



# BINOL-furo fused based triazoles macromolecule synthesis via click chemistry and its applications for sensing silver ions

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## Abstract:

The furo fused BINOL based triazole macromolecules were developed via click chemistry reaction protocol. It was evaluated as a cation sensor. Among the metal ions screened, macromolecule **7** exhibited good binding ability to Ag<sup>+</sup> ion. The addition of Ag<sup>+</sup> ion caused selective turn-off type fluorescence alterations. Anthracene units act as a PET donor and triazole works as an electron acceptor when the Ag<sup>+</sup> ion is bound by two triazole nitrogen atoms in the receptor. The experiment revealed that macromolecule **7** acts as a molecular switch for detecting Ag<sup>+</sup> ions.

**Keywords:** Furo fused BINOL, triazole, click chemistry, cation sensor, fluorescence, quenching, Ag<sup>+</sup> ion.

## Introduction:

BINOL-based ligands became pioneer macromolecules in the field of metal cation sensors.<sup>1-8</sup> Heavy metal ions can cause considerable damage to the surrounding environment and human health, hence the synthesis of highly selective cation sensors is in high demand in many industries today, including environmental, biological, and waste management.<sup>9-12</sup> The development of selective fluorescence chemosensors for detecting the presence of heavy and transition metal (HTM) ions has attracted a lot of interest. The BINOL substituted triazole molecules are prominently synthesized by click reaction protocols.

Sharpless and co-workers<sup>13</sup> coined the term "Click" chemistry in 2001 to characterize a new synthetic organic chemistry technique that allows reactive molecular building blocks to join together efficiently. "Click Chemistry" refers to reactions that are high yielding, broad in scope, produce only by-products that can be eliminated without chromatography, are stereospecific, easy to carry out, and can be carried out in easily removable or benign solvents. Gill et al.,<sup>14</sup> Li et al.<sup>15</sup> Moses and Moorhouse<sup>16</sup> and Wu and Fokin<sup>17</sup> have examined the general synthetic value of click chemistry across the fields. The Cu (I) catalysed azide-alkyne cycloaddition (CuAAC) is mentioned in the reviews as being relevant in a number of disciplines, including as one of many helpful in 1,3-dipolar cycloaddition reactions<sup>18</sup> and in the conversion of acetylenes<sup>19</sup> and azide<sup>20</sup>. In several sectors of materials synthesis, the great efficiency of "Click" chemistry has become highly essential and visible. "Click" chemistry has proved notably successful in the production of 1,2,3-triazoles via 1,3-dipolar cycloaddition between azides and alkynes, as Huisgen<sup>21</sup> initially reported. Silver is one of the most common surface water pollutants. Silver salts are normally utilized in topical ointments for burn patients because of the truth in their antimicrobial properties.<sup>22</sup>

Overuse of silver-containing medicines has raised concerns about silver accumulation in the liver and tissues, as well as its negative influence on patients.<sup>23</sup> Silver has received a lot of attention for its harmful impact on the environment, especially on organisms, because of its numerous usage and large prospects in the industry. Silver ions have been shown to attach to carboxyl groups in metabolites and inactivate sulfhydryl enzymes.<sup>24,25</sup> Thus, maintaining in view the function performed through silver in everyday life, easy and speedy sensing of silver in organic and environmental structures may be very important. Many views consisting of atomic absorption, inductively coupled plasma-mass atomic emission, fluorescence, and UV-vis absorption spectroscopy had been broadly hired to quantify hint quantities of silver ions.<sup>26</sup> Among those methodologies, fluorescence signalling is turning into one of the first alternatives as it's far quite touchy and easy which interprets binding occasions into tangible fluorescence signals.<sup>27</sup>

The fluorescence methodology is superior to other analytical methods because most fluorescent sensors can be utilised as cellular imaging reagents. As a result, a lot of time and effort has gone into developing fluorescent sensors that can be used for a variety of purposes. Several photophysical methods can be used to provide visual parameters that can be connected to the concentration of the analyte. A considerable spectrum shift in either the absorption or emission spectra becomes highly critical for high sensitivity and simplicity. However, the achievement of fluorescence enhancement with spectral shift for detecting silver ions<sup>28</sup> has been constrained until now due to the fact silver ions normally quench fluorescence emission through electron switch and intersystem crossing processes.<sup>29</sup>

