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Determination of trace uranyl ion by thermoresponsive porphyrin-terminated polymeric sensor

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ABSTRACT

Uranyl ion exists at trace levels in the environment and can cause severe adverse effects to human health. Therefore, it is desirable to develop analytical methods that can determine the trace uranyl ion in aqueous medium. We report here a new method using a thermo-responsive polymeric fluorescent sensor. Specifically, 5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin terminated poly(*N*-isopropylacrylamide) (TCPP-PNIPAM) was synthesized by controlled free radical polymerization for the detection of uranyl ion. The maximum fluorescence intensity at ~658 nm of TCPP-PNIPAM increases with molecular weights and is also closely related to the temperature. The polymeric sensor is sensitive to pH (1.0~5.0) with a fast responsive time (~3 min). Under optimized experimental conditions, the sensor exhibits a stable response for uranyl ion with high selectivity over a concentration range from 1.0×10^{-3} to 1.0×10^{-7} mol/L. For the trace uranyl ion (such as 1.0×10^{-8} or 10^{-9} mol/L), the determination could be successfully achieved after concentrating 100 times by centrifugation above 32 °C. The properties enable the polymeric sensor to have great potential for environmental application.

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1. Introduction

Uranium is a radioactive element that exists naturally in the environment [1]. Nowadays human beings have a high chance of

Abbreviations: (UO_2^{2+}), Uranyl ion; (THF), tetrahydrofuran; (TCPP-PNIPAM), 5,10,15,20-tetrakis(4-carboxyphenyl)-porphyrin terminated poly(*N*-isopropylacrylamide); (EPA), Environmental Protection Agency; (PNIPAM), poly(*N*-isopropylacrylamide); (TCPP), 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin; (RAFT), reversible addition-fragmentation chain transfer; (DMF), *N,N*-dimethylformamide; (EG), ethylene glycol; (AIBN), 2, 2'-Azobisobutyronitrile; (DDACT), *S*-1-dodecyl-*S'*-(α,α' -dimethyl-*a*"-acetic acid) trithiocarbonate; ($^1\text{H NMR}$), ^1H nuclear magnetic resonance; (HPPS), high-performance particle sizer; (FT-IR), Fourier transform infrared; (GPC), gel permeation chromatographer; (DCC), *N,N'*-dicyclohexylcarbodiimide; (DMAP), dimethylaminopyridine; (PDI), polydispersity; (LCST), low critical solution temperature

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being exposed to uranium that can cause severe adverse effects to human health [2,3], since uranium is one of the main sources in nuclear energy generation and enriched uranium is a major component in nuclear weapons. Uranium has many forms in aqueous solution, and the most soluble or bioavailable form is uranyl (UO_2^{2+}). The maximum contamination level of UO_2^{2+} in drinking water is defined as 1.30×10^{-7} mol/L by U.S. Environmental Protection Agency (EPA) [4]. Therefore, it is desirable to have simple and convenient analytical methods that can determine the uranyl present in the aqueous medium at trace level.

Many analytical techniques, such as inductively coupled plasma-mass spectrometry [5–7], atomic absorption spectrometry [8,9] require expensive and complicated instruments, making on-site real-time sensing difficult. Optical sensing approaches (e.g. laser fluorimetry [10,11], absorption [12,13], luminescence [14]) and electrochemical approaches [15,16] for the detection of environmental and biological uranium have been developed in the field of chemical sensors for several decades. Among the optical sensors, the fluorescence-based one is a very appealing technique for future practical applications due to its intrinsic sensitivity and high spatial resolution [17,18]. For example, Ganesh et al. reported the determination of uranium concentration in raffinate stream of Purex process during reprocessing of spent

nuclear fuel by using fluorescence enhancing reagent such as sodium pyrophosphate [19]; Angel et al. reported the detection of uranyl ion via fluorescence quenching and photochemical oxidation of calcein with the detection limit of 4.0×10^{-8} mol/L [20]; recently Liao et al. reported the separation and determination of trace uranium using a double-receptor sandwich supramolecule method based on immobilized salophen and fluorescence labeled oligonucleotide [21]. However, these methods always require additional chemicals (such as sodium pyrophosphate, calcein and oligonucleotide) or devices (such as ball lens [22]) to obtain high sensitivity and high selectivity.

Recently we noticed the fluorescence-signaling DNA aptamers and deoxyribozymes were used as novel biosensing moieties for heavy metal ions [23–25]. For example, Lu et al. reported a catalytic beacon sensor for UO_2^{2+} based on an in vitro-selected UO_2^{2+} -specific DNAzyme, and this method has a 45 pM detection limit and million-fold selectivity [26]. However, this kind of biosensors (such as the uranyl-specific DNAzyme) is costly due to the complication in vitro-selection. Therefore, it is still desirable to develop new simple and convenient methods with high sensitivity and high selectivity for the detection of trace uranium in the environment.

