A multi-functional chemosensor for highly selective ratiometric fluorescent detection of silver(I) ion and dual turn-on fluorescent and colorimetric detection of sulfide

Ji Hye Kang, Ju Byeong Chae and Cheal Kim

Department of Fine Chemistry, Seoul National University of Science and Technology, Seoul 139-741, Korea

A multi-functional chemosensor 1 as silver and sulfide detector was synthesized by the combination of octopamine and 4-dimethylaminocinnamaldehyde. Sensor 1 exhibited a ratiometric fluorescence emission for Ag\(^+\) from blue to sky. The binding mode of 1 and Ag\(^+\) turned out to be a 1:1 ratio as determined using Job plot and electrospray ionization (ESI) mass spectral analyses. The sensing mechanism of 1 with silver ion was unravelled by 1H NMR titrations and theoretical calculations. Sensor 1 also discerned sulfide by enhancing fluorescence intensity and changing colour from yellow to colourless in aqueous solution. The sensing properties of 1 toward S\(^2^-\) were investigated by using ESI-mass analysis, Job plot and 1H NMR titrations. Moreover, 1 could be used as a detector for sulfide in a wide pH range.

1. Introduction

To date, many researchers have studied many analytical methods for the detection of various analytes of metal ions and anions such as atomic absorption spectroscopy, surface-enhanced Raman scattering, ion-selective electrodes and inductively coupled plasma mass spectrometry [1–6]. However, these methods have required complicated procedures, operator and great expense [7–11]. In contrast, a chemosensor using fluorescent and colorimetric
responses has many advantages such as rapid signalling time, high selectivity and operational simplicity [12–18]. Therefore, it is worthwhile to design chemosensors for the detection of cations and anions.

Silver(I) is one of frequently used metals in the industrial field like imaging, electronics, pharmacy and photography as well as in real life like jewellery, table cutlery and filters for water purifiers [19,20]. However, superabundance of silver can cause a strong poison to organisms and environments [21,22]. For example, Ag\(^{+}\) which has a strong interaction with amino and sulfhydryl groups can easily form hazardous complexes with nucleic acids, amino acids and so on [23,24]. Therefore, it is an acute environmental pollutant owing to a large consumption of silver [25–27]. These facts led us to consider that it is of importance to determine silver(I) in the surrounding environment.

Sulfide in organisms has been known as an endogenous signalling molecule, which functions in various biological reactions [28,29]. For instance, S\(^{2-}\) can inhibit vascular smooth muscle cell proliferation, regulate apoptosis and interfere with insulin signalling [30,31]. Though sulfide is generated endogenously from l-cysteine, abnormal concentrations of sulfide in bio-systems can lead to serious trouble such as hypertension, diabetes, liver cirrhosis and Down’s syndrome [32–35]. Therefore, development of a sulfide detector has been receiving substantial attention [36,37].

Octopamine is associated with regulations of blood pressure and weight loss, and used as a sympathomimetic drug [38,39]. Thus, it is considered as a bio-friendly molecule. Cinnamaldehyde moiety is known to be a good chromophore and fluorophore which emits in the range of 400–550 nm [40–44]. Thus, we expected that a sensor containing both an octopamine moiety and a cinnamaldehyde one might act as a unique chemosensor.

Herein, we present a novel chemosensor 1 for targeting silver(I) and sulfide with various responses. Sensor 1 could detect Ag\(^{+}\) with red-shifted fluorescent emission from 449 (blue) to 488 nm (sky). The binding structure and mechanism of 1 with Ag\(^{+}\) were explained via Job plot and electrospray ionization (ESI) mass spectral analyses, \(^1\)H NMR titration and theoretical calculations. Moreover, 1 could be applied to sense S\(^{2-}\) with dual methods, which were the fluorescence turn-on and colour change from yellow to colourless. The sensing mechanism of 1 toward sulfide was described by using Job plot, ESI-mass analyses and \(^1\)H NMR titration.

2. Experimental

2.1. Materials and instrumentation

Sigma-Aldrich provided all the reagents of analytical and spectroscopic grade. Absorption spectra and emission spectra were recorded using Lambda L25 UV/Vis and LS45 fluorescence spectrometers (Perkin Elmer), respectively. A Varian spectrometer recorded \(^1\)H and \(^13\)C NMR spectra. ESI mass spectra were measured with a Thermo Finnigan ion trap instrument.

