Supplementary Material

for

Biomimetic sensitive elements for 2,4,6-trinitrotoluene tested on multilayered sensors

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Abstract: In spite of technological progress, most of the current techniques for 2,4,6-trinitrotoluene (TNT) detection are time consuming due to laborious sensor preparation. Thereby, the aim of this work was to enlarge the knowledge for preparing sensitive elements for TNT with the aid of molecular imprinting; a known technique used to deliver biomimetic materials. The study depicts first the auto-assembly mechanism of (TNT) with functional diamino-silanes (i.e. N-(2-aminoethyl)-3-aminopropyl methyl dimethoxysilane) *via* "double" Meisenheimer complexes. This mechanism is being described herein for the first time and applied further to obtain molecularly imprinted polymer (MIP) films for TNT recognition. For testing the potential application of films as chemical sensor elements, typical rebinding assays of TNT in liquid state and rebinding of TNT in vapour state, using multilayered sensor chips composed of quartz-chromium (Cr)-gold (Au)-titanium oxide (TiO_2), were employed. Batch rebinding experiments have shown that thinner films were more efficient on retaining TNT molecules, in the first 5 minutes with a specificity of about 1.90. The quartz-Cr-Au-TiO_2-MIP capacitive sensors, tested in vapour state, registered short response times (less than 25 seconds), low sensitivity to humidity and high specificity for TNT.

Keywords: 2,4,6-trinitrotoluene; double Meisenheimer complex; biomimetic sensitive elements; molecular imprinting; multilayered sensors; vapour state detection;

***Manuscript Section** 2.2. Synthesis of molecularly imprinted polymer (MIP) films for TNT recognition*

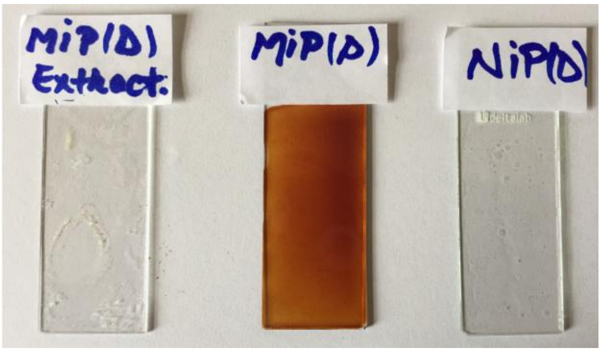


Figure S1: Films on glass slides: TNT-MIP (D) film after TNT extraction with the 1N HCl solution and TNT-MIP (D) film after deposition and maturation compared to the NIP (D) film;

***Manuscript Section** 2.3. Preparation of quartz-Cr-Au-TiO_2-MIP sensors*

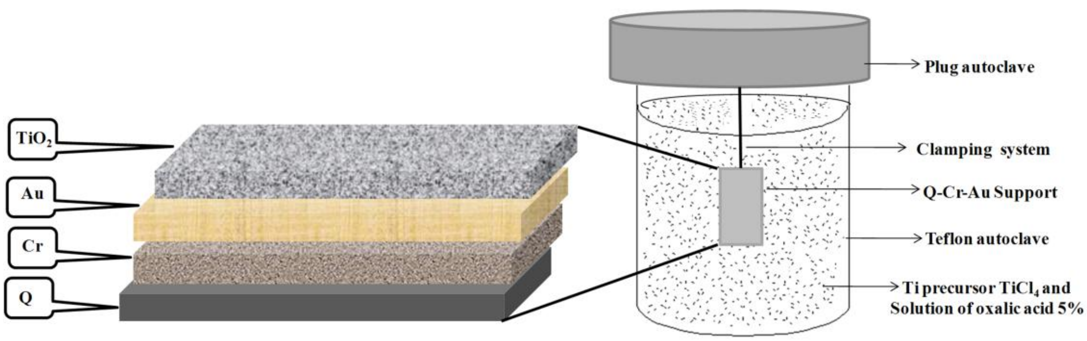
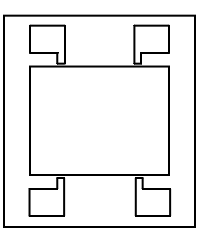


Figure S2: Schematic illustration of the in-situ hydrothermal method for obtaining the TiO2 films on the quartz-Cr-Au support

