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Supporting Information

Concomitant Site-Specific Incorporation of Silver(I) and Mercury(II) Ions into a DNA Duplex

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Author Contributions

B.J. Data curation: Lead; Investigation: Lead; Writing – original draft: Lead
J.M. Funding acquisition: Lead; Project administration: Lead; Supervision: Lead; Writing – review & editing: Lead.

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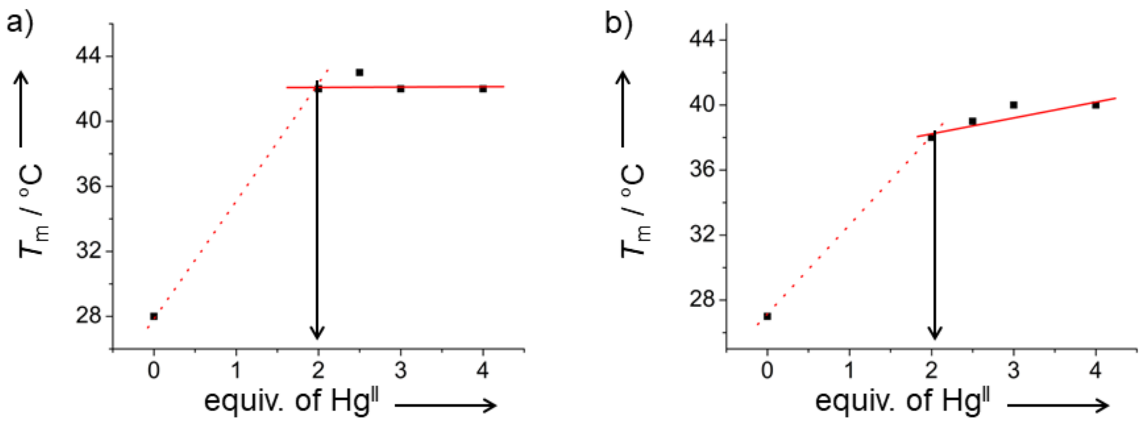

Figure S1. Increase in T_m depending on the equivalents of Hg^{II} added to a solution of duplex **I** at a) pH 5.5 (MES) and b) pH 6.8 (MOPS). Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM buffer.

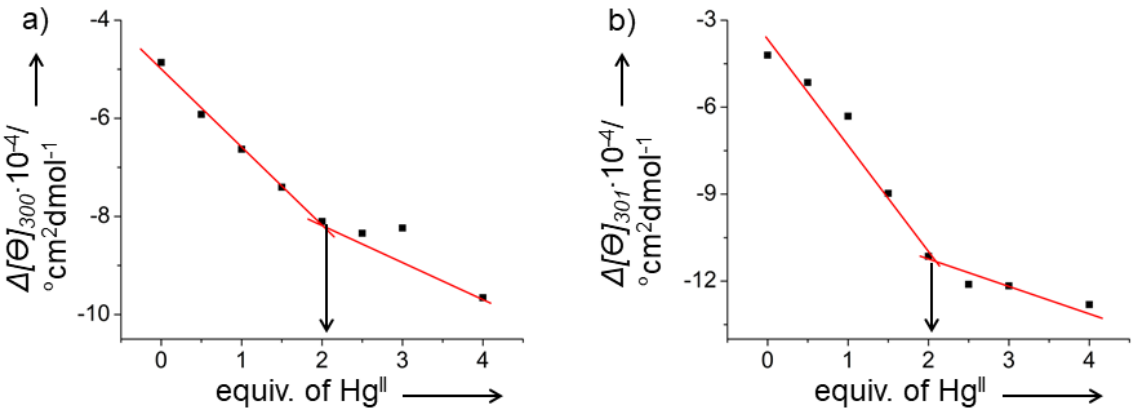

Figure S2. Change in molar ellipticity *[Θ]* depending on the equivalents of Hg^{II} added to a solution of duplex **I** a) at 300 nm and pH 5.5 (MES), b) at 301 nm and pH 6.8 (MOPS). Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM buffer.

