

Tris-Triazole Based Chemosensors for Selective Sensing of Pb²⁺ Ions

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A series of novel tris-triazole based neutral chemosensors (**4a-c**) have been synthesized *via* click reaction and characterized by various spectral techniques. All the synthesized triazoles were evaluated for their ion binding properties towards various cations (Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺) by UV-visible titration experiments. It was observed that the addition of Pb²⁺ ions to compound **4a** led to significant changes in UV-visible spectrum and a new UV band was observed at 262 nm. Further, the Job's plot confirmed the formation of 1:1 complex between compound **4a** and Pb²⁺. The synthesized chemosensor selectively sense Pb²⁺ ions in preference to other cations like Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺.

Keywords: 1,2,3-Triazoles, Click reaction, Chemosensors, Lead ions.

INTRODUCTION

Lead is known as the highly toxic metal ion present in soil, water bodies and air due to its frequent uses in our daily life in various forms like in storage batteries, cosmetics, paints, insulation, ceramics, electronic devices, plastics, construction materials and utilization in petroleum refining like sulfonation, halogenation, extraction, condensation, metallurgy [1-4]. Due to its non-biodegradable nature, trace of lead remains in soil, water system and food items [5], which causes serious health problems like infertility, increased blood pressure, nerve disorders, muscle and joint pain, irritability, memory or concentration loss, kidney disorders and mental retardation in humans [6-10]. Every year 143000 deaths and 0.6 % of the illnesses have been estimated due to lead poisoning [11]. In view of these hazardous health effects, monitoring and detection of lead ions is an area of intense research activity. Although, various methods are available for quantitative analysis of Pb(II) ions including atomic absorption spectrometry [12], inductively coupled plasma mass spectroscopy [13], inductively coupled plasma atomic emission spectroscopy [14] and anodic stripping voltammetry [15]. Most of these techniques involve difficult and long-lasting sample preparation, large amount of expendable materials, high initial cost, requirement of skilled operators which make these

techniques not easily accessible. In view of these, there is an urgent need to develop a sensitive, economical and easy to use monitoring technique for the detection of lead at low concentration.

In recent years, significant efforts have been made for the development of highly selective and sensitive fluorescent/colorimetric chemosensor molecules for the detection of Pb(II) ions in chemical and biological systems with advantages of reusability, high selectivity and sensitivity, real-time measurement and cost effectiveness [16-20]. In this context, triazole moiety is an attractive scaffold for designing and development of chemosensor molecules due to its ability to participate in hydrogen bonding and dipole-dipole interaction which can be used for sensing of metal ions. 1,2,3-Triazole have been used for stabilizing silver nanoparticles or used as capping agents for silver nanoparticles. These stabilized or capped silver nanoparticles are utilized for sensing and quantification of mercury ions either through mercury induced aggregation of silver nanoparticles or by the formation of Ag-Hg amalgam [21-23]. The literature survey revealed the use of 1,2,3-triazole derivatives for designing of sensing materials for sensing of toxic metal ions other than mercury are still rare despite their unique structural features [24-28]. In continuation of our research efforts devoted to ionic recognition [29-31], we are reporting herein, synthesis

of novel triazole derivatives (**4a-c**) via copper(I)-catalyzed alkyne-azide cycloaddition reaction which exhibited high selectivity and sensitivity towards Pb^{2+} ions compared to other metal ions.

EXPERIMENTAL

Propargyl alcohol, benzene-1,3,5-tricarbonyl trichloride, benzyl halides, 4-dimethylaminopyridine, cuprous iodide, microcrystalline cellulose were procured from Sigma Aldrich and used as received. All the melting points were recorded in an open capillary using LABCO melting point apparatus. IR spectra were recorded on SHIMADZU IR AFFINITY-I FT-IR spectrophotometer. The ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using BrukerAvance-III 400 nano bay spectrometer. The high-resolution mass spectra (HRMS) were recorded using Micromass LC-MS/MS QTOF SCIEX-QTOF spectrometer.

