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Paper

A NBD-based two-in-one Cu²⁺/Ni²⁺ chemosensor with differential charge transfer processes

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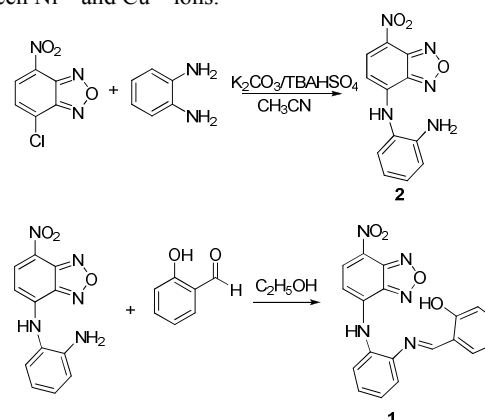
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A new multifunctional NBD-based probe has been developed having high sensitivity and selectivity towards Cu²⁺/Ni²⁺ over other metal ions over a wide pH range. The probe **1** could be used for the simultaneous estimation of Cu²⁺ and Ni²⁺ ions by changing its visible color change from yellow to blue and light green respectively in semi-aqueous system. The binding mode of probe **1** to Cu²⁺ and Ni²⁺ were determined to be 1:1 complexation stoichiometry through Job's plot. Ethylenediamine tetraacetate showed high selectivity towards the in situ-prepared Cu²⁺ complex over the Ni²⁺ complex, which is applied to distinguish Ni²⁺ and Cu²⁺ ions. The detection limits for Cu²⁺ ions 1.8 x 10⁻⁷ M and 1.1 x 10⁻⁶ M for Ni²⁺ ions were lower than WHO guidelines for drinking water. Moreover, probe **1** could be used as practical, visible colorimetric test kit for Cu²⁺ ions. The sensing mechanism of Cu²⁺ and Ni²⁺ ions has been supported by DFT-calculations.

Introduction

Colorimetric sensors are promising due to their simplicity, real-time and on-line analysis, especially a significantly lower capital cost compared with other closely related methods. Thus, research on metal-ion selective colorimetric chemosensors has attracted great attention from supramolecular chemists, and great achievements have been obtained.¹ Ni²⁺ is a significant environment pollutant yet an essential trace element in biological system.² Ni²⁺ is used in a wide variety of metallurgical processes such as electroplating, rods for arc welding, ceramics, dental prostheses, catalyst for hydrogenation and alloy production as well as Ni-Cd batteries. Ni²⁺ is an essential trace metal ion in biological system, which has relevance in biosynthesis and metabolism. For example, loss of nickel homeostasis is harmful to prokaryotic and eukaryotic organisms.³ Nevertheless, reports of Ni²⁺ chemosensors are very rare and out of which most of them are based on potentiometric methods.⁴ Copper also plays an important role in various biological processes and is also significant pollutant due to its widespread use.⁵ The exposure to high level of copper even for short period of time can cause gastrointestinal disturbance and long time exposure can cause liver or kidney damage.⁶ Many Cu²⁺ chemosensors have been reported and used for biological applications.⁷ It is pity that chemosensor for differential estimation of Cu²⁺ and Ni²⁺ ions has been very scarcely reported in literature.

In this work, we synthesized a new NBD-derived probe **1**, having the receptor linked through schiff base (Scheme 1).⁸ Schiff bases with π electrons in the C=N group and nitrogen in aromatic ring offer a good possibility for chelation with metal ions. The chelation to metal ions would enhance ICT (intramolecular charge transfer) transition or make LMCT (ligand to metal charge transfer) transition, which is utilized for the detection of metal ions. As expected, probe **1** showed excellent selectivity towards Ni²⁺ and Cu²⁺ in the presence of excess amounts of various competing metal ions. The probe **1**, in the presence of Cu²⁺ opened the new absorption channel at 585 nm and its associated visible color change from yellow to blue and in the presence of Ni²⁺ ions showed new absorption band at 607 nm band with visible color change from yellow to light green. We found that addition of ethylenediamine tetraacetate (EDTA) causes the revival of probe **1** absorption in case of Cu²⁺, provided the effective method for distinguishing between Ni²⁺ and Cu²⁺ ions.



