Bis-Organosilicon based receptor for detection of Hg²⁺ ions: Low detection limit and excellent selectivity

Gurjaspreet Singh, Pinky Satija, Akshpreet Singh, Kavita Chowdhary, Geetika Sharma, Mohit, Shilpy, Jandeep Singh, Jasbhinder Singh

 PII:
 S0022-328X(20)30360-0

 DOI:
 https://doi.org/10.1016/j.jorganchem.2020.121458

 Reference:
 JOM 121458

To appear in:

Journal of Organometallic Chemistry

Received date:1 July 2020Revised date:18 July 2020Accepted date:23 July 2020

Please cite this article as: Gurjaspreet Singh, Pinky Satija, Akshpreet Singh, Kavita Chowdhary, Geetika Sharma, Mohit, Shilpy, Jandeep Singh, Jasbhinder Singh, Bis-Organosilicon based receptor for detection of Hg²⁺ ions: Low detection limit and excellent selectivity, *Journal of Organometallic Chemistry* (2020), doi: https://doi.org/10.1016/j.jorganchem.2020.121458

This is a PDF file of an article that has undergone enhancements after acceptance, such as the addition of a cover page and metadata, and formatting for readability, but it is not yet the definitive version of record. This version will undergo additional copyediting, typesetting and review before it is published in its final form, but we are providing this version to give early visibility of the article. Please note that, during the production process, errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

© 2020 Published by Elsevier B.V.



Highlights

- Organosilicon based receptors have been synthesized using Claisen Schmidt and Click reaction.
- The synthesized sensor showed selectivity towards recognition of mercury ions.
- The detection limit of the sensor was calculated to be 0.10 μ M for Hg²⁺ ions.

Journal Pression

Bis-Organosilicon based receptor for detection of Hg²⁺ ions: Low detection limit and excellent selectivity

Gurjaspreet Singh^{a*}, Pinky Satija^a, Akshpreet Singh^b, Kavita Chowdhary^a, Geetika Sharma^b, Mohit^a, Shilpy^a, Jandeep Singh^c, Jasbhinder Singh^c

^aDepartment of Chemistry, Panjab University, Chandigarh-160014, India ^bDepartment of Chemistry, GGDSD College, Sector-32, Chandigarh-160032, India ^cDepartment of Chemistry, Lovely Professional University, Phagwara-144411, India

*Corresponding Author Prof. Gurjaspreet Singh Department of Chemistry, P.U., Chandigarh, India +91-0172-2534428, Email: gjpsingh@pu.ac.in

Abstract

Mercury Contamination represents a major environmental and health concern for which new eco-friendly solutions are desired. Azide–alkyne cycloaddition and Claisen Schmidt reaction were attempted to trigger a flavanone based bis-siloxyl hybrid materials. The synthesized bis-organosilicon compound was used as receptor for recognition of Hg (II) ions in semi aqueous medium. The presence of silicon makes the receptor impetus and has benefits in the field of nanochemistry. All the final compounds were recognized by spectroscopic techniques like IR, NMR and further corroborate by mass spectrometry.

Keywords: Azide alkyne cycloaddition reaction, Claisen Schmidt reaction, Organosilicon compound, Mercury ion

1. Introduction

The sensing of metal ions has arisen as area of escalating significance. In spite of great success in the development of various chemosensor, the tracking of cumulative concentration of toxic chemicals is still the current focus of research interest. Mercuric ion (Hg^{2+}) is one of the most hazardous and bioaccumulative heavy metal ion that causes grisly serious human health issues like cognitive and motor disorders, immunotoxic, genotoxic, neurototoxic