2.2. Synthesis of 1

Octopamine (194 mg) and triethylamine (TEA, 140 µl) were dissolved in 5 ml of methanol (MeOH). Then, 4-dimethylaminocinnamaldehyde (215 mg) was added dropwise into the reaction solution. The reaction mixture was stirred additionally for 1 h until the precipitate appeared. An orange precipitate obtained was filtered, washed three times with ethyl acetate, and dried to obtain the pure orange solid. The yield: 77.6%. \(^1\)H NMR (400 MHz, DMF-\(d_7\), ppm, 25°C): \(\delta\) 9.42 (s, 1H), 8.01 (d, \(J = 8\) Hz, 1H), 7.00 (d, \(J = 16\) Hz, 1H), 7.46 (d, \(J = 8\) Hz, 2H), 6.81 (d, \(J = 8\) Hz, 2H), 7.24 (d, \(J = 8\) Hz, 2H), 6.76 (d, \(J = 8\) Hz, 2H), 6.72 (m, 1H), 5.05 (s, 1H), 4.80 (t, \(J = 8\) Hz, 1H), 3.75 (d, \(J = 12\) Hz, 1H), 3.58 (t, \(J = 12\) Hz, 1H); \(^13\)C NMR (100 MHz, DMSO-\(d_6\), ppm, 25°C): \(\delta\) 164.5, 156.6, 151.3, 142.7, 135.1, 129.0, 127.7, 123.6, 123.4, 115.1, 112.4, 72.5, 69.3. ESI-MS: \(m/z\) calcd for C\(_{19}\)H\(_{22}\)N\(_2\)O\(_2\) + H\(^+\), 311.18; found, 311.28.

2.3. Fluorescence titrations

For Ag\(^{+}\), 1 ml of dimethylformamide (DMF) was used to dissolve 1 (1.6 mg) and 3 µl of 1 (5 mM) was diluted with 2.997 ml of DMF to afford a 5 µM concentration. Amounts of 0.8–10.6 µl of a stock AgNO\(_3\) solution (10 mM) in DMF were transferred to the sensor 1 solution (5 µM) prepared above. After mixing them for 10 s, fluorescence spectra were recorded.

For S\(^{2-}\), 1 ml of DMF was used to dissolve 1 (1.6 mg) and 6 µl of 1 (5 mM) was diluted with 2.994 ml of bis-tris buffer (pH = 7.0, 10 mM) to make a 10 µM concentration. Amounts of 1.5–15.0 µl of a stock Na\(_2\)S
solution (200 mM) in bis-tris buffer were transferred to the sensor 1 solution (10 µM) prepared above. After mixing them for 10 s, fluorescence spectra were recorded.

2.4. UV–visible titrations

For Ag+, 1 ml of DMF was used to dissolve 1 (1.6 mg) and 3 µl of 1 (5 mM) was diluted with 2.997 ml of DMF to make a 5 µM concentration. Amounts of 6.0–78.0 µl of a stock AgNO3 solution (10 mM) in DMF were transferred to the sensor 1 solution (5 µM) prepared above. After mixing them for 10 s, UV–visible spectra were recorded.

For S2−, 1 ml of DMF was used to dissolve 1 (1.6 mg) and 6 µl of 1 (5 mM) was diluted with 2.994 ml of bis-tris buffer (pH = 7.0, 10 mM) to make a 10 µM concentration. Amounts of 1.5–18.0 µl of a stock Na2S solution (200 mM) in bis-tris buffer were transferred to the sensor 1 solution (10 µM) prepared above. After mixing them for 10 s, UV–visible spectra were recorded.

2.5. Job plots

For Ag+, 1 ml of DMF was used to dissolve 1 (1.6 mg) and 180 µl of 1 (5 mM) was diluted with 29.82 ml of DMF to make a 30 µM concentration. Amounts of 2.7–0.3 ml of the 1 solution were taken and transferred to fluorescence cells. 60 µl of a stock Ag+ solution (10 mM) in DMF was diluted with 19.97 ml DMF. 0.3–2.7 ml of the Ag+ solution was added to each 1 solution. After mixing them for 10 s, fluorescence spectra were recorded.

For S2−, 1 ml of DMF was used to dissolve 1 (1.6 mg) and 420 µl of 1 (5 mM) was diluted with 29.58 ml of bis-tris buffer (pH = 7.0, 10 mM) to make a final concentration of 70 µM. Amounts of 2.7–0.3 ml of the 1 solution were taken and transferred to UV cells. 7 µl of a stock S2− solution (200 mM) in bis-tris buffer was diluted with 19.99 ml bis-tris buffer. 0.3–2.7 ml of the S2− solution was added to each 1 solution. After mixing them for 10 s, UV–visible spectra were recorded.

2.6. Competitive experiments

For Ag+, MNO3 (0.1 mmol; M = Na, K) or M(NO3)2 (0.1 mmol; M = Cd, Zn, Fe, Cu, Hg, Ni, Co, Mg, Pb, Mn, Ca, Pd) or M(NO3)3 (0.1 mmol; M = Fe, Al, In, Ga, Cr) or AuCl3 (0.1 mmol) was separately dissolved in DMF (5 ml). 4.5 µl of each metal-ion solution (20 mM) was diluted with 2.988 ml of DMF to give 6 equiv of metal ions. 9.0 µl of a stock Ag+ solution (10 mM) in DMF was taken and added to each metal-ion solution prepared above. Then, 1 ml of DMF was used to dissolve 1 (1.6 mg) and 3 µl of 1 (5 mM) was taken and added to the mixed solution prepared above to make a 5 µM concentration. After mixing them for 10 s, fluorescence spectra were recorded.

