A novel benzophenone-based colorimetric chemosensor for detecting Cu^{2+} and F^-

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MS received 5 November 2018; revised 9 December 2018; accepted 11 December 2018; published online 12 January 2019

Abstract. A novel selective colorimetric chemosensor **ANBP** ((E)-(2-(((8-hydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)methylene)amino)-5-nitrophenyl)(phenyl)methanone), based on the combination of benzophenone group and julolidine chromophore, was synthesized. Sensor **ANBP** showed rapid colorimetric responses toward Cu^{2+} (pale orange to pink) and F^- (orange to blue). The detection limit by **ANBP** to Cu^{2+} ($6.82 \mu\text{M}$) was far below WHO guideline value ($31.3 \mu\text{M}$). Moreover, **ANBP** could quantify Cu^{2+} in aqueous samples. 1:1 binding mode between **ANBP** and Cu^{2+} or F^- was proposed by ESI-mass analyses and Job plots. The remarkable color changes with Cu^{2+} and F^- resulted from the intramolecular charge transfer (ICT) effect, which was demonstrated by theoretical calculations.

Keywords. Fluoride; colorimetric chemosensor; copper ion; theoretical calculations.

1. Introduction

Optical chemosensors have several advantages such as fast response, low cost and high selectivity for detecting biologically important analytes.^{1,2} Due to these advantages, development of optical sensors for selective sensing of specific analytes including anions and metal ions has attracted much attention in medical, environmental, biological and industrial fields.^{3–5} In particular, as one of the optical chemosensors, colorimetric sensors are widely used to detect multiple analytes due to the use of cheap machines or no machine at all.^{6–8}

Copper ion (Cu^{2+}) is an indispensable transition metal in body, which plays crucial roles in various enzyme-catalyzed reactions and biological processes.^{9,10} However, abnormal levels of Cu^{2+} is associated with negative health effects such as hematological manifestations, stomach cramps, diarrhoea and pelvic inflammatory disease.^{11–13} Therefore, several sensors having specific functional groups for monitoring and for measurement of Cu^{2+} have been developed such as

quinazoline,¹⁴ thiourea,¹⁵ 1,8-naphthalimide,^{16,17} pyrene,¹⁸ and Schiff base derivatives.^{19,20}

Fluoride (F^-), one of the biologically important anions, is used considerably in the cure of osteoporosis and in dental care.²¹ Nevertheless, a high dose of F^- might lead to kidney failure and acute gastric problems in humans.²² For a healthy life, therefore, the development of an efficient method for recognizing F^- is of great importance.²³ Much progress has been achieved in F^- sensor including the unique functional groups such as pyrroles,²⁴ Lewis acid,^{25–28} urea and thiourea,^{29–32} amides,^{33,34} acridinium-salt³⁵ and polymer.^{36,37} However, many of them suffer from synthetic difficulties involving severe reaction conditions and expensive chemicals.

Benzophenone derivative has a diaryl ketone, which is a well-known chromophore with its distinct spectral properties.^{38,39} Julolidine moiety often exhibited a good colorimetric response with target analytes because it has excellent chromogenic properties.^{40,41} These facts led us to expect that the existence of both the benzophenone and the julolidine moieties in a

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chemosensor may show unique chromogenic properties to specific analytes. Therefore, we developed the sensor **ANBP** through a combination of the two groups to develop a new unique chemosensor.

Herein, we report a novel chemosensor **ANBP**, conjugating benzophenone moiety and julolidine chromophore. The sensor **ANBP** can detect Cu^{2+} by color change from pale orange to pink. Also, **ANBP** displayed a high selectivity to F^- through intense color change (orange to blue). It is noteworthy that the benzophenone-based selective Cu^{2+} and F^- colorimetric chemosensor is the first example to date. Additionally, the detection mechanisms of **ANBP** to Cu^{2+} and F^- were demonstrated by various spectroscopic investigations and theoretical calculations.

2. Experimental

2.1 Chemicals and instrumentation

Chemicals were purchased from the commercial sources. A Varian spectrometer was used to measure ^1H and ^{13}C NMR data. ESI-MS data were obtained on a Waters Acquity SQD quadrupole Mass machine. UV-Visible and fluorescent experiments were conducted with Perkin Elmer 2S UV/Visible and LS45 fluorescent machines.

