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LETTER

## Design of a dual sensing highly selective cyanide chemodosimeter based on pyridinium ring chemistry†

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**A new chemodosimeter, Quino-P, recognizes the strongly nucleophilic cyanide by dual colorimetric and fluorescence ‘off-on’ signalling responses. Noteworthy, several other anions, even in significantly higher concentrations, induce no detectable photophysical perturbations. The chemodosimeter mechanism involves formation of a C4-cyano adduct, which exhibits an uncommon phenomenon of enhanced internal charge transfer interaction.**

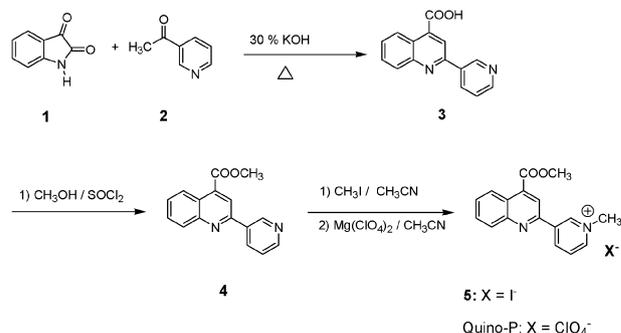
The development of optical chemosensors for anions of biological, environmental, and clinical concerns is currently under active investigation.<sup>1</sup> Among anions of interest, the trace detection of cyanide is of prime importance because of its lethal effects on livestock, mammals, humans and the environment.<sup>2</sup> Cyanide contamination in the environment is possible due to its widespread uses in synthetic fibres, resins, herbicides, gold-extraction and various metallurgy processes.<sup>3</sup> Moreover, incidences of cyanide poisoning in human and animals can also occur through ingestion of cyanogenic glycosides found in certain vegetables and dietary foodstuffs.<sup>4</sup> Cyanide exposure through accidental or intentional release in drinking water or food-chains can culminate in environmental damages and in humans, cyanide poisoning can result in convulsion, loss of consciousness, and even death.

A recent review by Yoon *et al.* summarizes the hitherto reported optical cyanide sensing strategy,<sup>5</sup> which includes H-bonding interaction, metal ion displacements, cyano-borane adduct formations, rearrangements and quantum dots. Besides, the strong nucleophilic character of CN<sup>−</sup> has also been harnessed to design internal charge transfer (ICT) based chemodosimeters carrying receptors, such as oxazine,<sup>6</sup> pyrylium salts,<sup>7</sup> squarane,<sup>8</sup> acridinium salt,<sup>9</sup> cyanine dye,<sup>10</sup>

trifluoroacetophenone,<sup>11</sup> dicyano-vinyl calix[4]pyrrole<sup>12</sup> and analogs.<sup>13</sup> Typically, these chromophores are specifically designed so as to undergo disruption in their  $\pi$ -conjugations upon irreversible addition of cyanide, offering color bleaching responses. However, ICT-based chemodosimeters capable of executing absorbance red shifts upon exposure to cyanide are indeed rare.<sup>6,14</sup>

Herein, we present a new chemodosimeter design that carries the requisite structural elements to convert the CN<sup>−</sup> binding event into an enhanced ICT process, delivering absorbance red shift and a high fluorescence turn-on response. The  $\pi$ -deficient pyridinium ring is well-known to react readily with a variety of carbon and hetero-atom nucleophiles to form the  $\pi$ -rich, 1,4-dihydropyridine (DHP) adducts, often with good regioselectivity.<sup>15</sup> Mimicking this aspect of the pyridinium ring chemistry, we have designed a novel CN<sup>−</sup> selective probe, Quino-P, incorporating a pyridinium ring as a CN<sup>−</sup> receptor, while a quinoline moiety is appended to serve as an electron withdrawing chromogenic unit.

The synthesis of Quino-P was readily accomplished by implementing Scheme 1. Base catalyzed condensation of isatin **1** with 3-acetylpyridine **2** afforded quinoline-pyridyl conjugate **3**, which upon esterification yielded **4**. Quaternization of **4** with CH<sub>3</sub>I in dry CH<sub>3</sub>CN afforded iodide salt **5**, which upon perchlorate anion exchange with Mg(ClO<sub>4</sub>)<sub>2</sub> gave the target, Quino-P as a pale yellow solid in good overall yield. A proposed CN<sup>−</sup> sensing mechanism is illustrated in Scheme 2.



