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PREPARATION AND ABSORPTION SPECTRAL PROPERTY OF A MULTIFUNCTIONAL WATER-SOLUBLE AZO COMPOUND WITH D-π-A STRUCTURE, 4-(4-HYDROXY-1-NAPHTHYLAZO)BENZOIC ACID

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A multifunctional water-soluble azo dye with the D-π-A conjugated structure, 4-(4-hydroxy-1-naphthylazo)benzoic acid (HNBA), was designed and synthesized using 1-naphanol as the electron donator, benzoic acid as the electron acceptor, and −N=N− as the bridging group. After its structure was characterized by FTIR, ^{1}H NMR, and element analysis, the UV-Vis absorption spectral performance of the target dye was studied in detail. The results showed that the dye, combining hydroxyl group, azo group, and carboxyl group, possessed excellent absorption spectral properties ($\varepsilon = 1.2 \cdot 10^4$ l·mol^{-1}·cm^{-1}) changing with pH and solvents. In particular, in polar and protonic water, it had excellent optical response to some metal ions, i.e., Fe^{3+} and Pb^{2+}, which might make it a latent colorimetric sensor for detecting heavy metal ions.

Keywords: *4-(4-hydroxy-1-naphthylazo)benzoic acid, preparation, absorption spectrum, colorimetric sensor.*

Introduction. With the repaid development of modern industry and agriculture, heavy metal pollution in the environment is getting more and more serious from coal-burning power plants, volcanic emissions, mining, solid-waste incineration, etc. So, different methods to determine metal ions have been developed, including atomic spectrometry [1], inductively coupled plasma mass spectrometry [2], reversed-phase high-performance liquid chromatography [3], electrochemistry [4], and fluorescent spectrophotometry [5]. Their excellent performances, however, are achieved at the expense of complicated and expensive instrumentation and cumbersome laboratory procedures, which cannot be applied straightforwardly and conveniently for rapid on-site analysis on a real-time basis [6–8].

Due to the low cost and simplicity of the experimental process, colorimetric detection has drawn particular attention for offering qualitative and quantitative information. Among all the chromophores identified, organic optical materials have attracted extensive attention because of their facile and scalable synthesis and tunable chemical and physical properties via molecular design and engineering [9–12]. Azo compounds possess more closely spaced energy levels and can absorb specific wavelengths in the visible range since as their electrons are extensively delocalized over aromatic rings and nitrogen atoms. By changing electron-donating and withdrawing substituents in the aryl ring, a plethora of multifunctional azo derivatives with different absorption intensities and absorption peaks has been designed, prepared, and applied in various fields such as nonlinear optics [13–15], light-emitting diodes [16–18], chemical sensors [19, 20], solar cells [21], biological-medical studies [22–24], and textile dyeing and the fashion industry [25, 26].

Owing to their special chromophoric nature and multi-dentate coordination ability, azo compounds containing multifunctional active moieties have attracted more and more attention. They have been widely utilized for metal complexation and spectroscopic determination of cationic species. Typically, Yun et al. [27] presented an easy naked-eye detection method for Fe^{3+} with the detection limit of 0.024 μg/ml, based on 1-nitroso-2-naphthol, an excellent color-forming chelating agent. Ebdelli et al. [28] developed a tetrakis(phenylazo) calix [4] arene derivative for coordinating Eu^{3+} with exceptional affinity. The stoichiometric ratio of the complexation between the ionophore and Eu^{3+} ions in acetonitrile has been determined too. Our group [19] also reported 4,4'-bis-(carboxyl-phenylazo)-dibenzo-18-crown-6 dye as a colorimetric sensor for Hg^{2+} determination. The dye, combining a crown ether ring and a carboxyl group, exhibited well-defined Hg^{2+}-selective ratiometric

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behavior, with the maximum absorption peak changing from 354 to 408 nm exclusively. The development of novel and efficient azo-based colorimetric sensing materials, remains a challenge.

Herein, an asymmetrical D-π-A conjugated azo compound, 4-(4-hydroxy-1-naphthylazo)benzoic acid (HNBA), was identified and prepared to improve its selective coordination ability and solubility, as well as its absorption spectral property. It was expected that the incorporation of strongly electron-donating 1-naphanol and electron-withdrawing benzoic acid moieties would endow the target azo with excellent absorption spectra. High coordination ability and solubility could also be realized by combining –COOH, –OH, and –N=N– groups as chelating and hydrophilic ones.

