Supplementary Data

For

A metronidazole-probe sensor based on imprinted biocompatible nanofilm for rapid and sensitive detection of anaerobic protozoan

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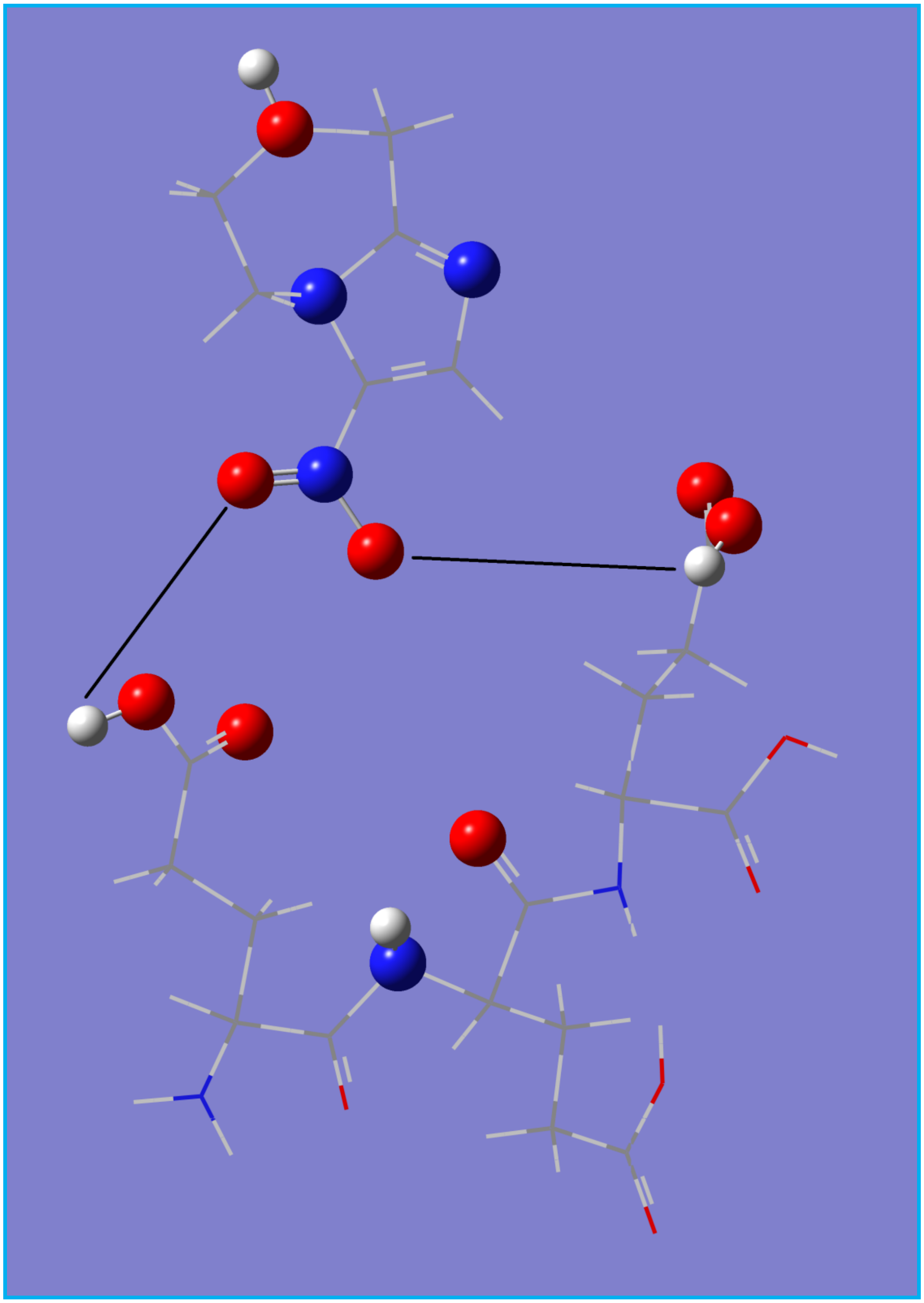

Figure S1: Optimized conformation of the one sided complex of MDZ-PGA by multilayer ONIOM method.