Scheme 1: Synthesis of Probe 1

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Electronic Supplementary Information (ESI) available: [Spectral data, competitive metal ion study and other supporting data, pH titration etc.
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Results and Discussion

Effect of Metal ions on absorption spectra of probe 1

To evaluate the binding affinity of probe **1** towards different metal ions UV-visible and fluorescence studies were performed in CH₃OH : H₂O:: 1:1 at pH 7.2 (HEPES buffer, 10⁻² M). The absorption spectrum of probe **1** (20 μM, CH₃OH: H₂O:: 1:1) is characterized by the two bands at 340 nm and 475 nm. Upon addition of 1000 μM of various metal ions such as Ba²⁺, Mg²⁺, Co²⁺, Al³⁺, Ni²⁺, Na⁺, K⁺, Ag⁺, Hg²⁺, Fe³⁺, Cu²⁺, Cr³⁺, Pb²⁺, Zn²⁺, Ca²⁺ etc. to probe **1** (20 μM, CH₃OH: H₂O:: 1:1, HEPES buffer) no significant visible or spectral change was observed except Cu²⁺ and Ni²⁺ ions. The presence of Cu²⁺ and Ni²⁺ ions showed the visible color change from yellow to blue and light green respectively (Figure 1 and Figure S6).

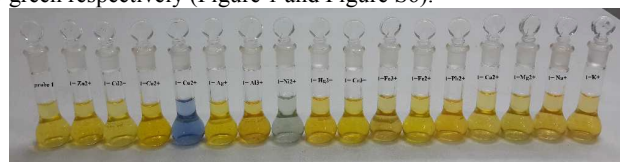


Figure 1: Visible color changes on addition of various metal ions to probe **1**.

Upon incremental addition of Cu²⁺ ions to the solution of probe **1** (20 μM), the absorption intensity of band at 475 nm and 340 nm decreased and concomitantly new absorption band at 585 nm and 415 nm reached to maximum at 1.0 equiv. of Cu²⁺ ions. Four clear isobestic points at 315 nm, 365 nm, 465 nm and 512 nm, indicating that only one product was generated from **1** upon binding to Cu²⁺ ions (Figure 2a). The ratios of absorption intensities at 585 and 475 nm (A_{585}/A_{475}) varies from 0.0167 to 3.0, which showed the 179-fold ratiometric change. Thus, probe **1** can be used to estimate 0.1 μM – 8 μM of Cu²⁺ ions. (Figure S7). The Job's plot analysis showed a 1:1 stoichiometry of Cu²⁺ to probe **1** (Figure S8). Based on UV-vis titration of probe **1** with Cu²⁺, the association constant (*K*) of **1** with Cu²⁺ was calculated by using spectral curve fit of the data using specfit 32. The *K* value was determined to be 3.62 × 10⁶ M⁻¹.

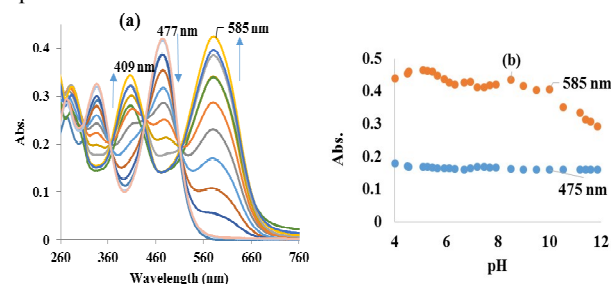


Figure 2: (a) Absorption spectra of probe **1** (20 μM, CH₃OH: H₂O:: 1:1, HEPES buffer) upon complexation with increasing concentration of Cu²⁺ ions. (b) Absorption changes (585 nm and 475 nm) of probe **1**.Cu²⁺ complex at different pH values (4-12).

