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Supporting Information

Relative Strand Orientation in a DNA Duplex Controls the Nuclearity of a Metal-Mediated Base Pair

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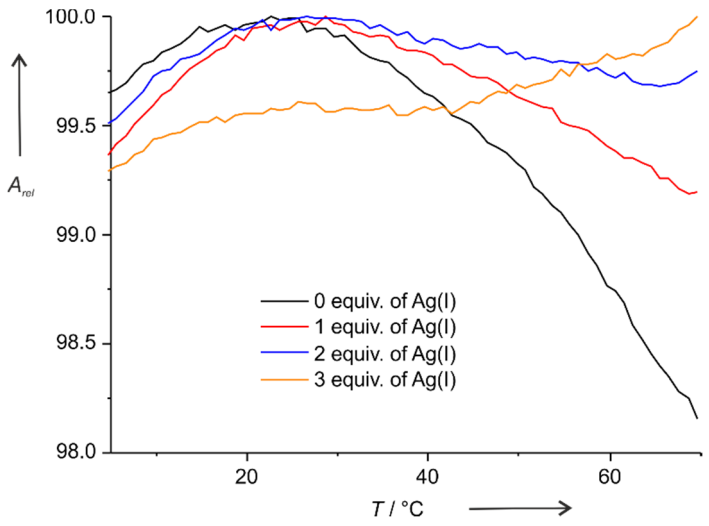


Figure S1. Melting curves of ODN2 in the presence of increasing amounts of Ag(I). Experimental conditions: 3 μM ODN2, 0→9 μM $AgClO_4$, 150 mM $NaClO_4$, 5 mM MOPS (pH 6.8). The absence of any cooperative melting is evident.

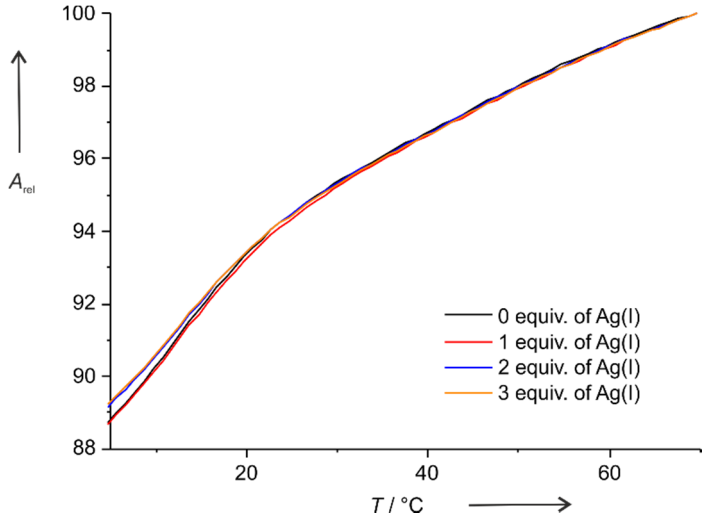


Figure S2. Melting curves of duplex **II** under near-neutral conditions in the presence of increasing amounts of Ag(I) (experimental conditions: 3 μM duplex, 0→9 μM $AgClO_4$, 500 mM $NaClO_4$, 5 mM MOPS (pH 6.8)). Evidently, no Ag(I)-mediated base pair is formed under these conditions. A comparison with the melting curves obtained at pH 5.5 (Figure 3a) clearly demonstrates two facts: 1) Slightly acidic conditions are essential for the formation of a stable parallel-stranded duplex with a metal-mediated base pair. 2) Even in the absence of Ag(I), the (highly unstable) duplex is more stable at lower pH, as evident from the larger hyperchromicity upon its melting (pH 5.5: 85% → 100%; pH 6.8: 89% → 100%).

