RESEARCH ARTICLE

LUMINESCENCE WILEY

A naphthyl thiourea-based effective chemosensor for fluorescence detection of Ag^+ and Zn^{2+}

Yuna Seo

| Sovoung Park | Gveongiin Kim | Minii Lee | Cheal Kim 💿

Department of Fine Chemistry, Seoul National University of Science and Technology (SNUT). Seoul, South Korea

Correspondence

Soyoung Park and Minji Lee, Cheal Kim, Department of Fine Chemistry, Seoul National University of Science and Technology (SNUT). Seoul 01811, South Korea. Email: soyp19@gmail.com; chealkim@snut.ac.kr

Funding information

The National Research Foundation of Korea, Grant/Award Numbers: 2018R1A2B6001686, NRF-2020R1A6A1A03042742

Abstract

A naphthyl thiourea-based effective chemosensor HNC, (E)-2-(2-hydroxy-3methoxybenzylidene)-N-(naphthalen-1-yl)hydrazine-1-carbothioamide, was synthesized. **HNC** showed quick responses toward Ag^+ and Zn^{2+} through marked fluorescence turn-on in different solvent conditions, respectively. Binding proportions of HNC to Ag^+ and Zn^{2+} were found to be 2:1 and 1:1, respectively. Detection limits of HNC for Ag^+ and Zn^{2+} were calculated as 3.82 and 0.21 μ M. Binding processes of HNC for Ag⁺ and Zn²⁺ were represented using Job's plot, DFT, ¹H NMR titration, and ESI-MS.

KEYWORDS

Ag⁺, calculations, chemosensor, fluorescent, thiourea, Zn²⁺

INTRODUCTION 1

 Ag^+ is a significant valuable metal ion and broadly used in industry, such as in the manufacturing of fungicides, in electronic and electrical applications, and in photographic production.^[1-5] These broad applications increase the amounts of Ag⁺ in environmental systems.^[6,7] Therefore, Ag⁺ could cause serious problems for humans.^[8] For instance, Ag⁺ can inactivate sulfur-containing enzymes and bind to imidazole, carboxyl, and amine moieties of diverse metabolites. Zn²⁺ is an abundant, essential metal ion in biology.^[9,10] For several decades, Zn²⁺ has been well recognized as an essential element in fundamental biological metabolisms such as growth and reproduction of living organisms and gene transcription.^[11-13] Therefore, an imbalance in Zn²⁺ levels may be related to pathological troubles.^[14,15] Particularly, excessive and deficiency levels of Zn²⁺ result in neurodegenerative problems such as iron deficiency, peripheral neuropathy, and Parkinson's disease.^[16] Therefore, effective sensing of Ag⁺ and Zn²⁺ has constantly attracted intensive attention in diverse areas.^[17–19]

To detect the transition metals such as Ag^+ and Zn^{2+} , several approaches such as electrochemistry, surfaces plasmon resonance spectroscopy and atomic absorption spectroscopy (AAS) have been developed.^[20-25] However, they demand time-consuming, sophisticated instruments and disciplined engineers.^[26-28] Conversely, fluorescence methods can readily and easily detect target ions with fast response and are easy to use.^[29-32]

The naphthyl group, one of the fluorophores, can be a valuable signal in part due to its excellent sensitivity and high quantum yield.^[33,34] The thiourea moiety with N and S atoms can act as a linker and chelate selectively soft metal ions via the hard-soft acid-base theory.^[35-37] In addition, O-vanillin has unique spectroscopic properties as a chromophore.^[38-40] Therefore, we expected that a naphthyl thiourea-based sensor with an O-vanillin moiety can effectively detect soft metal ions such as Ag^+ and Zn^{2+} with a strong and unique emission.

Here, we describe a naphthyl thiourea-based effective sensor HNC that could detect Ag⁺ and Zn²⁺ using different fluorescent colours, while chemosensors capable of detecting both Ag⁺ and Zn²⁺ are very rare. In particular, HNC showed the lowest detection limit (0.21 μ M) for Zn²⁺ among chemosensors for detecting both Ag⁺ and Zn^{2+} . HNC reacted with Ag^+ and Zn^{2+} at the ratios of 2:1 and 1:1, respectively. Considering Job's plot, ESI-MS, fluorescence, and UV-visible light titrations, calculations and ¹H NMR titration, detection processes of Ag⁺-2·HNC and Zn²⁺-HNC were illustrated.

