Tandem Detection of Sub-Nano Molar Level CN\(^{-}\) and Hg\(^{2+}\) in Aqueous Medium by a Suitable Molecular Sensor: A Viable Solution for Detection of CN\(^{-}\) and Development of the RGB-Based Sensory Device

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ABSTRACT: An inimitable urea-based multichannel chemosensor, DTPH \([1,5\text{-bis-(2,6-dichloro-4-(trifluoromethyl)phenyl)}\text{-carbonohydrazide}]\), was examined to be highly proficient to recognize CN\(^{-}\) based on the H-bonding interaction between sensor \(-\text{NH moity and CN}\(^{-}\) in aqueous medium with explicit selectivity. In the absorption spectral titration of DTPH, a new peak at higher wavelength was emerged in titrimetric analytical studies of CN\(^{-}\) with the zero-order reaction kinetics affirming the substantial sensor\(-\text{analyte interaction. The isothermal titration calorimetry (ITC) experiment further affirmed that the sensing process was highly spontaneous with the Gibbs free energy of } -26 \times 10^4 \text{ cal/mol. The binding approach between DTPH and CN}^{-}\text{ was also validated by more than a few experimental studies by means of several spectroscopic tools along with the theoretical calculations. A very low detection limit of the chemosensor toward CN\(^{-}\) \((0.15 \text{ ppm})\) further instigated to design an RGB-based sensory device based on the colorimetric upshots of the chemosensor in order to develop a distinct perception regarding the presence of innocuous or precarious level of the CN\(^{-}\) in a contaminated solution. Moreover, the reversibility of the sensor in the presence of CN\(^{-}\) and Hg\(^{2+}\) originated a logic gate mimic ensemble. Additionally, the real-field along with the in vitro CN\(^{-}\) detection efficiency of the photostable DTPH was also accomplished by using various biological specimens.

INTRODUCTION

The recognition of toxic anionic elements is an arena of colossal cognizance in the 21st century.\(^1\text{-}^7\) From the environmental perspective, cyanide (CN\(^{-}\)) is one of the most precarious anionic analytes which causes noxious effects on bio-organisms, specifically on mammals.\(^5,3\) It prevents to activate cytochrome C oxidase (COX) by binding with Fe in the protein, which results in the interdiction of cellular inhalation and cellular anoxia or hypoxia.\(^1\text{-}^3,8\text{-}^10\) Likewise, cyanide also upsurges the reactive oxygen species level and consequently the electron transportation sequence in mitochondria is blocked causing the inhibition in the synthesis of adenosine triphosphate. This toxic element as well causes hasty assassination and adversely invades the cardiovascular as well as the central nervous system.\(^2\) In this way, CN\(^{-}\) results in vomiting, convulsion, unconsciousness, and ultimately death.\(^1\) Even a trace amount of CN\(^{-}\) \((0.5\text{-}3.5 \text{ mg kg}^{-1} \text{ body weight})\) is sufficient to kill a human being.\(^6,11\) Inside the blood of a person affected by fire, the CN\(^{-}\) concentration should lie within 23–26 mM.\(^12\) According to WHO and USEPA the safe limit and maximum contaminant level (MCL) of cyanide is set to be 0.07 and 0.2 ppm, respectively.\(^1,8,13\)

Despite its dreadful toxicity, New Zealand and Australian Environmental and Conservation Council reported that approximately 2–4 g/L CN\(^{-}\) is essential for 99% of the inhabitants in the marine and freshwater.\(^1\) Some foods and plants like fruits, apple seeds, bitter almonds, and cassava roots also contain CN\(^{-}\).\(^1,2,13\) In contrast, cyanide has several significant roles in numerous industrial practices, such as gold mining; petrochemical production; metallurgy; metal electroplating and case-hardening; steel, resins, pesticides, and pharmaceuticals as well as fiber manufacturing and photography.\(^1,3,5,6,9,10,12\) Undeniably, around 1 million ton of CN\(^{-}\)-enriched products are manufactured per year for commercial

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purpose. In addition, CN\(^-\) is also used as terror substances and chemical warfare reagents. Therefore, the third world is at high risk, due to the rapid increase in the CN\(^-\) concentration in the drinking water on account of inundating. In this perspective, detection of CN\(^-\) has unremittingly obtained noteworthy consideration owing to its disastrous consequences on breathing organisms as well as on the environment.