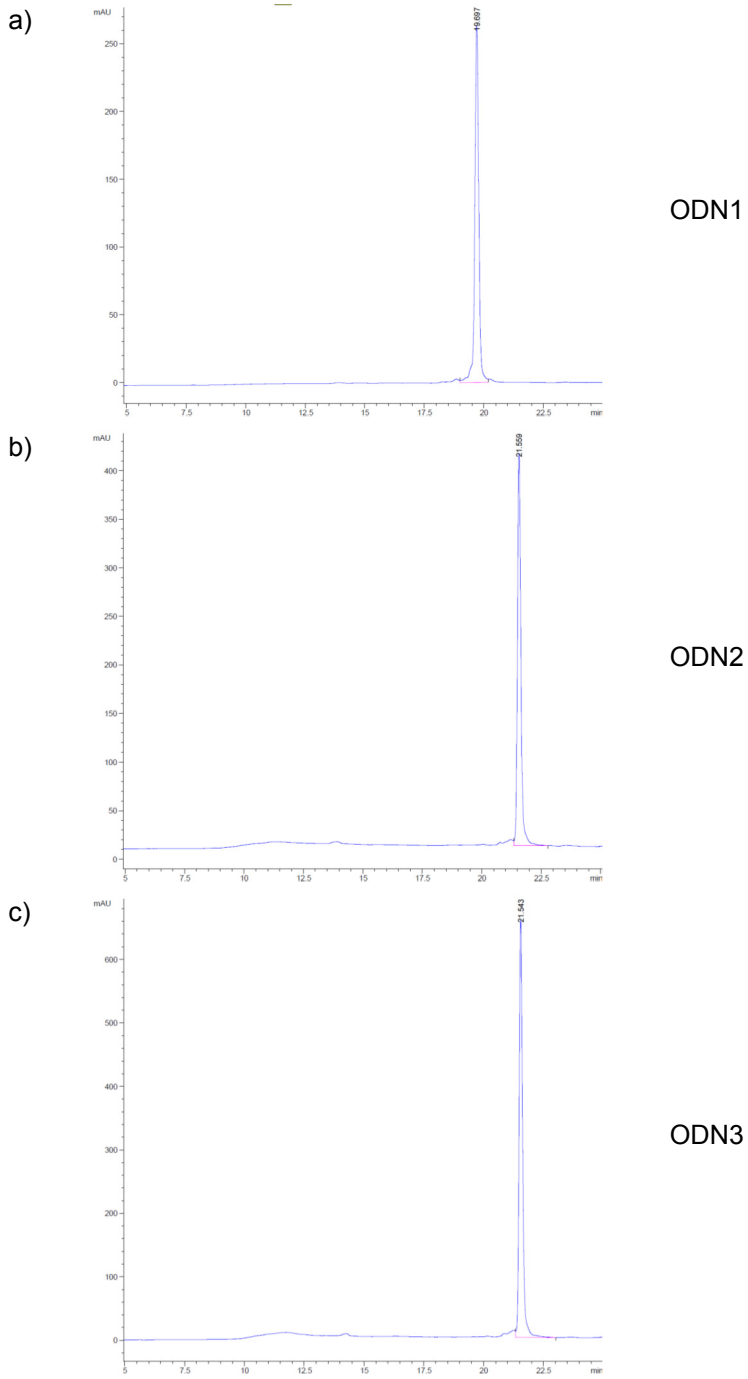


Figure S3. HPLC traces of purified oligonucleotides a) ODN1, b) ODN2, c) ODN3; *x* and *y* axes show the retention time and the UV absorbance at 254 nm, respectively. A Macherey-Nagel NUCLEODUR C18 HTec column (5 μm) was used in combination with the following eluents at a flow rate of 1 mL/min: triethylamine : acetic acid (1 : 1) 100 mM in water (solvent A) and triethylamine : acetic acid (1 : 1) 100 mM in water : CH_3CN (1 : 4) (solvent B). Gradient applied: 0–5 min, 3% B; 5–45 min, 3–40% B; 45–53 min, 100% B.

