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Colorimetric detection of histidine in aqueous solution by Ni^{2+} complex of a thiazolylazo dye based on indicator displacement mechanism

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Abstract

A colorimetric naked-eye chemosensor for histidine (His) was established by mixing a thiazolylazo dye and Ni^{2+} in a 1:1 molar ratio (TAMSMB-Ni^{2+}). Due to the interaction of Ni^{2+} with His, TAMSMB was regenerated upon the addition of His to TAMSMB-Ni^{2+} to lead a significant hypsochromic shift in absorption spectra accompanied by a visual color change from red to yellow which can be directly observed by the naked eye. On the other hands, other amino acids did not trigger any significant changes in absorption properties and solution color. Moreover, it exhibited the selective recognition of His without obvious interference from other amino acids. Thus, TAMSMB-Ni^{2+} can act as a simple and efficient colorimetric chemosensor for His with sensitivity and selectivity in aqueous solution.

Keywords: Colorimetric detection, Chemosensor, Histidine, Thiazolylazo dye, Nickel ion

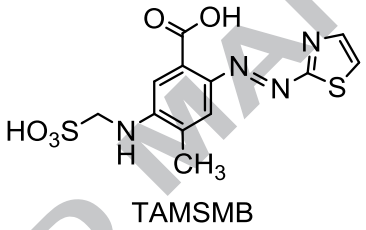
1. Introduction

The selective and sensitive detection of environmentally and biologically relevant important analytes including amino acids, anions, and metal ions has nowadays received considerable attention because of the involvement in a wide variety of biological processes.[1-20] Among amino acids, His is an indispensable constituent of proteins and plays an important role in the growth and repair of tissue.[21] His exists at the active site of many enzymes because its imidazole group can act as the chelate ligand and be dissociated at almost a neutral pH range.[22] Furthermore, it is a precursor of histamines and works as neurotransmitter or neuromodulator in both the brain and the central nervous systems.[23] A deficiency of His causes chronic kidney disease, Friedreich ataxia, epilepsy, and Parkinson's disease, whereas an excess of His induces metabolic disorders or histidinemia.[24-28] Thus, because abnormal levels of His in the body are closely associated with a variety of diseases, the selective and sensitive quantification of His in biological fluids can be of great interest and provide important information for clinical diagnosis.

Therefore, to date, several analytical methods including resonance light scattering,[29] surface enhanced Raman scattering,[30] capillary electrophoresis,[31] liquid chromatography,[32] electrochemistry,[33] fluorescence spectrometry,[34,35] and colorimetric assay[36] have been explored to analyze His quantitatively. Among these techniques, the colorimetric method has attracted much attention because of more advantages over the other techniques, such as the operational simplicity, convenience, low cost, and naked-eye visualization. However, to the best of our knowledge, despite the existence of His in aqueous media, not too much colorimetric chemosensors for the detection of His in pure aqueous solution have been reported in the literature.[37,38] Moreover, most of the reported chemosensors have been prepared by organic synthetic methods, while commercially available compounds offer several advantages in terms of cost effectiveness, simplicity, no need of organic synthesis process.

Compared with the colorimetric method based on the chromophore covalently bonded with the receptor, the indicator displacement assay (IDA) method based on the indicator-metal complex is a successful strategy due to no tedious organic synthesis by the simple combinations of indicators and metal ions in solution.[39] Recently, although many indicator-metal complexes have been utilized in sensing various anions and amino acids,[40-42] there have been few reports on chemosensors for the colorimetric detection of His by the IDA method.[42]

4-Methyl-5-(sulfomethylamino)-2-(2-thiazolylazo)benzoic acid (TAMSMB) has been utilized in clinical and chemical fields for quantitative determination of Cu^{2+} in serum.[43] It contains thiazolylazo and benzoic acid moieties as shown in Scheme 1, which is a commercially available and water-soluble colorimetric indicator for several metal ions such as Co^{3+} and Ni^{2+}.[44,45] Previous studies have reported that His acts as a ligand for Ni^{2+} in several proteins[46] and binds to Ni^{2+} to form the complex in aqueous solution.[34,37,47] Herein, we describe a chemosensor based on the TAMSMB-Ni^{2+} complex for selective and sensitive detection of His over other amino acids in aqueous solution under physiological conditions by the IDA method. TAMSMB is well known as a colorimetric detection reagent for several metal ions in aqueous solution. However, as far as we know, there is no report of a metal complex of TAMSMB which can detect analytes such as anions and amino acids by the IDA method. Notably, TAMSMB-based Ni^{2+} complex is the first example of a colorimetric probe for detecting His.



