

## Electronic Supplementary Information

### **K<sub>4</sub>[Fe(CN)<sub>6</sub>] immobilized anion sensitive protonated amine functionalized polysilsesquioxane films for ultra-low electrochemical detection of dsDNA**

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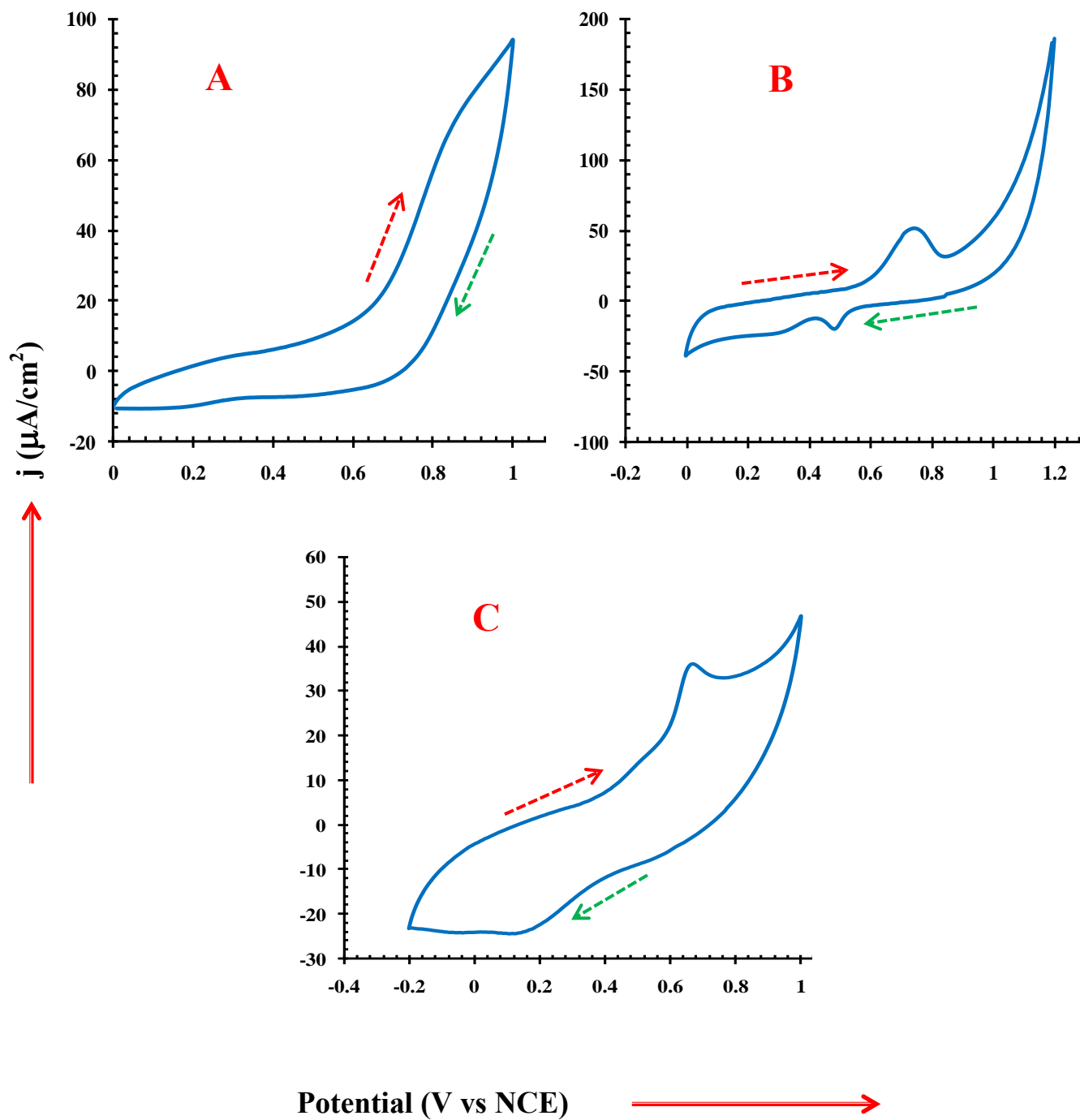
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**Table S1.** Electrochemical parameters calculated for different anions.