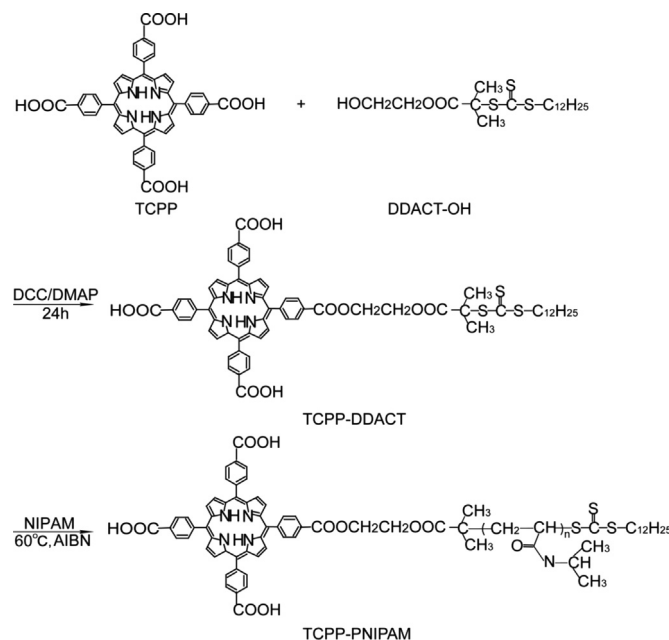
Porphyrin derivatives have been employed widely as fluorophores in probes owing to their excellent photophysical properties [27,28], but their applications were always limited by their poor solubility in water [29], which can lead to aggregation and function degradation. Recently Tian et al. [30] reported a random copolymer, poly(*N*-isopropylacrylamide-co-PtPorphyrin), consisting of *N*-isopropylacrylamide and platinum (II) phenylporphyrin units, behaving as an optical dual sensor for oxygen and temperature. However, the fluorescence intensity was low due to the aggregation quenching of the hydrophobic phenylporphyrins, and the molecular weights could not be controlled for the design of the sensor by this method.

We report here a new method using a thermo-responsive polymeric fluorescent sensor. Specifically, 5,10,15,20-tetrakis(4-carboxyphenyl) porphyrin (TCPP) terminated poly(*N*-isopropylacrylamide) (PNIPAM) was synthesized by controlled reversible addition-fragmentation chain transfer (RAFT) radical polymerization [31] (Scheme 1) for the detection of UO_2^{2+} . The carboxyl groups and the soluble PNIPAM polymer chain would improve the solubility of TCPP-PNIPAM in water, and the specific-coordination property of porphyrin with uranyl would endow the sensor a good selectivity. In general, porphyrin exhibits strong fluorescence in visible region owing to the conjugated double bond system and the high mobility of its π -electron [32], and the selective coordination with uranyl [33] would result in a decrease of porphyrin fluorescence. Furthermore, the thermo-responsive polymer PNIPAM has a hydrophilic coil-hydrophobic globule transition around 32 °C [34,35], which makes the aqueous solution be easily concentrated by the centrifugation above 32 °C for the effective detection of trace uranyl, thereby greatly extending the detection limit of this method. To the best of our knowledge, it is the first time to determine trace uranyl by thermo-responsive polymeric sensors.

2. Experimental section

2.1. Materials and reagents

N-isopropylacrylamide (NIPAM, 99%) was purchased from J&K Chemical Co. Ltd. and was purified by re-crystallization in benzene/*n*-hexane (3:1) before use. Tetrahydrofuran (THF, Sinopharm Chemical Reagent Co., Ltd., AR), *N,N*-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd., AR) and ethylene glycol



PNIPAM: *N*-isopropylacrylamide

TCPP: 5,10,15,20-Tetrakis(4-carboxyphenyl)porphyrin

DDACT: S-1-dodecyl-S'-(α,α' -dimethyl- α' -acetic acid) trithiocarbonate

Scheme 1. The schematic for the synthesis of TCPP-PNIPAM.

(EG, Sinopharm Chemical Reagent Co., Ltd., AR) were dried by molecular sieves (4 Å). 2, 2'-Azobisobutyronitrile (AIBN, Sinopharm Chemical Reagent Co., Ltd., CP) was purified by re-crystallization in methanol and dried in a vacuum oven at room temperature. TCPP was synthesized according to the standard Adler method [36] (Fig. S1, see Supporting Information). S-1-dodecyl-S'-(α,α' -dimethyl- α' -acetic acid) trithiocarbonate (DDACT) and DDACT-OH were synthesized according to the modified literature method [37] (Figs. S2 and S3, see Supporting Information). All other chemical agents were used as received.

2.2. Characterization methods

^1H nuclear magnetic resonance (^1H NMR) spectra were obtained on a Varian INVOA-400 instrument working at 300 MHz. The Z average size and the polydispersity index of the particles were measured by a Malvern HPP5001 high-performance particle sizer (HPPS). Fourier transform infrared (FT-IR) spectra were recorded on a Varian-1000 spectrometer: the samples were ground with KBr crystals and the mixture was then pressed into a pellet for IR measurement. The molecular weights and polydispersities of the homopolymers were determined with a Waters 1515 gel permeation chromatographer (GPC) equipped with refractive index detector, using HR1, HR3, and HR4 column with molecular weight range 100–500,000 calibrated with PS standard samples, and THF as the eluent at a flow rate of 1.0 mL/min operated at 30 °C. All fluorescence measurements were conducted on a FLS920 fluorescence spectrometer with the excitation wavelength of 425 nm with an emission wavelength range from 500 to 800 nm.

2.3. Synthesis of TCPP-DDACT

TCPP (1.19 g, 1.5 mmol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.205 g, 1.0 mmol) and dimethylaminopyridine (DMAP) (0.015 g, 0.12 mmol) were dissolved in dry THF (20 mL), and then DDACT-OH (0.414 g, 1.0 mmol) was added dropwise to the mixture over 2 h

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