Supporting Information

Exciton Delocalization in a DNA-Templated Organic Semiconductor Dimer Assembly

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Experimental Section

Synthesis and purification of the octaniline-DNA conjugate. A "click" reaction between the phenyl capped octaniline (compound 1) and the 2'-propargyl-modified DNA strand (strand B) was carried out on a CPG resin. The resin was transferred back to the CPG column for automatic DNA synthesis. The OH group on the 5' end of strand B was "capped" first (see Figure below), and strand A was then synthesized by standard oligonucleotide solid phase synthesis procedures. The Boc groups on octaniline were removed while the oligomer was attached to the CPG support, using microwave radiation: the reaction was carried out in 500 µL 1/1 trifluoroacetic acid/dichloromethane for 7 min at 25-35°C, and then washed three times with 500 µL dichloromethane. The octaniline-DNA conjugate was cleaved from the solid support in 500 µL 50

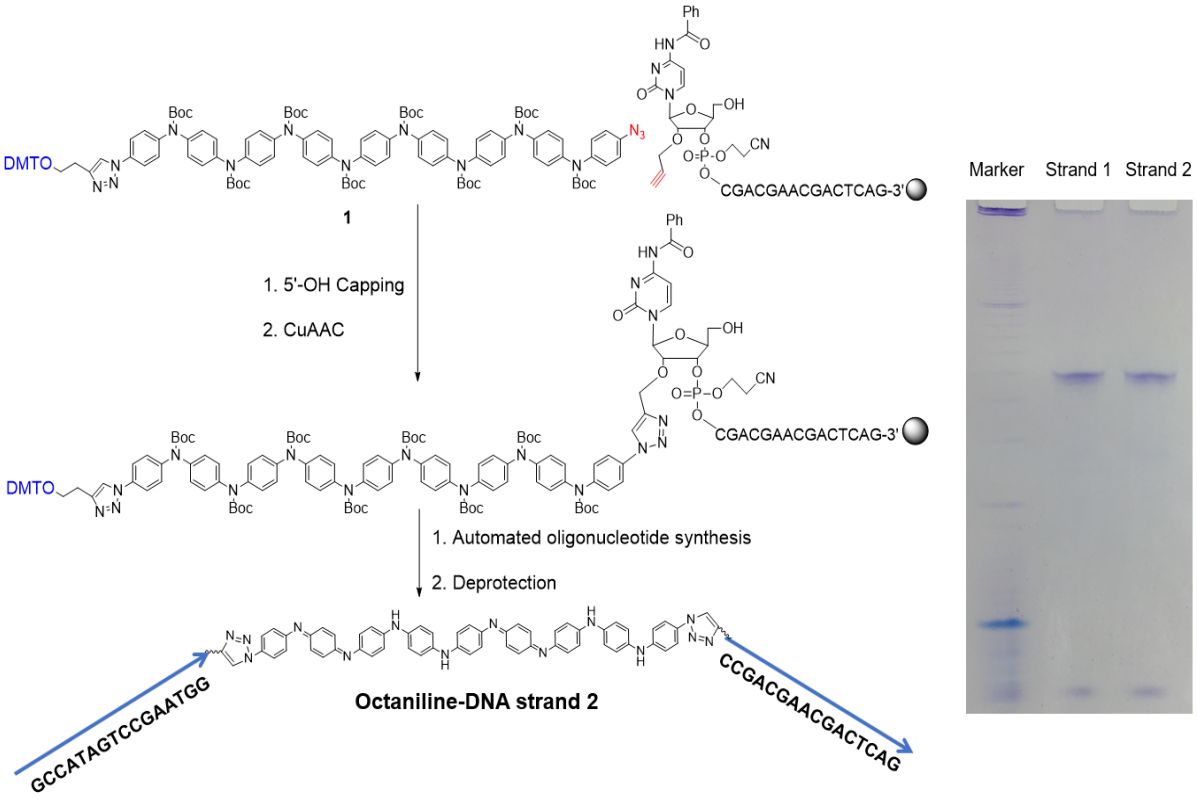


Figure S1. The synthesis of octaniline-DNA strand 2, and the denaturing gel electrophoresis of both octaniline-DNA strands. Compound 1 and octaniline-DNA strand 1 was prepared as in Ref. 1.

mM K_2CO_3 methanol solution overnight. The sample was dried down and dissolved in 500 μL DD H_2O, then desalted and concentrated using 3K spin filter from Millipore.

Octaniline-DNA strands purification. Octaniline-DNA strands were purified with 20% denaturing polyacrylamide gel at 55°C. The gels were placed on a silica TLC plate (w/UV254) that covered by the transparent film. The bands were visualized with a 254 nm UV light source. The target bands were identified, excised from the gels with a razor blade, and extracted with extraction buffer (500 mM ammonium acetate, 10 mM magnesium acetate and 1 mM EDTA) overnight. The eluates were filtered by 0.22 μm filter and then desalted and concentrated using 3K spin filter.

Unmodified DNA strands purification. DNA strands were purified with 20% denaturing polyacrylamide gel at 55°C. Ethidium bromide stained gels were illuminated with a 254 UV light source. The target band was identified, excised from the gels with a razor blade, and extracted with extraction buffer (500 mM ammonium acetate, 10 mM magnesium acetate and 1 mM EDTA) overnight. The eluates were subjected to extraction with n-butanol to remove the ethidium, followed by ethanol precipitation.

The preparation of DNA constructs in SDS buffer. DNA construct prepared by fast-annealing protocol was added with 1/9 volume of the SDS 1XTAE Mg (12.5 mM) buffer to adjust to the desired SDS concentration. For example, adding 0.5 μL of 6% SDS 1XTAE Mg (12.5 mM) buffer to 4.5 μL DNA construct. The mixtures were vortexed and centrifuged for 1 min to break the bubble.

The preparation of DNA constructs at lower pH. DNA construct prepared by fast-annealing protocol was added with 1/9 volume of 1XTAE Mg (12.5 mM) buffer (pH ~3) followed by vortexing. The pH of the resulting solution was measured with Millipore 4-7 pH strips.

UV-Vis measurement. The UV-Vis spectra of octaniline-DNA strands/constructs were collected using Nanodrop 2000 at room temperature, and the samples were recovered after the measurements.

Non-denaturing PAGE analysis. The DNA construct (4 μM) was dissolved in 10 μL of 1XTAE Mg (12.5 mM) buffer. 1 μL of 10X Tracking dye (contains 1XTAE Mg (12.5 mM), 50% glycerol and a trace amount of Bromophenol Blue and Xylene Cyanol FF) was added to the buffer. Polyacrylamide gels were prepared with desired concentrations and were run at the desired temperature. The gels were stained with stains-all solution afterward.