EXPERIMENTAL 2

2.1 General information

Chemicals (analytical and spectroscopic grade) were commercially provided from Sigma-Aldrich. ¹H and ¹³C NMR measurements were executed on a Varian 400 MHz machine. ESI-MS was provided with a Thermo MAX machine. UV-vis and fluorescence measurements were carried out using Perkin Elmer spectrometers (Lambda 25 and LS45).

2.2 | Synthesis of HNC

2.2.1 | Synthesis of NH

Hydrazine (4 × 10⁻³ mol) was added to 1-naphthyl isothiocyanate (3 × 10⁻³ mol) in CH₃CH₂OH (10 ml). After stirring the solution for 15 h, a white powder was obtained and rinsed with ethyl alcohol and ether. ¹H NMR (dimethyl sulphoxide (DMSO)-*d*₆): 9.21 (s, 1H), 7.90 (m, 2H), 7.81 (d, 1H, J = 8.1 Hz), 7.73 (s, 1H), 7.50 (m, 4H) 4.90 (s, 2H).

2.2.2 | Synthesis of HNC

O-Vanillin (0.076 g, 5×10^{-4} mol) was added to **NH** (0.108 g, 5×10^{-4} mol) in CH₃CH₂OH (10 ml). The solution was shaken for 13 h at 25°C. A white-coloured powder was filtered and rinsed with ether (510 mg; 30%). ¹H NMR (DMSO-*d*₆): 11.88 (s, 1H), 10.31 (s, 1H), 9.26 (s, 1H), 8.58 (s, 1H), 7.98 (m, 1H), 7.89 (m, 2H), 7.76 (m, 1H), 7.54 (m, 4H), 6.99 (m, 1H), 6.77 (m, 1H), 3.35 (s, 3H). ¹³C NMR (DMSO-*d*₆): δ 176.57, 147.82, 146.04, 139.67, 135.70, 133.61, 130.52, 127.97, 127.83, 126.83, 126.68, 126.33, 125.91, 125.33, 123.40, 120.74, 118.78, 112.86, 55.91 ppm. ESI-mass: cald for C₁₉H₁₇N₃O₂S + H⁺ ([**HNC** + H⁺])⁺: 576.18 found 576.34.

2.3 | Fluorescence and UV-visible light titrations

For Ag⁺, **HNC** (1 \times 10⁻⁵ mol) was dissolved in 1000 μ l DMSO, and 6.0 μ l of the **HNC** (1 \times 10⁻² M) was diluted with 2.994 ml DMSO solution to provide 20 μ M. Ag(NO₃) (2 \times 10⁻⁵ mol) was dissolved in 1000 μ l of DMSO. Next, 3-24 μ l of the Ag(NO₃) stock (2 \times 10⁻² M) was put into **HNC** (20 μ M). After 30 s, UV-visible and fluorescence spectra were taken.

For Zn²⁺, **HNC** (1 × 10⁻⁵ mol) was dissolved in 1000 μ l DMSO, and 6.0 μ l of the **HNC** (1 × 10⁻² M) was diluted with 2.994 ml buffer/MeCN solution (7:3, v/v, 0.1 M bis-tris, pH 7.0) to provide 20 μ M. Zn(NO₃)₂ (2 × 10⁻⁵ mol) was dissolved in MeCN (1 ml). 0.3–3.0 μ l of the Zn(NO₃)₂ stock (2 × 10⁻² M) was put into **HNC** (20 μ M). After 30 s, UV-visible and fluorescence spectra were taken.

2.4 | Quantum yields

Quantum yield (Φ) was derived from the following equation with quinine as standard: ($\Phi_F = 0.53$ in 100 mM H_2SO_4)^[41]

$$\Phi_{F(x)} = \Phi_{F(s)} \left(A_S F_X / A_X F \right) \left(n_x / n_s \right)^2$$

where F: area of fluorescence emission curve; s: standard; A: absorbance; n: refractive index of the solvent; x: unknown.

