Electronic Supplementary Material (ESI) for Analyst.

SUPPORTING INFORMATION

Electroanalytical profiling of cocaine samples by means of an electropolymerized molecularly imprinted polymer

Renata A. Grothe, Alnilan Lobato, Bassim Mounssef Jr., Nikola Tasić, Ataualpa A.C. Braga, Adriano O. Maldaner, Leigh Aldous, Thiago R.L.C. Paixão, and Luís Moreira Gonçalves

Figure S1. Electrocleaning of the electrode with aqueous sulfuric acid, 0.5 mol L^{-1}, 10 CV cycles from 0 V to +1.5 V vs. Ag|AgCl, with a scan rate of 100 mV s^{-1}.

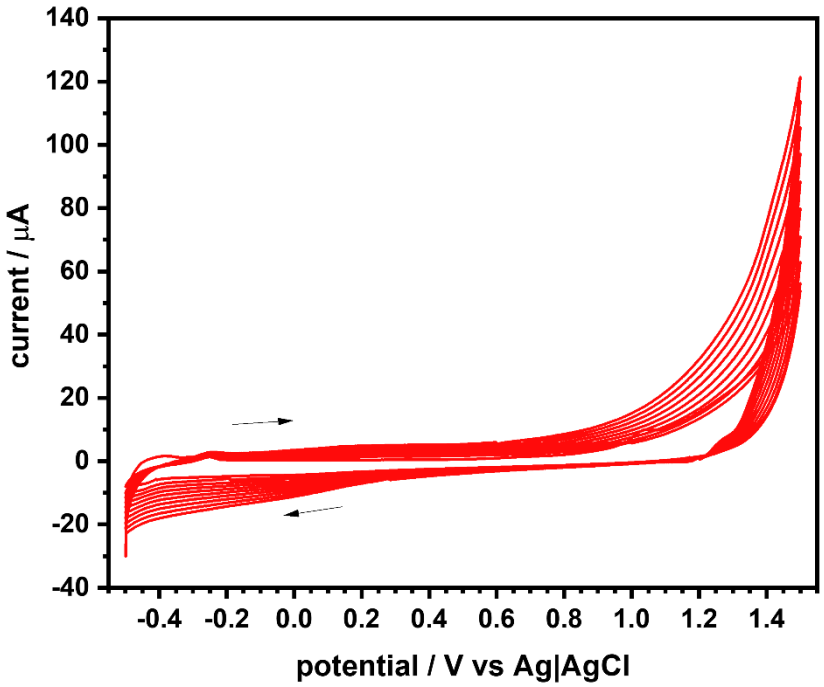

Figure S2. Electropolymerization process performed by 10 CV cycles from 0 V to +1.5 V vs. Ag|AgCl, at 50 mV s^{-1}, in the AHBA:BZC solution with 1:6 molar ratio ([AHBA] = 0.5 mmol L^{-1}, [BZC] = 3 mmol L^{-1}).

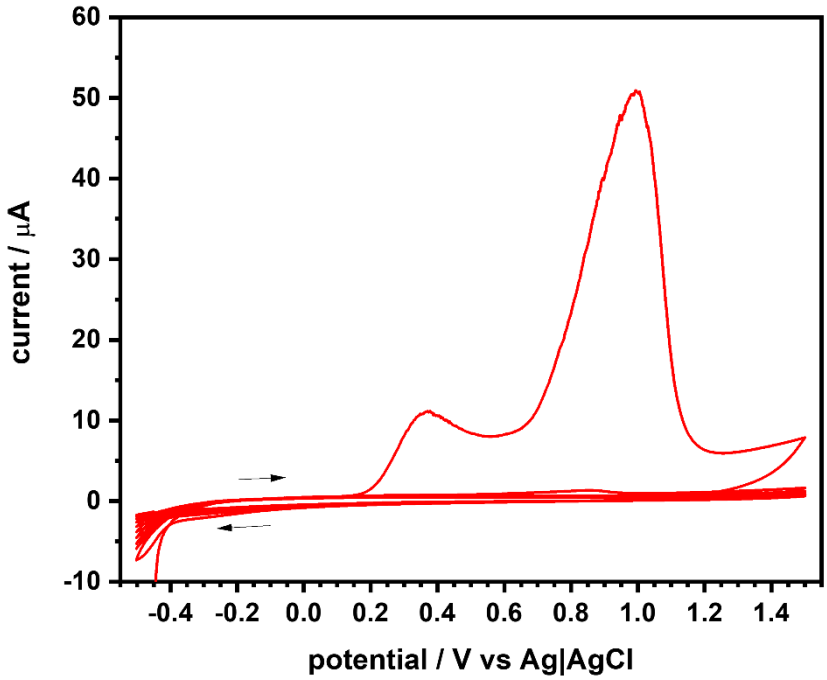

Figure S3. Template removal, 10 CV cycles in the potential range from -0.5 to +1.5 V in PBS with a scan rate of 200 mV s^{-1}.

