RSC Advances

Journal Name

ARTICLE TYPE

Colorimetric and near infrared fluorescent detection of cyanide by a new phenanthroimidazole–indolium conjugated probe†

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In this paper, a new dual colorimetric and fluorescent probe for cyanide anions was developed. This probe contains an electron−donating phenanthroimidazole moiety and a strong electron−withdrawing indolium derivative. The detection of cyanide was performed via the fast nucleophilic attack of cyanide to the indolium group of the probe, resulting in a rapid sensing process for cyanide with obvious color and fluorescence (at two different emission channels, one in visible region and one in near infrared 10 region) signal changes, and with high selectivity and sensitivity. The detection limit was found to be 26 nM in aqueous solution, and the application of this probe for cyanide detection in simulated wastewater samples were investigated.

Introduction

Cyanide ion (CN^-) is a well known extremely toxic anion and is of highly potential danger for mammals even in very low 15 concentrations.[1] The maximum permissive level of cyanide in drinking water is therefore set at as low as 1.9 μM by the World Health Organization (WHO).[2] Despite its high toxicity, cyanide is widely used in various industrial processes such as gold mining, electroplating, metallurgy and the synthesis of nylon, fibers and 20 others.[3] In this case, any accidental release of cyanide ions from these industrial processes can cause serious environmental disasters. Considering the highly toxic property of cyanide, as well as the continuing environmental concerns caused by its widespread industrial use, the sensitive and selective detection of 25 cyanide ions is of considerable importance, and as a result, much effort have been given into the development of reliable and efficient methods for cyanide detection in recent years.[4]

Although many methods have been proposed to detect cyanide such as using titrimetric, voltammetric, potentiometric, 30 chromatography and electrochemical methods, *etc*,[5] these methods often require complicated, time consuming sample pretreatment or need expensive equipment with high detection limits. More recently, optical methods using small molecular chemical probes have attracted more attention due to their many 35 appealing advantages.[4] In particular, probes especially those with dual colorimetric and fluorescent signal outputs are more attractive because they offer not only the convenient visual sensing by the "naked eye", but also provide simple, highly sensitive and low cost detection by fluorescent signal responses. 40 To construct cyanide selective chemical probes, two approaches of using coordination complex-based displacement and reaction-based chemodosimeters are generally used.[4] These approaches take advantage of two significant properties of cyanide, its high binding affinity towards copper ions and its 45 strong nucleophilicity. Among them, the reaction-based chemodosimeter approach has recently attracted particular attention to many research groups, due to many probes based on

this approach showed promising sensing behaviour for cyanide with high selectivity and sensitivity in aqueous solutions. The 50 most used reactions in chemodosimeters for cyanide include nucleophilic cyanide addition to electron-deficient carbon–carbon double bond,[6] to carbon–heteroatom double bond[7] and to heterocyclium derivatives[8]. These studies greatly advanced the research of cyanide recognition and sensing.

55 We are interested in developing new chemodosimeters for anion sensing. For example, by using the specific reactions such as hydrogen sulfide mediated thiolysis of dinitrophenyl ether and fluoride triggered cleavage of Si-O bond, we have developed new chemodosimeters for hydrogen sulfide[9a] and fluoride[9b], 60 respectively. Herein, we report a new dual colorimetric and fluorescent chemodosimeter for cyanide (probe **1** in Scheme 1), which is based on the fast nucleophilic attack of cyanide anions to the iminium carbon. This probe contains a conjugated phenanthroimidazole moiety with a positively-charged indolium 65 derivative, and was found highly reactive for cyanide anions to show rapid and distinct optical signal changes with high selectivity and sensitivity. The detection limit of this probe for CN^- was measured to be about 26 nM, which is well below the WHO cyanide standard in drinking water. Notably, this probe 70 shows significant detectable near infrared (NIR) fluorescent signal changes during cyanide detection. So far, NIR fluorescent probes for cyanide are very rare.[10] In addition, we also successfully applied this probe to detect cyanide in simulated wastewater samples, indicating that this probe has potential in 75 chemical and environmental applications for cyanide detection.
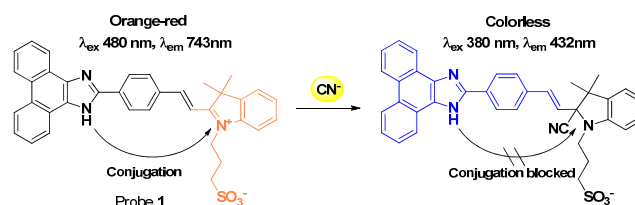

Scheme 1. Structure of probe **1** and sensing of cyanide.

