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Journal Name

ARTICLE

## Development of Hg<sup>2+</sup> sensor based on N'-[1-(pyridin-2-yl)ethylidene] benzenesulfonyl-hydrazide (PEBSH) fabricated silver electrode for environmental remediation

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N'-[1-(pyridin-2-yl)ethylidene]benzenesulfonylhydrazide (PEBSH) was synthesized via a simple condensation of 2-acetyl pyridine and benzene sulfonyl hydrazide in very good yield and crystallized in methanol. The characterization of title compound were accomplished using highly sophisticated spectroscopic techniques like, UV/VIS, IR, <sup>1</sup>H-NMR and <sup>13</sup>C-NMR. Finally the structure was determined with single crystal x-ray diffraction techniques for its further usage in detection of cations. Then a thin-layer of PEBSH onto flat-silver electrode (AgE) is deposited with conducting coating agents to fabricate a sensitive and selective Hg<sup>2+</sup> ions sensor in short response time in phosphate buffer phase. The fabricated cationic-sensor is also exhibited higher sensitivity, large-dynamic concentration ranges, long-term stability, and improved electrochemical performances towards mercury ions. The calibration plot is linear ( $r^2 = 0.9799$ ) over the large Hg<sup>2+</sup> concentration ranges (0.1 nM to 1.0 mM). The sensitivity and detection limit is  $\sim 2.1897 \mu\text{A}\cdot\text{mM}\cdot\text{cm}^{-2}$  and  $\sim 0.063 \text{ nM}$  (signal-to-noise ratio, at a SNR of 3) respectively. This novel effort is initiated a well-organize way of efficient cationic sensor development with conducting binder deposited flat-electrode for toxic pollutants in environmental and health-care fields in large scales.

Key words: Sulphonyl hydrazone; N'-[1-(pyridin-2-yl)ethylidene]benzenesulfonylhydrazide; Hg<sup>2+</sup> ions; I-V method; Silver electrode; Sensitivity,

### Introduction

Organic molecules with electron donor functional groups in them are of great interest in chemistry due to large number of applications in medicinal, biological [1], catalysis [2], environmental [3] and organometallic [4] chemistry by binding various metal elements. There are different functional groups which have capability to donate electron pairs like O-H and N-H. The N-H group is available in pyrole, pyrazole, pyrazoline and diazpine etc. The hydrazone derivatives belong to class of organic compounds which have also capability to bind metal

element via N-H linkage and applied in various biological [5] and commercial studies [6,7]. Caffeine based hydrazone derivatives were investigated as selective anticancer agents towards T-lymphoblastic leukaemia cells (T-LLC) [8]. Benzisothiazole hydrazone were synthesized and reported as anticancer agents [9]. Pyrimidine containing hydrazones were prepared and tested against *C. albicans* and *C. Glabrata* for antifungal activity [10]. Environmentally polluted cyanide and acetate ions were detected using the novel hydrozone derivatives [11]. Some hydrazone derivatives have effectively worked as hole-transporting materials also known as electroactive derivatives [12].

Pyridine containing molecules are well known for complexation due to availability of lone pair of electron available on nitrogen atom. Literature provide a reasonable references where pyridine ring was merged with the hdrazone system to form bi/tridentate chelating agents [13] which enhance the capability to extract the metal ions. Pyridine-2-aldehyde-2-quinolyhydrazone (PAQH) has been employed as a spectroscopic and flourimetric sensor for the detection of Pd [14], Co [15], Ni [16] and Zn [17]. 2-[(Pyridine-4-carbonyl)-hydrazono]-propionic acid was used as a ligand to drag Mn(II) metal. The *E* and *Z* form of pyridine-2-carbaldehyde-2'-

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pyridylhydrazone (PCPH), has been isolated and subjected for the complexation of Mn- and Re-halogenocarbonyls [18]. The supramolecular chemistry of some metal complexes of hydrozone system were explained using single crystal x-ray diffraction approach [19]. Tridentate ligands were synthesized with hydrazone backbone and used to co-ordinate iron and copper metals [20].

