Supporting Information

Footprints of Nanoscale DNA-Silver Cluster Chromophores *via* Activated-Electron Photodetachment Mass Spectrometry

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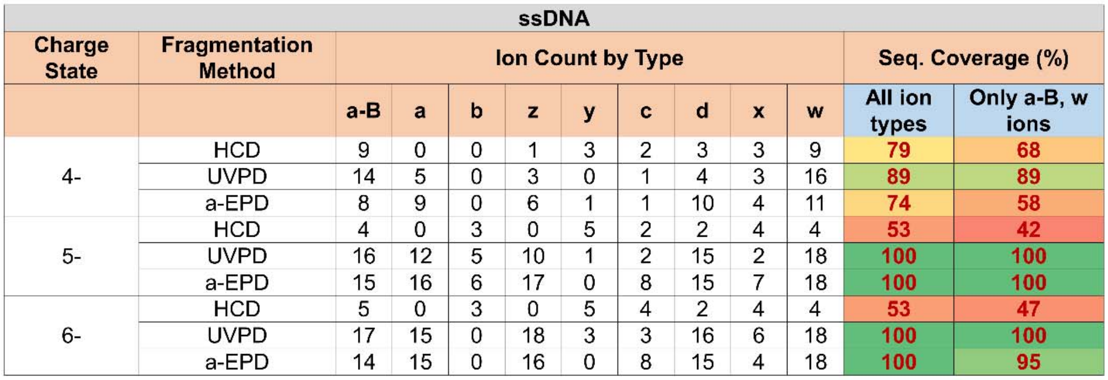
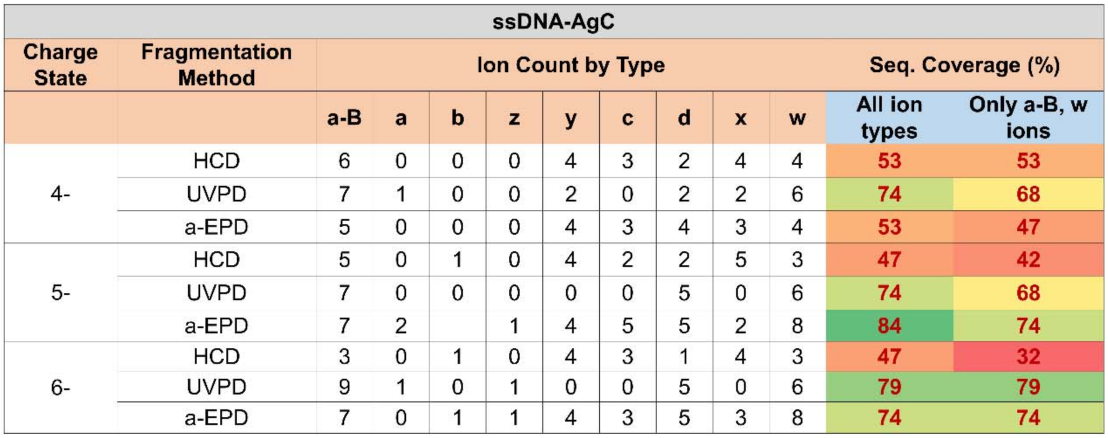
(a) **ssDNA**



ssDNA

Charge State	Fragmentation Method	Ion Count by Type									Seq. Coverage (%)	
		a-B	a	b	z	y	c	d	x	w	All ion types	Only a-B, w ions
4-	HCD	9	0	0	1	3	2	3	3	9	79	68
	UVPD	14	5	0	3	0	1	4	3	16	89	89
	a-EPD	8	9	0	6	1	1	10	4	11	74	58
5-	HCD	4	0	3	0	5	2	2	4	4	53	42
	UVPD	16	12	5	10	1	2	15	2	18	100	100
	a-EPD	15	16	6	17	0	8	15	7	18	100	100
6-	HCD	5	0	3	0	5	4	2	4	4	53	47
	UVPD	17	15	0	18	3	3	16	6	18	100	100
	a-EPD	14	15	0	16	0	8	15	4	18	100	95

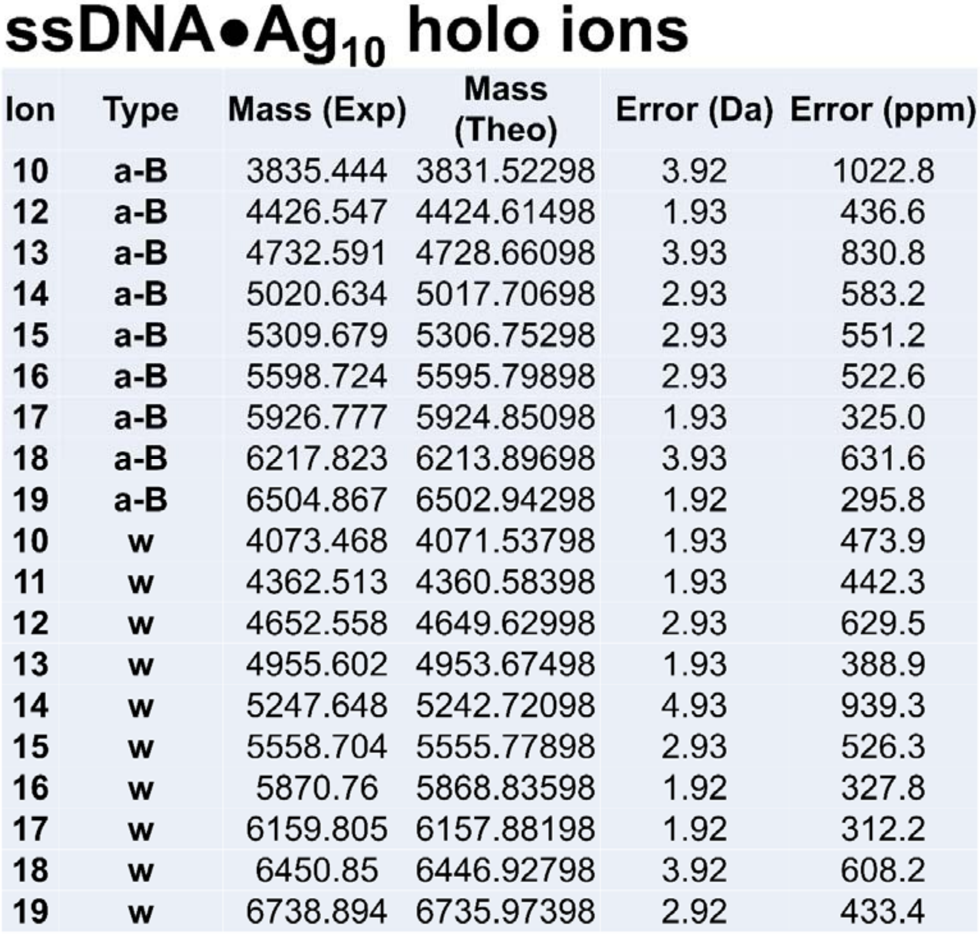
(b) **ssDNA•Ag_{10}**



ssDNA-AgC

Charge State	Fragmentation Method	Ion Count by Type									Seq. Coverage (%)	
		a-B	a	b	z	y	c	d	x	w	All ion types	Only a-B, w ions
4-	HCD	6	0	0	0	4	3	2	4	4	53	53
	UVPD	7	1	0	0	2	0	2	2	6	74	68
	a-EPD	5	0	0	0	4	3	4	3	4	53	47
5-	HCD	5	0	1	0	4	2	2	5	3	47	42
	UVPD	7	0	0	0	0	0	5	0	6	74	68
	a-EPD	7	2		1	4	5	5	2	8	84	74
6-	HCD	3	0	1	0	4	3	1	4	3	47	32
	UVPD	9	1	0	1	0	0	5	0	6	79	79
	a-EPD	7	0	1	1	4	3	5	3	8	74	74

Table S1. Summarized tables of ion type distributions and sequence coverage across various charge states and fragmentation methods for ssDNA CCC CAA CTC CTT CCC GCC AC **(a)** without and **(b)** with silver cluster. Above tables were used to create main text **Figure 2** and **Figure S23**.



ssDNA•Ag_{10} holo ions

Ion	Type	Mass (Exp)	Mass (Theo)	Error (Da)	Error (ppm)
10	a-B	3835.444	3831.52298	3.92	1022.8
12	a-B	4426.547	4424.61498	1.93	436.6
13	a-B	4732.591	4728.66098	3.93	830.8
14	a-B	5020.634	5017.70698	2.93	583.2
15	a-B	5309.679	5306.75298	2.93	551.2
16	a-B	5598.724	5595.79898	2.93	522.6
17	a-B	5926.777	5924.85098	1.93	325.0
18	a-B	6217.823	6213.89698	3.93	631.6
19	a-B	6504.867	6502.94298	1.92	295.8
10	w	4073.468	4071.53798	1.93	473.9
11	w	4362.513	4360.58398	1.93	442.3
12	w	4652.558	4649.62998	2.93	629.5
13	w	4955.602	4953.67498	1.93	388.9
14	w	5247.648	5242.72098	4.93	939.3
15	w	5558.704	5555.77898	2.93	526.3
16	w	5870.76	5868.83598	1.92	327.8
17	w	6159.805	6157.88198	1.92	312.2
18	w	6450.85	6446.92798	3.92	608.2
19	w	6738.894	6735.97398	2.92	433.4

Table S2. Table of identified holo ions from deconvoluted a-EPD spectrum of 6- charge state of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster. Table highlights systematic mass shifts of 1.9, 2.9, 3.9, and 4.9 Da observed for deconvoluted holo ions due to the interference of Ag isotope patterns with the utilized deconvolution method. This effect is also seen in the deconvoluted a-EPD spectra – instead of a single deconvoluted holo ion peak, we observe groups of holo ion peaks separated by multiples of 1.0 Da, further highlighting the systematic deconvolution mass errors that occur when ions containing silver atoms are deconvoluted. The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B or w_n in which the number n (listed in Ion column) represents the number of nucleotides contained in the fragment.

DNA	Sequence	Length (nt)	Exact Mass (Da)
ssDNA	CCC CAA CTC CTT CCC GCC AC	20	5876.003
hpDNA	CCC CAA CTC CTT CCC GCC TTT TGG CGG G	28	8424.389
ssDNA-AgC	CCC CAA CTC CTT CCC GCC AC + **AgC**	20	6945.054
hpDNA-AgC	CCC CAA CTC CTT CCC GCC TTT TGG CGG G + **AgC**	28	9493.440

Table S3. Sequences and masses of all DNA and DNA-AgC samples studied. All sequences are listed from 5’ to 3’ end, and DNA hairpin regions are underlined.

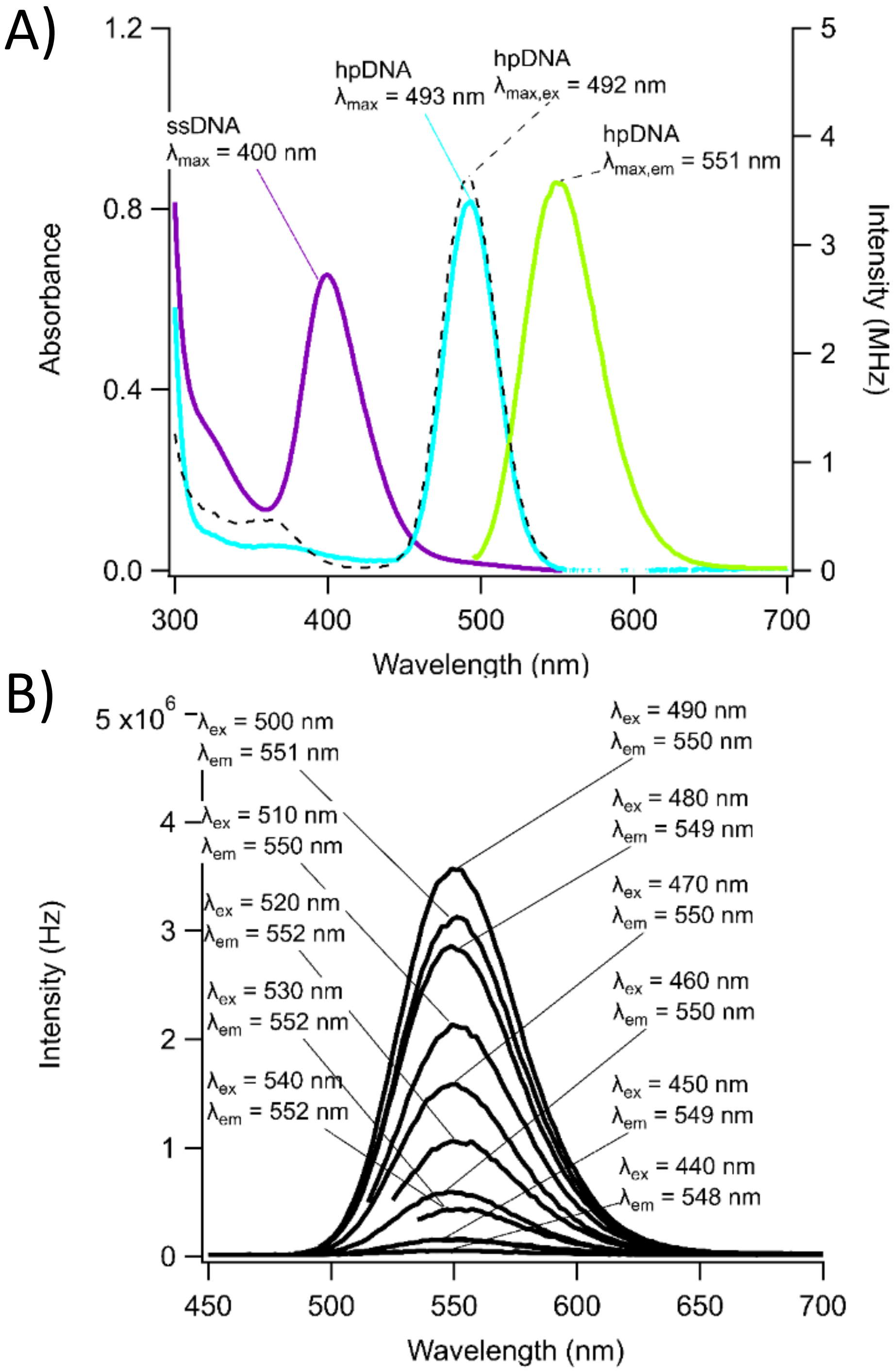


Figure S1. (A) Absorption spectra of the ssDNA-Ag_{10} complexes (solid violet) and the hpDNA – Ag_{10} complexes (solid blue). The excitation maximum and shape for the hpDNA-Ag_{10} complex (dotted black) match the absorption transition. The emission band for the hpDNA-Ag_{10} complex (solid green) has λ_{max} = 550 nm. (B) Emission spectra of hpDNA-Ag_{10}. The emission band does not shift over the range of excitation wavelengths from 440 nm to 540 nm. These overlapping spectra support a single type of cluster. Adopted from Reference 41.

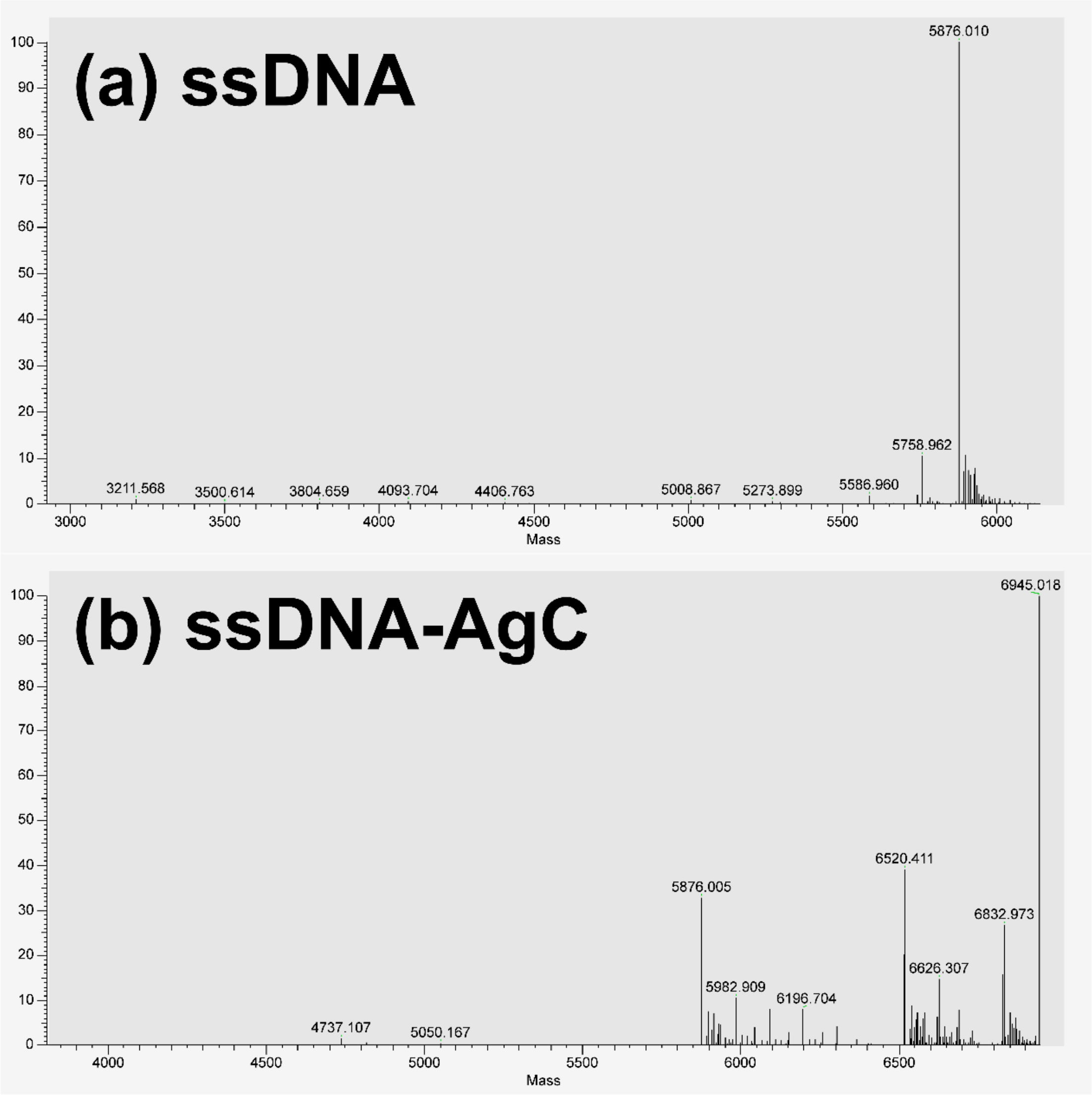


Figure S2. Negative-mode deconvoluted MS1 spectra of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC in 50 mM ammonium acetate **(a)** without and **(b)** with the AgC.