For S2−, tetraethylammonium salts (Br−, CN−, Cl−, F−, I−; 1.0 mmol) or tetrabutylammonium salts (BzO−, OAc−, Cl−, SCN−; 1.0 mmol) or sodium salts (Na xX) (X = H2PO4−, NO2−, SO42−, OH−, HSO3−; 1.0 mmol) were separately dissolved in 5 ml of bis-tris buffer. 13.5 µl (or 16.5 µl for colorimetric response) of each anion solution (200 mM) was diluted with 2.967 ml of bis-tris buffer to give 90 equiv (or 110 equiv for colorimetric response) of anions. 13.5 µl (or 16.5 µl for colorimetric response) of 1.5–15.0 µl of a stock S2− solution (200 mM) in bis-tris buffer was taken and added to each anion solution prepared above. Then, 1 ml of DMF was used to dissolve 1 (1.6 mg) and 6 µl of 1 (5 mM) was taken and added to the mixed solution prepared above to make a 10 µM concentration. After mixing them for 10 s, fluorescence and UV–visible spectra were recorded.

2.7. 1H NMR titrations

For Ag+, four NMR tubes of sensor 1 (0.01 mmol) dissolved in DMF-d7 were prepared, and then three different equivalents (1, 2 and 4 equiv) of AgNO3 dissolved in DMF-d7 were taken and added to each solution of sensor 1. After shaking the solutions for 10 s, 1H NMR spectra were recorded.

For S2−, three NMR tubes of sensor 1 (0.01 mmol) dissolved in DMF-d7/D2O (6:1, v/v) were prepared, and then two different equivalents (1 and 2 equiv) of Na2S dissolved in D2O were taken and added to each solution of sensor 1. After shaking the solutions for 10 s, 1H NMR spectra were recorded.

2.8. Theoretical calculations of 1 and 1–Ag+

The density functional theory (DFT) and time-dependent DFT (TD-DFT) methods were used for all theoretical calculations with the Gaussian 03 program [45–47]. The main atoms were applied for 6-31G
Scheme 1. Synthesis of 1.

3. Results and discussion

Sensor 1 was synthesized by combination of octopamine and 4-dimethylaminocinnamaldehyde with 77.6% yield in MeOH (scheme 1). Compound 1 was characterized with analytic methods such as ESI mass analysis and $^1$H and $^{13}$C NMR.

3.1. Fluorescence ratiometric response of 1 toward Ag$^+$

To study the fluorometric sensing abilities of 1, we conducted the selectivity experiment upon addition of 6 equiv of various metal ions such as Al$^{3+}$, In$^{3+}$, Zn$^{2+}$, Ga$^{3+}$, Cd$^{2+}$, Fe$^{2+}$, Fe$^{3+}$, Cu$^{2+}$, Mg$^{2+}$, Cr$^{3+}$, Ag$^+$, Co$^{2+}$, Hg$^{2+}$, Ni$^{2+}$, K$^+$, Na$^+$, Ca$^{2+}$, Pb$^{2+}$, Mn$^{2+}$, Pb$^{2+}$ and Au$^{3+}$ (figure 1). Excitation at 382 nm caused a fluorescence emission of 1 at 449 nm. In the presence of different metal ions, Al$^{3+}$ and Fe$^{3+}$ decreased the fluorescence intensity of 1, and Cu$^{2+}$, Ga$^{3+}$, In$^{3+}$ and Hg$^{2+}$ quenched it. Only Ag$^+$ showed a bathochromic shift from 449 to 488 nm. There were no or little spectral changes with the other metal ions. The results demonstrated that sensor 1 could be used as a selective ratiometric fluorescence sensor for detection of Ag$^+$. Importantly, the use of 1 as a ratiometric fluorescence sensor for Ag$^+$ might be
Figure 2. Fluorescence spectral changes of 1 (5 µM) with the addition of Ag⁺. Inset: plot of the fluorescence intensity at 488/449 nm versus the number of equiv of Ag⁺ added.

Figure 3. Fluorescence intensities (at 488/449 nm) of 1 (5 µM) with Ag⁺ (6 equiv) with various cations (6 equiv).

very meaningful, because only a few ratiometric fluorescence silver sensors have been reported to date [9,26,56–59].

The fluorescence titration of 1 with Ag⁺ was carried out (figure 2). The fluorescence intensity steadily decreased at 449 nm and gradually increased at 488 nm up to 6 equiv of Ag⁺. To demonstrate the sensing property of 1 toward Ag⁺, we performed UV–visible titration (electronic supplementary material, figure S1). Upon the addition of Ag⁺, the absorbance at 350 nm dwindled and the band at 400 nm increased steadily up to 12 equiv of Ag⁺. An isosbestic point was apparent at 368 nm, which suggested that 1 and Ag⁺ constituted a single species.

