

Supporting Information

**Insertion of a Bulky Rhodium Complex
into a DNA Cytosine-Cytosine Mismatch:
An NMR Solution Study**

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Table S1. NOE contacts of the free oligonucleotide d(CGGACTCCG). All chemical shifts are relative to DSS-d₆ ($\delta = 0.000$ ppm). The chemical shifts of the non-exchangeable and exchangeable protons were measured at 10 °C and 4 °C respectively. Experimental conditions: [dsDNA] = 2.32 mM, 50 mM Pi, 20 mM NaCl, pH = 6.10(2).

Residue	H6/H8	H1'	H5/H2/Me	H2'	H2''	H3'	H4'	H5'	H5''	NH / NH ₂
C1	7.615	5.758	5.929	1.852	2.352	4.692	4.062	3.962	3.705	8.334-7.245
G2	7.921	5.477	-	2.676	2.698	4.707	4.304	4.072	3.962	13.292
G3	7.799	5.648	-	2.647	2.755	5.037	4.414	4.194	4.133	12.804
A4	8.182	6.259	7.957	2.749	2.829	4.954	4.215	4.499	4.414	-
C5	7.261	5.721	5.404	2.431	1.772	4.695	4.102	4.365	4.047	-
T6	7.615	6.051	1.689	2.369	2.534	4.891	4.238	?	4.047	14.406
C7	7.603	6.002	5.721	2.153	2.448	4.823	4.175	4.108	?	8.481-6.961
C8	7.542	5.672	5.734	2.034	2.369	4.854	4.141	4.108	4.072	8.823-7.210
G9	8.019	6.222	-	2.681	2.386	4.719	4.210	4.145	4.096	13.230

Table S2. NOE connectivities of the Rh-bound oligonucleotide. All chemical shifts are relative to DSS-d₆ ($\delta = 0.000$ ppm). The chemical shifts of the non-exchangeable and exchangeable protons were measured at 10 °C and 4 °C respectively. The two nOe walks resulting from the loss of the C₂ symmetry in the central part of the oligonucleotide are indicated as a (blue) and b (green). For A₄, only the amino protons of the a and b strands were distinguishable. Experimental conditions: [dsDNA] = 1.62 mM, [Δ -Rh(bpy-*d*₈)₂chrysi³⁺] = 1.62 mM (1 equivalent per mismatch), 50 mM Pi, 20 mM NaCl, pH = 6.10(2). § Ambiguous assignment. Line broadening and overlaps render the distinction between H5' and H5'' uncertain.

Residue	H6/H8	H1'	H5/H2/Me	H2'	H2''	H3'	H4'	H5' / H5''	NH / NH ₂
C1	7.583	5.699	5.676	1.795	2.318	4.698	4.095 [§]	3.948 - 3.948	8.333-6.905
G2	7.908	5.441	-	2.619	2.619	5.022	4.192	4.192 - 4.026	13.222
G3	7.791	5.555	-	2.622	2.642	5.051	4.351	4.130 - 4.026	13.222
A4a	7.972	6.017	7.973	2.210	2.545	4.857	4.413	4.114 - 3.974	8.421-6.959
A4b	"	"	"	"	"	"	"	"	8.323-7.208
C5a	7.661	6.083	5.741	2.239	2.366	4.817	4.413	4.049 - 3.952	-
C5b	7.557	5.829	5.881	2.261	2.398	4.897	4.660	4.017 - 3.978	-
T6a	7.615	5.744	1.946	2.199	2.369	4.875	4.420	4.140 - 3.965	12.793
T6b	7.511	5.679	1.940	2.053	2.364	4.527	4.283	4.101 - 3.978	12.793
C7	7.557	5.715	5.786	2.097	2.443	4.840	4.156	4.101 - ?	8.743-7.227
C8	7.550	5.503	5.773	2.125	2.369	4.892	4.108	4.049 - ?	8.743-7.217
G9	7.973	6.147	-	2.704	2.368	4.694	4.192	4.121 - 4.065	12.793

Table S3. Chemical shifts of the hydrogens of the chrysi ligand in the absence and presence of mismatched DNA. All chemical shifts are relative to DSS- d_6 ($\delta = 0.000$ ppm). Experimental conditions: [dsDNA] = 1.62 mM, [Δ -Rh(bpy- d_8) $_2$ chrysi $^{3+}$] = 1.62 mM (1 equivalent per mismatch), 50 mM Pi, 20 mM NaCl, pH = 6.10(2). The chemical shifts of the non-exchangeable and exchangeable protons were measured at 10 °C and 4 °C respectively.

Proton	Unbound Δ -Rh(bpy- d_8) $_2$ chrysi $^{3+}$	DNA bound by Δ -Rh(bpy- d_8) $_2$ chrysi $^{3+}$
χ_0	8.703	13.032
χ_1	8.164	7.210
χ_2	7.516	7.018
χ_3	7.767	7.923
χ_4	8.242	6.188
χ_5	8.303	7.198
χ_6	8.303	7.934
χ_7	8.059	6.984
χ_8	7.515	7.241
χ_9	7.393	7.276
χ_{10}	7.889	7.364
χ_{11}	8.703	12.900

Table S4. Intermolecular nOe between Δ -Rh(bpy-*d*₈)₂chrysi³⁺ and the oligonucleotide. The two strands, resulting from the loss of the C₂ symmetry in the central part of the oligonucleotide, are marked a and b. Experimental conditions: [dsDNA] = 1.62 mM, [Δ -Rh(bpy-*d*₈)₂chrysi³⁺] = 1.62 mM (1 equivalent per mismatch), 50 mM Pi, 20 mM NaCl, pH = 6.10(2), D₂O, 10 °C.