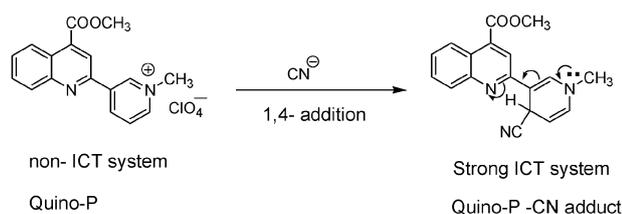
**Scheme 1** Synthesis of Quino-P.

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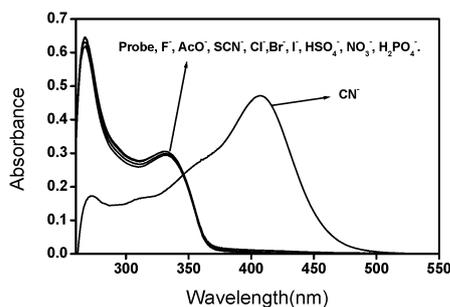
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† Electronic supplementary information (ESI) available: Spectra of compound **4** and Quino-P, competitive fluorescence binding, Job's plot, detection limit, D<sub>2</sub>O exchange, <sup>1</sup>H NMR interpretation of Quino-P and its cyanide adduct, <sup>13</sup>C NMR of Quino-P with added KCN and molecular modelling studies. See DOI: 10.1039/c0nj00715c



**Scheme 2** Proposed cyanide sensing mechanism.

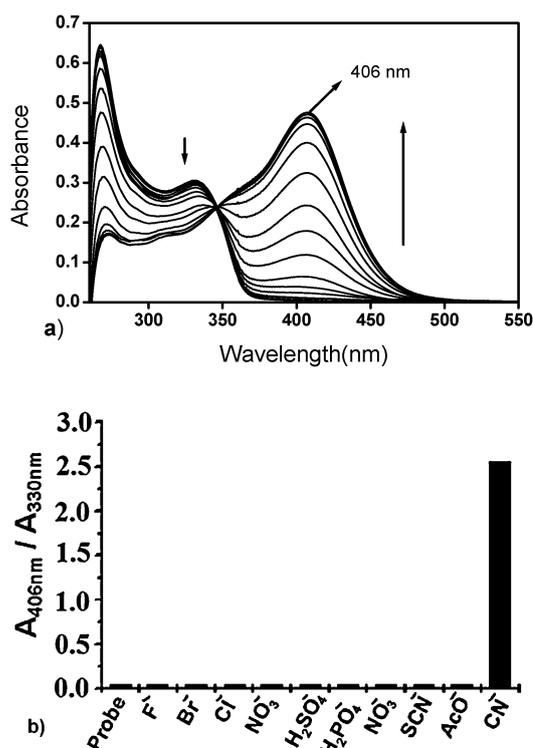


**Fig. 1** Absorption spectra of Quino-P ( $2.8 \times 10^{-5}$  M) in DMSO-H<sub>2</sub>O (7 : 3, v/v) in tris-HCl in the presence of TBA salts of F<sup>-</sup>, AcO<sup>-</sup>, SCN<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> at  $7.5 \times 10^{-2}$  M each, whereas CN<sup>-</sup> is  $7.6 \times 10^{-3}$  M.

Presuming regioselective reaction, the nucleophilic attack of cyanide on the C4 position of the pyridinium ring would form the corresponding cyano-1,4-DHP adduct. Being  $\pi$ -electron rich, the 1,4-DHP moiety in the resulting cyano-adduct is expected to engage in a push-pull interaction with the conjugated,  $\pi$ -deficient, quinoline ring. This phenomenon would provoke enhanced ICT interaction, thereby forming the basis of a potentially novel cyanide signalling protocol.

The sensitivity of Quino-P towards various anions, as their tetra-*n*-butylammonium (TBA) salts, was evaluated by optical spectral analysis. The absorption spectrum of Quino-P displayed maxima at 330 and 267 nm, attributable to the local excitations of pyridinium and quinoline rings, respectively. As shown in Fig. 1, the UV-vis profile of the probe ( $2.8 \times 10^{-5}$  M) in DMSO-H<sub>2</sub>O (7 : 3, v/v) in tris-HCl buffer pH 7.0 was essentially insensitive to each of F<sup>-</sup>, AcO<sup>-</sup>, SCN<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, up to  $7.5 \times 10^{-2}$  M, implying the absence of any detectable ground state interactions of these anions with the probe. In contrast, cyanide, at 10-fold lower concentration ( $7.6 \times 10^{-3}$  M), induced a significant interaction, as evidenced by an instant color change from the initial colorless to deep yellow, an event that allows selective visual detection of cyanide by the naked eye.

