Self-assembled monolayers of functional molecular nanowires: Electron transportation studies and application for electrochemical sensing of heavy metal ions

(UGC Reference No. 43-228/2014(SR))

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Final Project Report

Submitted to

University Grants Commission, New Delhi

By
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(January, 2019)

UNIVERSITY GRANTS COMMISSION
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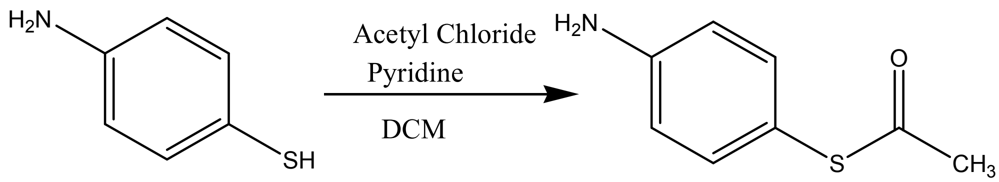
ज्ञान-विज्ञान विमुक्तये

PROFORMA FOR SUBMISSION OF INFORMATION AT THE TIME OF SENDING THE FINAL REPORT OF THE WORK DONE ON THE PROJECT

1.	**Name and Address of the Principal Investigator**	Dr. Inderpreet Kaur Department of Chemistry Guru Nanak Dev University, Amritsar-143005 E-mail: inderpreet11@yahoo.co.in Mob. No. 08427662766
2.	**Name and Address of the Institution**	Department of Chemistry Guru Nanak Dev University, Amritsar-143005
3.	**UGC Reference No. & Date**	43-228/2014(SR) dated 18.08.2015
4.	**Date of Implementation**	Sept. 16, 2015
5.	**Tenure of period**	Three years (From Sept. 2015 to June. 2018)
6.	**Total grant allocated** (Rs.)	12,18,600/-
7.	**Total grant received** (Rs.)	10,29,814/-
8.	**Final expenditure** (Rs.)	10,29,814/-
9.	**Title of the Project**	**Self-assembled monolayers of functional molecular nanowires: Electron transportation studies and application for electrochemical sensing of heavy metal ions**
10.	**Objectives of the project** The overall objectives of the proposal are: • To prepare multifunctional molecular wires with terminal thiol (SH) and incorporate sensory functions into the backbone which have affinity to form complex with metal ions such as copper(II), lead(II), mercury(II), etc. • To self-assemble the prepared multifunctional thiols on the various metal electrode surfaces such as gold, platinum, etc. to obtain self-assembled monolayers • To investigate the quality of SAMs in terms of degree of order and compactness using cyclic voltammetry (CV).	

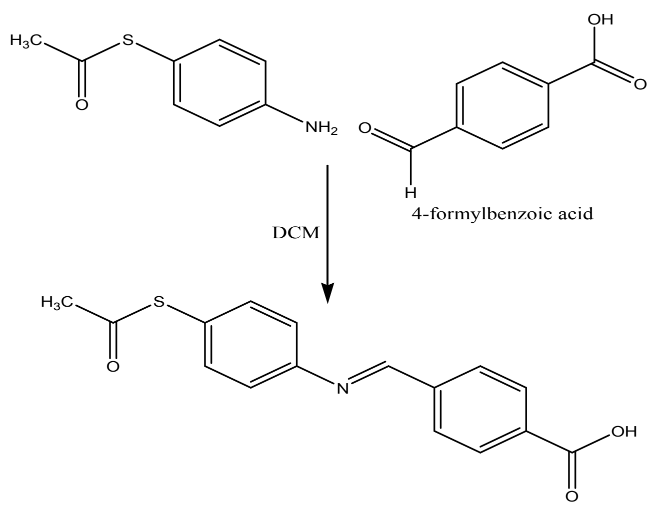
	• To quantify electron transport in ordered arrays of SAMs using electrochemical impedance spectroscopy (EIS). • To investigate the morphology of SAMs using Atomic Force Microscopy (AFM). • To confirm the binding of thiols on metal surface using FT-IR. • To utilize SAMs based metal surfaces as platforms for electrochemical sensing and determination of analyte metal ions in aqueous solutions. • To prepare chemically modified carbon paste electrodes (potentiometric sensors) based on thiol-gold nanoparticles for the potentiometric determination of metal ions in aqueous solutions. • To characterize the prepared sensors systematically in terms of various parameters such as slope, concentration range, detection limit, response time, functional pH range and selectivity. • To investigate the applications of prepared sensors for on-line monitoring of the heavy metal ions in environmental and biological samples.
11.	**Whether objectives were achieved (Give details)** Yes. All the objectives that were set have been achieved. In this project, multifunctional molecular nanowires with terminal thiol (SH) and sensory functional groups incorporated into the backbone/tail were prepared. The self-assembled monolayers (SAMs) of prepared molecular wires prepared on gold and platinum electrode surfaces and systematically studied for their quality, order, compactness and electron transportation properties using electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Further, all the SAMs would be imaged using atomic force microscope (AFM) to examine the topographic surface and a section analysis of height images gave root-mean-square (RMS) roughness. In addition, the binding of molecular wires on the gold surface will be confirmed using FT-IR Microscopy. The SAMs based electrodes will be applied as platform for the impedimetric sensing of heavy metal ions in aqueous media. Further, the gold nanoparticles coated self-assembled molecules would be applied as modifier to construct chemically modified carbon paste electrodes for heavy metal ions