TAMSMB

Scheme 1 Chemical structure of TAMSMB.

2. Results and discussions

The addition of Ni^{2+} or Cu^{2+} to TAMSMB resulted in the color change from yellow to red or blue, respectively, suggesting that TAMSMB can form the complexes with Ni^{2+} and Cu^{2+}, while other typical metal ions including Cd^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} yielded no color change of TAMSMB solution. Both of the TAMSMB-Ni^{2+} and TAMSMB-Cu^{2+} complexes were treated by His to return to an original yellow color, however, TAMSMB-Cu^{2+} were restored to TAMSMB even by treatment with cysteine (Cys). Therefore, we chose TAMSMB-Ni^{2+} for the selective colorimetric detection of His based on the IDA method.

Initially, to assess the optical properties of TAMSMB-Ni^{2+} complex formation, the absorption spectra were measured when aqueous solution of TAMSMB was titrated with Ni^{2+} in 10 mM phosphate buffer solution (pH 6.5) at room temperature (Fig. 1). The absorption spectrum of TAMSMB exhibited an absorption band centered at 475 nm in the absence of Ni^{2+}. As gradually increasing the concentration of Ni^{2+}, the absorbance at 475 nm decreased, while a new

red-shift absorption band centered at 552 nm appeared, with a significant visible color change from yellow to red. Thus, the absorption bathochromic shift of TAMSMB toward Ni^{2+} may be mainly attributed to the metal-to-ligand charge-transfer.

The stoichiometric ratio between TAMSMB and Ni^{2+} was evaluated through a Job's plot experiment to display the formation of the 1:1 stoichiometry complex between TAMSMB and Ni^{2+} (Fig. S1).[48] The association constant of Ni^{2+} to TAMSMB was found to be 4.39×10^4 M^{-1} (log *K*a = 4.64) using the Benesi–Hildebrand method (Fig. S2).[49]

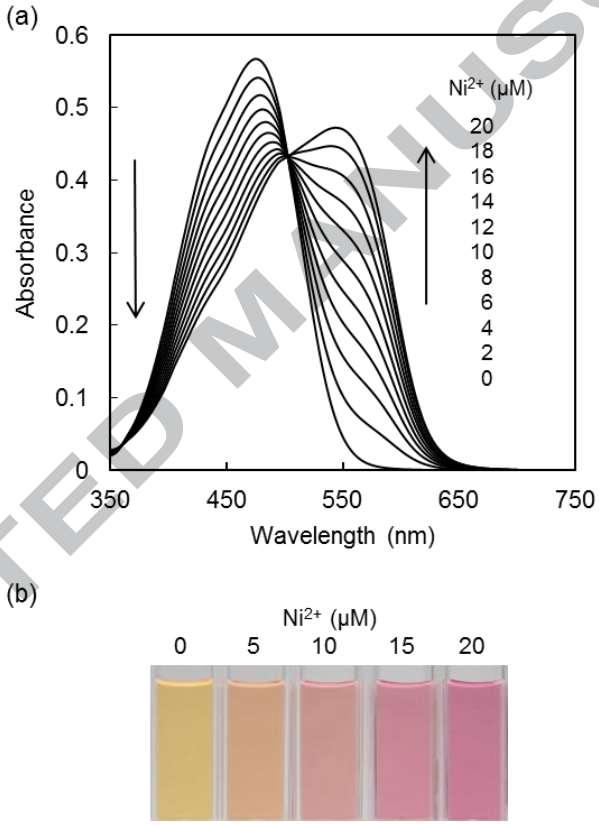


Fig. 1 (a) Absorption spectra of TAMSMB (20 μM) as a function of Ni^{2+} concentration in 10 mM phosphate buffer solution at pH 6.5. (b) The color changes of TAMSMB (20 μM) as a function of Ni^{2+} concentration in 10 mM phosphate buffer solution at pH 6.5.