Fig. 2a depicts the concentration dependent absorbance profile of Quino-P with the added CN<sup>-</sup> (0– $7.6 \times 10^{-3}$  M). The spectral response occurred instantly, and the probe's maximum at 330 nm was progressively red shifted to generate a new, more intense absorbance at 406 nm with incremental addition of cyanide. In addition, the higher energy band at 267 nm was also markedly diminished in its absorbance. Absorbance ratiometric analysis of CN<sup>-</sup> is possible using the ratio, 406 nm/330 nm (Fig. 2b). It may be noted that many known ICT based CN<sup>-</sup> chemodosimeters exhibit absorbance



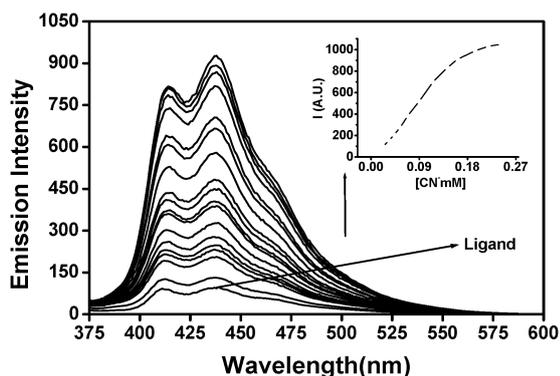
**Fig. 2** (a) Spectrophotometric response of Quino-P ( $2.8 \times 10^{-5}$  M) in DMSO-H<sub>2</sub>O (7 : 3, v/v) in tris-HCl at pH 7.0 with increasing TBACN (0– $7.6 \times 10^{-3}$  M). (b) Ratiometric response (406 nm/330 nm) of Quino-P ( $2.8 \times 10^{-5}$  M) towards anions.

blue shifts due to the  $\pi$ -conjugation break-down. By contrast, Quino-P delivers a rare phenomenon of absorbance red shift because of the inducement of a dominant ICT transition, as proposed in Scheme 2.

The emission spectrum of Quino-P ( $\lambda_{\text{ex}} = 345$  nm) displayed a broad band with a maximum at 435 nm, and the quantum yield, calculated with respect to anthracene ( $\Phi = 0.27$ ), was found to be 0.0041. The weak emission efficiency of Quino-P may be attributable to photoinduced electron transfer (PET) from the excited quinoline fluorophore to the redox active, pyridinium ion.<sup>16</sup> This proposition finds support in the fact that quinoline-pyridyl conjugate **4**, a neutral analog of the ionic Quino-P, fluoresces 12 times more intensely ( $\Phi = 0.054$ ) than Quino-P.

Evaluation of the fluorescence profile of the probe (1  $\mu$ M) with  $2.5 \times 10^{-3}$  M each of F<sup>-</sup>, AcO<sup>-</sup>, SCN<sup>-</sup>, HSO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Br<sup>-</sup>, Cl<sup>-</sup>, I<sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> revealed no evidence of interaction under the excited state condition as well. Noteworthy, a significant fluorescence 'on-off' response was induced by CN<sup>-</sup> at a significantly lower concentration. Fluorimetric titration (Fig. 3) revealed a linear increase in the emission intensity, until saturating at  $2.5 \times 10^{-4}$  M of CN<sup>-</sup>, the emission enhancement reached *ca.* 10 fold ( $\Phi = 0.046$ ) compared to that of the native probe (inset in Fig. 3).

The emission off-on response could be attributable to the transformation of a PET-capable pyridinium ring of the free receptor into one of the PET-disabled, electron rich DHP ring within the cyano-Quino-P adduct. The PET nature of the probe is also evident from the observation that the

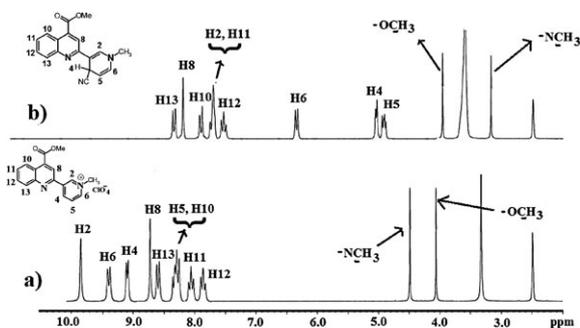


**Fig. 3** Fluorimetric titration of Quino-P (1  $\mu\text{M}$ ) in buffer DMSO with increasing  $\text{CN}^-$  cyanide ( $0\text{--}2.5 \times 10^{-4}$  M). Inset: emission enhancement as a function of  $\text{CN}^-$  concentration.

