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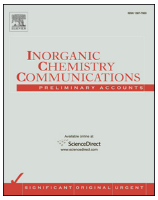

Short communication

A NBD-based highly sensitive and selective colorimetric chemosensor for Ni^{2+} and Cu^{2+}

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ABSTRACT

A new colorimetric chemosensor **1**, containing the 7-nitrobenzo-2-oxo-1,3-diazolyl (NBD) moiety and the phenol one connected through Schiff-base linkage, has been synthesized. Sensor **1** showed remarkable color changes from pink to orange and pale brown, respectively, upon selective binding to Ni^{2+} and Cu^{2+} that can be identified by the naked-eye. The binding modes of sensor **1** to Ni^{2+} and Cu^{2+} were determined to be 1:1 stoichiometries using a Job plot and ESI-mass analysis. The sensor **1** showed high sensitivity toward Ni^{2+} and Cu^{2+} with the detection limits of 0.48 μM and 0.26 μM, respectively. The recognition properties of the sensor **1** toward Ni^{2+} and Cu^{2+} were explained by using photophysical experiments and theoretical calculations. Practically, sensor **1** functioned as a visible test strip for Ni^{2+} and Cu^{2+}.

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Nickel is an essential trace element for supporting life, such as respiration, metabolism and biosynthesis [1]. Moreover, metallic nickel and its compounds are widely used in modern industries such as electroplating, rods for arc welding, pigments for paints, ceramics, surgical and dental prostheses, catalysts for hydrogenation and magnetic tapes of computers [2]. However, an oversupply of nickel in such industries can cause a variety of pathological effects in the human body as in a form of lung cancer, prostate cancer, larynx cancer, lung embolism, asthma and chronic bronchitis [3]. US EPA has classified nickel as one of 13 priority metal pollutants for its widespread use [4]. On the other hand, copper is the third most abundant essential trace element in the human body and it plays an important role in many fundamental physiological processes in organisms. However, unregulated overloading of copper can cause extremely negative health effects such as gastrointestinal disturbance and liver or kidney damage [5]. Therefore, the development of a novel chemosensor for the rapid and convenient detection of nickel and copper is of great importance [6–15]

Herein, we report a simple dual target chemosensor **1** based on the NBD moiety and phenol one connected via a Schiff-base linkage. Sensor **1** is highly responsive to Ni^{2+} and Cu^{2+} with remarkable color changes from pink to orange and pale brown, respectively, and it showed an excellent selectivity in the presence of other competing metal ions. Practically, **1** functioned as a colorimetric test strip for Ni^{2+} and Cu^{2+}. The sensing mechanisms of Ni^{2+} and Cu^{2+} were explained by theoretical calculations.

The compound **2** was synthesized by the substitution reaction of NBD chloride and hydrazine according to the literature method (see Supporting Information), and the sensor **1** was obtained by the condensing of **2** and salicylaldehyde with 52% yield in EtOH (Scheme 1). Both compounds **1** and **2** were characterized by ^{1}H NMR and ^{13}C NMR, ESI-mass spectroscopy, and elemental analysis. To explore the sensing behavior of sensor **1** toward metal ions, the absorption spectral changes to various metal ions including Al^{3+}, Ga^{3+}, In^{3+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Cr^{3+}, Hg^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+} and Pb^{2+} were investigated in CH_3CN solution (Fig. 1). The remarkable spectroscopic and visual responses of **1** were observed upon the addition of Ni^{2+} and Cu^{2+}, which were corresponded with color changes from pink to orange and pale brown, respectively. In contrast, no significant spectral or visible change was observed in the presence of other metal ions under the identical conditions. Importantly, this is the second example that an organo-chemosensor can operate for colorimetric detection of both Ni^{2+} and Cu^{2+}, to the best of our knowledge [16]. The binding properties of **1** with Ni^{2+} were studied by UV–vis titration (Fig. 2). Upon gradual increase of Ni^{2+} concentration, the band at 515 nm gradually shifted to 498 nm. At the same time, the absorption peak at 400 nm gradually decreased while the absorption intensities at 460 nm and 625 nm increased until it reached a limiting value (1.6 equiv). Moreover, the presence of a clearly defined isosbestic point at 425 nm implied that sensor **1** reacted with Ni^{2+} to form a stable complex.

