Contents lists available at ScienceDirect

Inorganica Chimica Acta

Research paper

Benzothiazole possessing reversible and reusable selective chemosensor for fluoride detection based on inhibition of excited state intramolecular proton transfer

Gargi Dhaka, Jasvinder Singh, Navneet Kaur *

Department of Chemistry, Panjab University, Chandigarh 160014, India

ABSTRACT

A series of three benzothiazole derivatives **BTBAs** based on aryl amide groups have been developed, whose photophysical properties were remarkably changed by the presence of –OCH$_3$ and –NO$_2$ groups at *para*-position of aryl amides. Among these chemosensors, **BTBA-OCH₃** showed fluoride selectivity in its absorbance and emission behavior among the various interfering anions, along with conspicuous color change from colorless to yellowish green color. Substantially red shifted absorption as well as fluorescence band of **BTBA-OCH₃** in DMSO, was observed upon addition of F⁻ ions. Inhibition of Excited State Intramolecular Proton Transfer (ESIPT) in sensor-anion deprotonated complex was suggested to be the signaling mechanism. ^{1}H NMR titrations of the sensor with F⁻ ions also supported deprotonation process. In particular, the spectral responses of this chemosensor could be tuned from side to side alternatively by adding F⁻ and HSO$_4^-$ anions in DMSO solvent.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

The discriminatory signaling of toxic ions in various environmental and chemical systems including living systems by chemosensors that translate molecular recognition into highly sensitive and simply detected signals has been keenly investigated [1–6]. However, the design and synthesis of artificial receptors that are capable of detecting anions have fetched much attention due to the vital roles that ions play in biology, environment and chemistry [7–10].

Among the anions, awareness about the vital role of fluoride ions in dental care, cure of osteoporosis, and involvement in hydrolysis of the nerve gas sarin has expanded in recent years. Fluoride also serves as an important agent in a number of military applications such as refinement of uranium in nuclear arms manufacturing. Owing to high charge density ratio, fluoride has peculiar chemical property to form strong hydrogen bonds with hydrogen-bond donors. Most of the reported fluoride sensors are based on colorimetric changes or fluorescence quenching. To date, examples of fluoride detection based on fluorescence enhancement are very rare [11–15]. Moreover, reviewing of the literature reveals that the majority of the sensor reports for fluoride ion detection are irreversible and only few scattered reports highlights reversible and reusable sensors to detect fluoride ion [1,14].

Different kinds of signaling mechanisms including internal charge transfer (ICT) [16–19], photoinduced electron transfer (PET) [20,21], metal-to-ligand charge transfer (MLCT) [22–23], excited state intramolecular proton transfer (ESIPT) [24,25], excimer/exciplex formation [26,27], fluorescence resonance energy transfer (FRET) [28–30] etc. have been invoked to design fluorescent chemosensors [31]. But, due to the same spectral outputs for anion-receptor interactions, the selectivity is always poor [32]. However, in the ESIPT phenomenon, by careful selection of the acidity and the hydrogen bonding ability of the protons, the biologically important anions can be distinguished from the different spectral outputs for anion-sensor interactions. In the ESIPT molecule, the formation of intramolecular hydrogen bond (IHB) takes place in the ground state between the H-bond donor group (–OH, –NH$_2$, etc.) and basic site (O,N) [33]. In the electronically excited state, this covalently attached proton migrates to a neighboring hydrogen-bonded atom which is less than 2 Å away.

In the design of anion receptors based on proton transfer, the ability of transfer of proton controls the selectivity between anions of similar basicity and surface charge density [29]. However, on addition of anions to fluorescent molecules possessing ESIPT phenomenon, the intermolecular proton transfer from ligand to anion may inhibit the intramolecular proton transfer.

* Corresponding author.
  E-mail addresses: neet_chem@yahoo.co.in, neet_chem@pu.ac.in (N. Kaur).

Here, we report new benzothiazole possessing chemosensors (**BTBA**, **BTBA-NO₂ and BTBA-OCH₃**) in which pK_a of the NH fragment is higher than an –OH group [34,35] and lower than an –NH₂ group [36] to have better anion selectivity and sensitivity. **BTBA** derivatives were prepared by treating **1** with different benzoyl chlorides in good yield and their anion binding properties were investigated by ^{1}H NMR, color changes, UV–vis and fluorescence titration analysis.

2. Material and methods

All reagents and chemicals were purchased from Aldrich and used without further purification. Solvents used for spectroscopic studies were purified by standard procedures before use. ^{1}H NMR spectra were recorded on a Bruker Advance II 400 at 400 MHz from solutions in DMSO-d_6. Absorption spectra were recorded on Shimadzu UV-240 spectrophotometer. Fluorescence spectra of solutions were recorded on Hitachi F-7000 equipped with 220–240 V Xe lamp.