Experimental. All the chemicals in the experiment were of AR grade and used as received from Sinopharm Chemical Reagent Co. Ltd. Water used throughout was doubly deionized. HNBA was synthesized as described below and a stock solution of $5.0 \cdot 10^{-3}$ mol/l HNBA was prepared using doubly deionized water at room temperature and stored at 4^oC. Phosphate buffers (PB) were prepared by mixing solutions of 0.01 mol/l H_3PO_4, 0.01 mol/l K_2HPO_4, 0.01 mol/l KH_2PO_4, or 0.01 mol/l KOH in a proper ratio to acquire the desired pH (pH 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0).

FTIR spectra of HNBA with KBr disc were acquired using a Nicolet NEXUS 870 FTIR spectrophotometer at room temperature in the region of 4000–500 cm^{-1}. ^1H NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 400 MHz using tetramethyl-silane (TMS) as the reference and D_2O as solvent. Elemental analyzes were conducted using an Elemental Vario EL-III apparatus. UV-vis spectra were recorded on a Lambda 35 UV/Vis spectrometer from 300 to 600 nm and the band-slit was set as 2.0 nm using a 1-cm square quartz cell. Also, a PHS-25 pH meter was used for the measurements.

According to [13, 29], *p*-aminobenzoic acid (0.72 g, 5 mmol) was dissolved in an ice-water solution of 15% sodium nitrite (0.38 g, 5.5 mmol). After cooling to 0°C, the solution was added to concentrated hydrochloric acid (1.2 ml) and stirred for 30 min. The excess nitrous acid was neutralized with about 5.0 mg urea. The mixture was then added dropwise to the 10 ml buffer solution (KH_2PO_4/Na_2HPO_4, pH 6) containing naphthol (0.73 g, 5 mmol) and stirred for another 2 h at 0–5°C. The resultant precipitate was filtered and purified by recrystallizing three times from ethanol to provide a dark red HNBA crystal with a yield of 88.9%.

IR (KBr), ν (cm^{-1}): ~2500–3500 (−COOH), 1705 (C=O), 1609 (N=N), 1278 (C–O); ^1H NMR (D_2O, 400 Hz) δ (ppm): 8.65 (d, J = 8.5 Hz, 1 H, Ar–H), 8.51 (d, J = 8.4 Hz, 1 H, Ar–H), 8.36 (d, J = 8.4 Hz, 1 H, Ar–H), 8.13 (d, J = 7.8 Hz, 1 H, Ar–H), 8.02 (d, J = 7.8 Hz, 1 H, Ar–H), 7.56 (t, J = 6.4 Hz, 1 H, Ar–H), 7.46 (t, J = 6.7 Hz, 1 H, Ar–H), 7.12 (t, J = 6.5 Hz, 1 H, Ar–H), 4.98 (s, 1 H, –OH). Anal. Calcd for $C_{17}H_{13}N_2SO_2$: H 4.14, C 69.86, N 9.58, S 9.77. Found: H 4.25, C 69.76, N 8.50, S 9.51.

Results and Discussion. To illustrate the effect of solvents on the absorption spectrum of HNBA, the UV-vis spectra in different polar solvents, i.e., N,N-dimethylformamide (DMF), tetrahydrofuran (THF), acetone, ethanol, and water were recorded with a concentration of $6.8 \cdot 10^{-5}$ mol/l as shown in Fig. 1. From Fig. 1, it is easy to see that HNBA has a strong and sharp absorption peak at *ca*. 524 nm with a molar absorptivity (ε) of $1.2 \cdot 10^4$ $l \cdot mol^{-1} \cdot cm^{-1}$ in polar and protonic water, attributed to the whole molecular D-π-A conjugated system. This means that HNBA may exist in the form of a single molecule, i.e., polar and protonic water is a good solvent for HNBA, in which HNBA can disperse enough owing to strong intermolecular interactions such as hydrogen bond interaction [1], whereas in polar nonprotonic acetone and THF, the absorption peaks show a hypsochromic shift by 34 and 36 nm to 490 and 488 nm with decreasing absorption intensity, respectively. According to the literature and our previous work [9, 10, 13, 30, 31], it is known that organic molecules with π-conjugated system could form two types of aggregates, H- and J-types, where the molecules are aligned in card-pack and slipped-stack manners, respectively. The H-type aggregation, in which the transition dipole moments of the chromophores are arranged in a parallel mode, yields a hypsochromic shift of the electronic absorption peak. On the other hand, in the J-type aggregates, the transition dipoles are arranged in a head-to-tail manner, leading to a bathochromic shift. Accordingly, the hypsochromic shifts of the absorption peaks for HNBA in polar and non-protonic acetone and THF could be attributed to the H-aggregation of azo molecules. For both ethanol and DMF, a new hypsochromic-shifted absorption peak emerges at ca. 459 and 608 nm besides the absorption at 501 nm. The reason may be that both ethanol and DMF are the transitional solvents for HNBA, in which there exist single-molecular forms and the H-aggregation or J-aggregation of HNBA, simultaneously.