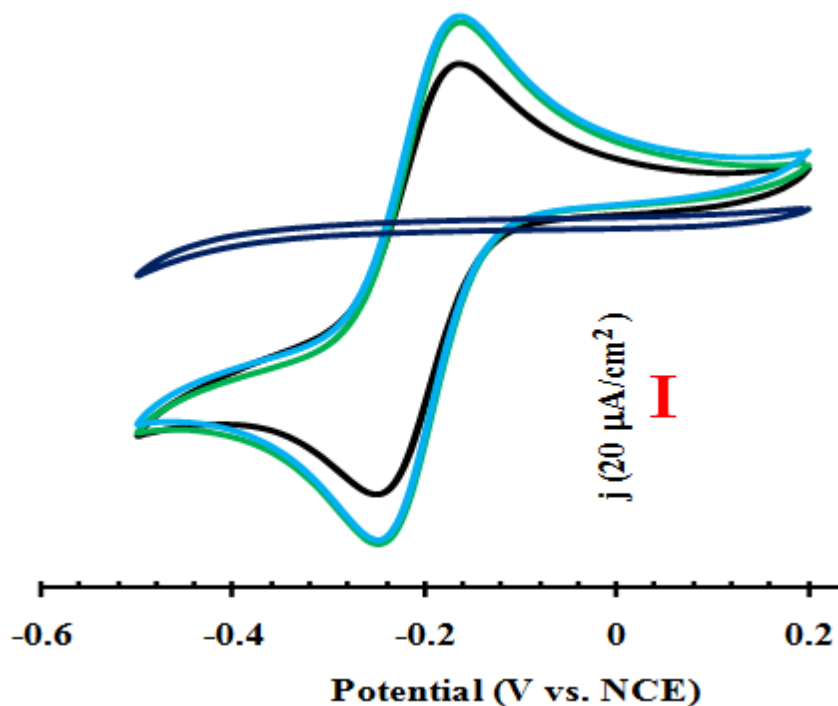
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**Table S3.** Analytical methods for DNA determination

**Scheme S1.** Mechanism of charge transport in  $[\text{Fe}(\text{CN})_6]^{4-}$  immobilized PSQs modified GC surface



**Fig. S1.** Cyclic voltammeteric response of different anionic redox couple immobilized GC/PSQs electrode in 100 mM  $\text{KNO}_3$  solution: A)  $[\text{Ru}(\text{CN})_6]^{3-}$  B),  $\text{AuCl}_4^-$  and C)  $\text{I}^-$

