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Proceedings

Picomolar Detection of Heavy Ions with Surface Acoustic Wave Sensors Functionalized with New Synthetized Anthracene Derivates[†]

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Abstract: 104 MHz-surface acoustic wave sensors have been functionalized with three new anthracenederivatives for the detection of mercury and copper heavy ions: 2,2-bis(4 anthracenylmethoxy)-1,1'-biphenyl (BP-AN), 9-([4-((4-(9anthrylmethoxy)phenyl)sulfanyl)methyl)methyl]anthracene (TDP-AN) and 4-(9-anthrylmethoxy) benzyl [4-(9-anthrylmethoxy) phenyl] sulfone (BPS-AN). Gravimetric results indicate that, compared to TDP-AN and BPS-AN, BP-AN based chemsensor has the highest affinity towards the two investigated ions. The corresponding sensitivities were of order of 3.67×10^8 °/M and 2.24×10^8 °/M for Hg²⁺ and Cu²⁺ respectively. The limit of detection of the BP-AN-SAW chemsensor, of order of 1 pM, is one of the lowest values ever reported in the literature. Experimental results were supported by quantum chemical calculations, based on the density functional theory.

Keywords: surface acoustic wave sensors; anthracene derivatives; DFT calculations

1. Introduction

Because of the severe pollution problems, which have affected many regions around the world, low levels' monitoring of copper and mercury ions became a societal and public health issue.

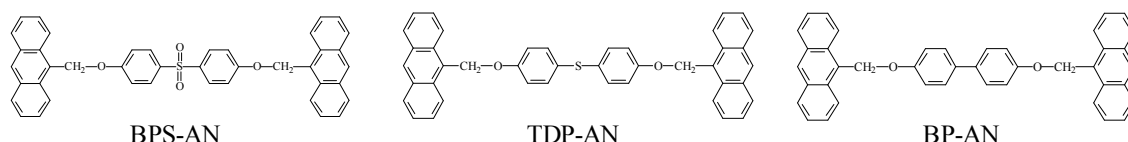
Despite their numerous advantages, conventional techniques respond less and less to the current demands in terms of measures' times and in-site analysis. Researches have therefore been oriented to the development of chemical and biological sensors to respond to all these requirements. Numerous functionalized organic and inorganic monolayers have been considered for Hg²⁺ and Cu²⁺ detection, such as DNA [1] antibodies [2] and ionic imprinted polymers [3]. In this study, we have chosen to functionalize surface acoustic wave (SAW) sensors with three new anthracene derivatives BP-AN, TDP-AN and BPS-AN. Several reasons have motivated this choice: - a relatively simple synthesis of these three molecules, - the possibility of several reuse of the same transducer, as all the investigated molecules are soluble in common organic solvents, - the rarity of anthracene derivatives' use for heavy ions detection - and the sensitivity and accuracy of SAW sensors [4,5].

Gravimetric measurements, supported by quantum chemical calculations, based on the density functional theory, were considered to investigate the affinity of the different anthracene molecules towards Hg^{2+} and Cu^{2+} ions.

2. Materials and Methods

2.1. Chemicals

Three new anthracene derivatives have been synthesized via the Williamson reaction: BP-AN, TDP-AN and BPS-AN. The main difference between them is related to the functional group between the three central phenyls (Scheme 1). These three molecules are soluble in chloroform.



Scheme 1. Chemical structure of BPS-AN, TDP-AN and BP-AN.

2.2. Gravimetric Measurements

The investigated 104 MHz SAW sensors consist of dual delay lines designed on a 36° rot lithium tantalate piezoelectric substrate. The phase difference between the reference and the sensing lines is the measured parameter. The measurement setup consists of a SAW sensor, a Kalrez flow cell, a PMMA cover, a peristaltic pump and a HP8711C network analyzer. Gravimetric measurements were repeated at least five times for each investigated anthracene based SAW sensor.

Before each experiment, a drop of 50 μL of a piranha solution (98% H_2SO_4 /30% H_2O_2 2:1 V/V) was deposited on the SAW's sensing area during 20 min to clean and activate it. The SAW device was then rinsed with ultrapure water and then with ethanol for 10 min. A 30 μL -drop of an anthracene molecule was after that deposited on the sensing zone and the device placed in an oven at 60°C during 15 min to improve the adhesion between the gold and the investigated anthracene derivatives.

2.3. DFT Calculations

The geometry of the three anthracene derivatives were first completely optimized with the Gaussian09 D.01 package using density functional theory (DFT) with the B3LYP hybrid functional at the basis set level of 6-31G (d, p) for anthracene derivatives and the LANL2DZ ECP base for copper (Cu) and Mercury (Hg) atoms [6]. The recently developed nonlocal van der Waals functional B3LYP-D3To has been used to include dispersion effects. Reactivity of Cu^{2+} and Hg^{2+} cations with anthracene derivatives was then investigated. The last step was dedicated to the determination of the most favorable adsorption site and the corresponding interaction energy.

3. Results and Discussion

3.1. Gravimetric Results

Phase-shift variations ($\Delta\Phi$) versus Hg^{2+} and Cu^{2+} concentration for BP-AN, TDP-AN and BPS-AN molecules are presented in Figure 1. Gravimetric results indicate that the affinity of BP-AN towards Hg^{2+} and Cu^{2+} ions is superior to that of TDP-AN and BPS-AN ones.

