Supporting Information

Single-molecule force spectroscopy of an artificial DNA duplex comprising a silver(I)-mediated base pair

Xinxin Tan¶, Stefanie Litau¶, Xi Zhang, and Jens Müller**

Dr. X. Tan, Prof. Dr. X. Zhang
Tsinghua University, Department of Chemistry, Key Lab of Organic Optoelectronics and Molecular Engineering, 100084 Beijing, P. R. China
E-mail: xi@mail.tsinghua.edu.cn

S. Litau, Prof. Dr. Jens Müller
Westfälische Wilhelms-Universität Münster, Institut für Anorganische und Analytische Chemie, Corrensstr. 28/30, 48149 Münster, Germany
E-Mail: mueller.j@uni-muenster.de

¶ These authors contributed equally to this work.

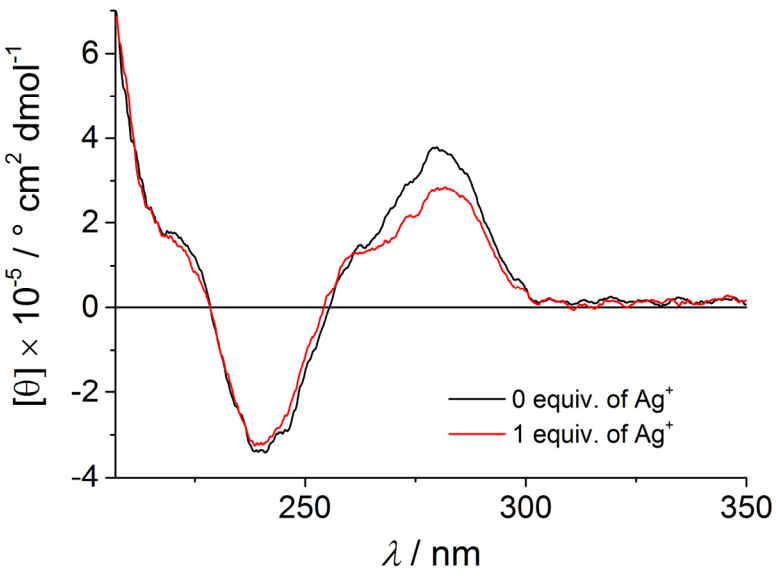

Figure S1. CD spectra of duplex **II** in the absence and presence of one equivalent of $AgNO_3$.

In both cases, the duplex adopts a B-DNA conformation.[1]