His is predicted to be able to remove Ni^{2+} from TAMSMB-Ni^{2+} to reproduce TAMSMB in that there have been some reports on the formation of a complex between His and Ni^{2+} in aqueous solution.[34,37,47] To investigate whether TAMSMB-Ni^{2+} can be utilized as a selective chemosensor toward His against other amino acids, the absorption spectral studies of TAMSMB-Ni^{2+} (20 μM) were conducted upon addition of 20 various amino acids (40

μM) including Ala, Arg, Asn, Asp, Cys, Gln, Glu, Gly, His, Ile, Leu, Lys, Met, Phe, Pro, Ser, Thr, Trp, Tyr, and Val in 10 mM phosphate buffer solution at pH 6.5 (Fig. 2). The addition of His to TAMSMB-Ni^{2+} gave rise to a characteristic colorimetric change as a decrease in the absorbance at 552 nm and an increase in the absorbance at 475 nm. Cys and Asp also induced slight spectral changes, which were very insignificant compared to the change induced by His. Amino acids other than His, Cys, and Asp yielded no dramatic changes in the absorption spectra of TAMSMB-Ni^{2+}. Thus, TAMSMB-Ni^{2+} can act as a selective colorimetric chemosensor for His through Ni^{2+} complex displacement mechanism.

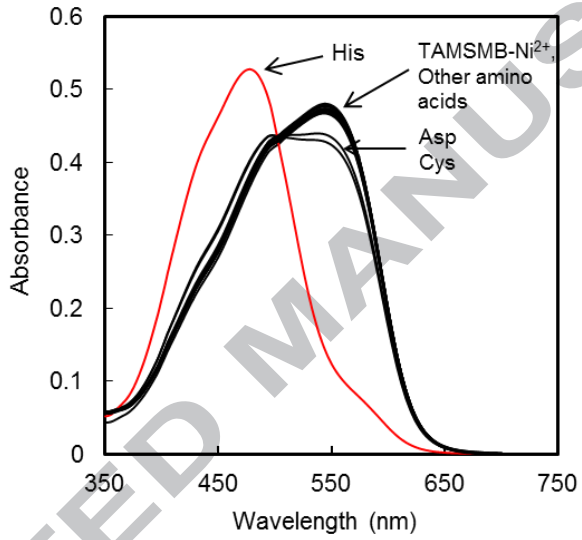


Fig. 2 Absorption spectra of TAMSMB-Ni^{2+} (20 μM) in the presence of various amino acids (40 μM) in 10 mM phosphate buffer solution at pH 6.5.

Moreover, to realize the Ni^{2+} displacement approach, the solution color and absorption spectral changes of TAMSMB-Ni^{2+} in the presence of various concentrations of His were also monitored (Fig. 3). Upon gradual addition of His into TAMSMB-Ni^{2+} (20 μM) significantly resulted in a gradual decrease in the absorbance at 552 nm with a hypsochromic shift, whereas the absorbance at 475 nm steadily increased and reached saturation at 4 equiv. (80 μM) of His (Fig. 3a). These spectral responses of TAMSMB-Ni^{2+} toward His were accompanied by a distinct visible color change from red to yellow, leading to the detection of His by the naked eye (Fig. 3c). Thus, the results indicated that TAMSMB-Ni^{2+} was recovered to TAMSMB by Ni^{2+} through a displacement mechanism with the formation of His and Ni^{2+} complex during the detection procedure of His. To determine the detection limit, from Fig. S3, the slope (*k*) of

straight line between the absorbance at 552 nm and His concentration was calculated to be 1.41×10^{-2} μM^{-1} (R^2 =0.9967). To estimate the S/N ratio, σ value was determined to be 2.29×10^{-3}. The detection limit of TAMSMB-Ni^{2+} for His was calculated to be 0.49 μM, which was comparable to those (0.05-5 μM) of previously reported sensors for His.[37,38,50-53]

Fig. 3c displays the color change of TAMSMB-Ni^{2+} with various concentrations of His. The solution color gradually turned from red to orange then yellow with an increase in His concentration from 0 μM to 40 μM. The red solution changed to orange color in the presence of 12 μM His, which meant that the detection limit by the naked eye could be as low as 12 μM. These detection limits of TAMSMB-Ni^{2+} for His are lower than the normal levels of His concentration (20 to 170 μM and 130 to 2100 μM in blood serum and urine, respectively).[54,55] Thus, the TAMSMB-Ni^{2+} complex could serve as a potential chemosensor for His with the visual observation.