2.2 Synthetic method of ANBP

((E)-2-(((8-hydroxy-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)methylene)amino)-5-nitrophenyl)(phenyl)methanone)

10 mL of acetic acid was used to dissolve 2-amino-5-nitrobenzophenone (1 mmol, 242 mg), and 8-hydroxyjulolidine-9-carboxaldehyde (1.2 mmol, 261 mg) was added to the acetic acid solution. After shaking it for 3 h, HCl (3 drops) were added and shaken for 30 h at 22 °C. The red precipitate solid was collected through filtration and washed with ethyl acetate and ether (373 mg, 84.5%). ^1H NMR in $\text{DMSO}-d_6$: δ 12.46 (s, 1H), 8.71 (s, 1H), 8.48 (d, J = 9.2 Hz, 1H), 8.27 (d, J = 2.4 Hz, 1H), 7.85 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 7.6 Hz, 2H), 7.72 (t, J = 7.6 Hz, 1H), 7.58 (t, J = 7.6 Hz, 2H), 6.98 (s, 1H), 3.33 (t, J = 11.6 Hz, 4H), 2.62 (t, J = 6.4 Hz, 4H), 1.85 (m, 4H). ^{13}C NMR in $\text{DMSO}-d_6$: δ 196.71 (1C), 191.67 (1C), 158.39 (1C), 156.25 (1C), 138.55 (1C), 134.47 (1C), 133.84 (1C), 131.90 (1C), 131.20 (1C), 130.95 (1C), 129.93 (1C), 128.85 (2C), 128.58 (2C), 117.12 (1C), 114.61 (1C), 113.40 (1C), 104.16 (1C), 49.53 (1C), 49.07 (1C), 26.52 (1C), 21.02 (1C), 19.93 (1C), 19.27 (1C), 7.30 (1C). ESI-MS (**ANBP**+ H^+): calcd, 442.18 (m/z); found, 442.18 (m/z).

2.3 Chromogenic Cu^{2+} sensing

2.3a UV-vis titration: Stock solutions of **ANBP** (1×10^{-2} M) and $\text{Cu}(\text{NO}_3)_2$ (0.1 M) were prepared in dimethylsulfoxide (DMSO). 3.0 μL of the **ANBP** was diluted

to a mixture (2.997 mL) of MeOH: bis-tris buffer (2:1) to give 0.01 mM. Titration experiments were performed by adding 3.0–45.0 μL of a stock $\text{Cu}(\text{NO}_3)_2$ to sensor **ANBP**. The solutions were stirred for 5 s before taking the UV-visible spectra.

2.3b Job plot: Stock solutions of **ANBP** (1×10^{-2} M) and $\text{Cu}(\text{NO}_3)_2$ (0.1 M) were prepared in DMSO. 120.0 μL of the **ANBP** and 6.0 μL of the Cu^{2+} were diluted to 39.88 mL and 19.99 mL of a mixture of MeOH: buffer (2:1) to give 30 μM , respectively. Then, 2.7, 2.4, 2.1, 1.8, 1.5, 1.2, 0.9, 0.6 and 0.3 mL of the diluted **ANBP** were added to cuvettes, and 0.3–2.7 mL of the diluted Cu^{2+} were transferred to each **ANBP**, separately. Cuvettes had a total 3 mL volume. The solutions were stirred for 5 s before taking the UV-visible spectra.

2.3c Competition test: Stock solutions of **ANBP** (0.01 M) and various cations (0.02 M) were prepared in DMSO and MeOH, respectively. 210 μL (0.02 M) of each cation was diluted to a mixture (2.745 mL) of MeOH: buffer (2:1), and 42 μL (0.1 M) of the Cu^{2+} was added to the solutions prepared above. 3.0 μL of **ANBP** was added to the mixed solution of each cation, which was stirred for 5 s before taking the UV-visible spectra.

