Figure 1S: *Selective Synthesis of a Violet-Absorbing Cluster Conjugate*
(A)-Absorption spectra of the sensor/cluster conjugate show that the absorption shoulder at 430 nm becomes less pronounced with lower relative concentrations of BH_4^-. (B)-Variations in the absorbance due to 1 equivalent of H_2O_2:oligonucleotide highlight the stability of the 400 nm absorbing species. These samples were formed in buffers supplemented with 200 mM $NaClO_4$ to monitor the response of a greater diversity of species. (C)-In comparison with samples in citric acid/citrate buffers at pH = 6.7 (Fig. 1A), similar behavior in analogous boric acid/borate buffers at pH = 8.0 (blue spectra) and cacodylic acid/cacodylate buffers at pH = 6.7 (red spectra, pH = 7) indicate the pH and buffer components do not influence the course of the reaction. The dotted lines correspond to 10 mM buffer components while the solid lines correspond to 10 mM buffer components with 200 mM $NaClO_4$.

Figure 2S: *Cluster Environment Transformed Through Hybridization.*
(A)-As opposed to the complement TCCAGCGGCGGG to the 3' recognition site on the sensor (dark red), the target strand CCCGCCGCTGGA does not cause the same spectral transformation, thus indicating that hybridization is needed for cluster transformation. (B)-Derivative absorbances at 400 nm (violet) and 720 nm (dark red) derived from the absorbance in Figure 1D show inflections at ~1 target:sensor. (C)-Variations in the absorbance response at 720 nm (left axis, dark red) and 400 nm (right axis, violet) with relative stoichiometry changes in the target concentration using 10 mM spermine in place of the 1 M $NaClO_4$ used in Figure 1D exhibit a faster response with the +3 charged spermine, thus indicating that it more effectively promotes hybridization through backbone neutralization. (D)-Absorption spectra acquired in 10 mM citric acid/citrate buffers without $NaClO_4$ (solid line), 200 mM $NaClO_4$ (dotted line), and 1 M $NaClO_4$ (dashed line) with 2 equivalents of target:sensor. With increasing amounts of $NaClO_4$, the cluster transformation becomes more favored.

Figure 3S: *Cluster Environment Transformed Through Hybridization.*
(A)-Absorption spectra were collected after heating to 60 ^oC, 70 ^oC, and 80 ^oC and then returning to 20 ^oC. At the higher temperatures, the absorption bands at 400 and 720 nm are diminished, indicative of cluster decomposition. (B)-Following purification of the sensor-cluster conjugate using size exclusion chromatography (violet spectrum), the complement was added to yield the same spectral transformation observed without purification (dark red spectrum) (see Fig. 1A). This similarity indicates that the cluster transformation is due exclusively to the 400 nm absorbing species. (C)-The spectral transformation is inhibited in a diluted sample (right axis, dotted line) in comparison with a more concentrated sample (left axis, solid line). This trend indicates that cluster changes through intermolecular transfer.

Figure 4S: *Alternate Sensors and Equivalent Binding Sites.*
Similar spectral responses to the target strand observed for the following alternate sensors indicate that common binding sites exist for the 400 nm and 720 nm absorbing clusters. The notation follows Table 1: T-S_B + S_{Bc} (6 base target/complement) (A), T-S_C + S_{Cc} (22 base recognition element for a cancer-related microRNA)[1] (B), T-S_D + S_{Dc} (19 base recognition element for the exon 6 of the human GAPDH gene)[2] (C), T-S_E + S_{Ec} (12 base recognition element for the terminus of the bacteriophage lambda genome)[3] (D), and G-S_E + S_{Ec} (E).

