An artificial base pair mediated by hydrogen bonding *and* metal-ion binding

*Fabian-Alexander Polonius and Jens Müller**

University of Dortmund, Department of Chemistry, 44227 Dortmund, Germany

jens.mueller@uni-dortmund.de

www.muellerlab.org

Supporting Information

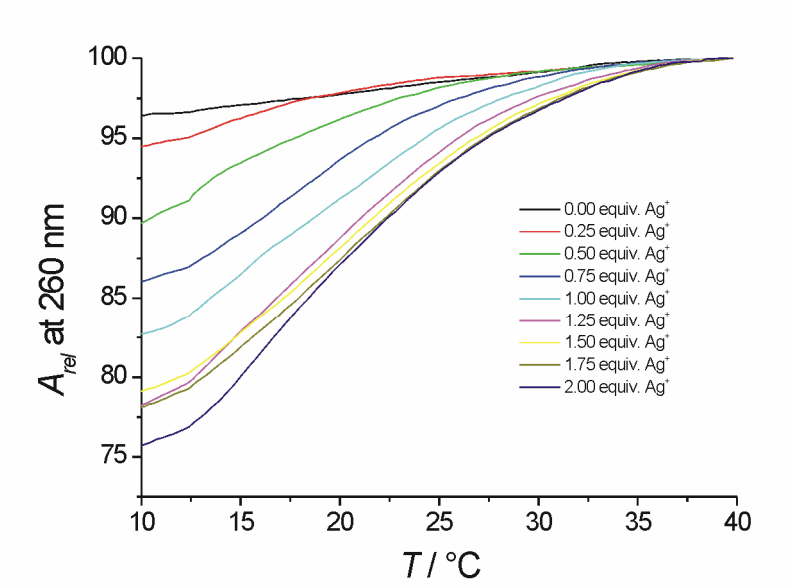

Figure S1: Melting curves of d(ADADADADA) · d(T_9) in the presence of various equivalents of $AgNO_3$. One equivalent of Ag^+ corresponds to one Ag^+ per 1-deazaadenine 2′-deoxyribonucleoside. Conditions: 1 µM d(ADADADADA), 1 µM d(T_9), 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

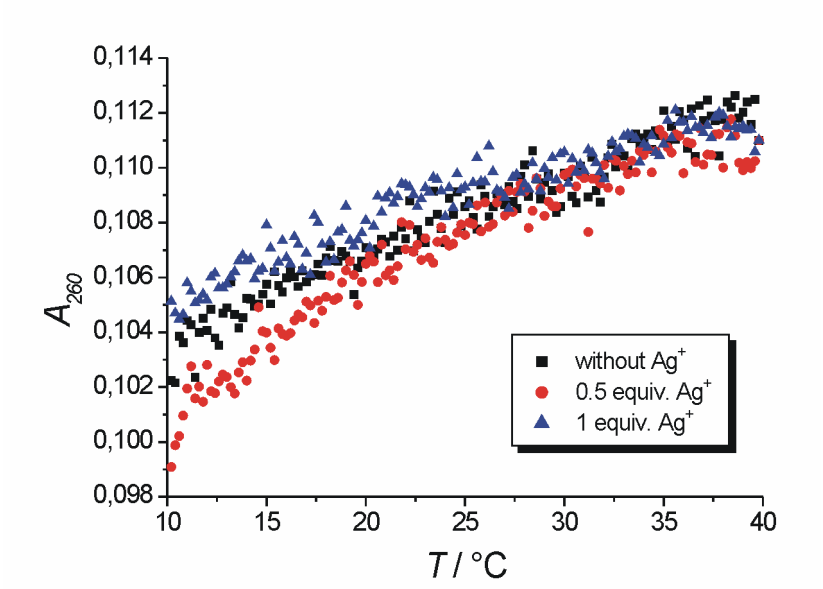

Figure S2: Melting curves of d(ADADADADA) in the presence of various equivalents of $AgNO_3$. For reasons of better comparability, one equivalent of Ag^+ corresponds to the same concentration of Ag^+ that was used with d(ADADADADA) · d(T_9). Conditions: 1 µM d(ADADADADA), 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