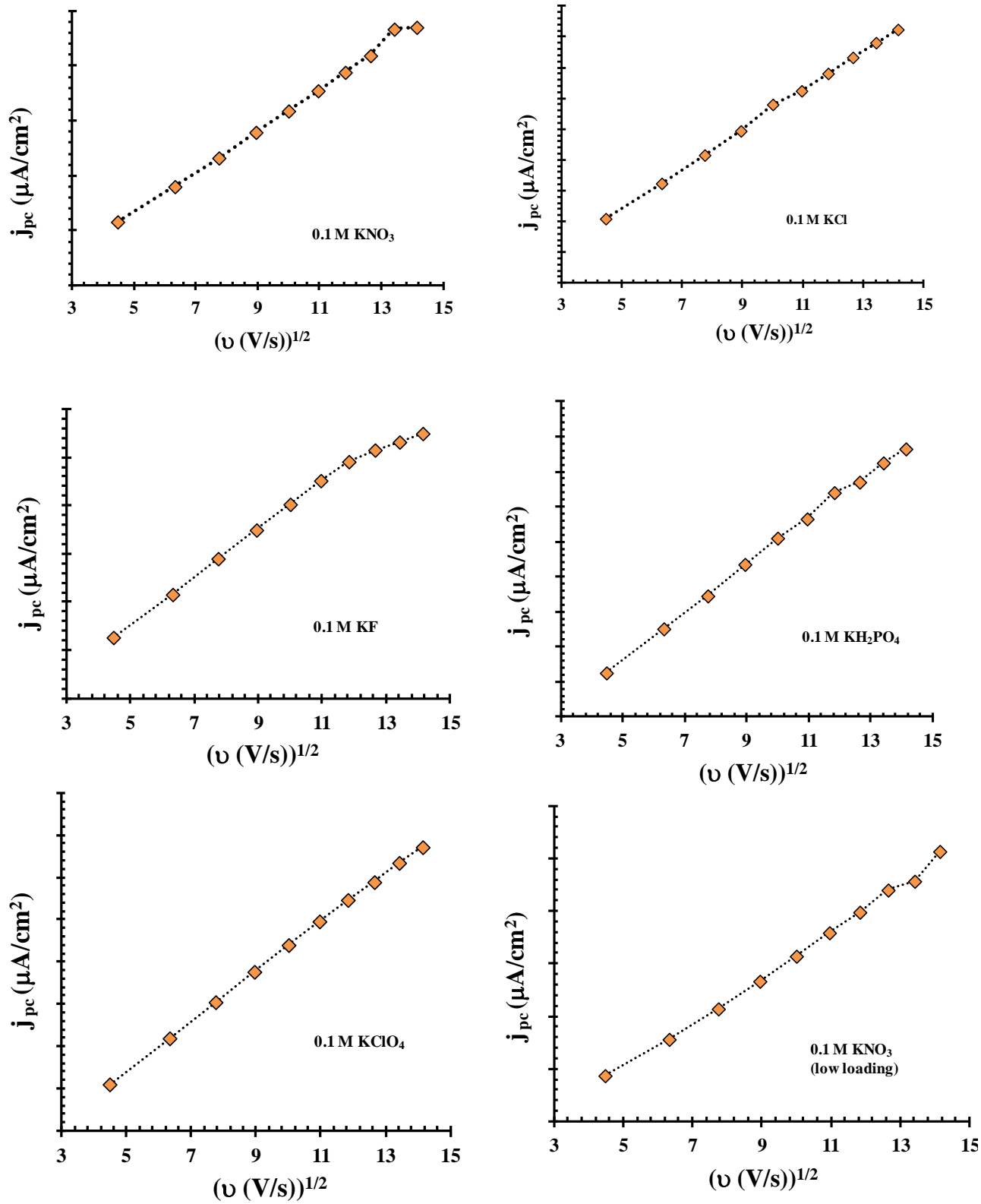


**Fig. S2.** Electrochemical response of  $[\text{Ru}(\text{NH}_3)_6]^{2+/3+}$  on GC surface in 0.1 M  $\text{KNO}_3$  (black), on GC/PSQs electrode in 0.1 M  $\text{KNO}_3$  (1 scan(cyan), 25 scan (green)) and GC/PSQs electrode response in 0.1 M  $\text{KNO}_3$  after electrochemical cycling (blue color).

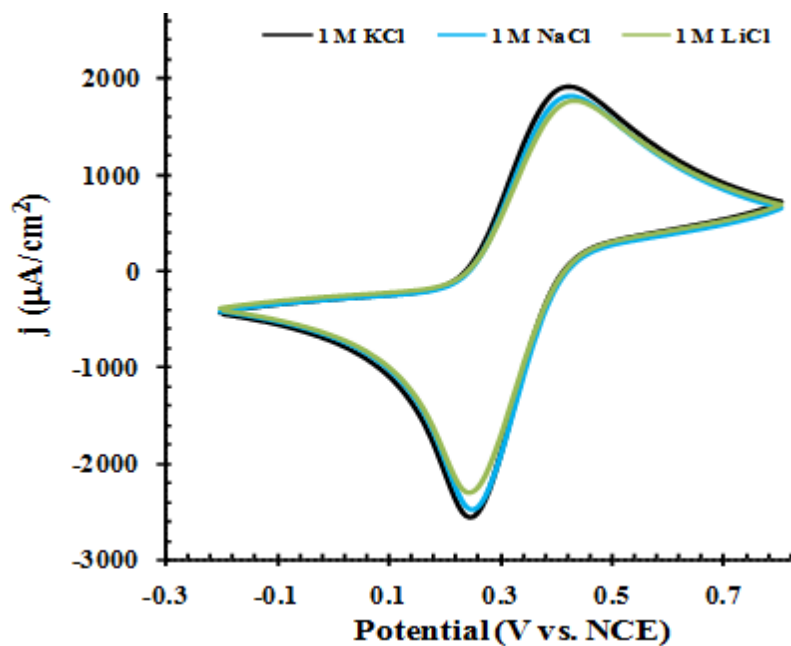
Calculation of surface coverage ( $\Gamma$ ) of the redox indicator was calculated using