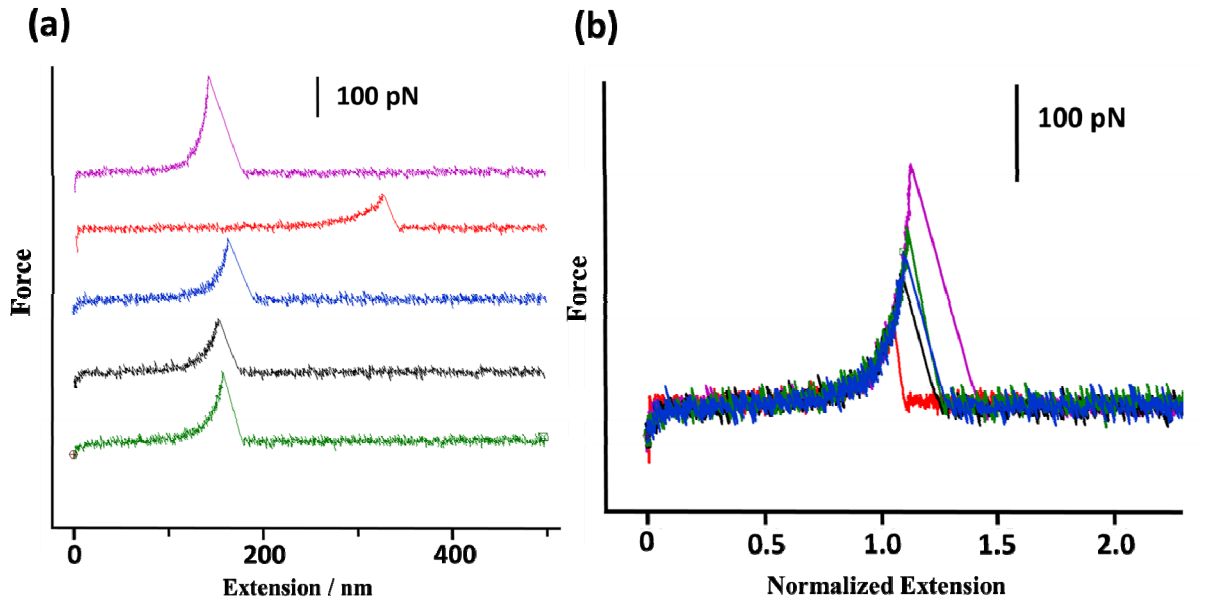

Figure S2. (a) Typical force curves obtained from the measurement of duplex **III**. (b) All the normalized force curves are superimposed well.

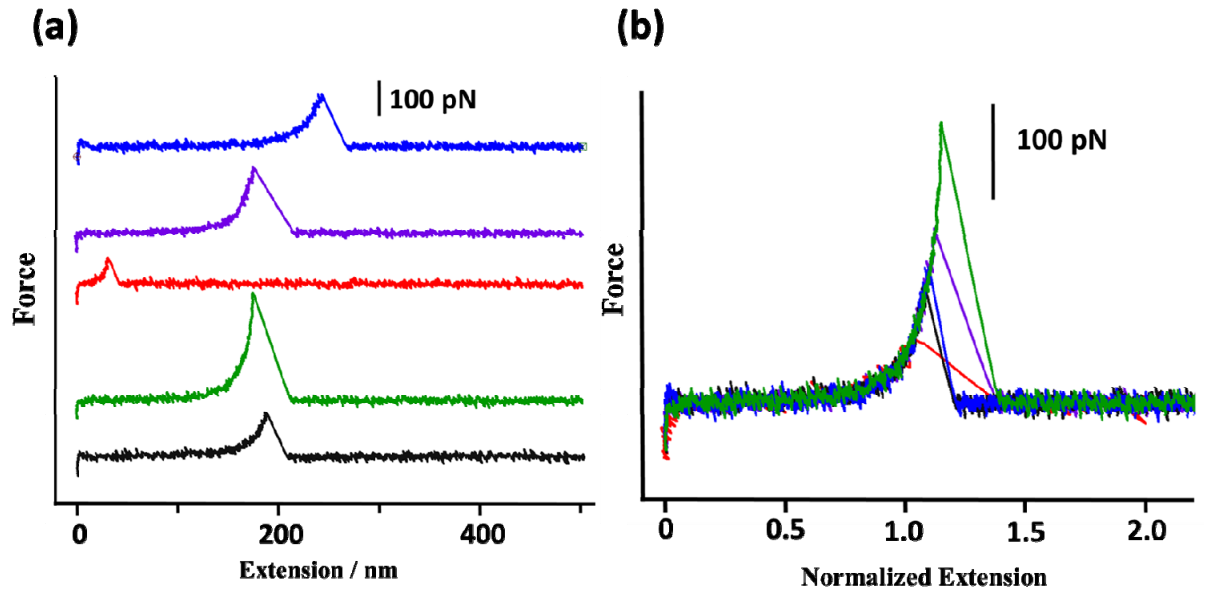

Figure S3. (a) Typical force curves obtained from the measurement of duplex **IV** in the absence of Ag^{+}. (b) All the normalized force curves are superimposed well.