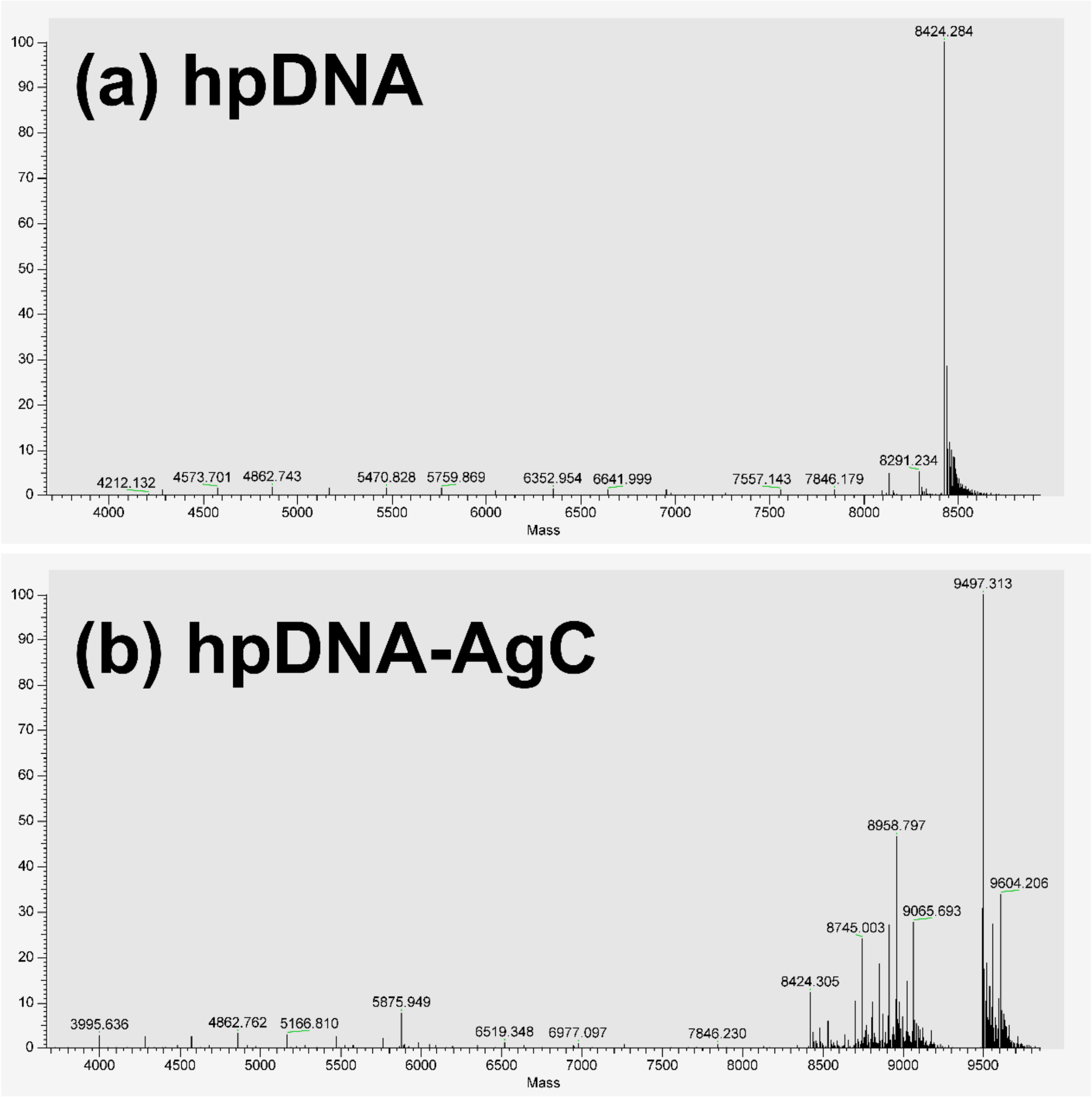


Figure S3. Negative-mode deconvoluted MS1 spectra of hairpin 28-mer oligonucleotide CCC CAA CTC CTT CCC GCC TTT TGG CGG G in 50 mM ammonium acetate **(a)** without and **(b)** with the Ag.

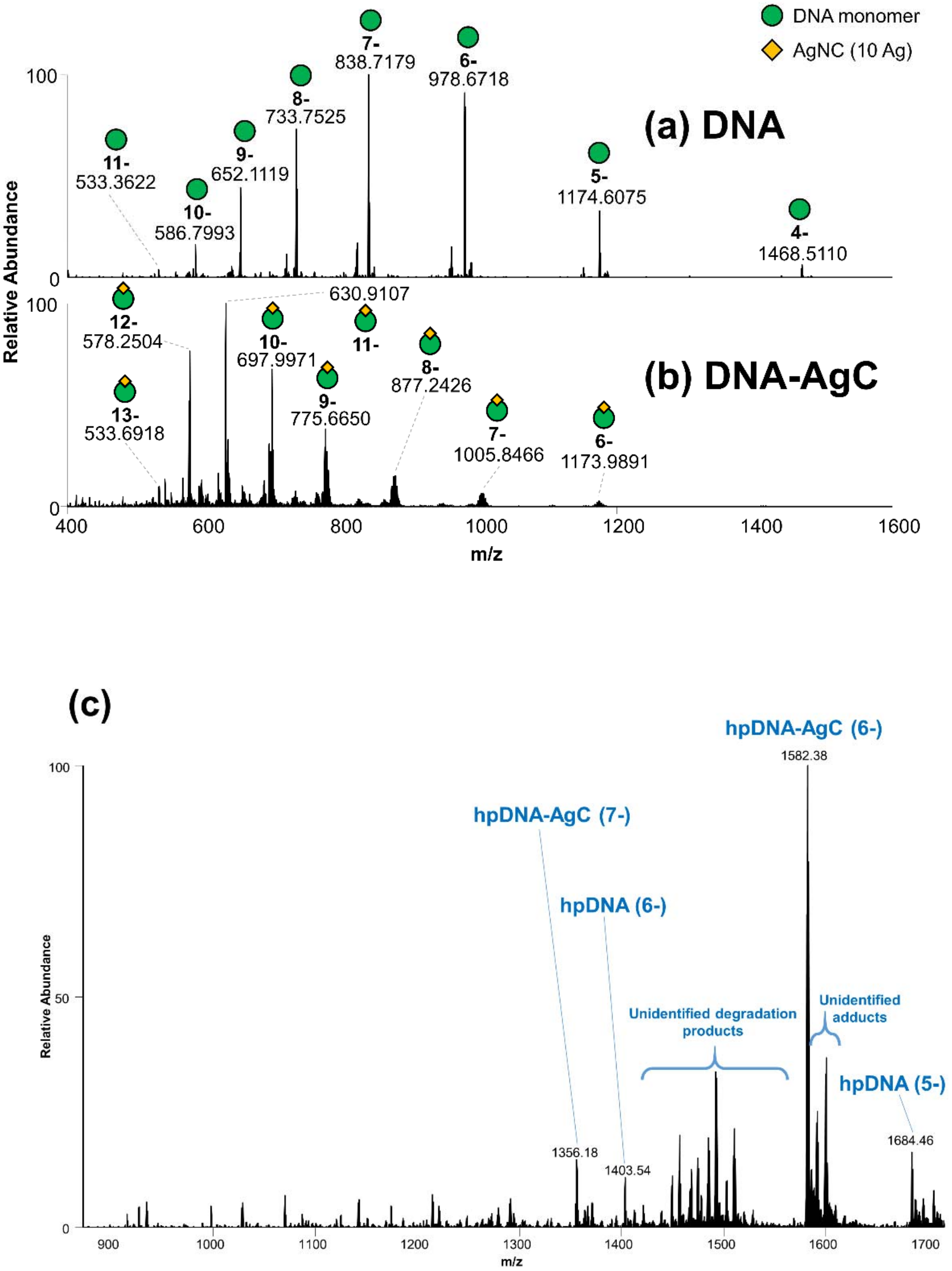


Figure S4. MS1 spectra of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC in 50:50 water:methanol (v/v) with 50 mM ammonium acetate **(a)** without and **(b)** with the AgC, highlighting the charge state shift observed for denaturing solvent compared to native solvent conditions (**Figure 1**), **(c)** assignment of contaminants in hpDNA-AgC MS1 spectrum (including bare hpDNA and unidentified degradation products).

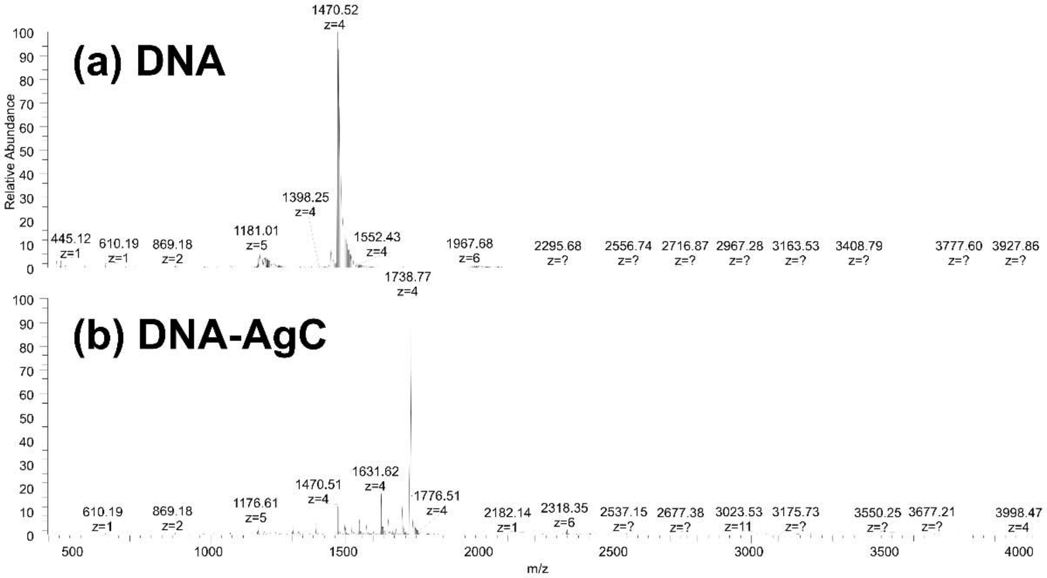
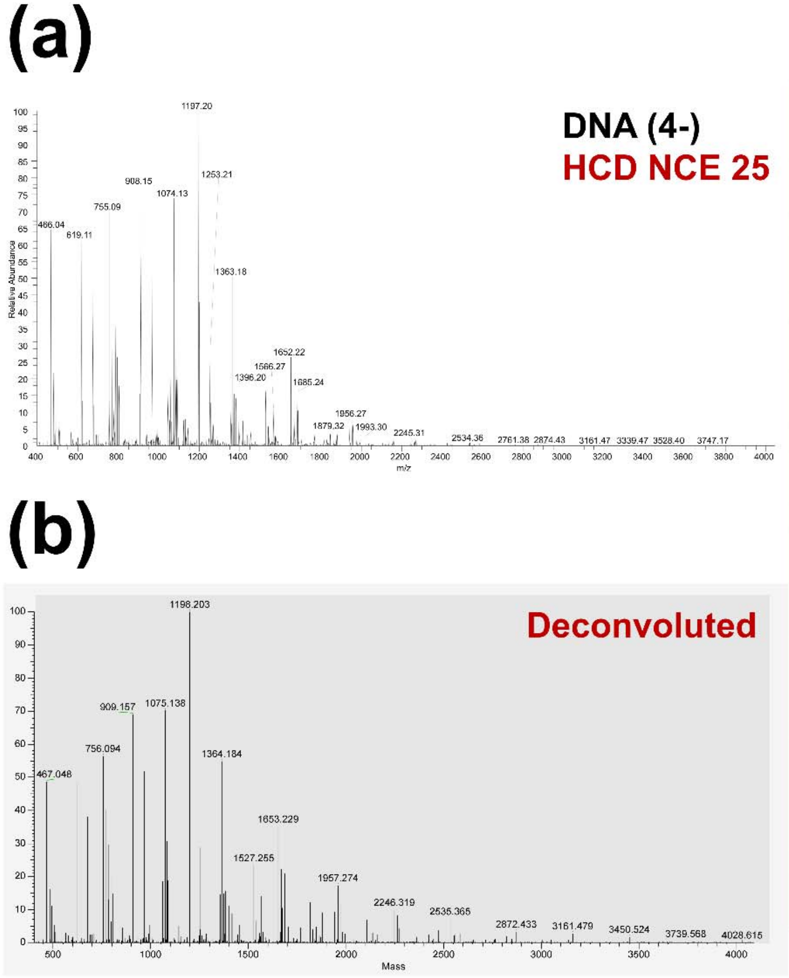


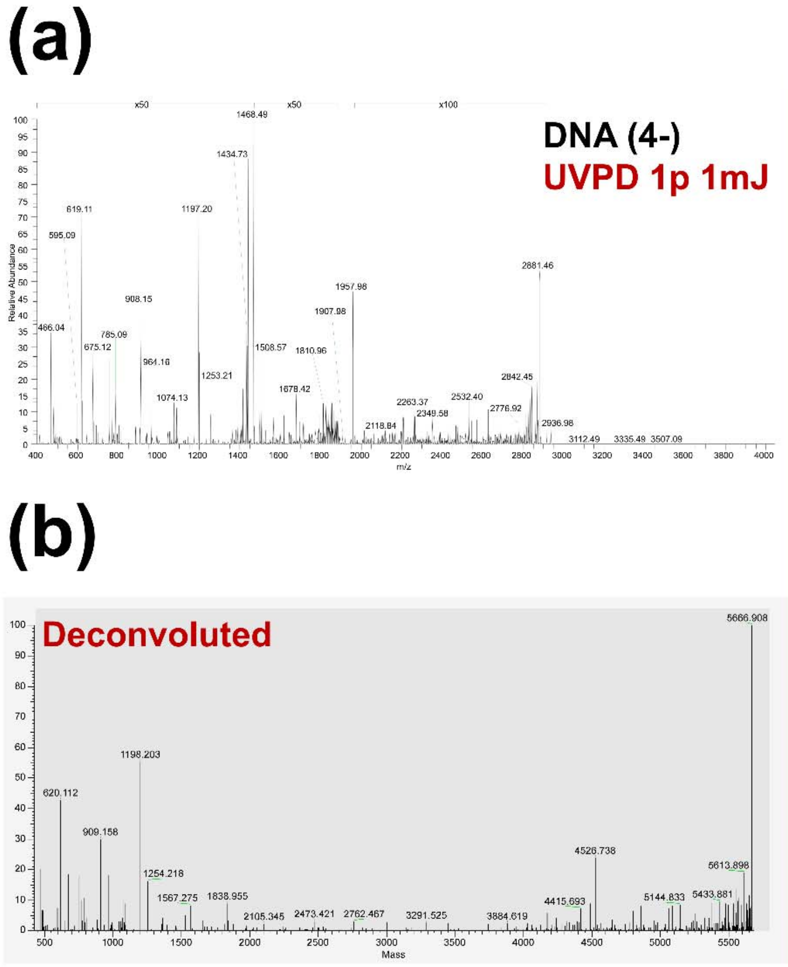
Figure S5. Positive-mode MS1 spectra of ssDNA CCC CAA CTC CTT CCC GCC AC **(a)** without and **(b)** with silver cluster.



