**Repeated and Folded DNA Sequences and Their Modular $Ag_{10}^{6+}$ Cluster**

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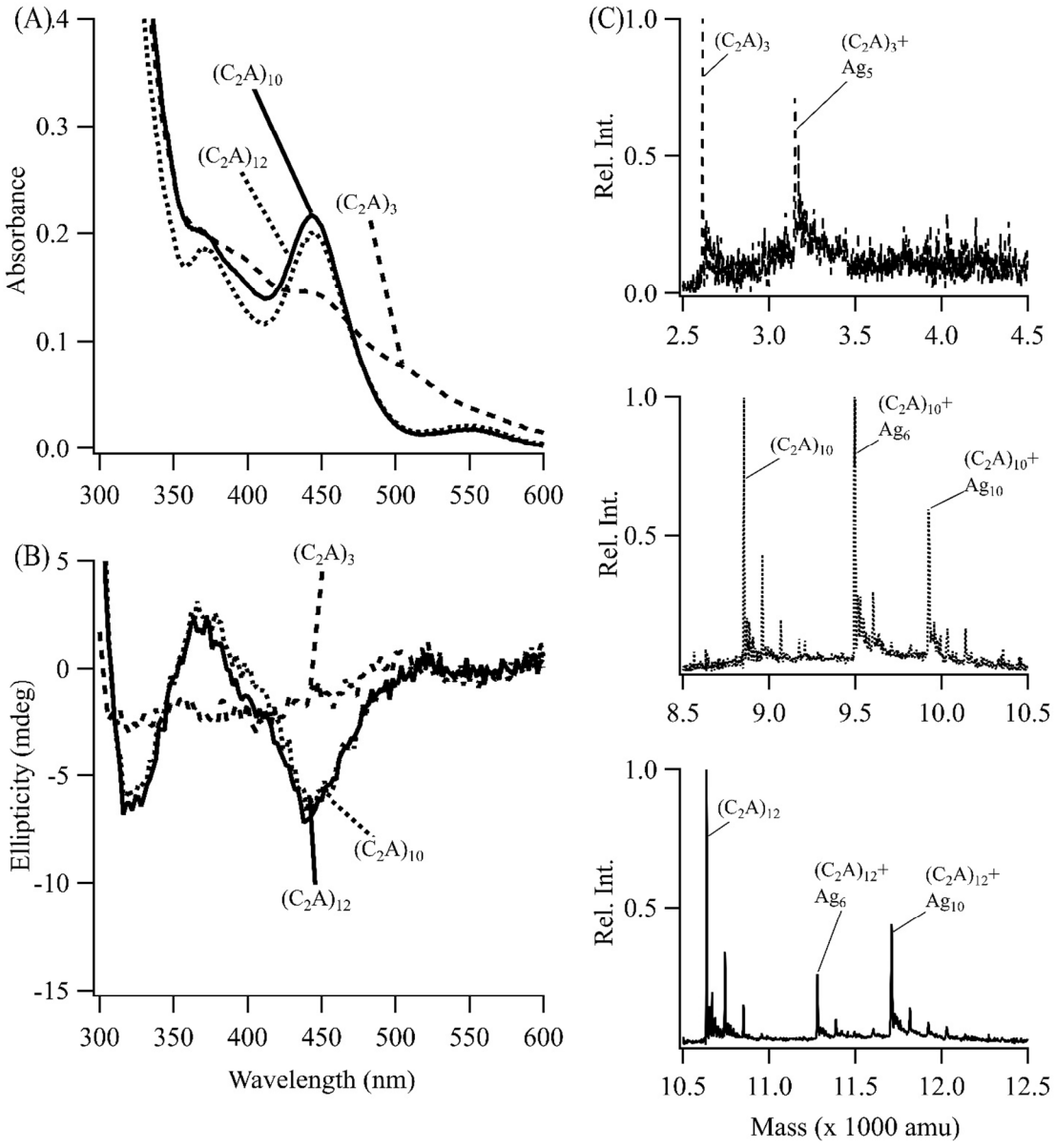


**Figure S1.** *A minimal DNA length develops $Ag_{10}^{6+}$ :* Absorption (A) and circular dichroism (B) spectra of $(C_2A)_3$ (dashed), $(C_2A)_{10}$ (dotted), and $(C_2A)_{12}$ (solid) oligoncleotides with silver clusters. (C) Mass spectra of $(C_2A)_{3,10,12}$ oligoncleotides with silver clusters. The spectra for the oligonucleotides $(C_2A)_{10}$ and $(C_2A)_{12}$ are simlar to those with $(C_2A)_6$ (see Figure 1).

