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A naphthalimide-quinoline based probe for selective, fluorescence ratiometric sensing of trivalent ions

Shyamaprosad Goswami*, Krishnendu Aich, Avijit Kumar Das, Abhishek Manna and Sangita Das

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A new naphthalimide-quinoline based probe (NAQ) is designed and synthesized and its structure is confirmed through single crystal analysis. It detects the trivalent ions (Fe^{3+} or Al^{3+} or Cr^{3+}) selectively among other alkali and transition metal ions studied. NAQ shows a distinct ratiometric fluorescence behavior upon addition of trivalent metal ions in CH_3CN-HEPES buffer solution (40/60, *v/v*, pH = 7.4). This fluorogenic sensing of NAQ to M^{3+} (M^{3+}= Fe^{3+} or Al^{3+} or Cr^{3+}) can be observed in naked eye, when illuminated under the UV light.

Introduction

In recent decade, the fluorogenic sensing of different metal ions have paid a great attention due to the advantages such as high sensitivity, selectivity, rapid response time and versatility.[1] A large number of chemosensors for divalent metal ions have been reported in the literature but only a few chemosensors for trivalent ions[2] are known. However, trivalent ions such as Fe^{3+}, Al^{3+} and Cr^{3+} play many important roles in the living organism. Iron in its trivalent form is indispensable for most organisms, as it is involved in both electron transfer and oxygen transport due to its sufficient redox potential and high affinity towards oxygen. High levels of Fe^{3+} within the body have been associated with increasing incidence of certain cancers and dysfunction of certain organs, such as the heart, pancreas, and liver.[3] Aluminum is the third most prevalent element and the most abundant metal in the earth's crust. Intake of excessive amounts of aluminium can be toxic to humans. Alzheimer's disease, osteoporosis, colic, rickets, gastrointestinal problems, interference with the metabolism of calcium, extreme nervousness, anemia, headaches, decreased liver and kidney function, memory loss, speech problems, softening of the bones, and aching muscles can all be caused by aluminium toxicity.[4] Trivalent chromium is one of the most important heavy metal elements. It is an essential nutrient for humans and plays an important role in the metabolism of carbohydrates, lipids, proteins, and nucleic acids.[5] Insufficient intake of Cr^{3+} increases the risk for diabetes and cardiovascular diseases, whereas excessive intake causes genotoxic effects.[6] So, there is a great need to develop a chemosensor which can detect the presence of trivalent cations in environmental and biological samples.

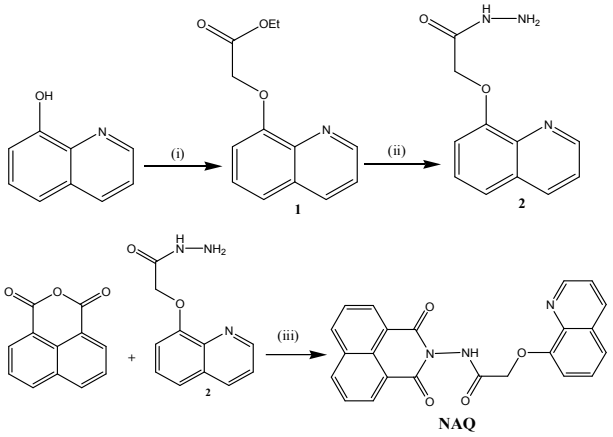
Recently, the development of fluorescence ratiometric probes for metal ions has attracted much attention since they allow the measurement of emission intensities at two different wavelengths. It is still a challenging task to design a ratiometric probe that selectively interacts with metal ions and show high ratiometric signals. Though many ratiometric chemosensors are reported for monovalent and divalent cations[7], surprisingly only a few are known for detection of trivalent ions.[2 (b, c, e), 7(b, f)]

In continuation of our research work to develop fluorescence sensor for biologically important substrates,[8] herein we report a new naphthalimide-quinoline based probe (NAQ) for selective detection of trivalent cations (Fe^{3+}, Al^{3+} and Cr^{3+}) based on ICT (internal charge transfer) mechanism. Experimental studies revealed that NAQ shows a selective fluorescence ratiometric behavior towards trivalent cations in CH_3CN-HEPES buffer solution (40/60, v/v, pH = 7.4).

