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Identification of a novel click-derived 1,2,3-triazole as selective Hg²⁺ ion detector: computational and experimental investigations

Rabail Ujan¹ · Nasima Arshad² · Fouzia Perveen³ · Pervaiz Ali Channar⁴ · Bhajan Lal⁵ · Mumtaz Hussain⁶ · Zahid Hussain⁶ · Aamer Saeed⁴ · Syeda Aaliya Shehzadi⁷

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Abstract

A new triazole-substituted compound (7), namely {5-((2-methyl-4-(3-methyl-4-(prop-2-ynyloxy) benzyl) phenoxy) methyl)-1-(3-(nitrophenoxy) propyl)-1h-1, 2, 3-triazole}, was synthesized through the coupling of azido and propargylated precursors via click approach using 1,3-dipolar cycloaddition reaction. This compound was further explored for its selectivity and sensitivity toward mercury (Hg²⁺) ions detection. Quantum chemical DFT calculations were performed to examine the adsorption of Hg(OOCCH₃)₂ on the surface of compound 7. The charge distributions before and after adsorption showed charge transfer from 7 to Hg(OOCCH₃)₂ which indicated that 7 was sensitive to Hg(OOCCH₃)₂ molecule for Hg⁺² detection. The lowing in energy gap (ΔE), higher electrical conductivity and increased density of states (DOS) after Hg(OOCCH₃)₂ adsorption further depicted the potential of 7 as a chemical sensor for Hg⁺² sensing. The photophysical potential of compound (7) was examined by employing a range of cations (Ba²⁺, Ca²⁺, Co²⁺, Hg²⁺, K⁺, Mg²⁺, Mn²⁺, Na⁺, NH⁴⁺ and Pd²⁺). A significant hyperchromic shift in compound 7 spectrum (UV/ and fluorescence) upon equimolar addition of Hg²⁺ ions indicated that the triazole-based compound (7) has exhibited selective interaction with Hg²⁺ ion in preference to other cations. The maximum chelation of compound (7) with Hg²⁺ was observed at *p*H 5.1 (slightly acidic medium). The compound (7) capability to recognize Hg²⁺ was observed even at 0.1 μ M detectable limit, indicating greater sensitivity of 7 toward Hg²⁺. No significant effect of competitive metal ions on 7 – Hg²⁺ complex further authenticated robust selectivity and sensitivity of 7 toward sensing Hg²⁺ ions. Binding mechanism indicated the formation of 2:1 complex of 7 - Hg²⁺. DFT and spectral findings complimented each other and proving the promising chemosensor candidacy of the compound 7 for Hg²⁺ ions.

Graphic abstract



Keywords Click-derived 1,2,3-triazole \cdot Chemosensor \cdot Selective Hg²⁺ detection \cdot Computational DFT studies \cdot Spectroscopic studies

🖂 Nasima Arshad

nasimaa2006@yahoo.com; nasima.arshad@aiou.edu.pk

Extended author information available on the last page of the article

Introduction

Heavy metals, especially mercury, lead, cadmium and arsenic (Hg, Pb, Cd, As), are very toxic to human health as well as the foremost threat to both terrestrial and aquatic life and hence always remain major concern in environmental and chemistry fields (Ali et al. 2019). Among all heavy metals, Hg is considered the most harmful and its accumulation within human and animal bodies may severely damage heart, brain, kidney and other important organs (Li et al. 2012). Methylmercury, the metabolized form of Hg²⁺ by aquatic microbes, has been reported to cause serious problems for human health and ecology (EPA Fact Sheet 2001). In many developing countries, including Pakistan, mercury concentration in drinking water has been detected above the permissible limit as recommended by US-EPA (Arshad and Imran 2017).

Development of chemical sensors is comparatively more recent, but it has proven to be most efficient and effective among other modern sensor technologies. Due to substantial sensitivity, selectivity, small size, dynamic range, easy measurement and low cost, chemical sensors have gained parallel attention to be used in environmental, industrial and medicinal monitoring and in defense/ public security as well (Wen 2016). As for as environmental issues are concerned, sensing and detection of heavy metals and other environmental toxins are one of the emerging strategies to explore new synthetic compounds as chemical sensors (Lvova 2020; Shabir et al. 2017). Spectroscopic, electrochemical, HPLC (high-performance liquid chromatography) and ICP-MS (inductively coupled plasma mass spectrometry) are the most employed and rapid techniques for chemical sensing and quantification of toxic metal ions including Hg ions (Suvarapu and Baek 2017).