In this background, exploration of neoteric cyanide-selective sensors capable to recognize trace level of CN\(^-\) in water, soil, food, air, and in biological samples is of today’s interest. Chromatography, spectrophotometry, mass spectrometry, Raman spectroscopy, flow injection amperometry, and potentiometry are some of the available technologies presently used for the detection of CN\(^-\) in several processed samples which are time-consuming and convoluted to be handled by untutored personnel. In this perspective, premeditated synthesis of more effectual and sensitive technique to recognize CN\(^-\) unservingly at lower level in different mediums is cynosure to the researchers. A number of artificial chemoreceptors containing Lewis acids, metallo receptors, protonated polyammonium macrocycles, guanidiniums, pyroles, amides, and organogels are explored for their recognition competence toward various anions. Most of the explored receptors bear very intricate structures which usually entail manifold synthetic procedures with comparatively lower yields. Nevertheless the organic chemosensors are not really proficient in water medium due to high hydration energy of the anions (\(\Delta G_{\text{bind}}\) for CN\(^-\) is \(-320\) kJ mol\(^{-1}\)) and effective rivalry of the H\(_2\)O molecules for the binding sites. In this background, exploration of potent multichannel chemosensors, capable of functioning in the presence of water is of certain interest.

The chemodosimetric approach, which employs the coordination interaction of CN\(^-\) to (i) a transition metal, (ii) an electronically deficient carbonyl moiety, or (iii) a coordinative unsaturated borane complexes are proficient methods with the intention of detecting cyanide in water. Still the chemodosimetric method has several disadvantages, such as delayed time, irreversibility, and requirement of high temperature to be activated for binding the cyanide ion to the suitable interactive part of the sensors. Even though innumerable compounds capable to provide H-bond forming units have been developed, which display strong attraction and selectivity toward CN\(^-\) in organic solvent, small molecular probes capable to proficiently sense CN\(^-\) through H-bonding interaction in aqueous phase are very scarce to date. Moreover most of the H-bonding receptors suffer from higher limit of detection and less selectivity. Therefore, in this work, we have introduced a unique urea-based chemosensor DTPH [1,5-bis(2,6-dichloro-4-(trifluormethyl)-phenyl)carbonohydrazide], capable to detect CN\(^-\) selectively at very low level in 9:1 ACN–water media (Scheme 1). To the extent of our awareness, urea-based chemosensors, capable to recognize CN\(^-\) selectively is scanty in the literature so far. The multichannel chemosensor proficiently recognized CN\(^-\) colorimetrically, fluorimetrically, and electrochemically due to the presence of four dissociable H containing \(-NH\) moieties in its skeleton. In addition, the premeditated presence of the electron-withdrawing –Cl and –CF\(_3\) groups at the ortho and para positions, respectively, regulated the binding affinity of the \(-NH\) moieties. The production of DTPH and the entire sensing phenomena were established by using quite a few sophisticated analytical instruments, for instance, ESI-MS, FT-IR, UV–vis, PL, CV, \(^1\)H NMR, and so on.

The thermodynamic characteristics of the sensing process were also noted by using isothermal titration calorimetry (ITC). \(^1\)H NMR studies in consort with the theoretical calculations provided rational evidence on the subject of the plausible interaction mode between the chemosensor and CN\(^-\). Moreover, the sensor–CN\(^-\) adduct showed high selectivity toward Hg\(^{2+}\), one among the most perilous and widely distributed metal ions in soil, water, and air. In addition, DTPH is successfully recognized CN\(^-\) in bitter almond seeds and fetal bovine serum (FBS), emboldening the usage of the chemosensor in our everyday-lives. Further, the chemosensor was also perceived to be capable to detect CN\(^-\) in the HeLa cells and human lungs carcinoma cells. Apart from these, an easy, instant, on-field, RGB-based sensory device has also been fabricated so as to recognize CN\(^-\) in both of its acceptable as well as excruciating concentration. Several color sensors are used in recent time so as to measure pH, color in the cosmetics, foods, beverages, printing, and so forth, where the light is divided into three primary colors: red (R), green (G), and blue (B). However, the explored colorimetric sensory devices are mainly comprised of a TCS color sensor and a developer board, which is relatively expensive. Therefore, in this work, some of the conventional techniques were modified in order to minimize the cost of the entire prototype and to make the device naive and user friendly. In this customized sensory device, various important segments, like TCS, microcontrollers, LED and so forth, were assimilated on a printed circuitry board and the performance of the developed integrated circuit board was optimized by using a reference ARDUINO.
The crystal of DTPH was obtained by careful evaporation of 1:1 DCM–hexane solvent mixture (Figure 1) (CCDC no. 1944265). DTPH was observed to be an asymmetrical molecule, where the \([(-\text{NH})_2\text{C}=\text{O}]\) group fashioned a connection amongst two chloro-fluoromethyl phenyl rings which were eventually nonplanar to each other. The C=O bond length was shown to be 1.22 Å and the N–H bond lengths were perceived to be 0.86 Å, whereas the C–N and N–N bond lengths were 1.34 and 1.37 Å, respectively, on both the contiguous sides. These findings affirmed that both the C–N and N–N bond distances were lesser than that of the urea and unsubstituted hydrazine moieties. Moreover, the C–Cl bond distances (1.73 Å) along with the C–F bond lengths (lied between 1.20 and 1.37 Å) were also found to be closed to the conventional C–Cl (1.77 Å) and C–F (1.35 Å) bond lengths, which put forward the existence of conjugation throughout the sensor molecule. There was an intramolecular interaction within the –Cl group of the phenyl part and the N center adjacent to the –CO group having the bond distance 2.93 Å. Two intermolecular interactions were also found to be transpired. One is the interaction amongst the O center of –CO of one molecule and the amide N of the adjacent molecule (bond distance: 2.81 Å), whereas another interaction was found to be emerged within the –Cl group of the phenyl moiety and the phenyl C center of the adjacent molecule (bond distance: 3.41 Å). However an intermolecular H bonding within the carbonyl O center and the amide H center was also found with the bond length of 2.02 Å. The existing intramolecular and intermolecular interactions finally formed an extended supramolecular 2D chain (Figure 1, Tables S1–S4; Supporting Information).\(^{43}\) Furthermore, the N–C(=O)–N and C–N–N bond angles were observed to be 114 and 125°, respectively, which affirmed the presence of strain within the sensor molecule.\(^{43,45}\)