NOEs from a strand	NOEs from b strand
χ 1 – T6aH2''	χ 7 – C5bH1' w
χ 1 – T6aH5'/H5''	χ 7 – T6bMe
χ 1 – T6aMe	χ 8 – C5bH4'
χ 2 – C5aH1'	χ 8 – C5bH5
χ 2 – C5aH4'	χ 8 – T6bMe
χ 2 – T6aH2'	χ 9 – C5bH4'
χ 2 – T6aMe	χ 9 – T6bH2''
χ 2 – T6aH5'/H5''	χ 9 – T6bMe
χ 3 – C5aH1'	χ 10 – T6bi
χ 3 – C5aH4'	χ 11 – T6bi
χ 3 – T6aMe	

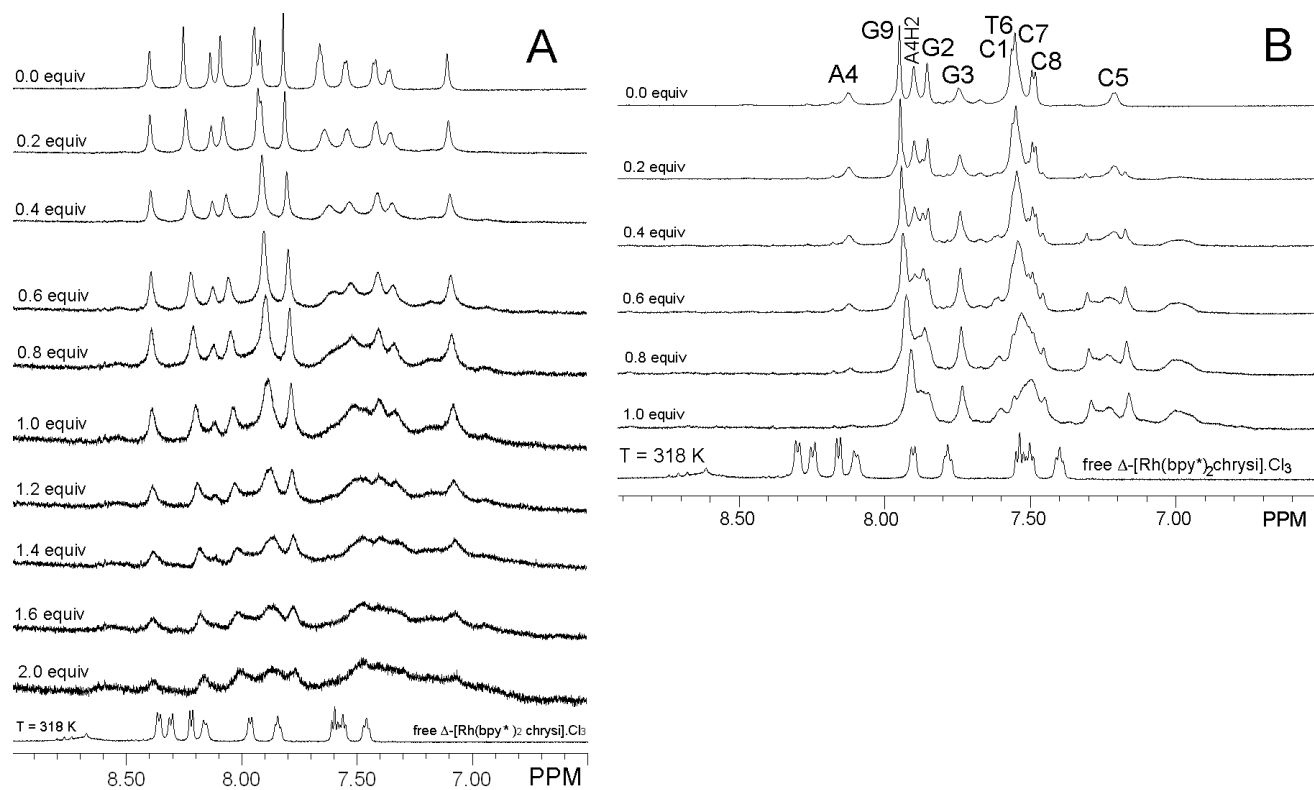


Figure S1. Titration of $\Delta\text{-Rh}(\text{bpy-}d_8)_2\text{chrysi}^{3+}$ to (a) an oligonucleotide containing two CA mismatches ($d(\text{CGATCGACCG})$, $T_m = 13^\circ\text{C}$) and (b) an oligonucleotide containing a single CC mismatch ($d(\text{CGGACTCCG})$, $T_m = 17.8^\circ\text{C}$). For clarification, only the aromatic region is represented. Experimental conditions: phosphate buffer, $I = 50\text{ mM}$, $T = 20^\circ\text{C}$, (a) $\text{pH} = 6.03$, (b) $\text{pH} = 6.10$.