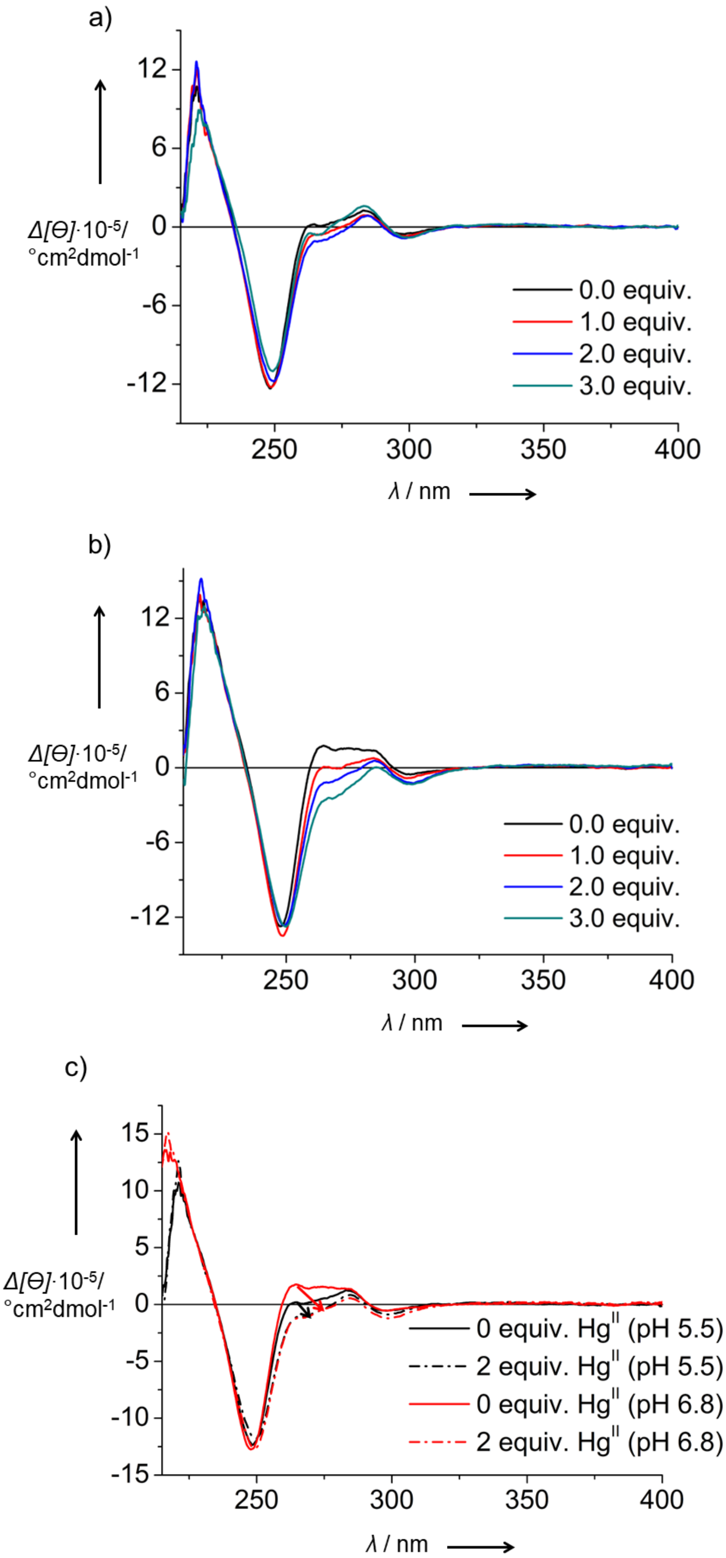

Figure S3. CD spectra of duplex **I** in the presence of increasing amounts of Hg^{II} at a) pH 5.5 (MES) and b) pH 6.8 (MOPS). Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM buffer. A hydrogenbonded **P**:**T** base pair is likely to be formed in the absence of transition metal ions (ref. 13c). The number of hydrogen bonds and hence the geometry of the base pair (and the local duplex conformation) is pH-dependent (ref. 13c). It is therefore not surprising that the CD spectra recorded at different pH values in the absence of Hg^{II} are not identical. Upon formation of the two Hg^{II}-mediated base pairs (i.e. in the presence of two Hg^{II} per duplex), the CD spectra are essentially identical again (Figure S3c). Excess Hg^{II} leads to different changes in the CD spectra, because it can potentially bind to the canonical nucleobases, where the availability of the binding sites is expected to be pH-dependent again.

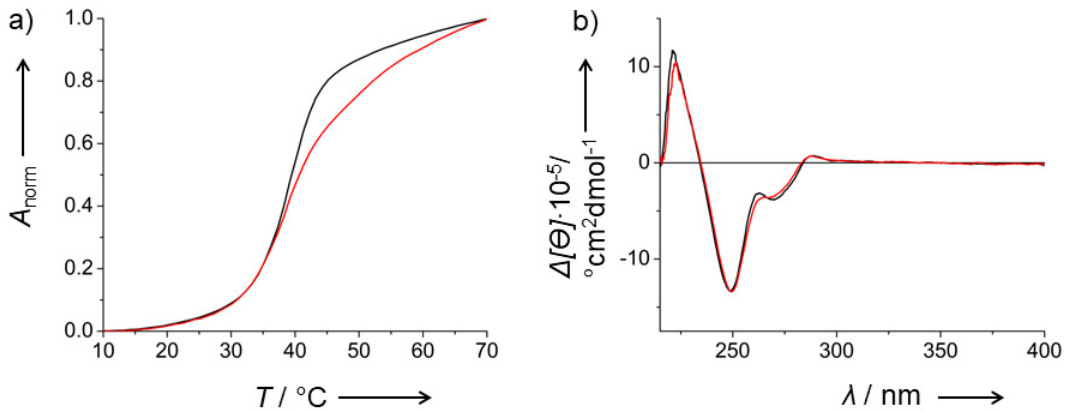

Figure S4. a) UV melting profiles of duplex **II** in the absence (black line) and presence (red line) of two Hg^{II} per duplex; b) CD spectra of duplex **II** in the absence (black line) and presence (red line) of two Hg^{II} per duplex. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MES (pH 5.5).