**Naked-Eye Observation.** In order to perform the visual colorimetric recognition experiment of DTPH, \(10^{-4}\) M sensor solution was prepared in ACN and \(10^{-5}\) M anion solutions were prepared in 9:1 ACN–H\(_2\)O medium. The anionic solutions were thereafter added separately to the sensor solutions by maintaining 1:1 ratio and interestingly the color of the sensor solutions turned into orange red from colorless upon addition of CN\(^-\), whereas the sensor remained intact in presence of the others anion (Figures S4 and S5; Supporting Information).

**Absorption Spectral Studies of DTPH with TBA\(^+\)CN\(^-\).** High photostability of a chemosensor is a good indication to be a competent contender in the arena of several chemical and biological experiments.\(^{46,47}\) In this perspective, time-dependent absorption studies were performed so as to assess the photostability of the colorimetric chemosensor. Amazingly DTPH was found to be almost unchanged upon keeping under UV lamp (255 nm) for 40 min (Figure 2b), which signified that DTPH was highly photostable and is advantageous for long-time experiments. Additionally, DTPH was also perceived to have no significant alteration in its absorbance spectra within a broad pH range of 5–12 (Figure S15, Supporting Information).

The UV–vis titration studies of DTPH were performed with \(10^{-5}\) M sensor solution prepared in ACN and \(10^{-4}\) M CN\(^-\) solution prepared in 9:1 ACN–H\(_2\)O medium. Here, the occurrence of water probably inhibited the deprotonation upon addition of CN\(^-\).\(^{15,26}\) From the absorption spectra, it was shown that the free sensor exhibited two peaks at 255 and 300 nm corresponding to the \(\pi-\pi^*\) and \(n-\pi^*\) transition, respectively, and the \(\pi-\pi^*\) transition also corroborated with the time-dependent density functional theory calculation (Figure S13; Supporting Information).\(^5\) Upon steady addition of CN\(^-\) to the sensor, a new peak was noticed to be emerged at 480 nm with simultaneous diminution of the initial peak and upsurge of the peak at 300 nm, affirming an charge-transfer transition within the –NH moiety of the sensor and CN\(^-\) (Figure 2a). Here, the H-bonding interaction between the sensor and CN\(^-\) triggered the increased electron density around the sensor which further reduced the energy gap between the molecular orbitals and therefore the absorbance wavelength increased causing the concomitant color change.\(^{25}\)
Herein, for the experimentation of low level CN\textsuperscript{−} detection, 0.18 ppm CN\textsuperscript{−} solution was added to the DTPH solution (10\textsuperscript{-3} M in ACN) by maintaining 1:1 stoichiometry ratio followed by the exposure to the RGB color sensor and the resultant R, G, and B values were found to be prominently increased from the reference input data. The nearly constant ΔR, ΔG, and ΔB values signified a stable response of DTPH toward CN\textsuperscript{−}. For low concentration of CN\textsuperscript{−}, the resulting sample attained a yellowish orange color due to the formation of new DTPH–CN\textsuperscript{−} adduct along with the appearance of a new peak at 450 nm upon addition of <0.2 ppm CN\textsuperscript{−}, whereas upon addition of higher amount of CN\textsuperscript{−}, the peak was shifted to 480 nm with significant diminution of the characteristic peak at 255 nm (Figure 4a). These findings indicated the significant color transition of the resulting chemosensor solution upon addition of different concentration of CN\textsuperscript{−} in consort with the prominent changes in the RGB values. Moreover, these interesting properties of DTPH incited to fabricate an easy, instant, on-field, RGB-based sensory device with the intention of monitoring the safer and precarious level of CN\textsuperscript{−} in various specimens. The changes in the RGB values correlating with the color changes of different concentration of CN\textsuperscript{−}-containing DTPH solutions were observed by taking the inherent RGB values of the chemosensor solution as the reference. The mounted RGB color sensor attached with the fabricated device detected the specific R, G, and B values of the input samples and processed through a coded microcontroller which was finally displayed on the digital display unit as high or low concentration of CN\textsuperscript{−}.