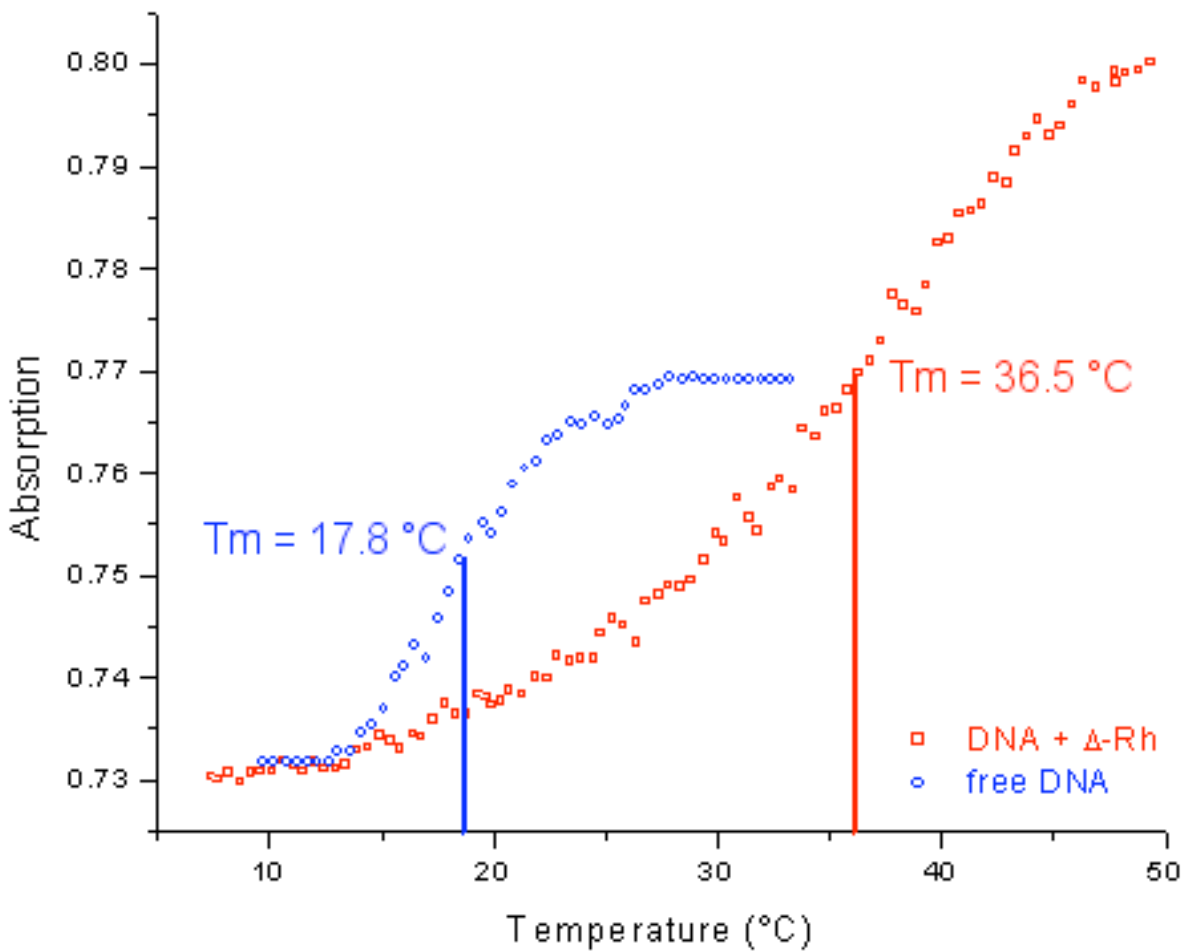


Figure S2. UV absorption at $\lambda = 260\text{ nm}$ of the free oligonucleotide (blue circle) and the metalloinsertor-bound DNA (red square). The T_m values represent the midpoint of the transition as obtained by fitting the melting profiles with a sigmoidal expression.