Results and discussion

NAQ was prepared through a high yielding synthetic route (overall yield = 80%), shown below in scheme 1. The intermediate 2 was prepared from 8-Hydroxyquinoline according to the procedure reported in the literature.[9] The molecular structure and purity of NAQ was established from different spectroscopic studies like ^1H NMR and ESI MS. In addition, the structure of the receptor (NAQ) has been confirmed through its single X-ray crystallographic analysis.

Scheme 1: Synthetic scheme of NAQ.



Reagents and conditions: (i) Ethyl chloroacetate, K_2CO_3, TBAB (tetra butyl ammonium bromide), Acetone, reflux, 4 h. (ii) Hydrazine hydrate, EtOH, reflux, 2 h. (iii) EtOH, reflux, 14 h.

The fluorometric behavior of NAQ is investigated upon addition of several metal ions such as Na^+, K^+, Mg^{2+}, Ba^{2+}, Ca^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Co^{2+}, Ni^{2+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+} and Cr^{3+} in CH_3CN-HEPES buffer solution (40/60, v/v, pH = 7.4). The emission spectrum of free NAQ (20 μM) showed a strong band with emission maxima positioned at 390 nm, upon excitation at

342 nm. There was no other emission band at any wavelength which indicates the absence of dual channel emission due to two different fluorophores (Fig. 1).

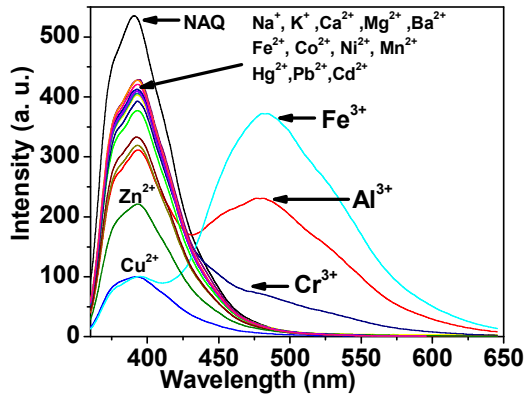


Fig. 1 Changes of emission spectra of NAQ (20 μM) upon addition of different metal ions (8 equivalents) in (CH_3CN-HEPES buffer, 40/ 60, *v/v*) solution at pH = 7.4.

As shown in Fig. 1, the binding of trivalent ions to NAQ caused a large red-shift (~94 nm) of emission spectra from 390 nm to 484 nm. Interestingly, the introduction of other common metal ions, no obvious red shift was observed in the emission spectra, revealed that this change was specific for trivalent cations only (Fig. 1).

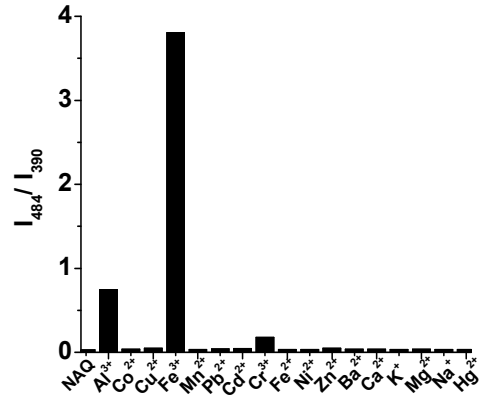


Fig. 2 The plot of the sensing indexes (I_{484}/I_{390}) of NAQ (20 μM) upon addition of different metal ions (8 equivalents) in (CH_3CN-HEPES buffer, 40/ 60, *v/v*) solution at pH = 7.4.

Upon addition of Cu^{2+} and Zn^{2+}, the maximum quenching of fluorescence intensity of NAQ has occurred. Other cations showed a little effect (quenching emission intensity) on the fluorescence spectra of NAQ. Severe quenching of the emission of NAQ was due to the chelation enhanced fluorescence quenching (CHEQ).[10] The values of the sensing index (I_{484}/I_{390}) for NAQ to Fe^{3+}, Al^{3+} and Cr^{3+} are 3.8, 0.8 and 0.2 respectively, whereas it is less than 0.05 for other metal ions (Fig. 2). It indicates the receptor is highly sensitive toward trivalent ions over other competing metal ions.