Results and discussion

1. Design and synthesis

The probe in this study was designed to contain an electron−donating phenanthroimidazole moiety and a strong electron−withdrawing positively-charged indolium derivative (Scheme 1), which are conjugated via a phenyl bridge to form a typical dye with intramolecular charge transfer (ICT) property. Phenanthroimidazole-based dyes have very convenient thermal stability and optical properties, and have been used to develop chemosensors for several anions and metal ions.[11] The indolium group was chosen because it can be used as a specific reaction site for cyanide.[8a-8g] The propanesulfonate residue introduced to the indolium group is used to improve the water solubility of the probe. As shown in scheme 1, the sensing of cyanide can be achieved by the nucleophilic addition of cyanide to the indolium moiety, as this would destroy the π−conjugation between indolium and phenanthroimidazole dye, block the ICT effect of the probe and give distinct changes for optical signal output.
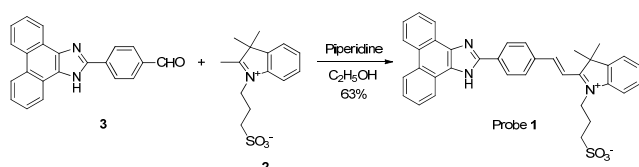
Scheme 2. Synthesis of probe **1**.

Probe **1** can be readily prepared via the condensation of 4-(1H-phenanthro[9,10-d]imidazol-2-yl)-benzaldehyde **3** with indolium derivative **2** in ethanol (Scheme 2). Both **2**[12] and **3**[11d] are known compounds, and they are prepared according to the previously published procedures. Structural identification of probe **1** was confirmed by NMR, IR and HR-MS spectroscopy. Detailed synthetic procedures and structure characterizations are given in the experimental section and in the ESI†.

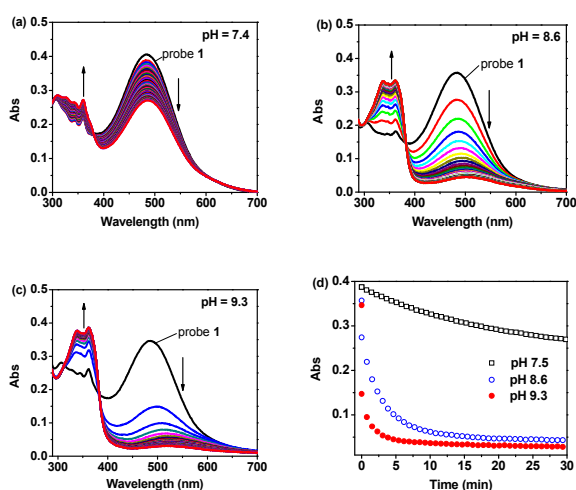## 2. Rapid, colorimetric and fluorescent detection of CN−

Fig. 1 The scanning kinetics of probe **1** (20 μM) upon addition of 5 equiv. of CN− in 1:1 MeOH–Tris·HCl buffer (10 mM) with the varied pH value at 25°C；(a) pH = 7.4, (b) pH = 8.6, (c) pH = 9.3. (d) The absorbance intensity changes of probe **1** at 486 nm in the presence of 5 equiv. CN− as a function of time at different pHs.

With probe **1** in hand, we first tested its sensing potential for CN−. The investigation experiments were explored in a MeOH–Tris·HCl buffer solution (10 mM, 1:1, v/v). Since the pK_a of HCN is 9.2 in water and the probe we designed to sense cyanide is based on the nucleophilic addition of cyanide anion to the indolium group, the pH of the reaction medium should have significant effect to the reaction efficiency. By examining the scanning kinetics of the reaction of probe **1** upon addition of cyanide under above conditions at different pHs, we did find that the reaction is highly pH−dependent, and become faster at higher pH. As shown in Fig. 1, the reaction is slow at pH 7.4 but can be completed within 5 min when the pH of the reaction is adjusted to 9.3. Thus, a 1:1 MeOH–Tris·HCl buffer (10 mM, pH = 9.3) at 25°C was chosen as the testing conditions to investigate the sensing ability of probe **1** for cyanide.
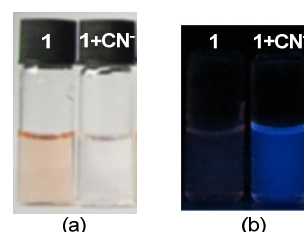