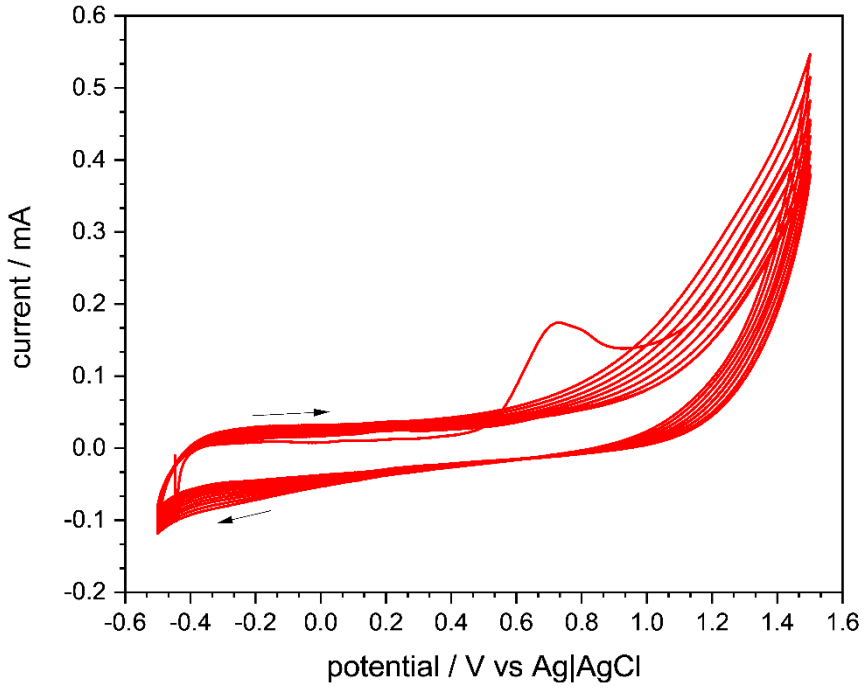

Figure S4. Cyclic voltammograms of 100 µmol L^{-1} of BZC, in PBS, at different scan rates (from 10 to 200 mV s^{-1}), from 0.0 to +1.5 V vs. Ag|AgCl. Inlay: Linear correlation between the oxidation peak current of the recorded cyclic voltammograms and the square root of the scan rate.