2.1. General procedure for fluorescence experiments

Stock solutions of the receptor **BTBAs** (10^{-2} M) and different anions (10^{-1} M) were prepared in DMSO. This stock solution was further diluted with DMSO and used further for different spectroscopic experiments. All the anions were added as their tetrabutylammonium salts for the different absorption and fluorescence experiments. Aliquots of anions under investigation were then injected into the sample solution through a rubber septum in the cap. The solutions were allowed to get stabilized after each addition, and were then scanned. Excitation wavelength was fixed at 365 nm in case of **BTBA** and 300 nm in case of **BTBA-OCH₃** and **BTBA-NO₂**.

2.2. General procedure for ^{1}H NMR experiments

For ^{1}H NMR titrations, two stock solutions were prepared in DMSO-d_6 (1.9×10^{-2} M), one of them containing host only and other containing an appropriate concentration of guest (F⁻). Aliquots of the two solutions were mixed directly in NMR tubes, which then was diluted to 0.5 mL with DMSO-d_6 if need be.

3. Experimental

3.1. Synthesis of N-(2-benzothiazol-2-yl)aniline (1)

Absolute ethanol was added to mixture of previously synthesized 2-(2′-nitrophenyl)benzothiazole (250 mg, 1 mmol) and SnCl₂·2H₂O (439 mg, 5 mmol) and refluxed at 70 °C for 5 h [37]. After completion of reaction (TLC), the crude product was separated and recrystallized to yield light yellow reduced product **1**. Yellow solid, mp (°C) 184, Yield (%) 70; IR (cm^{-1}) 3453.87 and 3284.13 (two sharp peaks, ν_{NH_2}), 1708.75, 1603.05 ($\nu_{C=N}$); ^{1}H NMR (DMSO, 400 MHz) δ: 6.67 (t, $J_1 = J_2 = 8.0$ Hz, 1H, ArH), 6.71 (d, $J = 8.0$ Hz, 1H, ArH), 7.15 (t, $J_1 = J_2 = 8.0$ Hz, 1H, ArH), 7.27 (t, $J_1 = J_2 = 8.0$ Hz, 1H, ArH), 7.38 (t, $J_1 = J_2 = 8.0$ Hz, 1H, ArH), 7.63 (d, $J = 8.0$ Hz, 1H, ArH), 7.63 (d, $J = 8.0$ Hz, 1H, ArH), 7.80 (d, $J = 8.0$ Hz, 1H, ArH), 7.89 (s, 2H, NH₂); ^{13}C NMR (CDCl₃, 75 MHz) δ (ppm): 169.24, 159.74, 146.78, 133.27, 131.82, 130.98, 126.04, 124.87, 122.48, 121.20, 116.91, 116.81, 115.28; ESI-MS: m/z (relative abundance, assignment) = 227.2 [(M+1)⁺].

3.2. Synthesis of N-(2-(benzothiazole-2-yl)phenyl)-4-methoxybenzamide (**BTBA-OCH₃**)

The mixture of **1** (250 mg, 1 mmol) and p-methoxybenzoyl chloride (245 mg, 1.3 mmol) in the presence of K₂CO₃ (183 mg,

1.2 mmol) was refluxed at 80 °C in dry CH₃CN with a catalytic amount of salt TBAHSO₄. After completion of reaction (TLC), the reaction mixture was allowed to cool down and then filtered off. The filtrate was evaporated using rotary evaporator to obtain the solid compound which was further recrystallized to yield pure **BTBA-OCH₃**. White solid, mp (°C) 190, Yield (%) 76; IR (cm^{-1}) 3117 (ν_{N-H}), 2917, 2844 (ν_{Ar-H} str.), 1670 ($\nu_{C=O}$), 1585 ($\nu_{C=N}$), 1429 (ν_{C-N}); ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 3.91 (s, 3H, –OCH₃), 7.24 (d, 2H, $J = 8.0$ Hz, ArH), 7.31 (t, 1H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.55 (t, 1H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.63 (t, 2H, $J_1 = J_2 = 8.0$ Hz, ArH), 8.06 (d, 1H, $J = 8.0$ Hz, ArH), 8.12 (d, 3H, $J = 8.0$ Hz, ArH), 8.21 (d, 1H, $J = 8.0$ Hz, ArH), 8.81 (d, 1H, $J = 8.0$ Hz, ArH), 12.9 (s, 1H, NH); ^{13}C NMR (CDCl₃, 100 MHz) δ (ppm): 170.1, 163.8, 162.6, 157.8, 138.7, 132.3, 132.1, 129.9, 127.7, 127.9, 126.7, 125.8, 123, 122.2, 121.9, 121.6, 120.8, 119.3, 113.9, 113.7, 55.5; ESI-MS: m/z (relative abundance (%), assignment) = 383.3 [100, (M+Na)⁺], 361.3 [(M+1)⁺].