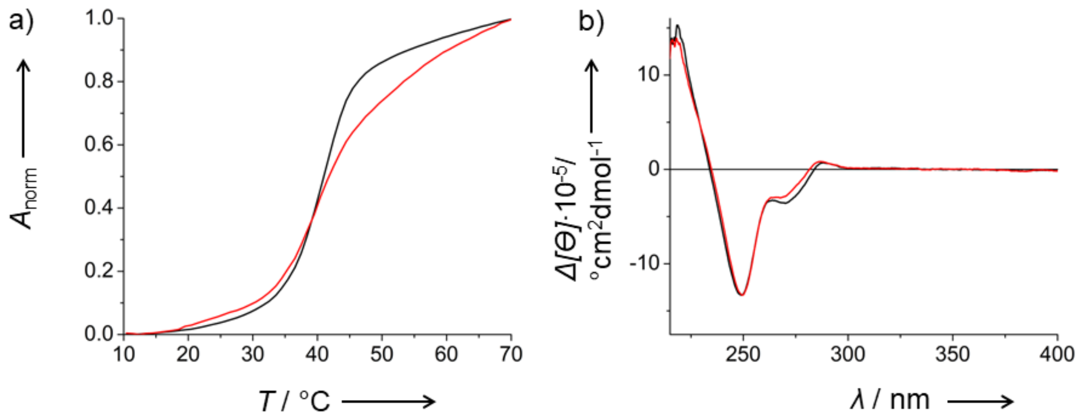

Figure S5. a) UV melting profiles of duplex **II** in the absence (black line) and presence (red line) of two Hg^{II} per duplex; b) CD spectra of duplex **II** in the absence (black line) and presence (red line) of two Hg^{II} per duplex. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MOPS (pH 6.8).

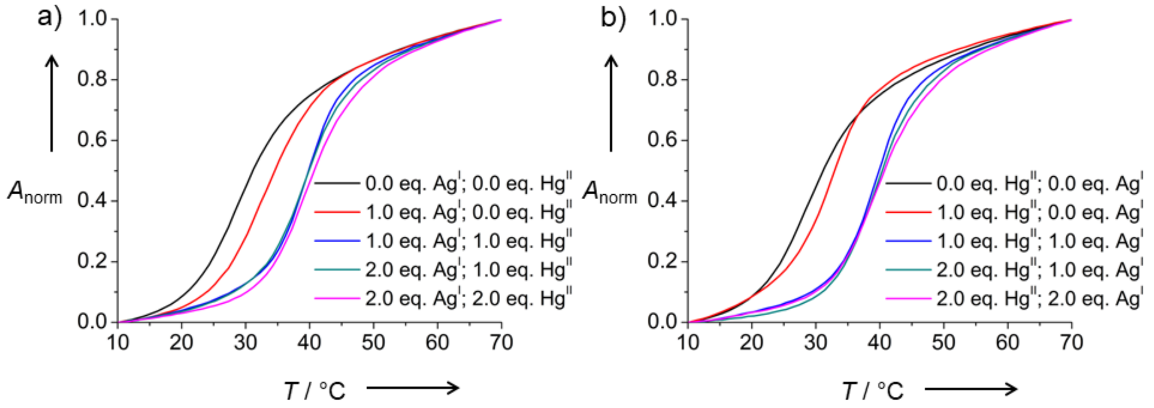

Figure S6. Melting profiles of duplex **IV** in the presence of increasing amounts of a) Ag^I and Hg^{II} and b) Hg^{II} and Ag^I. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MES (pH 5.5).

