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Supporting information

## Convertible and Conformationally Constrained Dinucleotides (C<sub>2</sub>NAs) Based on Neutral Dioxo-1,3,2-Oxaza-Phosphorinane Modified Backbone, Synthesis, Structural Studies, Behaviour Within Deoxyoligonucleotides and Conjugation

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Table S1: MALDI-Tof MS of oligonucleotides and retention time in HPLC (column Waters X-bridge OST  $C_{18}$  2.5  $\mu$ , 50 x 4.5mm, gradient 95% of A to 85% of A in B, A: TEAA buffer 50 mM, pH 7.0; B: ACN

Entry	Name	Seq	Mass Th	Mass Obs	Rt HPLC (min)
1 2	ODN1	GCGCTTGCCG CGGCAAGCGC	3020.0 3038.0	3016.9 3034.5	4.00 3.02
3	ODN2	GCGCTTGCCG	3084.1	3080.2	4.94
4	ODN 7	GCGC <mark>TT</mark> GCCG	3084.1	3080.5	4.94
5 6	ODN 3	GCGTTTTTTGCT AGCAAAAAACGC	3633.4 3656.5	3632.3 3655.0	5.17 4.13
7	ODN 4	GCGTTTTTTGCT	3697.4	3695.8	6.11
8	ODN 5	GCGTT <b>TT</b> TTGCT	3697.4	3695.3	6.23
9	ODN 6	GCGTTTTTTGCT	3697.4	3695.7	6.16
10	ODN 8	ATCCTATTTTTAGGAT	4861.2	4859.1	5.96
11	ODN 9	ATCCTATTTTAGGAT	4925.2	4921.9	6.68
12	ODN 10	ATCCTATTTTAGGAT	4925.2	4922.1	6.52
13	ODN 11	ATCCTAT <b>TT</b> TTAGGAT	4925.2	4921.6	6.88
14	0DN 12	ATCCTATTTTAGGAT	4925.2	4922.9	7.40
15	ODN 13	GAT TTG CAT A <b>TT</b> CAT GAG	5592.7	5590.5	6.92

16	f-ODN 2	GCGC <mark>TT</mark> GCCG Fluorescein	3544.4	3544.2	4.65
17	f-ODN 4	GCGTTTTT <mark>TT</mark> GCT I Fluorescein	4157.8	4151.9	6.10
18	f-ODN 10	ATCCTATT <mark>TT</mark> TAGGAT I Fluorescein	5385.6	5390.5	6.97
19	f-0DN 13	GAT TTG CAT A <mark>TT</mark> CAT GAG Fluorescein	6053.1	6124.5 (+3 Na)	6.83

## Figure S1: Typical HPLC profile and UV spectra of synthesis of f-ODN 4 from ODN 4 by CuAAC. a) t=o, b) t=1h and c) After NAP G25 filtration











Figure S6. Thermal denaturation curves for bulges made with GATTTGCATA*TT*CATGAG (Table 5) Abs where  $TT = \alpha, \beta$ -C<sub>2</sub>NA gauche(+), and ODN 14 to 20 of decreasing size.





Figure S8. Thermal denaturation curves for bulges made with GATTTGCATA*TT*CATGAG (Table 6) Abs where  $TT = \alpha, \beta$ -C<sub>2</sub>NA gauche(+), and ODN 21 to 26 of increasing size.



Figure S9. Thermal denaturation curves for ODNs conjugated with fluorescein and featuring Abs an  $\alpha$ ,  $\beta$ -C<sub>2</sub>NA.