To further check the practical applicability of probe **1** as a Cu²⁺ selective sensor, the competition experiments were performed (Figure S9). Upon addition of 1.0 equiv. of Cu²⁺ ions in the presence of 100 equiv. of other metal ions, there was no obvious interference of other metal ions. Thus, **1** could be used as selective colorimetric sensor for Cu²⁺ ions in the presence of most competing metal ions. The effect of pH on

absorption response of **1** to Cu²⁺ ions in series of solutions with pH values ranges from 2.5 to 13.0. The color of **1**.Cu²⁺ complex and absorption changes remained unaffected between pH 4.0-12.0. These results indicated that Cu²⁺ could be clearly detected using probe **1** over a wide pH range of 4.0-12.0 (Figure 2b and Figure S10).

Upon incremental addition of Ni²⁺ ions to the probe **1** (20 μM, CH₃OH: H₂O:: 1:1, HEPES buffer, pH = 7.0), the intensity of absorption band at 475 nm decreased and new absorption band was formed at 575 nm with a strong shouldered band at 607 nm associated with visible color change from yellow to light green (Figure 3). Four clear isobestic points were observed at 300 nm, 370 nm, 445 nm and 505 nm, indicating that only one product was generated from probe **1** upon binding to Ni²⁺. Job's plot analysis showed 1:1 stoichiometry for Ni²⁺ to probe **1** (Figure S11). The ratios of absorption intensities at 585 and 475 nm (A_{575}/A_{475}) varies from 0.0158 to 2.25 and showed 142-fold ratiometric change on addition of Ni²⁺ ions (Figure S12). The association constant was calculated based on UV-Vis titration by using Benesi hildebrand equation/spectral curve fit data (Figure S16-17). The *K* value was determined to be 3.03 × 10⁶ M⁻¹. The detection limit (3σ/*k*) of probe **1** was found to be 1.1 × 10⁻⁶ M, which was much lower than that recommended by WHO in drinking water.

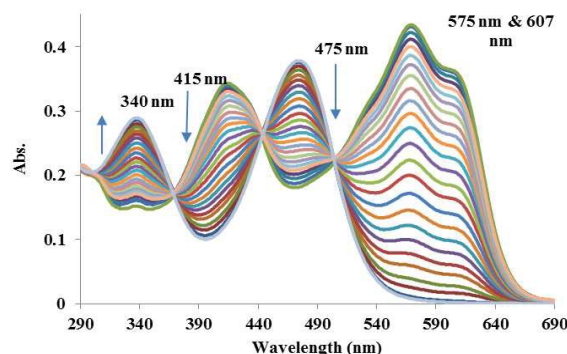


Figure 3: The effect of the addition of Ni²⁺ ions on UV-Vis spectrum of probe **1** (20 μM, CH₃OH: H₂O:: 1:1, HEPES buffer, pH = 7.0).

To further check the practical ability of probe **1** as Ni²⁺ sensor, competitive metal ion experiments were performed in the presence of 1.0 equiv. of Ni²⁺ and 50 equiv. of other interfering metal ions like Na⁺, K⁺, Ba²⁺, Mg²⁺, Ca²⁺, Co²⁺, Al³⁺, Ni²⁺, Ag⁺, Hg²⁺, Fe³⁺, Cu²⁺, Cr³⁺, Pb²⁺, Zn²⁺ etc., no significant interference was observed. There was some interference for detection of Ni²⁺, which was 10% for Co²⁺ and 12% for Fe³⁺ at higher equivalents (Figure S13). Nevertheless, the changes of color were still detectable in the presence of these interfering metal ions.

To examine the reversibility of binding of probe **1** with Cu²⁺ and Ni²⁺, experiments were performed in the presence of EDTA. On the addition of an aqueous solution of EDTA (2 equiv.) to the **1**.Cu²⁺ complex, the absorption band at 585 nm disappeared and simultaneously reappearance of the absorption maximum at 475 nm was observed. Again, on addition of Cu²⁺ to this solution mixture, having EDTA, the absorption band at 585 nm reappeared. Preferential binding of EDTA to Cu²⁺ led to the formation of Cu-EDTA and regeneration of the probe **1** and confirms the reversal binding of probe **1** to the Cu²⁺ ions

