Electronic Supplementary Information

DNA film thickness

The following expression was used to calculate the thickness of the DNA film on the gold electrode. The XPS spectrum from a freshly sputtered gold film is used as a intensity reference. In this formula, the observed intensity of the gold substrate signal, I_{Au}, is given by the intensity from a clean gold substrate, $I_{\mathrm{Au}}{}^{0}$, attenuated by the DNA film of thickness t [1] as

$$I_{Au} = I_{Au}^{0} \exp\left[-\frac{t}{L_{Au}}\right] \tag{S1}$$

Where, L_{Au} represents the film thickness and average practical effective attenuation length for electrons from Au in DNA film [1, 2].

Table S1 Equivalent circuit element values for DNA 3 films in the absence and presence of binding to different concentrations of Hg(II) ranging from 10^{-5} to 10^{-10} M. *represents change in charge transfer resistance (R_{CT}) values of DNA 3 before and after incubating with different concentrations of Hg(II). $\Delta R_{CT} = R_{CT}$ (after Hg(II) immersion) - R_{CT} (before Hg(II) immersion).

	R_s ($\Omega.cm^2$)	$C_{monolayer}$ (F/cm^2)	R_{CT} ($k\Omega.cm^2$)	R_x ($\Omega.cm^2$)	CPE (F/cm^2)	n	ΔR_{CT}* ($k\Omega.cm^2$)
DNA	3.4	7.73E-09	72.40	165.5	2.23E-07	0.97	-
1×10^{-5} M	3.3	6.09E-09	156.1	160.3	2.71E-07	0.96	83.7
1×10^{-6} M	3.4	6.34E-09	132.7	153.8	2.80E-07	0.97	60.3
1×10^{-7} M	3.2	6.43E-09	111.0	164.4	2.20E-07	0.97	38.6
1×10^{-8} M	3.4	6.94E-09	97.00	172.1	2.45E-07	0.96	24.6
1×10^{-9} M	3.3	7.07E-09	84.80	172.1	2.88E-07	0.95	12.4
1×10^{-10} M	3.1	7.21E-09	77.60	164.1	2.63E-07	0.96	5.20

