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A multifunctional colorimetric chemosensor for cyanide and copper(II) ions

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ABSTRACT

We designed and synthesized a new asymmetric chemosensor **1** based on the combination of salicylaldehyde moiety and 2-amino-3-(((E)-(8-hydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9yl)methylene)amino)maleonitrile followed by the condensation reaction of julolidine and 2,3-diaminomaleonitrile. The sensor **1** exhibited definite color changes from violet to pale yellow for CN^- and Cu^{2+} separately in different solvent systems. The phenomena possibly originated from blue shift generated by the intramolecular charge transfer (ICT) transition. The complex formations were proposed to be in 1:1 ratio, based on Job plot, ^1H NMR titration and ESI-mass spectrometry analysis. Furthermore, the multifunctional colorimetric sensing ability of **1** was theoretically explained by DFT and TDDFT calculations.

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1. Introduction

Anions are ubiquitous in nature and are involved in biological processes, in industrial and agricultural pollutions [1]. Hence, development of systems that can selectively and easily detect anions has received considerable attention in recent decades [2]. Among the various anions, cyanide is one of the primary concerns, because it is known as 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 [3–11]. Cyanide could be absorbed through lungs, gastrointestinal track and skin, leading to vomiting, convulsion, loss of consciousness, and eventual death [12–14]. Despite its toxicity, cyanide ions are widely used as raw materials or auxiliaries in the production of nylon, resins, herbicides, and in the extraction of gold [15,16], which release cyanide into the environment as a toxic contaminant. Thus, there is a need for an efficient sensing system to monitor cyanide concentration in the sources of contamination.

Recognition of heavy and transition metal ions by chemosensors has received considerable attention not only because of the important functions of heavy and transition metal ions, but also due to their potential toxicity toward the environment and biological systems [17,18]. Copper ion (Cu^{2+}) plays a key role in many physiological processes including gene expression and protein functioning [19], and is also required by human nervous system [20]. Indeed, copper homeostasis is strongly controlled by factors, including copper transport proteins and chaperones [21]. Thus, daily ingestion of copper is indispensable for our good health [22]. However, unregulated Cu(II) can cause many problems. Excess intake of Cu^{2+} causes disorders associated with neurodegenerative diseases including Alzheimer's, Parkinson's, Menke's, Wilson's, and prion diseases in human [23–25]. On the other hand, copper deficiency is associated with myelopathy [26]. Copper is also a significant metal pollutant due to its widespread use in life science, medicine, chemistry and biotechnology. The toxicity of copper ion has a harmful effect on microorganisms even at submicromolar concentration [27]. Therefore, the design and synthesis of highly sensitive and selective chemosensors for Cu^{2+} are still a great demand.

Among various approaches, such as fluorescence techniques and electrochemical methods for the detection of cyanide and copper ion, the most attractive approach focuses on novel colorimetric sensors, which allow naked-eye detection of the color change without resorting to the use of expensive instruments [28–31]. Colorimetric materials have certain advantages, such as low cost, rapid response

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rate, easy method and high selectivity [32–36]. Therefore, colorimetric sensors that are capable of recognizing both CN^- and Cu^{2+} in aqueous environment await development.

In this work, a new multi-functional chemosensor **1** was developed, which could selectively detect CN^- and Cu^{2+} based on the distinct color changes among a series of ions. Our strategy was based on the fact that 2,3-diaminomaleonitrile has a well-known unique electronic properties due to an intramolecular charge transfer (ICT) [37]. Therefore, the new asymmetric chemosensor **1** was designed and synthesized based on the combination of salicylaldehyde moiety and 2-amino-3-(((E)-(8-hydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9yl)methylene)amino) maleonitrile followed by the condensation reaction of julolidine and 2,3-diaminomaleonitrile. The resulting sensor **1** can detect CN^- by color change from violet to pale yellow via the 'naked-eye' with high selectivity in DMSO/bis-tris buffer (9:1, v/v). It also showed a colorimetric response toward Cu^{2+}, while there was no change in presence of other metal ions.

2. Experimental

2.1. General information

All the solvents and reagents (analytical and spectroscopic grade) were purchased from Sigma–Aldrich. ^1H and ^{13}C NMR spectra were recorded on a Varian 400 MHz and 100 MHz spectrometer and chemical shifts are recorded in ppm. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQ^{TM} Advantage MAX quadrupole ion trap instrument by infusing samples directly into the source using a manual method. The spray voltage was set at 4.2 kV, and the capillary temperature was set at 80 °C. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Elemental analysis for carbon, nitrogen, and hydrogen was carried out using a Flash EA 1112 elemental analyzer (thermo) at the Organic Chemistry search Center of Sogang University, Korea.

2.2. Synthesis of 2-amino-3-(((E)-(8-hydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9yl)methylene)amino)maleonitrile

2,3-Diaminomaleonitrile (0.11 g, 1 mmol) and 8-hydroxyjulolidine-9-carboxaldehyde (0.23 g, 1 mmol) were dissolved in 5 mL of ethanol. Then, three drops of hydrochloric acid was added into the reaction mixture, which was stirred for 3 h at room temperature. The brown powder was produced. The brown solid was collected by filtration, washed with diethyl ether and air-dried. Yield: 80%. ^1H NMR (400 MHz, DMSO-d_6) δ 11.95 (s, 1H), 8.24 (s, 1H), 6.77 (s, 1H), 4.48 (s, 2H), 3.30 (m, 4H), 2.68 (t, J = 8 Hz, 4H), 1.95 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.28, 155.89, 147.13, 130.42, 121.78, 115.30, 114.25, 113.52, 107.53, 105.17, 104.34, 49.43, 48.19, 26.49, 21.22, 20.33, 19.89 ppm. ESI-MS m/z $[M-H^+]^-$: calcd, 306.14; found, 306.20.