$$\Gamma = \frac{Q}{nFA} \quad (1)$$

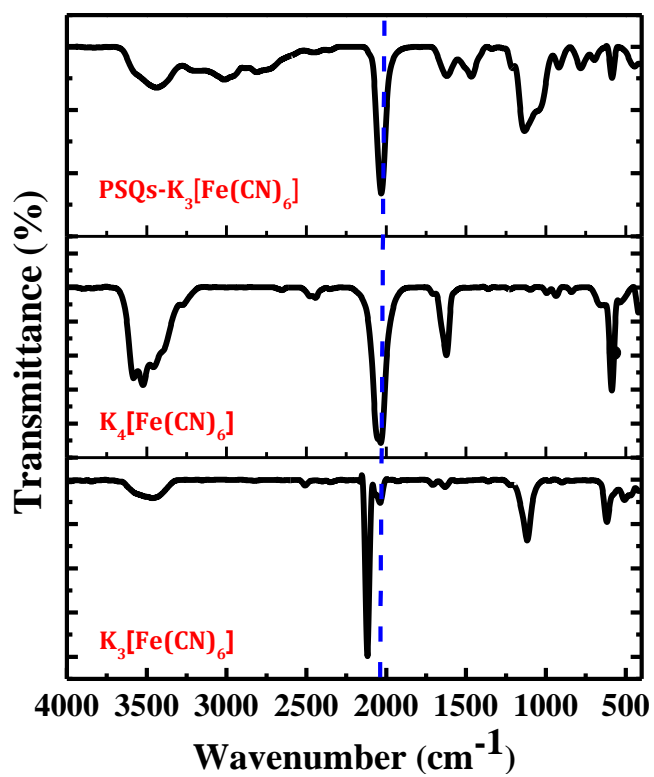
Where 'Q' is the columbic charge in (C) and n,F, A are number of electrons involved, faraday constant and area of the electrode used respectively.



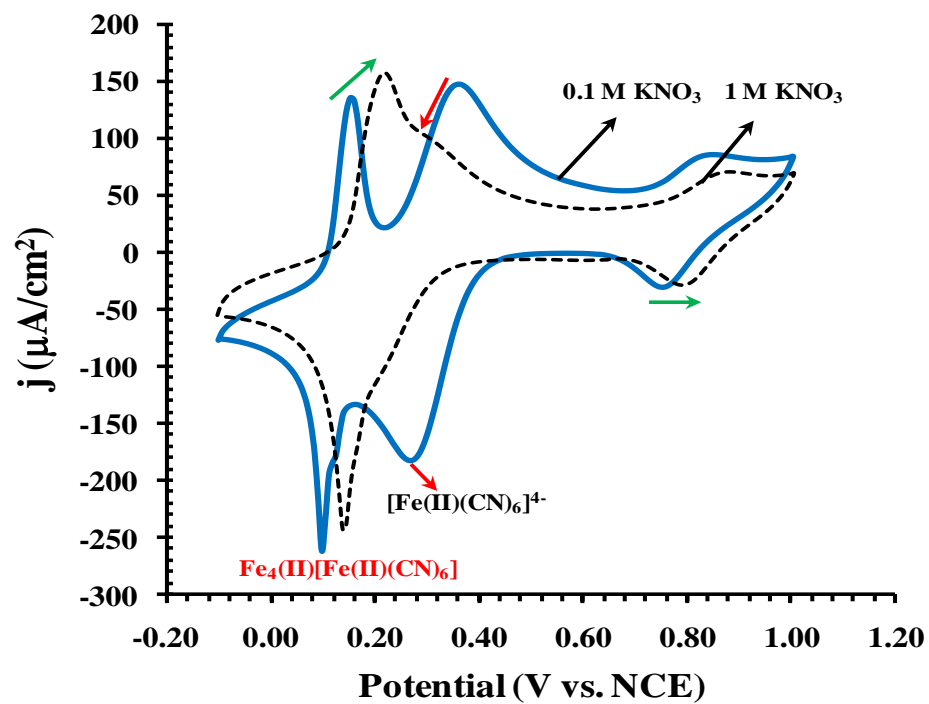
**Fig. S3.** A plot of peak current vs square root of scan rate for different anions at pH=5.



**Fig. S4.** Effect of cation on cyclic voltammetry response of  $[\text{Fe}(\text{CN})_6]^{4-}$  immobilized GC/PSQs electrode.



**Fig. S5.** FT-IR spectra of  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_6]^{3-}$  incorporated PSQs.



**Fig. S6.** Cyclic voltammetry response of partially converted PB containing ferri/ferro redox couple incorporated in GC/PSQs electrode against different concentration of  $\text{KNO}_3$  (0.1M to 1.0 M).

