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Development of a new chemosensor for Al^{3+} ion: Tuning of properties

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ABSTRACT

We have synthesized and characterized three Schiff-base molecules, namely, 1-(((2-hydroxybenzylidene)hydrazono)methyl)naphthalen-2-ol (**H_2L**), (1-(((2-hydroxy-5-nitrobenzylidene)hydrazono)methyl)naphthalen-2-ol (**H_2L-NO_2**) and 1-(((2-hydroxy-5-methylbenzylidene)hydrazono)methyl)naphthalen-2-ol) (**H_2L-Me**). Out of these three compounds, **H_2L-NO_2** has been found to be a selective fluorescent chemosensor for Al^{3+}. Fluorescence intensity of **H_2L-NO_2** at 517 nm (λ_{ex} = 390 nm) is increased significantly in the presence of Al^{3+}. Other relevant metal ions cannot induce considerable enhancement in its emission intensity. The enhancement has been explained using PET and CHEF mechanism. Quantum yield and life-time of **H_2L-NO_2** have increased in the presence of one equivalent of Al^{3+}. **H_2L-NO_2** forms 1:1 complex with the metal ion which is confirmed from Job's plot and ESI mass spectral analysis. Its sensitivity has been determined by 3σ method and found to be moderate. Emission intensity of **H_2L** and **H_2L-Me** does not increase appreciably in the presence of Al^{3+}. Presence of electron withdrawing group in **H_2L-NO_2** may be responsible for its aluminum sensing properties.

1. Introduction

Aluminum is one of the most available elements in earth's crust [1–3]. It is generally present as Al^{3+} ion. It has widespread applications in many areas of daily use. Aluminum utensils are used in domestic purpose. It is available in many products of paper [4], textile [5], food industries [6], etc. Aluminum is not essential for our body but several *anthropogenic* activities may lead to the accumulation of high concentration of this metal ion in biological systems. Use of Al-foil as food wrapper or Al-made utensils and intake of water with high metal ion concentration may have adverse health effects. As per WHO (World Health Organisation) recommendation, daily human intake of aluminum may be 2–10 mg depending on body weight [7–11]. It has relevance in stimulation of different diseases e.g. Alzheimer's disease, Parkinson's disease, amyotrophic lateral sclerosis, etc. and it is associated with the damage of the central nervous system [4–6,12]. Excessive aluminum concentration is toxic to flora and fauna. Thus, selective and sensitive detection of Al^{3+} becomes important to the researchers of chemical, biological and environmental sciences.

Detection of aluminum ion may be achieved by means a number of methods/instruments. But among them, fluorescence spectroscopy becomes most popular among the scientists because of its comparatively low cost, easy operation, high sensitivity, etc. Development of fluorescent chemosensors for Al^{3+} ion increases to address its sensibility and suitability of application in real samples [7–14]. But generation of chemosensors for this metal ion is not easy because of its poor ability to form coordination bond and strong hydrophilic character. However, it is a hard acid and favors binding with hard center [15]. Fluorescent chemosensors for Al^{3+} are mainly based on photoinduced electron transfer (PET), chelation-enhanced fluorescence (CHEF), Intraligand charge transfer (ICT) and excited-state intramolecular proton transfer (ESIPT) mechanisms. There are several other reports which describe development of different chemosensors for trivalent metal cations based on the above mentioned mechanisms [16–26].

After appearance of a report on aluminum sensing properties of a commercially available chemical, 2-hydroxy-1-naphthaldehyde [27], a number of Schiff-base molecules [28–31] using 2-hydroxy-1-naphthaldehyde as aldehyde were evolved as fluorescent chemosensor for Al^{3+} ion. Our most recent publication describes incorporation of 2-hydroxy-1-naphthaldehyde in functionalized mesoporous silica for detection and removal of Al^{3+} ion [32]. Tuning of properties of a chemosensor is important to get desired application. Presence of electron withdrawing group(s) or electron pushing group(s) on chemosensors has been used for the tuning of the properties. Mere presence of such group may have drastic effect on the sensing ability and sensitivity. They can affect excitation and emission energy of the probe. Sensor may become numb in their presence on the organic skeleton. In our previous report, we have shown that the presence of methyl group in the Schiff-base molecule makes it a selective fluorescent sensor for Al^{3+} while nitro group in place of methyl group turns it insensitive as the sensor [33].