Low pH non-denaturing PAGE analysis. The pH of 1XTAE Mg (12.5 mM) buffer were adjusted to pH ~5. The pH was measured with pH paper (Millipore 4-7 pH strips). Polyacrylamide gels with desired concentrations were prepared in pH ~5 1XTAE Mg (12.5 mM) buffer, which requires longer polymerization time. The gels were pre-run at pH ~5 for 20 min at 4 ˚C before the DNA samples were loaded.

The DNA samples (4 μM) were prepared at pH 7-8 in 1XTAE Mg (12.5 mM) buffer with the fast-annealing protocol. After stayed at the 4 ˚C for 30 min, the pH of DNA sample was adjusted to ~5. The pH of 10X Tracking dye was also adjusted to ~5 before the adding of Bromophenol Blue and Xylene Cyanol FF.

SDS non-denaturing PAGE analysis. Polyacrylamide gels with desired concentrations were prepared in 1XTAE Mg (12.5 mM) buffer contains 0.6% SDS. The DNA sample (4 μM, 9 μL)

was mixed with 1 μL of 1XTAE Mg (12.5 mM) buffer contains 6% SDS, and then added with 1 μL of 10X Tracking dye (contains 0.6% SDS). The gels were run in 1XTAE Mg (12.5 mM) buffer contains 0.6% SDS at the desired temperature.

Ferguson plot analysis. The DNA constructs were analyzed in different concentrations of non-denaturing gel. Four concentrations of gel were prepared in one experiment: 6%, 8%, 10%, 12%. The gels were run in parallel, in which same voltage and time were applied. The Ferguson plot analysis was carried out in different conditions, such as non-denaturing gel electrophoresis or low pH and SDS non-denaturing gel electrophoresis. The corresponding gel electrophoresis analysis was carried out with the protocols described above. For each data set, log(mobility) *vs* gel concentration was used to generate the Ferguson plot. The mobility was calculated by the equation: mobility = migration velocity (cm/s) / field strength (V/cm).

Strand displacement experiment. Step 1: IS construct with 8mer toehold overhangs (30 μM, 5 μL) was prepared with the fast-annealing protocol. The sample was used to collect CD and UV-Vis spectra and recovered for further use. Step 2: Two 12mer invasion strands (120 pmole) were dried down. Took 4 μL of the IS construct solution and added to the invasion strands sample. The sample was thoroughly mixed by pipetting, and the mixture was kept at room temperature overnight. The sample was then used to collect CD and UV-Vis spectra and recovered. Gel electrophoresis analysis of the sample in step 1 and the product in step 2 indicated the transition from IS to I0 construct, and I0 construct aggregated to the dimer.

Octaniline constructs with different compositions

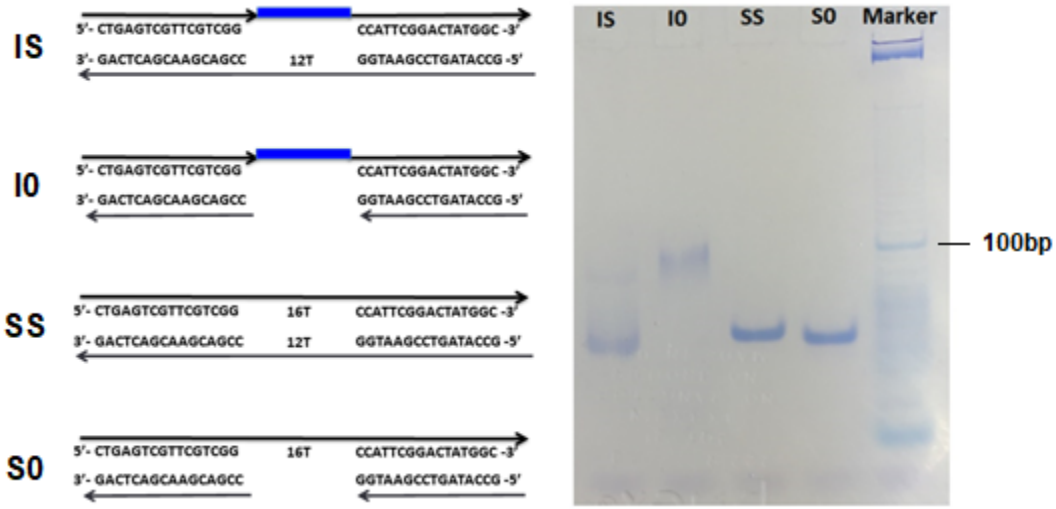


Figure S2. The non-denaturing PAGE analysis of different octaniline constructs at pH 7-8. The mobility of I0 construct is same to double-sized linear DNA duplex

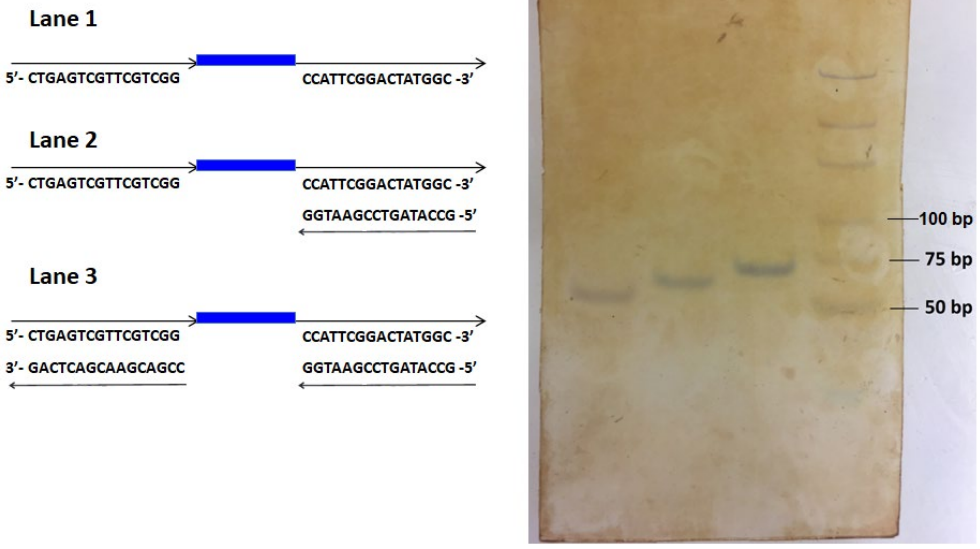


Figure S3. The 0.6% SDS non-denaturing PAGE analysis of the I0 construct and the control constructs. The mobility (size based on the marker) difference between these constructs indicates that the I0 construct exists as the monomer in SDS buffer.

