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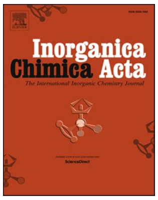

Research paper

‘Quick CuAAC’ Chemistry for Hg(II) and Mn(II) ion sensing via 9H-carbazole derivatives

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ABSTRACT

The synthesis of 1,2,3-triazole merged 9H–carbazole derivative is being reported with excellent yield but drastic reduction in the reaction time. The 1,2,3-triazole linker has been synthesized under thermal conditions within 20 min and yield of more than 90%, using Cu(I) as catalyst. Using UV–Vis spectral technique, the alkyne product displayed excellent detection capability towards Hg(II) and Mn(II) ions in methanol with the detection limit as low as 20 μM and 10 μM, respectively, whereas the triazolyl product can efficiently sense Cu(II) ions.

1. Introduction

Click chemistry has been extensively used since its discovery by Sir Sharpless and co-workers in 2001, and has gained worldwide applauds for simple reaction technique leading to the product formation with inoffensive by-products [1–3]. The reaction involves fusion of a terminal alkyne with an azide in the company of Cu(I) catalyst which undergoes 3 + 2 cycloaddition to 1,4 disubstituted 1,2,3-triazole as product [4–7]. The reaction has been efficiently carried out under thermal and photocatalytic [8–12] conditions to give products containing various donor sites from linkers and *N*-atom from triazole. The use of Copper(I) Catalyzed Alkyne-Azide Cycloaddition (CuAAC) reaction have created a library of molecules that can act as ion sensors [13–16], drug discovery [17–22], material and polymer science [23–24].

The last decade has witnessed booming research on (Scheme 1) the metal ion sensors with the exploitation of UV–Vis and/or Fluorescence spectroscopy, electrochemistry and atomic/emission absorption spectroscopy have been developed for detection of metal ions [25–28]. There have been immense efforts to synthesize a selective Hg(II) ion sensor from a low-cost material via highly efficient methodology which can be operational via simple instruments like UV–Vis spectrophotometer [29–33]. It has always been a great challenge to design a molecule that be produced within minutes in pure form and can be directly used for metal ion detection. The presence of conjugated system on carbazole derivative has led to an innovative design that can proficiently sense the presence of target metal ions.

There have been numerous reports on the conventional methodology of CuAAC reaction which proceed either under thermal or photochemical conditions. The optimized reaction time for thermal and photochemical cycloaddition reaction is typically varies from 3 to 12 h and 1–24 h, respectively. Thus, since the advent of CuAAC, there have been several modifications in the catalyst, reactants, temperature conditions, mole percent of catalyst, etc. to enhance the yield and improve the reaction [34–37]. But the reaction that yields 91% product within few minutes of reaction has not been reported so far. Herein we report first such Click reaction that occurs ‘quickly’ i.e. 15 times faster as compared to conventional synthesis, which further acts as a chromophore due to the existence of electron rich species in the product which have led to its role as Hg(II) ion sensor.

2. Experimental section

2.1. Synthesis of benzyl azide (1)

To a stirred solution of Benzyl chloride (5.0 ml, 4.34 mmol) in DMF (50 ml), Sodium azide (14.0 g, 21.7 mmol) was added slowly and the reaction mixture was stirred for 5 h at 90 °C. After completion of reaction, the mixture was quenched by the addition of ice–cold water and the

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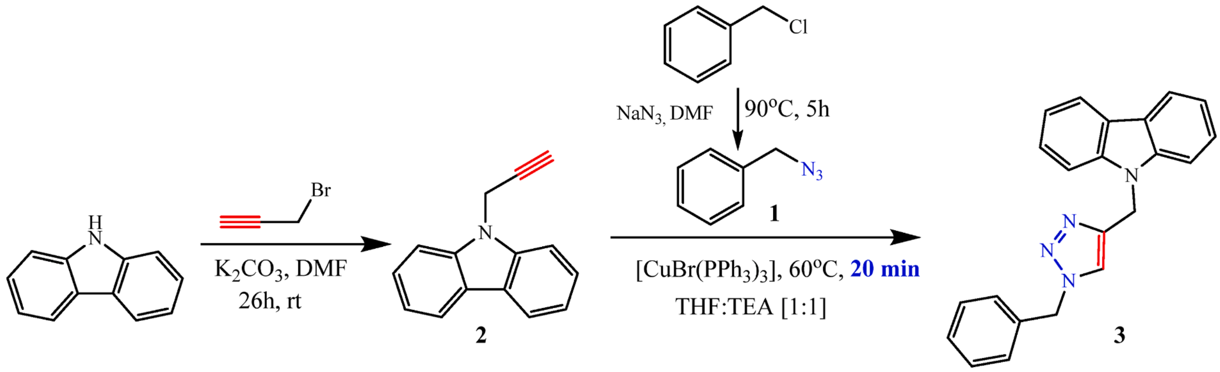

Scheme 1. Synthesis of 9–((1–benzyl–1*H* –1,2,3–triazol–4–yl)methyl)–9*H*–carbazole (3).

crude product was extracted using diethyl ether. The combined organic layers was dried over the anhydrous sodium sulphate; and in vacuum evaporation of the solvent yielded the desired compound. The product was isolated as yellow viscous oil. Yield: 88%; IR (neat, cm^{-1}): 3032 (–C═C–H), 2931 (–C–H), 2090 (–N═N═N–), 1674 (–C═C).