Click chemistry is a newer approach of synthesis and has been frequently employed to disclose click-derived chemosensors. These chemosensors are categorized by their detection mechanism along with structural features. In click chemistry, Cu(I)-catalyzed azide–alkyne cycloaddition is the most efficient and reliable reaction of binding two molecular building blocks. A wide range of chemical sensors contain click-derived triazoles, and their sensing ability is attributed to the recognition of both cations and anions (Lau et al. 2011).

Among triazole family, 1,2,3-triazole moiety has provided an upfront molecular linking approach implemented in various synthetic applications. 1,2,3-Triazole-based chemosensors, being simpler in synthesis with high sensitivity, have become the most important structural motif among various click-derived triazoles in chemical sensing field. The 1,2,3-triazole framework obtained by the click reaction has been utilized as binding sites for metal ions and anions (Chang et al. 2007; Hung et al. 2009a, b; Shehzadi et al. 2018). 1,2,3-Triazole-modified calix[4] crowns as binding sites for alkali/transition metal ions (Zhan et al. 2009), 1,2,3-triazole ring-appended chemosensor joined by anthraquinone and bis(2-azidoethoxy) ethane for the selective optical/electrochemical detection of Al³⁺ ions (Kim et al. 2010), hexapodal triazole, linked to a cyclophosphazene core rhodamine-based chemosensor for the selective determination of Hg^{2+} ions (Ozay et al. 2014), a reversible turn-off fluorescence chemosensor based on 2,7-bis(1,2,3-triazol-4-yl)methoxy)naphthalene for selective detection of Fe^{3+} ions (Singh et al. 2018), a 1,2,3-triazole-based thiosemicarbazide as a fluorescence chemodosimeter for Hg^{2+} ion detection (Lin et al. 2015) are the examples from some reported literature on triazolederived chemsensors for metal ion detection. There are many other reports on selective metal ion detections using 1,2,3-triazole-based chemosensors (Lau et al. 2011; Hrishikesan et al. 2011; Shi et al. (2013; Hung et al. 2009a, b). The structures of some representative bis 1,2,3-triazole chemosensors for detection of metal ions are given in Fig. 1 (Jabeen et al. 2016).

In the current study, we report the successful click synthesis of a new 1,2,3-triazole-substituted compound. This compound was further investigated computationally and experimentally for its sensitivity and selectivity toward Hg^{2+} ion detection.

Experimental

Apparatus, reagents and chemicals

Analytical grade chemicals, regents and solvents were used in experimental work, and all commercial products were purchased from Sigma-Aldrich. Compounds' synthesis was carried out by following the literature (Zhang et al. 2005). Column chromatography was performed with silica gel 60 from Fluka (0.043–0.06 mm) while thin layer chromatography (TLC) was carried out on 0.25 mm pre-coated glass plates (silica gel 60 F254, Merck AG, Darmstadt, Germany). Metal solutions were prepared from their respective salts. Deionized water (0.05 micro siemens) was obtained from HEJ analytical laboratory and used throughout the experiments. ¹H NMR was recorded on a Bruker Avance 300 MHz instrument. Chemical shifts (δ) in ppm and coupling constant (J) values in Hertz (Hz) were calculated. EI-MS spectra were observed on JEOL JMS600 mass spectrometer. FT-IR spectra of compounds were recorded on VECTOR 22 (Bruker) while absorption and emission spectra were recorded on UV-visible (Shimadzu 1800) and fluorescence (F-7000; Model FL2133-007) spectrophotometers, respectively, and the quartz cells used in these experiments were **Fig. 1** Some representative *bis* 1,2,3-triazole chemosensors for detection of metal ions (Jabeen et al. 2016)



of 1 cm path length. In fluorescence spectrophotometer, the instrumental parameters used were wavelength scan, emission scan mode, 2400 nm/s scan speed, 0.0 s time delay, 400 V PMT voltage, 0.5 s response time, 5.0 nm each EX-slit and EM slit, 200.0 nm EM start wavelength and 900 nm EM end wavelength.

Synthesis of 1-(3-Azidopropoxy)-3-Nitrobenzene (5)



Compound 2 was synthesized by dissolving of 3-nitrophenol (100 mg, 0.64 mmol) (1) in 10 ml acetone. After formation of clear solution, potassium carbonate (134 mg, 1.5 mmol) was added and stirred for 1 h at 55 °C. Then 1,3-dibromopropane (0.13 ml, 2 mmol) was added followed by heating to reflux for 5 h. After completion of reaction, 20 ml water and dichloromethane were added to separate the organic and aqueous phase. The organic phase was collected, dried and filtered, and solvent was removed through rotary evaporator to give 1-(3-bromopropoxy)-3-nitrobenzene (2) as transparent liquid. Without further purification 2 was treated with excess of NaN₃ in DMF for 2 h at room temperature. After

completion of reaction, DMF was removed by freeze drying and 1-(3-azidopropoxy)-3-nitrobenzene (5) was purified by column chromatography using hexane and dichloromethane (8:2, v/v) as eluent.