Procedure for the synthesis of tri(prop-2-yn-1-yl)benzene-1,3,5-tricarboxylate (2): To a stirred solution of propargyl alcohol (3.3 mmol) and 4-dimethylaminopyridine (3.3 mmol) in 30 mL of dichloromethane, benzene-1,3,5-tricarbonyl trichloride (1 mmol; dissolved in dichloromethane) was added drop wise at 0°C . The stirring of reaction mixture was continued till the completion of reaction, as monitored by TLC. After completion of the reaction, the reaction mixture was diluted with dichloromethane and the organic layer was washed with 2 N sulphuric acid (2×10 mL), water (2×10 mL) and brine (10 mL) and dried over anhydrous sodium sulphate. Dichloromethane was evaporated in vacuum to obtain the product.

Tri(prop-2-yn-1-yl)benzene-1,3,5-tricarboxylate (2): Off white solid, yield: 91 %, m.p.: $198-200^\circ\text{C}$. IR (KBr, ν_{max} , cm^{-1}): 3287, 3084 (*str.*), 2126 ($\text{C}=\text{C}$ *str.*), 1736 ($\text{C}=\text{O}$ *str.*, ester), 1655, 1609 ($\text{C}=\text{O}$ *str.*, ester), 1441, 1371, 1325, 1271, 1233 ($\text{C}-\text{O}$ *str.*, ester), 1152, 1107 ($\text{C}-\text{O}$ *str.*, ester), 999, 959, 932, 737, 689, 646). ^1H NMR (CDCl_3 , 400 MHz): δ 2.58 (t, 3H, alkyne CH), 5.01 (d, 6H, OCH_2), 8.98 (s, 3H, Ar-H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 53.15 (OCH_2), 75.64 (CH acetylene), 77.11 (C acetylene), 130.78 (Ar-C), 135.30, (Ar-C), 164.00 ($\text{C}=\text{O}$). HRMS: m/z ($\text{M}+\text{H}$) $^+$ calcd. for $\text{C}_{18}\text{H}_{12}\text{O}_6$: 325.0712, found: 325.0757.

General procedure for the synthesis of 1,2,3-tris-triazoles (4a-c): A mixture of alkyne **2** (1mmol), 4-substituted phenyl azides (**3a-c**) (3.6 mmol) and catalyst (100 mg) in 10 mL of water was stirred at 80°C until TLC analysis shows that the reaction is complete. The reaction mixture was cooled to room temperature, filtered and residues thus obtained were washed with ethyl acetate. Solvent was evaporated under high vacuum to get corresponding 1,2,3-tris-triazoles (**4a-c**) in good yield.

Tris((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methyl)benzene-1,3,5-tricarboxylate (4a): Off white solid, yield: 71 %, m.p.: $138-140^\circ\text{C}$. IR (KBr, ν_{max} , cm^{-1}): 3125 (C-H *str.*, triazole), 1732 ($\text{C}=\text{O}$ *str.*, ester), 1601, 1524, 1443, 1412, 1342, 1248 (C-O *str.*, ester), 1179, 1152 (C-O *str.*, ester) 1111, 1005, 962, 880, 820, 768, 741, 691, 629. ^1H NMR (CDCl_3 , 400 MHz): δ 5.61 (s, 6H, OCH_2), 8.23 (d, 6H, Ar-H, $J = 12$ Hz), 8.44 (d, 6H, Ar-H, $J = 8$ Hz), 8.71 (s, 3H, triazolyl-H), 9.17 (s, 3H, Ar-

H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 58.80 (OCH_2), 121.24 (C-5), 124.29, 125.98, 131.27, 134.44, 141.14, 143.71 (C-4), 147.26, 164.22 ($\text{C}=\text{O}$). HRMS: m/z ($\text{M}+\text{H}$) $^+$ calcd. for $\text{C}_{36}\text{H}_{24}\text{N}_{12}\text{O}_{12}$: 817.1715, found: 817.1651.