(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.127	676.128	1.5
4		965.173	965.174	1.0
5		1254.218	1254.220	1.6
6		1567.275	1567.277	1.3
7		1880.331	1880.334	1.6
9		2473.422	2473.426	1.6
10		2762.467	2762.472	1.8
13		3659.603	3659.610	1.9
14		3948.647	3948.656	2.3
8	z	2295.420	2295.414	2.6
3	y	829.192	829.193	1.2
4		1118.237	1118.239	1.8
5		1447.289	1447.291	1.4
2	c	578.091	578.099	13.8
5		1469.271	1469.248	15.7
2	d	596.101	596.103	3.4
3		885.146	885.150	4.5
4		1174.191	1174.196	4.3
2	x	602.102	602.103	1.7
3		891.147	891.150	3.4
5		1509.246	1509.249	2.0
2	w	620.112	620.113	1.6
3		909.157	909.159	2.2
4		1198.203	1198.205	1.7
5		1527.255	1527.257	1.3
6		1816.300	1816.303	1.7
7		2105.346	2105.349	1.4
10		3002.482	3002.487	1.7
11		3291.527	3291.533	1.8
13		3884.610	3884.624	3.6

Figure S6. (a) HCD spectrum of 4- charge state (*m/z* 1468) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-*B*, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

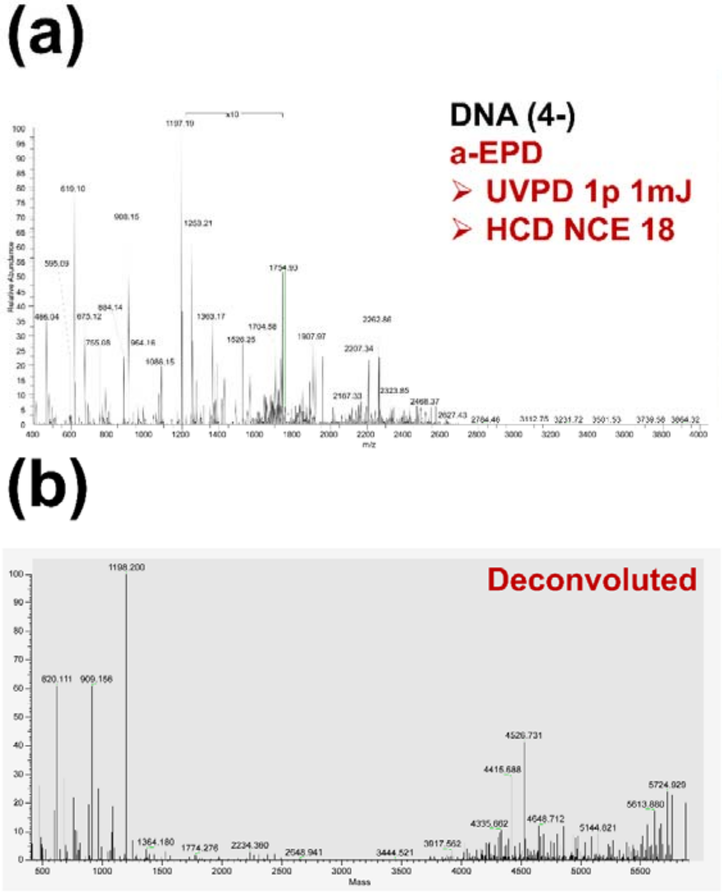


(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.127	676.128	1.5
4		965.172	965.174	2.1
5		1254.218	1254.220	1.6
6		1567.275	1567.277	1.3
7		1880.330	1880.334	2.1
9		2473.421	2473.426	2.0
10		2762.467	2762.472	1.8
13		3659.603	3659.610	1.9
14		3948.648	3948.656	2.0
15		4237.697	4237.702	1.2
16		4526.738	4526.748	2.2
17		4855.792	4855.800	1.6
18		5144.833	5144.846	2.5
19		5433.881	5433.892	2.0
2	a	497.117	497.118	2.0
16		4676.757	4676.795	8.1
17		4965.824	4965.841	3.4
18		5254.875	5254.888	2.5
19		5567.928	5567.945	3.1
2	z	521.128	521.129	1.9
18		5278.890	5278.899	1.7
19		5567.945	5567.945	0.0
2	c	578.091	578.099	13.8
2	d	596.101	596.103	3.4
3		885.146	885.150	4.5
14		4157.669	4157.681	2.9
17		5064.805	5064.826	4.1
2	x	602.102	602.103	1.7
3		891.147	891.150	3.4
18		5359.795	5359.873	14.6
2	w	620.112	620.113	1.6
3		909.158	909.159	1.1
4		1198.203	1198.205	1.7
5		1527.255	1527.257	1.3
6		1816.299	1816.303	2.2
7		2105.345	2105.349	1.9
8		2394.394	2394.395	0.4
10		3002.479	3002.487	2.7
11		3291.525	3291.533	2.4
13		3884.619	3884.624	1.3
14		4173.664	4173.670	1.4
15		4486.716	4486.728	2.7
16		4799.777	4799.785	1.7
17		5088.820	5088.831	2.2
18		5377.864	5377.877	2.4
19		5666.908	5666.923	2.6

Figure S7. (a) UVPD spectrum of 4- charge state (*m/z* 1468) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

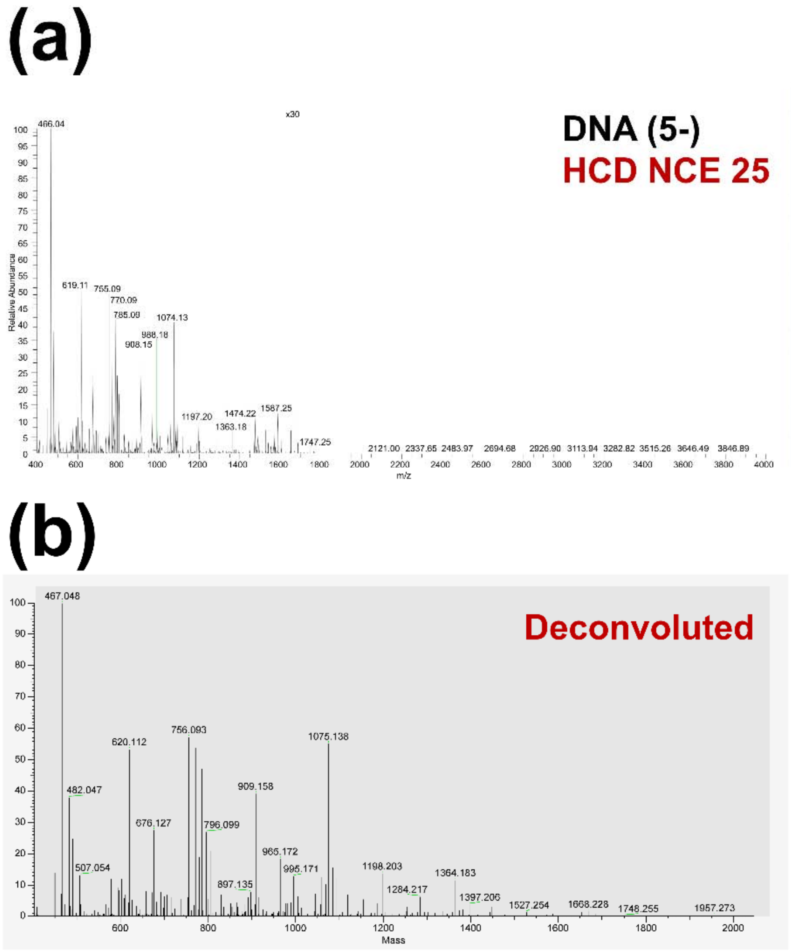
(a)



(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.126	676.128	3.0
4		965.170	965.174	4.1
5		1254.215	1254.220	4.0
6		1567.271	1567.277	3.8
15		4237.691	4237.702	2.6
16		4526.731	4526.748	3.8
17		4855.778	4855.800	4.5
18		5144.821	5144.846	4.9
2	a	497.116	497.118	4.0
3		786.160	786.164	5.1
4		1075.205	1075.211	5.6
5		1388.261	1388.268	5.0
14		4058.635	4058.696	15.0
15		4347.690	4347.742	12.0
16		4676.758	4676.795	7.9
17		4965.800	4965.841	8.3
19		5567.915	5567.945	5.4
2	z	521.127	521.129	3.8
3		810.172	810.176	4.9
4		1099.216	1099.222	5.5
5		1428.267	1428.275	5.6
16		4700.761	4700.806	9.6
19		5567.915	5567.945	5.4
4	y	1118.234	1118.239	4.5
17	c	5046.815	5046.817	0.4
2	d	596.100	596.103	5.0
3		885.145	885.150	5.6
4		1174.189	1174.196	6.0
5		1487.246	1487.254	5.4
13		3868.615	3868.635	5.2
14		4157.664	4157.681	4.1
15		4446.713	4446.728	3.4
16		4775.759	4775.780	4.4
18		5353.868	5353.873	0.9
19		5666.892	5666.930	6.7
3	x	891.145	891.150	5.6
4		1180.190	1180.196	5.1
5		1509.242	1509.249	4.6
17		5070.806	5070.826	3.9
2	w	620.111	620.113	3.2
3		909.156	909.159	3.3
4		1198.200	1198.205	4.2
5		1527.252	1527.257	3.3
13		3884.612	3884.624	3.1
14		4173.656	4173.670	3.4
15		4486.714	4486.728	3.1
16		4799.765	4799.785	4.2
17		5088.806	5088.831	4.9
18		5377.856	5377.877	3.9
19		5666.892	5666.923	5.5

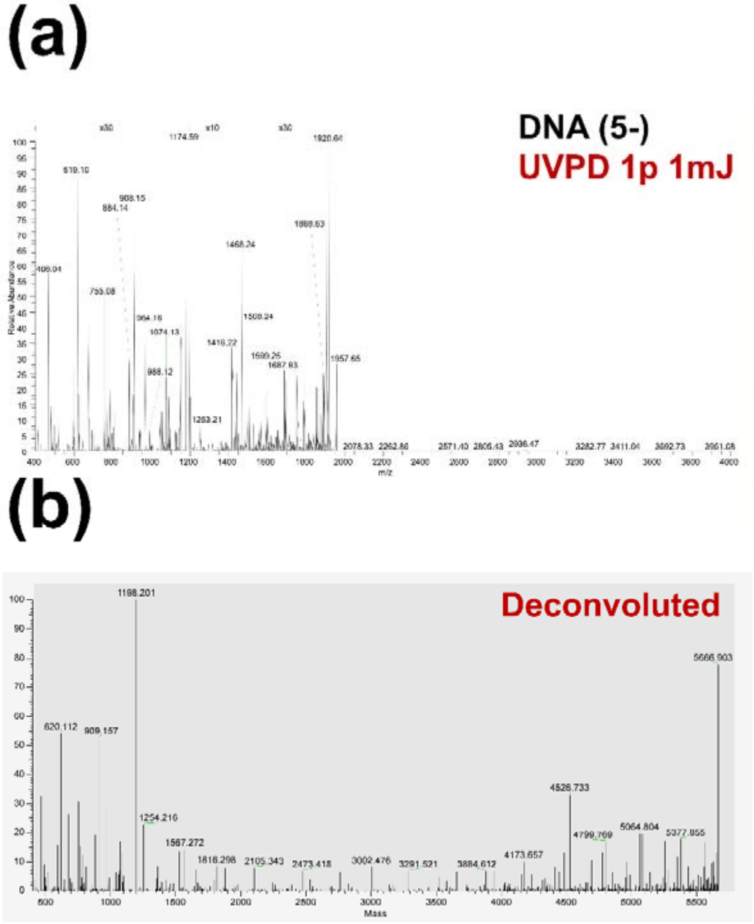
Figure S8. (a) a-EPD spectrum of 4- charge state (UVPD of 4- of *m/z* 1468, HCD of subsequent 3•- of *m/z* 1957) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.



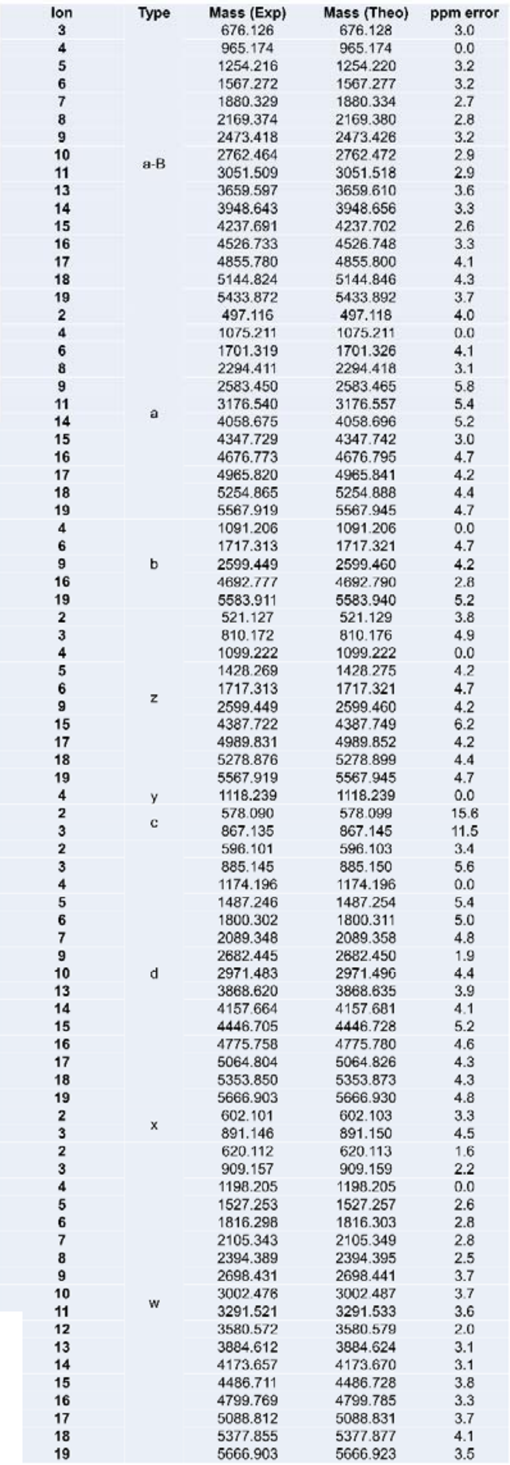
(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.127	676.128	1.5
4		965.172	965.174	2.1
5		1254.218	1254.220	1.6
6		1567.274	1567.277	1.9
3	b	802.170	802.160	12.5
4		1091.214	1091.206	7.3
6		1717.328	1717.321	4.1
2	y	540.146	540.147	1.9
3		829.192	829.193	1.2
4		1118.237	1118.239	1.8
5		1447.289	1447.291	1.4
6		1736.330	1736.337	4.0
2	c	578.091	578.099	13.8
3		867.136	867.145	10.4
2	d	596.101	596.103	3.4
3		885.146	885.150	4.5
2	x	602.102	602.103	1.7
3		891.147	891.150	3.4
4		1180.192	1180.196	3.4
5		1509.246	1509.249	2.0
2	w	620.112	620.113	1.6
3		909.158	909.159	1.1
4		1198.203	1198.205	1.7
5		1527.254	1527.257	2.0

Figure S9. (a) HCD spectrum of 5- charge state (*m/z* 1174) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

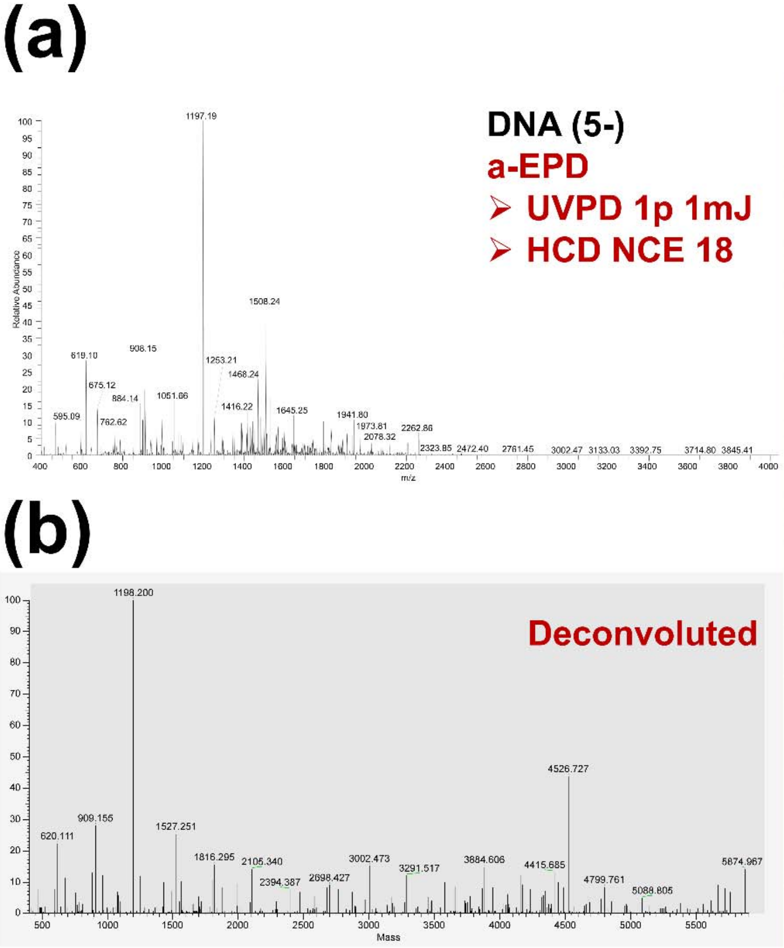


(c)