For information on the binding mode of 1 with Ag⁺, Job plot and ESI mass spectrometry analyses were executed. Job plot [60] showed the 1:1 stoichiometric ratio (electronic supplementary material,
**Figure 4.** $^1$H NMR titrations of 1 with the addition of Ag$^{+}$ (0, 1, 2 and 4 equiv).

**Figure 5.** Energy-minimized proposed structures of (a) 1 and (b) 1–Ag$^+$ complex.

The positive-ion mass spectrum indicated the formation of 1 + Ag$^+$ + 11 solvents [m/z: 727.32; calcd, 727.31] (electronic supplementary material, figure S3). The association constant of 1 with Ag$^+$ was determined to be $7.00 \times 10^4$ M$^{-1}$ using Li’s equation [61] based on the fluorescence titration

The dihedral angle (1O, 2C, 3N, 4C): $-150.925^\circ$

The dihedral angle (1O, 2C, 3N, 4C): $-157.525^\circ$
Scheme 2. The proposed fluorescent sensing mechanism of Ag⁺ by 1.

Figure 6. (a) Fluorescence and (b) absorption spectra of sensor 1 (10 µM) with different anions in buffer (bis-tris, pH = 7.0, 10 mM). (c) The colour changes of sensor 1 (10 µM) with various anions.

Figure 7. (a) Fluorescence and (b) absorption spectral changes of 1 (10 µM) with increasing concentrations of S²⁻. Inset: plot of (a) fluorescence at 368 nm and (b) absorbance at 470 nm versus the number of equiv of S²⁻ added.

Data (electronic supplementary material, figure S4). The detection limit was calculated to be 1.49 µM (electronic supplementary material, figure S5) via 3σ/slope [62].

To ascertain the functional application prospect of 1, the competition test was conducted in the presence of assorted metal ions such as Al³⁺, In³⁺, Zn²⁺, Ga³⁺, Cd²⁺, Cu²⁺, Mg²⁺, Fe²⁺, Fe³⁺, Cr³⁺, Ag⁺, Co²⁺, Hg²⁺, Ni²⁺, Na⁺, Mn²⁺, K⁺, Pb²⁺, Ca²⁺, Pd²⁺ and Au³⁺ (figure 3). Most metal ions did...
not show interferences to sense silver ion, and Pd\(^{2+}\) and Au\(^{3+}\) interfered about 30%. These results demonstrated that the sensor 1 was very selective for detection of Ag\(^{+}\).

We implemented the \(^1\)H NMR titrations to further understand the binding properties of 1 toward Ag\(^{+}\) (figure 4). Upon addition of 4 equiv of Ag\(^{+}\) to 1, most of the protons showed down-field shifts while proton H\(_{12}\) and H\(_{13}\) displayed no shift. In particular, protons H\(_{4}\), H\(_{8}\), H\(_{9}\) and H\(_{10}\) exhibited large down-field shifts. These chemical shifts indicated that the oxygen atom of the ethyl moiety and the nitrogen atom of the imine might associate with silver ion.

To further investigate the sensing mechanism of 1 with Ag\(^{+}\), the DFT and TD-DFT calculations were applied. First, we executed the geometric optimizations of 1 and 1–Ag\(^{+}\) complex (figure 5). Ag atom was applied to the LANL2DZ/ECP, and the main atoms were employed to the B3LYP/6-31G(d,p) method. Energy-minimized structures of 1–Ag\(^{+}\) and 1 species showed folded structures with the dihedral angles of 1O, 2C, 3N, 4C = −150.925° and −157.525°, respectively. Next, the electronic transitions of 1 and 1–Ag\(^{+}\) complex were examined at the optimized geometries (S\(_0\)). For 1, the main MO contribution was calculated to be the HOMO → LUMO transition (372.52 nm, electronic supplementary material, figure S6), which was assigned to be the intramolecular charge transfer. For 1–Ag\(^{+}\) complex, the main MO contribution was calculated to be the HOMO → LUMO transition (398.69 nm, electronic supplementary material, figure S7), which displayed the ligand-to-metal charge-transfer. These results showed that the binding of 1 with Ag\(^{+}\) caused a bathochromic shift (372.52 to 398.69 nm) and generated the shift of fluorescence intensity (449 to 488 nm) (electronic supplementary material, figure S8). Based on the analysis of Job plot, ESI mass, \(^1\)H NMR titrations and theoretical calculations, the sensing mechanism of 1 with Ag\(^{+}\) is described in scheme 2.