In continuation to our interest in the development and exploration of chemosensors for small cations [34–37], we report here the

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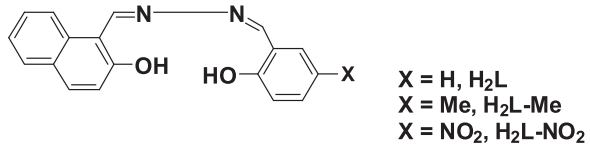

Scheme 1. Structures of H_2L, H_2L-NO_2 and H_2L-Me.

synthesis, characterization and spectral properties of three Schiff-base molecules, namely, 1-(((2-hydroxybenzylidene)hydrazono)methyl) naphthalen-2-ol (**H_2L**), (1-(((2-hydroxy-5-nitrobenzylidene)hydrazono) methyl)naphthalen-2-ol (**H_2L-NO_2**) and 1-(((2-hydroxy-5-methylbenzylidene)hydrazono)methyl)naphthalen-2-ol) (**H_2L-Me**) (Scheme 1). Electron withdrawing and electron pushing groups are introduced to **H_2L** to examine their effects on spectral behavior. **H_2L-NO_2** has been found as a selective and sensitive fluorescence chemosensor for Al^{3+} ion while **H_2L** and **H_2L-Me** are unable to detect this metal ion. **H_2L** has been as reported a ratiometric pH sensor earlier [38].

2. Experimental section

2.1. Materials and physical methods

2-Hydroxy-1-naphthaldehyde and 5-nitro-2-hydroxybenzaldehyde were purchased from Sigma Aldrich and used without further purification. All other reagents were obtained from commercial sources and used as received. Solvents used for spectroscopic studies were purified and dried by standard procedures before use [39]. NMR spectra of the compounds were recorded on either a Bruker 500 MHz spectrometer or a Bruker 300 MHz spectrometer. FT-IR spectra were obtained on a Perkin Elmer spectrometer (Spectrum Two) with the samples by attenuated total reflectance (ATR) technique. Elemental analysis was carried out with a 2400 Perkin Elmer Series-II CHN analyzer. The ESI-MS spectra were recorded on Qtof Micro YA263 mass spectrometer. Absorption spectra were studied using a Shimadzu UV 2100 spectrophotometer. Emission spectra were recorded on a Horiba make Fluoromax-4C spectrofluorimeter. Luminescence lifetime measurements were carried out using a time-correlated single photon counting set up from Horiba Jobin-Yvon. The luminescence decay data were collected on a Hamamatsu MCP photomultiplier (R3809) and were analyzed using the IBH DAS6 software.

Emission quantum yields (Φ) of **H_2L-NO_2** and its Al^{3+} complex were determined by using the formula:

$$\Phi_{sample} = \{(OD_{standard} \times A_{sample} \times \eta^2_{sample})/(OD_{sample} \times A_{standard} \times \eta^2_{standard})\} \times \Phi_{standard}$$

where A is the area under the emission spectral curve, OD is optical density of the compound at the excitation wavelength and η is the refractive index of the solvent, quantum yield of standard (quinine sulfate) (Φ = 0.546 in water, λ_{ex} = 350 nm) [40].

1-(Hydrazonomethyl)naphthalen-2-ol was synthesized following published procedure [1,41,42].

2.2. Synthesis of (1-(((2-hydroxy-5-nitrobenzylidene)hydrazono)methyl) naphthalen-2-ol (H_2L-NO_2)

1.0 mmol (0.186 g) of 1-(hydrazonomethyl)naphthalen-2-ol was dissolved in 20 mL of acetonitrile in a 100 mL round bottom flask. To it, 1.0 mmol (0.167 g) of 2-hydroxy-5-nitro benzaldehyde was added slowly. Then the mixture was stirred for 24 h to obtain a deep yellow solid crystalline product. It was filtered and washed with cold acetonitrile and then dried in desiccators. Data for **H_2L-NO_2**: yield: 75% (0.251 g); C, H, N analysis: anal. Calc. for $C_{18}H_{13}N_3O_4$: C, 64.47; H, 3.91; N, 12.53; found C, 64.32; H, 3.81; N, 12.66; ESI-MS^+ (*m/z*): 330.09 (**H_2L-NO_2** + H^+); FT-IR (Wavenumber, cm^{-1}: 1629, 1484, 1341, 1219, and 777); ^{1}H NMR (in DMSO-d_6) (δ, ppm): 12.83 (s, 1H), 12.26 (br, s, 1H), 9.93 (s, 1H), 9.11 (s, 1H), 8.74 (s, 1H), 8.62 (d, 1H, *J* = 8.5), 8.26 (d, 1H, *J* = 8.9), 8.03 (d, 1H, *J* = 8.5), 7.90 (d, 1H, *J* = 8.1), 7.59 (t, 1H, *J* = 7.5), 7.42 (t, 1H, *J* = 7.2), 7.25 (d, 1H, *J* = 8.9), 7.17 (d, 1H, *J* = 9.0); ^{13}C NMR (DMSO-d_6) δ (ppm): 108.79, 117.98, 119.21, 119.55, 122,27, 124.37, 125.80, 128.53, 129.41, 132.79, 135.69, 140.59, 159.27, 160.47, 160.94, 163.49 and 164.07.