Mercury is one of the most tarnished heavy metals [21], which originated serious environmental and health problems [22]. Owing to such concerns, attention in designing and constructing cationic sensors with extremely high selectivity and sensitivity for  $Hg^{2+}$  has been experiencing an expansion. Till today, sensors based on small organic molecules [23], DNA [24], protein [25], oligonucleotide [26], and alkyne oxymercuration [27] have been developed and tested the mercury ions. Many of these approaches have limitations such as non-specific interference from competing metal ions, time consuming, lower-water solubility, un-economical, elevated working temperatures, or a nitrogen-purge buffer which cause inconvenience for mercury detection in biological samples. The development of simple, reliable, and sensitive methods for the detection of toxic metallic ions for environmental safety, protection, food quality control, and human health [28]. There are several hazardous cations have been classified as "priority pollutants" by both the United States Environmental Protection Agency (USEPA) and the European Commission. Mercury elements are comparatively in waste streams of diverse large-scale processing and manufacturing where they serve as precursor materials in various industries such as coal mining, crude oil refining, paper bleaching, and production of dyes, resins, plastics, explosives, detergents, pharmaceuticals, pesticides, and herbicides [29, 30]. In difference, several metallic constituents of plant origin have been originated to display a broad range of attractive physiological characteristics [31, 32]. Recent determination methods such as spectrophotometry, fluorimetry, gas or liquid chromatography, mass spectrometry and capillary electrophoresis are usually perceptible and consistent but possess limitations, such as being expensive, time-consuming and requiring pre-concentration and extraction steps that increase the risk of sample loss and generation of other hazardous byproducts [33]. Electrochemical sensing of toxic mercury compounds represents a promising approach that can be utilized to complement already existing methods owing to collective characteristics such as high sensitivity and selectivity, low cost, simple instrumentation and potential for miniaturization [34, 35]. As we were already involved in the synthesis of sulfonamides [36-40] so, here, we synthesized a very new tridentate ligand  $N'$ -[1-(pyridin-2-yl)ethylidene]benzenesulfonohydrazide (PEBSH) Scheme 1, with the capacity to bind metal element via nitrogen of pyridine and sulphonyl hydrazone system. Scifinder and Cambridge structural database fail to provide any single reference about the synthesis of this new molecule. PEBSHs based on silver electrodes are used for sensing  $Hg^{2+}$ , wherein compound containing nitrogen and oxygen atoms are incorporated into the side chains of conjugated system and where the coordination of mercury ion to oxygen and nitrogen atoms leads to inter-chain

p-p interactions for  $Hg^{2+}$  detection [41]. As mercury is highly carcinogenic and serious to health and environment, it is urgently required to fabricate a simple and reliable sensor with PEBSH. Consequently, the mercury sensing properties of PEBSH films have been investigated and explained in term of fabrication and their typical characteristics. The simple fabrication technique is used for the preparation of PEBSH on flat AgE with conducting coating binders, which is measured by simple and reliable I-V technique. To best of our knowledge, this is the first report for sensitive detection of  $Hg^{2+}$  ions with sulphonyl hydrazone using simple I-V technique in short response time.

## Experimental

Benzenesulphonylhydrazine (1 g) was purchased from Kochlight laboratories Ltd. Colonbrook bucks England, 2-acetylpyridine (0.65 g) obtained from Acros organic, New Jersey USA. Analytical grade solvents (Chloroform, Ethanol) were taken from BDH VWR international Poole, BH15, 1TD, England. All these were used without any further purification. Analytical grade of  $HgCl_2$ ,  $Al_2(SO_4)_3$ , ethyl acetate,  $Ba(NO_3)_2$ ,  $CaCl_2$ ,  $CdSO_4$ , disodium phosphate ( $Na_2HPO_4$ ),  $Ce(NO_3)_2$ ,  $Co(NO_3)_2$ , butyl carbitol acetate,  $CrCl_3$ ,  $KCl$ ,  $MgCl_2$ ,  $Na_2SO_3$ ,  $NiCl_2$ ,  $SbCl_3$ ,  $SnCl_2$ ,  $Y(NO_3)_3$ ,  $ZnSO_4$ , and monosodium phosphate ( $NaH_2PO_4$ ) was used and purchased from Sigma-Aldrich Company, USA. Stock solution of 0.1 M  $Hg^{2+}$  ions solution was prepared from the purchased chemical. A Stuart Scientific SMP3, version 5.0 melting point apparatus (Bibby Scientific Limited, Staffordshire, UK) was used to record the melting point, and the reported m.p. is uncorrected.  $^1H$ -NMR &  $^{13}C$ -NMR spectra were recorded on an AVANCE-III 600 MHz instrument (Bruker, Fallanden, Switzerland) at 300 K, and chemical shifts are reported in ppm with reference to the residual solvent signal. FT-IR spectra were recorded as neat on a Thermo Scientific NICOLET iS50 FT-IR spectrometer (Thermo Scientific, Madison, WI, USA). UV-vis. studies were performed by using Evolution 300UV/VIS spectrophotometer (Thermo Scientific). I-V technique was executed with fabricated AgE throughout the all experiments by using Electrometer (Kethley, 6517A, Electrometer, USA) at room conditions. Caution! Mercury is toxic. Only a small amount of this material was used and prepared the required solution and handled with care.

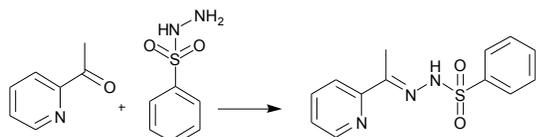
### Synthesis of $N'$ -[1-(pyridin-2-yl)ethylidene]benzenesulfonohydrazide (PEBSH):

The mixture of Benzenesulphonylhydrazine (1g, 5.8 mmol) and 2-acetylpyridine (0.65 g, 5.8 mmol) was refluxed in ethanol for 2 hours. Then it was allow to cool at room temperature, precipitate obtained were filtered and washed with cold ethanol. The product obtained were crystalized from ethanol, and ethylacetate (50:50), yield: 93%, m.p. 136-137 °C.