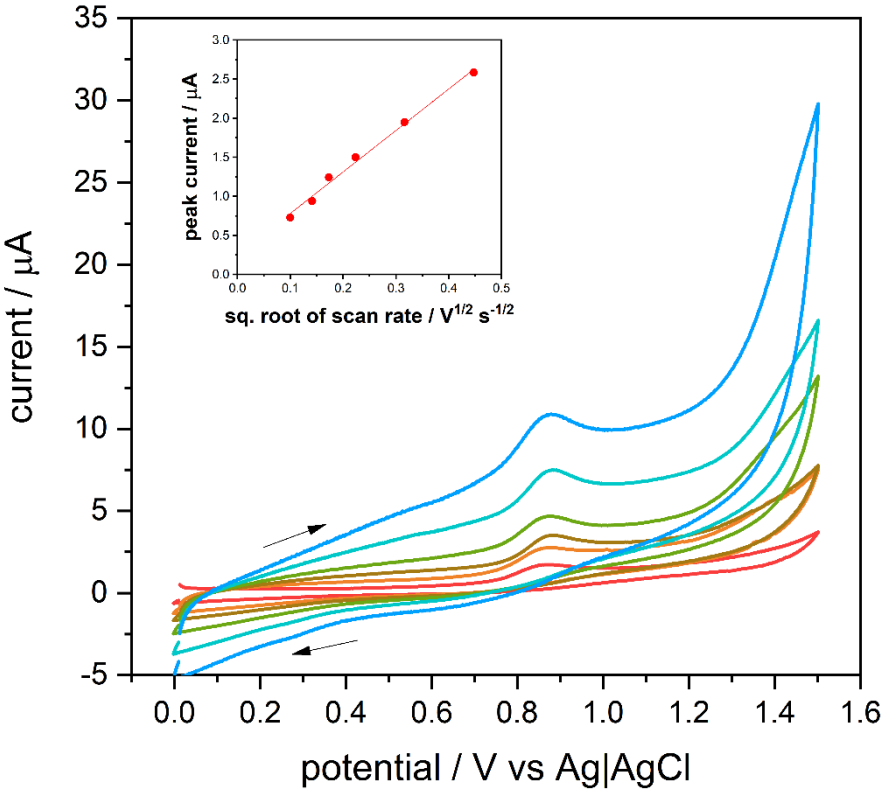

Figure S5. Cyclic voltammograms of 100 µmol L^{-1} of BZC, in different pHs (a universal buffer solution was used), at a scan rates from 10 to 25 mV s^{-1}, from 0.0 to +1.5 V vs. Ag|AgCl.