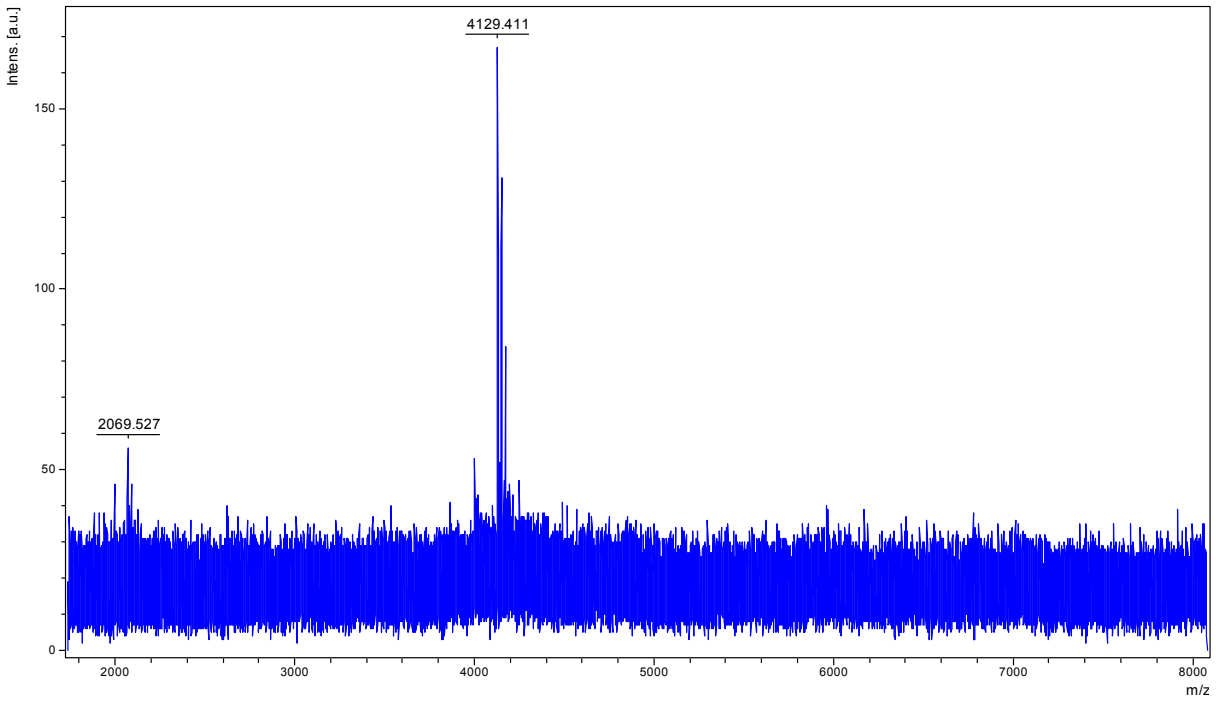


Figure S4. MALDI-ToF mass spectrum of ODN1. Calcd for ($C_{132}H_{158}N_{65}O_{69}P_{12}$) [*M*+H]$^+$: 4129 Da.

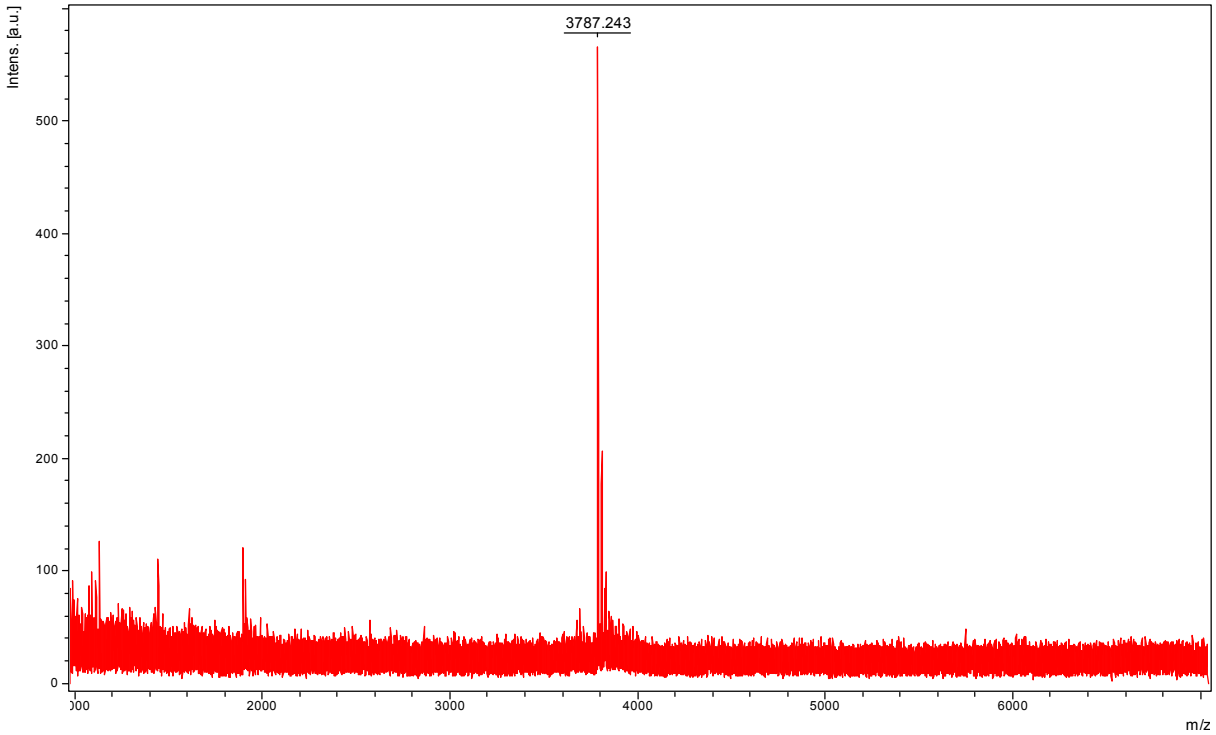


Figure S5. MALDI-ToF mass spectrum of ODN2. Calcd for ($C_{123}H_{163}N_{33}O_{82}P_{12}$) [*M*+H]$^+$: 3787 Da.

