

Supporting Information

Molecularly imprinted polymers electrochemical sensing: the effect of inhomogeneous binding sites on the measurements. Comparison between imprinted polyaniline versus nanoMIP-doped polyaniline electrodes for the EIS detection of 17 β -estradiol.

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1. Investigation of electrochemical behaviour of E2

Preliminary investigation of the electrochemical behaviour of the target analyte 17 β -estradiol (E2) at the bare screen-printed gold electrode was assessed by CV. Ideally the target analyte/template used to prepare electropolymerized MIPs should be inert and it should not actively participate in the MIP layer formation. Figure S1 shows a flat voltammogram without any peaks indicating that in the range of -0.5 V and +0.8 V the analyte is not a redox compound. This is crucial as it indicates that any resulting polyaniline layers are void of any interferences from the template.

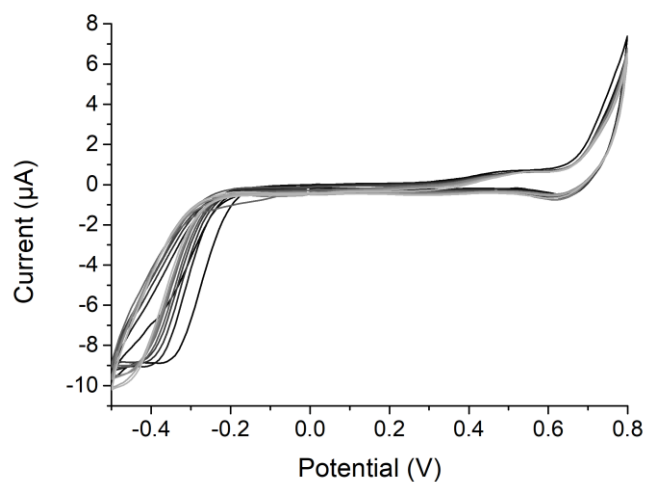


Figure S1. CV of E2.