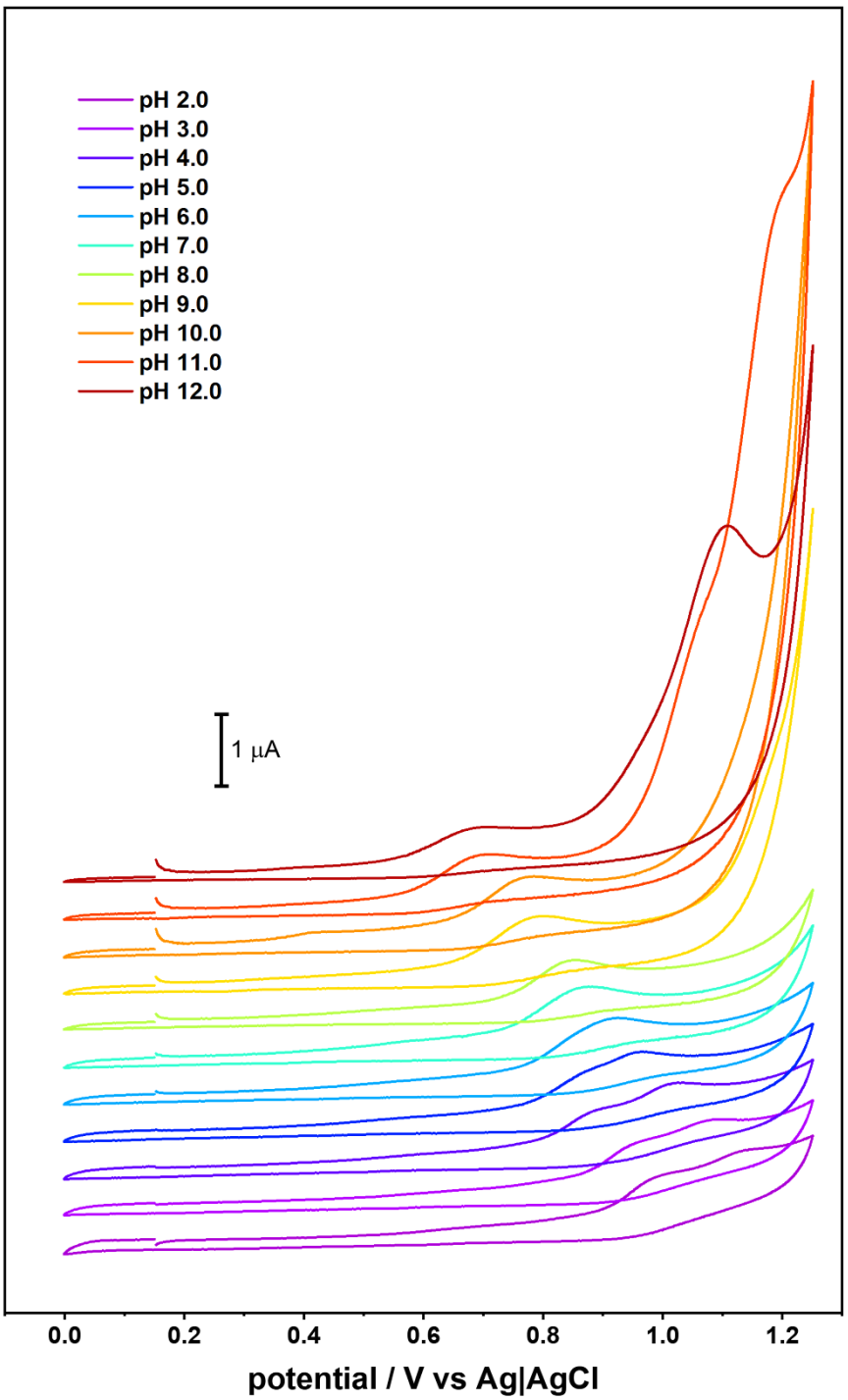

Figure S6. Peak potential and peak current variation with pH (data obtained from the voltammograms from Figure S4).

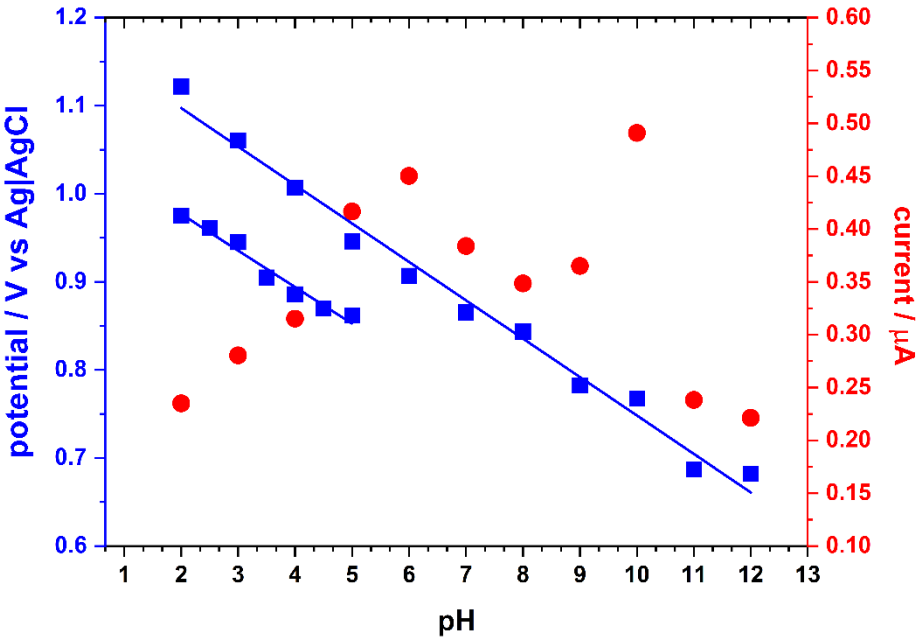

Figure S7. SWVs (potential range from +0.5 to +1.5 V, at a frequency of 25 Hz, pulse amplitude of 20 mV and step potential of 2.5 mV) right after electropolymerization and after the electrocleaning (i.e. template removal) process. Baseline correction with moving average level 2.

