Alumina-Modified Glassy Carbon Electrode: A Robust Platform for Accurate Nimodipine Detection in Pharmaceutical Applications

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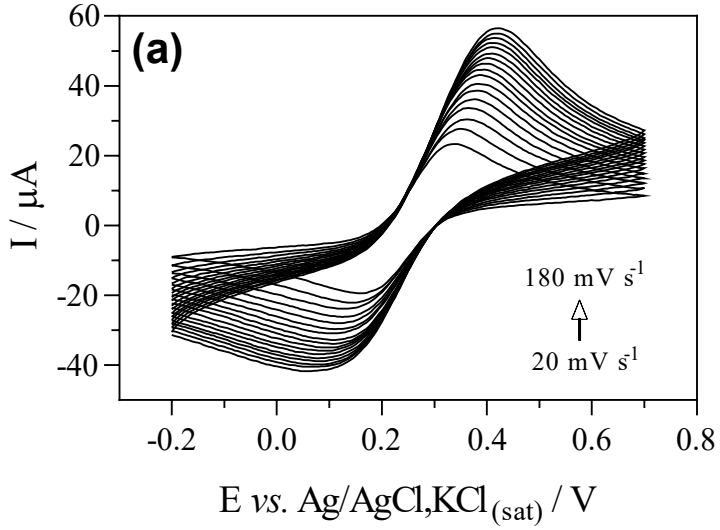
SUPPLEMENTARY INFORMATION



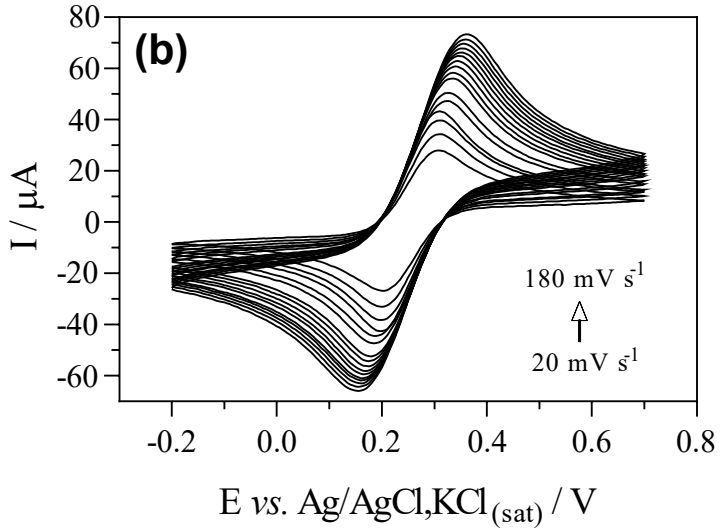
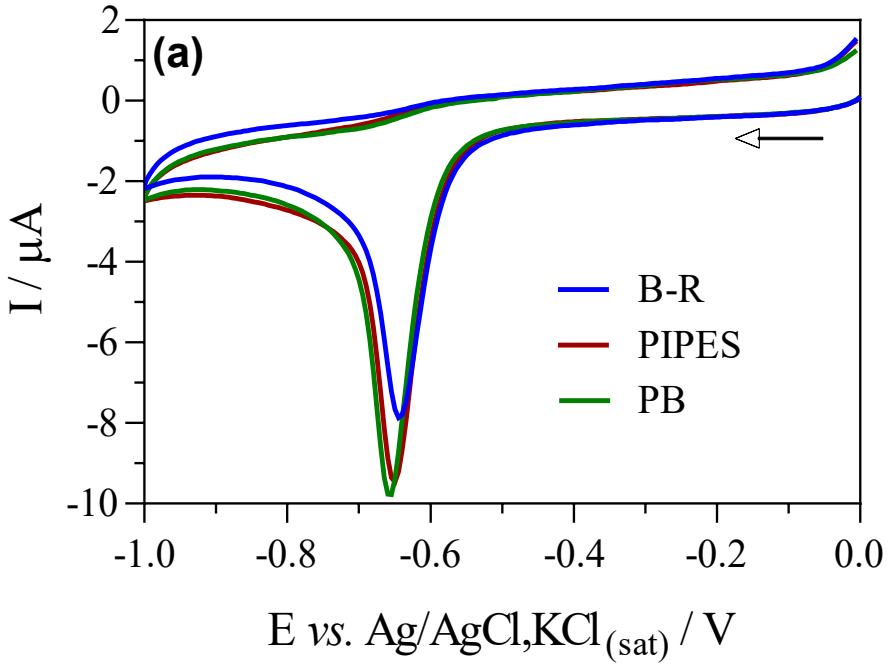
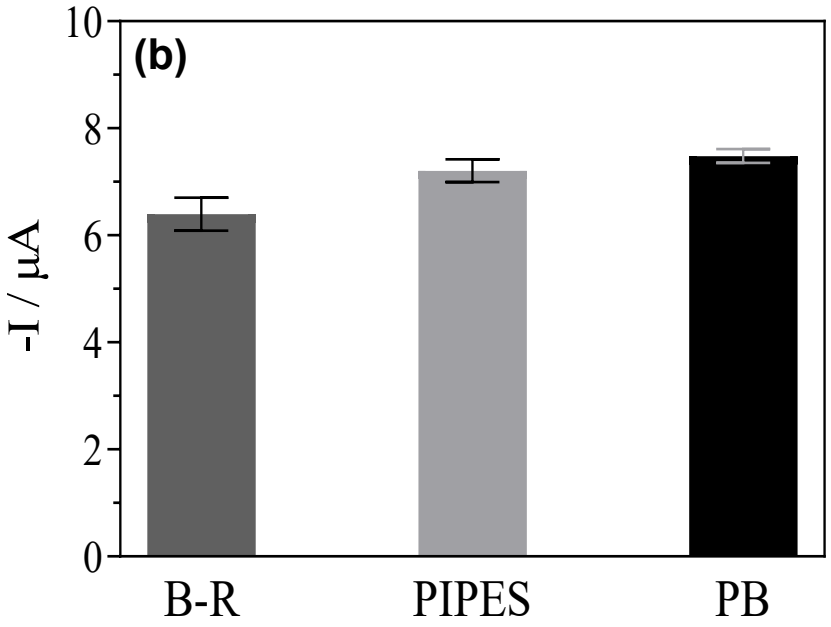


Figure S1. Cyclic voltammetry for (a) GCE/WP and (b) GCE/AP in $K_3Fe(CN)_6/K_4Fe(CN)_6$ 5 mmol L^{-1} at different scan rates.