(a)



(b)

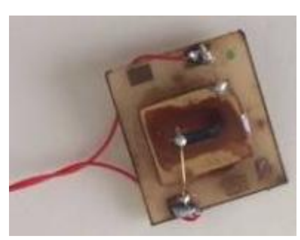


Figure S3: Description of the sensor assembly: a) Lay-out of the Electronic Mask (EM) and **b)** EM-Q-Cr-Au-TiO_2-MIP Sensor

Manuscript Section *3.3. Batch rebinding studies for films deposited on glass slides*

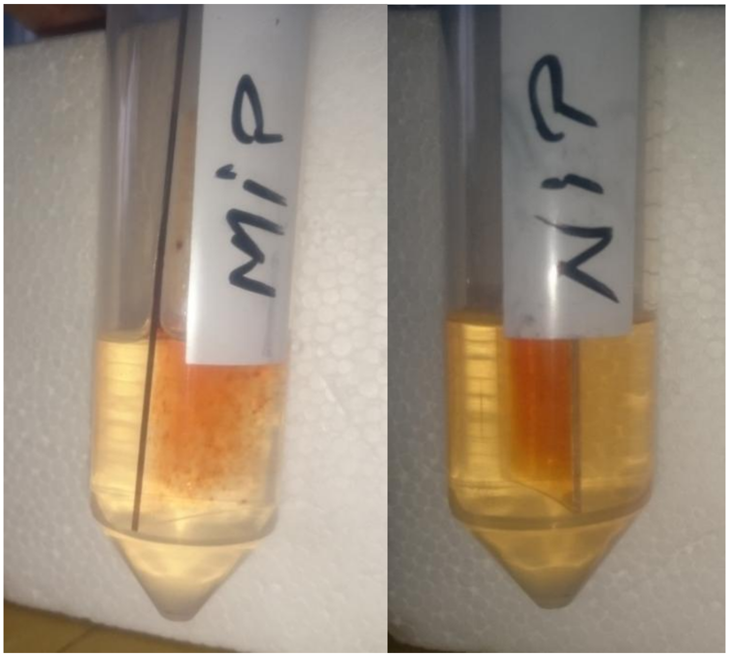


Figure S4: TNT-MIP (D) films and NIP (D) after 120 minutes of contact with the TNT solution 0.02 g L^{-1}.

Manuscript Section *3.6. TNT detection in vapour state using quartz-Cr-Au-*TiO_2*-MIP sensors*