(Figure 4a). Interestingly, the alternate addition of Cu^{2+} and EDTA to probe **1** gave rise to switchable change in the absorbance at 585 nm and can be repeated more than 5 times by the alternate addition of Cu^{2+} and EDTA to probe **1** (Figure 4b). However, no absorption reversal was observed when EDTA was added to the probe **1**. Ni^{2+} complex (Figure S14). This indicated that EDTA is not able to remove Ni^{2+} from the **1**. Ni^{2+} complex and hence cannot restore the absorption of probe **1**. EDTA has high selectivity towards the in situ prepared Cu^{2+} complex over Ni^{2+} complex, which can be applied to distinguish Ni^{2+} and Cu^{2+} .

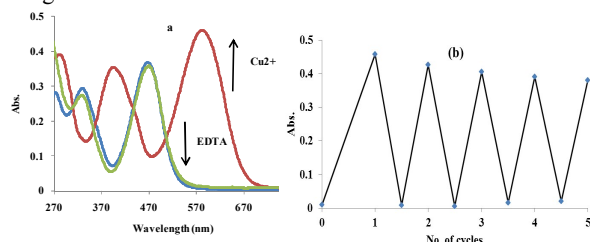


Figure 4: (a) The absorption response showing the reversibility of (a) Cu^{2+} ($10\ \mu\text{M}$) coordination to probe **1** by EDTA ($20\ \mu\text{M}$) (b) switchable behaviour in the absorbance at 585 nm by the alternate addition of Cu^{2+} and EDTA to probe **1**.

To further investigate the practical application of probe **1**, test kits were prepared by immersing wattman filter paper into the solution of probe **1** and were dried under vacuum. Then spot of different concentrations the Cu^{2+} solutions on this paper strips showed the visible color changes to blue. Thus this paper strips can be used for the sensing of copper ions (Figure 5). Moreover one another experiment was performed to show the application of this probe in which probe **1** solution was adsorbed onto silica gel 60-10 mesh. The presence of different concentration of Cu^{2+} ions showed the drastic color changes. Thus this probe can be used to sense and quantify the Cu^{2+} ions through these test kits as well.

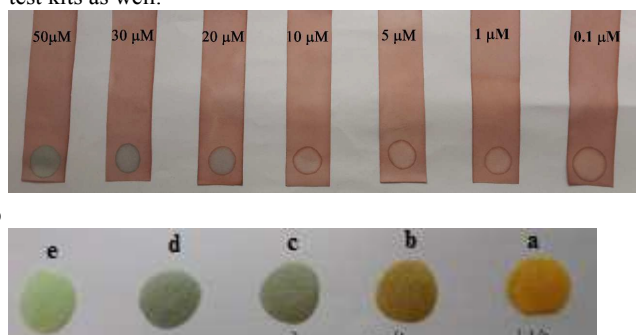


Figure 5: Photographs of filter paper coated (upper) with probe **1** ($80\ \mu\text{M}$) and its color changes (in circle) in the presence of different concentration of Cu^{2+} ions. Lower: Color change of silica gel coated with probe **1** in increasing concentration of Cu^{2+} ions (a) probe **1** only; (b) **1** + $2\ \mu\text{M}$ Cu^{2+} ; (c) **1** + $4\ \mu\text{M}$ Cu^{2+} ; (d) **1** + $6\ \mu\text{M}$ Cu^{2+} ; (e) **1** + $10\ \mu\text{M}$ Cu^{2+} .

Effect of Metal ions on emission spectra of probe **1**

The excitation of probe **1** ($20\ \mu\text{M}$, $\text{CH}_3\text{OH}:\text{H}_2\text{O}::1:1$, HEPES buffer) at 340 nm, showed a very weak emission. Upon addition of various metal ions like Ba^{2+} , Mg^{2+} , Co^{2+} , Al^{3+} , Ni^{2+} ,

Na^+ , K^+ , Ag^+ , Hg^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Pb^{2+} , Zn^{2+} , Ca^{2+} etc, no significant change was observed except in the presence of Al^{3+} ions (Figure 6a). Upon incremental addition of Al^{3+} to the solution of probe **1**, the emission was turned “on” at 510 nm which achieved the plateau after $50\ \mu\text{M}$ of Al^{3+} ions due to CHEF effect (Figure 6b). The Cu^{2+} and Ni^{2+} due to the paramagnetic effect showed the emission quenching which could not be determined due to the weak emission of probe **1**.

