Electronic Supplementary Material (ESI) for Dalton Transactions.

Competitive formation of DNA linkage isomers by a trinuclear platinum complex and the influence of pre-association

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Supporting Information

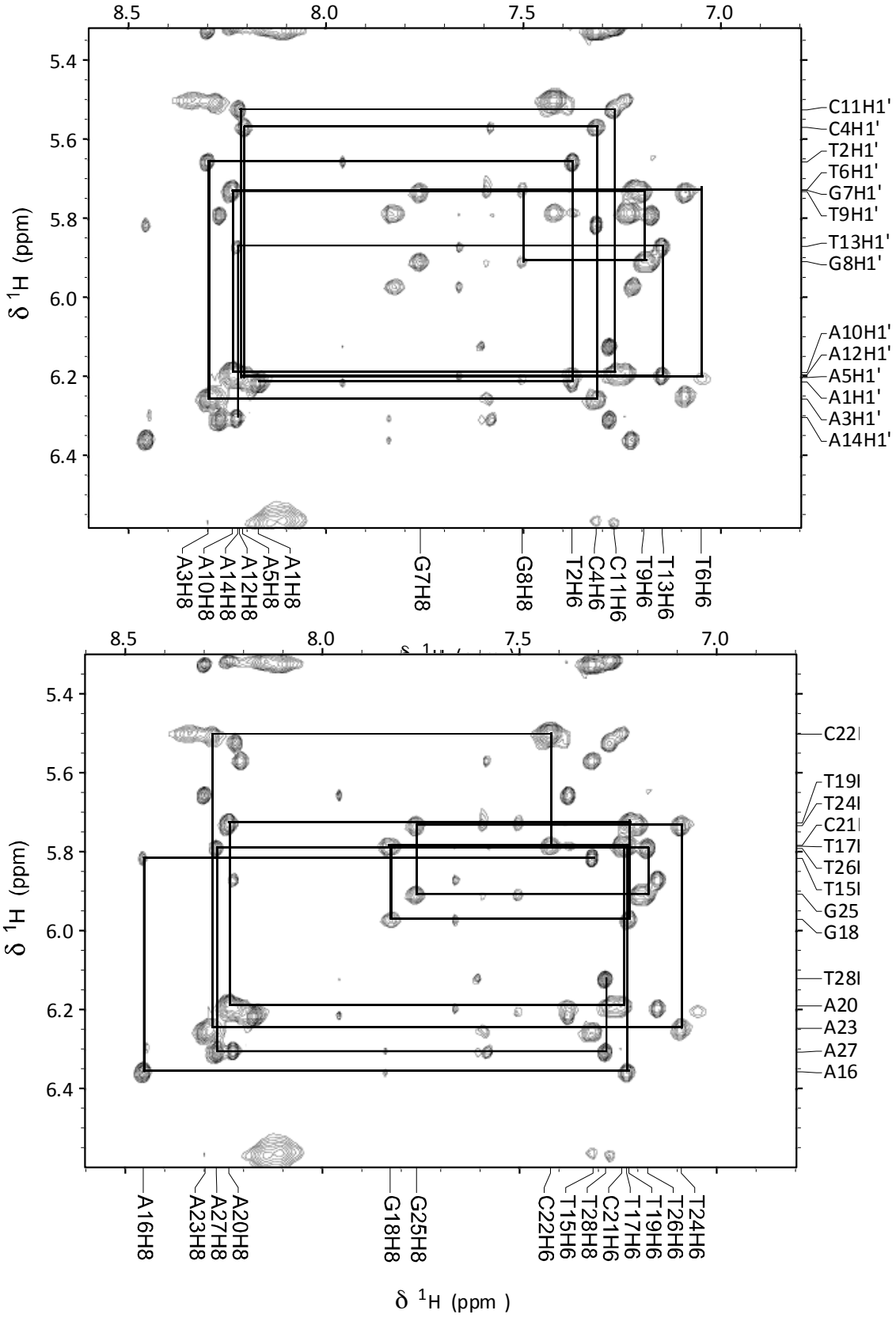

Figure S1a. Contour plot of the 2D ^{1}H NOESY NMR spectrum (mixing time = 150 ms) of duplex **I** (in 200 mM NaOAc, 5% D_2O in H_2O) at 298 K, showing the H6/H8 aromatic (8.5 – 6.9 ppm) to sugar ring H1′ (6.6 – 5.4 ppm) connectivities. The sequential NOESY assignment walks are shown for the –GG- strand (**Ia**) and for the complementary –CC- strand (**Ib**) and are in accordance with the published data (J. A. Parkinson, Y. Chen, Z. Guo, S. J. Berners-Price, T. Brown and P. J. Sadler, *Chem. Eur. J.*, 2000, 6, 3636-3644).

Table S1 – ^{1}H NMR chemical shifts of duplex **I** (298 K) showing the shifts that occur on addition of **0** (2:1 ratio).[a]