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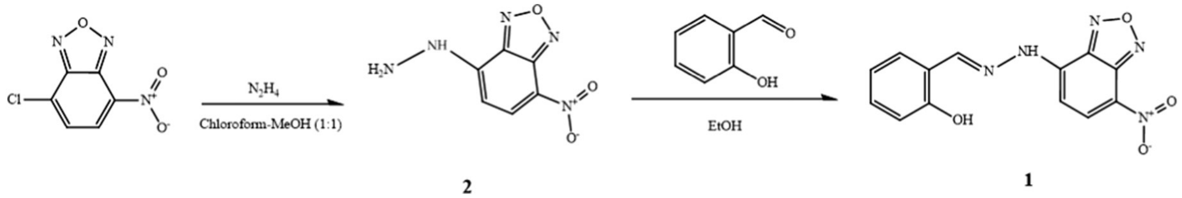

Scheme 1. Synthesis of **1**.

To determine the stoichiometric ratio of **1** and Ni^{2+}, Job plot analysis [17] was carried out using absorption titration experiments in the presence of various molar fractions of Ni^{2+} (Fig. S1). When the molar fraction of Ni^{2+} was 0.5, the absorbance at 550 nm reached an extreme value, suggesting that the complex formation between **1** and Ni^{2+} has a stoichiometric ratio of 1:1. The ESI-mass analysis of a mixture of **1** and Ni^{2+} also revealed the formation of a 1:1 complex through the metal coordination interaction, with the peak at $m/z = 432.12$ (Fig. S2). It corresponded to the coordination structure of $[\mathbf{1} + Ni^{2+} - H^{+} + CH_3CN + 2H_2O]^{+}$ (calcd: 432.04). On the basis of the 1:1 stoichiometry and UV–vis titration data, the binding constant of **1**-Ni^{2+} complex was determined to be 5.7×10^4 from Benesi-Hildebrand equation (Fig. S3) [18]. The detection limit ($3\sigma/K$) [14] of sensor **1** as a colorimetric sensor for the analysis of Ni^{2+} was found to be 0.48 μM (Fig. S4). Thus, it is useful to detect the submicromolar concentration of Ni^{2+}, which belongs to the range found in many chemical and environmental systems.

One of the important criterion for a selective sensor is the ability to detect a specific ion in the presence of other competing ions. The absorbance (at 625 nm) of **1**-Ni^{2+} complex remained unperturbed in the presence of different cations such as Al^{3+}, Ga^{3+}, In^{3+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Mg^{2+}, Cr^{3+}, Ag^{+}, Hg^{2+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+} and Pb^{2+} (Fig. S5), while Cu^{2+} did show some interference. The results indicated that the presence of most background ions exerted no interference to the detection of Ni^{2+}.

UV–vis titrations of **1** with Cu^{2+} were also conducted (Fig. 3). Upon gradual increase of the Cu^{2+} concentration, the absorption band at 500 nm gradually decreased and the band at 400 nm increased. A new

