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A single chemosensor for the detection of dual analytes Cu^{2+} and S^{2-} in aqueous media

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A multifunctional colorimetric chemosensor **1**, *N*-(2-((2,4-dinitrophenyl)amino)phenyl)-2-((2-hydroxyethyl)amino)acetamide was synthesized and used to sense Cu^{2+} and S^{2-} in aqueous solution. The sensor **1** showed highly selective colorimetric responses to Cu^{2+} and S^{2-} by immediately changing its color from pale yellow to light green and pink, respectively, without any interference from other metal ions and anions. Especially, **1** can detect Cu^{2+} (10.1 μM) below the guideline (31.5 μM) of WHO. Moreover, the sensor **1** could be used to quantify Cu^{2+} ion in water samples. The sensing mechanism of Cu^{2+} by **1** were proposed to be a metal-to-ligand charge-transfer (MLCT) with the experimental results and theoretical calculations, and that of S^{2-} by **1** proposed to be a deprotonation process.

1. Introduction

The design of artificial synthetic probes that can selectively recognize metal ions, anions and neutral species in chemical, clinical, environmental, and biological samples has gained considerable notice of researcher worldwide.[1–4]

Copper, the third most plentiful essential trace element found in the human physiology and one of the foremost metals known to humans, is indispensable for carrying out several necessary processes both in the plants and animals.[5,6] However, copper in excessive amounts could exhibit toxicity by causing oxidative stress and disorders associated with neurodegenerative diseases including Menkes, Wilson's, Parkinson's, Alzheimer's, and prion diseases.[7–16] In recent years, copper has been also suspected to cause kidney and liver damage.[17,18] Based on these reports, the World Health Organization (WHO) has set the maximum allowable level of copper in drinking water at 31.5 μM.[19] Therefore, the development of copper probes with high sensitivity and selectivity capable of rapidly monitoring Cu^{2+} has attracted considerable attention and is in high demand.

As a member of the reactive sulfur species family, hydrogen sulfide (H_2S) has drawn much attention due to its effects on environmental toxins and poisons for centuries.[20] It is largely generated in coal and natural gas processing, petroleum industries, biogas production, automobile tail gas, and sewage treatment plants.[21,22] On the other hand, several studies have shown that H_2S participate in many physiological processes, such as angiogenesis, vasodilation, regulation of inflammation, neuromodulation, and apoptosis.[23–26] In addition, it has also proved that abnormal H_2S production is linked to human diseases such as Alzheimer's disease, Down's syndrome, hypertension, and liver cirrhosis.[27–30] Therefore, the quantitative detection of H_2S is of great significance for both environmental and biological systems.[31]

Several methods, such as electrochemical, fluorescence techniques, inductively coupled plasma emission spectroscopy, inductively coupled plasma mass spectroscopy and atomic absorption spectroscopy have been used to detect metal ions and anions.[32–40] Most of these methods require intricate and expensive procedures, while colorimetric methods can simply and conveniently monitor target ions in the visible range with high sensitivity, low cost, simplicity, and rapidity.[41–45]

Dinitrobenzene with an electron acceptor part ($-NO_2$ group) has been frequently used in recent years as the chromogenic dye in chemosensors.[46–48] In addition, the chromogenic dye with NH_2CH_2OH moiety is usually water-soluble. Therefore, we designed and synthesized a new receptor **1**, based on the combination of the dinitrobenzene and the aminoethanol moieties, which was expected to endow it with a unique photophysical properties and water solubility.

Herein, we report on a new receptor **1**, which was synthesized by coupling 2-chloro-*N*-(2-((2,4-dinitrophenyl)amino)phenyl) acetamide with aminoethanol (Scheme 1). The receptor **1** detected

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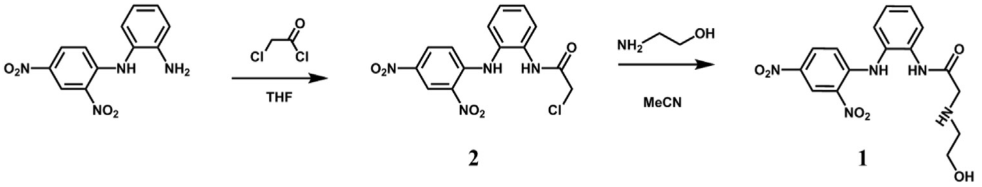

Scheme 1. Synthetic procedure of **1**.

Cu^{2+} by color change from pale yellow to light green and S^{2-} from pale yellow to pink in aqueous solution. The detection mechanisms were proposed for Cu^{2+} with metal-to-ligand charge-transfer (MLCT) and for S^{2-} with the deprotonation process.

2. Experimental

2.1. General information

All the solvents and reagents (analytical grade and spectroscopic grade) were obtained from Sigma–Aldrich and used as received. N^1-(2,4-Dinitrophenyl)benzene-1,2-diamine was synthesized according to the literature method.[49] ^1H NMR and ^{13}C NMR spectra were recorded on a Varian 400 and 100 MHz spectrometer. Chemical shifts (δ) were reported in ppm, relative to tetramethylsilane $Si(CH_3)_4$. Absorption spectra were recorded at room temperature using a Perkin Elmer model Lambda 25 UV/Vis spectrometer. Electrospray ionization mass spectra (ESI-mass) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using a Vario micro cube elemental analyzer (ELEMENTAR) in laboratory center of Seoul National University of Science and Technology, Korea.

