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A phenothiazine-based colorimetric chemodosimeter for the rapid detection of cyanide anions in organic and aqueous media†

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A novel, phenothiazine-based chemodosimeteric probe **PCP 1** has been developed and studied as a cyanide selective indicator in organic and aqueous media. Complete colour bleaching was observed due to nucleophilic addition of cyanide to the tricyanovinyl moiety of **PCP 1**, which results in the disruption of the extended conjugate and turn-off the intramolecular charge transfer process.

Introduction

The development of chemosensors and chemodosimeters for anions, an integral part of our biological system, is an area of emerging interest in supramolecular and anion coordination chemistry.[1] Among various anions, CN^- is particularly important due to its extreme toxicity towards mammals.[2] The rapid absorption of CN^- within blood and its binding with Fe^{3+}, an active site of cytochrome c, inhibits cellular respiration in mammalian cells, leading to vomiting, convulsions, loss of consciousness, and eventual death.[3] Despite this grey side, the industrial use of cyanide salts in gold mining, electroplating, metallurgy, and production of organic chemicals, synthetic fibers or resins remains widespread.[4] However, the accidental release of cyanide might lead to very serious problems. Thus a convenient and robust detection of CN^- is of crucial importance.

To date, considerable efforts have been devoted to develop optical sensors for CN^-, in which a change in colour or fluorescence intensity is monitored.[5] Among them, colorimetric sensors are especially appealing as the signalling events can be detected by naked eye.[6] Nevertheless, most of the chromogenic systems for CN^- suffer from their limited sensing features only in organic solvents as well as low sensitivity employing high concentration of CN^- (>1.9 μM), which is not permissible, specifically, in drinking water (≤1.9 μM) as suggested by World Health Organization (WHO).[7] In this context, it is critical to search for a sensor paradigm that combines the operational benefits of instrumentation free and cost-effective protocol with the convenience in aqueous solution, whilst retaining high selectivity and sensitivity for rapid CN^- detection.

Since its first appearance in 1883,[8] 10*H*-phenothiazine (PTZ) **3** has found rising applications as electrophoric sensors in supramolecular assemblies for photo-induced electron transfer (PET),[9] electrically conducting charge-transfer composites,[10] polymers,[11] donor–acceptor arrangements,[12] organic light-emitting diodes (OLEDs),[13] multifunctional sensors,[14] and also as chromophores in dye-sensitized photovoltaic cells.[15] Despite this influential "aura" of PTZ core, the PTZ-based chromogenic systems for anions are relatively scarce.[16] Furthermore, to the best of our knowledge, PTZ-based cyanide chemosensors or chemodosimeters are still unprecedented. In continuation of our interest in the unswerving recognition of biologically important analytes,[17] herein, we disclose a simple yet robust and novel phenothiazine-based chemodosimeteric probe, 10-butyl-3-tricyanovinyl-10*H*-phenothiazine, **PCP 1** for the rapid, sensitive and selective detection of cyanide anions in organic and aqueous media.

Results and discussion

The structure and synthesis of **PCP 1** is outlined in Scheme 1. Briefly, the reaction of **3** with *n*-butyl bromide in anhydrous acetone followed by tricyanovinylation of 10-butyl-10*H*-phenothiazine **2** with TCNE in anhydrous DMF–THF mixture (1 : 1 v/v) furnished **PCP 1** in moderate yield. The structure and purity of **PCP 1** along with **2** and 3-tricyanovinyl-10*H*-phenothiazine **4**‡

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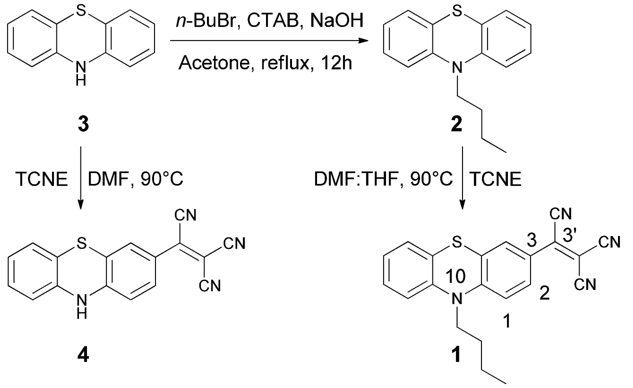
† Electronic supplementary information (ESI) available: Experimental procedures for the synthesis, spectral data, and copies of ^1H NMR and ^{13}C NMR of **PCP 1** and **4**; data for UV-vis absorption experiments; theoretical calculation results; and other relevant data. See DOI: 10.1039/c4ra06440b



Scheme 1 Synthesis of **PCP 1** and **4**.

