Supporting Information

Electrochemical Detection of 9-Hydroxyfluorene Based on the Direct Interaction with Hairpin DNA

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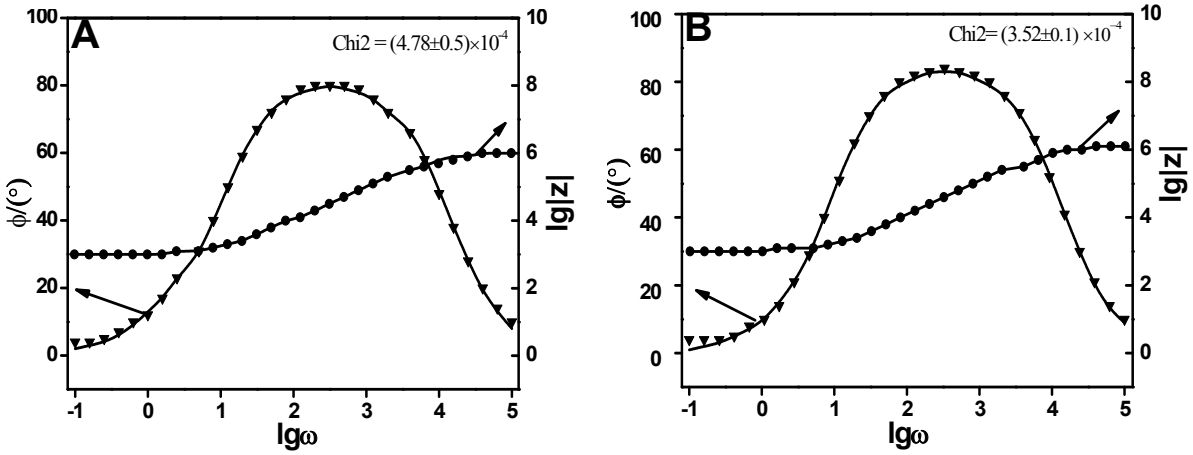

Fig. S1. Bode plots (lg|Z| (●) *vs*. lgω and ϕ (▼) *vs*. lgω) for films of hairpin DNA (1) before (A) after (B) incubated with 550 nM 9-OHFLU for 30min. Measured data were shown as symbols with calculated fit to the equivalent circuit as solid lines.

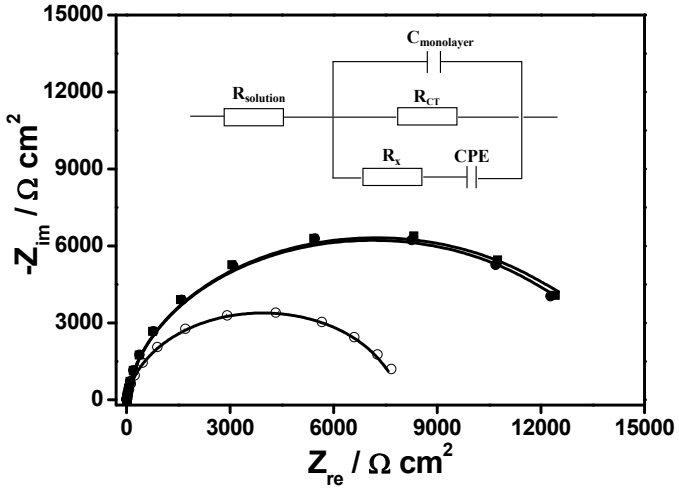

Fig. S2. Representative Nyquist plots ($-Z_{im}$ *vs*. Z_{re}) for films of hairpin DNA (1) (○) hybridization with DNA (2) to formed matched ds-DNA(1+2) before (●) and after (■) incubated with 550 nM 9-OHFLU for 30 min. Measured data were shown as symbols with calculated fit to the equivalent circuit (shown inset of Figure 1) as solid lines.