	H6		H8		H2				Me		H1'		H2'		H2''		NH		H4(1)		H4(2)	
A1			8.17	(0.00)	7.95	(-0.03)					6.20	(-0.02)	2.65	(-0.01)	2.80	(0.00)						
T2	7.37	(-0.01)							1.45	(-0.01)	5.58	(-0.06)	2.16	(-0.01)	2.40	(-0.03)						
A3			8.31	(0.00)	7.64	(0.03)					6.24	(-0.01)	2.75	(0.02)	2.90	(-0.01)						
C4	7.34	(0.01)					5.36	(0.03)			5.46	(-0.08)	2.06	(-0.01)	2.36	(-0.04)			6.58	(0.01)	8.07	(-0.04)
A5			8.25	(0.03)	7.53	(0.01)					6.20	(0.01)	2.68	(0.04)	2.88	(-0.01)						
T6	7.09	(0.04)							1.41	(0.05)	5.59	(-0.09)	1.87	(-0.03)	2.25	(-0.03)	13.50	(-0.01)				
G7			7.80	(0.03)							5.53	(-0.10)	2.68	(0.04)	2.68	(-0.01)	12.67	(0.08)				
G8			7.67	(0.05)							5.90	(-0.01)	2.51	(0.02)	2.70	(-0.01)	12.67	N/A				
T9	7.20	(-0.01)							1.42	(0.05)	5.57	(-0.12)	2.03	(-0.03)	2.32	(-0.11)	13.45	(0.00)				
A10			8.29	(0.03)	7.62	(0.20)					6.14	(-0.04)	2.76	(0.07)	2.85	(-0.01)						
C11	7.33	(0.05)					5.41	(0.08)			5.43	(-0.06)	2.01	(0.01)	2.32	(-0.01)			6.62	(0.04)	8.11	(-0.04)
A12			8.25	(0.03)	7.71	(0.04)					6.19	(0.00)	2.63	(0.04)	2.82	(0.02)						
T13	7.16	(-0.00)							1.53	(0.03)	5.82	(-0.04)	1.89	(-0.02)	2.23	(-0.02)						
A14			8.22	(-0.01)	7.59	N/A					6.30	(0.00)	2.47	(0.01)	2.67	(0.01)						
T15	7.32	(0.01)							1.58	(0.02)	5.79	(-0.02)	1.79	(0.01)	2.20	(-0.00)						
A16			8.46	(0.00)	7.83	(-0.01)					6.33	(-0.01)	2.88	(0.00)	2.99	(-0.02)						
T17	7.25	(0.01)							1.45	(0.01)	5.71	(-0.05)	2.14	(-0.02)	2.43	(-0.04)	13.36	(0.03)				
G18			7.85	(0.03)							5.92	(-0.03)	2.61	(0.03)	2.69	(-0.03)	12.45	(0.05)				
T19	7.23	(0.01)							1.46	(0.05)	5.57	(-0.11)	2.04	(-0.03)	2.31	(-0.14)	13.48	(0.05)				
A20			8.29	(0.03)	7.60	(0.18)					6.14	(-0.04)	2.76	(0.09)	2.85	(-0.02)						
C21	7.31	(0.04)					5.32	(0.07)			5.79	(0.00)	1.97	(-0.03)	2.36	(-0.04)			6.45	(0.02)	7.91	(-0.04)
C22	7.45	(0.01)					5.57	(0.05)			5.30	(-0.15)	2.08	(-0.00)	2.35	(-0.04)			6.73	(0.04)	8.30	(-0.04)
A23			8.31	(0.02)	7.65	(0.10)					6.23	(0.00)	2.72	(0.05)	2.92	(-0.01)						
T24	7.14	(0.04)							1.48	(0.03)	5.64	(-0.04)	2.05	(-0.00)	2.37	(-0.01)	13.36	(-0.12)				
G25			7.80	(0.03)							5.89	(-0.00)	2.57	(0.02)	2.67	(-0.01)	12.41	(0.05)				
T26	7.19	(0.01)							1.45	(0.02)	5.73	(-0.03)	2.00	(0.01)	2.36	(-0.03)	13.48	(0.12)				
A27			8.30	(0.03)	7.65	(0.03)					6.31	(0.00)	2.77	(0.03)	2.85	(0.01)						
T28	7.29	(-0.01)							1.55	(0.00)	6.12	(0.00)	N/A	N/A	N/A	N/A						

[a] Numbers in brackets are the changes in chemical shift of the protons of the duplex upon addition of 2 mol. equiv. of the complex, i.e. $\Delta\delta = \delta$ (**I**:**0**) – δ (**I**).

Table S2 – Energies of minimised structures from the production dynamics simulation of **0** (non-relativistic DFT Hirshfeld charges) docked at the G18 site of duplex **I**.

Time (ps)	Energy (cal mol^{-1})
491 – 520	-1.7770×10^5
1631 – 1660	-1.7818×10^5
4601 – 4630	-1.7781×10^5
4961 – 4990	-1.7789×10^5
6371 – 6400	-1.7769×10^5
6731 – 6760	-1.7767×10^5
7871 – 7900	-1.7780×10^5
9161 – 9190	-1.7790×10^5

Table S3 – Energies of minimised structures selected from the production dynamics simulation of **0** (non-relativistic DFT Hirshfeld charges) with the GG duplex with the complex docked at the G25 site.

Time (ps)	Energy (cal mol^{-1})
491 – 520	-2.0295×10^5
1181 – 1210	-2.0283×10^5
1631 – 1660	-2.0252×10^5
3161 – 3190	-2.0238×10^5
4481 – 4510	-2.0261×10^5
6191 – 6220	-2.0291×10^5
6761 – 6790	-2.0243×10^5
7811 – 7840	-2.0293×10^5
8831 – 8860	-2.0248×10^5
9551 – 9580	-2.0302×10^5

Scientist equation file used in the fitting of combined monofunctional and combined product species of ^{15}N-**1** with duplex **I**.

```
// MicroMath Scientist Model File
// Simplified - combined total for product and monofunctional
IndVars: T
DepVars: A, B, C, D, L
Params: KAB, KBC, KCD,
A'=-KAB*A
B'=KAB*A-KBC*B*L
C'=KBC*B*L-KCD*C
D'=KCD*C
L'=-KBC*B*L
// A=1, B=aqua/Cl (2), C=monofunctional (3,4), D=product (5), L= duplex I
// Initial Conditions
T=0.0
A=0.0016
B=0.000
C=0.000
D=0.0
L=0.002
***
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