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Construction of a DNA Origami Based Molecular Electro-optical Modulator

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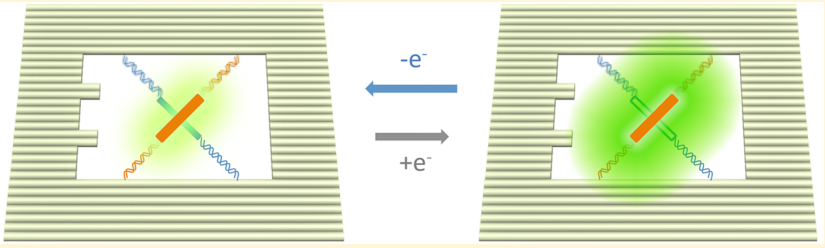
Supporting Information



ABSTRACT: An electro-optical modulator was constructed using a DNA nanostructure scaffold with oligomers of poly(phenylenevinylene) and polyaniline. A molecular device containing one each of the functional molecules was assembled in a DNA origami. The constructs formed an "X" shape and were visualized by atomic force microscopy. In response to redox reconfiguration, the device reversibly altered fluorescence signal output. This molecular self-assembly strategy provides opportunities to make unique material composites that are difficult to achieve by blending. The strategy offers a "plug and play" format that may lead to many new functions.

KEYWORDS: *DNA origami, conductive polymers, polyaniline, poly(phenylenevinylene), molecular electro-optical modulator*

Constructing functional molecular devices is a major focus of nanotechnology, particularly DNA nanotechnology.[1−4] In past decades, molecular devices were constructed with certain privileged materials; nanoparticles were used to construct optical devices;[5−9] and carbon nanotubes were templated by DNA origami to form a molecular transistor.[10] The functionality of molecular devices can certainly be expanded by introducing new materials into the DNA world. In recent years, conjugated polymers have also been organized by DNA nanostructures. Poly(*p*-phenylenevinylene) was organized on DNA origami to form nanowires,[11] and our previous work has organized the oligomer of polyaniline into designed three-dimensional (3D) DNA lattices.[12] During the preparation of this Letter, it was reported that polythiophene was immobilized on a DNA origami surface and that the fluorescence intensity of the polymers was tuned by controlling interchain aggregation of the backbones.[13] However, the use of well-defined molecules of such materials to construct molecular devices has not been reported, nor has the inclusion of two very different organic oligomers within the same DNA scaffold.

In this work, we introduce a prototype of a DNA based molecular electro-optical modulator constructed from two different kinds of organic semiconductors: a poly(phenylenevinylene) heptamer (HPV) and an octamer of polyaniline (OANI).[14−17] There are two major parts of this molecular device. The scaffold is similar to the DNA origami used by Sugiyama et al.[18,19] The scaffold was used to template the oligomers, while also acting as a "photo frame" when collecting images of the molecular device. The electronic components, two organic semiconductors, were assembled into the DNA origami and brought into approximate proximity (Figure 1). In the device, HPV acts as the emitter to transfer optical "input" into the fluorescent signal, while OANI acts as the modulator that governs the device's "output".

The electronic components were synthesized stepwise. Symmetric molecules of OANI and HPV with the azide groups at each end were prepared and covalently attached to DNA strands. The synthesis of the DNA−oligomer conjugates is shown in Figure 2a using HPV as an example. The copper-catalyzed azide−alkyne cycloaddition (CuAAC) between HPV and oligonucleotide strands containing a nonterminal 2′-*O*-propargyl ribosyl residue on the solid support leads to a doubly "clicked" major product. The resulting DNA−HPV conjugate is thus also symmetric and contains the same DNA sequence at each end.