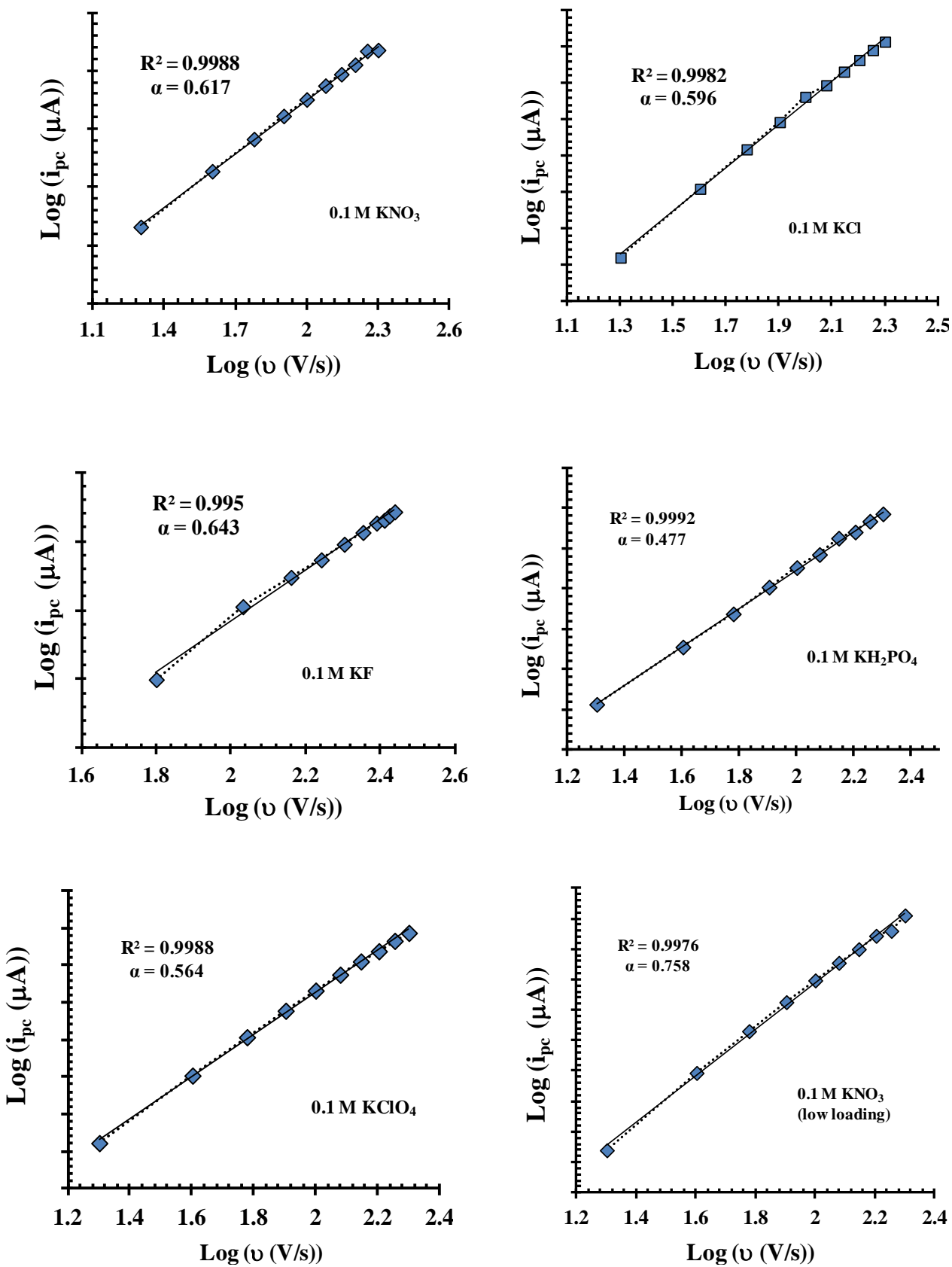
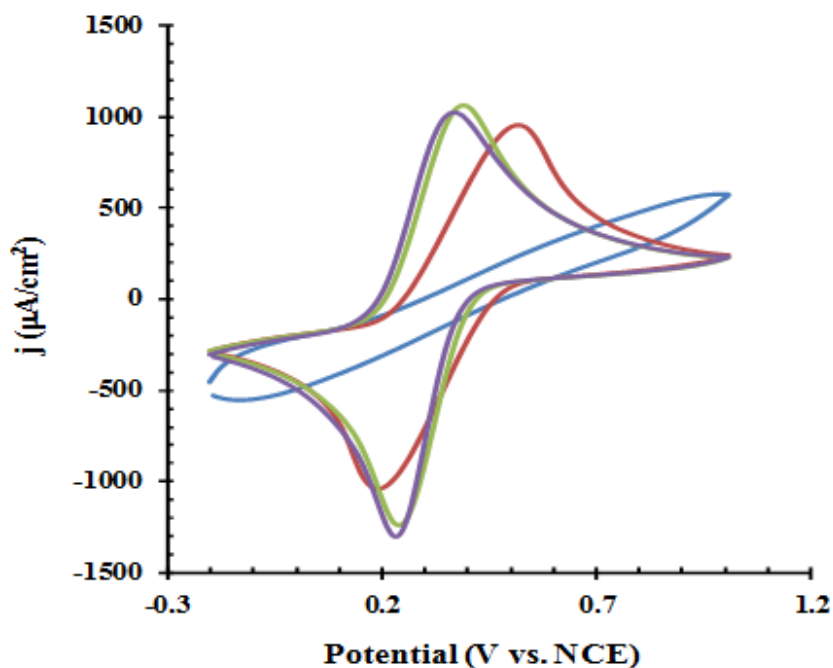