For both investigated cations, the limit of detection (LOD) of the BP-AN SAW chemsensor was found of order of 1 pM, one of the lowest values ever reported in literature, while those of BPS-AN and TDP-AN SAW sensors were in the nanomolar range (Table 1)

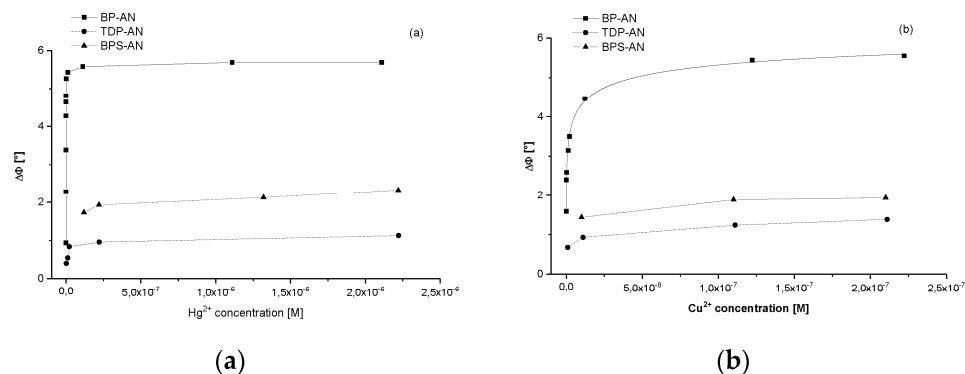


Figure 1. Phase-shift variations ($\Delta\Phi$) for BP-AN, TDP-AN and BPS-AN derivatives versus. (a) Hg^{2+} concentration (b) Cu^{2+} concentration.

Sensitivity values were calculated from the slope of the initial part of each phase/concentration curve and gathered in Table 1. These values indicate that the sensitivities of BP-AN-SAW sensor towards both investigated cations are superior, by about two orders of magnitude, to those of BPS-AN and TDP-AN ones, highlighting thus the high affinity between BP-AN and Hg^{2+} and Cu^{2+} ions.

Table 1. Calculated sensitivities towards Hg^{2+} and Cu^{2+} ions and estimated limit of detection of SAW sensors functionalized with anthracene derivatives.

	S (°/M)		LOD (M)	
	Cu^{2+}	Hg^{2+}	Cu^{2+}	Hg^{2+}
BP-AN	2.24×10^8	3.67×10^8	10^{-12}	10^{-12}
TDP-AN	0.51×10^6	2.34×10^6	10^{-9}	2×10^{-9}
BPS-AN	5.8×10^5	2.3×10^5	10^{-8}	10^{-8}

3.2. Chemical Calculations

Frontier Molecular Orbital theory was first tested to understand the type of interactions involved between anthracene molecules and Cu^{2+} and Hg^{2+} ions. The key parameter is the energy difference between highest occupied orbital (HOMO) and the lowest unoccupied orbital (LUMO) levels of both reactants. Calculations (results not shown here) indicate that the lowest ΔE values are those corresponding to cation/BP-AN complexes. BP-AN is consequently the most reactive anthracene derivative against copper and mercury cations. We have after that optimized the possible cations' adsorption sites. The interaction energies E_{int} were calculated from the relation:

$$E_{\text{int}} = E_{\text{Complex}} - (E_{\text{Anthracene}} + E_{\text{Metal}}) + E_{\text{BSSE}} \quad (1)$$

where E_{Complex} is the total energy of copper or mercury cation, $E_{\text{Anthracene}}$ is the total energy of anthracene molecules, E_{Metal} is the energy of isolated metal cations and E_{BSSE} is the energy of the basis set superposition error. The most stable complexes are presented in Figure 2 and the corresponding interaction energies are summarized in the Table 2.

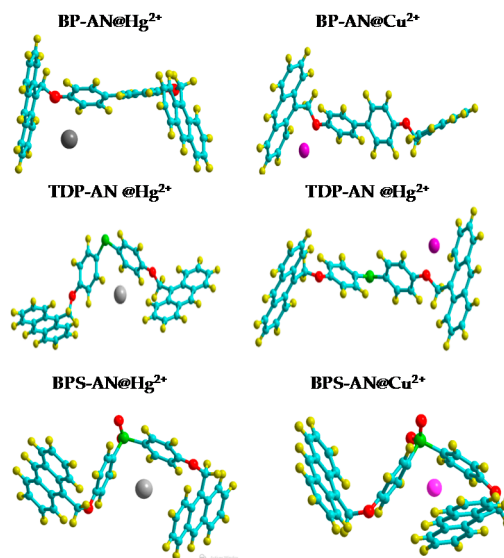


Figure 2. Optimized Hg^{2+} -anthracene and Cu^{2+} anthracene complexes. S, green; O, red; C, blue; H, yellow; Cu, violet; Hg, dark gray sphere.

For all the investigated complexes, the interaction energies values are negative which indicate that the adsorption is exothermic. Calculations indicate also that the adsorption energies of Cu^{2+} and Hg^{2+} on BP-AN are superior to those on TDP-AN and BPS-AN confirming thus the experimental gravimetric results.

Table 2. Adsorption energies of metal cations on anthracene derivatives (E_{int}) in kJ/mol.

	E_{int} (kJ/mol)	
	Cu^{2+}	Hg^{2+}
BP-AN	−1370.28	−1102.71
TDP-AN	−991.51	−923.94
BPS-AN	−939.05	−882.67

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

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