The one-step, double CuAAC reaction on the solid support is not limited to HPV. An OANI−DNA conjugate was also prepared in the same way (Figure 2b), and the molecular mass of both compounds was confirmed by MALDI-TOF mass spectrometry. A smaller molecule (phenyl-capped dimeric oligoaniline) with an azide group at each end was also used to prepare the symmetric double DNA conjugate as the major product (Figure S3), indicating the generality of this strategy. It was reported previously that similar double attachment reactions were also observed with DNA and peptides on a solid support, by using different reactions such as phosphoramidite

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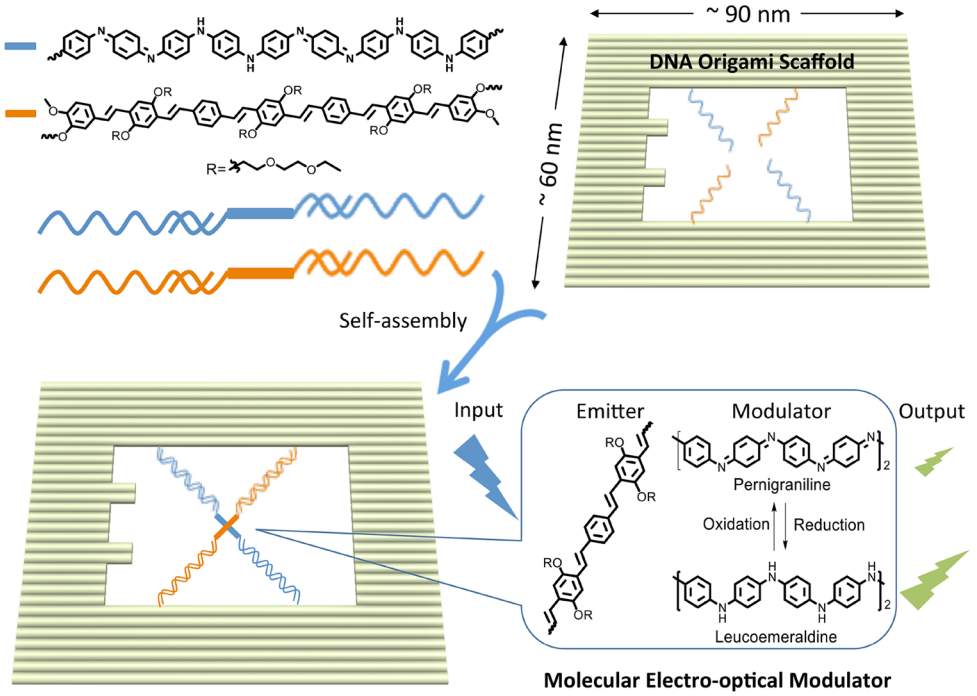

Figure 1. Construction of a DNA origami-based molecular electro-optical modulator. HPV-DNA and OANI-DNA conjugates were templated by a DNA origami scaffold to form an "X" shape. HPV and OANI molecules located proximally in the center of the assembly formed a molecular electro-optical device. OANI acts as a modulator to tune the fluorescence intensity of OPV in response to the change in a redox environment.