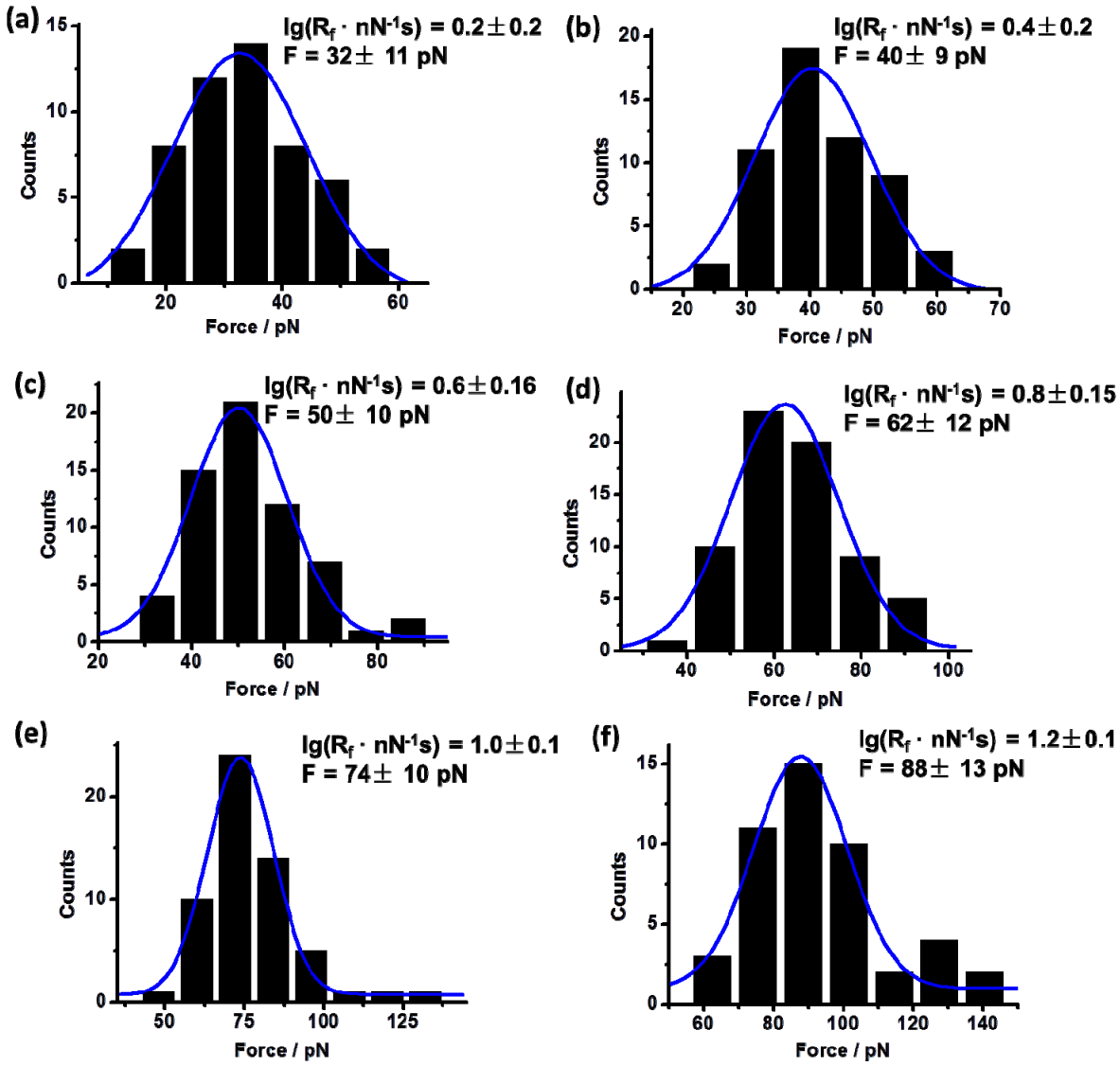

Figure S4. The most probable rupture forces of duplex **III** under different R_f. For building up histogram a, b, c, d, e, f, the number of force curves is 52, 56, 62, 68, 57, and 47, respectively.