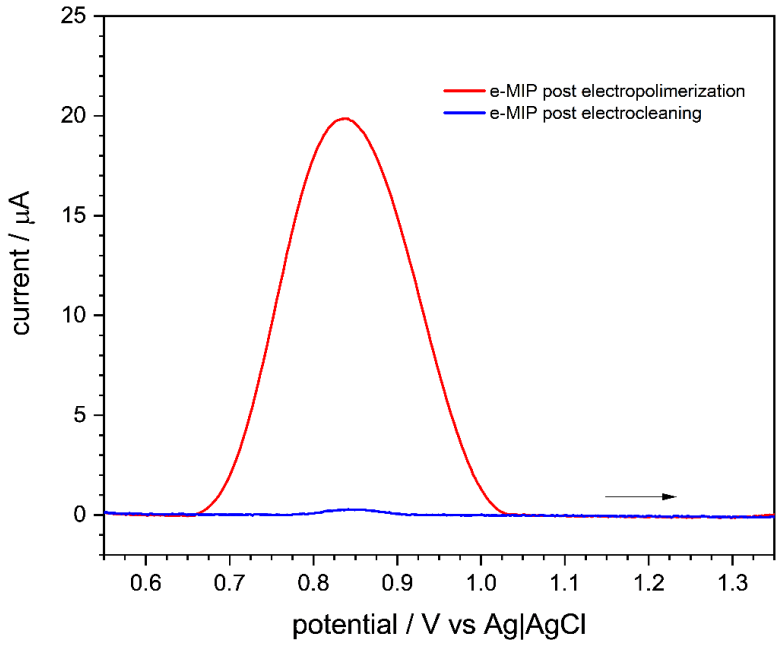

Figure S8. Optimization studies. A) AHBA/BZC ratio performed on the GCE-MIP device, peak current obtained by SWV of PBS after incubation in a BZC solution, 30 µmol L^{-1} (polymerization conditions: 0.50 mmol L^{-1} 3,4-AHBA, from 1.5 to 3.5 mmol L^{-1} BZC, 50 mV s^{-1}, 10 cycles and 45 min of incubation); B) Electropolymerization scan rate study performed on the GCE-MIP device, peak current obtained by SWV of PBS after incubation in a BZC solution, 30 µmol L^{-1}, (polymerization conditions: 0.50 mmol L^{-1} 3,4-AHBA, 3.0 mmol L^{-1} BZC, 10 cycles and 45 min of incubation) C) Electropolymerization number of cycles study performed on the GCE-MIP device, peak current obtained by SWV of PBS after incubation in a BZC solution, 30 µmol L^{-1} with different number of cycles of polymerization (polymerization conditions: 0.50 mmol L^{-1} 3,4-AHBA, 3.0 mmol L^{-1} BZC, 50 mV s^{-1} and 45 min of incubation); D) Incubation time study performed on the GCE-MIP device, peak current obtained by SWV of PBS (pH 7.4) after different times of incubation in a BZC solution, 30 µmol L^{-1}, at pH = 7.4 (polymerization conditions: 0.50 mmol L^{-1} 3,4-AHBA, 3.0 mmol L^{-1} BZC, 10 cycles and scan rate of 50 mV s^{-1}. For A, B and C: potential range from +0.5 to +1.5 V, at a frequency of 25 Hz, pulse amplitude of 20 mV and step potential of 2.5 mV, baseline correction with moving average level 2.

