

Electronic Supplementary Information

5-phenyl-dipyrromethane and 5-(4-pyridyl)-dipyrromethane as modular building blocks for bio-inspired conductive Molecularly Imprinted Polymer (cMIP). An Electrochemical and Piezoelectric investigation.

S. Susmel^a and C. Comuzzi^b,

^a Department of Food Science and Technology, Analytical Chemistry Group, University of Udine, Via Sondrio 2/A-33100 Udine-Italy

^b Department of Chemistry, Physics and Environment, University of Udine, Via Cotonificio 108-33100 Udine-Italy

The CV of 5-ph-Dp and 5-py-Dp recorded in the scan rate range 0.05 to 0.8 V s⁻¹ were reported in Figure S1 and Figure S2. The data extrapolated from the scan rate were reported in Figure S1.1 for ph-derivative and Figure S2.2 for the py-derivative, respectively.

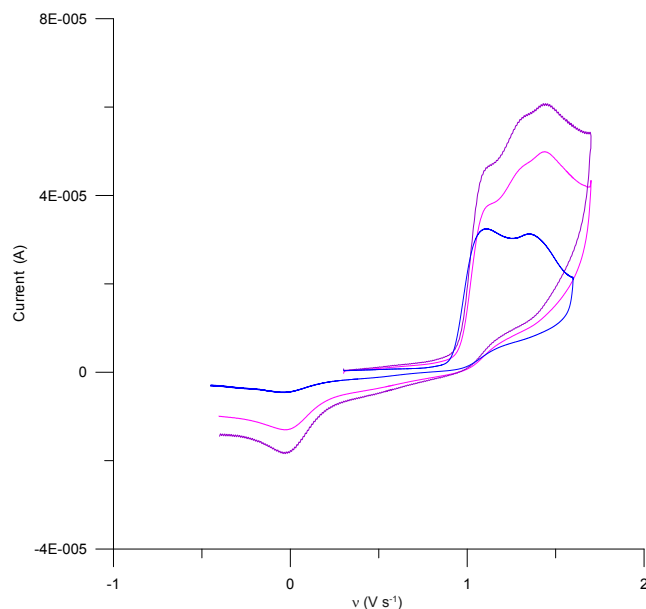
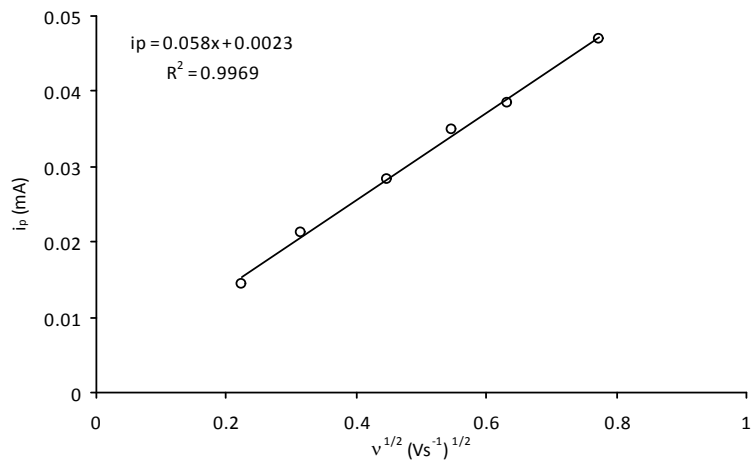
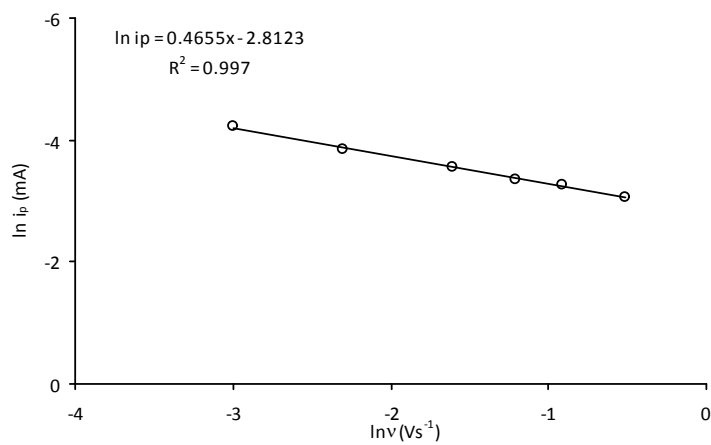


Figure S1: CV of 5-ph-Dp 1mM recorded at Pt-WE vs Ag/AgCl, Cl⁻_{sat} in AN + 0.05 M TBAP at a) 0.1 V s⁻¹ (blue line); b) 0.3 V s⁻¹ (pink) ; c) 0.6 V s⁻¹ (purple).