the appearance of a broad spectra at 450 nm affirming the formation of the adduct. Consequently, $\Delta R$ and $\Delta G$ values increased with time very slightly, whereas the $\Delta B$ remained unchanged throughout the experimentation (Figure 4c). Similarly, for higher concentration of CN$^-$, prominent changes were observed in RGB values as well as in the absorption spectra of the chemosensor. The changes in the color noticed by human eyes are not exactly similar to the absorption spectral responses. $^{51}$ The broad range in spectra covering the blue, greenish blue, blue green, and green color which is detected by an instrument is observed as their harmonized colors (yellow, orange, red orange, and red, respectively) by the human eyes. $^{51}$ Therefore, with the increasing CN$^-$ concentration, the color range red shifted from the blue region absorption spectra and thus an increase in the green and red filter photodiode signal, as well as decrease in the blue filter photodiode was observed from the lower concentration of CN$^-$ containing solution. As a result, the R and G values were perceived to be increased essentially. Again the $\Delta R$ and $\Delta G$ values increased with time, whereas compared to lower concentration of CN$^-$ solution, the $\Delta G$ values were continuously increased up to the saturation point in a spontaneous manner (Figure 4d).

Furthermore, to affirm the noticeable changes, the RGB values were expressed with reference to the total change in color ($\Delta C$) by the Euclidean distance equation

$$\Delta C = \sqrt{(\Delta R)^2 + (\Delta G)^2 + (\Delta B)^2}$$

where $\Delta R$, $\Delta G$, and $\Delta B$ are the changes in R, G, and B values from the reference values, correspondingly. (Figure 4c) The $\Delta C$ value remained unchanged up to 15 min for the low concentration of CN$^-$ solution, whereas, for higher concentration of CN$^-$, the $\Delta C$ value became nearly constant after a certain times affirming the quick and firm response of DTPH toward CN$^-$. $^{42,52}$ Therefore, all of these findings implied that the RGB sensor signals adequately correlated with the optical as well as the absorption spectral upshots of different concentration of DTPH--CN$^-$ adduct.

**Overture toward the Electronic Circuit Fabrication.** The resindable outcome of DTPH and CN$^-$ in the presence of Hg$^{2+}$ can imitate numerous logical functions, which can be useful to accomplish several molecular level mathematical calculations. $^{31,33-36}$ The creation of molecular level logical operation is principally originated from some spectroscopic responses of the given chemical inputs so that an intricate circuit can be efficient to unravel several computational complexities. $^{57}$ At the present time, alterable switches are of significant importance owing to their substantial requirement in the information technology.

Introducing anionic as well as cationic inputs can produce a discrete spectral change, which instigated us to utilize DTPH, CN$^-$, and Hg$^{2+}$ to constitute a three-input coalescent circuitry (Figure S8; Supporting Information). In this case, upon addition of Hg$^{2+}$, the orange red colored solution of DTPH-CN$^-$ adduct turned into the colorless solution of DTPH by releasing CN$^-$ from the host–guest assembly, whereas upon further addition of CN$^-$ the orange red coloration of the solution returned and this cyclic colorimetric turn-off-on occurrences of the DTPH-CN$^-$ solution by the addition of Hg$^{2+}$ was continued significantly up to seven times. The spectroscopic outcomes of DTPH with entering analytes like CN$^-$ and Hg$^{2+}$ are tabulated in Table S5 (Supporting Information). The sensor itself possessed absorbance spectra at 255 nm (OUTY1), while in the presence of CN$^-$ the sensor resulted in the absorbance spectra at 480 nm (OUTY2). Upon addition of Hg$^{2+}$, the spectroscopic response at 255 nm was regenerated with consequent diminution of the peak at 480 nm, whereas various others competitive metal ions (Zn$^{2+}$, Cd$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Pb$^{2+}$) were irresponsive toward the DTPH-CN$^-$ solution (Figures S16 and S17, Supporting Information). Therefore, OUTY2 was in the ON stage if both the input 1 (DTPH) and input 2 (CN$^-$) were present. Conversely, in the presence of an inhibitor input 3 (Hg$^{2+}$), the output signal at OUTY2 was OFF and OUTY1 was ON, which further reproduced the free sensor. Succinctly, OUTY2 was in the ON state when both the In 1 and In 2 were present and the addition of In 3 caused the OUTY2 to be turned off (OUT =

