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Synthesis and characterization of 1,2,3-triazoles-linked urea hybrid sensor for selective sensing of fluoride ion

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Abstract

Two urea-linked 1,2,3-triazole based sensors (**5a** and **5b**) have been synthesized by 1,3-dipolar cycloaddition between 1-(4-fluorophenyl)-3-(prop-2-yn-1-yl)urea (**2**) and phenyl azides (**4a-4b**) *via* copper(I)-catalyzed click reaction. The synthesized sensors **5a** and **5b** have been evaluated for their sensing ability towards anions (F, Br⁻, Cl⁻, I⁻, H₂PO₄⁻ and AcO⁻) and cations (Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺) through UV-Visible, fluorescence and NMR spectral techniques. It was observed that sensor **5a** exhibited selective sensing for F⁻ ion with a bathochromic shift in absorption spectrum and showed fluorescence "turn-on" behavior in the emission spectroscopy. The UV-Visible experiments exhibited that **5a** interact with F⁻ ion with a stability constant (K) of 2.058×10^4 M⁻¹ and detection limit of **5a** for F⁻ ions was found to be 65.76±0.45µM. Furthermore, these results were also supported by density functional theory (DFT) calculations.

Keywords: Urea, triazoles, receptor, anion, fluoride ion.

1. Introduction

Selective sensing of anions by designed chemosensors has gained considerable interest because of their important role in various chemical [1], biological and industrial processes [2]. The design and development of efficient colorimetric sensors for biologically important anions is an important area of research [3]. In particular, development of artificial chemosensors capable of

selective fluoride sensing are of high significance [4] because it is an essential element for the human body and is used to treat dental caries osteoporosis and enamel demineralization [5,6]. The excess ingestion of the fluoride ions in our body lead to chronic and acute toxicity like skeletal or dental fluorosis, urolithiasis, stomach ulcers, etc [7-10]. Due to the physiological, pathological, and toxicological effects of fluoride ion, much attention has been devoted for the development of fluorescent/colorimetric chemosensors for sensing of fluoride ion in chemical and biological systems with high selectivity, sensitivity, real-time measurement and cost effectiveness [11-13]. A number of cyclic and acyclic sensors [14-17] containing precise alignment of amides, urea, thiourea, pyrazole, triazole, etc. have been synthesized for the recognition of fluoride ions [18-19]. These artificial chemosensors sense anions by triggering photophysical properties of chromophores while interacting with anions which result in significant changes either in colour or in fluorescence [20-22]. It is well known that fluoride ion forms strong hydrogen bond with hydrogen bond donors at low concentration while high concentration of fluoride ion induces deprotonation. In this context, urea derivatives are excellent hydrogen bond donors thereby reported to exhibit various biological activities [23-25]. Moreover, numerous urea based chemosensor molecules have been reported as naked-eye fluoride ion sensors [26-29].

On the other hand, 1,4-disubstituted 1,2,3-triazole derivatives were studied extensively in supramolecular [30] and coordination chemistry [31] due to their ease of synthesis *via* click reaction and exceptional abilities to exhibit various noncovalent interactions including hydrogen bonding, π - π stacking and C-H··· π interactions with guest molecules [32]. 1,2,3-Triazoles exhibit high dipole moment value which allow them to form hydrogen bonding with the guest entity. The C₅-H group of triazole ring also shows weak hydrogen bond donating ability with anions. Additionally, 1,2,3-triazole derivatives were also reported as potential chelating ligands for flouride ion. On the basis of aforementioned, herein, we report synthesis of urea-triazole hybrids (**5a**-**5b**) from urea linked terminal alkyne and phenyl azides. The binding studies revealed that **5a** act as chromofluorogenic sensor for F⁻ ions in preference to Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Br⁻, Cl⁻, I⁻, H₂PO₄⁻ and AcO⁻ ions.

2. Results and Discussion

2.1 Synthesis and Characterization of 1,2,3-Triazole-Linked Urea Hybrid Sensors

The urea-linked 1,2,3-triazoles **5a** and **5b** were synthesized in three steps (scheme 1). Firstly, 1-(4-fluorophenyl)-3-(prop-2-yn-1-yl)urea (**2**) was synthesized from 4-flouro phenyl isocyanate (**1**) and propargyl amine using triethylamine in dichloromethane. The other precursors, phenyl azides (**4a-4b**) were prepared from classical diazotization-azidation of aniline derivatives [33]. In the final step, 1-(4-fluorophenyl)-3-(prop-2-yn-1-yl)urea (**2**) and phenyl azides (**4a-4b**) were subjected to azide-alkyne 1,3-dipolar cycloaddition reaction in presence of catalytic amount of copper sulphate and sodium ascorbate in water:DMF to furnish urea-linked 1,2,3-triazoles (**5a** and **5b**) in high yield.



