

o-Phenylenediamine as a reaction-based probe for the fluorescent detection of Ce(IV) ions

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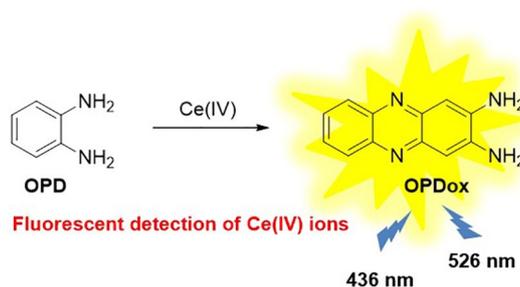
Abstract

o-Phenylenediamine as a new fluorescent probe is designed for detecting Ce(IV) ions. The mechanism of detection relies on the oxidative activity of Ce(IV) ions, which can promote the oxidative cyclization of *o*-Phenylenediamine leading to the formation of fluorescent 2,3-diaminophenazine and giving a more than 150-fold fluorescence enhancement. Furthermore, the *o*-Phenylenediamine fluorescent probe was effectively used for the detection of Ce(IV) ions in river water, tap water, rainwater, and lateritic soil from Ganzhou.

Keywords

Ce(IV) ions, detection, fluorescence analysis, *o*-phenylenediamine, reaction-based probe

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Introduction

Cerium (Ce), the most abundant rare-earth element, has been widely used in industry as a polishing powder, as a phosphor agent, as magnets, as a catalyst, and as a ceramic colorant.^{1–3} Although Ce(III) exists naturally in cerium fluorocarbonate minerals, during the process of mineral extraction and metallurgy, Ce(III) is usually converted into Ce(IV) for easier extraction in the post-treatment stage.^{4–6} This process further increases the exposure of Ce(IV) to the community. High concentrations of Ce ions are known to be harmful to the environment and human health.^{7,8} For instance, long-term exposure to Ce(IV) ions would probably lead to dysfunction in circulatory systems, the immune system, and the central nervous system in humans.⁹ Therefore, accuracy, precision, and rapid determination of Ce(IV) ions are very important for the environment and in clinical applications.

Various instruments are commonly used for the detection of Ce ions, such as X-ray fluorescence,¹⁰ inductively coupled plasma atomic emission spectrometry (ICP-AES),¹¹

spectrophotometry,¹² neutron activation analysis (NAA),¹³ inductively coupled plasma mass spectrometry (ICP-MS), and electrochemical methods.^{14,15} However, these methods possess several shortcomings, such as high cost, long processing times, and complex sample preparation. Recently, fluorescence sensors have become a powerful tool for the detection of important analytes in the environment and in

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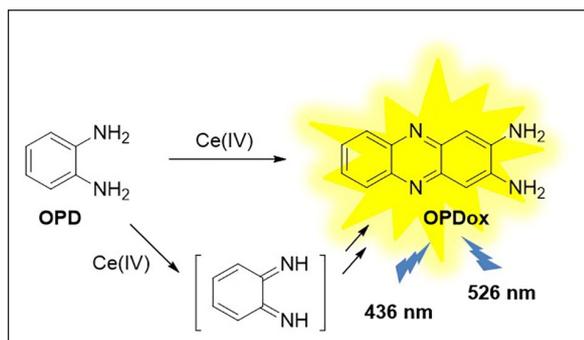
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Scheme 1. Reaction principle for the detection of Ce(IV) ions.

organisms because of their simplicity and high sensitivity.^{16–20} Up to now, several fluorescence sensors have been exploited to detect the Ce ions.^{21–25} However, some of these methods are restricted by toxic inorganic nanomaterials, low sensitivity, or low selectivity. Recently, a rhodamine-based probe²⁶ and a Schiff base probe²⁷ have been reported for the recognition of Ce(IV) ions, respectively. The two probes both show high selectivity and sensitivity, but with relatively complex molecular structures. We also reported a cascade-reaction-based fluorescence probe for the detection of Ce(IV) ions.²⁸ Ce(IV) ions can oxidize 2-naphthol, which subsequently reacts with *o*-phenylenediamine (OPD) to produce fluorescent benzo[*a*]phenazine. Although this method is efficient for the fluorescence detection of Ce(IV) ions, multistep reactions are inconvenient for detecting ions. Therefore, it is necessary to develop a rapid, sensitive, and efficient Ce(IV)-ion-sensing platform.