$^1H$ -NMR: (850 MHz) ( $CDCl_3$ ) $\delta$ : 14.65 (1H, broad, NH), 8.53 (1H, d, Ar-H,  $J = 8.5$ ), 8.04 (2H, d, Ar-H,  $J = 10.2$ ), 7.97 (1H, d, Ar-H,  $J = 8.5$ ), 7.67 (1H, dd, Ar-H,  $J = 8.5, 8.5$ ), 7.60 (1H, t, Ar-H,  $J = 8.5, 8.5$ ) 7.53 (2H, t, Ar-H,  $J = 10.2, 10.2$ ), 7.24 (1H, dd, Ar-H,  $J = 10.2, 10.2$ ), 2.29 (3H, s,  $CH_3$ )  $^{13}C$ -NMR: (850 MHz) ( $CDCl_3$ ) $\delta$ : 154.35, 153.00, 148.39, 138.38, 136.40, 133.38, 129.07, 128.02, 124.06, 120.71, 11.40. IR  $\nu_{max}$ : 3159, 2636, 2323, 2160, 2050, 1978, 1565, 1450, 1399,

1311, 1159, 1053, 910, 753, 722, 685, 578, 551  $\text{cm}^{-1}$ . UV/VIS  $\lambda_{\text{max}} = 281 \text{ nm}$ .

**Scheme 1:** Synthesis of  $\text{N}'$ -[1-(pyridin-2-



yl)ethylidene]benzenesulfonylhydrazide (PEBSH)

#### Preparation and fabrication of AgE with PEBSH:

Phosphate buffer solution (PBS, 0.1 M) at pH 7.0 is prepared by mixing of equi-molar concentration of 0.2 M  $\text{Na}_2\text{HPO}_4$  and 0.2 M  $\text{NaH}_2\text{PO}_4$  solution in 100.0 mL de-ionize water at room conditions. AgE is fabricated with PEBSH using butyl BCA and EA as a conducting binder. Then it is kept in the oven at 35.0 °C for 3 hour until the film is completely dried, stable, and smooth. A cell is assembled with PEBSH/binders/AgE and Pd-wire as a working and counter electrodes respectively. As received  $\text{HgCl}_2$  is diluted to make various concentrations (0.1 nM to 0.1 M) in DI water and used as a target analyte. The ratio of current versus concentration (slope of calibration curve) is used to calculate the  $\text{HgCl}_2$  sensitivity. Detection limit is evaluated from the ratio of 3N/S (ratio of Noise $\times$ 3 vs. Sensitivity) from the linear dynamic range of calibration curve. Electrometer is used as a constant voltage sources for I-V measurement in simple two electrode system. Amount of 0.1M PBS was kept constant in the beaker as 10.0 mL throughout the chemical investigation. The PEBSH is fabricated and employed for the detection of  $\text{Hg}^{2+}$  ions in liquid phase. I-V response is measured with PEBSH/AgE film.

#### Crystallography:

The solid material of molecule was crystalized under slow evaporation. Sample was screened out under microscope to get a crystal with appropriate sizes, Table 1. Then it was fixed on tip of glass needle with the help of locally available glue to mount on Agilent SuperNova (Dual source) Agilent Technologies Diffractometer, equipped with graphite-monochromatic Cu/Mo  $K\alpha$  radiation for data collection. The data collection was accomplished using CrysAlisPro software [42] at 296 K under the Mo  $K\alpha$  radiation. The structure solution was performed using SHELXS-97 [43] and refined by full-matrix least-squares methods on  $F^2$  using SHELXL-97 [43], in-built with WinGX [44]. All non-hydrogen atoms were refined anisotropically by full-matrix least squares methods [43]. Figures were drawn using PLATON [45] and ORTEP-3 [46].

The molecules have three different kind of hydrogen atoms. The aromatic C-H hydrogen atoms were positioned geometrically and treated as riding atoms with C-H = 0.93 Å and Uiso(H) = 1.2 Ueq(C) carbon atoms. The methyl hydrogen atoms were positioned geometrically with  $C_{\text{methyl}}\text{-H} = 0.96 \text{ Å}$  and Uiso(H) = 1.5 Ueq(C) for methyl carbon atom. The N-H = 0.89(2) Å, hydrogen atom was located with difference fourier map and refined using riding model with Uiso (H) = 1.2 Ueq(N). The cif has been submitted to CCDC and got CCDC

numbers as 1063027 for molecules I-III respectively, the data can be obtained free of cost freely from CCDC bank.

## Results and discussion

In order to comprehend the spatial geometry and other inter- and intra-molecular interactions in the unit cell, we have determined the crystal structure of molecule I. The ORTEP diagram of title compound is shown in Figure 1. The molecule consist of two aromatic rings i.e. benzene ring (C1-C6) and pyridine heterocyclic ring (C8-C12/N3). Both of these rings are oriented at dihedral angle of 57.21 (8)°. Unit cell dimensions and other crystal structure parameters are given in Table 1, while the selected bond lengths and bond angles are shown in Tables S1 & S2. The molecules undergo two different intermolecular interactions, in first case N1-H1N...O2 type classical interaction connects the molecules along  $a$  axes to form long chains Figure 2, Figure S1, Table 2. These chains were connected through another C12---H12...O1 non-classical hydrogen bonding interaction with  $d\text{H...O} = 2.49 \text{ Å}$  and symmetry operation is  $\frac{1}{2}+X, \frac{1}{2}-Y, 1+Z$ , along  $c$  axes. The O1-S1-O2 angle is 119.90(11) which is in accordance with already published sulfonamide structures and represents that the geometry around sulphur atom is distorted tetrahedral.