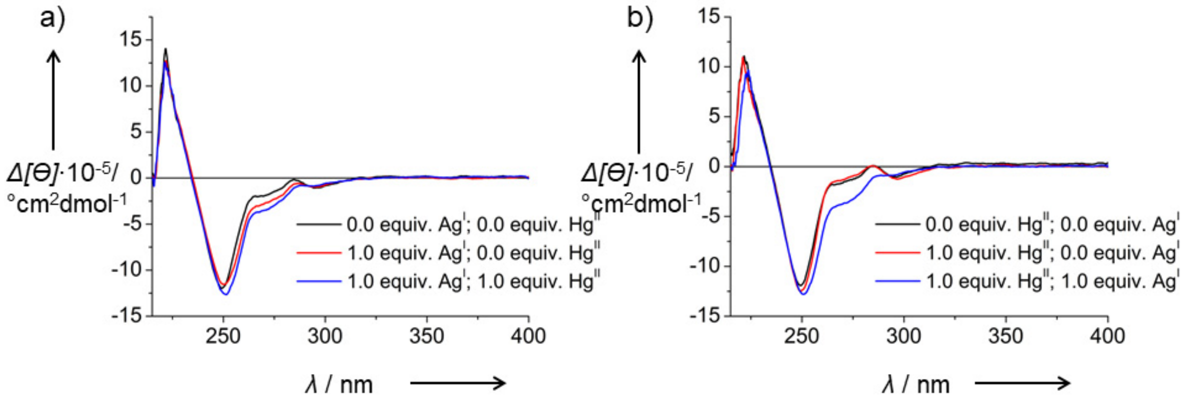

Figure S7. CD spectra of duplex **IV** in the presence of increasing amounts of a) Ag^I and Hg^{II} and b) Hg^{II} and Ag^I. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MES (pH 5.5).

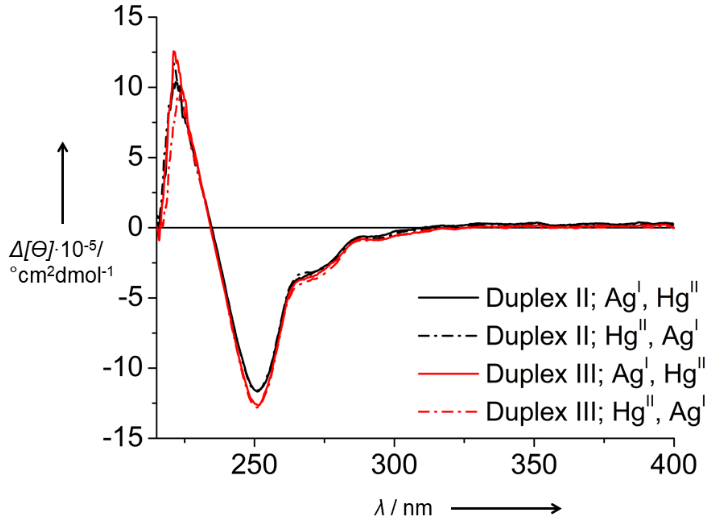

Figure S8. CD spectra of duplexes **III** and **IV** after the formation of a heterometallic assembly via the addition of one equivalent of Ag^{I} and one equivalent of Hg^{II}. The CD spectra are essentially identical. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MES (pH 5.5).

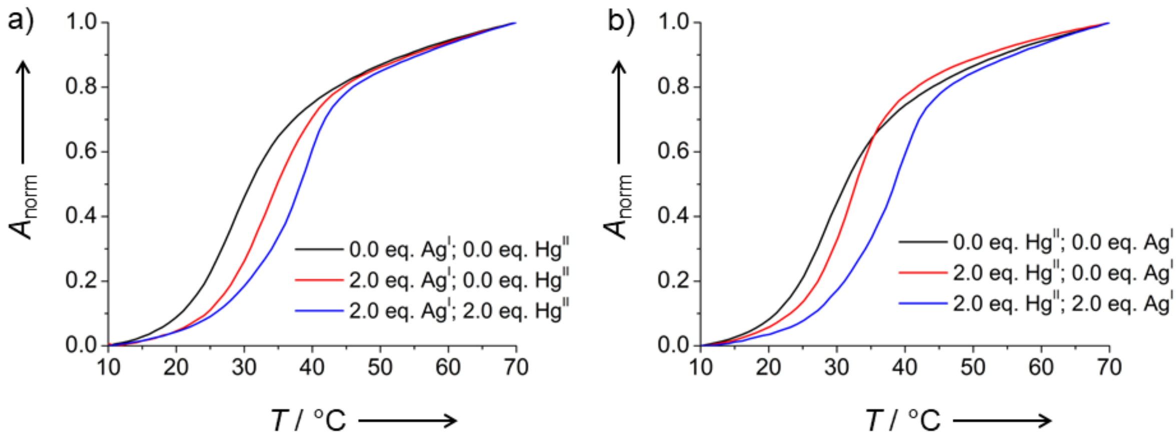

Figure S9. UV melting profiles of duplex **III** in the presence of a) excess Ag^{I} and Hg^{II} and b) excess Hg^{II} and Ag^{I}. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MES (pH 5.5).