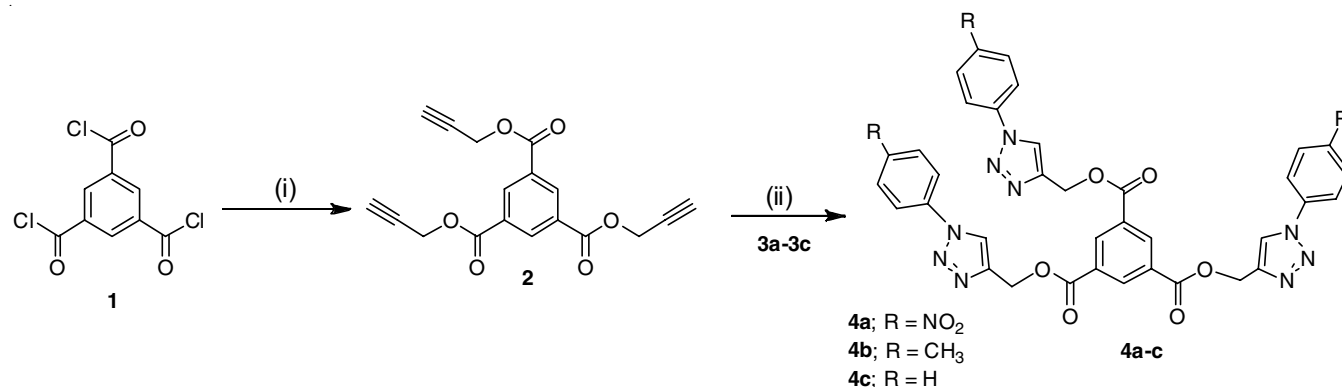
Tris((1-(*p*-tolyl)-1H-1,2,3-triazol-4-yl)methyl)benzene-1,3,5-tricarboxylate (4b): Off white solid, yield: 71 %, m.p.: $219-221^\circ\text{C}$. IR (KBr, ν_{max} , cm^{-1}): 3136 (C-H *str.*, triazole), 1730 ($\text{C}=\text{O}$ *str.*, ester), 1614, 1559, 1520 (C-O *str.*, ester), 1447, 1379, 1319, 1234 (C-O *str.*, ester), 1144, 1109, 1043, 984, 818, 741, 694, 662, 523. ^1H NMR (CDCl_3 , 400 MHz): δ 2.44 (s, 9H, CH_3), 5.61 (s, 6H, OCH_2), 7.33 (d, 6H, Ar-H, $J = 8$ Hz), 7.63 (d, 6H, Ar-H, $J = 8$ Hz), 8.12 (s, 3H, triazolyl-H), 8.91 (s, 3H, Ar-H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 21.10 (CH_3), 58.67 (OCH_2), 120.64 (C-5), 122.52, 130.28, 130.97, 134.54, 135.22, 139.16, 142.84 (C-4), 164.76 ($\text{C}=\text{O}$). HRMS: m/z ($\text{M}+\text{H}$) $^+$ calcd. for $\text{C}_{39}\text{H}_{33}\text{N}_9\text{O}_6$: 724.2632, found: 724.2502.

Tris((1-phenyl-1H-1,2,3-triazol-4-yl)methyl)benzene-1,3,5-tricarboxylate (4c): Off white solid, yield: 71 %, m.p.: $188-190^\circ\text{C}$. IR (KBr, ν_{max} , cm^{-1}): 3140 (C-H *str.*, triazole), 1728 ($\text{C}=\text{O}$ *str.*, ester), 1599 ($\text{C}=\text{N}$ *str.*), 1562, 1504, 1445, 1383, 1325, 1234 (C-O *str.*, ester), 1148, 1107 (C-O *str.*, ester), 1043, 972, 833, 760, 694, 525. ^1H NMR (CDCl_3 , 400 MHz): δ 5.62 (s, 6H, OCH_2), 7.47 (t, 3H, Ar-H, $J = 8$ Hz), 7.55 (t, 6H, Ar-H, $J = 7.7$ Hz), 7.76 (d, 6H, Ar-H, $J = 8$ Hz), 8.17 (s, 3H, triazolyl-H), 8.91 (s, 3H, Ar-H). ^{13}C NMR (CDCl_3 , 100 MHz): δ 58.67 (OCH_2), 120.82, 122.61 (C-5), 129.01, 129.79, 130.98, 135.20, 136.89, 142.95 (C-4), 164.69 ($\text{C}=\text{O}$). HRMS: m/z ($\text{M}+\text{H}$) $^+$ calcd. for $\text{C}_{36}\text{H}_{27}\text{N}_9\text{O}_6$: 682.2163, found: 682.2026.