fluorescence amplification is not accompanied by any emission wavelength shift.<sup>17</sup> A competitive fluorescence experiment was used to verify the unique chemodosimeter action of Quino-P towards  $\text{CN}^-$  only. Addition of  $2.5 \times 10^{-3}$  M each of  $\text{F}^-$ ,  $\text{AcO}^-$ ,  $\text{SCN}^-$ ,  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{I}^-$  and  $\text{H}_2\text{PO}_4^-$  did not detectably alter the fluorescence profile of Quino-P recorded in the presence of  $2.5 \times 10^{-4}$  M of  $\text{CN}^-$ . Thus, a potential clearly exists in the probe to selectively discriminate cyanide even when other anions may be present in higher concentrations (ESI†).

The strong nucleophilicity of cyanide and the aqueous measurement capability of the probe ensure that the optical interferences, frequently encountered from the strongly hydrated, weakly nucleophilic or acidic anions, are not observed.<sup>18</sup> The Job's plot showed a 1 : 1 binding stoichiometry and the apparent association constant,  $\log K$ , was found to be 3.95. The detection limit of  $\text{CN}^-$ , derived from the emission data, was found to be  $1.6 \mu\text{M}$  (ESI†).

Though we presumed a regioselective 1,4-cyanide addition, competitive reactions on the other reactive C2 and C6 of the pyridinium ring cannot be entirely ruled out. To establish the actual binding mode, we carried out  $^1\text{H}$  NMR analysis of the probe without and with added five equiv. of KCN in  $\text{DMSO-d}_6\text{-D}_2\text{O}$ . The proton assignments for Quino-P and its cyano-adduct are shown in Fig. 4a and b, respectively (for NMR interpretation, see ESI†). The NMR data indicated the formation of C4-Quino-P- $\text{CN}^-$  adduct with complete regioselectivity. As shown in Fig. 4b, the cyanide addition



**Fig. 4** 300 MHz  $^1\text{H}$  NMR of (a) Quino-P. (b)  $^1\text{H}$  NMR Quino-P + 5 equiv. of KCN in 70 : 30 (v/v)  $\text{DMSO-d}_6\text{-D}_2\text{O}$ .

causes pronounced upfield shifts ( $\delta$  1.34 to 4.05) of the  $\text{N-CH}_3$  and the pyridinium ring protons because of the charge neutralization.

Though not directly involved in the cyanide reaction, some of the quinoline ring as well as  $-\text{CO}_2\text{CH}_3$  protons also experience discernible upfield shifts in the range of  $\delta$  0.12 to 0.55. These upfield shifts obviously reflect an increase in charge density on the quinoline ring, and thus provide a further confirmation of the presence of the ICT interaction in the Quino-P +  $\text{CN}^-$  adduct. Consistent with the  $^1\text{H}$  NMR results, the  $^{13}\text{C}$  NMR of the probe also displayed prominent upfield shifts of the  $\text{N-CH}_3$  signal as well as those of the pyridyl ring carbons after adding KCN (ESI†).

In conclusion, we have disclosed a new and efficient chemodosimeter design, which has the in-built structural features to deliver absorbance red shift by undergoing a unique ICT process, and the fluorescence turn-on signalling by cancellation of the PET, post-cyanide addition. The unique selectivity of cyanide is evident since many potentially competing anions pose no detectable optical interferences even in excess concentrations. The NMR analysis confirms the regioselective C4 addition of cyanide, and in agreement with the experimental findings, the theoretical studies (ESI†) support a strong tendency towards  $\pi$ -conjugation in the Quino-P- $\text{CN}^-$  adduct. The detection limit of  $1.6 \times 10^{-6}$  M is satisfactory for cyanide monitoring up to the toxic threshold of  $1.9 \mu\text{g}$  in drinking water recommended by WHO.

## Experimental

### Reagents and instrumentation

Reagents and solvents used were purchased from S.D. Fine Chemicals, India, or Sigma-Aldrich. IR spectra were recorded using a Perkin-Elmer FT-IR spectrometer and pellets were made by using KBr.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on BRUKER model Avance II 300 of 300 MHz. UV-vis spectra were recorded using a Shimadzu UV-vis recording spectrophotometer, model no. UV-2401PC. Fluorescence studies were carried out using a Shimadzu spectrofluorimeter, model no. RF-5301PC. The slit-width was set at 3 nm for both excitation and emission and the PMT detector voltage was 700 V.

