A highly selective colorimetric sensor to Fe^{3+} and Co^{2+} in aqueous solutions

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Abstract Five aromatic azo dyes with hydroxyl groups (1–5) were designed and synthesized by coupling reactions. The relationships between structures of the compounds and the spectroscopic properties were investigated. The absorption spectra of these compounds upon titration with K⁺, Ca²⁺, Al³⁺, Mg²⁺, Ni²⁺, Mn²⁺, Cd²⁺, Cr³⁺, Fe³⁺, Cu²⁺, Zn²⁺, Co²⁺, Hg²⁺, and Pb²⁺ ions in neutral aqueous solutions were reported. The results are coincident with the calculation results using the density functional theory method. The high selectivity, excellent water solubility and simple synthetic process make 1-[(2-Hydroxyl)phenylazo]-2-naphthol (5) a potential sensor for sensing Fe³⁺ and Mn²⁺ with the naked eye. 1-[(2-hydroxyl)phenylazo]-2-naphthol-6-sulfonic acid (3) shows high selectivity for the colorimetric detection of Fe³⁺ and Co²⁺ among the tested metal ions. The detection limitations of **3** for determining Co²⁺ and Fe³⁺ were calculated to be 2.8 × 10⁻⁷ and 5.6 × 10⁻⁷ mol/L, respectively.

Keywords Azo compounds · Colorimetric sensing · Metal ions · Water-soluble · DFT calculations

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Introduction

Although some metal ions play important roles in various biological processes, they can cause serious environmental pollution and healthy problems if high concentrations are introduced into the soil, groundwater and the human body [1-6]. Therefore, the design and synthesis of new sensors with high sensitivity and selectivity for metal ions have attracted considerable attention [6-10]. Molecules with fluorophore and/or chromophore are the most frequently reported sensors for metal ions based on the differences in their photophysical properties, such as the absorption and fluorescence signals, before and after the interaction with metal ions. Fluorescent sensors report the presence of metal ions via fluorescence quenching, fluorescence enhancement or shift of the emission maximum. But fluorescent sensors have some disadvantages such as the interfering background fluorescence, the quenching from the competing metal ions and even the incompatibility of the sensors with water [11-13]. In addition, some fluorescent sensors need to be excited with ultraviolet light, which cannot penetrate deeply into biological samples and can damage or trigger autofluorescence from such samples [14–16]. Colorimetric sensors infer the presence of metal ions via change of absorbance at the absorption maxima. In theory, the detection limitation of fluorescence sensors can be 10⁶ times lower than that of the colorimetric sensors because the fluorescence signal can be enhanced by increasing the excitation energy. However, excellent colorimetric sensors can recognize metal ions by using the cheap absorption spectrometers or even the naked eye instead of expensive instruments. Work in this area is still of great challenge and interest.

Aromatic azo dyes have been widely investigated as colorimetric sensors for metal ions [17-21]. They are generally synthesized by a simple coupling reaction of a diazonium salt and an aromatic compound. The absorption spectra of the aromatic azo dyes are related to the two substituted aromatic rings conjugated with an azo group. It is possible to design and synthesize colorimetric sensors with an absorption maximum in the visible and near infrared regions, which is the requirement for sensing in vivo. Most reported azo sensors use nitrogen- or sulfur-containing groups as receptors of metal ions based on the interaction of metal ions with N or S atoms, which possibly decrease the selectivity of the sensors due to the strong interaction ability of N and S atoms with metal ions [22, 23]. In addition, the structurally complex and hydrophobic properties of some aromatic azo sensors limit their applications. It is still necessary to design and synthesize highly selective, structurally simple and hydrophilic colorimetric sensors for metal ions. In connection with our previous work on sensors for ions [15, 24, 25], five aromatic azo dyes with hydroxyl groups (1-5, Fig. 1) were synthesized. The weak interaction ability and hydrophilic property of the hydroxyl group make it possible to improve the selectivity and solubility in aqueous solutions. And the colorimetric responses of **1–5** to K^+ , Ca^{2+} , Al^{3+} , Mg^{2+} , Ni^{2+} , Mn^{2+} , Cd^{2+} , Cr^{3+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Hg²⁺, and Pb²⁺, which are frequently concerned with vital processes, in Tris-HCl buffer solutions are investigated.



