



An azaindole–hydrazine imine moiety as sensitive dual cation chemosensor depending on surface plasmon resonance and emission properties



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ABSTRACT

A novel azaindole-based colorimetric and fluorescent sensor with an attached hydrazine group (L) was synthesized and characterized by FT-IR, NMR, and CHNS analyses. L exhibited high colorimetric selectivity and sensitivity toward Ag^+ ions over other common cation solutions (Ag^+ , Na^+ , K^+ , Ba^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Cr^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Sr^{2+} , Zn^{2+} , and Al^{3+}) in ethanol:HEPES buffer (1:9, v/v) solution. Upon addition of Ag^+ ions, the maximum absorption band of L displayed a red shift from 332 to 400 nm. The efficient electron transfer ability of the molecular receptor L lead to the easy formation of silver nanoparticles (AgNPs) that manifested naked eye detection through color change of solution from colorless to yellow. The AgNPs thus obtained using organic compound L as stabilizer were characterized by light scattering, zeta potential and transmission electron microscopy (TEM). Meanwhile, the results of fluorescence titration experiments illustrated that the sensor functions as “turn-off” receptor upon selective binding with Fe^{2+} . Comparative studies revealed that quenched emission originated from selective chelation of Fe^{2+} ions with the lone pair of the azaindole receptor's nitrogen atom and causes enhanced PET process Both B.-H. plot and emission spectra analysis reveals a 1:2 stoichiometric relationship between L and the added Fe^{2+} ions. The designed probe L permitted accurate detection of respective Ag^+ and Fe^{2+} down to 2.8 nM and 2.17×10^{-7} M with rapid response times. Finally, by using Ag^+ and Fe^{2+} ions as chemical inputs and the absorbance and emission response as outputs, logic circuits are constructed at the nanoscale level.

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1. Introduction

A great deal of research is now being directed for the designing of organic materials with specific binding geometries for cations [1–5]. Creative designing of the reactive probes that show altered optical response upon change in the chemical surroundings has been used for constructing highly selective molecular switches and chemosensors [6–9]. Aromatic moieties incorporated with different heterocyclic rings present a special class of luminescent receptors due to their excellent optoelectronic features, good thermal stability as well as selective binding events [10–13]. These unique properties make organic probes as most promising candidates for various sensing applications. However, their applicability is insufficient due to their tedious operational conditions, consumptive nature and cytotoxicity [14–16]. Shedding light on all these issues, the main requirement of smart probes that can potentially facilitate sensing of charged species by relatively simple and

convenient formats is still to be accomplished. With the rapid development of technology in the past few years, unique structural array of azaindole derivatives have attracted much attention from the scientific community. Azaindoles are bicyclic azaaromatic molecules having special place in synthetic chemistry due to their highly pronounced pharmacological and biological activities as well as key structural element in various natural products [17–19]. These compounds seem to have an edge over all the other probes because of their enhanced sensitivity to the chemical transformations in local environment [20]. A variety of sophisticated azaindole hosts bearing functional groups such as carboxylic acid, amide or diaminotriazine are known to offer selective and directional sites for metal complexation [21–23]. However, to the best of our knowledge, this feature has hardly been explored in chemosensing studies for recognition of hazardous chemicals in aqueous phase. Introduction of an azaindole skeleton into the molecular probe can be expected to give favorable selective and irreversible photochemical transitions. By judicious incorporation of a suitable receptive binding unit, judicious incorporation of a suitable receptive binding unit for conversion of analytes (e.g., metal ion) to nanoparticles (metal nanoparticles) in solution phase [24,25].

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Attachment of organic chromophores favors stability as well as surface functionality to these nanoentities that offer tunable changes in their surface plasmon resonance (SPR). Such ease of capping allows one to tailor the coupling between π electron cloud of probe and surface plasmon of metal leading to gradual optical transitions, which can be probed by various sensing methods [26–28]. Plasmonic colorimetric assays, in particular, have opened various ways for the ultrasensitive and quantification analyte detection ranging from ions and small molecules to large proteins. In addition, these unique distance-dependent optical properties can be chemically programmed to induce visual color change and the detection is successful at lower concentration of the analyte [29,30]. Therefore, extreme sensitivity of such sensing platforms presents rapid and portable quantification of various biological and chemical analytes without complicated instrumentation, resulting into a relatively more selective sensor.

Herein, we report facile synthesis of imine moiety (L) by simply functionalizing the carbaldehyde substituted azaindole backbone with hydrazine groups. Spectroscopic characterization of the obtained receptor L has been done using various techniques as IR, UV, ^1H NMR and fluorescence spectroscopy. The performance of new azaindole probe and the implication of measurement methodology is demonstrated by monitoring ionic species in mixed aqueous media and its response to various parameters by monitoring optoelectronic transitions. Our objective is to explore a new pathway for preparing stable Ag colloids solution based on electrochemical scheme that display spectroscopic transformations associated with the surface plasmon resonance (SPR). Implementation of this approach largely depends upon the dual function of azaindole derivative L favoring reduction of silver ions and their stabilization as nanoparticles. Immediate synthesis of monodispersed AgNPs allows rapid naked eyes analysis and explores optical transitions even at nanomolar concentrations. However, in the second part, we highlight the utilization of azaindole binding sites for selective sensing and quantification of Fe^{2+} ions using emission spectroscopy. Further, selective chelation of this organic molecule with Fe^{2+} ions triggers photoinduced electron transfer (PET) which facilitates fluorescence quenching. In analytical chemistry, such a combination is unique and no report is available on the use of azaindole probe showing chromogenic and fluorogenic signaling towards Ag^+ and Fe^{2+} , respectively.