Scheme 1. Synthesis of 5a-5b: (i) Propargyl amine, triethylamine, DCM. (ii) HCl, NaNO₂, DCM, NaN₃, 0 °C. (iii) Phenyl azides (4a-4b), CuSO₄.5H₂O, sodium ascorbate, DMF:H₂O, rt.

The synthesized triazole derivatives **5a** and **5b** were characterized using FTIR, ¹H NMR, ¹³C NMR and HRMS techniques. For example, FTIR spectrum of compound **5a**, displayed two bands at 1669 cm⁻¹ and 3158 cm⁻¹ due to carbonyl stretching and C-H stretching of triazole ring, respectively. The ¹H NMR spectrum of compound **5a** exhibited two singlets at δ 10.54 and δ 8.33 due to OH and triazolyl protons, respectively. The NH protons of urea moiety of **5a** resonated at δ 8.63 ppm and δ 6.65 ppm, respectively. In ¹³C NMR spectrum of **5a**, carbonyl carbon exhibited a peak at δ 158.60 ppm, while, signal of methylene carbon was observed at δ 35.28 ppm. The C-5 and C-4 carbons atoms of the triazole moiety were observed at δ 120.02 ppm and δ 145.71 ppm respectively. The HRMS analysis of **5a** exhibited molecular ion peak at

328.1423 $(M+H)^+$ which is consistent with molecular formula. Similarly, analytical and spectral data of compound **5b** was laid in agreement to the assigned structure.

2.2 Sensing Behaviour of Synthesized Compounds Using UV-Visible Spectroscopic Method

The sensing abilities of **5a-5b** were investigated by absorption, emission and NMR studies towards different cations and anions. The UV-Visible spectroscopic experiments were performed with **5a** by adding tetrabutylammonium salts of F⁻, Br⁻, Cl⁻, I⁻, H₂PO₄⁻ and AcO⁻ ions and perchlorate salts of Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺ ions in DMSO. The UV-Visible spectrum of **5a** showed a band at 305 nm which was shifted to a new absorption band at 343 nm on addition of fluoride ions as shown in **Fig. 1** whereas other ions including Br⁻, Cl⁻, I⁻, H₂PO₄⁻ and AcO⁻ anions and Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺ metal ions did not produce any change in absorption spectrum. The observed sensing ability of **5a** towards fluoride ion was examined in the presence of other tested anions and cations and no interference of other ions was obtained in absorption studies.



Fig. 1. UV-Visible spectra of **5a** (1×10^{-4} M in DMSO) upon addition of F⁻, Br⁻, Cl⁻, I⁻, H₂PO₄⁻, AcO⁻, Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺ ions (25×10^{-4} M in DMSO)

As shown in UV-Visible titration spectra in **Fig. 2**, upon gradual addition of fluoride ions (0.0-6.0 equiv.) in solution of **5a**, the intensity of absorption maxima of **5a** at 305 nm was decreased and a new band at 343 nm was started to become visible. These results indicated the interaction between receptor and fluoride ion which led to deprotonation of acidic amide NH group of urea of **5a** thereby causing a red shift of 38 nm mainly because of intramolecular charge transfer (ICT) phenomenon between anion-urea [34].



Fig. 2. The absorption titration spectra of **5a** (0.1 mM) with 0.0 to 6.0 equiv. of F (2.5 mM) ions in DMSO solution

Stability constant (K) between triazole-linked urea sensor (**5a**) and F⁻ ion was calculated from UV-Visible titration data (y = 6E-05x+1.235 9, $R^2 = 0.996$) using Benesi–Hildebrand equation and found to be 2.058×10^4 M⁻¹ (**Fig. 3**). Furthermore, the detection limit of **5a** was calculated from the equation LOD = 3α /S for the fluoride anion and was found to be $65.76\pm0.45 \mu$ M. Here, α is the standard deviation of blank measurements (0.002517) and S is the slope of calibration curve (**Fig. 4**) of the UV-Visible titrations.