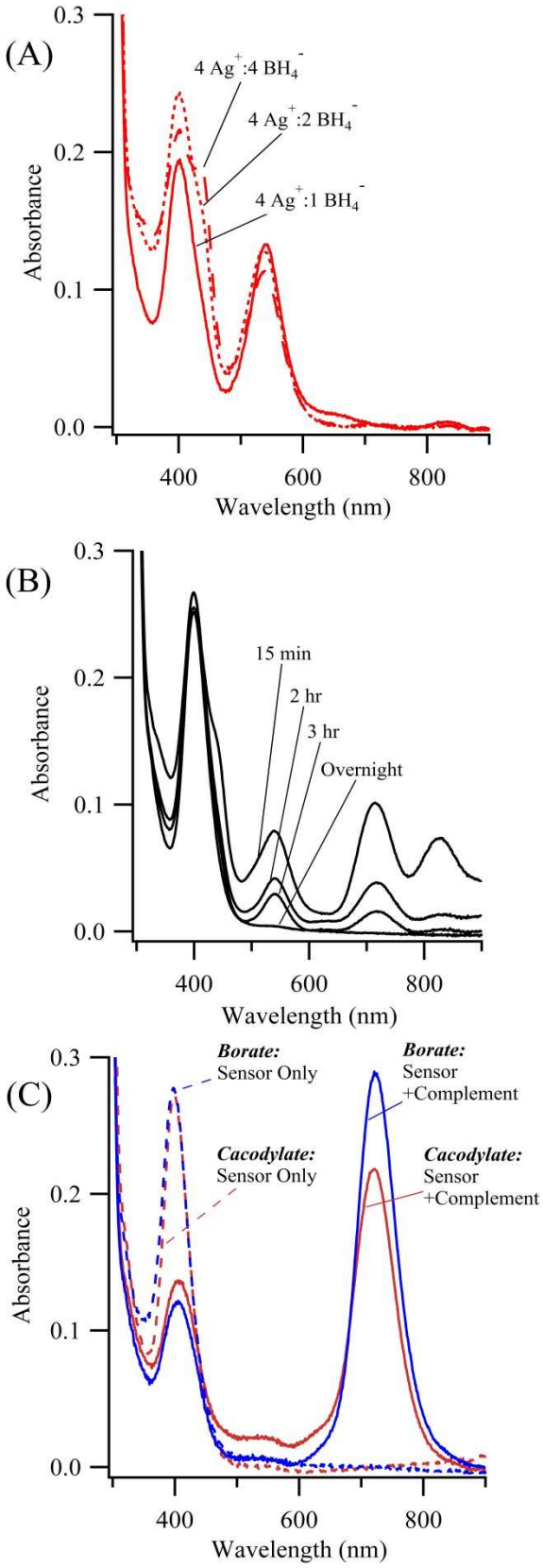
(A)
4 Ag+:4 BH4-
4 Ag+:2 BH4-
4 Ag+:1 BH4-
Absorbance
Wavelength (nm)
(B)
15 min
2 hr
3 hr
Overnight
Absorbance
Wavelength (nm)
(C)
Borate:
Sensor Only
Borate:
Sensor
+Complement
Cacodylate:
Sensor Only
Cacodylate:
Sensor
+Complement
Absorbance
Wavelength (nm)

