Supporting Information

Electrochemical Impedance Study the Interaction of Metal Ion with Unlabeled PNA

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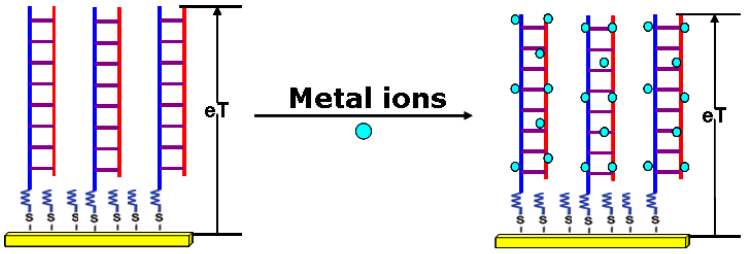
Scheme 1. Unlabeled PNA-PNA binding with metal ions



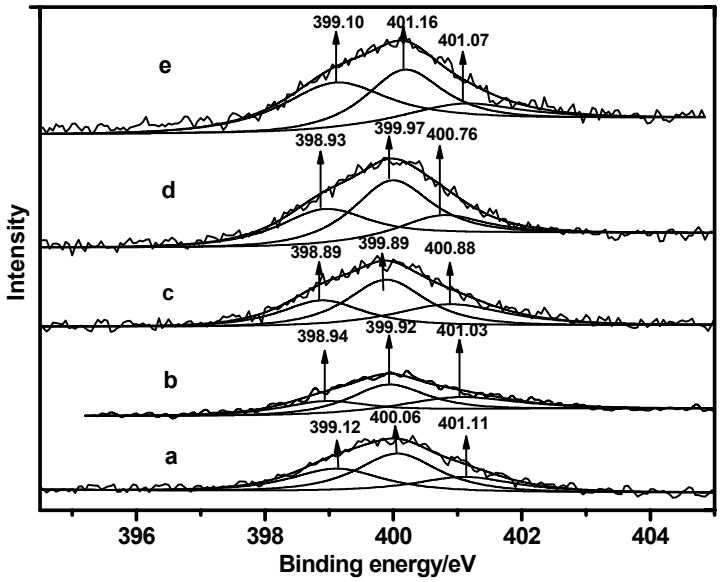


Figure S1. XPS high resolution spectra of the fitted curves for N1s: PNA(I)-PNA(II) in absence (a) and in presence of Co^{2+}(b), Ni^{2+}(c), Zn^{2+} (d) and Mg^{2+}(e). The binding energies were summarized as shown in Table 1.

Tabel S1 Experimental binding energies for different chemical states of N involved in PNA(I)-PNA(II) duplex			
Samples	-N= conjugated in base (eV)	-NH_2 and nonconjugated N in base (eV)	N in PNA backbone (eV)
PNA(I)-PNA(II)	399.12	400.06	401.11
PNA(I)-PNA(II)+Mg^{2+}	399.10	400.16	401.07
PNA(I)-PNA(II)+Zn^{2+}	398.93	399.97	400.76
PNA(I)-PNA(II)+Ni^{2+}	398.89	399.84	400.84
PNA(I)-PNA(II)+Co^{2+}	398.94	399.92	401.03

N 1s spectra are composed of three peaks: two peaks centered at 399.12 and 400.06 eV are assigned to –N= conjugated, –NH_2 and nonconjugated N in base respectively,[1] and the third peak centered at 401.11 eV is contributed from N in PNA backbone.[2] In presence of Zn^{2+}, Ni^{2+}, and Co^{2+}, N1s binding energies contributed from N in bases centered at 399.12 and 400.06 eV are shifted to lower binding energies, which is indicative of metal ions interacting with the nucleobases involving the N7 of purines or the N3 of pyrimidines.[3-4] In addition, N1s peaks centered at 401.11 eV contributed from PNA backbone are also shifted to lower binding energies for in presence of Zn^{2+}, Ni^{2+}, and Co^{2+}, which demonstrated that metal ions probably associated with N in PNA backbone. But for in presence of Mg^{2+}, N1s peaks centered at 401.07 eV, 399.12 eV and 400.06 eV is almost unchanged compared to that PNA(I)-PNA(II), which is indicative of Mg^{2+} not binding with PNA.