Fig. 3.The Benesi–Hildebrand plot of measured absorbance $[1/(A-A_0)]$ at 343 nm versus $1/[F^-]$ (M⁻¹)



Fig. 4. Determination of detection limit for F anion; Absorbance vs. F concentration (M) plot for 5a receptor (65.8 μ M)

2.3 Sensing Behaviour of 5a Using Fluorescence Spectroscopic Method

The sensitivity of **5a** for fluoride ion was also examined by exploring its fluorescence spectra in DMSO:CH₃CN (1:9, v/v) solution. The fluorescence experiments were performed from 350 nm to 600 nm using silt width of 10 nm. The sensor **5a** showed emission peak at 425 nm when excited at 325 nm. A distinct change in the emission spectrum was obtained in presence of fluoride ions while other tested metal ions and anions (Br⁻, Cl⁻, I⁻, H₂PO₄⁻, AcO⁻, Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺) did not exhibit any noticeable changes in emission spectrum under similar experimental conditions. It was found that continue addition of F ion to a solution of **5a**, a steady increase in emission intensity was observed at 425 nm as shown in **fig. 5**. These observations are consistent with the previous report [35-37] which advised that fluorescence "turn-on" behaviour may be the result of hydrogen bonding in between **5a** and F⁻ ion at initial addition of F⁻ ions whereas further addition of F⁻ ions led to deprotonation of amide (–NH) protons which facilitated the π to π^* transitions responsible for enhancement behaviour of **5a**.



Fig.5. Fluorescence titration spectra of **5**a in DMSO:CH₃CN 1:9 v/v (10 mM) with 0.0–6.0 equiv. of F^- ions at 25°C

2.4 Sensing Behaviour of Synthesized Compounds Using ¹H Nuclear Magnetic Resonance Spectroscopic Method

To get more details about interaction mechanism of receptor **5a** with F ions, proton NMR titration of **5a** with fluoride ions in DMSO-d₆ were performed. The OH, NH protons of urea and CH proton of trizole ring of **5a** were observed at δ 10.54, 8.68, 6.66 and δ 8.34 ppm, respectively which shifted to downfield on addition of tetrabutyl ammonium fluoride. It was interesting to observe that addition of more than 3.0 equivalent of TBAF, the signals of OH and NH protons of urea were disappeared, whereas CH proton of triazolyl moiety was continuously shifted to downfield as shown in **Fig.6**. These observations indicated that initially F ion interacted with OH, NH protons of urea and CH proton of trizole ring through hydrogen bonding while further addition of F⁻ ions resulted in deprotonation of OH and NH protons of urea. The existence of CH proton of triazolyl moiety in presence of excess of F⁻ ion showed the involvement CH of proton only in hydrogen bond interactions. The deprotonation of OH and NH protons induces an upfield shift of aromatic protons due to through-bond propagation of electron density.



Fig.6. Proton NMR titration spectra of 5a upon addition of various equiv. of TBAF in DMSO-d₆

Similarly, the sensing behavior of **5b** was also investigated for different ions such as F⁻, Br⁻, Cl⁻, Γ , H₂PO₄⁻, AcO⁻, Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺ under similar experimental condition by comparing their UV-Visible and NMR studies before and after addition of these ions. The result of UV-visible experiment clearly revealed that **5b** does not exhibit any significant changes in absorption spectrum in presence of these ions as shown in Figure S13 and S14 (Supporting information). On the other hand, it was interesting to observe that NMR titration experiment of **5b** with fluoride ion shows that only N-H protons of **5b** at δ 8.63 and 6.64 ppm were disappeared in presence of F- ion. These experiments suggested that interactions between **5b** and F⁻ are weaker in comparison to sensor **5a**, thereby no significant changes were recorded in UV spectra. Also, the presence of phenolic proton (-OH) and C-H proton of trizole moiety of **5a** play significant role in strong binding of F- ion

Density Functional Theory (DFT) Study

The interaction between receptor **5a** with fluoride anion was theoretically investigated exploiting the DFT. The geometries of chemosensor and fluoride anion were optimized without symmetry constraints using Gaussian 09 program [38-39] at B3LYP/6-311G(d,p) level of theory (**Fig.7-8**). Absorption properties of these compounds were predicted at the same level. In general, the bond lengths of N–H and H–F bonds were reported around 0.98 and 0.92 Å, respectively. In the optimized structure of chemosensor (**Fig. 7**), the N4-H26 and N2-H25 bond distances are 1.00

