


 Cite this: *RSC Adv.*, 2019, **9**, 22053

 Received 20th May 2019
 Accepted 5th July 2019

 DOI: 10.1039/c9ra03776d
rsc.li/rsc-advances

A cascade reaction-based switch-on fluorescent sensor for Ce(IV) ions in real samples[†]

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We herein report a cascade reaction-based switch-on fluorescence sensor for Ce(IV) ions. The mechanism is based on the ability of Ce(IV) ions to oxidize β -naphthol, which condenses with *o*-phenylenediamine to generate fluorescent benzo[a]phenazine. The sensor achieved a 200-fold fluorescence enhancement and was successfully applied to real sample detection.

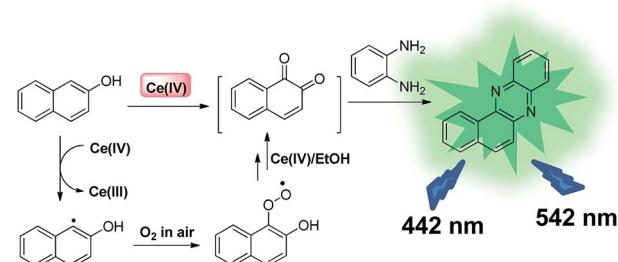
Cerium (Ce) is the most abundant rare-Earth element and has been widely used as polishing powders, fluorescent powders, magnets, catalysts and a ceramic colorant in industry.^{1,2} Although Ce(III) is the most abundant type of cerium in the Earth, Ce(IV) can be more easily extracted and separated from cerium fluorocarbonate mineral. Furthermore, the oxidation processes to convert Ce(III) to Ce(IV) during the post-treatment stage further increases the exposure of Ce(IV) to the community.^{3–5} High concentration of Ce is known to be an environmental hazard and to have acute toxicity to seeds.^{6,7} Prolonged exposure to Ce(IV) ions will cause malfunctions in the human body, particularly with the circulation systems, immune systems and central nervous systems.⁸ Therefore, accurate and rapid determination of Ce(IV) ion is of significant interest for both environmental and clinical applications.

Over the centuries, instrument-based methods have been employed for detection of the Ce(IV) ion, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS), radiochemical neutron activation, and electrochemical methods.^{9,10} However, these methods generally have drawbacks including high cost, long processing time, complicated sample preparation and instrumental complexity. Meanwhile, fluorescent sensors are powerful tools for detecting environmentally and biologically significant analytes in the presence of interfering matrices, by virtue of their simplicity and high sensitivity.^{11–20} To date, a wide variety of fluorescent sensors have been developed for monitoring Ce ions.^{21–25} However, these methods are typically limited by the uses of toxic inorganic nanomaterials, low sensitivity and low selectivity. Therefore, the

development of a fast, sensitive and efficient sensing platform for Ce(IV) ions is highly desirable.

Over the past years, fluorescence properties of benzo[a]phenazine and its derivatives have received considerable attention in organic synthesis, materials and analytical chemistry.^{26–30} Inspired by their promising properties, we herein developed a novel Ce(IV) probe based on Ce(IV)-promoted oxidation/condensation/cyclization to generate highly fluorescent benzo[a]phenazine. It is noteworthy that the Ce(IV) ion has been extensively studied as an oxidant in various chemical reactions.³¹ In this work, the Ce(IV) ion is used as a single-electron oxidant to facilitate the reaction with OPD, followed by the generation of a fluorescent product.³² In the presence of Ce(IV) ions, BNO is oxidized into naphthalene-1,2-dione and then condensed with *o*-phenylenediamine (OPD) to form fluorescent benzo[a]phenazine (Scheme 1). To our knowledge, this is the first detection method using the Ce(IV) ion based on the Ce(IV)-mediated cascade reaction.

This sensing system is comprised of β -naphthol (BNO) and *o*-phenylenediamine (OPD). First, we investigated the fluorescence changes of a mixture of BNO and OPD in organic solvent in the presence of Ce(IV) ions. To study solvent effects, a series of organic solvents, including acetonitrile (ACN), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), ethanol (EtOH), and



Scheme 1 Principle of the Ce(IV)-mediated cascade reaction for the detection of Ce(IV) ions.

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ra03776d



tetrahydrofuran (THF) were used. BNO (50 μ M) was first mixed with Ce(iv) (120 μ M), followed by adding OPD (40 μ M) for 3 h at room temperature (rt). The result showed that a strong fluorescence enhancement was observed in EtOH (Fig. 1a).