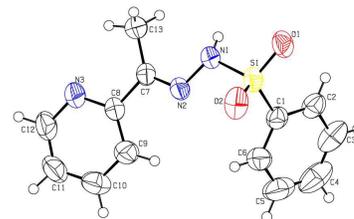


Figure 1: ORTEP diagram of 1, thermal ellipsoids were drawn at 50% probability level.

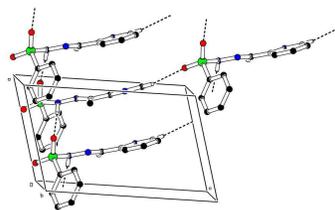


Figure 2: A perspective view showing intermolecular hydrogen bonding interaction via dashed lines.

#### Spectroscopic discussion:

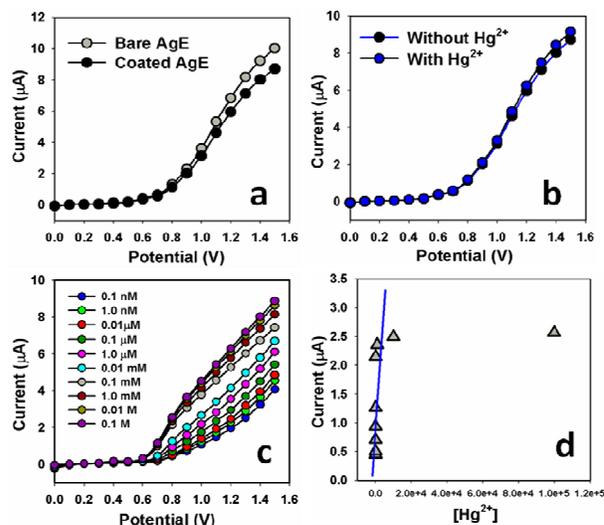
The target molecule was synthesized via simple condensation reaction of 2-acetylpyridine and benzene sulfonyl hydrazine **Scheme 1**. We have characterized this using various spectroscopic techniques and finally structure was determined by single crystal x-ray diffraction studies. Figure S2, show the respective  $^1\text{H}$ NMR and  $^{13}\text{C}$ NMR values in supplementary material. The molecule has three different kind of protons i.e. NH,  $\text{CH}_3$  and aromatic. Three methyl protons shows singlet at  $\delta$  2.29, the NH appeared at 14.65 while the aromatic protons are perfectly located in their low field are with the range  $\delta$  7.23-8.53. Although it is difficult to predict the each and every aromatic proton in a molecule without 2-D NMR but the purity of our synthesized compound was good enough to identify

these on the basis of chemical shifts ( $\delta$ ), proton environment and coupling constant ( $J$ ). We have two aromatic rings in the molecule first one is phenyl and other is pyridine. Phenyl ring has five proton which appeared in three different signals i.e. a doublet at  $\delta$  8.04 shows two protons with coupling constant  $J = 10.2$  Hz, a triplet at  $\delta$  7.53 also shows the presence of two protons with coupling constant  $J = 10.2$  Hz and thirdly a doublet of doublet at  $\delta$  7.24 represent a single proton Figure S4. The four protons of pyridine are appeared in four separate signals at  $\delta$  8.53 with  $J = 8.5$ , at  $\delta$  7.60 Hz as triplet with  $J = 8.5$  Hz, at  $\delta$  7.67 as triplet with  $J = 8.5$  Hz and at  $\delta$  7.97 as doublet of doublet with  $J = 8.5$  Hz. Similarly assignment to identify carbon atoms was accomplished as C-methyl observed at 11.40. All other aromatic carbon was appeared in their respective region Figure S2. UV/VIS values were measured in chloroform quantitatively and the spectra was scanned within the range of 200-600 nm. The concentration of solution was  $4.97 \times 10^{-5}$  molar. The  $\lambda_{\max}$  observed is 281 nm, Figure S3, which is due to the  $\pi$ - $\pi^*$  transition of C=NH (imine) functional group of title compound. The IR spectroscopy revealed the structure by defining functional groups through various stretching and bending peaks observed in particular areas of spectrum Figure S4. The N-H stretching peak appeared at  $3159 \text{ cm}^{-1}$  nm with low intensity while N-H wagging seemed at  $685 \text{ cm}^{-1}$ . The C=N (imine) peaks due to stretching vibrations appeared at  $1565$  &  $1582 \text{ cm}^{-1}$ . S=O stretching vibrations appeared with low intensity at  $1311 \text{ cm}^{-1}$ . C-H stretching, bending and rocking vibrations were observed at  $2636 \text{ cm}^{-1}$ ,  $753 \text{ cm}^{-1}$  and  $910 \text{ cm}^{-1}$  respectively. C=C stretching and bending vibrations were simulated at  $1450$  and  $1053 \text{ cm}^{-1}$ .