A



B

C

Figure S1.1: 5-ph-Dp 1mM: A) dependence of the anodic peak current (i_{pa}) on the square root of potential scan rate (v); B) dependence of i_{pa} on the potential scan rate in double logarithm coordinates C) variation of the scan rate normalised current ($i_p/v^{1/2}$) with scan rate

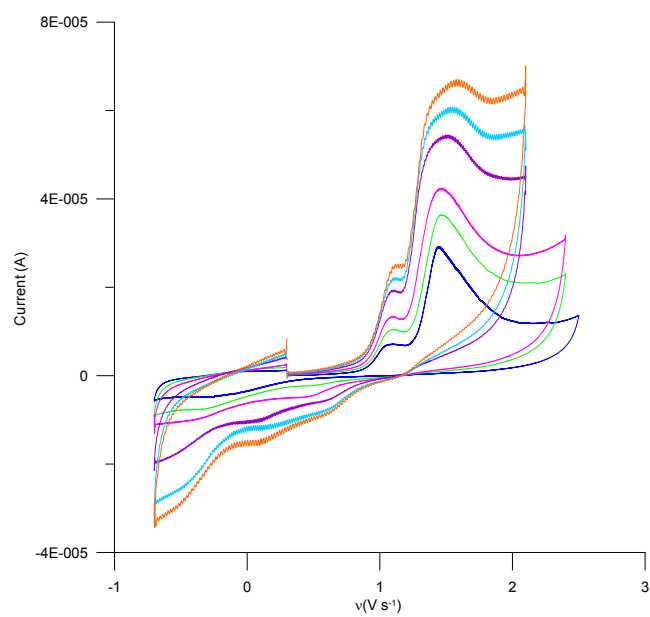


Figure S2: CV of 5-py-Dp 1mM recorded at Pt-WE vs Ag/AgCl, Cl_{sat} in AN + 0.05 M TBAP at a) 0.1 V s⁻¹ (blue line); b) 0.2 V s⁻¹ (light green); c) 0.3 V s⁻¹ (pink); d) 0.6 V s⁻¹ (purple); e) 0.8 V s⁻¹ (light blue); f) 1 V s⁻¹(orange)