A series of control experiments were performed to study the role of different components in this sensing system. The results showed that no fluorescence enhancement was found in the absence of any of the components (Fig. 1b). Moreover, UV-vis absorption spectra exhibited a strong absorption band between 300 nm and 400 nm, but only when all components were present (Fig. S1†). Furthermore, when the reaction was carried out at millimolar levels in the detection system, the final product benzo[a]phenazine was obtained with structure confirmed by ^1H / ^{13}C NMR and melting point (Fig. S2†). To verify the reaction mechanism, the naphthalene-1,2-dione intermediate also was isolated and characterized by NMR (Fig. S3†). Therefore, the proposed method is capable of sensing Ce(iv) ions.

Considering the importance of incubation time in a sensing system, we next investigated the change of fluorescence intensity against different incubation times. In the presence of Ce(iv) ions (120 μ M), the fluorescence intensity of the system increased with longer incubation time, reaching a steady state at 3 h. In contrast, only negligible fluorescence enhancement was observed in the absence of Ce(iv) ions. Therefore, 3 h was chosen as the optimized incubation time for subsequent experiments (Fig. 2).

The sensitivity of an analytical method is very important for its application. So, we examined fluorescence responses of our method to various concentrations of Ce(iv) ions. The system containing BNO (50 μ M) was incubated with indicated concentrations of Ce(iv) ions at rt for 1 h and followed by adding OPD (40 μ M) for 3 h. As shown in Fig. 3a, the fluorescence intensity of the system increased with the concentration of Ce(iv) (8–160 μ M). Upon the addition of Ce(iv) ions, the sensor displayed more than a 200-fold fluorescence enhancement. A good linear relationship was established in a range of 16–88 μ M, and the limit of detection (LOD) was calculated as 1.23 μ M, according to $\text{LOD} = 3\sigma/s$.

To verify the good selectivity of this method, a range of common metal ions (Al^{3+} , Ba^{2+} , Ag^+ , Ca^{2+} , Cr^{3+} , Co^{2+} , K^+ , Mg^{2+} , Na^+ , Fe^{3+} , Mn^{2+}) and rare-Earth metal ions (Dy^{3+} , Gd^{3+} , La^{3+} , Nd^{3+} , Tb^{3+} , Y^{3+} , Ce^{3+}) were investigated. The results showed that

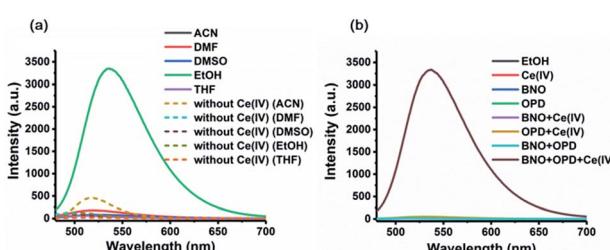


Fig. 1 Fluorescence emission spectra ($E_{\text{x}} = 442$ nm) of the sensing system containing 50 μ M BNO and 40 μ M OPD, with and without 120 μ M Ce(iv), in the indicated organic solvents with 0.5% H_2O (a), and the emission spectra of control experiments under various conditions (b).

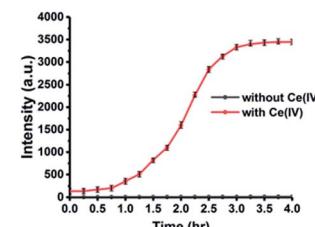


Fig. 2 Fluorescence intensity of the system in the presence and absence of Ce(iv) ions over the indicated time. The concentration of BNO is 50 μ M, with 40 μ M OPD, and 120 μ M Ce(iv) ions in EtOH containing 0.5% H_2O . The fluorescence was monitored at 15 min intervals and collected at a wavelength of 542 nm.

only Ce(iv) ions triggered a significant fluorescence enhancement, and encouragingly even Ce^{3+} only slightly enhanced the fluorescence of the system (Fig. 4). However, other common and rare-Earth metal ions exhibited low fluorescence enhancement. To demonstrate the specificity of the sensor to Ce(iv) ions, a competition experiment was carried out by adding Ce(iv) ions (120 μ M) to a system having the same concentration of other cations. No significant fluorescence change was observed, indicating that this reaction-based method possess great potential to detect Ce(iv) ions even in the presence of other common interfering cations. These results demonstrated high selectivity of this method towards the Ce(iv) ion, which can be attributed to the special single-electron oxidation property of the Ce(iv) ion.