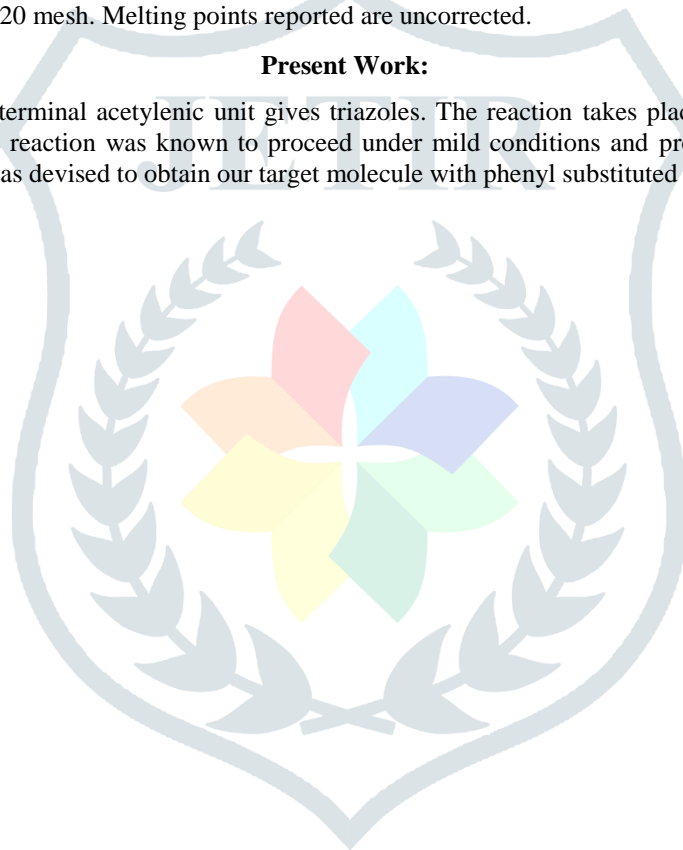
### **Experimental:**

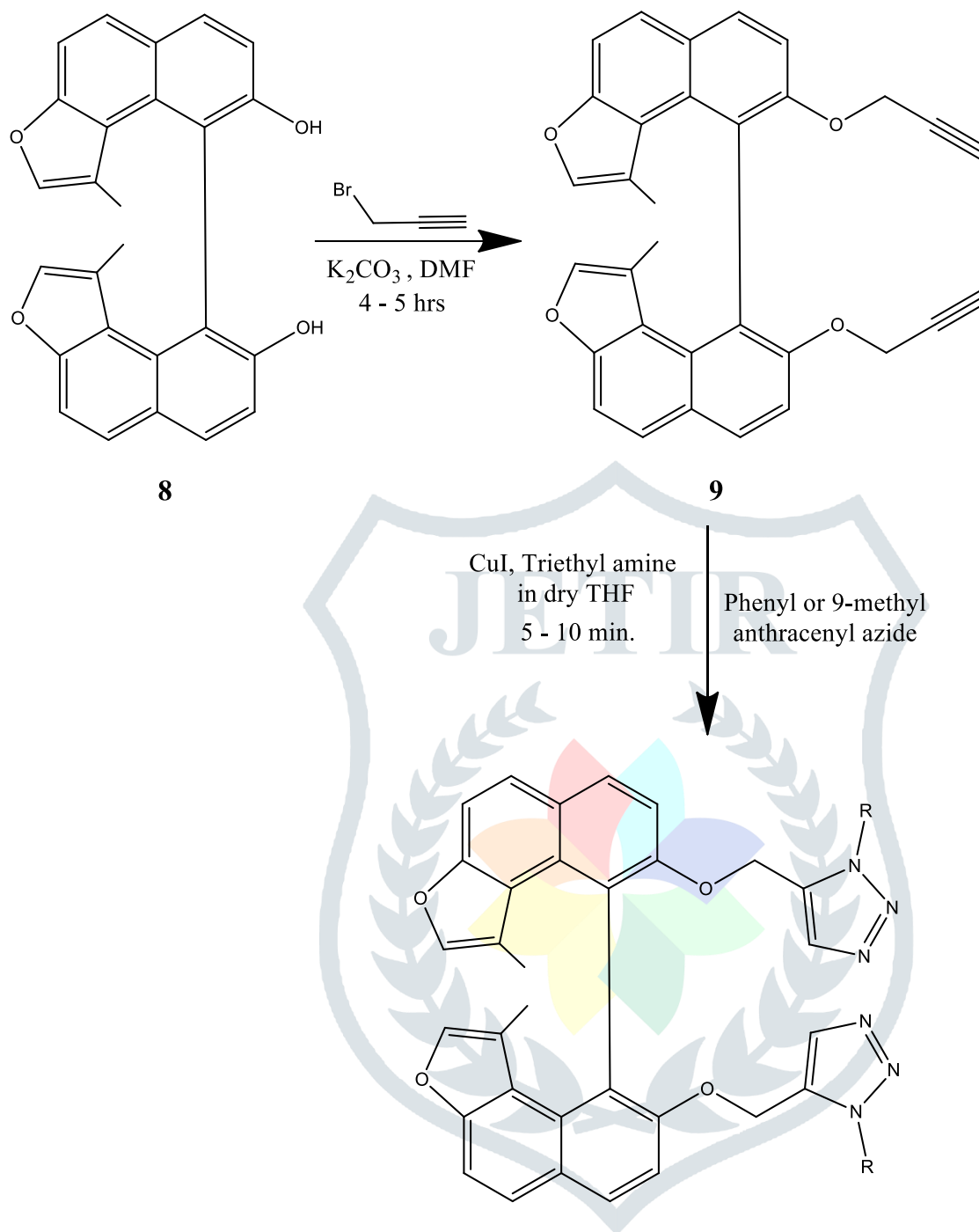
#### **Material and Instruments:**

The Spectral grade solvents were purchased from S. D. Fine Chemicals (India) and used as received. IR spectra were recorded on PERKIN ELMER FTIR Spectrometer and <sup>1</sup>H NMR spectra were recorded on 300 MHz Bruker, AV II 300 of 300 MHz, using TMS as internal standard. Chemical shifts were given in ppm relative to an internal reference for CDCl<sub>3</sub>. <sup>13</sup>C NMR spectra were recorded on 75 MHz Bruker, AV II 300 spectrometer. GC-MS spectrum was recorded on Thermo Finnigan LCQ DECA XP (Ion Trap). Reagents were of AR grade and used without further purification were purchased from Sigma-Aldrich. Column chromatography was performed on silica gel 60-120 mesh. Melting points reported are uncorrected.

#### **Present Work:**

The reaction of aryl azide with terminal acetylenic unit gives triazoles. The reaction takes place via a click chemistry pathway catalyzed by Cu(I) catalyst. The reaction was known to proceed under mild conditions and provide good yields. Based on this premise, the following scheme was devised to obtain our target molecule with phenyl substituted 1,2,3-triazole derivatized methyl-substituted furo-fused BINOL.





Where,

R = Phenyl (**6**) or 9-methyl anthracenyl (**7**) group