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**Figure 4.** (a) Absorption spectral response of DTPH in presence of different concentration of CN$^-$ solution; (b) change of $\Delta C$ values with time; change in $\Delta R$, $\Delta G$, and $\Delta B$ values with time (c) for the low concentration and (d) high concentration of CN$^-$ containing solution.
0) and OUTY1 to be turned on, forming a NOT gate. As shown in the Table S5, methodical observation of the absorbance spectral response at 255 and 480 nm by the chronological addition of CN\(^-\) (In 2) and Hg\(^{2+}\) (In 3) to the sensor produced an INHIBIT logic function. Moreover, the chemosensor possessing this type of anion–cation dual responses up to seven cycles can be an optimistic prospect toward the exploration of a prospective molecular logic gate mimic device (Figures 5 and S9; Supporting Information).

**Emission Spectral Studies of DTPH with TBA\(^+\)CN\(^-\).**

The luminescence experiments of DTPH with CN\(^-\) were performed with the same solutions of sensor and CN\(^-\) as taken for the absorbance studies. The nonfluorescent chemosensor exhibited an in firm emission spectrum at 355 nm by the excitation at 290 nm, which concomitantly up surged upon consecutive addition of CN\(^-\) along with the simultaneous red shifting of the peak position (Figure S10; Supporting Information). The bathochromic spectral shift of the sensor in presence of CN\(^-\) clearly suggested the favorable ICT process.58–62 Additionally, the turn-on fluorescence response in presence of CN\(^-\) may be the consequence of the constraint in the PET as a result of the sensor–CN\(^-\) interaction.63–66

**Electrochemical Studies of DTPH with TBA\(^+\)CN\(^-\).**

Cyclic voltammetric titration of DTPH upon continuous addition of CN\(^-\) was performed by using 10\(^-3\) M DTPH solution prepared in ACN and 10\(^-4\) M CN\(^-\) solution made in 9:1 ACN–H\(_2\)O solvent.67,68 Three-electrode electrochemical cell was used to carry out the experiment, and tetrabutylammonium hexafluorophosphate (TBAPF\(_6\)) was used as the supporting electrolyte. The free sensor showed an oxidation peak at 0.405 V (current height \(\sim 1.72 \times 10^{-6} \) A). After interaction with CN\(^-\), the initial peak started to decrease in current height and after addition of 0.118 mM CN\(^-\) the peak was found to be shifted to 0.415 V (current height \(\sim 3.1 \times 10^{-6} \) A) (Figure S11; Supporting Information) connoting the restraint in PET within the sensor molecule.

**1H NMR Titration of DTPH with TBA\(^+\)CN\(^-\).**

The 1H NMR titration studies of DTPH in the presence of CN\(^-\) were performed in DMSO-\(d_6\) solvent to acquire an explicit conjecture regarding the plausible binding mode of CN\(^-\) with the sensor (Figure 6).69,70 In the 1H NMR spectra, it was observed that the sensor owns two \(-\text{NH}\) proton signals at 8.56 and 7.51 ppm, corresponding to the \(-\text{NH}_4\) and \(-\text{NH}_8\) protons, respectively, and the lingering aromatic protons were observed to be emerged at 7.7 ppm. Upon gradual addition of CN\(^-\), the \(-\text{NH}\) protons were started to diminish in intensity with simultaneous broadening, signifying a strong H-bonding interaction between CN\(^-\) and the \(-\text{NH}\) moiety of DTPH.71 Moreover, the spectra further showed that the peak corresponding to more dissociable \(-\text{NH}_4\) proton was completely diminished by only 0.06 mM addition of CN\(^-\) while the \(-\text{NH}_8\) proton disappeared by 0.08 mM CN\(^-\) addition. These findings further affirmed that CN\(^-\) interacted more strongly with the more polarizable \(-\text{NH}_4\) proton followed by the \(-\text{NH}_8\) protons (Scheme 2).

