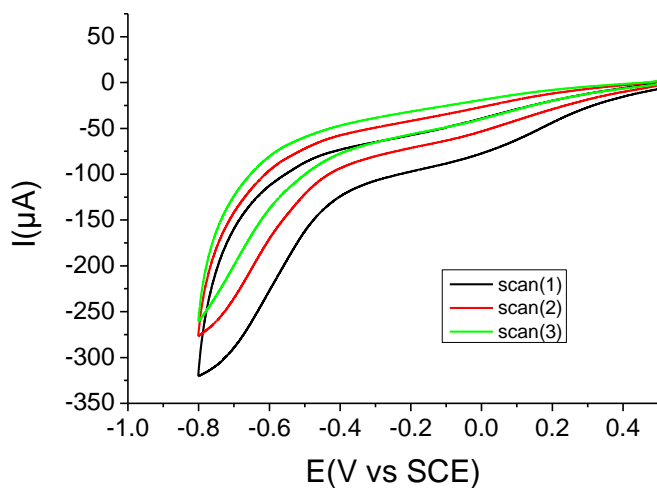


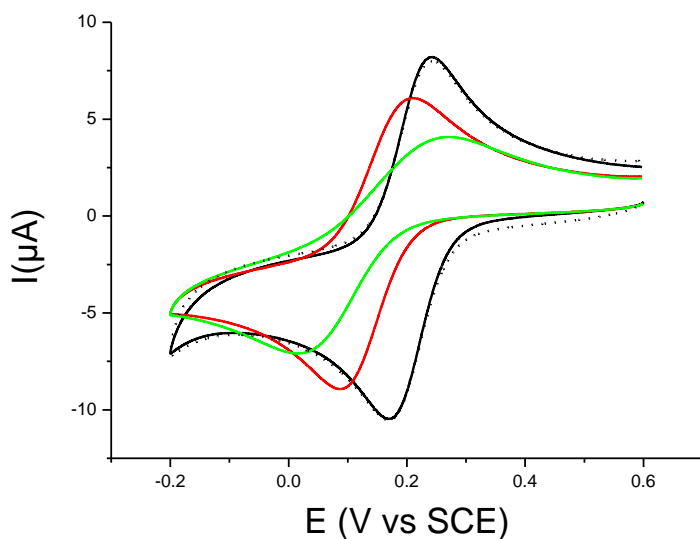
**Reductive electrografting of in situ produced diazopyridinium cations: tailoring the interface between carbon electrodes and electroactive bacterial films.**

Hassiba Smida, Estelle Lebègue, Jean-François Bergamini, Frédéric Barrière, Corinne Lagrost

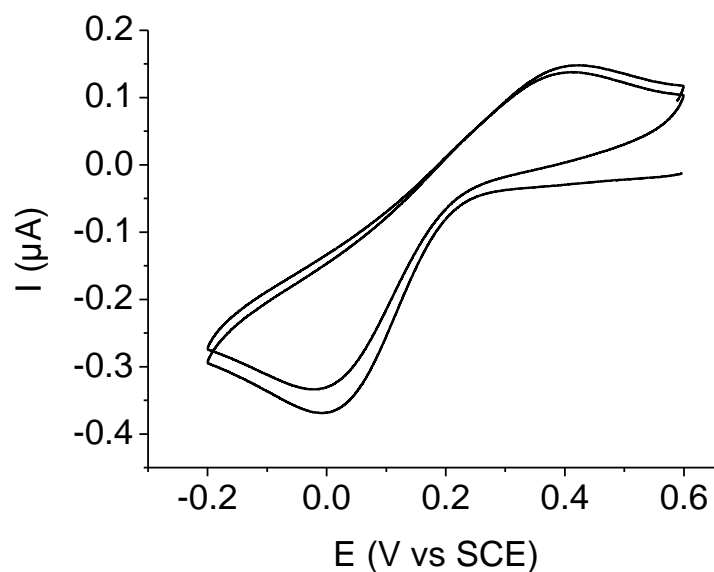
Université de Rennes 1, CNRS UMR n° 6226, Sciences Chimiques de Rennes, Equipe MaCSE,  
France