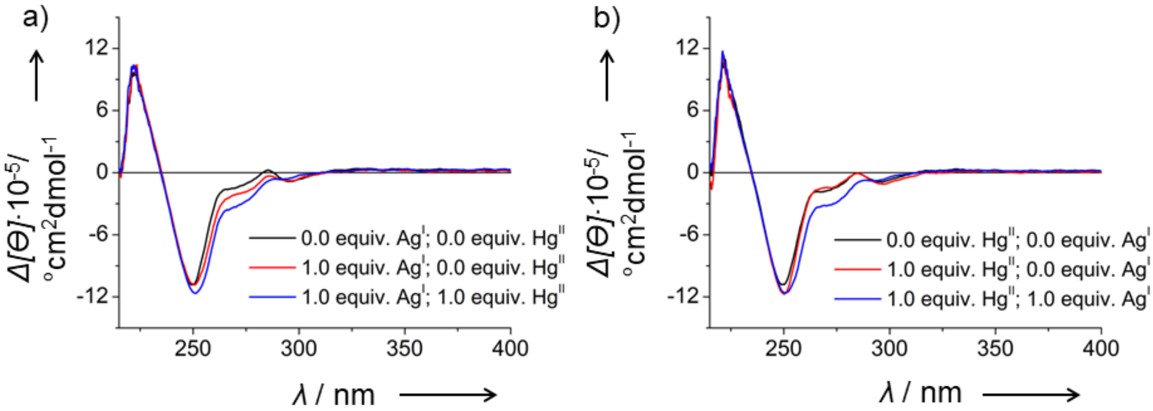

Figure S10. CD spectra of duplex **III** in the presence of increasing amounts of a) Ag^{I} and Hg^{II} and b) Hg^{II} and Ag^{I}. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MES (pH 5.5).

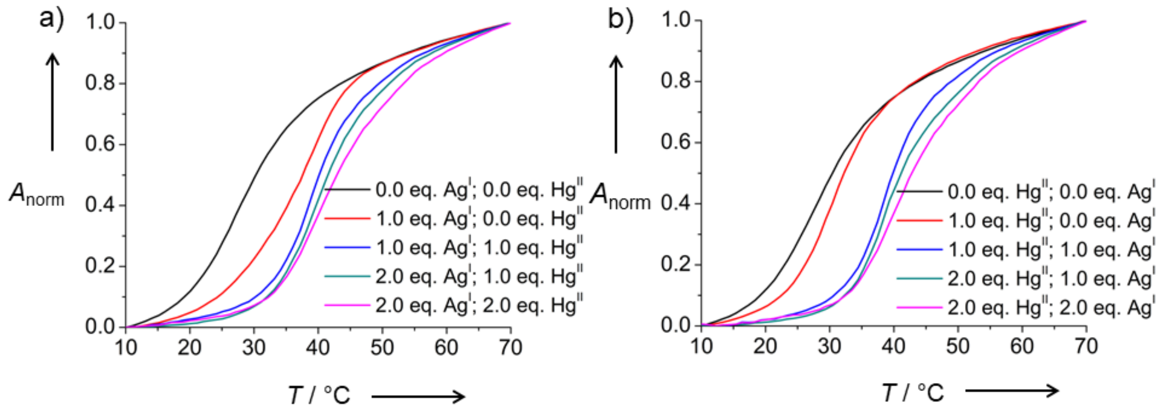

Figure S11. UV melting profiles of duplex **III** in the presence of increasing amounts of a) Ag^{I} and Hg^{II} and b) Hg^{II} and Ag^{I}. Conditions: 2 µM duplex, 500 mM $NaClO_4$, 2.5 mM $Mg(ClO_4)_2$, 5 mM MOPS (pH 6.8).

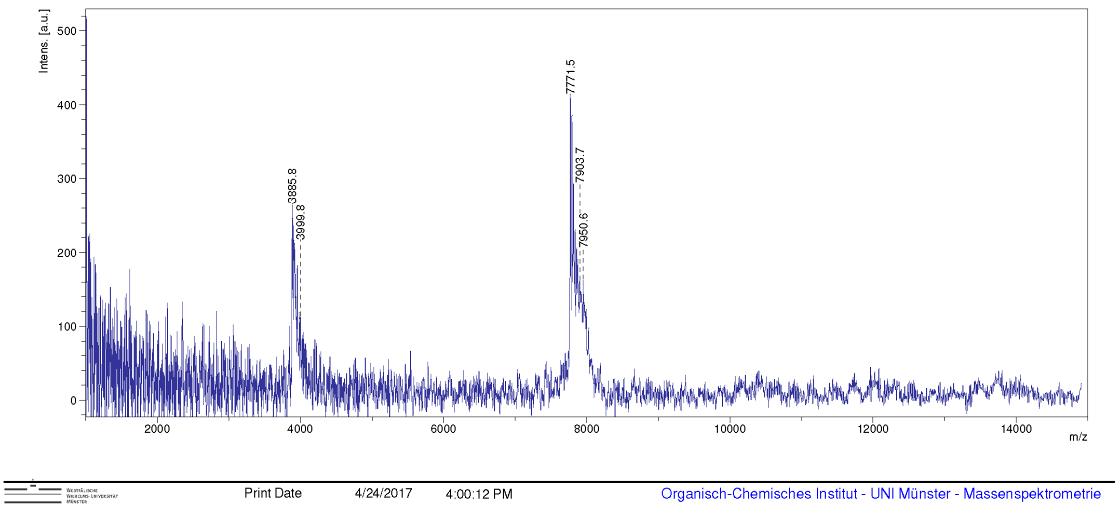

Figure S12. MALDI-ToF mass spectrum of ODN1.