#### Synthesis of propargyl derivatives of methyl substituted furo-fused BINOL (9)

Methyl substituted furo-fused BINOL **8** (5.2mmol) and propargyl bromide (7.8mmol) were taken in dry DMF solvent (20ml) in presence of anhydrous potassium carbonate (5.2mmol) in a round bottom flask which was heated on the steam bath for 4-5 hours. The progress of the reaction was monitored by TLC. The reaction mixture was poured into crushed ice. The obtained solid product was filtered, washed with water, and purified with column chromatography using silica gel.

**Yield:** 57.75%

**M.P.:** 133-135<sup>0</sup> C.

**FTIR (KBr):** 3457, 3126, 2926, 2113, 1613, 1453, 1241cm<sup>-1</sup>.

**<sup>1</sup>H NMR** (300 MHz, CDCl<sub>3</sub>): δ 1.18 (s, 2H; for 2 CH units), 2.79(s, 6H; for 2 CH<sub>3</sub>), 4.23 (s, 4H; for 2 CH<sub>2</sub>), 7.24-7.27 (d, 2H; 2 ArH, J=8.7Hz), 7.52-7.55(d, 2H, 2 ArH, J= 8.7Hz), 7.57 (s, 2 H, ArH), 7.63-7.66 (d, 2 H, 2 ArH, J= 8.7Hz), 7.78-7.81 (d, 2H, 2 ArH J= 8.7Hz)

$^{13}\text{C}$  NMR (75MHz  $\text{CDCl}_3$ ):  $\delta$  16.85, 57.76, 76.09, 78.39, 112.34, 113.14, 117.01, 117.57,

120.75, 126.27, 128.22, 129.24, 129.31, 142.78, 152.14, 156.11

ESI MS:  $m/z$ :  $[\text{M}]^+$  470

### Click reaction of propargyl derivative of methyl substituted furo- fused BINOL and phenyl azide (6)

Propargyl derivative of methyl substituted furo-fused BINOL (1 eq) was stirred with copper iodide (1 eq) in dry THF for 5-10min, then added phenyl azide (1 eq) and triethylamine (1 eq). The mixture was stirred overnight. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was evaporated. The obtained solid product was filtered, washed with water, and purified with column chromatography using silica gel.