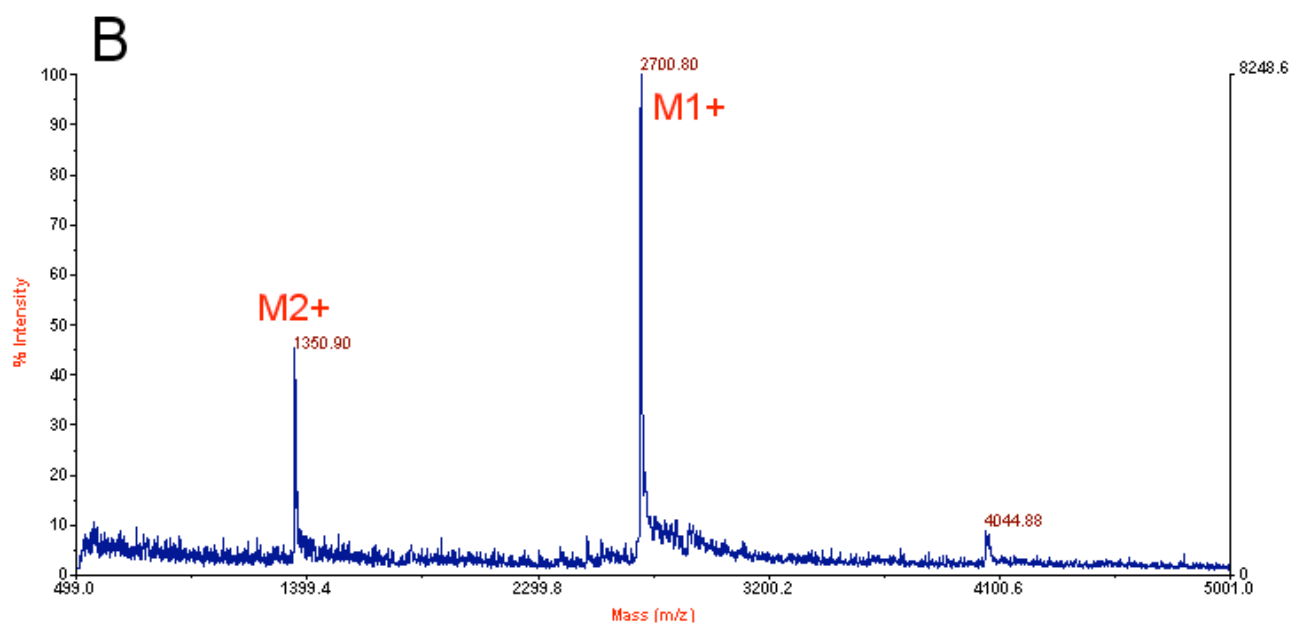


Figure S3. Photocleavage induced by the metalloinsertor. (a) MALDI-TOF mass spectrum obtained after 1 hour of irradiation with a solar simulator. The products correspond to cleavage at the T₆ neighboring the CC mismatch. (b) MALDI-TOF mass spectrum obtained on an identical sample without photo-irradiation. The M¹⁺ and M²⁺ peaks correspond to the uncleaved 5'-CGGACTCCG-3' oligonucleotide.