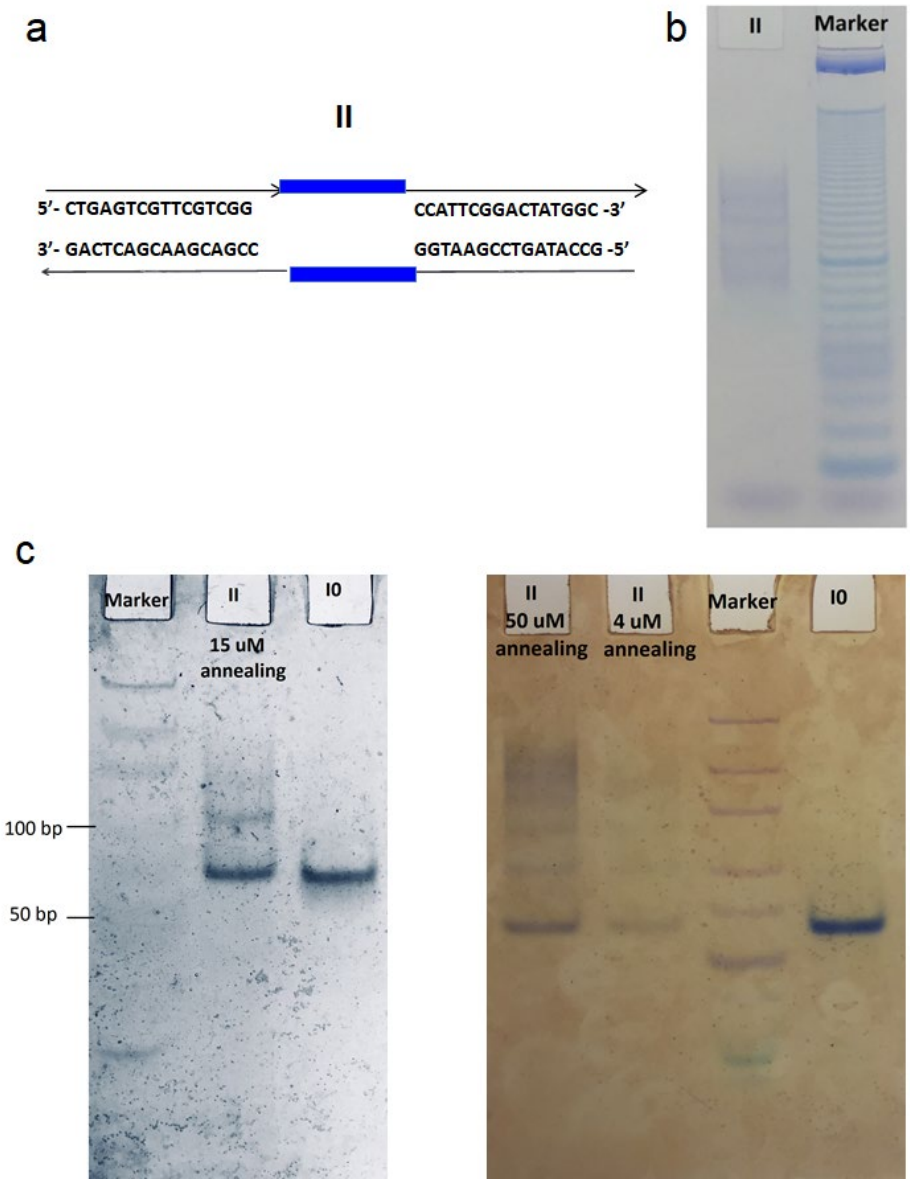


Figure S4. The non-denaturing PAGE analysis of octaniline II construct in different conditions. a, The II construct. b, The non-denaturing PAGE analysis of II construct shows the construct exists as multiple species. c, The 0.6% SDS non-denaturing PAGE analysis of the II and I0 constructs. The mobility of the monomer state of II construct is similar to I0 in 0.6% SDS non-denaturing PAGE, while there are still lower-mobility species, which indicates the multiple species exist in b are resulted from both aggregation and cross-reaction.

Octaniline I0 construct and DNA four-arm junction as the control

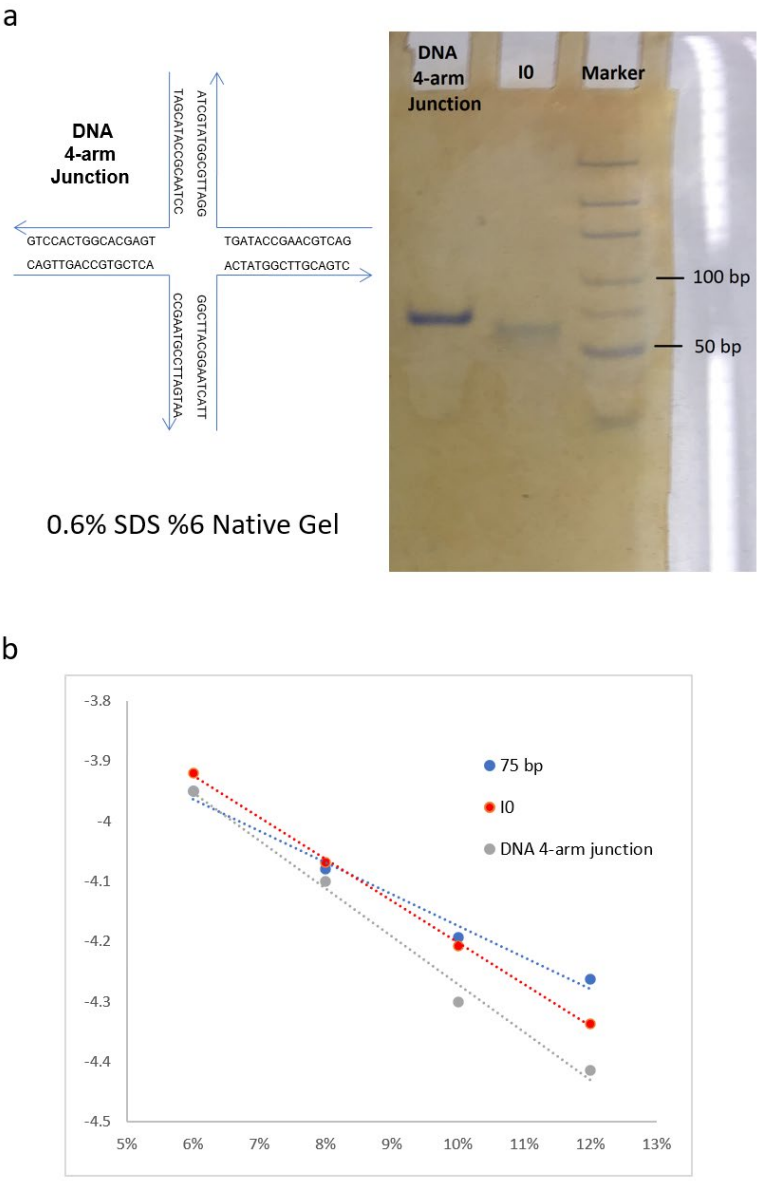


Figure S5. Ferguson plot analysis of I0 in SDS condition. a, The SDS non-denaturing PAGE analysis of DNA 4-arm junction and I0 construct. b, The Ferguson plot of DNA 4-arm junction, I0 construct compared to 75 bp linear DNA duplex.