In order to better understand the sensing mechanism, absorption and fluorescence experiments of NAQ (20 μM) were conducted with different concentrations of Fe^{3+}, Al^{3+} and Cr^{3+} (0 – 8 equivalents) (Fig. 3). As shown in Fig. 2, the addition of Fe^{3+} elicited a gradual decrease at 390 nm and a simultaneous increase (~22 fold) in a new red shifted emission band at 484 nm with an obvious iso-emission point at 432 nm. This indicates a clear ratiometric fluorescence response of the probe towards Fe^{3+}. The fluorescence intensity ratios of the receptor at 484 nm and 432 nm (I_{484}/I_{432}) increased linearly ($R^2 = 0.9822$) with the amount of Fe^{3+} in the range of 0 – 60 μM (Fig. 3, Inset). From the fluorescence titration experiments, the detection limit of the probe for Fe^{3+} was evaluated and determined to be 20 μM, using the equation DL = K × Sb_1/S, where K = 3, Sb_1 is the standard deviation of the blank solution and S is the slope of the calibration curve[11] (see ESI).

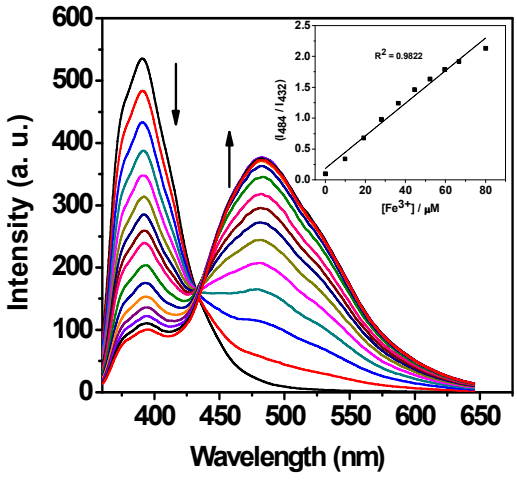


Fig. 3 Fluorescence spectra of NAQ (20 μM) upon titration with Fe^{3+} (0 to 8 equivalents) in CH_3CN-HEPES buffer (40/ 60, *v/v*, pH = 7.4) solution. λ_{ex} = 342 nm. Inset: fluorescence intensity ratio (I_{484} / I_{432}) as function of [Fe^{3+}].

On increasing the concentration of Al^{3+} (0 to 8 equivalents) to solution of NAQ (20 μM), we observed that the similar quenching of fluorescence intensity at 390 nm and enhancement (~12 fold) at 484 nm has occurred (Fig. 4). In case of Cr^{3+}, the quenching (at 390 nm) and enhancement (at 484 nm, ~4 fold) of emission intensity was both minor, in the same experimental condition (Fig. 5). Further increasing of the concentration of Fe^{3+} or Al^{3+} or Cr^{3+} did not lead to any enhancement of emission intensity at 484 nm. The limit of detection of NAQ for Al^{3+} and Cr^{3+} was determined from fluorescence titration data (23 μM and 25 μM respectively) (see ESI).

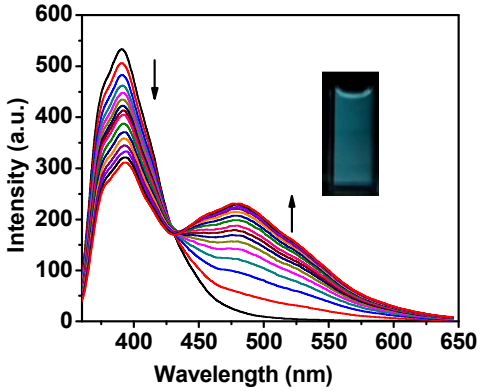


Fig. 4 Fluorescence spectra of NAQ (20 μM) upon titration with Al^{3+} (0 to 8 equivalents) in CH_3CN-HEPES buffer (40/ 60, *v/v*, pH = 7.4) solution. λ_{ex} = 342 nm. Inset: Emission color changes of NAQ (20 μM) after addition of Al^{3+} (80 μM) under UV light.