(a)
I / µA
E vs. Ag/AgCl,KCl (sat) / V
B-R
PIPES
PB


(b)
-I / µA
B-R
PIPES
PB

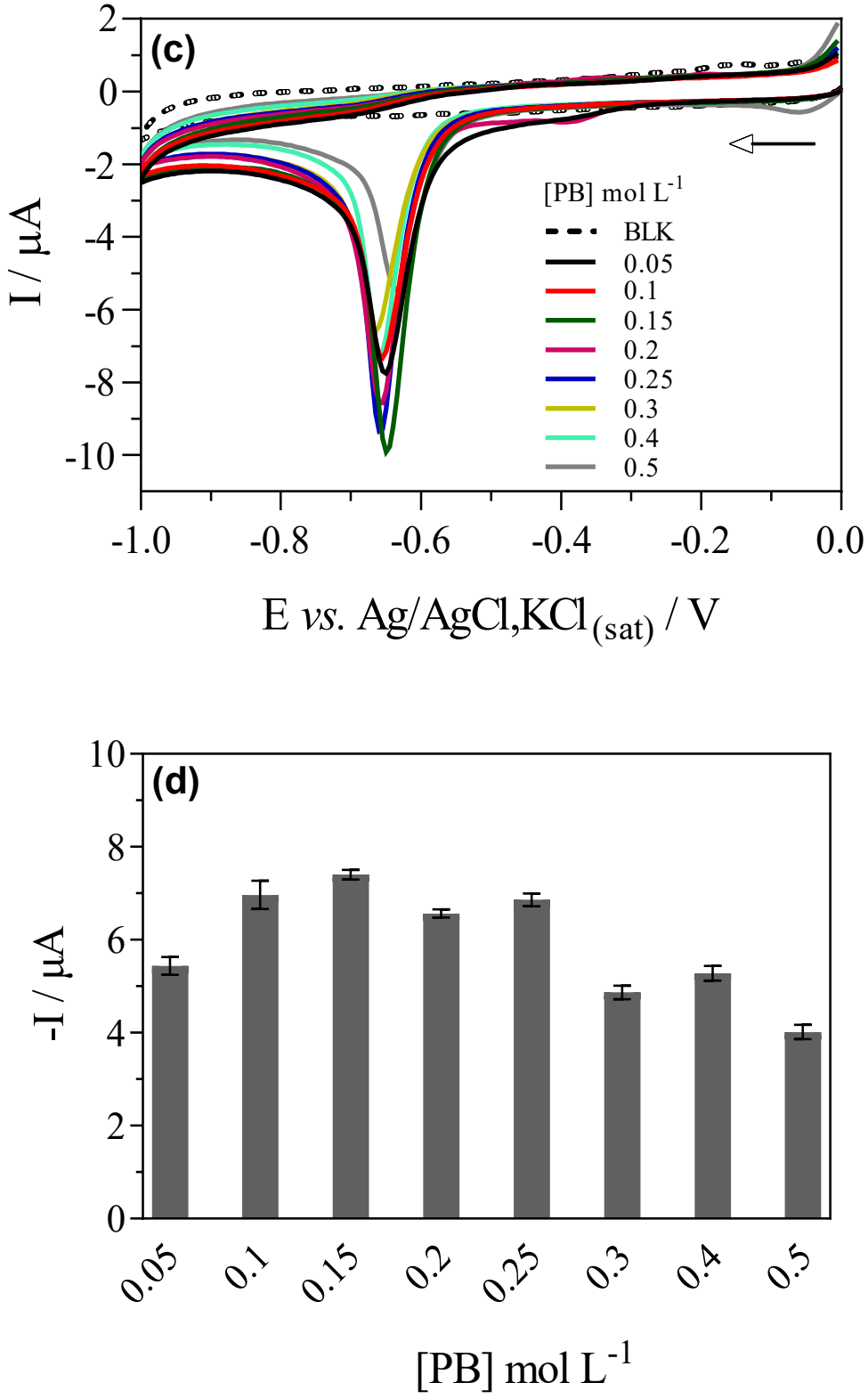
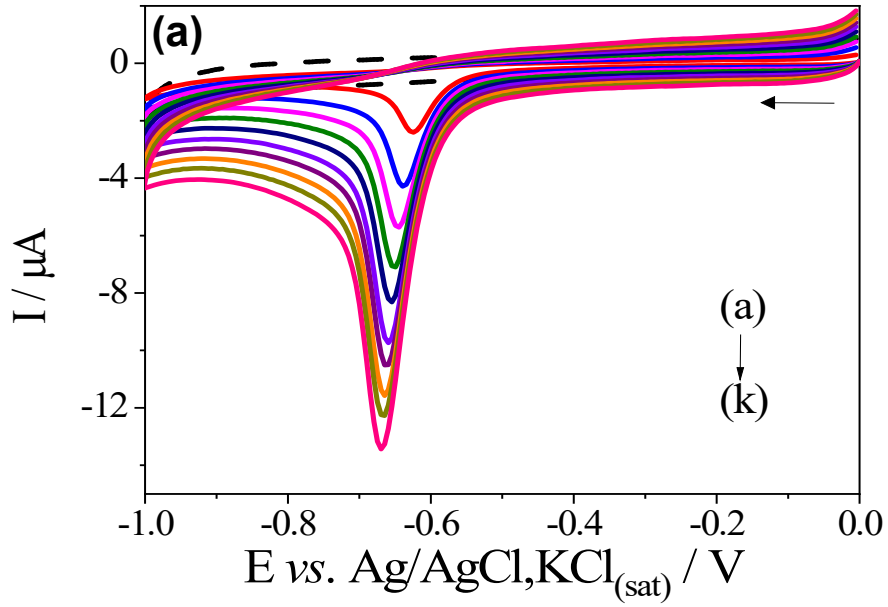
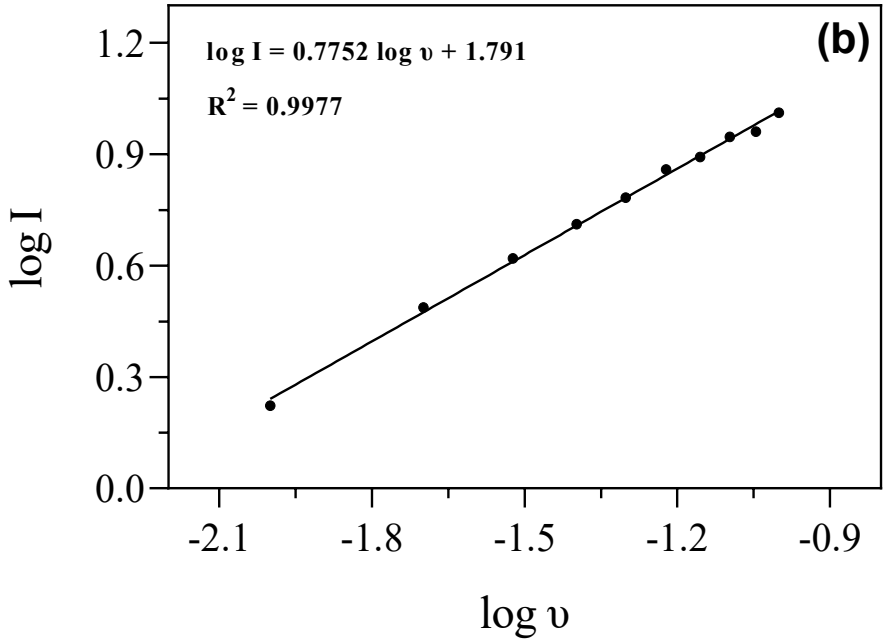


Figure S2. (a) Cyclic voltammetry study for 25 µmol L^{-1} NMP in buffer solutions, such as B-R, PIPES and PB at pH 6 (0.1 mol L^{-1}) and (b) its correspondent bar graph for each cathodic current intensity on GCE/AP (υ = 50 mV s^{-1}); n = 3. (c) Comparisons of 25 µmol

L^{-1} NMP between different PB concentrations and (d) the bar chart for the current sign obtained on GCE/AP (υ = 50 mV s^{-1}); n = 3.


(a)
0
-4
-8
-12
I / μA
(a)
(k)
-1.0
-0.8
-0.6
-0.4
-0.2
0.0
E vs. Ag/AgCl,KCl(sat) / V


log I = 0.7752 log υ + 1.791
R2 = 0.9977
(b)
1.2
0.9
0.6
0.3
0.0
log I
-2.1
-1.8
-1.5
-1.2
-0.9
log υ