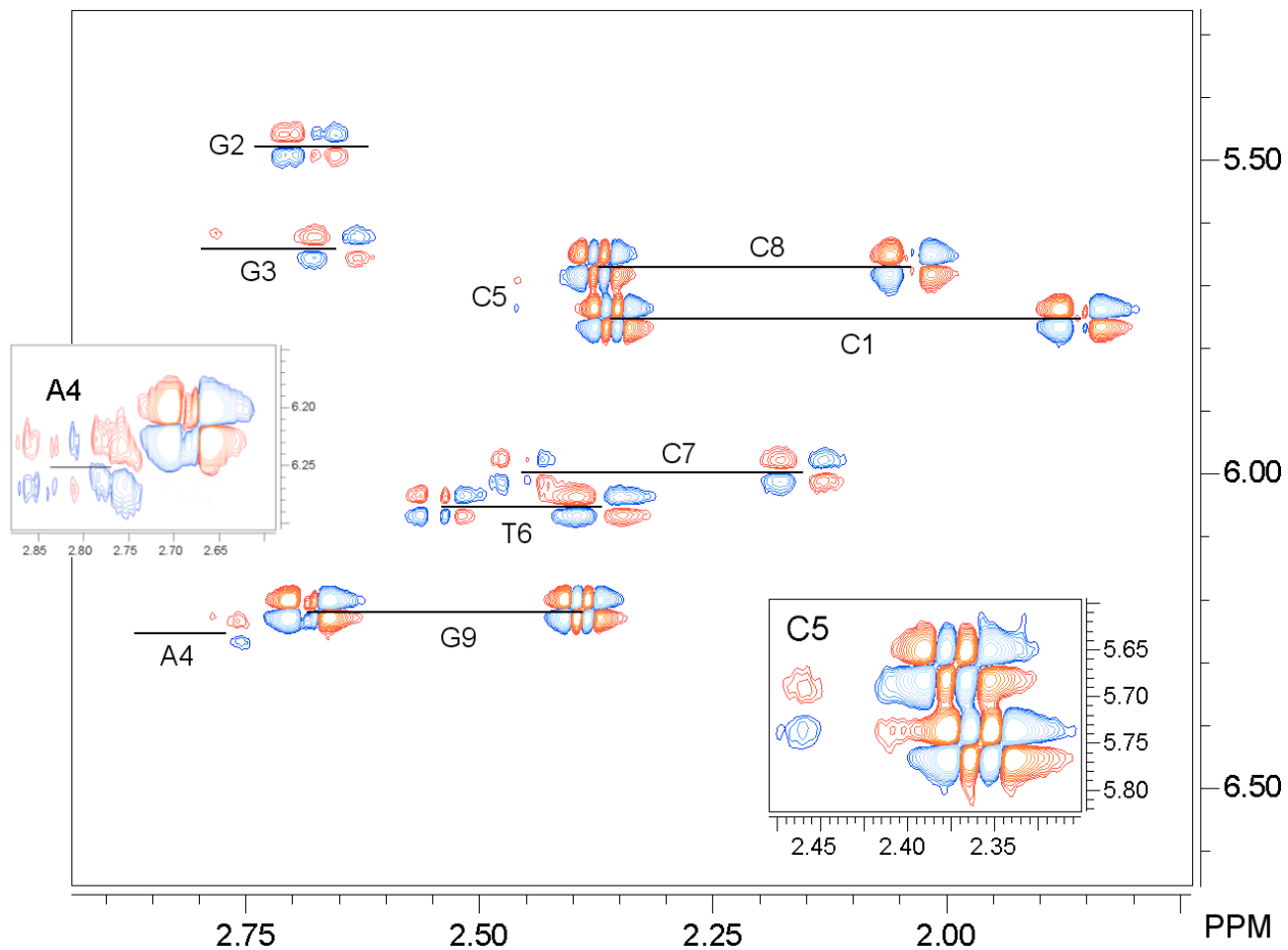


Figure S4. 2D DQF-COSY sub-spectrum of the free oligonucleotide at 10 °C ($F2 \times F1 : H2'-H2'' \times H1'$). The crosspeak patterns indicate the conformation of the sugars. All sugars, including that of the mismatched cytosine, maintain the C_2' -endo pucker. Inserts: the crosspeaks associated to the A4 and C5 sugars are only visible at a lower signal-to-noise resolution.

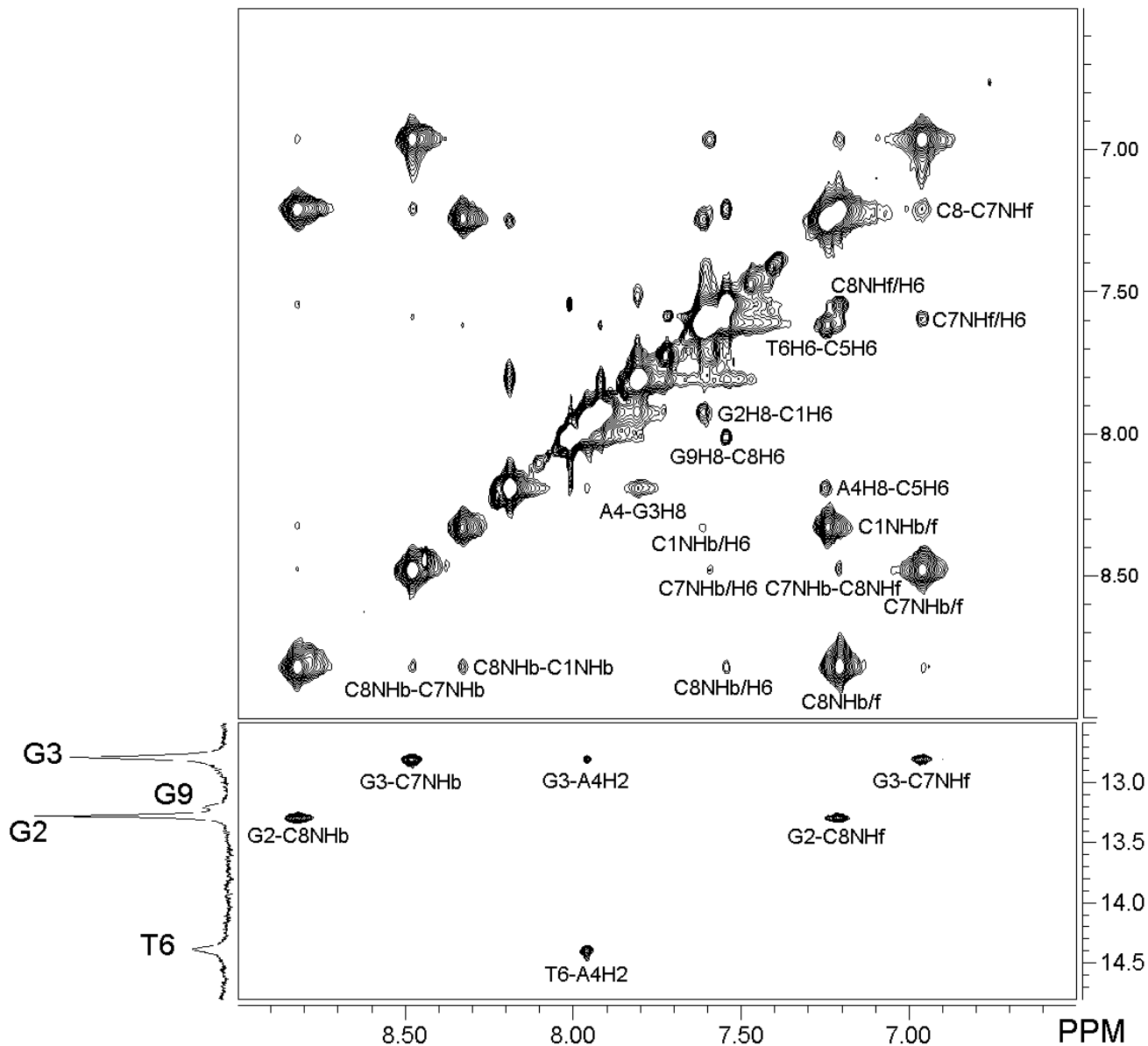


Figure S5. NOESY sub-spectra and assignments of the nOe contacts between the exchangeable protons of the free oligonucleotide (upper part: F2 \times F1 : aromatic + amino \times aromatic + amino; lower part: F2 \times F1 : aromatic + amino \times imino). The chemical shifts and the crosspeaks of the imino and amino protons indicate that all bases are Watson-Crick paired. No correlation is observed for the C-C mismatch, suggesting that the two cytosines are probably paired by a single hydrogen bond in a Wobble-type conformation. NHb and NHf correspond to the bound and free amino protons respectively. Experimental conditions: H₂O, 4 °C, 300 ms mixing time.