2.3d pH effect: Buffer solutions with different pH (2–12) were prepared by using KOH and HCl in the buffer. After making the desired pH, 3 μL (0.01 M) of **ANBP** in DMSO was added to a mixture (2.997 mL) of MeOH: bis-tris buffer (2:1) of each pH to produce 10 μM . After the addition of 42 μL of $\text{Cu}(\text{NO}_3)_2$ (0.1 M) to the solution prepared above, it was stirred for 5 s before taking the UV-visible spectra.

2.3e Measurement of Cu^{2+} : UV-visible measurement of Cu^{2+} was conducted by adding 3 μL (10 mM) of a stock **ANBP** and 0.1 mL (0.1 M) of the buffer to a sample solution (2.897 mL). The solution was stirred for 5 s before taking the UV-visible spectra.

2.4 Chromogenic F^- sensing

2.4a UV-visible titration: Stock solutions of **ANBP** (0.01 M) and tetraethylammonium fluoride (TEAF, 0.1 M) were prepared in DMSO. 6 μL of the **ANBP** was diluted with 2.994 mL *N,N*-dimethylformamide (DMF) to give 0.02 mM. Titration experiments were conducted by adding 6–66 μL of a stock TEAF to sensor **ANBP** solution. The solutions were stirred for 5 s before taking the UV-visible spectra.

2.4b Job plot: Stock solutions of **ANBP** (0.01 M) and TEAF (0.1 M) were prepared in DMSO. 80 μL of the **ANBP** and 4 μL of the TEAF were diluted by adding 39.92 mL and 19.99 mL of DMF to give 20 μM , respectively. Then, 2.7, 2.4, 2.1, 1.8, 1.5, 1.2, 0.9, 0.6 and 0.3 mL of the diluted **ANBP** were added to cuvettes, and 0.3–2.7 mL of the diluted F^- were added to each **ANBP**, separately. Cuvettes had a total 3.0 mL volume. The solutions were stirred for 5 s before taking the UV-visible spectra.

Scheme 1. Synthetic method for **ANBP**.

2.4c Competition experiment: Stock solutions of **ANBP** (0.01 M) and various anions (0.1 M) were prepared in DMSO and DMF, respectively. 60 μ L of each anion (0.1 M) was diluted by addition of 2.874 mL DMF, and then 60 μ L of the F^- (0.1 M) was added to the solution. After 6.0 μ L of the **ANBP** was added to a mixture of each anion, the solutions were stirred for 5 s before taking the UV-visible spectra.

2.4d 1H NMR and ^{19}F NMR titrations of ANBP with F^- : For 1H NMR titrations, four different equivalents (0, 0.5, 1.0 and 10.0) of TEAF in DMSO- d_6 were added to four NMR tubes of sensor **ANBP** (17.6 mg, 4×10^{-2} mmol) in DMSO- d_6 (2.8 mL). 1H NMR spectra were obtained after a minute.

For ^{19}F NMR titrations, two different equivalents (0 and 5.0) of TEAF in DMSO- d_6 were added to two NMR tubes of sensor **ANBP** (1.3 mg, 2.9×10^{-3} mmol) in DMSO- d_6 (590 μ L). ^{19}F NMR spectra were obtained after a minute.

2.4e Calculations: Calculation results were obtained using the Gaussian 09 program.⁴² The optimized forms of **ANBP**, **ANBP**- Cu^{2+} and **ANBP**- F^- were calculated using DFT method. Becke, three-parameter, Lee-Yang-Parr's gradient (B3LYP) was used for hybrid functional and the 6-31G(d,p) used as a basis set.^{43–46} The 6-31G(d,p) was applied to the atoms of C, H, N, O and LANL2DZ was applied to Cu^{2+} for an effective core potential (ECP).^{47–49} All structures presented showed local minima in optimized structures since the imaginary frequencies were not observed. The solvent effects of DMF and MeOH were considered with Cossi-Barone's Conductor-like polarization continuum model (CPCM).^{50,51} TD-DFT was calculated for studying the electronic states of singlet excited state in the ground state geometries of the three structures. Thirty singlet states were used for calculation.

3. Results and Discussion

ANBP was synthesized by a condensation reaction of 2-amino-5-nitrobenzophenone and 8-hydroxyjulolidine-9-carboxaldehyde in acetic acid with hydrochloric acid as a catalyst (Scheme 1). **ANBP** was characterized by 1H NMR, ^{13}C NMR, and ESI-MS.