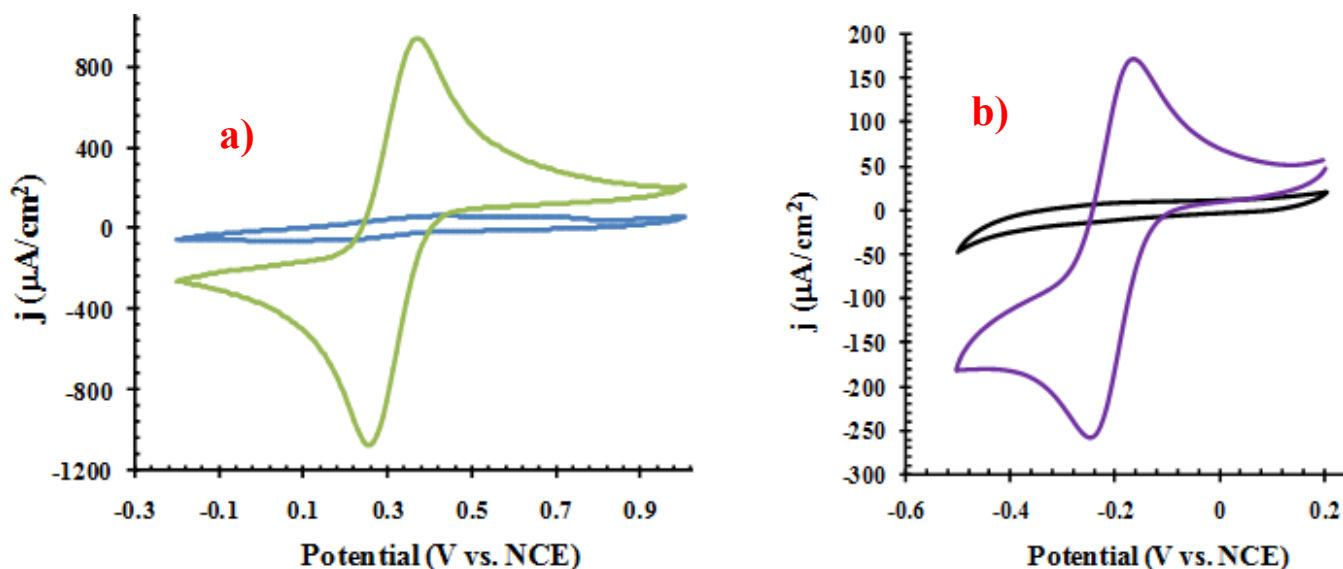