Yield: 72%

M.P.:  $198^{\circ}\text{C}$

FTIR (KBr): 3108, 1717, 1667, 1466, 1209  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.44 (s, 6H; 2  $\text{CH}_3$ ), 4.15 (s, 4H; 2  $\text{CH}_2$ ), 6.15 (s, 2H; 2 ArCH), 7.04-7.87 (m, 20H; ArH,)

$^{13}\text{C}$  NMR (75MHz  $\text{CDCl}_3$ ):  $\delta$  16.88, 29.68, 64.63, 112.28, 112.91, 113.97, 117.52, 117.58,

120.76, 126.06, 126.36, 128.88, 129.36, 129.45, 129.60, 129.86, 130.22, 142.77, 152.62, 156.11

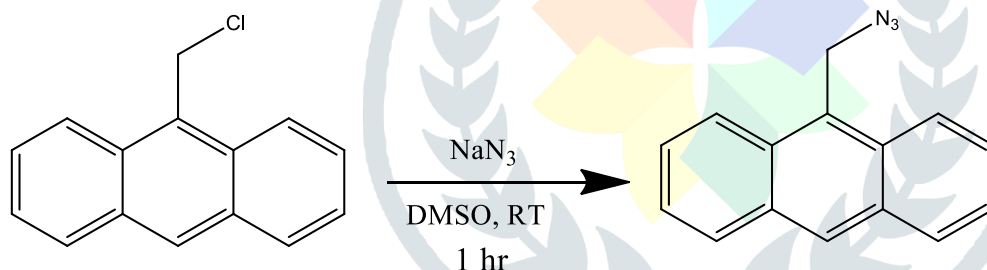
ESI MS:  $m/z$ :  $[\text{M}]^+$  708

### Synthesis of 9-methyl Anthracenyl azide

9-Methylene chloride was reacted with sodium azide in DMSO. The reaction was completed within 1 hr. The product was isolated in good yield and was characterized by the appearance of azide band at  $2074\text{ cm}^{-1}$  in the IR spectrum and methylene group was found to be singlet at  $\delta$  5.63 in  $^1\text{H}$  NMR scan.

Yield: 62.80%

M.P.:  $84-85^{\circ}\text{C}$ .



FTIR (KBr ): 2917, 2209, 2074, 1238  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  5.63 (s, 2H;  $\text{CH}_2$ ), 7.49-7.54 (t, 2H; ArH, ), 7.60-7.65(t, 2H,

ArH, ), 8.03-8.06(d, 2H, ArH), 8.32-8.34 (d, 2H, ArH, ), 8.50 (s, 1H, ArH)

$^{13}\text{C}$  NMR (75MHz  $\text{CDCl}_3$ ):  $\delta$  38.97, 123.41, 125.22, 126.90, 127.69, 129.25, 129.29, 129.98, 131.47

ESI MS:  $m/z$ :  $[\text{M}]^+$  233

### Click reaction of propargyl derivative of methyl substituted furo- fused BINOL and 9-Anthracenylmethyl azide (7)

Propargyl derivative of methyl substituted furo-fused BINOL (1 eq) was stirred with copper iodide (1 eq) in dry THF for 5-10min, then added 9-Anthracenylmethyl azide (1 eq) and triethylamine (1 eq). The mixture was stirred overnight. After completion of the reaction as monitored by TLC, the solvent was evaporated. Then water was added, and solid precipitated was filtered out. Cycloadduct was purified using a silica gel column.

Yield: 68%

M.P.:  $210^{\circ}\text{C}$ .