2.3. Synthesis of receptor *1*

2-Amino-3-(((E)-(8-hydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido [3,2,1-ij]quinolin-9yl)methylene)amino)maleonitrile (0.31 g, 1 mmol) and salicylaldehyde (0.11 mL, 1 mmol) were dissolved in 5 mL of acetonitrile. Two drops of H_3PO_4 were added to the reaction solution and it was stirred for 12 h at room temperature until a dark green precipitate appeared. The resulting precipitate was filtered and washed twice with CH_3CN. The yield: 0.16 g (39.0%). ^1H NMR ($CDCl_3$, 400 MHz); δ 12.90 (s, 1H), 12.36 (s, 1H), 8.71 (s, 1H), 8.40 (s, 1H), 7.45 (m, 2H), 7.11 (d, J = 8.0 Hz, 1H), 6.98 (t, J = 8.0 Hz, 1H), 6.81 (s, 1H), 3.36 (m, 4H), 2.82 (t, J = 6.4 Hz, 2H), 2.70 (t, J = 6.0 Hz, 2H), 1.97 (m, 4H). ESI-MS m/z $[M-H^+]^-$: calcd, 410.16; found, 410.07. Anal. Calcd. for $C_{24}H_{21}N_5O_2$ (411.17): C, 70.06; H, 5.14; N, 17.02. Found: C, 69.78; H, 5.27; N, 17.43%.

2.4. UV–vis titrations

For CN^-, **1** (1.2 mg, 0.003 mmol) was dissolved in DMSO (1 mL) and 10 μL (3 mM) of it were diluted to 2.99 mL with DMSO/bis-tris buffer (9:1, v/v) to make a final concentration of 10 μM. Tetraethylammonium (TEA) cyanide (0.03 mmol) was dissolved in DMSO (1 mL) and 1–30 μL of the CN^- ion solution (30 mM) were transferred to the solution of **1** (10 μM) prepared above. After mixing them for a few seconds, UV–vis spectra were obtained at room temperature.

For Cu^{2+}, **1** (1.2 mg, 0.003 mmol) was dissolved in CH_3CN (1 mL) and 10 μL (3 mM) of it were diluted to 2.99 mL with CH_3CN to make a final concentration of 10 μM. $Cu(NO_3)_2$ (0.03 mmol) was dissolved in CH_3CN (1 mL) and 1–16 μL of the Cu^{2+} ion solution (30 mM) were transferred to the solution of **1** (10 μM) prepared above. After mixing them for a few seconds, UV–vis spectra were obtained at room temperature.

2.5. Job plot measurements

For CN^-, **1** (1.2 mg, 0.003 mmol) and TEACN (0.5 mg, 0.003 mmol) were dissolved in DMSO (1 mL), respectively. 0.10 mL of the receptor **1** solution were diluted to 29.90 mL of DMSO/bis-tris buffer (9:1, v/v) to make the concentration of 10 μM. The CN^- solution was diluted in the same way. 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5 and 0 mL of the receptor **1** solution were taken and transferred to vials. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the CN^- ion were added to each receptor solution separately. Each vial had a total volume of 5 mL. After shaking the vials for a few minutes, UV–vis spectra were taken at room temperature.

For Cu^{2+}, **1** (1.2 mg, 0.003 mmol) and $Cu(NO_3)_2$ (0.7 mg, 0.003 mmol) were dissolved in CH_3CN (1 mL), respectively. 0.10 mL of the receptor **1** solution were diluted to 29.90 mL of CH_3CN to make the concentration of 10 μM. The $Cu(NO_3)_2$ solution was diluted in the same way. 5, 4.5, 4, 3.5, 3, 2.5, 2, 1.5, 1, 0.5 and 0 mL of the receptor **1** solution were taken and transferred to vials. 0, 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 and 5 mL of the Cu^{2+} ion were added to each receptor solution separately. Each vial had a total volume of 5 mL. After shaking the vials for a few minutes, UV–vis spectra were taken at room temperature.

2.6. Competition with other metal ions or anions

For CN^-, **1** (1.2 mg, 0.003 mmol) was dissolved in DMSO (1 mL) and 10 μL of this solution (3 mM) were diluted to 2.99 mL with DMSO/bis-tris buffer (9:1, v/v) to make the final concentration of 10 μM. Stock solutions (30 mM) of the tetraethylammonium salts of F^-, CN^-, Cl^-, Br^- and I^- and the tetrabutylammonium salts of AcO^-, $H_2PO_4^-$, BzO^-, N_3^- and SCN^- anions were prepared in DMSO. 30 μL of each anion solution (30 mM) were taken and added to 2.96 mL of the solution of receptor **1** (10 μM) to give 30 equiv. of anions. Then, 30 μL of TEACN solution (30 mM) were added to the mixed solution of each anion and **1** to make 30 equiv. After mixing them for a few seconds, UV–vis spectra were obtained at room temperature.

For Cu^{2+}, **1** (1.2 mg, 0.003 mmol) was dissolved in CH_3CN (1 mL) and 10 μL of this solution (3 mM) were diluted with 2.99 mL of CH_3CN to make the final concentration of 10 μM. MNO_3 (M = Na, K, Ag, 0.02 mmol) or $M(NO_3)_2$ (M = Mn, Co, Ni, Cu, Zn, Cd, Mg, Ca, Hg, Pb, 0.02 mmol) or $M(NO_3)_3$ (M = Fe, Cr, Al, Ga, In, 0.02 mmol) or $M(ClO_3)_2$ (M = Fe, 0.02 mmol) were dissolved in DMSO (1 mL). 22.5 μL of each metal solution (20 mM) were taken and added to 3 mL of the solution of receptor **1** (10 μM) to give 15 equiv. of metal

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