and 1.01 Å, respectively and comparable with the reported data. The optimized structures of chemosensor and fluoride anion show that the N–H bond lengths vary from 1.00 Å to 1.56 Å (N14-H33) and 1.01 Å to 2.99 Å (N16-H34) (see **Fig. 8**). Therefore, it can be realized from these data that deprotonation of the acidic N–H protons of urea based chemosensor and the formation of HF. The DFT studies revealed that the interaction mechanism mediated through abstraction of proton from the host. The frontier molecular orbitals (FMOs) of the chemosensor and fluoride anion were examined to understand the modifications in the electronic structure of deprotonated chemosensor, as depicted in **Fig. 9**. It is observed that the HOMO and LUMO are localized on different parts. It can be seen in **Fig. 9** that the HOMO of chemosensor is mostly restricted on the fluoropheny 1-1,2,3-triazole-urea part whereas the LUMO is present on the contradictory site. After adding two fluoride ions to chemosensor, main part of HOMO and LUMO reposition on urea linkage which reveals more reactivity in host molecule. For chemosensor, the energy gap between these two MOs is 5.15 eV and after the deprotonation with fluoride ions, the energy gap decreased to 1.74 eV.



Fig. 7. Optimized structure of chemosensor with some bond lengths (Å) calculated using the B3LYP/6-311G(d,p)method. Yellow: C; Pink: N; Blue: H; red: O; Light orange: F.



Fig. 8. Optimized structure of chemosensor–F⁻ with some bond lengths (Å) calculated using the B3LYP/6-311G(d,p)method. Yellow: C; Pink: N; Blue: H; red: O; Light orange: F.



Fig. 9. Frontier orbitals of chemosensor and chemosensor–F⁻ calculated using the B3LYP/6-311G(d,p) method

3. Experimental

3.1 Instrumentation, Analysis and Starting Material

The melting points (°C) of derivatives were recorded in open capillary. IR spectra of all compounds were obtained on SHIMAZDU IR AFFINITY-I FT-IR spectrophotometer. The ¹H NMR (400 MHz) and ¹³C NMR (100 MHz) spectra were recorded using TMS as an internal standard on Bruker Avance-III 400 nano bay spectrometer. HRMS spectra were acquired on LC-MS/MS QTOF SCIEX-QTOF spectrometer. All the reactants, metal perchlorates and tetrabutylammonium salt were procured from sigma Aldrich and used without further purification.

3.2 Procedure for the Synthesis of urea-linked terminal alkyne (2)

To a stirred solution of propargylamine (1.1 mmol) and triethylamine (1.1 mmol) in 30 mL of dichloromethane (DCM), 4-flouro phenyl isocyanate (1) (1 mmol; in dichloromethane) was added drop wise at 0 °C and the reaction mixture was allowed to stir at room temperature. After completion of the reaction (confirmed by TLC), the reaction mixture was diluted with dichloromethane and the DCM layer was washed with 2N sulphuric acid, water, brine solution and dried over anhydrous sodium sulphate. Further, DCM layer was concentrated to dryness to yield terminal alkyne (2) in good yield.

1-(4-fluorophenyl)-3-(prop-2-yn-1-yl)urea (2): off white solid, 81% yield, Mp: 168-170°C. IR (KBr, v_{max}/cm^{-1}): 3325 (C-H alkyne), 3177 (NH str), 3113, 3073, 3017, 2914, 2120 (C=C str), 1886 (C=O str), 1638 (C=O str, amide), 1609, 1533 (C=C str), 1506, 1456, 1414, 1354, 1304, 1242, 1217, 1157, 1126, 1098, 1057. ¹H NMR (CDCl₃, 400 MHz): δ 3.09 (t, *J* = 2.4 Hz, 1H, alkyne CH), 3.86-3.88 (dd, 2H, CH₂), 6.45 (t, *J* = 4.0 Hz, 1H, NH), 7.05-7.09 (m, 2H,Ar-H), 7.38-7.41 (m, 2H, Ar-H) 8.61 (s, 1H, NH). ¹³C NMR (CDCl₃, 100 MHz): δ 29.71 (NCH₂), 75.14 (CH-acetylene), 77.77 (C-acetylene), 115.64, 115.87, 133.36, 158.00 (C=O), 160.42 (C-F). HRMS: m/z (M+H)⁺ calculated for C₁₀H₁₀FN₂O 193.0777, found: 193.0810.

3.3 General procedure for the synthesis of phenyl azides (4a-4b)

The organic azides **4a** and **4b** were synthesized from anilines by classical diazotization-azidation reaction as reported [33].

