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Design of Surface Acoustic Wave Sensors Functionalized with Bisphenol S Based Molecules for Lead Ions Detection †

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† Presented at the Eurosensors 2018 Conference, Graz, Austria, 9–12 September 2018.

Published: 26 November 2018

Abstract: This study concerns the design of surface acoustic wave sensors functionalized with bisphenol S based molecules for lead ions detection. (4-hydroxyphenyl, 4′-benzyloxyphenyl) sulfone (M1), (4-hydroxyphenyl,4′-anthrylmethyloxyphenyl) sulfone (M2) and (4,4′-bis (anthrylmethyloxyphenyl)) sulfone (M3) were synthesized and then drop-coated on the SAWs sensing areas. Gravimetric results indicate that the limit of detection of the three sensors is in the picomolar range and that the M3/SAW sensor has the highest affinity towards lead ions compared to M1/SAW and M2/SAW. Density functional theory (DFT) calculations were investigated to support experimental results and to understand the nature of interactions involved between lead ions and the three synthetized molecules.

Keywords: surface acoustic wave sensors; lead ions; density functional theory calculations

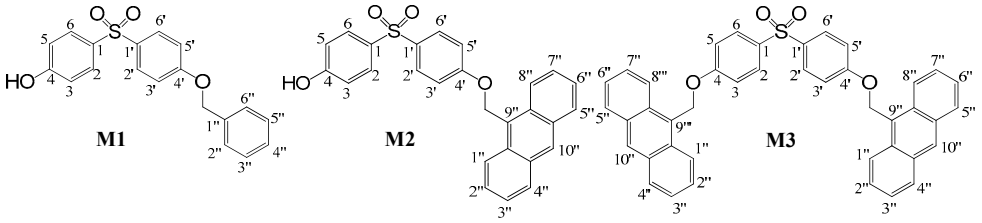
1. Introduction

Among the large variety of heavy metal ions, lead is considered as one of the most toxic ones because of its stability in contaminated sites and its toxicity. Its presence in drinking-water is a consequence of its wide use in plumbing and metal fittings in buildings [1]. Accordingly, several studies have been oriented towards the development of chemical sensors for lead monitoring. Among these devices, surface acoustic wave (SAW) sensors are probably the most promising ones in terms of sensitivity, high accuracy, and possibility of performing real time measurements [2]. Several organic and inorganic monolayers, such as DNA, aptamers and ion imprinted polymers, have been considered for lead II ions detection. In this study, we have chosen to functionalize the sensing area of SAW sensors with three new molecules synthetized from bisphenol S reagent: (M1), (M2) and (M3). The main difference between them is related to the terminal groups making it possible to vary both the geometric shape and the distribution of the electronic cloud all along the molecule under consideration. The achieved gravimetric results were supported by quantum chemical calculations based on the density functional theory.

2. Materials and Methods

2.1. Synthesis of M1, M2 and M3 Molecules

Bis (4-hydroxyphenyl) sulfone was dissolved in DMF, then potassium carbonate was added to the solution and stirred for 10 min at room temperature. After addition of benzyl chloride or 9-(chloromethyl) anthracen, the reaction was activated by microwave irradiation (4 × 1 min, 500 W, 140 °C). M1, M2 and M3 compounds were obtained after classical treatment and purification. The molecular structures of the three molecules are presented in Schema 1.



Schema 1. Chemical structure of M1, M2 and M3 molecules.

2.2. Instrumentation

The developed gravimetric sensor consists of dual delay lines fabricated on 36° rot lithium tantalate piezoelectric substrates. The sensitive area and interdigital transducers (IDTs) were realized by evaporation of (20/80) nm Cr/Au layers [3]. The IDTs were patterned with a periodicity of λ = 40 μm which corresponds to an operating frequency of about 104 MHz. The measurement setup consists of a (M1, M2 or M3) coated SAW sensor, a Kalrez® flow cell, a PMMA cover including inlets and outlets, a peristaltic pump, and a HP8214 network analyzer to monitor phase output versus time at a fixed frequency.

Before the functionalization step, a drop of a piranha solution (2:1 (*v*/*v*) 98% H_2SO_4/30% H_2O_2) was deposited on the sensing area during 20 min. The SAW devices were then rinsed with ultra-pure water and then with ethanol for 10 min. A 30 μL-drop of the considered molecule (M1, M2 or M3) was after that deposited on the sensitive zone, and the device placed into an oven, at 60 °C during 15 min, to evaporate the chloroform solvent.