Encouraged by the excellent sensitivity and selectivity of this sensing system, we next investigated its ability to detect Ce(iv) ions in real samples. First, a water sample from the Ganjing River (pH = 7.9) was collected and used in this work. Upon the addition of a water sample containing Ce(iv) ions (16 μ M) into the sensing system, an obvious fluorescence enhancement was observed with a RSD of 0.92% (Fig. 5a). Moreover, we further explored its application to the detection of Ce(iv) ions in a lateritic soil sample collected from Ganzhou (pH = 5.4). The samples were pre-treated according to a reported method.³³ The results showed that Ce(iv) ions (24 μ M) could induce a significant luminescence enhancement with a RSD of 0.93% (Fig. 5b).

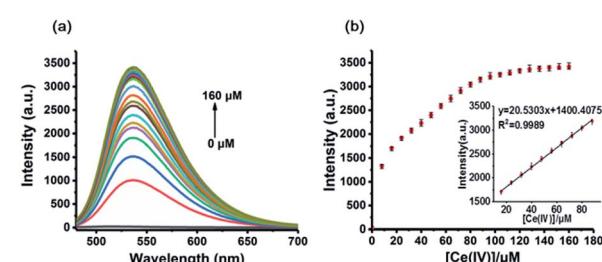


Fig. 3 (a) Fluorescence responses of the system to various concentrations of Ce(iv) ions. The concentration of BNO is 50 μ M, with 40 μ M OPD, and the concentration of Ce(iv) ions was in the range of 8–160 μ M. (b) Fluorescence responses at 542 nm of the system to various concentrations of Ce(iv) ions. The inset shows the linear correlation between fluorescence intensity and the concentration of Ce(iv) ions (16–88 μ M). $\lambda_{\text{ex}} = 442$ nm, $\lambda_{\text{em}} = 542$ nm.



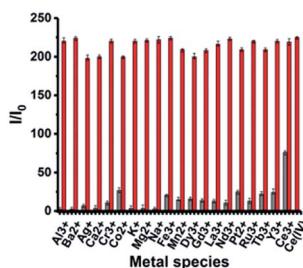


Fig. 4 Fluorescence intensity upon the addition of different metal species (Al^{3+} , Ba^{2+} , Ag^+ , Ca^{2+} , Cr^{3+} , Co^{2+} , K^+ , Mg^{2+} , Na^+ , Fe^{3+} , Mn^{2+} , Dy^{3+} , Gd^{3+} , La^{3+} , Nd^{3+} , Tb^{3+} , Y^{3+} , Ce^{3+} , $\text{Ce}(\text{IV})$). The black bars represent the addition of 120 μM concentrations of different anions to the sensing system. The red bars represent the subsequent addition of 120 μM $\text{Ce}(\text{IV})$ ions to the system. $\lambda_{\text{ex}} = 442 \text{ nm}$, $\lambda_{\text{em}} = 542 \text{ nm}$.

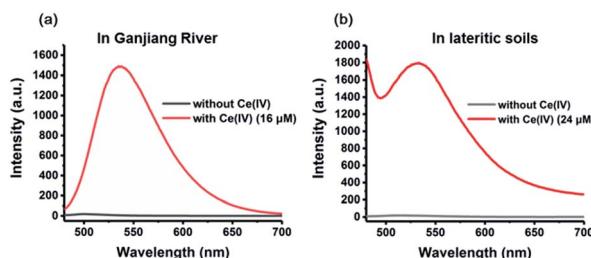


Fig. 5 Emission spectra of the sensing system with and without $\text{Ce}(\text{IV})$ ions in (a) a water sample from the Ganjiang River and (b) lateritic soil samples.

Taken together, we have successfully demonstrated the applicability of this sensing system to detect $\text{Ce}(\text{IV})$ ions in the presence of those complex matrices.

Conclusions

In this work, we report a switch-on fluorescence system for the detection of $\text{Ce}(\text{IV})$ ions. A cascade reaction-based platform is based on the ability of $\text{Ce}(\text{IV})$ to oxidize BNO, followed by condensation/cyclization with OPD to form fluorescent benzo[*a*]phenazine. After optimization, the probe exhibited a linear range of 8–160 μM , with a limit of detection of 1.23 μM at a signal-to-noise ratio (S/N) of 3. The system selectively detected $\text{Ce}(\text{IV})$ ions over 18 cations and showed a more than 200-fold enhancement of the fluorescence signal. We also successfully demonstrated its applicability for the detection of $\text{Ce}(\text{IV})$ ions in real samples, including river water from the Ganjiang River and lateritic soil from Ganzhou. It is anticipated that further optimization could lead to the development of an improved sensor with great potential for the *in situ* monitoring of $\text{Ce}(\text{IV})$ ions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This work is supported by the Natural Science Foundation of China (No. 21762018 and 51564021), and the Program of Qingjiang Excellent Young Talents of Jiangxi University of Science and Technology.

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