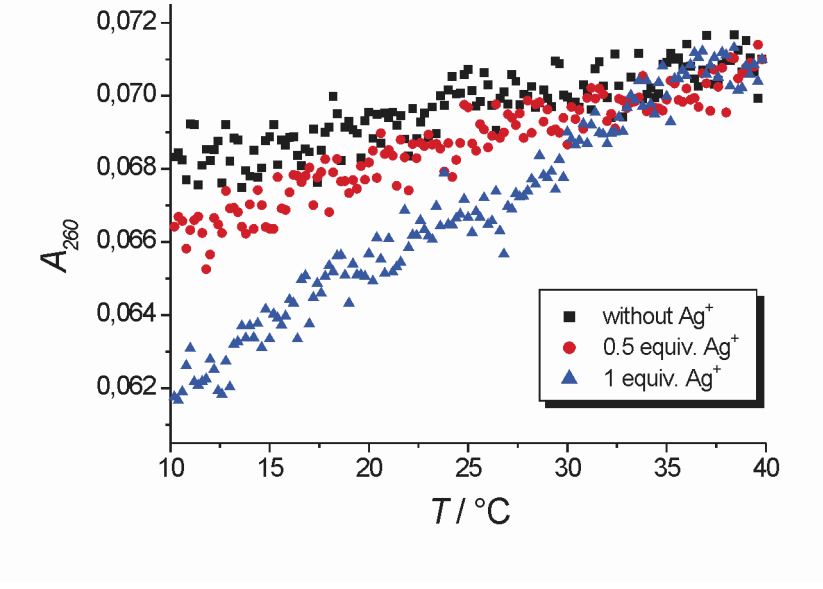

Figure S3: Melting curves of d(T_9) in the presence of various equivalents of $AgNO_3$. For reasons of better comparability, one equivalent of Ag^+ corresponds to the same concentration of Ag^+ that was used with d(ADADADADA) · d(T_9). Conditions: 1 µM d(T_9), 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

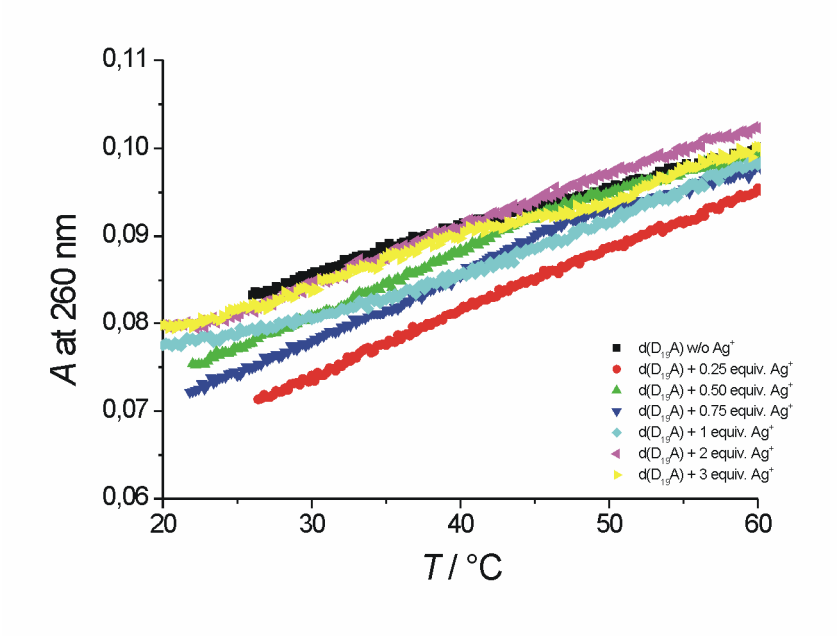

Figure S4: Melting curves of $d(D_{19}A)$ in the presence of various equivalents of $AgNO_3$. One equivalent of Ag^+ corresponds to one Ag^+ per nucleoside. Conditions: 0.5 µM $d(D_{19}A)$, 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