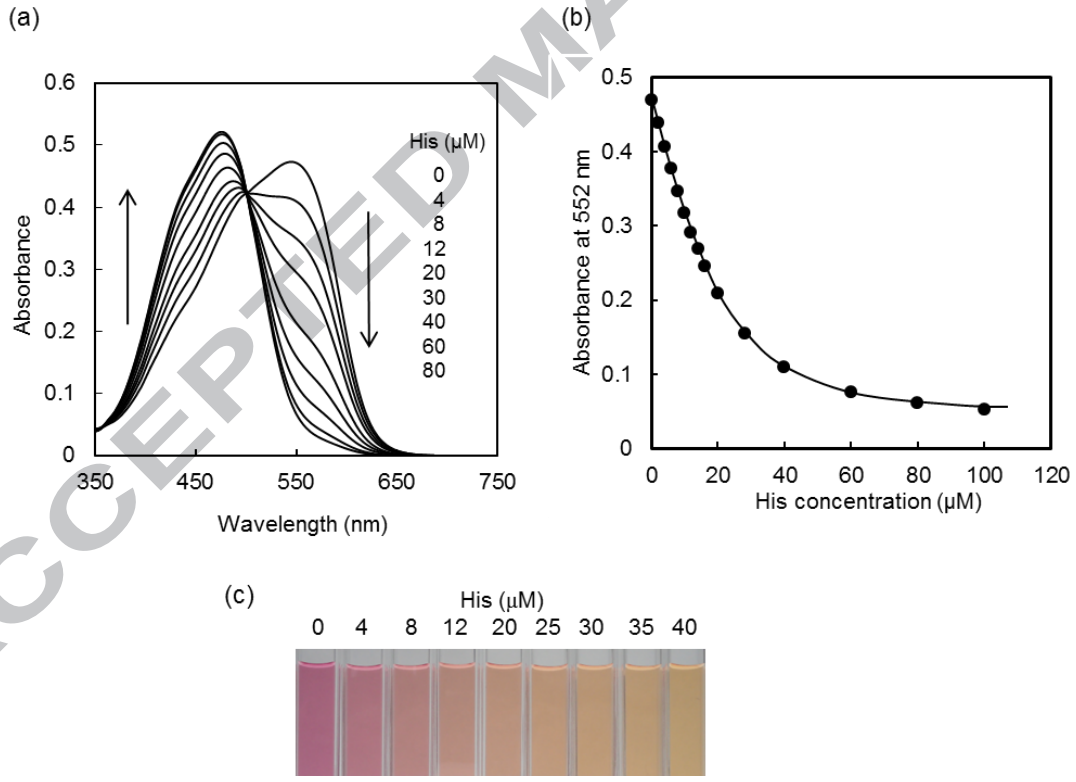


Fig. 3 (a) Absorption spectra of TAMSMB-Ni^{2+} (20 μM) as a function of His concentration in 10 mM phosphate buffer solution at pH 6.5. (b) Absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) as a function of hisidine concentration in 10 mM phosphate buffer solution at pH 6.5. (c) The color changes of TAMSMB-Ni^{2+} (20 μM) as a function of His concentration in 10 mM phosphate buffer solution at pH 6.5.

To estimate the stoichiometry between His and Ni^{2+}, a Job's plot experiment between His and TAMSMB-Ni^{2+} was carried out (Fig. S4). We can find when the molar fraction of His was 0.5, the absorbance difference (ΔA) at 552 nm reached a maximum, implying the formation of a 1:1 complex between His and Ni^{2+}. The binding constant for the formation of the His-Ni^{2+} complex was determined to be $K_b = 2.28 \times 10^5$ M^{-1} (log $K_b = 5.36$) by non-linear least squares fitting of the absorption titration data of TAMSMB-Ni^{2+} (552 nm) with His utilizing a 1:1 competitive binding equilibrium model (Fig. S5).[56,57] Since the binding constant (K_b) for the interaction of His and Ni^{2+} is approximately 5-fold higher than that (K_a) for the interaction of TAMSMB and Ni^{2+}, the transfer of Ni^{2+} from TAMSMB to His can thermodynamically favorably occur.