The UV-Vis and CD spectra of octaniline I0 construct

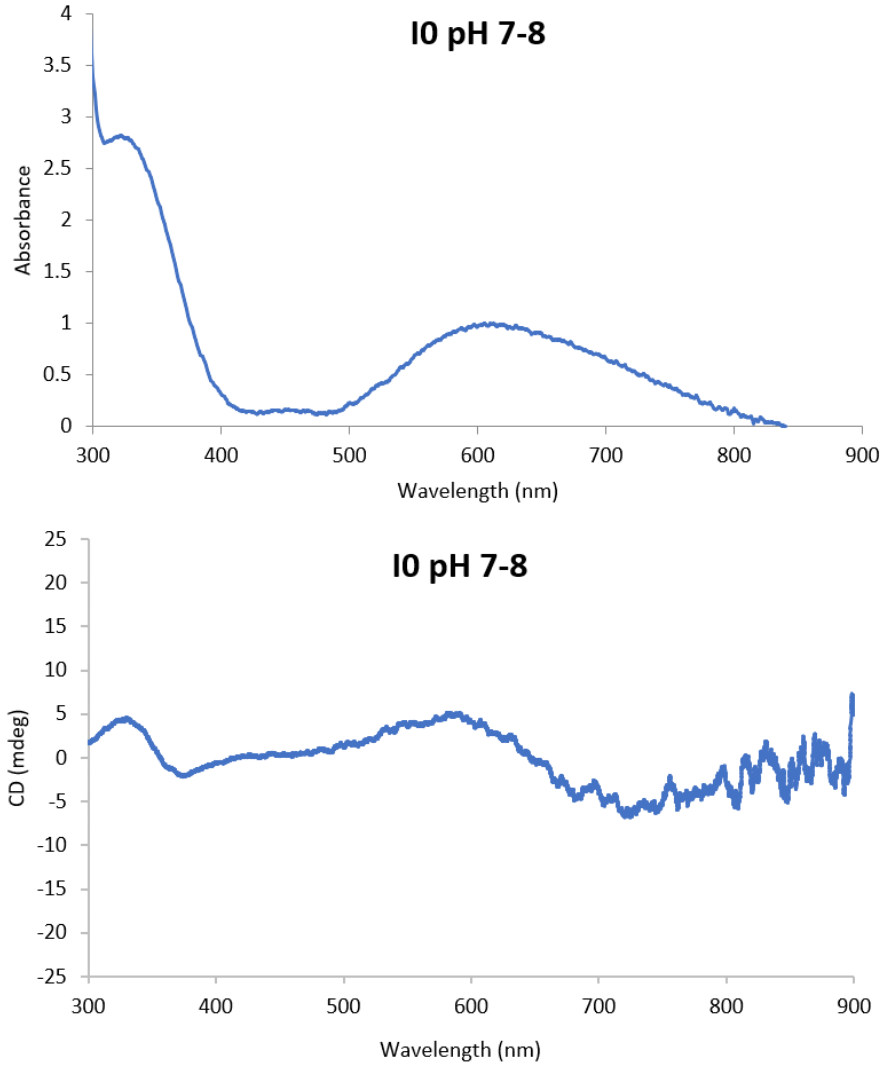


Figure S6. UV-Vis and CD of octaniline construct I0 at neutral pH. The I0 construct exists in the dimer state $(I0)_2$ based on PAGE analysis.