**Application: Detection of  $\text{Hg}^{2+}$  ions with PEBSH/AgE:**

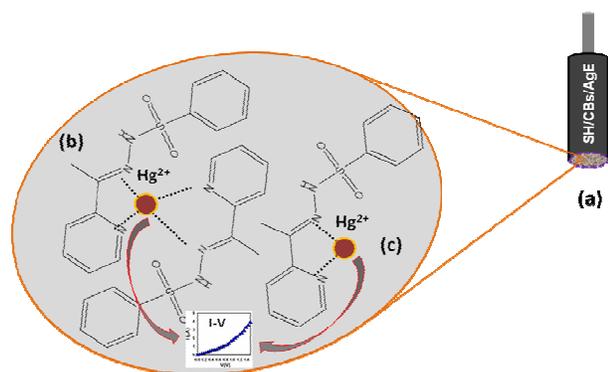
The potential application of PEBSH assembled onto AgE as cationic sensors (especially  $\text{Hg}^{2+}$  ions analyte in buffer system) has been executed for measuring and detecting target chemical. Enhancement of the PEBSH/AgE as cationic sensors is in the initial stage and no other reports are available. The PEBSH/AgE sensors have advantages such as stability in air, non-toxicity, chemical inertness, electro-chemical activity, simplicity to assemble, ease in fabrication, and chemo-safe characteristics. As in the case of  $\text{Hg}^{2+}$  ions sensors, the incident of rationale is that the current response in I-V method of PEBSH/AgE considerably changes when aqueous  $\text{Hg}^{2+}$  ions analytes are adsorbed. The PEBSH/AgE was applied for fabrication of cationic-sensor, where  $\text{Hg}^{2+}$  ions were measured as target analyte. The fabricated-surface of PEBSH sensor was prepared with conducting binders (EC & BCA) on the AgE surface. The fabricated AgE electrode was put into the oven at low temperature ( $35.0 \text{ }^\circ\text{C}$ ) for 3.0 hrs to make it dry, stable, and uniform the surface totally. The PEBSH was employed for the detection of  $\text{Hg}^{2+}$  ions in liquid phase. I-V responses were measured with sulphonyl hydrazone coated thin-film (in two electrodes system). In experimental section, it was already outlined the  $\text{Hg}^{2+}$  ions sensing protocol using the PEBSH/AgE modified electrode. The concentration of  $\text{Hg}^{2+}$  ions was varied from 0.1 nM to 0.1 M by adding de-ionized water at different proportions.

Here, Fig. 3(a) is represented the I-V responses for uncoated-AgE (gray-dotted) and PEBSH/AgE (black-dotted) electrodes. In PBS system, the PEBSH/AgE electrode shows that the reaction is reduced slightly owing to the presence of PEBSH on bare-AgE surface. A considerable enhancement of current value with applied potential is demonstrated with fabricated PEBSH/AgE in presence of target  $\text{Hg}^{2+}$  ions analyte, which is presented in Fig. 3(b). The black-dotted and blue-dotted curves were indicated the response of the fabricated film before and after injecting  $25.0 \text{ } \mu\text{L}$   $\text{Hg}^{2+}$  solution in  $10.0 \text{ mL}$  PBS solution respectively. Significant increases of current are measured after injection of target component in regular interval. I-V responses to varying  $\text{Hg}^{2+}$  ions concentration on thin PEBSH/AgE were investigated (time delaying, 1.0 sec; response time, 10s) and presented in the Fig. 3(c). Analytical parameters (such as sensitivity, detection limit, linearity, and linear dynamic range etc) were calculated from the calibration curve (current vs. concentration), which was presented in Fig. 3(d). A wide range of  $\text{Hg}^{2+}$  ions concentration was selected to study the possible detection limit (from calibration curve), which was examined in  $0.1 \text{ nM}$  to  $0.1 \text{ M}$ . The sensitivity was calculated from the calibration curve, which was close to  $\sim 2.1897 \text{ } \mu\text{A} \cdot \text{mM} \cdot \text{cm}^{-2}$ . The linear dynamic range of the PEBSH/AgE sensor was employed from  $0.1 \text{ nM}$  to  $1.0 \text{ mM}$  (linearly,  $r^2=0.9948$ ), where the detection limit was calculated about  $0.016 \pm 0.002 \text{ nM}$  (ratio,  $3\text{N}/\text{s}$ ). The PEBSH/AgE was exhibited mesoporous behaviors, where the electrical resistance decreases under the presence of target  $\text{Hg}^{2+}$  ions in PBS phase. The film resistance was decreased gradually (increasing the resultant current) upon increasing the  $\text{Hg}^{2+}$  ions concentration in bulk system.



**Figure 3.** I-V responses of (a) AgE (without PEBSH) and PEBSH/AgE (with PEBSH); (b) PEBSH/AgE (in absence of  $\text{Hg}^{2+}$  ions) and  $\text{Hg}^{2+}$  ions/PEBSH/AgE (in presence of  $\text{Hg}^{2+}$  ions); (c) concentration variations ( $0.1 \text{ nM}$  to  $0.1 \text{ M}$ ) of  $\text{Hg}^{2+}$  ions, (d) calibration plot of PEBSH fabricated silver electrode (at  $+0.5 \text{ V}$ ).