3.1 Colorimetric study for cations

The cation sensing capability of sensor **ANBP** was examined by UV-vis absorption spectral changes with diverse cations (Mg^{2+} , Ga^{3+} , Mn^{2+} , In^{3+} , K^+ , Zn^{2+} , Na^+ , Fe^{3+} , Cd^{2+} , Co^{2+} , Cr^{3+} , Pb^{2+} , Ni^{2+} , Cu^{2+} , Ca^{2+} , Fe^{2+} , and Al^{3+}) in a mixture of MeOH:buffer (2:1) (Figure 1). Compound **ANBP** showed a unique spectral change for Cu^{2+} compared to other cations. With Cu^{2+} , the absorbance centered at 475 nm disappeared and two new absorption peaks at 550 and 750 nm appeared. It could be also recognized by the naked eye through color change from pale orange to pink. This indicated that sensor **ANBP** can act as a Cu^{2+} indicator.

To understand the detailed chemosensing properties between sensor **ANBP** and Cu^{2+} , UV-vis titration was carried out by the addition of Cu^{2+} ions to **ANBP** (Figure 2). Stepwise addition of Cu^{2+} decreased the absorbance of 475 nm, whereas increasing the absorbance at 550 and 750 nm. Two well-defined isosbestic points at 420 and 504 nm indicated the production of only one complex between **ANBP** and Cu^{2+} .

A Job plot analysis⁵² was carried out to examine the binding ratio of **ANBP** and Cu^{2+} (Figure S1, Supplementary Information). It gave a 1:1 complexation, which was further confirmed by an ESI-MS spectrometry method (Figure S2, Supplementary Information). The positive mass data of **ANBP** with Cu^{2+} exhibited the value of $m/z = 581.09$, reminiscent of **ANBP**- H^+ + Cu^{2+} + DMSO [calcd, $m/z = 581.10$]. With all the results of analysis, namely, UV-visible titration, ESI-MS method and Job plot, the possible sensing mechanism of Cu^{2+} by **ANBP** is proposed (Scheme 2).

To investigate the practical applicability for the quantitative measurement of Cu^{2+} by **ANBP**, a calibration curve was constructed (Figure 3). A good linearity was obtained, based on the absorbance of **ANBP** vs. Cu^{2+} concentration (0–40 μ M) ($R^2 = 0.9906$ ($n = 3$)), suggesting that **ANBP** could be used for the quantitative analysis of Cu^{2+} . The detection limit of 6.82 μ M ($3\sigma/\text{slope}$) for Cu^{2+} was obtained with the

Figure 1. (a) Absorption and (b) color changes of **ANBP** (10 μM) with diverse cations.

Figure 2. Absorption spectral changes of **ANBP** (10 μM) upon the addition of 0–150 equiv. of Cu^{2+} .

calibration data.⁵³ This value is far below the WHO guideline (31.3 μM) for the Cu^{2+} ion.⁵⁴ Application of Benesi-Hildebrand equation gave the association constant (K) of $4.5 \times 10^2 \text{ M}^{-1}$ ⁵⁵ (Figure S3, Supplementary Information). Sensor **ANBP** was applied to water samples for the practical applicability to Cu^{2+} (Table 1). Satisfactory R.S.D. values and recoveries were observed

for the water samples. The results demonstrated that **ANBP** can be efficiently used for the measurement of Cu^{2+} level in environmental and chemical applications.

To investigate the ability of **ANBP** as colorimetric indicator for Cu^{2+} , the competitive tests were carried out in the presence of Cu^{2+} and various metal ions (Figure S4, Supplementary Information). On the addition of **ANBP** to Cu^{2+} (140 equiv.) with other cations (140 equiv.), some cations showed little inhibition (Al^{3+} , In^{3+} , Fe^{2+} and Fe^{3+}). In addition, sensing ability of **ANBP** to Cu^{2+} was investigated over a broad pH range (2.0–12.0) (Figure S5, Supplementary Information). The absorbance and color of the **ANBP**- Cu^{2+} were maintained in the range of pH 7.0 to 11.0, which suggested that **ANBP** may detect Cu^{2+} by the naked eye or UV-visible spectra over the broad pH range.