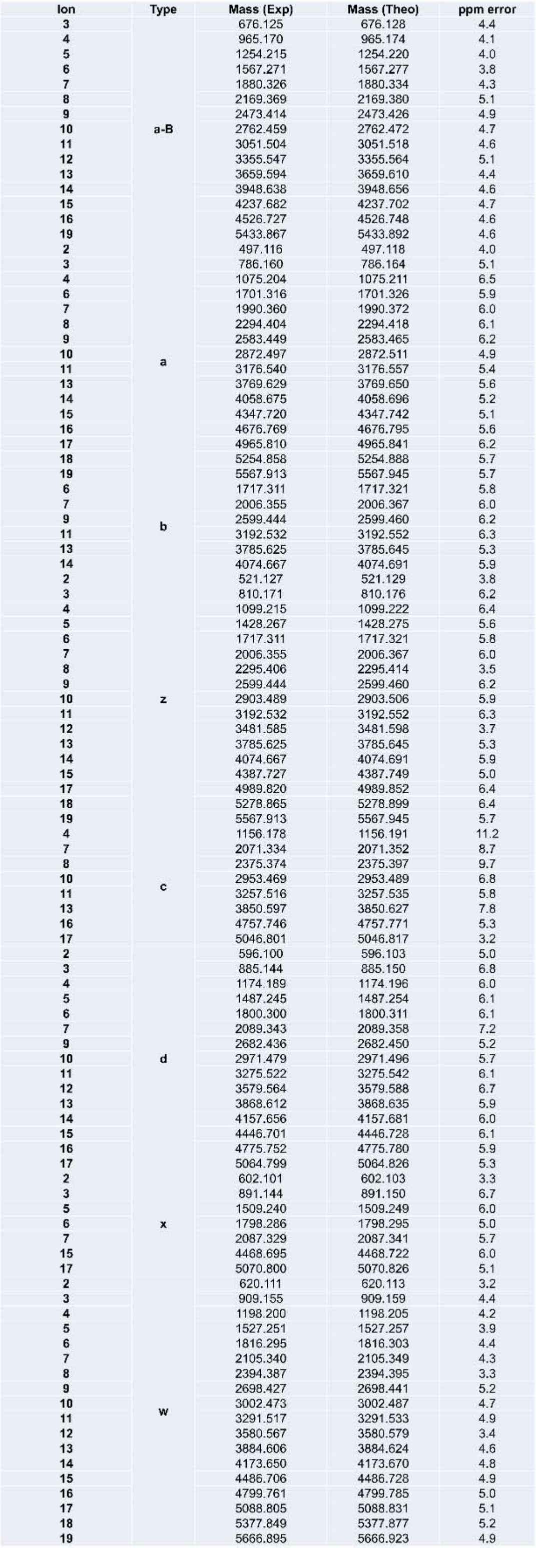


Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.126	676.128	3.0
4		965.174	965.174	0.0
5		1254.216	1254.220	3.2
6		1567.272	1567.277	3.2
7		1880.329	1880.334	2.7
8		2169.374	2169.380	2.8
9		2473.418	2473.426	3.2
10		2762.464	2762.472	2.9
11		3051.509	3051.518	2.9
13		3659.597	3659.610	3.6
14		3948.643	3948.656	3.3
15		4237.691	4237.702	2.6
16		4526.733	4526.748	3.3
17		4855.780	4855.800	4.1
18		5144.824	5144.846	4.3
19		5433.872	5433.892	3.7
2	a	497.116	497.118	4.0
4		1075.211	1075.211	0.0
6		1701.319	1701.326	4.1
8		2294.411	2294.418	3.1
9		2583.450	2583.465	5.8
11		3176.540	3176.557	5.4
14		4058.675	4058.696	5.2
15		4347.729	4347.742	3.0
16		4676.773	4676.795	4.7
17		4965.820	4965.841	4.2
18		5254.865	5254.888	4.4
19		5567.919	5567.945	4.7
4	b	1091.206	1091.206	0.0
6		1717.313	1717.321	4.7
9		2599.449	2599.460	4.2
16		4692.777	4692.790	2.8
19		5583.911	5583.940	5.2
2	z	521.127	521.129	3.8
3		810.172	810.176	4.9
4		1099.222	1099.222	0.0
5		1428.269	1428.275	4.2
6		1717.313	1717.321	4.7
9		2599.449	2599.460	4.2
15		4387.722	4387.749	6.2
17		4989.831	4989.852	4.2
18		5278.876	5278.899	4.4
19		5567.919	5567.945	4.7
4	y	1118.239	1118.239	0.0
2	c	578.090	578.099	15.6
3		867.135	867.145	11.5
2	d	596.101	596.103	3.4
3		885.145	885.150	5.6
4		1174.196	1174.196	0.0
5		1487.246	1487.254	5.4
6		1800.302	1800.311	5.0
7		2089.348	2089.358	4.8
9		2682.445	2682.450	1.9
10		2971.483	2971.496	4.4
13		3868.620	3868.635	3.9
14		4157.664	4157.681	4.1
15		4446.705	4446.728	5.2
16		4775.758	4775.780	4.6
17		5064.804	5064.826	4.3
18		5353.850	5353.873	4.3
19		5666.903	5666.930	4.8
2	x	602.101	602.103	3.3
3		891.146	891.150	4.5
2	w	620.112	620.113	1.6
3		909.157	909.159	2.2
4		1198.205	1198.205	0.0
5		1527.253	1527.257	2.6
6		1816.298	1816.303	2.8
7		2105.343	2105.349	2.8
8		2394.389	2394.395	2.5
9		2698.431	2698.441	3.7
10		3002.476	3002.487	3.7
11		3291.521	3291.533	3.6
12		3580.572	3580.579	2.0
13		3884.612	3884.624	3.1
14		4173.657	4173.670	3.1
15		4486.711	4486.728	3.8
16		4799.769	4799.785	3.3
17		5088.812	5088.831	3.7
18		5377.855	5377.877	4.1
19		5666.903	5666.923	3.5

Figure S10. (a) UVPD spectrum of 5- charge state (*m/z* 1174) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm).

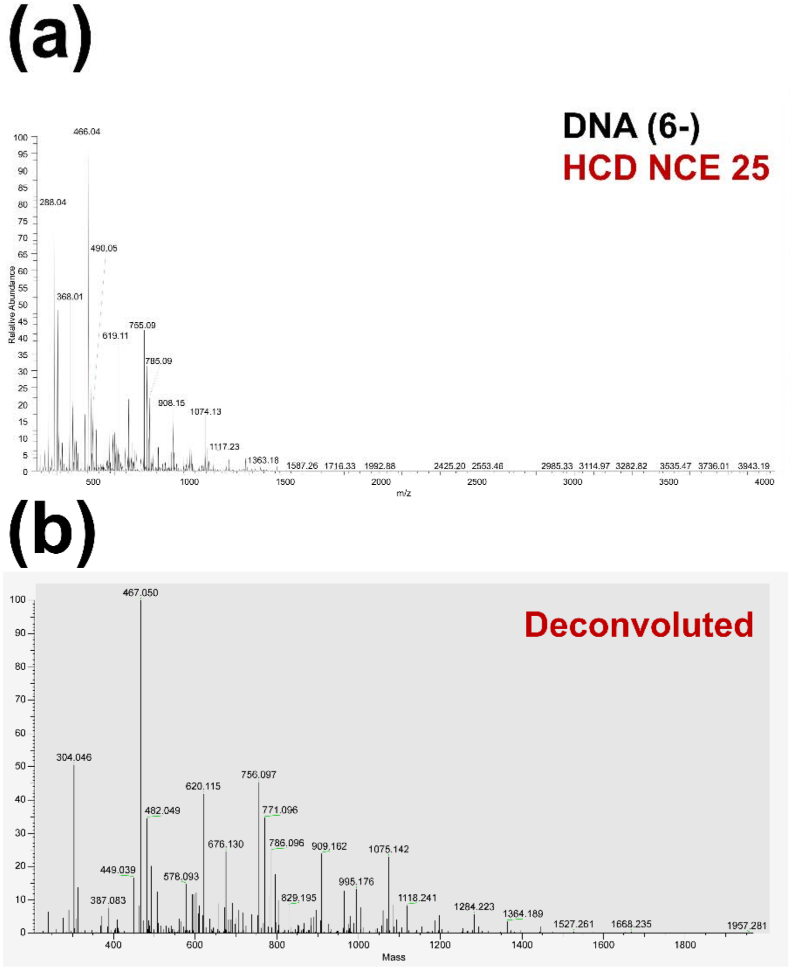


(c)



Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.125	676.128	4.4
4		965.170	965.174	4.1
5		1254.215	1254.220	4.0
6		1567.271	1567.277	3.8
7		1880.326	1880.334	4.3
8		2169.369	2169.380	5.1
9		2473.414	2473.426	4.9
10		2762.459	2762.472	4.7
11		3051.504	3051.518	4.6
12		3355.547	3355.564	5.1
13		3659.594	3659.610	4.4
14		3948.638	3948.656	4.6
15		4237.682	4237.702	4.7
16		4526.727	4526.748	4.6
19		5433.867	5433.892	4.6
2	a	497.116	497.118	4.0
3		786.160	786.164	5.1
4		1075.204	1075.211	6.5
6		1701.316	1701.326	5.9
7		1990.360	1990.372	6.0
8		2294.404	2294.418	6.1
9		2583.449	2583.465	6.2
10		2872.497	2872.511	4.9
11		3176.540	3176.557	5.4
13		3769.629	3769.650	5.6
14		4058.675	4058.696	5.2
15		4347.720	4347.742	5.1
16		4676.769	4676.795	5.6
17		4965.810	4965.841	6.2
18		5254.858	5254.888	5.7
19		5567.913	5567.945	5.7
6	b	1717.311	1717.321	5.8
7		2006.355	2006.367	6.0
9		2599.444	2599.460	6.2
11		3192.532	3192.552	6.3
13		3785.625	3785.645	5.3
14		4074.667	4074.691	5.9
2	z	521.127	521.129	3.8
3		810.171	810.176	6.2
4		1099.215	1099.222	6.4
5		1428.267	1428.275	5.6
6		1717.311	1717.321	5.8
7		2006.355	2006.367	6.0
8		2295.406	2295.414	3.5
9		2599.444	2599.460	6.2
10		2903.489	2903.506	5.9
11		3192.532	3192.552	6.3
12		3481.585	3481.598	3.7
13		3785.625	3785.645	5.3
14		4074.667	4074.691	5.9
15		4387.727	4387.749	5.0
17		4989.820	4989.852	6.4
18		5278.865	5278.899	6.4
19		5567.913	5567.945	5.7
4	c	1156.178	1156.191	11.2
7		2071.334	2071.352	8.7
8		2375.374	2375.397	9.7
10		2953.469	2953.489	6.8
11		3257.516	3257.535	5.8
13		3850.597	3850.627	7.8
16		4757.746	4757.771	5.3
17		5046.801	5046.817	3.2
2	d	596.100	596.103	5.0
3		885.144	885.150	6.8
4		1174.189	1174.196	6.0
5		1487.245	1487.254	6.1
6		1800.300	1800.311	6.1
7		2089.343	2089.358	7.2
9		2682.436	2682.450	5.2
10		2971.479	2971.496	5.7
11		3275.522	3275.542	6.1
12		3579.564	3579.588	6.7
13		3868.612	3868.635	5.9
14		4157.656	4157.681	6.0
15		4446.701	4446.728	6.1
16		4775.752	4775.780	5.9
17		5064.799	5064.826	5.3
2	x	602.101	602.103	3.3
3		891.144	891.150	6.7
5		1509.240	1509.249	6.0
6		1798.286	1798.295	5.0
7		2087.329	2087.341	5.7
15		4468.695	4468.722	6.0
17		5070.800	5070.826	5.1
2	w	620.111	620.113	3.2
3		909.155	909.159	4.4
4		1198.200	1198.205	4.2
5		1527.251	1527.257	3.9
6		1816.295	1816.303	4.4
7		2105.340	2105.349	4.3
8		2394.387	2394.395	3.3
9		2698.427	2698.441	5.2
10		3002.473	3002.487	4.7
11		3291.517	3291.533	4.9
12		3580.567	3580.579	3.4
13		3884.606	3884.624	4.6
14		4173.650	4173.670	4.8
15		4486.706	4486.728	4.9
16		4799.761	4799.785	5.0
17		5088.805	5088.831	5.1
18		5377.849	5377.877	5.2
19		5666.895	5666.923	4.9

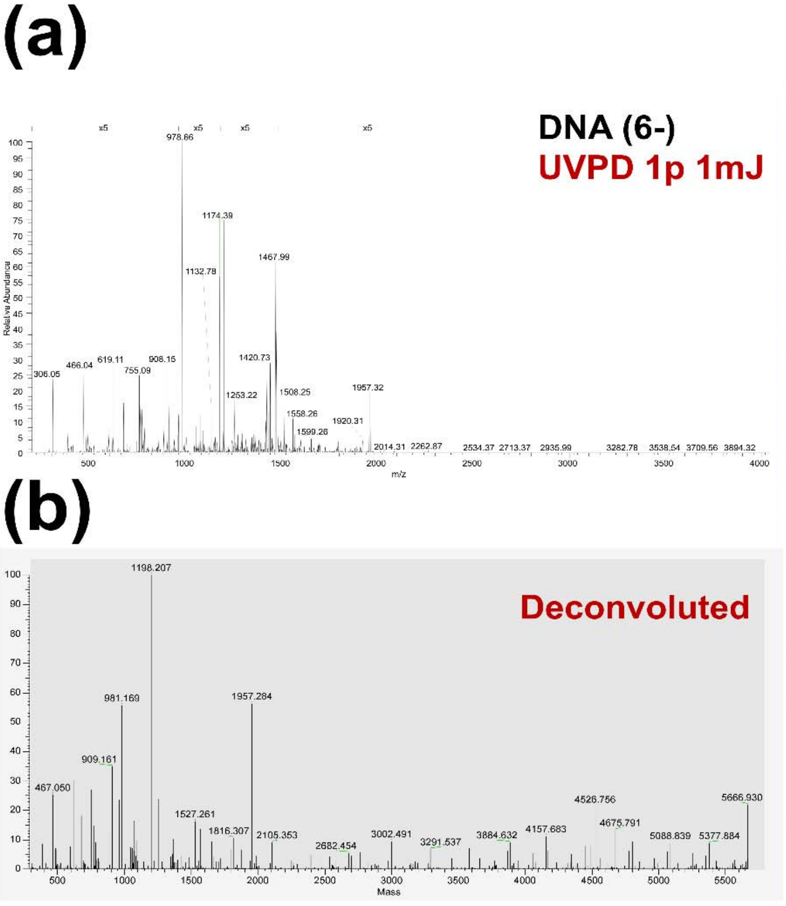
Figure S11. (a) a-EPD spectrum of 5- charge state (UVPD of 5- of *m/z* 1174, HCD of subsequent 4•- of *m/z* 1468) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm).



(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
2	a-B	387.083	387.082	2.6
3		676.130	676.128	3.0
4		965.177	965.174	3.1
5		1254.223	1254.220	2.4
6		1567.280	1567.277	1.9
3	b	802.173	802.160	16.2
4		1091.219	1091.206	11.9
6		1717.336	1717.321	8.7
2	y	540.149	540.147	3.7
3		829.195	829.193	2.4
4		1118.241	1118.239	1.8
5		1447.295	1447.291	2.8
6		1736.339	1736.337	1.2
2	c	578.093	578.099	10.4
3		867.140	867.145	5.8
4		1156.186	1156.191	4.3
5		1469.276	1469.248	19.1
2	d	596.104	596.103	1.7
3		885.150	885.150	0.0
2	x	602.104	602.103	1.7
3		891.151	891.150	1.1
4		1180.197	1180.196	0.8
5		1509.248	1509.249	0.7
2	w	620.115	620.113	3.2
3		909.162	909.159	3.3
4		1198.208	1198.205	2.5
5		1527.261	1527.257	2.6

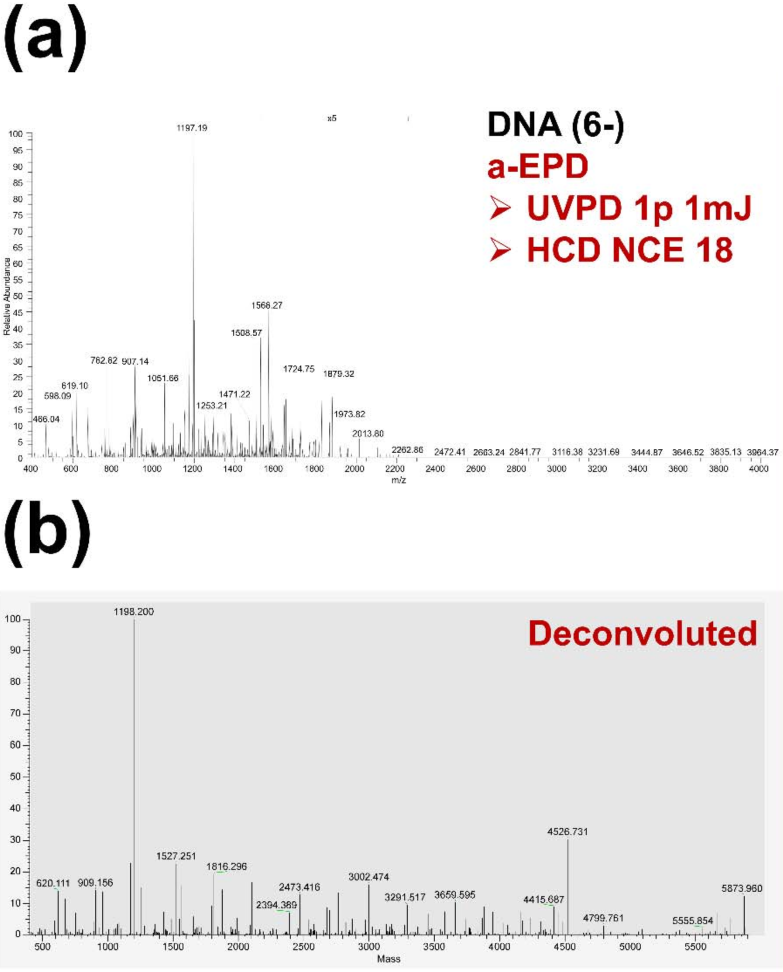
Figure S12. (a) HCD spectrum of 6- charge state (*m/z* 978) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