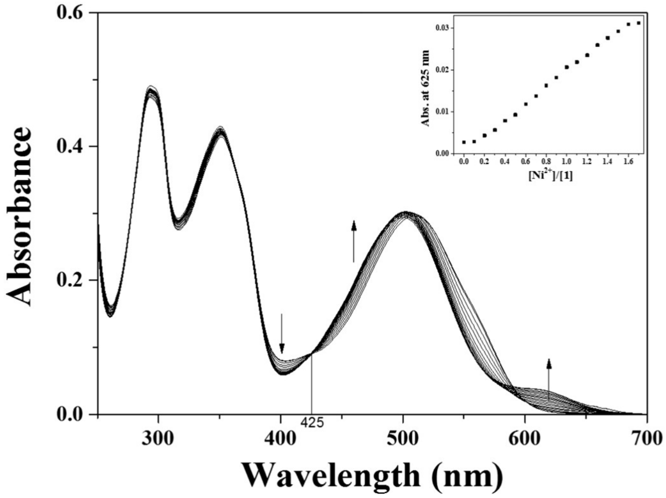

Fig. 2. Absorption spectral changes of **1** (20 μM) in the presence of different concentrations of Ni^{2+} ions.

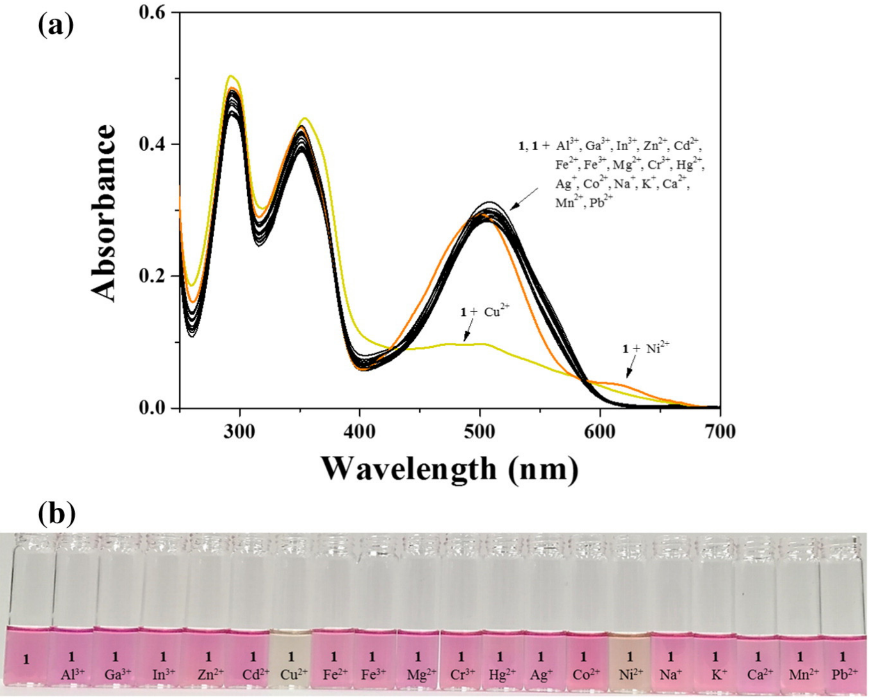

Fig. 1. (a) Absorption spectral changes of **1** (20 μM) in the presence of 1.6 equiv. of different metal ions. (b) The color changes of **1** (20 μM) upon addition of various metal ions (1.6 equiv). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

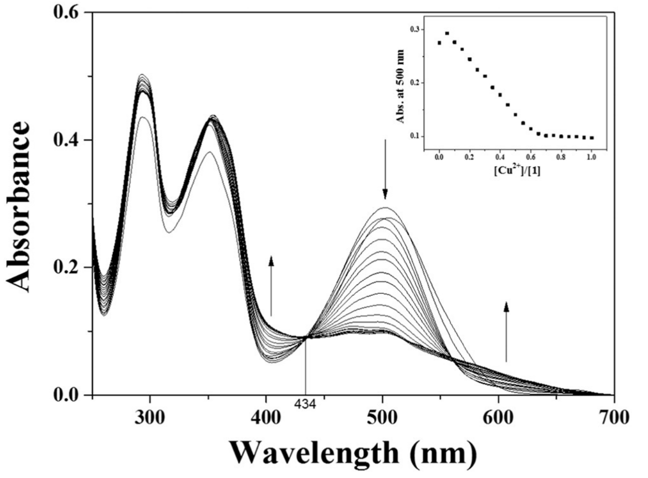

Fig. 3. Absorption spectral changes of **1** (20 μM) in the presence of different concentrations of Cu^{2+} ions.