Characterization data

Yield: 60%; R_f Value: 0.8 cm; 3187 (SP² C-H stretching), 2959 (SP³ C–H stretching), 2105 (C–N), 1570, 1434 (C=C aromatic), 1153 (C–O); ELMS: m/z 224 (M⁺:C₉H₁₀N₄O₃, calc. 222), m/z 180 (C₉H₁₀NO₃), m/z 152 (C₇H₆NO₃), m/z139 (C₆H₄NO₃); ¹H NMR (300 MHz, CDCl₃): δ 7.81 (d, 1H, J=8.1 Hz, Ar–<u>H</u>), 7.71 (t, 1H, J=4 Hz, Ar–<u>H</u>), 7.41 (t, 1H, J=7.438–7.384 Hz, Ar–<u>H</u>), 7.21 (dd, 1H, J=2.1, 1.8 Hz, Ar–<u>H</u>), 4.19 (t, 2H, J=7.2 Hz, PhOCH₂CH₂), 3.59 (t, 2H, J=6.3 Hz, PhOCH₂CH₂CH₂Br), 2.37 (m, 2H, PhOCH₂CH₂CH₂Br).

Synthesis of Bis(3-Methyl-4-(Prop-2-Yn-1-Yloxy) Phenyl)Methane (6)



100 mg (0.44 mmol) 4,4'-methylene *bis*(2-methylphenol) (4) was dissolved in 10 ml of ethanol and addition of 181 mg (3 mmol) K_2CO_3 . After stirring for 45 min at 60 °C, 0.15 ml

(4 mmol) of propargyl bromide (5) was added. The reaction mixture was heated to reflux for six hours. The reaction was monitored with TLC using hexane: DCM (2: 8, v/v)). The workup of final product was carried out in the mixture of dichloromethaneand water (1:1, v/v). Dichloromethane was evaporated through rotary, followed by silica gel column chromatography to give 6 as white solid.

Characterization data

Yield: 90%; melting point: 55 °C; R_f Value: 0.73; IR (KBr): (PhOCH₂CCH = 3295 cm⁻¹), (PhOCH₂CCH = 2117 cm⁻¹), (PhOCH₂CCH = 1128 cm⁻¹). EI.MS: *m/z* 304 (M⁺ C₂₁H₂₀O₂, calc. 304.15), *m/z* 289 (C₂₀H₁₇O₂), *m/z* 265 (C₁₈H₁₇O₂), *m/z* 237 (C₁₆H₁₃O₂), *m/z* 225 (C₁₅H₁₃O₂) ¹H NMR (300 MHz, CDCl₃): δ 6.95 (dd, 2H *J* = 9, 6.5 Hz, Ar–H), 6.8 (d, 2H *J* = 6.5 Hz, Ar–H), 4.65 (d, 4H *J* = 2.1 Hz PhOCH₂CCH), 3.78 (s, 2H PhCH₂Ph), 2.46 (t, 2H *J*=2.1 Hz, PhOCH₂CCH), 2.21 (s, 6H, PhCH₃).

Synthesis of Target Compound 5-((2-Methyl-4-(3-Methyl-4-(Prop-2-Ynyloxy) Benzyl) Phenoxy) Methyl)-1-(3-(Nitrophenoxy) Propyl)-1H-1, 2, 3-Triazole (7)



100 mg (0.33 mmol) of *bis* (3-methyl-4-(prop-2-ynyloxy) phenyl)methane was dissolved in 10 ml DMF. After formation of clear solution, 60 mg (0.7 mmol) 1-(3-azidopropoxy)-3-nitrobenzene was added, with the addition of azide, copper sulfate pentahydrate and sodium ascorbate were added into the solution. The reaction was heated to reflux at 60 °C for12 hours. Color of reaction changed from green to brown. Reaction was monitored through TLC analysis. DMF was evaporated through freeze drying and filtered through filter paper. Dichloromethane is added in the reaction mixture, and filtration was performed. Solvent was evaporated and separated by silica gel column chromatography using hexane and ethyl acetate (4: 6, v/v).