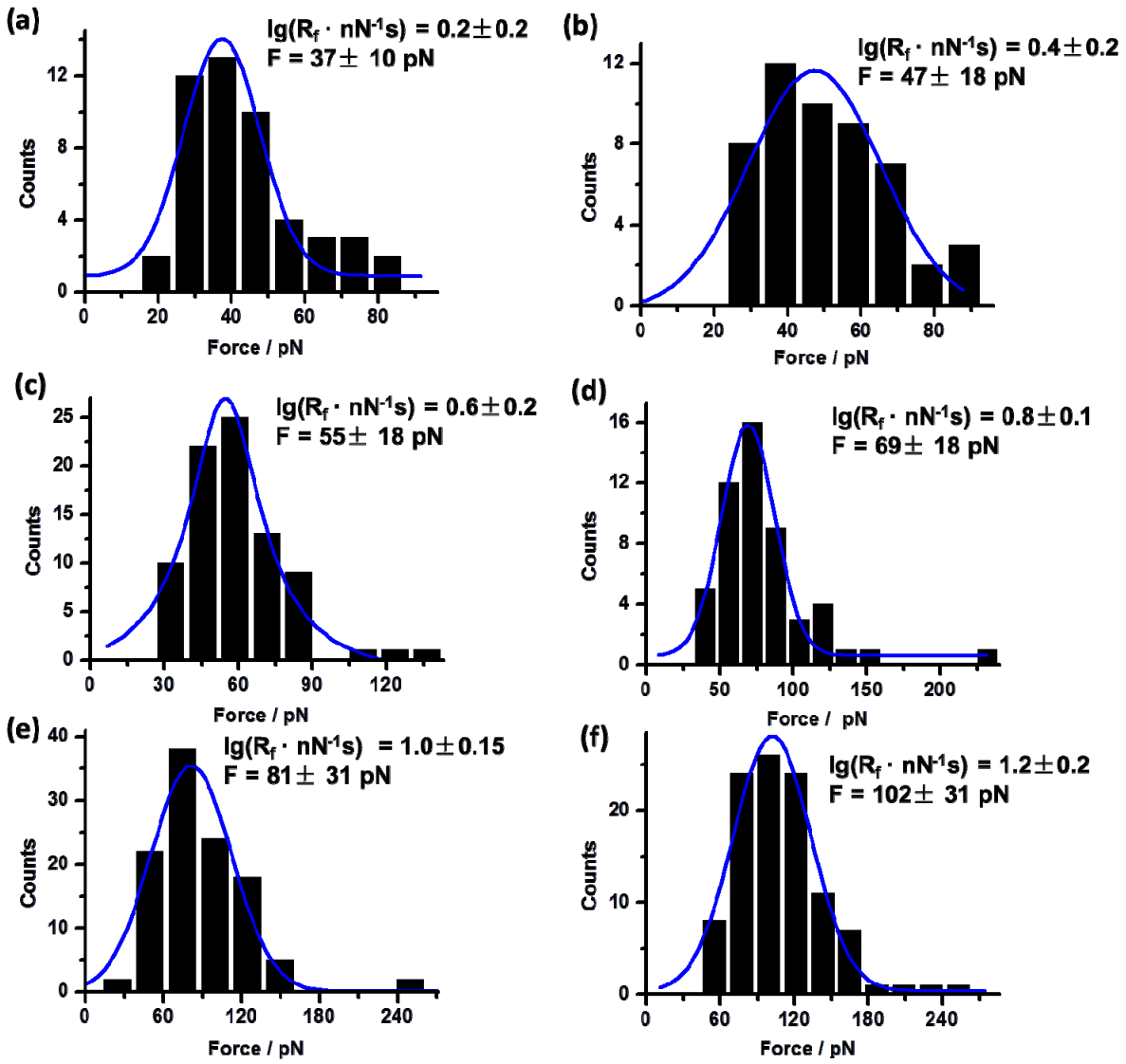

Figure S5. The most probable rupture forces of duplex **IV** in the presence of Ag^+ under different R_f. For building up histogram a, b, c, d, e, f, the number of force curves is 49, 51, 82, 52, 110, and 104, respectively.

