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Selective Colorimetric and "Turn-on" Fluorimetric Detection of Cyanide Using a Chemodosimeter Comprising Salicylaldehyde and Triphenylamine Groups

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Keywords: Sensors / Chromophores / Charge transfer / Anions / Cyanides

Chemodosimeters **S1** and **S2** having salicylaldehyde and triphenylamine functionalities were synthesized, and the changes in their absorption and emission properties in the presence of anions were evaluated. **S1** and **S2** act as selective colorimetric and fluorimetric molecular probes for sensing and signalling cyanide. The signal transduction mechanism was investigated by UV/Vis absorption, emission, and NMR spectroscopy, and was supported by DFT calculations. The interaction between the receptors and cyanide ions causes large changes in both colour and emission intensity. A significant enhancement in fluorescence intensity was caused by the better nucleophilicity of the cyanide and by the carbonyl activation by the phenol proton of the salicylaldehyde group in the dosimeter through an intramolecular hydrogen bond. Intramolecular charge transfer from the negatively charged quinonoidal fragment to the triarylamine group was responsible for the colorimetric response. The detection limits were found to be 1.55 and 0.72 μM for **S1** and **S2**, respectively, with fluorimetric enhancement factors of 350 and 25.

Introduction

Anions play important roles in biology, medicine, catalysis, and in the environment.[1] Recently, considerable attention has been paid to the development of selective optical signalling systems for anionic species.[2] Among the various anions, cyanide is one of the most concerning due to its high toxicity to human and aquatic life.[3] The worldwide production of cyanide in the various industries is 1,400,000 tons per year[4] due to its applications in the production of nitriles, nylon, acrylic plastics and gold extraction processes.[5]

Several colorimetric and fluorimetric probes for cyanide have been reported in recent literature,[6] and there are several common approaches to the design of selective probes for cyanide ions. Copper complexes have successfully been used as a cyanide probe due to the affinity of Cu^{II} towards cyanide.[7] Cyanide addition to Zn^{II}–porphyrin,[8,6b] Ru^{II}–complex,[9,6l] boronic acid derivatives,[10,6k] and CdSe quantum dots[11] have also been exploited as detection methods. Other strategies such as hydrogen-bonding interactions,[12,6a] deprotonation,[13] and luminescence lifetime measurements[7a] have also been used to design selective probes for cyanide. Due to the exceptional nucleophilicity of cyanide, nucleophilic substitution by cyanide is one of the most important methods for probing its presence. Addition of cyanide to an activated aldehyde group is one of the important strategies used to develop probes that are selective to cyanide only.[14] Colorimetric sensors are always important because the presence of analyte can be rapidly confirmed visually. There are several literature reports of colorimetric probes for cyanide but colorimetric as well as "turn-on" fluorimetric probes for cyanide are very few.[15]

Here we have designed and synthesized two compounds, **S1** and **S2**, as probes for cyanide comprising salicylaldehyde and triphenylamine functionalities. The nucleophilic reactivity of CN^- towards the salicylaldehyde moiety was exploited to detect cyanide selectively. Triphenylamine functionality is incorporated to generate colorimetric changes through intramolecular charge transfer (ICT). The synthesis of **S1** and **S2** was based on reported synthetic strategies and was straightforward and high yielding. Anion recognition properties of **S1** and **S2** were studied in aqueous tetrahydrofuran (THF) solution towards several anions such as CN^-, AcO^-, F^-, Cl^-, Br^-, $H_2PO_4^-$, NO_2^-, N_3^-, HS^- and ClO_4^- as their tetrabutylammonium salt. Both **S1** and **S2** showed selective colorimetric and "turn-on" fluorimetric sensitivity towards CN^-.

Results and Discussion

Synthesis of S1 and S2

Compounds **S1** and **S2** were synthesized in high yield by the protocol shown in Scheme 1. Compound **1** was prepared by following the reported procedure.[16] Stannylation of **1** followed by Stille coupling between stannyl derivative