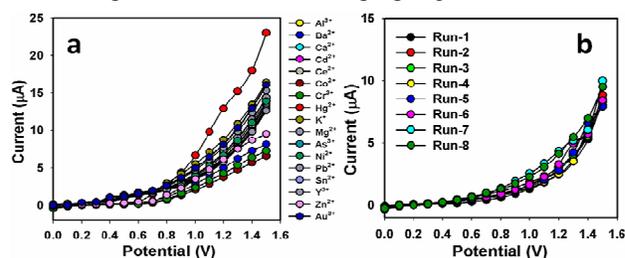
I-V characteristic of the PEBSH is activated as a function of  $\text{Hg}^{2+}$  ions concentration at room conditions, where improved current response is observed. In the Scheme-2(a), the mechanism of  $\pi$ - $\pi$  interaction between PEBSH and target analyte is well presented here. As obtained, the current response of the PEBSH-film is increased with the increasing concentration of  $\text{Hg}^{2+}$  ions, however similar phenomena for toxic chemical detection have also been reported earlier [47-53]. For a low concentration of  $\text{Hg}^{2+}$  ions in liquid medium, there is a smaller surface coverage of  $\text{Hg}^{2+}$  ions molecules on PEBSH/AgE film and hence the surface reaction proceeds steadily. By increasing the  $\text{Hg}^{2+}$  ions concentration, the surface reaction is increased significantly (gradually increased the response as well) owing to surface area (assembly of PEBSH/AgE) contacted with  $\text{Hg}^{2+}$  ions molecules. Further increase of  $\text{Hg}^{2+}$  ions concentration on PEBSH/AgE surface, it is exhibited a more rapid increased the current responses, due to larger area covered by  $\text{Hg}^{2+}$  ions and the  $\pi$ - $\pi$  interaction of the functional groups (lone pairs of nitrogen). The  $\pi$ - $\pi$  interaction could be approaches as per the schematic view, inter-molecular scheme 2(b) and intra-molecular scheme 2(c) interaction of the sulphonyl hydrazones as per explained by Masoumi et al [54]. Usually, the surface coverage of  $\text{Hg}^{2+}$  ions on PEBSH/binders/AgE surface is reached to saturation, based on the regular enhancement of current responses. To support the binding of  $\text{Hg}^{2+}$  with sensor PEBSH, FTIR studies were carried out, as per request. It is quite evident from the study that, as the addition of  $\text{Hg}^{2+}$  with PEBSH, it is shifted the  $-\text{NH}-$  characteristic peak towards lower frequency region, due to attachment or conjugation of  $\text{Hg}^{2+}$  ions into PEBSH, which caused the interaction of  $-\text{NH}-$  present in the PEBSH (Figure S5).



**Scheme 2.** Mechanism of the probable interaction of  $\text{Hg}^{2+}$  with PEBSH with conducting binders embedded onto flat-AgE. (a) Fabricated electrode and (b)  $\pi$ - $\pi$  inter-molecular, and (c)  $\pi$ - $\pi$  intra-molecular bonding interactions between lone-pair of nitrogen (PEBSH) and  $\text{Hg}^{2+}$ .

Interference (for selectivity) was studied for  $\text{Hg}^{2+}$  ions sensor in presence other chemicals like  $\text{Al}^{3+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ce}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{As}^{3+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Y}^{3+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Au}^{3+}$  using the PEBSH embedded on flat AgE (Figure 4a). The concentrations of all analytes are kept constant at  $0.1\ \mu\text{M}$  level

in PBS system. Here, it is clearly demonstrated the PEBSH/AgE sensor is most selective toward  $\text{Hg}^{2+}$  ions compared with other chemicals. The excellent selectivity is ascribed to the reasons are terminal functional groups have strong and stable interaction with  $\text{Hg}^{2+}$  resulting in the increase the current response in I-V system. Dual or more complex matrix were investigated in presence of various analytes with target matrix and presented in ESM (Figure S6). To check the reproducibly and storage stabilities, I-V response for PEBSH/AgE sensor was examined (Figure 4b). After each experiment, the fabricated PEBSH/AgE substrate was washed thoroughly with the phosphate buffer solution and observed that the current response was not significantly decreased. The sensitivity was retained almost same of initial sensitivity up to few days, after that the response of the fabricated PEBSH/AgE electrode gradually decreased. The  $\text{Hg}^{2+}$  ions sensor based on PEBSH/AgE is displayed good repeatability as well as reproducibility with good stability for over week and no major changes in sensor responses are found. After a week, the ionic sensor response with PEBSH/AgE was slowly decreased, which may be due to the weak-interaction between fabricated PEBSH active functional sides and  $\text{Hg}^{2+}$  ions. The significant result was achieved by PEBSH/AgE, which can be employed as proficient electron mediators for the development of efficient cationic sensors. Actually the response time was around 10.0 sec for the fabricated PEBSH/AgE to reach the saturated steady-state level. The higher sensitivity of the fabricated PEBSH/AgE could be attributed to the excellent absorption (assembly of PEBSH/binders/AgE) and adsorption ability (surface of PEBSH/binders/AgE), high catalytic-decomposition activity, and good biocompatibility of the PEBSH. The estimated sensitivity of the fabricated sensor is relatively higher and detection limit is comparatively lower than previously reported chemical sensors based on other nano-composite or nano-materials modified electrodes measured by I-V systems [55-58]. Due to PEBSH/binders/AgE, it provides a favorable micro-environment for the  $\text{Hg}^{2+}$  ions detection with good quantity. The high sensitivity of PEBSH/AgE provides high electron communication features which enhanced the direct electron transfer between the active sites of PEBSH and AgE. The PEBSH/AgE system is demonstrated a simple and reliable approach for the detection of toxic chemicals. It is also revealed that the significant access to a large group of chemicals for



wide-range of ecological and biomedical applications in environmental and health-care fields respectively.