2. CVs of electrodeposition of aniline for imprinted PANI electrode and nanoMIPs-doped PANI electrode

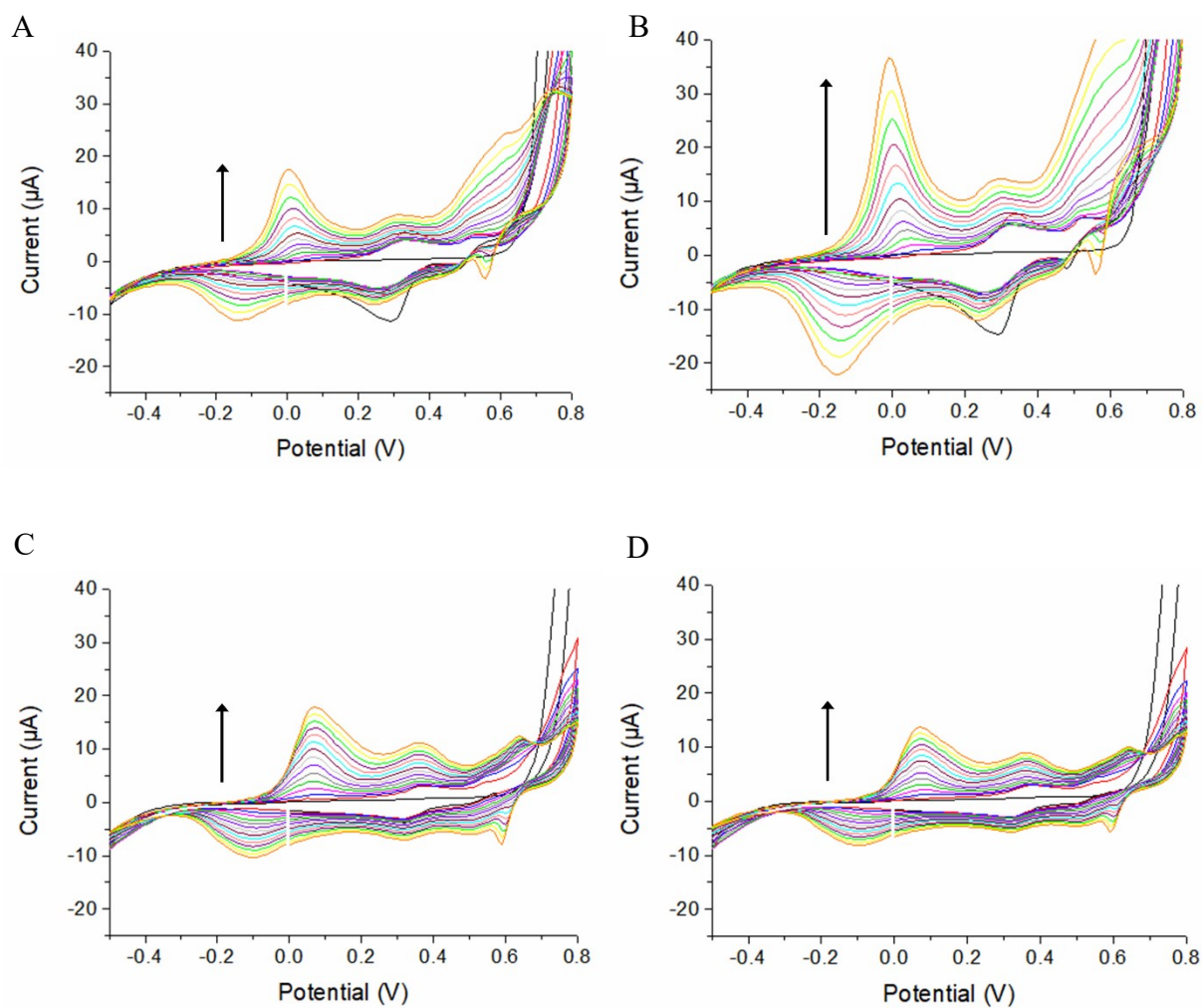


Figure S2. CV of (A) imprinted PANI layer, (B) PANI control, (C) nanoMIPs-doped PANI and (D) NPs control.

3. Fitting with PSTrace software

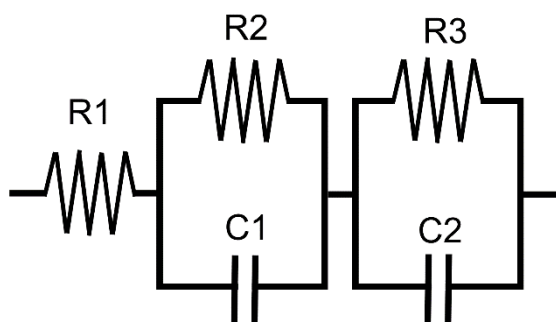


Figure S3. Equivalent circuit used for the fitting of Nyquist plot in PSTrace Software.