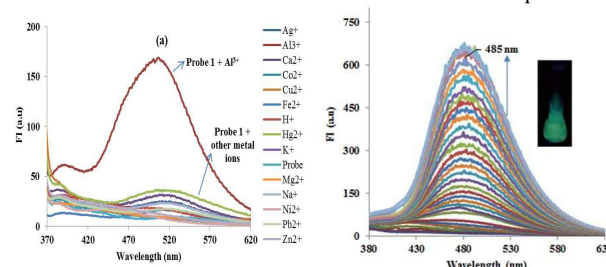
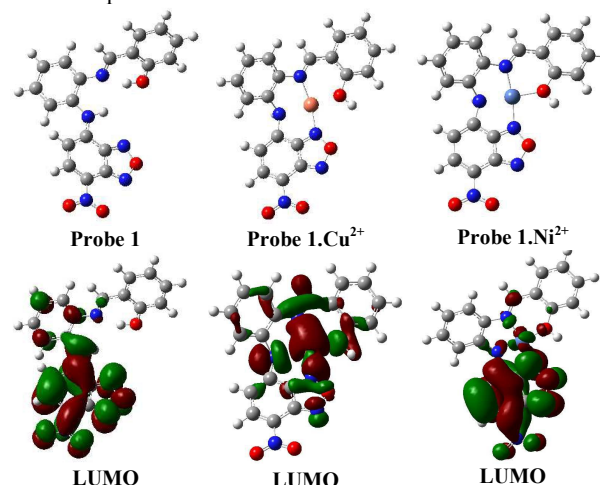


Figure 6: The fluorescence response of probe **1** ($20\ \mu\text{M}$, $\text{CH}_3\text{OH}:\text{H}_2\text{O}::1:1$, HEPES buffer, $\text{pH} = 7.0$) (a) in the presence of various metal ions ($50\ \text{equiv.}$); (b) Titration of Al^{3+} ions on excitation at 340 nm.

To check the practical ability of probe **1** as selective Al^{3+} sensor, we carried out competitive experiments in the presence of $10\ \mu\text{M}$ of Al^{3+} and 1mM of other interfering metal ions like Ba^{2+} , Mg^{2+} , Co^{2+} , Al^{3+} , Ni^{2+} , Na^+ , K^+ , Ag^+ , Hg^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Pb^{2+} , Zn^{2+} , Ca^{2+} etc., no significant interference was observed in both the cases as shown in Figure S15.

TD-DFT Calculations

To understand the sensing mechanism of Cu^{2+} and Ni^{2+} binding with probe **1**, theoretical calculations⁹ were performed in parallel to the experimental studies. As Job plots analysis showed the 1:1 stoichiometric ratio in both the cases so, all theoretical calculations were performed with 1:1 stoichiometry. The significant structural properties of energy minimized structure are shown in Figure 7. The structure optimization of probe **1** with Cu^{2+} and Ni^{2+} showed that the complex attained the planarity and form symmetrical square planar complexes. These optimized structures clearly predicted the LMCT process in the complexes.



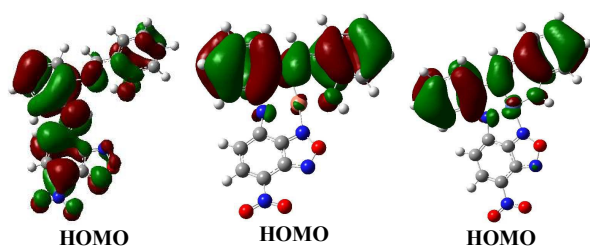


Figure 7: Energy minimizes structure and frontier molecular orbital contribution of probe **1** and its complexes with Cu^{2+} and Ni^{2+} .