**Figure 4.** Selectivity studied with various analytes using PEBSH/AgE. (a) I-V responses of various analytes and (b) Current responses of analytes at  $+0.5\text{V}$  ( $\text{Hg}^{2+}$  ions); Analyte

concentration was taken at 0.1  $\mu\text{M}$ . Potential range: 0 to +1.5 V; Delay time: 1.0 s

## Conclusions

We have synthesized new PEBSH derivative for its application as detection of toxic metal ions. The molecule was characterized completely using spectroscopic and single crystal diffraction approaches. Analytical performances of  $\text{Hg}^{2+}$  ions sensor using PEBSH/AgE are investigated by reliable I-V method in terms of sensitivity, detection limit in short response time as well as reproducibility. This extensive research is performed in terms of preparation and characterization of PEBSH and applied for the  $\text{Hg}^{2+}$  ions sensor using I-V method. The novel idea imparts high selectivity and fast detection for mercury ion to the PEBSH fabricated AgE-probe. Potentially, the same concept might be applied to the creation of new sensors for monitoring other ions. Hence, this approach is introduced a new route for efficient toxic ionic sensor development in environmental and healthcare fields.

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## References

1. A.I. Mosa, A.A. Emara, J.M. Yousef and A.A. Saddiq, *Spectrochim. Acta A*, 2011, 81, 35-45.
2. S. Fukuzumi, *Pure Appl Chem*, 2007, 79, 981-991.
3. X.-B. Zhang, Z. Wang, H. Xing, Y. Xiang and Y. Lu, *Anal. Chem.*, 2010, 82, 5005-5011.
4. K. Roztocki, D. Matoga and J. Szklarzewicz, *Inorg. Chem. Commun.*, 2015, 57, 22-25.
5. V. Suryanti, M. Bhadbhade, H.M. Chawla, E. Howe, P. Thordarson, D.S. Black and N. Kumar, *Spectrochim. Acta Part A*, 2014, 121, 662-669.
6. S. Dalapati, Md.A. Alam, S. Jana and N. Guchhait, *J. Fluor Chem.*, 2011, 132, 536-546.
7. A.N. Kent, *Tetrahedron Lett.*, 2012, 53, 5616-5618.
8. R. Kaplánek, M. Jakubek, J. Rak, Z. Kejík, M. Havlík, B. Dolenský, I. Frydrych, M. Hajdúch, M. Kolář, K. Bogdanová, J. Králová, P. Džubák and V. Král, *Bioorg. Chem.*, 2015, 60, 19-29.
9. E.B. Lindgren, M.A. de Brito, T.R.A. Vasconcelos, M.O. de Moraes, R.C. Montenegro, J.D. Yoneda and K.Z. Leal, *Eur. J. Med. Chem.*, 2014, 86, 12-16.
10. M. Donna, N.A. Cammarata, G. Backes, G.E. Palmer and B.S. Jursic, *Bioorg. Med. Chem.*, 2014, 22, 813-826.
11. V.K. Gupta, A.K. Singh, and N. Gupta, *Sensors Actuat. B*, 2014, 204, 125-135.
12. A. Bieliauskas, V. Getautisb, V. Martynaitisb, V. Jankauskas, E. Kamarauskas, S. Krikstolaityte and A. Sackus, *Synthetic Met.*, 2013, 179, 27-33.
13. R.W. Frei, G.H. Jamro and O. Navratil, *Anal. Chim. Acta*, 1971, 55, 125-133.
14. R.E. Jensen and R.T. Pflaum, *Anal. Chim. Acta*, 1967, 37, 397-400.
15. S.P. Singhal and D.E. Ryan, *Anal. Chim. Acta*, 1967, 37, 91-96.
16. B.K. Afghan, D.E. Ryan, *Anal. Chim. Acta*, 1968, 41, 167-170.
17. R.E. Jensen, and R.T. Pflaum, *Anal. Chim. Acta*, 1966, 38, 1268-1269.
18. J.G. Dunn and D.A. Edwards, *J. Organomet. Chem.*, 1973, 61, 323-328.
19. S. Naskar, S. Naskar, R.J. Butcher and S.K. Chattopadhyay, *Inorg. Chim. Acta*, 2010, 363, 3641-3646.
20. V. Oleg, P.N. Palamarciuc, M.D. Bourosh, J.L. Revenco, Y.A. Simonov and R. Clérac, *Inorg. Chim. Acta*, 2010; 363: 2561-2566.
21. Z. Zhang, Q. Fan, P. Sun, L. Liu, X. Lu, B. Li, Y. Quan and W. Huang, *Macromol. Rapid Commun.* 2010, 31, 2160-2165.
22. Caballero, R. Martinez, V. Lloveras, I. Ratera, J. Vidal-Gancedo, K. Wurst, A. Tarraga, P. Molina and J. Veciana, *J. Am. Chem. Soc.*, 2005, 127, 15666-15667.
23. E.M. Nolan and S.J. Lippard, *Chem. Rev.*, 2008, 108, 3443-3480.
24. X.X. Xue, F. Wang, and X.G. Liu, *J. Am. Chem. Soc.*, 2008, 130, 3244-3245.
25. P. Chen, C. He, *J. Am. Chem. Soc.*, 2003, 126, 728-729.
26. Ono, H. Togashi, *Angew. Chem. Int. Ed*, 2004, 43, 4300-4302.
27. F. Song, S. Watanabe, P.E. Floreancig and K. Koide, *J. Am. Chem. Soc.*, 2008, 130, 16460-16461.
28. D.A. Oriero, I.O. Gyan, B.W. Bolshaw, I.F. Cheng and D.E. Aston, *Microchem. J.*, 2015, 118, 166-175.
29. F. Karim and A.N.M. Fakhruddin, *Rev. Environ. Sci. Biotechnol.*, 2012, 11, 261-274.
30. W. Rajesh and T.K. Kaneto, *Sensor Actuat. B*, 2004, 102, 271-277.
31. N. Balasundram, K. Sundram, S. Samman, *Food Chem.*, 2006, 99, 191-203.
32. S.H. Choi, J.H. Yang and J.C. Lee, *J. Sensors*, 2009, 916515, 1-9.
33. Arecchi, M. Scampicchio, S. Drusch and S. Mannino, *Anal. Chem. Acta*, 2010, 659, 133-6.
34. D.W. Kimmel, G. LeBlanc, M.E. Meschievitz, and D.E. Cliffel, *Electrochemical sensors and biosensors Anal. Chem.*, 2012, 84, 685-707.
35. N.J. Ronkainen, H.B. Halsall and W.R. Heineman, *Chem. Soc. Rev.*, 2010, 39, 1747-1763.
36. O.A. Blatova, A.M. Asiri, Z.M. Al-amshany, M.N. Arshad and V.A. Blatov, *New J. Chem.*, 2014, 38, 4099-4106.
37. M. Shafiq, I.U. Khan, M. Zia-ur-Rehman, M.N. Asghar, A.M. Asiri and M.N. Arshad, *Asian J. Chem.*, 2012, 24, 4799-4803.
38. M.N. Arshad, W.A. Siddiqui, I.U. Khan and A.M. Asiri, *J. Chil. Chem. Soc.*, 2014, 59, 2697-2700.
39. M.N. Arshad, T. Mahmood, A.M. Asiri, K.A. Alamry, M.A. Gilani, K. Ayub and A.S. Birinji, *Spectrochim. Acta Part A*, 2015; 142: 364-74.
40. M.N. Arshad, O. Sahin, M. Zia-ur-Rahman, I.U. Khan, A.M. Asiri and H.M. Rafique, *J. Struct. Chem.*, 2013, 54, 437-442.
41. C. Qin, X. Wu, B. Gao, H. Tong, and L. Wang, *Macromolecules*, 2009, 42, 5427-5429.
42. Agilent (2012). *CrysAlis PRO*. Agilent Technologies, Yarnton, England.
43. G.M. Sheldrick, *Acta Cryst.*, 2008, A64, 112-122.
44. L.J. Farrugia, *J Appl Cryst.*, 2012, 45, 849-854.
45. A.L. Spek, *Acta Cryst.*, 2009, D65, 148-155.
46. L.J. Farrugia, *J. App. Cryst.*, 1999, 32, 837-838.