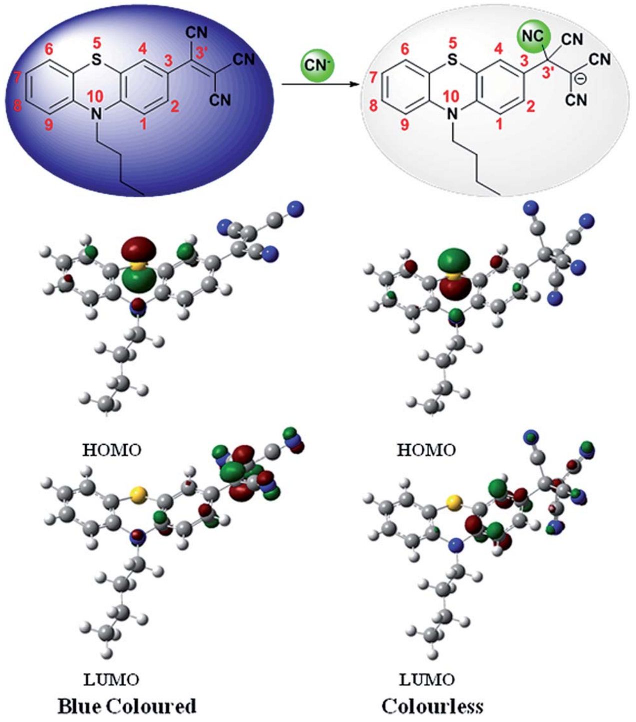


Fig. 1 Upper panel: proposed product obtained from the reaction of CN$^-$ with **PCP 1**; lower panel: calculated HOMO and LUMO distribution of **PCP 1** and its CN$^-$ adduct.

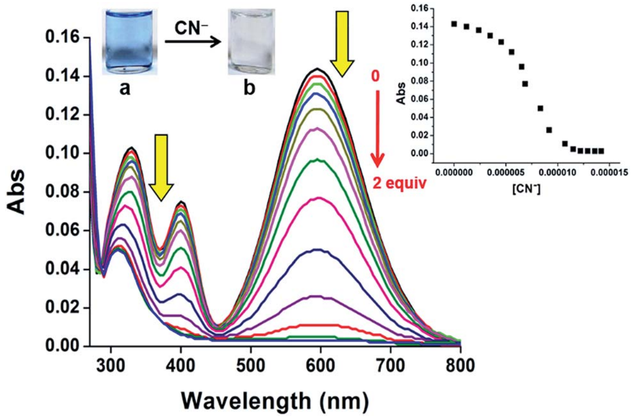


Fig. 2 UV-vis absorption spectral changes of **PCP 1** (5.0×10^{-6} M) upon addition of increasing amount of CN$^-$ (as tetrabutylammonium salt; 0 → 2 equiv.) in DCM. Inset (left): (a) a solution of **PCP 1** (5 μM in DCM). (b) Addition of 2 equiv. of CN$^-$ to solution (a). Inset (right): titration profile of the observed changes at $\lambda = 600$ nm.

were unambiguously confirmed by ^{1}H and ^{13}C NMR spectroscopy (see ESI†). It is worthwhile to mention here that the protection of 10N–H in **3** as well as attachment of tricyanovinyl (TCV) motif to the PTZ core completely switched-off the original blue fluorescence of **3**, and consequently **PCP 1** and **4** appeared as non-fluorescent but colorimetric sensors.