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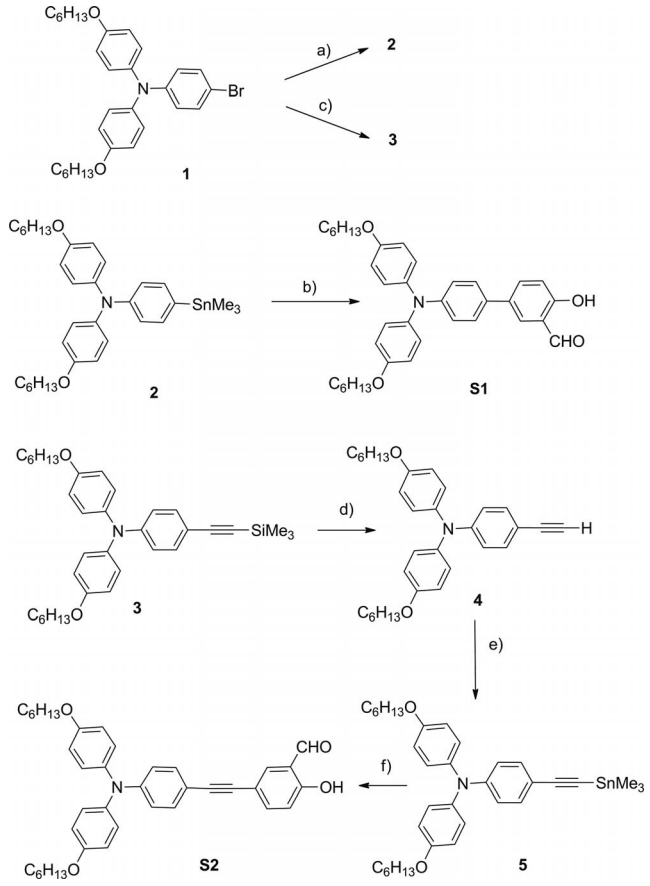
2 and 5-bromosalicylaldehyde, afforded **S1** with good yield. Sonogashira coupling of **1** and ethynyltrimethylsilane in anhydrous THF afforded **3**. Compound **5** was synthesized by desilylation of **3** followed by stannylation of **4**. Stille coupling of **5** and 5-bromosalicylaldehyde afforded **S2** in high yield.



Scheme 1. Synthetic routes to **S1** and **S2**. *Reagents and conditions:* (a) *n*BuLi (1.1 equiv.), Me_3SnCl (1.1 equiv.), THF, –78 °C, 72%; (b) 5-bromo-2-hydroxybenzaldehyde, $[Pd(PPh_3)_4]$, toluene, reflux, 24 h, 68%; (c) CuI, $[Pd(PPh_3)_2Cl_2]$, Et_3N, ethynyltrimethylsilane, THF, 80%; (d) K_2CO_3, MeOH, room temp., overnight, 90%; (e) *n*BuLi (1.1 equiv.), Me_3SnCl (1.1 equiv.), –78 °C, THF, 78%; (f) 5-bromo-2-hydroxybenzaldehyde, $[Pd(PPh_3)_4]$, toluene, reflux, 24 h, 72%.

Colorimetric Detection

The anion-sensing properties of **S1** and **S2** were studied in aqueous THF (THF/H_2O = 95:5). **S1** and **S2** showed absorption maxima at 326 and 346 nm, respectively; **S2** showed a 20 nm redshift in absorption maxima due to extended conjugation by an extra acetylene group compared with that of **S1**. The solution of **S1** and **S2** was treated with a fixed amount of different anions (5 equiv., added as tetrabutylammonium salts) and the absorption spectra were recorded. Addition of CN^- caused a marginal bathochromic shift of the high-intensity peak in the UV/Vis absorption spectra of **S1** and **S2** (Figure 1), however, an additional low-intensity, broad peak appeared in the region

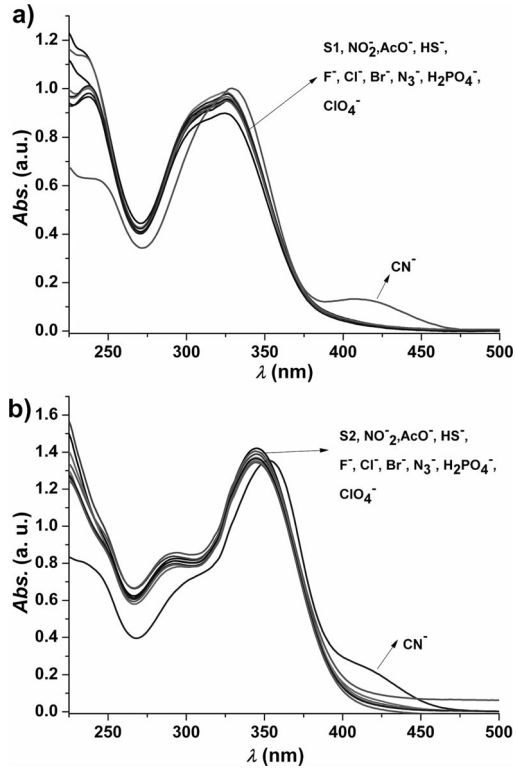


Figure 1. UV/Vis spectra of 0.1 mM solutions of (a) **S1** and (b) **S2** in THF/water mixture (95:5) upon addition of different anions (5 equiv.).