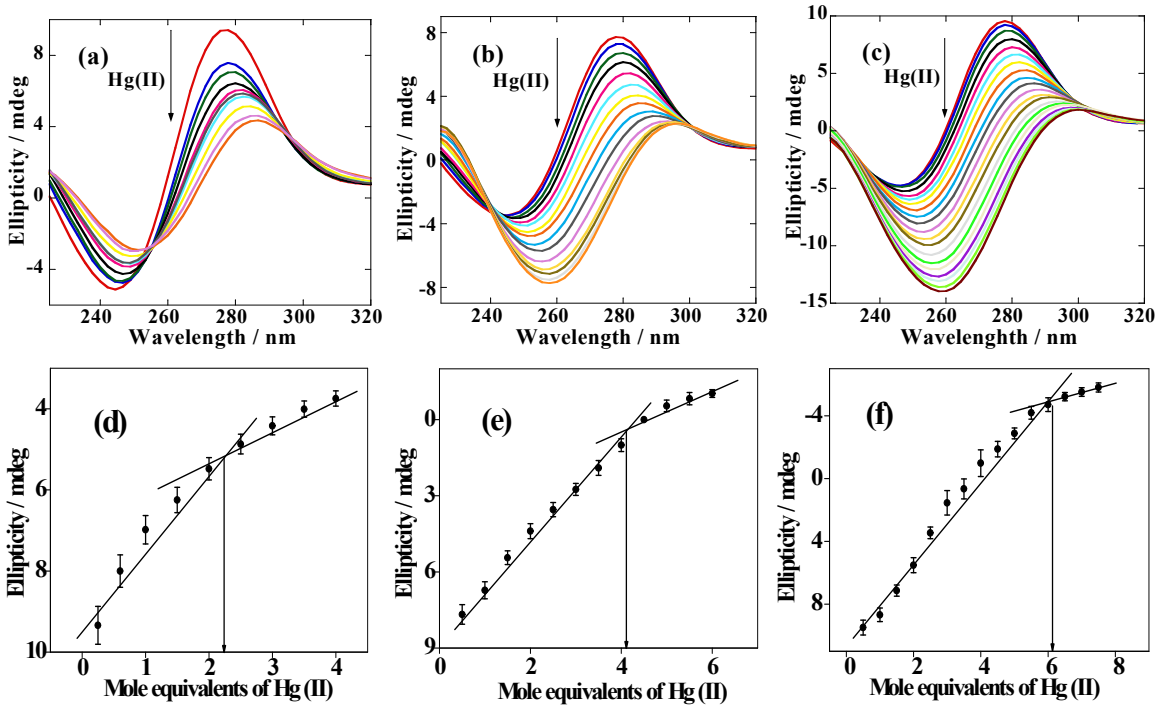

Fig. S1 CD spectra of (a) DNA 1 (b) DNA 2 and (c) DNA 3 at 5.0 μM concentration in the absence and presence of increasing concentration of Hg(II) from 0.25 to 4.0, 0.5 to 6.0 and 0.5 to 8.0 equivalents in 20 mM MOPS buffer solution containing 150 mM $NaClO_4$ at pH~7.4, respectively. Plots (d), (e) and (f) represent the variation of ellipticity *vs.* mole equivalents of Hg(II) for DNA 1, DNA 2 and DNA 3 respectively.

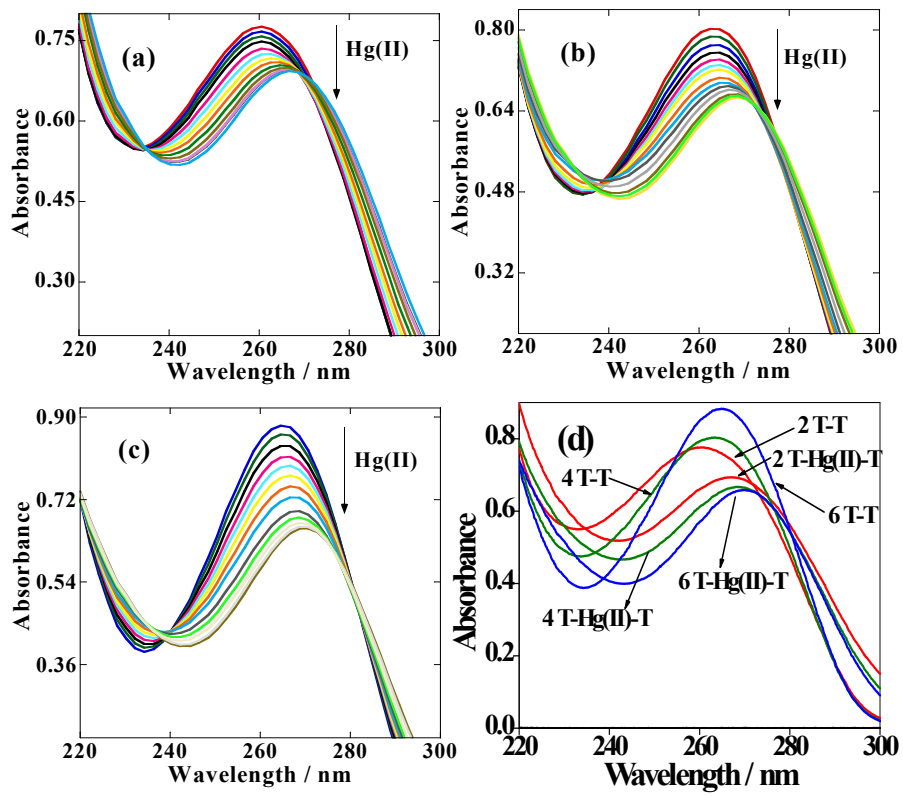

Fig. S2 UV-visible spectra of (a) DNA 1 (b) DNA 2 and (c) DNA 3 at 5.0 μM concentration in the absence and presence of increasing concentration of Hg(II) from 0.25 to 4.0, 0.5 to 6.0 and 0.5 to 8.0 equivalents in 20 mM MOPS buffer solution containing 150 mM $NaClO_4$ at pH~7.4, respectively; (d) UV-visible spectra of DNAs with different T-T mismatches in the absence and presence of Hg(II).