2.5 | Job's plot

For Ag⁺, **HNC** (1 × 10⁻⁵ mol) was dissolved in 1000 µl DMSO. 150 µl of the **HNC** (1 × 10⁻² M) was diluted with 29.85 ml DMSO solution to provide 50 µM. Next, 0.3-2.7 ml of the diluted **HNC** was put into cuvettes. Ag(NO₃) (2 × 10⁻⁵ mol) was dissolved in 1000 µl of DMSO; 75 µl of the Ag⁺ (2 × 10⁻² M) was diluted with 29.925 ml DMSO solution to make 50 µM; 0.3-2.7 ml of the diluted Ag⁺ was put into each **HNC**. After 30 s, fluorescence spectra were measured.

For Zn²⁺, **HNC** (1 × 10⁻⁵ mol) was dissolved in 1000 μ l DMSO; 150 μ l of the **HNC** (1 × 10⁻² M) was diluted with 29.85 ml buffer/ MeCN solution (7:3) to make 50 μ M; 0.3–2.7 ml of the diluted **HNC** was put into cuvettes; 75 μ l of the Zn²⁺ (2 × 10⁻² M) was diluted with 29.925 ml buffer/MeCN solution (7:3) to make 50 μ M. 0.3–2.7 ml of the diluted Zn²⁺ was put into each **HNC**. After 30 s, fluorescence spectra were measured.

2.6 | Competition experiments

HNC $(1 \times 10^{-5} \text{ mol})$ was dissolved in 1000 µl DMSO. Next, 20 µmol of various metals (Ni(NO₃)₂, Pb(NO₃)₂, Fe(NO₃)₃, In(NO₃)₃, NaNO₃, Mn(NO₃)₂, Cr(NO₃)₃, KNO₃, Zn(NO₃)₂, Ga(NO₃)₃, Cd(NO₃)₂, Cu(NO₃)₂, Mg(NO₃)₂, Hg(NO₃)₂, Co(NO₃)₂, Ca(NO₃)₂, Fe(NO₃)₂ and Al(NO₃)₃) were also dissolved in 1000 µl DMSO.

For Ag⁺, 36.0 µl of each cation (2 × 10⁻² M) and 36.0 µl of Ag⁺ (2 × 10⁻² M) was put into 3000 µl DMSO; 6 µl of **HNC** solution (1 × 10⁻² M) was put into the mixed solutions. For Zn²⁺, 2.4 µl of each cation (2 × 10⁻² M) and 2.4 µl of Zn²⁺ (2 × 10⁻² M) were transferred into 3000 µl of buffer/MeCN solution (7:3). After 30 s, fluorescence spectra were measured.

2.7 | ¹H NMR titration

Three NMR tubes of **HNC** (7.0 mg, 2×10^{-5} mol) dissolved in DMSO- d_6 (1000 µl) were made, and 0–1.0 equivalents of AgNO₃ dissolved in DMSO- d_6 (1000 µl) were added to the solution of **HNC**. ¹H NMR titration data were obtained after mixing the solution for 20 s.

For Zn²⁺, two NMR tubes of **HNC** (7.0 mg, 2×10^{-5} mol) dissolved in DMSO- d_6 (200 µl) and CD₃CN (500 µl) were made, and 0–1 equivalents of Zn(NO₃)₂ dissolved in DMSO- d_6 (1000 µl) were added to the solution of **HNC**. ¹H NMR titration data were obtained after mixing the solution for 20 s.

2.8 | Calculations

All calculations for HNC, Ag^+-2 ·HNC and Zn^{2+} -HNC were performed with the Gaussian 16 W program.^[42] The B3LYP/6-31G (d,p)^[43-46] basis set was used for HNC and the LANL2DZ basis was applied for Ag^+ and Zn^{2+} .^[47-49] Imaginary frequencies were not discovered in HNC, Ag^+-2 ·HNC and Zn^{2+} -HNC, signifying that these structures

defined local minima. The integral equation formalism variant (IEFPCM) was used to consider the solvent effects of dimethyl sulfoxide and acetonitrile.^[50,51] The transition states and energy levels of HNC, Ag⁺-2·HNC and Zn²⁺-HNC were obtained through TD-DFT.

3 | RESULTS AND DISCUSSION

HNC was provided with the imine formation of O-vanillin with **NH** in ethyl alcohol (Scheme 1) and affirmed by ¹H and ¹³C NMR and ESI-MS. The sensing abilities of **HNC** to Ag^+ and Zn^{2+} were examined with varied analytical tools such as UV-vis spectroscopy, fluorescence spectroscopy, ESI-MS, ¹H NMR titration, DFT calculation.