Fig. 1 The structures of 1-5

Experimental

Materials

All chemicals are commercially available with AR grade and are used without further purification. 6-Naphthenol-2-sulfonic acid was synthesized according to the literature using naphthalene-2,6-disulfonic acid as a starting material [26, 27].

Syntheses

General procedures for preparation of 1–5 are as follows [28].

In a 100-mL beaker, 10.0 mmol compounds with an NH_2 group were dissolved in a mixed solvent of 10 mL deionized water and 4 mL concentrated hydrochloric acid. Then, the solution was cooled 0 °C. A solution of 10.2 mmol sodium nitrite dissolved in 2 mL deionized water was added dropwise into the above solution. The temperature of the solution was controlled below 5 °C during the process. The resulted solution was stirred for another 15 min after the addition was finished. The excess sodium nitrite was decomposed by a proper amount of urea.

Next, 10.0 mmol of the coupling compound was dissolved in a mixed solvent of 10 mL deionized water and 5 mL 10 % sodium hydroxide in a 200-mL beaker. The mixture was cooled to 0 °C, and then the benzenediazonium solution of the above step was added dropwise into the solution. The temperature of the system was controlled below 5 °C, and the pH of the reaction solution was kept around 10 with 10 % sodium carbonate. After the addition, the solution was stirred for another 1.5 h at room temperature. Then, the pH was adjusted to 7 using 1 M hydrochloric acid and allowed to stand for 2 h. The red precipitate was filtered out, washed with distilled water twice, and dried in vacuo. The crude product was purified by column chromatography on silica gel, using methylene chloride as eluent.

1-[(2-Hydroxyl)phenylazo]-2,4-diphenol (1)

Yield: 85.4 %. ¹H NMR (400 MHz, DMSO- d_6 , TMS): $\delta = 12.65$ (s, 1H), 11.39 (s, 1H), 10.46 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 7.68 (d, J = 12.0, 1H), 7.30

2726

(t, J = 8.0 Hz, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.96 (t, J = 8.0 Hz, 1H), 6.46 (d, J = 8.0 Hz, 1H), 6.36(d, J = 4.0 Hz, 1H) (Fig. S1, Supplementary material). MS (EI): m/z = 229.0 (M-1) (100 %). IR (KBr, cm⁻¹): 3,473, 1,629, 1,581, 1,425, 1,465 (N=N). Elem. Anal. C₁₂H₁₀N₂O₃: Calcd. C 62.60, H 4.38, N 12.17. Found: C 62.62, H 4.65, N 11.61.

1-[(2-Hydroxymethyl)phenylazo]-2,4-diphenol (2)

Yield: 80.5 %. ¹H NMR (400 MHz, DMSO- d_6 , TMS): 14.10 (s, 1H), 10.63 (s, 1H), 7.72 (d, J = 8.0 Hz, 1H), 7.66 (d, J = 12.0 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.25 (d, J = 8.0 Hz, 1H), 7.06 (t, J = 8.0 Hz, 1H), 6.51 (d, J = 8.0 Hz, 1H), 6.29 (d, J = 2.0 Hz, 1H), 3.94 (s, 3H) (Fig. S2, Supplementary material). MS (EI): m/z = 243.1 (M-1). IR (KBr, cm⁻¹): 3,439, 1,627, 1,598, 1,502, 1,465. Elem. Anal. C₁₃H₁₂N₂O₃: Calcd. C 63.93, H 4.95, N 11.47. Found: C 63.60, H 5.19, N 10.84.