3.2 Colorimetric study for anions

The spectroscopic behaviors of chemosensor **ANBP** were investigated with various anions (I^- , H_2PO_4^- , CN^- , N_3^- , Br^- , OAc^- , Cl^- , SCN^- , F^- , and BzO^- ; Figure 4). On addition of various anions, there are significant spectral and colorimetric changes (orange to blue) with F^- and small changes (orange to green)

Scheme 2. Possible structure of **ANBP**-Cu²⁺.

Figure 3. Determination of the detection limit based on a change in the absorbance at 550 nm: **ANBP** (10 μM) with Cu²⁺.

with CN[−], whereas other anions showed no effect. The observations indicated that **ANBP** could be a colorimetric indicator for F[−].

The sensing property of **ANBP** with F[−] was performed by UV-visible experiments (Figure 5). Addition of F[−] into **ANBP** led the decrease of the absorption band of 475 nm and the increase of a new absorption band at 615 nm. An isosbestic point appeared at 531 nm which was suggestive of the production of a UV-vis active species.

Job plot analysis⁵² gave a 1:1 ratio between **ANBP** and F[−] (Figure S6, Supplementary Information). To get more information on the complexation of **ANBP** with F[−], ¹H NMR and ¹⁹F NMR titration studies were carried out. In the ¹H NMR titrations (Figure 6), the addition of fluoride (1.0 equiv.) to **ANBP** led the upfield shift of the hydroxyl proton (H₁₄) and aromatic protons. Excess addition of fluoride (10.0 equiv.) caused the disappearance of the hydroxyl proton (H₁₄) and the appearance of a new peak (FHF[−]) at 16.12 ppm. In the ¹⁹F NMR titrations (Figure S7, Supplementary Information), the addition of fluoride (5.0 equiv.) led

the generation of the peak FHF[−] at −143.2 ppm with a singlet corresponding to free F[−] at −102.7 ppm. These results led us to propose the deprotonation of **ANBP** by F[−] to produce FHF[−] species. The proposal was further confirmed by an ESI-MS experiment (Figure S8, Supplementary Information). Negative-ion mass data of **ANBP** with F[−] exhibited the value of m/z = 440.22, reminiscent of **ANBP**-H⁺ [calcd, m/z = 440.16]. With the UV-visible and ¹H NMR titration, ESI-mass method and Job plot, the possible detection process of F[−] by **ANBP** was proposed (Scheme 3).

Application of Benesi-Hildebrand equation gave the binding constant (*K*) of 1.8 × 10² M^{−1} for **ANBP** with F^{−55} (Figure S9, Supplementary Information). Detection limit (3σ/slope)⁵³ of **ANBP** for F[−] ion turned out to be 55.2 μM (Figure S10, Supplementary Information). Additionally, detection limits of colorimetric chemosensors previously reported for detecting both Cu²⁺ and F[−] were compared to our results in Table S1 (Supplementary Information). Moreover, to examine the interference of other competitive anions on **ANBP**-F[−] species, the competitive experiments were performed in the presence of fluoride mixed with anions (I[−], N₃[−], CN[−], Cl[−], BzO[−], Br[−], OAc[−], SCN[−] and H₂PO₄[−]; Figure 7). Upon the addition of fluoride with other anions, the coexisting anions did not inhibit the colorimetric sensing of fluoride by **ANBP** except for H₂PO₄[−]. H₂PO₄[−] showed 50% reduction of the absorbance of **ANBP**-F[−] species.