2.2. Synthesis of 9–(prop–2–ynyl)–9H–carbazole (2)

In a 100 ml of round bottom flask, Carbazole (1.0 g, 5.98 mmol) was dissolved in 20 ml DMF by continuous stirring till homogenous solution. It was followed by addition of dry K_2CO_3 (5.0 g, 36.1 mmol) and propargyl bromide dropwise (0.92 g, 0.837 ml, 7.74 mmol) within 5 min. The reaction mixture was stirred continuously for 26 h at room temperature. The completion of reaction was monitored using TLC (hexane: ethyl acetate (4:1)). Upon completion of reaction, the mixture was quenched by pouring into ice cold water. The creamy yellow solid product formed was filtered and dried for further use. Yellow powder; Yield: 99%; Anal. Calcd. for $C_{15}H_{11}N$ (%): C, 87.77; H, 5.40; N, 6.82; Found (%): C, 87.12; H, 5.23; N, 6.12; Melting point: 83–84℃; IR (neat, cm^{-1}): 3261 (–C≡C–H), 3045 (–C═C–H), 2924 (–C–H), 2115 (–C≡C), 1591 (–C═C), 784 (ortho subs.); ^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.05$ (d, $J = 7.8$ Hz, 2H), 7.47–7.40 (m, 4H), 7.23 (ddd, $J = 8.0$, 6.9, 1.3 Hz, 2H), 4.91 (d, $J = 2.5$ Hz, 2H), 2.18 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 139.93$ (s), 125.99 (s), 123.36 (s), 120.54 (s), 119.68 (s), 108.82 (s), 77.95 (s), 72.32 (s), 32.32 (s).

2.3. Synthesis of 9–((1–benzyl–1H –1,2,3–triazol–4–yl)methyl)–9H–carbazole (3)

The compound (2) (1.0 g, 4.8 mmol) was taken in a two-necked round bottom flask, THF:TEA (1:1) was added with continuous stirring, followed by the addition of benzyl azide(1) (0.6 ml, 4.8 mmol) and 0.01 g of [CuBr(PPh_3)$_3$] catalyst was added in it. The reaction mixture was refluxed at 60℃ for 20 min; instantaneously white color precipitates were formed. Solution was filtered and from residue, the desired product was obtained. It was dried at room temperature. The product was isolated as off white solid. Yield: 91%; Light Brown; Anal. Calcd. for $C_{22}H_{18}N_4$ (%): C, 78.08; H, 5.36; N, 16.56; Found (%): C, 77.34; H, 5.04; N, 16.01; Melting point: 150–151℃; IR (neat, cm^{-1}): 3047 (–C═C–H), 2939 (–C–H), 1591 (–C═C), 1384 (–N═N); ^{1}H NMR (400 MHz, $CDCl_3$ $\delta = 8.04$ (d, $J = 7.8$ Hz, 2H), 7.39 (d, $J = 3.1$ Hz, 4H), 7.25–7.20 (m, 5H), 7.07–7.04 (m, 2H), 6.97 (s, 1H), 5.52 (s, 2H), 5.24 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) $\delta = 140.09$ (s), 134.47 (s), 129.05 (s), 128.69 (s), 127.87 (s), 126.00 (s), 123.10 (s), 121.51 (s), 120.44 (s), 119.47 (s), 108.86 (s), 54.07 (s), 38.93 (s).

Table 1
Optimized reaction conditions to carry out Quick Click Chemistry under thermal conditions.

Entry	Reaction Duration (min)	Temperature (°C)	Yield (%)
1	40	25	0
2	80	25	0
3	160	25	0
4	320	25	0
5	5	60	20
6	10	60	55
7	15	60	90
8	**20**	**60**	**91**
9	5	80	19
10	10	80	53
11	15	80	88

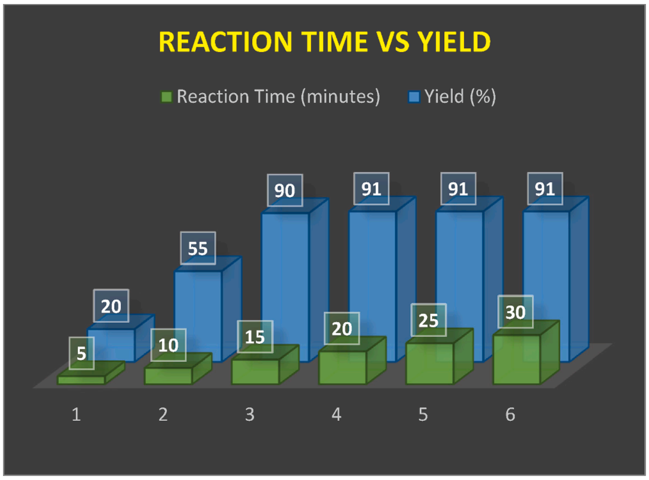

Fig. 1. Graphical representation of yield of conversion of reactants into 1,2,3-triazole product with time.

3. Result and discussion

3.1. Synthesis

The synthesis of 1–(azidomethyl)benzene (1) was carried out from the nucleophilic substitution reaction of Benzyl chloride with Sodium Azide. 9*H*–carbazole was transformed into its terminal alkyne derivative i.e. 9–(prop–2–ynyl)–9*H*–carbazole (2) by the reaction with propargyl bromide in DMF facilitated by base K_2CO_3. Azide (1) and Alkyne (2) were coupled via copper–catalyzed alkyne–azide cycloaddition reaction [CuAAC] yielding more than 90% of 9–((1–benzyl–1*H*–1,2,3–triazol–4–yl)methyl)–9*H*–carbazole (3) as