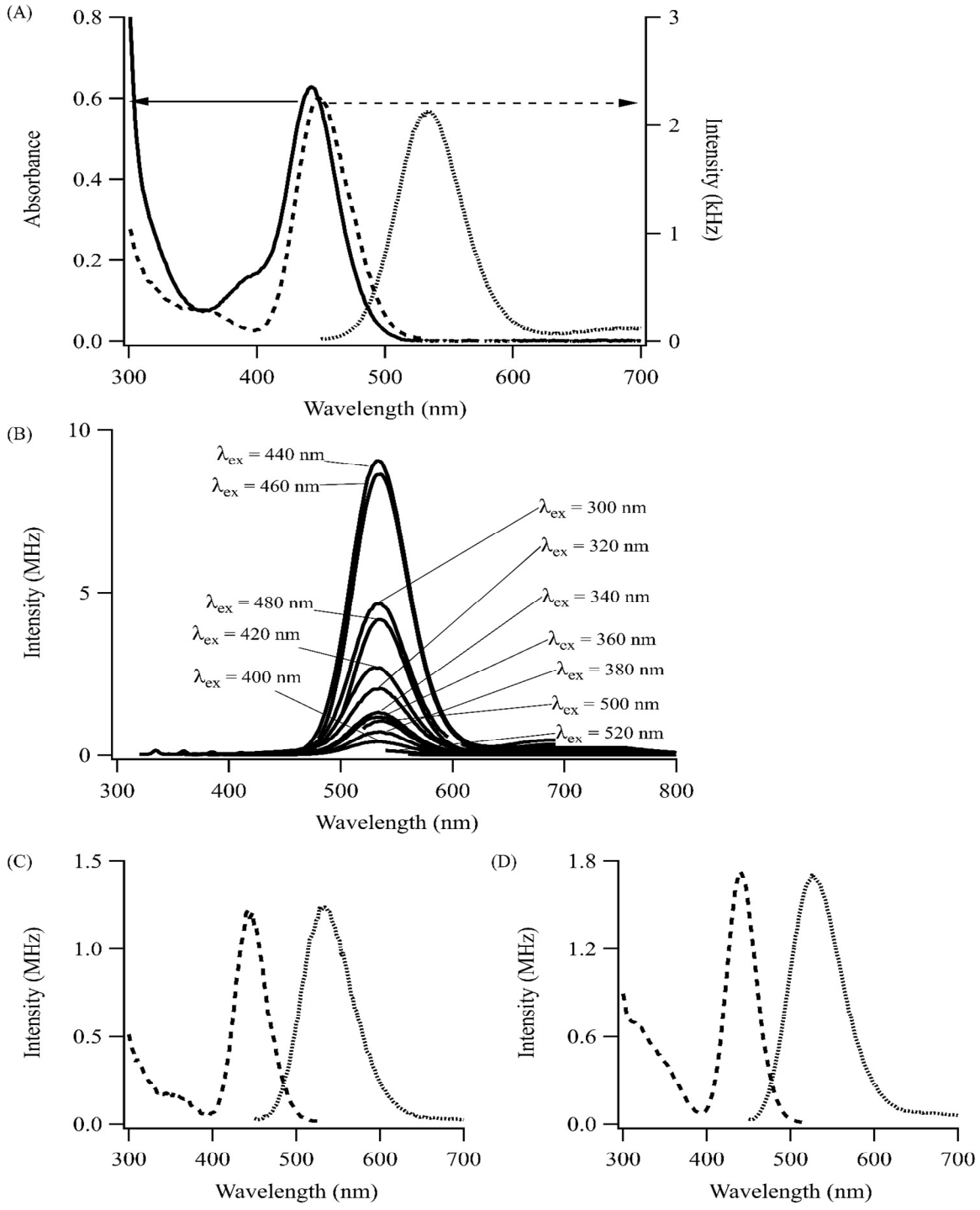


**Figure S2.** *A minimal DNA length develops $Ag_{10}^{6+}$ :* (A) Absorption (solid), excitation (dashed), and emssion (dotted) spectra of the cluster with $(C_2A)_7$. A 6 nm shift the absorption and excitation maxima may indicate a mixture of species, and we are currently investigating these spectra. (B) Emission spectra acquired with excitation wavelvenths of 300- 600 nm. A consistent emission band indicates that a single emissive species forms. (C and D) Excitation (dashed) and emission (dotted) spectra for the clusters with $(C_2A)_4$ and $(C_2A)_5$, respectively. Similar spectra develop with the longer $(C_2A)_x$ seqeunces and thus suggest that the $Ag_{10}^{6+}$ cluster has a smaller subuit that is emissive.

