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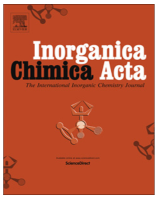

Research paper

Highly selective hydrazone based reversible colorimetric chemosensors for expeditious detection of CN⁻ in aqueous media

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ABSTRACT

Herein we have described the design and syntheses of two novel hydrazone based N, O donor Schiff-base colorimetric sensors $\mathbf{L_1}$ and $\mathbf{L_2}$ for selective sensing of cyanide ions in 2:1 CH_3CN-H_2O mixture. $\mathbf{L_1}$ and $\mathbf{L_2}$ have been characterized by ^1H NMR, IR spectroscopy, HRMS spectrometry and elemental analyses. Interactions of $\mathbf{L_1}$ and $\mathbf{L_2}$ with CN^- provide remarkable color change from yellow to red (for $\mathbf{L_1}$) and yellow to pink (for $\mathbf{L_2}$) along with change in the absorption maxima, enabling naked-eye sensing of CN^- ion, without use of any expensive equipment. From the job's plot analyses, HRMS spectral studies and ^1H NMR analyses, 1:1 binding stoichiometry of chemosensor $\mathbf{L_1}$ and 1:2 binding stoichiometry of chemosensor $\mathbf{L_2}$ towards cyanide ion have been confirmed. The detection limits reach up to 1.3 μM for $\mathbf{L_1}$ and 1.0 μM for $\mathbf{L_2}$ which are lower than the maximum permissible level of CN^- in drinking water set by WHO. The other competitive anions (OAc^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, NO_2^-, NO_3^-, HSO_4^-, N_3^-, CO_3^{2-}, PO_4^{3-}, S^{2-}, and BO_3^{3-}) showed very negligible interference for detection of cyanide at that concentration level. The sensing mechanism has further been confirmed by DFT studies. Both the chemosensors $\mathbf{L_1}$ and $\mathbf{L_2}$ have been successfully applied for the determination of CN^- ions in real water samples and simulated urine samples.

1. Introduction

The development of chemosensors for anions has become a subject of intense research interest, because anions play important roles in a wide range of environmental, clinical, chemical, and biological applications [1–5]. Among the various anions, cyanide is one of the maximum concerned, because it is one of the most rapidly acting and powerful poisons. Its toxicity results from its propensity to bind to the iron in cytochrome *c* oxidase, interfering with electron transport and resulting in hypoxia [6–11]. Cyanide could be absorbed through the lungs, gastrointestinal tract and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death [12–14]. In spite of its toxicity, its application in various areas as raw material for synthetic fibers, resins, herbicides, and the gold extraction process is unavoidable [15–17], which releases cyanide into the environment as a toxic contaminant. Thus, there is a need for an effective sensing system to monitor cyanide concentration from pollutant sources. Among various approaches such as fluorescence techniques and electrochemical methods for the detection of cyanide, the most attractive approach focuses on novel colorimetric cyanide sensors, which allow naked-eye detection of the color change without resorting to the use of expensive instruments [18–21]. Colorimetric materials have advantages such as low cost, a rapid response rate, easy detection and high selectivity [22–26]. Therefore, colorimetric sensors that are capable of recognizing cyanide in an aqueous environment are of current interest.

Hydrazone derivatives form an important class of most widely used organic compounds and have versatile applications in various advanced fields including the ink jet printing [27], pigments [28], photography [29], molecular recognition [30], multidentate ligands [31] and fluorescent materials [32]. These are also found to be significant due to their extensive applications in pharmaceutical and biological activities like anticancer, anti-inflammatory, antibacterial, antifungal, antimalarial, antitubercular activities [33], and potential inhibitor for various enzymes [34]. Hydrazones containing chromophoric group like nitro are having hydrogen donor capability and are reported as good anion receptors [35,36]. The success of hydrazone derivatives is also due to the simplicity of their synthesis, to the many possibilities presented by variation of the diazo compounds and coupling components, the generally high molar extinction coefficient as well as to the good light and wet fastness properties [37]. Although many optical

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sensors for cyanide detection have been reported based on H-bonding interaction [38], nucleophilic addition reaction [39], metal complex displacement approach [40], most of them suffer from various limitations such as lengthy synthetic protocol, severely interference from F^- and AcO^-. In these connections and in continuation to our earlier research [41], we have reported here two novel reversible chromogenic chemosensors $\mathbf{L_1}$ and $\mathbf{L_2}$ containing hydrogen donor for the detection of CN^- in 2:1 CH_3CN-H_2O mixture. Interactions of $\mathbf{L_1}$ and $\mathbf{L_2}$ with CN^- provide remarkable color change from yellow to red (for $\mathbf{L_1}$) and yellow to pink (for $\mathbf{L_2}$).