Blue-shift in UV-Vis of I0 dimer aggregate

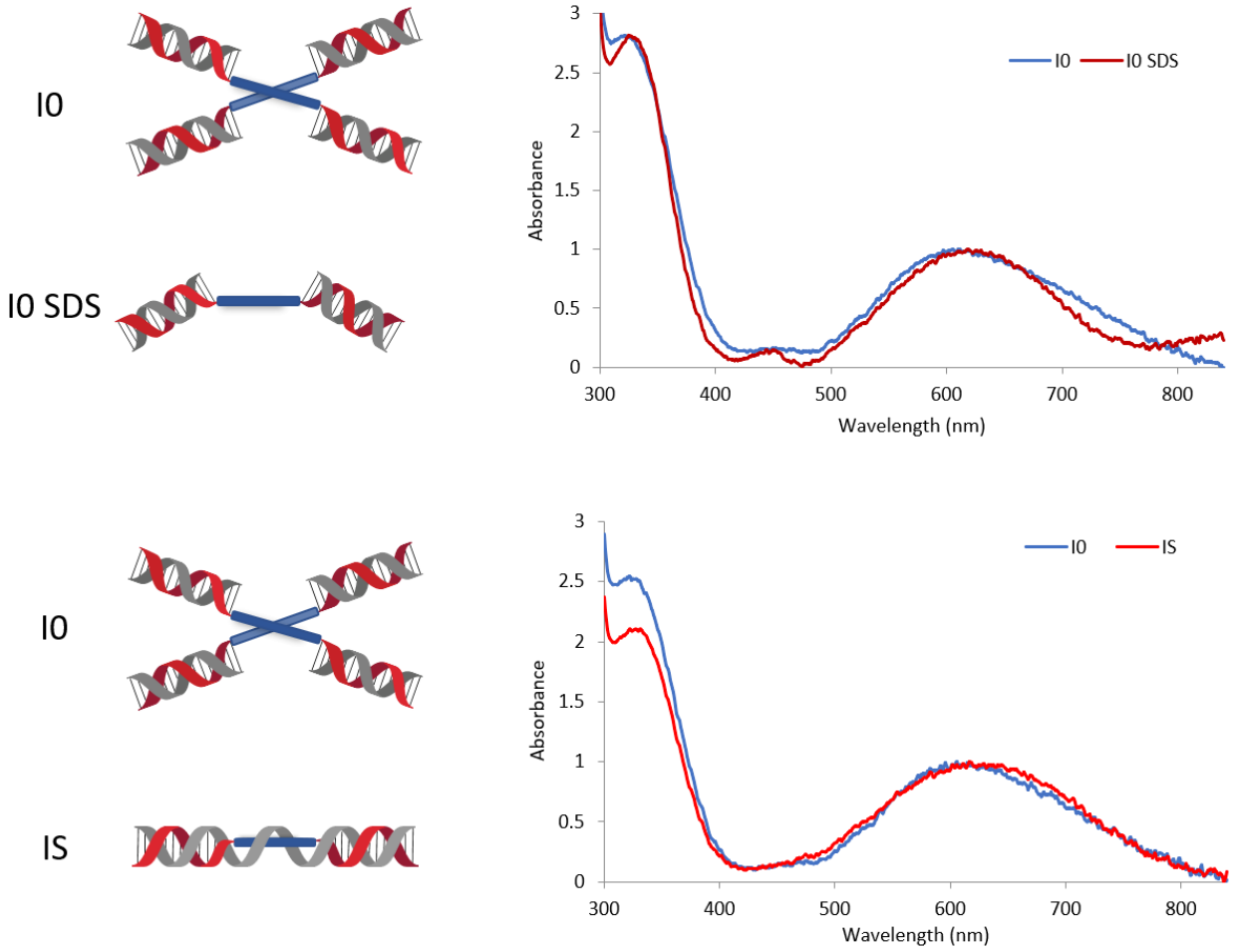
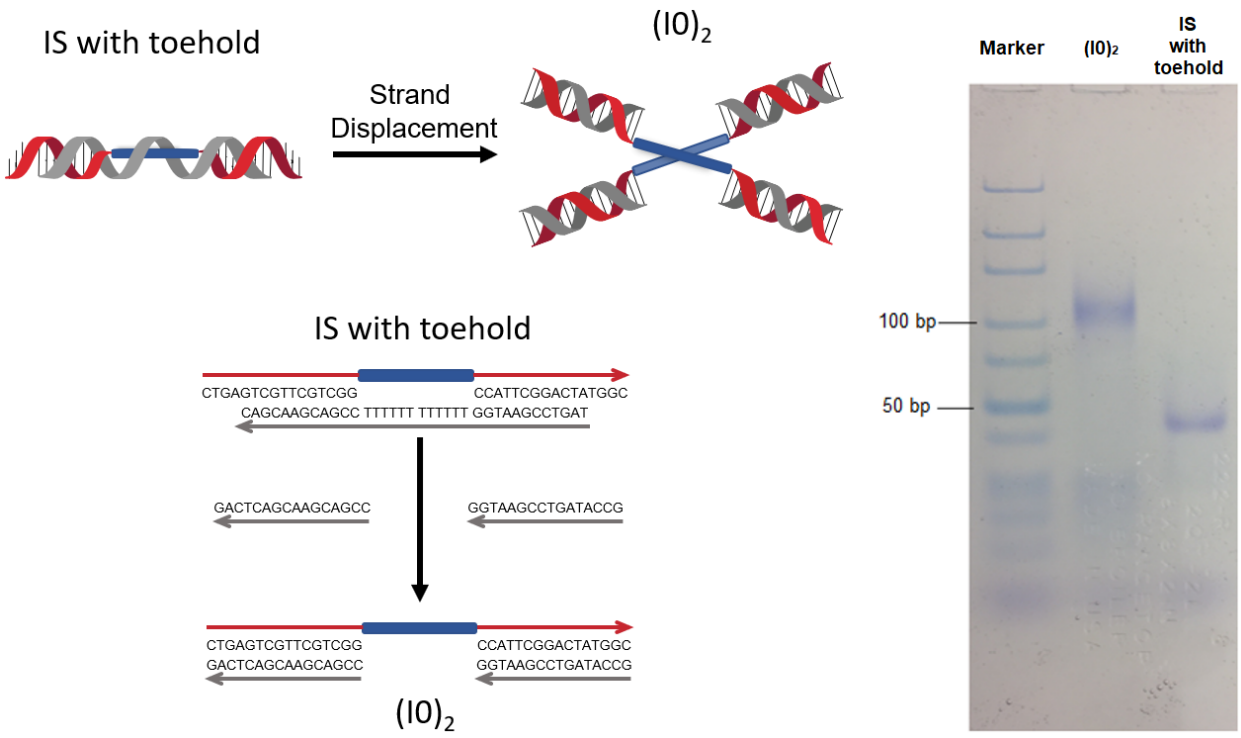


Figure S7. The blue-shift in the UV-Vis of I0 dimer. Top: The comparison between the UV-Vis of $(I0)_2$ and I0 (in SDS buffer). Bottom: The comparison between the UV-Vis of $(I0)_2$ and IS. The UV-Vis peak around 620 nm of I0 dimer show blue shift compared to both kind of monomers: I0 (in SDS) and IS.


IS with toehold
Strand Displacement
$(I0)_2$
IS with toehold
CTGAGTCGTTCGTCGG
CCATTCGGACTATGGC
CAGCAAGCAGCC TTTTTT TTTTTT GGTAAGCCTGAT
GACTCAGCAAGCAGCC
GGTAAGCCTGATACCG
CTGAGTCGTTCGTCGG
GACTCAGCAAGCAGCC
CCATTCGGACTATGGC
GGTAAGCCTGATACCG
$(I0)_2$
Marker
$(I0)_2$
IS with toehold
100 bp
50 bp

Spectral theory analysis for the octaniline dimer aggregate

The Frenkel Hamiltonian for a pair of chromophores, labeled 1 and 2, is given by

$$H = E_0\left(a_1^\dagger a_1 + a_2^\dagger a_2\right) + J(a_1^\dagger a_1 + a_2^\dagger a_2) \quad (1)$$

Here $a_1^\dagger$ and $a_2^\dagger$ are the exciton creation operators for chromophores 1 and 2 respectively and, here, are taken to satisfy Bose commutation relations. The first term on the right side of the equation accounts for the energy associated with excitons occupying chromophores 1 and 2. The coefficient E_0 is the energy difference between a chromophore's ground state and its first optically allowed excited state. The second term accounts for the exchange energy associated with transferring an exciton from one chromophore to the other. The coefficient J is the exchange energy. This term arises from the interaction between the transition dipoles of chromophore 1 and 2. The one-exciton energy eigenstates are

$$|S\rangle = \frac{1}{\sqrt{2}}\left(a_1^\dagger + a_2^\dagger\right)|0\rangle \quad (2)$$

$$|A\rangle = \frac{1}{\sqrt{2}}\left(a_1^\dagger - a_2^\dagger\right)|0\rangle, \quad (3)$$

where $|0\rangle$ is the system ground state. The energy eigenvalues of these states are

$$E_s = E_0 + J \quad (4)$$

$$E_A = E_0 - J, \quad (5)$$

respectively. In contrast to the Hamiltonian Eq. (1) the Frenkel Hamiltonian for a single isolated chromophore, say chromophore 1, is $H_1 = E_0 a_1^\dagger a_1$. The one exciton eigenstate for this Hamiltonian is $a_1^\dagger|0\rangle$ and has the energy eigenvalue E_0. From this it is evident that the absorption peak of a chromophore monomers, centered at E_0 will be split into two peaks centered at $E_0 - J$

and $E_0 + J$ when to such chromophores are brought into proximity. The difference between the two peaks is $2J$ and is referred to as the Davydov splitting. The electromagnetic field couples to the chromophores *via* the transition dipole. The transition dipole of chromophore 1 can be written as

$$\boldsymbol{\mu}_1 = \mu \mathbf{n}_1 + \left(a_1^{\dagger} + a_1\right) \tag{6}$$

where μ is the magnitude of the transition dipole and the unit vector $\mathbf{n_1}$ is the orientation vector for the dipole. This will generally lie along the long axis of the molecule. One has a similar expression for the transition dipole $\boldsymbol{\mu_2}$ for chromophore 2. The total transition dipole moment μ is the sum of the individual transition dipole moments.