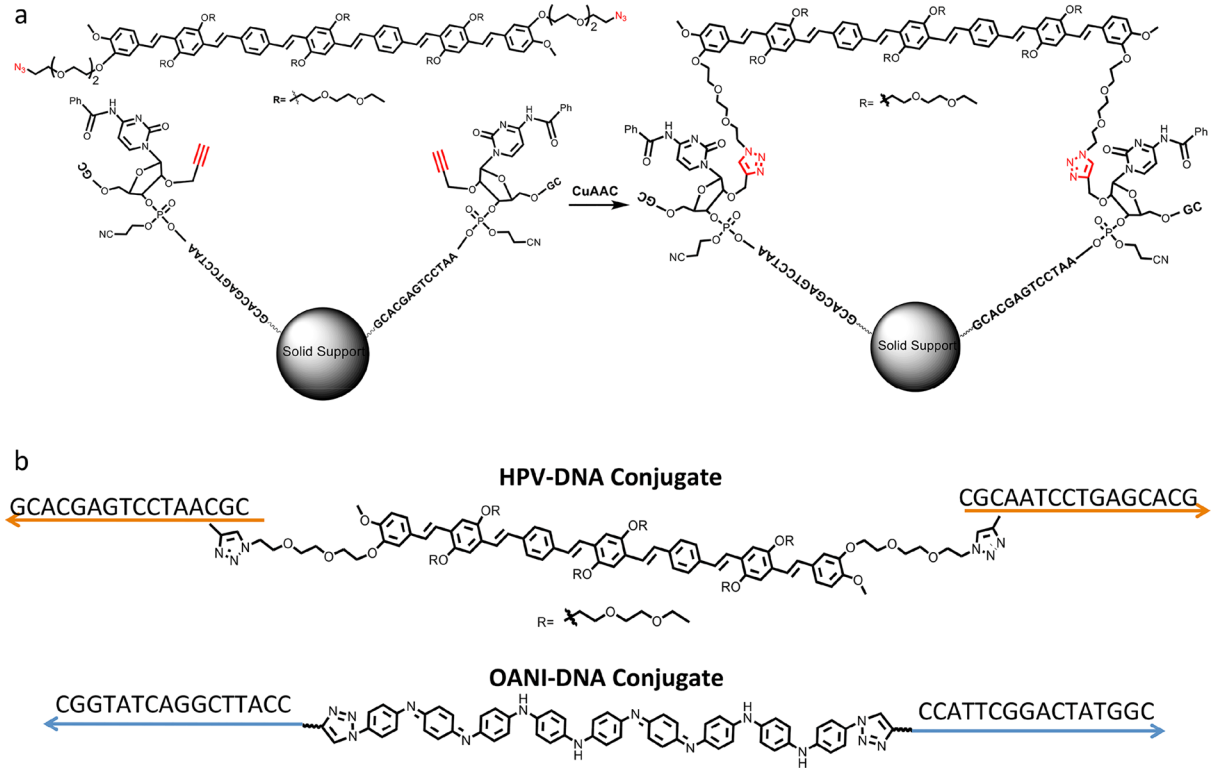

Figure 2. Synthesis of HPV−DNA and OANI−DNA conjugates on the solid support. (a) The schematic depiction of a one-step, double CuAAC reaction on the solid support using HPV as an example. The doubly attached products were cleaved from the resin afterward. Note: the removal of Boc is necessary prior to cleavage from the solid support for OANI. (b) The structures and sequences of HPV−DNA and OANI−DNA conjugates. Note that the OPV attachment point is not terminal, but at the antepenultimate position of the DNA molecule.

chemistry[20] or amide coupling reactions,[21] respectively. The advantage of the double CuAAC reaction shown here is that the position of modification is not restricted to the end of the DNA strand, which may provide more options when designing structures of DNA−oligomer conjugates. Figure 2b highlights the attachment of the OANI at a terminal residue and the OPV three residues from the terminus; with our strategy, any nucleotide can, in principle, serve as the attachment point.

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We first incorporated the HPV and OANI–DNA conjugates into the DNA origami scaffold to form homo "X" constructs. The conjugates must contain two copies of DNA from double CuAAC conjugation, or they would not show the "X" constructs visible in Figures S9 and S10. The HPV–OANI "X" shown in Figure 3 was constructed in a similar manner, with DNA

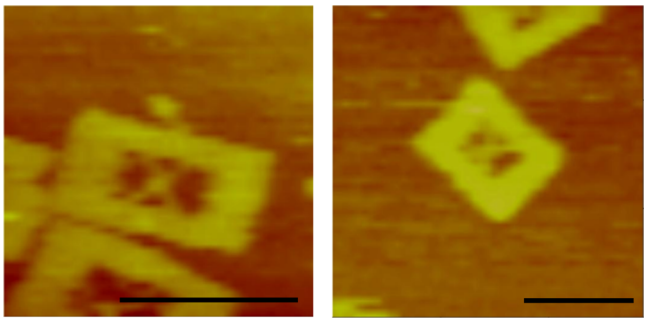

Figure 3. Atomic force microscopy characterization of the molecular device. The "X" shape appears in the middle of the origami scaffold, which indicates the formation of the device. Scale bars: 100 nm.

sequences of two template strands (blue and orange in Figure 1) orthogonal to each other (see Supporting Information). The yield of origami formation with both oligomers present was ~20%.[22]

The intrinsic optical properties of HPV and OANI–DNA conjugates made them an ideal pair for us to construct an electro-optical modulator. Our design is to control the energy transfer from HPV to OANI by tuning the oxidation state of OANI, thus switching the "output" signal of the device. The maximum emission wavelength of HPV is 520 nm and therefore overlaps with the UV–vis spectrum of the OANI–DNA conjugate in the oxidized form but not the reduced form. In Figure 4a, the redox active region of OANI UV–vis spectrum