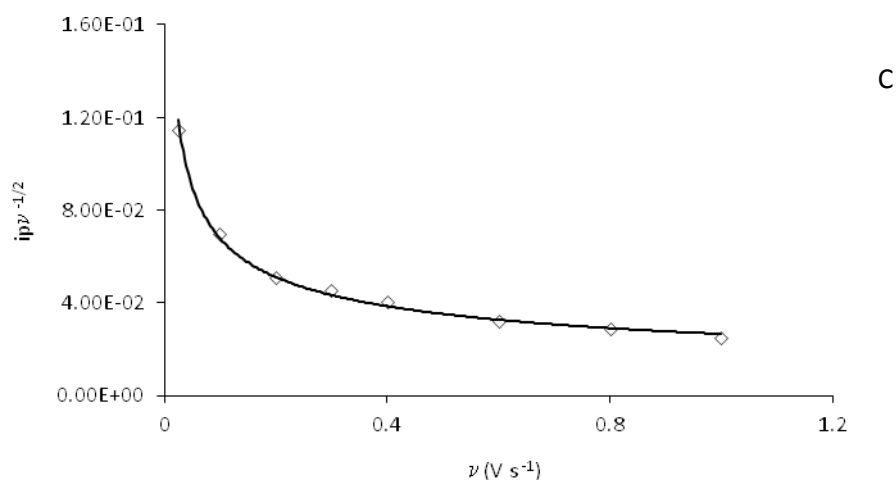
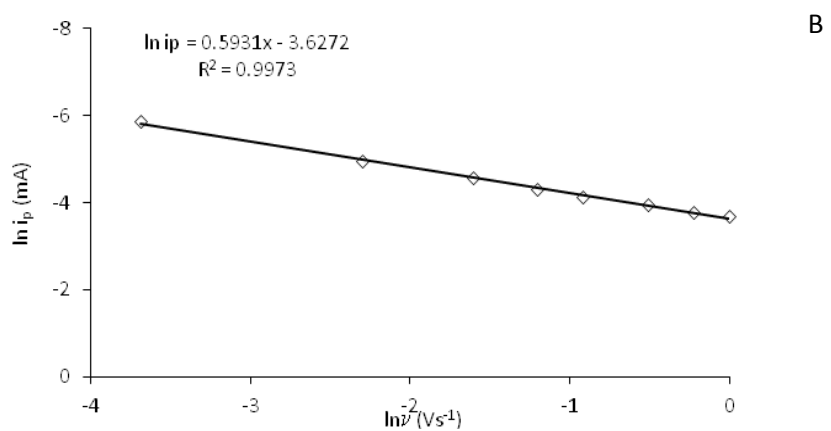
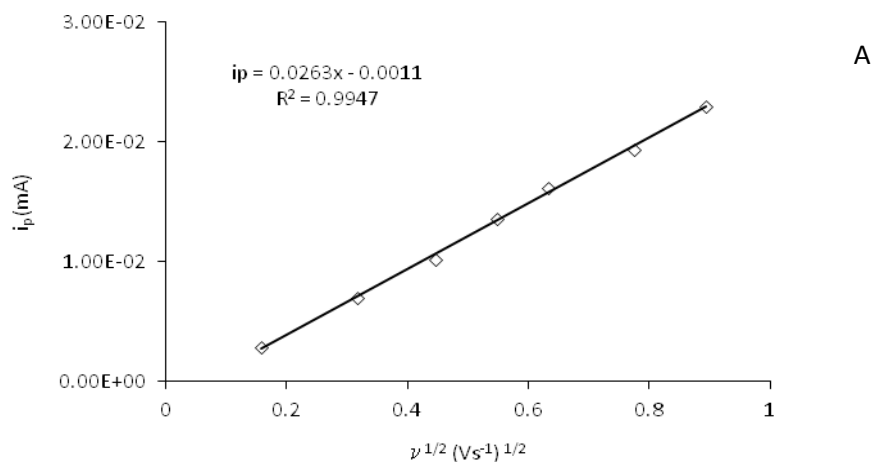


Figure S2.2: 5-py-Dp 1 mM: A) dependence of the anodic peak current (i_{pa}) on the square root of potential scan rate (v); B) dependence of i_{pa} on the potential scan rate in double logarithm coordinates C) variation of the scan rate normalised current ($i_p/v^{1/2}$) with scan rate.

CV of 5-py-DP in the presence of tosylate, as stabilizer of radical cation was also recorded (Figure S3). The shielding of the positive charge is responsible for the cathodic shift of both oxidation processes. Moreover, the ip related to radical cation formation turns to $n_{app} = 2$.