In recent years, the luminescent properties of 2,3-diaminophenazine (OPDox) have received extensive attention in the fields of analytical chemistry, organic synthesis, and materials chemistry.^{29–32} Notably, the Ce(IV) ions have been generally studied as a single-electron oxidant in various reactions.^{33,34} As an efficient single-electron oxidizer, Ce(IV) can efficiently promote the oxidative cyclization of OPD to generate OPDox.^{35–37} In this work, as a continuation of our ongoing studies on reaction-based fluorescent probes,^{38–41} OPD is used as a reaction-based fluorescent probe for the detection of Ce(IV) ions. In this detection process, OPD can be rapidly oxidized by Ce(IV) ions to an imine, which then undergoes as a further intermolecular cycloaddition to form the product OPDox which possesses yellow fluorescence, thus realizing the fluorescent detection of Ce(IV) ions (Scheme 1).

Results and discussion

The solvent for the reaction of Ce(IV) ions and OPD was first investigated, including MeCN, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), EtOH, CH₂Cl₂, and H₂O. In the experiment, OPD (40 μM) was mixed with Ce(IV) ions (0.4 μM) for 1 h at room temperature. It was observed that the effect of the solvent was significant, and the maximum fluorescence enhancement was observed in MeCN (Figure 1(a)). Control experiments were carried out in order to investigate the effect of the various components in the sensing system. It was thus shown that enhancement

in fluorescence only occurred when both Ce(IV) and OPD were present in the system (Figure 1(b) and (c)).

Furthermore, only when OPD and Ce(IV) ions were present, a strong absorption band between 350 and 550 nm could be found in the nature of UV-Vis absorption spectrum (Figure S1). To confirm the product, the detection reaction was performed at a millimolar level, and the OPDox product was obtained with the structure being confirmed by ¹H/¹³C NMR spectroscopy (Figure S2 and S3). At the same time, bright yellow fluorescence could be observed with the naked eye via irradiation with an ultraviolet lamp at 365 nm (Figure 1(b)) when OPD (1 mM) and Ce(IV) ions (1 mM) were mixed at room temperature. Hence, OPD as a new and practical probe for the sensing Ce(IV) ions was studied in further detail.

In order to ascertain the optimal sensing system, varying MeCN/H₂O ratios were investigated for the luminescence response of the detection reaction. The highest luminescence enhancement was obtained with a 4:1 MeCN/H₂O ratio (Figure 2). However, the luminescence rate started to decrease slowly thereafter. The incubation time was then investigated. It can be found that the fluorescence intensity of the system containing Ce(IV) ions increases with an extended incubation time and reaches a steady state at 3 h (Figure 3). However, no obvious fluorescence enhancement was measured without the Ce(IV) ions. We therefore chose a 4:1 MeCN/H₂O as the best mixed solvent and 3 h as the optimal incubation time.

Sensitivity is of importance for an analytical method. Hence, the fluorescence responses of the detection method to various concentrations of Ce(IV) ions were examined in detail. At room temperature, a system containing OPD (40 μM) was uniformly mixed with different concentrations of Ce(IV) ions (Figure 4). A highest 150-fold increase in fluorescence was obtained on increasing the concentration of Ce(IV) ions (0–88 μM). Two linear relationships were established at ranges of 0.4–4 μM ($R^2=0.9979$) and 5–36 μM ($R^2=0.9988$), respectively. At low Ce(IV) concentrations, OPD was converted into fluorescent OPDox and could be rapidly detected, resulting in a high sensitivity of the fluorescence response. At higher Ce(IV) concentrations, more fluorescent product was formed and the reaction proceeded over a larger time window. This, together with the higher fluorescence intensity, resulted in a lower slope. Therefore, the probe exhibited different linear correlations at different Ce(IV) concentration ranges. According to the limit of detection (LOD) = 3σ/s, 26 nM of the LOD was calculated. Compared to our previous work,²⁶ this method shows a wider detection range and a lower LOD.