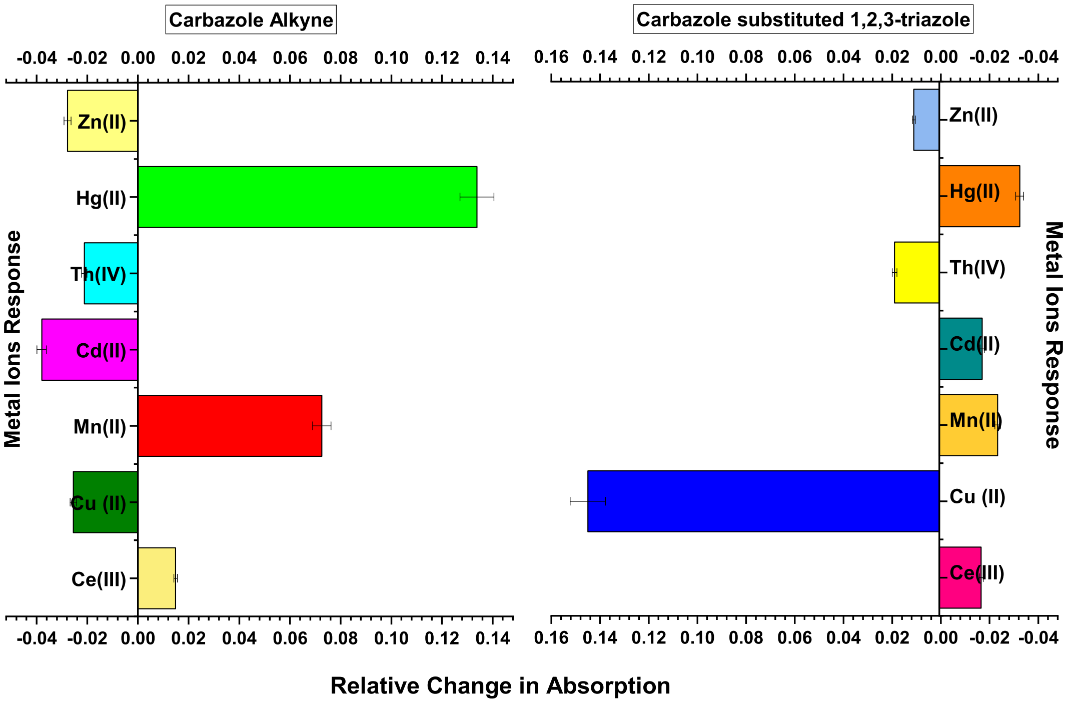

Fig. 2. Metal ion sensing response of compound (2) with different metal salts, in methanol solvent at $\lambda_{max} = 283$ nm, by the successive addition of 29 equiv. 10 mM solution of Mn(II) ions and 14 equiv. 10 mM solution of Hg(II) ion solution. Right side: probe (3) with variant ions solution at 303 nm, positive result with successive addition of 30 equivalent 1 mM solution of Cu (II) ions.

product. This strategy is based on the selectively efficient $[CuBr(PPh_3)_3]$–THF–Et_3N chemical set–up enhancing the speed of cycloaddition reaction from conventional 300 min to less than 20 min.

3.2. Optimization of time and product yield

The optimization of the reaction conditions was performed to evaluate the minimum time required for the maximum yield and many trial reactions were carried out, as tabulated in the Table 1 and represented in Fig. 1. The analysis of results indicates that the reaction did not initiate at the room temperature even when in spite of stirring it for conventional standard time of 5 h. As soon as the reaction was warmed and the temperature was raised to 60 °C, there was significant advancement in the progress of reaction within few minutes of thermal equilibrium. The formation of white solid with first few minutes of reaction confirmed the progress of reaction. With the advancement of time, the reaction was found to be complete within 20 min. Thereafter, insignificant increase in the amount of product was recorded. Any increase in temperature and time did not affect the yield of reaction. From this study, it was concluded that the reaction was complete within first very few minutes and thus the nomenclature was termed as “Quick Click” reaction. This reaction is first of its kind to be carried out within such a short span and with high yield and have not been reported so far to the best of our knowledge.

3.3. Spectroscopic analysis

3.3.1. IR spectroscopy

The newly synthesized compounds were examined by Infra–Red Spectroscopy in the range of 4000–400 cm^{-1} as a neat spectrum. The IR spectrum of the synthesized compounds was as expected and each signal can be assigned to a specific bond stretch/bend. The spectra of starting material Carbazole and its alkyne (2) were analyzed and the two new signals at 3261 cm^{-1} corresponding to $-C\equiv\mathbf{C}-\mathbf{H}$ and 2115 cm^{-1} for $-\mathbf{C}\equiv\mathbf{C}-$ group originated in the spectrum of compound (2) confirmed the presence of terminal alkyne in product. In case of Benzyl azide (1), a sharp signal at 2090 cm^{-1} corresponds to the azide group $-N_3$ in the product. Upon cycloaddition between alkyne and azide, the absorption band at 3261 cm^{-1} ($-C\equiv\mathbf{C}-\mathbf{H}$), 2115 cm^{-1} ($-\mathbf{C}\equiv\mathbf{C}$) along with a signal at 2090 cm^{-1} for $-N_3$ goes missing in the IR spectrum of Carbazole linked 1,2,3–triazole (3). Along with, the appearance of new signals at 3047 cm^{-1} ($-C=\mathbf{C}-\mathbf{H}$) and 1384 cm^{-1} ($-\mathbf{N}=\mathbf{N}$) support the 5-membered heterocycle formation. From this cumulative analysis, the generation of 1,2,3–triazole ring with less time duration of the click reaction is established.

3.3.2. NMR spectroscopy

^{1}H NMR studies confirm the formation of expected azide (1), alkyne (2) and triazole (3) with good yield. All protons in the synthesized compounds can be identified in spectra and assigned a value in NMR. The ^{1}H NMR of compound (2) is in agreement with the expected result due to absence of –NH signal of Carbazole which was substituted by terminal alkyne propyne group. Moreover, the presence of signal at 2.18 ppm (t, $J = 2.5$ Hz, 1H) for 1H of $-C\equiv\mathbf{C}-\mathbf{H}$ and 4.91 ppm (d, $J = 2.5$ Hz, 2H) for 2H of $-CH_2$ signifies the successful nucleophilic substitution reaction. The transformation of alkyne (2) into bi-substituted 1,2,3-triazole (3) can be further established from the disappearance of ^{1}H NMR signal for 1H of $-C\equiv\mathbf{C}-\mathbf{H}$ at 2.18 ppm and popping-up of a new singlet peak at 6.97 ppm for 1H of $-C=\mathbf{C}-\mathbf{H}$ of triazole ring, clearly indicating the complete cyclisation of reactants. Moreover, the signal due to $-\mathbf{CH_2}-$ from propargyl group shows an upward shift from 4.91 ppm in alkyne (2) to 5.24 ppm in 5-membered ring product due to decrease in electron density due to linkage to aromatic heterocyclic ring.

