Sensors and Actuators B 202 (2014) 645–655

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

A single chemosensor for multiple target anions: The simultaneous detection of CN^- and OAc^- in aqueous media

Ga Rim You[a,b], Gyeong Jin Park[a,b], Seul Ah Lee[a,b], Ye Won Choi[a,b], Yong Sung Kim[a,b], Jae Jun Lee[a,b], Cheal Kim[a,b,*]

[a] Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea
[b] Department of Interdisciplinary Bio IT Materials, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form 19 May 2014
Accepted 28 May 2014
Available online 5 June 2014

Keywords:
Cyanide
Acetate
Naked-eye detection
Colorimetric
Fluorimetric

ABSTRACT

A multifunctional fluorescent and colorimetric chemosensor **1** (*Z*)-1-((benzo[*d*]thiazol-2-ylimino)methyl)naphthalen-2-ol for the detection of both CN^- and OAc^- in aqueous solution has been developed. This sensor could simultaneously detect two anions through fluorogenic (CN^-) and chromogenic (CN^- and OAc^-) methods. The sensor could function as a "turn-on" fluorescence receptor only to CN^-. In addition, the sensor displayed an obvious color change from yellow to colorless upon selective binding with CN^- through a nucleophilic addition mechanism. Moreover, the sensor also showed color change from yellow to orange upon deprotonation with OAc^-. This is the first report that sensor **1** is able to detect simultaneously both CN^- and OAc^- by two different detection modes.

1. Introduction

Anion recognition is an area of growing interest in supramolecular chemistry [1–9], due to the importance of several anions in biological, environmental and chemical processes. Among various anions, acetate and cyanide have been intensively studied owing to their important roles in our life.

Cyanide is one of the most concerned, because it is known as one of the most rapidly acting and powerful poisons. For instance, cyanide can binds heme cofactors to inhibit the process of cellular respiration in mammals [10–13]. Also, even very small amounts of the cyanide cause diseases of the vascular, cardiac, visual, endocrine, central nervous and metabolic systems [14]. In spite of its extreme toxicity, cyanide is used in many industries such as gold mining, electroplating, metallurgy, and polymer production such as nitriles, nylon, and acrylic plastics which produce nearly 140,000 tons of cyanide per year worldwide [15–19].

Acetate ions also play an important role in living organisms such as acetyl coenzyme A. Sodium acetate is involved in biological process like enzyme metabolism and used as main ingredient in some medicines. In addition, the production of acetic acid from fermentation process is the main component present in vinegar used in foods [20–22].

For these reasons, therefore, considerable effort has been devoted to the development of novel methods for the detection of acetate and cyanide in the past decade. For examples, as acetate can form strong hydrogen bonds, various chemosensors containing acidic NH and OH groups have been developed to detect acetate. Meanwhile, the detection of cyanide has been accomplished through various approaches such as transition metals [23–25], boron center [26,27] and CDSe quantum dots [28], hydrogen-bonding interactions [29,30], deprotonation [31], luminescence lifetime measurement [32] and nucleophilic addition reactions [33–38]. Single probes for multiple targets are, recently, being actively considered because of the advantages such as potential cost and analytical time reduction [39,40,30,41–43]. However, analytes sometimes tend to interfere with each other when responding to single molecular sensors in the same signaling channel. Therefore, an ideal single-molecule sensor is able to sense more than one species in different signaling channels, without the interference between analytes [44–51]. Nevertheless, a single molecular sensor which can selectively detect and distinguish more than one

* Corresponding author at: Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-743, Republic of Korea.
Tel.: +82 2 970 6693; fax: +82 2 973 9149.
E-mail addresses: chealkim@seoultech.ac.kr, chealkim@snut.ac.kr, chealkim20@daum.net (C. Kim).

http://dx.doi.org/10.1016/j.snb.2014.05.124
0925-4005/

anionic species through different signaling channels has been still rarely reported.

Herein, we report on development of a single molecular anion sensor **1** based on naphtholic Schiff base bearing an aminobenzothiazole group, which can selectively detect acetate and cyanide via colorimetric and fluorescent channels, without the interference between the two analytes. Mechanistic studies demonstrate that two different signaling mechanisms operate for the detections of acetate and cyanide.