effects, damages to the central nervous system, endocrine system, kidney, acrodynia, Hunter–Russell syndrome, Minamata disease, Alzheimer's disease, DNA damage and mitosis impairment which can be attributed to easy coordination with biological ligands such as proteins, DNA and enzymes [1-7]. The major sources of this pollutant are power plants, oil refining, fertilizer industries, gold mining, ore processing, industrial wastes, solid waste incineration, combustion of fossil fuels, wood pulping, rubber processing, coal and fossil fuel combustion and solid waste incineration [8-10]. World Health Organization (WHO) has prescribed limit regarding maximum contamination level for mercury in drinking water, which is ~ 2μ g L⁻¹[11-12]. Although there are various analytical tools to detect Hg²⁺ ions such as atomic absorption/emission spectroscopy, electrochemical, voltammetric, potentiometric and inductively coupled plasma mass spectrometry (ICP-MS), but these require expensive and sophisticated instrumentation, are time consuming and laboratory based, which curb their application in Hg²⁺ monitoring [13-14]. Hence new detection methods are required which have advantages such as cost effective, practical, real time monitoring, facile, sensitive, selective and sustainable and uses eco friendly materials [15-16].

Therefore, we were motivated to take the next step for improvement of simple and elegant chemosensor to track Hg^{2+} with high sensitivity and efficacy. Our quest is about the synthesis of a silicon based complex molecular system for the tracking of Hg^{2+} ions in the semi aqueous medium. The insertion of two triazole rings *via* click reaction into the functional system imparts multiple coordination sites to the receptor. The chemosensor reported here has high potential for tracking Hg(II) ions and produces biodegradable and non-toxic byproducts. Moreover, the presence of organosilicon unit in the prepared chemosensor can lead to the construction of silicon capped nanoparticles which can equip the receptor to have advanced applications.

2. Experimental Aspects

2.1. Materials and methods

Propargyl bromide (Aldrich), 4-hydroxyacetophenones (AVRA), 4-hydroxy -3-methoxy acetophenone (Alfa Aesar), 2-hydroxy naphthaldehyde (Alfa Aesar), potassium carbonate (Avra), sodium hydroxide (Avra), [CuBr(PPh₃)₃](Aldrich), 3-chloropropyl triethoxysilane (Aldrich), Sodium azide (Avra) were used as received. 3-Azidopropyltriethoxysilane (AzPTES) was prepared from (3-chloropropyl)triethoxysilane and Sodium azide according to a procedure reported in the literature. Infrared spectrum was obtained on a Thermo Scientific

Fischer spectrometer. The NMR spectra (¹H and ¹³C) were recorded on a BRUKER (400 MHz) spectrometer. JASCO V-530 double beam spectrophotometer is used for electronic spectral measurements. The Schlenk technique was engaged to perform reactions under nitrogen atmosphere.

2.2.Synthesis of acetylinic napthaldehyde and acetophenone

In 5 ml DMF, 2-hydroxy naphthaldehyde was dissolved followed by the addition of anhydrous K_2CO_3 . The resulting suspension was stirred for 30 min and the colour change from brown to olive green was observed. To this, addition of propargyl bromide was done and the resultant mixture was again allowed to stir for 16 h. The workup was done by ice cold water leading to the formation of brown coloured precipitates of acetylinic naphaldehyde. Similar procedure was followed for preparation of acetylinic acetophenone.

2.3.Synthesis of acetylinic chalcones (5a and 5b)

To ethanolic solution of substituted acetylenic acetophenone (1.0 eq), 10 ml of NaOH (5% w/v) was added. After stirring for 20 min, ethanolic solution of the acetylinic naphthaldehyde (1.0 equiv) was added dropwise and the solution was stirred for a period of 5h. Mustard coloured precipitates were obtained, filtered, recrystallized using ethanol to afford the crystalline product.

Synthesis of 5a: Yellow solid, M.P.: 118-121°C, Yield: 95 %. IR(cm⁻¹): 3285 (C=C-H), 2124 (C=C), 1653 (C=O), 1169, 1268 (O-CH₂).¹H(CDCl₃, 400 MHz,): $\delta = 8.45$ -8.48 (d, J = 15.7 Hz, 1H, H β), 7.41-8.30(m,10H,Ar-H), 7.08-7.11 (d, J = 15.7 Hz, 1H, H α), 4.94(d, J=2.5Hz, - OCH₂(Naphthalene)), 4.81 (d, J = 2.4 Hz, 2H, -OCH₂(phenyl)), 4.01(s, 3H, -OCH₃),2.57-2.61 (m, J = 2.5 Hz, 2H, -C=CH). ¹³C (CDCl₃, 101 MHz): $\delta = 189.4$, 161.1, 154.8, 136.4, 131.2, 130.8, 128.4, 127.7, 124.2, 123.5, 118.7, 114.6, 114.3, 77.8, 76.0, 69.5, 57.1, 55.3.