FTIR (KBr): 3188, 2974, 1515, 1296, 833  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.67 (s, 6H; 2  $\text{CH}_3$ ), 5.35 (s, 4H; 2  $\text{CH}_2$ ), 6.54 (s, 2H; 2  $\text{CH}_2$ )

7.50-8.26 (m, 28H; ArH)

$^{13}\text{C}$  NMR (75MHz acetone):  $\delta$  22.36, 31.37, 63.20, 120.97, 121.17, 121.26, 121.47, 122.62,

124.48, 125.92, 126.94, 127.09, 128.51, 128.91, 129.24, 129.32, 129.65, 129.68, 129.93, 130.50,

130.61, 131.08, 142.90, 143.14, 143.24

ESI MS:  $m/z$ :  $[\text{M}]^+ 93$

## Result and Discussion

### Photophysical responses of methyl substituted furo-fused BINOL based methylene anthryl substituted triazole (7) on interaction with metal ions

The methyl substituted furo-fused BINOL based methylene anthryl-substituted triazole unit (7) when excited at  $\lambda$  330 nm gave fluorescence emission at 452 nm was relatively not affected through pH value ranges from 4 to 9. As a result, the molecule was discovered to be an organic solvent and pH stable, making it a potentially viable chemosensor material.

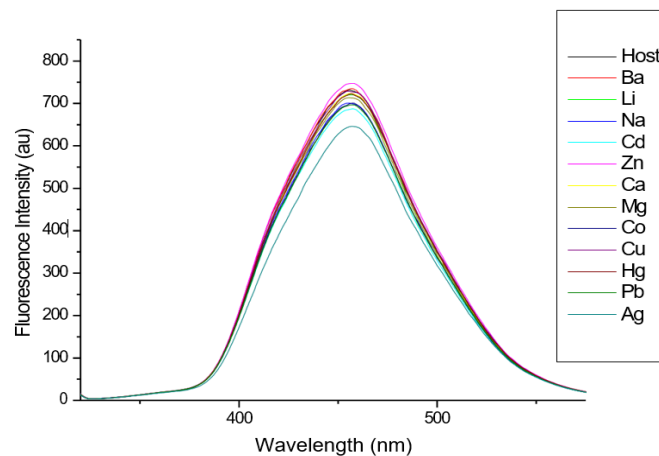
The optical sensitivity methyl substituted furo-fused BINOL based anthryl substituted triazole (7) unit towards various metal ions was evaluated by fluorescence spectral analysis.

#### Fluorescence spectral studies:

Excitation of methyl substituted furo-fused BINOL based triazole unit ( $1 \times 10^{-5}$  M) in acetonitrile at  $\lambda_{\text{max}}$  330 nm produced an emissive band centered at 452 nm with a Stokes shift of 122 nm. The fluorescent response of compound 7 toward certain common metal ions in acetonitrile was tested ( $[1] = 1.0 \times 10^{-5}$  mol/L,  $[M] = 1.0 \times 10^{-5}$  mol/L). The addition of 1 equivalent of  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Ba}^{2+}$  had no discernible influence on fluorescence emission ( $\lambda_{\text{max}} = 330$  nm), as shown in Figure 1.

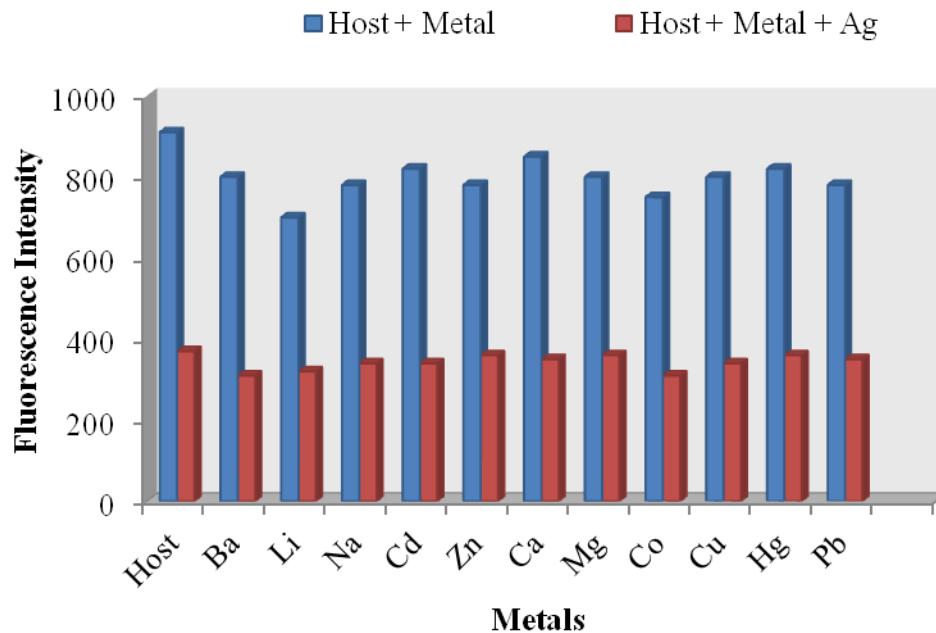
However, fluorescent quenching was seen when 1 equivalent of  $\text{Ag}^+$  was added to the solution of 7, indicating that compound 7 had a particular response with  $\text{Ag}^+$  due to the chelation enhanced fluorescence quenching (CHEQ) effect.