Characterization data

Physical state: gummy solid; yield: 35%; R_f value: 0.7 cm; IR (KBr): (PhOCH₂CCH = 3297 cm⁻¹), (PhOCH₂CCH = 2117 cm⁻¹), (PhOCH₂CCH = 1130 cm⁻¹), (ArCH₂CN = 2453 cm⁻¹); EI.MS: *m/z* 526 (M⁺ C₃₀H₃₀N₄O₅, calc. 528), *m/z* 509 (C₃₀H₂₈N₄O₅), *m/z* 266 $(C_{18}H_{17}O_2)$, *m/z* 227 $(C_{15}H_{14}O_2)$; ¹H NMR (300 MHz, CDCl₃): δ 8.23 (s, 1H), 7.80 (d, 1H), 7.68 (s, 1H), 7.50 (t, 1H, J = 8.2 Hz), 7.37 (dd, 1H J = 2.1 Hz), 7.00 (m, 6H), 5.08 (s, 2H), 4.73(d, 2H), 4.57 (t, 2H, J = 6.6 Hz), 4.10 (t, 2H, J = 5.7 Hz), 3.71 (s, 2H), 3.50 (s, 1H), 2.33 (m, 2H), 2.08 (d, 6H, J = 12.9 Hz).

Computational analysis

Computational studies were performed using DFT by SCM-ADF modeling suite 2018. Optimization, molecular orbital calculations, density of state calculations and adsorption of Hg(OOCCH₃)₂ on compound 7 were investigated using (LDA-GGA) due to Becke (Becke 1988) and Perdew (Perdew 1986). The double zeta (DZ) basis sets demonstrated the electron density consisting at good level of accuracy by keeping frozen core of nitrogen, carbon, oxygen and Hg atoms small. Scalar relativistic corrections were incorporated through the zeroth-order regular approximation (Nosheen et al. 2020). Presently, PW91 functional was implemented to determine energetic and electron transfer due to adsorption of $Hg(OOCCH_3)_2$ on 7. Optimized geometries and adsorption energies were based on equilibrium geometry calculations. The adsorption energies were calculated by following equation.

$$\Delta E_{\rm ads} = E_{\rm complex} - (E_1 + E_2)$$

Here, E_{complex} refers to the energy of the Hg(OOCCH₃)₂ on 7, and E_1 and E_2 refer to the energy of optimized compound 7 and Hg(OOCCH₃)₂, respectively. ΔE_{ads} refers to adsorption energy of the system.

General procedure for spectroscopic measurements

Initially, one millimolar stock solution of 7 was prepared in DMSO and DMF, separately, and spectrum was recorded, individually. The target compound 7 showed good result in DMF than DMSO; hence further work was proceeded with the solution of 7 in DMF. Stock solutions of all metals in one millimolar concentration were prepared in deionized water. The absorption and emission spectra of compound 7 in the presence of metal ions were recorded using equimolar concentrations (0.5 µM each) in DMF/H₂O (1:1, v/v ratio). The mixing of 7 and metal ions was done within the cuvette, and each spectrum was recorded after 5 min. For Hg^{2+} ion detection, 0.1–1000 μ M concentrations of Hg^{2+} were added, separately, into 0.5 µM solution of 7, stirred, stay for five minutes, and then analyzed through spectrophotometer. The rest of the other titrations and experiments were performed according to the same conditions.

Results and discussion

Chemistry

The synthesis of target compound 7 was achieved according to Scheme 1, (Jabeen et al. 2016). Initially, 3-nitrophenol (1) was reacted in refluxing acetone with 1,3-dibromopropane in the presence of K_2CO_3 as base to achieve compound 2 which on further treatment with NaN₃ produced 1-(3-azidopropoxy)-3-nitrobenzene (5). In another reaction, compound (4), namely 4,4'-methylenebis(2-methylphenol), was treated with propargyl bromide in refluxing acetone to prepare compound (6). In final step, the Cu(I)-catalyzed cycloaddition of (5) with *bis*(3-methyl-4-(prop-2-yn-1yloxy)phenyl)methane (6) yielded the target compound 7 in 86% yield after column chromatographic purification.