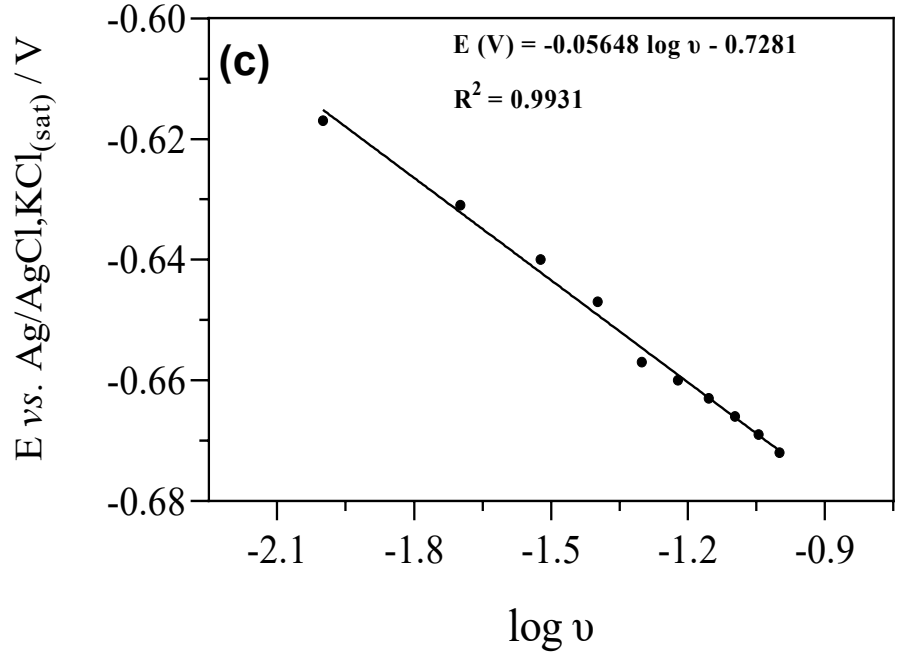
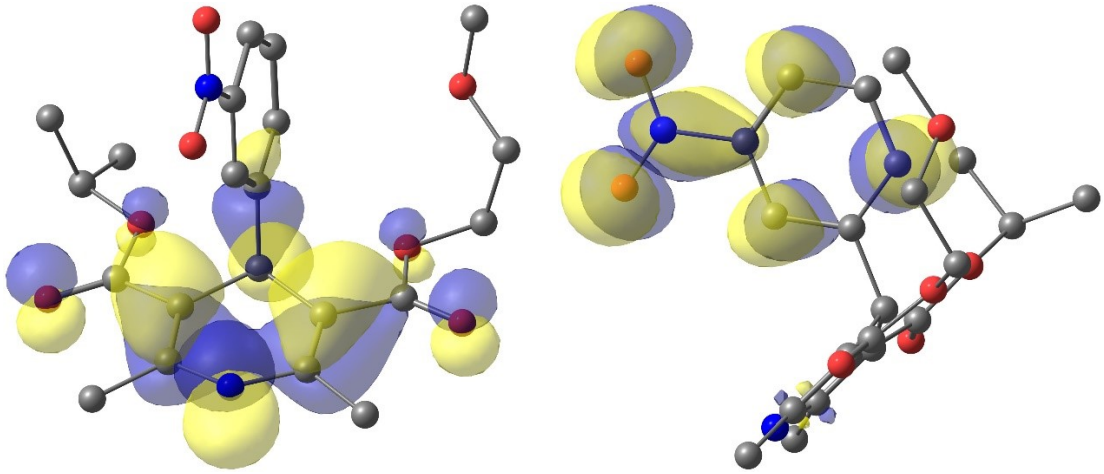


Figure S3. (a) CV for NMP 25 μmol L^{-1} in PB 0.15 (pH 6) for towards scan rates: (a), BLK, (b) 10, (c) 20, (d) 30, (e) 40, (f) 50, (g) 60, (h) 70, (i) 80, (j) 90 and (k) 100 mV s^{-1}. Plot graphs of (b) log I *vs.* log υ and (c) E *vs.* log υ.



(a) **(b)**

Figure S4. Frontier molecular orbitals; (a) HOMO and (b) LUMO of NMP. The gray, red, and blue spheres represents carbon, oxygen, and nitrogen atoms, respectively. The hydrogen atoms were suppressed for sake of clarity.

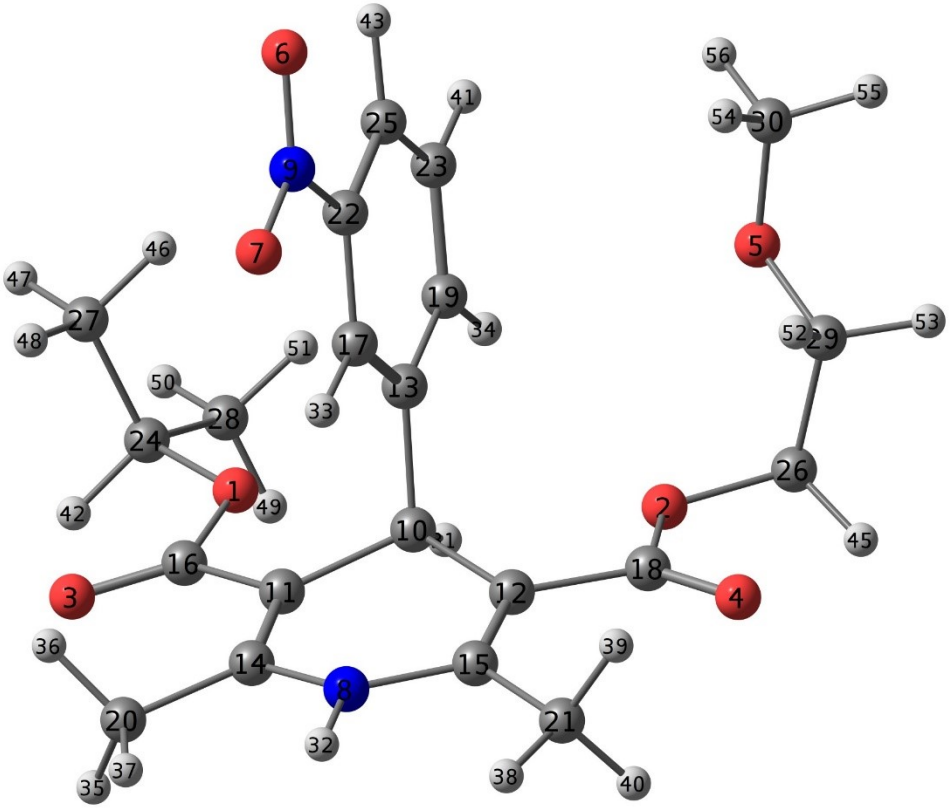


Figure S5. Atom labels of NMP optimized at BP86/Def2-TZVPPD-D3BJ level of theory.