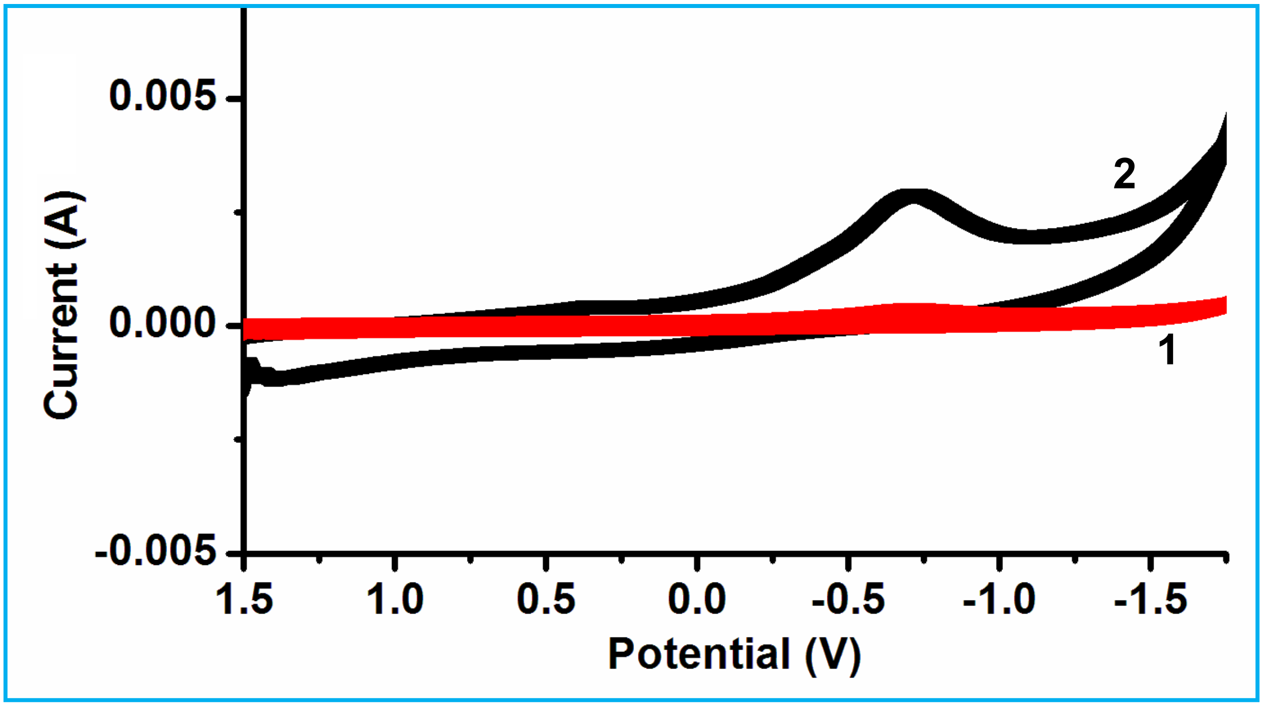

Figure S2: Template rebinding study on MDZ-imprinted (run 1) and non-imprinted (run 2) polymer modified PGEs.

Table S1: Comparative studies of surface roughness factor on modified and bare electrodes.

S.N.	Types of electrode	I_p (μA)	A (cm^2)	A_{geom} (cm^2)	$R_f = A/ A_{geom}$
1.	Bare PGE	203	0.061	0.094	0.648
2.	PGA modified PGE	167	0.046	0.094	0.489
3.	AuNPs/PGA modified PGE	298	0.074	0.094	0.797

