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Quinoline-based chemosensor for fluoride and acetate: A combined experimental and DFT study

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ABSTRACT

A novel quinoline-based chemosensor **L** was synthesized and characterized by HRMS, FTIR, ^{1}H NMR and ^{13}C NMR. The anion recognition ability of **L** towards different anions was investigated by experimental (naked-eye, UV–visible, fluorescence and ^{1}H NMR) and theoretical (B3LYP/6-31G(d,p)) methods. In the presence of F^- and AcO^-, **L** showed naked-eye detectable colour change from light yellow to orange brown with the appearance of a new charge transfer band at ~530 nm in the absorption spectra while a remarkable enhancement was observed in the fluorescence spectra. The spectral titration with TBAOH and ^{1}H NMR study showed the binding nature of anion with **L** to follow deprotonation mechanism.

1. Introduction

Chemosensors provide a powerful method for studying molecular recognition and thus they have wide applications in biological, environmental, clinical, industrial and chemical processes [1–3]. The development of chromogenic receptors for anion sensing is a relatively new area of research in supramolecular chemistry [4,5] and also challenging owing to the large size (lower charge to radius ratio), high solvation, pH sensitivity and wide range of different geometries (such as spherical, linear, trigonal, tetrahedral, and octahedral, etc.) of anions. Among the different anions, fluoride is attracting huge interest, as it is a biologically important anion that shows beneficial effects on human physiology such as prevention of dental caries and treatment of osteoporosis [6]. Similarly, acetate also plays a major role in daily life because carboxylates are critical components in numerous metabolic processes [7] and also used as a food additive. Initially, anion recognition was mainly achieved by using charged host molecules, such as protonated polyamines or azamacrocycles [8], guanadinium [9] and metal complexes [10]. Recently, neutral receptors with binding groups such as amides [11], carbamides [12], urea/thioureas [13], amidoureas [14], pyrroles [15], indoles [16], calixpyrroles [17] and phenols/catechols [18] have been employed for the selective recognition and detection of anions. Also, efforts are made to develop anion selective optical sensors based on the dual-modes responses (absorbance and fluorescence). Hitherto, many anion selective receptors have been reported on the basis of a variety of signalling mechanisms such as photo-induced electron transfer (PET) [19–22], excimer or exciplex [23,24], intramolecular charge transfer (ICT) [25–27], metal-to-ligand charge transfer (MLCT) [28,29], fluorescence resonance energy transfer (FRET) [30] and excited state proton transfer (ESPT), etc. [31–35].

Herein, we have designed a quinolone-based integrated receptor **L** (Scheme 1) containing both hydrogen-bond donor groups and a chromogenic unit. The anion recognition properties of the receptor towards different anions were studied experimentally by naked-eye, UV–visible, fluorescence and ^{1}H NMR methods. The receptor showed selectivity towards fluoride and acetate among the tested anions by 'turn-on' responses. To the best of our knowledge, the quinolone-based sensors reported so far involves complicated synthesis [36], and are based on anion-induced fluorescent quenching [37].

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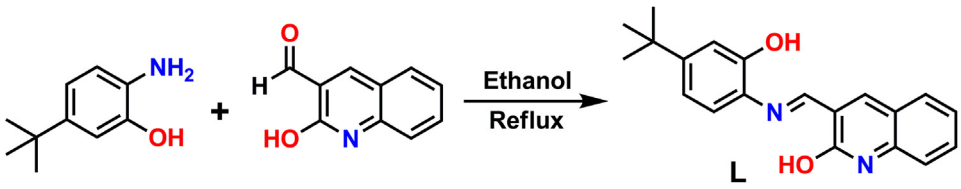

Scheme 1. Synthesis of receptor **L**.

2. Experimental

2.1. Materials and methods

All analytical grade chemicals and reagents were procured from SD Fine Chemical Ltd. (Mumbai, India) and were used without further purification. All anions were used in the form of *n*-tetrabutylammonium (TBA) salts. The reactions were monitored by thin layered chromatography (TLC) using 0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light. ^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz Varian mercury plus spectrometer. Chemical shifts were expressed in δ (ppm) using TMS as an internal standard. Mass spectral data were obtained with a micromass-Q-TOF (YA105) spectrometer.

2.2. Synthesis of **L**

2-Hydroxyquinoline-3-carbaldehyde (1 g, 6 mmol) and 2-amino-5-(*tert*-butyl)phenol (1.04 g, 6 mmol) were added to ethanol (10 ml). The reaction mass was refluxed for 5–6 h. After completion of the reaction, the solution was cooled to room temperature and the solvent was evaporated under reduced pressure to obtain the solid. It was purified by recrystallization in ethanol and dried in oven at 50 °C. Yield = 1.21 g, 62%. Melting point: 240 °C; FT-IR (KBr, cm^{-1}): 3303, 3152, 3104, 2954, 2898, 1652, 1580, 1501, 1207, and 1160; ^{1}H NMR (500 MHz, DMSO-d_6, ppm, Me_4Si): δ = 1.29 (s, 9H, $-CH_3$), 6.85 (d, J = 8.0 Hz), 7.14 (dd, J = 8.5H, 1 Hz), 7.16 (s, J = 2.0 Hz, 1H), 7.25 (t, J = 15.0, 7.5 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 8.5, 15.5 Hz, 1H), 7.84 (d, J = 7.5 Hz, 1H), 8.88 (s, 1H), 8.94 (s, 2H, —OH, —CH=N), 12.13 (s, 1H, —OH); ^{13}C NMR (100 MHz, DMSO-d_6, ppm, Me_4Si): 31.31, 33.82, 115.18, 115.60, 116.14, 119.01, 122.40, 124.54, 126.81, 129.35, 131.65, 136.78, 137.68, 139.64, 141.83, 148.94, 153.22, and 161.59; HRMS calculated for $C_{20}H_{20}N_2O_2$: 320.1502; Found: 321.1576 $[M+H]^+$.