Table S2. Equivalent circuit element values for PNA(I) films in absence and presence of metal ions*

	equivalent circuit elements						
	R_s ($\Omega\cdot cm^2$)	**$C_{monolayer}$** ($\mu F\cdot cm^{-2}$)	**R_{CT}** ($\Omega\cdot cm^2$)	**R_x** ($\Omega\cdot cm^2$)	**CPE** ($\mu F\cdot cm^{-2}$)	**n**	**ΔR_{CT}** ($\Omega\cdot cm^2$)
ss-PNA	6.4(0.1)	15.4(1.0)	1343(17)	4.0(0.2)	21.1(1.1)	0.8(0.01)	—
+Ni^{2+}	6.4(0.1)	16.0(0.3)	805(20)	4.3(0.1)	26.0(2.0)	0.8(0.02)	538(6)
+Co^{2+}	6.3(0.1)	16.2(0.6)	826(15)	4.1(0.1)	28.5(1.0)	0.8(0.04)	517(5)
+Zn^{2+}	6.4(0.1)	16.5(1.2)	830(20)	4.3(0.1)	25.0(0.7)	0.8(0.04)	513(7)
Buffer[a]	6.5(0.1)	15.8(0.5)	1052(15)	5.0(0.3)	28.1(1.4)	0.8(0.02)	291(3)
+Mg^{2+}	6.6(0.1)	13.9(0.2)	1343(20)	3.8(0.1)	19.1(1.2)	0.8(0.01)	0(10)

* The values in parentheses represent the standard deviations from at least 5 electrode measurements.

[a] PNA(I) with Zn^{2+}, Ni^{2+}, Co^{2+} incubating in blank buffer solution for 1day

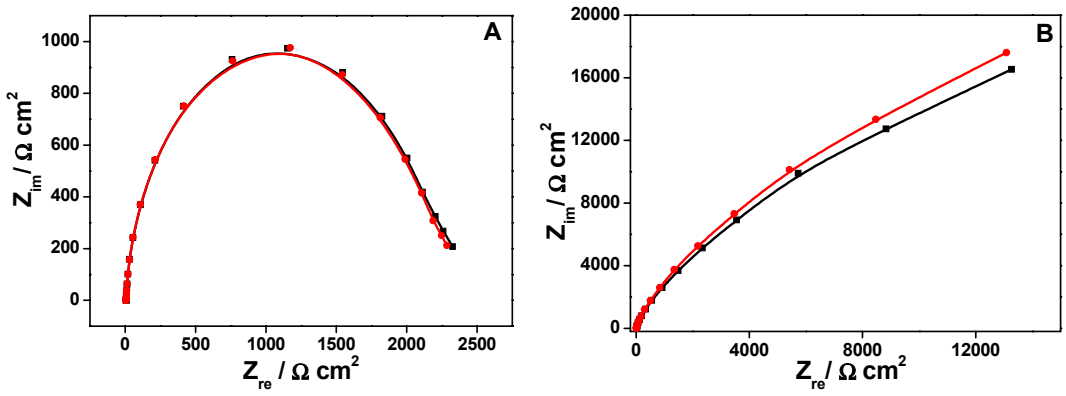


Figure S2. Representative Nyquist plots (-Zim vs Zre) for films of 15-mer duplex of PNA(I)-PNA(II) with $[Fe(CN)_6]^{3-/4-}$ as redox probe (A) and with $[Ru(NH_3)_6]^{2+/3+}$ as redox probe (B) in absence (—) and presence of 0.4 mM Mg^{2+} (—).

