Supplementary Material (ESI) for Analyst

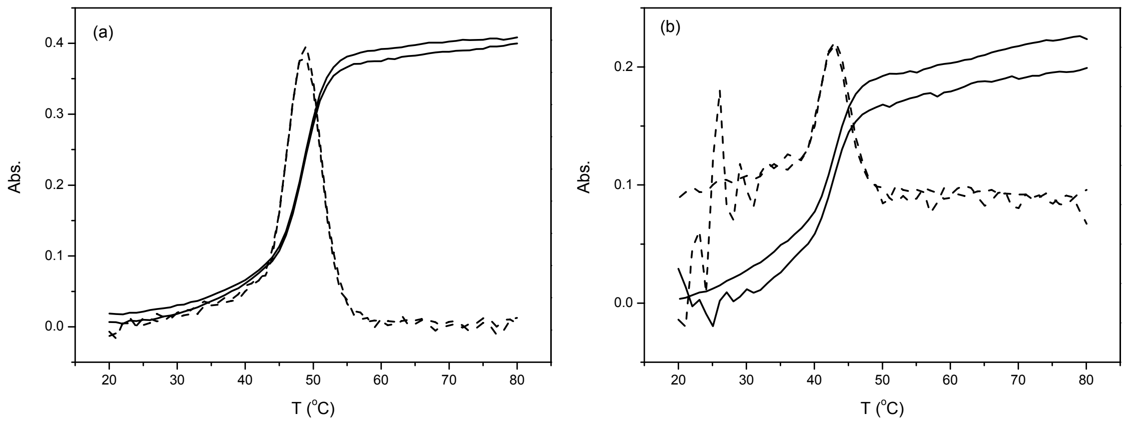
Electronic Supporting Information

Interaction of Metal Ions and DNA Films on Gold Surfaces: An Electrochemical Impedance Study

Xiaomin Bin and *Heinz-Bernhard Kraatz*[*]

Department of Chemistry, University of Western Ontario, 1151 Richmond Street London, Ontario, Canada N6A 5B7

Figure S1. Melting curves of ds-DNA **1+2** (a) and **1+3** (b) solution in 50 mM Tris-ClO_4 (pH 8.6).



The solid lines are two trials of melting curves, and the dotted lines are the differential curves of the melting curve. From the peak position of the differential curves, the melting points of ds-DNA **1+2** and **1+3** are 49°C and 43 °C, respectively.

Figure S2. Equivalent circuits used to fit impedance spectra of ds-DNA monolayer. (A) for impedance spectra of matched ds-DNA films without diffusion; (B) for impedance spectra of ds-DNA monolayer with diffusion part. R_s, solution resistance; C_m or Q_m, capacitance or CPE of monolayer; R_{ct}, charge-transfer resistance; R_x and Q, defects in the monolayer; Q_d and R_d, a combination of two parallel diffusion-like elements which give information about the diffusion through the DNA monolayer.