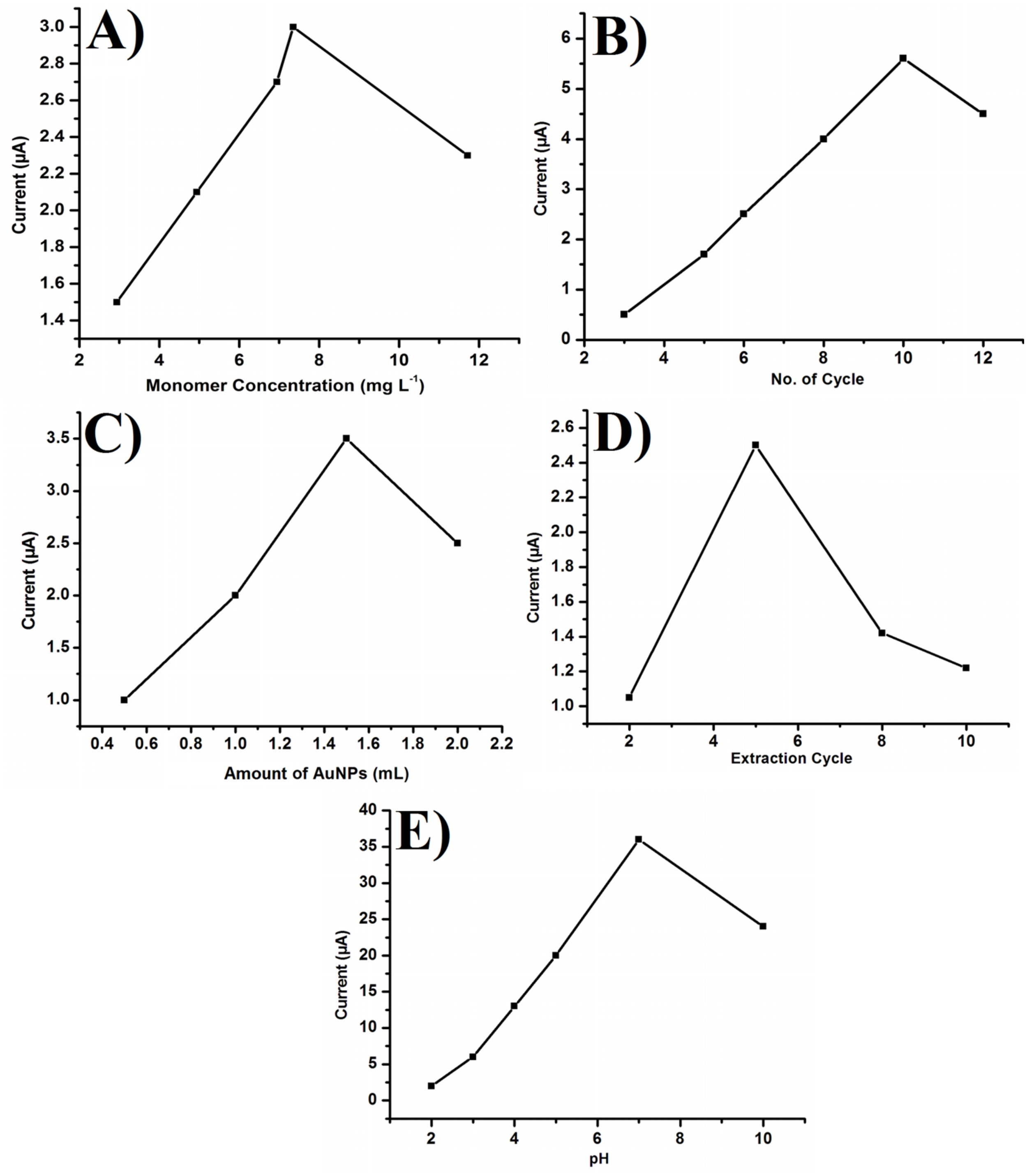

Figure S3: Optimization of different parameters affecting sensor development: (A) monomer concentration, (B) number of cycle for electro-polymerization of glutamic acid, (C) amount of AuNPs, (D) number of cycle for MDZ extraction, and E) pH of supporting electrolyte.