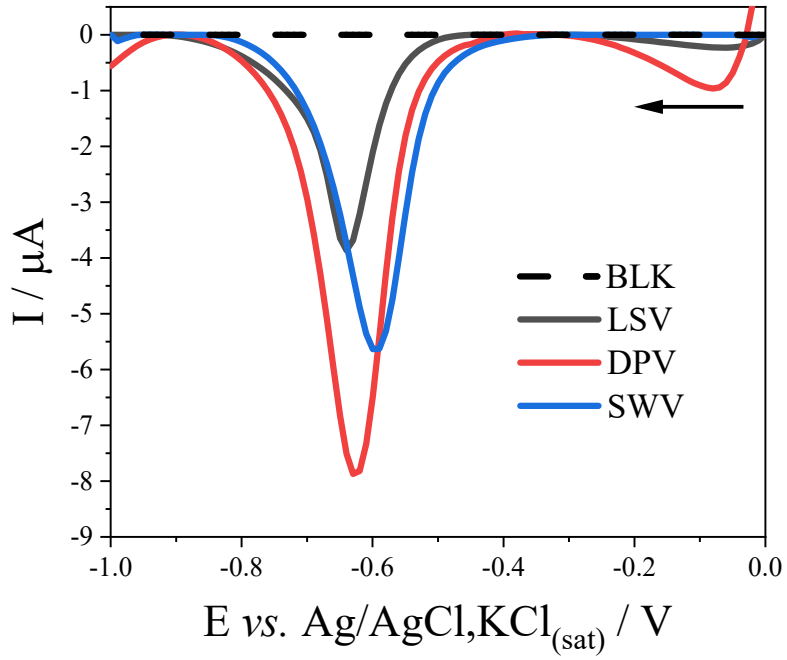
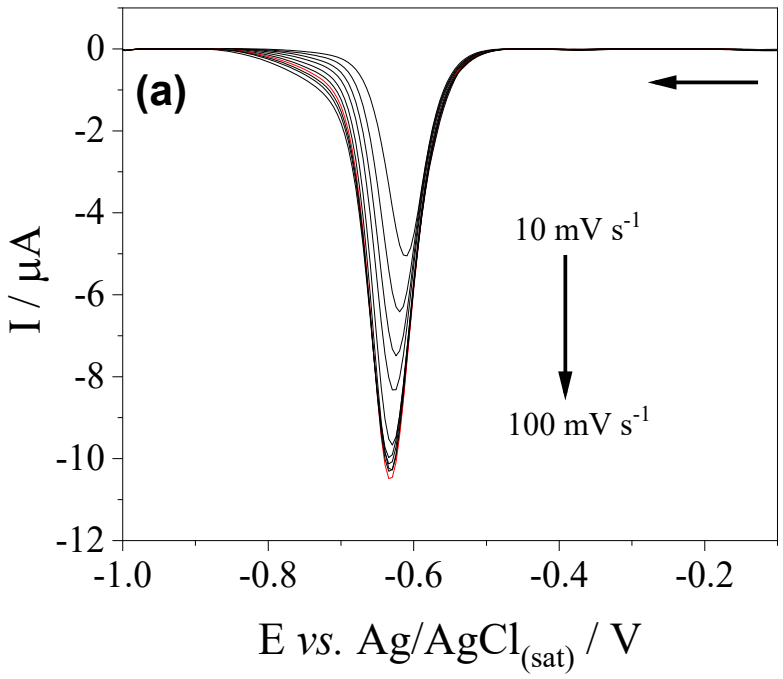
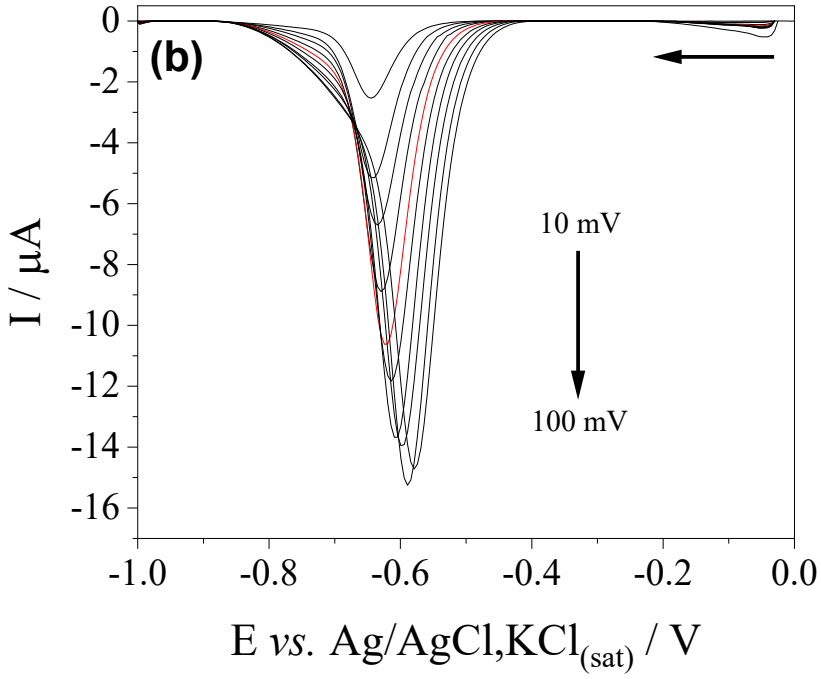
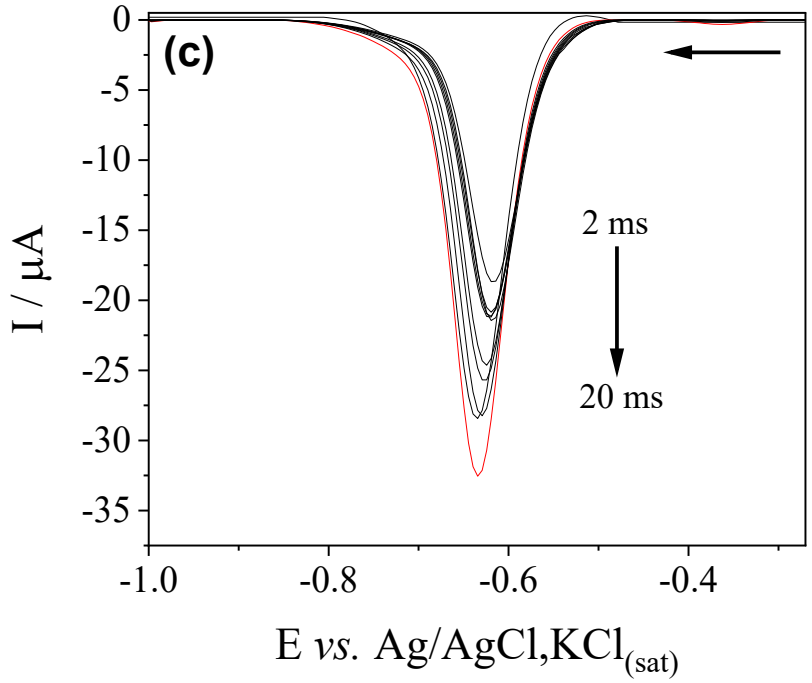
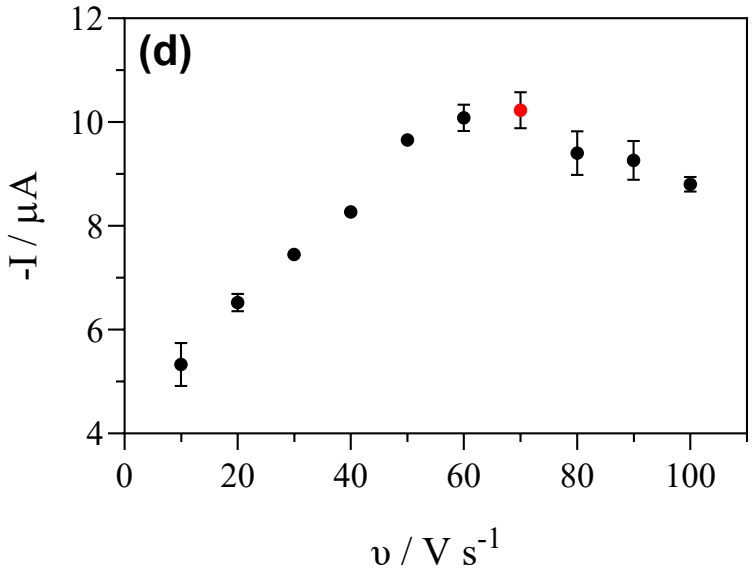


Figure S6. Baseline corrected voltammograms obtained from LSV, DPV and SWV for NMP 25 µmol L^{-1} in PB 0.15 mol L^{-1} (pH 6) with GCE/AP sensor (υ = 50 mV s^{-1}).


(a)
10 mV s-1
100 mV s-1
I / µA
E vs. Ag/AgCl(sat) / V


(b)
10 mV
100 mV
I / µA
E vs. Ag/AgCl,KCl(sat) / V


(c)
0
-5
-10
-15
-20
-25
-30
-35
I / µA
2 ms
20 ms
-1.0
-0.8
-0.6
-0.4
E vs. Ag/AgCl,KCl(sat)