^{13}C NMR spectra completely support the data obtained from ^{1}H NMR for all the synthesized compounds. All the desired carbon signals were obtained in accordance to the expected results. Carbon NMR for terminal alkyne (2) exhibits two prominent signals at 77.95 ppm for $-\mathbf{C}\equiv CH$ and at 72.32 ppm for $-C\equiv CH$ group indicating that the desired compound was formed successfully. The complete conversion of alkyne (2) into product (3) was confirmed by the absence of signals at 77.95 ppm for $-\mathbf{C}\equiv CH$ and 72.32 ppm for $-C\equiv\mathbf{C}H$ and appearance of new signal at 140.09 ppm for $-\mathbf{C}=CH$ of triazole ring and at 123.10 ppm for $-C=\mathbf{C}H$.

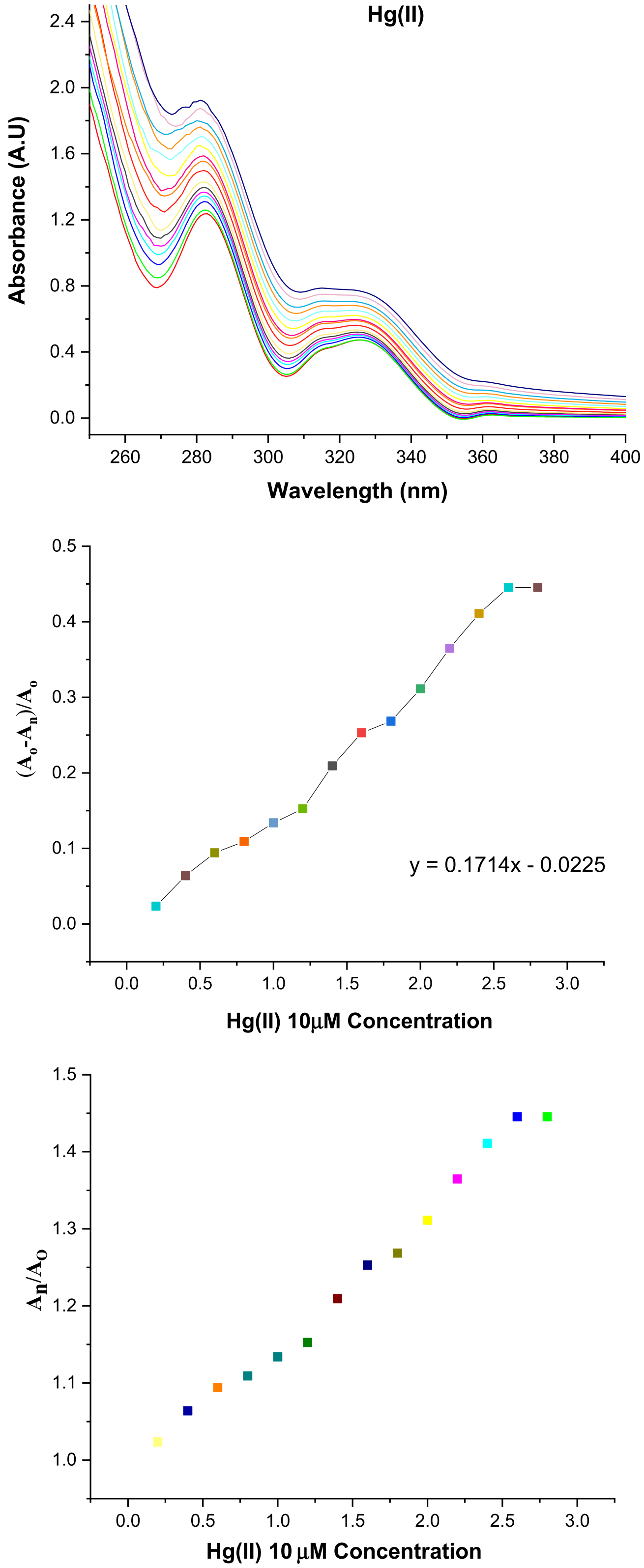

Fig. 3. (a) Metal ion detection was recorded with successive addition of 14 equiv. 10 mM solution of Hg(II) ions solution at $\lambda_{max} = 283$, using methanol solvent. (b) Relative change in absorption maxima (A_n/A_o), (A_o = Absorption maxima of compound (2); A_n = Absorption maxima with successive addition of Hg(II) ions). (c) The correlation plot, $(A_0–A_n)/A_0$ vs Concentration of Hg(II), to obtained lowest detection limit of Hg(II).

