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Research paper

Condensation product of 2-hydroxy-1-napthaldehyde and 2-aminophenol: Selective fluorescent sensor for Al^{3+} ion and fabrication of paper strip sensor for Al^{3+} ion

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ABSTRACT

The condensation product of 2-hydroxy-1-napthaldehyde and 2-aminophenol (**L**), in 1:1 (*v*/*v*) CH_3OH: H_2O acts as selective fluorescent sensor for Al^{3+}. The fluorescence intensity of **L** at emission wavelength 517 nm**,** when excited with 360 nm photons, increases on interaction with Al^{3+} by *ca.* 7-fold. Under UV lamp, **L** shows light yellow fluorescence on interaction with Al^{3+} visible to bare eyes. Metal ions – Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+}do not interfere. The increase in fluorescence intensity is due to the quenching of photoinduced electron transfer (PET) process prevailing in **L**. The fluorescent and UV/Visible spectral data analysis showed a 1:1 complexation between **L** and Al^{3+} with $\log\beta = 4.532$ (β = binding constant) and detection limit 10^{-5} M. DFT and TDDFT calculations also confirm 1:1 interaction between **L** and Al^{3+}. **L** has been successfully applied in fluorescent imaging of Al^{3+} in live rat L6 myoblasts cells and as paper strip fluorescent sensor for Al^{3+} in aqueous medium.

1. Introduction

In the earth crust, lithosphere consists of Aluminium (Al) in 8.3% which is considered to be third most abundant element after oxygen and silicon [1]. Aluminium compounds are widely used in textile industries, paper industries, in making utensils, in alloys [2], water purification, automobiles [3] etc. Due to its low density and therefore low weight, high strength, superior malleability, easy machining, excellent corrosion resistance, good thermal and electrical conductivity Al is the second most widely used metal after iron [4]. Although it is quite useful but it has got some adverse effects too. Al^{3+} when consumed in surplus amount may lead to neurodegenerative disease like Alzheimer disease, Parkinson disease [5], bone abnormalities etc. Therefore the detection of Al^{3+} is of great environmental as well as biological importance [6]. Fluorescent sensors have attracted a lot of scientific interest [7] due to their easy applicability, reasonable cost, higher sensitivity, simple instrumentation etc in comparson to other highly sophisticated techniques like atomic absorption and emission spectroscopy, spectrophotometry, electrochemistry, electrochemiluminescence etc [8,9].

As fluorescent sensor, simple Schiff base ligands, have gained recent interest for different metal ions including Al^{3+}. This is basically due to their relatively easy one or two steps synthesis [10–12]. Schiff bases recently reported as "off-on" fluorescent sensor for Al^{3+} are based on – 2-Hydroxyacetophenone and ethylenediamine [13], thiazoleand salicylaldehyde [14]; 2-hydroxyethylether-2-nitrophenol and salicylaldehyde [15], 8-hydroxyjulolidine-9- carboxaldehyde and benzohydrazide [16]; 2-hydroxyaniline and 2 hydroxybenzaldehyde [17]; salicylhydrazide and ortho-phthalaldehyde [18]; salicylaldehyde and 4,4-difluoro-4-bora-3a,4adiaza-s-indacene [19]; thiophene-2-carboxylic acid hydrazide [20]; 8-hydroxyquinoline-7-carbal-dehyde and 4-aminopyrine [21]; 2-methyl quinoline-4-carboxylic hydrazide and 8-formyl-7-hydroxyl-4-methyl coumarin [22]; perylenebisimide and di(2-(salicylideneamino))ethylamine [23]; 4-aminoantipyrine and salicylaldehyde, 4-aminoantipyrine and 2-hydroxy-1 naphthaldehydeantipyridine [24]; Rhodamineethylenediamine and 1,8-naphthalic anhydride [25] etc.

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In this paper we have reported new fluorescent sensor for Al^{3+} derived from the condensation of 2-hydroxy-1-napthaldehyde and 2-aminophenol in absolute alcohol. The sensor is selective for Al^{3+} while metal ions – Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+} do not interfere. The interaction of sensor with Al^{3+} results bare eye visible light yellow fluorescence under UV lamp. The sensor is applicable to live rat L6 myoblasts cells and has been used to obtain paper strip fluorescent sensor for Al^{3+} in aqueous medium.

2. Experimental

2-Hydroxy-1-napthaldehyde and DMSO-d_6 are from Sigma Aldrich, 2-aminophenol and metal salts were either from Merck or Loba Chemie. The metal salts except $Pb(NO_3)_2$, $CaCl_2$ and $HgCl_2$ were sulphates. Metal salt solutions (0.01M) were prepared in doubly distilled water obtained from quartz double distillation plant.

The FT-IR spectra were recorded in a Perkin Elmer RXI spectrometer as KBr pellets, NMR and ^{13}C NMR spectra were recorded on a Bruker Ultra Shield 300 MHz spectrophotometer using DMSO-d_6 as solvent. The fluorescence and UV/Visible spectra were recorded in HITACHI 2500 and Shimadzu UV 1800 spectrophotometer respectively using quartz cuvette (1 cm path length).

2.1. Synthesis and characterization of the sensor (L)

L has been reported as an intermediate towards the synthesis of a duel sensor for Al^{3+} and CN^- [26]. 0.02 mol (0.035 g) of 2-hydroxy-1-napthaldehyde and 0.02 mol (0.022 g) of 2-aminophenol were dissolved in 10 mLC_2H_5OH in a 50 mL round bottom flask and allowed to stir for 8 h. Yellowish precipitate was obtained, solvent was evaporated in a rota evaporator to obtain the product which was recrystallized from CH_3OH. Yield: 70%.