3.1 | Fluorescence sensing for Ag⁺

The fluorescence sensing variation of **HNC** was studied toward varied cations such as Ca^{2+} , Fe^{3+} , In^{3+} , Cd^{2+} , Cr^{3+} , Cu^{2+} , Mg^{2+} , Ga^{3+} , Hg^{2+} ,

(a)

Ag⁺, Pb²⁺, Co²⁺, Na⁺, Al³⁺, Ni²⁺, Zn²⁺, K⁺, Mn²⁺ and Fe²⁺ in DMSO (Figure 1). On addition of the cations (12 equiv) into **HNC** ($\Phi = 0.0051$), only Ag⁺ exhibited the striking fluorescence increment ($\Phi = 0.0214$) at 340 nm, whereas other metals showed no or slight variations. These results indicated that sensor **HNC** was clearly able to distinguish Ag⁺.

To analyze the photophysical characteristic of **HNC**, the fluorescence and UV-vis titrations of **HNC** with Ag⁺ were conducted (Figures 2 and 3). The incremental addition of Ag⁺ to **HNC** caused a striking emission increment at 436 nm with saturation at 12 equiv of Ag⁺. Upon the addition of Ag⁺ (0-12 equiv) to **HNC** for UV-vis titration (Figure 3), the absorption at 330 nm was diminished, and two definite isosbestic points at 302 and 361 nm appeared. The detection limit of **HNC** for Ag⁺ was provided to be 3.82 μ M (3 σ /k) with fluorescence titration (Figure S1).^[52]

Job's plot test was performed to determine the association proportion of **HNC** with Ag⁺ (Figure S2). A maximal intensity showed up at the molar fraction of 0.7, which means that one Ag⁺ may combine with two **HNC**.^[53] The structure of the Ag⁺-2·**HNC** complex was



EtOH



FIGURE 2 Fluorescence variations of **HNC** (20 μ M) with increment of Ag⁺. Inset: Fluorescence intensity (at 436 nm) as the amount of Ag⁺ (blue line = **HNC** and red line = Ag⁺- 2·**HNC**)



SCHEME 2 Structure of Ag⁺-2·HNC

12

600

containing varied cations (12 equiv), most of them did not interfere with the detection of Ag⁺ using **HNC**, while for Fe³⁺, Fe²⁺ and Hg²⁺ inhibited *c*. 30–50% and Cu²⁺ inhibited completely. Additionally, we checked the reversibility of **HNC** to Ag⁺, but it was not successful.

3.2 | Spectroscopic response of HNC to Zn^{2+}

The fluorescence spectra of **HNC** with varied cations (Co²⁺, Ga³⁺, K⁺, Cu²⁺, Pb²⁺, Ca²⁺, Ga³⁺, Na⁺, Al³⁺, Mn²⁺, Fe²⁺, Cr³⁺, Ni²⁺, Fe³⁺, Mg² ⁺, Cd²⁺, Ag⁺, In³⁺and Zn²⁺) were measured in buffer/MeCN solution (7:3, v/v). As shown in Figure 4, **HNC** ($\Phi = 0.0137$) and **HNC** with most cations exhibited a small emission at 480 nm ($\lambda_{ex} = 380$ nm). Alternatively, **HNC** with Zn²⁺ exhibited a marked greenish-blue fluorescence response ($\Phi = 0.0864$). Therefore, **HNC** could work as an effective fluorescence sensor for detecting Zn²⁺. Conversely, at this stage it is not clear why **HNC** detects only Ag⁺ in DMSO and only Zn²⁺ in buffer/MeCN solution (7:3, v/v), respectively.

To analyze the chemosensing properties of **HNC** to Zn^{2+} , fluorescence and UV-visible light titrations were carried out (Figures 5 and 6). The emission of **HNC** at 480 nm increased up to the 0.8 equiv of Zn^{2+} (Figure 5). In Figure 6, the absorbance peak at 330 nm constantly decreased up to 0.8 equiv of Zn^{2+} . Two absolute isosbestic

FIGURE 3 Absorption variations of HNC (20 μ M) with increment of Ag⁺ (blue line = HNC and red line = Ag⁺-2·HNC)

350

Wavelength (nm)

400

450

300

proved with ESI-MS (Figure S3). The intensity of 809.25 (*m/z*) was consistent with the $[2 \cdot HNC + Ag^+]^+$ [calcd, 809.11]. Moreover, the ¹H NMR titration demonstrated a clear interaction of HNC and Ag⁺ (Figure S4). On addition of Ag⁺ into HNC, the protons, H₁, H₆, H₇, and H₈, were greatly shifted down field, while the protons attached to the benzene and the naphthyl moieties were moved slightly down field. These outcomes led us to propose that Ag⁺ may coordinate with the S of C=S and the N of imine. Job's plot, ESI-MS analysis and ¹H NMR titration suggested that Ag⁺ would react with two HNC (Scheme 2).

