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Electropolymerization of Amino-Derived Silicon Phthalocyanines for Chemical Sensing Applications

Mélanie Cyr[1,2], Gabriele Magna[3], Francesco Pizzoli[3], Alessandro Mita[3], Lorena Di Zazzo[3],
Roberto Paolesse[3], Benoît Lessard[2], Jaclyn Brusso[1]
[1] Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, ON K1N 6N5, Canada
[2] Department of Chemical and Biological Engineering, University of Ottawa, Ottawa, ON K1N 6N5, Canada
[3] Department of Chemical Sciences and Technology, University of Rome Tor Vergata, 00133 Rome, Italy

Corresponding Author's e-mail address: roberto.paolesse@uniroma2.it

Summary:

Silicon phthalocyanines (SiPcs) are a versatile class of organic semiconductors for applications in organic thin film transistors (OTFTs) and organic photovoltaics (OPVs) due to their simple synthesis, easy tunability and high charge transport characteristics. Herein, a novel class of electropolymerized SiPcs have been synthesized and incorporated in both mass-based and conductometric sensors. The results indicated that not only were both sensor types successful in recognizing various gases and volatile organic compounds, but partial selectivity was also achieved in the conductometric sensors with high sensitivity for CO_2 and trimethylamine gases.

Keywords: Electropolymerization, phthalocyanines, electronic nose, quartz microbalance, interdigitated electrode

Introduction:

Organic sensors provide a cost-effective alternative to conventional inorganic sensors for analyte detection with low temperature manufacturing and simple operation, with small form factor.[1] Phthalocyanines is an exciting class of small molecules organic semiconductor with high thermal and chemical stability that can be synthesized in a few high yielding steps. Phthalocyanines can also interact with redox active species through electron transfer, making them great candidates for various sensing applications. Silicon Phthalocyanines (SiPc) are tetravalent molecules which can be easily functionalized through axial coupling leading to changes in solubility, solid state packing and tuning frontier molecular orbital energy levels.[2]

Electropolymerization of amino-derived porphyrin and corrole materials via cyclic voltammetry is a facile and effective method in fabricating polymeric films onto conductometric sensors, for gas sensing and electronic nose applications.[3] The polymer forms via a phenazine bridge catalyzed by aminophenyl groups on the materials. The work presented herein looks at the electropolymerization of novel *para*, *meta* and *ortho* oriented bis(aminophenoxy) silicon phthalocyanines (SiPcs), where the formation of the phenazine linkers occurs at the axial position rather than the periphery of the phthalocyanine. This will create a linear polymer where the SiPc cores will be parallel to one another, which can be ideal for charge transfer within the polymer material. The SiPc polymers (poly-SiPc) were polymerized and characterized on both quartz microbalances (QMBs) for mass-based sensing and interdigitated electrodes (IDEs) for conductometric sensing against gases and volatile organic compounds (VOCs) for the very first time.

Materials and methods:

The synthesis of the amino-derived silicon phthalocyanines (SiPcs) was done using a similar synthetic pathway for other previously synthesized SiPc derivates.[4] The poly-SiPcs are produced via electropolymerization using either cyclic voltammetry (CV) or chronoamperometry (CA) techniques. Polymers were deposited firstly on indium tin oxide (ITO) glass to characterize the optoelectronic properties of the polymer films, followed by deposition on QMB and IDE (Figure 1A). During the deposition, the ITO glass or electrodes were immersed in a 1 mM monomeric solution of the amino-derived SiPc in dichlorobenzene (DCB)