The response time is an important property for practical application. The time dependences of absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) in the presence of different concentrations of His (10, 20, and 40 μM) were investigated (Fig. 4). The absorbance began to decrease immediately after the addition of His and then remained unchanged after about 60 s in each case, demonstrating fast response time of TAMSMB-Ni^{2+} toward His.

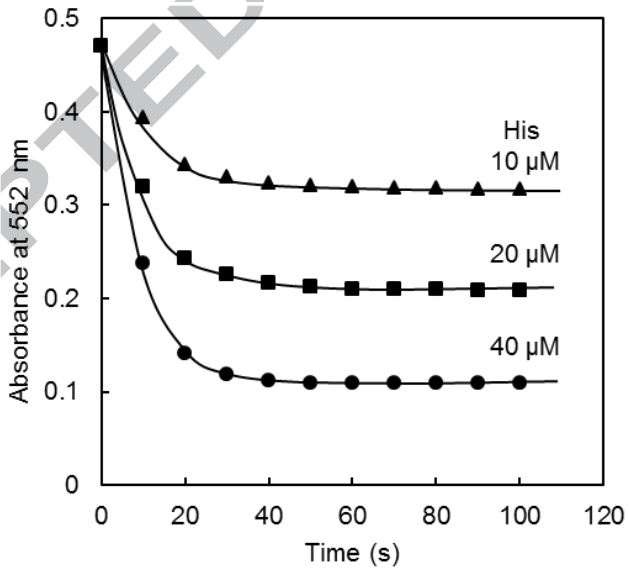


Fig. 4 Plots of the absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) as a function of hisidine concentration in 10 mM phosphate buffer solution at pH 6.5 in the presence of His (10, 20, and 40 μM) as a function of time.

To verify practicality of TAMSMB-Ni^{2+} as a selective colorimetric chemosensor for His, competition experiments with His and the other amino acids were conducted in 10 mM phosphate buffer at 6.5 (Fig. 5). Compared

to TAMSMB-Ni^{2+} containing only His, no obvious changes in the absorbance at 552 nm were observed with the other amino acids. This result demonstrated that other amino acids did not interfere with the absorption change induced by His, confirming the sensing ability of TAMSMB-Ni^{2+} for His could not be significantly affected by the coexistence of other amino acids.