47. M.M. Rahman, S.B. Khan and A.M. Asiri, PLoS ONE, 2014, 9, e85036.
48. X.L. Cheng, H. Zhao, L.H. Huo, S. Gao and J.G. Zhao, Sensor Actuat. B, 2004, 102, 248-252.
49. J.K. Srivastava, P. Pand, V.N. Mishra and R. Dwivedi, J. Nat. Gas Chem, 2011, 20, 179-183.
50. M.M. Rahman, S.B. Khan and A.M. Asiri, Microchim. Acta., 2015, 182, 487-494.
51. M.M. Rahman, S.B. Khan and A.M. Asiri, Electrochim. Acta., 2013, 112, 422-430.
52. M.M. Rahman, A. Jamal, S.B. Khan and M. Faisal, J. Phys. Chem. C, 2011, 115, 9503-9510.
53. M.M. Rahman, A. Jamal, S.B. Khan and M. Faisal, ACS Appl. Mat. Interf., 2011, 3, 1346-1351.
54. Masoumi, M.S. Gargari, G. Mahmoudi, B. Miroslaw, B. Therrien, M. Abedi and P. Hazendonk, J. Mol. Struct., 2015, 1088, 64-69.
55. M.M. Rahman, S.B. Khan and A.M. Asiri, K.A. Alamry, A.A.P. Khan, A. Khan, M.A. Rub, N. Azum Microchim. Acta., 2013. 180. 675-685.
56. M.M. Rahman, A. Jamal, S.B. Khan, M. Faisal and A.M. Asiri, Microchim. Acta, 2012, 178, 99-106.
57. M.M. Rahman, S.B. Khan, G. Gruner, M.S. Al-Ghamdi, M.A. Daousn and Asiri AM. Electrochim. Acta., 2013, 103, 143-150.
58. M.M. Rahman, A. Jamal, S.B. Khan and M. Faisal, Biosens. Bioelectron., 2011, 28, 127-134.