The structures of synthesized starting compounds 5, 6 and target compound 7 were confirmed via spectroscopic techniques. The EI-MS of compound 2 showed the molecular ion peak at 261 Da (Fig. S2), while ¹H-NMR spectrum showed three peaks in aromatic region comprising four aromatic protons. The two triplets at 3.5 ppm and 4.1 ppm were assigned to N₃CH₂ and –OCH₂ protons, respectively (Fig. S3). The molecular ion peak of bis (5-methyl-2-(prop-2-ynyloxy) phenyl) (6) was observed at 304 Da in the EImass spectrum (Fig. S4). Further structural confirmation was observed by ¹H-NMR spectrum where a doublet at 4.6 ppm was assigned for CH₂ protons of propargyl group. The CH₂ group between two phenyl rings resonated at 3.7 ppm as singlet, while acetylenic proton appeared at 2.4 as triplet due to coupling with propargylic CH₂ group (Fig. S5). The structural confirmation of final compound 7 was also performed by both MS and NMR. The molecular mass of the compound 7 was deduced from EI-MS spectrum showing a quite intense molecular ion peak at 526 Da (Fig. S6). The successful ring closure to form 1,2,3-triazole was confirmed by ¹H-NMR spectrum showing a singlet of CH of triazole ring in the downfield region at 8.2 ppm. The other aromatic protons appeared in the region of 7.8–6.8 ppm (Fig. S7).

Computational studies on compound 7 for Hg²⁺ ion detection

Firstly, single-point energy (SPE) was assessed to find the correct spin multiplicities (SMs) for the compound 7 and Hg(OOCCH₃)₂. After that, 7 and Hg(OOCCH₃)₂ molecule were optimized geometrically using equilibrium geometry calculations. The total charge of $Hg(OOCCH_3)_2$ molecule was taken as zero to assign equilibrium geometry that has a singlet multiplicity (SM). In order to determine the stable configuration, the Hg(OOCCH₃)₂ molecule was placed above the 7. To understand the energetic behavior of the Hg(OOCCH₃)₂ adsorption, adsorption energies were calculated and are presented in Table 1. The adsorption energy, (ΔE_{ads}) , for 7 - Hg(OOCCH₃)₂ complex was computed as -6.09 eV which revealed that adsorption Hg(OOCCH₃)₂ on 7 was exothermic and indicated effective sensing of $Hg(OOCCH_3)_2$ molecule. The O-Hg and C=O bond lengths of adsorbed Hg(OOCCH₃)₂ molecule were calculated to be 2.75 Å and 1.63 Å when adsorbed on 7 structure, these values being larger than respective bond lengths of free $Hg(OOCCH_3)_2$ molecule revealing that mercury acetate has been effectively sensed and detected by 7. The distances between O-Hg and C=O for Hg(OOCCH₃)₂ molecule were computed as 2.21 Å and 1.25 Å, respectively, before adsorption. Similarly, plane of encircled ring of compounds 7 was tilted by an angle 78.910 after adsorption of Hg(OOCCH₃)₂ which showed effective sensing of mercury by 7.



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		Compound 7	Hg(OOCCH ₃) ₂	Complex [7 - Hg(OOCCH ₃) ₂]
Bond lengths	B.L	_	O–Hg = 2.21 Å C=O = 1.25 Å	O–Hg = 2.75 Å C=O = 1.63 Å
Energies/eV	E	$E_1 = -400.91$	$E_2 = -189.0$	$E_{complex} = -596.00$
Adsorption energies /eV	$\Delta E_{ m ads}$	-	-	-6.09
MO's	$E_{\rm HOMO}$	-6.02		-1.04
	$E_{\text{HOMO-1}}$	-6.23		-2.74
	$E_{\rm LUMO}$	- 5.25		-0.62
	$E_{\text{LUMO+1}}$	-3.70		-0.30
	$\Delta E_{\text{HOMO-LUMO}}$	0.77		0.417
	$\Delta E_{\mathrm{HOMO-1-LUMO+1}}$	2.53		2.44

Table 1 Geometric and electronic parameters of the optimized compound 7 and its complex with $(Hg(OOCCH_3)_2 \text{ calculated by using DFT at PW91 functional and DZ basis set}$

Additionally, the structural variation and Mullikan charges analysis of atoms of 7 before and after adsorption of Hg(OOCCH₃)₂ are shown in Fig. 2. Flipping of circled moiety at angle of 45°, while the charge distribution, i.e., -0.186 on O atom before adsorption and -0.144 on this atom after adsorption, indicated that charge transfer from 7 to Hg(OOCCH₃)₂ took place during process of chemical sensing, as shown in Fig. 2.

