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Volatile organic molecules adsorption by thin solid films of self-assembled molecular cavitands

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Extensive researches in chemical sensor area involve the search and investigation of novel sensing techniques, approaches and materials. One of the most important problems under creation of sensory systems is the choice of appropriable sensitive materials for coating of sensor. The promising organic materials for sensor applications are calixarenes because of their nano-size structure, excellent sorption abilities and selectivity, long time stability, technological feasibility. Attractive feature of calixarene molecules is ability to form “host-guest” complexes with various anions, cations and organic molecules. Specific chemical stucture of calixarenes molecules modified with different functional groups provides researchers with possibility of meeting any requirements in terms of sensitivity and selectivity towards definite volatile organic compounds.

Up to date, sensor applications of calixarene layers have been proposed for a few transducer types, e.g. Quartz Crystal Microbalances (QCM) [1], ion Selective Field Effect Transistors (ISFET) [2] and another principle, which is based on conductivity modulation of discontinuous gold films (DGFs) on a dielectric substrate [3].

This work reports on the results of investigation of adsorption of volatile organic molecules by the novel functionalysation calixarenes (CA). 8-channel QCM sensor system with all necessary equipment (gas cell, gas-supplying system and electronic circuits, etc.) designed in our laboratory has been used in experiments. Influence of introduction of various functional groups into calixarene molecule macrocycle to sensitivity towards different organic molecules has been analyzed. Sensors coated with phosphorous-containing calixarenes showed a high sensitivity and an excellent selectivity towards volatile organic compounds (aromatics, chlororganics, ketones and aliphatic alcohols). Sensor response was found to be depended on chemical structure of calixarenes under study, particularly, on the substituting group of molecule. Good sensor response has been obtained for phosphorylated CA compounds. Concentration dependencies and sensitivity thresholds of sensors have been obtained. Concentration dependencies in the range 500 – 10000 ppm were recalculated from kinetic curves and represented good linearity. Detection limit of several analytes was less than 10 ppm. Films of the phosphorylated calixarenes showed fast and reversible adsorption to wide range of analyte except the situation, when stable complex “host-guest” was formed.

Study of influence of films thickness and its quality and uniformity on VOC’s adsorption has been carried out as well. It turned out that the quantity of absorbed volatile molecules grew in a linear manner with an increasing of film thickness. No evident slowing down in kinetic adsorption has been observed. Thus, it can be concluded that adsorption mechanism is rather of bulky than surface type.

Summarizing all mentioned above we can say that thin solid films of self-assembled molecular cavitands possess a good affinity towards various VOCs and consequently they are very promising materials which can be used as sensitive layers for QCM sensors. As it was shown, varying numbers of arilic fragments (i.e. size and shape of cavity) as well as binding different functional groups to upper and lower rims, it is possible to change significantly sensitivity of sensor towards given analyte from practically total insensibility to possibility of registering very small amount of analyte (less than 100 ppm). We should especially emphasize very high sensitivity of calixarenes containing functional groups with phosphorus that makes ones attractive in terms of application in sensory systems.

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