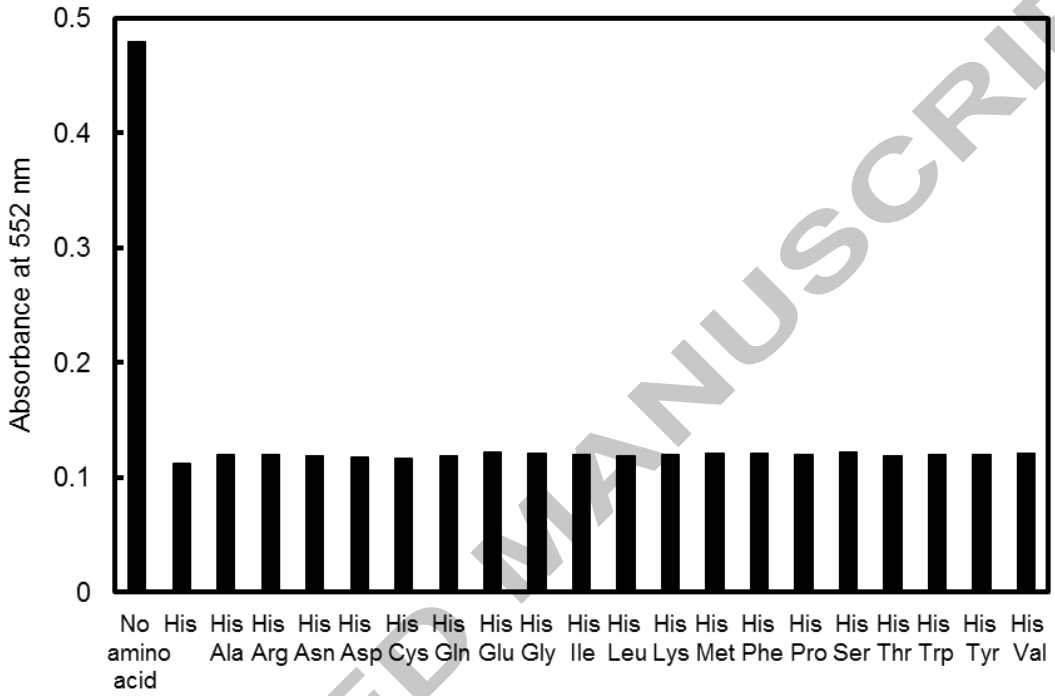


Fig. 5 Competitive selectivity of TAMSMB-Ni^{2+} (20 μM) toward His (40 μM)) in the presence of other amino acids (40 μM) in 10 mM phosphate buffer solution at pH 6.5.

The effects of pH on the absorption response in the presence of His or Cys were investigated in aqueous solution with pH values ranging from 4 to 11 as shown in Fig 6. The presence of His gave rise to remarkable color changes in the TAMSMB-Ni^{2+} solution from red to yellow between pH 6.5 and 9, while the colorimetric changes almost disappeared below pH 5 and above pH 11. The addition of Cys to TAMSMB-Ni^{2+} resulted in the color changes from red to yellow between pH 7 and 10. Therefore, pH 6.5 was selected as the optimal pH value in the light of an effective colorimetric response and a selective detection of His.

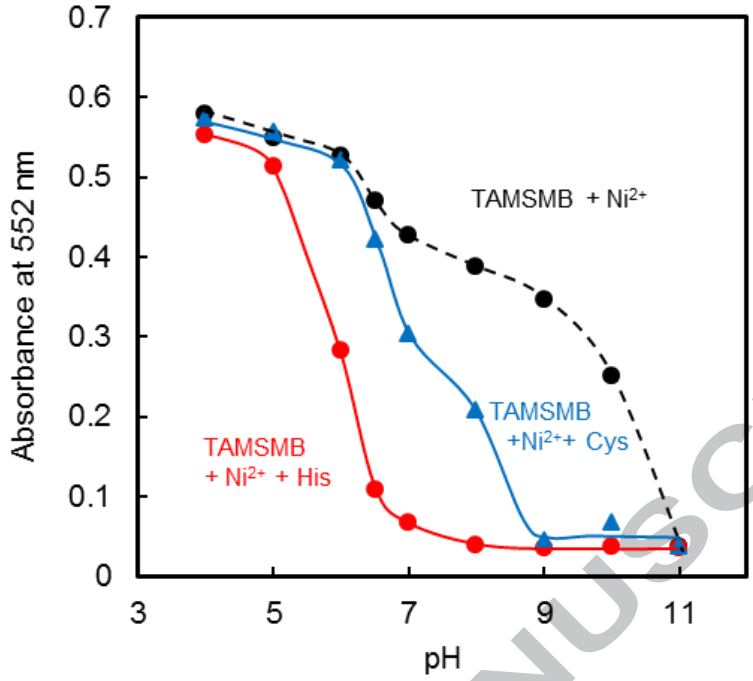


Fig. 6 Absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) and in the presence of His (40 μM) or Cys (40 μM) as a function of pH in 10 mM buffer solution.

The reversible responsive property of TAMSMB-Ni^{2+} to His in aqueous solution is very important for practical application. In order to examine the reversibility of TAMSMB-Ni^{2+} toward His, when Ni^{2+} was added to the solution of TAMSMB-Ni^{2+} in the presence of His, the absorption maximum shift from 475 to 552 nm with the color change from yellow to red, which indicated the production of TAMSMB-Ni^{2+} (Fig. 7). Subsequently, upon addition of His to the solution again, although TAMSMB was regenerated by the release of Ni^{2+}, the absorbance at 552 nm gradually increased with the number of addition, suggesting that the reversibility declined with an increase in the cycle.