Synthesis of 5b: Yellow solid, M.P.: $132^{\circ}C-135^{\circ}C$, Yield: 93 %. IR(cm⁻¹): 3294 (C=C-H), 2124 (C=C), 1659 (C=O), 1169, 1265 (O-CH₂).¹H (CDCl₃, 400 MHz): $\delta = 8.45-8.48$ (d, J = 15.7 Hz, 1H, H β), 7.42-8.32 (m, 9H, Ar-H), 7.11-7.14 (d, J = 15.4 Hz, 1H, H α), 4.94(d, J=2.3Hz, -OCH₂(Naphthalene)), 4.89 (d, J = 2.2 Hz, 2H, -OCH₂(phenyl)), 2.56-2.60 (m, J = 2.3 Hz, 2H, -C=CH). ¹³C (CDCl₃, 101 MHz,): $\delta = 189.3$, 150.3, 149.4, 136.9, 134.5, 132.4, 131.2, 128.4, 127.5, 124.7, 123.5, 122.5, 118.5, 114.3, 112.4, 111.2, 78.4, 76.0, 63.0, 56.4.

2.4.Synthesis of organotriethoxysilanes (6a and 6b)

To the solvent mixture of 1:1 THF/Et₃N taken in a two-neck round bottomed flask, bis acetylinic chalcone (1 equiv) was treated with 2 mol of AzPTES with a pinch of catalyst [CuBr(PPh₃)₃] loading and the mixture was refluxed at 60°C for 5 h. After cooling, the reaction mixture was filtered to separate catalyst. Bis-1,4 triazole linked chalcone triethoxysilane was extracted by solvent evaporation, which was followed by addition of ether to obtain mustard coloured solid product.

Synthesisof 6a: Mustard Yellow, Charring above 250°C.Yield: 94 %. IR(cm⁻¹): 2876, 2921, 2962 (propyl chain), 1658 (C=O), 1598(C=C), 1013, 743(Si-O).¹H NMR (CDCl₃, 400 MHz): δ = 8.35-8.39 (d, *J* = 15.7 Hz, 1H,H β), 7.20-8.18 (m, 11H, Ar-H), 6.98-7.00(d, *J* = 15.8 Hz, 1H, H α), 5.36(s, 2H,-OCH₂(Naphthalene)), 5.20 (s, 2H, -OCH₂(phenyl)), 4.23-4.31(m, 4H,-N₃CH₂-), 3.65-3.75 (m,12H, -OCH₂CH₃), 1.89-1.98 (m, 4H, -CCH₂C-), 1.07-1.15 (m, 18H, -OCH₂CH₃), 0.45-0.55 (m, 4H, -SiCH₂-).¹³C NMR (CDCl₃, 101 MHz): δ =189.1, 161.7, 155.3, 143.3, 136.7, 132.9, 130.9, 129.3, 128.5, 127.3, 124.1, 122.9, 118.0, 114.5, 63.2, 61.5, 58.9, 52.2, 23.9,18.1, 7.3. ESI-TOF-MS (m/z): 815(M-OCH₂CH₃).

Synthesisof 6b: Mustard Yellow, Charring above 250°C, Yield:91 %. IR(cm⁻¹): 2974 (C=C-H), 1652 (C=O), 1595(C=C), 1074, 751 (Si-O). ¹HNMR(CDCl₃, 400 MHz,): δ = 8.43-8.47 (d, J = 15.3 Hz, 1H,H β), 7.42-8.26 (m, 10H, Ar-H), 7.14-7.16(d, J = 15.3 Hz, 1H, H α), 5.47(s,2H,OCH₂(Naphthalene)), 5.38(s,2H,-OCH₂(phenyl)), 4.31-4.38(m,4H,-N₃CH₂-), 3.95(s,3H,-OCH₃), 3.69-3.85 (m,12H, -OCH₂CH₃), 1.95-2.05 (m, 4H, -CCH₂C-), 1.16-1.26 (m, 18H, -OCH₂CH₃), 0.53-0.63 (m, 4H, -SiCH₂-). ¹³C NMR (CDCl₃, 101 MHz): δ = 187.8, 138.0, 131.9, 130.7, 121.9, 121.6, 113.2, 94.9, 61.3, 56.9, 51.1, 28.4, 23.2, 17.0, 6.3. ESI-TOF-MS (m/z): 845(M-OCH₂CH₃).