The probe **1** in the presence of Ni^{2+} ion form the more planar stable square planar complex than the Cu^{2+} ion which can be clearly predicted from the bond distances of metal with four heteroatoms involved in formation of square planar complex (Table S1). Due to this reason, addition of ethylenediamine tetracetate (EDTA) caused the revival of probe **1** absorption changes in case of Cu^{2+} but not in case of Ni^{2+} .

To interpret further the absorption properties of probe **1** and its complexes with Cu^{2+} and Ni^{2+} , TD-DFT calculations were performed. In case of probe **1**, the main molecular orbital contribution of first lowest excited state was determined for HOMO $\rightarrow$ LUMO transition (450 nm), which indicated the intramolecular charge transfer schiff moiety to NBD moiety.

In case of probe **1**. Cu^{2+} complex, the 6th and 7th excited state (550 nm and 545 nm) were found to be relevant to color change (yellow to blue) showing predominant LMCT and ICT. In case of probe **1**. Ni^{2+} complex, 8th and 9th excited states (585 nm and 590 nm) was found to be related to metal-to-ligand charge transfer (MLCT), and its contribution to lowest-energy excitation was around 20 %. Such excitation corresponds to charge transfer from excited Ni^{2+} centre to NBD and Schiff base moieties. These transitions were found to be relevant to color change (yellow to light green) showing predominant ICT and MLCT. These studies clearly predicted the differential charge transfer in the complexes.

Conclusion

NBD-based probe **1** was developed for the detection of Cu^{2+} and Ni^{2+} ions in semi-aqueous system. The probe **1** could be used for the simultaneous estimation of Cu^{2+} and Ni^{2+} ions by changing its visible color change from yellow to blue and light green respectively in semi-aqueous system. The binding mode of probe **1** to Cu^{2+} and Ni^{2+} were determined to be 1:1 complexation stoichiometry through Job's plot. The detection limits for Cu^{2+} ions 0.1 μM – 8 μM and 0.5 μM – 10 μM for Ni^{2+} ions were lower than WHO guidelines for drinking water. Moreover, probe **1** could be used as practical, visible colorimetric test kit for Cu^{2+} ions. The sensing mechanism of Cu^{2+} and Ni^{2+} ions were supported by DFT-calculations.

Experimental

General Experiment Conditions: All reagents were purchased from commercial suppliers and used without further purification. TLC analyses were performed on silica gel plates and column chromatography was conducted over silica gel (mesh 100–200). ^1H NMR spectra were recorded using JEOL

A1 spectrometers operating at 400 MHz. ^{13}C NMR spectra were recorded at 100 MHz. All chemical shifts are reported in ppm relative to the TMS as an internal reference. UV-vis studies were carried out on a Shimadzu 2600 machine using slit width of 1.0 nm and matched quartz cells. Fluorescence spectra were determined on a Varian Cary Eclipse fluorescence spectrometer. Stock solution of dyad **1** was prepared at 10^{-3} M in distilled CH_3OH . The resulting solution was shaken well before recording the absorption spectra. All absorption and fluorescence scans were saved as ACS II files and further processed in ExcelTM to produce all graphs shown. Solutions of **1** were typically 20 μM for UV-vis studies. Stability constants were determined by fitting the absorption spectra recorded during the titrations of the receptor with metals ions and by using Benesi hildebrand equation.

Synthesis of Compound 2: The compound **2** was obtained through the reaction between 4-Chloro-7-nitro-1, 2, 3-benzoxadiazole (NBD-Cl) and *o*-phenylenediamine in the presence of potassium carbonate, TBAHSO₄ in acetonitrile. The solution was refluxed for 5 hrs and reaction was monitored through TLC. After completion of reaction, the reaction mixture was extracted with chloroform. The residue was purified through column chromatography to get pure product **2** in 70% yield as a reddish brown solid; Mpt. 220 $^\circ\text{C}$. ^1H NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$, 400 MHz, ppm): δ 9.90 (s, 1H, NH), 8.42 (m, 1H, ArH), 7.20 (m, 2H, ArH), 6.92 (m, 1H, ArH), 6.81 (m, 1H, ArH) 6.10 (m, 1H, ArH); ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$, 100 MHz, ppm): 144.2, 143.7, 143.2, 142.6, 136.2, 128.6, 126.7, 123.0, 121.6, 117.8, 116.5, 100.8.