RESULTS AND DISCUSSION

The synthesis of 1,2,3-tris-triazoles (**4a-c**) was achieved by synthetic protocol as depicted in **Scheme-I**. In the first step, tri(prop-2-yn-1-yl)benzene-1,3,5-tricarboxylate (**2**) was synthesized from benzene-1,3,5-tricarbonyl trichloride (**1**) and propargyl alcohol using *N,N*-dimethylaminopyridine in dichloromethane [32]. The other precursor 4-substituted phenyl azides (**3a-c**) were prepared by classical diazotization-azidation of unsubstituted aniline. The synthesized 4-substituted phenyl azides (**3a-c**) were subsequently reacted with tri(prop-2-yn-1-yl)benzene-1,3,5-tricarboxylate (**2**) using cellulose supported cuprous iodide nanoparticles [33] in water to furnish desired 1,2,3-tris-triazoles (**4a-c**) in good yield at 80°C .

The structures of synthesized tris-triazoles (**4a-c**) were confirmed on the basis of their FTIR, ^1H NMR, ^{13}C NMR and HRMS data. For example, FTIR spectrum of compound **4a**, displayed bands at 1732 and 3125 cm^{-1} assigned for carbonyl stretching band and C-H stretching of triazole, respectively. The ^1H NMR spectrum of compound **4a** exhibited two singlets at δ 5.70 and δ 8.0 which were assigned to methylene group and triazolyl protons, respectively. In ^{13}C NMR spectrum of compound **4a**, appearance of peaks at δ 58.80, δ 143.71 and δ 121.24 due to methylene carbons, C-4 and C-5 carbon atoms of the triazole ring further corroborated the assigned structure. The mass spectrum of compound **4a** showed a peak at 817.1651 ($\text{M}+\text{H}$) $^+$ is in good agreement with the molecular formula of the synthesized compound. Similarly, analytical and spectral data of compounds (**4b** and **4c**) was laid in agreement to the assigned structure.



Scheme-I: Synthesis of target compounds **4a-c**: Reagents and conditions: (i) propargyl alcohol, N,N-dimethyl amino pyridine. (ii) Phenyl azides (**3a-3c**), cuprous iodide nanoparticles catalyst and water (10 mL), 80 °C

The ion recognition properties of synthesized receptor (**4a**) were investigated by UV-visible studies in DMSO/CH₃CN (1:9 v/v) solvent system. The binding interactions of receptor **4a** were investigated upon addition of perchlorates of different ions such as Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺ and Ni²⁺ to standard solution of receptor **4a**. However, a marked shift in absorption spectrum of receptor **4a** was observed upon addition of lead perchlorate as shown in Fig. 1. The absorption spectrum of receptor **4a** in the presence of Pb²⁺ ions was almost unaffected by the presence of other competing metal ions. The addition of Pb²⁺ ions to a solution of receptor **4a** led to gradually decrease in the intensity at 310 nm and appearance of new absorption band at 262 nm. The observed blue shift indicated that Pb²⁺ ion interact with carbonyl oxygen atom and nitrogen atom of triazole moiety of receptor **4a**. These results were consistent with the observation from the various triazole based chemosensors reported in literature [34-36].

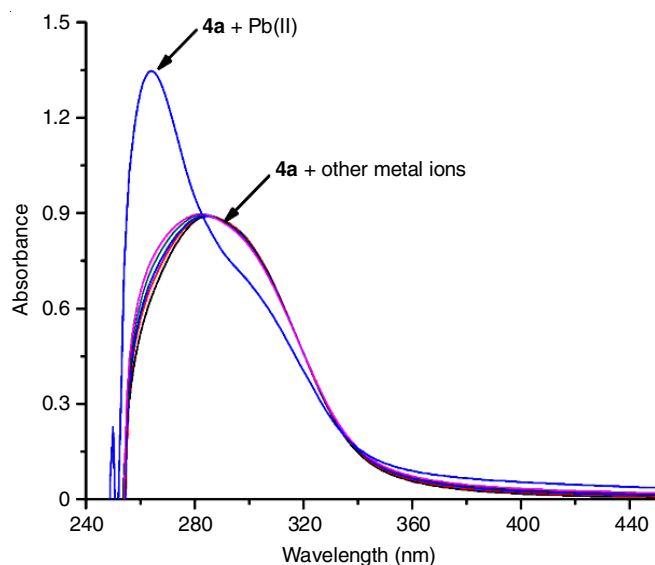


Fig. 1. Absorption spectra of **4a** (12 μM) upon addition of various ions as Cu²⁺, Zn²⁺, Ca²⁺, Co²⁺, Cd²⁺, Hg²⁺, Pb²⁺, Ni²⁺ in DMSO/CH₃CN (1.0:9.0 v/v)