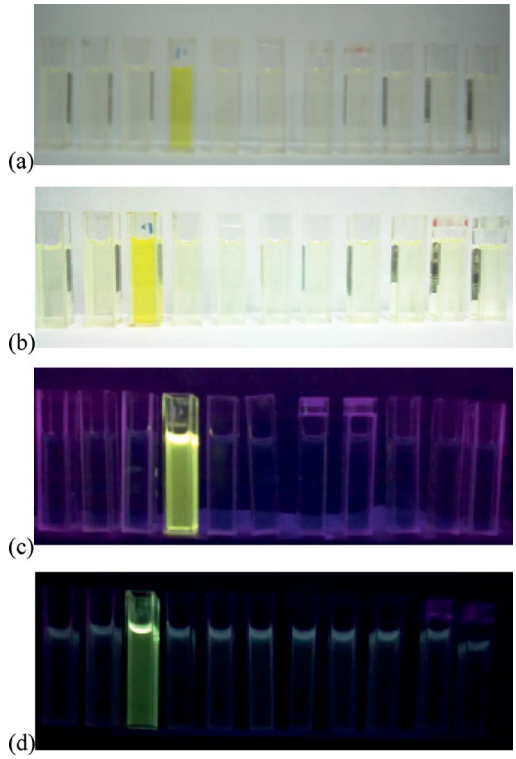


Figure 2. Colorimetric and fluorometric responses of the dosimeter (10 μM) in the presence of 5 equiv. of different anions: (a) colorimetric and (c) fluorimetric for **S1** (from left to right: $H_2PO_4^-$, ClO_4^-, CN^-, F^-, AcO^-, Br^-, Cl^-, NO_2^-, N_3^-, HS^-); (b) colorimetric and (d) fluorimetric for **S2** (from left to right: $H_2PO_4^-$, CN^-, F^-, ClO_4^-, AcO^-, Br^-, Cl^-, NO_2^-, N_3^-, HS^-).

400–450 nm, which was responsible for the visible colour change (from colourless to yellow; Figure 2, a and b). With the addition of increasing amounts of tetrabutylammonium cyanide (from 0.1 to 20 equiv.) to a solution of **S1** and **S2**, the intensity of both the peaks steadily enhanced (Figure 3).

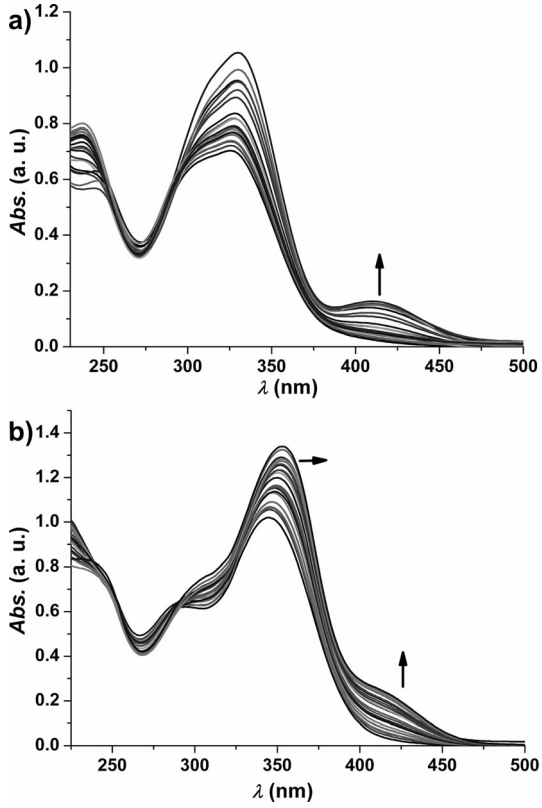


Figure 3. Changes in the UV/Vis spectra of 3.3 μM solutions of **S1** (a) and **S2** (b) upon addition of increasing amounts of cyanide (0.1 to 20 equiv.) in THF/water.

To explain the origin of the colorimetric response, we have performed DFT calculations on **S1** and its product on treatment with cyanide, **S1**-CN.[17] Geometry optimization of **S1** and **S1**-CN were performed at the B3LYP/6-31G(d) level[18] and these optimized geometries were subsequently considered for single point TD-DFT calculations at the B3LYP/TZVP level.[19] Geometry optimization of **S1**-CN from various probable structures converged on the same geometry, which corresponds to phenolic H transfer to formyl oxygen, as shown in the structures of **S1**-CN. These results were supported by ^{1}H NMR spectroscopy studies. As a result, a negative charge moved on the phenolic oxygen, converting it into a partial quinonoidal structure for which the negative charge can be more effectively delocalized over the conjugated system. TD-DFT[20] calculations indicated the origin of the broad low intensity peak in the region of 400–450 nm as a charge-transfer band from the negatively charged quinone part to the triarylamine fragment (Figure 4). The calculated transition at 439 nm with an oscillator strength f = 0.0272 corresponds to HOMO→LUMO+1 (Table S1 in the Supporting Information).