FTIR (KBr)**:**1592 cm^{-1} ($\nu_{c=N}$); 3444 cm^{-1} ($\nu_{o\text{-}H}$); 2922 cm^{-1} ($\nu_{c\text{-}H\ aliphatic}$); 1512 cm^{-1}($\nu_{c=c}$).

HRMS: *m*/*z* 264.1.

^{1}H NMR (300MH$_z$, DMSO-d_6, δppm, TMS): 15.69 (d***J*** = 9 Hz,1H); 10.38 (br,1H); 9.47 (d***J*** = 9.6 Hz,1H); 8.36 (d***J*** = 8.4 Hz,1H); 7.92 (d, ***J*** = 7.5 Hz,1H); 7.79 (d***J*** = 9.6 Hz,1H); 7.66 (d***J*** = 7.8 Hz,1H); 7.49–7.46 (m,1H); 7.27–7.25 (m,1H); 7.12–7.07 (m,1H); 6.99 6.93 (m,2H), 6.76 (d***J*** = 9.3 Hz,1H).

^{13}CNMR (75 MHz, DMSO-d_6, δppm, TMS): 177.9, 149.4, 148.4, 138.1, 134.0, 129.1, 128.5, 128.2, 126.8, 125.9, 125.2, 123.1, 119.9, 119.8, 117.6, 116.0, 107.7.

2.2. Preparation of solutions

For sensing studies stock solution of **L** was prepared as 2×10^{-5} M in 1:1 (*v*/*v*) $CH_3OH:H_2O$. Metal ions solutions were also prepared as 0.1 M in 1:1 (*v*/*v*) $CH_3OH:H_2O$. Fluorescent titrations were done by pipetting out 2 mL of solution of **L** in 1 cm quartz cell and by adding appropriate amount of metal ion using micro pipette. For reversibility studies the concentration of $EDTA^{2-}$ was made 0.1 M and added using micropipette.

2.3. DFT calculations

From the available experimental data the structure of **L**:Al^{3+} complex was predicted and confirmed by DFT calculation. The **L** and **L**:Al^{3+} complex were fully optimized using B3LYP [29] function. For **L** basis set 6-311G and for **L**:Al^{3+} metal complex basis set LanL2DZ were used in the program Gaussian 09 [30]. The stability of the complex was confirmed by the vibrational energy calculation with same level of theory. TD-DFT calculations were performed to find out first three probable transitions of **L**:Al^{3+} complex.

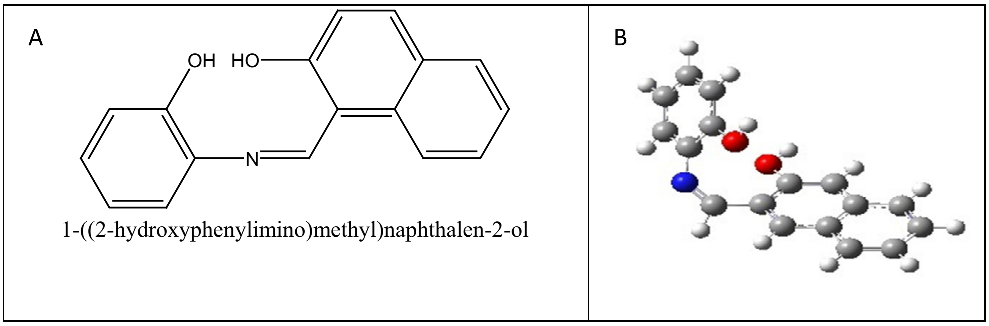
2.4. Cytotoxicity studies

To test the cytotoxicity of the compound 'A', a 3-(4,5-dimethylthiazol-2-yl)-2,Sdiphenyl tetrazolium bromide (MTT) assay was performed using the standard procedure. After treatment of the L6 cells with concentration ranging from (10–300) μM of compound A, 100 μl of MTT solution (5 mg ml^{-1} phosphate-buffered saline (PBS) was added to each well of a 96-well culture plate and incubated continuously at 37 °C for 4 h. All the media was removed from the wells post incubation and replaced with 100 μl of DMSO for solubilising the blue-violet intracellular formazan crystals produced. Absorbance of the solution measured at 595 nm using a microtiter plate reader. The values obtained were the mean (±standard deviation) of three separate experiments. The cytotoxicity was calculated as a percentage of cell viability when compared to untreated control cells and expressed in terms of IC50.

3. Results and discussion

Scheme 1 A shows the chemical structure, based on different spectral data, of the synthesised sensor 1-((2-hydroxyphenylimino)methyl)naphthalene-2-ol (**L**). The DFT optimised structure of **L** has been shown in Scheme 1B.

The fluorescent spectrum of **L** (2×10^{-5} M) was recorded in 1:1 (*v*/*v*) $CH_3OH:H_2O$ with excitation wavelength 360 nm. The maximum emission peak was observed at λ_{max}value 517 nm. The fluorescence spectra of 2×10^{-5} M solution of **L** was also recorded at different added concentrations of metal ions – Na^+, K^+, Al^{3+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Pb^{2+}, Cd^{2+} and Hg^{2+}. Significant enhancement in fluorescence intensity (*ca.* 7-fold) was observed only in case of Al^{3+}. Fig. 1 shows the fluorescence spectra of **L** in presence of different metal ions when metal ion to **L** concentration



Scheme 1. Chemical structure of L (A) and DFT optimised structure of L (B).