Synthesis of 6a+Hg complex: In a 50 ml RBF containing dry acetonitrile, equimolar amount of 6a and anhydrous mercuric chloride were added and the contents were stirred for 2 hrs. The obtained precipitates were filtration, washed with acetonitrile and dried to yield the desired complex which was then characterized by IR spectrum.

3. Results and Discussion

3.1.Synthesis

We have used base catalyzed Claisen-Schmidt reaction for preparation of naphthaldehyde based chalcones. Commercially available hydroxy-acetophenones were reacted with

propargyl bromide using K_2CO_3 as base in DMF. The intermediate acetylenes underwent aldol condensation with acetylinic naphthaldehyde in the presence of 5% NaOH solution resulting into Bis-acetylinic chalcones (5a, 5b) in high yields. These bis-acetylinic chalcones underwent click chemistry with 3-azidopropyltriethoxysilane (3-AzPTES) using [CuBr(PPh₃)₃] as catalyst to afford Bis-1,2,3-triazole blended triethoxysilanes (6a, 6b) (Scheme 1).



Scheme 1: Synthesis of chalcone allied bis-triazole encapped organosilanes (6a and 6b).
Reagents and conditions: (i) K₂CO₃, DMF, 16h stir (ii) 5% NaOH Solution, Ethanol, 5h stir (iii) 3-azidopropyltriethoxysilane, THF:TEA (1:1) (iv) [CuBr(PPh₃)₃], 5h reflux

3.2. Spectroscopic analysis

In IR spectroscopy, C=O stretching vibrations of carbonyl bond appeared in the range of 1660-1652 cm⁻¹. The signal appeared around 2100 cm⁻¹ and 3300 cm⁻¹ is due to bis alkynes, 5a and 5b respectively and disappearance of this region in silanes 6a and 6b endorse the cyclization of alkynyl moiety into triazole unit. Moreover, stretching vibrations in the range of 2975-2964 cm⁻¹ are due to C=CH of the triazole ring which also adds on to the confirmation of [2+3] cycloaddition. In ¹H NMR spectra, Doublets at around 6.98-7.16 ppm and 8.35-8.49 ppm corresponding to α and β hydrogen atoms respectively with a J value of 15-16Hz endorse the (E)-configuration of the chalcones. Alkynyl proton appears at around δ \approx 2.4 ppm that upon cyclization with 3-AzPTES shows a shift to $\delta = 7.3-7.7$ ppm which corroborates the cyclization of alkynyl moiety into triazole unit. Due to presence of unsymmetrical aromatic rings, OCH₂ protons associated with naphthalene ring appeared at 4.81-4.89ppm and OCH₂ protons linked with phenyl ring appeared at 4.9. The shifting of -OCH₂ protons of acetylene group from $\delta = 4.81$ -4.94 ppm (5a and 5b) to $\delta \approx 5.20$ -5.47 ppm (6a and 6b) validate the formation of cyclised product. Also, a major shift in the protons of the carbon attached with the azide group in 3-AzPTES from 3.2 ppm to 4.2 ppm authenticates the formation of the desired product. The ethoxy groups of the silanes manifest multiplets in the range 1.10-1.20 ppm and 3.69-3.79 ppm respectively. Similar shifting is scrutinized in the carbon spectrum of the respective compounds. In ¹³C NMR spectra of the compounds, the carbonyl carbon appears as the least shielded carbon in the region $\delta = 184-189$ ppm. The vinyl carbons of the chalcone moiety appear at $\delta = 120-124$ ppm and $\delta = 142.1-144.9$ ppm for α and β carbons respectively. Two carbons of alkynyl moiety (5a and 5b) appear in the range of δ = 76.0-78.8 ppm that shift around δ = 119.4-122.9 ppm and δ = 136.6-143.0 ppm in cyclised compounds (6a and 6b) justify the cyclization of alkyne functionality into triazole unit. The HRMS spectrum of synthesized Bis-triazole chalcone blended organosilane (6a) showed a signal at m/z 815 corresponding to [M-OCH₂CH₃].