Fig. 2 (a) Color changes of probe **1** (20 μM) upon addition of 100 μM CN− in MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1 : 1, v/v). (b) Emission color changes of probe **1** (20 μM) upon addition of 100 μM CN− in MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1 : 1, v/v) under a 365 nm UV light.
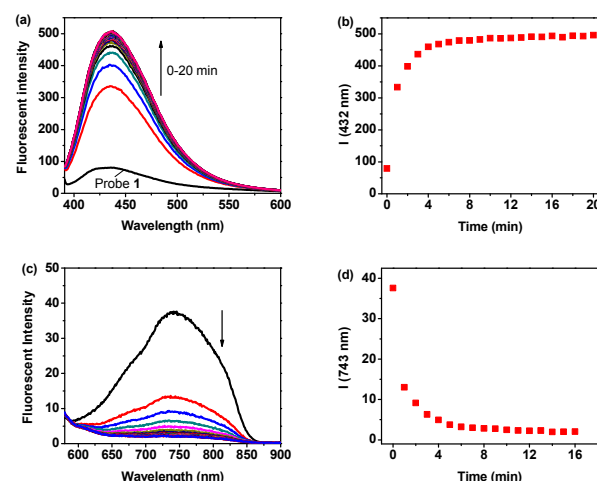

Fig. 3 Time-dependent fluorescence spectra changes of probe **1** (20 μM) upon addition of 100 μM CN− in 1:1 MeOH–Tris·HCl buffer (10 mM, pH 9.3) at 25°C. (a) Excited at 380 nm, d_{ex} = 5 nm, d_{em} = 10 nm. (b) Fluorescence intensity changes at 432 nm against time. (c) Excited at 480 nm, d_{ex} = 10 nm, d_{em} = 10 nm. (d) Fluorescence intensity changes at 743 nm against time.

Along with the fast reaction at pH 9.3, we can see that probe **1** shows an absorption maximum at 486 nm with an extinction coefficient of ~16,700 $M^{-1}cm^{-1}$, and as the reaction progresses, the absorption band at 486 nm gradually decreases, while the peak at 361 nm and 338 nm increase until reach saturation after 5 min (Fig. 1c). A well isosbestic point at 385 nm was observed, indicating that probe **1** gradually changed into another species in the reaction mixture. Meanwhile, we observed

a distinct color change of the reaction mixture from orange-red to colorless, and the solution started to show a bright blue fluorescence (Φ = 0.034, ESI†) if observed under a 365 nm light (Fig. 2). All these optical responses are highly visible to the naked eye, indicating that probe **1** can be used as a dual colorimetric and fluorescent sensor for rapid detection of CN^- in aqueous solution.

The fluorescence spectra changes of probe **1** with 5 equiv. of CN^- were also examined. As shown in Fig. 3, when excited at 380 nm, probe **1** in 1:1 MeOH–Tris·HCl buffer (10 mM, pH = 9.3) at 25 °C shows a weak fluorescence centred at 432 nm (Φ = 0.014, ESI†), and this emission peak gradually enhances as time goes on, until a saturation was observed at about 5 min after mixing with CN^- (Fig. 3a and 3b). Notably, when the solution is excited at 480 nm, probe **1** showed a detectable near infrared (NIR) emission signal changes at 743 nm, and addition of CN^- to the probe **1** solution results in a gradual decrease in the NIR emission peak (Fig. 3c and 3d). The fluorescence enhancement at 432 nm and decrease at 743 nm indicate the destruction of the π−conjugation between indolium and phenanthroimidazole dye, and the recovery of the fluorescence of the phenanthroimidazole moiety. Therefore, probe **1** can offer fluorescent detection of cyanide at two different emission channels, one in the visible range, and another in the NIR range. It's worth noting that NIR fluorescent probes have many advantages, which were well stated in recent reviews,[13] however, NIR fluorescent probes for CN^- are very limited in the literature.[10]