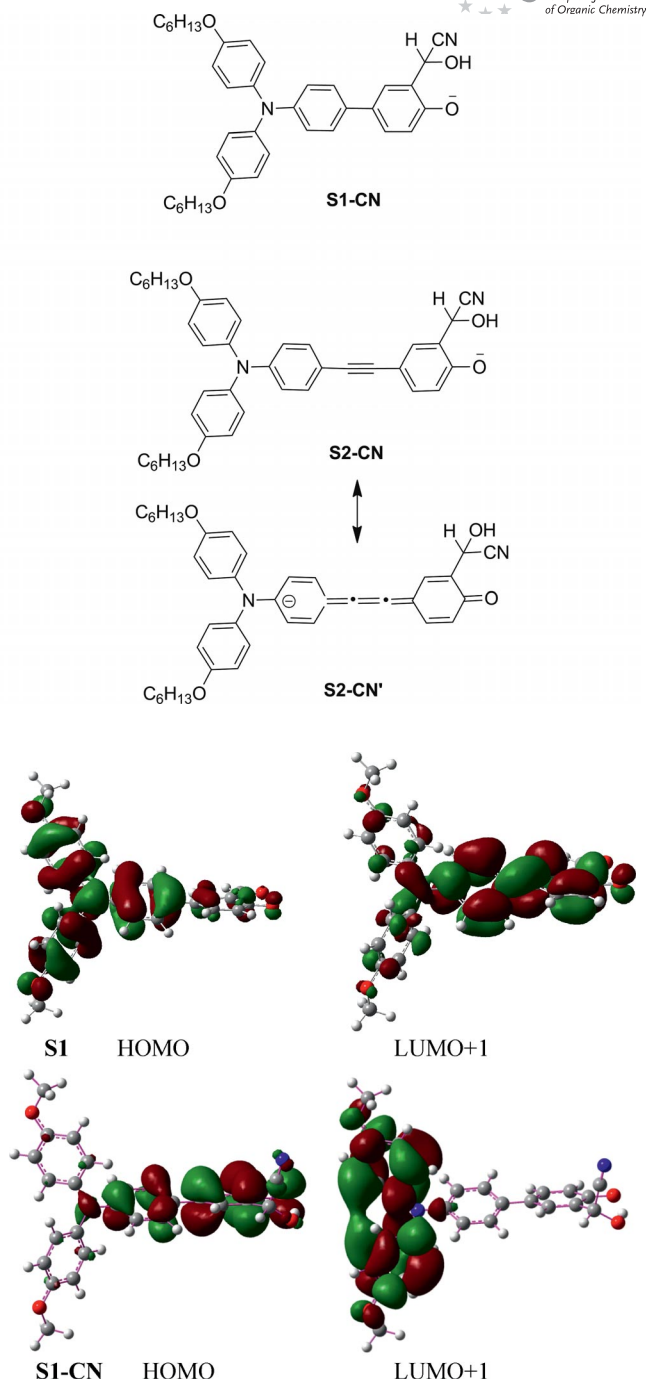


Figure 4. DFT generated molecular orbital of **S1** and **S1**-CN (HOMO and LUMO+1) at B3LYP/6-31G(d).

Fluorimetric Detection

Compounds **S1** and **S2** showed emission maxima at 428 (λ_{ex} = 326 nm) and 465 nm (λ_{ex} = 346 nm), respectively, with very low quantum yields [**S1** (0.08%) and **S2** (0.9%)] with respect to quinine sulfate. The large Stokes shifts of 102 and 119 nm for **S1** and **S2**, respectively, can be ascribed to excited state proton transfer (ESPT).[21] The ESPT process opens the ways for nonradiative deactivation and is responsible for the very weak fluorescence of **S1** and **S2**.[21] By adding an excess of anions (5 equiv.) to the solutions of

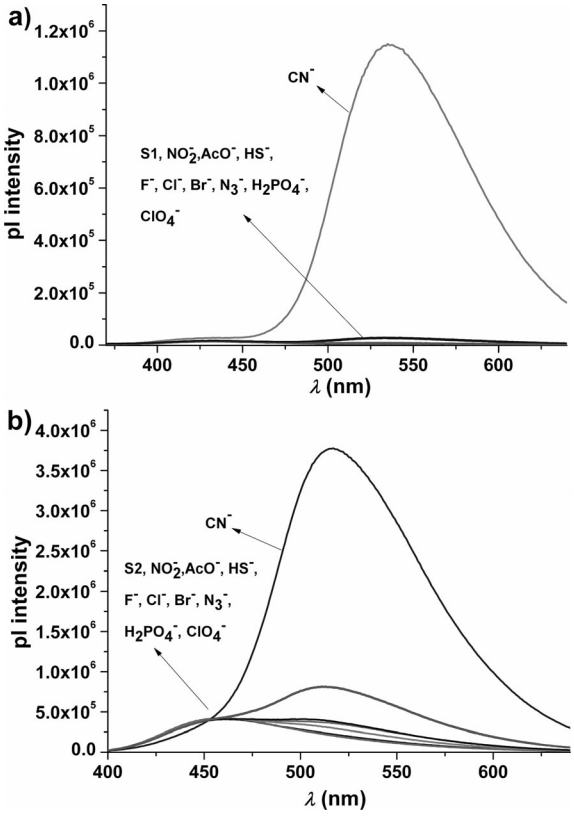


Figure 5. Emission spectra of 3.3 μM solutions of (a) **S1** and (b) **S2** in THF/water mixture (95:5) upon addition of different anions (5 equiv.).