3.3. Photophysical study

The UV-Vis absorption spectra of bis-triazole-triethoxysilanes (6a) were recorded in Acetonitrile: H₂O (9:1) mixture at room temperature with concentration of 10 μ M. The UV-Visible response of 10 μ M of chalcone blended organosilane (6a) in the presence of 10 mM of various metals ions (Al³⁺, Cr³⁺, Ce³⁺, Fe²⁺, Hg²⁺, Zn²⁺, Cd²⁺, Cu²⁺, Co²⁺, Ni²⁺, Mn²⁺, Mg²⁺, Ca²⁺, Na⁺, K⁺ etc.) was analyzed under identical conditions. Gratifyingly, only Hg²⁺ caused a decrease in the absorbance of compound 6a which suggests the specificity of this sensing system towards Hg²⁺ ions as shown in Fig 1. The prepared receptor worked selectively only

with Hg^{2+} ions can be attributed to the same cage size of the molecule as is the size of Hg^{2+} ions. The size of other metal ions is different from the molecule resulting in the selective sensing of Hg^{2+} ions.



Fig 1: Variations in absorption spectrum of receptor (6a) solution in the presence of different metal ions

To figure out the variation of UV–Vis spectra, we studied separately the absorption spectra of chalcone blended triazolesilane (6a) in the presence of Hg^{2+} ions. Upon sequential addition of Hg^{2+} ions, the systematic changes in the absorption spectra of compound 6a in CH₃CN:H₂O (9 : 1; v/v) was observed and the absorption peaks at 373nm, 332nm and 295nm were blue-shifted and broadened as shown in Fig 2.



Fig 2: Variation in UV–Vis absorption spectrum of receptor(6a) upon gradual addition of Hg^{2+}



Fig 3: Bar graph representation at 373nm of Silane (6a) in the presence of various metal ions

Such an excellent selectivity and specificity may be attributed to the fact that Hg^{2+} has much stronger affinity towards nitrogen and oxygen atoms as hard-soft interaction is more favored here and may form coordination complex. Moreover, other metal ions have showed a negligible change in absorbance (Fig. 3) even at higher concentration. Further, Job's plot indicates 1:2 stoichiometry of complexation between the bis-triazolesilane (6a) and Hg^{2+} (Fig 4).



The detection limit is calculated using the equation $3\sigma/K$, where σ is the standard deviation and K is the slope of the plot of Hg²⁺ and the value was found to be 0.10μ M. The association constant of the mercury complex formed in solution has been evaluated by using the standard Benesi–Hildebrand equation (Fig. 5) and is found to be $3.06 \times 10^7 M^{-1}$.



Fig 5: B-H Plot for sensor 6a

Various chemosensor have been employed for the recognition of Hg^{2+} ions as shown in Table 1. The observations pave the way for the silicon based probe to assess the Hg^{2+} ions.

Table 1: Comparison of few reported sensors for Hg^{2+} ions with the present receptor

Receptor	Measured Signal	Stiochiometry	LOD	Reference
Pyrene based	Fluorescence	1:1	7.8nM	[18]
receptor)			
Carbon	Fluorescence	1:1	42nM	[19]
Nanoparticle				
BODIPY	Fluorescence	1:1	108nM	[20]
Thiophene based	UV-Vis/Fluorescence	2:1	20μΜ	[21]
Schiffs base				
Silicon based	UV-Vis	1:2	0.10 µM	Present
Receptor				Study

3.4. Probable Binding mechanism

Scheme 2 displays the sensing strategy of the chalcone blended organosilane (6a) toward the target metal ion Hg^{2+} . The silane have a flexible structure and the presence of multiple donor sites like nitrogens in the triazole rings and carbonyl oxygen, in a single entity enhance the binding ability towards Hg^{2+} ions.