$$\boldsymbol{\mu}_1 = \boldsymbol{\mu}_1 + \boldsymbol{\mu}_2 \tag{7}$$

It is evident from this discussion that the absorbance of a dimer chromophore complex will depend on the orientation vectors $\mathbf{n}_1$ and $\mathbf{n}_2$ for the two chromophores. In the discussion to follow it is assumed that the chromophore complexes are in solution and, hence, the results given are those obtained by averaging over all chromophore complex orientations. Due to the coupling of the electronic degrees of freedom with the vibronic degrees of freedom, the spectral lines are broadened. Here it is assumed that the broadening is the same for all spectral peaks and the line shape function f is a Gaussian:

$$f(E) = \pi e^{-E^2/2\Gamma^2}, \tag{8}$$

where Γ is the linewidth parameter. The extinction spectrum of a chromophore monomer complex can then be written as

$$\epsilon_M(E) = \epsilon_M^p f(E - E_0), \tag{9}$$

where ϵ_M^p is the extinction coefficient at the absorbance peak maximum. The extinction spectrum of the chromophore dimer complex is given by

$$\epsilon_D(E) = \epsilon_M^p[|\mathbf{n}_1 + \mathbf{n}_2|\, f(E - E_s) + |\mathbf{n}_1 - \mathbf{n}_2|^2\, f(E - E_A)], \tag{10}$$

The spectrum of the circular dichroism, which is the difference in the extinction spectrum of left-circularly polarized light and right-circularly polarized light, is given by

$$CD(E) = \frac{4\pi r}{\lambda}\epsilon_M^p(\mathbf{n}_1 \times \mathbf{n}_2)\cdot\mathbf{n}_{12}[\, f(E - E_s) - f(E - E_A)], \tag{11}$$

where $\mathbf{n}_{12}$ is the unit vector pointing from the center of chromophore 1 to the center of chromophore 2, r is the distance between the centers of the two chromnophores, and λ is the wavelength of light in the medium in which the chromophores reside. This equation is valid for the case when $r \ll \lambda$. To further restrict the model the chromophores in the dimer complex will be taken to be aligned so that the distance between their centers is the distance of the closest approach. As a consequence, $\mathbf{n}_{12}$ is perpendicular to $\mathbf{n}_1$ and to $\mathbf{n}_2$, and it can be taken to be parallel to $\mathbf{n_1} \times \mathbf{n_2}$. The angle θ between $\mathbf{n}_1$ and $\mathbf{n}_2$ is defined by writing

$$\sin(\theta) = \mathbf{n}_1 \times \mathbf{n}_2 \tag{12}$$

and

$$\cos(\theta) = \mathbf{n}_1 \cdot \mathbf{n}_2 \tag{13}$$

Equations (10) and (11) then become

$$\epsilon_D(E) = 4\epsilon_M^p\left[\, f(E - E_s)\cos^2\left(\frac{\theta}{2}\right) + f(E - E_A)\sin^2\left(\frac{\theta}{2}\right)\right] \tag{14}$$

and

$$CD(E) = \frac{4\pi r}{\lambda}\epsilon_M^p[\, f(E\, -\, E_s) -\, f(E\, -\, E_A)]\sin(\theta)\,. \qquad (15)$$

Equations (9), (14) and (15) together with Eq. (8) are used to extract J, θ and r from the data.

Data analysis was performed by simultaneously fitting the absorbance data and CD data for the I0 construct used in the strand displacement experiment to Eqs. (14) and (15) to extract the parameters E_0, J, Γ, θ and r. Values obtained for the parameters are given in the table below.

Table 1, Parameter values obtained by fitting the I0 absorbance and CD data.

Parameter	Value
E_0	2.0 eV
J	0.11 eV
Γ	0.22 eV
θ	34°
r	0.53 nm

Taking octaniline length l to be 4 nm, the distance between the ends is given by $l \sin\left(\frac{\theta}{2}\right) = 1.2$ nm, which does not seem unreasonable given that duplex DNA is 2 nm wide. Although the model provides a satisfactory fit to the data and yields reasonable values for the parameters, the assumptions underlying the model should be kept in mind. The model assumes the octaniline molecules are stiff rods. It assumes that the molecules adopt a configuration in which the distance between the centers of the two octaniline is small compared to the length of the molecules. It

assumes that the aggregates adopt a single conformation rather than an ensemble of conformations. And, it assumes that vibronic coupling has little effect on the absorbance and CD spectrum peak positions and shapes. To refine the model, independent data, especially structure data, would provide valuable constraints. Never-the-less, clear indications of coherent exciton exchange giving rise to exciton delocalization has been observed.