3.3 DFT/TD-DFT calculations

The energy-optimized molecular structures of **ANBP**, **ANBP**-Cu²⁺, and **ANBP**-F[−] are shown in Figure S11, Supplementary Information. **ANBP** showed a twisted structure (the dihedral angle 5C, 6C, 7C, 8C = −166.823°; Figure S11(a), Supplementary Information). As the carbonyl group of the benzophenone moiety binds to Cu²⁺, the structure of **ANBP**-Cu²⁺ complex represented a significant dihedral angle change (5C, 6C, 7C, 8C = −30.142°) (Figure S11(b), Supplementary

Table 1. Determination of Cu^{2+} .^a

Sample	Cu^{2+} added (μM)	Cu^{2+} found (μM)	Recovery (%)	R.S.D. (n = 3) (%)
Tap water	0.0	0.0	—	—
	20.0	20.1	100.4	2.90
Drinking water	0.0	0.0	—	—
	20.0	20.3	101.3	2.78

^aConditions: $[\text{ANBP}] = 10 \mu\text{M}$ in $\text{MeOH}:\text{buffer}$ (2:1, pH 7.0).

Figure 4. (a) Absorption and (b) color changes of **ANBP** (20 μM) upon the addition of diverse anions.

Information). **ANBP-F⁻** showed a slight change of the dihedral angle ($5\text{C}, 6\text{C}, 7\text{C}, 8\text{C} = -129.403^\circ$) (Figure S11(c), Supplementary Information).

Based on these structures, TD-DFT calculations were conducted for analyzing electronic transition characters (Figures S12–S16, Supplementary Information). The major transition of **ANBP** occurred from HOMO $\rightarrow$ LUMO (Figure S12, Supplementary Information), and the main transition of the **ANBP-Cu²⁺** complex did from HOMO $\rightarrow$ LUMO (α) and HOMO $\rightarrow$ LUMO+1 (β) (Figure S13, Supplementary Information). In the case of **ANBP**, ICT was observed from the julolidine moiety to the benzophenone one (Figure S14,

Supplementary Information). **ANBP-Cu²⁺** complex showed both ligand-to-metal charge transfer (LMCT) and ICT characters. Therefore, a sensing mechanism for Cu^{2+} might be due to the enhancement of ICT character. The red shift ($536.05 \text{ nm} \rightarrow 549.26 \text{ nm}$) is consistent with the experimental data.

For **ANBP-F⁻**, the main transitions occurred from HOMO-1 $\rightarrow$ LUMO and HOMO $\rightarrow$ LUMO (Figure S15, Supplementary Information). The transitions showed ICT character, which was enhanced more than that of **ANBP**. Although the HOMO $\rightarrow$ LUMO transition of **ANBP** is similar to that of **ANBP-F⁻**, it seems that HOMO-1 $\rightarrow$ LUMO transition

Figure 5. Absorption changes of ANBP (20 μM) upon the addition of 0–110 equiv. of F^- .

Figure 7. Absorption changes for competitive selectivity of ANBP (20 μM) towards F^- (100 equiv.) with diverse anions (100 equiv.).

Figure 6. ^1H NMR titration of ANBP with F^- .

Scheme 3. Possible sensing mechanism of ANBP for F^- .

partially affected enhancement of ICT (Figure S16, Supplementary Information). Therefore, the sensing mechanism of F^- by **ANBP** might be due to the enhancement of ICT character via the deprotonation. The redshift from 536.05 nm to 577.82 nm is also matched with the experimental data. Based on UV-vis titration, Job plot, 1H NMR titration, and theoretical calculations, possible binding structures and detection mechanisms for Cu^{2+} and F^- were proposed in Schemes 2 and 3.

4. Conclusions

A novel benzophenone-based sensor **ANBP**, based on the combination of the benzophenone and the julolidine chromophores, was designed and synthesized. Sensor **ANBP** could sense Cu^{2+} by a color change from pale orange to pink in aqueous solution. The detection limit (6.82 μM) of **ANBP** to Cu^{2+} was far below that (31.3 μM) recommended by WHO. Importantly, sensor **ANBP** showed its potential for practical application in real samples. Moreover, sensor **ANBP** could exhibit high selectivity for F^- by a color change from orange to blue. DFT studies supported the experimental data and the proposed detection mechanisms. Interestingly, **ANBP** is the first benzophenone-based colorimetric indicator for the simultaneous sensing of Cu^{2+} and F^- .

Supplementary Information (SI)

Supplementary data (Table S1 and Figures S1–S16) associated with this article is available at www.ias.ac.in/chemsci.

Acknowledgements

We acknowledge the National Research Foundation of Korea (NRF-2018R1A2B6001686).

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