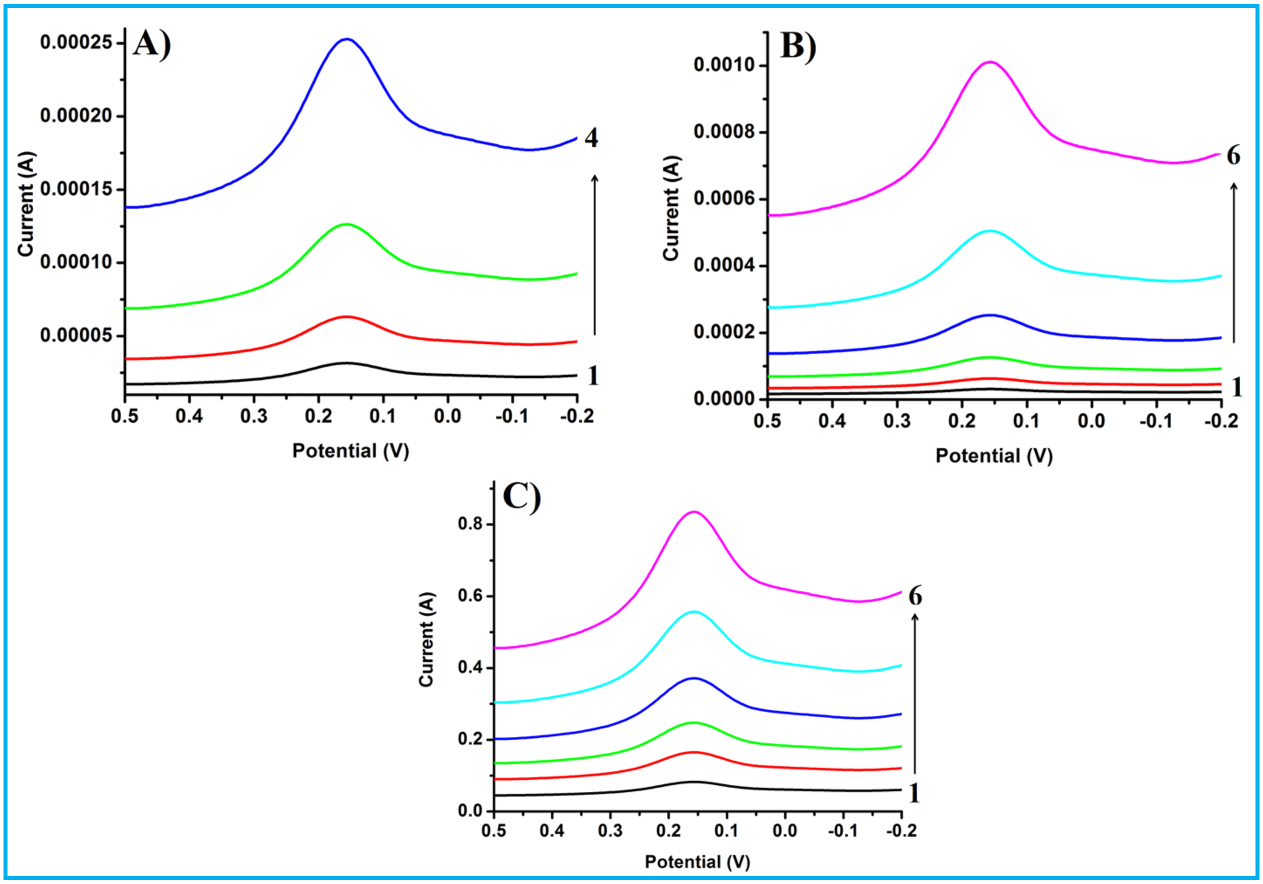

Figure S4: DPSV runs for different concentration of MDZ in a potential range between +0.5 to −0.2 V in optimized condition (with 50mV modulation amplitude, 50ms pulse width and 5mV step potential): (A) 0.098 to 0.98 mg L^{-1}, (B) 1.0 to 12.0 mg L^{-1}, and (C) 30 to 130.0mg L^{-1}.