The anthracene units may operate as PET donors while the triazole group acts as electron acceptors when  $\text{Ag}^+$  is bound by two triazole nitrogen atoms of the receptor. As a result, 7 can act as a molecular switch for detecting  $\text{Ag}^+$  ions, exhibiting  $\text{Ag}^+$ -selective switching-off signaling properties.



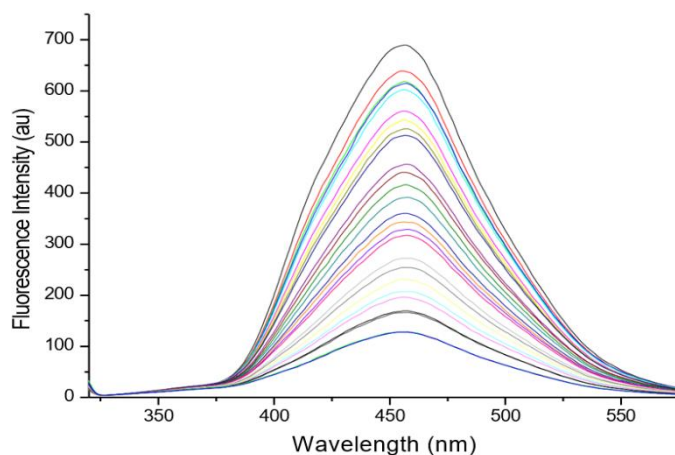
**Figure 1:** The fluorescent spectra of host in the presence of various metal ions  $\text{Ag}^+$ ,  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{Cd}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  at 1:1 equivalent ratio.

Figure 2 shows the competition experiment, which involved adding  $\text{Ag}^+$  (1mM) to the acetonitrile solution of HOST 7 in the presence of another metal ion. The excitation wavelength was set to 330 nm for all measurements, and the emission was observed at 452 nm. In the presence of other metal ions, no significant changes in the fluorescence quenching efficiency of  $\text{Ag}^+$  were observed, demonstrating that HOST can be utilized as a selective  $\text{Ag}^+$  sensor that is unaffected by other metal ions, particularly  $\text{Hg}^{2+}$ .



**Figure 2:** Fluorescent response of **HOST 7** (20  $\mu\text{L}$ ) with various other metal ions. Blue bars represent the addition of various metal ions (1mM) to **HOST** solution (20  $\mu\text{L}$ ), red bars represent subsequent addition of  $\text{Ag}^+$  (1mM) to the former solution.

With the information provided above, it can be inferred that **HOST 7** is a good fluorogenic sensing material for detecting  $\text{Ag}^+$  ions. We evaluated the decrease in fluorescence intensity after serial additions of aliquots of an acetonitrile solution of  $\text{Ag}^+$  ion to the diluted **HOST 7** solution in acetonitrile to study the quenching behaviour of  $\text{Ag}^+$  ion in detail. Figure 3 illustrates the fluorescence spectra of **HOST 7** after varied quantities of  $\text{Ag}^+$  were added. The fluorescence intensity of **7** decreased gradually as  $[\text{Ag}^+]$  increased in the titration. After the amount of  $\text{Ag}^+$  reached 30 equivalent, the lowered speed of fluorescence slowed down, and the fluorescence emission intensity barely changed.



**Figure 3:** Fluorescence spectra of **HOST 7** ( $1.0 \times 10^{-5}$  mol/L in acetonitrile) upon addition of increasing concentration of  $\text{Ag}^+$  ions in acetonitrile with an excitation at 330 nm.