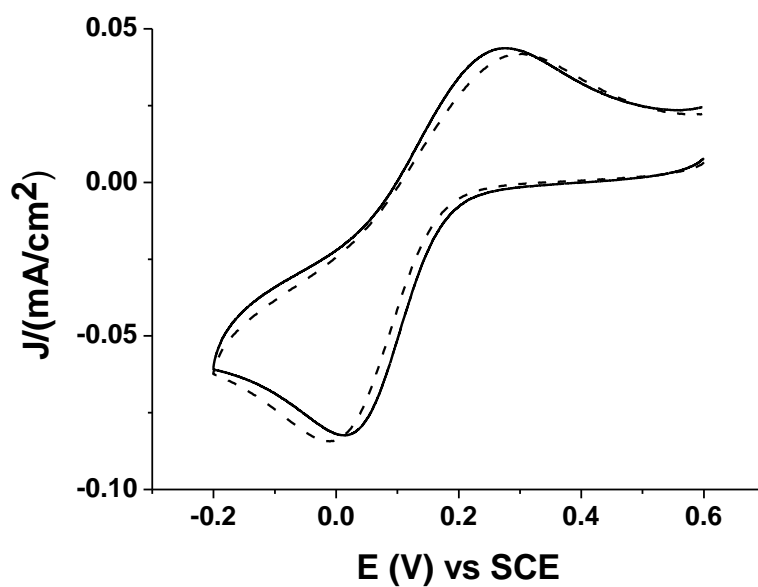
**Figure S1.** Cyclic voltammograms at a glassy carbon electrode for the reduction of 4-diazopyridinium cations in situ produced from 20 mM 4-aminopyridine in aqueous 0.5 M HCl in the presence of 40 mM NaNO<sub>2</sub>. Scan rate is 0.05 V s<sup>-1</sup>.



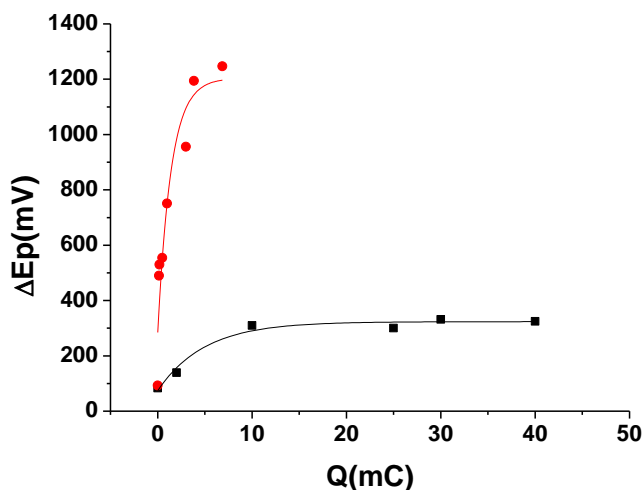
**Figure S2.** Cyclic voltammetry of 1 mM ferricyanide in aqueous 0.1 M KCl at a bare glassy carbon electrode (black dotted line), at a modified electrode as described in figure S1 at different pH. pH = 2 (black solid line), pH = 7.5 (red solid line), pH = 9 (green solid line). Scan rate is 0.05 V s<sup>-1</sup>.



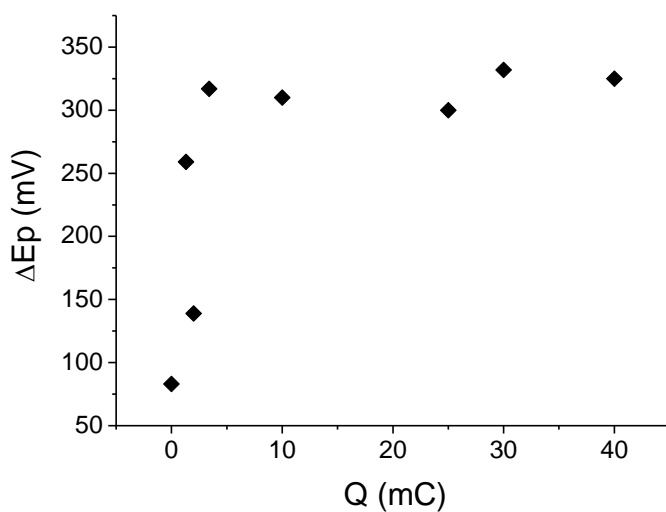
**Figure S3:** Cyclic voltammograms of 1 mM ferricyanide in aqueous 0.1 M KCl solution at pH = 9 for a gold electrode modified from electrografting of 4-diazopyridinium cations