The method was also applied to solid-phase conditions. The letters of “Ce” were written on a thin-layer chromatography (TLC) aluminum sheet using the reaction solution of OPD and Ce(IV) ions as an “ink” (Figure 5). When the solvent was dried, we observed the TLC sheet under daylight and UV 254 and 365 nm irradiation. Compared with the reaction solution that did not contain any Ce(IV) ions, the “Ce” containing both OPD and Ce(IV) ions emits bright yellow fluorescence under 365 nm UV irradiation. Therefore, this method serves as a visual fluorescence probe for Ce(IV) ions.

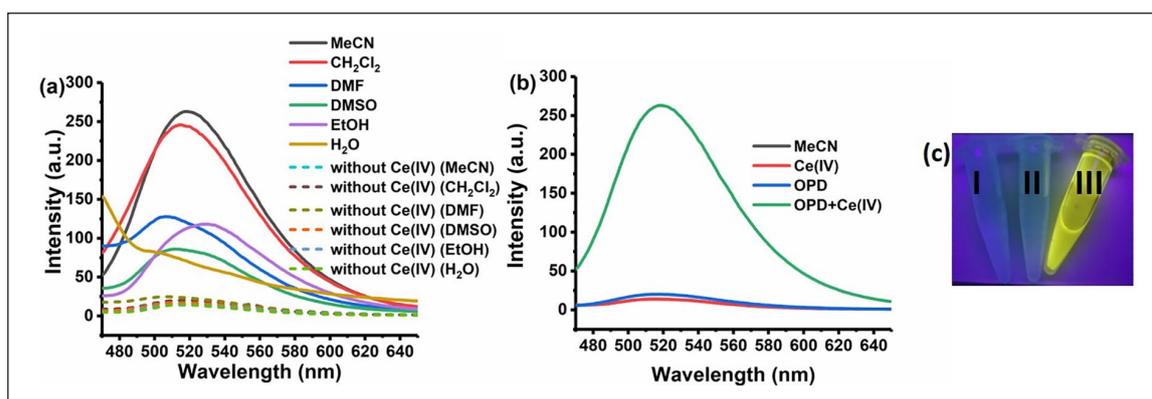


Figure 1. Fluorescence emission spectra ($\lambda_{ex} = 436$ nm) of the sensing system containing $40 \mu\text{M}$ OPD, (a) with or without Ce(IV) ions ($0.4 \mu\text{M}$) in the indicated solvents and (b) the emission spectra of the control experiments in MeCN. (c) Photographs of 1 mM of Ce(IV) (I), 1 mM of OPD (II), and 1 mM of Ce(IV) with 1 mM of OPD (III) under 365 nm UV illumination.

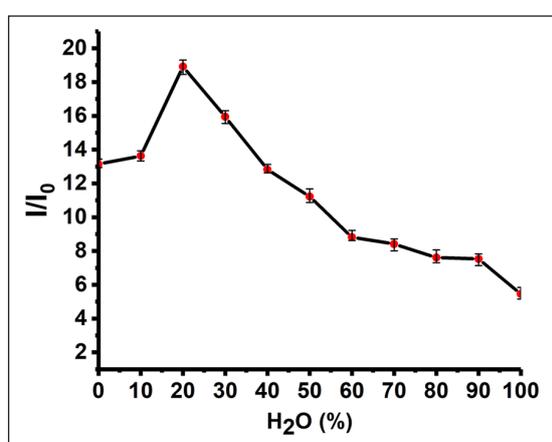


Figure 2. Fluorescence enhancement of OPD ($40 \mu\text{M}$) with $0.4 \mu\text{M}$ of Ce(IV) ions in various percentages of water in MeCN.