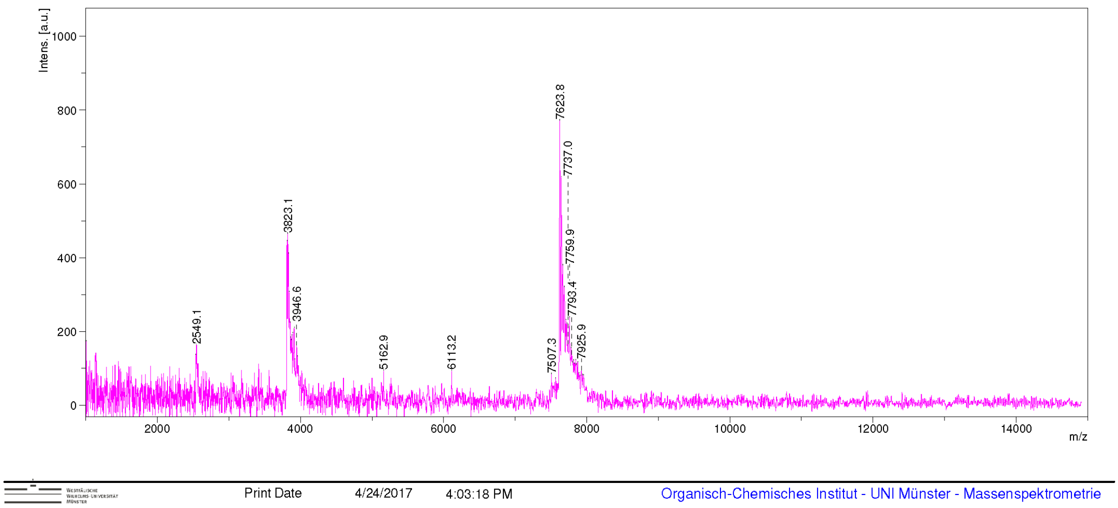

Figure S13. MALDI-ToF mass spectrum of ODN2.

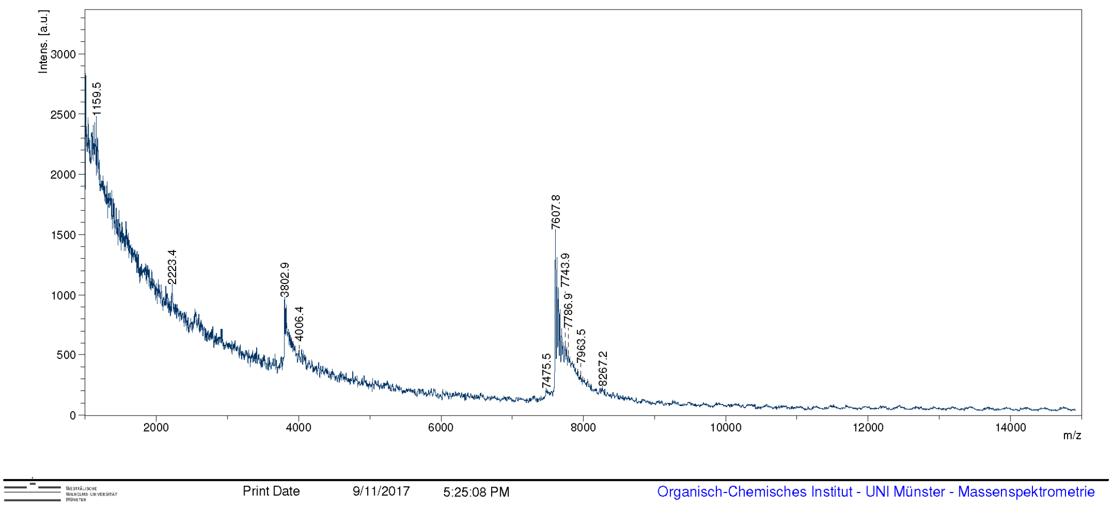

Figure S14. MALDI-ToF mass spectrum of ODN3.