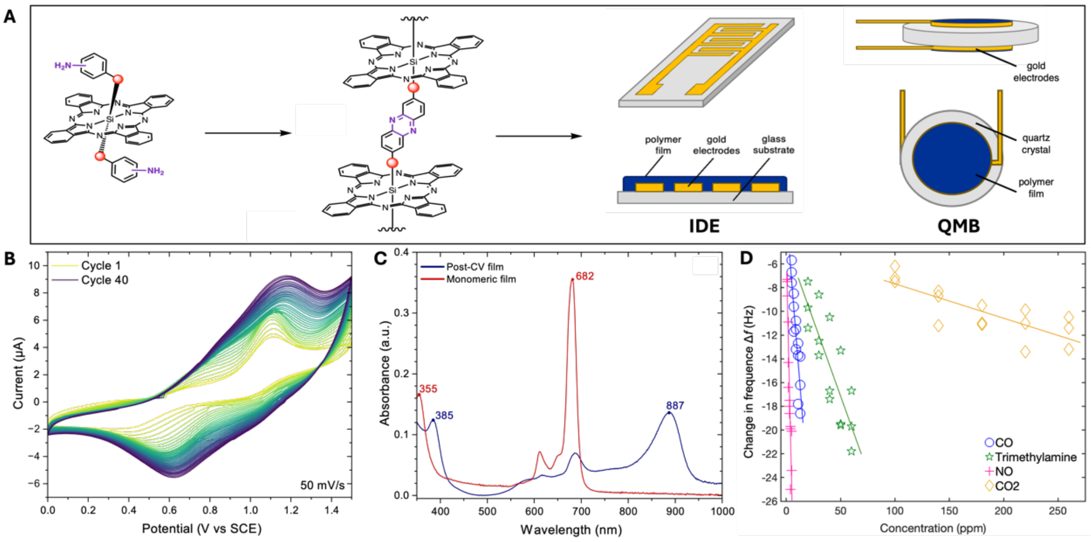

Figure 1. A) Polymerization process of amino-derived SiPc and visual representation of the film growth onto QMB and IDE electrodes. B) Typical cyclic voltammogram upon polymer formation. C) UV-vis-NIR characterization of the polymer film on ITO glass versus the starting monomer. D) Characteristic curves of para-SiPc polymer to CO, TMA, NO and CO_2.

containing 0.1 M of tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. For the testing of the sensors, QMBs and IDEs are enclosed in a chamber connected to a mass flow controller regulated to deliver specific gas concentrations blended with N_2. The QMB and IDEs are tested against carbon monoxide (CO), carbon dioxide (CO_2), nitric oxide (NO), trimethylamine (TMA), H_2O, toluene, hexane, ethanol, pentanol, triethylamine (TEA), and acetic acid (AcOH). The fundamental oscillation frequency (for QMB) and resistances (for IDE) of the sensors are measured at 1 sample/s with a proper electronics or multichannel multimeter connected to a computer; delta frequencies or relative resistance changes in responses have been considered as features, and data analysis is performed in Matlab®.

Results and discussion:

Three amino-derived SiPc monomers were synthesized, where the amino groups vary from the *para, meta* and *ortho* positions, to further evaluate the ease with which the material polymerizes depending on its positioning. The materials were characterized via UV-vis-NIR spectroscopy and spectroelectrochemistry which confirmed successful polymerization of the *para* and *ortho* derivatives only (CV and UV-vis spectra seen in Figures 1B and 1C).

The sensing performances of the polymer films formed via CV and CA on QMBs were investigated by testing gases (CO, CO_2, NO, TMA) and VOCs (H_2O, Toluene, Hexane, EtOH, PentOH, TEA, AcOH). Results showed that although all QMBs were successful in sensing all analytes, slight differences in the selectivity can be observed when comparing polymers from the *para* and *ortho* derivatives (an example of the response curve for a QMB sensor against gases can be seen in Figure 1D). Furthermore, when tested as an array, the principal component analysis (PCA) demonstrates that the films formed from either CV or CA will also have some difference in the correlation of their detection, thus allowing for the sensors to work together and gain selectivity as an electronic nose.

For the IDE sensors, the sensitivity of each poly-SiPc IDE has been shown to vary when tested under darkness and under light, with an increased signal response when subjected to analytes under visible light (white LED). The IDEs were tested firstly against varying concentrations of gases (CO, CO_2, NO, TMA) mixed with N_2, from which selectivity for CO_2 and TMA gases was apparent. Further ongoing testing is being conducted with this series of sensors under synthetic air and at varying humidity levels to evaluate their responding potential under realistic environmental conditions.

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