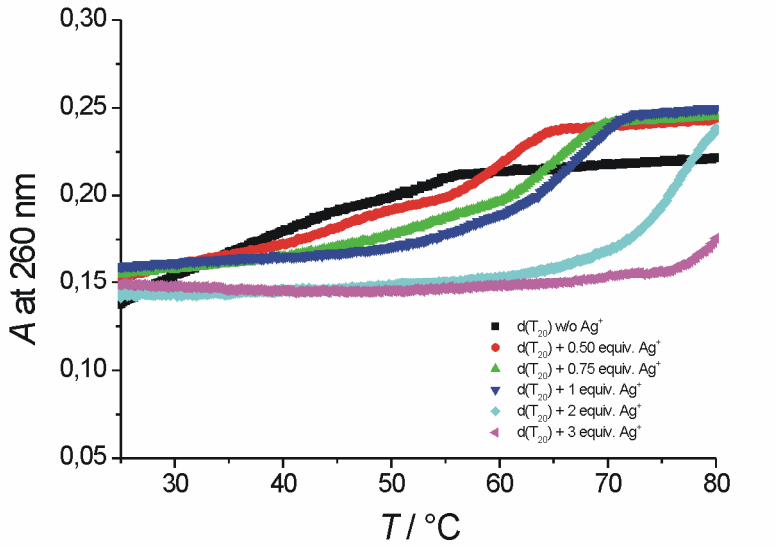

Figure S5: Melting curves of $d(T_{20})$ in the presence of various equivalents of $AgNO_3$. One equivalent of Ag^+ corresponds to one Ag^+ per nucleoside. Conditions: 1 µM $d(T_{20})$, 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

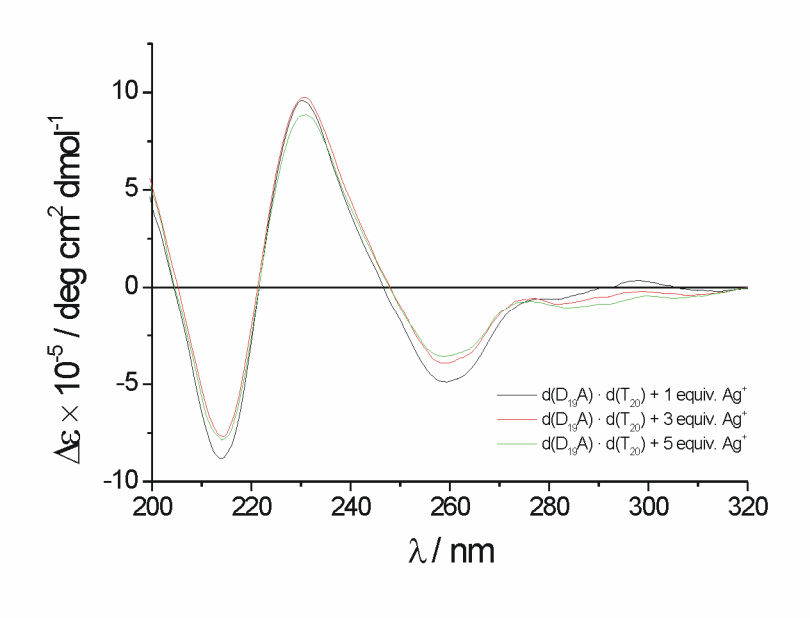

Figure S6: CD spectra of $d(D_{19}A) \cdot d(T_{20})$ in the presence of various equivalents of $AgNO_3$. One equivalent of Ag^+ corresponds to one Ag^+ per base pair. Conditions: 3 µM $d(D_{19}A)$, 3 µM $d(T_{20})$, 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