Fig. S7. Log plot of current vs scan rate for different anions at pH=5.

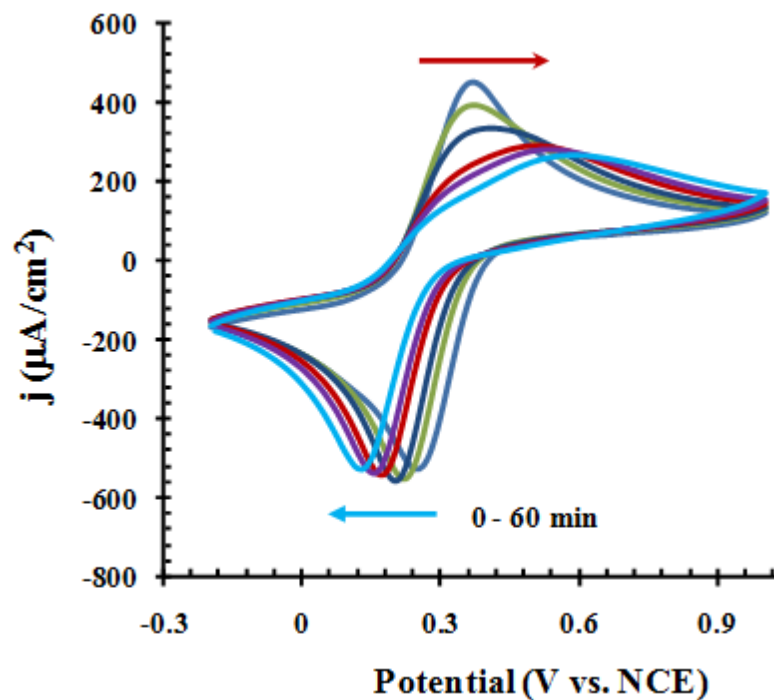




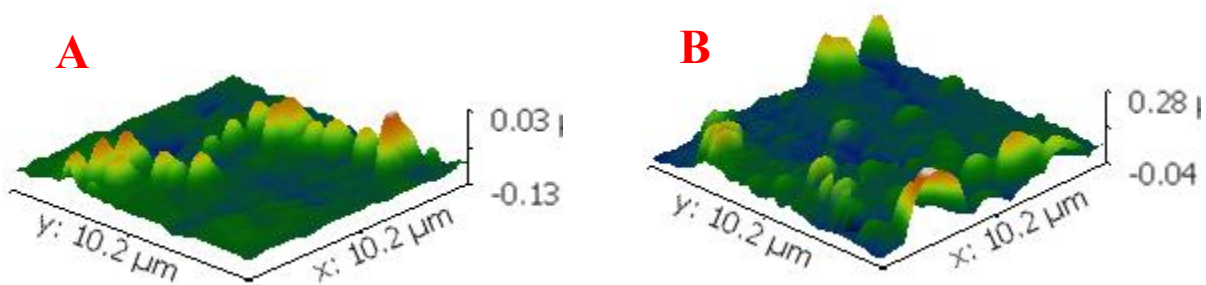
**Fig. S8.** Electrochemical response of  $[\text{Fe}(\text{CN})_6]^{4-}$  immobilized GC/PSQs in different concentration of KCl, 1 mM (blue), 10 mM (red), 30 mM (green) and 50 mM (violet). [Redox free solution]



**Fig. S9.** CV response of GC/ PSQs in 0.1 M  $\text{KNO}_3$  after dipping in 1 mM dsDNA (60 min) a) blue line after electrochemical cycling in ferricyanide (50 cycle) and green line is  $[\text{Fe}(\text{CN})_6]^{3-/4-}$  response on GC surface, b) black line is after electrochemical cycling in  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  and violet line is  $[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$  response on GC surface.



**Fig. S10.** CV response of  $[\text{Fe}(\text{CN})_6]^{4-}$  incorporated GC/PSQs film after dipping in 1 mM dsDNA (0 min, 5 min, 10 min, 20 min, 30 min and 60 min) in 0.1 M  $\text{KNO}_3$  solution



**Fig. S11.** AFM images of before (A) and after dsDNA (B) adsorbed  $[\text{Fe}(\text{CN})_6]^{4-}$  incorporated GC/PSQs electrode.

**Table S1.** Electrochemical parameters calculated for different anions.

Anions	$E^0$	$\Delta E_p$ (V)	$\alpha$
KNO <sub>3</sub>	0.30	0.097	0.61
KCl	0.32	0.097	0.59
KF	0.27	0.095	0.64
KClO <sub>4</sub>	0.31	0.132	0.56
KH <sub>2</sub> PO <sub>4</sub>	0.25	0.092	0.47

**Table S2.** Surface coverage ( $\theta$ ) and exchange current density ( $j_0$ ) values derived from impedance results.

Equilibrium exchange current density of redox indicator with increasing surface concentration of dsDNA was calculated using the equation given below. The parameters present in the equation has its own significance gas constant (R), temperature (T), number of electrons involved (n), Faraday constant (F), area of the electrode (A) and charge transfer resistance ( $R_{ct}$ )

$$j_0 = \frac{RT}{nFAR_{ct}} \quad (2)$$

dsDNA concentration	$\theta$ [%]	$j_0$ (A.cm <sup>-2</sup> )	SD (%)
0	0	1.746x10 <sup>-3</sup>	5.81 x10 <sup>-5</sup>
0.5 aM	54.6	7.922x10 <sup>-4</sup>	3.04x10 <sup>-6</sup>
1 aM	72.8	4.745x10 <sup>-4</sup>	6.86x10 <sup>-6</sup>
1 fM	83.3	2.899x10 <sup>-4</sup>	8.79x10 <sup>-6</sup>
1 pM	87.8	2.115x10 <sup>-4</sup>	4.23x10 <sup>-6</sup>
1 nM	90.8	1.594x10 <sup>-4</sup>	2.67x10 <sup>-6</sup>
1 $\mu$ M	92.3	1.329x10 <sup>-4</sup>	9.12x10 <sup>-6</sup>
1 mM	93.3	1.155x10 <sup>-4</sup>	7.45x10 <sup>-6</sup>