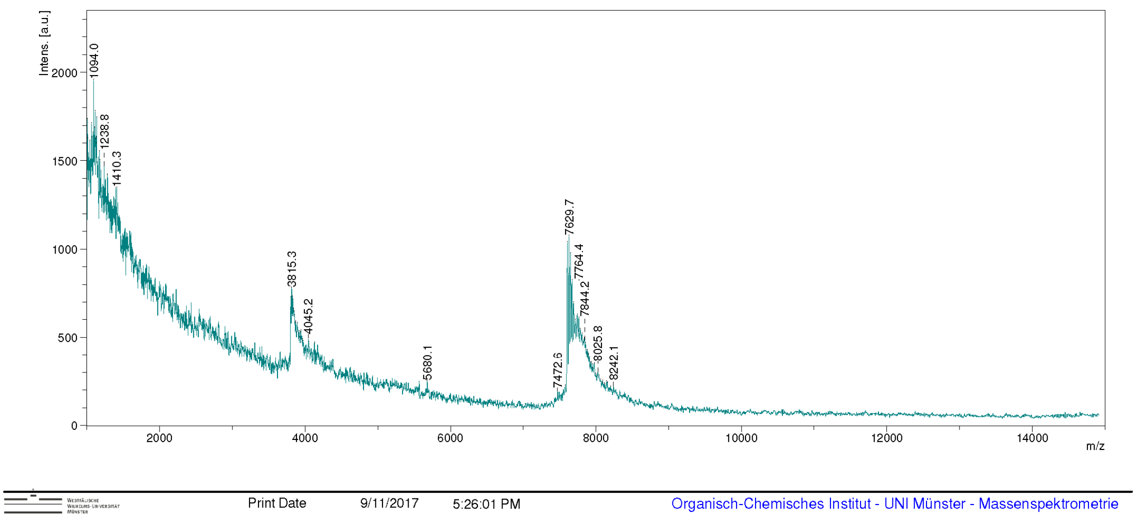

Figure S15. MALDI-ToF mass spectrum of ODN4 (7629.7 corresponds to $[M+Na]^+$).

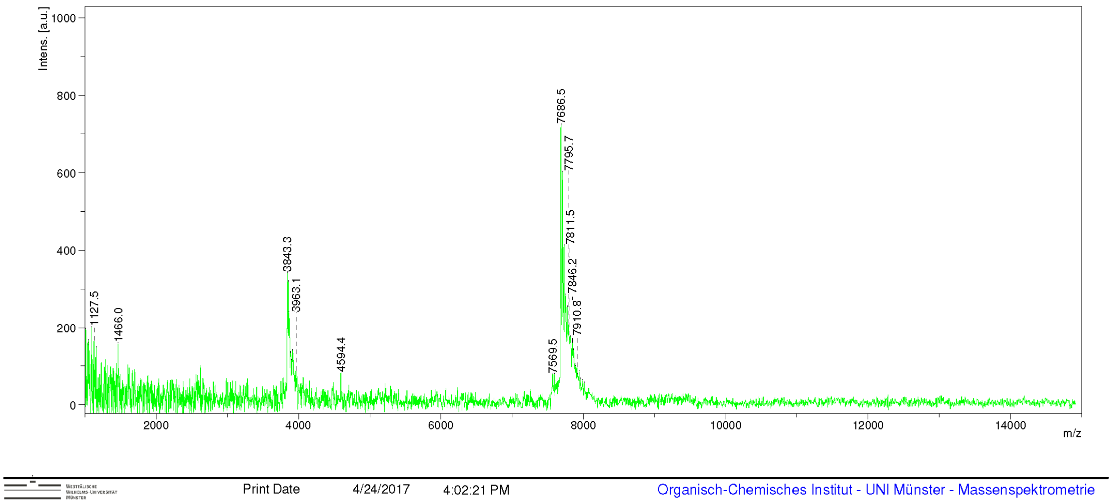

Figure S16: MALDI-ToF mass spectrum of ODN5.

Table S1. Melting temperature T_m of duplex **II** in the absence and presence of Hg^{II} at pH 5.5 and 6.8.

	0 equiv.	2 equiv.	ΔT_m (0→2)
pH 5.5	39 °C	38 °C	−1 °C
pH 6.8	42 °C	41 °C	−1 °C

Table S2. Melting temperature T_m of duplex **IV** upon the stepwise addition of Ag^I and Hg^{II} in steps of one equivalent each (pH 5.5).

Order of titration	$\boldsymbol{T_m}$	**Order of titration**	$\boldsymbol{T_m}$
0.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	28 °C	0.0 equiv. Hg^{II}; 0.0 equiv. Ag^I	28 °C
1.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	33 °C	1.0 equiv. Hg^{II}; 0.0 equiv. Ag^I	33 °C
1.0 equiv. Ag^I; 1.0 equiv. Hg^{II}	39 °C	1.0 equiv. Hg^{II}; 1.0 equiv. Ag^I	40 °C
2.0 equiv. Ag^I; 1.0 equiv. Hg^{II}	39 °C	2.0 equiv. Hg^{II}; 1.0 equiv. Ag^I	40 °C
2.0 equiv. Ag^I; 2.0 equiv. Hg^{II}	39 °C	2.0 equiv. Hg^{II}; 2.0 equiv. Ag^I	40 °C

Table S3. Melting temperature T_m of duplex **III** upon the stepwise addition of Ag^I and Hg^{II} in steps of one equivalent each (pH 5.5).