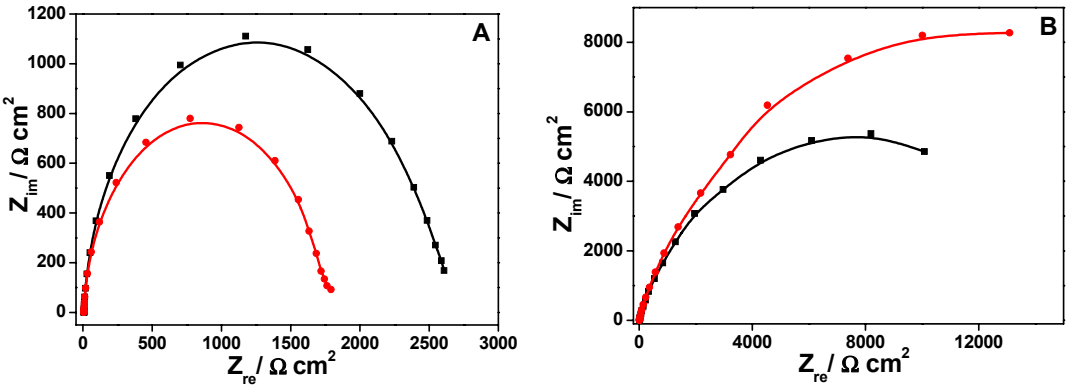


Figure S3. Representative Nyquist plots (-Zim vs Zre) for films of 15-mer duplex of PNA(I)-PNA(II) (A) with $[Fe(CN)_6]^{3-/4-}$ as redox probe and (B) with $[Ru(NH_3)_6]^{2+/3+}$ as redox probe in absence (—) and presence of 0.4 mM Ni^{2+} (—).

Tabel S3 the sequence of DNA probe, PNA and DNA targets	
Name	Squence
ss-DNA	5'HO-$(CH_2)_6$-S-S-$(CH_2)_6$-GTC-ACG-ATG-GCC-CAG 3'
Complementary PNA	(C) CAG-TGC-TAC-CGG-GTC (N)
Complementary DNA	3' CAG-TGC-TAC-CGG-GTC 5'

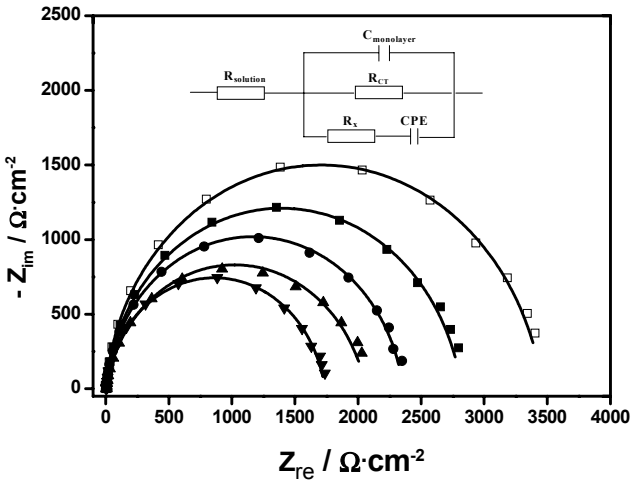


Figure S4. Representative Nyquist plots ($-Z_{im}$ vs Z_{re}) for films of 15-mer ssDNA-PNA(□);ssDNA-PNA incubating with 0.4mM divalent metal ions Mg^{2+} (■),Zn^{2+} (●),Co^{2+}(▲),Ni^{2+}(▼) for 2h. Measured data are shown as symbols with calculated fit to the equivalent circuit as solid lines. The measured data are fit to the equivalent circuit; R_s, solution resistance; $C_{monolayer}$, capacitance of the DNA/PNA monolayer; R_{CT}, charge-transfer resistance of DNA/PNA monolayer; R_x and CPE, resistance and nonlinear capacitor accounting for defects in the films.