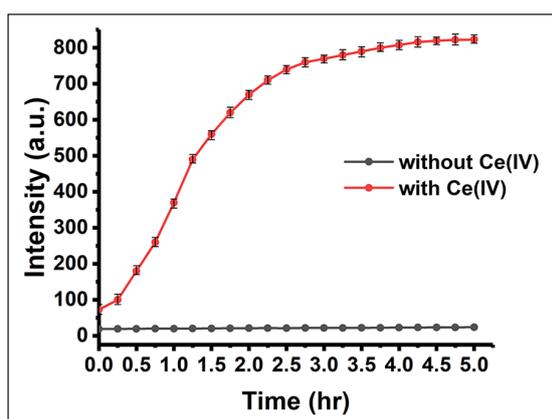


Figure 3. The fluorescence intensity of the system in the presence and absence of Ce(IV) ions with the indicated time. The concentration of Ce(IV) ions is 0.4 and $40 \mu\text{M}$ for OPD in MeCN containing 20% H_2O . The fluorescence was monitored at 15 min intervals and collected at a wavelength of 526 nm .

To show the excellent selectivity of this sensing method, 19 common cations, 11 common anions, and 15 rare-earth cations were all investigated (Figure 6). It can be found that only Ce(IV) ions ($0.4 \mu\text{M}$) gave an obvious enhancement in the fluorescence. As for other ions, only a slight fluorescence

enhancement was obtained, even at a concentration of $20 \mu\text{M}$. The specificity of the probe for Ce(IV) ions was also excellently observed from a competition experiment conducted by mixing Ce(IV) ions ($0.4 \mu\text{M}$) in a system with another ion ($20 \mu\text{M}$). Comparable fluorescence enhancements indicated that this organic reaction-based probe possesses high selectivity toward Ce(IV) ions.

A Job's plot experiment was carried out for the determination of the stoichiometric ratio of the interaction between Ce(IV) ions and OPD (Figure 7). The 2:1 ratio obtained from the Job's plot experiment is consistent with the reaction mechanism.

Finally, the detection of Ce(IV) ions was studied in real samples using the fluorescent probe. Samples of Ganjiang River water, tap water, rainwater, and lateritic soils were collected and pretreated according to previous methods.^{42,43} When exogenous Ce(IV) ions ($19.2 \mu\text{M}$) were added to the samples, significant luminescence intensities were observed. As shown in Table 1, recovery rates of 94.78% and 93.68% could be obtained in Ganjiang River water and tap water samples, respectively. Higher recovery rates of 97.39% and 98.77% were obtained for rainwater and lateritic soils samples, respectively. These results show that our fluorescent detection method can be applied for Ce(IV) ions sensing in real samples with good sensitivity.

Conclusion

In this work, a reaction-based switch-on fluorescent probe for Ce(IV) ions has been reported. The reaction is based on a tandem oxidation-cyclization reaction between the OPD and Ce(IV) ions, forming fluorescent OPDox. A maximum 150-fold fluorescence enhancement is observed in response to Ce(IV) ions, with good selectivity and sensitivity. Its applicability can provide a platform for the development of the next-generation Ce(IV)-ion probes for use in real-world scenarios.

Experimental

General instrumentations and materials

The UV-Vis spectra were recorded on an ultraviolet spectrophotometer (UV-2550). Emission spectra were performed