Fig. 1S

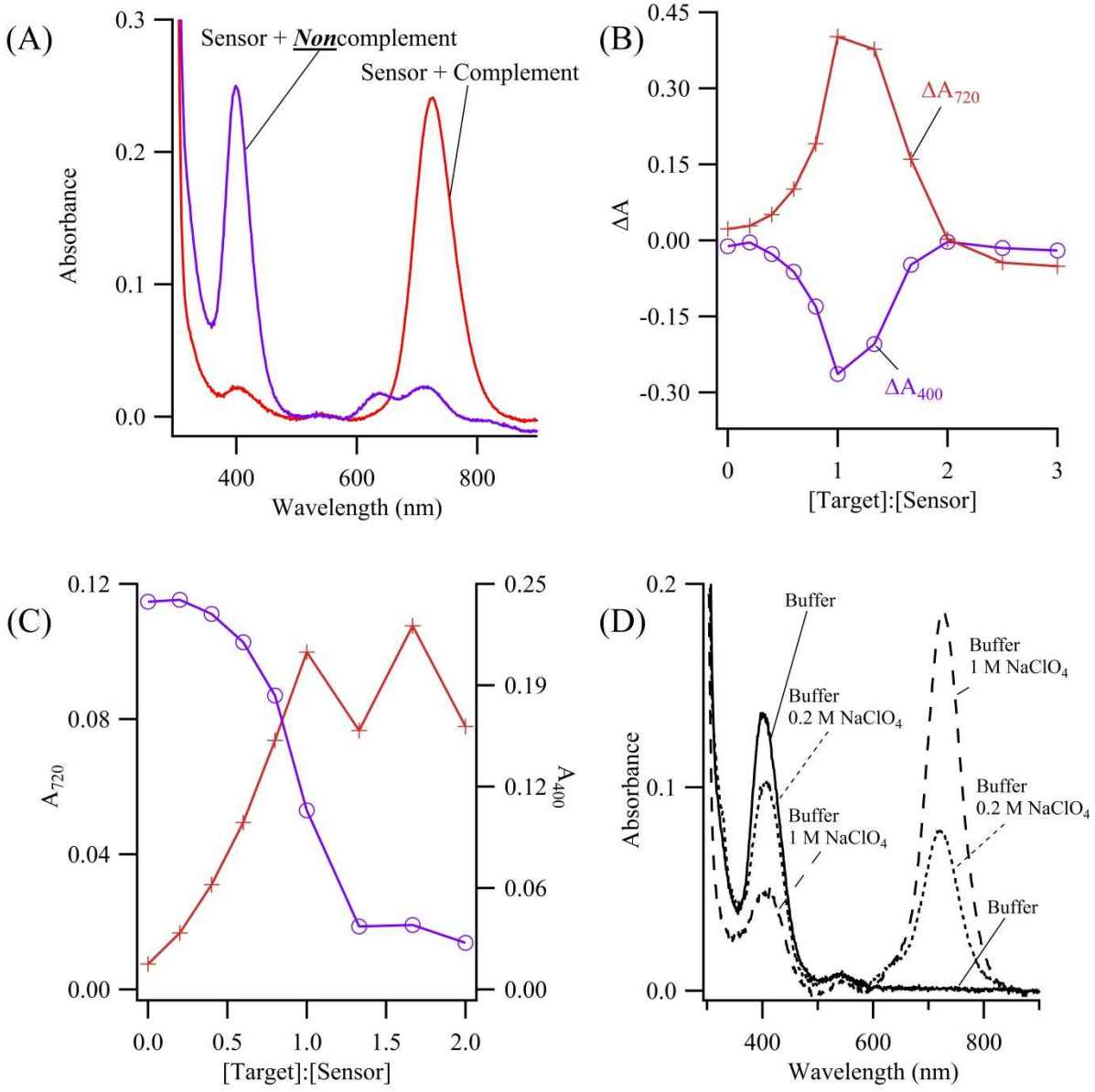
(A)
Sensor + Noncomplement
Sensor + Complement
Absorbance
Wavelength (nm)
(B)
ΔA720
ΔA400
ΔA
[Target]:[Sensor]
(C)
A720
A400
[Target]:[Sensor]
(D)
Buffer
Buffer 0.2 M NaClO4
Buffer 1 M NaClO4
Buffer 1 M NaClO4
Buffer 0.2 M NaClO4
Buffer
Absorbance
Wavelength (nm)