(d)
12
10
8
6
4
-I / µA
0
20
40
60
80
100
υ / V s-1

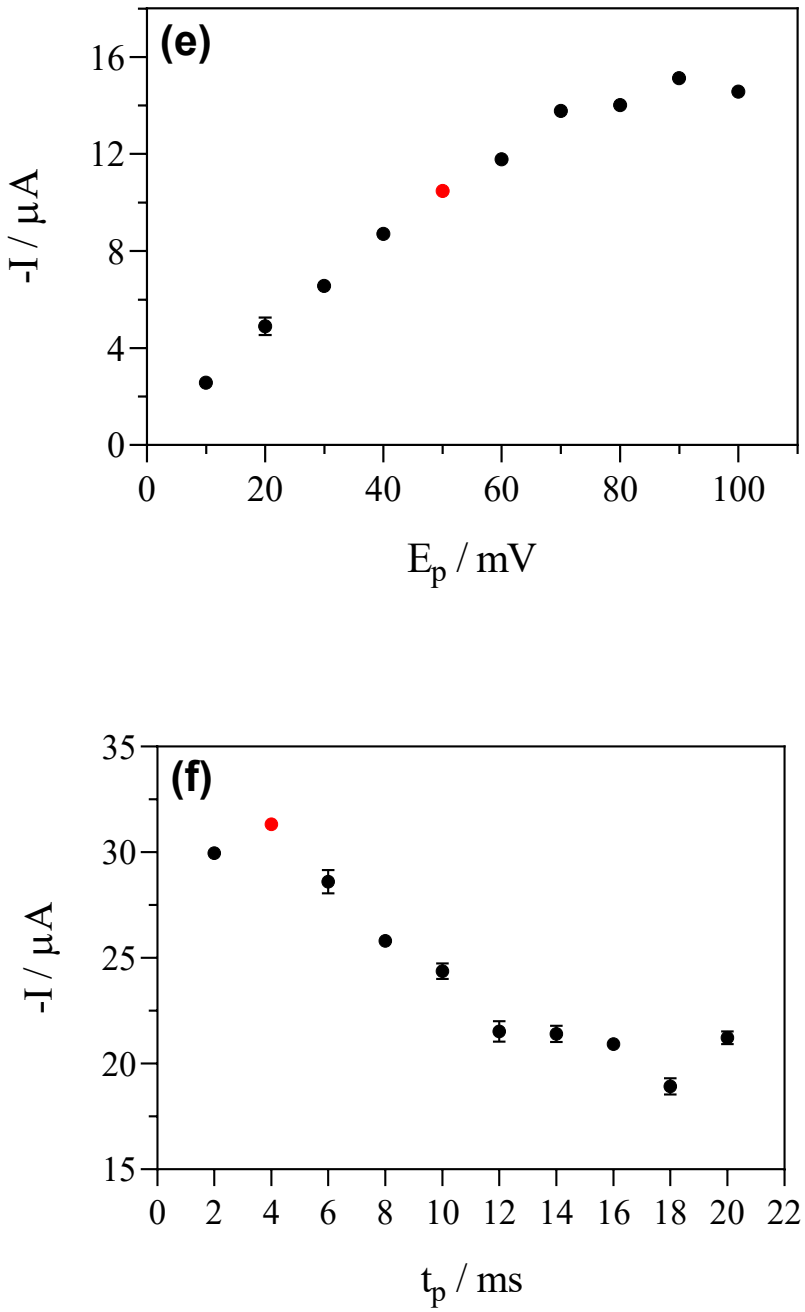
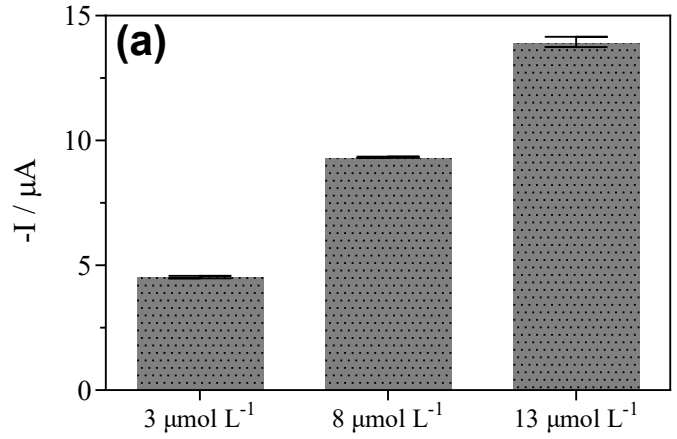
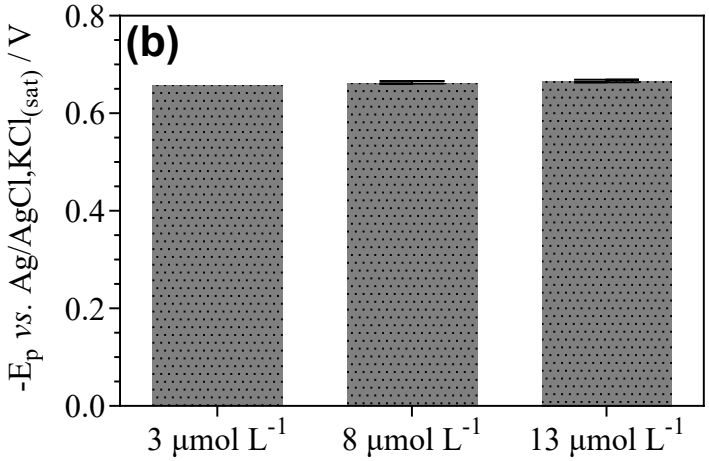
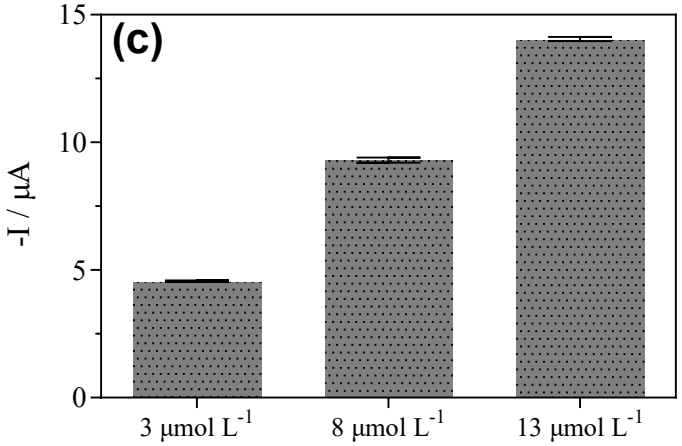


Figure S7. Baseline corrected voltammograms obtained by the optimization of DPV parameters for NMP 40 µmol L^{-1} in PB 0.15 mol L^{-1} (pH 6) with GCE/AP sensor for (a) E_p = 50 mV, t_p = 5 ms and υ between 10 and 100 mV s^{-1}; (b) t_p = 5 ms, υ = 70 mV s^{-1} and E_p between 10 and 100 mV and (c) υ = 70 mV s^{-1}, E_p = 50 mV and t_p between 2 and 20 ms. Plot graphs of (d) −I *vs.* υ (*n* = 3), (e) −I *vs.* E_p (*n* = 3) and (f) −I *vs.* t_p (*n* = 3).


(a)
15
10
5
0
-I / µA
3 µmol L-1
8 µmol L-1
13 µmol L-1


(b)
0.8
0.6
0.4
0.2
0.0
-Ep vs. Ag/AgCl,KCl(sat) / V
3 µmol L-1
8 µmol L-1
13 µmol L-1


(c)
15
10
5
0
-I / µA
3 µmol L-1
8 µmol L-1
13 µmol L-1

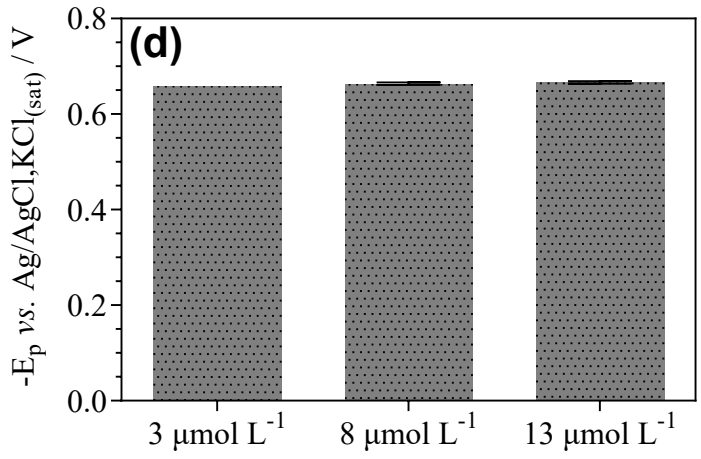
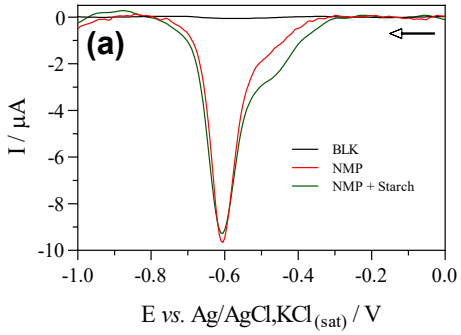
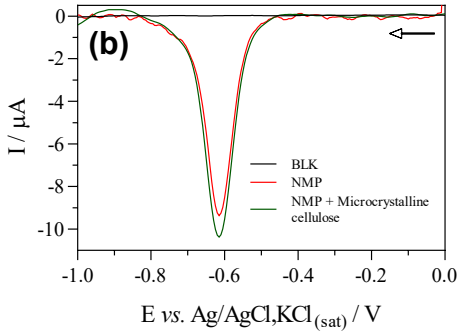
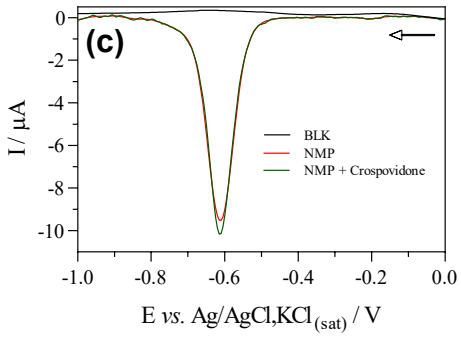
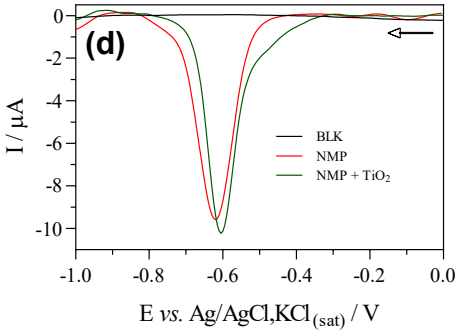