2.2. Synthesis of 2-chloro-*N*-(2-((2,4-dinitrophenyl)amino)phenyl)acetamide (2)

The N^1-(2,4-dinitrophenyl)benzene-1,2-diamine (0.27 g, 1 mmol) and 2-chloroacetylchloride (0.16 mL, 2 mmol) were dissolved in 5 mL of tetrahydrofuran. Then, this solution was stirred for 1 h at room temperature. The yellow powder produced was filtered, washed using ethanol and diethyl ether, and air-dried. The yield: 0.28 g (80%, solid) and mp=100–102 °C. IR (KBr): (cm^{-1})= 3284(m), 3054(w), 1658(m), 1558(m), 1496(s), 1420(w), 1334(s), 1131(m), 1062(w).[†] ^1H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 9.90 (s, 1H), 8.91 (d, J=4 Hz, 1H), 8.21 (d, J=8 Hz, 1H), 7.74 (d, J=8 Hz, 1H), 7.47 (m, J=8 Hz, 2H), 7.38 (t, J=8 Hz, 1H), 6.77 (d, J=8 Hz, 1H), 4.20 (s, 2H) ppm. ^{13}C NMR (100 MHz, DMSO-d_6) δ 165.9, 147.4, 136.9, 133.9, 131.8, 130.9, 130.3, 128.5, 128.5, 126.9, 125.6, 123.6, 117.1, 43.3 ppm.[‡] The ^{13}C NMR spectrum of **2** was well consistent with that obtained from theoretical expectation.[§]

2.3. Synthesis of *N*-(2-((2,4-dinitrophenyl)amino)phenyl)-2-((2-hydroxyethyl)amino)acetamide (1)

The **2** (0.35 g, 1 mmol) and ethanolamine (0.09 mL, 1.5 mmol) were dissolved in 5 mL of acetonitrile. Then, triethylamine (0.14 mL, 1 mmol) was added into the reaction mixture, which was stirred for 5 d at room temperature. The solvent was removed under reduced pressure to obtain orange oil, which was purified by silica gel column chromatography (9:1 v/v $CHCl_3/CH_3OH$). The yield: 0.129 g (34%, oil) and IR (KBr): (cm^{-1})=3252(m), 3104(w), 2923(m), 1673(m), 1585(s), 1505(s), 1420(m), 1329(s), 1270(m), 1129(m).[†] ^1H NMR (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 8.90 (d, J=4 Hz, 1H), 8.20 (d, J=8 Hz, 1H), 8.00 (d, J=8 Hz, 1H), 7.42 (m, J=8 Hz, 2H), 7.29 (t, J=8 Hz, 1H), 6.69 (d, J=8 Hz, 1H), 4.43 (t, J=8 Hz, 1H), 3.22 (m, J=8 Hz, 2H), 3.19 (s, 2H), 2.37 (t, J=8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 171.1, 147.5, 136.9, 134.8, 131.6, 130.5, 129.4, 128.8, 128.6, 125.8, 123.7, 123.5, 117.1, 60.5, 52.8, 52.0 ppm.[‡] ^1H NMR spectrum of **1** was well consistent with that obtained from theoretical expectation.[¶] ESI-MS m/z $[M+H^+]^+$: calcd, 376.12; found, 376.13. Elemental Anal. Calcd (%) for $C_{16}H_{17}N_5O_6$: C, 51.20; H, 4.57; N, 18.66; Found: C, 51.14; H, 4.43; N, 18.27.

2.4. UV–vis titration

For Cu^{2+}; receptor **1** (3.75 mg, 0.01 mmol) was dissolved in dimethylsulfoxide (DMSO, 1 mL) and 9 μL of the receptor **1** (10 mM) was diluted to 2.991 mL of bis–tris buffer/DMSO (7/3, v/v) to make the final concentration of 30 μM. $Cu(NO_3)_2\cdot 2.5H_2O$ (2.4 mg, 0.01 mmol) was dissolved in DMSO (1 mL). 0–81 μL of the $Cu(NO_3)_2$ solution (10 mM) was transferred to the receptor **1** solution (30 μM) prepared above. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

For S^{2-}; receptor **1** (3.75 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 9 μL of the receptor **1** (10 mM) was diluted to 2.991 mL of bis–tris buffer/DMSO (3/2, v/v) to make the final concentration of 30 μM. Sodium sulfide nonahydrate (24.01 mg, 0.1 mmol) was dissolved in bis–tris buffer (1 mL). 0–130.5 μL of the S^{2-} solution (100 mM) was transferred to the receptor **1** solution (30 μM) prepared above. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

2.5. Job plot measurement

For Cu^{2+}; receptor **1** (3.75 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 300 μL of the receptor **1** (10 mM) was diluted to 29.7 mL of bis–tris buffer/DMSO (7:3, v/v) to make the final concentration of 100 μM. $Cu(NO_3)_2\cdot 2.5H_2O$ (2.4 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 300 μL of the Cu^{2+} solution (10 mM) was diluted to 29.7 mL of bis–tris buffer/DMSO (7:3, v/v) to make the final concentration of 100 μM. 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, and 0.5 mL of the **1** solution were taken and transferred to vials. 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 mL of the Cu^{2+} solution were added to solutions of **1** prepared above. Each vial had a total volume of 5 mL. After shaking the vials for a few seconds, UV–vis spectra were taken at room temperature.

For S^{2-}; receptor **1** (3.75 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 300 μL of the receptor **1** (10 mM) was diluted to 29.7 mL

[†] We provided physical state, melting point, IR and the yield of compounds **1** and **2** in Sections 2.2 and 2.3.

[‡] We provided the J values for multiplets in ^1H NMR and corrected the digit of ^{13}C NMR in Sections 2.2 and 2.3.

[§] The ^{13}C NMR spectrum of **2** was satisfied with its the molecular structure. Therefore, we added some comments on it in Section 2.2.

[¶] The ^1H NMR spectrum of **1** was satisfied with its the molecular structure. Therefore, we added some comments on it in Section 2.3.

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