**Infrared Spectroscopic Studies of DTPH with TBA\(^+\)CN\(^-\).**

The detection of CN\(^-\) by DTPH was further ascertained with the help of infrared spectroscopic studies (Figure S6; Supporting Information). The IR experiment was executed by adding 1 equivalent TBACN with the sensor. The free sensor displayed two characteristic peaks at 3410 and 1670 cm\(^{-1}\), confirming the presence of \(-\text{NH}\) and \(-\text{CO}\) groups in the framework. After addition of CN\(^-\), a new peak was engendered at 2100 cm\(^{-1}\), indicating a significant interaction of

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**Figure 5.** Fabrication of logic gate by altering inputs of NAND–NOT–NOR logic functions for DTPH with CN\(^-\) and Hg\(^{2+}\).

**Figure 6.** 1H NMR titration spectra of DTPH in the presence of TBACN in DMSO-\(d_6\).
Scheme 2. Plausible Binding Mode of DTPH and CN$^-$

DTPH with CN$^-$.$^{72}$ The disappearance of the $-\text{NH}$ peak asserted the interaction of CN$^-$ with the $-\text{NH}$ moiety of the chemosensor. Moreover, the peak corresponding to $-\text{CO}$ group along with the others peak were found to be broadened attributing to the increase in the charge density within the system.

Isothermal Titration Calorimetric Studies of DTPH with TBA$^+\text{CN}^-$. In order to get clear insights regarding the thermodynamic parameters subsumed in the interaction between DTPH and CN$^-$, ITC experiment has been effectuated at 25 °C which directly determines the alteration in enthalpy ($\Delta H$), binding constant ($K$), and stoichiometry ($n$).$^{73}$ The calorimetric titration plot is depicted in Figure 7.

![ITC plot of DTPH in presence of TBACN.](image)

On the other hand, in the case of 1:2 DTPH$–\text{CN}^-$ interaction, when CN$^-$ interacted with both of the $-\text{NH}_2$ hydrogen of N4 and N19 along with the $-\text{NH}_2$ hydrogen of N7, the distances between CN$^-$ and hydrogen were measured to be 2.16 Å (for N4 hydrogen), 1.97 Å (for N19 hydrogen), and 1.93 Å (for N7 hydrogen). Moreover, the $-\text{NH}$ bond lengths of N4, N19, and N7 were lengthened to 1.022, 1.032, and 1.038 Å, respectively. On the other hand, when CN$^-$ attached with the $-\text{NH}_2$ hydrogen of N21 along with the $-\text{NH}_2$ hydrogens of N4 and N19, the distance between CN$^-$ and $-\text{NH}$ were observed to be 1.92 Å (for N21 hydrogen), 1.93 Å (for N4 hydrogen), and 2.16 Å (for N19 hydrogen). Simultaneously the $-\text{NH}$ bond distances of the N4, N19, and N21 were also stretched from their initial distances to 1.038, 1.022, and 1.031 Å correspondingly. On the other hand, when $-\text{CN}^-$ interacted with both of the $-\text{NH}_2$ hydrogen, the distances between CN$^-$ and hydrogens were shown to be 1.93 Å for each and the $-\text{NH}$ bond lengths were extended to 1.04 Å for N21 and 1.38 Å for N7 (Figure 8, Tables S7–S9; Supporting Information).

Real-Time Applications of DTPH To Recognize CN$^-$. With the purpose of exploring the real-time usability of the calculations exclusively agreed with the experimental finding.$^{80,81}$ In free DTPH, the $-\text{NH}$ bond distances were observed to be 1.015 Å for $-\text{NH}_1$ and 1.019 Å for $-\text{NH}_2$, which were found to be lengthened and the HOMO–LUMO gap along with the energy of the free DTPH was also lowered down in the presence of CN$^-$, affirming the H-bonding host–guest interaction and the consequent appearance of the UV–vis spectra at a longer wavelength (Figure S12, Table S6; Supporting Information).$^8$ The $^1\text{H}$ NMR spectra revealed that CN$^-$ interacted with the sensor through H-bonding interaction with both of the $-\text{NH}_1$ and $-\text{NH}_2$ hydrogens, which was also established in the DFT calculations. In case of the 1:1 host–guest interaction between the $-\text{NH}_2$ hydrogen of DTPH and CN$^-$, the distances of CN$^-$ with both of the $-\text{NH}_1$ hydrogen were found to be 2.02 Å, and the $-\text{NH}_2$ bond lengths were extended to 1.03 Å from 1.015 Å. Likewise, when CN$^-$ interacted with the $-\text{NH}_2$ hydrogen, the distances between the H and CN$^-$ were perceived to be 1.91 Å while the $-\text{NH}_1$ bond distances were elongated to 1.038 Å from 1.019 Å (Figure 8, Tables S7–S9; Supporting Information).