Table S1. Equivalent Circuit Element Values for Films of Hairpin DNA (1), ds-DNA (1+2) before and after Incubating with 550 nM 9-OHFLU [b]

	Circuit elements						
	R_s ($\Omega \cdot cm^2$)	C_{film} ($\mu F \cdot cm^{-2}$)	R_{CT} ($\Omega \cdot cm^2$)	R_x ($\Omega \cdot cm^2$)	CPE ($\mu F \cdot cm^{-2}$)	n	ΔR_{CT} ($\Omega \cdot cm^2$)
Hairpin DNA (1)	7.5(0.2)	7.4(0.4)	7897(11)	5.2(0.4)	22.4(0.5)	0.90(0.01)	
ds-DNA(1+2)	6.7(0.1)	10.2(0.3)	14248(20)	10.1(0.7)	27.3(1.4)	0.91(0.03)	
ds-DNA(1+2) + 9-OHFLU	6.7(0.1)	10.3(0.4)	14460(17)	10.3(0.8)	27.3(1.7)	0.91(0.03)	212 (36)

[b] The values in parentheses represent the standard deviations from at least five electrode measurements.

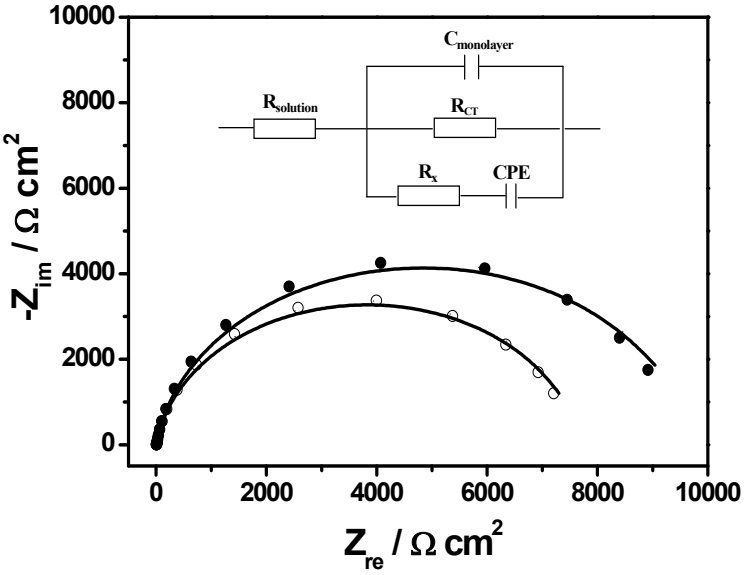

Fig. S3. Representative Nyquist plots ($-Z_{im}$ *vs*. Z_{re}) for films of ss-DNA (3) before (○) and after incubated with 550 nM 9-OHFLU for 30min (●). Measured data were shown as symbols with calculated fit to the equivalent circuit (shown inset of Fig. 1) as solid lines.

Table S2. Equivalent Circuit Element Values for Films of ss-DNA (3) before and after incubated with 550 nM 9-OHFLU [c]

	Circuit elements						
	R_s ($\Omega \cdot cm^2$)	C_{film} ($\mu F \cdot cm^{-2}$)	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(3)	6.8(0.2)	7.4(0.4)	7669(50)	9.9(2.4)	26.6(3.0)	0.89(0.01)	--
ss-DNA(3) +9-OHFLU	6.9(0.0)	7.5(1.5)	9695(83)	10.7(0.1)	26.3(4.9)	0.89(0.00)	2026(52)

[c] The values in parentheses represent the standard deviations from at least five electrode measurements.

Table S3. Chemical Shifts of -OH in 9-OHFLU before and after Interacting with Nucleobases in D_2O

	Chemical shifts (ppm)			
	9-OHFLU	**9-OHFLU+ A**	**9-OHFLU + T**	**9-OHFLU +C**
δ(OH)	5.749	5.586	5.692	5.689
Δδ(OH)	--	0.163	0.057	0.060

Table S4. Chemical Shifts of -NH group of A, T, G, C before and after Interacting with 9-OHFLU in d_6-DMSO

	Chemical shifts (ppm)				
	A	**T**	**G**		**C**
	N^6	**N^3**	**N^1**	**N^2**	**N^4**
δ(NH)	7.078	10.986	10.454	6.254	7.029
δ (NH)+9-OHFLU	7.115	10.998	10.473	6.271	7.052
Δδ(NH)	0.037	0.012	0.019	0.017	0.023

