



Novel indole based dual responsive “turn-on” chemosensor for fluoride ion detection



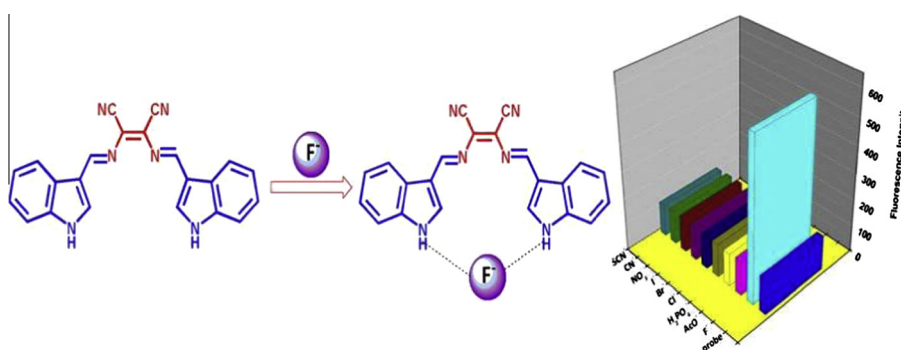
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HIGHLIGHTS

- The receptor DN was synthesized by a simple method with high yield.
- The detection limit of F^- by DN was very low (2.73×10^{-7} M).
- The reversible behavior of the receptor DN towards F^- was studied.
- The remarkable red shift fluorescence spectra was further supported by DFT calculations.

GRAPHICAL ABSTRACT



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ABSTRACT

An efficient new dual channel chemosensor 2,3-bis((E)-(1H-indole-3-yl)methyleneamino)maleonitrile (DN) which exhibits selective sensing of F^- ions in DMSO, was synthesized by a facile one step condensation reaction of indole-3-carboxaldehyde with diaminomaleonitrile. The probe DN was characterized by elemental analysis, 1H , ^{13}C -NMR, ESI-MS and IR spectral techniques. Upon addition of F^- , DN induces remarkable changes in both absorption and fluorescence spectra on the basis of charge transfer mechanism. The receptor DN serves for highly selective, sensitive detection of F^- without the interference of other relevant anions. The Job's plot analysis indicates the binding stoichiometry to be 1:1 (host/guest).

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Introduction

Recent years witness burgeoning interest on the development of new chemosensors for the selective recognition of anions [1–5], cations [6–10] or neutral molecules due to its crucial and potential application in the biological, chemical, environmental, industrial and pathological processes [11–14]. Fluoride ion is drawing a unique attention among anions because of its small size, good basicity, high electronegativity, and tendency to form strongest H-bond with $-NH$ or $-OH$ groups [15]. Fluoride ions

are widely used in dental care [16] as it has ability to prevent Osteoporosis [17], demineralization [18].

Fluorosis, arising due to over-accumulation of fluoride in the bones [19–21], has been linked with high levels of fluoride in drinking water. High concentration of fluoride in human body resulted in number of diseases such as urolithiasis, gastric and kidney disorders [22], Alzheimer's disease [23], neurotransmitter biosynthesis inhibition [24]. Apart from the biological significance, it can also act as prospective catalyst in organic and inorganic synthesis [25] and involved in the detection of chemical warfare agents [11]. These features of fluoride have made its detection at very low levels is of crucial importance. Among methods available anion receptors with chromogenic and fluorogenic perturbations

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have several advantages due to their high sensitivity, specificity [26,27], low detection limit [28]; besides require no expensive equipment [29].

Anion-selective receptors based on indoles [30], bisindole [31], carbazole [32], nitrophenyl [33], quinine [34] and nitrobenzene/azo groups [35] moieties have been reported to recognize the anions via H-bonding or deprotonation of protons on the receptor [36,37]. The receptors containing the N–H fragment as the binding site for fluoride ion are frequently reported in the literature [38,39]. Recently reported Indole-based receptors exhibited high selectivity in their anions binding capability [40–46].

This has led to design and synthesize a new indole based sensor, 2,3-bis((1H-indol-3-yl)methyleneamino)maleonitrile [DN] for anion recognition. The receptor was synthesized by a simple Schiff base condensation reaction between indole-3-carboxaldehyde and diaminomaleonitrile in good yield (Scheme 1). The receptor was systematically and fully characterized by ^1H , ^{13}C -NMR, ESI-MS, IR and elemental analysis (Figs. S1–S5, see supplementary information). The receptor behaves as both colorimetric and fluorimetric sensor for fluoride ions with high selectivity through H-bonding interaction between –NH protons and fluoride anion.

Materials and methods

Materials

All reagents for synthesis obtained commercially were used without further purification. In the titration experiments, tetrabutylammonium salts were used as the anion source, stored in a desiccator under vacuum and used without further purification. Solvents used were of spectroscopic grade.

