugated polymers offers attractive optical and electrical properties. Thus conjugated polymers, for instance, poly(phenylene vinylene) (PPV) [24], poly(phenylene ethylene) (PPE) [25], polydiacetylene (PDA) [26], polythiophene (PT) [27,28] and polyfluorene (PF) [29] have been widely reported as a colorimetric or fluorescence chemosensors. However, most reported conjugated polymers exhibit rather poor solubility in water probably due to their low charge densities which compete with the aromatic $\pi-\pi$ stacking of the hydrophobic backbones [30]. This limits their applicability for biomolecular detection, water quality monitoring, etc. More recently, cationic PTs and their derivatives have received much attention due to their good water solubility and attractive optical properties. Electrostatic force-induced conformational change in PT backbone often leads to color as well as the fluorescence intensity changes. Adenosine triphosphate (ATP) is one of the reported anionic molecules that induced significant color and fluorescence intensity change upon non-covalent bonding with cationic PTs and their derivatives [31]. However, electrostatic complex of homopolymer PTs and ATP may not be ideal for detection of trivalent metal ions due to either irreversible complexation and/or weak interaction. Therefore, a rationally designed and synthesized PT random copolymer is utilized in this study for complexation with ATP and subsequently for selective and sensitive detection of Al^{3+}.

The synthesized PT random copolymer was incubated with negatively charged ATP to form a complex based on the electrostatic self-assembly [32,33]. The color of resulting solution changed immediately (from yellow to purple), and the fluorescence intensity was quenched to around 15% of its original intensity. Addition of Al^{3+} resulted in the recovery of color (from purple to yellow) and fluorescence intensity due to the disassembly of PT-ATP complex as a result of strong affinity between Al^{3+} and ATP [34]. The formation of Al^{3+}-ATP complex triggered the transformation from a planar π-stacking morphology of PT copolymer to a random coiled morphology, thus resulting in recovery of color and fluorescence of PT copolymer. The proposed methodology enabled selective and sensitive detection of Al^{3+} without sophisticated instrumentation. We furthermore demonstrate similar responses to Al^{3+} in tap water, illustrating the applicability for drinking water quality monitoring, as water from the tap is typically used for drinking either as it is or upon boiling.

2. Experiment section

A novel water soluble PT monomer (m1, m2) and copolymer (CP) were synthesized adopting the protocol reported previously [35–37]. The structure of monomers (m1, m2) and CP is shown in

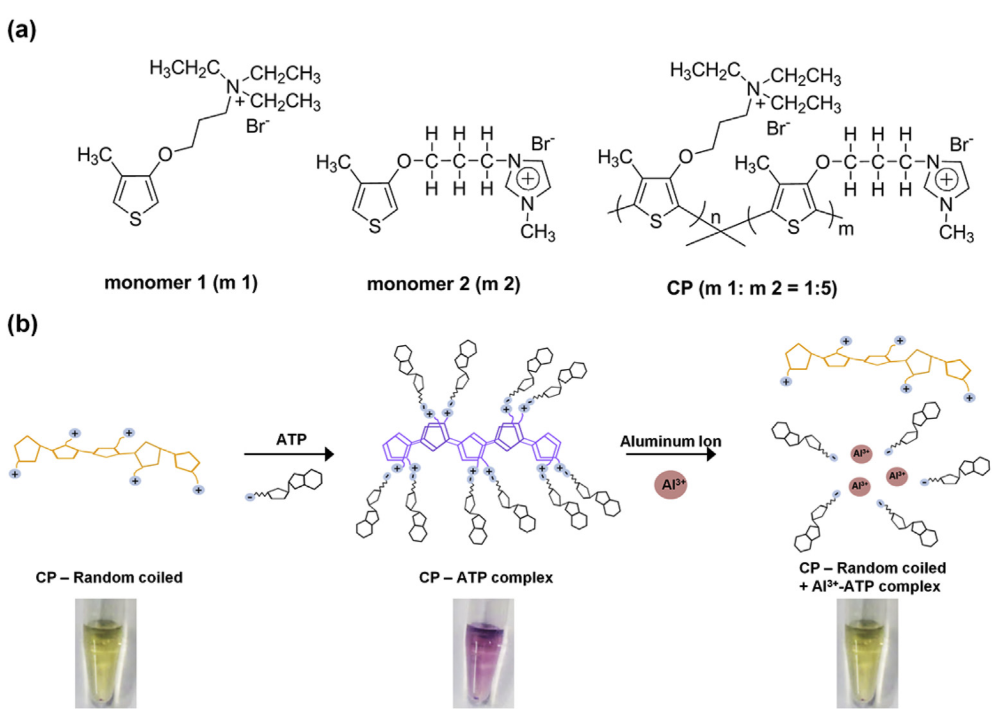

Fig. 1. (a) Structure of monomer 1, monomer 2, and its copolymer (CP). (b) principle of Al^{3+}detection. For clarity, the substituted groups are not shown.