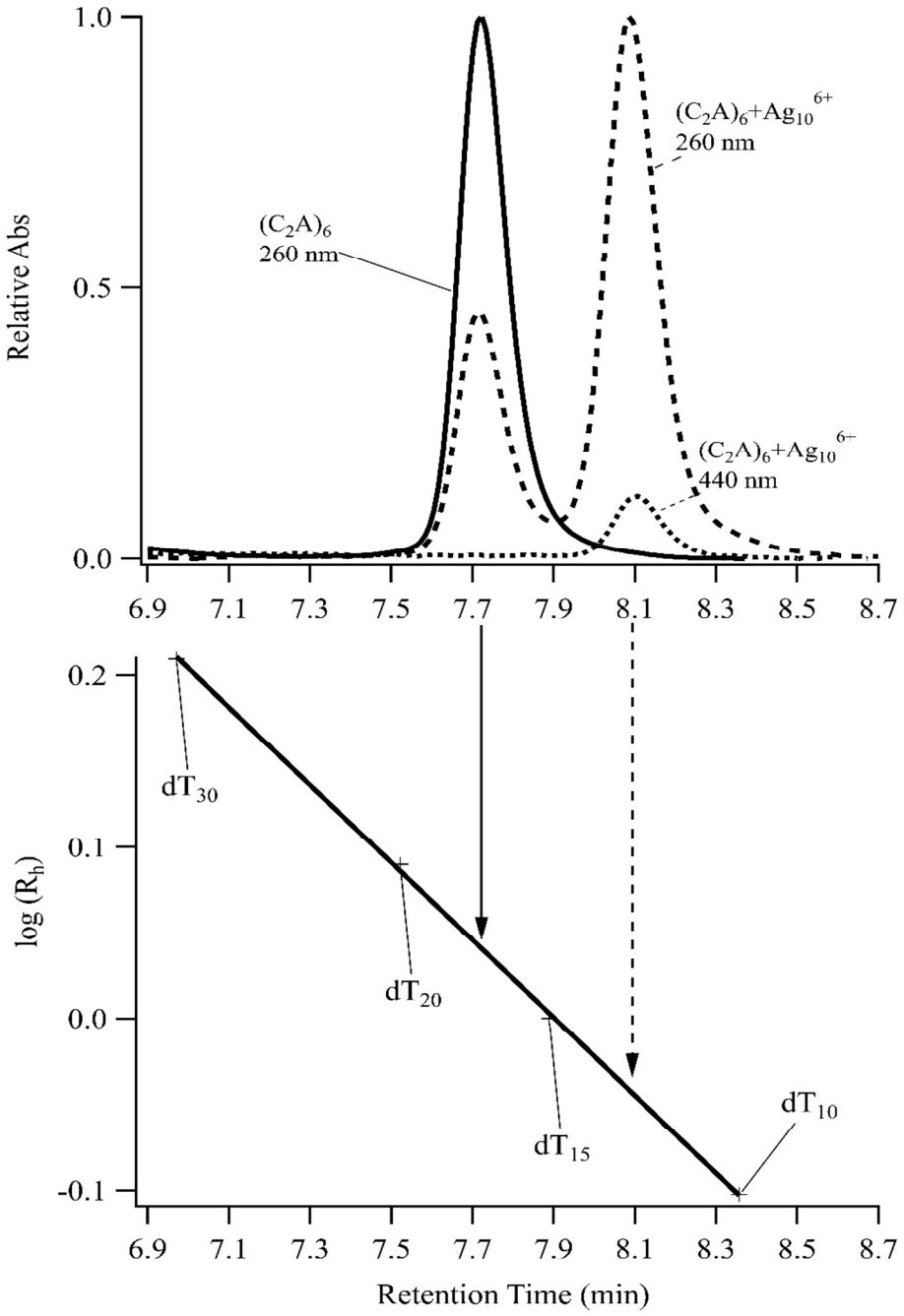


**Figure S3:** *A minimal DNA length develops $Ag_{10}^{6+}$:* (A) Size exclusion chromatographs of 30 μM solution of $(C_2A)_6$ (Solid) and $(C_2A)_6$-$Ag_{10}^{6+}$ (dashed) in 10 mM citrate buffer with 40 mM $NaClO_4$. For $(C_2A)_6$-$Ag_{10}^{6+}$, the two peaks are the unlabeled strand and the strand with the cluster. The dotted line was acquired at 440 nm, which corresponds to the absorption of the cluster. The peaks due to the DNA and cluster lie within 0.02 min, which supports a single type of cluster conjugate. (B) A calibration curve relates the retention times to the hydrodynamic radii using single-stranded thymine oligonucleotides $dT_{10}$, $dT_{15}$, $dT_{20}$, and $dT_{30}$.