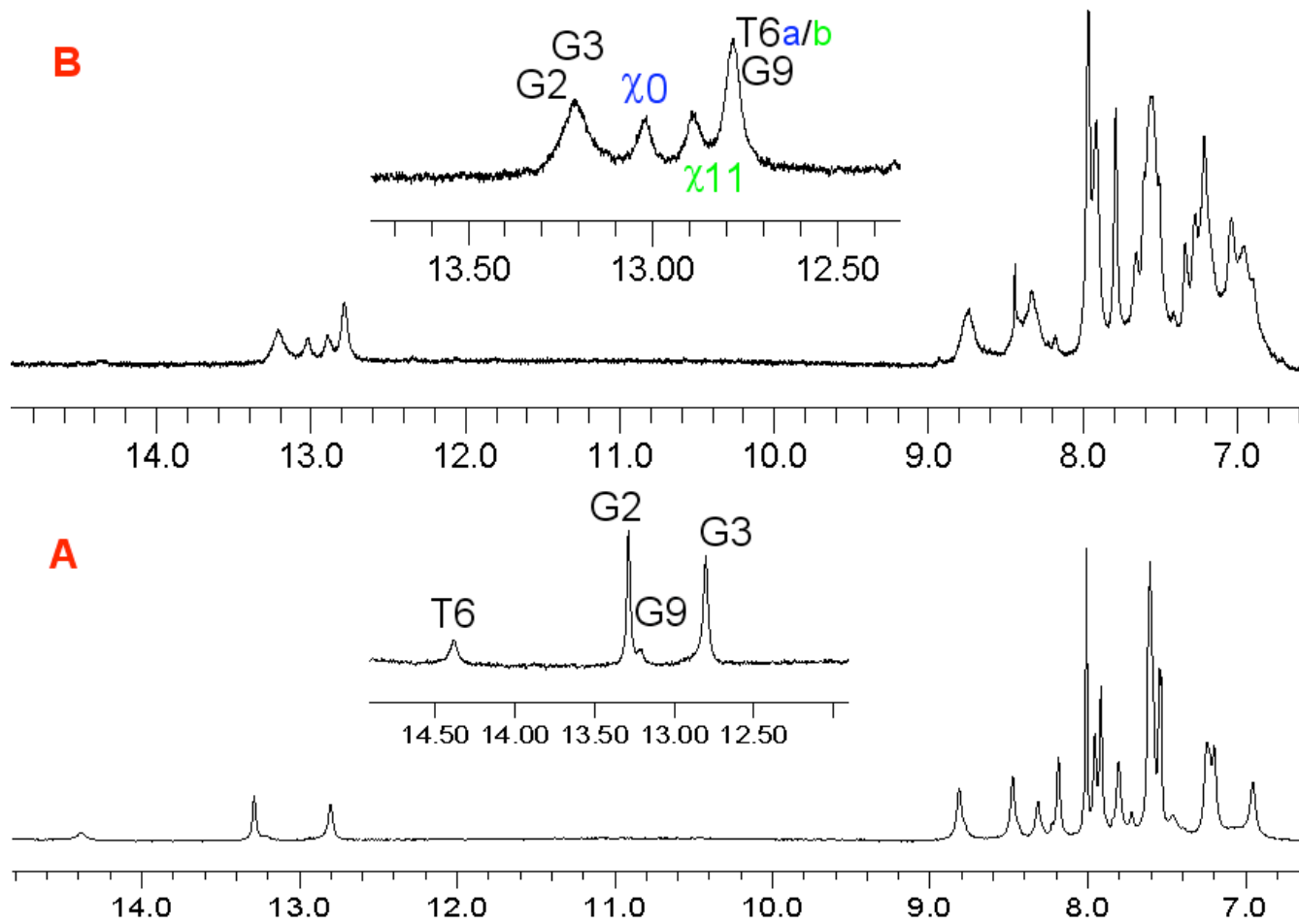


Figure S6. 1D ^1H sub-spectra of the aromatic, amino and imino protons of (a) the free oligonucleotide and (b) $\Delta\text{-Rh}(\text{bpy-}d_8)_2\text{chrysi}^{3+}$ inserted in the DNA-Rh adduct. Experimental conditions, H_2O , 4°C .