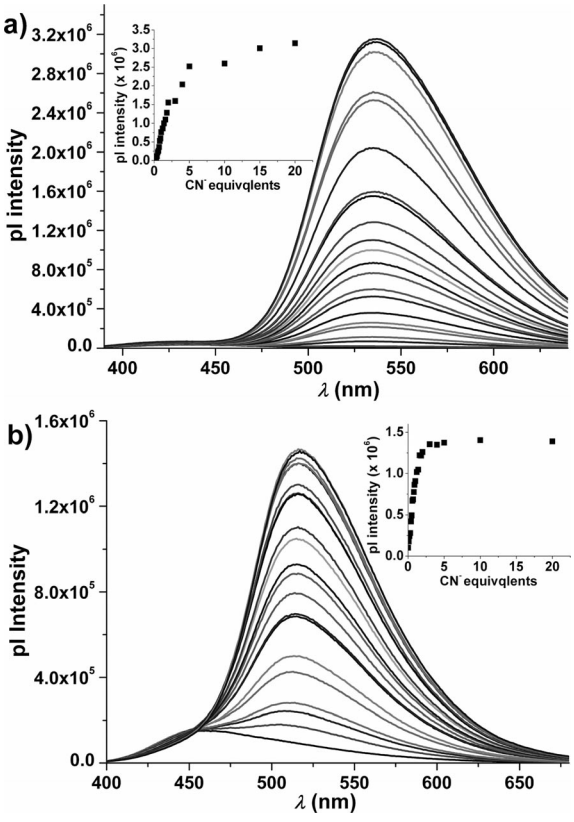


Figure 6. Fluorescence titration spectra of 3.3 μM solutions of (a) **S1** and (b) **S2** upon addition of cyanide from 0.1 to 20 equiv.

S1 and **S2**, emission spectra were recorded. Only the inclusion of cyanide ions led to emission with high intensity at 534 and 516 nm for **S1** and **S2**, respectively, whereas the presence of other anions did not lead to any significant enhancement in emission intensity (Figure 5). The cyanoalkoxide anion (deprotonated cyanohydrins) generated after addition of cyanide to the formyl group, exchanges the phenolic proton. This process inhibits ESPT and leads to strong emission after addition of cyanide ions to **S1** and **S2**. The change in emission spectra led to visible detection under a 360 nm UV lamp with clear yellow fluorescence (Figure 2, c and d). In cyanide titration experiments with **S1** and **S2** and increasing amounts of cyanide (from 0.1 to 20 equiv.), the intensity of the peaks at 534 and 516 nm, respectively, were gradually enhanced (Figure 6). According to the previous theoretical study,[21] it is expected that local excited states of **S1**-CN and **S2**-CN are not involved in the ESPT process and thus strong fluorescence was obtained. We note that after cyanide addition the emission peak for **S2** appeared at shorter wavelength than that of **S1**. This can be ascribed to the contribution of allene-type structure **S2**-CN′ to the phenoxide ion **S2**-CN (formed by the proton transfer of deprotonated cyanohydrins). The allene-type structure restricts the conjugation and, as a result, the fluorescent enhancement factor for **S2** is less than that of **S1**.

To visualise the emission response of **S1** to the different ions, a bar diagram of F/F_0 of different anions at 534 nm was plotted (Figure 7). The enhancement factor in the in-

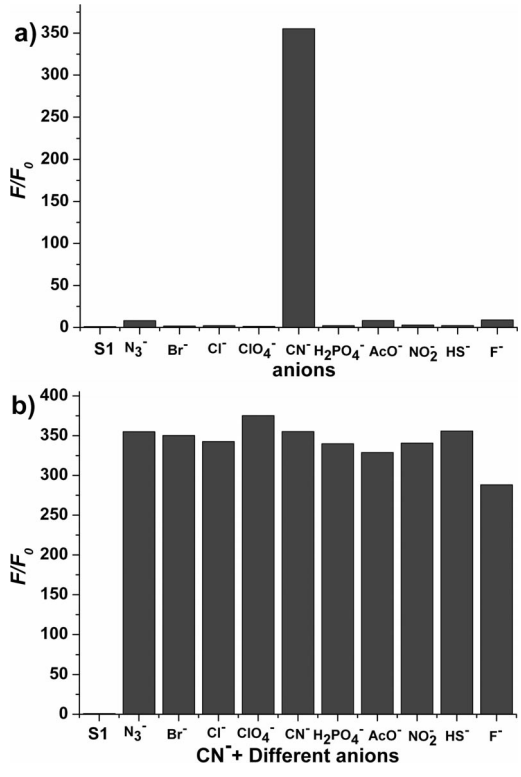


Figure 7. Fluorescence responses of (a) **S1** (3.3 μM) upon addition of various anions (5 equiv.) in THF/water solution, (b) **S1** (3.3 μM) to CN^- (1 equiv.) containing various anions (5 equiv.). λ_{ex} = 326 nm, Slit: 2.5 nm/2.5 nm.

tensity of the emission peak of **S1** at 534 nm on addition of cyanide is 350, whereas other anions did not show any significant change in the emission intensity (Figure 7, a; for **S2** see the Supporting Information, Figure S7). To check the detection dependence of CN^- in the presence of other competitive anions, we carried out titration experiments with **S1**, **S2**, cyanide (1 equiv.) and competitive anions (5 equiv.). It was clearly seen that there was no detectable change in the fluorimetric (Figure S3 and S4 in the Supporting Information) or colorimetric (Figure S5 and S6 in the Supporting Information) detection of cyanide in the presence of other anions. From part b of Figure 7 it is clear that emission intensity remains nearly unchanged in the presence of competitive anions.