band at 600 nm appeared with an isosbestic point at 434 nm, which indicated that the only one complex was formed between **1** and Cu^{2+}. The stoichiometry of the **1**-Cu^{2+} complex was determined by Job plot [17] and ESI-mass spectrometry analysis. The Job plot for the binding of **1** and Cu^{2+} exhibited a 1:1 stoichiometry (Fig. S6). The positive-ion mass spectrum confirmed the formation of $[\mathbf{1} + Cu^{2+} - H^{+} + CH_3OH]^{+}$ based on the presence of a peak at $m/z = 393.20$ (calcd: 393.01) (Fig. S7). The association constant was calculated to be $1.3 \times 10^5\ M^{-1}$ from a Benesi-Hildebrand plot (Fig. S8) [18]. This value is within the range of those (10^2–10^9) reported for Cu^{2+}-binding sensors. The detection limit [19] of the **1** for Cu^{2+} was determined to be 0.26 μM (Fig. S9).

To utilize **1** as an ion-selective colorimetric chemosensor for Cu^{2+}, the effect of competing metal ions was carried out (Fig. 4). Upon addition of 1.0 equiv. of Cu^{2+} in the presence of other metal ions (1.0 equiv) such as Al^{3+}, Ga^{3+}, In^{3+}, Zn^{2+}, Cd^{2+}, Fe^{2+}, Fe^{3+}, Cr^{3+}, Mg^{2+}, Hg^{2+}, Ag^{+}, Co^{2+}, Ni^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mn^{2+} and Pb^{2+}, coexistent metal ions exerted no interference to the detection of Cu^{2+}.

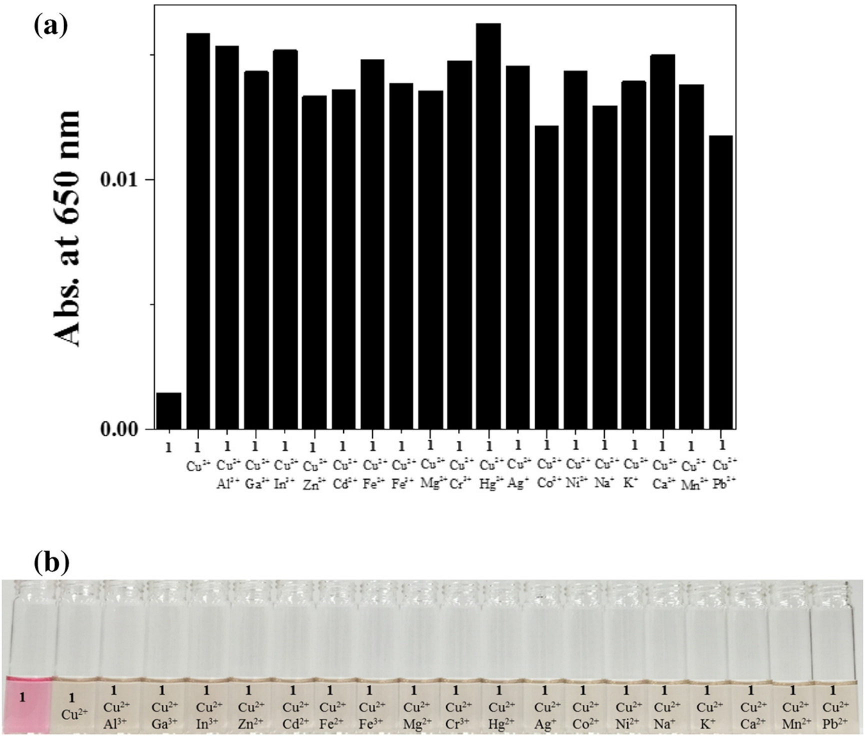

Fig. 4. (a) Competitive selectivity of **1** (20 μM) toward Cu^{2+} (1.0 equiv) in the presence of other metal ions (1.0 equiv). (b) The color changes of **1** (20 μM) in the presence of Cu^{2+} (1.0 equiv) and other metal ions (1.0 equiv).