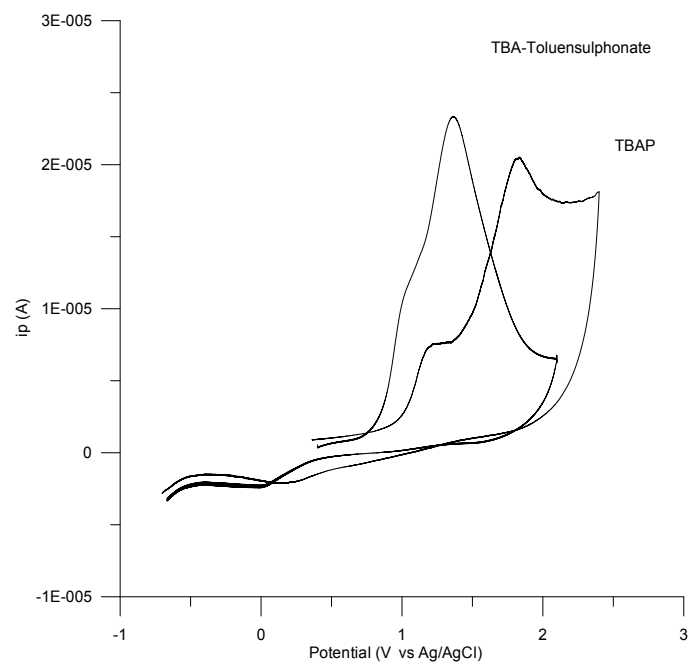


Figure S3: CV of 1 mM of 5-py-Dp recorded in TBA-tosylate compared to that obtained in tetrabutylammonium-perchlorate. Both voltamograms were obtained at Pt-WE vs Ag/AgCl, Cl^-_{sat} . Scan rate 0.1 Vs^{-1} .

The EQCM profile of both 5-ph-DP cNIP (Fig. S4, solid line) and 5-ph-DP cMIP (Fig. S4, dashed line), shows that the film increased regularly its thickness.

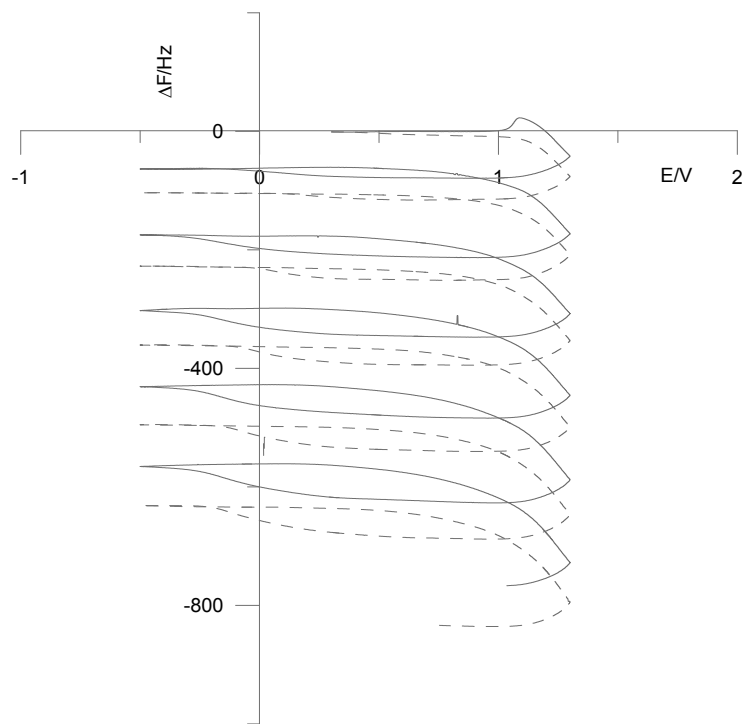


Figure S4: 5-ph-DP deposition at Pt quartz crystal electrode to obtain cNIP (solid line) and cMIP (dashed line)

The control DPV of non-imprinted poly-5-ph-DP (Fig. S4A, solid line) showed the film oxidation at + 0.3 V and a single well defined overoxidation peak at + 1.2 V. However, the DPV profile of 5-ph-DP-cMIP (Fig. S4A-dashed line) presented a prewave at + 0.9 V and the peak at + 1.2V shifted at + 1.35V and its ip intensity increased of about 25%. It was estimated, by comparison of microgravimetric and DPV data, that poly-5-ph-DP was able to trap 2.75×10^{-9} mol cm^{-2} of SA. The DPVs show also that c-MIP was able to bind reversibly SA (Fig. S4A-dotted line) which was extracted in AN added with 1% HAc (v/v) (Fig. S4A-dashed-dotted line) .