To achieve more information, the kinetics of probe **1** at different concentrations of CN^- from 0 to 200 µM were also measured. As shown in Fig. S1a (ESI†), probe **1** is reasonably stable under the test conditions, and the speed of the signal change is influenced by concentration of CN^-. We can see that higher concentration of the CN^- promotes the reaction. For example, the reaction competed at about 15 min and 5 min, when the concentration of CN^- is used at 40 µM and 100 µM, respectively. Although the reaction became slower and signal saturation time was found to be more than 15 min under stoichiometric conditions, distinct signal changes are also observed within a few minutes. Similar results can be found if monitor the reaction by fluorescence intensity changes, either at 432 nm or 743 nm (Fig. S1b and S1c, ESI†)
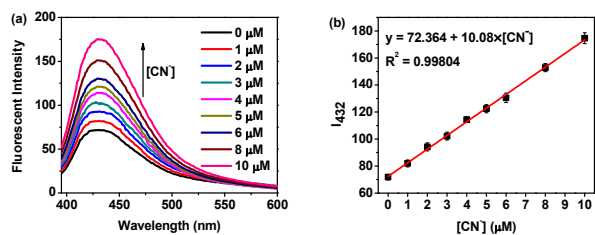
3. The detection limit

Fig. 4 (a) Fluorescence spectra changes of probe **1** (20 µM) upon addition of different concentrations of CN^- in MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1 : 1, v/v) at 25°C. Final concentration of CN^-: 0, 1, 2, 3, 4, 5, 6, 8, 10 µM. (b) A linear calibration curve between the fluorescent intensity at 432 nm (I_{432}) and the concentration of CN^- in the range of 0 to 10 µM. Each spectrum was collected at 10 min after CN^- addition. λ_{ex} = 380 nm, slit width: d_{ex} = 5 nm, d_{em} = 10 nm.

Furthermore, measuring of the absorbance or fluorescence change of the probe **1** solution after 10 min upon addition of different concentrations of KCN revealed that saturation occurred when CN^- was added more than 5 equiv. to the concentration of probe **1** (Fig. S2-S4, ESI†). To get insight into its sensitivity, the detection limit of probe **1** for CN^- was determined based on the fluorescence titration. As shown in Fig. 4, a linear calibration curve can be found between the fluorescent intensity changes at 432 nm and the concentration of CN^- in the range of 0 to 10 µM (R^2 = 0.99804). Thus, the detection limit of probe **1** for CN^- is measured to be about 26 nM based on the signal to noise ratio (S/N) = 3 under the test conditions, which demonstrates that probe **1** is operable well below the WHO cyanide standard in drinking water (1.9 µM). Therefore, this result indicates that probe **1** is a highly sensitive fluorescent probe for cyanide anions.

4. The selectivity

Selectivity is a key factor for a probe. The above results showed that probe **1** not only provides a sensitive colorimetric and fluorescent signal changes for CN^-, but also offers a rapid sensing process for CN^- in aqueous solution. In this case, one question must be answered: how about the selectivity? To evaluate the selectivity of probe **1** for CN^-, we chose a set of anionic species as interference ions, such as F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NO_3^-, HSO_4^-, AcO^-, SCN^-, CO_3^{2-}, HCO_3^-, NO_2^-, N_3^-, S^{2-}, $H_2PO_4^-$, PO_4^{3-}, ClO_4^- and cysteine (Cys). A colorimetric assay is firstly explored, as this method is most convenient. As shown in Fig. S5 (ESI†), among various analytes, only CN^- resulted in an obvious color change, as well as the fluorescence color change to the probe **1** solution, indicating that probe **1** has high selectivity for CN^- over these interference ions.
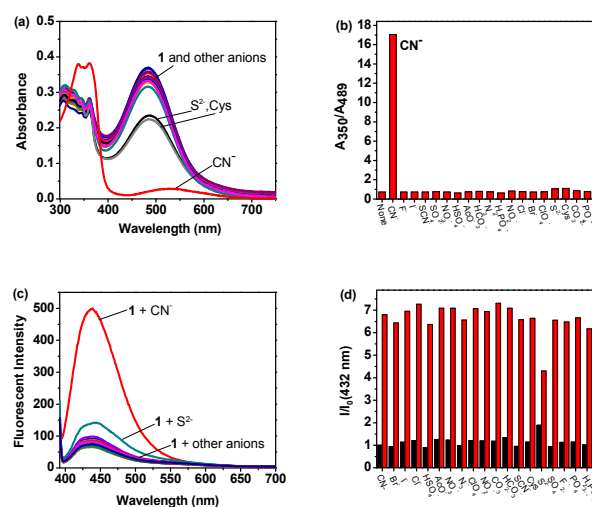