3.4 General Procedure for the synthesis of urea-linked 1,4-disubstitutesd 1,2,3-triazoles (5a-5b)

A mixture of phenyl azide (1mmol), alkyne 2 (1mmol), and copper sulphate (0.1 mmol) and sodium ascorbate (0.2 mmol) in DMF:water (8:2) was stirred at room temperature. After completion of the reaction (monitored by TLC), an ice cold aqueous solution of ammonia: ammonium chloride (9:1) was added to the reaction mixture. The precipitates thus obtained were filtered and dried to yield the desired 1,4-disubstituted 1,2,3-triazoles (**5a-5b**) in good yield.

1-(4-fluorophenyl)-3-((1-(2-hydroxyphenyl)-1H-1,2,3-triazol-4-yl)methyl)urea (5a): Light brown solid, 87% yield, Mp: 210-212°C. IR (KBr, v_{max}/cm^{-1}): 3361 (OH str), 3290 (NH str), 3158 (C-H str, triazole), 1669 (C=O str), 1579 (C=O str, amide), 1511 (C=C str), 1475, 1313, 1277, 1230, 1090. ¹H NMR (DMSO, 400 MHz): δ 4.43 (d, J = 5.6 Hz, 2H, NCH₂), 6.66 (t, J = 4.0 Hz, 1H, NH), 6.99 (t, J = 7.2 Hz, 1H, Ar-H), 7.04-7.12 (m, 3H, Ar-H), 7.31-7.36 (m, 1H, Ar-H), 7.39-7.43 (dd, J = 4.0 Hz, 1H, 2H, Ar-H), 7.59-7.60 (m, 1H, Ar-H), 8.33 (s, 1H, triazolyl-H), 8.63 (s, 1H, NH), 10.54 (s, 1H, OH). ¹³C NMR (DMSO, 100 MHz): δ 35.28 (CH₂), 115.46, 115.68, 117.53, 119.78, 119.85, 120.02 (C-5), 124.59, 125.06, 125.48, 130.47, 137.21, 145.71 (C-4), 149.95, 155.63, 156.28, 158.60 (C=O). HRMS: m/z (M+H)⁺ calculated for C₁₆H₁₄FN₅O₂ 328.1210, found: 328.1423.

1-(4-fluorophenyl)-3-((1-phenyl-1H-1,2,3-triazol-4-yl)methyl)urea (5b): Light yellow solid, 89% yield, Mp: 198-200°C. IR (KBr, v_{max} /cm⁻¹): 3312 (NH str), 3134 (C-H str, triazole), 1636 (C=O str), 1612 (C=O str, amide), 1571 (C=C str), 1509, 1467, 1306, 1219 , 1052. ¹H NMR (CDCl₃, 400 MHz): δ 4.32 (d, J = 5.6 Hz, 2H, NCH₂), 6.56 (t, J = 5.6 Hz, 1H, NH), 7.06 (t, J = 8.8 Hz, 2H, Ar-H), 7.31-7.40 (m, 7H, Ar-H), 8.00(s, 1H, triazolyl-H), 8.58 (s, 1H, NH). ¹³C NMR (CDCl₃, 100 MHz): δ 39.99 (CH₂), 119.79, 120.01 (C-5), 124.70, 124.77, 125.14, 133.42, 134.46, 140.81, 141.77 (C-4), 160.74 (C=O), 161.54. HRMS: m/z (M+H)⁺calculated for C₁₆H₁₄FN₅O 312.1261, found: 312.1460.

4 Conclusion

In conclusion, urea-linked 1,2,3-triazoles (**5a** and **5b**) have been synthesized *via* 1,3-dipolar cycloaddition between 1-(4-fluorophenyl)-3-(prop-2-yn-1-yl)urea (**2**) and phenyl azides (**4a-4b**). The sensor **5a** exhibited significant selectivity for F^- ion in presence of other competing anions and cations as revealed by UV-Visible, fluorescence and NMR titration experiments. The Benesi–Hildebrand plot revealed that sensor **5a** interacts with F^- with stability constant K of

 2.058×10^4 M⁻¹ and detection limit of 65.8 μ M ranges. Further, fluorescence, NMR experiments and density function theory calculations rationalized the experimental results.

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Highlights

- Synthesis of 1,2,3-Triazole-linked urea hybrids using click reaction.
- Compound 5a exhibited selective sensing for F ion in preference to different ions. •
- Binding properties were studied by UV-Visible, Fluorescence and NMR titration ٠ experiments.
- DFT studies also supported the experimental results. •

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Declaration of Interest Statement

Authors declare no conflict of interest

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