2. Experimental

2.1. General information

Melting points were determined on an X-4 digital melting-point apparatus and not corrected. UV–Visible spectra were recorded on a Shimadzu UV 1800 spectrophotometer using a 10 mm path length quartz cuvette. ^1H NMR spectra of ligand $\mathbf{L_1}$ and $\mathbf{L_2}$ were recorded on a Bruker Ultra shield 200 using $CDCl_3$ at room temperature and NMR titrations were carried out dissolving $\mathbf{L_1}$ and $\mathbf{L_2}$ in DMSO d^6 and cyanide salts in D_2O. The chemical shifts are reported in δ values (ppm) relative to TMS. High resolution mass (HRMS) spectra were recorded on a Waters mass spectrometer using mixed solvent HPLC methanol and triple distilled water. All the chemicals and metal salts were purchased from Merck and the counter ion was used as nitrate for metal and sodium for anions.

2.2. Synthesis and characterization of the probe $\mathbf{L_1}$

To 25 mL of an anhydrous methanol solution of benzil (0.420 g, 2 mmol), 2,4-(dinitrophenyl)hydrazine (0.396 g, 2 mmol) was added. The resulting pale yellow mixture was refluxed for 6 h, under dry condition. Then it was slowly cooled to room temperature. Yellow crystalline solid separated out, which was filtered *off* and dried in air. Yield, 0.546 g (70%); mp 178 °C Anal. found (calc. for $C_{20}H_{14}N_4O_5$): C, 61.54 (61.53%); H, 3.62 (3.61%); N, 14.35 (14.33%). EI-MS: *m*/*z* 390.10 (M^+, 100%) (Fig. S1). FTIR/cm^{-1} (KBr): 3441(br), 3269(m), 3112 (w), 2926(w), 1657(w) ($>C{=}O$), 1621(vs) ($C{=}N$), 1592(s), 1506(s), 1413(m), 1342(s), 1306(s), 1227(m), 1012(m), 940(w), 840(w), 747(w), 589(w) (Fig. S2). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 11.91 (s, 1H), 9.08 (s,1H), 8.41 (d, 1H), 8.21 (d, 1H), 7.94 (d, 2H), 7.69 (m, 3H), 7.42–7.51 (m, 2H) (Fig. S3). ^{13}C NMR (200 MHz, $CDCl_3$, TMS): δ 194.27, 151.42, 144.62, 139.07, 135.53, 134.57, 130.81, 129.86, 129.43, 129.02, 127.21, 123.75, 123.21, 116.57, 115.25 (Fig. S4). UV–VIS $\lambda_{\mathbf{max}}$/nm (ε/$dm^{\mathbf{3}}$ mol^{-1} cm^{-1})($CH_\mathbf{3}CN$): 374 (45,600).

2.3. Synthesis and characterization of the probe $\mathbf{L_2}$

For the synthesis of the probe $\mathbf{L_2}$, the azo dye 2-(4-nitrophenyl)-diazenyl-2-hydroxybenzaldehyde (**1**) was prepared first by the following way.

The diazonium salts from aniline derivatives were prepared in good yield according to the previously described methods [42] with slight modification. After completion of diazotization reaction, in a second flask, salicylaldehyde was dissolved in water containing sodium hydroxide and sodium carbonate and cooled to 0 °C in an ice bath. The diazonium solution was slowly added to the phenolate solution in basic medium by adjusting the pH at 7.5–8.5 over 30–45 min. The resulting solution was stirred for 1–2 h in an ice bath and then allowed to reach room temperature to obtain a precipitate. The precipitate was collected and was washed several times with cool water after acidified of the solution (pH = 5.5–6.5) by addition of diluted HCl. The precipitate was finally recrystallized in MeOH/H_2O to obtain the pure product.