In the first step, the anion recognition behaviour of **4** (5.0×10^{-5} M) towards certain anions (as their tetrabutylammonium salts) was tested in DCM solution. In particular, the absorption spectroscopic titrations of **4** with most basic F$^-$, AcO$^-$, and $H_2PO_4^-$ as well as CN$^-$ induced typical spectral shifts attributable to the normal N–H-anion hydrogen bonding interactions. Concomitantly, the DCM solution of **4** exhibited a colour change from blue to turquoise blue in the presence of F$^-$, AcO$^-$, $H_2PO_4^-$, and CN$^-$ and thus the selectivity of **4** towards particular anion such as CN$^-$ was seriously in question (see ESI†).

Based on the quantum chemical calculations at the semi empirical level,[18] it was envisioned that by protecting 10N–H of **3**, CN$^-$ could preferentially attack at the C3′-position (charge density = −0.011; see ESI†) of the TCV motif in **PCP 1**. In an attempt to better understand this phenomenon, structural optimization of the structures were carried out by DFT calculations at B3LYP/6-311++G** level.[18] As demonstrated in Fig. 1 (lower left panel), the optimized structure of **PCP 1** has extended π conjugation between the phenyl and TCV groups. Notably, the HOMO of **PCP 1** was delocalized onto the sulphur atom, and the LUMO was delocalized over the TCV group indicating that intramolecular charge transfer (ICT) from sulphur atom to TCV group could occur.

Whereas **2** is transparent, **PCP 1** bearing a TCV-motif exhibits a blue colour in DCM solution ($\lambda_{max} = 600$ nm). Thus, the expected nucleophilic attack of CN$^-$ should result in interruption of π conjugation, which would influence the UV-vis absorption with apparent loss in colour. The initial evidence for the nucleophilic addition of CN$^-$ to **PCP 1** was assessed by high resolution mass spectrometry in which a peak at *m*/*z* 382.1129 corresponding to **PCP 1**–CN$^-$ adduct was observed (Fig. S14†). In fact, absorption spectroscopic titrations of **PCP 1** with CN$^-$ resulted in significant changes in the UV-vis spectra (Fig. 2). In particular, the disappearance of the visible bands (complete bleaching), instead of a shift, pointed out to a chemical reaction between CN$^-$ and **PCP 1** in a chemodosimeter fashion as proposed in Fig. 1.

In order to further evaluate the nature of the reaction of cyanide with **PCP 1**, we monitored the ^{1}H NMR spectral changes produced *via* the gradual addition of CN$^-$ in $(CD_3)_2SO$ at room temperature. As shown in Fig. 3a, all the aromatic proton signals exhibited an up-field shift after addition of ~1 equiv. of CN$^-$. The striking difference corresponded to the aromatic