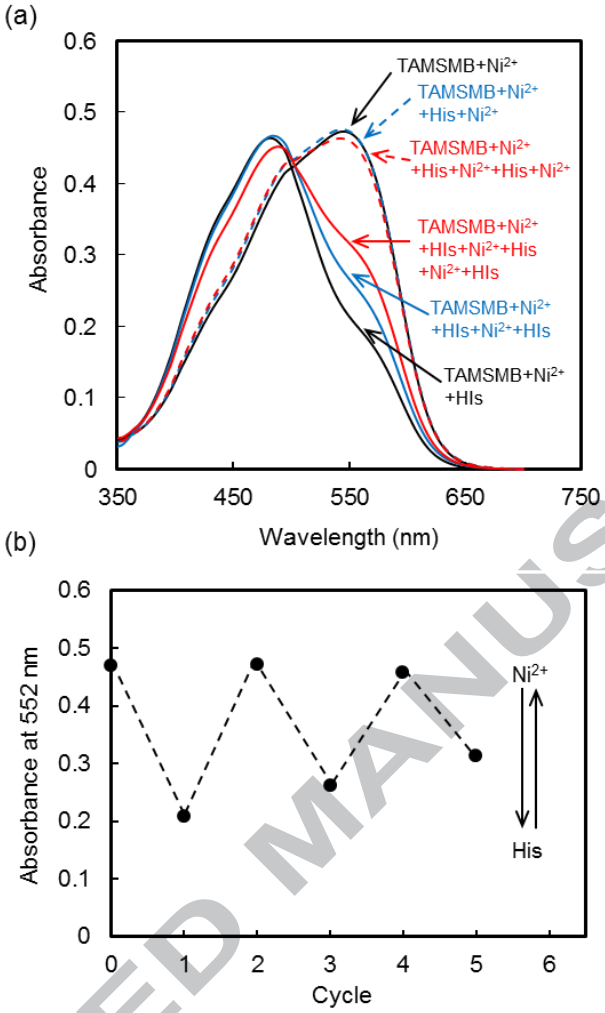
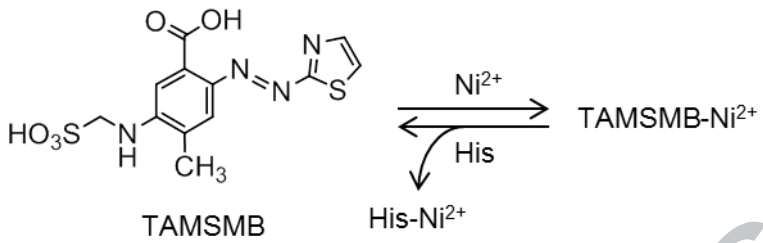


Fig. 7 (a) Absorption spectra of TAMSMB-Ni^{2+} (20 μM) after the sequential addition of His (20 μM) and Ni^{2+} (20 μM) in10 mM phosphate buffer solution at pH 6.5. (b) Reversible changes in absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) after the sequential addition of His (20 μM) and Ni^{2+} (20 μM).

Upon addition of Ni^{2+}, the absorption maximum of TAMSMB exhibited a red shift with color change from yellow and red. TAMSMB could be combined with Ni^{2+} in aqueous solution with pH values ranging from 4 to 6.5 as previously reported.[45] Additionally, from the Job's plot between TAMSMB and Ni^{2+} (Fig. S1), TAMSMB could form the complex with Ni^{2+} in a 1:1 stoichiometric ratio (TAMSMB-Ni^{2+}). Subsequently, although the addition of His to the TAMSMB-Ni^{2+} solution resulted in the color change from red to yellow, the amino acids other than His caused no or insignificant color changes. There have been some reports on the complex formation between His and Ni^{2+} in aqueous solution. [34,37,47] The Job's plot between TAMSMB-Ni^{2+} and His exhibited a 1:1 stoichiometry for the His-Ni^{2+} complex

formation (Fig. S4). It can be presumed from these findings that TAMSMB-Ni^{2+} was regenerated to TAMSMB by the release of TAMSMB through a displacement mechanism with the 1:1 binding stoichiometry between interaction between His and Ni^{2+} (Scheme 2).



Scheme 2 Possible proposed sensing mechanism of TAMSMB-Ni^{2+} toward His.