Stoichiometry, ^{1}H NMR Spectroscopic Studies, Selectivity, and Detection Limits

Nucleophilic attack on the aldehyde group should also satisfy 1:1 probe and cyanide stoichiometry. The result obtained from a Job plot supports the formation of a 1:1 receptor–CN^- adduct (for **S1**, see part a of Figure 8 and for **S2**, see Figure S8). Furthermore, we investigated the ^{1}H NMR spectra of **S1** (Figure 8, b) and **S2** (Figure S19 in the Supporting Information) in the presence of cyanide anions and compared it with that of **S1** and **S2**, respectively. The aldehyde proton of **S1** and **S2** at around δ = 10.3 ppm was shifted upfield to δ = 5.8 and 5.5 ppm, respectively, for **S1** and **S2** upon cyanide addition at room temperature. This chemical shift was consistent with cyanohydrin formation due to nucleophilic attack of the cyanide on the formyl group of the dosimeter. The detection limits obtained from the fluorimetric study were 1.55 (**S1**) and 0.72 μM (**S2**) (Figure S1 and S2).[22] Thus **S1** and **S2** are efficient probes for very low concentrations of cyanide.

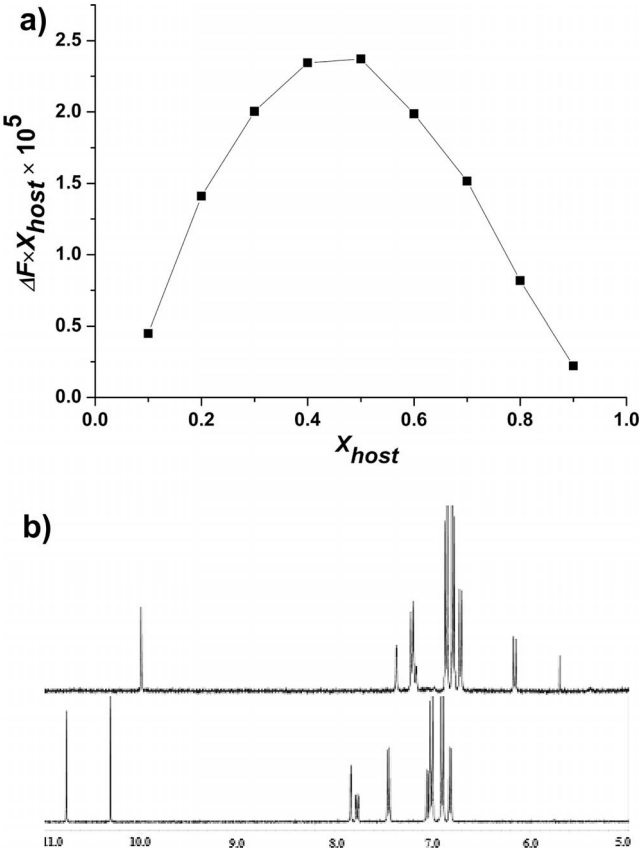


Figure 8. (a) Job plot of **S1** with CN^-; (b) ^{1}H NMR spectral change of the dosimeter upon addition of cyanide anions: (below) sensor **S1** only, and (above) sensor and CN^- (10 equiv.) in [D_6]DMSO.

Conclusions

Chemodosimeters **S1** and **S2**, comprising salicylaldehyde and triphenylamine functionalities, act as a selective colorimetric and "turn-on" fluorimetric sensor for cyanide in aqueous THF with a very low detection limit (<2 μM) and high fluorescence intensity enhancement factor (ca. 350-fold). A significant enhancement in fluorescence intensity was caused by the better nucleophilicity of the cyanide and the carbonyl activation by the phenol proton of the salicylaldehyde group in the dosimeter through an intramolecular hydrogen bond. Intramolecular charge transfer from the negatively charged quinone part to the triarylamine fragment is responsible for the colorimetric response. The detection limits were 1.55 and 0.72 μM for **S1** and **S2**, respectively, with fluorimetric enhancement factors of 350 and 25.

Experimental Section

Materials and General Methods: All reactions were performed under an argon atmosphere to maintain dry conditions. Anhydrous toluene and THF were collected from Na and benzophenone. All reagents were purchased from commercial sources and used without further purification. Compounds **S1** and **S2** were readily prepared by the synthetic protocol shown in Scheme 1. 1-(Hexyloxy)-4-iodobenzene was synthesized from 4-iodophenol by following the reported literature.[23] All the new compounds were characterised by conventional methods (^{1}H, ^{13}C NMR, HRMS). Emission and absorption spectra were recorded with Fluoromax-3 and HITACHI U-4100 UV/Vis/NIR spectrophotometers, respectively. NMR spectroscopic data were recorded with Bruker Advance 500 MHz and Jeol ECS 400 MHz spectrometers with either $CDCl_3$ or [D_6]DMSO as solvent.