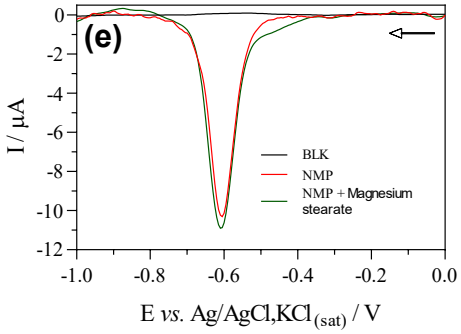
Figure S8. Current and peak potential monitoring for (a,b) intra-day and (c,d) inter-day repeatability study for three different concentrations of NMP, such as 3, 8 and 13 µmol L^{-1} in PB 0.15 mol L^{-1} (pH 6) with GCE/AP sensor for DPV (υ = 70 mV s^{-1}, E_p = 50 mV and t_p = 4 ms); *n* = 7.

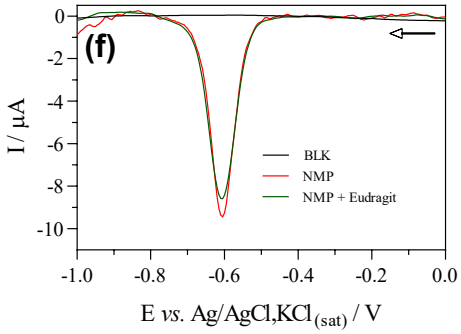

(a)
BLK
NMP
NMP + Starch
I / µA
E vs. Ag/AgCl,KCl(sat) / V

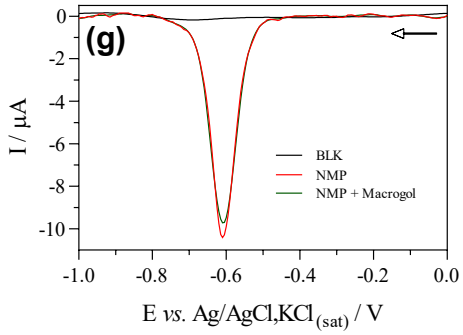

(b)
BLK
NMP
NMP + Microcrystalline cellulose
I / µA
E vs. Ag/AgCl,KCl(sat) / V

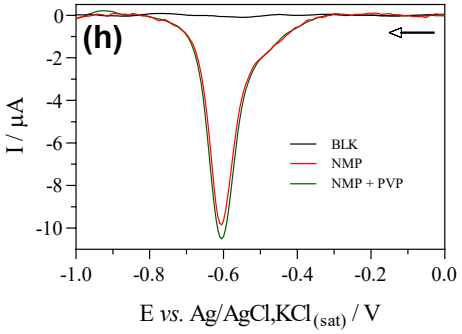

(c)
BLK
NMP
NMP + Crospovidone
I / µA
E vs. Ag/AgCl,KCl(sat) / V

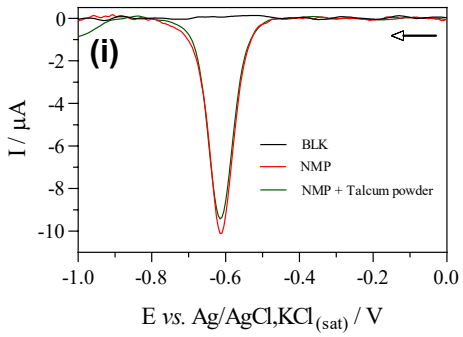

(d)
BLK
NMP
NMP + TiO2
I / µA
E vs. Ag/AgCl,KCl(sat) / V


(e)
BLK
NMP
NMP + Magnesium stearate
I / µA
E vs. Ag/AgCl,KCl(sat) / V


(f)
BLK
NMP
NMP + Eudragit
I / µA
E vs. Ag/AgCl,KCl(sat) / V


(g)
BLK
NMP
NMP + Macrogol
I / µA
E vs. Ag/AgCl,KCl(sat) / V


(h)
BLK
NMP
NMP + PVP
I / µA
E vs. Ag/AgCl,KCl(sat) / V



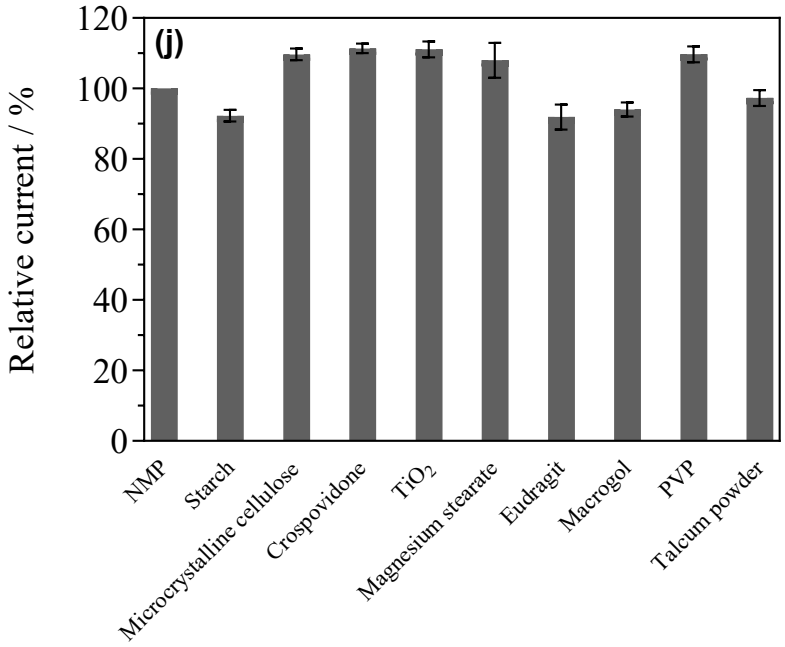


Figure S9. DP normalized voltammograms obtained in PB 0.15 mol L^{-1} (pH 6) with GCE/AP sensor for NMP in the presence of potential interferences, such as (a) starch, (b) microcrystalline cellulose, (c) crospovidone, (d) TiO_2, (e) magnesium stearate, (f) eudragit, (g) macrogol, (h) PVP and (i) talcum powder. (j) The relative current (%) for each potential interferent (n = 3).