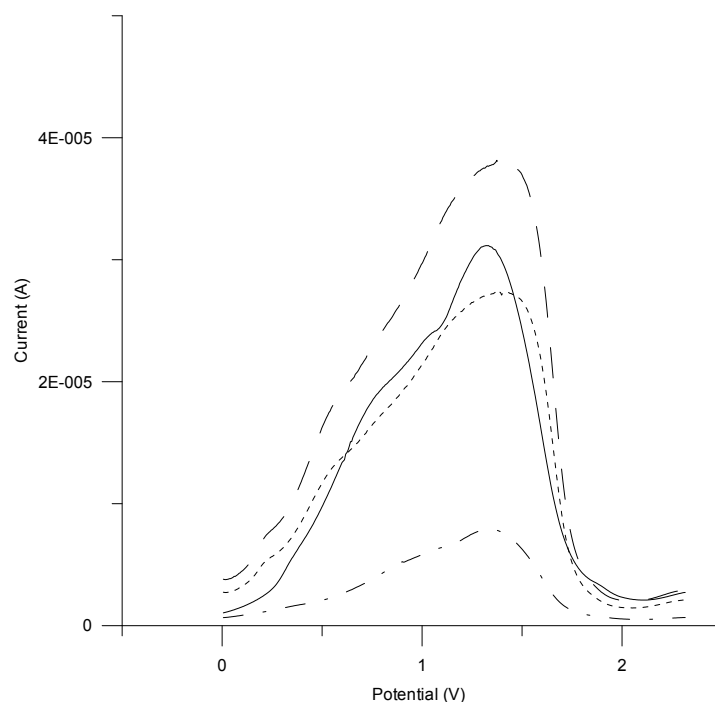


Figure S 4A: DPV of homo-poly-5-ph-DP cNIP (solid line), cMIP (dashed line), c-MIP after SA removal (dash-dot line), cMIP SA rebind (dotted line). cMIP monomer/template ratio = 1:1. Pt-quartz crystal WE in AN + 0.05 M TBAP vs. Ag/AgCl; scan rate 0.10 V s^{-1}

The profiles of mass variation (Fig. S5, solid line) showed that the mass increase of poly-5-py-DP was confined just to the anodic part of the scan. The EQCM (Fig. 5-dashed line) profiles of poly-5-py-DP showed the inclusion of SA as increasing cathodic current and as contemporary lowering of the frequency shift due to the mass deposition at the crystal surface. As for cNIP, the deposition process after ca. 17 cycles becomes less efficient and inversely related to the number of cycles.

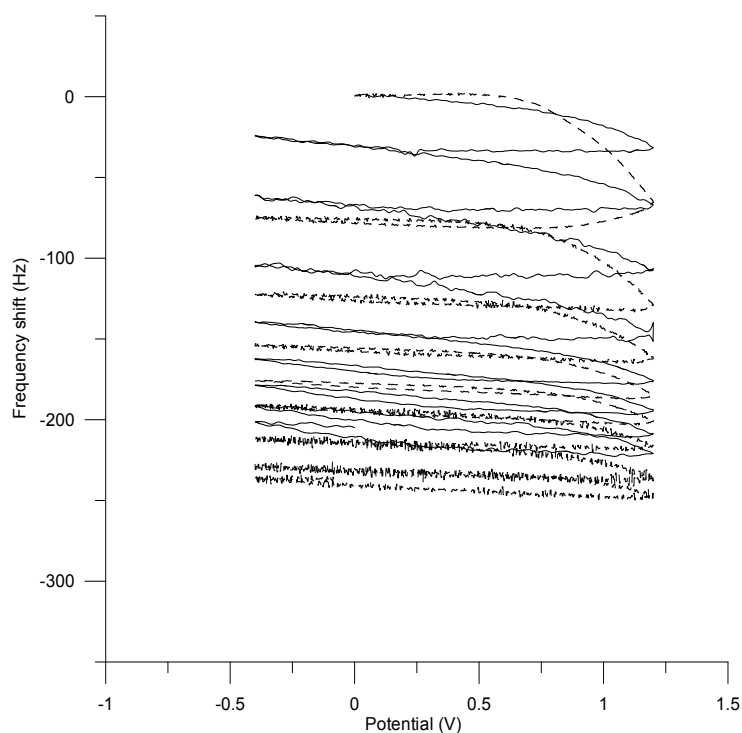


Figure S5: Δf (Hz) profile of homo-poly-5-py-DP (cNIP as solid line) and homo-poly-5-py-DP + SA (cMIP as dashed line); cMIP monomer/template ratio = 1:1. Pt- quartz crystal WE in AN + 0.05 M TBAP vs. Ag/AgCl; Scan rate 0.1 Vs⁻¹

The DPV control voltammetry of non-imprinted poly-5-py-DP shows an oxidation process at + 0.2 V followed by two overoxidation processes at + 1.2 V and + 1.4 V with similar ip (Fig. S5A, solid line). In py-cMIP the uptake of SA was observed as oxidation wave at + 1.6 V (Fig. S5A, dashed line) and it was reversibly bound (Fig. S5A dotted line) after extraction with AN containing 1% HAc (v/v) (Fig. S5A –dashed-dotted line). The comparison of cNIP and cMIP suggests the inclusion of SA while the similarity of the two poly cMIP obtained from the singular monomers indicate that the SA uptake does not change the deposition of the film.