To 25 mL of an anhydrous methanol solution of benzildihydrazone (0.238 g, 1 mmol), the azo dye, 2-(4-nitrophenyl)diazenyl-2-hydroxybenzaldehyde (**1**, 0.542 g, 2 mmol) was added. The resulting yellow mixture was refluxed for 6 h, under dry condition. Then it was slowly cooled to room temperature. Yellow crystalline solid separated out, which was filtered *off* and dried in air. Yield, 0.543 g (73%); mp > 200 °C Anal. found (calc. for $C_{40}H_{28}N_{10}O_6$): C, 64.50 (64.52%); H, 3.75 (3.79%); N, 18.85 (18.81%). HRMS: 744.22 (M, 100%) (Fig. S5). FTIR/cm^{-1} (KBr): 3444(br), 3059(w,br), 1614(vs) ($C{=}N$), 1516 (vs), 1317(vs), 1344(m), 1279(m), 1116(m), 860(m), 689(w) (Fig. S6). ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 11.58 (s, 2H) 8.91 (s, 2H), 8.35 (m, 5H), 7.94–8.00 (m, 12H), 7.49 (m, 5H), 6.99 (s, 2H) (Fig. S7). UV–VIS: λ_{max}/nm(ε/$dm^{\mathbf{3}}$ mol^{-1} cm^{-1})($CH_\mathbf{3}CN$): 314 (37 800); 374 (44 450).

2.4. UV–Vis titrations

The chemosensors $\mathbf{L_1}$ (3.90 mg, 0.01 mmol) and $\mathbf{L_2}$ (7.44 mg, 0.01 mmol) were dissolved in acetonitrile-water solvent mixture (2:1, v/v, 10 mL) and 30 μL of them were diluted to 3 mL with the solvent mixture to make a final concentration of 10 μM. Sodium cyanide (0.1 mmol) was dissolved in 10 mL of triple distilled water and 1.5–90 μL of the anions solution (10 mM) were transferred to the solutions of $\mathbf{L_1}$ and $\mathbf{L_2}$ (10 μM) prepared above. After mixing them for a few seconds, UV–Vis spectra were obtained at room temperature.

2.5. Colorimetric test kit

Chemosensors $\mathbf{L_1}$ (3.90 mg, 0.01 mmol) and $\mathbf{L_2}$ (7.44 mg, 0.01 mmol) were dissolved in acetonitrile-water solvent mixture (2:1, v/v) (10 mL) to get 1 mM solution. Test kits were prepared by immersing filter-papers into these solutions (1 mM), and then dried in air to get rid of the solvent. CN^- and different anions (OAc^-, F^-, Cl^-, Br^-, I^-, $H_2PO_4^-$, NO_2^-, NO_3^-, HSO_4^-, N_3^-, CO_3^{2-}, PO_4^{3-}, S^{2-}, and BO_3^{3-}; 0.001 mmol) were dissolved in acetonitrile-water solvent mixture (2:1, v/v, 10 mL) to prepare 0.1 mM solution. The test kits prepared above were dipped into above-mentioned acetonitrile-water mixture (2:1, v/v) of cyanide ion and other anions and then dried at room temperature.

2.6. Computational details

The GAUSSIAN-09 Revision C.01 program package was used for all calculations [43]. The gas phase geometries of the compound was fully optimized without any symmetry restrictions in singlet ground state with the gradient-corrected DFT level coupled with the hybrid exchange-correlation functional that uses Coulomb-attenuating method B3LYP [44]. Basis set 6-31++G was found to be suitable for the whole molecule.

3. Results and discussion

3.1. Synthesis and structures of $\mathbf{L_1}$ and $\mathbf{L_2}$

Receptor $\mathbf{L_1}$ was obtained in good yield (70%) by the 1:1 condensation reaction of benzil and 2,4-(dinitrophenyl) hydrazone in anhydrous methanol, whereas the receptor $\mathbf{L_2}$ was prepared by the 1:2 condensation reaction of the azo dye 2-(4-nitrophenyl)diazenyl-2-hydroxybenzaldehyde and benzildihydrazone. Both the probes were characterized by ^1H NMR, IR and HRMS spectrometry and elemental analyses. Optimized geometries and surface plots of