The UV-visible binding interaction of receptor **4a** and Pb²⁺ ions were investigated by monitoring absorption changes upon gradual addition of lead perchlorate to a solution of receptor **4a** in DMSO-CH₃CN (1.0:9.0 v/v) solvent system. The UV-

visible titration experiments show upon addition of Pb²⁺ ions to 12.0 μM solution of receptor **4a** leads to step-wise decrease of 310 nm peak with appearance of new peak at 262 nm which reached its limiting value on addition of 1.0 equivalent of Pb²⁺ ions as shown in Fig. 2. In addition to this, appearance of a well defined isosbestic point at 344 nm in UV-visible spectrum attributed the formation of single reactive intermediate between the receptor **4a** and Pb²⁺ ion in equilibrium and thus formation of 1:1 complex between receptor **4a** and Pb²⁺ ion.

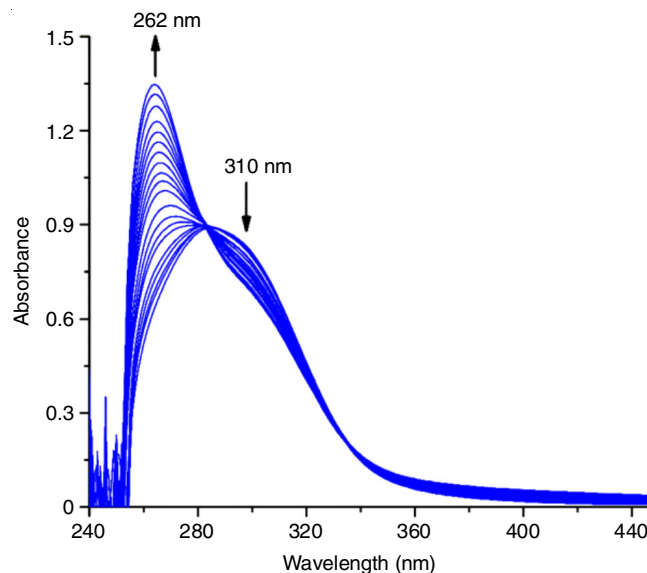


Fig. 2. Absorption titration spectra of **4a** (12 μM) with gradual addition of Pb²⁺ ions in DMSO-CH₃CN(1.0:9.0 v/v) solution

To find out stoichiometry of the complex between receptor **4a** and Pb²⁺ ion, an isomolar concentration of receptor **4a** and Pb²⁺ ion was made and the absorbance change at 262 nm was monitored spectrophotometrically (Job's continuous variation plots) as shown in Fig. 3. Quantitative analysis through Job's continuous variation plot exhibit a inflection point for Pb²⁺ ion at the mole fraction of 0.5, thereby suggesting the formation of 1:1 complex between receptor **4a** and Pb²⁺ ion.

As indicated from the Benesi-Hildebrand plot of measured absorbance [1/(A-A₀)] versus 1/[Pb²⁺] a linear correlation (R² = 0.99457) exists between measured absorbance [1/(A-A₀)] versus 1/[Pb²⁺]. These results are also consistent with a 1:1 association stoichiometry between host **4a** and guest Pb²⁺ ion

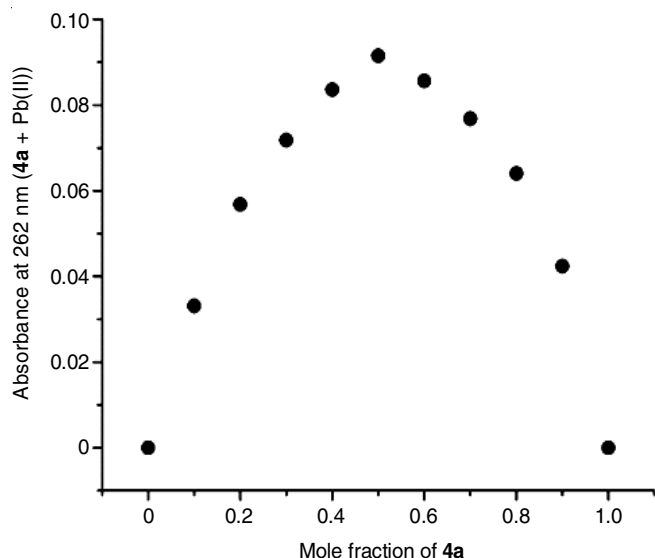


Fig. 3. Job's plot of **4a** with Pb^{2+} ion at 262 nm determined by UV-visible experiments in DMSO- CH_3CN (1.0:9.0 v/v) solvent system