Compound 2: *n*BuLi (1.6 M in hexane, 2.8 mL) was added slowly to a solution of **1** (2.1 g, 4 mmol) in THF (50 mL) at –78 °C under a nitrogen atmosphere and the mixture was stirred for 2 h at the same temperature. $SnMe_3Cl$ (1 M in hexane, 2.2 mL, 2.2 mmol) was added slowly at –78 °C and stirred for 10 min at same temperature, then stirred at room temp. overnight. The reaction was quenched by adding water (50 mL) and the product was extracted with ethyl ether. The organic layer was separated, dried with sodium sulfate, and concentrated by using a rotary evaporator. The ^{1}H NMR spectrum was recorded in $CDCl_3$ and the crude product was used for the next step without further purification. Conversion (72%) was calculated on the basis of ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.37 (s, 9 H), 0.90 (t, J = 6.7 Hz, 6 H), 1.33 (m, 8 H), 1.41 (m, 4 H), 1.76 (m, 4 H), 3.92 (t, J = 6.7 Hz, 4 H), 6.80 (d, J = 9.1 Hz, 4 H), 6.90 (d, J = 8.5 Hz, 2 H), 7.05 (d, J = 9.1 Hz, 4 H), 7.39 (d, J = 8.5 Hz, 2 H) ppm.

Compound S1: 5-Bromo-2-hydroxybenzaldehyde (202 mg, 1 mmol) was dissolved in a dry three-necked round-bottomed flask and a solution of **2** (1 g) in toluene (25 mL) was added, the solution was purged with nitrogen for 10–15 min, then $[Pd(PPh_3)_4]$ (100 mg) was added. The reaction mixture was heated to 110 °C under nitrogen for 24 h, then cooled to room temp. and toluene was evaporated by rotary evaporator. The crude mixture was directly loaded onto a column and the product was separated by flash column chromatography (ethyl acetate/hexane); yield 384 mg (68%); pale-yellow solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.86 (t, J = 6.7 Hz, 6 H), 1.30 (m, 8 H), 1.41 (m, 4 H), 1.67 (m, 4 H), 3.92 (t, J = 6.7 Hz, 4 H), 6.81 (d, J = 8.5 Hz, 2 H), 6.89 (d, J = 9.1 Hz, 4 H), 7.00 (d, J = 9.1 Hz, 4 H), 7.04 (d, J = 8.5 Hz, 1 H), 7.44 (d, J = 9.1 Hz, 2 H), 7.75–7.77 (m, 1 H), 7.83 (d, J = 1.8 Hz, 1 H), 10.29 (s, 1 H), 10.74 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 22.1, 25.2, 28.7, 31.1, 67.5, 115.3, 117.8, 119.6, 123.3, 125.7, 126.5, 126.6, 130.4, 131.3, 133.9, 139.9, 147.6, 155.2, 159.6, 191.5 ppm. HRMS (ESI): m/z calcd. for $C_{37}H_{43}NO_4^+$ 565.3192 [M$^+$]; found 565.3184.

Compound 3: To a mixture of $[PdCl_2(PPh_3)_2]$ (70 mg, 0.10 mmol) and CuI (38 mg, 0.2 mmol) in THF (40 mL) were added successively **1** (2.10 g, 0.4 mmol), trimethylsilyl acetylene (624 μL, 4.4 mmol), and NEt_3 (20 mL). The resulting mixture was stirred for 18 h at room temp. The dark solution was evaporated under reduced pressure and the resulting black solid was extracted with CH_2Cl_2 and further purified by chromatography on silica gel (hexane) to give **3**; yield 1.75 g (80%); yellowish oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.23 (s, 9 H), 0.93 (t, J = 6.7 Hz, 6 H), 1.33 (m, 8 H), 1.41 (m, 4 H), 1.76 (m, 4 H), 3.93 (t, J = 6.4 Hz, 4 H), 6.80 (d, J = 8.5 Hz, 2 H), 6.82 (d, J = 8.8 Hz, 4 H), 7.05 (d, J = 8.8 Hz, 4 H), 7.24 (d, J = 8.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 0.1, 14.0, 22.5, 25.7, 29.2, 31.5, 68.2, 92.1, 105.8, 113.6, 115.3, 118.9, 127.0, 132.7, 139.9, 148.9, 155.8 ppm. HRMS (ESI): m/z calcd. for $C_{35}H_{47}NO_2Si^+$ 541.3376 [M$^+$]; found 541.3371.