Fig. 5 The selectivity of probe **1** for CN^-. (a) UV-vis spectra changes of probe **1** (20 µM) in the presence of various anions. (b) Relative absorbance intensity changes of probe **1** at 350 nm and 489 nm (A_{350}/A_{489}) for various anions. (c) Fluorescent spectra changes of probe **1** (20 µM) in the presence of various anions. (d) Relative fluorescence (I/I_0) of probe **1** at 432 nm for various anions. Black bars represent the addition of a single analyte, red bars represent the subsequent addition of CN^- (100 µM) to the mixture. All spectra were recorded 10 min after the addition of anions in MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1 : 1, v/v) at 25°C. The concentration: 100 µM for S^{2-}, Cys, CN^- and 1 mM for other anions. For fluorescent measurement, λ_{ex} = 380 nm, d_{ex} = 5 nm, d_{em} = 10 nm.

To obtain more details, the UV-vis and fluorescent spectra changes of probe **1** towards these anionic species were then explored and the results are shown in Fig. 5. From Fig. 5, we can see that significant UV-vis spectra change and large fluorescence enhancement of the probe **1** solution were only observed upon addition of CN⁻. In contrast, other anions did not show any significant interference except a small disturbance from S^{2-} and Cys, which is probably due to the similar addition mechanism. The selectivity of probe **1** for CN⁻ can be well illustrated in Fig. 5b and Fig. 5d, via comparing the relative absorption ratio at 350 nm and 489 nm (A_{350}/A_{489}) or the relative fluorescent intensity ratio at 432 nm (I/I_0) for each analyate. Moreover, detection of CN⁻ was also examined in the presence of various anions, and the results showed that distinct fluorescence signal changes can be still observed after subsequent addition of CN⁻ to the probe **1** solutions in presence of various anions including S^{2-} and Cys, indicating detection of CN⁻ using probe **1** in the presence of these interfering anions is still effective (Fig. 5d). Therefore, all these investigations indicate that probe **1** is highly selective for CN⁻.

5. The sensing mechanism

The optical changes of probe **1** in the presence of CN⁻ suggest that the conjugation structure of probe **1** between the phenanthroimidazole moiety and the positively charged indolium group was blocked by nucleophilic addition of CN⁻ to probe **1**. In addition, the well defined isosbestic point at 385 nm in Fig. 1 indicates the formation of a **1**–CN adduct. Job's plot analysis of the UV-vis titrations revealed that a maximum absorbance intensity change is at about 0.5 mole fraction (Fig. S6, ESI†), which is in line with the proposed 1 : 1 binding stoichiometry.
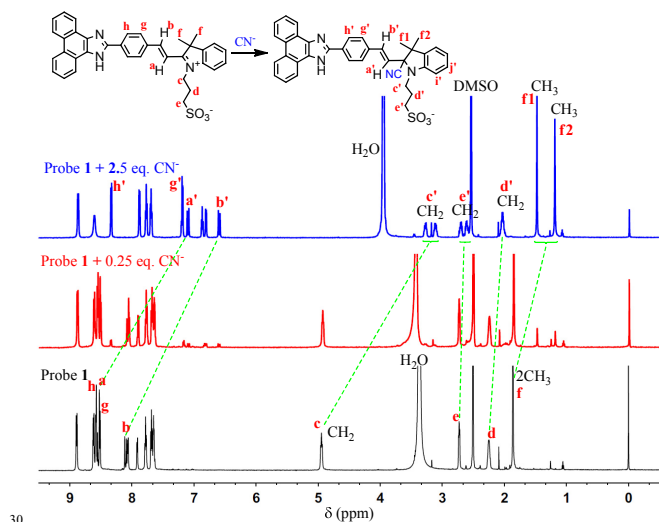

Fig. 6. ¹H NMR spectra changes of probe **1** with addition of CN⁻. For an enlarged image to see the change of each proton, see Fig. S7, ESI†.