3.2. Fluorogenic and colorimetric responses of 1 toward S\(_{2}^{2−}\)

We examined the fluorescent and colorimetric sensing abilities of 1 in the presence of different anions such as Cl\(^{−}\), CN\(^{−}\), F\(^{−}\), Br\(^{−}\), I\(^{−}\), OAc\(^{−}\), H\(_2\)PO\(_4\)^{−}, N\(_3\)^{−}, BzO\(^{−}\), SCN\(^{−}\), NO\(_2\)^{−}, SO\(_4^{2−}\), OH\(^{−}\), HSO\(_3^{−}\) and
**Figure 9.** $^1$H NMR titrations of 1 with the addition of $S^{2−}$ (0, 1 and 2 equiv).

$S^{2−}$ in bis-tris buffer (pH = 7.0, 10 mM, figure 6). The enhanced emission was shown only for sulfide with an excitation of 266 nm, whereas 1 and other anions exhibited no fluorescence emission (figure 6a). Also, there were no or little spectral changes for 1 and other anions (figure 6b), while 1 with $S^{2−}$ showed a significant decrease of absorbance at 470 nm, which induced a colour change from yellow to colourless. This observation could be explained as follows. $F^{−}$ with a strong basicity and hydrogen bonding character could form hydrogen bonding to excess water molecules instead of the deprotonation of any phenolic OH of sensor 1. In contrast, $S^{2−}$ with a strong basicity and less hydrogen bonding character might deprotonate more acidic phenolic proton of 1 instead of forming hydrogen bonds with less acidic water molecules, and then, showing colour change. These results suggested that sensor 1 had ability as a superior fluorogenic and colorimetric chemosensor for sulfide. Importantly, there are only a few sensors for the detection of $S^{2−}$ with a dual method [32,63–65]. In addition, this is a first instance that a single chemosensor can recognize both silver(I) and sulfide, to the best of our knowledge.

We executed the fluorescence and UV–visible titrations of 1 with $S^{2−}$ (figure 7). Upon the addition of $S^{2−}$, the fluorescent intensity at 368 nm gradually increased up to 90 equiv of $S^{2−}$ (figure 7a). In UV–visible titration (figure 7b), the absorbance at 260 nm increased, and the band at 470 nm steadily decreased with an isosbestic point at 272 nm. The tendency of dwindling absorbance at 470 nm was continued up to 110 equiv of $S^{2−}$. These results demonstrated that 1 reacted with sulfide to form a single species.

To understand the interaction properties of 1 with $S^{2−}$, we conducted Job plot and ESI mass spectrometry analyses. Job plot [60] showed the 1:1 stoichiometric ratio of 1 with $S^{2−}$ (electronic supplementary material, figure S9). The negative-ion mass spectrum indicated the formation of 1 – H$^+$ [m/z: 309.35; calcld, 309.16] (electronic supplementary material, figure S10). On the basis of fluorescence titration data, the association constant of 1 and sulfide was calculated to be $1.82 \times 10^{3}$ M$^{−1}$ using Li’s equation [61] (electronic supplementary material, figure S11). The detection limit was determined to be 14.8 µM (electronic supplementary material, figure S12) by $3σ$/slope [62].

We checked the practical abilities of 1 for sensing $S^{2−}$ in the presence of other anions. For fluorescence recognition (electronic supplementary material, figure S13), CN$^{−}$, Br$^{−}$, BzO$^{−}$, SO$_4^{2−}$ and OH$^{−}$ displayed interferences of 30, 80, 55, 63, and 64%. However, CN$^{−}$, BzO$^{−}$, SO$_4^{2−}$ and OH$^{−}$ still showed discernible fluorescence emission. For colorimetric recognition (figure 8), all of the anions showed no inhibition
of S$^{2-}$. These results explained that 1 could detect effectively S$^{2-}$ without disturbance of other anions using two methods together.

For further information for practicality of 1, we investigated the pH dependence of 1 for detection of sulfide. For fluorescence response (electronic supplementary material, figure S14a), sensor 1 could recognize the sulfide in pH range of 3 to 7. For colorimetric response (electronic supplementary material, figure S14b), sensor 1 could discern S$^{2-}$ in pH range of 4 to 10. These observations suggested that S$^{2-}$ could be well detected by 1 under both acid and base conditions by increasing fluorescence intensity and changing colour, respectively.

$^1$H NMR titrations were conducted to further examine the sensing mechanism of 1 with S$^{2-}$ (figure 9). Hydroxyl protons were not observed due to the D$_2$O solvent. As the concentration of sulfide increased, H$_2$, H$_3$ and H$_5$ showed up-field shifts. There was no shift for other protons. These results suggested that the hydroxyl proton of the phenol group of 1 might be deprotonated by sulfide, inducing the fluorescence enhancement. Based on the analysis of Job plot, ESI mass and $^1$H NMR titration, we depict the sensing mechanism of 1 toward S$^{2-}$ in scheme 3.