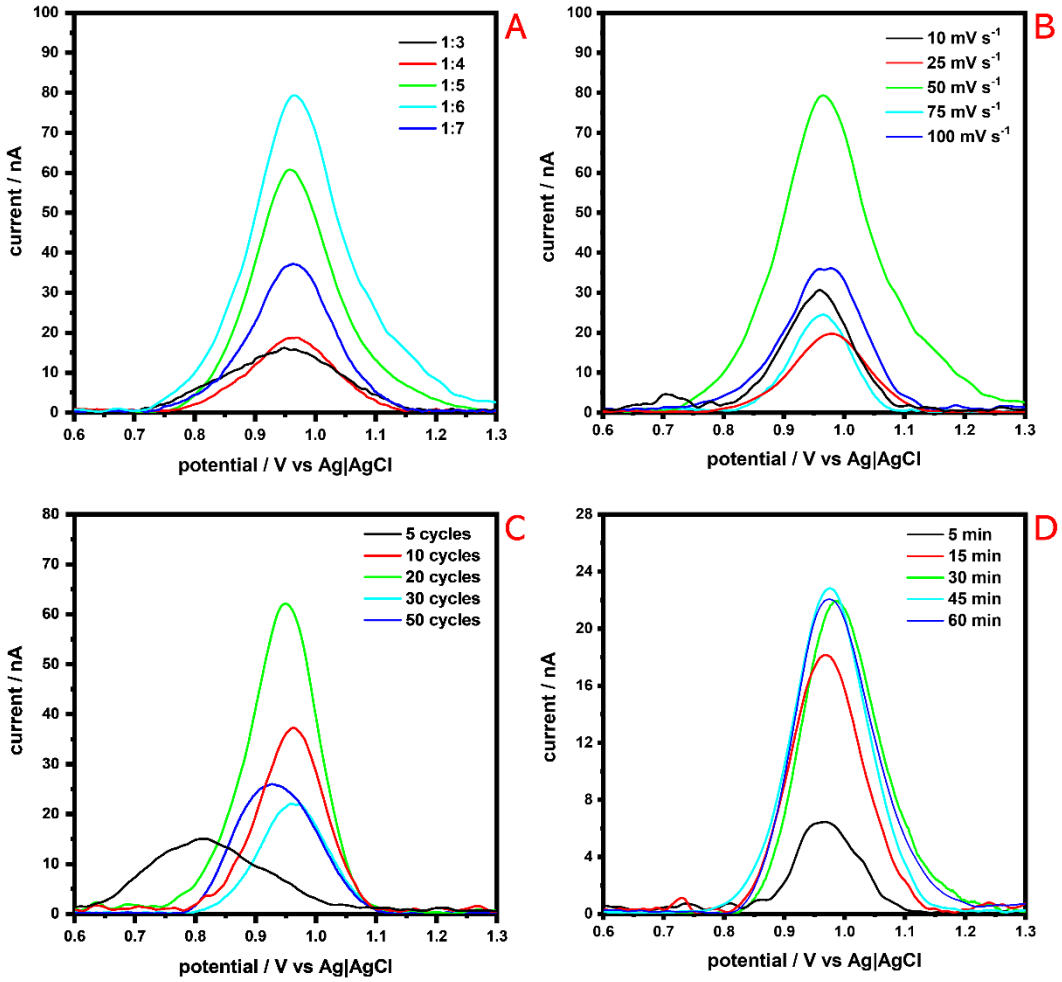

Figure S9. Left to right, top to bottom: cavities formed in the presence of BZC from least stable to third most stable (energies in kcal mol^{-1}).

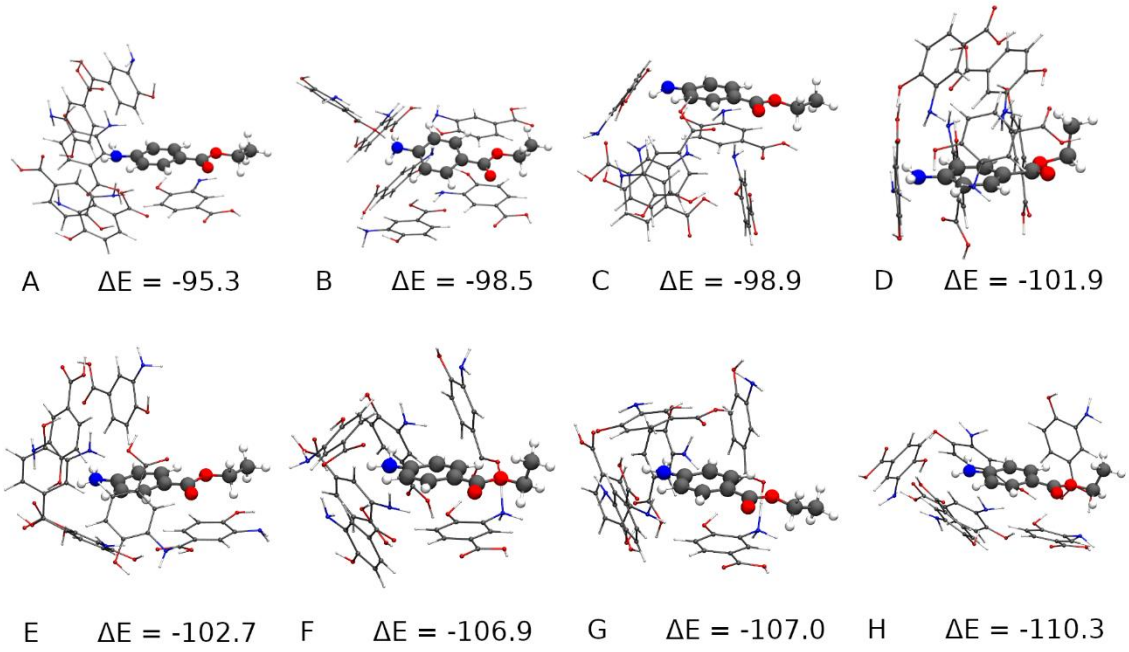

Figure S10. Calibration curve of the artificial urine samples.