12.	**Achievements from the project:** In this project, multifunctional molecular nanowires with terminal thiol (SH) and sensory functional groups incorporated into the backbone/tail were prepared and assembled on the surface of Au and Pt electrodes. The self-assemble monolayers so formed were characterized using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM). Molecular wires possess thiol head groups which allow SAM formation through the bond formation between sulfur of thiol group and gold electrode. The other donor atoms in backbone and on the surface of SAM have capacity to interact with metal ions in solution. Keeping this in view, Au-SAM electrodes were investigated as a platform for sensing of metal ions in aqueous solution, using EIS. Impedimetric sensor for detection of copper (II) and cobalt(III) have been successfully developed. The sensors developed could serve as a as simple, reliable and sensitive method for the electrochemical detection of heavy metals different environmental and biological samples.
13.	**Summary of the findings (500 words)** The proposed work can be divided into three parts: **<u>Part 1: Synthesis of Multifunctional Molecular Wires</u>:** In this project, multifunctional molecular nanowires with terminal thiol (SH) and sensory functional groups incorporated into the backbone/tail were prepared. The synthesis of multifunctional molecular wires was carried out in three steps: (1) Protection of thiol group; (2) Condensation reaction of protected thiol and (3) Deprotection of protected thiol to achieve final product. For example, in order to prepare molecular wire **1**, the reaction was carried out in following three steps**:** **1. Protection of thiol group of 4-aminothiol:** To protect thiol group, 4-aminothiol was refluxed with acetyl chloride and pyridine in dichloromethane (DCM) for 24 hrs at 25-30°C. The completion of reaction was monitored using TLC.



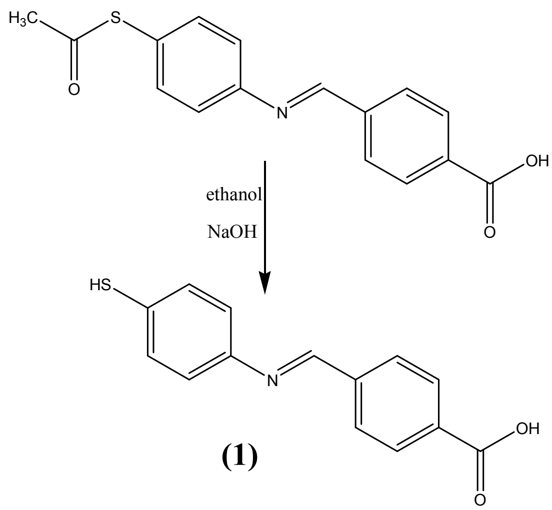
2.Condensation of protected aminothiol wih4-formyl benzoic:

Added 4-formyl benzoic acid to the product of 1st step in DCM and refluxed it for 16hrs at 35-40˚C. Checked the reaction progress by again TLC.



3. Deprotection of thioacetate group of the condensation product to final Product:

Dissolved the product of 2nd step in ethanol in two neck round bottom flask under inert atmosphere. Added NaOH solution in dropwise fashion then reflux contents for 2 hrs at 70-80 ˚C and neutralized the mixture with degassed 2M HCl solution and transferred the contents to a separatory funnel under inert atmosphere. Added degassed diethyl ether and degassed water to the separatory funnel before separating the organic layer. Washed the organic layer with degassed water and dried over sodium sulphate to remove moisture content. Then remove the solvent at 40˚C using a rotary evaporator. The product can be stabilized by adding small amount of 4-tert-butylcatechol.