4. Conclusion

We designed a new multifunctional chemosensor 1 for detection of silver(I) and sulfide. Silver(I) with 1 showed the ratiometric fluorescence from blue to sky. 1 bound to Ag$^+$ with a 1:1 ratio, which was determined by Job plot and ESI mass analyses. The limit of detection turned out to be 1.49 µM and there was no interference for sensing silver(I) by 1. The sensing properties were understood via $^1$H NMR titrations and DFT calculations. In addition, sensor 1 recognized sulfide with an obvious fluorescence enhancement and colour change from yellow to colourless. The sensing mechanism of 1 with S$^{2-}$ was studied through ESI mass, Job plot and $^1$H NMR titration. In particular, this is a first instance that a single chemosensor can recognize both silver(I) and sulfide, to the best of our knowledge.

Data accessibility. All of the data in this study are included in figures and electronic supplementary material, and freely available.

Authors’ contributions. J.H.K. carried out the laboratory work and data analyses. J.B.C. performed parts of the laboratory work and revised the manuscript. J.H.K. and C.K. discussed the results and also wrote and revised the manuscript. All authors gave final approval for publication.

Competing interests. We declare we have no competing interests.

Funding. The National Research Foundation of Korea (NRF) (NRF-2018R1A2B6001686) is gratefully acknowledged. We also gratefully acknowledge the support of the work by MOE (Korea Ministry of Environment) as ‘The Chemical Accident Prevention Technology Development Project’ (No. 2016001970001).

Acknowledgements. The authors are grateful to the Seoul National University of Science and Technology for providing laboratory facilities.