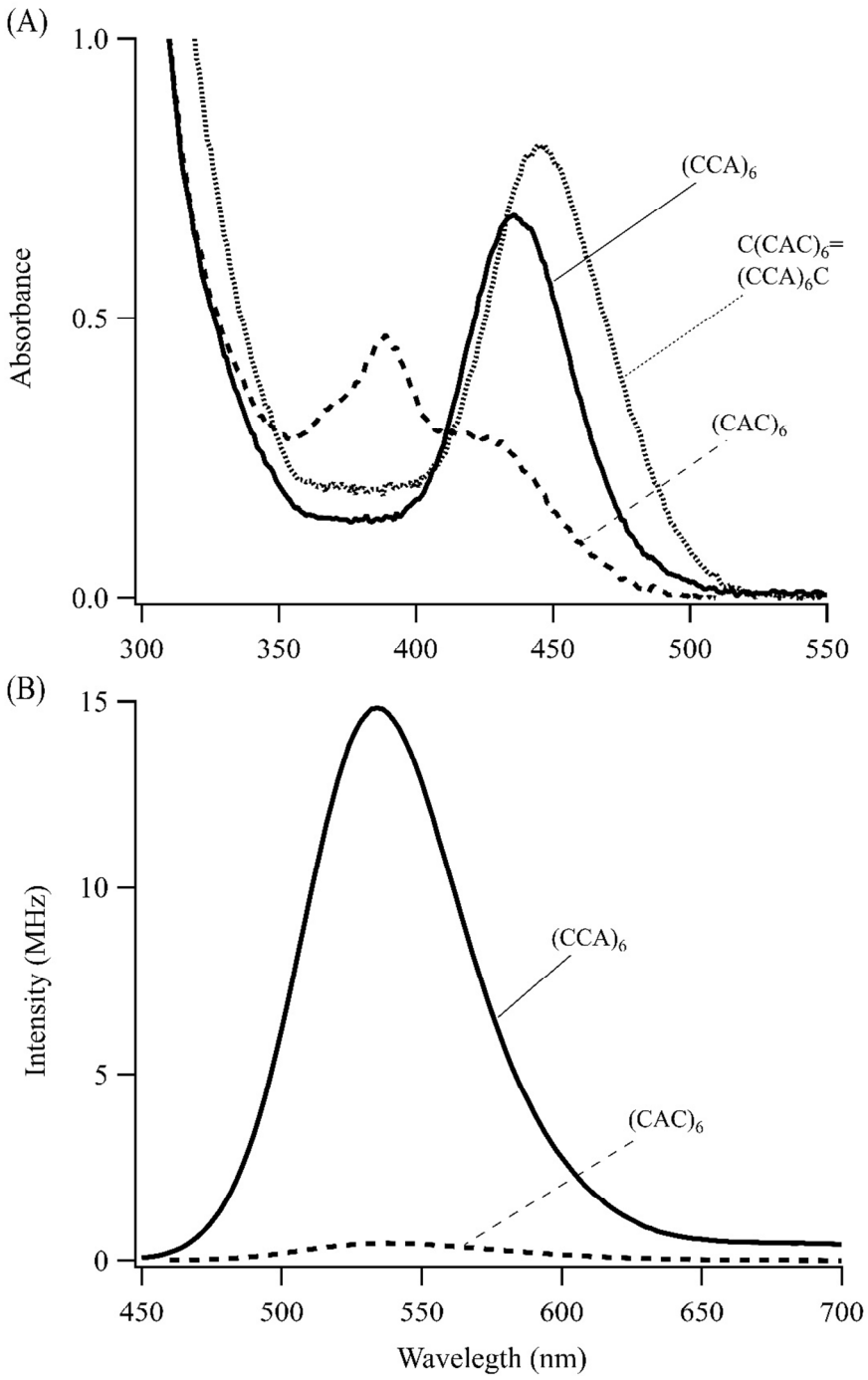


**Figure S4.** *A minimal DNA length develops* $Ag_{10}^{6+}$ *:* (A) Absorption spectra of $(C_2A)_6$ (solid), $(CAC)_6$ (dashed), and $(C(CAC)_6$ (dotted) oligoncleotides with silver clusters. (B) Emission spectra of $(C_2A)_6$ (solid) and $(CAC)_6$ (dashed) oligonucleotides. Permuting the sequence alters the favored environment for the silver clusters.

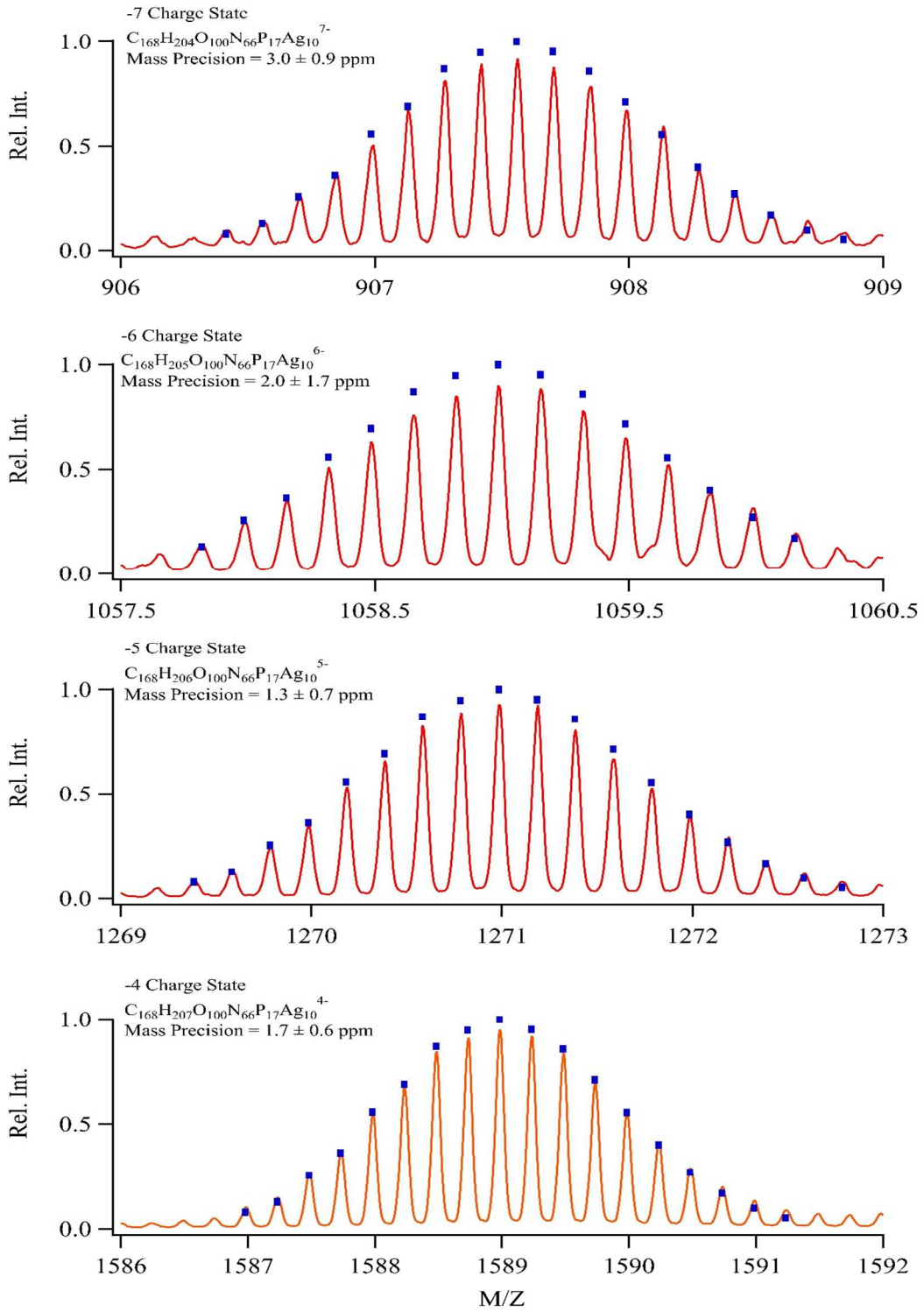


**Figure S5:** *A minimal DNA length develops $Ag_{10}^{6+}$:* Expanded views of the -4 to -7 charge states for $(C_2A)_6/Ag_{10}^{6+}$ complexes. The isotopologue masses were predicted using the specific formulas, and the blue tick marks represent the predicted masses from these formulas (see each graph). The fully protonated strand has the formula $C_{168}H_{217}O_{100}N_{66}P_{17}$.