2.3. Calculation Methods

Chemical calculations were performed by means of the Gaussian 09 D.01 package [4] using the density functional theory (DFT) method. The geometries were fully optimized at the B3LYP/GEN level by using 6-31G (d, p) basis set for the carbon (C), oxygen (O), hydrogen (H) and sulfur (S) atoms and LANL2DZ ECP basis set for lead (Pb), copper (Cu) and Mercury (Hg) atoms [5]. All the computations reported in this paper were performed using the dispersion-including B3LYP-D3 method to adequately describe the dispersion interactions between a particle and its neighbors in a given radius, via a simple pair-wise force field summed to the pure DFT energy[6].

3. Results and Discussion

3.1. Gravimetric Results

For the three designed (M1, M2 and M3)/SAW sensors, Pb^{2+} ions injection led to a phase decrease, indicating that each of the investigated molecules recognizes the analyte. A typical gravimetric response (i.e., phase shift versus time) after the injection of a 10^{-11} M of Pb^{2+} solution is presented in Figure 1a.

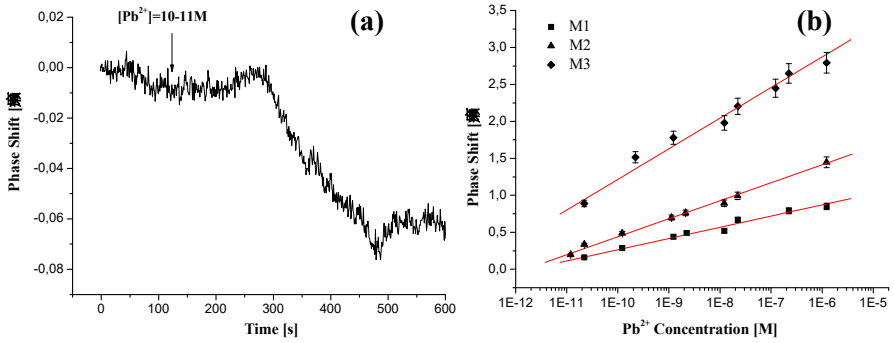


Figure 1. (**a**) Phase variations versus time after the injection of a solution of 10^{-11} M of Pb^{2+} on the sensing area of a M1/SAW sensor (**b**) Semi-logarithmic phase-shift variations (ΔΦ) versus lead ions concentration for the M1, M2 and M3/SAW sensors.

The calibration curves of the (M1, M2 andM3)/SAW sensors in a semi-logarithmic scale, are presented in Figure 1b; the further corresponding sensitivities are gathered in Table 1. Results indicate that the affinity of M3 towards Pb^{2+} ions is superior to that of M1 and M2. The limit detection of the three sensors are in the picomolar range; the lowest one is that of the M3/SAW sensor.

Table 1. Estimated sensitivities (S) and limits of detection of M1, M2 and M3 based SAW sensors.

	S [°/M]	LOD
M1	0.151 ± 0.005	22 pM
M2	0.243 ± 0.007	12 pM
M3	0.414 ± 0.019	22 pM

3.2. Density Functional Theory (DFT) Calculations

Quantum chemical calculations, based on the density functional theory (DFT) with the B3LYP functional, were carried out to understand the interaction phenomena involved between the different entities and to explain the ability of M1, M2 and M3 molecules to capture lead ions. The geometry of the three molecules were completely optimized, prior to the determination of the most stable adsorption sites of lead cations.

The interaction energies E_{int} were calculated from Equation (1):

$$E_{int} = E_{Complex} - (E_{Mi} + E_{lead}) + E_{BSSE}, \quad (1)$$

where $E_{Complex}$ is the total energy of lead cations adsorbed on the different molecules, E_{Mi} is the total energy of a given $M_{i=1,2,3}$ molecules, E_{lead} is the energy of isolated lead cations and E_{BSSE} is the energy of the basis set superposition error.

The most stable geometries of the different complexes are presented in Figure 2, and the corresponding calculated energies are gathered in Table 2.