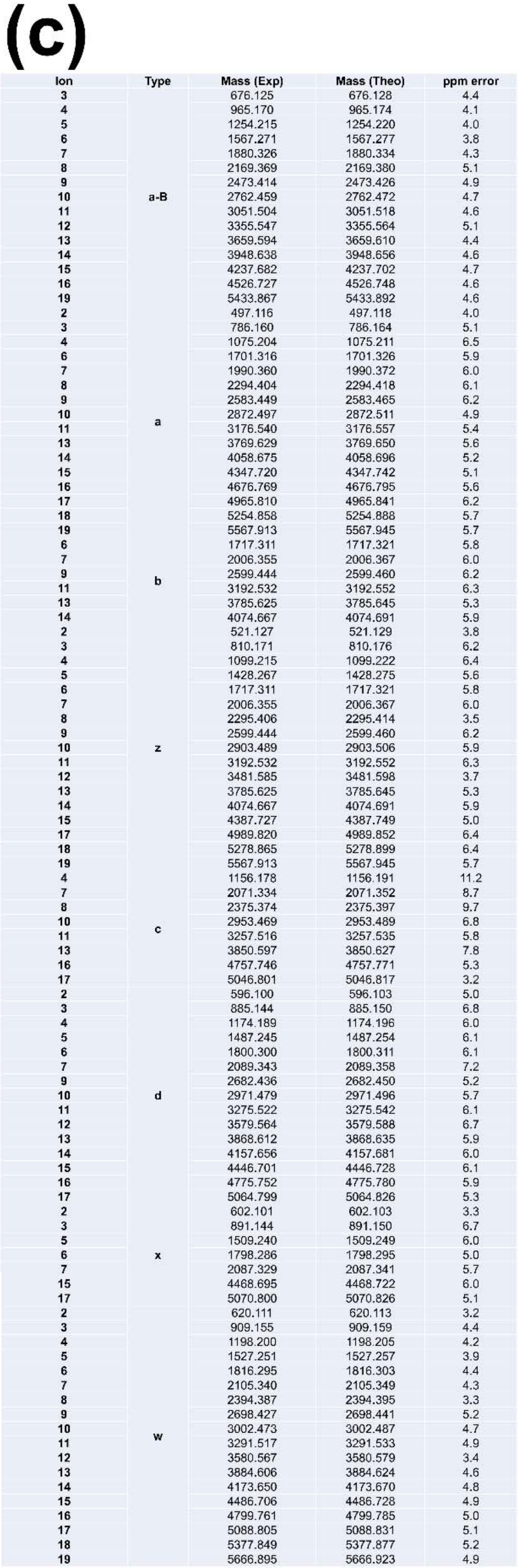


(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
2	a-B	387.083	387.082	2.6
3		676.130	676.128	3.0
4		965.177	965.174	3.1
5		1254.223	1254.220	2.4
6		1567.281	1567.277	2.6
7		1880.339	1880.334	2.7
8		2169.385	2169.380	2.3
9		2473.431	2473.426	2.0
10		2762.478	2762.472	2.2
11		3051.523	3051.518	1.6
12		3355.568	3355.564	1.2
13		3659.617	3659.610	1.9
14		3948.662	3948.656	1.5
15		4237.711	4237.702	2.1
16		4526.748	4526.748	0.0
18		5144.854	5144.846	1.6
19		5433.902	5433.892	1.8
2	a	497.119	497.118	2.0
4		1075.211	1075.211	0.0
5		1388.269	1388.268	0.7
6		1701.327	1701.326	0.6
7		1990.373	1990.372	0.5
8		2294.419	2294.418	0.4
9		2583.466	2583.465	0.4
11		3176.558	3176.557	0.3
13		3769.652	3769.650	0.5
14		4058.699	4058.696	0.7
15		4347.749	4347.742	1.6
16		4676.795	4676.795	0.0
17		4965.844	4965.841	0.6
18		5254.894	5254.888	1.1
19		5567.950	5567.945	0.9
2	z	521.130	521.129	1.9
3		810.177	810.176	1.2
4		1099.223	1099.222	0.9
5		1428.276	1428.275	0.7
6		1717.322	1717.321	0.6
7		2006.368	2006.367	0.5
8		2295.421	2295.414	3.0
9		2599.462	2599.460	0.8
10		2903.508	2903.506	0.7
11		3192.553	3192.552	0.3
12		3481.606	3481.598	2.3
13		3785.647	3785.645	0.5
14		4074.689	4074.691	0.5
15		4387.753	4387.749	0.9
16		4700.806	4700.806	0.0
17		4989.854	4989.852	0.4
18		5278.900	5278.899	0.2
19		5567.950	5567.945	0.9
8	y	2314.429	2314.429	0.0
10		2922.524	2922.521	1.0
16		4719.819	4719.819	0.0
2	c	578.093	578.099	10.4
14		4139.673	4139.673	0.0
16		4757.771	4757.771	0.0
2	d	596.104	596.103	1.7
3		885.150	885.150	0.0
4		1174.197	1174.196	0.9
5		1487.254	1487.254	0.0
6		1800.313	1800.311	1.1
7		2089.358	2089.358	0.0
9		2682.454	2682.450	1.5
10		2971.497	2971.496	0.3
11		3275.543	3275.542	0.3
13		3868.636	3868.635	0.3
14		4157.683	4157.681	0.5
15		4446.731	4446.728	0.7
16		4775.780	4775.780	0.0
17		5064.832	5064.826	1.2
18		5353.875	5353.873	0.4
19		5666.930	5666.930	0.0
1	x	289.046	289.046	0.0
2		602.104	602.103	1.7
3		891.151	891.150	1.1
5		1509.249	1509.249	0.0
16		4781.780	4781.780	0.0
18		5359.892	5359.873	3.5
2	w	620.115	620.113	3.2
3		909.161	909.159	2.2
4		1198.207	1198.205	1.7
5		1527.261	1527.257	2.6
6		1816.307	1816.303	2.2
7		2105.353	2105.349	1.9
8		2394.403	2394.395	3.3
9		2698.443	2698.441	0.7
10		3002.491	3002.487	1.3
11		3291.537	3291.533	1.2
12		3580.589	3580.579	2.8
13		3884.632	3884.624	2.1
14		4173.676	4173.670	1.4
15		4486.733	4486.728	1.1
16		4799.785	4799.785	0.0
17		5088.839	5088.831	1.6
18		5377.884	5377.877	1.3
19		5666.930	5666.923	1.2

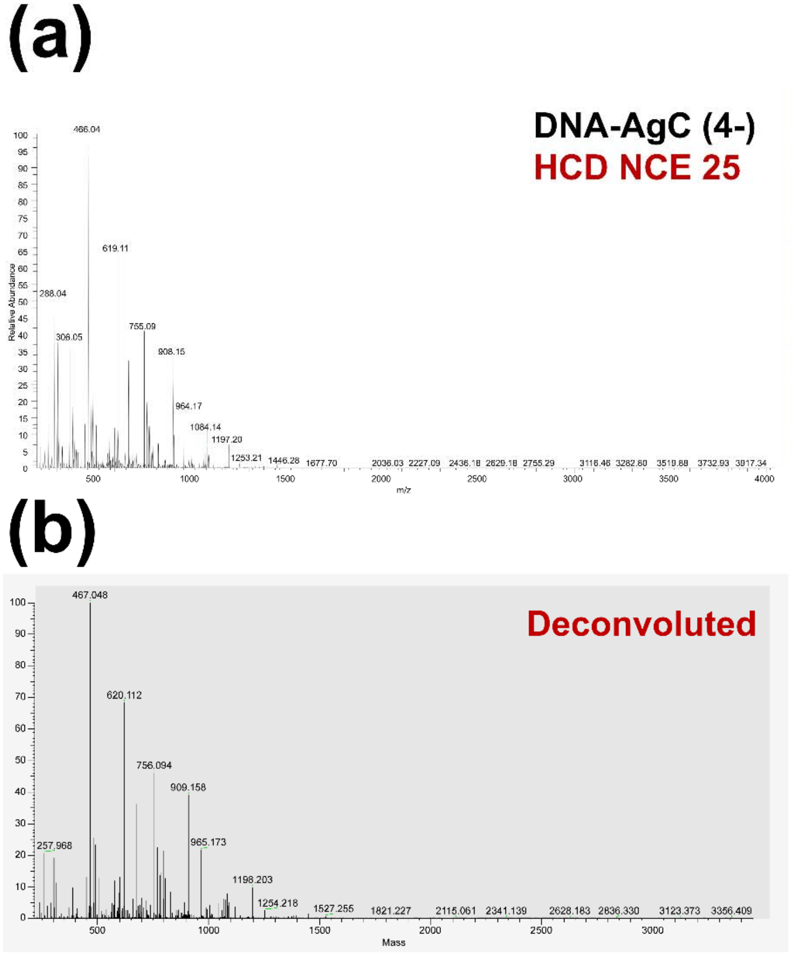
Figure S13. (a) UVPD spectrum of 6- charge state (*m/z* 978) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm).





Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.125	676.128	4.4
4		965.170	965.174	4.1
5		1254.215	1254.220	4.0
6		1567.271	1567.277	3.8
7		1880.326	1880.334	4.3
8		2169.369	2169.380	5.1
9		2473.414	2473.426	4.9
10		2762.459	2762.472	4.7
11		3051.504	3051.518	4.6
12		3355.547	3355.564	5.1
13		3659.594	3659.610	4.4
14		3948.638	3948.656	4.6
15		4237.682	4237.702	4.7
16		4526.727	4526.748	4.6
19		5433.867	5433.892	4.6
2	a	497.116	497.118	4.0
3		786.160	786.164	5.1
4		1075.204	1075.211	6.5
6		1701.316	1701.326	5.9
7		1990.360	1990.372	6.0
8		2294.404	2294.418	6.1
9		2583.449	2583.465	6.2
10		2872.497	2872.511	4.9
11		3176.540	3176.557	5.4
13		3769.629	3769.650	5.6
14		4058.675	4058.696	5.2
15		4347.720	4347.742	5.1
16		4676.769	4676.795	5.6
17		4965.810	4965.841	6.2
18		5254.858	5254.888	5.7
19		5567.913	5567.945	5.7
6	b	1717.311	1717.321	5.8
7		2006.355	2006.367	6.0
9		2599.444	2599.460	6.2
11		3192.532	3192.552	6.3
13		3785.625	3785.645	5.3
14		4074.667	4074.691	5.9
2	z	521.127	521.129	3.8
3		810.171	810.176	6.2
4		1099.215	1099.222	6.4
5		1428.267	1428.275	5.6
6		1717.311	1717.321	5.8
7		2006.355	2006.367	6.0
8		2295.406	2295.414	3.5
9		2599.444	2599.460	6.2
10		2903.489	2903.506	5.9
11		3192.532	3192.552	6.3
12		3481.585	3481.598	3.7
13		3785.625	3785.645	5.3
14		4074.667	4074.691	5.9
15		4387.727	4387.749	5.0
17		4989.820	4989.852	6.4
18		5278.865	5278.899	6.4
19		5567.913	5567.945	5.7
4	c	1156.178	1156.191	11.2
7		2071.334	2071.352	8.7
8		2375.374	2375.397	9.7
10		2953.469	2953.489	6.8
11		3257.516	3257.535	5.8
13		3850.597	3850.627	7.8
16		4757.746	4757.771	5.3
17		5046.801	5046.817	3.2
2	d	596.100	596.103	5.0
3		885.144	885.150	6.8
4		1174.189	1174.196	6.0
5		1487.245	1487.254	6.1
6		1800.300	1800.311	6.1
7		2089.343	2089.358	7.2
9		2682.436	2682.450	5.2
10		2971.479	2971.496	5.7
11		3275.522	3275.542	6.1
12		3579.564	3579.588	6.7
13		3868.612	3868.635	5.9
14		4157.656	4157.681	6.0
15		4446.701	4446.728	6.1
16		4775.752	4775.780	5.9
17		5064.799	5064.826	5.3
2	x	602.101	602.103	3.3
3		891.144	891.150	6.7
5		1509.240	1509.249	6.0
6		1798.286	1798.295	5.0
7		2087.329	2087.341	5.7
15		4468.695	4468.722	6.0
17		5070.800	5070.826	5.1
2	w	620.111	620.113	3.2
3		909.155	909.159	4.4
4		1198.200	1198.205	4.2
5		1527.251	1527.257	3.9
6		1816.295	1816.303	4.4
7		2105.340	2105.349	4.3
8		2394.387	2394.395	3.3
9		2698.427	2698.441	5.2
10		3002.473	3002.487	4.7
11		3291.517	3291.533	4.9
12		3580.567	3580.579	3.4
13		3884.606	3884.624	4.6
14		4173.650	4173.670	4.8
15		4486.706	4486.728	4.9
16		4799.761	4799.785	5.0
17		5088.805	5088.831	5.1
18		5377.849	5377.877	5.2
19		5666.895	5666.923	4.9

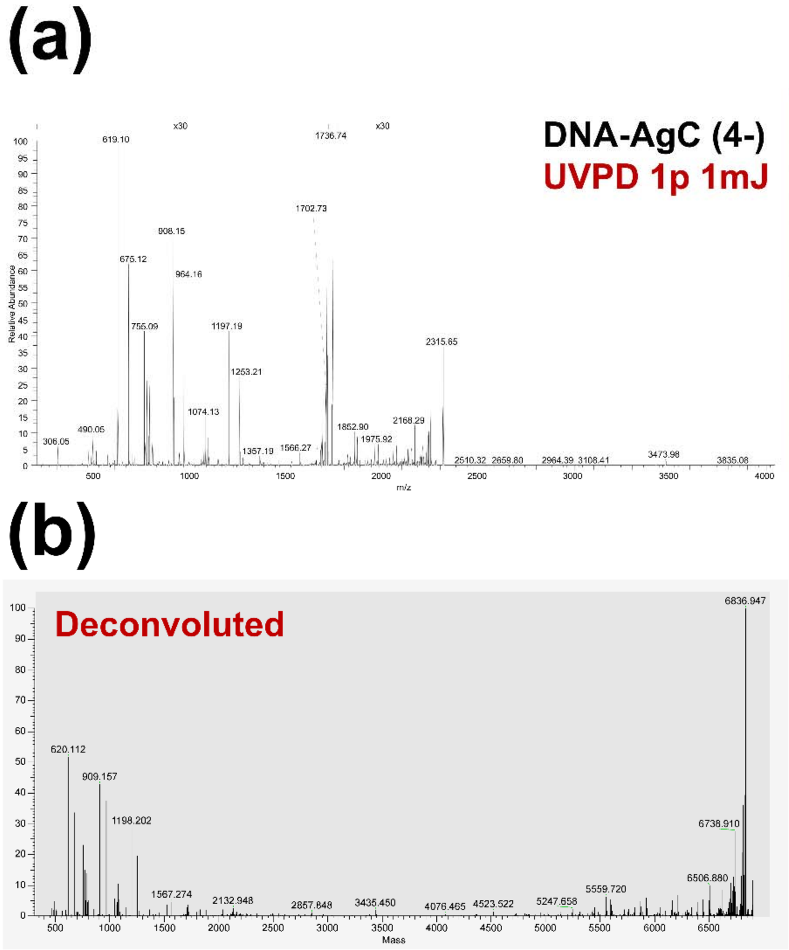
Figure S14. (a) a-EPD spectrum of 6- charge state (UVPD of 6- of *m/z* 978, HCD of subsequent 5•- of *m/z* 1174) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm).



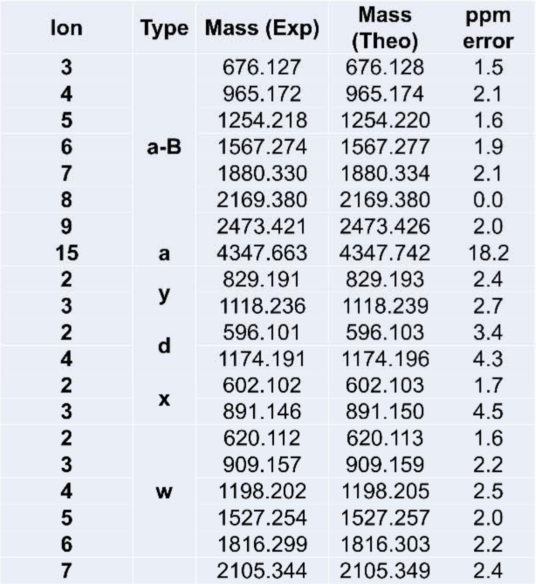
(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
2	a-B	387.082	387.082	0.0
3		676.127	676.128	1.5
4		965.173	965.174	1.0
5		1254.218	1254.220	1.6
6		1567.274	1567.277	1.9
7		1880.330	1880.334	2.1
2	y	540.146	540.147	1.9
3		829.192	829.193	1.2
4		1118.237	1118.239	1.8
5		1447.289	1447.291	1.4
2	c	578.091	578.099	13.8
3		867.136	867.145	10.4
4		1156.181	1156.191	8.6
2	d	596.101	596.103	3.4
3		885.147	885.150	3.4
2	x	602.102	602.103	1.7
3		891.147	891.150	3.4
4		1180.192	1180.196	3.4
5		1509.245	1509.249	2.7
2	w	620.112	620.113	1.6
3		909.158	909.159	1.1
4		1198.203	1198.205	1.7
5		1527.255	1527.257	1.3

Figure S15. (a) HCD spectrum of 4- charge state (*m/z* 1736) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.