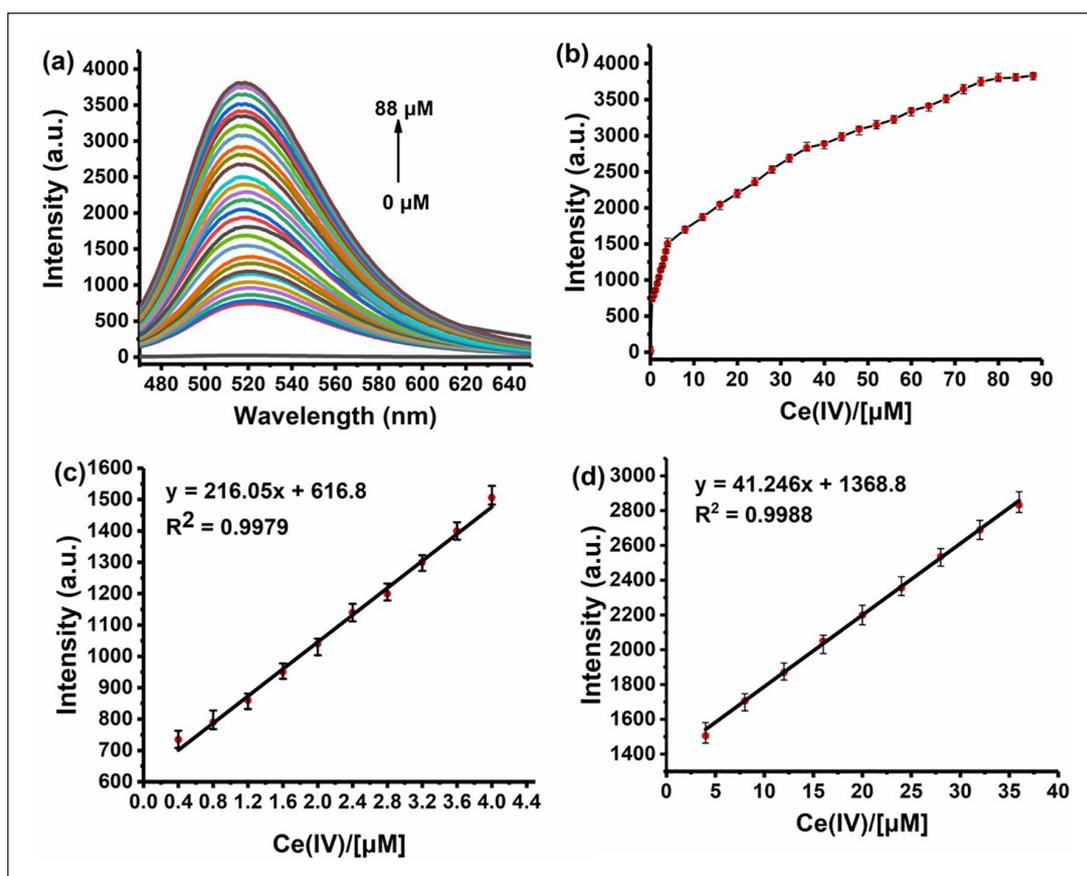


Figure 4. (a) Fluorescence responses of the system to various concentrations of Ce(IV) ions. The concentration of OPD is 40 μM and the concentration of Ce(IV) ions is in the range of 0–88 μM . (b) Fluorescence responses at 526 nm of the system at various concentrations of Ce(IV) ions (1–120 μM). The linear correlation between fluorescence intensity and the concentration of Ce(IV) ions (c) 0.4–4 μM and (d) 5–36 μM . $\lambda_{\text{ex}} = 436 \text{ nm}$, $\lambda_{\text{em}} = 526 \text{ nm}$.

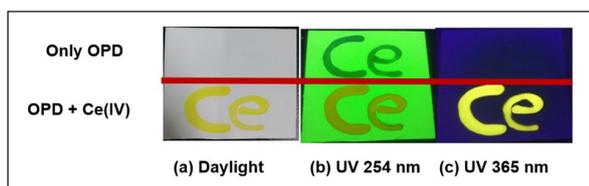


Figure 5. Photographs of TLC sheets with letters written using OPD (top row) or OPD–Ce(IV) (bottom row) as “ink” recorded under (a) daylight and UV light at (b) 254 nm and (c) 365 nm.