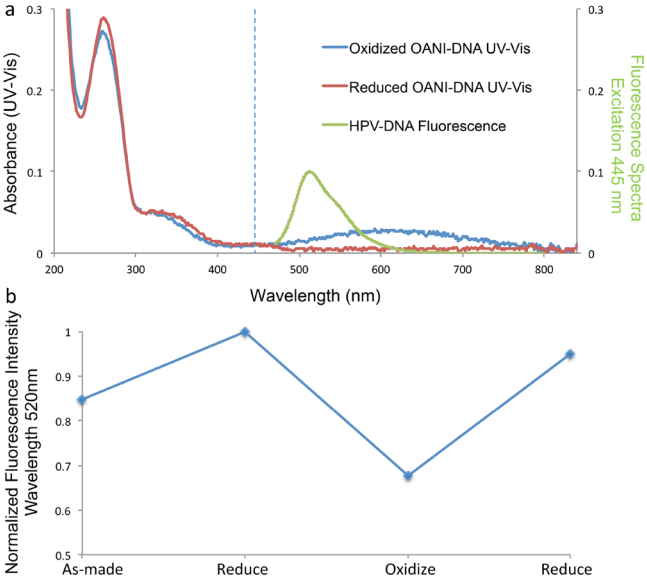

Figure 4. Optical response of the molecular electro-optical modulator in DNA origami. (a) The superimposition of the fluorescence spectrum of HPV–DNA conjugate over the UV–vis spectra of OANI–DNA conjugate. The UV–vis spectrum of OANI in the oxidized state overlaps with the fluorescence spectrum of OPV, while there is almost no overlap at the reduced form. (b) Fluorescence intensity of HPV (measured at wavelength 520 nm, normalized) was tuned by the oxidation states of OANI inside the device.

overlaps with the fluorescence emission spectrum of HPV perfectly. Moreover, the excitation wavelength of HPV does not overlap with the redox-active region of OANI, which makes it an ideal match.

Monitoring the fluorescence spectrum of the HPV–OANI modulator in the DNA origami under different redox conditions has demonstrated a working device. The oxidation state of OANI was tuned by adding reducing and oxidizing reagents, sodium ascorbate and ammonium persulfate, respectively. The "output" signal clearly depends on the oxidation state of OANI and can be switched back and forth. The strongest fluorescence intensity was obtained by reducing OANI, whereas oxidation of OANI led to a decrease of fluorescent intensity of about 40% as shown in Figure 4b. However, since it is difficult to evaluate the percentage of the unpaired HPV in the sample, the efficiency of the device is not quantitative. An intensity change of 40% is consistent with the overall yield of the origami assembly, as an appreciable amount of origami containing a single HPV unit would be present (and cannot be purified away readily), which would not be quenched by the redox reaction.

Experiments also showed that two electronic components being brought into proximity and their response to redox reconfiguration are essential to the modulating function of our device. The fluorescence intensity of the two electronic components shown in Figure 1 does not respond to sodium ascorbate without the DNA origami scaffold (Figure S14). However, HPV and OANI–DNA conjugates were tethered together by a long complementary DNA strand in a preliminary experiment, and the fluorescence intensity was switched back and forth similar to our device (see Figures S15 and S16). It is worth mentioning that the change of fluorescence intensity of our device is not abrupt, it is a process that slows down with the passage of time. For example, when the device was treated with sodium ascorbate, the fluorescence intensity mostly increased during the first 5 min and barely changed after 20 min (Figure S12). Moreover, the fluorescent signal change is faster when reducing OANI and slower when oxidizing it; this is similar to our observation when reducing/oxidizing OANI (by color in another system[12] or UV–vis in Figures S7 and S8).

In conclusion, we have successfully constructed a molecular device that acts as an electro-optical modulator using a "bottom-up" strategy. Conjugation of oligomer bis(azides) resulted in products with oligomers centered between two identical DNA sequences that were successfully incorporated into an origami framework. Two separate organic oligomers were located proximally to each other within one origami unit, and redox cycling modulated the brightness of the HPV unit. We anticipate further refinements in such structures to increase yield and structural control of the functional assemblies. A variety of devices can be imagined using such an approach.[23,24]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.8b00332.

Description of OANI and HPV-DNA conjugates synthesis, design of DNA origami, atomic force microscopy images, and redox tuning of the device's fluorescence experiments (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. X.W., C.L., D.N., and R.S. carried out experiments. N.C.S. and J.W.C. initiated and directed the project.

Notes

The authors declare no competing financial interest.

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