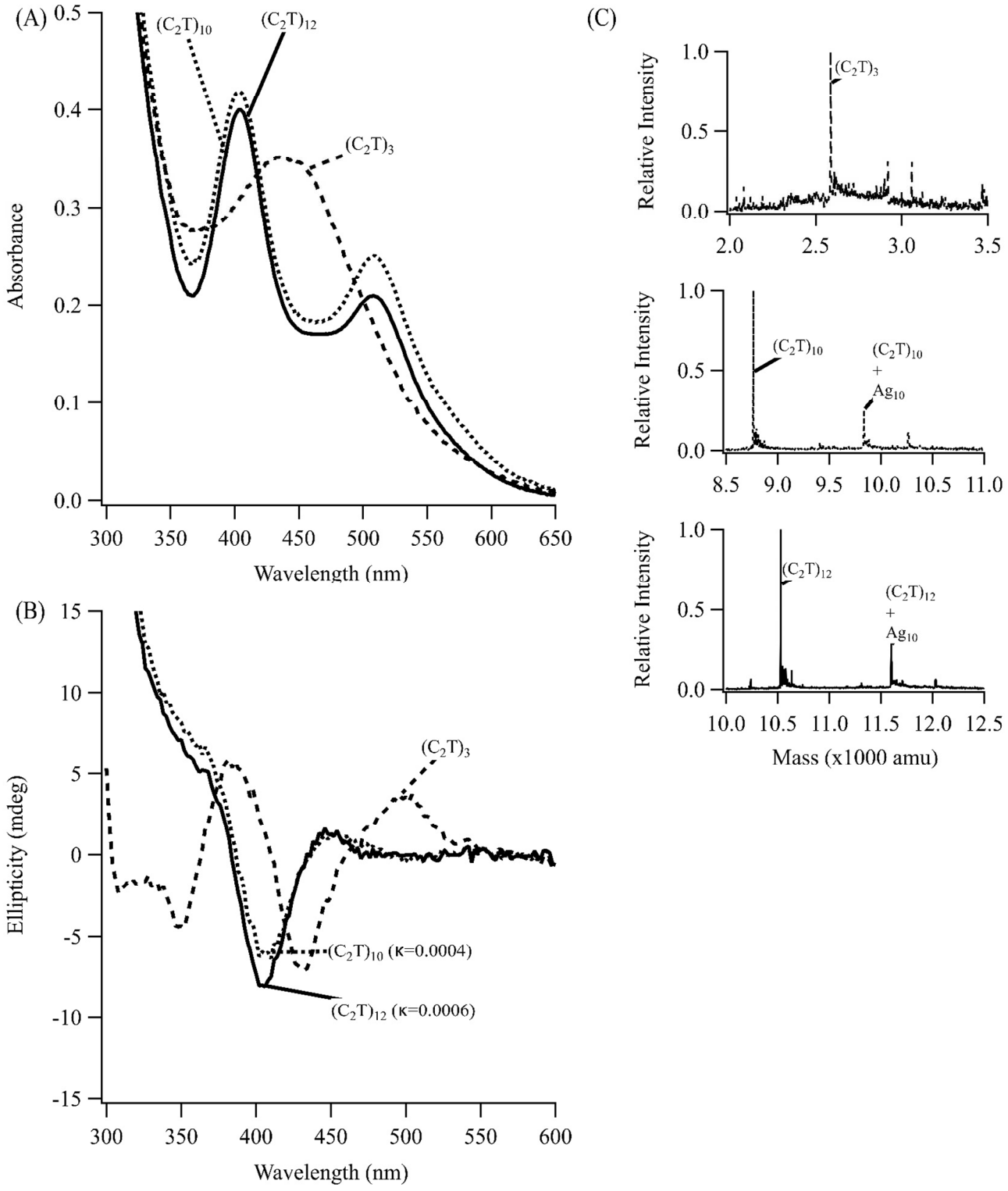


**Figure S6.** *A minimal DNA length develops $Ag_{10}^{6+}$ :* Absorption (A) and circular dichroism (B) spectra of $(C_2T)_3$ (dashed), $(C_2T)_{10}$ (dotted), and $(C_2T)_{12}$ (solid) oligoncleotides with silver clusters. (C) Mass spectra of $(C_2T)_{3,10,12}$ oligoncleotides with silver clusters. The spectra for the oligonucleotides $(C_2T)_{10}$ and $(C_2T)_{12}$ are simlar to those with $(C_2T)_6$ (see Figure 2).