2. Experimental

2.1. Materials

Reactants 7-azaindole-3-carboxaldehyde and hydrazine were purchased from commercial supplier (Sigma). Metal ion solutions (Ag^+ , Na^+ , K^+ , Ba^{2+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Cr^{3+} , Fe^{2+} , Mg^{2+} , Mn^{2+} , Ni^{2+} , Sr^{2+} , Zn^{2+} , and Al^{3+}) were prepared from their nitrates in double distilled water. All the reagents were obtained from Alfa Aesar Chemical. 4-(2-Hydroxyethyl)-1-piperazineethanesulfonic acid (HEPES) buffer and ethanol of HPLC grade was obtained from Sigma Aldrich. All the reagents were used as received throughout the work. Buffer solutions were prepared using HEPES and proper amount of aqueous NaOH and HCl under adjustment by a pH meter.

2.2. Methods

FT-IR spectra IR spectra were recorded on a Thermo Scientific Nicolet iS 50 in the region $4000\text{--}400\text{ cm}^{-1}$.

^1H NMR spectra were collected on a Bruker DRX 400 spectrometer in CDCl_3 with tetramethylsilane as internal reference.

2.3. Absorbance and photoluminescence measurements

The electronic absorption and steady-state fluorescence emission spectra were obtained on Jasco V-530 and Hitachi-F7000 with a xenon lamp, respectively. A 3.5 ml Quartz cuvette with 10 mm path length having 3 ml of solution was used for the spectral measurement. The excitation and emission wavelengths were 340 and 415 nm with scan rate of 500 nm min^{-1} and 10 nm slit widths. For absorption spectra, the data were collected by scanning over 240–500 nm range with scan rate of 480 nm min^{-1} .

2.4. pH studies

The pH of solutions was examined with a Mettler Toledo Digital pH meter, which was calibrated with standard pH buffer solutions.

2.5. XRD analysis

The structural characterization was done by X-ray diffractometer (XRD; PANalytical X'Pert PRO) measured with $\text{Cu K}\alpha$ radiations ($\lambda = 1.54178\text{ \AA}$) in the range of $20\text{--}80^\circ$ with scan speed of 8° min^{-1} .

2.6. Transmission electron microscopy (TEM) images

Morphology and dimensions of the Ag nanoparticles was examined by Hitachi H-7500 TEM. For TEM studies carbon-coated 200 mesh copper grid was dipped into a solution of dispersed SB capped ZnO NPs in methanol.

2.7. Particle size analysis

The particle size of nanoparticles was determined by Photon Correlation Spectroscopy (PCS) using Malvern Zetasizer Nano S90 (Malvern Instruments, Malvern, UK). The instrument measured hydrodynamic diameter by means of 4 mW He–Ne Laser operating at 633 nm and measured at a scattering angle of 90° at 25°C .

2.8. Zeta potential

The zeta potential (ZP) which reflects the electric charge on the particle surface, was determined by Microtac Nanotracc Wave at 25°C .

2.9. Synthesis of azaindole Schiff base L

A mixture of hydrazine (1 mmol, 10 ml) and 7-azaindole-3-carbaldehyde (1 mmol, 10 ml) was prepared in absolute ethanol with molar ratio 1:2. Solution was kept under reflux for 3 h. The completion of reaction was confirmed through TLC. The resulting solution was cooled to room temperature. The yellow precipitates were obtained, filtered-off and then recrystallized from hot ethanol. The complete reaction scheme for the formation of ligand is shown in Scheme 1. Elemental analysis. Found: C, 66.26; H, 4.24; N, 29.32%. Required: C, 66.66; H, 4.19; N, 29.16%. FT-IR (KBr plates, cm^{-1}): 3036–2982 w (C–H stretch), 1630 s ($\nu\text{ C}=\text{N}$), 1604–1492 m (ring stretching) (cm^{-1}) (where w = weak; ν = very; s strong; m = medium; br = broad). ^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.2–8.32 (aromatic H, m, 9H), 8.85 (CH=N, s, 1H), 12.11 (NH, s, 1H) (Fig. S1 supplementary data). UV–vis (ethanol:water (1:1, v/v)): $\lambda_{\text{max}} = 222, 286$ and 332 nm . Fluorescence (ethanol:water (3:7, v/v)): $\lambda_{\text{exc}} = 340\text{ nm}$, $\lambda_{\text{em}} = 415\text{ nm}$.

2.10. Recognition studies

The detection of ions was carried out by employing sensor (L) in mixed aqueous system using absorption and fluorescence

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