1-[(2-Hydroxyl)phenylazo]-2-naphthol-6-sulfonic acid (3)

Yield: 65.5 %. ¹H NMR (400 MHz, DMSO- d_6 , TMS): 16.44 (s, 1H), 10.75 (s, 1H), 8.52 (d, J = 12.0 Hz, 1H), 8.0–8.05 (m, 3H), 7.85 (d, J = 8.0 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H), 7.16 (m, 1H), 7.05 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 12 Hz, 1H) (Fig. S3, Supplementary material). MS (EI) m/z = 343.5(M–1). IR (KBr,cm⁻¹): 3,416, 1,618, 1,546, 1,459, 1,466. Elem. Anal. C₁₆H₁₂N₂O₅S: Calcd. C 55.81, H 3.51, N 8.14, S 9.31. Found: C 56.03, H 4.06, N 7.80, S 9.06.

1-Phenylazo-2-naphthol-6-sulfonic acid (4)

Yield: 85.7 %. ¹H NMR (400 MHz, DMSO- d_6 , TMS): 15.76 (s, 1H), 8.50 (d, 1H, J = 8.0 Hz), 8.03 (d, 2H, J = 8.0 Hz), 7.88 (d, J = 8.0 Hz, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.39 (t, J = 8.0 Hz, 1H), 6.94 (d, J = 8.0 Hz, 1H) (Fig. S4, Supplementary material). MS (EI): m/z = 327 (M-1). IR (KBr, cm⁻¹): 3,441, 1,620, 1,549, 1,499, 1,457. Elem. Anal. C₁₆H₁₂N₂O₄S: Calcd. C 58.53, H 3.68, N 8.53, S 9.77. Found: C 57.99, H 4.01, N 8.03, S 9.19.

1-[(2-Hydroxyl)phenylazo]-2-naphthol (5)

Yield: 83.6 %. ¹H NMR (400 MHz, DMSO- d_6 , TMS): 16.41 (s, 1H), 10.66 (s, 1H), 8.53 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 8.0 Hz, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.61 (t, J = 8.0 Hz, 1H), 7.46 (t, J = 8.0 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.06 (d, J = 8.0 Hz, 1H), 7.02 (d, J = 8.0 Hz, 1H), 6.86 (d, J = 8.0 Hz, 1H) (Fig. S5, Supplementary material). MS (EI): m/z = 263.2(M-1). IR (KBr, cm⁻¹): 3,441, 1,617, 1,594, 1,491, 1,446. Elem. Anal. C₁₆H₁₂N₂O₂: Calcd. C 72.72, H 4.58, N 10.60. Found: C 72.69, H 4.64, N 10.53.

General methods

UV–Vis absorption spectra were recorded using a TU-1901 Ultraviolet–visible double-beam spectrometer. ¹H NMR spectra were measured on a Bruker advance DPX-400 MHz resonance spectrometer. IR spectra were obtained using a NEXUS-470 Fourier infrared spectrometer. Electrospray ionization mass spectra were measured on a LC/MSD–Trap–XCT system. Elemental analyses were carried on a Flash EA 1112 elemental analyzer.

Procedures of metal ion sensing

The nitrate salts of metal ions K⁺, Ca²⁺, Al³⁺, Mg²⁺, Ni²⁺, Mn²⁺, Cd²⁺, Cr³⁺, Fe³⁺, Cu²⁺, Zn²⁺, Co²⁺, Hg²⁺, and Pb²⁺ were used to evaluate the sensing properties of **1–5** to metal ions in Tris–HCl buffer (0.05 M, pH 7.1). Stock solutions of the metal ions were prepared in deionized water with the concentration of 1 mmol/L. The solutions of **1–5** were prepared in Tris–HCl buffer with concentrations around 10^{-5} mol/L for spectroscopic measurements. In the titration experiments, 3 mL solution of **1–5** was added into the quartz optical cell with an optical path length of 1 cm, respectively. The stock solution of each metal ion was added into the cell step by step via a pipette. The absorption spectra were collected after stirring for 2 min of each addition.