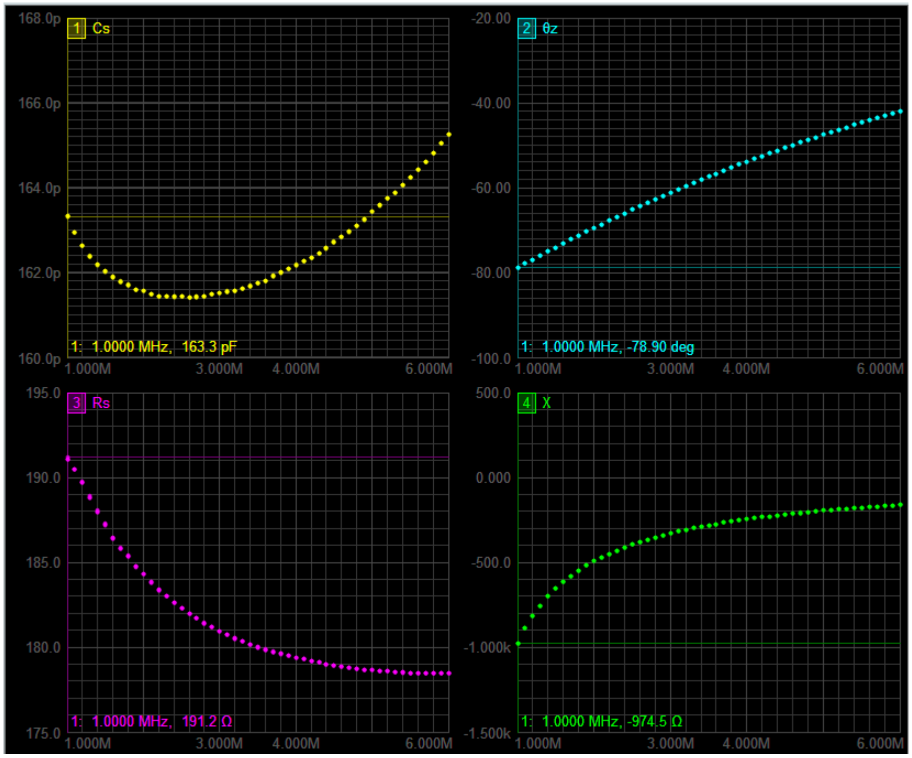


Figure S5: Experimental data (RLC) for the Test Set N°1. Electrical characteristics of tested EM-Q-Cr-Au-TiO_2-MIP Sensor, Humidity max 5% (pure dry air), 26 °C, absence of TNT

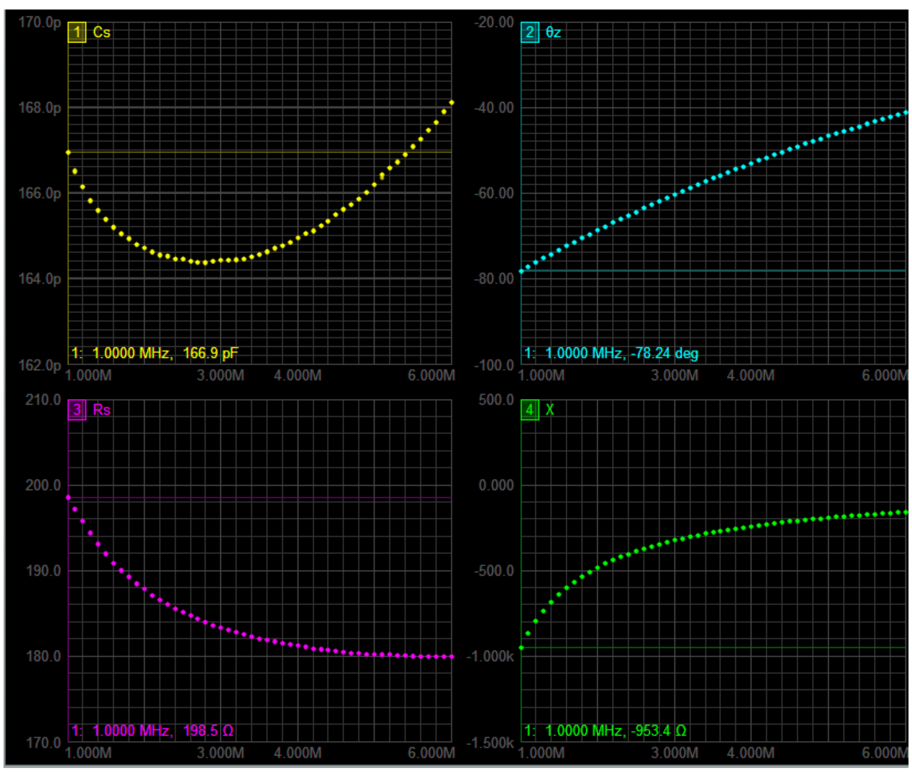


Figure S6: Experimental data (RLC) for the Test Set N°2. Electrical characteristics of tested EM-Q-Cr-Au-TiO2-MIP Sensor, Humidity 31%, 26 °C, absence of TNT