The molecular orbital (HOMO and LUMO) representations for 7 before and after Hg(OOCCH₃)₂ adsorption are represented in Fig. 3. It is apparent from the data in Table 1 and from Fig. 3 that the HOMO–LUMO gap decreased from 0.77 eV to 0.417 eV after adsorption. The decrease in ΔE value after adsorption of Hg(OOCCH₃)₂ on compound 7 revealed enhanced electrical conductivity according to following equation (Bhuvaneswari et al. 2018).

$$\sigma = AT^{3/2} \exp\left(\frac{-E_g}{2kT}\right)$$

where σ is the electrical conductivity, *A* is the constant, ΔE is energy gap, *k* is the Boltzmann's constant and *T* is the temperature. The increased electrical conductivity of the structure after adsorption is demonstrated that compound 7 could be considered a potential sensor for Hg(OOCCH₃)₂ detection. The distribution of isodensities on 7 also changed after adsorption of Hg(OOCCH₃)₂, as obvious from Fig. 3. For HOMO and LUMO orbitals, isodensities on compound 7 were shifted close to Hg(OOCCH₃)₂ highlighting the regions of compound 7 involved in sensing mercury acetate. Shifting of isodensities toward Hg(OOCCH₃)₂ revealed that aniline part of compound 7 is involved in sensing Hg(OOCCH₃)₂.

It is apparent from Fig. 3 that before adsorption HOMO densities were concentrated on six-membered benzene ring structure along ether linkage and LUMO isodensities were concentrated on nitrobenzene ring. However, after adsorption of Hg(OOCCH₃)₂, HOMO isodensities were shifted to nitrobenzene of compound 7 and LUMO isodensities were shifted on Hg(OOCCH₃)₂ depictive of the fact that 7 acted as donor and Hg(OOCCH₃)₂ performed as acceptor for electric charge. For HOMO-1, a decrease was observed in orbital densities distribution on 7, whereas LUMO + 1 was concentrated on same position before and after adsorption. Hence, according to HOMO, LUMO, HOMO-1 and LUMO + 1 isodensities distributions compound 7 acted as donor and Hg(OOCCH₃)₂ was considered to be acceptor.

Another important electronic descriptor calculated was the density of states (DOS) which is fundamentally the number of different electronic states at a particular energy level that electrons are allowed to occupy (Yong et al. 2016). The density of states (DOS) plots for optimized structure of 7 before and after Hg(OOCCH₃)₂ adsorption are represented in Fig. 4. The most significant application of the DOS plots is to prepare a demonstration of molecular orbitals, the bonding, anti-bonding or non-bonding nature of the orbitals and their interactions (Yong et al. 2016). The region of the curves on lower negative side indicated LUMOs and on greater negative side showed HOMOs, as shown in Fig. 4.

Comparison of the graphs before and after adsorption showed that intensity of DOS on LUMOs side increased due to electron density transfer from HOMO of 7 to the LUMO of complex of 7 with Hg(OOCCH₃)₂; as a result, population of LUMOs was increased. Figure 4 demonstrates that there was appearance of one more state at 4.7 eV due to which HOMO-LUMO was decreased. This decrease was responsible for increase in electrical conductivity. After adsorption, smoothness in the DOS peaks indicated that electron transfer process became gradual which played important role in electrical conductivity change.



Fig. 2 Optimized structure and Mullikan charge distributions of (top) compound 7 and (bottom) $Hg(OOCCH_3)_2$ adsorbed on 7 calculated at LDA-GAA level theory and PW91 functional

Selective detection of Hg²⁺ lon by UV and fluorescence spectroscopy

Selective recognition property of receptor 7 toward various metals ions such as Bi³⁺, K⁺, Yb³⁺, Na⁺, Sn²⁺, Ba²⁺, Rb²⁺, Zn²⁺ and Hg²⁺ has been studied. Initially, absorption spectrum of 7 was recorded and a broadband with maxima at $\approx 275-285$ nm was observed, as shown in Fig. 5. The broader peak may be attributed to various n – π^* and $\pi - \pi^*$ transitions (Shabir et al. 2017). Then absorption spectra of 7 have been recorded in the presence of each metal ions, separately, and shown in Fig. 5 (only shown for 7 - Hg^{2+} complex). A significant rise in the absorption peak intensity of 7 (0.5 µM) was observed in the presence of equimolar concentration of Hg^{2+} ions. The percent hyperchromism was evaluated to be 50% which indicated interaction of compound 7 toward Hg^{+2} . Similar experiments were performed with other metals, but no significant changes in absorption intensity were observed in compound 7 spectrum as observed with Hg^{+2} ions. These results pointed toward selectivity of compound 7 toward Hg^{+2} ions.