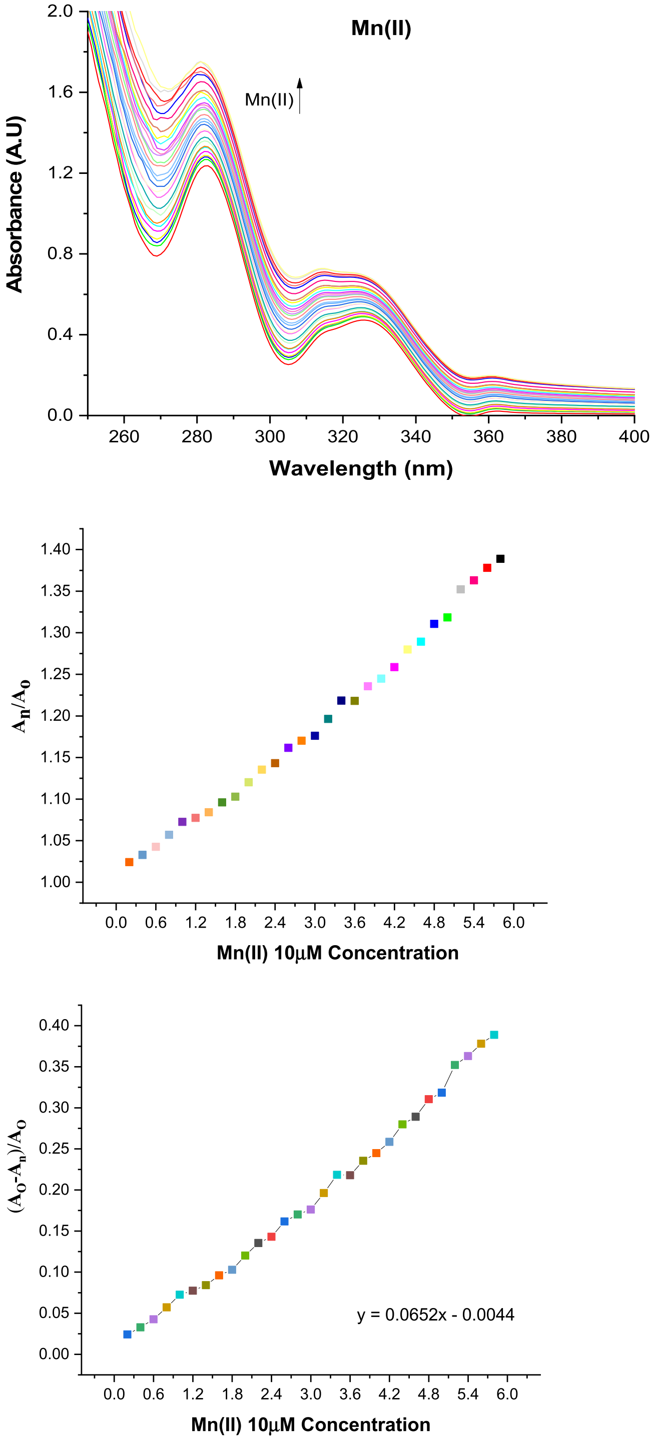

Fig. 4. (a) Metal ion detection was recorded with successive addition of 29 equiv. 10 mM solution of Mn(II) ions solution at $\lambda_{max} = 283$ nm, using methanol solvent. (b) Relative change in absorption maxima (A_n/A_o), (A_o = Absorption maxima of compound [2]; A_n = Absorption maxima with successive addition of Mn(II) ions). (c) The correlation plot, $(A_o–A_n)/A_o$ vs Concentration of Mn(II), to obtained lowest detection limit of Mn(II).

Thus, the spectroscopic data confirms the conversion of linear chained reactants to di-substituted cyclic product.

3.3.3. UV–vis spectra and metal ion sensing

The absorbance spectral properties of final product (3) were examined solvatochromically using chloroform, dimethyl sulfoxide, dimethylformamide and methanol as solvents. The studies concluded that

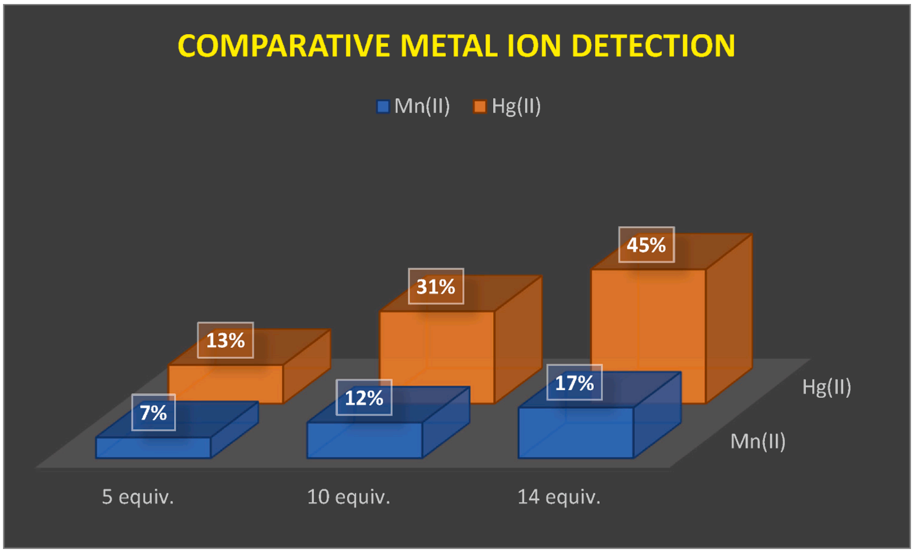

Fig. 5. Graphical representation of comparative metal ion detection by the 9H–carbazole derivative for Hg(II) and Mn(II).

methanol was ideal solvent for use, owing to high solubility and better detection studies. To record the metal–ion effect on absorption spectrum, the standard solution of 1,2,3-triazole (3) with the concentration of 0.2 mM in methanol was prepared. Same way, metal salt stock solutions of Thorium (IV), Cerium (IV), Zinc (II), Cadmium (II), Copper (II), Mercury (II), and Manganese (II) were prepared with 1 mM concentration. To access absorbance spectra, the metal salt solution was added dropwise in cuvette containing already 2 ml of standard solution of synthesized compound. The UV–Visible spectra were recorded at addition of one equivalent of metal salt solution in standard solution of compound (3). Among the spectrally analysed set of metal ions, the compound (3) exhibited significant shift in absorption maxima intensity but negligible change was observed in absorption wavelength maxima with Mercury (II) and Manganese (II) ions, as shown in Fig. 2.

3.3.4. *Response of compound (2) towards Hg(II) ions*

The results of UV–vis spectra of Hg(II) titration presented a unique response, with a swift increase in the absorption maxima associated with an increase in absorbance value keeping value of wavelength constant. The maximum absorbance value was achieved, by the successive addition 14 equiv. 10 mM solution of Hg(II) ions as shown in Fig. 3. The changes in value of wavelength can be decayed because of this, the unique behavior of Hg(II) ions can be explained as there is increase in number of electronic transitions keeping energy gap between HOMO and LUMO constant, due to which absorbance value increases from 1.2543 to 1.81291 . The lowest detection limit of Hg(II) ions, was calculated using the plot of $(A_o - A_n)/A_o$ vs concentration of Hg(II) ions, the detection limit 20 μM of Hg (II) was obtained as shown in Fig. 3 (c).

3.3.5. *Response of compound (2) towards Mn(II) ions*

The UV–vis spectra displayed an increase in absorption maxima upon successive addition 29 equiv. 10 mM solution of Mn(II) ions. It was analyzed that, there is an increase in absorbance value that is 1.2616 to 1.7523, whereas the concentration of compound (2) was decreased by the slowly addition of metal salt solution as shown in Fig. 4. The reason behind this can be attributed to increase in the number of electrons in transition from HOMO to LUMO. The energy gap between HOMO and LUMO remains same because in UV–Visible spectra there is no desirable change was detected in the wavelength. The lowest detection limit of Mn (II) ions, was calculated using the plot of (Ao–An)/Ao vs concentration of Mn(II) ions, the detection limit 10 μM of Mn (II) was obtained as shown in Fig. 4 (c).