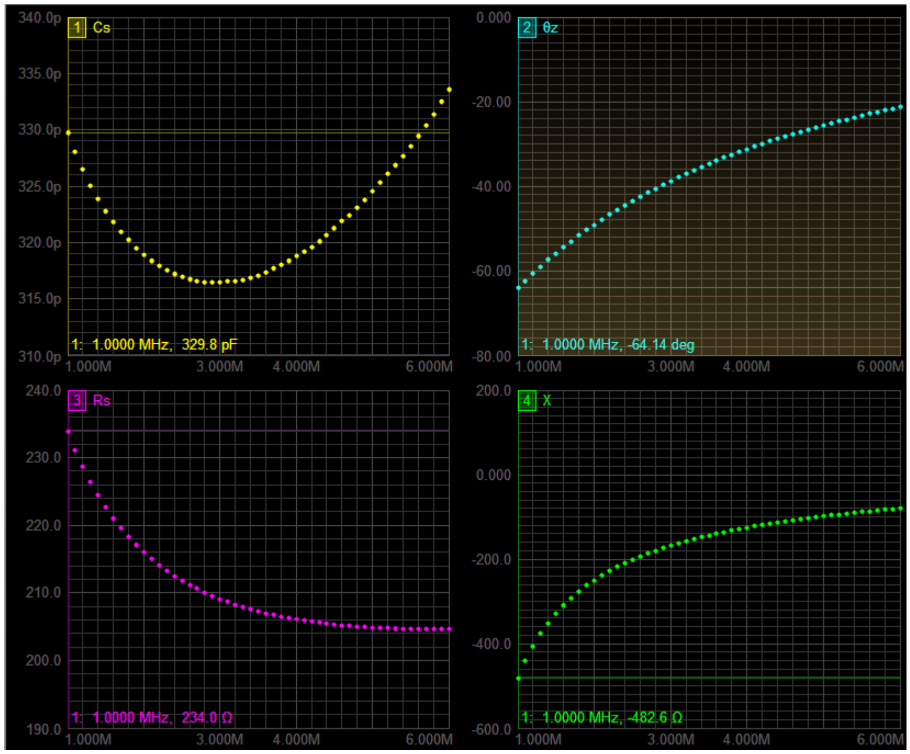


Figure S7: Experimental data (RLC) for the Test Set N°3. Electrical characteristics of tested EM-Q-Cr-Au-TiO2-MIP Sensor, Humidity max 5% (pure dry air), 26 °C, 0.2 mgL^{-1} TNT in the air flow

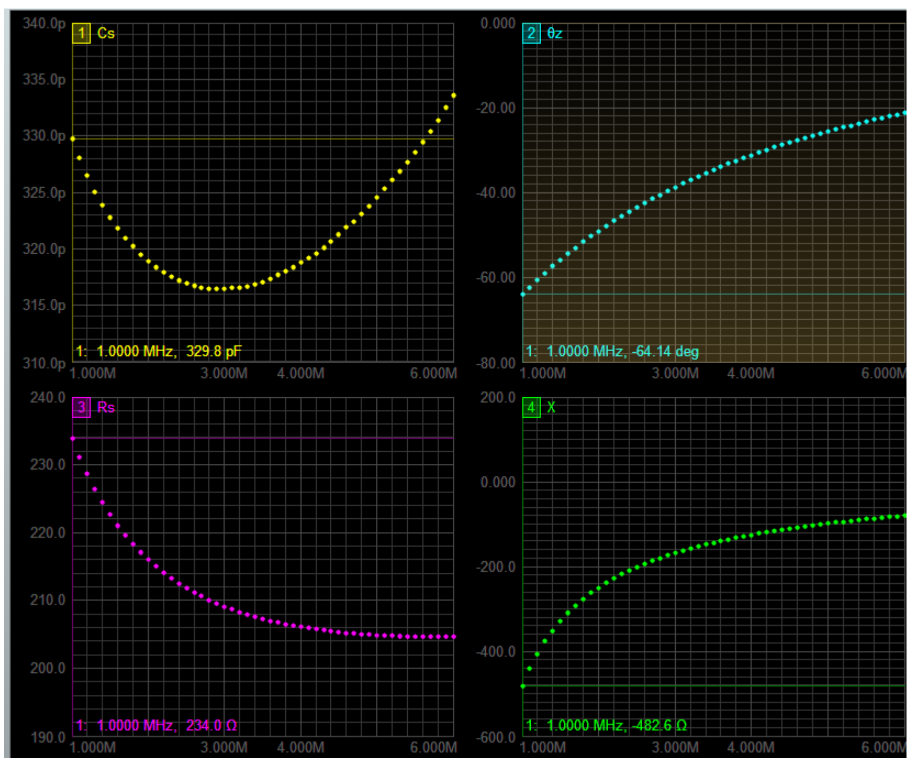


Figure S8: Experimental data (RLC) for the Test Set N°4. Electrical characteristics of tested EM-Q-Cr-Au-TiO2-MIP Sensor, Humidity max 5% (pure dry air), 26 °C, TNT: DNB = 0.2: 0.2 (mgL^{-1}/ mgL^{-1}) in the air flow