Supplementary Information

Stable and reproducible nano-electrospray ionization of aqueous

solutions and untreated biological samples using ion current limitation

combined with polarity reversing

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Figure S1. The effect of LTQ ion injection time on the total ion signal intensity for PR-R-nESI-MS of cytochrome c (120 μ g/mL) in 0.1% formic acid in the *m/z* range 50-2000.



Figure S2. nESI current vs. applied voltage during the analysis of cytochrome c (120 μ g/mL) in 0.1 % formic acid aqueous solution both in positive (a& b) and (c&d) negative ion mode without and with the use of 10 G Ω resistor in series with high voltage power supply.



Figure S3. Positive and negative ion mode mass spectra of native proteins by PR-RnESI-MS using a pulled glass capillary as nESI emitter: cytochrome c (120 μ g/mL) (a, b), and myoglobin (167 μ g/mL) (c, d), both& in 100 mM NH₄Ac aqueous solution. A 1 μ L sample solution has been used for the analysis of nanospray stability. The experimental parameters (high voltage and the distance of two electrodes) for nanospray has been maintained as discussed in the experimental section.