Instrumental methods

The NMR spectra were recorded on a Bruker(Avance) instrument operating at 300 MHz in DMSO- d_6 with TMS as an internal reference. Chemical shifts were expressed in ppm and coupling constants (J) in Hz. UV–visible absorption spectra were recorded on JASCO V-550 spectrophotometer. All fluorescence measurements were made on an F-4500 Hitachi fluorescence spectrophotometer with slit width 5 nm used for both excitation and emission. FT-IR spectra were recorded on FT-IR spectrophotometer (8400S SHIMADZHU) in the range of 4000–400 cm^{-1} using KBr discs. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed in the positive ion as well as negative ion mode on a liquid chromatography-ion trap mass spectrometer (LCQ fleet, Thermo Fischer Instruments Limited, US). Elemental analysis was carried out in a Perkin-Elmer 4100 elemental analyzer.

Synthesis of receptor DN

An ethanolic solution of 1H-Indole-3-carboxaldehyde (1.45 g, 10 mmol) was added to a solution of diaminomaleonitrile (1.08 g, 10 mmol) in ethanol at room temperature. The resulting solution

was heated to reflux for 5 h. After the completion of reaction, the reaction mixture was cooled to room temperature. The precipitated compound was collected, washed with EtOH and dried. The orange solid obtained was further purified by recrystallizing from EtOH. Yield 80%. ^1H NMR (300 MHz, DMSO- d_6 , TMS): δ (ppm) = 12.10(br, 2H), 9.94(s, 2H), 8.46(d, 2H, J = 7.8 Hz), 8.29(s, 2H), 7.15–8.15(m, 6H); ^{13}C NMR (75 MHz, DMSO- d_6 , TMS): δ (ppm) = 152.9, 138.8, 137.6, 124.7, 124.5, 123.8, 123.3, 122.5, 121.9, 121.2, 118.6; IR (KBr, cm^{-1}): ν (N–H) 3361, ν (C=N) 1616, ν (C≡N) 2236, ν (C–H) 2925, ν (C=C) 1642; Anal. Calcd for $\text{C}_{22}\text{H}_{14}\text{N}_6$: C, 72.92; H, 3.89; N, 23.19; found: C, 72.32; H, 3.56; N, 23.23; MS(ESI): 363 (M + H) $^+$.

Computational details

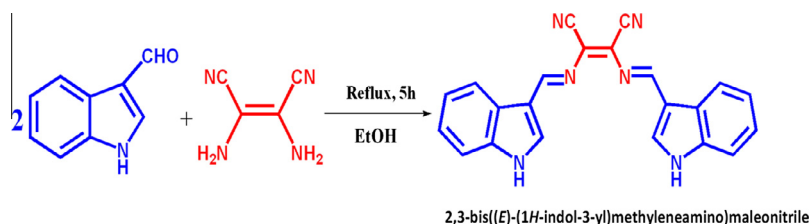
Density functional theory (DFT) calculations were carried out with B3LYP-6-31G and B3LYP/LanL2DZ basis set using Gaussian 03 program package to confirm the UV–visible and fluorescence changes upon the addition of F-anions. The TD-DFT calculations on the optimized geometries of DN & DN.F $^-$ was performed using the above basis set in order to obtain the electronic behavior and oscillator strength for the corresponding transitions.

Results and discussion

The evaluation of recognition behavior of sensor DN with various anions was primarily investigated by UV–vis spectroscopy, color changes, fluorescence titration and ^1H NMR spectroscopy. The spectrophotometric titrations were performed in DMSO solution having a series of anions namely AcO^- , H_2PO_4^- , HSO_4^- , Cl^- , Br^- , I^- , NO_3^- , SCN^- and CN^- as n-tetrabutylammonium ($n\text{-Bu}_4\text{N}^+$) salts. The addition of fluoride causes conspicuous color change from yellowish orange to red (Fig. 1); other tested anions did not induce any color change. The UV–vis spectral response upon addition of various anions towards receptor DN was investigated. Only F $^-$ give detectable changes in the absorption spectrum (Fig. S6). However, changes in the absorption spectrum of DN were not observed with the addition of other anions.

As depicted in Fig. 2, the receptor DN exhibited an absorption band at 386 nm in DMSO. Upon stepwise addition of fluoride, a band at 348 nm decreases steadily while a new band emerging at 456 nm increased steadily in its intensity. The two prominent isobestic points at 345, 419 nm during the titration indicate that a single component such as anion-receptor complex is produced. These responses are mainly due to high electronegativity of the fluoride and its small size than other halide ions. Thus, DN selectively detects F $^-$ over other anions colorimetrically.

Furthermore, fluoride sensing performance of DN with same set of anions was also carried out in DMSO. The fluorescence color change with F $^-$ was given in Fig. 1. As shown in the Fig. S7, the fluorescence spectrum of DN is also interesting. Upon excitation at 375 nm, the receptor DN displayed a weak emission band at 460 nm with a fluorescence quantum yield of $\phi_f = 0.021$. With an incremental addition of fluoride anions to DN, an intense emission band emerged at 493 nm; Using fluorescein as standard the



Scheme 1. The synthetic route of receptor DN.

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