Binding constant of **HNC** with Ag^+ was provided to be $5 \times 10^8 \text{ M}^{-1}$ with Li's equation (Figure S5),^[54] which is in the scope of those (10^2 to 10^9) formerly reported for Ag^+ sensors. The practicable sensing ability of **HNC** for Ag^+ was executed with a competition test (Figure S6). On addition of **HNC** to Ag^+ solution (12 equiv)





FIGURE 5 Fluorescence variations of **HNC** (20 μ M) with increment of Zn²⁺. Inset: Fluorescence emission (at 480 nm) as the amount of Zn²⁺ (blue line = **HNC** and red line = Zn²⁺ -**HNC** (0.8 equiv))

points appeared at 269 and 353 nm, indicating binding of **HNC** with Zn²⁺. Using fluorescence titrations, the detection limit of Zn²⁺ with **HNC** was obtained as 0.21 μ M (3 σ /k) (Figure S7).^[55] Interestingly, **HNC** has the lowest detection limit for Zn²⁺ among chemosensors for detecting both Ag⁺ and Zn²⁺ (Table S1).

To determine the complexation ratio of **HNC** and Zn^{2+} , Job's plot test was performed (Figure S8). The highest value appeared at molar fraction of 0.5, which meant the formation of a 1:1 complex of **HNC** with Zn^{2+} . This was verified with ESI-MS analysis (Figure S9). The intensity of 492.08 (*m*/*z*) was proposed to be [**HNC**-H⁺ + DMSO + Zn^{2+}]⁺ (calcd, 492.04) in the positive-ion peak. Moreover, the ¹H NMR titration demonstrated a clear interaction of **HNC** and Zn^{2+}

(Figure S10). On addition of Zn^{2+} into **HNC**, the protons, H₁, H₆, H₇, and H₈, were slightly shifted down filed. These outcomes led us to propose that Zn^{2+} may coordinate with the O molecule of the phenol group, the S of C=S and the N of the imine. The analysis of Job plot, ESI-mass and ¹H NMR titration proposed the appropriate binding formation of Zn^{2+} -**HNC** (Scheme 3).

The binding constant of **HNC** with Zn²⁺ was obtained as $5.3 \times 10^4 \text{ M}^{-1}$ with the Benesi-Hildebrand equation (Figure S11).^[56] To determine whether **HNC** effectively detects to Zn²⁺ in solution including other metal ions, competition experiments were conducted (Figure S12). Most metal ions did not inhibit the detection of **HNC** with Zn²⁺, while Cu²⁺, Fe²⁺ and Fe³⁺ showed fluorescence



FIGURE 6 Absorption variations of **HNC** (20 μ M) with increment of Zn²⁺ (blue line = **HNC** and red line = Zn²⁺-**HNC**)



SCHEME 3 Structure of Zn²⁺-HNC



Dihedral angle (1N, 2N, 3C, 4S) : 2.40 °

quenching of 30–50%. The pH response of Zn^{2+} -**HNC** was obtained at various pH ranges (6.0–9.0) (Figure S13). The result exhibited a large fluorescence increment at pH 7.0–9.0, indicating that **HNC** could detect Zn^{2+} over the pH range 7.0–9.0. Additionally, we checked the reversibility of **HNC** to Zn^{2+} , but this was not successful.

3.3 | Theoretical calculations for Ag⁺

To further understand the sensing mechanism of **HNC** to Ag⁺, calculations were carried out. The energy-optimized patterns of **HNC** and Ag⁺-2·**HNC** are shown in Figure 7. **HNC** had a dihedral angle of 2.40 (1 N, 2 N, 3C, 4S), whereas Ag⁺-2·**HNC** had a dihedral angle of -6.76 (1 N, 2 N, 3C, 4S). The interaction of **HNC** and Ag⁺ induced a distortion in the structure of **HNC**.