The stoichiometry of the complex system was determined to be 1: 1, indicating the development of a 1: 1 complex, based on changes in the fluorometric response in the presence of various concentrations of  $\text{Ag}^+$ . A Job plot analysis was performed to further demonstrate the binding ratio between **HOST 7** and  $\text{Ag}^+$ . A 1: 1 binding was further confirmed by Job's plot analysis. (Figure 4)

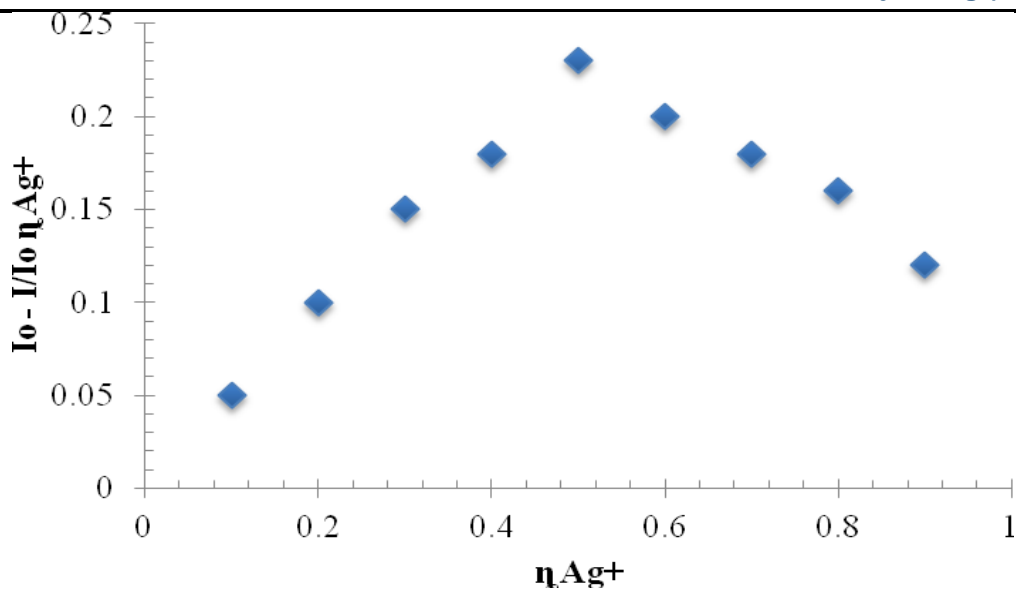


Figure 4: Job's Plot

The Sterne Volmer constant,  $K_{sv}$ , is related to quenching efficiency and is obtained by measuring quantifiable changes in fluorescence using the Sterne Volmer equation. We got good binding and selectivity as indicated ( $K_{sv}=2.9 \times 10^5 \text{ M}^{-1}$ ).