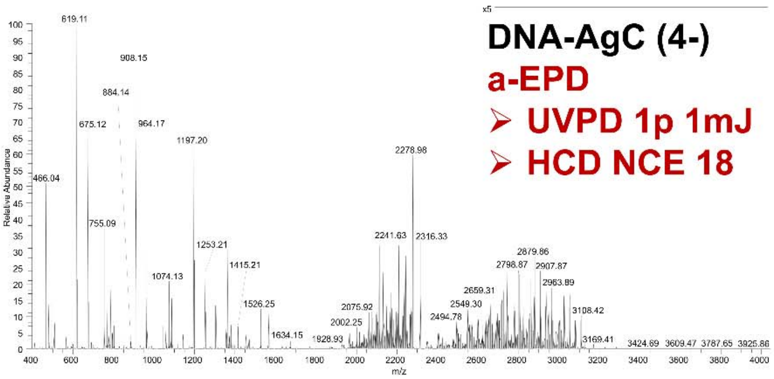
(c)



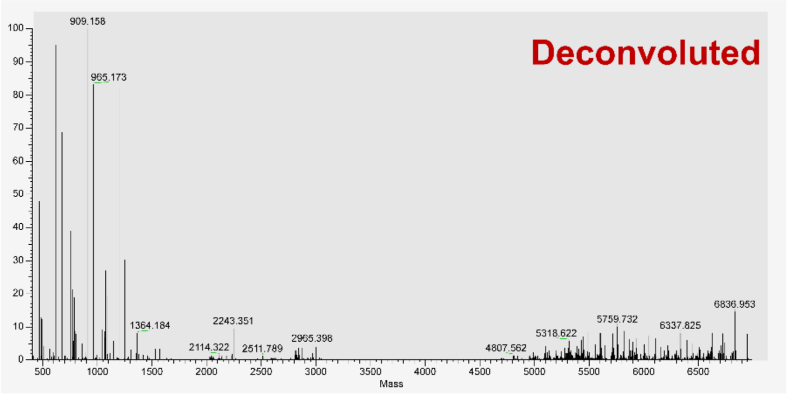
Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.127	676.128	1.5
4		965.172	965.174	2.1
5		1254.218	1254.220	1.6
6		1567.274	1567.277	1.9
7		1880.330	1880.334	2.1
8		2169.380	2169.380	0.0
9		2473.421	2473.426	2.0
15	a	4347.663	4347.742	18.2
2	y	829.191	829.193	2.4
3		1118.236	1118.239	2.7
2	d	596.101	596.103	3.4
4		1174.191	1174.196	4.3
2	x	602.102	602.103	1.7
3		891.146	891.150	4.5
2	w	620.112	620.113	1.6
3		909.157	909.159	2.2
4		1198.202	1198.205	2.5
5		1527.254	1527.257	2.0
6		1816.299	1816.303	2.2
7		2105.344	2105.349	2.4

Figure S16. (a) UVPD spectrum of 4- charge state (*m/z* 1736) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

(a)



(b)

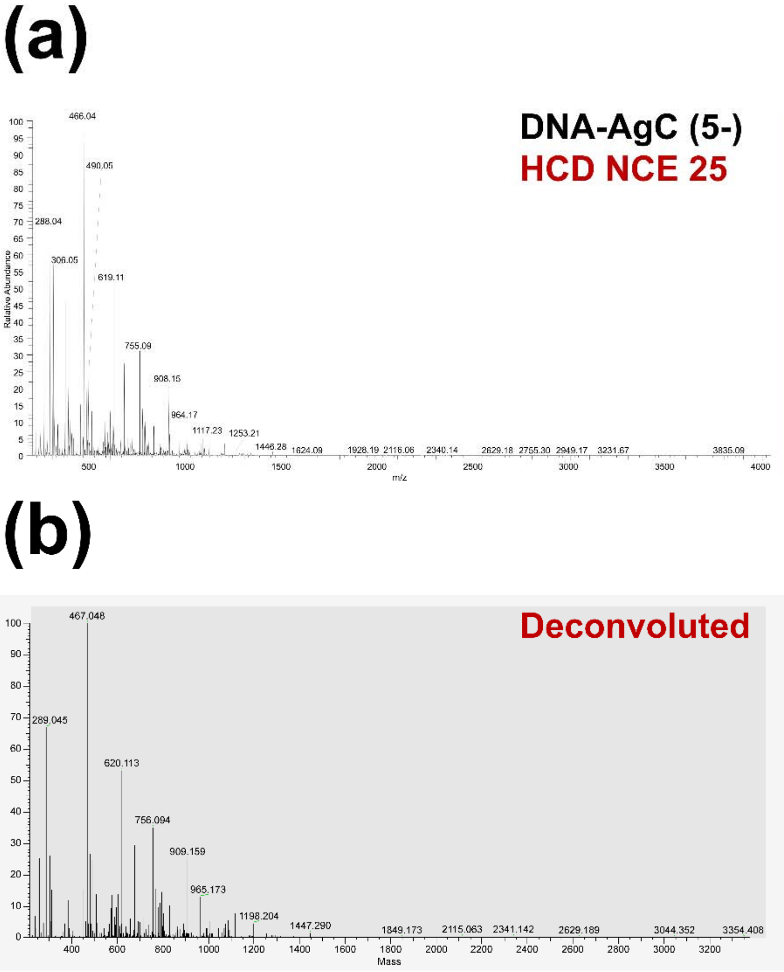


(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.128	676.128	0.0
4		965.173	965.174	1.0
5		1254.219	1254.220	0.8
6		1567.276	1567.277	0.6
7		1880.332	1880.334	1.1
2	y	540.147	540.147	0.0
3		829.192	829.193	1.2
4		1118.237	1118.239	1.8
5		1447.290	1447.291	0.7
2	c	578.091	578.099	13.8
3		867.136	867.145	10.4
17		5046.740	5046.817	15.3
2	d	596.102	596.103	1.7
3		885.147	885.150	3.4
4		1174.192	1174.196	3.4
17		5064.727	5064.826	19.5
2	x	602.102	602.103	1.7
3		891.148	891.150	2.2
4		1180.193	1180.196	2.5
2	w	620.113	620.113	0.0
3		909.158	909.159	1.1
4		1198.204	1198.205	0.8
5		1527.256	1527.257	0.7

Figure S17. (a) a-EPD spectrum of 4- charge state (UVPD of 4- of *m/z* 1736, HCD of subsequent 3•- of *m/z* 2315) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm).

The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

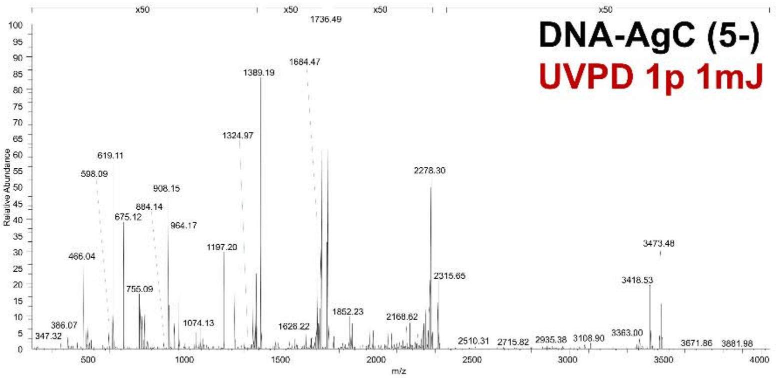


(c)

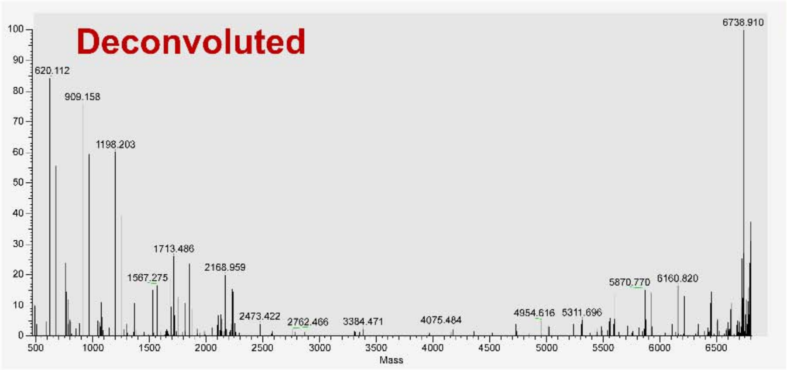
Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
2	a-B	387.082	387.082	0.0
3		676.128	676.128	0.0
4		965.173	965.174	1.0
5		1254.219	1254.220	0.8
6		1567.275	1567.277	1.3
3	b	802.171	802.160	13.7
2	y	540.147	540.147	0.0
3		829.192	829.193	1.2
4		1118.238	1118.239	0.9
5		1447.290	1447.291	0.7
2	c	578.091	578.099	13.8
3		867.137	867.145	9.2
2	d	596.102	596.103	1.7
3		885.147	885.150	3.4
1	x	289.045	289.046	3.5
2		602.102	602.103	1.7
3		891.148	891.150	2.2
4		1180.193	1180.196	2.5
5		1509.247	1509.249	1.3
2	w	620.113	620.113	0.0
3		909.159	909.159	0.0
4		1198.204	1198.205	0.8

Figure S18. (a) HCD spectrum of 5- charge state (*m/z* 1389) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

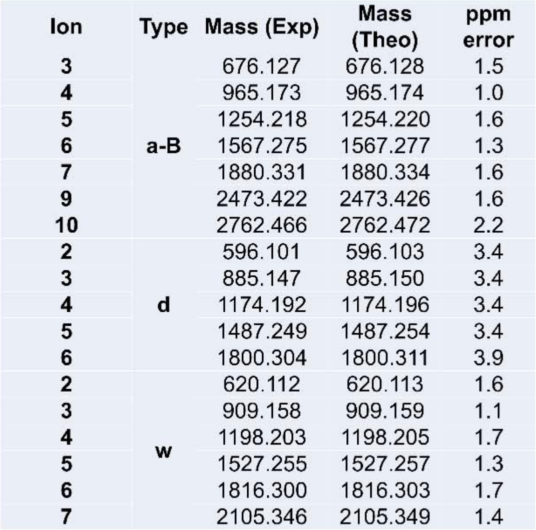
(a)



(b)

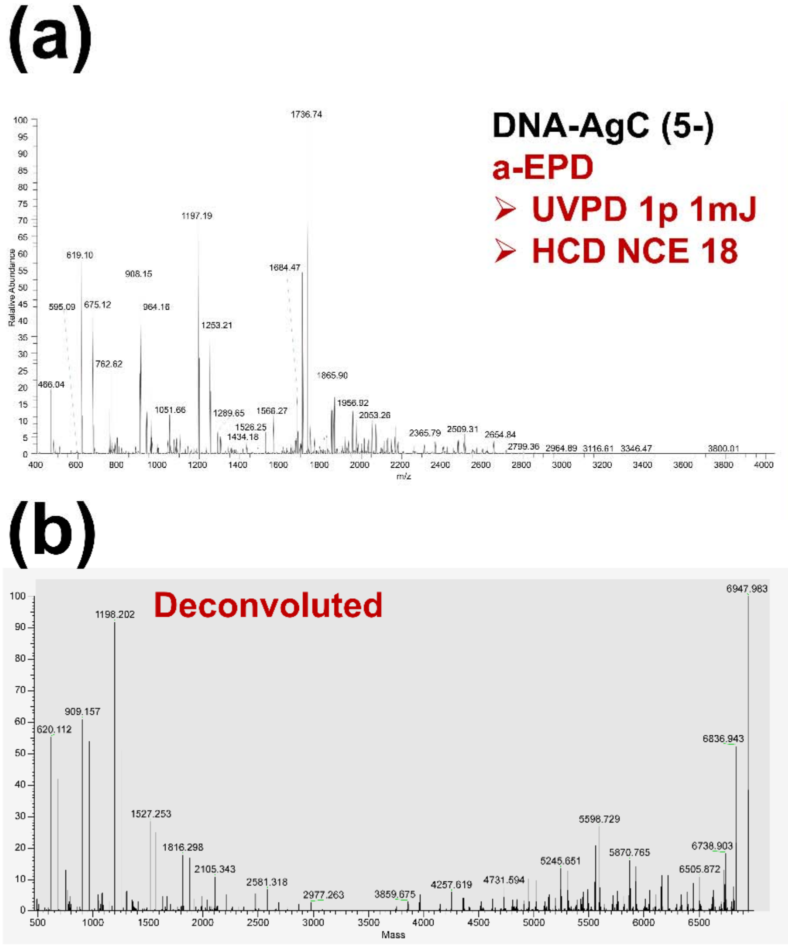


(c)

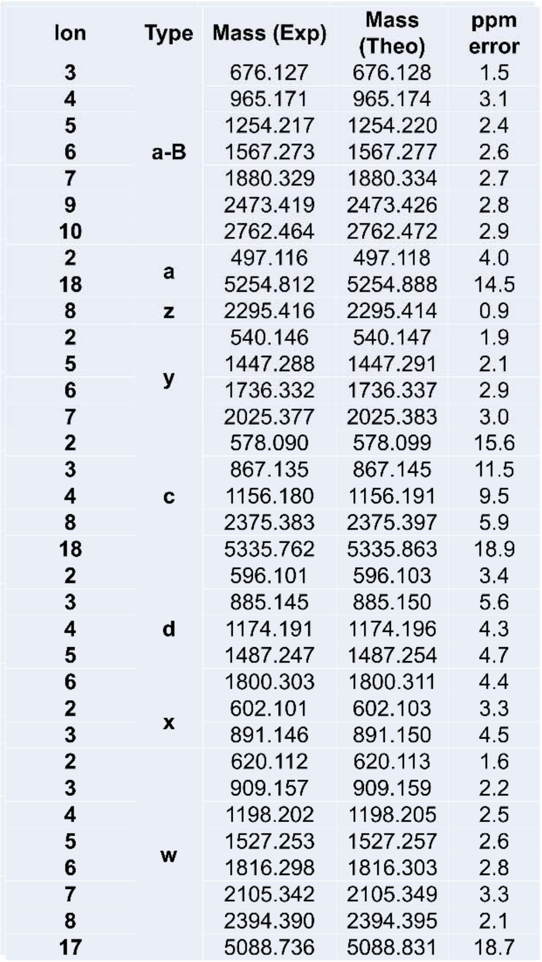


Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.127	676.128	1.5
4		965.173	965.174	1.0
5		1254.218	1254.220	1.6
6		1567.275	1567.277	1.3
7		1880.331	1880.334	1.6
9		2473.422	2473.426	1.6
10		2762.466	2762.472	2.2
2	d	596.101	596.103	3.4
3		885.147	885.150	3.4
4		1174.192	1174.196	3.4
5		1487.249	1487.254	3.4
6		1800.304	1800.311	3.9
2	w	620.112	620.113	1.6
3		909.158	909.159	1.1
4		1198.203	1198.205	1.7
5		1527.255	1527.257	1.3
6		1816.300	1816.303	1.7
7		2105.346	2105.349	1.4

Figure S19. (a) UVPD spectrum of 5- charge state (*m/z* 1389) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

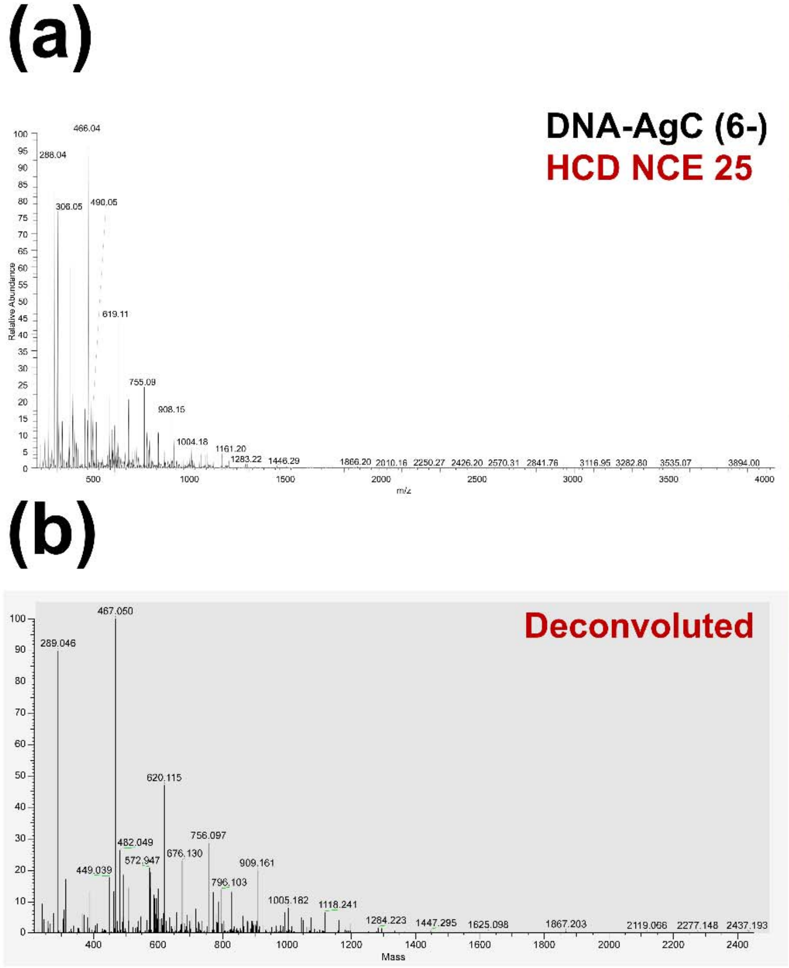


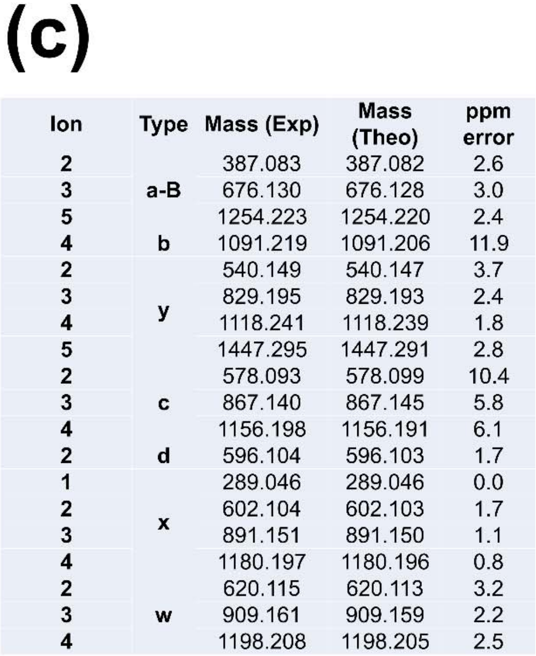
(c)



Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.127	676.128	1.5
4		965.171	965.174	3.1
5		1254.217	1254.220	2.4
6		1567.273	1567.277	2.6
7		1880.329	1880.334	2.7
9		2473.419	2473.426	2.8
10		2762.464	2762.472	2.9
2	a	497.116	497.118	4.0
18		5254.812	5254.888	14.5
8	z	2295.416	2295.414	0.9
2	y	540.146	540.147	1.9
5		1447.288	1447.291	2.1
6		1736.332	1736.337	2.9
7		2025.377	2025.383	3.0
2	c	578.090	578.099	15.6
3		867.135	867.145	11.5
4		1156.180	1156.191	9.5
8		2375.383	2375.397	5.9
18		5335.762	5335.863	18.9
2	d	596.101	596.103	3.4
3		885.145	885.150	5.6
4		1174.191	1174.196	4.3
5		1487.247	1487.254	4.7
6		1800.303	1800.311	4.4
2	x	602.101	602.103	3.3
3		891.146	891.150	4.5
2	w	620.112	620.113	1.6
3		909.157	909.159	2.2
4		1198.202	1198.205	2.5
5		1527.253	1527.257	2.6
6		1816.298	1816.303	2.8
7		2105.342	2105.349	3.3
8		2394.390	2394.395	2.1
17		5088.736	5088.831	18.7