4. Preparation of imprinted PANI layer and PANI control

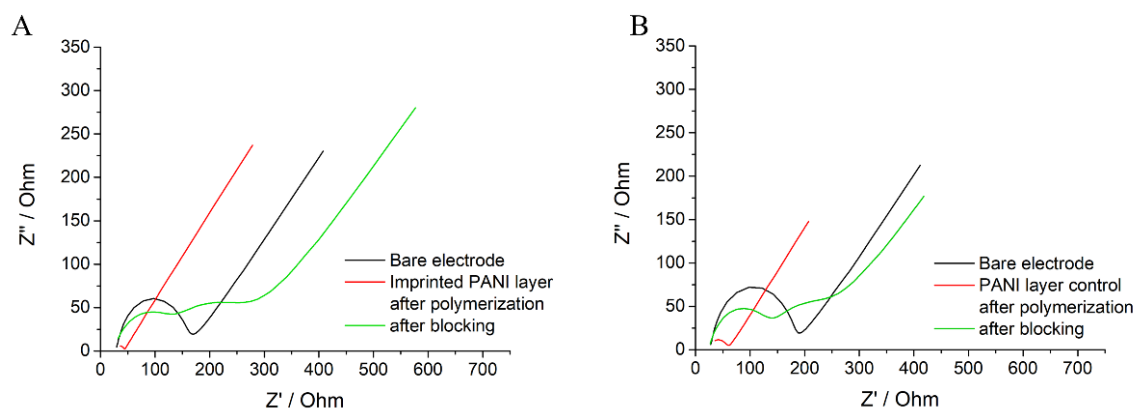


Figure S4. Nyquist plot of Imprinted PANI layer (A) and PANI control (B) after the electropolymerization and after the blocking step.

5. Dynamic Light Scattering (DLS) of nanoMIPs

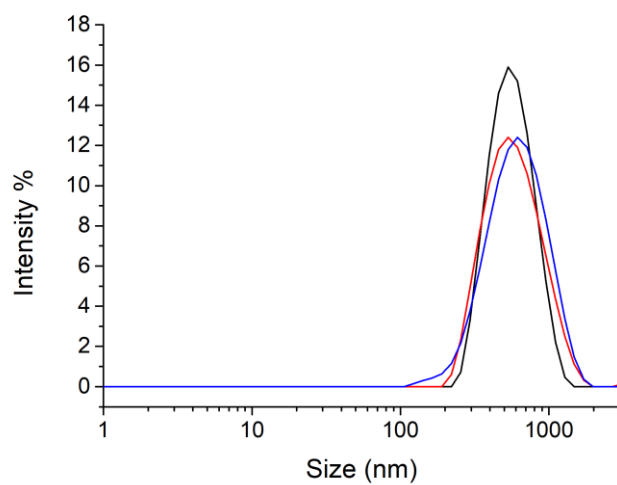


Figure S5. Example of DLS measurements of nanoMIP.

Table S1. Parameters obtained from DLS measurements of nanoMIP.