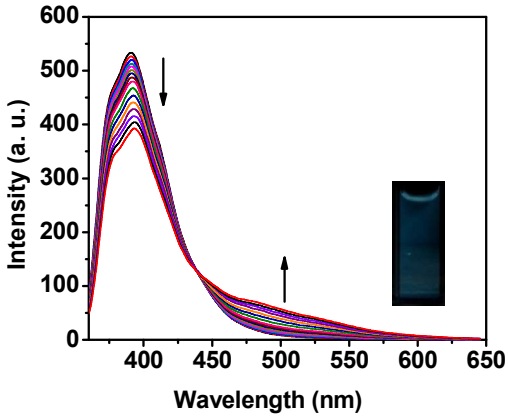


Fig. 5 Fluorescence spectra of NAQ (20 μM) upon titration with Cr^{3+} (0 to 8 equivalents) in CH_3CN-HEPES buffer (40/ 60, *v/v*, pH = 7.4) solution. λ_{ex} = 342 nm. Inset: Emission color changes of NAQ (20 μM) after addition of Cr^{3+} (80 μM) under UV light.

To utilize NAQ as a selective sensor for trivalent ions, the effect of competing metal ions was studied using 3 equivalents of Fe^{3+} and 10 equivalents of the interfering metal ions. As shown in Fig. 6, no significant variation in the emission spectra at 484 nm was observed by the addition of interfering metal ions, i.e. Fe^{3+} can be easily detected in presence of all of the competing metal ions by means of its ratiometric response to NAQ. The competition experiments were also performed using Al^{3+} and Cr^{3+} and the results were similar as Fe^{3+} (see ESI). Thus it is concluded that NAQ can be used as a selective fluorescence ratiometric sensor for trivalent cations. Job's plot of emission spectra obtained for NAQ-M (M = Fe^{3+}, Al^{3+} and Cr^{3+}) system clearly indicates the formation of a 1:1 stoichiometry (see ESI).

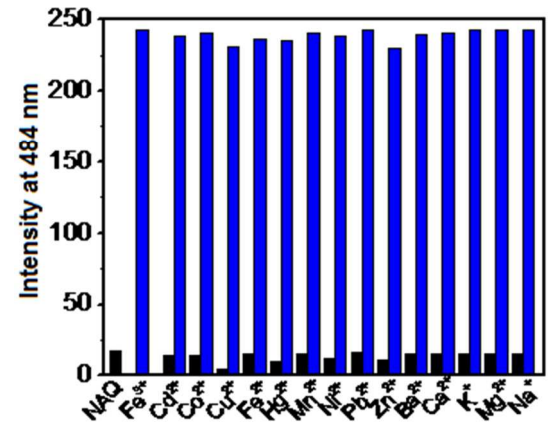
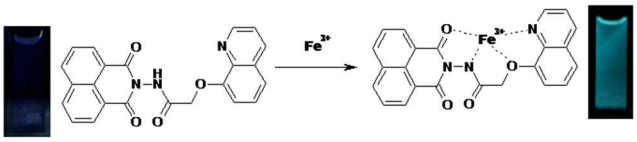


Fig. 6 Metal ion selectivity profile of the receptor (20 μM): (black bars) change of emission intensity of receptor + 10 equiv M^{n+}; (blue bars) change of emission intensity of receptor + 10 equiv M^{n+}, followed by 3 equiv Fe^{3+} at 484 nm.