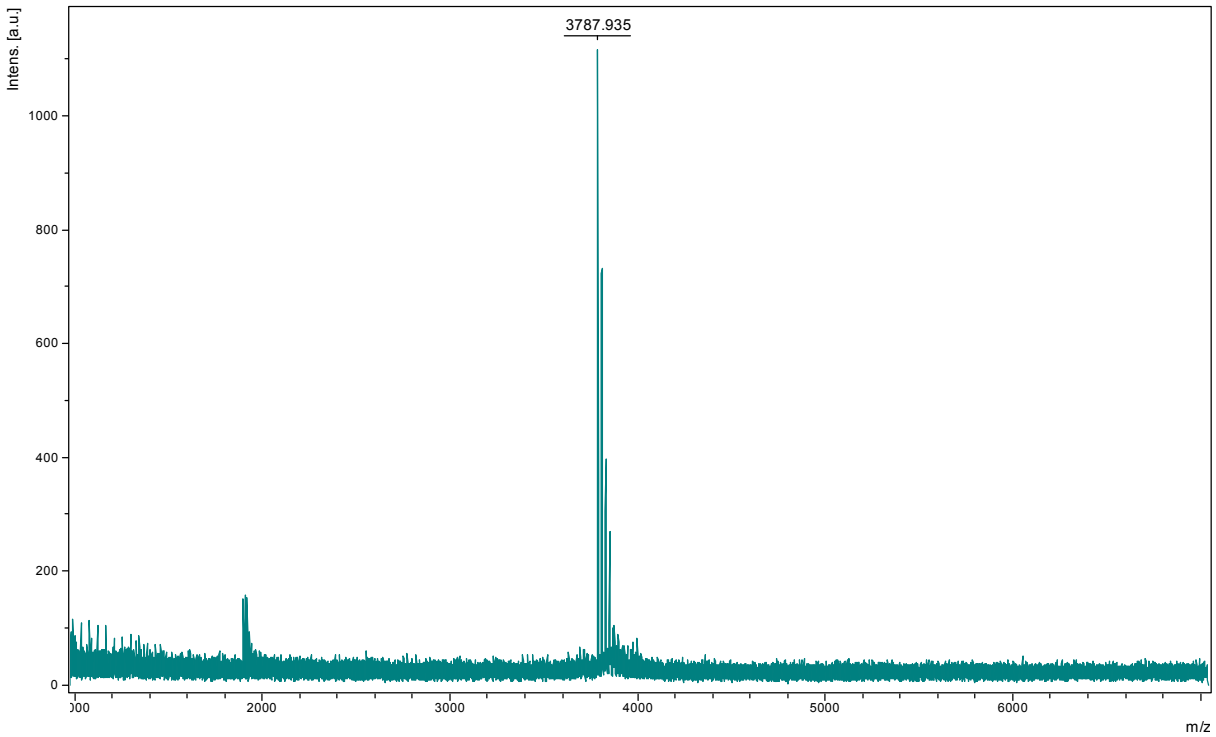
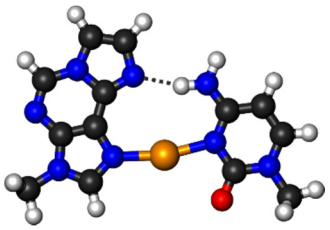


Figure S6. MALDI-ToF mass spectrum of ODN3. Calcd for ($C_{123}H_{163}N_{33}O_{82}P_{12}$) [*M*+H]$^+$: 3787 Da.

Computational methods

For the DFT calculations, the GAUSSIAN 09 package[1] was used, where the Kohn-Sham molecular orbitals were calculated using the PBE0 hybrid exchange-correlation functional[2] and SDD basis set.[3]

Cartesian coordinates of the geometry-optimized structures



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Ag	-0.607700	-0.730900	0.000100
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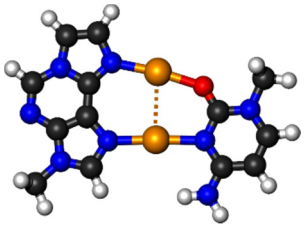

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H	-6.046700	-2.138000	0.000000
H	-4.575100	-2.620100	-0.886400
H	-4.577200	-2.618500	0.891000

References

[1] GAUSSIAN 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

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