2.3. Synthesis of 1-(((2-hydroxybenzylidene)hydrazono)methyl) naphthalen-2-ol (H_2L)

H_2L was synthesized by following the same procedure adopted for **H_2L-NO_2** except 2-hydroxybenzaldehyde was used in place of 2-hydroxy-5-nitrobenzaldehyde. Data for **H_2L**: yield: 70% (0.203 g); C, H, N analysis: anal. Calc. for $C_{18}H_{14}N_2O_2$: C, 74.52; H, 4.86; N, 9.66; found C, 74.42; H, 4.81; N, 9.60; ESI-MS^+ (*m/z*): 291.14 (**H_2L** + H^+); FT-IR (Wavenumber, cm^{-1}: 1620, 1577, 1471, 1272, 1184, and 742); ^{1}H NMR (in DMSO-d_6) (δ, ppm): 12.86 (s, 1H), 11.15 (s, 1H), 9.88 (s, 1H), 9.06 (s, 1H), 8.60 (d, 1H, *J* = 8.4), 8.00 (d, 1H, *J* = 8.9), 7.89 (d, 1H, *J* = 7.8), 7.70 (d, 1H, *J* = 7.5), 7.58 (t, 1H, *J* = 7.5), 7.37–7.43 (m, 2H), 7.24 (d, 1H, *J* = 8.9), 6.94–7.00 (m, 2H); ^{13}C NMR (in DMSO-d_6) δ (ppm): 108.84, 117.09, 118.66, 119.22, 120.07, 122.17, 124.30, 128.30, 128.52, 129.39, 131.58, 132.76, 133.66, 135.31, 159.12, 160.64, 162.29, 162.91.

2.4. Synthesis of 1-(((2-hydroxy-5-methylbenzylidene)hydrazono)methyl) naphthalen-2-ol) (H_2L-Me)

H_2L-Me was synthesized by following the same procedure followed for **H_2L-NO_2** except 2-hydroxy-5-methylbenzaldehyde was used in place of 2-hydroxy-5-nitrobenzaldehyde. Data for **H_2L-Me**: yield: 72% (0.219 g); C, H, N analysis: anal. Calc. for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20; found C, 74.84; H, 5.21; N, 9.28; ESI-MS^+ (*m/z*): 305.12 (**H_2L-Me** + H^+); FT-IR (Wavenumber, cm^{-1}: 1617, 1584, 1464, 1225 and 777); ^{1}H NMR (in DMSO-d_6) (δ, ppm): 12.89 (s, 1H), 10.89 (br, s, 1H), 9.87 (s, 1H), 9.00 (s, 1H), 8.57 (d, 1H, *J* = 8.6), 8.01 (d, 1H, *J* = 8.9), 7.89 (d, 1H, *J* = 7.5), 7.58 (t, 1H, *J* = 7.0), 7.50 (s, 1H), 7.42 (t, 1H, *J* = 7.2), 7.20–7.25 (m, 2H), 6.89 (d, 1H, *J* = 8.3), 2.26 (s, 3H); ^{13}C NMR (in DMSO-d_6) δ (ppm): 20.42, 108.86, 116.97, 118.37, 119.22, 122.15, 122.15, 124.30, 128.31, 128.51, 128.63, 129.39, 131.16, 132.76, 134.44, 135.25, 157.00, 160.60, 162.13, 162.67.

2.5. Fluorescence sensing experiments

The fluorescence sensing studies of the Schiff-base molecules were carried out in the presence of different cations in 10 mM HEPES buffer in water: methanol (1:9, *v/v*) (pH = 7.4) at room temperature. Nitrate salts of different cations (Al^{3+}, Na^+, K^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, Hg^{2+}, Zn^{2+}, Cd^{2+}, Cr^{3+}, Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Ga^{3+} and In^{3+}) were used for spectroscopic experiments. Typically, for an absorption or emission titration, the probe and different metal salts were mixed in a way so that the final concentration of the probe became 40 μM with desired concentrations of the metal ion.

3. Results and discussion

3.1. Synthesis and characterization

H_2L, **H_2L-NO_2** and **H_2L-Me** have been synthesized following similar reaction method (Scheme s1). One eqv. of 2-hydroxy-1-naphthaldehyde has been allowed to react with one eqv. of hydrazine and we have obtained the product with one free NH_2 group. This free amino group undergoes condensation with one eqv. of aldehyde functionality (2-hydroxybenzaldehyde for **H_2L**, 5-nitro-2-hydroxybenzaldehyde for **H_2L-NO_2** and 5-methyl-2-hydroxybenzaldehyde for **H_2L-Me**) for the formation of final product. These compounds have been characterized