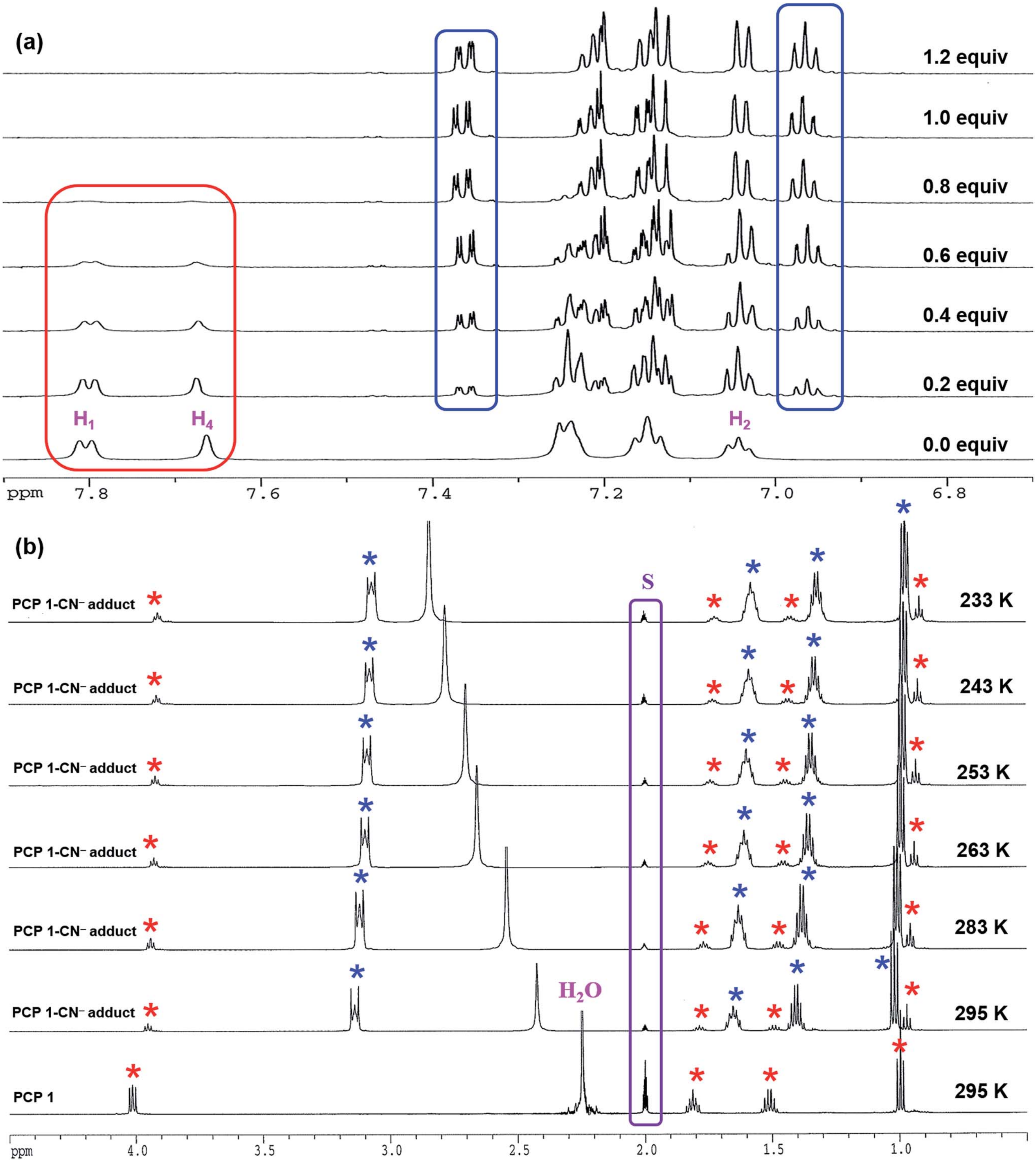


Fig. 3 (a) Partial ^{1}H NMR (600 MHz, $(CD_3)_2SO$) spectral changes seen upon the addition of 0–1.2 equiv. of CN^- to **PCP 1** (10.0 mM). In red: signals disappearing. In blue: signals appearing during titration; (b) selected region of ^{1}H NMR (600 MHz, CD_3CN) of **PCP 1** at room temperature (RT) and **PCP 1**–CN^- adduct at temperatures ranging from RT (295 K) to −40 °C (233 K). Red stars: signals due to *N*-butyl chain of **PCP 1**. Blue stars: signals due to *N*-butyl chains of tetrabutylammonium cyanide. S denotes solvent.

protons (H_1; 7.80 and H_4; 7.66 ppm) which completely disappeared, whereas two new signals appeared at δ 7.35 and 6.96 ppm, respectively. These observations suggest a nucleophilic attack at the C3′-position as the likely mechanism for the interaction between **PCP 1** and CN^-. Furthermore, the absence of a signal at ~3.5–3.9 ppm, corresponding to the C–H proton of the malononitrile group, indicated possible formation of a stabilized anionic species.

Occasionally, the C–H proton attached to the dicyano carbon is not observed leading to misinterpretation of the obtained results. Taking this into account, the proposed reaction pathway for CN^- sensing was unambiguously confirmed by recording ^1H NMR spectra of **PCP 1**–CN^- adduct in CD_3CN at temperatures ranging from 283 K to 233 K and comparing with the ^1H NMR spectra of **PCP 1**–CN^- adduct at room temperature (295 K). As can be seen in Fig. 3b, most resonances due to the N-terminated butyl chain protons of both the **PCP 1**–CN^- adduct and tetrabutylammonium cyanide experienced a noticeable up-field shifting upon successively decreasing the temperature from 295 K to 233 K. Nevertheless, no new proton signal was recognized during the course of low temperature NMR study.