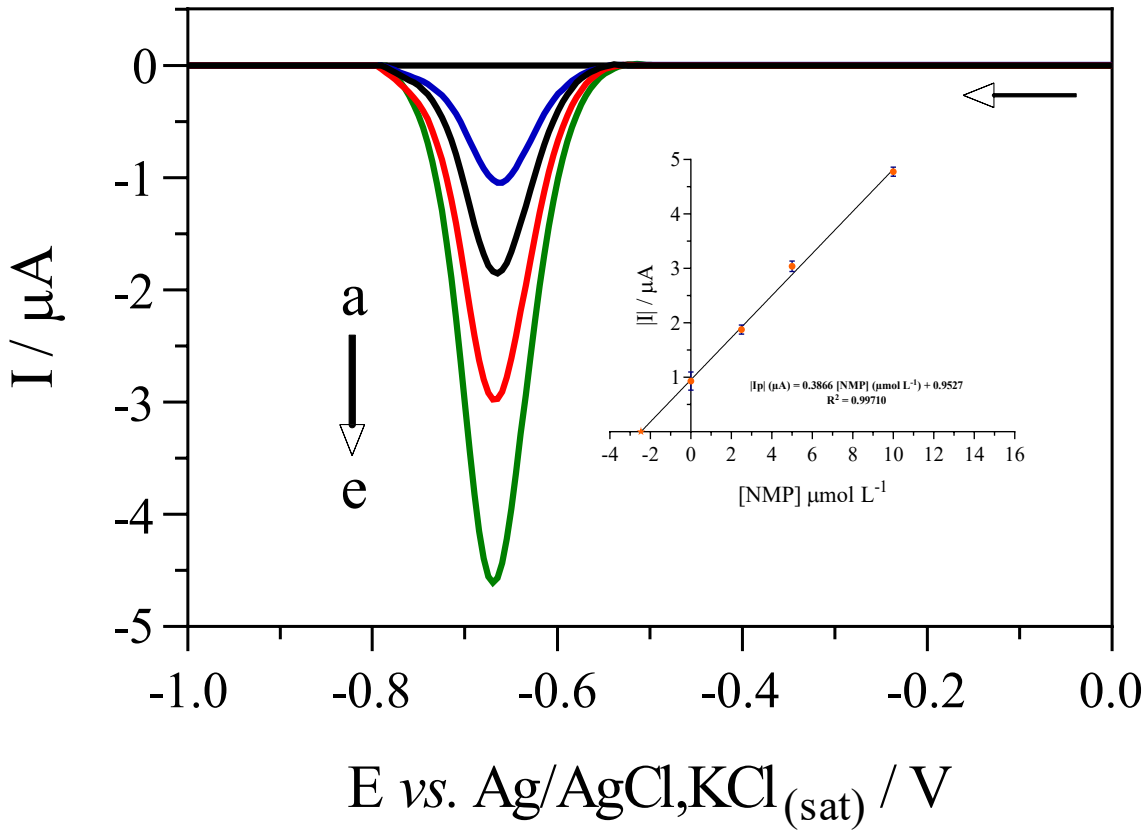
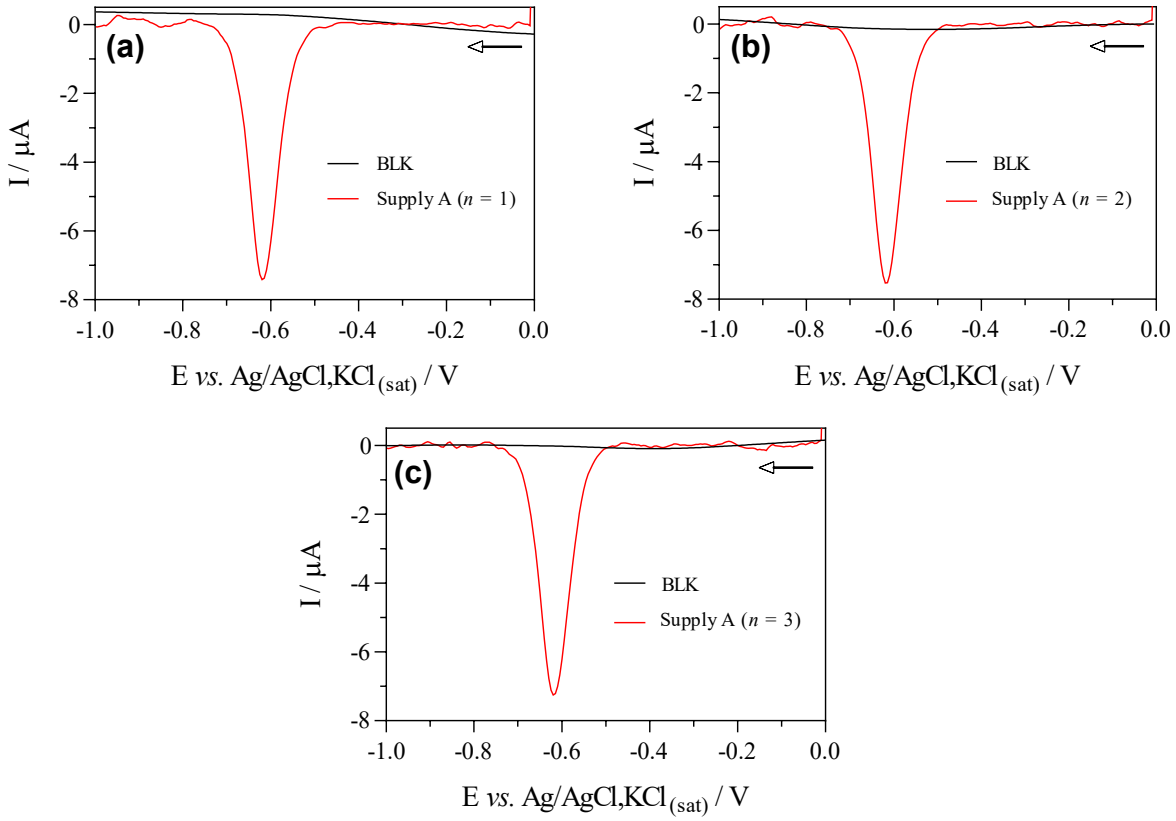


Figure S10. DP voltammograms obtained in 0.15 mol L^{-1} PB (pH 6.0) for NMP quantification in pharmaceutical tablets and the respective standard addition plot for (a) blank, (b) sample, (c) 2.5, (d) 5.0 and (e) 10.0 µmol L^{-1} of NMP (*inset*); n = 3.


(a)
BLK
Supply A (n = 1)
(b)
BLK
Supply A (n = 2)
(c)
BLK
Supply A (n = 3)
I / µA
E vs. Ag/AgCl,KCl(sat) / V

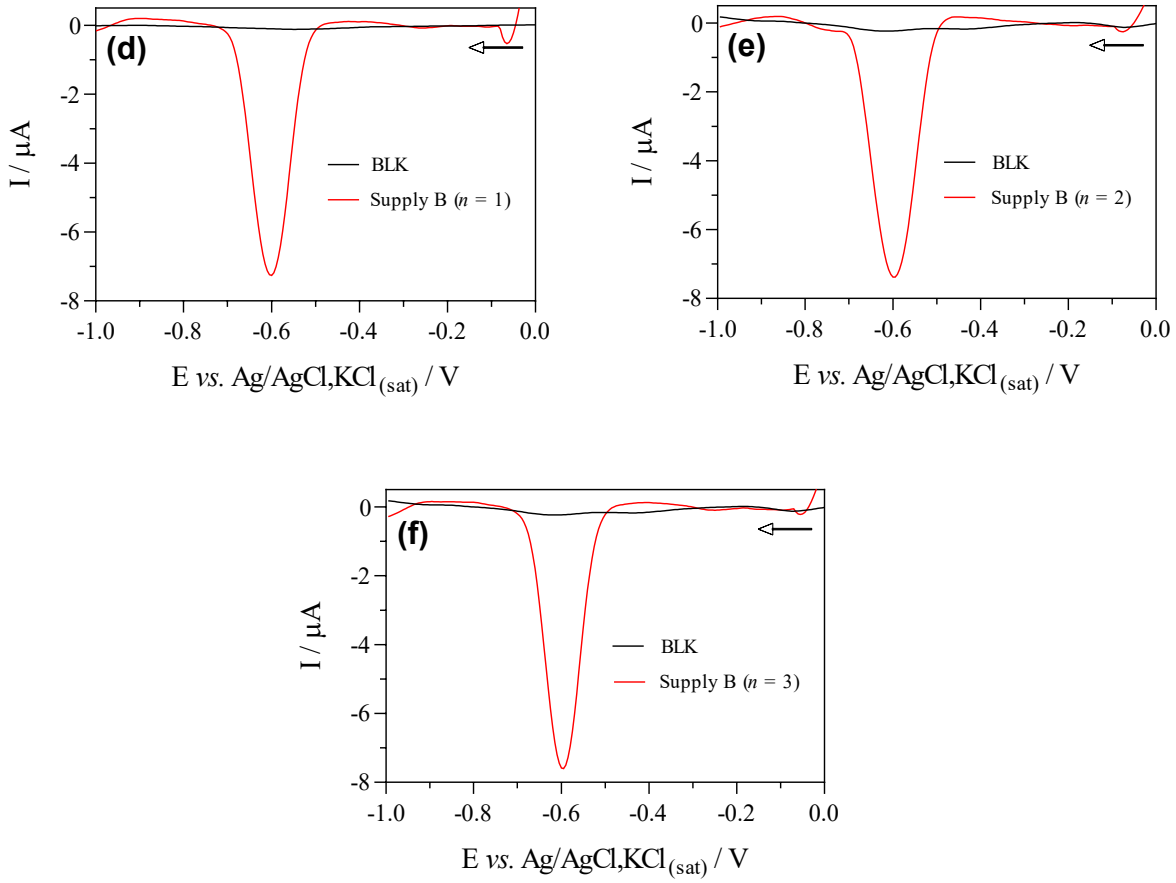

(d)
BLK
Supply B (n = 1)
(e)
BLK
Supply B (n = 2)
(f)
BLK
Supply B (n = 3)
I / µA
E vs. Ag/AgCl,KCl(sat) / V

Figure S11. DP normalized voltammograms obtained in PB 0.15 mol L^{-1} (pH 6) with GCE/AP sensor for NMP in supply A (a-c) and supply B samples (d-f) in triplicate for each one.