Figure S20. (a) a-EPD spectrum of 5- charge state (UVPD of 5- of *m/z* 1389, HCD of subsequent 4•- of *m/z* 1736) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

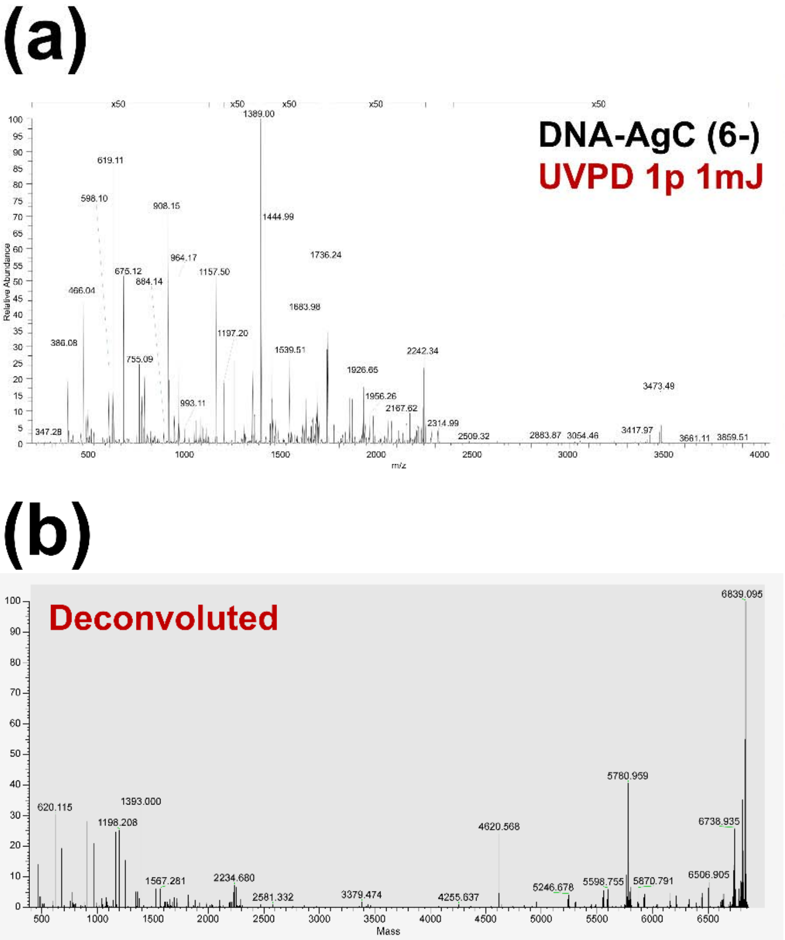




(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
2		387.083	387.082	2.6
3	a-B	676.130	676.128	3.0
5		1254.223	1254.220	2.4
4	b	1091.219	1091.206	11.9
2		540.149	540.147	3.7
3	y	829.195	829.193	2.4
4		1118.241	1118.239	1.8
5		1447.295	1447.291	2.8
2		578.093	578.099	10.4
3	c	867.140	867.145	5.8
4		1156.198	1156.191	6.1
2	d	596.104	596.103	1.7
1		289.046	289.046	0.0
2	x	602.104	602.103	1.7
3		891.151	891.150	1.1
4		1180.197	1180.196	0.8
2		620.115	620.113	3.2
3	w	909.161	909.159	2.2
4		1198.208	1198.205	2.5

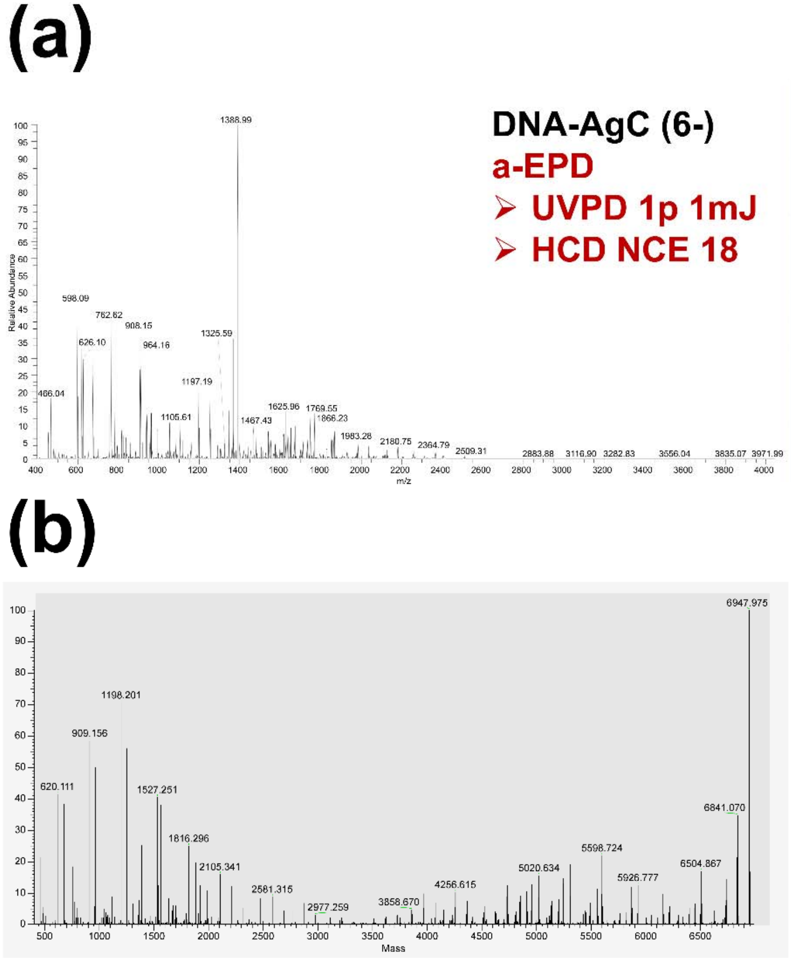
Figure S21. (a) HCD spectrum of 6- charge state (*m/z* 1157) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.



(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
2	a-B	387.083	387.082	2.6
3		676.130	676.128	3.0
4		965.177	965.174	3.1
5		1254.223	1254.220	2.4
6		1567.281	1567.277	2.6
7		1880.339	1880.334	2.7
8		2169.380	2169.380	0.0
9		2473.432	2473.426	2.4
10		2762.477	2762.472	1.8
5	a	1388.270	1388.268	1.4
2	z	521.130	521.129	1.9
2	d	596.104	596.103	1.7
3		885.150	885.150	0.0
4		1174.196	1174.196	0.0
5		1487.255	1487.254	0.7
6		1800.311	1800.311	0.0
2	w	620.115	620.113	3.2
3		909.162	909.159	3.3
4		1198.208	1198.205	2.5
5		1527.261	1527.257	2.6
6		1816.307	1816.303	2.2
7		2105.354	2105.349	2.4

Figure S22. (a) UVPD spectrum of 6- charge state (*m/z* 1157) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

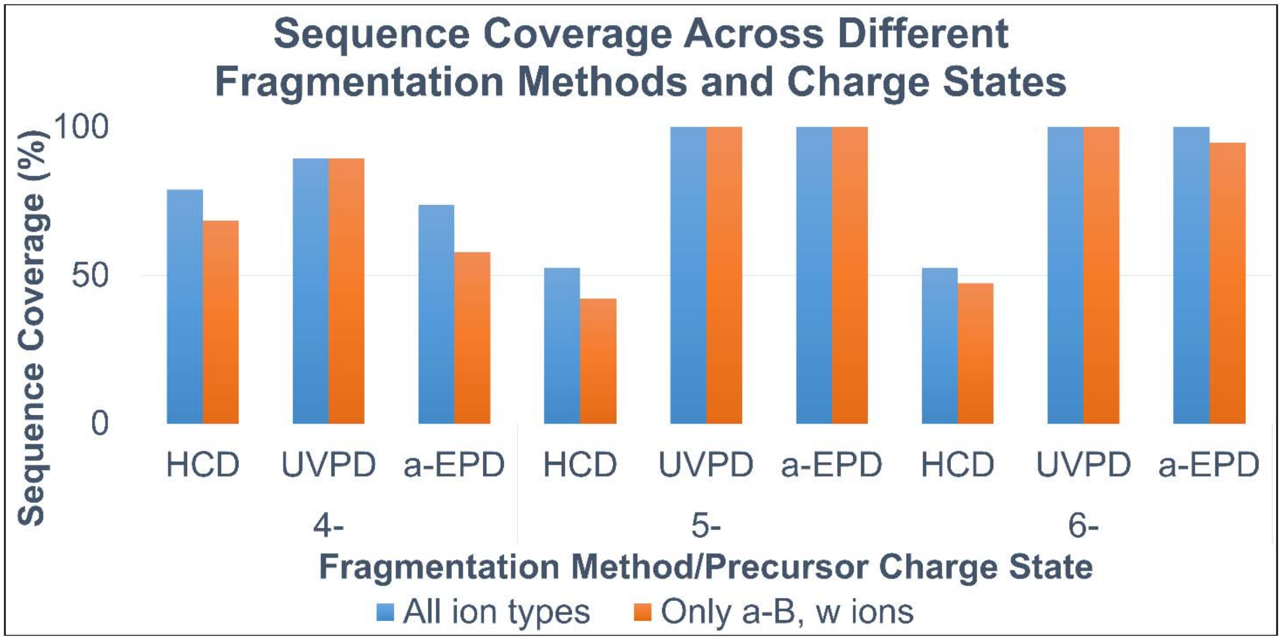


(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
3	a-B	676.126	676.128	3.0
4		965.171	965.174	3.1
5		1254.216	1254.220	3.2
6		1567.271	1567.277	3.8
7		1880.327	1880.334	3.7
9		2473.416	2473.426	4.0
10		2762.461	2762.472	4.0
17	b	4981.835	4981.836	0.2
8	z	2295.413	2295.414	0.4
3	y	829.190	829.193	3.6
4		1118.235	1118.239	3.6
5		1447.286	1447.291	3.5
7		2025.375	2025.383	3.9
2	c	578.090	578.099	15.6
3		867.135	867.145	11.5
18		5335.761	5335.863	19.1
2	d	596.100	596.103	5.0
4		1174.189	1174.196	6.0
5		1487.246	1487.254	5.4
6		1800.300	1800.311	6.1
9		2682.435	2682.450	5.6
2	x	602.101	602.103	3.3
3		891.146	891.150	4.5
5		1509.241	1509.249	5.3
2	w	620.111	620.113	3.2
3		909.156	909.159	3.3
4		1198.201	1198.205	3.3
5		1527.251	1527.257	3.9
6		1816.296	1816.303	3.9
7		2105.341	2105.349	3.8
8		2394.385	2394.395	4.2
10		3002.474	3002.487	4.3

Figure S23. **(a)** a-EPD spectrum of 6- charge state (UVPD of 6- of *m/z* 1157, HCD of subsequent 5•- of *m/z* 1388) of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC with silver cluster, **(b)** deconvoluted spectrum and **(c)** tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.

(a) ssDNA



(b) ssDNA-AgC

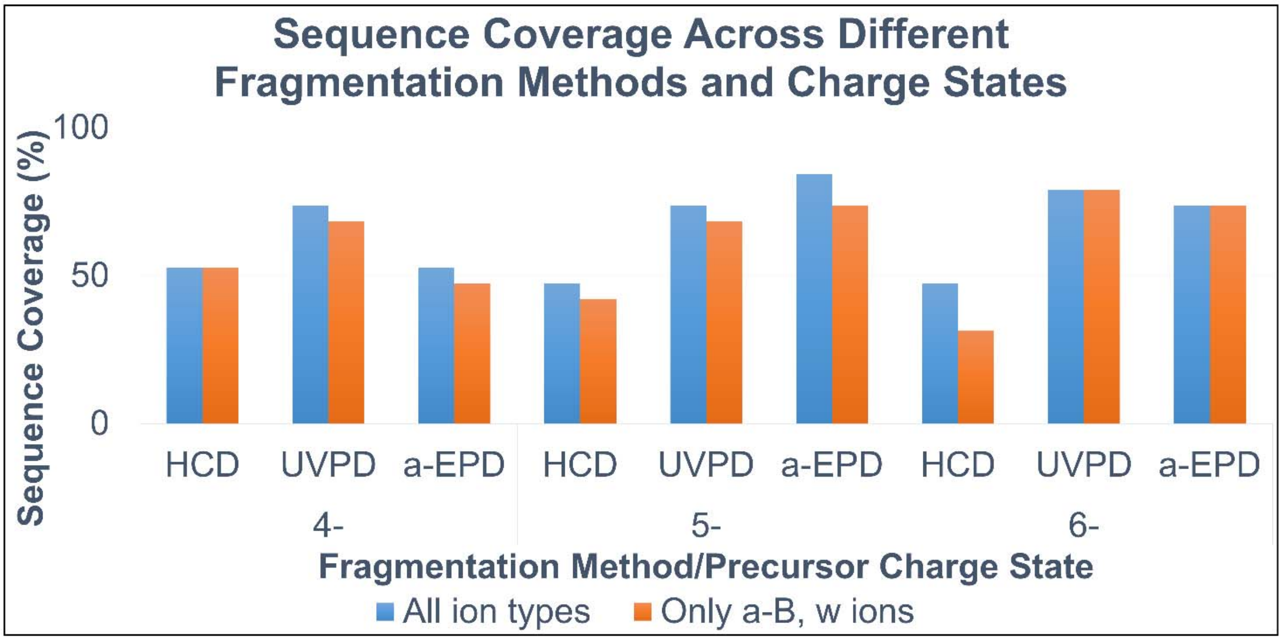
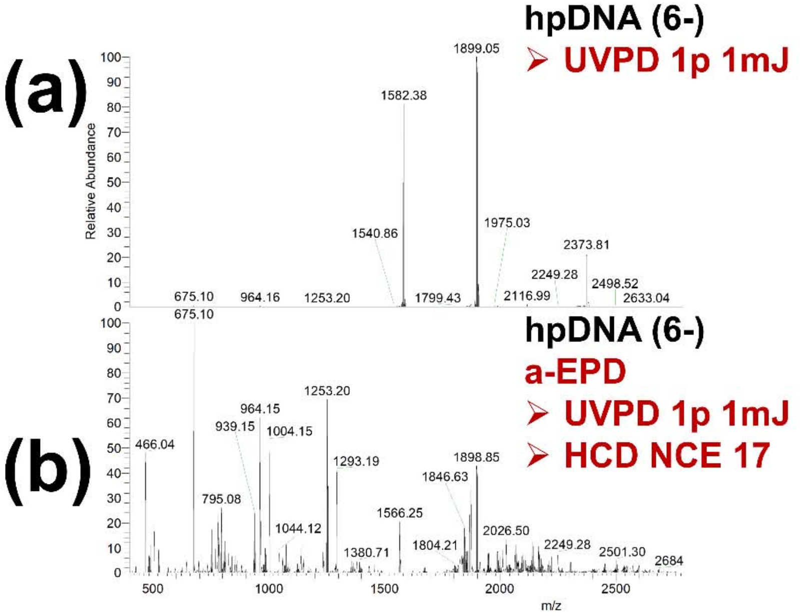


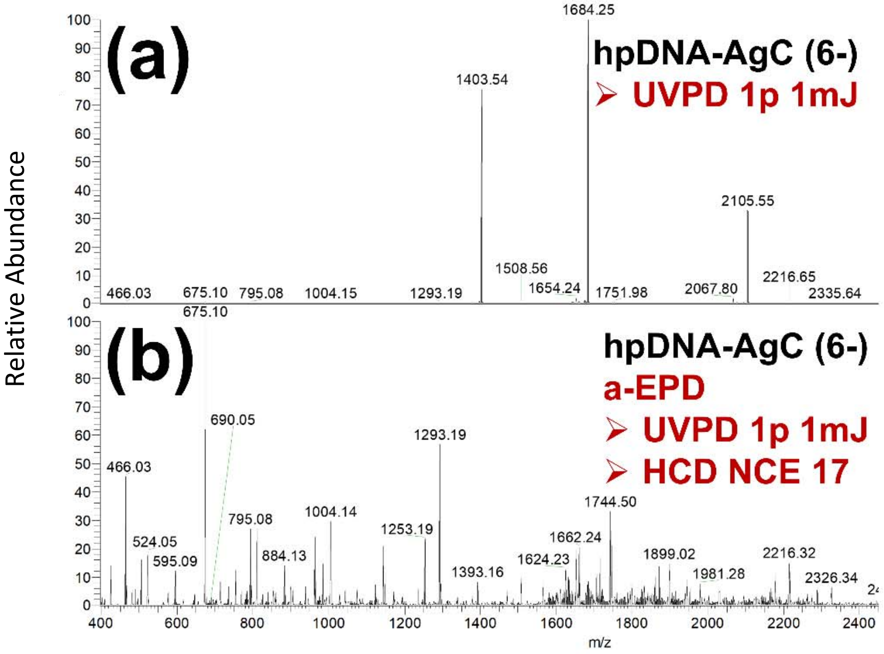
Figure S24. Bar graphs of single stranded 20-mer oligonucleotide CCC CAA CTC CTT CCC GCC AC sequence coverage for **(a)** lone DNA and **(b)** DNA-silver cluster sample across different fragmentation methods and charge states. Graphs show calculated sequence coverage when all ion types are included (blue) and when solely *a-B* and *w* ions are included (orange).