The dimer of I0 construct at lower pH

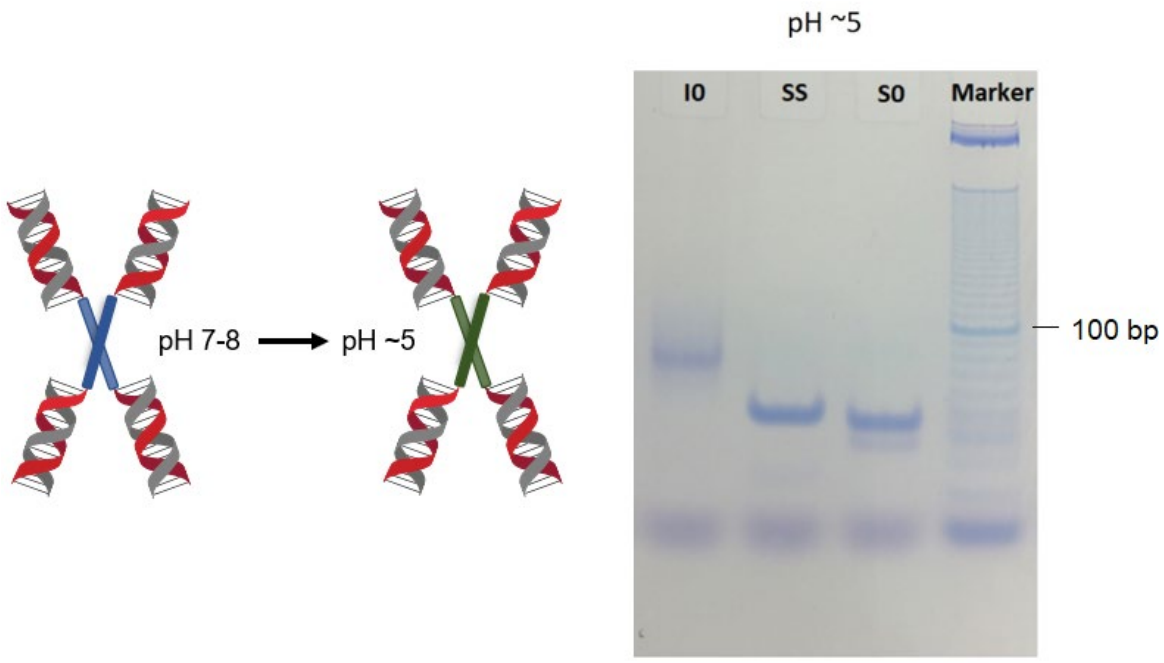


Figure S9. Non-denaturing PAGE analysis shows I0 exists as $(I0)_2$ at lower pH (pH ~5).

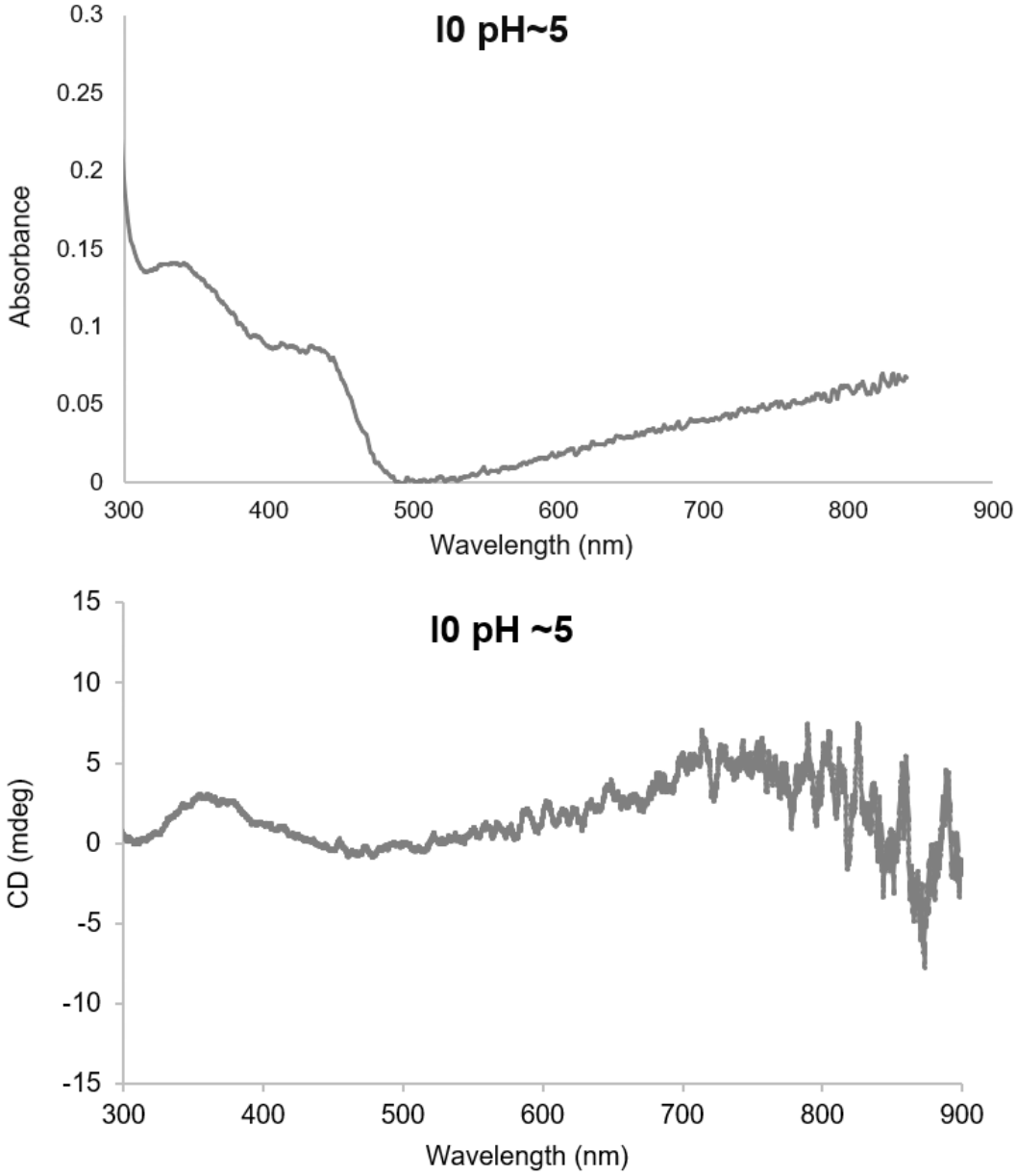


Figure S10. UV-Vis and CD of octaniline construct I0 at lower pH (pH ~5). The I0 construct exists in the dimer state $(I0)_2$ based on PAGE analysis.