Order of titration	T_m	Order of titration	T_m
0.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	29 °C	0.0 equiv. Hg^{II}; 0.0 equiv. Ag^I	28 °C
1.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	33 °C	1.0 equiv. Hg^{II}; 0.0 equiv. Ag^I	34 °C
1.0 equiv. Ag^I; 1.0 equiv. Hg^{II}	39 °C	1.0 equiv. Hg^{II}; 1.0 equiv. Ag^I	40 °C
2.0 equiv. Ag^I; 1.0 equiv. Hg^{II}	39 °C	2.0 equiv. Hg^{II}; 1.0 equiv. Ag^I	40 °C
2.0 equiv. Ag^I; 2.0 equiv. Hg^{II}	39 °C	2.0 equiv. Hg^{II}; 2.0 equiv. Ag^I	40 °C

Table S4. Melting temperature T_m of duplex **III** upon the stepwise addition of Ag^I and Hg^{II} in steps of two equivalents each (pH 5.5).

Order of titration	T_m	Order of titration	T_m
0.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	28 °C	0.0 equiv. Hg^{II} 0.0 equiv. Ag^I	28 °C
2.0 equiv. Ag^I 0.0 equiv. Hg^{II}	34 °C	2.0 equiv. Hg^{II} 0.0 equiv. Ag^I	32 °C
2.0 equiv. Ag^I 2.0 equiv. Hg^{II}	40 °C	2.0 equiv. Hg^{II} 2.0 equiv. Ag^I	39 °C

Table S5. Melting temperature T_m of duplex **III** upon the stepwise addition of Ag^I and Hg^{II} in steps of one equivalent each (pH 6.8).

Order of titration	T_m	Order of titration	T_m
0.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	27 °C	0.0 equiv. Hg^{II}; 0.0 equiv. Ag^I	28 °C
1.0 equiv. Ag^I; 0.0 equiv. Hg^{II}	37 °C	1.0 equiv. Hg^{II}; 0.0 equiv. Ag^I	31 °C
1.0 equiv. Ag^I; 1.0 equiv. Hg^{II}	40 °C	1.0 equiv. Hg^{II}; 1.0 equiv. Ag^I	38 °C
2.0 equiv. Ag^I; 1.0 equiv. Hg^{II}	41 °C	2.0 equiv. Hg^{II}; 1.0 equiv. Ag^I	39 °C
2.0 equiv. Ag^I; 2.0 equiv. Hg^{II}	42 °C	2.0 equiv. Hg^{II}; 2.0 equiv. Ag^I	41 °C

Table S6. Oligonucleotides used for the investigation of Hg^{II}-mediated hetero base pairing and DNA-programmed heterometallic assembly.

	Sequences used for the investigation	*Entry*	*[M+H]⁺ / Da*	
			Calcd.	*Found*
Duplex I	5'-d(AAA AAA AAA **P**TA ATT TT**P** AAT ATT T)-3' *Chemical formula*: $C_{262}H_{310}N_{96}O_{139}P_{24}$	**ODN1**	7773	7772
	5'-d(TTT TTT TTT **T**AT TAA AA**T** TTA TAA A)-3' *Chemical formula*: $C_{250}H_{318}N_{77}O_{155}P_{24}$	**ODN2**	7624	7624
Duplex II	5'-d(AAA AAA AAA **A**TA ATT TT**A** AAT ATT T)-3' *Chemical formula*: $C_{250}H_{311}N_{98}O_{141}P_{24}$	**ODN5**	7684	7687
	5'-d(TTT TTT TTT **T**AT TAA AA**T** TTA TAA A)-3' *Chemical formula*: $C_{250}H_{318}N_{77}O_{155}P_{24}$	**ODN2**	7624	7624
Duplex III	5'-d(AAA AAA AAA **P**TA ATT TT**P** AAT ATT T)-3' *Chemical formula*: $C_{262}H_{310}N_{96}O_{139}P_{24}$	**ODN1**	7773	7772
	5'-d(TTT TTT TTT **C**AT TAA AA**T** TTA TAA A)-3' *Chemical formula*: $C_{249}H_{317}N_{78}O_{154}P_{24}$	**ODN3**	7608	7608
Duplex IV	5'-d(AAA AAA AAA **P**TA ATT TT**P** AAT ATT T)-3' *Chemical formula*: $C_{262}H_{310}N_{96}O_{139}P_{24}$	**ODN1**	7773	7772
	5'-d(TTT TTT TTT **T**AT TAA AA**C** TTA TAA A)-3' *Chemical formula*: $C_{249}H_{317}N_{78}O_{154}P_{24}$	**ODN4**	7608	7608