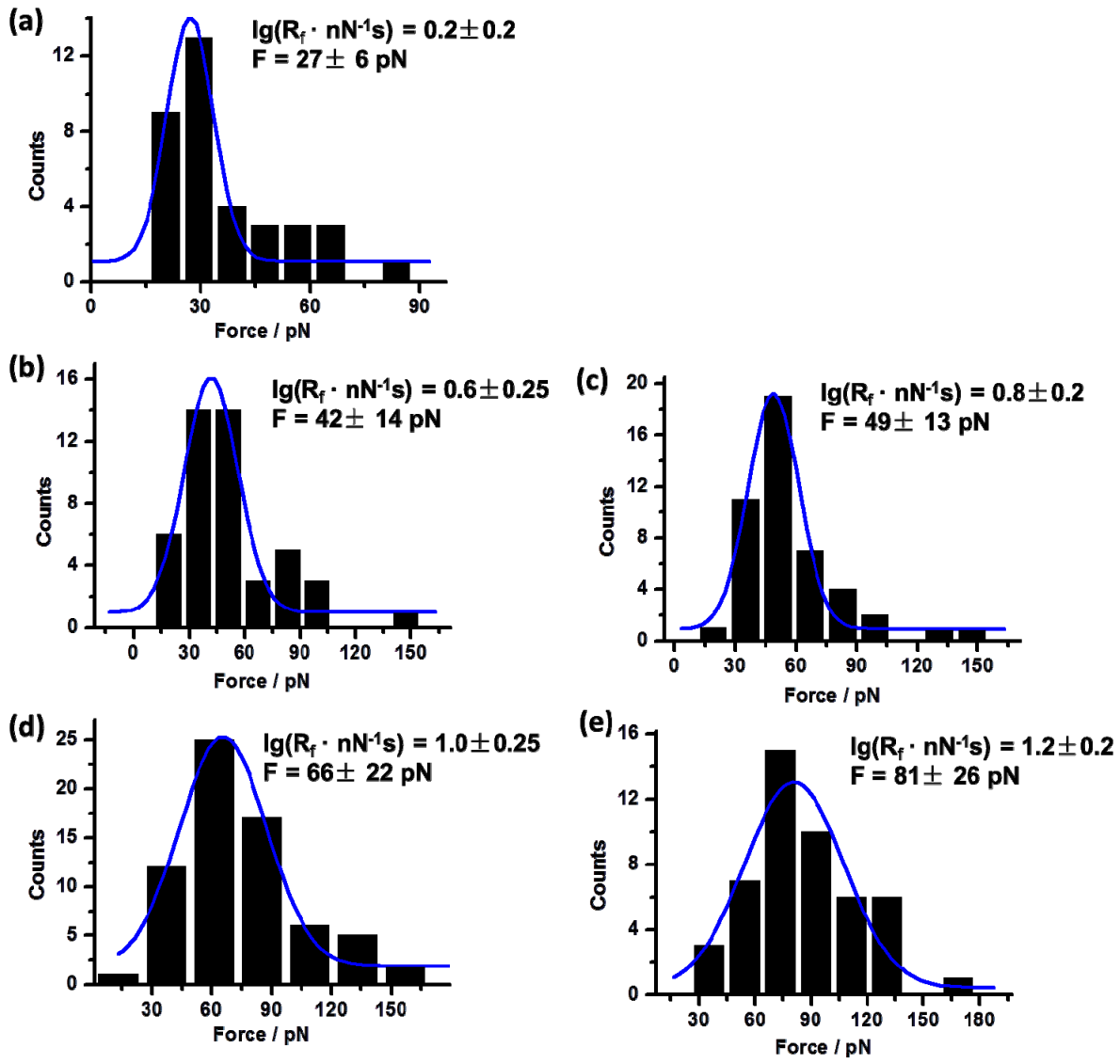

Figure S6. The most probable rupture forces of duplex **IV** in the absence of Ag^+ under different R_f. For building up histogram a, b, c, d, e, the number of force curves is 35, 46, 46, 68, and 48, respectively.