For an acidic HNBA molecule, the pH of the system will have a more significant influence on its existing formation and so make its absorption spectrum changed. Here the effect of pH on the absorption spectrum was investigated in polar and protonic water with a pH range of ~3.0–10.0. As shown in Fig. 2, it is interesting to find that when the pH is within 5.0 and 7.0, the absorption at 524 nm is the strongest and nearly unchanged. When the pH is less than 4.0, the absorption intensity at 524 nm decreases greatly and becomes bathochromic-shifted as well. The reason may be that weak acidic HNBA coagulates (H-aggregation) under the strong acid condition. While the pH increases to more than 7.0, its absorption peak

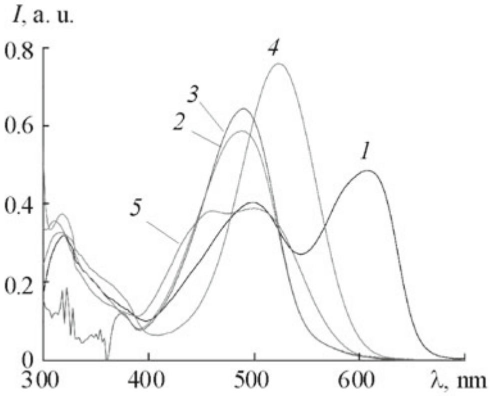

Fig. 1. The UV-Vis spectra of HNBA in polar solvents: DMF (1), THF (2), acetone (3), water (4), and ethanol (5) in $6.8 \cdot 10^{-5}$ mol/l.

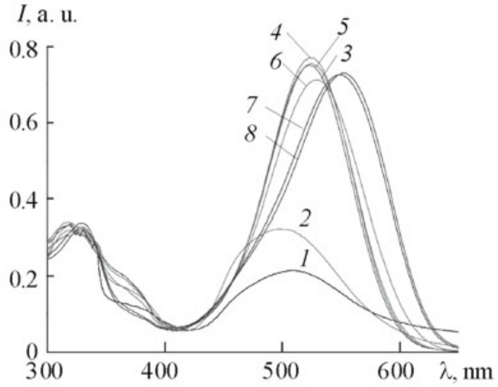

Fig. 2. Effect of pH on the UV-Vis spectra of HNBA (from top to bottom: 3.0 (1), 4.0 (2), 5.0 (3), 6.0 (4), 7.0 (5), 8.0 (6), 9.0 (7), 10.0 (8)).

has a bathochromic shift and the absorption intensity decreases a little. The reason may be that −COOH and −OH groups in HNBA molecules could change slowly into COO^- and O^- ions with increase in pH, which enlarges the whole molecular π-conjugated system, augments the molecular electron density, but reduces the molecular dipole moment. This phenomenon indicates that HNBA will possess the best optical absorption property under a wide pH range.

To demonstrate the application of HNBA, we investigated its spectral response to some environmentally relevant metal ions, i.e., K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Ni^{2+}, Cd^{2+}, Cu^{2+}, Co^{3+}, Al^{3+}, Hg^{2+}, Pb^{2+}, and Fe^{3+} at the same concentration of $6.8 \cdot 10^{-5}$ mol/l in aqueous solutions under pH 6.0. After the addition of different metal ions above, the relative changes in absorption spectra were recorded as shown in Fig. 3. From Fig. 3, we can easily see that monovalent metal ions and most of the common divalent metal ions tested have nearly no effects on the absorption spectra of HNBA, while, under the same conditions, high-valence Al^{3+} can produce a small hypsochromic shift of the absorption spectra of HNBA; in particular, Fe^{3+} can produce a hypsochromic shift of 16 nm from 524 to 508 nm. More importantly, environmentally toxic heavy metal ions such as Hg^{2+} and especially Pb^{2+} can greatly decrease the absorption intensity with an obvious hypsochromic shift to 466 nm to form a camel peak. The reason may be that high-valence Al^{3+} and Fe^{3+} and divalent Hg^{2+} and Pb^{2+}, with strong soft acidic properties, could selectively coordinate with −COOH, −OH, or −N=N−, which will distort the whole D-π-A molecular configuration and decrease the coplanar system or degree of conjugation.