Compound 4: To a stirred solution of **3** (1.08 g, 2 mmol) in CH_3OH (30 mL) was added K_2CO_3 (28 mg, 0.2 mmol). The mixture was stirred for 24 h at room temp., concentrated, and the residue was diluted with Et_2O and washed with water (3 × 30 mL). The organic phase was dried with Na_2SO_4, filtered, and concentrated by rotary evaporator. The resulting organic compound was purified by filtration through a silica gel column (hexane/CH_2Cl_2) to afford **4**; yield 844 mg (90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.8 Hz, 6 H), 1.33 (m, 8 H), 1.44–1.47 (m, 4 H), 1.78 (m, 4 H), 2.98 (s, 1 H), 3.92 (t, J = 6.4 Hz, 4 H), 6.80 (d, J = 8.5 Hz, 2 H), 6.83 (d, J = 9.1 Hz, 4 H), 7.05 (d, J = 8.5 Hz, 4 H), 7.24 (d, J = 9.1 Hz, 2 H) ppm. ^{13}C NMR,(100 MHz, $CDCl_3$): δ = 14.0, 22.5, 25.7, 29.2, 31.5, 68.2, 84.3, 112.3, 115.3, 118.7, 127.1, 132.8, 139.8, 149.2, 155.9 ppm. HRMS (ESI): m/z calcd. for $C_{32}H_{39}NO_2^+$ 469.2981 [M$^+$]; found 469.2974.

Compound 5: Compound **4** (940 mg, 2 mmol) and anhydrous THF (40 mL) were taken in a 100 mL three-necked round-bottomed flask. The reaction mixture was cooled to –78 °C and nBuLi (1.6 M in hexane, 1.4 mL) was added slowly to the cold mixture and the mixture was stirred for 1 h at the same temperature. $SnMe_3Cl$ (1 M in hexane, 2.2 mL) was added slowly and the reaction mixture was kept at room temp. overnight. The reaction was quenched by adding water (25 mL) and the product was extracted with ethyl ether. The organic layer was separated, dried with sodium sulfate, and concentrated by using a rotary evaporator. The ^{1}H NMR spectrum was recorded in $CDCl_3$ and crude product was used for the next step without further purification. Conversion (78%) was calculated on the basis of ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.28 (s, 9 H), 0.86 (t, J = 6.8 Hz, 6 H), 1.30 (m, 8 H), 1.42–1.45 (m, 4 H), 1.72 (m, 4 H), 3.88 (t, J = 6.4 Hz, 4 H), 6.80–6.84 (m, 6 H), 6.97 (d, J = 8.8 Hz, 4 H), 7.20 (d, J = 8.8 Hz, 2 H) ppm.

Compound S2: 5-Bromo-2 hydroxy benzaldehyde (202 mg, 1 mmol) was taken in a dry three-necked round-bottomed flask and a solution of **5** (1.2 mg) in toluene (25 mL) was added. The solution was purged with nitrogen for 10–15 min, then $[Pd(PPh_3)_4]$ (100 mg) was added. The reaction mixture was heated to 110 °C under nitrogen for 24 h, then cooled to room temp. and toluene was evaporated by rotary evaporator. The crude mixture was directly loaded onto a column and the product was separated by flash column chromatography (ethyl acetate/hexane); yield 384 mg (72%); pale-yellow solid. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 0.87 (t, J = 6.8 Hz, 6 H), 1.30 (m, 8 H), 1.46 (m, 4 H), 1.69 (m, 4 H), 3.93 (t, J = 6.4 Hz, 4 H), 6.67 (d, J = 8.5 Hz, 2 H), 6.92 (d, J = 9.1 Hz, 4 H), 7.00 (d, J = 8.5 Hz, 1 H), 7.05 (d, J = 9.1 Hz 4 H), 7.29 (d, J = 8.5 Hz, 2 H), 7.59 (m, 1 H), 7.71 (d, J = 2.4 Hz, 1 H), 10.24 (s, 1 H), 11.09 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.7, 29.2, 31.6, 68.2, 86.0, 89.6, 113.1, 115.3, 115.8, 117.9, 118.9, 120.4, 127.15, 132.2, 136.5, 139.7, 139.8, 148.9, 155.9, 160.9, 196.2 ppm. HRMS (ESI): m/z calcd. for $C_{39}H_{43}NO_4^+$ 589.3192 [M$^+$]; found 589.3184.

Computational Details: All electronic structure calculations were carried out using the Gaussian 09[17] program suite. Geometry optimisations were performed at the B3LYP/6-31G(d) level.[18] The triple-ζ valence quality with one set of polarization functions (TZVP)[19] was chosen as basis sets for single point TD-DFT[20] calculations on the optimised geometries using the 6-31G(d) basis set.

UV/Vis and Fluorescence Titration Procedure: In absorption and emission titration experiments, the total volume of solution was fixed to 3 mL. The response to cyanide anion is very fast, therefore, spectra were recorded immediately after the addition of cyanide.

Supporting Information (see footnote on the first page of this article): Graphs of detection limits for **S1** and **S2**, sensitivity of cyanide to **S2**, Jobs plot for **S2**; copies of the ^{1}H and ^{13}C NMR spectra and computational details.

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