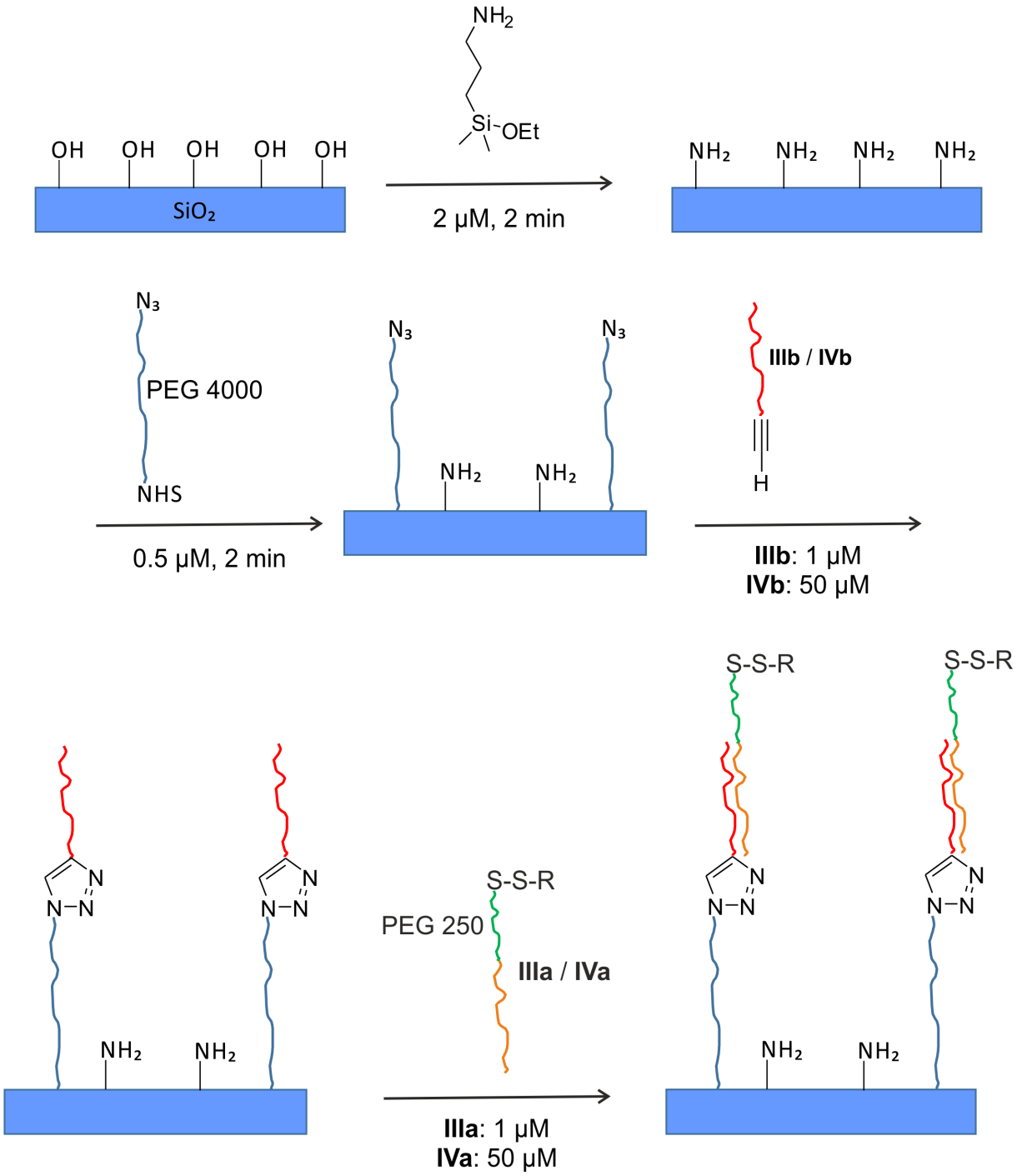

Figure S7. Stepwise modification of the SiO_2 surface with oligonucleotide duplexes **III** and **IV**, respectively.