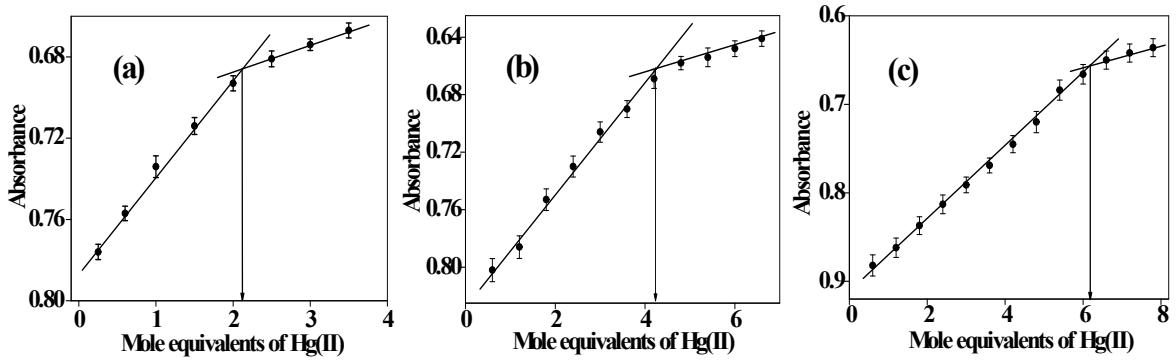

Fig. S3 Variation of absorbance *vs.* mole equivalents of Hg(II) for (a) DNA 1; (b) DNA 2 and (c) DNA 3, respectively.

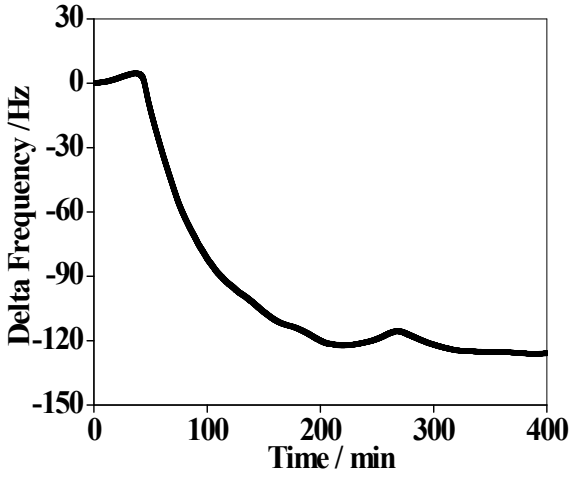

Fig. S4 Monitoring adsorption of DNA 3 from solution onto a gold surface using quartz crystal microbalance (QCM). The concentration of DNA injected was 25 μM and the measurement was carried out at room temperature.

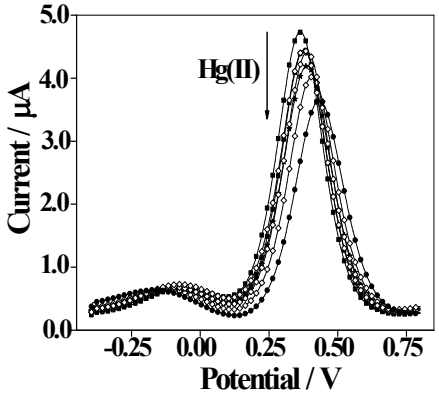

Fig. S5 Differential pulse voltammetric titrations corresponding to the films of DNA 3 before (■) and after incubating in buffer solution (20 mM MOPS buffer solution containing 150 mM $NaClO_4$ at pH~7.4) containing Hg(II) with concentrations ranging from 10^{-5} (●), 10^{-6} (▲), 10^{-7} (O) and 10^{-8} (★), 10^{-9} (◇) and 10^{-10} M (⊳).

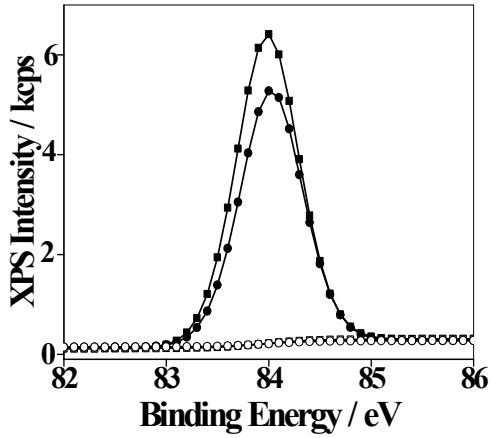

Fig. S6 High resolution XPS spectra of DNA 3 for Au $4f_{7/2}$ peak before (—■—) and after (—●—) incubating with 10 μM Hg(II).