2. Experimental

2.1. Materials and instrumentation

All the solvents and reagents (analytical and spectroscopic grade) were obtained from Sigma Aldrich and used as received. NMR spectra were recorded using a Varian 400 spectrometer. Chemical shifts (δ) were reported in ppm, relative to tetramethylsilane $Si(CH_3)_4$. Electrospray ionization mass spectra (ESI-MS) were collected on a Thermo Finnigan (San Jose, CA, USA) LCQTM Advantage MAX quadrupole ion trap instrument. Absorption spectra were recorded at 25 °C using a Perkin Elmer model Lambda 2S UV/Vis spectrometer. Fluorescence measurements were performed on a Perkin Elmer model LS45 fluorescence spectrometer. Elemental analysis for carbon, nitrogen, and hydrogen was carried out using a Flash EA 1112 elemental analyzer (thermo) at the Organic Chemistry Research Center of Sogang University, Korea.

2.2. Synthesis of receptor *1*

A solution of 2-aminobenzothiazole (0.15 g, 1.1 mmol) in absolute ethanol was added to a solution containing 2-hydroxy-1-naphthaldehyde (0.25 g, 1 mmol) in absolute ethanol. Two drops of HCl were added into the reaction solution and it was stirred for 12 h at room temperature. A yellow precipitate was filtered, washed several times with ethanol and dried in vacuum to obtain the pure yellowish solid. Yield: 0.22 g (72.3%). mp = 230–235 °C. IR (cm^{-1}, KBr pellet): 3623 (b, ν_{O-H}), 2160 (w), 2023 (w), 1974 (w), 1605 (w, $\nu_{N=C}$), 1594(w, $\nu_{N=C}$), 1551(m), 1511 (w), 1467 (m, ν_{S-C}), 1426 (m), 1387 (w), 1349 (w), 1313 (m), 1248 (w), 1208 (m), 1144 (s), 1083 (w), 819 (s), 739 (s), 661 (m), 533 (m), ^{1}H NMR (400 MHz, CD_3Cl, 25 °C): δ = 13.71 (s, 1H), 10.16 (s, 1H), 8.31 (d, J = 8.5 Hz, 1H), 8.00 (d, J = 8.1 Hz, 1H), 7.94 (d, J = 9.1 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 7.7 Hz, 1H), 7.50 (t, J = 7.7 Hz, 1H), 7.40 (m, 2H), 7.20 (s, 1H); ^{13}C NMR (400 MHz, DMSO-d_6): 169.89, 165.75, 163.81, 151.192, 138.89, 134.50, 132.02, 129.93, 129.68, 128.42, 127.42, 125.88, 125.10, 123.13, 123.07, 122.56, 120.04, 110.48; ESI-MS m/z ($M-H^+$): calcd, 303.06; found, 303.06; Anal. calcd for $C_{18}H_{12}N_2OS$ (304.37): C, 71.03; H, 3.97; N, 9.20. Found: C, 70.79; H, 3.86; N, 9.57.

2.3. UV–vis titrations

For CN^-; receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (dimethyl sulfoxide, 1 mL) and 3 μL of the receptor **1** (10 mM) were diluted to 2.997 mL of DMSO/bis-tris buffer (8/2, v/v, containing 10 mM bis-tris, pH = 7.0) to make the final concentration of 10 μM. Tetraethylammonium cyanide (165.6 mg, 0.1 mmol) was dissolved in DMSO/bis-tris buffer (8/2, v/v; 1 mL). 0.3–9 μL of the CN^- solution (100 mM) were transferred to the receptor solution (10 μM) prepared above. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

For OAc^-; receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 3 μL of the receptor **1** (10 mM) were diluted to 2.997 mL of DMSO/bis-tris buffer (8/2, v/v) to make the final concentration of 10 μM. Tetrabutylammonium acetate (322.6 mg, 0.1 mmol) was dissolved in DMSO/bis-tris buffer (8/2, v/v; 1 mL). 0.3–14.1 μL of the OAc^- solution (100 mM) were transferred to the receptor solution (10 μM) prepared above. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