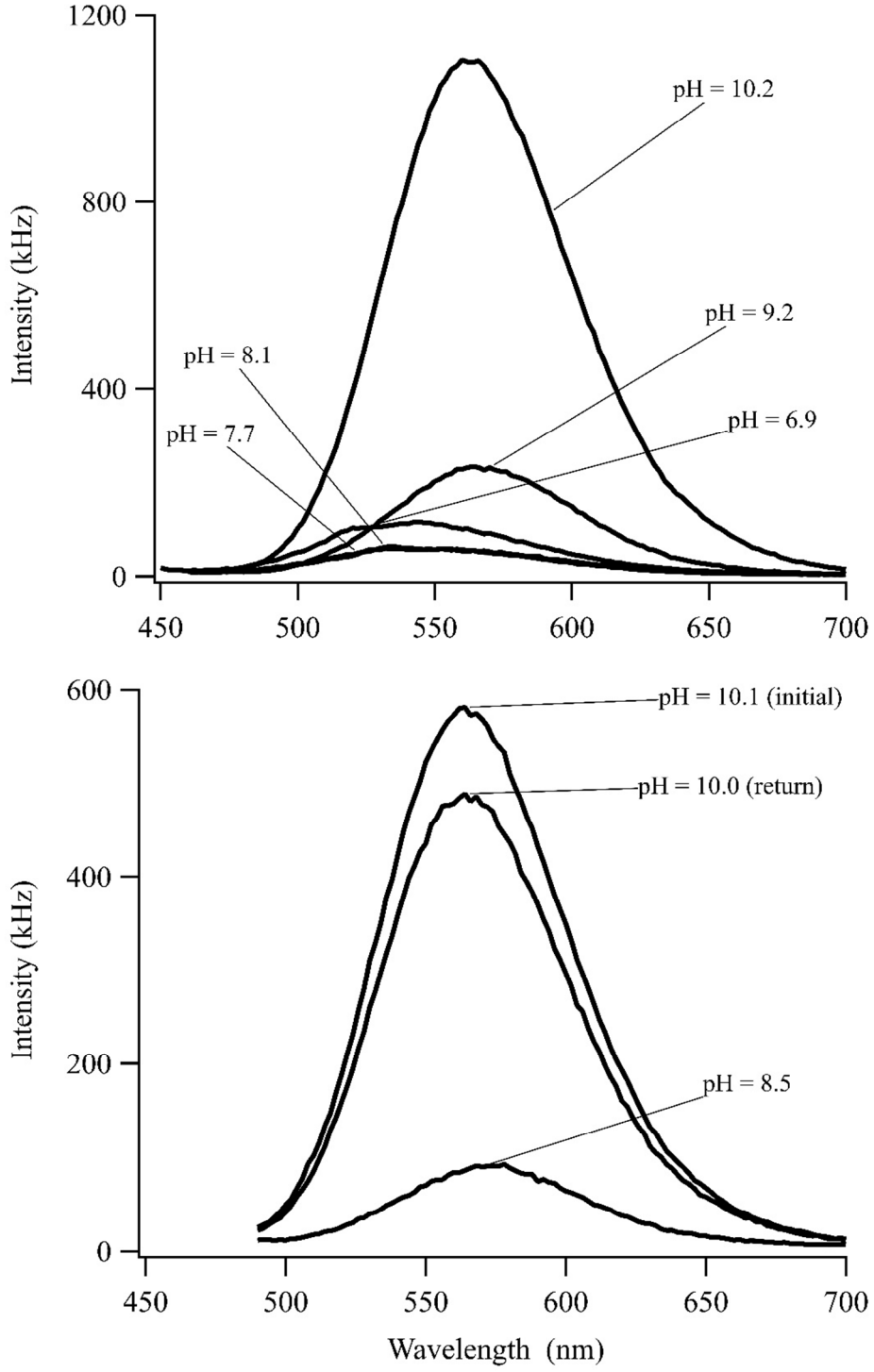


**Figure S7:** *Multiple nucleobases coordinate* $Ag_{10}^{6+}$: (A) Fluorescence spectra of $(C_2T)_6$ at different pH values. The maximum change occurs from pH = 9.2 to 10.2, which brackets the $pK_a$ ~ 9.7 for the N3 of thymine. (B) Fluorescence intensity is strong at high pH, quenches at low pH, and recovers at high pH. Collectively, these spectra suggest that the cluster and $H^+$ compete for the N3 binding site in thymine.

