Supplementary Materials: Selectivity and Efficiency of Conductive Molecularly Imprinted Polymer (c-MIP) Based on 5-Phenyl-Dipyrromethane and 5-Phenol-Dipyrromethane for Quorum Sensing Precursors Detection

Sabina Susmel and Clara Comuzzi

Crystal structure of QscR, a Pseudomonas aeruginosa quorum sensing signal receptor.



Figure S1. Schematization of AHLs binding pocket, as described in [15].

Electropolymerization of 5-ph-DP and 5-pOH-DP

The electropolymerization ability of 5-ph-DP was already investigated by EQCM measurements in which both the cyclic voltammetry and frequency shift due to the mass deposition of quartz crystal were recorded in parallel [14]. The conductive non imprinted polymer (cNIP) of 5-ph-DP was prepared by cycling the potential between -0.8 V and 1.2 V (vs. Ag/Ag⁺) at a scan rate of 50 mVs⁻¹. A mass of 1.11 × 10⁻⁵ g·cm⁻² (4.99 × 10⁻⁸ mol·cm⁻²) was obtained at the Pt-quartz crystal electrode (Figure S2A). The EQCM technique was adopted to assess the ability of 5-pOH-Dp to form polymers, as well (Figure S2B). Figure 2B shows the cyclic voltammograms obtained for 1×10^{-3} mol·L⁻¹ of 5-pOH-DP in 0.05 mol·L⁻¹ of TBAP/AN using the potential cycling between -0.8 V and 1.2 V (vs. Ag/Ag⁺) at a scan rate with a potential of 50 mVs-1. For comparison, cMIP obtained with 5-pOH-DP and Acetyl-HS as the template, both with a concentration of 1 mM, is reported in Figure 2B, as well. On the first cycle, the oxidation peak at about 0.8 V is assigned to the oxidation of the dipyrromethane unit to its radical cation. The coupling of the radicals and the film formation was confirmed during the second (and subsequent) cycle as a broad anodic peak grown at about +0.2 V due to the oxidation of the formed film of poly-5-pOH-DP. The increase of the current density at both oxidation potentials (0.8 V and +0.2 V) with the number of cycles is an indication of the electropolymerisation process which was confirmed through the mass increase measured as the frequency shift (Figure 2A,B, insert). A mass of 1.7×10^{-5} gr·cm⁻² of poly-5-pOH-DP was obtained with 6 voltage sweeps (cNIP).



Figure S2. (**A**) cNIP (red line) and cMIP (blue line) of 5-pH-DP at the Pt-quartz crystal electrode. Monomer concentration 1×10^{-3} mol·L⁻¹, template acetyl-HS in concentration 1×10^{-3} mol·L⁻¹ in AN/0.05 mol·L⁻¹ TBAP, scan rate 50 mVs⁻¹, Ag/Ag⁺ non-aqueous RE. Inset: frequency variation measured during the cNIP electrodeposition and cMIP; (**B**) cNIP (red line) and cMIP (blue line) of 5-pOH-DP at the Pt-quartz crystal electrode. Monomer concentration 1×10^{-3} mol·L⁻¹, template acetyl-HS in concentration 1×10^{-3} mol·L⁻¹, template acetyl-HS in concentration 1×10^{-3} mol·L⁻¹ in AN/0.05 mol·L⁻¹ TBAP, scan rate 50 mVs⁻¹, Ag/Ag⁺ non-aqueous RE. Inset: frequency variation measured during the cNIP electrodeposition and cMIP.



Figure S3. Net frequency shift variation measured at each single sweep as the difference between cMIP and cNIP.

Typical QCM response obtained for a cMIP sensor prepared using the monomer and template, both with concentrations of 1 mM, as it was the more efficient ratio for template inclusion.



Figure S4. Typical QCM response measured during the rebinding test. The acetyl-HS-analyte was added in solution at a concentration of 3.7×10^{-7} M (-97.5 Hz) and 1.8×10^{-7} M (-53 Hz). Pt-quartz-crystal modified with poly-5-pOH-DP imprinted with acetyl-HS. Both the monomer in solution and acethyl-HS for cMIP preparation were at concentrations of 1 mM. Extraction was performed with 10% HAc + AN + 0.05 M TBAP.