References

1. Fu Y, Li P, Kang XY, Liu YY, Li GF, Ye F. 2016 A novel 1,8-naphthalimide derivative as an efficient silver(I) fluorescent sensor. J Lumin. 178, 156–162. (doi:10.1016/j.jlumin.2016.05.023)
2. Tang L, Cai M, Huang Z, Zhong K, Hou S, Bian Y, Nandhakumar R. 2013 Rapid and highly selective relay recognition of Cu(II) and sulfide ions by a simple benzimidazole-based fluorescent sensor in water. Sens. Actuators B 185, 188–194. (doi:10.1016/j.snb.2013.04.109)
3. Gao C, Liu X, Jin X, Wu L, Xie Y, Liu W, Yao X, Tang Y. 2013 A retrievable and highly selective fluorescent sensor for detecting copper and sulfide. Sens. Actuators B 185, 125–131. (doi:10.1016/j.snb.2013.04.110)
4. Xiao H, Zhang Y, Zhang W, Li S, Xu R. 2016 Two novel dyes containing spirobifluorene and triphenylamine: synthesis, one- and two-photon excited fluorescence and applications as probes for silver ions, water and cell imaging. Sens. Actuators B 231, 469–475. (doi:10.1016/j.snb.2016.04.101)
5. Min CH, Na S, Shin JE, Kim JK, Jo TG, Kim C. 2017 A new Schiff-based chemosensor for chromogenic
sensing of Cu(II), Cd(II) and S(II) in aqueous solution: experimental and theoretical studies. New J. Chem. 41, 3991–3999. doi:10.1039/CN10045E
6. Jiménez-Morales A, Galván JC, Aranda P. 2002. A new silver-ion selective sensor based on a polythiacyanine-ether entrapped by sol–gel. Electrochem. Acta 47, 2281–2287. doi:10.1016/S0013-4686(02)00606-3
7. Hammoud HH, El Shazly S, Sonji G, Sonji N, Boushaid KH. 2013. Thiophene aldehyde-diaminouracil Schiff base: a novel fluorescent probe for detection and quantification of cupric, silver and ferric ions. Spectrochim. Acta A 150, 94–103. doi:10.1016/j.saa.2015.05.038
8. Sirajuddin Nayab P, Shkir M, Gull P, Al Faify S. 2017 A novel ratiometric fluorescent H 2 S probe based on tandem naphthoic substitution/cyclization reaction and its bioimaging. Dyes Pigmen. 146, 287–292. doi:10.1016/j.dyepig.2017.07.016
9. Chen C et al. 2016 A simple benzimidazole quinoline-conjugate fluorescent chemosensor for highly selective detection of Ag(I). Tetrahedron 72, 3980–3985. doi:10.1016/j.tet.2016.05.020
10. Lee SY, Bok KH, Kim C. 2017 A fluorescence ‘turn-on’ chemosensor for Hg(II) and Ag(I) based on NBD-(7-nitrobenzo-2-oxa-1,3-diazole). J. Adv. 290–299. doi:10.1021/acs.jsa.6b04087
11. Velmurugan K, Thamilselvan A, Antony R, Kannan VR, Tang L, Nandhakumar R. 2017 Imidazoquinolineone bearing thiol probe for fluorescent electrochemical sensing of Ag and relay recognition of proline. J. Photochem. Photobiol. A 333, 130–141. doi:10.1016/j.jphotochem.2016.10.025
12. Affoue A, Parveen SDS, Kumar BS, Pitchumani K. 2015 Selective sensing of silver ion using berberine, a naturally occurring plant alkaloid. Sens. Actuators B 204, 170–175. doi:10.1016/j.snb.2014.09.042
13. Li L-Q, Gao L-J. 2016 A novel naphthylamine based fluorescent sensor for Ag(I) recognition. Spectrochim. Acta A 152, 426–430. doi:10.1016/j.saa.2015.07.097
14. Li WT, Wu GY, Ou WJ, Li Q, Lou JC, Qin L, Yao H, Zhang YMA, Wei TB. 2017 A colorimetric and reversible fluorescent chemosensor for Ag(I) in aqueous solution and its application in IMPLICATION logic gate. Sens. Actuators B 239, 671–678. doi:10.1016/j.snb.2016.08.016
15. Ghosh A et al. 2016 Tuning of azine derivatives for selective recognition of Ag(I) with the inhibition tracking of endophytic bacteria in rice root tissue. Dalton Trans. 45, 19491–19499. doi:10.1039/C6DT03170J
16. Shi W, Chen Y, Chen X, Xie Z, Hui Y. 2016 Simple-structured, hydrazinecarbothioamide derivative dual-channel optical probe for Hg(II) and Ag +. J. Lumine. 174, 56–62. doi:10.1016/j.jlumin.2016.01.012
17. Shen W, Wang L, Wu M, Bao X. 2016 A fluorescent derivative FLC as a chemosensor for Hg(II) and Ag(I) and its application in living-cell imaging. Inorg. Chem. Commun. 70, 107–110. doi:10.1016/j.inoche.2016.05.001
18. Zhang C, Wang R, Cheng L, Li B, Ni Y, Li Y. 2016 A redox-nucleophilic dual-reactable probe for highly selective and sensitive detection of Hg(II): synthesis, spectroscopy and bioimaging. Sci. Rep. 6, 30148. doi:10.1038/srep30148
19. Jin X et al. 2016 Novel fluorescent-based fluorescence probe for detecting Hg(II) and its real applications in blood plasma and biological imaging. Anal. Chem. 88, 111–211. doi:10.1021/acs.analchem.6b04087
20. Joo DH, Mok JS, Bae GH, Oh SE, Kang JH, Kim C. 2017 Colormetric detection of Cu(II) and fluorescent detection of PO 4 3− and S 2− by a multifunctional chemosensor. Ind. Eng. Chem. Res. 56, 8399–8407. doi:10.1021/acs.iecr.7b03115
21. Xu Q, He L, Wei H, Lin W, Liu X. 2018 An ICT-based hydrogen sulfide sensor with good water solubility for fluorescence imaging in living cells. J. Fluoresc. 28, 5–11. doi:10.1007/s10895-015-1622-5
22. Das AK, Goswami S, Dutta G, Maity S, Kanti Mandal T, Khansa K, Bhattacharya N. 2016 A concentration dependent auto-relay-recognition by the same analyte: a dual fluorescence switch-on by hydrogen sulfide via Michael addition followed by reduction and staining for bio-activity. Org. Biomol. Chem. 14, 570–576. doi:10.1039/C5OB02088E