Fig. 2S

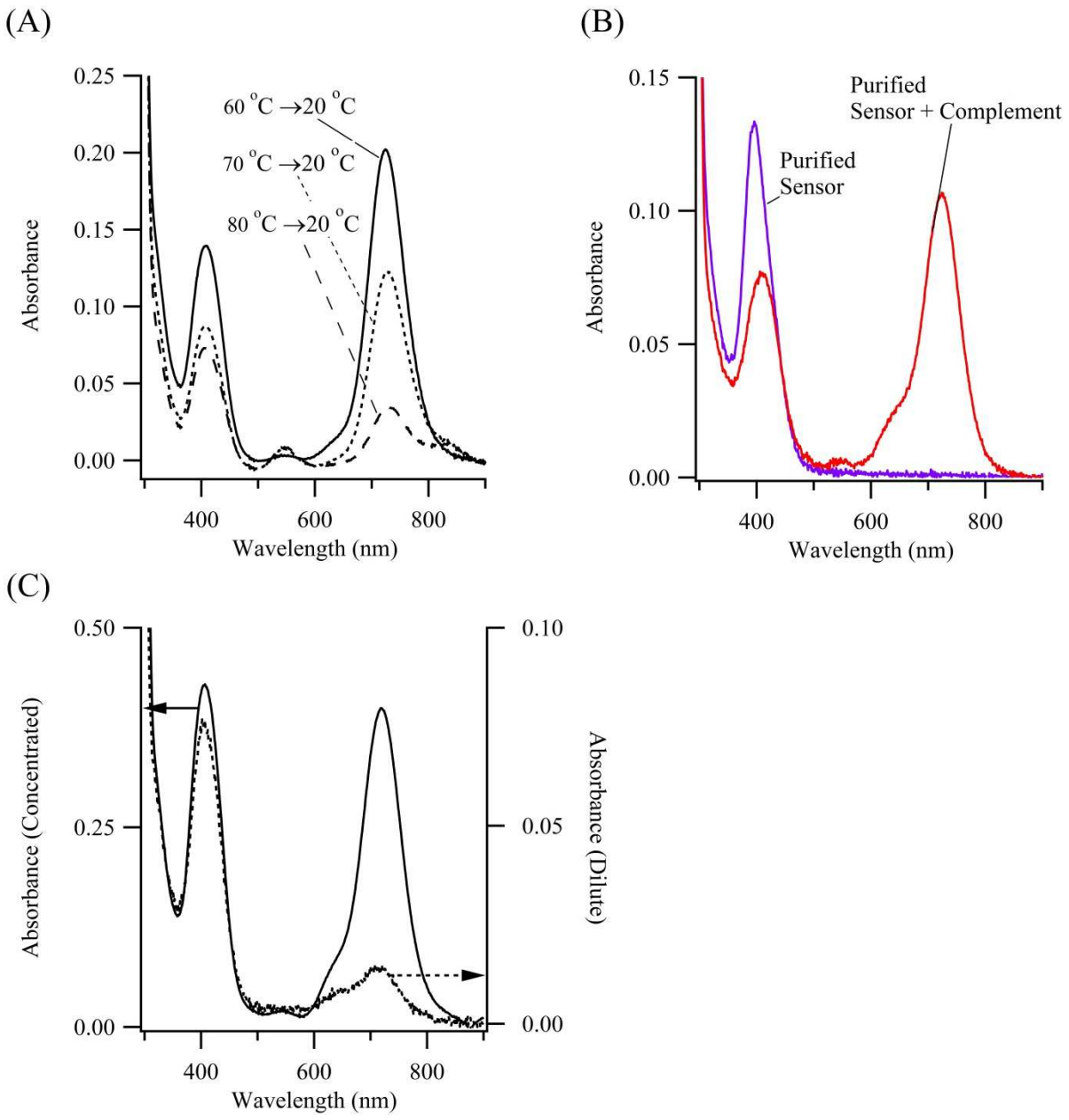
(A)
0.25
0.20
0.15
0.10
0.05
0.00
Absorbance
60 °C →20 °C
70 °C →20 °C
80 °C →20 °C
400
600
800
Wavelength (nm)
(B)
0.15
0.10
0.05
0.00
Absorbance
Purified
Sensor + Complement
Purified
Sensor
400
600
800
Wavelength (nm)
(C)
0.50
0.25
0.00
Absorbance (Concentrated)
0.10
0.05
0.00
Absorbance (Dilute)
400
600
800
Wavelength (nm)