Fig. 3 Schematic molecular orbital (MO) diagram of (Left) compound 7 (Right) compound 7 with adsorbed Hg(OOCCH₃)₂ showing HOMO, LUMO and HOMO–LUMO energy gap (ΔE)



Fig. 4 The density of states (DOS) **a** for optimized structure of (Left) compound 7 (Right) compound 7 with adsorbed $Hg(OOCCH_3)_2$ calculated at LDA-GGA level of theory

To further authenticate the DFT and UV findings for the selectivity of targeted compound (7) toward Hg^{+2} ions, fluorescence study was conducted because the compound 7 showed fluorescence in UV region. The excitation spectrum was conducted by scanning the wavelength from 200 to 500 nm and maximum emission was observed for the compound 7 at wavelength 275 nm with excitation wavelength of 250 nm. By using the selected excitation wavelength, then emission spectrum was taken in the presence and absence of various metal ions, as shown in Fig. 6.



Fig. 5 Absorption spectra of compound 7 only and 7 - Hg^{2+}



Fig. 6 Fluorescence spectra of receptor 7 without and in the presence of metal ions

Upon addition of one equivalent of each metal ions into the receptor 7, separately, only Hg^{2+} displayed a significant enhancement in excitation intensity at 275 nm, whereas other tested metal ions did not induce such substantial changes in the fluorescence intensity of sensor 7. The changes in emission spectrum of 7 in the presence of other metal ions are less significant and indicated that receptor 7 exhibits a higher selective response toward the Hg^{2+} ion over the other tested metal ions. The reason for metal ion chelation of compound 7 could be attributed to the presence of lone pair of electrons on the nitrogen atom of triazole group. Nitrogen, being its high electronegativity, may drag the electrons toward itself and enhances the electron density on the ring and hence may resulted in covalent bond formation with metal ions.

Concentration study

Furthermore, the recognition limit of compound 7 for Hg^{+2} ion was explored through concentration study. The fluorescence titration of receptor 7 with Hg^{2+} was carried out, and spectra were taken under parallel experimental conditions



Fig. 7 Fluorescence spectra of receptor 7 with increasing concentration of Hg^{2+} ion



Fig. 8 Effect of pH on emission spectra of compound 7

by varying the concentration of mercury from 0.1 μ M to 1000 μ M; meanwhile, the concentration of compound 7 was kept constant, as shown in Fig. 7. It is clear from Fig. 7 that even at lowest Hg²⁺ concentration (0.1 μ M) the fluorescence intensity of 7 has significant value. However, an increase in fluorescence intensity could be observed with increasing Hg²⁺ concentrations. These results clearly demonstrate that receptor 7 shows higher selective and sensitive binding capability toward Hg²⁺ as detectable changes in the intensity have been observed even with 0.1 μ M concentration of Hg²⁺ ions. The limit of detection was calculated to be 0.06 μ M by using slope of the straight-line equation by applying the formula: LOD=3.3×S.D/ slope.

Effect of pH

The effect of *p*H on binding ability of ligand 7 with Hg^{2+} ion was investigated in DMF, as shown in Fig. 8. The variations in *p*H were induced by addition of hydrochloric acid and sodium hydroxide while the concentration of compound 7 was kept constant at 0.5 μ M. An increase in fluorescence

intensity was observed when *p*H was increased from 1.7 to 5.1. Maximum intensity was observed at pH 5.1, while, by increasing *p*H above 8.0, a pronounced drop in the peak intensity was observed. Maximum rise in fluorescence intensity of 7 - Hg²⁺ adduct till slightly acidic pH (5.1) and then quenching in the fluorescence intensity in basic pH (8.0–11) showed that compound can display maximum binding in acidic media compared to basic one. Supramolecular complex formation between ligand and metal ions is highly dependent on the pH of the medium. The maximum enhancement in absorption intensity of sensor 7 upon interaction with Hg²⁺ was recorded at pH 5.1 while in high



Fig.9 Fluorescence emission response of 7-Hg complex (0.5 μ M) in the presence of one equivalent of various metal ions in 0.05 M in DMF solution at pH 5.1



Fig. 10 ¹H-NMR spectrum of 7 and 7 - Hg²⁺ complex

acidic or basic medium the increases in absorption intensity are lower as compared to neural pH medium. This change in absorption intensity of compound 7-Hg²⁺ complex is possibly due to protonation and deprotonation process which destabilized the complex formation.