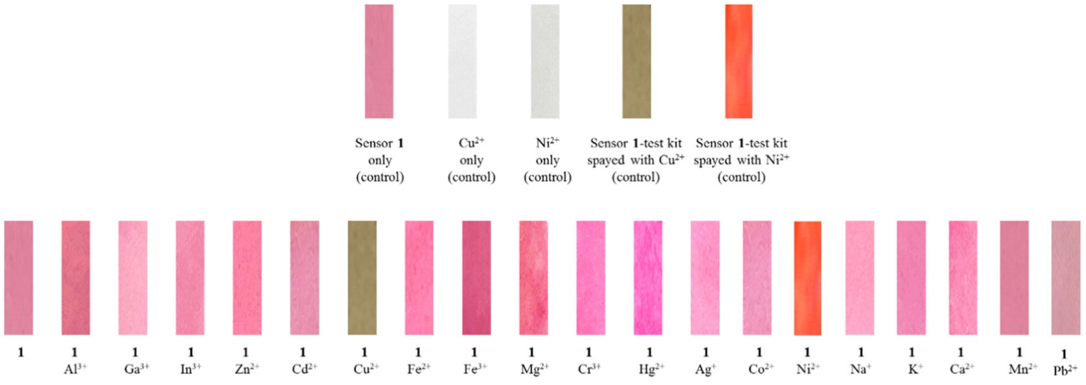

Fig. 5. Photographs of the filter papers coated with **1** for the detection of Ni^{2+} and Cu^{2+}. Sensor-**1** test strips (100 μM) immersed in various metal ions (20 μM).

Motivated by the favorable features of sensor **1** in solution, colorimetric test strips were prepared (Fig. 5). When the test strips coated with **1** were immersed in various metal-ion solutions, only Ni^{2+} and Cu^{2+} showed the distinct visible color changes from pink to orange and brown, respectively. Therefore, **1** could be used for "in the field" measurements of Ni^{2+} and Cu^{2+} that did not require any additional equipment.