	Value
Z-average (d.nm)	553.3
PdI	0.275
Intercept	0.937

6. Isothermal Titration Nano Calorimetry (ITC) of nanoMIP

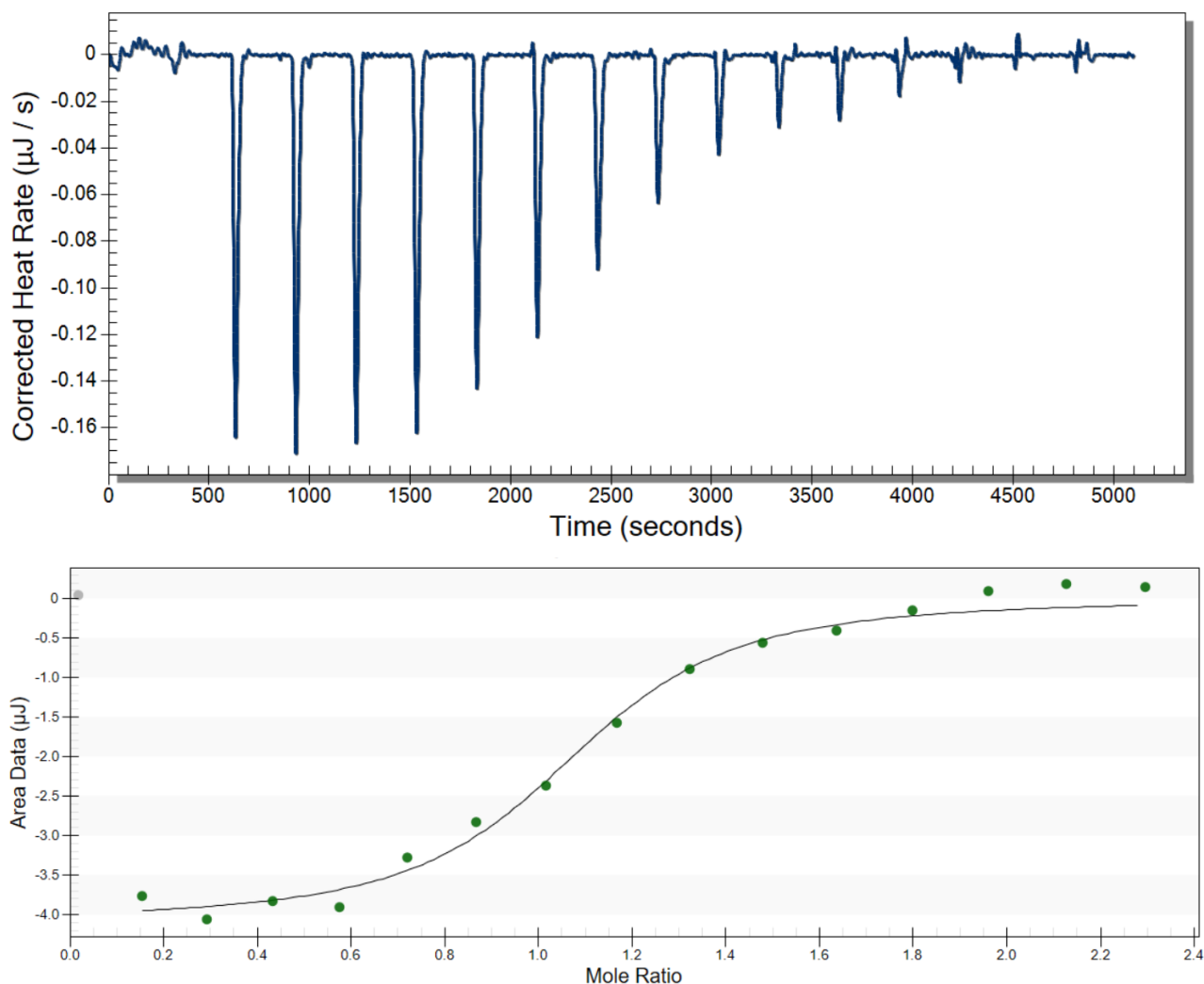


Figure S6. Upper panel: Raw ITC profile of nanoMIPs titrated with the template E2. Lower panel: integrated heats plotted as a function of the molar ratio nanoMIPs/E2 (green circles) and fitting of the data with an independent sites model.

Table S2. ITC fitting parameters.

Parameters	Value
K_d (M)	1.172×10^{-8}
n	1.029
ΔH (kJ/mol)	-380.8
ΔS (J/mol·K)	-1125

7. Structure of interferents

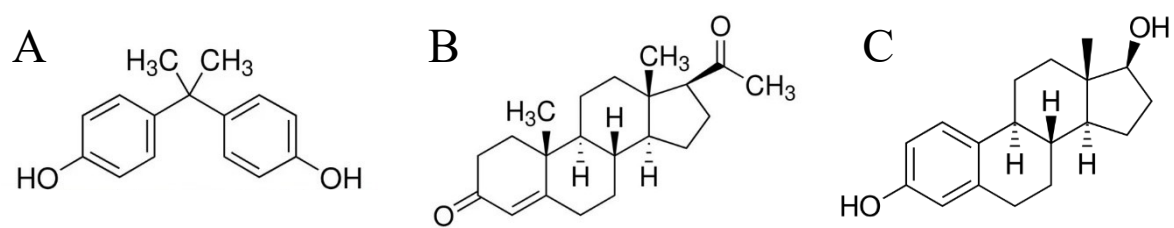


Figure S7. Molecular structure of Bisphenol A (A), Progesterone (B) and 17 β -Estradiol (C).

8. Real sample measurements

Table S3. Normalized Rct of NanoMIP-doped PANI electrode tested in real sample

	E2 (ng/mL)	Normalized Rct
PBS	0.1	0.151 ± 0.0032
	1	0.249 ± 0.0037
	10	0.370 ± 0.0032
Wastewater	0.1	0.144 ± 0.0024
	1	0.240 ± 0.0049
	10	0.350 ± 0.0042



DSSPACE

<https://dspace.org/>

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