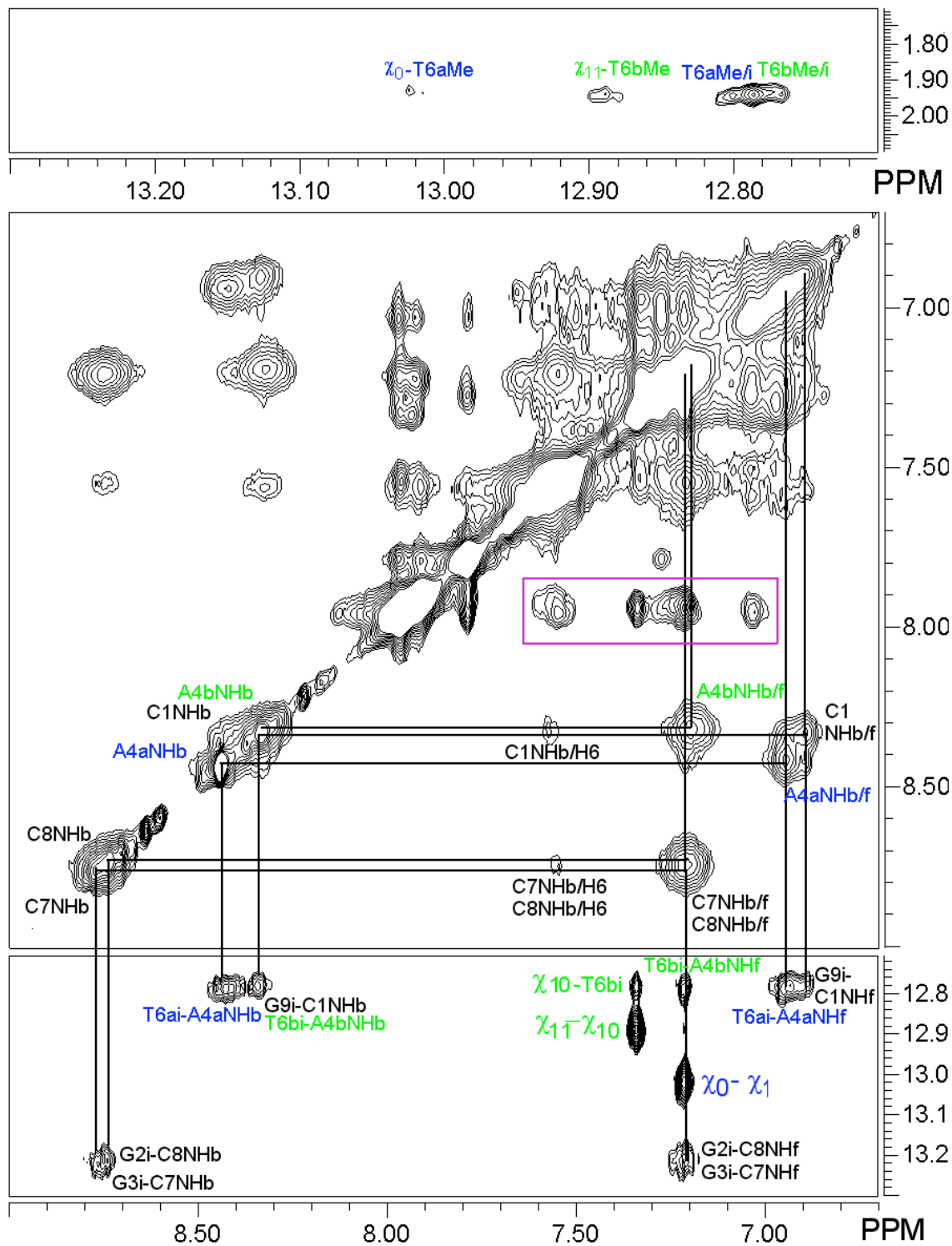


Figure S7. NOESY sub-spectra and assignments of the NOE contacts between the exchangeable protons of the Rh-bound DNA. (lower part: F2 \times F1 : aromatic + amino \times imino; medium part: F2 \times F1 : aromatic + amino \times aromatic + amino; upper part: F2 \times F1 : imino \times T6Me groups). NHb and NHf correspond to the bound and free amino protons respectively. Loss of the C₂ symmetry in the central part of the oligonucleotide results in two unequivalent strands labeled a (blue) and b (green). Intramolecular nOe correlations between chrysi protons (labelled χ) are indicated by a purple rectangle. Experimental conditions: H₂O, 4 °C, 300 ms mixing time.