2.3. UV–visible and fluorescence experiments

UV–visible spectra were recorded on a PerkinElmer Lamda 25 UV–VIS spectrophotometer. Fluorescence spectra were recorded on a Varian Cary Eclipse fluorescence spectrophotometer using freshly prepared solutions. The absorption and emission spectra were recorded using a quartz cell of 1-cm path length. The emission spectra were recorded between 400 and 675 nm by exciting the receptor at 400 nm. Excitation and emission slit width was kept at 5, and the data were smoothen using Savitzky–Golay smoothing filter. All the experimental parameters were kept constant throughout in order to have precision and accuracy.

Stock solutions of the anions (1.0×10^{-3} M) and **L** (1.0×10^{-4} M) were prepared in DMSO. Spectral titrations were carried out by taking a fixed concentration of **L** directly into the cuvette and then the incremental amount of anions ($[F^-]$ and $[AcO^-] = 1.0 \times 10^{-3}$ M) was added by using micropipette. After each aliquot addition of anions, the spectra were recorded. The change in absorbance at 530 nm was plotted against anion concentrations to obtain useful results. Job's plot was plotted using equimolar concentration (1.0×10^{-4} M) of **L** and anion.

3. Results and discussion

The receptor **L** was synthesized by refluxing the mixture of 2-hydroxyquinoline-3-carbaldehyde and 2-amino-5-(*tert*-butyl)phenol (1:1 molar ratio) in ethanolic medium (Scheme 1). The synthesized receptor **L** was characterized by various spectral (FTIR, ^{1}H NMR, ^{13}C NMR, and HR-MS) data (Figs. S1–S4). Then, the very first indication for the anion sensing ability by **L** was observed from the naked-eye detectable visible colour changes (Fig. 1). The receptor **L** showed a remarkable colour change from light yellow to orange brown on addition of 10 equiv. of F^- and AcO^- anion in DMSO. The colour change of **L** on interaction with F^- and AcO^- can be explained by the fact that the intramolecular charge transfer (ICT) process occurred between the phenolic oxygen and the electron withdrawing quinoline ring with the formation of a hydrogen bonded complex between the hydroxyl groups of **L** and the anion added. A slight colour change was also depicted in the case of $H_2PO_4^-$ but it was not prominent as for F^- and AcO^-. However, no intense colour changes were observed in the presence of other anions such as Cl^-, Br^-, I^-, ClO_4^- and HSO_4^-. Simultaneously, the interactions of **L** towards different anions were studied using UV–visible spectrophotometer (Fig. 1). In the absence of anions, receptor **L** showed two absorption bands, one at 303 nm due to π–π^* transition in azomethine group (—CH=N—) and second band at 400 nm is due to overall intramolecular charge transfer (ICT) and/or due to the equilibrium between the tautomeric forms (ketoamine–phenolimine). Upon the addition of F^- and AcO^-, there was a dramatic change in the spectra of **L**. A new charge transfer band at ~530 nm was appeared which indicates the formation of the host–guest complex between **L** and F^-/AcO^- that increases the conjugation in the receptor. Similarly, $H_2PO_4^-$ also showed a slight change in the spectrum of **L**. However, other anions such as Cl^-, Br^-, I^-, ClO_4^- and HSO_4^- induced no detectable photophysical perturbations even in significantly higher concentrations.

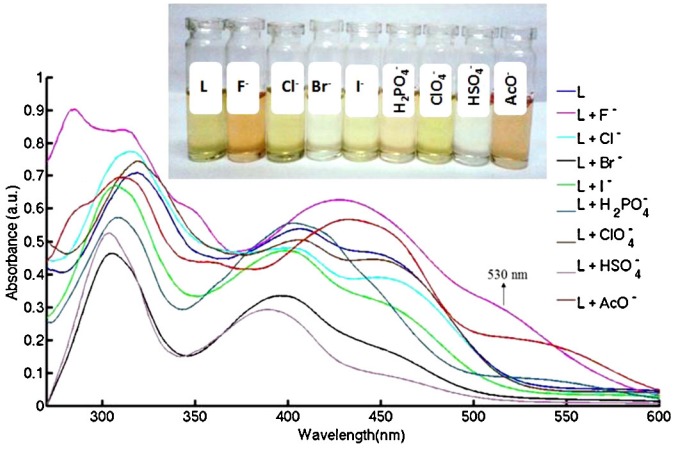

Fig. 1. UV–visible spectral changes of **L** in the presence of different anions ([**L**] = 50 μM, [Anion] = 500 μM) in DMSO. Inset showing the colour change of **L** on addition of different anions (10 equiv.).