Results and discussion

Absorption spectra studies

The absorption spectra of 1–5 in Tris–HCl buffer, as shown in Fig. 2, are dominated by a band in the visible region (400–700 nm) due to the π – π * transitions of the compounds along the conjugated long axes and a band in the ultraviolet region (200–300 nm) due to the absorption of the phenyl or naphthyl group in these compounds, respectively. The absorption maxima of 3–5 in the visible region are red-shifted compared to those of 1 and 2 due to their larger π conjugated systems.





The absorption maximum in the visible region of 1 (462 nm) is 12 nm red-shifted compared to that of 2 (450 nm) due to the less steric effect of 1 than 2. The absorption maximum in the visible region of 3 (502 nm) is 18 nm red-shifted compared to 4 (484 nm) due to the donating effect of the hydroxyl group on the benzene ring of 3. The absorption maximum in the visible region of 3 is 40 nm blue-shifted compared to that of 5 (542 nm) because of the strong electron-withdrawing effect of the sulfonic acid group on naphthyl ring. These substituents effects of the aromatic azo dyes on the absorption spectra could greatly help us to design sensors to metal ions with proper absorption maxima.

Metal cations selectivity studies

The absorption spectra of **1** (15 μ mol/L) in Tris–HCl (pH 7.1) buffer solution upon titration of Fe³⁺ and Pb²⁺ are illustrated in Fig. 3a, b, respectively. Upon addition of Fe³⁺, the absorbance at 462 nm decreased greatly (Fig. 3a). Additions of Ni²⁺, Mn²⁺, Cd²⁺, and Hg²⁺ to the solution of **1** decrease the absorbance at 462 nm in different degrees without any red-shifting. Addition of Pb²⁺ caused a simultaneous decrease in the absorbance at 462 nm with red-shifting (Fig. 3b). Addition of Cu²⁺, Co²⁺ and Zn²⁺ to the solution of **1** resulted in the same absorption responses of **1** to Pb²⁺, whereas additions of K⁺, Ca²⁺, Al³⁺, Mg²⁺, and Cr³⁺ to the solution of **1** caused little change of the absorption spectrum of **1**. The results show that **1** is not a good sensor because the sensitivity was poor and no apparent color change occurred upon addition of the tested metal ions.

The absorption properties of **3** upon titrations of the mentioned metal ions were studied in order to determine the effect of the substitutes on the selectivity of sensors. Figure 4a, b illustrates the effects upon addition of Fe^{3+} and Co^{2+} on the absorption spectra of **3** (60 µmol/L). As shown in Fig. 4a, the absorption band at 502 nm of **3** was gradually decreased upon addition of Fe^{3+} and finally disappeared. At the same time, a new absorption band, accompanied by an isobestic absorption point at 460 nm, at the blue side was gradually formed. As shown in Fig. 4b, the



Fig. 3 Absorption spectra of 1 (15 μ mol/L) upon titration of Fe³⁺ (0–30 μ mol/L) (a) and Pb²⁺ (b) in Tris–HCl buffer solution



Fig. 4 Absorption spectra of 3 (60 μ mol/L) upon titration of Fe³⁺ (a) and Co²⁺ (b) in Tris–HCl buffer solution

absorption spectra of **3** upon titration of Co^{2+} showed decreases at 502 nm and 270 nm; at the same time, the absorption band at 502 nm was split into two bands, with the more intense transition shifting to longer wavelength. The red-shift indicates that interaction of **3** and Co^{2+} leads to a reduction of the HOMO–LUMO gap [29]. The absorption isobestic points in the titration spectra indicate the formation of the 1:1 complexes. The detection limitations of **3** for determining Co^{2+} and Fe^{3+} , at which the value of A₀/A equal to 1.1, were calculated to be 2.8×10^{-7} and 5.6×10^{-7} mol/L, respectively. The absorption spectra of **3** upon titration of K⁺, Mg²⁺, Ca²⁺, Cr³⁺, Cd²⁺, Cu²⁺, Zn²⁺, Pb²⁺, and Hg²⁺ changed little. The results indicated that compound **3** shows high colorimetric selectivity to Fe³⁺ and Co²⁺, but almost no response to the other metal ions.