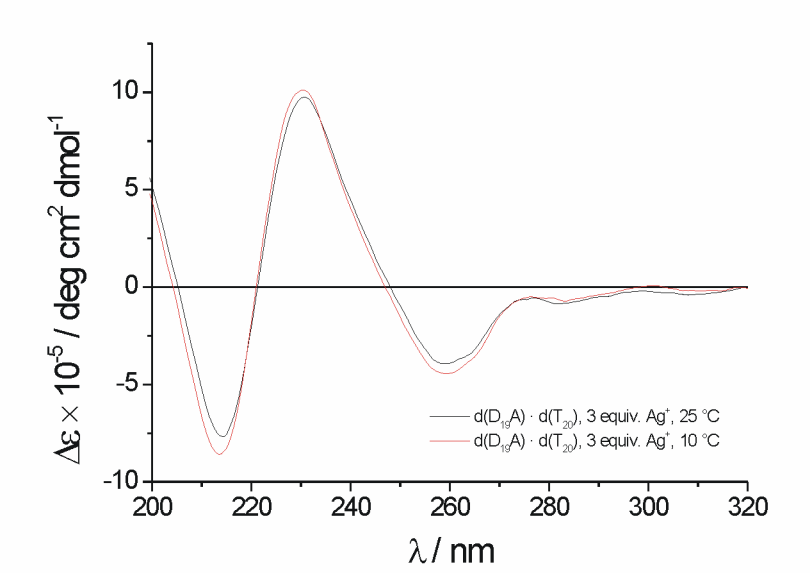

Figure S7: CD spectra of $d(D_{19}A) \cdot d(T_{20})$ in the presence of 3 equiv. of $AgNO_3$, recorded at 25°C and 10°C, respectively. One equivalent of Ag^+ corresponds to one Ag^+ per base pair. Conditions: 3 µM $d(D_{19}A)$, 3 µM $d(T_{20})$, 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

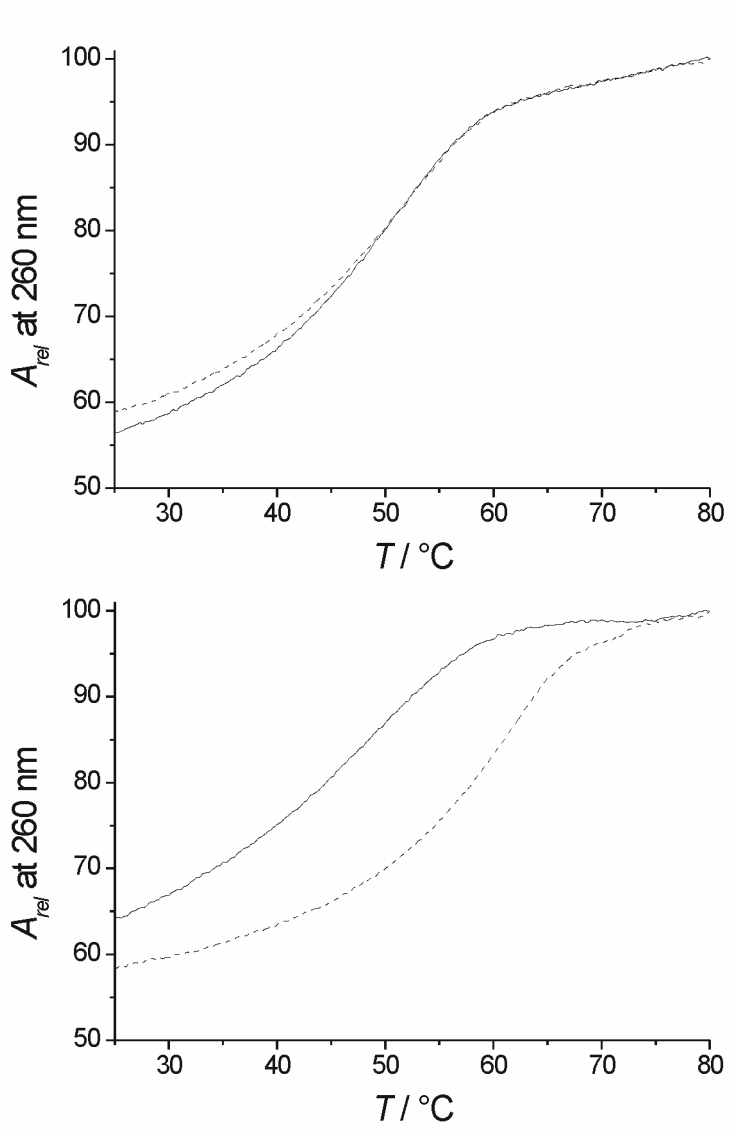

Figure S8: Denaturing (solid line) and renaturing (broken line) profiles of $d(D_{19}A) \cdot d(T_{20})$ in the presence of 1 (top) and 3 equiv. (bottom) of $AgNO_3$. One equivalent of Ag^+ corresponds to one Ag^+ per base pair. Conditions: 1 µM $d(D_{19}A)$, 1 µM $d(T_{20})$, 1 M $NaClO_4$, 5 mM MOPS pH 6.8.