3.4. *Comparative data*

The comparative results of metal ion detection by 9H–carbazole derivative for Hg(II) and Mn(II) ions prove that the detection of Hg(II) ions is nearly 2.5 times more effective in comparison to Mn(II) ions, as shown in Fig. 5. In spite of detection of both these ions with d [5] (Mn (II)) and d [10] (Hg(II)) system at wavelength of 283 nm, this difference can be attributed to the binding of metal ion to the ligand. In terms of HSAB principle, Hg(II) acts as soft acid and Mn(II) acts as hard acid and the ligand contains donor *N*-atoms which are in resonance within the 5-membered ring making them lesser hard due to utility of unpaired electrons. As a result Hg(II) ions bind better to ligand as compared to Mn (II) ions in the similar fashion.

3.5. *Response of compound (3) towards Cu(II) ions*

To examine the response of carbazole triazole towards metal ion sensing, different type of metals ion such as Zn(II), Hg(II), Th(IV), Cd(II), Mn(II), Cu(II) and Ce(III) at 1 mM concentration were prepared in methanol and investigated with the solution of 0.2 mM Carbazole triazole in methanol. The outcome of UV–Visible data showed that only Cu (II) ion was bearing quenching sensations with a unique stimulated changes in absorbance values while rest of metal ions were demonstrating negligible quenching with target molecule as shown in bar graph Fig. 2. The studies performed with remaining ions were not remarked with “turn-on” quenching, except Cu(II) ion which exhibit “turn-on” retort for absorption at 303 nm accompanied by hyperchromic shift with the difference of 0.14 in absorbance value , in contrast at λ_{max} 339 nm and 325 nm absorbance was gradually decreased with the addition of metal ion solution, which was assigned to “turn-off” response as shown in Fig. 6(a). Isosbestic point was rise at 320 nm due to this “turn-on” and “turn-off” phenomena. The reason for this distinctive sensing attributes to the electronic configuration of Cu (II) that is [Ar] $3d^9$ and the presence of 3 electronegative atoms in probe ligand that is nitrogen which made interaction with Cu and complete the octet as $3d^{10}$ via ligand to metal charge transfer, because of this the lowest detection limit of testing of Cu(II) ions is 23.5 μM Fig. 6(c).

3.6. *Mechanism of metal ion sensing*

Among the various metal ions examined, the modulations in the absorption behaviour of 9H-carbazole derivatives has been observed only on complexation with Hg(II), Mn(II) and Cu(II) ions. These are transition metal ions having large number of vacant orbitals in their outermost shell as well as inner d-orbitals and consequently have strong tendency to form complexes by accepting electron pairs through coordinate bonding from ligands having N/O/S as donor atoms. The 9H-carbazole derivatives 2 & 3 reported in the present research work are enriched with nitrogen as donor atoms to bind with metal ions. Electron transfer from ligand to metal ion changes the electronic and/or molecular structure of ligand and results into fluctuation in absorption maxima that can be measured with UV–Visible spectroscopy. The extent and nature of modulation either 'Turn-on' or 'Turn-off' depends upon the nature of metal ion.