**Table S3.** Analytical methods for DNA determination

DNA detection methods	Techniques	Detection limits
<b>Electrochemical methods</b>		
1) Potentiometric detection	Potentiometry	10 pM <sup>1</sup>
2) DNA hybridization (Nano ensembles, Electroactive and magnetic beads, conducting polymer etc.,)	Voltammetry	5 aM <sup>2</sup> , 400 fM <sup>3</sup> , 1 fM <sup>4</sup> & 20 aM <sup>5</sup>
3) Electronic transduction	Impedance	200 aM <sup>6</sup> , 3.5x10 <sup>-13</sup> M <sup>7</sup> , 0.5 nM <sup>8</sup>
<b>Fluorescence spectroscopy</b>		
<b>Colorimetric analysis</b>		
		1 aM <sup>9</sup> , 4.5 fM <sup>10</sup> 20 aM <sup>11</sup> , 100 pM <sup>12</sup>

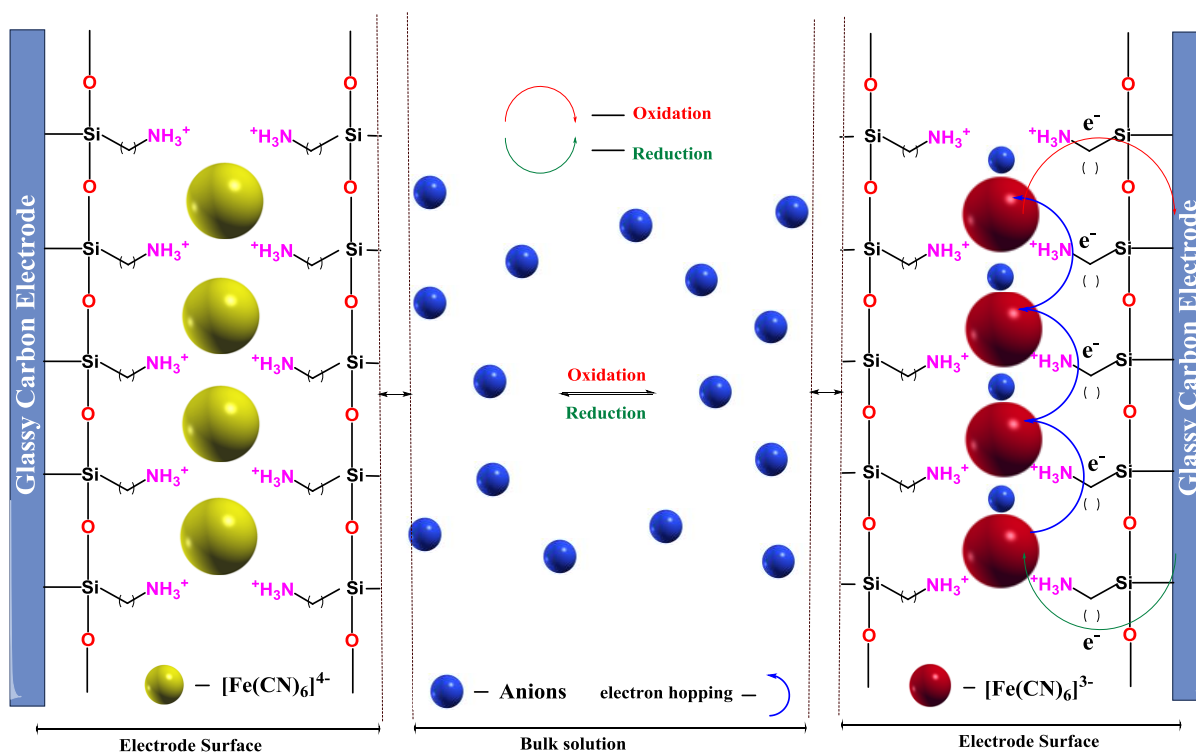
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**Scheme S1.** Mechanism of charge transport in  $[\text{Fe}(\text{CN})_6]^{4-}$  immobilized PSQs modified GC surface.