Fig. 3S

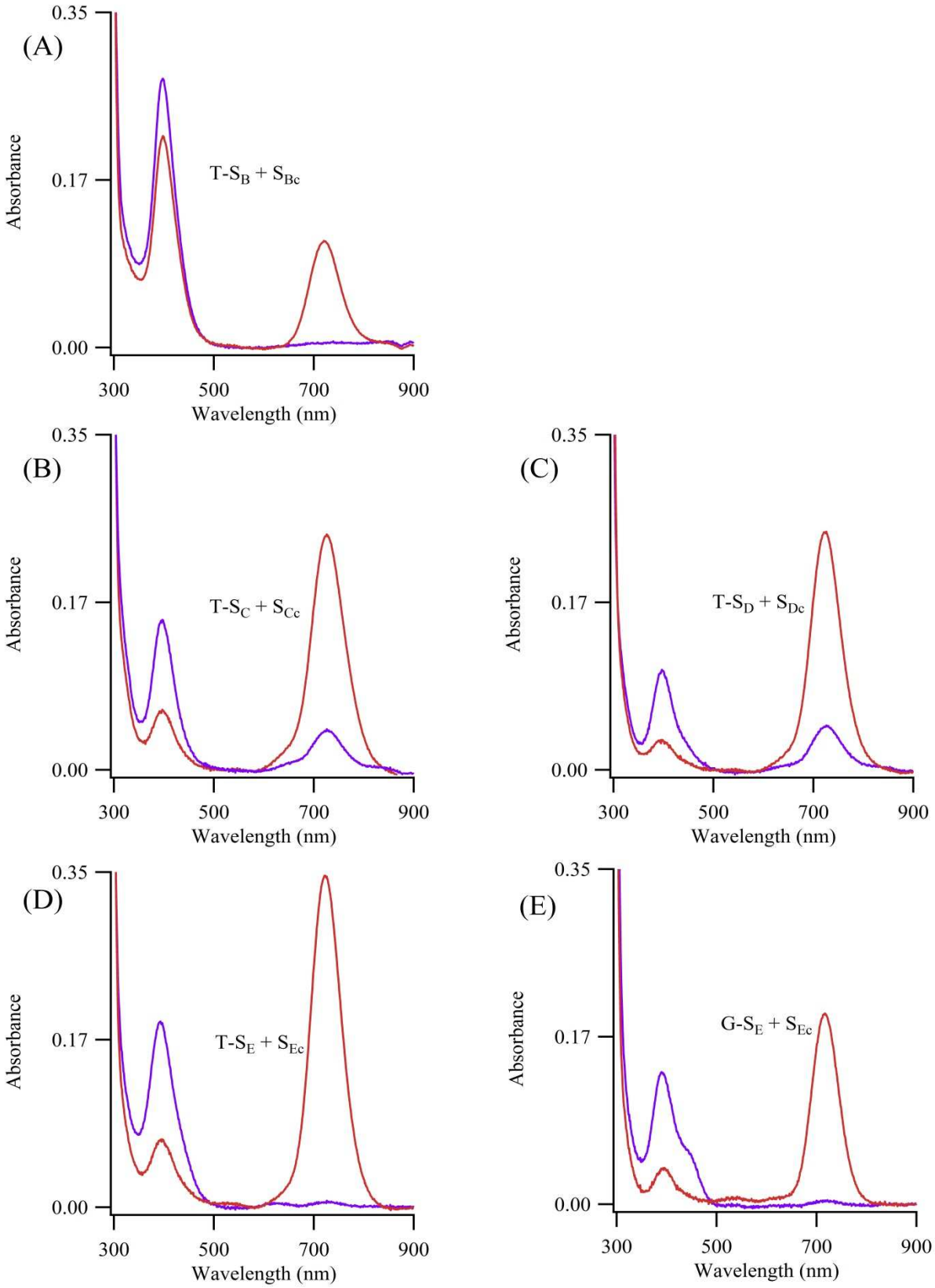
(A)
T-S$_B$ + S$_{Bc}$
(B)
T-S$_C$ + S$_{Cc}$
(C)
T-S$_D$ + S$_{Dc}$
(D)
T-S$_E$ + S$_{Ec}$
(E)
G-S$_E$ + S$_{Ec}$
Absorbance
0.35
0.17
0.00
300
500
700
900
Wavelength (nm)

Fig. 4S

References

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3. Nichols, B. P.; Donelson, J. E., 178-Nucleotide sequence surrounding the cos site of bacteriophage lambda DNA. *J. Virol.* **1978,** *26* (2), 429-34.