23. Tang L, Zhang Z, Yan B. 2016 A N-[(2-hydroxyethyl) piperazine dangled 2,5-diphenyl-1,3,4-oxadiazole-based fluorescent sensor for selective relay recognition of Cu(II) and sulfide in water. Luminescence 31, 1456–1460. doi:10.1007/s10967-016-0238
24. Ryu KY, Lee UJ, Kim JK, Park DY, Kim C. 2016 Colorimetric chemosensors for multiple targets, Cu(II), Cd(II) and S(II). J. 16, 586–1657. doi:10.1039/C5RA27555A
25. Li J, Yin C, Huo F. 2015 Chromogenic and fluorogenic chemosensors for hydrogen sulfide: review of detection mechanisms since the year 2009. J. Adv. 5, 219–2206. doi:10.1016/j.jraita8076
26. Zhao Q, Kang J, Wen Y, Huo F, Zhang Y, Yin C. 2016 Turn-on fluorescent probe for detection of Hg(II) and its applications in bioimaging. Spectrochim. Acta A 159, 9–12. doi:10.1016/j.saa.2017.08.002
27. Huo F, Zhang Y, Ning P, Meng Y, Huo F. 2017 A novel isophorone-based red-emitting fluorescence probe for selective detection of sulfide anions in water for in vivo imaging. J. Mater. Chem. B 5, 2798–2803. doi:10.1039/C7TB02996E
28. Stohs SJ. 2015 Physiological functions and pharmacological and toxicological effects of p-octapine. Drug Chem. Toxicol. 38, 106–112. doi:10.1080/01480545.2014.90069
29. Haller CA, Benowitz NL, Jacob P. 2005 Hemodynamic effects of ephedra-free weight-loss supplements in humans. Am. J. Med. 118, 998–1003. doi:10.1016/j.amjmed.2005.02.034
30. Kumar M, Kumar N, Bhalla V. 2011 FRET-induced nanomolar detection of Fe(III) based on cinnamaldehyde-rodamine derivative. Tetrahedron Lett. 52, 4333–4336. doi:10.1016/j.tetlet.2011.06.044
31. Jung JM, Kim C, Harrison RG. 2018 A dual sensor selective for Hg(II) and cysteine detection. Sens. Actuators B 255, 275–2763. doi:10.1016/j.snb.2017.09.090
32. Samanta S, Datta BK, Boral M, Nandan A, Das G. 2016 A multi-responsive turn-on fluorescent probe to sense Zn(II), Cd(II) and Pb(II) - left-right-center emission signal switch. Analyst 141, 4388–4393. doi:10.1039/C4AN00345A
33. Kar C, Samanta S, Goswami S, Ramesh A, Das G. 2015 A single probe to sense Al(III) colorimetrically and Cd(II) by turn-on fluorescence in physiological conditions and live cells, corroborated by X-ray crystallographic and theoretical studies. Dalton Trans. 44, 4122–4132. doi:10.1039/C4DT03438B
34. Pal S, Sen B, Lohar S, Mukherjee M, Banerjee S, Chattopadhyay P. 2015 Effect of metal oxidation state on FRET: a C(II) silent but selectively C(II) responsive fluorescent reporter and its bioimaging applications. Dalton Trans. 44, 1761–1768. doi:10.1039/C4DT02368G
35. Becker AR. 1993 Density-functional thermochromistry. III. The role of exact exchange. J. Chem. Phys. 98, 5648–5652. doi:10.1063/1.466491
46. Lee CT, Yang W, Parr RG. 1988 Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev. B 37, 785–789. (doi:10.1103/PhysRevB.37.785)
47. Frisch MJ et al. 2009 Gaussian 03, Revision C.02. Wallingford, CT: Gaussian, Inc.
48. Hanharran PC, Pople JA. 1973 The influence of polarization functions on molecular orbital hydrogenation energies. Theor. Chim. Acta 28, 213–222. (doi:10.1007/BF00533485)
49. Franci MM, Pietro Wi, Hehre WJ. 1982 Self-consistent molecular orbital methods. XXIII. A polarization-type basis set for second-row elements. J. Chem. Phys. 77, 3654–3665. (doi:10.1063/1.444267)
50. Hay PJ, Wadt WR. 1985 Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys. 82, 270–283. (doi:10.1063/1.440799)
51. Wadt WR, Hay PJ. 1985 Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys. 82, 284–299. (doi:10.1063/1.448800)
52. Hay PJ, Wadt WR. 1985 Ab initio effective core potentials for molecular calculations. Potentials for K to Au including the outermost core orbitals. J. Chem. Phys. 82, 299–310. (doi:10.1063/1.448975)
53. Barone V, Cossi M. 1998 Quantum calculation of molecular energies and energy gradients in solution by a conductor solvent model. J. Phys. Chem. A 102, 1995–2001. (doi:10.1021/jp9716997)
54. Cossi M, Barone V. 2001 Time–dependent density functional theory for molecules in liquid solutions. J. Chem. Phys. 115, 4708–4717. (doi:10.1063/1.1394921)
55. O’boyle NM, Tenderholt AL, Langner KM. 2008 cclib: a library for package-independent computational chemistry algorithms. J. Comput. Chem. 29, 839–845. (doi:10.1002/jcc.20823)
56. Takashima I, Kanegae A, Sugimoto M, Ojida A. 2014 Aza-crown-ether-appended xanthene: selective ratiometric fluorescent probe for silver(1) ion based on arenne–metal ion interaction. Inorg. Chem. 53, 7080–7082. (doi:10.1021/ic500980j)
57. Zhu M, Zhou Y, Liang Y, Li L, Qi D, Bai M, Chen Y, Du H, Bian Y. 2014 Synergistic coupling of fluorescent ‘Turn-Off’ with spectral overlap modulated FRET for ratiometric Ag + sensor. Inorg. Chem. 53, 12 186–12 190. (doi:10.1021/ic50234Ab)
58. Kursunlu AN, Güler E. 2017 Novel fluorescent sensor for silver(I) based on the 3,4-bis-triazole Bodipy via dual-click chemistry. J. Mol. Struct. 1134, 345–349. (doi:10.1016/j.molstruc.2017.01.003)
59. Zhang W, Kang J, Li F, Wang H, Tang B. 2015 Dual signaling molecule sensor for rapid detection of hydrogen sulfide based on modified tetraphenylethylene. Anal. Chem. 87, 8964–8969. (doi:10.1021/acs.analchem.5b02169)