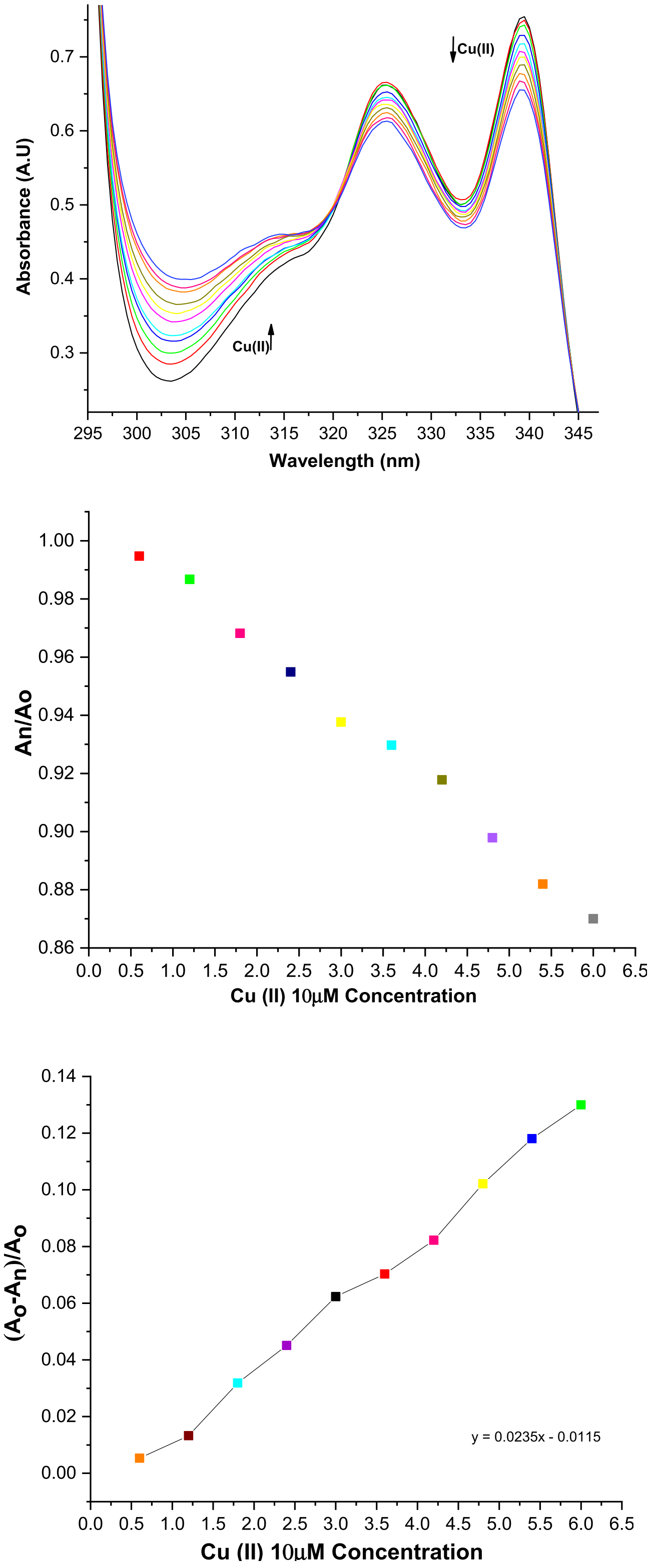

Fig. 6. (a) Metal ion detection was recorded with successive addition of 30 equiv. 1 mM solution of Cu(II) ions solution at $\lambda_{max} = 339$ nm, using methanol solvent. (b) Relative change in absorption maxima (A_n/A_o), (A_o = Absorption maxima of compound (3); A_n = Absorption maxima with successive addition of Cu(II) ions). (c) The correlation plot, (A_o-A_n)/A_o vs concentration of Cu(II), to obtain lowest detection limit of Cu(II).

4. Conclusions

The use of click chemistry for the synthesis of 1,2,3–triazole having Carbazole moiety via copper–catalyzed click approach was successfully demonstrated. The resulting synthesized compounds were characterized by IR spectroscopy and NMR (^{1}H and ^{13}C) spectroscopy. All techniques proved that all the synthesized structures were in alignment with the expected results. Results obtained from UV–Vis spectra of compound (2) gives a valuable data. The compound (2) have capability to detect Mn (II) and Hg (II) ions, it was confirmed by observing the increase in absorbance value by addition of 29 equiv. 10 mM solution of Mn(II) ions and 14 equiv. 10 mM solution of Hg(II) ions. The compound (2) gave detection limit 10 μM of Mn (II) and 20 μM of Hg (II). Moreover compound (3) was effectively detected Cu(II) ion among all the inspected metal ions and it depicted uncommon alteration in absorbance value by the consecutive addition of 1 mM solution of Cu (II) ions, which gave 23.5 μM lowest detection limit of Cu(II) ion.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ica.2021.120560.

References

[1] C.W. Tornoe, C. Christensen, M. Meldal, Peptidotriazoles on solid phase: 1,2,3–triazoles by regiospecific Cu (I)–catalyzed 1,3–dipolar cycloaddition of terminal alkynes to azides, J. Org. Chem. 67 (2002) 3057.
[2] H.C. Kolb, M.G. Finn, K.B. Sharpless, Click chemistry: diverse chemical function from a few good reactions, Angew. Chem., Int. Ed. Engl. (2004, 2001,) 40.
[3] C.D. Hein, X.M. Liu, D. Wang, Click Chemistry, a powerful tool for pharmaceutical sciences, Pharm. Res. 10 (2008) 2216.
[4] V.V. Rostovtsev, L.G. Green, V.V. Fokin, K.B. Sharpless, A Stepwise Huisgen Cycloaddition Process: Copper(I)–Catalyzed regioselective "Ligation" of Azides and Terminal Alkynes, Angew. Chem. Int. Ed. 41 (2002) 2596.
[5] N. Kaur, G. Singh, J. Singh, A. Singh, P. Satija, G. Kaur, J. Singh, Molecular keypad controlled circuit for Ce^{3+} and NO_3^- ions recognition by mw synthesized silicon embedded organic luminescent sensor, RSC Adv. 8 (2018) 36445.
[6] G. Singh, P. Satija, G. Sharma, J.S. Shilpy, First report of silver ion recognition via a silatrane-based receptor: excellent selectivity, low detection limit and good applicability, New J. Chem. 43 (2019) 5525.
[7] P. Neeraja, S. Srinivas, K. Mukkanti, P.K. Dubey, S. Pal, 1H–1,2,3-Triazolyl-substituted 1,3,4-oxadiazole derivatives containing structural features of ibuprofen/naproxen: Their synthesis and antibacterial evaluation, Bio. Med. Chem. Lett. 26 (2016) 5212.
[8] Y. Jiang, D. Kong, J. Zhao, W. Zhang, W. Xu, W. Li, G. Xu, A simple, efficient thermally promoted protocol for Huisgen-click reaction catalyzed by CuSO4. 5H2O in water, Tetrahedron Lett. 55 (2014) 2410.
[9] G. Singh, J. Singh, S.S. Mangat, A. Arora, Three-step pathway towards bis(1,2,3-triazolyl-γ-propylsilatranes) as Cu^{2+} fluorescent sensor, via 'Click Silylation', Tetrahedron Lett. 55 (2014) 2551.
[10] P. Kaur, B. Lal, N. Kaur, G. Singh, A. Singh, G. Kaur, J. Singh, Selective two way Cd (II) and Co(II) ions detection by 1,2,3–triazole linked fluorescein derivative, J. Photochem. & Photobio. A: Chemistry 382 (2019) 111847, https://doi.org/10.1016/j.jphotochem.2019.05.010.

[11] G. Kaur, G. Singh, J. Singh, Photochemical tuning of materials: A click chemistry perspective, Mat. Today Chem. 8 (2018) 56.

[12] G. Singh, S.S. Mangat, H. Sharma, J. Singh, A. Arora, A.P.S. Pannu, N. Singh, Design and syntheses of novel fluorescent organosilicon-based chemosensors through click silylation: detection of biogenic amines, RSC Adv. 4 (2014) 36834.

[13] G. Singh, A. Arora, S.S. Mangat, J. Singh, S. Chaudhary, N. Kaur, D.C. Lazarte, Synthesis and characterization of modified Schiff base silatranes (MSBS) via 'Click Silylation', J. Mol. Struct. 1079 (2015) 173.

[14] G. Singh, S.S. Mangat, J. Singh, A. Arora, R.K. Sharma, Synthesis of polyfunctional triethoxysilanes by 'click silylation, Tetrahedron Lett. 55 (2014) 903.

[15] G. Singh, J. Singh, J. Singh, S.S. Mangat, Design of selective 8–methylquinolinol based ratiometric Fe^{2+} and $Fe^{3+}/H_2PO_4^-$ fluorescent chemosensor mimicking NOR and IMPLICATION logic gates, J. luminescence. 165 (2015) 123.