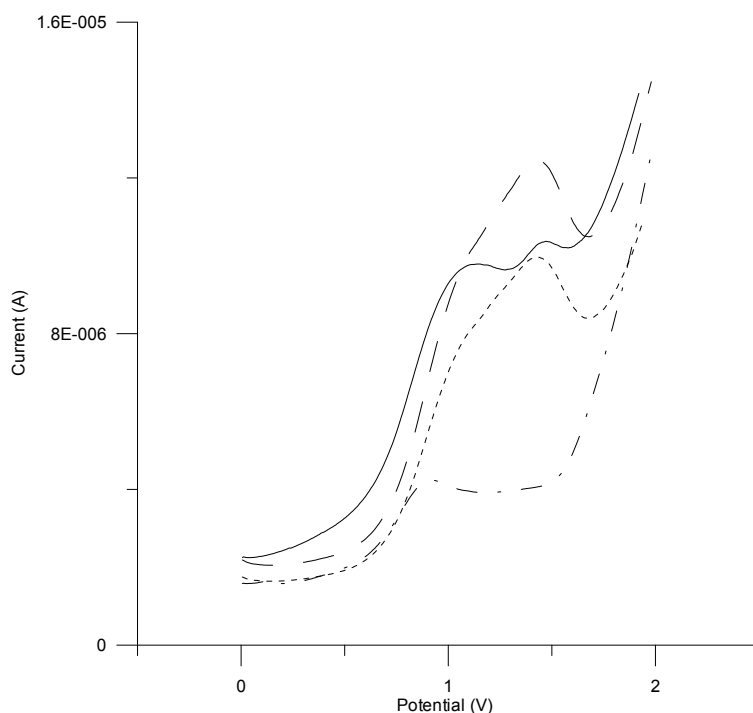


Figure S5A: DPV of homo-poly-5-py-DP cNIP (solid line), cMIP (dashed line), c-MIP after SA removal (dash-dot line), cMIP SA rebind (dotted line). cMIP monomer/template ratio = 1:1. Pt-quartz crystal WE in AN + 0.05 M TBAP vs. Ag/AgCl; Scan rate 0.10 Vs⁻¹

When the two monomers were mixed to form the copolymer, the EQCM frequency shift (Fig. S6- solid line) shows that the deposition of co-cNIP was confined to the anodic part of the cycles. The template inclusion was confirmed by EQCM frequency shift (Fig. S6, dashed line) in which the mass deposited at each cycle increased, compared to co-cNIP.