(1)

Following the same procedure, multifunctional molecular wires shown in **Figure 1** were prepared. Multifunctional molecular nanowires with terminal thiol (SH) and sensory functional groups incorporated into the backbone/tail will be prepared as mentioned in **scheme 1**. These molecular wires **1 – 4** consist of terminal –SH group which possesses strong affinity for binding with the metal surfaces like gold and the backbone consist of functional groups which have capacity to bind with analyte metal ions. For each thiol, different spacers such as saturated spacer (**a, b, c**), phenyl ring spacer (**d**) and heterocyclic ring spacer (**e** and **f**) will be incorporated to prepare molecular wires having structurally different backbones. The characterization of the molecular wires for the confirmation of their molecular structure and purity were made by techniques such TLC, IR, NMR, MS and elemental analysis.

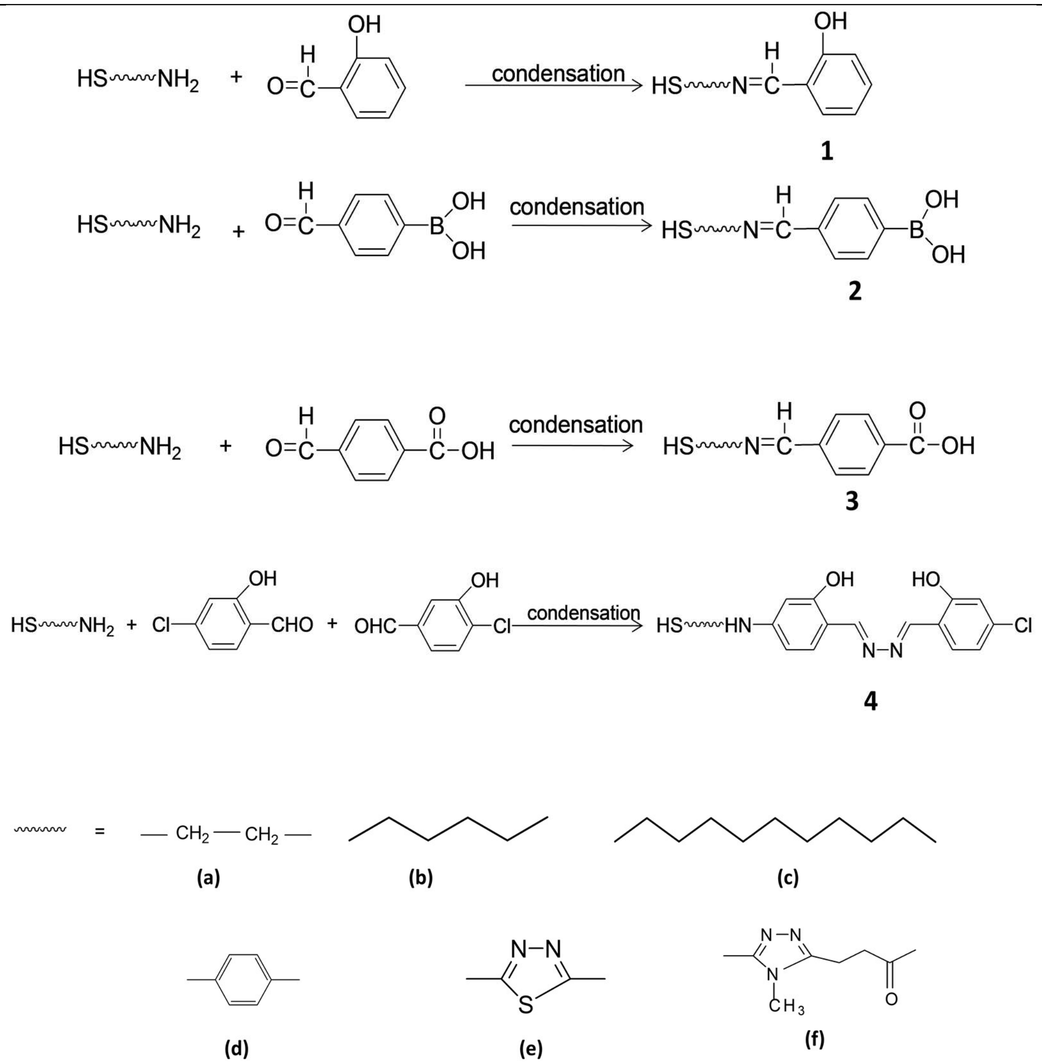


Figure 1: Structures of multifunctional molecular nanowires

Part 2: Preparation of Self-assembled monolayers

The self-assembled monolayers (SAMs) of prepared molecular wires were prepared on gold and platinum electrode surfaces by immersing the clean metal electrodes in 1.0 mM solution of nanowire for appropriate duration at room temperature. All the self-assembled monolayers on metal electrode surfaces were systematically studied for their quality, order, compactness and electron transportation properties using electrochemical techniques such as cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Further, all the SAMs were imaged using atomic force microscope

(AFM) to examine the topographic surface and a section analysis of height images gave root-mean-square (RMS) roughness. In addition, the binding of molecular wires on the gold surface were confirmed using FT-IR Microscopy.

The study of self-assembled monolayers can be divided into two sections:

(A) Electrochemical Studies:

(i) Cyclic voltammetry: Cyclic voltammetry (CV) was used to investigate the quality of self-assembled monolayers (SAMS) on the electrodes. This well established electrochemical technique, enabled us to examine the integrity and compactness of self-assembled monolayers (SAMS) on the electrodes. The screening of performance of SAM with different probes is necessary was also carried out in order to characterize their integrity and passivating properties. Hence, the passivating behavior of self-assembled monolayers of various nanowires on metal electrodes in the presence of two different redox probe molecules such as $K_3[Fe(CN)_6]$ and $[Ru(NH_3)_6]Cl_3$, was also investigated.