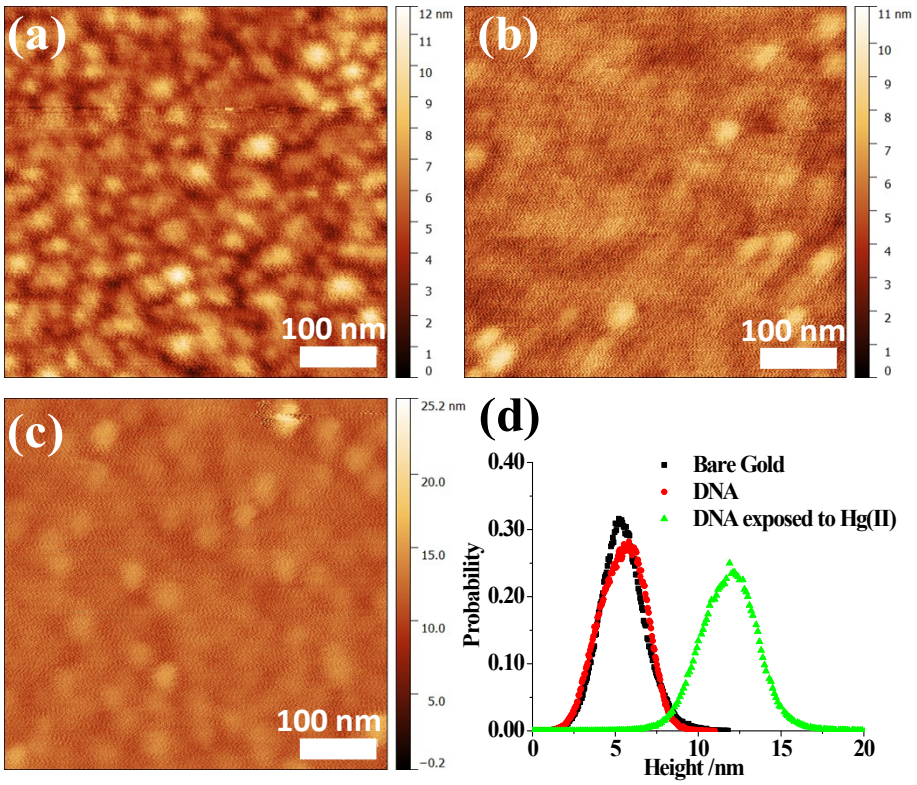

Fig. S7 (a) Atomic force microscopy images of bare gold surface and surfaces modified with DNA (b) before and (c) after expose to the 10 μM Hg(II). The images were obtained using contact mode AFM under ambient condition. The height distributions are shown in plot (d).

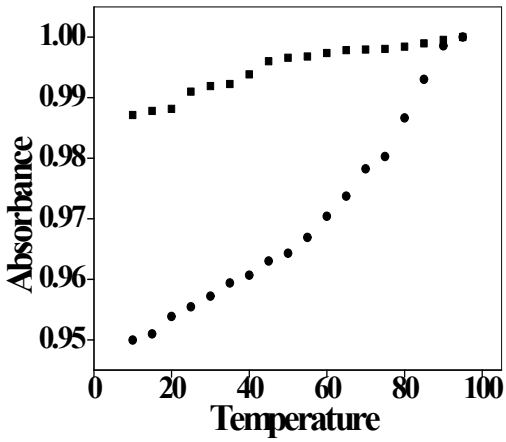

Fig. S8 Normalized UV melting curves of DNA 3 at 5.0 μM in the absence (■) and presence (●) of 6.0 equivalents of Hg(II) in 20 mM MOPS buffer solution containing 150 mM $NaClO_4$ at pH~7.4.