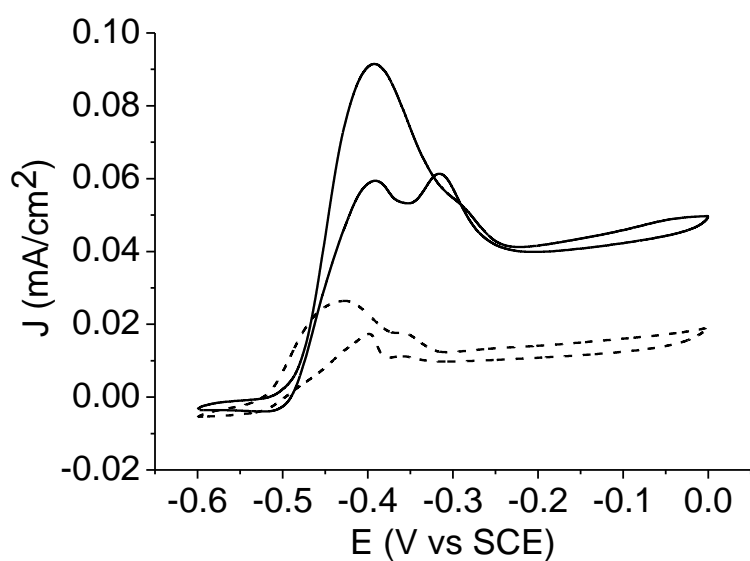
**Figure S4.** Cyclic voltammograms of the reduction of 1 mM ferricyanide (in 0.1 M KCl and 10 mM phosphate buffer adjusted to pH=9 with NaOH) onto glassy carbon electrode modified electrografting of pyridine-4-diazonium cations with a charge consumption equal to  $Q = 1.3 \text{ mC}$  (solid line) and  $Q = 3.4 \text{ mC}$  (dashed line). Scan rate is 0.05  $\text{V s}^{-1}$



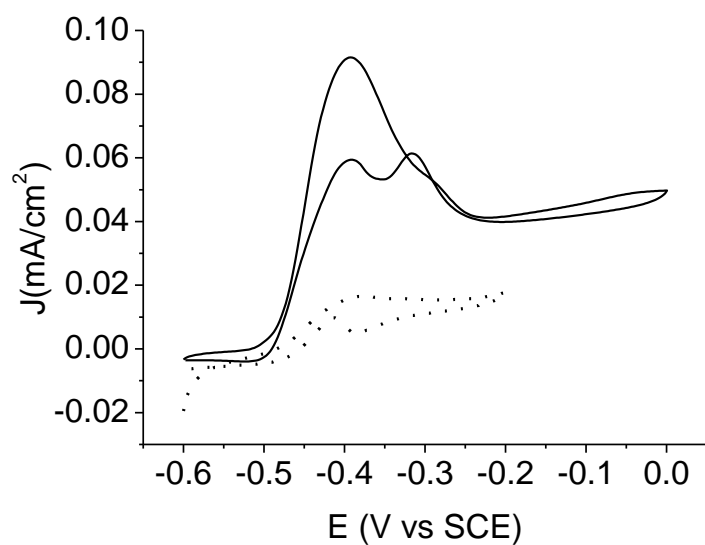
**Figure S5.** Variation of  $\Delta E_p$  (peak to peak separation) for the ferricyanide/ferrocyanide electrochemical response at glassy carbon modified through electrografting of diazopyridinium cations (black curve) or of benzenediazonium cations (red curve) as a function of the charge consumed ( $Q$ ) during the electrografting process. Solid lines are only for guiding eye purpose. Diazopyridinium and benzenediazonium cations were *in situ* produced in acidic 0.5 M HCl in the presence of 2 eq.  $\text{NaNO}_2$  from 4-aminopyridine and aniline, respectively.



**Figure S6.** Variation of  $\Delta E_p$  (peak to peak separation) for the ferricyanide/ferrocyanide electrochemical response at glassy carbon modified through electrografting of 4-diazopyridinium cations as a function of the charge consumed ( $Q$ ) during the electrografting process.



**Figure S7.** Cyclic voltammograms under acetate saturation conditions of biofilms after 2 days of development on a bare graphite electrode in the absence (dashed line) and in the presence of 0.1 mM of pyridine in the anolyte (solid line).



**Figure S8.** Cyclic voltammograms under acetate saturation conditions of biofilms on a bare graphite electrode in the presence of 0.1 mM of pyridine in the anolyte after 2 days of development (solid line) and after a week (dashed line).