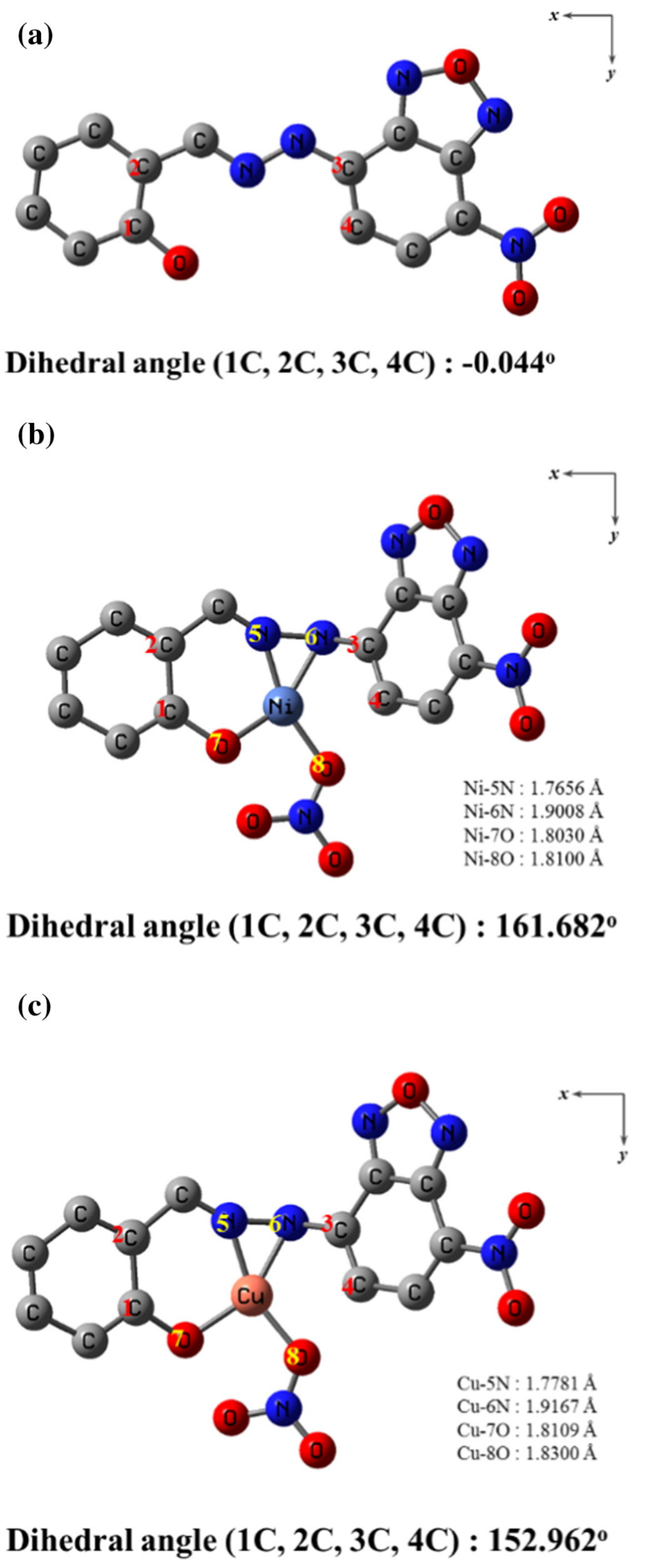

Fig. 6. Energy minimized structures of (a) **1**, (b) **1**-Ni^{2+} complex and (c) **1**-Cu^{2+} complex.

In order to understand the sensing mechanisms of **1** toward Ni^{2+} and Cu^{2+}, density functional theory (DFT) and time dependent-density functional theory (TD-DFT) calculations were conducted. All optimizations were carried out using the B3LYP/6-31G(d, p) method basis set on the Gaussian 03 program. The calculated energy-minimized structures of **1**, **1**-Ni^{2+} and **1**-Cu^{2+} species are shown in Fig. 6. The energy-minimized structure of **1** showed a planar structure with the dihedral angle of 1C, 2C, 3C, 4C = −0.044° (Fig. 6a). **1**-Ni^{2+} complex exhibited a tetra-coordinated structure with the dihedral angle of 1C, 2C, 3C, 4C = 161.682°. Three coordination sites were satisfied by the 5N, 6N and 7O donor of **1**, and a NO$_3^-$ occupied one site (Fig. 6b). For **1**-Cu^{2+} complex, Cu^{2+} was coordinated to 5N, 6N, 7O of **1** and an oxygen atom of NO$_3^-$ with the dihedral angle of 1C, 2C, 3C, 4C = 152.962° (Fig. 6c). To further interpret the electronic and absorption properties of **1**, **1**-Ni^{2+} and **1**-Cu^{2+} complexes, TD-SCF calculations were conducted from GEN basis set. In free sensor **1**, the main molecular orbital (MO) contribution of the 1st lowest excited state was determined for the HOMO → LUMO transition (496.69 nm, Fig. S10). The HOMO spread out the whole molecule of **1**, and LUMO was on the NBD group, which indicated an intra-molecular charge transfer (ICT). In **1**-Ni^{2+} complex, the 5th excited state was found to be related to the color change (497.49 nm, Fig. S11). The MO of the HOMO – 2 was mainly located at the metal-centered orbital while the LUMO was localized on the NBD moiety (Fig. S12), which corresponds to metal-to-ligand charge-transfer (MLCT) and causes the color change from pink to orange. In **1**-Cu^{2+} complex, the 13th excited state was found to be relevant to the color change from pink to pale brown (437.69 nm, Fig. S13). The MOs of the HOMO (α) and HOMO – 1 (β) mainly lied in the phenol moiety while the LUMO + 1 (α) and LUMO + 1 (β) spread around the NBD moiety (Fig. S14). Their transitions were assigned to ICT transition. The changes in absorption spectra due to complex formation are also reflected in the theoretically calculated spectra of **1**, **1**-Ni^{2+} and **1**-Cu^{2+} complexes (Fig. S10, S11 and S13). With the integration of information obtained from Job plot, ESI-mass spectroscopy analysis and theoretical calculations, the binding modes of **1**-Ni^{2+} and **1**-Cu^{2+} complexes are depicted in Scheme 2.