Based on the energy-optimized patterns, TD-DFT calculations were implemented to investigate molecular orbital transitions and electronic transition states of **HNC** and Ag^+-2 ·**HNC**. For **HNC**, the main absorption was identified as the second excited state, which originated from the HOMO \rightarrow LUMO transition (341.51 nm), showing the intramolecular charge transfer (ICT) characteristic (Figures S14 and S15). For Ag^+-2 ·**HNC**, the main molecular orbital contribution of the 1st excited state was determined for the HOMO \rightarrow LUMO transition (367.10 nm), showing the ICT characteristic (Figures S15 and S16). Considering the similar ICT characteristics and molecular



Dihedral angle (1N, 2N, 3C, 4S) : -6.76 °







Dihedral angle (1N, 2N, 3C, 4S) : -3.15 °



FIGURE 8 Energy-optimized patterns of (a) **HNC** and (b) Zn²⁺-**HNC**

orbital transitions of the two compounds, the chelation of Ag⁺ with **HNC** induced a decrease in the HOMO-LUMO energy gap of Ag⁺-2·**HNC** compared with that of **HNC**, which was consistent with the red shift in the UV-visible spectra. The decrease in the energy gap could be the cause of the fluorescence enhancement. Therefore, the fluorescence response of the Ag⁺-2·**HNC** complex could be demonstrated by the chelation-enhanced fluorescence (CHEF) effect. Integrating all the results from the Job's plot, calculations, ¹H NMR titration, and ESI-MS, we suggested a sensing mechanism for Ag⁺-2·**HNC** (Scheme 2).

3.4 | Theoretical calculations for Zn²⁺

To illustrate the sensing process of **HNC** for Zn^{2+} , calculations were made. The energy-optimized patterns of **HNC** and Zn^{2+} -**HNC** are shown in Figure 8. **HNC** with a distorted structure displayed a dihedral angle of 177.64 (10, 2 N, 3 N, 4S), which resulted from the rotation of the naphthyl group. Zn^{2+} -**HNC** with a more flatted structure had a dihedral angle of -0.97 (1 N, 2 N, 3C, 4S), which resulted from a small rotation of the naphthyl group in the formation of the complex.

To examine molecular orbitals and transition energies, TD-DFT calculations were conducted through energy-optimized patterns of HNC and Zn^{2+} -HNC. For HNC, the main absorption appeared from the HOMO-1 \rightarrow LUMO transition (335.73 nm; Figures S17 and S18), indicating ICT characteristics. As indicated from the most relevant colour change in Zn^{2+} -HNC, the excited state (386.18 nm) mainly originated from HOMO \rightarrow LUMO with ICT characteristics



Dihedral angle (1N, 2N, 3C, 4S) : -0.97 °



(Figures S18 and S19). Due to similar orbital characteristics in two compounds and the formation of the rigid form after binding to Zn²⁺, the fluorescence change process can be inferred by CHEF effect. The restriction of nonradiative transition and improvement of radiative transition occurred during the formation of the metal complex. Furthermore, the change in the HOMO-LUMO energy gap corresponded to the bathochromic movement in UV-visible experiments. Taking into consideration Job's plots, calculations, ¹H NMR titration, and ESI-MS, we suggested a conceivable detection mechanism for Zn²⁺-**HNC** (Scheme 3).

4 | CONCLUSION

We demonstrated an effective naphthyl thiourea-based fluorescence sensor **HNC** that showed a selective fluorescence turn-on mechanism for Ag⁺ and Zn²⁺ over the varied metal ions. The complexation ratio of **HNC** with Ag⁺ and Zn²⁺ were calculated to be 2:1 and 1:1. **HNC** could be applied to sense Zn²⁺ and Ag⁺ at low detection limits (0.21 and 3.82 μ M). Importantly, **HNC** has the lowest detection limit for Zn² ⁺ among chemosensors for detecting both Ag⁺ and Zn²⁺. Sensing processes of **HNC** to Ag⁺ and Zn²⁺ were elucidated using fluorescence titration, UV-vis, ESI-MS, DFT, and ¹H NMR titration.

ACKNOWLEDGEMENTS

The National Research Foundation of Korea (NRF-2020R 1A6A1A03042742 and 2018R1A2B6001686) is gratefully acknowledged.