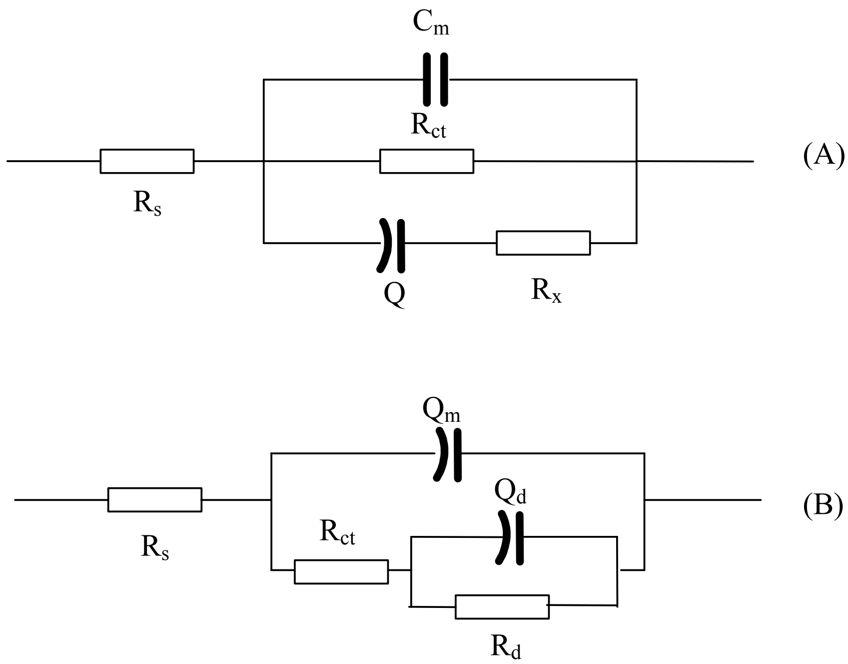


Table S1. Equivalent circuit element values for 25 base pair ds-DNA films in the absence and presence of metal ions, and extensively rinsed ds-DNA films on the gold electrode surface. Unit: R_s, R_x: (Ω●cm^2); R_{ct}: (kΩ●cm^2); C_m: (μF●cm^2); CPE(Yo) ($Ss^{-0.5}cm^{-2}$)

	Ca^{2+}			Mg^{2+}			Al^{3+}		
	ds-DNA	Ca-DNA	rinsed	ds-DNA	Mg-DNA	rinsed	ds-DNA	Al-DNA	rinsed
R_s	0.6(0.3)	0.6(0.2)	0.7(0.3)	0.6(0.4)	0.7(0.4)	0.7(0.4)	0.6(0.2)	0.7(0.2)	0.5(0.2)
C_m	6.9(1.3)	--	9.5(2.0)	5.2(2.2)	--	3.7(1.5)	4.8(2.4)	4.3(1.6)	4.1(1.9)
CPE (Y_o) 10^5	1.7(0.3)	3.3(1.3)	2.6(0.8)	1.7(0.9)	2.2(2.0)	0.9(0.5)	1.3(0.1)	1.5(0.2)	1.6(0.4)
n	0.91(0.04)	0.92(0.01)	0.94(0.01)	0.91(0.01)	0.92(0.03)	0.92(0.03)	0.91(0.01)	0.94(0.01)	0.95(0.01)
R_{ct}	6.16(0.70)	0.45(0.31)	4.61(0.14)	5.85(0.53)	1.21(0.37)	5.75(0.88)	5.21(0.46)	2.58(0.34)	2.73(0.66)
R_x	0.9 (0.8)	--	0.8(0.6)	2.0(1.0)	--	3.5(1.0)	2.2(1.1)	1.4(0.5)	0.6(0.2)
	La^{3+}			Ni^{2+}			Cu^{2+}		
	;-DNA	a-DNA	nsed	;-DNA	i-DNA	nsed	;-DNA	u-DNA	nsed
s	5(0.1)	6(0.2)	7(0.3)	8(0.2)	7(0.3)	0.7(0.3)	0.8(0.2)	0.8(0.2)	8(0.2)
m	1(3.3)		7(1.0)	5(2.8)	0(1.2)	1.3(0.3)	2.1(0.2)	1.7(0.3)	5(0.2)
PE (Y_o) 10^5	3(1.3)	9(1.1)	2(0.8)	7(1.3)	1(0.7)	1.1(0.8)	1.3(0.7)	1.7(0.3)	5(0.3)
	91(0.04)	89(0.02)	93(0.01)	91(0.04)	92(0.04)	0.94(0.02)	0.93(0.03)	0.93(0.03)	95(0.01)
ct	55(0.37)	65(0.67)	26(0.30)	60(0.13)	76(1.0)	4.06(0.88)	6.06(0.77)	2.85(0.41)	07(0.34)
x	9(1.0)		8(0.2)	0(0.4)	5(0.6)	0(0.4)	9(0.3)	9 (0.2)	8(0.3)
	Zn^{2+}			Cd^{2+}			Hg^{2+}		
	ds-DNA	Zn-DNA	rinsed	ds-DNA	Cd-DNA	rinsed	ds-DNA	Hg-DNA	rinsed
R_s	0.6(0.2)	0.6(0.2)	0.7(0.1)	0.6(0.2)	0.7(0.3)	0.7(0.2)	0.6(0.3)	0.7(0.3)	0.6(0.2)
C_m	2.7(1.4)	3.3(1.1)	1.3(0.5)	4.8(2.4)	--	4.2(1.8)	5.0(1.4)	--	1.5(0.4)
CPE (Y_o) 10^5	1.2(0.3)	1.5(0.2)	1.4(0.4)	1.3(0.5)	1.5(0.8)	1.3(0.9)	1.4(0.3)	3.0(1.0)	1.6(0.5)
n	0.92(0.04)	0.95(0.01)	0.95(0.01)	0.94(0.01)	0.89(0.01)	0.91(0.01)	0.91(0.03)	0.82(0.05)	0.90(0.01)
R_{ct}	5.71(0.50)	3.40(0.70)	3.65(0.66)	5.35(0.12)	0.79(0.16)	1.43(0.33)	5.83(0.23)	0.55(0.39)	5.09(0.83)
R_x	2.0(0.7)	1.3(0.5)	1.3(0.5)	3.1(1.2)	--	2.9(0.5)	3.0(1.3)	--	2.4(1.0)