A theoretical calculation has been carried out to further confirm the reaction mechanism between HNBA and the high-valence Al^{3+} and Fe^{3+} and divalent Hg^{2+} and Pb^{2+} with strong soft acidic property. Taking Fe^{3+} as an example, we show the structures of HNBA coordinating with Fe^{3+} before and after in Fig. 4. The data were optimized using the B3LYP/6-31G level of theory and method implemented in the Gaussian 03 suite of program [32]. From the results, we can easily find that the terminal phenyl ring is greatly distorted, and the dipole moment changes accordingly from 4.1115 to 9.5957 D once Fe^{3+}

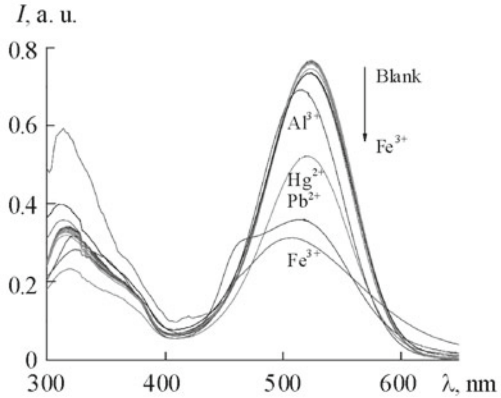

Fig. 3. Effects of different metal ions on the UV-Vis absorption spectra of the target dye (from top to bottom: blank, K^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ag^+, Ni^{2+}, Cd^{2+}, Cu^{2+}, Co^{3+}, Al^{3+}, Hg^{2+}, Pb^{2+}, and Fe^{3+}).

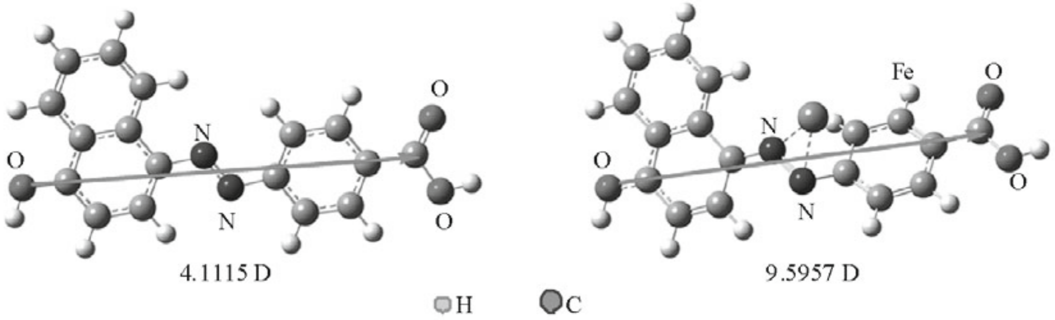

Fig. 4. Optimized geometries and dipole moments of HNBA before (a) and after the action of Fe^{3+} (b).

coordinates with nitrogen atoms in –N=N– bonds in HNBA. The coordination with Fe^{3+} accordingly results in damage of the original conjugated system and so the absorbance at 524 nm decreases and even disappears due to the hypsochromic or bathochromic shifts.

Conclusions. A water-soluble D-π-A conjugated azo compound, 4-(4-hydroxy-1-naphthylazo)benzoic acid (HNBA), is designed and prepared. HNBA possesses a strong and sharp absorption peak at ca. 524 nm with a molar absorptivity (ε) of $1.2 \cdot 10^4$ $l \cdot mol^{-1} \cdot cm^{-1}$ in polar and protonic water and remains very stable under weak acidic or neutral conditions (pH ~5.0–7.0). There are obvious H-aggregation or J-aggregation effects in most other polar solvents, such as DMF, THF, acetone, and even ethanol, in which their absorption peaks are hypsochromic- or bathochromic-shifted accordingly. More importantly, some high-valence metal ions and heavy metal ions, for example, Fe^{3+} and Pb^{2+}, can produce a hypsochromic shift and decrease selectively the absorption peak of HNBA. The action mechanism between HNBA and metal ion was confirmed and deduced by experimental data and theoretical calculations. The target azo HNBA can be a latent sensor for colorimetric detection for some of the heavy metal ions mentioned.

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