3. Conclusion

In summary, we have successfully developed the Ni^{2+} complex with a commercially available organic dye TAMSMB as a colorimetric chemosensor for selective detection of His. TAMSMB bound to Ni^{2+} in a 1:1 stoichiometric ratio, resulting in a significant bathochromic shift with a remarkable color change from yellow to red. The TAMSMB-Ni^{2+} complex could detect His selectively through the regeneration of original TAMSMB by the interaction of Ni^{2+} with His. The detection could be done within 60 s with the detection limits of 0.49 μM and 12 μM by absorption and naked-eye methods, respectively, which are lower than the normal levels of His. Moreover, interference studies confirmed the high selectivity of the TAMSMB-Ni^{2+} colorimetric probe for His with little interference by other amino acids.

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Figure captions

Scheme 1 Chemical structure of TAMSMB.

Scheme 2 Possible proposed sensing mechanism of TAMSMB-Ni^{2+} toward His.

Fig. 1 (a) Absorption spectra of TAMSMB (20 μM) as a function of Ni^{2+} concentration in 10 mM phosphate buffer solution at pH 6.5. (b) The color changes of TAMSMB (20 μM) as a function of Ni^{2+} concentration in 10 mM phosphate buffer solution at pH 6.5.

Fig. 2 Absorption spectra of TAMSMB-Ni^{2+} (20 μM) in the presence of various amino acids (40 μM) in 10 mM phosphate buffer solution at pH 6.5.

Fig. 3 (a) Absorption spectra of TAMSMB-Ni^{2+} (20 μM) as a function of His concentration in 10 mM phosphate buffer solution at pH 6.5. (b) Absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) as a function of hisidine concentration in 10 mM phosphate buffer solution at pH 6.5. (c) The color changes of TAMSMB-Ni^{2+} (20 μM) as a function of His concentration in 10 mM phosphate buffer solution at pH 6.5.

Fig. 4 Plots of the absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) as a function of His concentration in 10 mM phosphate buffer solution at pH 6.5 in the presence of His (10, 20, and 40 μM) as a function of time.

Fig. 5 Competitive selectivity of TAMSMB-Ni^{2+} (20 μM) toward His (40 μM) in the presence of other amino acids (40 μM) in 10 mM phosphate buffer solution at pH 6.5.

Fig. 6 Absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) toward His (40 μM) or Cys (40 μM) as a function of pH in 10 mM buffer solution.

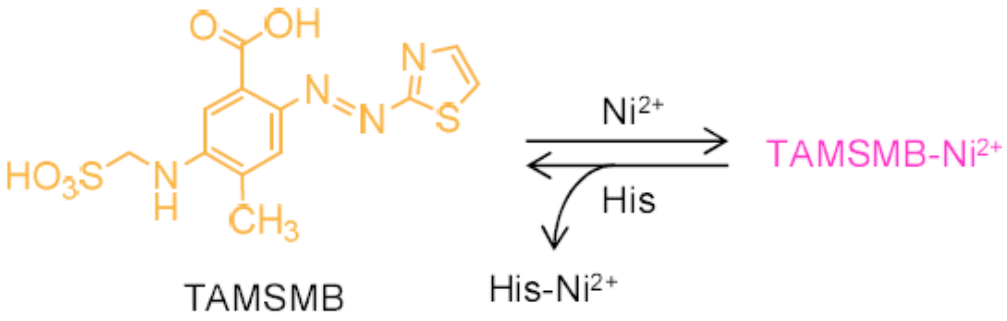
Fig. 7 (a) Absorption spectra of TAMSMB-Ni^{2+} (20 μM) after the sequential addition of His (20 μM) and Ni^{2+} (20 μM) in10 mM phosphate buffer solution at pH 6.5. (b) Reversible changes in absorbance at 552 nm of TAMSMB-Ni^{2+} (20 μM) after the sequential addition of His (20 μM) and Ni^{2+} (20 μM).

Highlights

1) A colorimetric chemosensor for histidine was developed using a TAMSMB-based Ni^{2+} complex in aqueous solution.

2) It could selectively detect histidine by color change from red to yellow.

3) It showed a fast response toward histidine.



Graphical Abstract