[16] G. Singh, S. Rani, A. Arora, S. Girdhar, J. Singh, A. Saroa, D. Aulakh, M. Wriedt, Organosilatranes with thioester-anchored heterocyclic ring assembly: Cu^{2+} ion binding and fabrication of hybrid silica nanoparticles, RSC. Adv. 5 (2015) 65963.

[17] K.S.S. Praveena, E.V.V.S. Ramarao, Y. Poornachandra, C.G. Kumar, N.S. Babu, N.Y. S. Murthy, S. Pal, Assembly of Quinoline, Triazole and Oxime Ether in a Single Molecular Entity: A Greener and One–pot Synthesis of Novel Oximes as Potential Cytotoxic Agents, Lett. Drug Des. Discov. 13 (2016) 210.

[18] N. Kuntala, J.R. Telu, V. Banothu, S.B. Nallapati, J.S. Anireddy, S. Pal, Novel benzoxepine–1,2,3–triazole hybrids: synthesis and pharmacological evaluation as potential antibacterial and anticancer agents, Med. Chem. Commun. 6 (2015) 1612.

[19] J. Mareddy, K.S.S. Praveena, N. Suresh, A. Jayashree, S. Roy, D. Rambabu, N.Y. S. Murthy, S. Pal, A Remarkably Faster Approach Towards 1,2,3–Triazolyl Quinolines Via. CuAAC in Water: Their Crystal Structure Analysis and Antibacterial Activities, Lett. Drug Des. Disc. 10 (2013) 343.

[20] A. Rani, G. Singh, A. Singh, U. Maqbool, G. Kaur, J. Singh, CuAAC-ensembled 1,2,3-triazole-linked isosteres as pharmacophores in drug discovery: review, RSC Adv. 10 (2020) 5610.

[21] J. Mareddy, S.B. Nallapati, J. Anireddy, Y.P. Devi, L.N. Mangamoori, R. Kapavarapu, S. Pal, Synthesis and biological evaluation of nimesulide based new class of triazole derivatives as potential PDE4B inhibitors against cancer cells, Bio. Med. Chem. Lett. 23 (2013) 6721.

[22] A.A.M. Alkhaldi, M.A. Abdelgawad, B.G.M. Youssif, A.O. Gendy, H.P.D. Koning, Synthesis, antimicrobial activities and GAPDH docking of novel 1, 2, 3-triazole derivatives, J. Pharma. Res. 18 (2019) 1101.

[23] G. Singh, S.S. Mangat, J. Singh, A. Arora, M. Garg, Synthesis of novel 1,2,3-triazole based silatranes via "click silylation", J. Organomet. Chem. 769 (2014) 124.

[24] M.A. Tasdelen, G. Yilmaz, B. Iskin, Y. Yagci, Photoinduced free radical promoted copper (I)-catalyzed click chemistry for macromolecular syntheses, Macromolecules 45 (1) (2012) 56–61.

[25] G. Singh, J. Singh, S.S. Mangat, J. Singh, S. Rani, Chalcomer assembly of optical chemosensors for selective Cu^{2+} and Ni^{2+} ion recognition, RSC Adv. 5 (2015) 12644.

[26] H. Jain, N. Deswal, A. Joshi, C.N. Ramachandran, R. Kumar, Triazole–appended pyrano[2,3–c]pyrazolone based colorimetric chemosensors for recognition of Fe^{3+} ions and their molecular logic gate behavior, Anal. Methods 11 (2019) 3230.

[27] K.B. Kim, G.J. Park, H. Kim, E.J. Song, J.M. Bae, C. Kim, A novel colorimetric chemosensor for multiple target ions in aqueous solution: simultaneous detection of Mn(II) and Fe(II), Inorg. Chem. Comm. 46 (2014) 237.

[28] R. Peng, Y. Xu, Q. Cao, Recent advances in click-derived macrocycles for ions recognition, Chinese Chem. Lett. 29 (2018) 1465.

[29] W. He, R. Liu, Y. Liao, G. Ding, J. Li, W. Liu, L. Wu, H. Feng, A new 1,2,3-triazole and its rhodamine B derivatives as a fluorescence probe for mercury ions, Anal. Biochem. 598 (2020), 113690.

[30] L.N. Liu, H. Tao, G. Chen, Y. Chen, Q.Y. Cao, An amphiphilic pyrene-based probe for multiple channel sensing of mercury ions, J. Lumin. 203 (2018) 189.

[31] M. Sulak, A.N. Kursunlu, B. Girgin, O.O. Karakus, E. Guler, A highly selective fluorescent sensor for mercury (II) ion based on Bodipy and Calix[4]arene bearing triazolenaphthylene groups; synthesis and photophysical investigations, J. Photochem. Photobiol. A Chem. 349 (2017) 129.

[32] Y.C. Hsieh, J.L. Chir, H.H. Wu, P.S. Chang, A.T. Wu, A sugar–aza–crown ether–based fluorescent sensor for Hg^{2+} and Cu^{2+}, Carbohydr. Res. 344 (2009) 2236.

[33] P. Rani, K. Lal, V.D. Ghule, R. Shrivastava, Green Synthesis of Triazole-Based Chemosensors and their Efficacy Towards Mercury Sensing, Current Analy. Chem. 16 (2020) 738.

[34] S. Chassaing, V. Beneteaub, P. Paleb, When CuAAC 'Click Chemistry' goes heterogeneous, Catal. Sci. Technol. 6 (2016) 923.

[35] S. Neumann, M. Biewend, S. Rana, W.H. Binder, The CuAAC: Principles, Homogeneous and Heterogeneous Catalysts, and Novel Developments and Applications, Macromol. Rapid Commun. 41 (2020) 1900359.

[36] P. Saini, G. Singh, G. Kaur, H. Singh, J. Singh, Robust and Versatile Cu (I) metal frameworks as potential catalysts for azide-alkyne cycloaddition reactions : Review, Mol. Catal. 504 (2021), 111432.

[37] M. Meldal, F. Diness, Recent Fascinating Aspects of the CuAAC Click Reaction, Trends Chem. 2 (2020) 569.