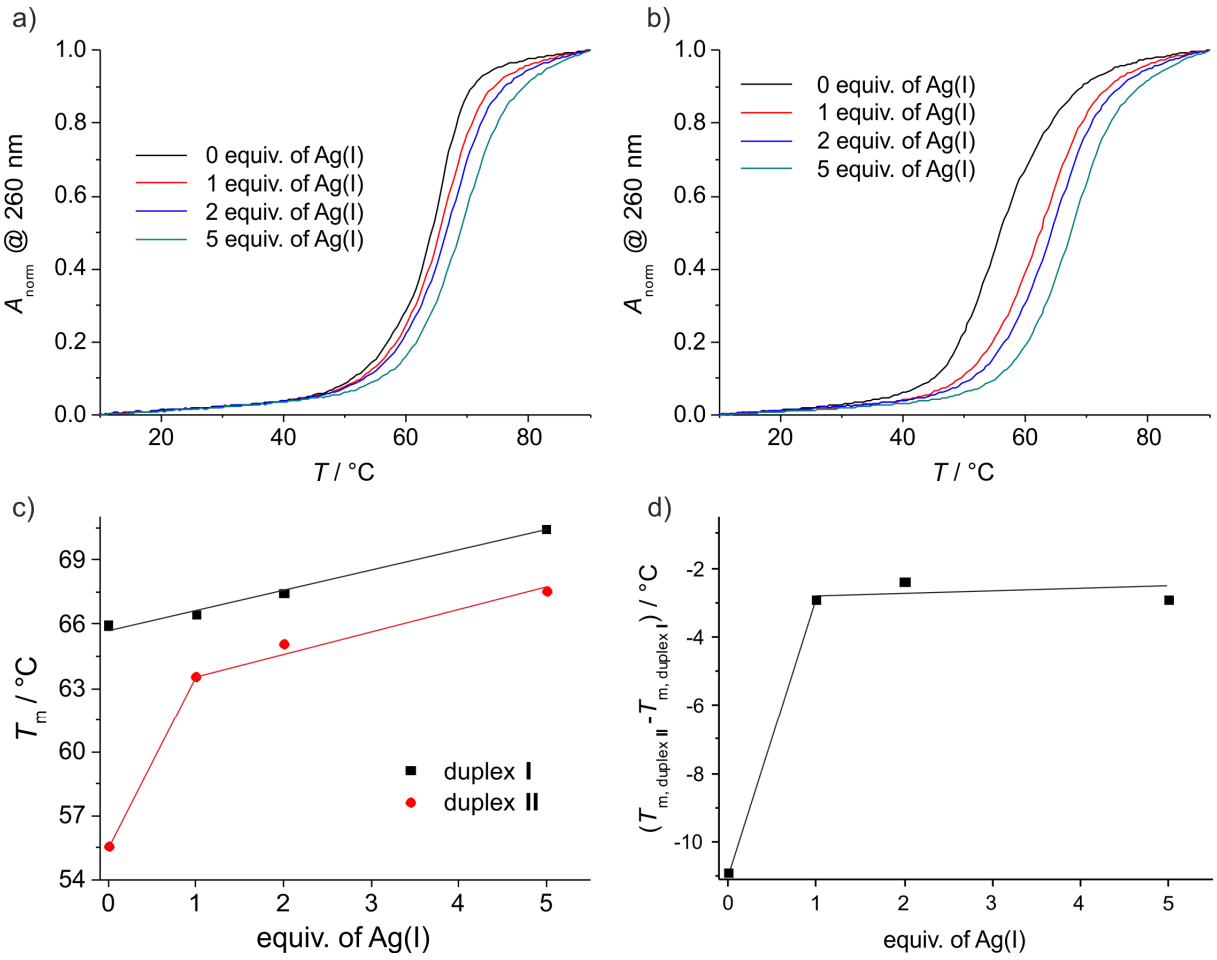

Figure S8. a) UV melting curves of duplex **I** in the presence of increasing amounts of Ag(I); b) UV melting curves of duplex **II** in the presence of increasing amounts of Ag(I); c) melting temperatures as derived from the respective UV melting curves, clearly showing the significant stabilization of duplex **II** upon the addition of the first equivalent of Ag(I); d) differences in the melting temperatures of duplexes **II** and **I** upon the addition of increasing amounts of Ag(I) (identical to inset in Figure 2).

In the SMFS experiments, the gold-coated AFM cantilevers were kept into contact with the substrates for 1 s. Here, Au-S coordination bond or even a covalent bond could form. According to the reference, the most probable rupture forces of the Au-S bond with different interaction times are 0.69 nN at 1.0 s, 0.76 nN at 2.0 s, 1.09 nN at 3.0 s and 1.01 nN at 8.0 s, respectively, indicating the shifting of bond types from coordinate to covalent.[2] Even in the isolated single monosulfides system that can form only Au-S coordination bond, the most probable rupture force is larger than 450 pN, and the force value is independent on the interaction time, as shown in Figure S9. Therefore, the Au-S bond is much stronger than the forces holding together the DNA duplex, and the weakest part of the polymer bridge is the DNA duplex.