on a fluorescence spectrometer (F-4600). Error limits were estimated: λ ($\pm 1 \text{ nm}$), τ ($\pm 10\%$), and ϕ ($\pm 10\%$). The solvents were distilled from standard drying agents. Unless otherwise stated, commercial reagents purchased from Alfa Aesar, Acros, and Aldrich chemical companies were used without further purification. Purification of reaction products was carried out by flash chromatography using Qing Dao Sea Chemical Reagent silica gel (200–300 mesh). ^1H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer and referenced internally to the residual proton resonance in DMSO- d_6 with tetramethylsilane (TMS; $\delta = 0.00 \text{ ppm}$) as the internal standard. Chemical shifts were reported as parts per million (ppm) in the δ scale downfield from TMS. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet),

m (multiplet), dd (doublet of doublet), and bs (broad singlet). ^{13}C NMR spectra were recorded on Bruker spectrometer with complete proton decoupling, and chemical shifts were reported in ppm from TMS with the solvent as the internal reference (DMSO- d_6 , $\delta = 39.5 \text{ ppm}$).

Detection method

The OPD was added into MeCN to a final concentration of 40 μM . Different concentrations of Ce(IV) ions were then added to MeCN containing OPD (40 μM) in a cuvette. Then, emission spectra were recorded after 3-h incubation in the range of 460–650 nm at $\lambda_{\text{ex}} = 436 \text{ nm}$, and the slit width is 10 nm/20 nm.

Preparation of real samples

Ganjiang River water was collected from the Ganjiang River. Tap water was collected from chemistry laboratory. Rainwater was collected from Ganzhou. Ce(IV) ions were spiked into various water samples to obtain sample solutions with 19.2 μM of Ce(IV) ions. Lateritic soils were collected from Ganzhou. Ce(IV) ions (0.05 mmol) were spiked into 5 g of soil and stirred well before use. Then, the sample was extracted with water. After filtration, the sample was diluted to obtain a solution with 19.2 μM of Ce(IV) ions.

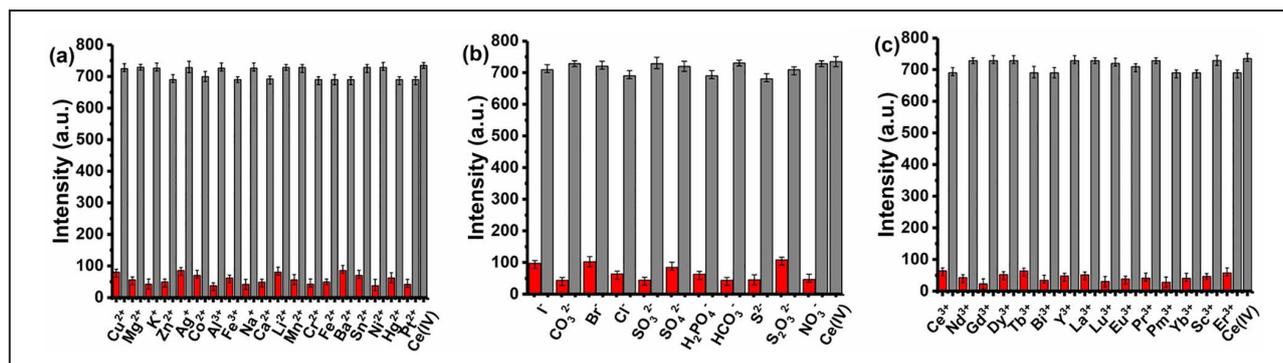


Figure 6. Fluorescence intensity upon addition of 19 common cations (a) (Cu^{2+} , Mg^{2+} , K^+ , Zn^{2+} , Ag^+ , Co^{2+} , Al^{3+} , Fe^{3+} , Na^+ , Ca^{2+} , Li^{2+} , Mn^{2+} , Cr^{3+} , Fe^{2+} , Ba^{2+} , Sn^{2+} , Ni^{2+} , Hg^{2+} , and Pt^{2+}), (b) 11 common anions (I^- , CO_3^{2-} , Br^- , Cl^- , SO_3^{2-} , SO_4^{2-} , HSO_4^- , HCO_3^- , S^{2-} , $\text{S}_2\text{O}_3^{2-}$, NO_3^-), and (c) 15 rare-earth cations (Ce^{3+} , Nd^{3+} , Gd^{3+} , Dy^{3+} , Tb^{3+} , Bi^{3+} , Y^{3+} , La^{3+} , Lu^{3+} , Eu^{3+} , Pr^{3+} , Pm^{3+} , Yb^{3+} , Sc^{3+} , and Er^{3+}). The red bars represent the addition of $20\ \mu\text{M}$ of different ions to the sensor system. The black bars represent the subsequent addition of $0.4\ \mu\text{M}$ Ce(IV) ions to the system. $\lambda_{\text{ex}} = 436\ \text{nm}$, $\lambda_{\text{em}} = 526\ \text{nm}$.