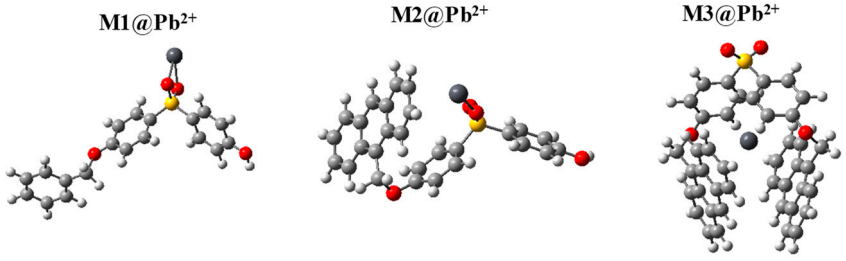


Figure 2. Optimized molecular structures of Pb^{2+}/(M1, M2 and M3) complexes. S: yellow; O: red; C: gray; H: white; Pb^{2+}: dark gray.

Calculation indicate that the M3@Pb^{2+} adsorption energy is higher than that of M1 and M2 complexes, confirming thus the better affinity of M3 towards lead ions. This might be correlated to the "cage like shape" of the M3 molecule, which favors lead cations capture.

Table 2. Interaction energies (E_{int}) of lead ions on M1, M2 and M3 molecules (in kJ/mol).

	Eint (kJ/mol)
M1	−677.15
M2	−749.03
M3	−840.16

3.3. Selectivity Investigations

Selectivity tests were investigated with the M3/SAW sensor, as it presents the best metrological parameters for Pb^{2+} detection. For this investigation, we considered two divalent cations which largely coexist with lead in real media: copper (Cu^{2+}) and mercury (Hg^{2+}) The phase shift value obtained after complete saturation of the sensor, $\Delta\Phi_S$, and estimated sensitivities of the M3/SAW device, to Pb^{2+}, Cu^{2+} and Hg^{2+} ions, are gathered in Table 3.

Table 3. "Saturated" phase variation $\Delta\Phi_S$ and sensitivity values of the M3/SAW sensor towards Pb^{2+}, Cu^{2+} and Hg^{2+} ions.

	$\Delta\Phi_S$ [°]	S [°/M]
Pb^{2+}	3.27 ± 0.16	0.41 ± 0.02
Cu^{2+}	1.95 ± 0.10	0.16 ± 0.03
Hg^{2+}	1.18 ± 0.06	0.18 ± 0.01

Results indicate that the sensitivity of the M3/SAW sensor to Pb^{2+} ions is more than twice greater than that to Hg^{2+} and Cu^{2+}, showing the relative selectivity of this sensor toward lead ions. Nevertheless, sensitivities to copper (II) and mercury (II) are sufficient to detect also these ions at low concentrations. M3/SAW sensors can thus be used at the first level of analysis and control chain for heavy metals monitoring in rivers and wastewaters.

4. Conclusions

Surface acoustic wave sensors functionalized with three new bisphenol S based molecules have been designed for lead ions detection. Gravimetric results indicate that 4,4′-bis (anthrylmethyloxyphenyl) sulfone (M3) presents the best affinity towards Pb^{2+}. Sensitivity and limit of detection of the M3/SAW sensor were of order 0.41°/M and 22 pM respectively. Selectivity tests indicate that the affinity of the M3/SAW device to Pb^{2+} ions is higher than to Hg^{2+} and Cu^{2+} ones.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Chemical Safety of Drinking Water: Assessing Priorities for Risk Management. Available online: http://apps.who.int/iris/bitstream/10665/43285/1/9789241546768_eng.pdf?ua=1&ua=1 (accessed on 30 June 2018).
2. Mujahid, A.; Dickert, F.L. Surface Acoustic Wave (SAW) for Chemical Sensing Applications of Recognition Layers. *Sensors* **2017**, *24*, 2716, doi:10.3390/s17122716.
3. Fourati, N.; Seydou, M.; Zerrouki, C.C.; Singh, A.; Samanta, S.; Maurel, F.; Aswal, D.K.; Chehimi, M. Ultrasensitive and Selective Detection of Dopamine Using Cobalt Phthalocyanine Nanopillar-Based Surface Acoustic Wave Sensor. *ACS Appl. Mater. Interfaces* **2014**, *6*, 22378–22386.
4. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; et al. *Gaussian 09, Version D.01*; Gaussian, Inc.: Wallingford, CT, USA, 2013.

5. Feller, D. The Role of Databases in Support of Computational Chemistry Calculations. *J. Comput. Chem.* **1996**, *17*, 1571–1586.
6. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104–154123.