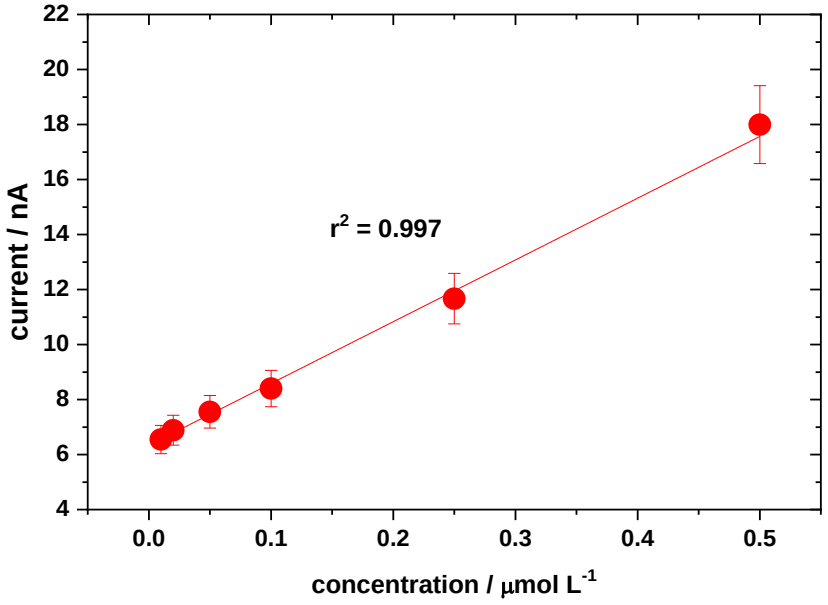

Figure S11. Integration of areas of the polymerization process, 10 CV cycles from 0 V to +1.5 V vs. Ag|AgCl, at 50 mV s^{-1}, in the AHBA:BZC solution with 1:6 molar ratio ([AHBA] = 0.5 mmol L^{-1}, [BZC] = 3 mmol L^{-1}).

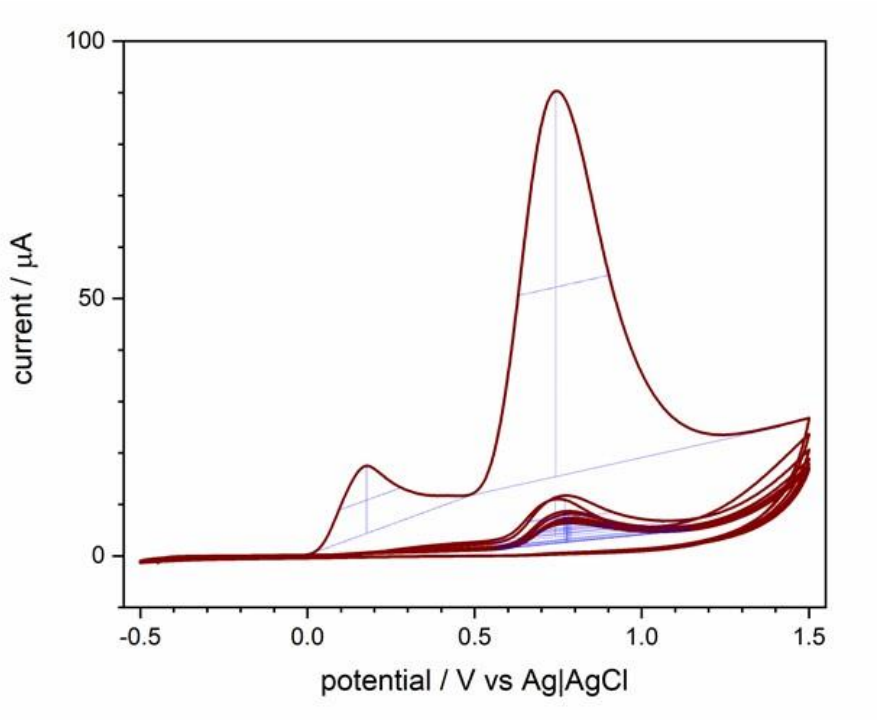

Table S1. Composition of the analyzed samples.

sample	compound (%, m/m)								
	BZC	**phenacetin**	**caffeine**	**lidocaine**	**aminopyrine**	**cocaine**	**cis-cinamoilcocaine**	**trans-cinamoilcocaine**	**ά***
#1	3.9	-	0	-	-	5.7	0.3	-	90.1
#2	27.6	-	31.4	-	-	9.1	0.6	0.6	30.7
#3	55.1	0.8	-	-	-	26.4	0.3	0.2	17.2
#4	1.1	9.5	3.0	-	-	3.6	0.3	0.3	82.2
#5	4.6	4.0	7.5	2.8	0.7	12.8	0.7	0.4	66.5
#6	8.8	1.4	-	-	0.2	61.2	3.0	2.1	23.3
#7	4.0	52.3	-	-	-	32.3	2.2	2.4	6.8

*unknown compounds