Based on these observations, structural optimization of the structure for the **PCP 1**–CN^- adduct was carried out (Fig. 1). In sharp contrast to **PCP 1**, the LUMO distribution on the vinyl group was significantly reduced and localized to only the phenyl group of PTZ core. Therefore, the nucleophilic addition of CN^- to the TCV group in **PCP 1** prevents ICT and results in complete bleaching of the colour.

To evaluate the cyanide selective nature of **PCP 1**, absorption spectral changes caused by the addition of other anions including F^-, Cl^-, Br^-, I^-, HSO_4^-, NO_3^-, $H_2PO_4^-$ and AcO^- were studied. Specifically, 10 equiv. of each anion were added to a DCM solution of **PCP 1** (5 μM) and incubated for 5 min at 25 °C, before being subjected to spectral analysis. Most of these anions did not cause any significant changes in the UV-vis absorption and the colour of the solution remained intact. However, in addition to cyanide, **PCP 1** also exhibited UV-vis absorption changes (though weak) after addition of F^-, indicating that F^- acts as a strong competitor of CN^- under these conditions (Fig. 4).

To understand the interaction mode between **PCP 1** and F^-, the additional ^1H NMR titration experiment was carried out (Fig. S16†). Surprisingly, unlike CN^-, the addition of F^- to the $(CD_3)_2SO$ solution of **PCP 1** elicited only negligible changes in the ^1H NMR spectra. In particular, the aromatic protons (H_1 and H_4) in **PCP 1** did not experience any possible shielding over the course of F^- titration. Nevertheless, a considerable decrease in the intensity of H_1 and H_4 was realized, and accompanied by some splitting in the remaining aromatic protons in **PCP 1**. These results suggest that F^- does not react with **PCP 1** in a scientific manner but possibly has some degradation effect on the same.

In order to verify the competing assay of F^-, time-dependent absorption spectral changes were monitored in the presence of F^- and CN^- (5 equiv.) in DCM at $\lambda = 600$ nm. After the addition of F^-, the absorbance intensity decreased only by 50% and reached a podium within 10 min. On the contrary, after the addition of CN^-, a remarkable reduction (>99%) in the intensity of the 600 nm absorption band could be observed within 60 s of mixing demonstrating the high reactivity of CN^- over F^- (Fig. S17†).

Although CN^- caused profound spectral changes than F^-, the latter also displayed colour bleaching in DCM and thus chromo (visual) selectivity of **PCP 1** towards CN^- was still in question. It is well known that the nucleophilicity/basicity of anions, in particular, F^- is greatly decreased in water due to its high solvation effect.[19]

Taking this into account, we retested the CN^- selectivity of **PCP 1** in aqueous solution adopting a surfactant-assisted protocol.[20] Although **PCP 1** has poor solubility in water yet readily dissolves in aqueous solution containing the neutral surfactant, Triton X-100. To test the cyanide selectivity in aqueous medium, **PCP 1** in THF (100 μL, 2×10^{-5} M)§ was added to water mixture containing Triton X-100 (1×10^{-2} M) and the resulting solutions were used to monitor the UV-vis spectral changes before and after the addition of F^- and CN^-. After 10 min of incubation, only the solution that included CN^- exhibited ~70% reduction in absorption intensity (Fig. 5). This observation is sharply in contrast to what observed in DCM solution and can be attributed to the cyanide induced solvation process. In addition, relatively lower hydration energy for CN^-