Table S1. Fukui index of all atoms of NMP calculated at BP86/Def2-TZVPPD-D3BJ.

Atom	f^-	f^+	f^0	Δf
1(O)	0.0110	0.0057	0.0084	-0.0053
2(O)	0.0115	0.0066	0.0091	-0.0049
3(O)	0.0504	0.0358	0.0431	-0.0146
4(O)	0.0484	0.0365	0.0425	-0.0119
5(O)	0.0358	-0.0022	0.0168	-0.0380
6(O)	0.0399	0.1006	0.0703	0.0607
7(O)	0.0192	0.0943	0.0568	0.0751
8(N)	0.0635	0.0102	0.0369	-0.0533
9(N)	0.0070	0.0574	0.0322	0.0504
10(C)	0.0146	0.0054	0.0100	-0.0092
11(C)	0.0654	0.0178	0.0416	-0.0476
12(C)	0.0626	0.0178	0.0402	-0.0448
13(C)	-0.0003	0.0144	0.0071	0.0147
14(C)	0.0302	0.0320	0.0311	0.0018
15(C)	0.0290	0.0335	0.0312	0.0045
16(C)	0.0166	0.0200	0.0183	0.0034
17(C)	-0.0012	0.0152	0.0070	0.0164
18(C)	0.0175	0.0213	0.0194	0.0038
19(C)	0.0036	0.0458	0.0247	0.0422
20(C)	0.0135	0.0120	0.0127	-0.0015
21(C)	0.0131	0.0124	0.0128	-0.0007
22(C)	0.0107	0.0202	0.0154	0.0095
23(C)	0.0147	0.0291	0.0219	0.0144
24(C)	0.0051	0.0037	0.0044	-0.0014
25(C)	0.0205	0.0414	0.0310	0.0209
26(C)	0.0099	0.0070	0.0084	-0.0029
27(C)	0.0054	0.0030	0.0042	-0.0024

28(C)	0.0051	0.0048	0.0050	-0.0003
29(C)	0.0104	0.0028	0.0066	-0.0076
30(C)	0.0128	0.0031	0.0080	-0.0097
31(H)	0.0292	0.0106	0.0199	-0.0186
32(H)	0.0321	0.0147	0.0234	-0.0174
33(H)	-0.0005	0.0096	0.0046	0.0101
34(H)	0.0064	0.0226	0.0145	0.0162
35(H)	0.0188	0.0183	0.0185	-0.0005
36(H)	0.0171	0.0129	0.0150	-0.0042

Table S2. Fukui index of all atoms of NMP calculated at BP86/Def2-TZVPPD-D3BJ.

Atom	f^-	f^+	f^0	Δf
37(H)	0.0175	0.0145	0.0160	-0.0030
38(H)	0.0177	0.0149	0.0163	-0.0028
39(H)	0.0166	0.0142	0.0154	-0.0024
40(H)	0.0179	0.0177	0.0178	-0.0002
41(H)	0.0141	0.0235	0.0188	0.0094
42(H)	0.0101	0.0102	0.0102	0.0001
43(H)	0.0157	0.0265	0.0211	0.0108
44(H)	0.0140	0.0109	0.0124	-0.0031
45(H)	0.0134	0.0112	0.0123	-0.0022
46(H)	0.0024	-0.0023	0.0000	-0.0047
47(H)	0.0152	0.0143	0.0148	-0.0009
48(H)	0.0020	0.0005	0.0013	-0.0015
49(H)	0.0052	0.0068	0.0060	0.0016
50(H)	0.0138	0.0128	0.0133	-0.0010
51(H)	0.0025	0.0006	0.0015	-0.0019
52(H)	0.0077	-0.0015	0.0031	-0.0092
53(H)	0.0231	0.0138	0.0185	-0.0093
54(H)	0.0102	-0.0031	0.0035	-0.0133
55(H)	0.0202	0.0133	0.0168	-0.0069
56(H)	0.0116	0.0041	0.0078	-0.0075

SI – xyz data.

Molecule: **NMP**
O -3.726814000 -0.369948000 -0.447073000
O -0.503887000 -3.636910000 -1.383886000
O -4.121409000 0.521380000 1.614689000
O 1.107655000 -4.346175000 0.065468000
O 0.466431000 -2.881961000 -4.076852000
O 2.156437000 3.101324000 -1.187350000
O 1.821944000 2.211543000 0.783447000
N -0.599690000 -1.577294000 2.837245000
N 1.631251000 2.271876000 -0.436831000
C -1.446109000 -1.624292000 0.140807000
C -2.220902000 -0.914913000 1.243024000
C -0.423185000 -2.600243000 0.709116000
C -0.762680000 -0.602329000 -0.766063000
C -1.744823000 -0.865364000 2.520917000
C 0.006716000 -2.497063000 2.001880000
C -3.438736000 -0.181126000 0.876753000
C 0.107429000 0.339870000 -0.212459000
C 0.160077000 -3.607233000 -0.179674000
C -0.998085000 -0.577612000 -2.145805000
C -2.347105000 -0.108935000 3.667726000
C 1.087892000 -3.311258000 2.648897000
C 0.712429000 1.282626000 -1.039671000
C -0.389879000 0.380928000 -2.960733000
C -4.808820000 0.433561000 -1.007889000
C 0.475875000 1.326520000 -2.414467000
C 0.049601000 -4.522393000 -2.380813000
C -4.257228000 1.805179000 -1.375091000

C -5.333411000 -0.346623000 -2.201237000

C 1.099632000 -3.820206000 -3.214708000

C 1.413342000 -2.078062000 -4.764059000

H -2.152978000 -2.180465000 -0.485619000

H -0.279966000 -1.539862000 3.798504000

H 0.317811000 0.360925000 0.854847000

H -1.661727000 -1.322155000 -2.581654000

H -3.362354000 -0.464035000 3.881839000

H -2.444790000 0.955652000 3.426644000

H -1.731814000 -0.219805000 4.571570000

H 1.198854000 -3.038151000 3.707528000

H 2.046939000 -3.164294000 2.138284000

H 0.869311000 -4.383156000 2.577444000

H -0.592444000 0.389815000 -4.030985000

H -5.581125000 0.534129000 -0.232584000

H 0.964644000 2.086128000 -3.019558000

H -0.799765000 -4.820067000 -3.007526000

H 0.487334000 -5.399942000 -1.888563000

H -3.436240000 1.704531000 -2.098481000

H -5.046378000 2.422526000 -1.825774000

H -3.883955000 2.323111000 -0.483566000

H -5.691616000 -1.337948000 -1.895844000

H -6.167948000 0.195253000 -2.665906000

H -4.546188000 -0.477962000 -2.956659000

H 1.824861000 -3.313483000 -2.551524000

H 1.656749000 -4.572234000 -3.808633000

H 2.003815000 -1.464077000 -4.060348000

H 2.106687000 -2.694265000 -5.365653000

H 0.853045000 -1.416201000 -5.434272000

Table S3. Optimization of DPV parameters for the determination of NMP.

Parameter	**Mode/Interval**	**Selected**
Technique	LSV, DPV, SWV	DPV
Scan rate / υ	10 – 100 mV s^{-1}	70 mV s^{-1}
Pulse potential / E_p	10 – 100 mV	50 mV
Pulse time / t_p	2 – 20 ms	4 ms