Upon binding with trivalent ions, NAQ showed a new emission band at 484 nm. The complex formation of NAQ with Fe^{3+} or Al^{3+} or Cr^{3+} modulated the ICT efficiency of the fluorophore and thereby result the ratiometric change in fluorescence. The probable host-guest complex formation of NAQ with Fe^{3+} is shown in scheme 2. Noteworthy, the ratiometric sensing process can readily be detected not only by fluorescence spectroscopy but also by the naked eye experiment. In absence of trivalent cations, NAQ (20 μM) showed blue emission, but M^{3+} (Fe^{3+}or Al^{3+} or Cr^{3+}) (80 μM) change its original blue emission to a bluish-green emission under UV light, that facilitates its quick naked eye detection (Scheme 2).

Scheme 2: Probable binding mode of the receptor (NAQ) with Fe^{3+}



UV-vis spectrum of the free receptor (20 μM) is characterized by a clear band centred at 338 nm in CH_3CN-HEPES buffer (40/ 60, *v/v*, pH= 7.4) solution. Upon titration of NAQ (20 μM) with Fe^{3+} (0- 10 equivalents), the absorption maxima increase slightly with an isosbestic point at 240 nm which indicates formation of a new species (see ESI). UV-vis titration experiment of NAQ with Al^{3+} and Cr^{3+} were also performed. The absorption spectra were characterized by two isosbestic points at 243 nm and 263 nm respectively in each case, indicating the complex formation of NAQ with Al^{3+} and Cr^{3+} (see ESI).

Single crystals of the sensor (NAQ) suitable for X-ray diffractometry were obtained by dissolving powder of the pure compound in $CHCl_3$/ MeOH (1:1) and slow evaporation of the solution free from vibrations. The perspective view of the receptor (NAQ) with atom numbering scheme is shown in Fig.7.

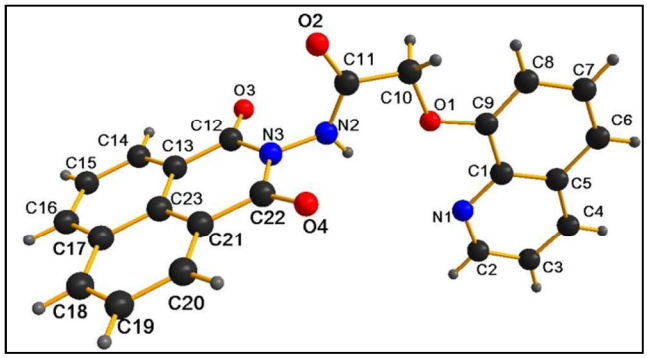


Fig.7 A molecular view of NAQ in solid state with atom numbering scheme.

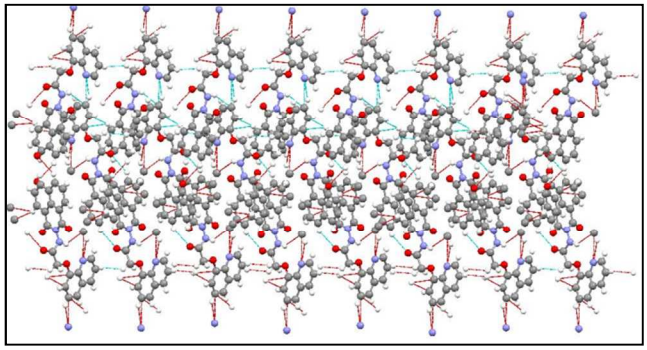


Fig. 8 Crystal packing diagram of the receptor (NAQ).

Selected metrical parameters are given in Table 1 (see ESI). The lattice is orthrhombic in nature with Pbca symmetry and the unit

cell consists of eight molecules. The crystal packing diagram is shown in Fig. 8. The plane containing three rings of naphthalimide moiety makes a dihedral angle with quinoline moiety of 78.56°. In NAQ, O1 and O2 atoms are in '*trans'* position with respect to C10-C11 bond whereas N3 and O2 atoms are in '*cis'* position with respect to N2-C11 bond. The torsion angle between the O1-C10-C11 plane and C10-C11-O2 is 173.51(15)^0. The distance between H9 and O1 is 2.1Å, which confirms the existence of intramolecular H-bonding between H9 and O1 in NAQ.