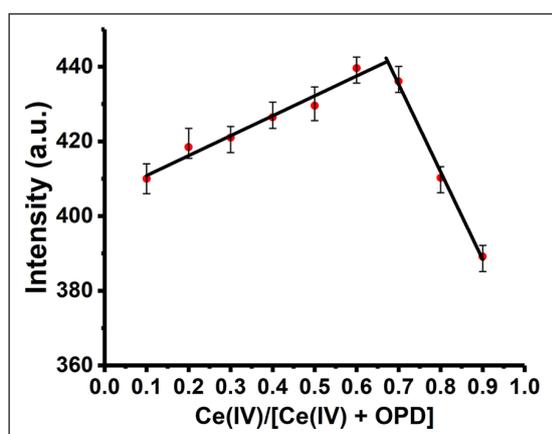


Figure 7. Job's plot for determining the stoichiometry of Ce(IV) ions and OPD; the total concentration of Ce(IV) ions and OPD was $100\ \mu\text{M}$. Molar fraction is given by $[\text{Ce(IV)}]/([\text{Ce(IV)}] + [\text{OPD}])$.

Table I. Investigations on the detection of Ce(IV) ions in water samples and lateritic soil samples.^a

Samples	pH	Added amount (μM)	Found amount (μM)	Standard deviation (μM)	RSD (%), $n = 3$	Recovery (%), $n = 3$
Ganjiang River water	8.07	19.20	18.20	0.65	1.91	94.78
Rain water	6.21	19.20	17.99	1.22	2.31	93.68
Tap water	5.49	19.20	18.70	0.43	0.95	97.37
Lateritic soils	5.40	19.20	18.96	0.23	0.46	98.77

RSD: relative standard deviation.

^aResults for the determination of Ce(IV) ions in real samples.

Experimental conditions: $\text{MeCN}/\text{H}_2\text{O}$ ($v/v = 4:1$); OPD ($40\ \mu\text{M}$), Ce(IV) ($19.2\ \mu\text{M}$).

Detection of OPD in real samples

Real samples (water samples and soil samples) were added to a sensing system containing OPD ($40\ \mu\text{M}$) in MeCN containing 20% H_2O . Then, the mixture solution was incubated at room temperature for 3 h. Emission spectra were

measured in the range of 460–650 nm with an excitation wavelength at 436 nm, and the slit width is 10 nm/20 nm.

Synthesis of 2,3-diaminophenazine

OPD (0.5 mmol) and Ce(IV) ions (0.6 mmol) were added into a round bottom flask, and then, solvent $\text{MeCN}/\text{H}_2\text{O}$ ($v/v = 4:1$) was added. The mixture was stirred at room temperature for 3 h. Then, the mixture was quenched with saturated NaCl solution, extracted by EtOAc , and dried over Na_2SO_4 . The crude product was purified by flash column chromatography to provide the corresponding yellowish-brown product 2,3-diaminophenazine, and the yield was 89%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ 7.87 (dd, $J = 6.5, 3.4\ \text{Hz}$, 2H), 7.53 (dd, $J = 6.5, 3.4\ \text{Hz}$, 2H), 6.88 (s, 2H), 6.31 (s, 4H); ^{13}C NMR (101 MHz, $\text{DMSO}-d_6$) δ 144.81, 142.16, 140.08, 127.87, 127.06, 102.15.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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Supplemental material

Supplemental material for this article is available online.

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