DFT calculations

The structure of the silver(I)-mediated base pair built from 1-deazaadenine and thymine has been modeled by DFT calculations. To save computing time, 9-methyl-1-deazaadenine and the 1-methylthyminate anion have been used to model 1-deaza-2'-deoxyadenosine and the thymidinate anion. Starting from different geometries, the calculations converge to a planar structure in which the silver(I) ion is located between the N7 position of 9-methyl-1-deazaadenine and the N3 position of deprotonated thymidine. As expected, the exocyclic amino group of deazaadenine and the carbonyl group of thymine are found to be within hydrogen bonding distance (N···O: 2.87 Å; NH···O: 1.93 Å, N–H···O: 149.1°).

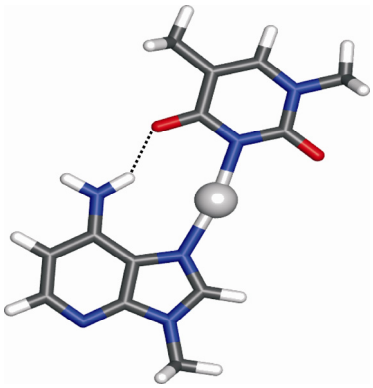

Figure S9: Geometry-optimized structure of the metal-ion mediated base pair formed from 9-methyl-1-deazaadenine, the 1-methylthyminate anion and silver(I). The dotted line represents a hydrogen bond.

Calculations have been performed with an adapted version (QUILD)[1] of the Amsterdam Density Functional Program (ADF version 2006.01).[2-4] The frequency analysis of the final geometry-optimized structure shows one imaginary frequency of 13.7 cm^{-1} that is associated with the rotation of the methyl groups and hence is an "allowed" imaginary frequency.

[1] M. Swart, F. M. Bickehaupt, *Int. J. Quant. Chem.* **2006**, *106*, 2536-2544

[2] G. te Velde, F. M. Bickelhaupt, S. J. A. van Gisbergen, C. Fonseca Guerra, E. J. Baerends, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001,** *22*, 931-967.

[3] C. Fonseca Guerra, J. G. Snijders, G. te Velde, E. J. Baerends, *Theor. Chem. Acc.* **1998**, *99*, 391-403.

[4] ADF2006.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com

Table S1: Cartesian coordinates of geometry-optimized structure shown in Figure S9

N	-3.940410	1.276518	0.000000
C	-5.056236	0.478217	0.000000
N	-6.298131	1.148736	0.000000
C	-6.364414	2.520005	0.000000
C	-5.261318	3.314183	0.000000
C	-3.959090	2.655598	0.000000
O	-2.883851	3.303637	0.000000
O	-5.022009	-0.755876	0.000000
C	-5.324343	4.813467	0.000000
C	-7.499791	0.318590	0.000000
H	-7.372201	2.935757	0.000000
H	-4.812052	5.227006	0.880060
H	-6.362980	5.168869	0.000000
H	-4.812052	5.227006	-0.880060
C	2.385153	2.874962	0.000000
C	3.514527	2.057015	0.000000
N	3.504009	0.709285	0.000000
C	2.261519	0.228289	0.000000
C	1.038692	0.927593	0.000000
C	1.068885	2.347274	0.000000
N	1.921149	-1.120871	0.000000
C	0.563717	-1.192055	0.000000
N	-0.006576	0.006712	0.000000
N	-0.022038	3.144111	0.000000
H	4.501437	2.521720	0.000000
C	2.868654	-2.224891	0.000000
H	0.028002	-2.133382	0.000000
H	-1.007258	2.841480	0.000000
H	0.115031	4.145793	0.000000
H	-8.378613	0.971395	0.000000
H	-7.517195	-0.327095	-0.886204
H	-7.517195	-0.327095	0.886204
H	2.315351	-3.168797	0.000000
H	3.505851	-2.169828	-0.889869
H	3.505851	-2.169828	0.889869
AG	-2.036664	0.470209	0.000000
H	2.517401	3.957001	0.000000