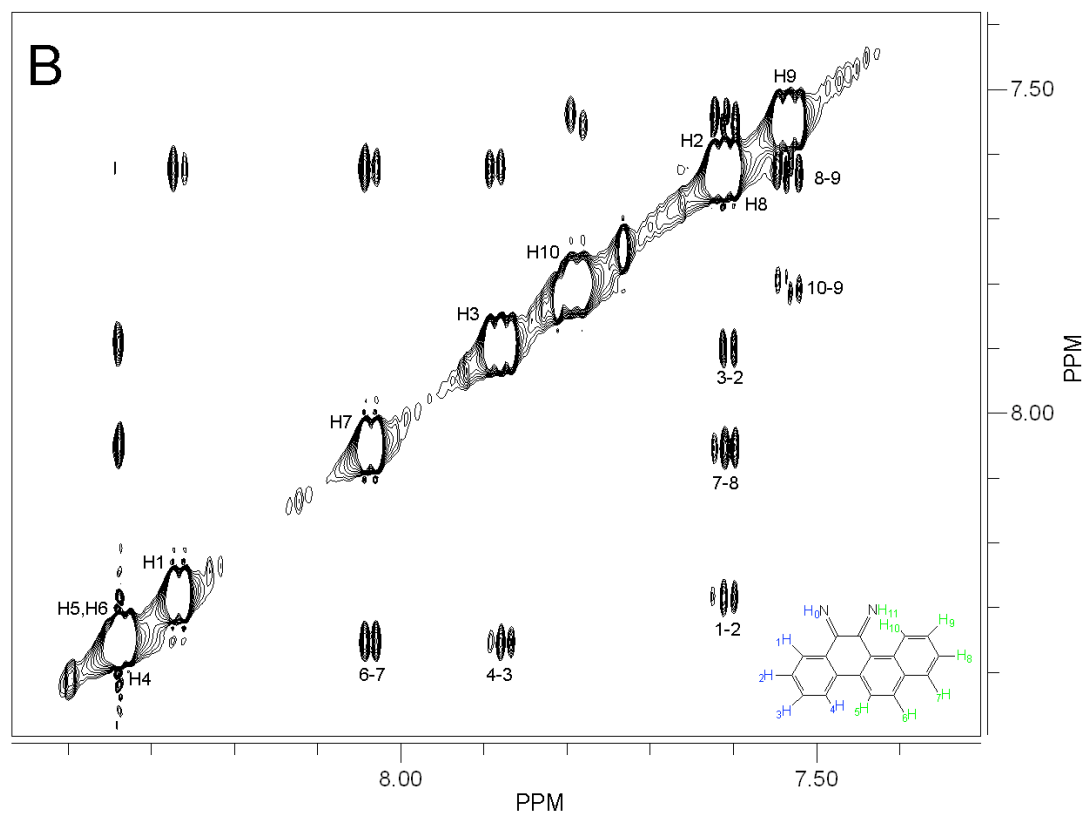
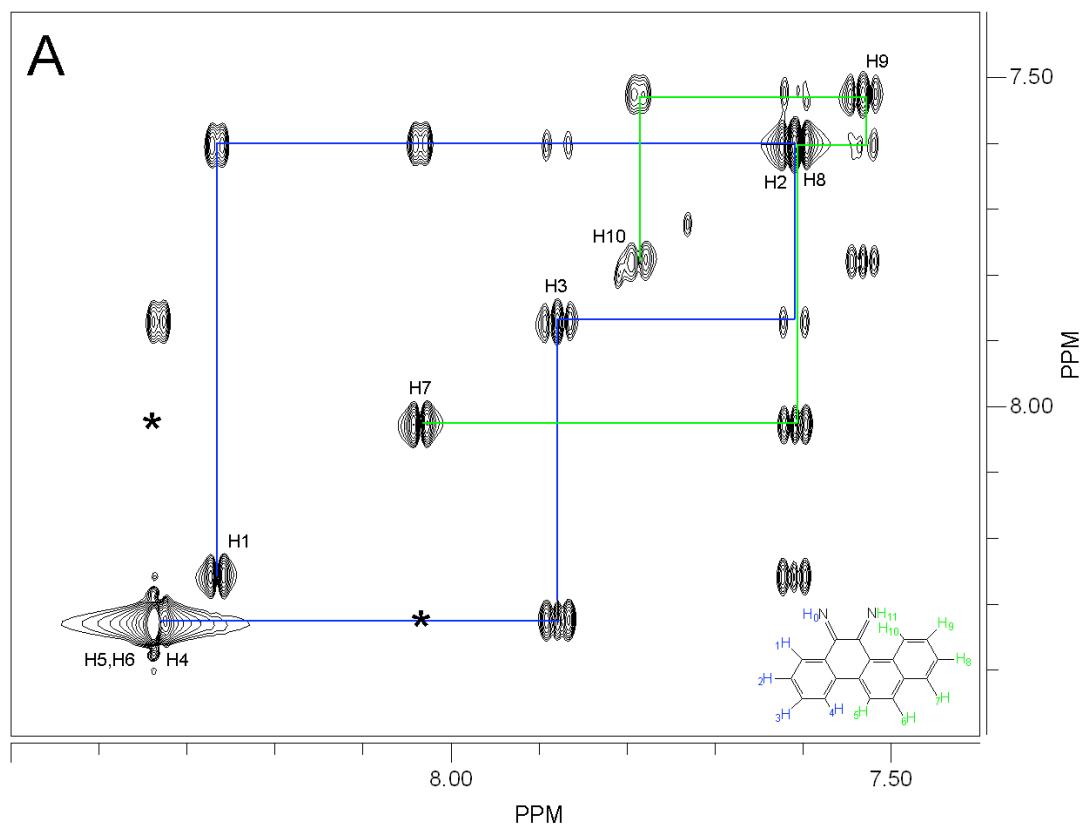


Figure S8. (a) COSY and (b) NOESY sub-spectra and assignments of the aromatic protons of the chrysi ligand of unbound Δ -Rh(bpy-*d*₈)₂chrysi³⁺ (D₂O, 20 °C). In the COSY spectrum two chains of scalar correlations match the two spin systems of the ligand. * Weak correlations observable only at low signal-to-noise resolution.