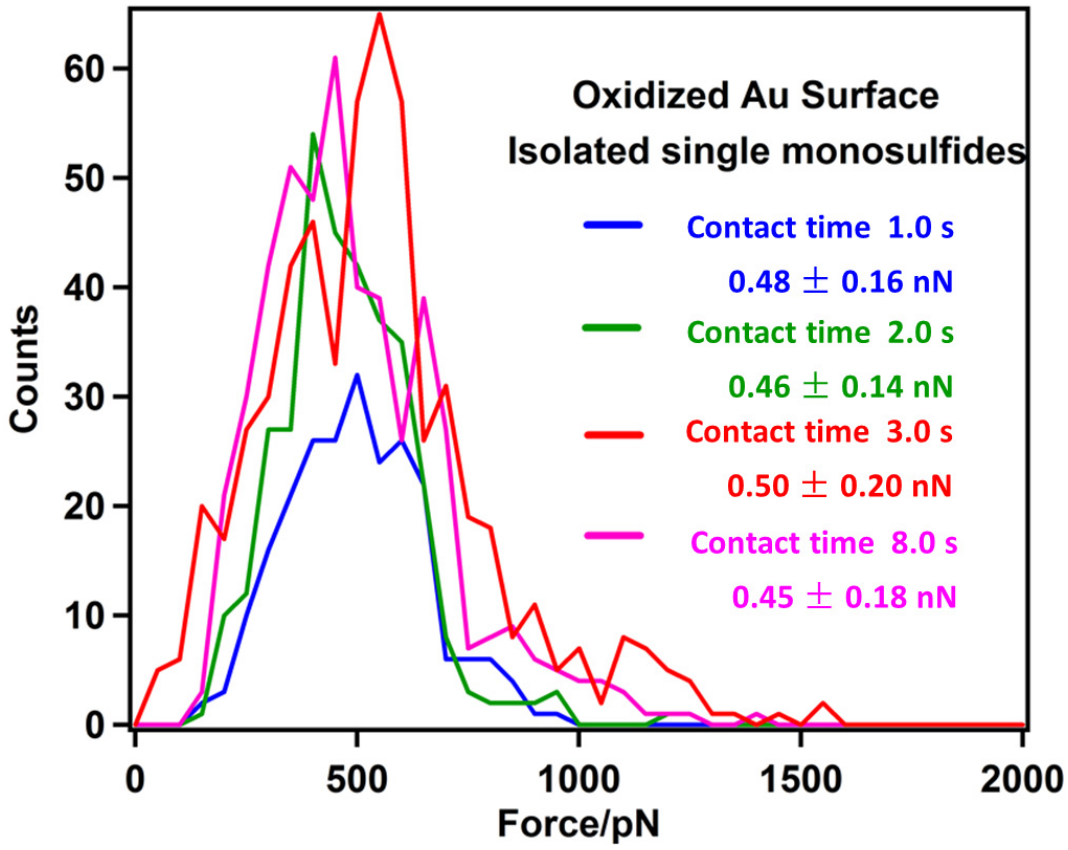

Figure S9. The most probable rupture force of Au-S coordination bond is larger than 450 pN, and the force value is independent on the interaction time.

Table S1. Modification of SiO_2 substrates characterized by XPS.

Atom	C_{1s}	O_{1s}	Si_{2p}	N_{1s}	P_{2p}	S_{2p}	Ag_{3d}
% Before step 1	16.46	60.57	22.97	-	-	-	-
% After step 1	15.33	1.96	60.36	22.34	-	-	-
% After step 2	24.59	51.91	20.71	2.79	-	-	-
% After step 3							
III b	20.00	56.86	20.23	2.58	0.34	-	-
IV b	22.14	55.63	19.12	2.74	0.38	-	-
% After step 4							
duplex **III**	23.89	54.32	17.23	3.14	0.36	1.06	-
duplex **IV**	31.89	43.42	16.31	4.88	0.31	3.20	-
duplex **IV** in the presence of Ag^+	31.01	43.33	15.13	5.11	0.84	1.98	2.60

References

1 Vorlíčková, M.; Kejnovská, I.; Bednářová, K.; Renčiuk, D.; Kypr, J. Circular dichroism spectroscopy of DNA: from duplexes to quadruplexes. *Chirality* **2012**, *24*, 691–698.

2 Xue, Y.; Li, X.; Li, H.; Zhang, W. Quantifying thiol–gold interactions towards the efficient strength control. *Nat. Commun.* **2014**, *5*, 4348.