Figure 8. Geometry-optimized structures of 1:1 interactions between DTPH and CN$^-$. On the other hand, in the case of 1:2 DTPH$–\text{CN}^-$ interaction, when CN$^-$ interacted with both of the $-\text{NH}_2$hydrogen of N4 and N19 along with the $-\text{NH}_2$ hydrogen of N7, the distances between CN$^-$ and hydrogen were measured to be 2.16 Å (for N4 hydrogen), 1.97 Å (for N19 hydrogen), and 1.93 Å (for N7 hydrogen). Moreover, the $-\text{NH}$ bond lengths of N4, N19, and N7 were lengthened to 1.022, 1.032, and 1.038 Å, respectively. On the other hand, when CN$^-$ attached with the $-\text{NH}_2$ hydrogen of N21 along with the $-\text{NH}_2$ hydrogens of N4 and N19, the distance between CN$^-$ and $-\text{NH}$ were observed to be 1.92 Å (for N21 hydrogen), 1.93 Å (for N4 hydrogen), and 2.16 Å (for N19 hydrogen). Simultaneously the $-\text{NH}$ bond distances of the N4, N19, and N21 were also stretched from their initial distances to 1.038, 1.022, and 1.031 Å correspondingly. On the other hand, when $-\text{CN}^-$ interacted with both of the $-\text{NH}_2$ hydrogen, the distances between CN$^-$ and hydrogens were shown to be 1.93 Å for each and the $-\text{NH}$ bond lengths were extended to 1.04 Å for N21 and 1.38 Å for N7 (Figure 9, Tables S10–S12; Supporting Information).

Real-Time Applications of DTPH To Recognize CN$^-$. With the purpose of exploring the real-time usability of the...
chemosensor in our day-to-day lives, 1.5 g of crushed bitter almond seeds were mixed with 5 mL of distilled water, and the solution was kept under stirring for around 1 h. The mixture was then kept to be stabilized. After that the solution was tested with 1 mM DTPH solution. Amusingly, the color of the sensor solution changed from colorless to orange red upon the addition of the filtered bitter almond solution. Moreover, in the UV−vis spectra of the DTPH−bitter almond solution, a peak at 480 nm was observed, confirming the sensing ability of the sensor toward CN− present in the bitter almond seeds (Figure 11a).

Apart from the bitter almond seed, the chemosensor was also found to be proficient to recognize CN− in the FBS tainted with CN−. At first, 0.5 mM CN− was spiked with the fresh FBS procured from HiMedia and centrifuged for 5 min at 3000 rpm. Thereafter, the supernatant was examined with 1 mM DTPH solution and amusingly the color of the solution turned from colorless to orange red. The CN−-spiked FBS-containing DTPH solution was also examined in the UV−vis spectra, and the peak at around 480 nm suggested that the colorimetric change was undeniably as a result of the existence of CN− in the serum (Figure 11b).

Live Cell Imaging Studies of DTPH To Recognize CN−. The intracellular CN− detection efficiency of the probe, DTPH, was also investigated by using HeLa cells as well as human lung carcinoma cell lines (A549). The fluorescence microscopy images were completely in good agreement with the fluorescence spectral characteristic of the DTPH−CN− adduct (Figures 12 and S14, Supporting Information). From the confocal microscopy images, it was perceived that the initially nonluminescent chemosensor turned into cyan emissive by the addition of CN−, which was completely consistent with the fluorescence titration experiment of the chemosensor in the presence of CN−, asserting that the chemosensor possesses a noteworthy efficiency to recognize CN− in the cell mediums also. Moreover, the MTT assay further revealed that 80% cells were viable when the concentration of the chemosensor was 100 μM.

Concise Comparative Studies with Some Hitherto Explored Effective Sensors. A number of inimitable sensing properties and applicability of DTPH compared to several newly explored CN− sensors have been elucidated in Table S14 (Supporting Information). From the table, it can be...
clearly shown that some of the explored chemosensors are comparable with DTPH in terms of detection limit and binding affinity, but the RGB-based colorimetric sensory device is not reconnoitered in the others work. Additionally, most of the explored chemosensors are revealed to be dual channel chemosensors, capable to detect CN\textsuperscript{−} by colorimetrically and/or fluorimetrically, while DTPH, being a multi-channel chemosensor, can recognize CN\textsuperscript{−} colorimetrically, fluorimetrically as well as electrochemically.