8 WILEY LUMINESCENCE The Journal of Biological and Chemical Luminescence

ORCID

Cheal Kim 🝺 https://orcid.org/0000-0002-7580-0374

REFERENCES

- [1] Y. Zhang, D. Wang, C. Sun, H. Feng, D. Zhao, Y. Bi, Dyes Pigm. 2017, 141, 202.
- [2] L. Q. Li, L. J. Gao, Spectrochim. Acta Part a Mol. Biomol. Spectrosc. 2016, 152, 426.
- [3] P. Su, Z. Zhu, J. Wang, B. Cheng, W. Wu, K. Iqbal, Y. Tang, Sens. Actuators, B 2018, 273, 93.
- [4] R. Saravanan, M. Mansoob Khan, V. K. Gupta, E. Mosquera, F. Gracia, V. Narayanan, A. Stephen, *J. Colloid Interface Sci.* 2015, 452, 126.
- [5] R. Saravanan, N. Karthikeyan, V. K. Gupta, E. Thirumal, P. Thangadurai, V. Narayanan, A. Stephen, *Mater. Sci. Eng. C* 2013, 33, 2235.
- [6] C. Chen, H. Liu, B. Zhang, Y. Wang, K. Cai, Y. Tan, C. Gao, H. Liu, C. Tan, Y. Jiang, *Tetrahedron* **2016**, *72*, 3980.
- [7] Z. E. Chen, H. Zhang, Z. Iqbal, Spectrochim. Acta, Part a 2019, 215, 34.
- [8] S. Y. Lee, K. H. Bok, C. Kim, RSC Adv. 2017, 7, 290.
- [9] D. Maity, T. Govindaraju, Chem. Commun. 2012, 48, 1039.
- [10] J. M. Jung, D. Yun, H. Lee, K. T. Kim, C. Kim, Sens. Actuators, B 2019, 297, 126814.
- [11] A. Pandith, N. Uddin, C. H. Choi, H. S. Kim, Sens. Actuators, B 2017, 247, 840.
- [12] Y. Bian, M. Cai, P. ZHou, J. Zhao, K. Zhong, S. Hou, L. Tang, RSC Adv. 2013, 37, 16802.
- [13] A. Manna, S. Paul, A. K. Maity, P. Saha, C. K. Quah, H. K. Fun, S. Goswami, RSC Adv. 2014, 4, 34572.
- [14] Y. Chen, Y. Bai, Z. Han, W. He, Z. Guo, Chem. Soc. Rev. 2015, 44, 4517.
- [15] J. M. Jung, J. H. Kang, J. Han, H. Lee, M. H. Lim, K. T. Kim, C. Kim, Sens. Actuators, B 2018, 267, 58.
- [16] N. Narayanaswamy, D. Maity, T. Govindaraju, Supramol. Chem. 2011, 23, 703.
- [17] L. Tang, X. Dai, K. Zhong, D. Wu, X. Wen, Sens. Actuators, B 2014, 203, 557.
- [18] N. Bhuvanesh, S. Suresh, J. Prabhu, K. Kannan, V. Rajesh Kannan, R. Nandhakumar, Opt. Mater. 2018, 2018, 123.
- [19] S. Kim, H. Lee, J. B. Chae, C. Kim, Inorg. Chem. Commun. 2020, 118, 108044.
- [20] Y. Q. Fan, P. P. Mao, L. Liu, J. Liu, Y. M. Zhang, H. Yao, Q. Lin, T. B. Wei, Chem. Eur. J. 2018, 24, 777.
- [21] C. Lim, M. An, H. Seo, J. H. Huh, A. Pandith, A. Helal, H. S. Kim, Sens. Actuators, B 2017, 241, 789.
- [22] A. Manna, D. Sarkar, S. Goswami, C. K. Quah, H. K. Fun, RSC Adv. 2016, 6, 57417.
- [23] Q. Lin, K. P. Zhong, J. H. Zhu, L. Ding, J. X. Su, H. Yao, T. B. Wei, Y. M. Zhang, *Macromolecules* **2017**, 50, 7863.
- [24] T. H. Ma, M. Dong, Y. M. Dong, Y. W. Wang, Y. Peng, Chem. Eur. J. 2010, 16, 10313.
- [25] M. Mukhopadhyay, D. Banerjee, A. Koll, A. Mandal, A. Filarowski, D. Fitzmaurice, R. Das, S. Mukherjee, J. Photochem. Photobiol. A 2005, 175, 94.
- [26] H. J. Jung, N. Singh, D. Y. Lee, D. O. Jang, Tetrahedron Lett. 2010, 51, 3962.
- [27] J. B. Chae, D. Yun, S. Kim, H. Lee, M. Kim, M. Hee, K. Kim, C. Kim, Spectrochim. Acta, Part a 2019, 219, 74.
- [28] V. K. Gupta, N. Mergu, L. K. Kumawat, A. K. Singh, *Talanta* 2015, 144, 80.
- [29] Y. W. Choi, G. R. You, J. J. Lee, C. Kim, Inorg. Chem. Commun. 2016, 63, 35.
- [30] D. Y. Lee, N. Singh, D. O. Jang, Tetrahedron Lett. 2010, 51, 1103.