2.4. Fluorescence titration

Receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 6 μL of this solution (10 mM) were diluted with 2.994 mL of DMSO/bis-tris buffer (8/2, v/v) to make the final concentration of 20 μM. Tetraethylammonium cyanide (165.6 mg, 0.1 mmol) was dissolved in DMSO (1 mL) and 3–60 μL of this CN^- solution (100 mM) were transferred to the receptor solution (20 μM) prepared above. After mixing them for a few seconds, fluorescence spectra were taken at room temperature.

2.5. Job plot measurement

For CN^-; Receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (1 mL). 15, 13.5, 12, 10.5, 9, 7.5, 6, 4.5, 3, 1.5 and 0 μL of the receptor **1** solution were taken and transferred to vials. Each vial was diluted with DMSO/bis-tris buffer (8/2, v/v) to make a total volume of 2.985 mL. Tetraethylammonium cyanide (1.66 mg, 0.01 mmol) was dissolved in DMSO/bis-tris buffer (8/2, v/v; 1 mL). 0, 1.5, 3, 4.5, 6, 7.5, 9, 10.5, 12, 13.5, and 15 μL of the tetraethylammonium cyanide solution were added to each diluted receptor **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few minutes, UV–vis spectra were taken at room temperature.

For OAc^-; Receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (1 mL). 15, 13.5, 12, 10.5, 9, 7.5, 6, 4.5, 3, 1.5, and 0 μL of the receptor **1** solution were taken and transferred to vials. Each vial was diluted with DMSO/bis-tris buffer (8/2, v/v) to make a total volume of 2.985 mL. Tetrabutylammonium acetate (3.23 mg, 0.01 mmol) was dissolved in DMSO/buffer (8/2, v/v; 1 mL). 0, 1.5, 3, 4.5, 6, 7.5, 9, 10.5, 12, 13.5, and 15 μL of the tetrabutylammonium acetate solution were added to each diluted receptor **1** solution. Each vial had a total volume of 3 mL. After shaking the vials for a few minutes, UV–vis spectra were taken at room temperature.

2.6. Competition with other anions

For CN^-; receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 9 μL of this solution (10 mM) were diluted with 2.976 mL of DMSO/bis-tris buffer (8/2, v/v) to make the final concentration of 30 μM. Tetraethylammonium salts of F^-, Cl^-, Br^-, and I^-, and tetrabutylammonium salts of OAc^- $H_2PO_4^-$, N_3^-, SCN^- and BzO^- (0.1 mmol) were dissolved in DMSO (1 mL). 15 μL of each anion solution (100 mM) were taken and added to 2.985 mL of the solution of receptor **1** (30 μM) to give 17 equiv. of anions. Tetraethylammonium cyanide (165.6 mg, 0.1 mmol) was dissolved in DMSO (1 mL). Then, 15 μL of tetraethylammonium cyanide solution (100 mM) were added into the mixed solution of each anion and **1** to make 17 equiv. After mixing them for a few seconds, UV–vis spectra were taken at room temperature.

For OAc^-; receptor **1** (3.04 mg, 0.01 mmol) was dissolved in DMSO (1 mL) and 9 μL of this solution (10 mM) were diluted with 2.976 mL of DMSO/bis-tris buffer (8/2, v/v) to make the final concentration of 30 μM. Tetraethylammonium salts of F^-, CN^-, Cl^-, Br^-, and I^-, and tetrabutylammonium salts of $H_2PO_4^-$, N_3^-,SCN^- and BzO^- (0.10 mmol) were dissolved in DMSO (1 mL). 15 μL of each anion solution (100 mM) were taken and added to 2.985 mL of the solution of receptor **1** (30 μM) to give 17 equiv. of anions. Tetrabutylammonium acetate (322.6 mg, 0.1 mmol) was dissolved in DMSO (1 mL). Then, 15 μL of tetrabutylammonium acetate solution (100 mM) were added into the mixed solution of each anion