The absorption spectra of 2 and 4 did not change much upon the titration of even 7 equivalents of the tested metal ions, indicating weak or no interactions between 2 or 4 and the tested metal ions. The absorption spectra of 5 (30 μ mol/L) in Tris-HCl (pH 7.1) buffer solutions upon titration of metal ions afforded much different behaviors of 1. The absorbance at 542 nm decreased and finally disappeared upon addition of Fe^{3+} to the solution of 5, while at the same time a new absorption peak at the blue side was gradually formed (Fig. 5a) and four absorption isobestic points were presented at 221, 253, 480, and 650 nm, respectively. The color of the solution changed from orange to light vellow as shown in Fig. 6. The absorption spectra of 5 upon titration of Cu^{2+} caused a blue-shift and an accompanying decrease of the absorbance at 542 nm (Fig. 5b). At the same time, the color of the solution changed from orange to purplish red. The blue-shift indicates that the interaction of 5 with Cu^{2+} increases the HOMO-LUMO gap. The absorption spectra of 5 upon titration of Co²⁺ showed a decrease in the absorbance of the visible band and an increase in the absorbance around 270 nm, while at the same time the visible absorption band was clearly split into two bands (Fig. 5c). The reason is probably that the interaction between Co²⁺ and the sensor weakens the conjugated properties of the molecule and leads to a new blue-shift band. Similar phenomena have been reported [29, 30]. Mn^{2+} induced a great decrease of the absorption band of 5 (Fig. 5d) with obvious color change. However, the addition of K^+ , Mg^{2+} , Ca^{2+} , Ni^{2+} , Al^{3+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} , and Hg^{2+} induced only a little change of the absorption spectrum of 5



Fig. 5 Absorption spectra of of 5 (30 μ mol/L) upon titration of Fe³⁺ (0–60) μ mol/L (**a**), Cu²⁺ (**b**), Co²⁺ (**c**), and Mn²⁺ (**d**) in Tris–HCl buffer solutions



Fig. 6 Colors of the solutions of 5 when 1 equiv. metal ions were added

without obvious apparent color change. The colors of the solutions of **5** are shown in Fig. 6 when 1 equiv. metal ions were added. The color of **5** changed to yellow upon addition of Fe^{3+} and light brown upon addition of Mn^{2+} . We can see that compound **5** is suitable for detection of Fe^{3+} and Mn^{2+} in aqueous solutions by the naked eye.

DFT calculations

In general, the binding of metal ions with the conjugate molecules will enlarge the conjugation length of the systems, which will induce a red-shift of the absorption

spectra. The absorption spectra of **1** upon titration of Co^{2+} , Cu^{2+} , Zn^{2+} , and Pb^{2+} generated large red-shifts, whereas no shift were observed upon titration of Fe^{3+} and Hg^{2+} . However, the absorption spectra of **5** upon titration of Co^{2+} , Cu^{2+} and Fe^{3+} afforded blue-shifts, and a similar phenomenon was observed in the absorption spectra of **3** upon titration of Fe^{3+} . In addition, the absorption band at 542 nm of **5** upon titration of Co^{2+} was split into two bands. According to these facts, we presume that the binding of the metal ions to the sensors has two effects: (1) enlarging the conjugation length of the systems, and (2) weakening the conjugated properties of the molecule. The absorption spectra afford blue-shift if the former effect dominates the overall effects. To verify this presumption, the molecular structures and the electronic density distributions of the HOMO orbitals of **1**, **3** and **5** before and after the binding of Cu^{2+} were calculated using the DFT method at B3LYP level. The basis set used for C, H, N and O atoms was 6-31 g, and Lanl2DZ



Fig. 7 Electronic density distributions of the HOMO orbitals for 1 (a, b), 3 (c, d) and 5 (e, f) before and after binding to Cu^{2+}



Fig. 8 Electronic density distributions of the HOMO orbitals for 1 (left) and 3 (right)

was used for the Cu atom. All the calculations were carried out using the Gaussian 03 program [31].