3.3. Synthesis of N-(2-(benzothiazole-2-yl)phenyl)benzamide (**BTBA**)

BTBA has been synthesized in similar manner as described the synthesis of **BTBA-OCH₃**. White solid, mp (°C) 160, yield (%) 76; IR (cm^{-1}) 3649 (ν_{N-H}), 3064 (ν_{Ar-H}), 1672 ($\nu_{C=O}$), 1615 ($\nu_{C=N}$), 1433 (ν_{C-N}); ^{1}H NMR (CDCl₃, 400 MHz) δ (ppm): 7.13 (t, 1H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.37 (t, 1H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.47 (t, 2H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.51–7.55 (m, 3H, ArH), 7.85 (t, 2H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.92 (d, 1H, $J = 8.0$ Hz, ArH), 8.15 (d, 2H, $J = 8.0$ Hz, ArH), 8.98 (d, 1H, $J = 8.0$ Hz, ArH), 13.3 (s, 1H, NH); ^{13}C NMR (CDCl₃, 100 MHz) δ (ppm): 169, 166.3, 161.1, 152.8, 138.5, 137.3, 135.6, 133.5, 132.5, 132, 131.9, 129.9, 129.8, 129.2, 128.7, 127.8, 126.7, 125.9, 123.3, 122.3, 121.6, 120.9, 119.4; ESI-MS: m/z (relative abundance (%), assignment) = 331.31 [100, (M + 1)⁺].

3.4. Synthesis of N-(2-(benzothiazole-2-yl)phenyl)-4-nitrobenzamide (**BTBA-NO₂**)

BTBA-NO₂ has been synthesized in similar manner as described the synthesis of **BTBA-OCH₃**. Brown solid, mp (°C) 150, Yield (%) 80; IR (cm^{-1}) 3117 (ν_{N-H}), 2978 (ν_{Ar-H}), 1687 ($\nu_{C=O}$), 1605 ($\nu_{C=N}$), 1430 (ν_{C-N}); ^{1}H NMR (DMSO, 400 MHz) δ (ppm): 7.34 (t, 2H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.53 (t, 1H, $J_1 = J_2 = 8.0$ Hz, ArH), 7.60 (d, 1H, $J = 8.0$ Hz, ArH), 7.65 (d, 1H, $J = 8.0$ Hz, ArH), 8.04 (d, 1H, $J = 8.0$ Hz, ArH), 8.12 (t, 1H, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, ArH), 8.40 (d, 2H, $J = 8.0$ Hz, ArH), 8.55 (d, 2H, $J = 8.0$ Hz, ArH), 8.90 (d, 1H, $J = 8.0$ Hz, ArH), 13.4 (s, 1H, NH); ^{13}C NMR (CDCl₃, 100 MHz) δ (ppm): 169.1, 163.9, 132.4, 129.9, 128.9, 127.1, 124.1, 123.9, 122.1, 121.7, 120.9, 119.6; ESI-MS: m/z (relative abundance (%), assignment) = 376.33 [100, (M+1)⁺].

4. Result and discussion

Scheme 1 outlines the synthesis of the BTBA derivatives, **BTBA**, **BTBA-NO₂** and **BTBA-OCH₃**. The refluxing of **1** with different benzoyl chlorides, in dry CH₃CN, gave different **BTBA** derivatives containing amide linkage i.e. **BTBA**, **BTBA-NO₂** and **BTBA-OCH₃**. The desired products were explicitly characterized by NMR spectra (^{1}H NMR, ^{13}C NMR), IR and Mass spectrum (Figs. S1–S9).

Photophysical properties of chemosensors **BTBA**, **BTBA-NO₂** and **BTBA-OCH₃** in DMSO solution have been summarized in Table S1. The normalized UV–vis absorption and photoluminescence spectra of these three chemosensors in DMSO have been shown in Fig. 1, which shows the large stokes shifts and complete lack of spectral overlap of all the three derivatives, that are the characteristic features of an ESIPT based chemosensor. The stokes shift follows the order as **BTBA-OCH₃** (87 nm) > **BTBA-NO₂** (79 nm) > **BTBA** (70 nm). In the case of fluorescence spectrum, **BTBA-OCH₃** exhibited