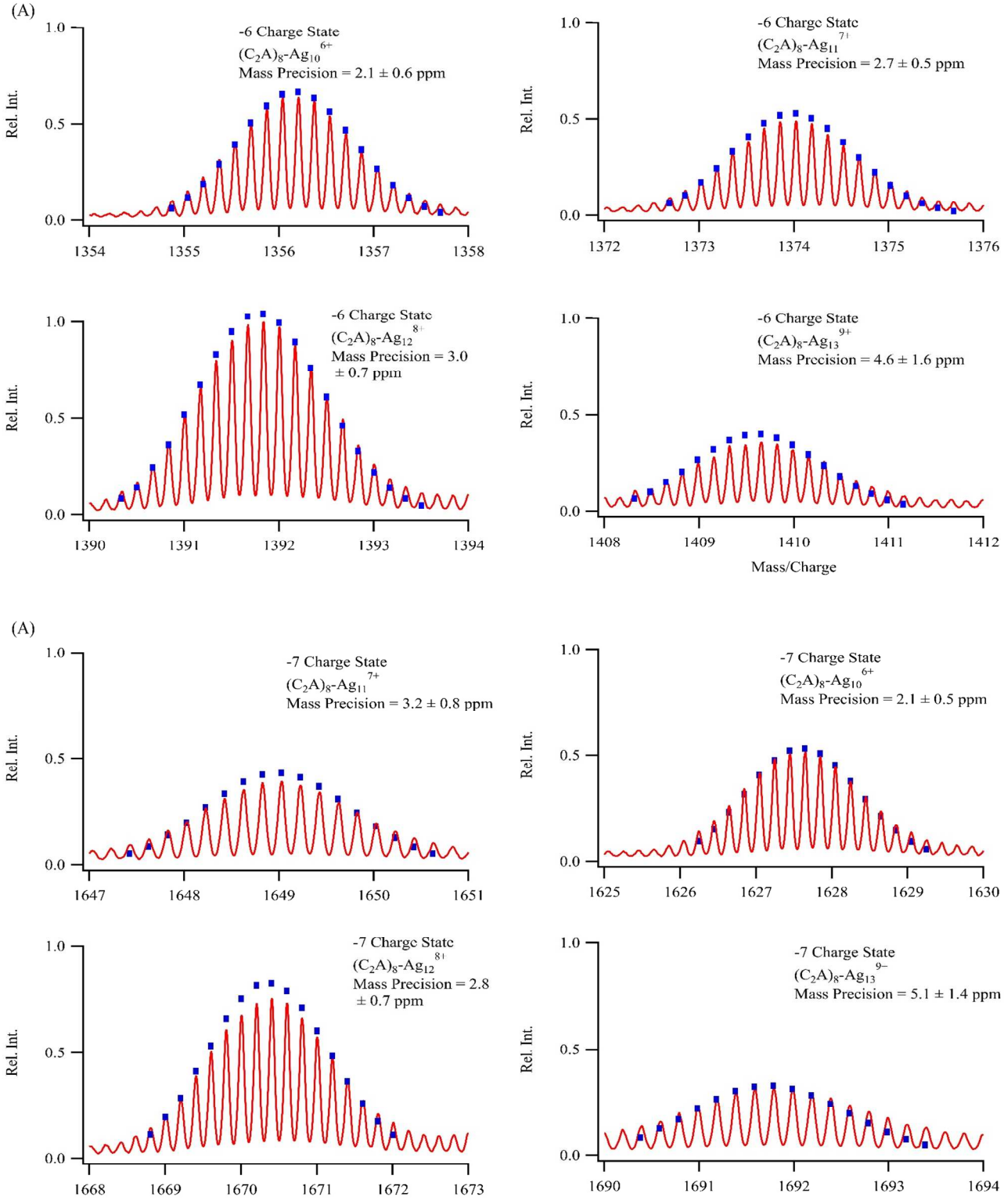


**Figure S8:** *Multiple nucleobases coordinate $Ag_{10}^{6+}$:* Expanded views of the -6 and -7 charge states for $(C_2A)_8$-$Ag_{10}^{6+}$, -$Ag_{11}^{7+}$, -$Ag_{12}^{8+}$, and -$Ag_{13}^{9+}$ complexes. The isotopologue masses were predicted using the specific formulas for these complexes and are indicated by the blue tick marks. The fully protonated strand has the formula $C_{224}H_{289}O_{134}N_{88}P_{23}$.

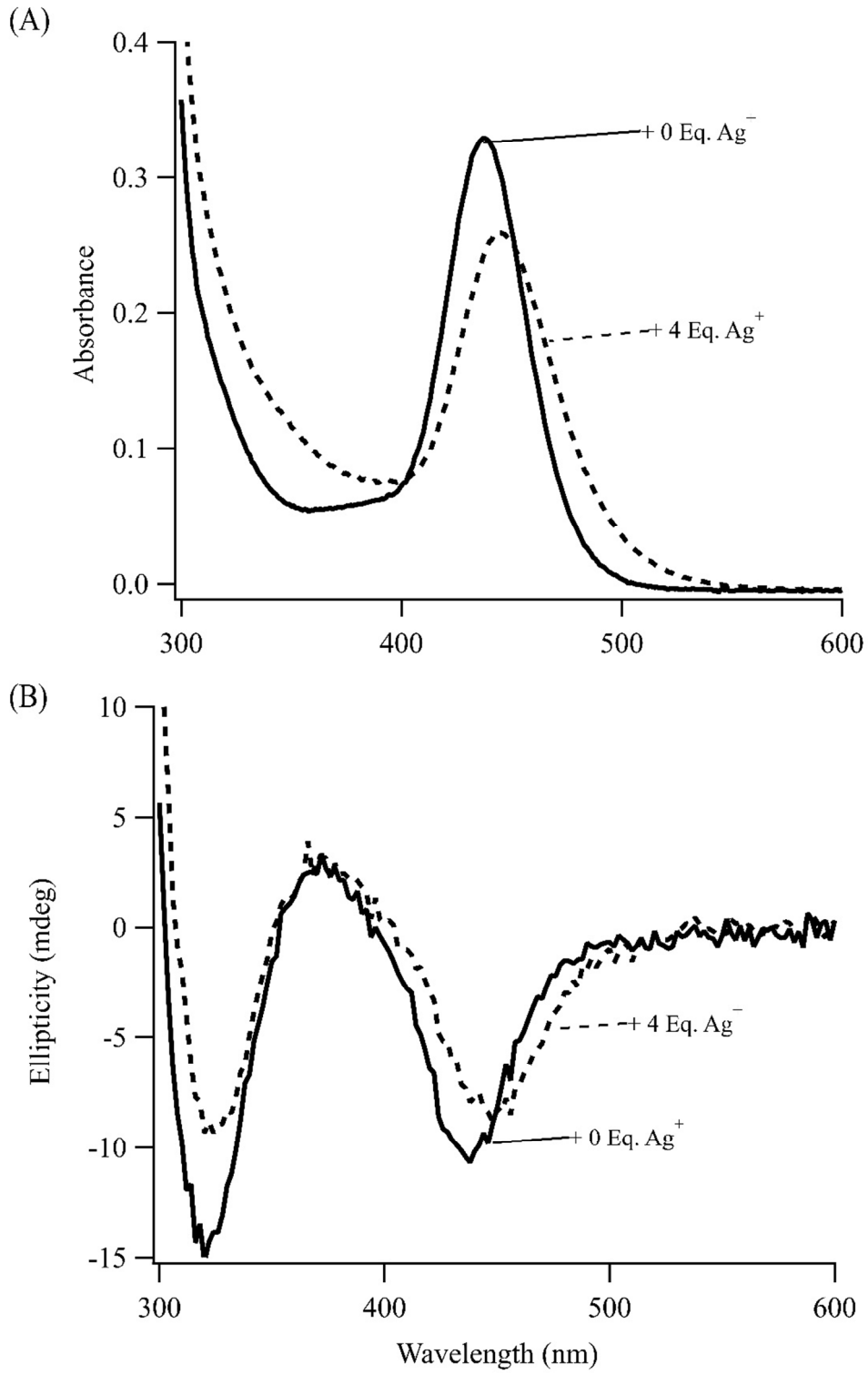


**Figure S9:** *Longer strands add $Ag^+$:* (A) Absorption and Circular Dichroism (B) spectra of the $(C_2A)_6$-$Ag_{10}^{6+}$ complex before and after adding 4 equivalents of $Ag^+$ followed by dialysis.