CD spectra of octaniline-DNA single strand

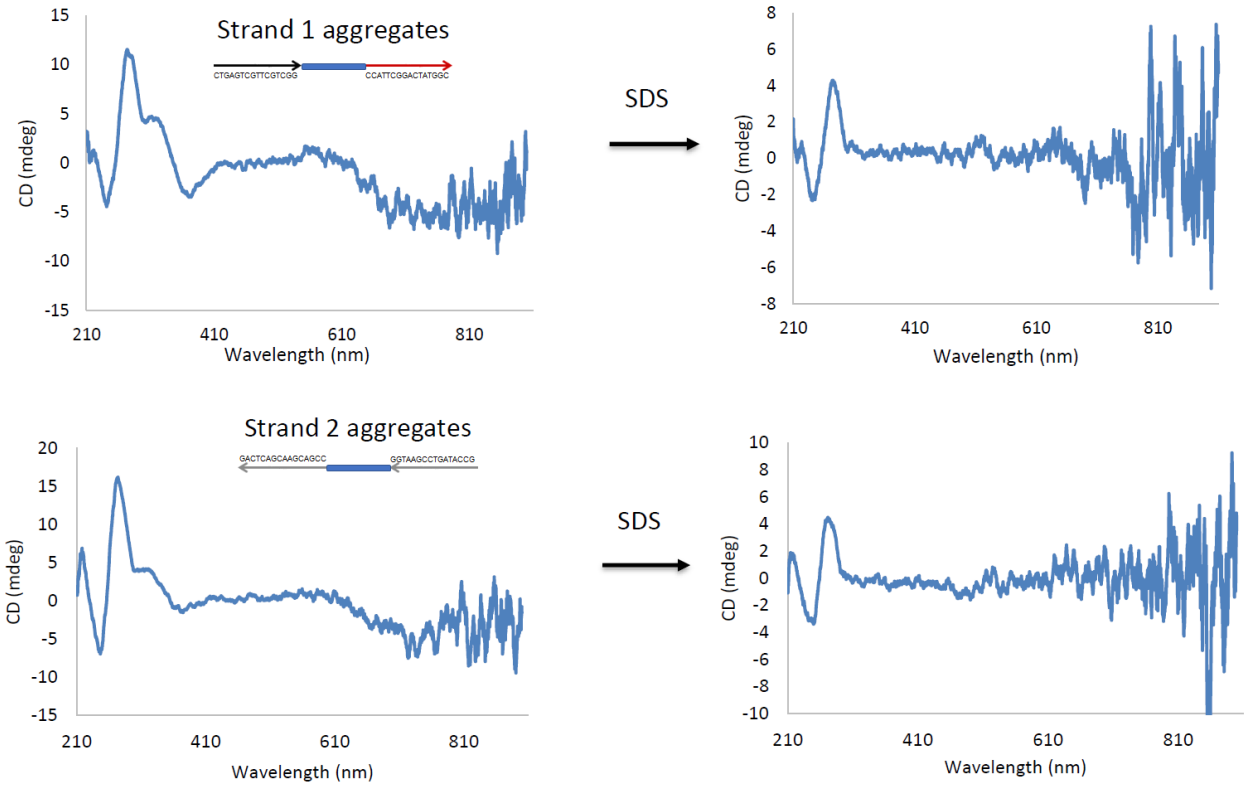


Figure S11. CD spectra of octaniline single strand before and after treating with SDS (0.6%).

CD spectra of II construct

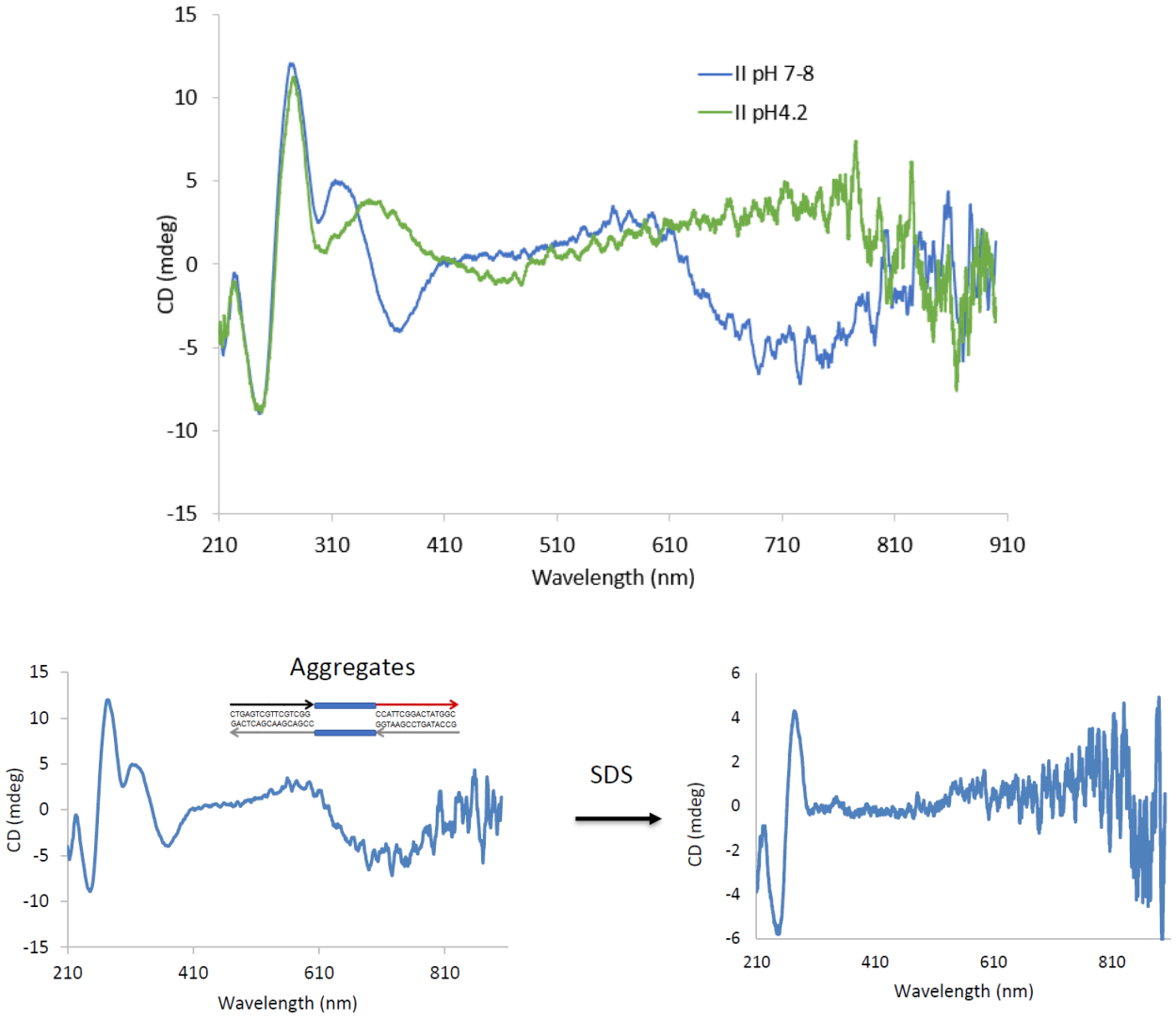


Figure S12. CD spectra of II construct at different pH (top), and the CD spectra of II construct before and after treating with SDS (0.6%).

References

1. Wang, X.; Sha, R. J.; Kristiansen, M.; Hernandez, C.; Hao, Y. D.; Mao, C. D.; Canary, J. W.; Seeman, N. C., An Organic Semiconductor Organized into 3D DNA Arrays by "Bottom-Up" Rational Design. *Angewandte Chemie-International Edition* **2017,** *56* (23), 6445-6448.