(ii) Electrochemical Impedance spectroscopy: Electrochemical impedance spectroscopy (EIS) is a powerful additional technique for analyzing the surface of the self-assembled monolayer on the metal electrode as it provides quantitative information about the structural integrity of monolayers. In EIS, sinusoidal potential sweeps with the frequencies varying from 0.1 Hz to 100 KHz to the metal electrode or metal-SAM electrode. EIS measurements were carried out in two parts: (a) Firstly, at open circuit potentials, where there was no overpotential at the SAM coated metal electrodes, in order to investigate the electron charge transfer due to the defects within the monolayers. In second part, the DC potential was applied over a wide range on SAM coated electrode. The Zplot software was used to collect, plot and interpret the raw impedance data. The Nyquist plots were fitted using equivalent Randles circuit models and the electron transportation properties of self-assembled monolayers were also evaluated.

(B) Morphological studies:

(i) AFM studies: The surfaces of self-assembled monolayers were characterized using atomic force microscopy (AFM) in terms of roughness of the surface of monolayers.

	(ii) FT-IR studies: The binding of molecular wires on the metal surface was confirmed by using FT-IR. **(3) Application of Self-assembled monolayers as platforms for electrochemical sensing** The SAMs based electrodes were applied as platform for the sensing of metal ions in aqueous media. Further, the gold nanoparticles coated self-assembled molecules were also applied as modifier to construct chemically modified carbon paste electrodes for heavy metal ions. Both types of sensors so prepared were characterized in terms parameters: measuring range, slope, detection limit, response time, functional pH range and selectivity. **Practical Application:** The practical significance of SAM based impedimetric and potentiometric sensors was tested by using them for estimation of heavy metal ions under investigation in different environmental samples such as water, soil, food crops - wheat grains and rice grains.
14.	**Contribution to society:** For the analysis of heavy metals in environmental and biological samples, various expensive techniques are being used. Development of suitable sensors will be very useful as these sensors developed could serve as a as simple, reliable and sensitive method for the electrochemical detection of heavy metals different environmental and biological samples.
15.	**Whether any Ph.D. Enrolled/Produced out of the project** Yes, the Project Fellow, Miss. Sarbjeet Kaur is enrolled as a Ph.D. student.
16.	**No. of the publication out of project:** Three (in Process) Work is under compilation for publications.

(PRINCIPAL INVESTIGATOR) **(REGISTRAR/PRINCIPAL)**