Conclusions

In summary, we report here a new probe for selective recognition of trivalent cations. It shows distinct ratiometric fluorescence response towards trivalent cations only over other alkali and HTM ions studied. This ratiometric fluorescence change can be observed by naked eye also after illumination under the UV light. It worked nicely in mixed solvent media and at a physiological pH range.

Experimental

General methods

Chemicals and solvents used for the synthesis of the receptor were purchased from Sigma-Aldrich chemicals Private Limited and used without further purification. Silica gel (100-200 mesh, Merck) was used for column chromatography. Melting points were determined on a hot-plate melting point apparatus in an open-mouth capillary and are uncorrected. ^{1}H-NMR spectra was recorded on JEOL, 400 MHz instrument. For NMR spectra, $CDCl_3$ was used as solvent using TMS as an internal standard. Chemical shifts are expressed in δ units and ^{1}H–^{1}H and ^{1}H–C coupling constants in Hz. UV-vis titration experiments was performed on a JASCO UV-V530 spectrophotometer and fluorescence experiment was done using PerkinElmer LS 55 fluorescence spectrophotometer using a fluorescence cell of 10 mm path. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer, using KBr discs. The X-ray data were collected using a Bruker-APEX II SMART CCD diffractometer with the graphite monochromated Mo-Kα radiation (λ = 0.71073) at a detector distance of 5 cm and with APEX2 software.

General method of UV-vis and fluorescence titration:

By UV-vis method

For UV-vis titrations, stock solution of the receptor (20 μM) was prepared in [(acetonitrile / water), 40/60, v/v] (at 25°C) in HEPES buffered solution. The solution of the guest cations using their chloride and nitrate [Al $(NO_3)_3.9H_2O$] salts in the order of 4 x 10^{-4}M, were prepared in deionized water using HEPES buffer at pH = 7.4. Solutions of various concentrations containing sensor and increasing concentrations of cations were prepared separately. The spectra of these solutions were recorded by means of UV-vis methods.

By fluorescence method

For fluorescence titrations, stock solution of the sensor was prepared as same as UV-vis titration. The solution of the guest cations using their salts in the order of 4 x 10^{-4}M, were prepared in deionized water. Solutions of various concentrations containing sensor and increasing concentrations of cations were prepared separately. The spectra of these solutions were recorded by means of fluorescence methods.

Methods for the preparation of the receptor

NAQ: A mixture of 1, 8-naphthalic anhydride (270 mg, 1.36 mmol) and **2** (300 mg, 1.38 mmol) in dry ethanol was stirred for 14 h at reflux. After evaporation of the solvent the residue was poured into ice water. Resulting precipitate was filtered and purified through silica gel column chromatography using 4% methanol in chloroform (*v/v*) as eluent. (400 mg, 72%) [m.p = >300^0 C (decomposed)]. **IR (cm^{-1}):** 822, 887, 1118, 1187, 1234, 1377, 1497, 1589, 1687, 1728. **^{1}H NMR (400 MHz, $CDCl_3$):** δ 5.005 (s, 2H), 7.193 (d, 1H), 7.551 (m, 4H), 7.768 (t, *J* = 7.64 Hz, 4H), 8.254 (d, *J* = 6.08 Hz, 2H), 8.645 (d, *J* = 7.32 Hz, 1H), 8.822 (s,1H). **TOF MS** (ESI, positive): calcd. for $C_{23}H_{15}N_3O_4$ [M$^+$] (m/z): 397.38; found: 397.98.

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Notes and references

Department of Chemistry, Bengal Engg. and Science University, Shibpur, Howrah-711 103, INDIA. Fax: +91 33 2668 2916; Tel:+91 33 2668 2961-3; E-mail: spgoswamical@yahoo.com

†Electronic Supplementary Information (ESI) available: [Job plot, association constant determination, detection limit determination,metal ion selectivity profile of NAQ, 1H NMR, ESI MS spectroscopy, fluorescence titration spectra of the receptor with different metal ions, UV-vis titration spectra of NAQ with Fe^{3+}, Al^{3+} and Cr^{3+}, X-ray data]. See DOI: 10.1039/b000000x/

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