Study of Interference of Other Metals on 7 – Hg^{2+} Complex

The selectivity of a chemosensor for a particular analyte is an important parameter in practical applications. To further verify the high selectivity of receptor 7 as a responsive sensor for Hg^{2+} , competitive experiments were performed by screening the addition of various interfering metal ions (such as Ba^{+2} , Bi^{+3} , Zn^{+2} , Yb^{+2} , Co^{+2} , Cu^{+2} , Fe^{+2} , K^{+1} , Na^{+1} , NH_4^{+1} , Ni^{+2} , Pb^{+2} , Sb^{+3} and Sn^{+2}) to 7- Hg^{2+} solution The spectra have shown no significant effect on fluorescence emission of 7- Hg^{2+} complex in the presence of competitive metal ions, as shown in Fig. 9. These responses illustrate that receptor 7 displays robust selectivity and sensitivity toward sensing Hg^{2+} ions.

Binding mechanism

Further ¹H-NMR spectrum of 7 was recorded after the addition of Hg²⁺ ion and compared with individual ¹H-NMR spectrum of 7 to see the binding site and the binding mechanism of ligand to metal, as shown in Fig. 10. No significant shift in ppm value of protons was observed. The prominent peak of triazole was observed at 8.229 ppm without mercury,



and very small change has been observed with mercury in case of ¹H-NMR peak at 7.682 ppm. It revealed that might be middle nitrogen of triazole involved in the binding to the metal. However, when 0.5 equivalent of $Hg(OAc)_2$ was added, the absorption band was decreased significantly and hypochromic shift of the absorption spectra was observed (Fig. 10), showing the formation of dimer of ligand in the ground state. Based on this observation, a 2:1 complex formation was proposed with binding site being nitrogen of triazole ring and oxygen of 3-nitrophenyl ring.

Conclusions

A novel click-derived 1,2,3-triazole chemosensor (7) was synthesized and characterized by FT-IR, El-MS and by ¹H NMR and further studied for the selective detection of Hg²⁺ ions. Computational and experimental approaches were used to explore the chemical sensing capability of the compound 7 toward Hg²⁺ ions. Variation in structural and electronic characteristics of 7 based on adsorption energy values, bond distances and angles, Frontier molecular orbital demonstrations and DOS analysis was done by computational DFT calculations. Changes in the charges of Hg $(OOCCH_3)_2$ molecule after adsorption on 7 indicated that charge transfer was happened from 7 to Hg(OOCCH₃)₂ adsorbate, making Hg(OOCCH₃)₂ as electron acceptors. Theoretical findings, i.e., decrease in HOMO-LUMO gap, while enhancement in the electrical conductivity after adsorption, predicted 7 as prospective candidates for the detection of the Hg(OOCCH₃)₂ molecule. The optical/sensing properties of compound 7 were experimentally studied by UV-visible and fluorescence spectroscopy. The recognition ability and profile of compound 7 were screened for various cations like (Bi³⁺, K⁺, Yb³⁺, Na⁺, Sn²⁺, Ba²⁺, Rb²⁺, Zn²⁺, Fe³⁺, Ni²⁺, Pb^{3+} , Ba^{2+} , Cu^{2+} and Hg^{2+}) using their respective salts. All spectral findings revealed that compound 7 is highly selective and sensitive toward Hg²⁺ ions as compared to other ions. ¹H NMR spectrum taken for 7 - Hg²⁺ revealed the formation of 2:1 complex. In summary, theoretical and experimental findings indicated that the compound 7 has characteristics of good selectivity and sensitivity and could act as a promising chemosensor candidate for Hg^{2+} ion detection.

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Declarations

Conflict of interest Authors declare that there is no conflict of interest.

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Authors and Affiliations

Rabail Ujan¹ · Nasima Arshad² · Fouzia Perveen³ · Pervaiz Ali Channar⁴ · Bhajan Lal⁵ · Mumtaz Hussain⁶ · Zahid Hussain⁶ · Aamer Saeed⁴ · Syeda Aaliya Shehzadi⁷

- ¹ M. A. Kazi Institute of Chemistry, University of Sindh, Jamshoro 76080, Pakistan
- ² Department of Chemistry, Allama Iqbal Open University, Islamabad 44000, Pakistan
- ³ Research Center for Modeling and Simulations, National University of Sciences and Technology (NUST), Islamabad, Pakistan
- ⁴ Department of Chemistry, Quaid-I-Azam University, Islamabad 45320, Pakistan

- ⁵ Institute of Chemistry, Shah Abdul Latif University, Khairpur 66020, Pakistan
- ⁶ Department of Chemistry, University of Karachi, Karachi 75270, Pakistan
- ⁷ Sulaiman Bin Abdullah Aba Al-Khail-Centre for Interdisciplinary Research in Basic Sciences (SA-CIRBS), International Islamic University, Islamabad 44000, Pakistan