## **Supplementary Data:**

## **Electrochemical Studies.**

Electrochemical impedance technique has been employed to investigate the charge transfer processes occurring at electrode/solution interfaces. Fig. 1a reveals the charge transfer resistance (Nyquist diameter "R<sub>CT</sub>") of bare gold (i), PNA/Au bioelectrode (ii) and (iii) DNA hybridized PNA/Au bioelectrodes, respectively. It can be seen that the  $R_{CT}$  value of PNA/Au bioelectrode obtained as 115  $\Omega$  (curve ii) which is smaller than that for the bare gold ( $R_{CT}$  309  $\Omega$ , curve i), indicating the immobilization of PNA molecules to the gold surface. This decrease in the value of R<sub>CT</sub> can be attributed to the presence of  $\text{FeCN}_6^{3-/4-}$  in the solution. The potential generated at the open circuit and the pH of the buffer solution might be causing the polarization of NH group in PNA backbone resulting in the positive charge on the surface (1,2). The polarization on surface attracts the negative charge of  $FeCN_6^{3-/4-}$  resulting in smaller charge transfer resistance from solution to electrode surface.<sup>24</sup> The R<sub>CT</sub> value for the DNA hybridized PNA/Au bioelectrode increases up to 187  $\Omega$  (curve iii). The observed increase in the value of R<sub>CT</sub> can be attributed to the hindrance caused by the presence of negative charge, originating from the backbone of DNA after hybridization on the surface of electrode. The presence of this negative charge on electrode causes the repulsion between the similarly charged redox couple of system increasing the charge transfer processes occurring at the electrode/solution interface(3). Therefore; this increase in R<sub>CT</sub> value on interaction of PNA with DNA confirms the DNA hybridization.

Fig. 2b shows the cyclic voltamogrammes of blank gold, PNA/Au bioelectrode and DNA hybridized PNA/Au bioelectrode in the range of -0.7 to 0.8 V. The oxidation current of the bare gold electrode (curve i) is 164.6  $\mu$ A which increases after PNA immobilization (curve (ii), 1047  $\mu$ A) indicating the formation of PNA SAM onto gold surface. The increase in the value of current can be attributed to the presence of NH group in the backbone of the PNA, which on polarization under experimental conditions generates the positive charge and attracts the negative charge of FeCN<sub>6</sub><sup>3-/4-</sup> in the solution facilitating the reaction of redox probe. In curve (iii, Fig. 2b) (I = 709  $\mu$ A) the oxidation current decreases when PNA/Au bioelectrode hybridizes to DNA confirming the reaction as hybridization brings the negative charge of DNA backbone on the surface of electrode resulting in repulsion in charges on the surface and of the redox probe. The results of the cyclic voltammetric studies are in agreement with the impedance studies.





Fig. 1: (a) Impedance Nyquist plot and (b) Cyclic voltammograms of (i) Bare gold (Au) electrode, (ii) PNA/Au bioelectrode and (iii) DNA hybridized PNA/Au bioelectrode in 50 mM, pH 7.0, 0.9% NaCl) containing 5 mM  $\text{Fe}(\text{CN})_6^{3-/4-}$ .

## **References:**

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