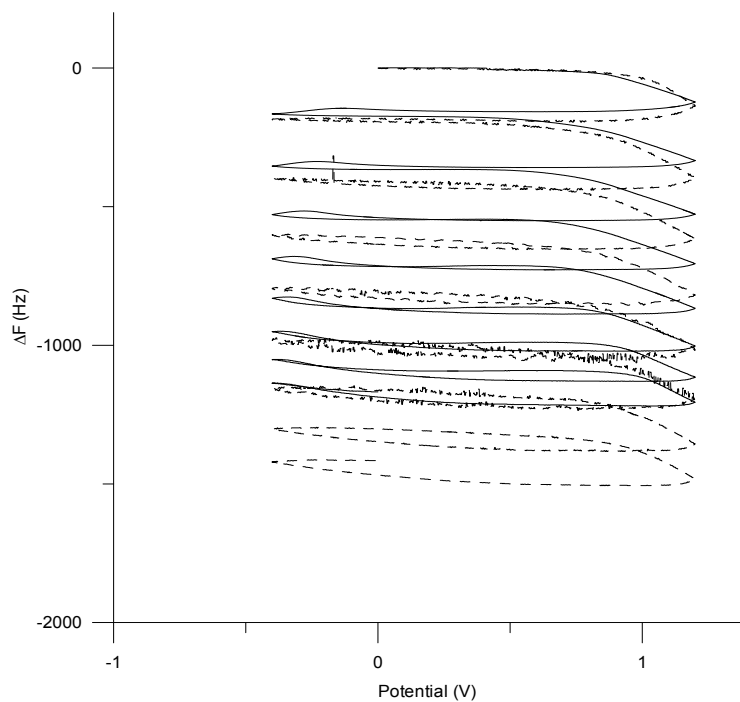


Figure S 6: Δf (Hz) profile of co-polymer (cNIP as solid line) and co-polymer + SA (cMIP as dashed line). Monomers feed ratio = 1; SA 1.5 mM. Pt- quartz crystal WE in AN + 0.05 M TBAP vs. Ag/AgCl ; Scan rate 0.10 Vs^{-1}

However, the DPV profiles (Fig. S6A-solid line) for the copolymer cNIP, obtained with a monomer feed ratio of 1:1, prove that both monomers were involved in the polymer backbone formation. In fact, peaks due to the overoxidation of both poly-5-py-DP and poly-5-ph-DP were evident with a higher ipa compared to that offered by the singly polymerized monomers.

The co-cMIP was prepared by mixing two monomers in a different ratio respect to a fixed amount of SA (1.5 mM) and the 1:1 feed ratio gave the higher copolymer deposition. The DPV profile (Fig. S6A-dashed line) confirmed the co-polymerization of the monomers as well as the SA inclusion in co-cMIP.

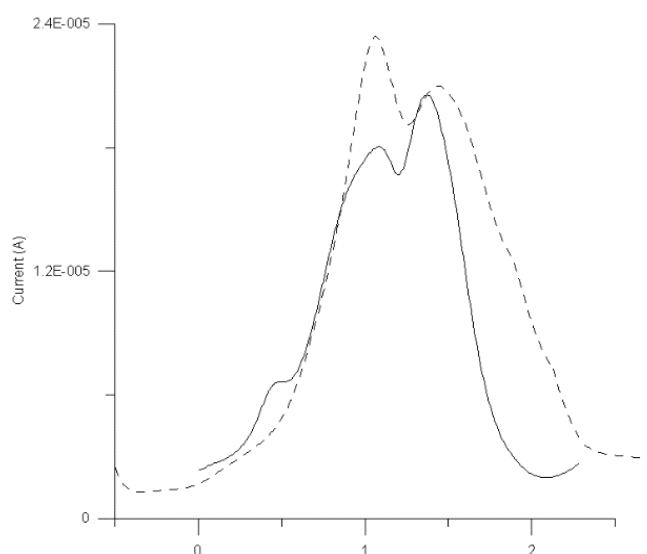


Figure S 6A: DPV of copolymer cNIP (solid line) and cMIP (dashed line). Monomers feed ratio = 1; SA 1.5 mM. Pt- quartz crystal WE in AN + 0.05 M TBAP vs. Ag/AgCl ; scan rate 0.10 Vs⁻¹

The Pt-quartz crystal modified by poly-5-ph-Dp was also utilised to measure the film thickness by profilometer (Figure S7). It was observed a linear correlation between the number of electropolymerisation cycles and the polymer thickness so, a layer of 2.7 nm per cycle was esteemed to deposit. The reported image shows that the film growth uniformly onto the electrode surface.

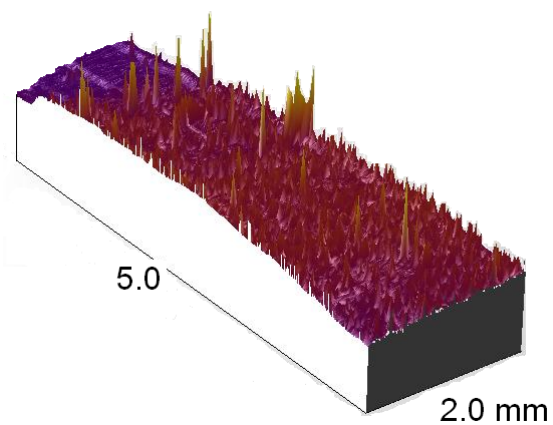


Figure S7: Profilometry measurement of poly-5-ph-Dp thickness