### Synthesis

Compound **3** was prepared by modifying the literature procedure as follows. Isatin **1** (1 mmol, 147 mg) and 3-acetylpyridine **2** (1.5 mmol, 182 mg) were refluxed in 30% aqueous KOH (20 mL) for 10 h. Then, the reaction mixture was cooled in ice-bath and acidified with acetic acid to precipitate acid **3** as a buff-white solid. After filtration, the solid was washed with cold water, then methanol, and air-dried to afford compound **3** in 80% yield (200 mg). mp  $315\text{--}317^\circ\text{C}$  [Lit.<sup>19</sup> mp  $316\text{--}318^\circ\text{C}$ ].

To a stirred solution of compound **3** (2.5 mmol, 625 mg) in dry MeOH (20 mL) was added an excess of thionyl chloride (3.75 mmol, 0.5 mL) drop-wise at  $0^\circ\text{C}$ . The reaction was allowed to warm to room temperature for 30 min and then refluxed for 5 h. Methanol was distilled out and the residual

solid recrystallised from  $\text{CHCl}_3$  : pet. ether (1 : 1 v/v) to afford compound **4** in 76% yield (500 mg), mp 95–96 °C, IR (KBr;  $\text{cm}^{-1}$ ): 3057, 2956, 1728, 1590, 1508, 1482, 1459, 1345, 1257, 1203, 1016, 794, 774.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  4.1 (s, 3H), 7.57 (m, 2H), 7.69 (t, 1H,  $J = 8.4$ ), 7.83 (t, 1H,  $J = 9.3$ ), 8.25 (d, 1H,  $J = 9.3$ ), 8.42 (s, 1H), 8.67 (d, 1H,  $J = 9.9$ ), 8.7 (d, 1H,  $J = 12.9$ ), 9.46 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  52.83, 119.70, 123.79, 124.20, 125.49, 128.34, 130.22, 130.32, 134.35, 134.99, 135.922, 148.42, 149.28, 150.23, 153.81, 166.44. Mass  $m/z$  value = 265. Anal. Calcd for  $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_2$ : C, 72.72; H, 4.54; N, 7.69%. Found: C, 72.99; H, 4.39; N, 7.48%.

Compound **4** (1 mmol, 264 mg) was dissolved in dry acetonitrile (5 mL) and  $\text{CH}_3\text{I}$  (5 mmol, 0.31 mL) was added. The reaction was left at room temperature for 2 days to afford the quaternized salt **5** as a yellow solid in nearly quantitative yield. The obtained iodide **5** was redissolved in warm acetonitrile (5 mL) and  $\text{Mg}(\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (250 mg) dissolved in 2 mL was added. The reaction mixture was vigorously stirred at room temperature for 24 h and then refrigerated overnight. The desired product, Quino-P was obtained as a light yellow solid in 80% yield (291 mg), mp 256–257 °C, IR (KBr;  $\text{cm}^{-1}$ ): 3038, 2951, 1718, 1584, 1503, 1472, 1418, 1258, 1204, 1153, 1017, 777, 666.

$^1\text{H}$  NMR ( $\text{DMSO}-d_6$ - $\text{D}_2\text{O}$ ):  $\delta$  4.06 (s, 3H), 4.49 (s, 3H), 7.84 (t, 1H,  $J = 7.7$ ), 7.97 (t, 1H,  $J = 7.5$ ), 8.29 (m, 2H), 8.62 (d, 1H,  $J = 8.7$ ), 8.7 (s, 1H), 9.1 (d, 1H,  $J = 6$ ), 9.4 (d, 1H,  $J = 8.1$ ), 9.87 (s, 1H).  $^{13}\text{C}$  NMR ( $\text{DMSO}-d_6$ - $\text{D}_2\text{O}$ ):  $\delta$  48.77, 53.66, 119.96, 124.37, 125.86, 128.26, 130.046, 130.41, 131.76, 137.45, 137.81, 143.08, 145.19, 146.29, 148.60, 150.54, 166.41. Mass  $m/z = 279$  [minus perchlorate ion]. Anal. Calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_2\text{O}_5\text{Cl}$ : C, 53.89; H, 3.96; N, 7.39; Cl, 9.37%. Found: C, 53.83; H, 3.68; N, 7.62; Cl, 9.13%.

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