Synthesis of Compound 1: The compound **2** and 2-hydroxybenzaldehyde was stirred in ethanol at 60 $^\circ\text{C}$ for 4 hrs. The solid of probe **1** was separated which was filtered and washed with ethanol to get pure probe **1** in 80% yield as a yellow solid. Mpt. 220 $^\circ\text{C}$. ^1H NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$, 400 MHz, ppm): δ 12.49 (s, 1H, CHN), 10.44 (s, 1H, NH), 8.71 (s, 1H, ArH), 8.42 (d, 1H, $J = 8.72$ Hz, ArH), 7.52 (m, 1H, ArH), 7.43(m, 4H, ArH), 6.96 (m, 1H, ArH), 6.87 (d, 1H, $J = 8.24$ Hz, ArH), 6.33 (d, 1H, $J = 8.72$ Hz, ArH); ^{13}C NMR ($\text{CDCl}_3 + \text{DMSO}-d_6$, 100 MHz, ppm): 195.3, 164.1, 160.6, 144.6, 144.2, 143.4, 136.7, 133.6, 132.7, 131.3, 129.0, 127.9, 127.1, 123.4, 119.8, 119.1, 119.1, 116.9, 101.5 (Scheme 1 and Figure SI 1-5).

DFT Calculations

DFT calculations using Becke three parameter exchange /Lee-yang-Parr correlation hybrid functional (B3LYP) with 6-31G (d,p) and 6-31G** + LanL2DZ basis sets as implemented in the Gaussian 09 suite programs were carried out for the geometry optimization of probe **1**, probe **1**. Cu^{2+} and probe **1**. Ni^{2+} complex. The energies and oscillator strengths of lowest-energy electronic transitions, which involves the calculation of excited-state energies of complex, were obtained using time dependent DFT (TD-DFT) with the same basis sets.

Acknowledgement

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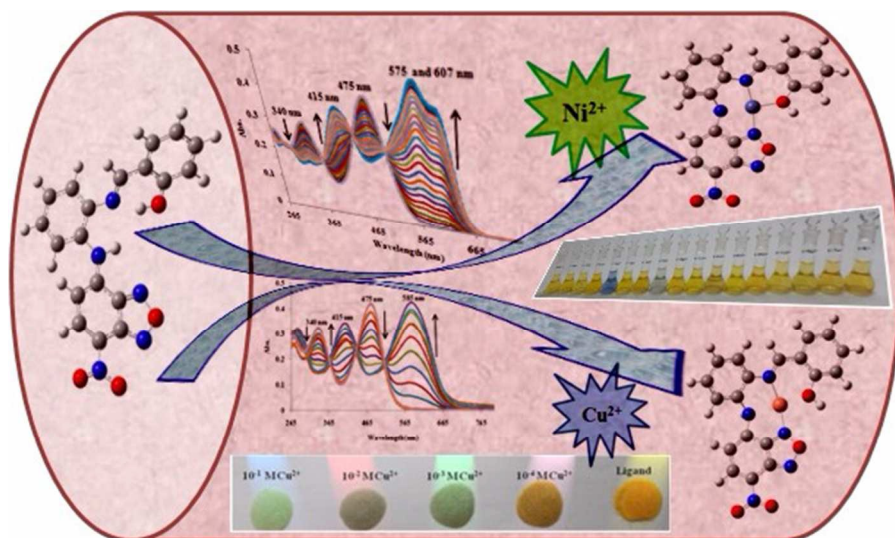
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Graphical Abstract

A NBD-based two-in-one $\text{Cu}^{2+}/\text{Ni}^{2+}$ chemosensor with differential charge transfer processes

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A new multifunctional NBD-based probe for differential sensing of $\text{Cu}^{2+}/\text{Ni}^{2+}$ ions through visible color changes in semi-aqueous system