- [31] V. K. Gupta, A. K. Singh, L. K. Kumawat, Sens. Actuators, B 2014, 195, 98.
- [32] V. K. Gupta, N. Mergu, L. K. Kumawat, A. K. Singh, Sens. Actuators, B 2015, 207, 216.
- [33] G. J. Park, M. M. Lee, G. R. You, Y. W. Choi, C. Kim, Tetrahedron Lett. 2014, 55, 2517.
- [34] J. H. Lee, J. H. Lee, S. H. Jung, T. K. Hyun, M. Feng, J. Y. Kim, J. H. Lee, H. Lee, J. S. Kim, C. Kang, K. Y. Kwon, J. H. Jung, *Chem. Commun.* 2015, 51, 7463.
- [35] E. J. Jun, K. M. K. Swamy, H. Bang, S. Kim, J. Yoon, Tetrahedron Lett. 2006, 47, 3103.
- [36] Z. Zhang, S. Lu, C. Sha, D. Xu, Sens. Actuators, B 2015, 208, 258.
- [37] P. Alaei, S. Rouhani, K. Gharanjig, J. Ghasemi, Spectrochim. Acta, Part a 2012, 90, 85.
- [38] Y. N. Guo, X. H. Chen, S. Xue, J. Tang, Inorg. Chem. 2011, 50, 9705.
- [39] M. Andruh, Dalton Trans. 2015, 44, 16633.
- [40] M. Sarwar, A. M. Madalan, C. Tiseanu, G. Novitchi, C. Maxim, G. Marinescu, D. Luneau, M. Andruh, New J. Chem. 2013, 37, 2280.
- [41] L. Tang, Z. Zheng, Y. Bian, J. Biol. Chem. Lumin. 2016, 31, 1456.
- [42] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, D. J. Fox, *Gaussian* 16, *Revision* C.01, Gaussian, Inc, Wallingford CT 2016.
- [43] A. D. Becke, J. Chem. Phys. 1993, 98, 5648.
- [44] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- [45] P. C. Hariharan, J. A. Pople, Theor. Chim. Acta 1973, 28, 213.
- [46] M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, J. Chem. Phys. 1982, 77, 3654.
- [47] P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 270.
- [48] W. R. Wadt, P. J. Hay, J. Chem. Phys. 1985, 82, 284.
- [49] P. J. Hay, W. R. Wadt, J. Chem. Phys. 1985, 82, 299.
- [50] V. Barone, M. Cossi, J. Phys. Chem. A 1998, 102, 1995.
- [51] M. Cossi, V. Barone, J. Chem. Phys. 2001, 115, 4708.
- [52] D. Kim, S. Y. Na, H. J. Kim, Sens. Actuators, B 2016, 226, 227.
- [53] P. Job, Ann. Chim. 1928, 9, 113.
- [54] R. Yang, K. Li, K. Wang, F. Zhao, N. Li, F. Liu, Anal. Chem. 2003, 75, 612.
- [55] A. Kim, C. Kim, New J. Chem. 2019, 43, 7320.
- [56] H. A. Benesi, J. H. Hildebrand, J. Am. Chem. Soc. 1949, 71, 2703.

SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Y. Seo, S. Park, G. Kim, M. Lee, C. Kim, *Luminescence* **2021**, 1. <u>https://doi.org/10.1002/bio.</u> 4114