The calculation results showed that the molecules with *trans*-configurations of compounds 1, 3 and 5 have lower energy than their *cis*-configurations. Therefore, most of the molecules take *trans*-configurations at normal conditions. The electronic density of the HOMO orbital is localized around the -N=N- group before binding to Cu^{2+} (Fig. 7a), and delocalized around the molecule after binding to Cu^{2+} (Fig. 7b) for 1. Cu^{2+} greatly involves the conjugation system, which enlarges the conjugation length of 1. This result is in agreement with the absorption spectra of 1 exhibiting a red-shift upon addition of Cu^{2+} . The electronic density of the HOMO orbital of **3** is delocalized around the molecule with a little more around the -N=N- group than the other position (Fig. 7c). The electronic density of the HOMO orbital of 3 after binding to Cu^{2+} is localized on the sulfonic acid group (Fig. 7d), and Cu^{2+} is not involved in the conjugation of the system. The electronic density of the HOMO orbital of 5 is delocalized around the molecule with a little more around the -N=Ngroup than the other position (Fig. 7e), which indicates a great conjugation bridge for the -N=N- group, whereas the electronic density of the HOMO orbital of 5 after binding to Cu²⁺ was clearly transferred to the phenyl and naphthanyl groups from the -N=N- group (Fig. 7f). Also, Cu^{2+} is slightly involved in the conjugation system, indicating the weakening of the conjugation length. This is the reason that the absorption spectra of 5 afforded a blue-shift upon addition of Cu^{2+} .

One of the N atoms in the -N=N- groups of 1-5 can be involved in coordinating with metal ions together with the hydroxyl groups on the aromatic rings. Two hydroxyl groups of 1, 3 and 5 can be involved in coordinating with the equivalent metal cation. Only one hydroxyl group of 2 and 4 can be involved in coordinating with one equivalent of the metal cation. Therefore, 1, 3 and 5 have better sensitivity than 2 and 4. The sulfonic acid group of 3 reduces the electronic density of the hydroxyl group on the naphthalene ring, thus reducing its metal cation coordinating ability compared to that of 5. Thus, 3 has better metal ions selectivity than 5.

NMR analysis

In general, the coupling constants for aromatic signals are typically 0–1 Hz for para coupling, 1–3 Hz for meta coupling, and 7–9 Hz for ortho coupling, respectively.

However, the hydrogen atoms on the benzene or naphthyl ring, which have been circled in Fig. 8, show a J value of 12 Hz for coupling constant. The electronic density on these carbons by DFT calculations is found to be very high, which makes the connected hydrogen show a large coupling constant in their ¹H NMR spectra. The other hydrogen atoms show normal coupling constants of 8 Hz for ortho coupling and 2 Hz for meta coupling.

Conclusions

Five aromatic azo dyes with hydroxyl groups were designed and synthesized by coupling reactions. The absorption spectra of the sensors upon titration with K⁺, Ca^{2+} , Al^{3+} , Mg^{2+} , Ni^{2+} , Mn^{2+} , Cd^{2+} , Cr^{3+} , Fe^{3+} , Cu^{2+} , Zn^{2+} , Co^{2+} , Hg^{2+} , and Pb^{2+} ions, which are frequently concerned with vital processes, in neutral aqueous solutions were reported. The relationship between their structures and spectroscopic properties were investigated. Compounds 1 and 5 could afford proper responses upon titration of different metal ions, but the selectivity of them was not outstanding. Compound 3 shows high selectivity for the detection of Fe^{3+} and Co^{2+} among the tested metal ions. The results are also supported by the calculation results using the DFT method. The high selectivity, excellent water solubility and simple synthetic process make 3 applicable in vivo for sensing Fe^{3+} and Co^{2+} .

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