¹H NMR and mass spectroscopy were further used to investigate the potential interaction mechanism of probe **1** with cyanide anions. The ¹H NMR titrations spectra of probe **1** upon addition of cyanide anions were shown in Fig. 6. We can see that addition of 0.25 equivalent of cyanide ions to the probe solution at room temperature resulted in appearance of several upfield-shifted peaks. When KCN was added more than one equivalent, the spectra showed significant signal changes for

several different protons, including protons bonded to aromatic and vinylic carbons, and as well as to the saturated carbons. For example, the doublet peaks corresponding to vinylic proton at a-position shifted from 8.57 ppm ($J = 16.2$ Hz) to 7.11 ppm ($J = 16.2$ Hz), while the vinylic proton at b-position shifted from 8.10 ppm ($J = 16.2$ Hz) to 6.60 ppm ($J = 16.2$ Hz). The triplet peak at 4.95 ppm corresponding to the two protons (Hc) in one of the three CH₂ groups that adjacent to indolium moiety in probe **1** shifted to 3.12-3.29 ppm, forming two set of multiplet peaks, meanwhile, the singlet peak corresponding to protons in the two CH₃ groups in probe **1** shifted from 1.86 ppm (6H, Hf) to 1.49 ppm (3H, Hf1) and 1.20 ppm (3H, Hf2), forming two set of singlet peaks. All these information indicate the nucleophilic attack of a cyanide anion to the iminium carbon in probe **1** and formation of the **1**-CN adduct,[8a-8g] in which the positive charged indolium moiety changed into a near neutral indole derivative, thus lose its strong electron−withdrawing property and as a consequence, several proton's signal upfield shifted. In addition, the **1**-CN adduct can be isolated, and its structure characterizations by ¹H NMR, IR, MS analysis further proved the structure (Fig. S8-10, ESI†).

6. The practical applications

To demonstrate the practical utility of probe **1**, the ability to detect CN⁻ in tap water and simulated wastewater samples was tested. As shown in Fig. 7, the fluorescence responses of probe **1** for CN⁻ in tap water and simulated wastewater were in good agreement with that in distilled water, indicating that probe **1** has potential in chemical and environmental applications for the detection of cyanide anions.
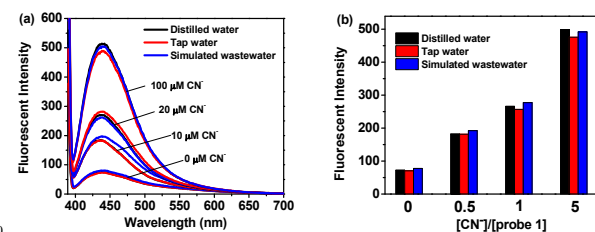

Fig. 7 Fluorescence detection of different concentrations of CN⁻ in 'distilled water', 'tap water', and 'simulated wastewater' by probe **1** (20 μM) MeOH–Tris·HCl buffer (10 mM, pH = 9.3, 1 : 1, v/v) at 25 °C. Final concentration of CN⁻: 0, 10, 20, 100 μM. The simulated wastewater sample contains: $[KCl] = 2.8 \times 10^{-4}$ M, $[MgCl_2] = 2.9 \times 10^{-4}$ M, $[CaCl_2] = 2.5 \times 10^{-4}$ M, $[NaF] = 1.6 \times 10^{-5}$ M, $[Na_3PO_4] = 1.1 \times 10^{-4}$ M, $[Na_2SO_4] = 2.1 \times 10^{-4}$ M, $[NaNO_3] = 4.8 \times 10^{-4}$ M, $[NaHCO_3] = 1.2 \times 10^{-3}$ M.

Experimentals

General

All reagents were purchased from commercial suppliers and used without further purification. All solvents were purified prior to use. All aqueous solutions and buffers were prepared with using distilled water that had been passed through a Millipore-Q ultrapurification system. Buffers used for different pHs were 2-Amino-2-hydroxymethyl-propane-1,3-diol (Tris) by addition of moderate amount of hydrochloric acid, and the pH was measured before experiments. TLC analysis was performed using precoated plates. Column chromatography was performed using silica gel (200-300 mesh) using eluents in the indicated v:v ratio. Melting