In conclusion, we have synthesized a new chemosensor **1**, based on the NBD and the phenol group connected via a Schiff-base linkage. Sensor **1** could be used for the simultaneous detection of Ni^{2+} and Cu^{2+} through its visible color changes from pink to orange and pale brown, respectively. The 1:1 stoichiometries of **1** toward Ni^{2+} and Cu^{2+} were confirmed by the Job plot and ESI-mass analysis. The detection limits were calculated to be 0.48 μM for Ni^{2+} and 0.26 μM for Cu^{2+}, respectively. The sensing mechanisms of **1** toward Ni^{2+} and Cu^{2+} were explained by DFT calculations. Based on the colorimetric response of **1** to Ni^{2+} and Cu^{2+}, test strips containing **1** were fabricated, which exhibited the obvious color changes from pink to orange and brown, respectively. Therefore, sensor **1** will offer an important guidance to the development of single sensors for recognizing both Ni^{2+} and Cu^{2+}.

Acknowledgements

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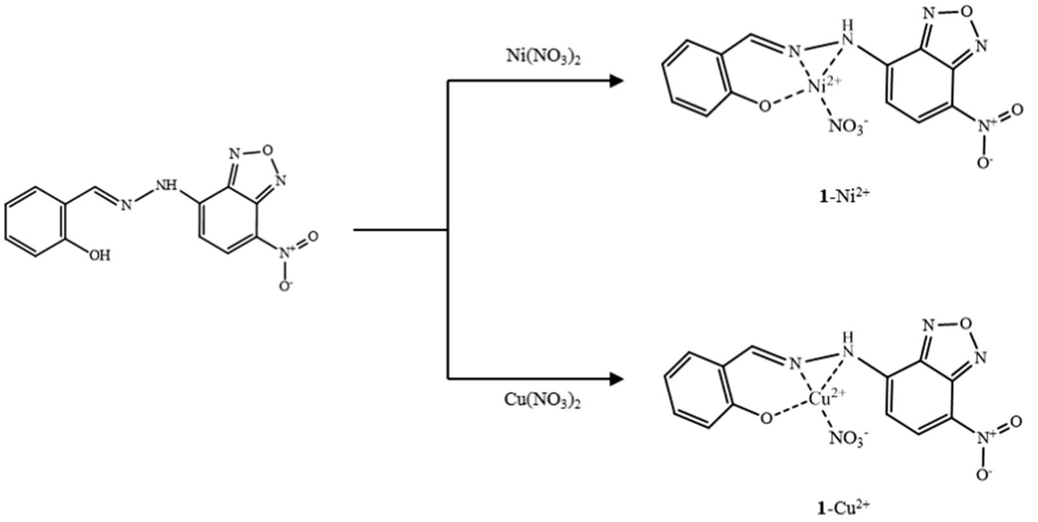
Appendix A. Supplementary material

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.inoche.2017.01.024.



Scheme 2. Proposed binding modes of **1**-Ni^{2+} and **1**-Cu^{2+} complexes.

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