Table S4. Equivalent circuit element values for ss-DNA+PNA films in absence and presence of metal ions*

	equivalent circuit elements						
	R_s ($\Omega\cdot cm^2$)	**$C_{monolayer}$** ($\mu F\cdot cm^{-2}$)	**R_{CT}** ($\Omega\cdot cm^2$)	**R_x** ($\Omega\cdot cm^2$)	**CPE** ($\mu F\cdot cm^{-2}$)	**n**	**ΔR_{CT}** ($\Omega\cdot cm^2$)
ss-DNA+PNA	5.8(0.1)	22.8(2.0)	3539(80)	13.2(2.2)	18.9(1.2)	0.8(0.01)	—
$+Zn^{2+}$	6.0(0.1)	26.3(2.5)	2213(40)	14.0(1.0)	21.1(1.0)	0.8(0.02)	1326(20)
$+Ni^{2+}$	5.8(0.1)	19.5(1.3)	1816(15)	7.9(0.3)	23.5(0.6)	0.8(0.01)	1723(8)
$+Co^{2+}$	5.7(0.1)	20.2(1.9)	2124(25)	8.3(0.6)	22.9(1.3)	0.8(0.01)	1415(13)
$+Mg^{2+}$	5.9(0.1)	22.8(1.0)	2816(102)	9.6(0.5)	22.4(1.5)	0.8(0.01)	723(10)

* The values in parentheses represent the standard deviations from at least 5 electrode measurements.

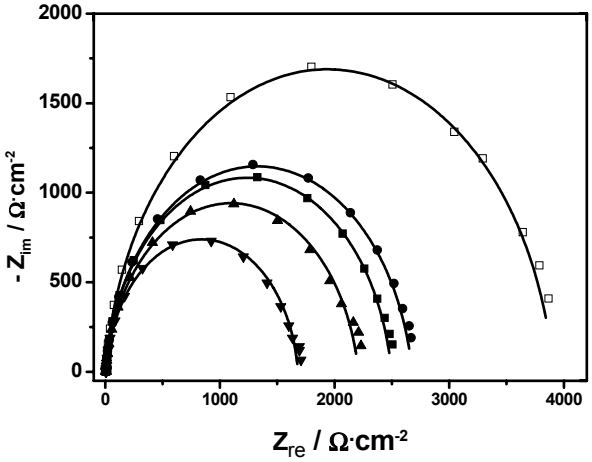


Figure S5. Representative Nyquist plots ($-Z_{im}$ vs Z_{re}) for films of 15-mer ssDNA-DNA(□); ssDNA-DNA incubating with 0.4 mM divalent metal ions Mg^{2+}(■),Zn^{2+}(●),Co^{2+}(▲),Ni^{2+}(▼) for 2h. Measured data are shown as symbols with calculated fit to the equivalent circuit shown inset Figure S4 as solid lines

Table S5. Equivalent circuit element values for ss-DNA-DNA films in absence and presence of metal ions*

	equivalent circuit elements						
	R_s	$C_{monolayer}$	R_{CT}	R_x	CPE	n	ΔR_{CT}
	($\Omega \cdot cm^2$)	($\mu F \cdot cm^{-2}$)	($\Omega \cdot cm^2$)	($\Omega \cdot cm^2$)	($\mu F \cdot cm^{-2}$)		($\Omega \cdot cm^2$)
ss-DNA-DNA	7.0(0.1)	12.0(0.3)	3904(70)	6.0(0.1)	18.3(0.4)	0.9(0.05)	—
$+Zn^{2+}$	7.0(0.1)	13.0(0.3)	2533(90)	5.4(0.2)	21.0(0.8)	0.9(0.01)	1371(29)
$+Ni^{2+}$	6.9(0.1)	8.5(0.5)	1673(25)	5.6(0.3)	21.4(1.4)	0.9(0.01)	2231(50)
$+Co^{2+}$	7.0(0.1)	9.8(0.4)	2201(80)	4.2(0.2)	19.9(0.1)	0.9(0.03)	1703(40)
$+Mg^{2+}$	6.9(0.1)	12.3(0.8)	2437(53)	6.6(0.4)	19.1(0.1)	0.9(0.01)	1467(60)

* The values in parentheses represent the standard deviations from at least 5 electrode measurements.

References:

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