points were determined using an X-4 apparatus and are not corrected. IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrophotometer as KBr pellets and were reported in cm^{-1}. NMR spectra were measured on Varian Mercury 400 and 600 instruments, operating at 400 or 600 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Coupling constants (J values) are reported in hertz. Electrospray mass spectra (ESI-MS) were acquired on Agilent 1100 Series LC/MS ion trap mass spectrometers and 6530 Accurate-Mass QTOF spectrometer coupled to an Agilent HPLC 1200 series (Agilent Technologies). UV-vis spectra and fluorescent spectra were recorded on an Agilent Cary 100 UV-vis spectrophotometer and an Agilent Cary Eclipse fluorescence spectrophotometer, respectively, and both spectrophotometers are equipped with a temperature controller. Standard quartz cuvettes with a 10 mm lightpath were used for all UV-vis spectra and fluorescent spectra measurements.

Procedures for CN$^-$ sensing: Stock solutions of probe **1** (0.2 mM) were prepared in CH$_3$OH (HPLC grade). Stock solutions (0.1 M) of the anions were prepared in water. UV/vis and fluorescence titration experiments were performed using 20 μM of probe **1** in 10 mM of Tris·HCl buffer (contains 50% CH$_3$OH, v/v) solution with varying concentrations of the anions at 25 °C.

Synthesis of probe 1

4-(1H-phenanthro[9,10-d]imidazol-2-yl)-benzaldehyde **3** (161 mg, 0.5 mmol) and 2,3,3-trimethyl-1-(propan-3-sulfonyl) indolenine **2** (140.5 mg, 0.5 mmol) were dissolved in ethanol (30 ml), 10 μL piperidine was added to the solution. The mixture was then heated under reflux for 24 h. After cooling the solid was collected, washed with anhydrous ethanol, acetone and diethyl ether, then dried, giving a brown solid (184 mg, yield: 63%). Mp. > 300 °C; ^{1}H NMR (600 MHz, DMSO-d$_6$) δ 13.77 (s, 1H), 8.89 (d, J = 8.2 Hz, 2H), 8.62 (d, J = 7.8 Hz, 2H), 8.58 (d, J = 8.2 Hz, 2H), 8.57 (d, J = 16.2 Hz, 1H), 8.52 (d, J = 8.2 Hz, 2H), 8.10 (d, J = 16.2 Hz, 1H), 8.06 (d, J = 7.0 Hz, 1H), 7.91 (d, J = 7.4 Hz, 1H), 7.78 (t, J = 7.2 Hz, 2H), 7.69 (t, J = 7.5 Hz, 2H), 7.65 (m, 2H) 4.95 (t, J = 7.5 Hz, 2H), 2.73 (t, J = 5.4 Hz, 2H), 2.25 (m, 2H), 1.86 (s, 6H). ^{13}C NMR (100 MHz, CF$_3$COOD + CDCl$_3$) δ 183.2, 153.2, 144.5, 140.6, 138.8, 132.0, 130.5, 129.6, 129.1, 128.8, 127.5, 124.7, 122.0, 119.8, 119.2, 116.4, 115.4, 113.6, 110.7, 54.0, 48.4, 46.3, 26.4, 24.3. IR (KBr, cm^{-1}): 3442 (br, NH), 3045, 1585, 1560, 1531, 1468, 1432, 1403, 1373, 1312, 1275, 1176, 1040, 953, 760, 727. HR-MS (ESI): m/z, calcd for C$_{36}$H$_{32}$N$_3$O$_3$S$^+$ (M + H)$^+$ 586.2159; Found 586.2156.

Conclusions

In summary, we developed a new highly reactive dual colorimetric and fluorescent chemodosimeter for cyanide. This new probe can be easily prepared and shows fast responses with distinct color and fluorescence signal changes both in visible and NIR region, and with high selectivity and sensitivity for cyanide ions. The detection limit was found to be 26 nM using fluorescent detection. We also demonstrated that this probe can be used to detect cyanide in simulated wastewater samples. Thus, it provides a new promising dual colorimetric and fluorescent sensor for rapid detection of cyanide and has potential in chemical and environmental applications.

Notes and references

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† Electronic Supplementary Information (ESI) available: [NMR and Mass spectra, and additional UV and fluorescence data]. See DOI: 10.1039/b000000x/
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Graphical abstract for contents page:

A new dual colorimetric and fluorescent probe was developed for rapid detection of cyanide anions with high selectivity and sensitivity.