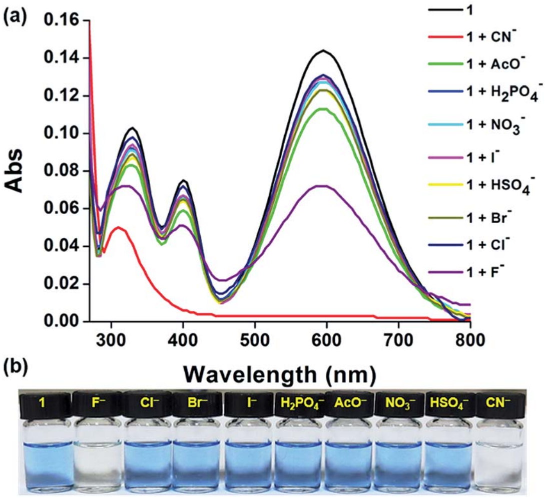


Fig. 4 (a) UV-vis spectral changes of **PCP 1** (5.0×10^{-6} M) and (b) corresponding colour responses seen upon the addition of 10 equiv. of various anions (as their tetrabutylammonium salts) in DCM.

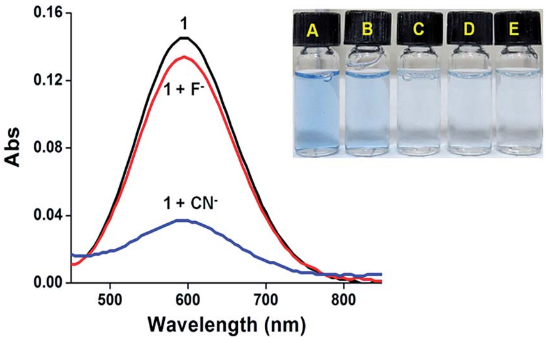


Fig. 5 Changes in the visible band ($\lambda = 600$ nm) of **PCP 1** (2×10^{-5} M) in water with Triton X-100 (1×10^{-2} M) in the presence of 5 equiv. of F^- and CN^-. Inset: colour changes of **PCP 1** (A; 1 μM) in Triton X-100-water solution in the presence of 1 μM (B), 1.5 μM (C), 2.5 μM (D), and 5 μM (E) of NaCN after 10 min of incubation.

($\Delta H_{\rm hyd} = -67$ kJ mol^{-1}) than that of F$^-$ ($\Delta H_{\rm hyd} = -505$ kJ mol^{-1}) further explains the CN$^-$ selectivity in aqueous environment.[21]

Colorimetric detection of micromolar concentrations of inorganic CN$^-$ (NaCN) and F$^-$ (NaF) was then evaluated using **PCP 1** in surfactant-assisted water solution (Inset: Fig. 5; for F$^-$, see Fig. S18†). In particular, **PCP 1** was found to exhibit a successful response, manifested in significant bleaching within 1.5 μM of cyanide concentration. As shown in Fig. S19,† A good linear relationship ($R^2 = 0.9875$) between the absorption intensity and the CN$^-$ concentration could be obtained. The detection limit was then calculated to be 1.56×10^{-6} M according to the following equation: detection limit = $3S/\rho$, where S is the standard deviation of blank measurements, ρ is the slope between intensity *versus* CN$^-$ concentration. This result indicates that the colorimetric detection limit by **PCP 1** is in good agreement with WHO guidelines (1.9 μM) for cyanide toxicity.

Conclusions

In summary, we have successfully designed and demonstrated that the phenothiazine-based chemodosimeteric probe, **PCP 1**, can be synthesized and such systems, as currently produced, are selective for CN$^-$, especially, in aqueous media. Although several colorimetric probes for CN$^-$ detection have been reported, most utilize organic solvents as the major detection medium usually containing a very low percentage of water (≤20% by volume). This is one of the very few colorimetric probes described for CN$^-$ detection in surfactant-assisted pure water. Consequently, **PCP 1** appears to be a practical system for colorimetric detection of CN$^-$ in aqueous media. Design and synthesis of more sensitive PTZ-based chemodosimeters or chemosensors for diverse sensing applications including cyanide anion are currently in progress.

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Notes and references

‡ The synthesis of **4** has been though previously reported, the NMR structural characterization as well as anion recognition properties of **4** are unprecedented (for details; see ESI†).

§ The optimized concentration, approaching nearly identical absorbance of **PCP 1** as was in DCM (5×10^{-6} M).

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