Scheme 2: Proposed binding mode for sensor 6a with Hg^{2+} ion

4. Conclusion

In this work, we have developed sensitive, simple, rapid, and cost-effective sensing system that hold great practical relevance for detection of mercury ions in semi aqueous medium with low detection limit of 0.10μ M. The sensor is based on Organosilicon compounds which have been synthesized by employing Claisen Schmidt and Click Chemistry approach. We expect that the developed sensor may offer opportunity for the fundamental research and applications in the field of living sciences.

Conflict of Interest

There is no conflict of interest.

Acknowledgements

The authors are thankful to the DST (Inspire Fellowship), DST-PURSE and CSIR (01(2950)/18/EMR-11) for providing financial support.

There is no conflict of interest.

References

- [1] J. Du, M. Liu, X. Lou, T. Zhao, Z. Wang, Y. Xue, J. Zhao and Y. Xu, *Anal. Chem.* 84 (2012) 8060–8066.
- [2] K. Bera, A. K. Das, M. Nag and S. Basak, Anal. Chem. 86 (2014) 2740-2746.
- [3] C. W Liu, C. C. Huang and H. Tsung Chang, Anal. Chem. 81 (2009) 2383–2387.
- [4] A. Malek, K. Bera, S. Biswas, G. Perumal, A. K. Das, M. Doble, T. Thomas and E. Prasad, Anal. Chem. 91 (2019) 3533-3538.
- [5] P. Wu, Y. Liu, Y. Liu, J. Wang, Y. Li, W. Liu and J. Wang, *Inorg. Chem.* 54 (2019) 11046–11048.
- [6] A. T. Afaneh and G. Schreckenbach, J. Phys. Chem. A 119 (2015) 8106-8116.
- [7] S. Hussain, S. De and P. K. Iyer, ACS Appl. Mater. Interfaces. 5 (2013) 2234-2240.
- [8] S. Kumari and G. S. Chauhan, ACS Appl. Mater. Interfaces. 6 (2014) 5908-5917.
- [9] D. Singhal, N. Gupta and A. K. Singh, RSC Adv. 5 (2015) 65731.
- [10] E. M. Nolan and S. J. Lippard, J. Am. Chem. Soc. 125 (2013) 14270-14271.
- [11] P. K. Sarkar, N. Polley, S. Chakrabarti, P. Lemmens, and S. K. Pal, ACS Sens. 1 (2016) 789–797.
- [12] S. A. Shahamirifard and M.Ghaedi, New. J. Chem. 41 (2017) 11533.
- [13] M. Lan, J. Zhang, Y. S. Chui, P. Wang, X. Chen, C. S. Lee, H. L. Kwong and W. Zhang, ACS Appl. Mater. Interfaces 6 (2014) 21270–21278.
- [14] T. Minami, Y. Sasaki, T. Minamiki, P. Koutnik, P. Anzenbacher and S. Tokito, *Chem. Commun.* 51 (2015) 17666.
- [15] N. A. Azmi, S. H. Ahmad and S. C. Low, RSC Adv. 8 (2018) 251.
- [16] G. Fang, M. Xu, F. Zeng and S. Wu, Langmuir. 26 (2016) 17764–17771.
- [17] A. Bianco, M. Maggini, M. Nogarole and G. Scorrano, Eur. J. Org. Chem. 13 (2006) 2934–2941.

- [18] L. N Liu, H. Taa, G. Chen, Y. Chen and Q. Y. Cao, J. Luminescence, 203 (2018) 189–194.
- [19] M. Lan, J. Zhang, Y. S. Chui, P. Wang, X. Chen, C. S. Lee, H. L. Kwong and W. Zhang, ACS Appl. Mater. Interfaces 6 (2014) 21270-21278.
- [20] S. Madhu, R. Kalaiyarasi, S. K. Basu, S. Jadhav and M. Ravikanth, J. Mater. Chem. C 2 (2014) 2534.
- [21] D. Singhal, N. Gupta and A. K. Singh, RSC Adv. 5 (2015) 65731.

Journal Prevention