S1. Optimization of deposition potential and deposition time

Deposition potential and deposition time are very important parameters in the electrochemical analysis. Herein, optimization of deposition potential and deposition time is also performed. The DPSV current for 0.1 mgL^{-1}MDZ was found to be increasing with the increase of deposition time up to 60s and then became constant. This indicated that the uptake of MDZ at MIP electrode surface was quite facile, and the saturation occurred very fast. For the DPSV measurements, accumulation potential was optimized to be−0.5 V, any value higher or lower than this potential cause reduction in peak current.

S2. Adsorption study of MDZ

On the surface of PGE, chronocolumetry technique was applied to calculate the surface coverage (Γ^0) and diffusion coefficient (D) of the MDZ. According to the integrated Cottrell equation, the relation between charges (Q) vs. square root of time ($t^{1/2}$) can be described as follows [S1]:

$$Q = 2nFAC(Dt)^{1/2}\pi^{-1/2} + Q_{ads} + Q_{dl} \qquad (1)$$

$$Q_{ads}=nFA\tau^0 \qquad (2)$$

$$I_p = \frac{n^2F^2I^0A\vartheta}{4RT} \qquad (3)$$

Where, A is the geometrical area of electrode that is ($9.4 \times 10^{-2} cm^2$), C is the concentration (14.2μM) of MDZ, Q_{dl} is the double layer charge, Q_{ads} is the Faradaic oxidative charge and other symbols have their usual meanings. Q_{dl} is assumed not changed in the presence and absence of MDZ in our total experiments. For MDZ–MIP, Q_{dl} and total charge (Q_{dl} +Q_{ads}) is evaluated from the respective intercepts of the Anson plots (Q vs. $t^{1/2}$) in the absence and presence of MDZ. The values of n and Γ^0 can be obtained as 4.0 and $1.06 x 10^{-9}$ mol cm^{-2}, respectively using equations 1-3. In the present instance, Γ^0 reflects the total surface coverage of MDZ analyte (1.05×10^{-10} mol or 6.05×10^{13} molecules) specifically bound to MIP cavities (each molecule per cavity). From the slope of the Anson plot 'D' values can be calculated for MDZ is found to be $2.47 \times 10^{-3} cm^2 s^{-1}$ for MDZ–MIP. The higher 'D' values may be explaining the surface diffusivity of the template on the different modified electrodes.

S3. Kinetic study of MDZ

According to the Butler-Volmer model of electrode kinetics, the values of rate constant (k_s) indicates that the rate of kinetics, required time for equilibrium and electron transfer coefficient (α) is used to describe the symmetry between the reverse electron transfer steps. Under investigation, potential shifting with scan rate supports the irreversibility of the electrochemical reaction. Peak potential of an irreversible process obeys the following equations [S2]:

$$\alpha n = \frac{1.857RT}{F(E_p - E_{\frac{p}{2}})} \qquad (4)$$

$$E_p = E_{\frac{p}{2}} - b(0.52 - 0.51\log_b d - \log k_s + 0.5\log v) \qquad (5)$$

$$b = \frac{2.303RT}{\alpha nF}$$

(6)

Where, b = 2.303RT/α nF, α = electron transfer co-efficient, n = no. of electron, E_p = peak potential, D = diffusion co-efficient, υ = scan rate.

Let us think in terms of energy barriers between the oxidized form and the reduced form as Ox + e- = Red, the free energy of the reactants can changed by increasing or decreasing the potential applied to the electrode. The extent to which the free energy changes contributes to a change in the activation energy is dependent on the magnitude of α, which ranges from 0 to 1. Herein, the estimated values of α and $k_{s,}$ for the reduction of MDZ at MIP-modified PGE were found to be 0.1986 and 0.232 cm s^{-1}, respectively using above equations (4-6). Therefore, the lower value of α (<0.5) suggests the irreversibility of the process, whereas the higher value of k_s indicates a fast kinetics due to the role of MIP-cavities present at the electrode surface.

Reference:

S1. A. Bard, L.R. Faulkner, Electrochemical Methods Fundamentals and Application, second ed., John Wiley and Sons, New York, 1980.

S2. E. Laviron, General expression of the linear potential sweep voltammogram in the case of diffusion less electrochemical system, J. Electroanal. chem. 101 (1979)19-28.