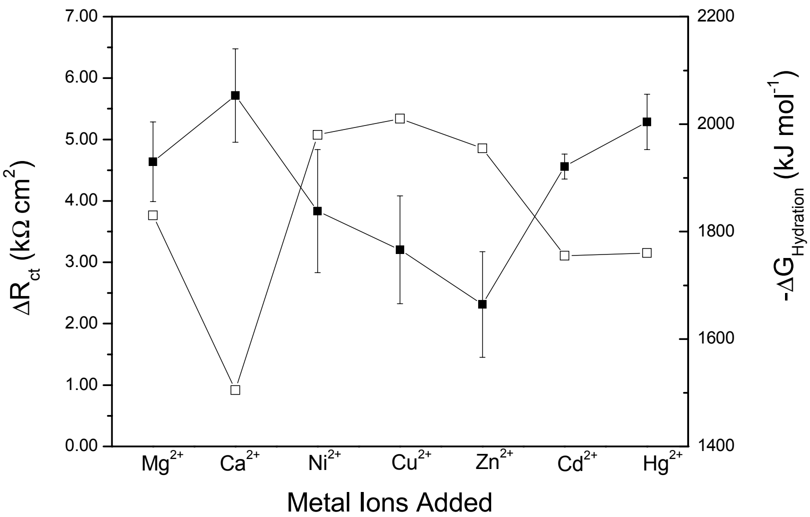
Table S2. Equivalent Circuit Element Values for 25 mer bare ds-DNA in the presence of Ca^{2+}, Mg^{2+}, La^{3+}, $Cd^{2+}$and Hg^{2+} respectively. *

		Ca^{2+}	Mg^{2+}	La^{3+}	Cd^{2+}	Hg^{2+}
	R_s	0.6(0.2)	0.7(0.4)	0.6(0.2)	0.7(0.3)	0.7(0.3)
Q_m	CPE (Y_o) 10^5	3.3(1.3)	2.2(2.0)	2.9(1.1)	1.5(0.8)	3.0(1.0)
	n	0.92(0.01)	0.92(0.03)	0.89(0.02)	0.89(0.01)	0.82(0.05)
	R_{ct}	0.45(0.31)	1.21(0.37)	0.65(0.67)	0.79(0.16)	0.55(0.39)
Q_d	CPE (Y_o)10^3	8.4(6.8)	1.0(0.5)	2.6(1.5)	0.9(0.2)	0.8(0.2)
	n	0.81(0.14)	0.72(0.11)	0.75(0.11)	0.84(0.05)	0.65(0.07)
	R_d	96(63)	410(310)	197(114)	229(90)	478(127)

* The impedance spectra were simulated by equivalent circuit as shown in inset of Figure 1b, a parallel combination of Q_d and R_d, which provides information about diffusion through the ds-DNA film, is in series with R_{ct}, the resistance of charge transfer.[1] Where R_s is the solution resistance and Q_m represents a non-ideal or leaky ds-DNA film.

1. M. Dijksma, B. A. Boukamp, B. Kamp and W. P. van Bennekom, *Langmuir*, 2002, **18**, 3105-3112.

Figure S3. The relevance of $\Delta R_{ct}(1)$ and free energy of hydration of divalent metal ions.



The above figure shows that the $\Delta R_{ct}(1)$ (■) values are relatively inverse proportional to the free energy of hydration ($-\Delta G_{Hydration}$) (□) for the divalent metal ions. The $-\Delta G_{Hydration}$ data was from[1]

Supplementary Material (ESI) for Analyst

Figure S4. Nyquist plots (Z_{img} vs. Z_{re}) of a 25 base pair fully matched DNA (**1**+**2**) (squares) monolayer and mismatch DNA (**1**+**3**) (circuits) assembled on gold microelectrode. In the absence of (filled) and in the presence of (unfilled) (a) Ca^{2+}; (b) Zn^{2+}; (c) Cd^{2+} and (d) Hg^{2+}. Black solid lines were fitting curves by corresponding equivalent circuits.