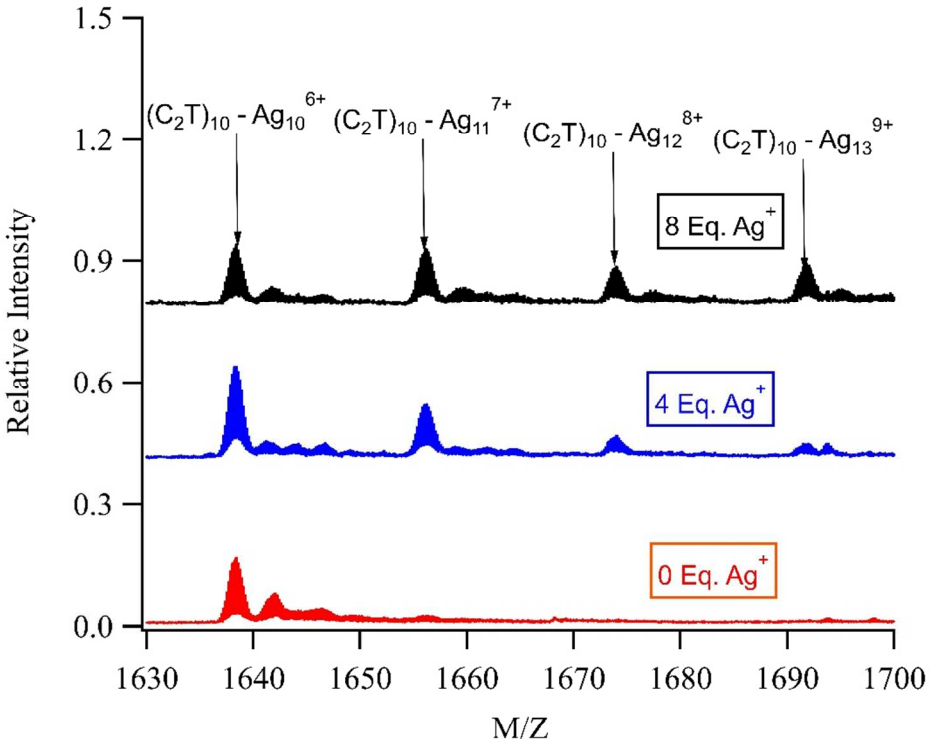


**Figure S10:** *Longer strands add $Ag^+$:* (A) Mass spectra of the -6 charge state of the $(C_2T)_6$-$Ag_{10}^{6+}$ cluster without and with 4 and 8 added equivalents of $Ag^+$:$(C_2T)_{10}$ followed by 100-fold dilution and dialysis. The mass spectra show higher order complexes $(C_2T)_{10}$-$Ag_{10}^{6+}$, -$Ag_{11}^{7+}$, -$Ag_{12}^{8+}$, and -$Ag_{13}^{9+}$.

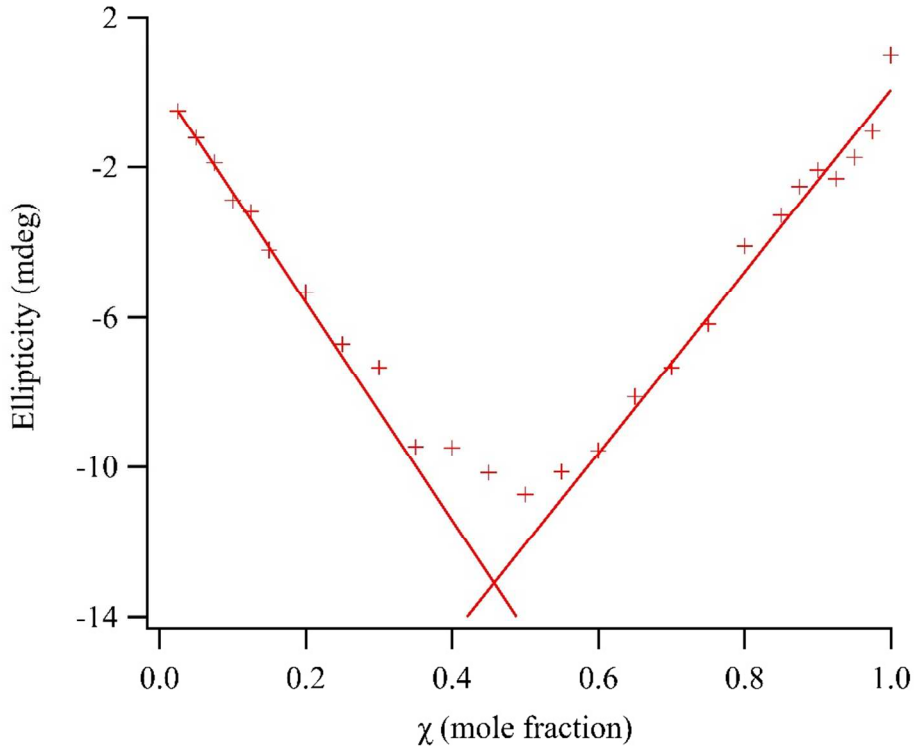


**Figure S11:** *Longer strands accumulate $Ag^+$ :* (A) Continuous variation analysis for $Ag^+$ binding to native $(C_2A)_6$. The concentration of oligonucleotide is based on the $C_2A$ repeats, and the total concentration of $Ag^+$ and $C_2A$ is 36 μM. The ellipticity was measured at 260 nm and the χ is the mole fraction with respect to $C_2A$. Linear extrapolations from the two limiting concentrations intersect at $\chi \sim 0.46$.