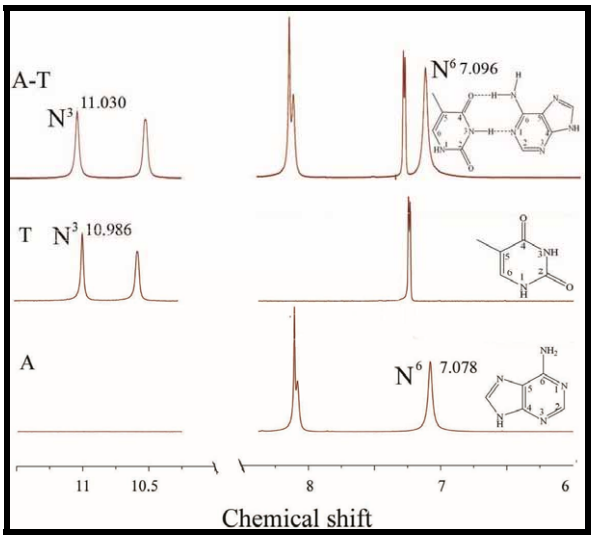

Fig. S4. ^{1}H NMR spectra of thymine, adenine and mixture with each equal molar in the d_6-DMSO. Chemical shifts were reported in parts per million (ppm) relative to tetramethylsilane as the internal standard (0.00 ppm).

Table S5. R_{CT} and ΔR_{CT} for Hairpin DNA (1) Films before and after interacting with 9-OHFLU[d]											
Circuit elements	9-OHFLU										
	0 nM	0.55nM	1nM	2nM	5.5 nM	27.5nM	55 nM	110 nM	275 nM	550 nM	1.1 μM
R_{CT} ($\Omega \cdot cm^2$)	7897	7944	7955	7974	7991	8133	8337	8784	9334	10480	10519
	(11)	(7)	(13)	(28)	(6)	(44)	(11)	(78)	(6)	(39)	(6)
ΔR_{CT}($\Omega \cdot cm^2$)	0	47(7)	58(12)	77(12)	94(6)	236(45)	440(10)	887(77)	1837(5)	2583(39)	2622(6)

[d] The values in parentheses represent the standard deviations from at least five electrode measurements.

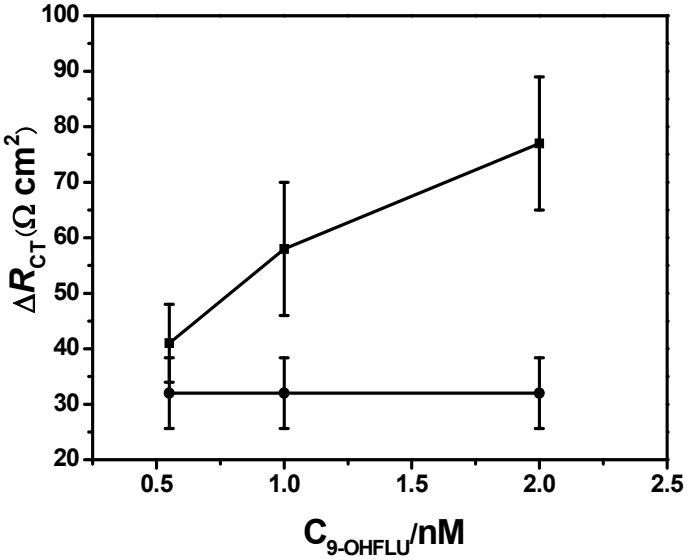

Fig. S5. Relationship between ΔR_{CT} and the concentrations of 9-OHFLU (■) ranged from 0.5 nM to 2 nM in Tris-buffer solution. The line (●) as the blank control group represented the values of ΔR_{CT} after and before incubating hairpin DNA (1) films in the solutions without 9-OHFLU. Error bars are derived from a minimum of five electrodes.

Table S6. Comparison of reported methods and the proposed method for 9-OHFLU determination

Methods	Detection limit (nM)	Recovery (%)	Reference
GC-MS	0.33	--	1
	0.13/0.74	70-74	2
	1.2	85.2	3
	1.1	70-130	4
	11	98-121	5
GC-GC-FID	0.2	69	6
LC-MS	38.5	87±6.9	7
	55	--	8
LC-DAD	2.2	103-110	9
This method	1	--	this report
	4[e]	96-102[e]	this report

[e] Detection limit and recovery in real water samples.

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