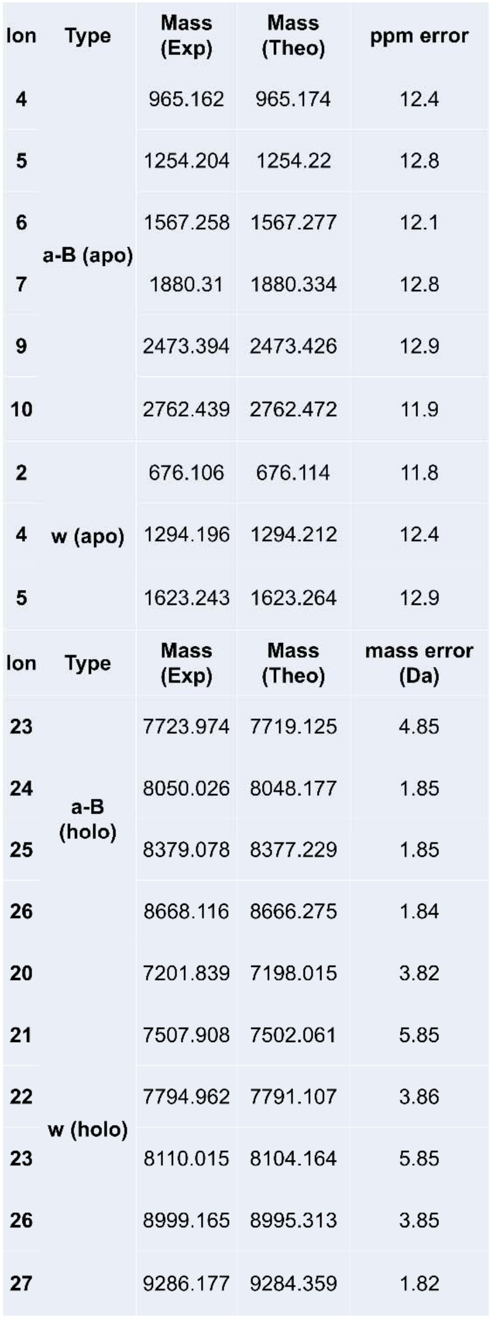
(c)

Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
4	a-B (apo)	965.159	965.174	15.5
5		1254.201	1254.22	15.1
6		1567.254	1567.277	14.7
7		1880.306	1880.334	14.9
9		2473.388	2473.426	15.4
10		2762.43	2762.472	15.2
11		3051.472	3051.518	15.1
13		3659.555	3659.61	15.0
14		3948.596	3948.656	15.2
15		4237.637	4237.702	15.3
16		4526.681	4526.748	14.8
17		4855.729	4855.8	14.6
18		5144.768	5144.846	15.2
24		6979.019	6979.127	15.5
25		7308.067	7308.179	15.3
26		7597.109	7597.225	15.3
27		7926.151	7926.277	15.9
2	w (apo)	676.104	676.114	14.8
3		1005.151	1005.166	14.9
4		1294.193	1294.212	14.7
5		1623.239	1623.264	15.4
6		1952.285	1952.317	16.4
7		2256.326	2256.362	16.0
8		2560.37	2560.408	14.8
9		2864.411	2864.454	15.0
10		3168.451	3168.499	15.1
11		3457.495	3457.545	14.5
12		3746.532	3746.591	15.7
15		4653.666	4653.736	15.0
18		5550.794	5550.873	14.2
23		7035.003	7035.114	15.8
24		7348.056	7348.171	15.7
26		7926.151	7926.263	14.1

Figure S25. (a) UVPD spectrum of 6- charge state (*m/z* 1403) and (**b**) a-EPD spectrum of 6- charge state (UVPD of *m/z* 1403 followed HCD of 5•- charge state of *m/z* 1684) of hpDNA sample CCC CAA CTC CTT CCC GCC TTT TGG CGG G; (**c**) tabulated sequence ion assignments and mass error values (ppm). The columns entitled Ion and Type indicate the assignment of the fragment ion: a_n-B, c_n, d_n, x_n, y_n, w_n, z_n, in which the number n (listed in the Ion column) represents the number of nucleotides contained in the fragment. Ions are grouped by type.



(c)



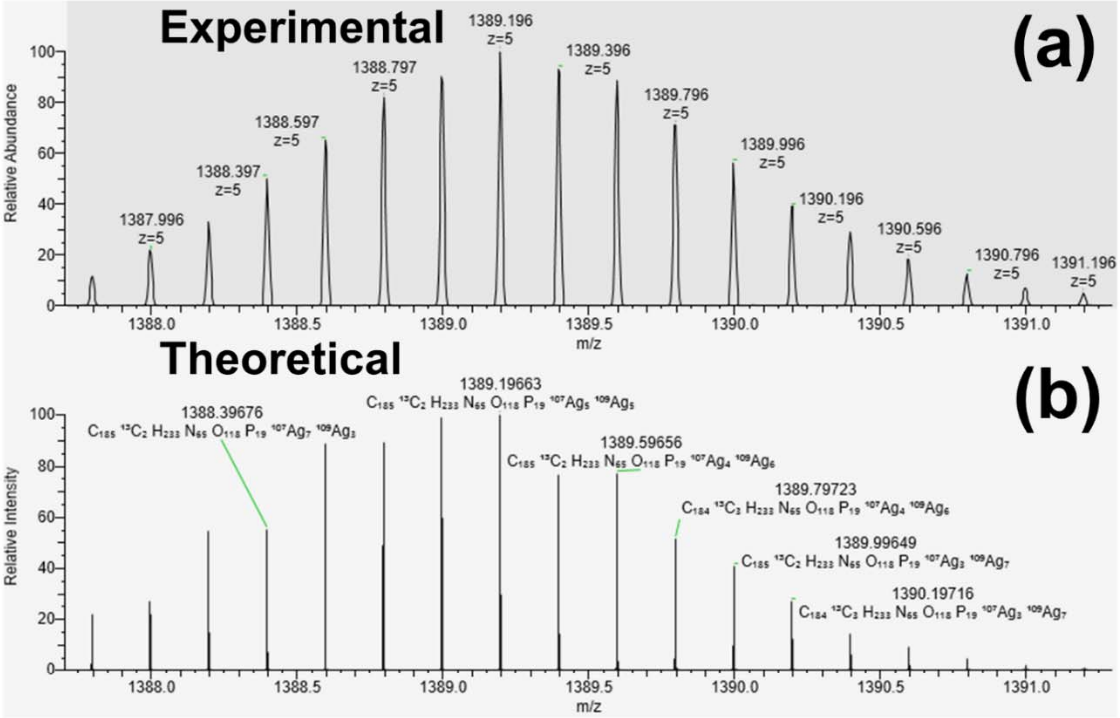
Ion	Type	Mass (Exp)	Mass (Theo)	ppm error
4	a-B (apo)	965.162	965.174	12.4
5		1254.204	1254.22	12.8
6		1567.258	1567.277	12.1
7		1880.31	1880.334	12.8
9		2473.394	2473.426	12.9
10		2762.439	2762.472	11.9
2	w (apo)	676.106	676.114	11.8
4		1294.196	1294.212	12.4
5		1623.243	1623.264	12.9

Ion	Type	Mass (Exp)	Mass (Theo)	mass error (Da)
23	a-B (holo)	7723.974	7719.125	4.85
24		8050.026	8048.177	1.85
25		8379.078	8377.229	1.85
26		8668.116	8666.275	1.84
20	w (holo)	7201.839	7198.015	3.82
21		7507.908	7502.061	5.85
22		7794.962	7791.107	3.86
23		8110.015	8104.164	5.85
26		8999.165	8995.313	3.85
27		9286.177	9284.359	1.82

Figure S26. (a) UVPD spectrum of 6- charge state (*m/z* 1582) and (**b**) a-EPD spectrum of 6- charge state (UVPD of *m/z* 1582 followed HCD of 5•- charge state of *m/z* 1899) of hpDNA-AgC sample CCC CAA CTC CTT CCC GCC TTT TGG CGG G; (**c**) tabulated sequence ion assignments and mass error values (ppm for apo ions, Da for holo ions). Holo ions once again show systematic mass error values of 1.8, 2.8, 3.8, 4.8, 5.8 Da due to interference of AgC with isotopic deconvolution algorithm.

$C_{187}H_{244}N_{65}O_{118}P_{19}Ag_{10}$ (neutral)

$\boxed{C_{187}H_{\underline{233}}N_{65}O_{118}P_{19}Ag_{10}^{5-}}$ *(-11 (H^+) + 6 (Ag^+) = -5)*



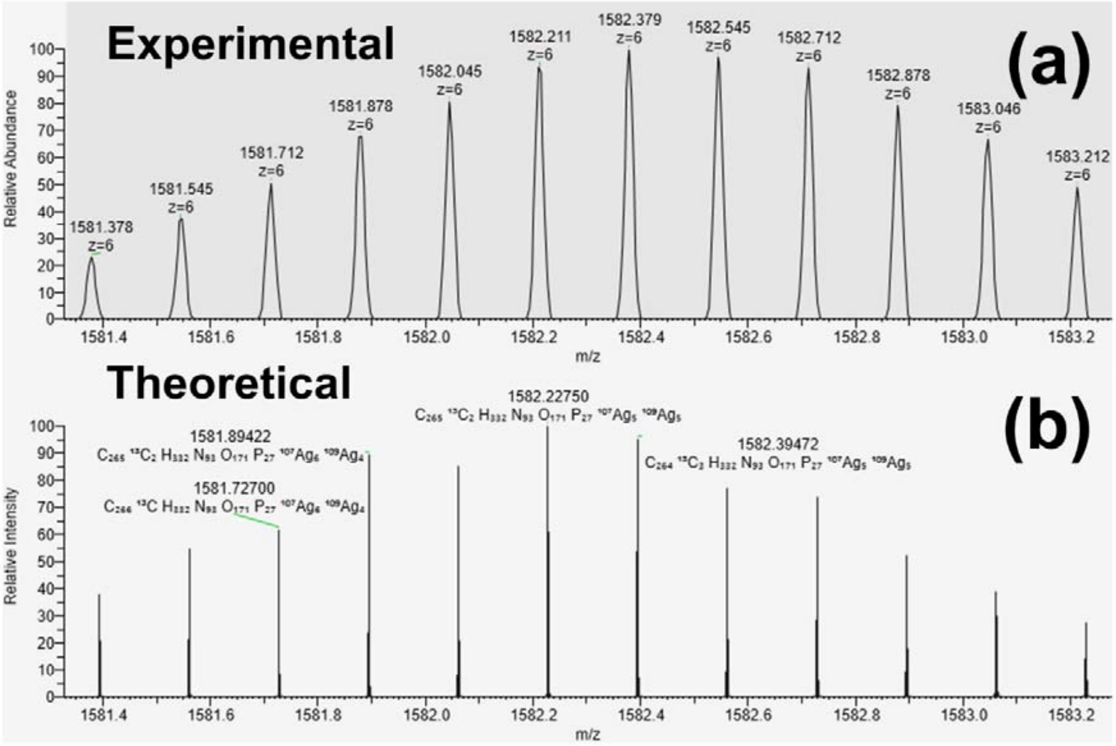
(c)

ssDNA+Ag10 (5- charge state)												
Exp m/z	1387.996	1388.197	1388.397	1388.597	1388.797	1388.997	1389.196	1389.396	1389.596	1389.796	1389.996	1390.196
Theo m/z	1387.995	1388.196	1388.397	1388.596	1388.797	1388.996	1389.197	1389.396	1389.597	1389.797	1389.996	1390.197
ppm error	0.7	0.7	0.0	0.7	0.0	0.7	-0.7	0.0	-0.7	-0.7	0.0	-0.7

Figure S27. (a) Experimental and (b) theoretical isotopic distributions of ssDNA-AgC (5- charge state) along with (c) calculated ppm error values. The results highlight the contribution of the partially oxidized Ag_{10}^{6+} cluster to overall negatively-charged DNA-AgC complex.

$C_{267}H_{344}N_{93}O_{171}P_{27}Ag_{10}$ (neutral)

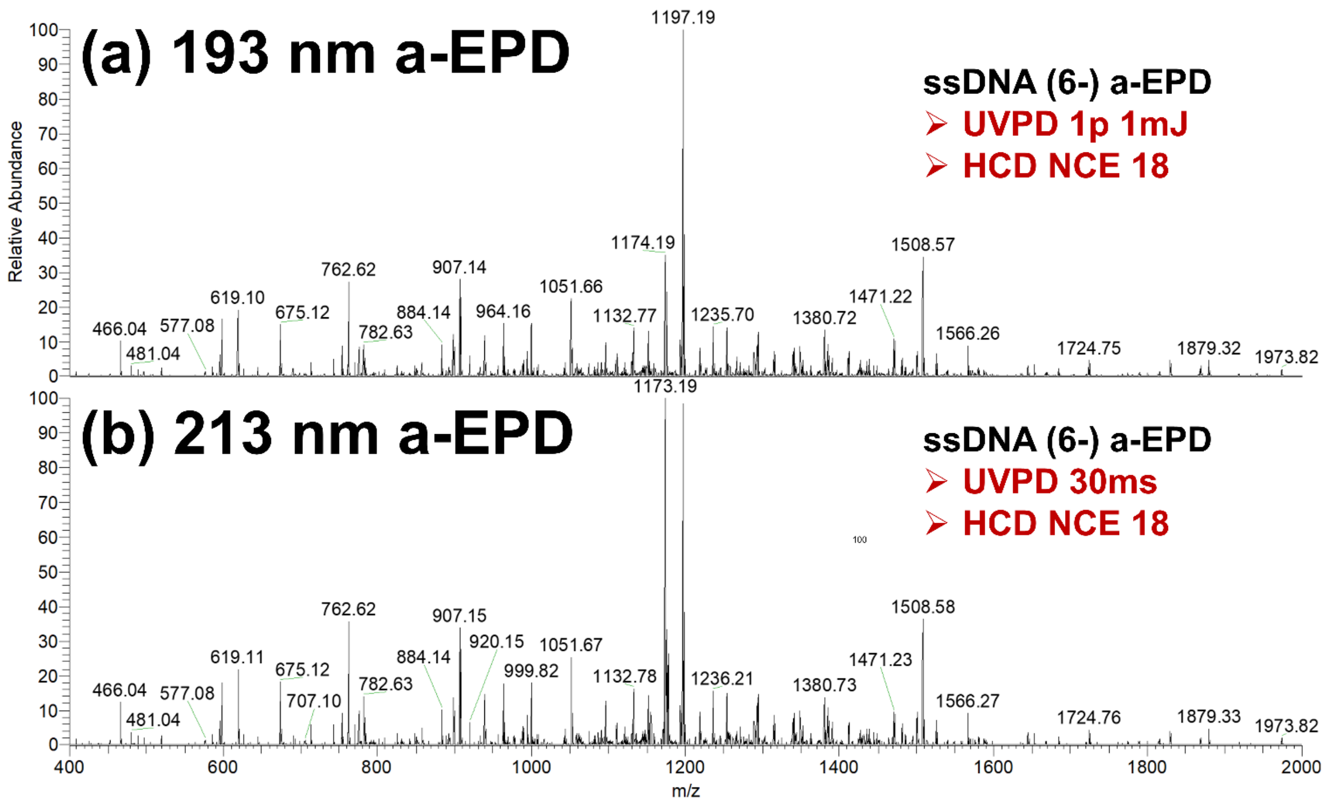
$\boxed{C_{267}H_{\underline{332}}N_{93}O_{171}P_{27}Ag_{10}^{6-}}$ *$(-12\ (H^{+}) + 6\ (Ag^{+}) = -6)$*

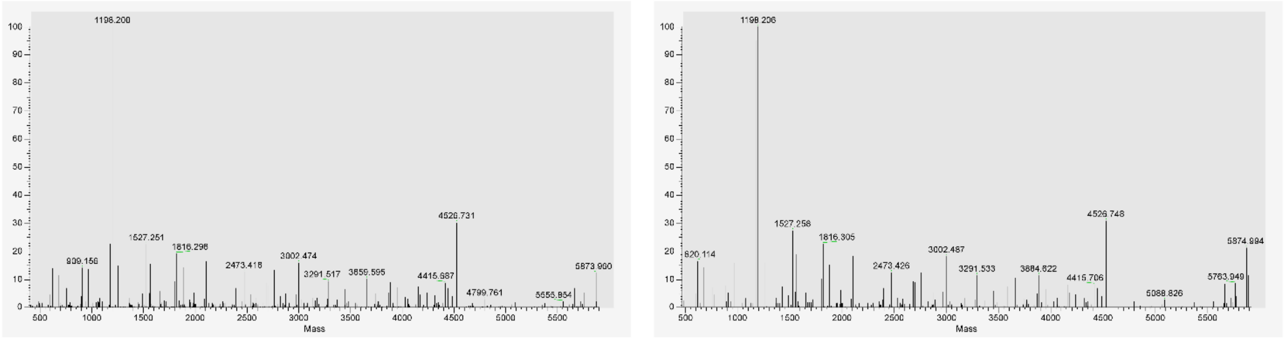


(c)

hpDNA+Ag10 (6- charge state)											
Exp m/z	1581.545	1581.712	1581.878	1582.045	1582.211	1582.379	1582.545	1582.712	1582.878	1583.046	1583.212
Theo m/z	1581.561	1581.727	1581.894	1582.061	1582.228	1582.395	1582.561	1582.728	1582.895	1583.061	1583.229
ppm error	10.1	9.5	10.3	10.4	10.4	9.9	10.0	10.1	10.9	9.7	10.4

Figure S28. (a) Experimental and (b) theoretical isotopic distributions of hpDNA-AgC (6- charge state) along with (c) calculated ppm error values. The results highlight the contribution of the partially oxidized Ag_{10}^{6+} cluster to overall negatively-charged DNA-AgC complex





(c) 193 nm a-EPD Deconvoluted

(d) 213 nm a-EPD Deconvoluted

Figure S29. Comparison of 213 and 193 nm a-EPD for characterization of the 6- charge state of the ssDNA (CCC CAA CTC CTT CCC GCC AC): **(a)** 193 nm a-EPD spectrum, **(b)** 213 nm a-EPD spectrum, **(c)** deconvoluted 193 nm a-EPD spectrum, **(d)** deconvoluted 213 nm a-EPD spectrum. a-EPD was performed *via* UVPD of the 6- charge state (*m/z* 978), and subsequent HCD of the 5•- ion (*m/z* 1174).