(Fig. 4). Moreover, the binding constant (K_f) of **4a**- Pb^{2+} , determined from increasing intensity at 262 nm was found to be $5.5 \times 10^5 \text{ M}^{-1}$ using Benesi-Hildebrand plot. Furthermore, detection limit of triazole **4a** for the detection of Pb^{2+} ions was found to be $2.89 \times 10^{-6} \text{ M}$. The detection limit was calculated from the equation $\text{LOD} = 3\alpha/S$. Here, α means the standard deviation of blank measurements and S means the slope of calibration curve of UV-visible titrations.

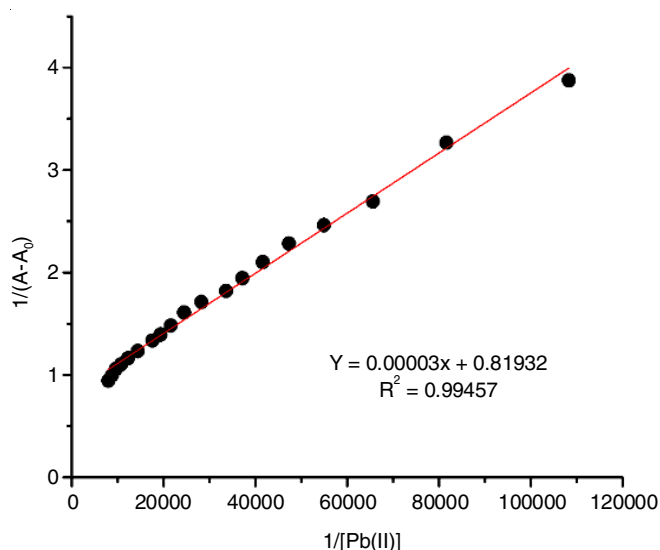
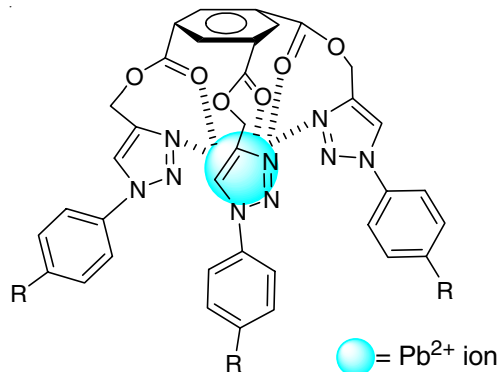


Fig. 4. Benesi-Hildebrand graph of absorbance $[1/(A-A_0)]$ at 262 nm versus $1/[\text{Pb}^{2+}]$

Similarly, the sensing behaviour of receptors **4b** and **4c** ($R = \text{H}$ and $R = \text{CH}_3$) was investigated for different ions such as Cu^{2+} , Zn^{2+} , Ca^{2+} , Co^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} and Ni^{2+} by comparing their UV-visible absorption spectra after and before the addition of these ions. It has been observed that receptors **4b** and **4c** exhibited little or no shift in absorption band after the addition of these ions. A possible binding model for receptor **4a**- Pb^{2+} complex is shown in **Scheme-II**, which is being explored further with the help of computational and spectroscopic methods.



Scheme-II: Possible binding model of **4a** with Pb^{2+} ion

Conclusion

In conclusion, we have synthesized some triazole based chemosensor molecules (**4a-c**) via copper(I)-catalyzed alkyne-azide cycloaddition reaction. The UV-visible titration studies revealed that compound **4a** selectively sense Pb^{2+} ions in preference to Cu^{2+} , Zn^{2+} , Ca^{2+} , Co^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} and Ni^{2+} ions. The Job's continuous variation plots and Benesi-Hildebrand plot suggested 1:1 binding stoichiometry between compound **4a** and Pb^{2+} ion with a detection limit of $2.89 \times 10^{-6} \text{ M}$.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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