**CONCLUSIONS**

In compendium, a hydrazine-functionalized colorimetric, fluorimetric, and electrochemical chemosensor DTPH was prepared by using some inexpensive reagents, and the chemosensor showed high sensitivity toward the prejudicial CN\textsuperscript{−} anion in aqueous medium. More than a few experimental as well as the theoretical outcomes affirmed that the photostable chemosensor can recognize CN\textsuperscript{−} owing to the H-bonding interaction between the sensor –NH moiety and –CN\textsuperscript{−} anion. Enthused by this very low detection limit (0.15 ppm), a portable RGB-based colorimetric sensory device has also been developed, which was proficient to coherently differentiating the safe and unsafe levels of CN\textsuperscript{−} in a solution. Moreover, the spontaneity of the sensing phenomenon was further asserted by the ITC experiment. The sensing ability of the DTPH--CN\textsuperscript{−} adducts toward the noxious Hg\textsuperscript{2+} among several others competitive metal ions further impelled to formulate a logic gate mimic ensemble. In addition, DTPH also revealed high efficiency to detect CN\textsuperscript{−} in the bitter almond seed, which made it a proficient CN\textsuperscript{−} selective chemosensor in the field of real-world application. Moreover, the efficacious CN\textsuperscript{−} sensing ability of DTPH in FBS made it feasible to detect CN\textsuperscript{−} in real biotic samples. Additionally, the excellent intracellular CN\textsuperscript{−} detection efficiency of DTPH made it a noteworthy contender in the realm of bio-sensing applications.

**EXPERIMENTAL SECTION**

**Materials and Method.** All of the preparatory materials (chemicals and solvents) were commercially obtainable and procured from Sigma-Aldrich. The analytical grade reagents were used devoid of any further refinement. All TBA salts of anions and the metal ion salts were also purchased from Sigma-Aldrich. All of the preparatory materials were used devoid of any further refinement. All TBA salts of anions and the metal ion salts were also purchased from Sigma-Aldrich and used deprived of any decontamination.

**Apparatus.** The ESI-MS was recorded in Advion’s CMS Expression (having serial number: 3013-0140) compact mass spectrometer. The IR spectra were effectuated in PerkinElmer FT-IR Spectrum 100 spectrophotometer. \textsuperscript{1}H NMR spectra were carried out in Bruker 400 MHz spectrometer. The SCXRD analysis was performed by using Bruker D8 Venture along with a photon detector. CARY60 and PerkinElmer LS-4S spectrophotometer were used to perform the adsorption and fluorescence experiments. Photostability and kinetic studies were accomplished in UV–Vis Cary-100 System having serial number EL08063728. Cyclic voltammetry studies were executed in the CH instrument. The ITC experiment was performed in Malvern Instruments (model VP-ITC). The fluorescence microscopy images were captured by using Nikon make confocal laser scanning microscopy (Model: Al(R)).

**Synthesis of DTPH and Characterization.** The synthesis of DTPH was carried out entirely in the inert atmosphere. At first, 2,6-dichloro-4-(trifluoromethyl) phenyl hydrazine (2 mM) was dissolved in 50 mL dry dichloromethane (DCM). After complete dissolution, 2 mM triphosgene was added to the solution along with the subsequent addition of a saturated NaHCO\textsubscript{3} solution. The mixture was then kept under stirring and after constant shaking for around 12 h the white colored product was obtained by using a separating funnel, and it was then washed by using distilled water (Scheme S1; Supporting Information). Finally the solid compound was washed and purified by hexane. Single crystals are obtained by evaporating DCM and hexane mixture after 3 days. The constitution of the compound was confirmed by ESI-MS, IR, \textsuperscript{1}H NMR, and single-crystal X-ray studies (Figures S1–S3; Supporting Information). Yield: 390 mg, 76%; mp 209 °C; (m/z) calc, S13.94 for C\textsubscript{14}H\textsubscript{12}Cl\textsubscript{4}F\textsubscript{6}N\textsubscript{4}O; found, 514.5 \{DTPH + H\textsuperscript{+}\}; \textsuperscript{1}H NMR (400 MHz, DMSO-\textsubscript{d\textsubscript{6}}, Me\textsubscript{4}Si): δ 8.56 (s, 2H), 7.7(d, 4Ar-H), 7.747 (s, 2H). The DTPH--CN\textsuperscript{−} adduct was also confirmed from mass spectroscopy (Figure S18, Supporting Information).

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04311.

Hydrazine-functionalized CN\textsuperscript{−} sensors: P.B. contents include characterizations of the chemosensor and its sensing responses toward CN\textsuperscript{−}; and fabrication of logic gate and geometry optimized upshots (PDF)

Crystallographic data 1944265 (CIF)

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