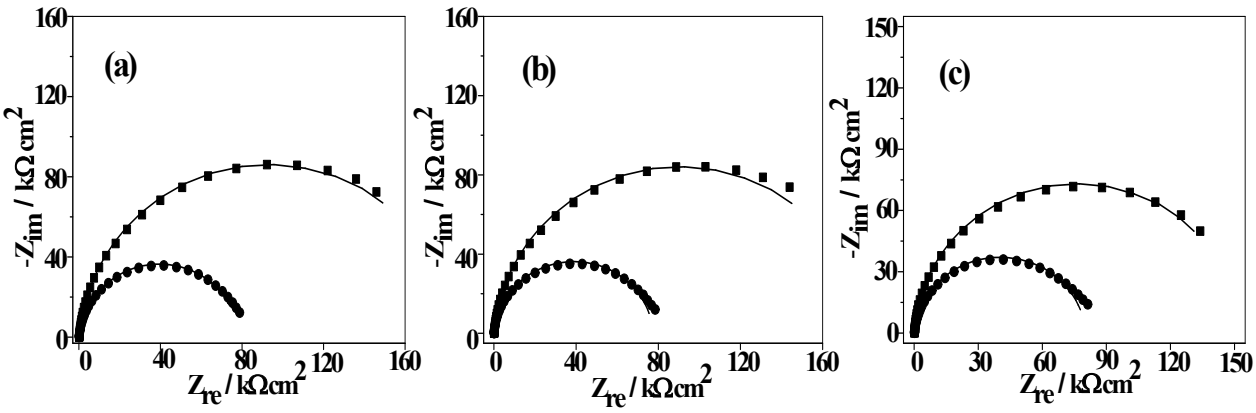

Fig. S9. Representative Nyquist plots ($-Z_{im}$ *vs.* Z_{re}) for DNA 3 before (●) and after incubating (■) in different concentrations of humic acid (a) 1 mg/L (b) 5 mg/L and (c) 10 mg/L and same concentration of 10 μM Hg(II) solution. The measurement was carried out in an electrolyte containing. 1.0 mM $[Fe(CN)_6]^{3-/4-}$ as the redox probe in 20 mM MOPS buffer solution containing 150 mM $NaClO_4$ at pH = 7.4.

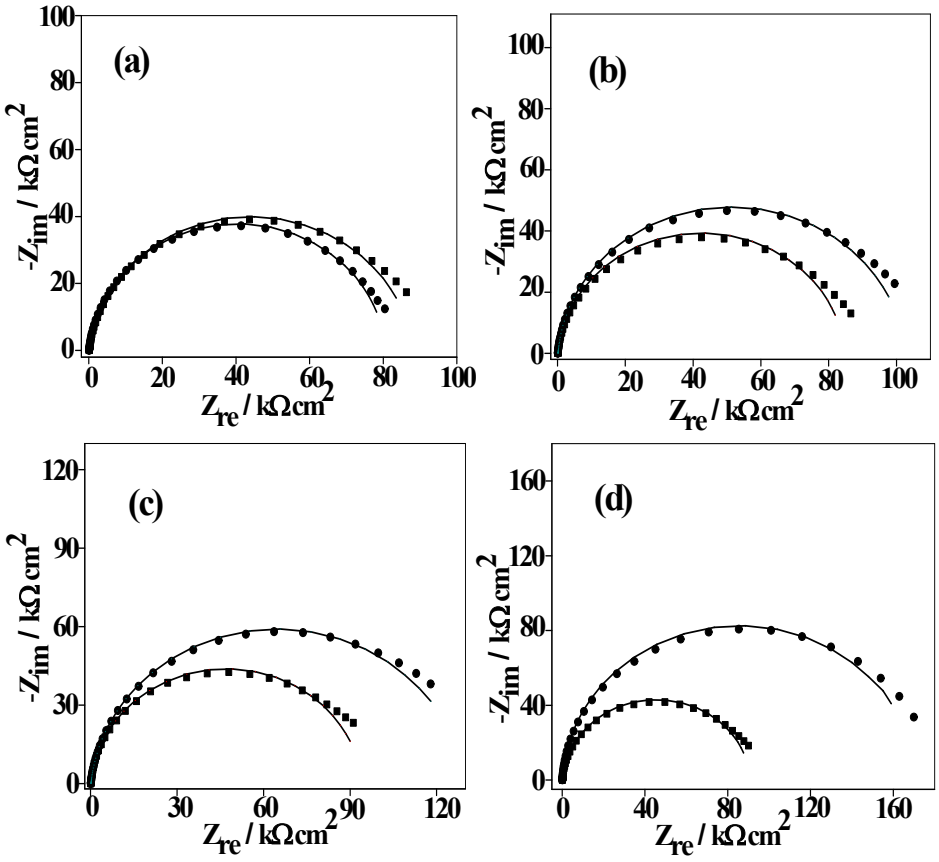

Fig. S10 Representative Nyquist plots ($-Z_{im}$ *vs.* Z_{re}) for DNA 3 before (■) and after incubating (●) in different spiked concentrations of Hg(II) in Ontario lake water (a) 10^{-10} M; (b) 10^{-9} M; (c) 10^{-7} M and (d) 10^{-5} M. The measurement was carried out in an electrolyte containing 1.0 mM $[Fe(CN)_6]^{3-/4-}$ as the redox probe in 20 mM MOPS buffer solution containing 150 mM $NaClO_4$ at pH~7.4.

References

1. D. M. Petrovykh, H. K.-Suda, M. J. Tarlov, L. J. Whitman, *Langmuir*, 2004, **20**, 429-440.
2. C. J. Powell, A. Jablonski, *Surf. Interface Anal.*, 2002, **33**, 211-229.