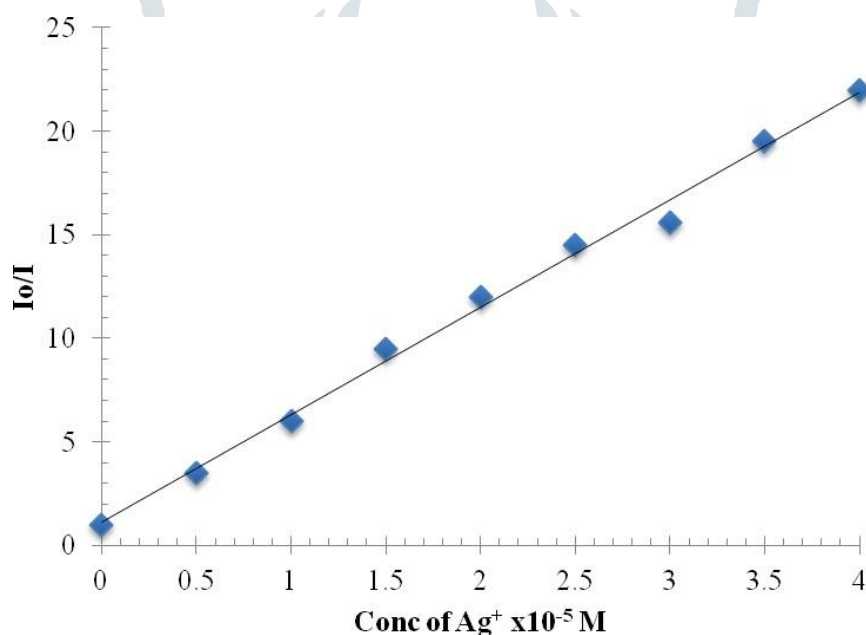
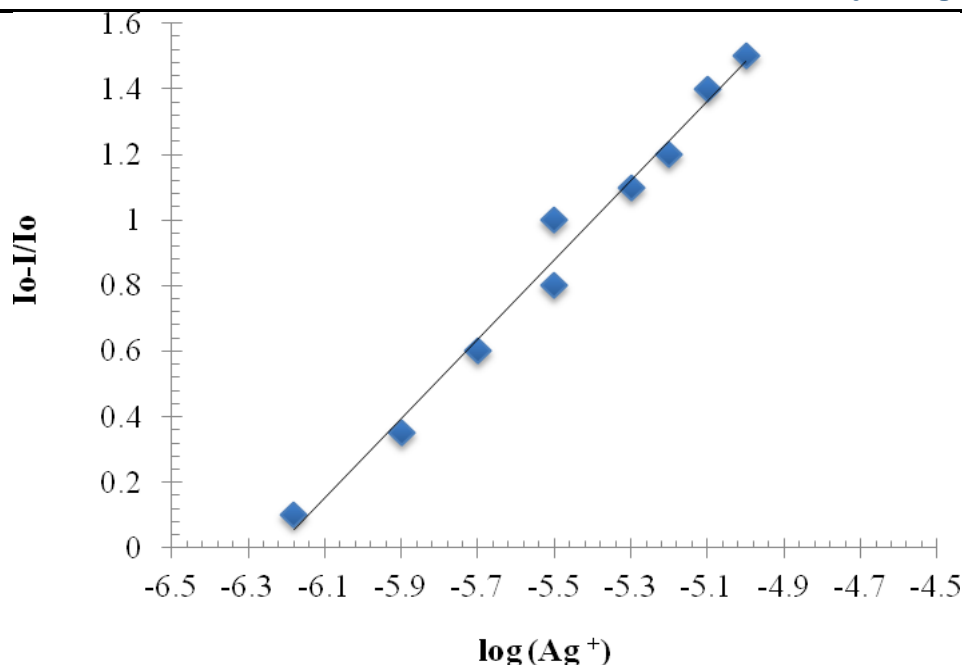


Figure 5: Stern Volmer plot

The detection limit of 7 towards  $Ag^+$  was determined using emission intensity data. (The limit of detection is defined as the minimum concentration that can be detected with a high degree (>99) of certainty). As per the literature protocol, the detection limit was calculated using the semilogarithmic plot of  $I-I_0/I_0$  (where  $I_0$  is the initial emission intensity and  $I$  emission intensities at 452 nm after adding the metal ion) against  $\log [Ag^+]$ . As shown in **Figure 6**, the antilog of the point at which this line intercepts the ordinate axis has been taken as the detection limit and is found to be  $2.3 \times 10^{-5} \text{ M}$ . The detection limit calculated is comparable with the values reported for several  $Ag^+$  selective sensors.



**Figure 6:** Determination of detection limit of  $\text{Ag}^+$  by fluorescence for 7

### Conclusion

Heavy metal ions can cause considerable damage to the surrounding environment and human health, hence the synthesis of highly selective cation sensors is in high demand in many industries today, including environmental, biological, and waste management. The development of selective fluorescence chemosensors for detecting the presence of heavy and transition metal (HTM) ions has attracted a lot of interest. Silver is one of the most common surface water pollutants. Based on the literature reports two molecules were identified as potential  $\text{Ag}^+$  sensors. The synthesis of both these molecules, methyl substituted furo-fused BINOL based triazole with phenyl substitution (**6**) and methyl substituted furo-fused BINOL based triazole with anthryl substitution (**7**), was achieved by 'Click chemistry' protocol. The molecules synthesized were adequately characterized by spectral analyses. Both these molecules were evaluated for selective metal ion sensing by employing several metal ions. Compound **6** did not exhibit any useful levels of metal sensing ability. Compound **7**, however, was found to be a useful  $\text{Ag}^+$  sensor. Compound **7**, was fluorescence active and hence fluorescence was used as a detection tool.  $\text{Ag}^+$  almost completely quenched its fluorescence due to a ligand to metal electron or energy transfer process. With this kind of excessive selectivity and sensitivity, **HOST 7** ought to function a fluorescent ON-OFF sensor for  $\text{Ag}^+$ .

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### Author contribution

Sandeep Bhagwan Kotwal and Dnyaneshwar Purushottam Gholap: writing and editing original manuscript.

### Conflicts of interest

The authors declare no conflict of interest.

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