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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Article
Cite This: J. Am. Chem. Soc. 2019, 141, 11923−11928
pubs.acs.org/JACS

Organizing End-Site-Specific SWCNTs in Specific Loci Using DNA

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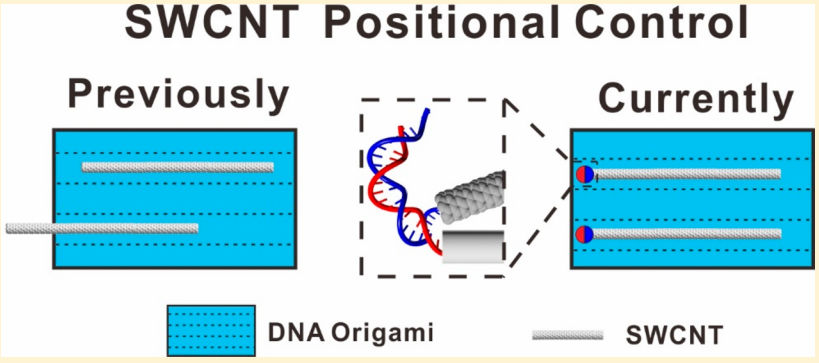
Supporting Information



ABSTRACT: Single-wall carbon nanotubes (SWCNTs) are known to embody many desirable features for nanoelectronic and photonic applications, including excellent electronic and optical properties and mechanical robustness. To utilize these species in a bottom-up nanotechnological approach, it is necessary to be able to place them in precise absolute positions within a larger framework, without disturbing the conduction surface. Although it is well-known how to orient one or two nanotubes on a DNA origami, precise placement has eluded investigators previously. Here, we report a method of attaching a strand of DNA on the reactive end of a SWCNT, and then of using that DNA strand to place the nanotube at a specific site on a 2D DNA origami raft. We demonstrate that it is possible to place one or two nanotubes on such a DNA origami raft.

INTRODUCTION

Single-wall carbon nanotubes (SWCNTs) offer many potential advantages for the construction of nanoelectronics and photonic devices.[1−5] They have been shown to be excellent conductors and semiconductors of charge and are known to be mechanically strong.[6] One of the key problems that prevents their convenient utility is the inability to organize them in specific directions at specific points.[7] A key advance was made by Zheng et al.,[8] when they discovered that it is possible to solubilize SWCNTs in aqueous medium by wrapping them in DNA, as well as discovering that different DNA sequences could be used to separate different species of SWCNTs.[9,10] A further advance was reported by Maune et al., who in 2010 used the solubilizing DNA to orient two SWCNTs in a perpendicular orientation on a DNA origami construct.[11] What remained lacking following their work was the ability to place one end of a SWCNT in a specific location.[12−14] Here, we report a method to derivatize one end of a SWCNT and demonstrate that two SWCNTs can be precisely located on a DNA origami construct. This method is not based on perturbing the surface lattice on the sides of the SWCNT, thus leaving the properties of the nanotube intact.

The way we have managed to place an end on the SWCNT at a specific site is to exploit the chemical functionality present at one end of it.[15] We conjectured that a DNA-solubilized SWCNT would have one of the DNA strands close to the reactive end. If that end was reactive with a complementary chemistry, it seemed likely that a DNA strand could be attached to the end covalently. As a consequence, we placed an amino group on the end of the DNA molecule that was solubilizing the SWCNT. This amino group can react with a carboxylic acid group on the SWCNT to produce an amide bond. This chemistry is illustrated in Figure 1. A similar approach has been used recently by Palma et al.[16,17] So as to localize the tip as closely as possible and to minimize any

Received: March 29, 2019
Published: July 8, 2019

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DOI: 10.1021/jacs.9b03432
J. Am. Chem. Soc. 2019, 141, 11923−11928

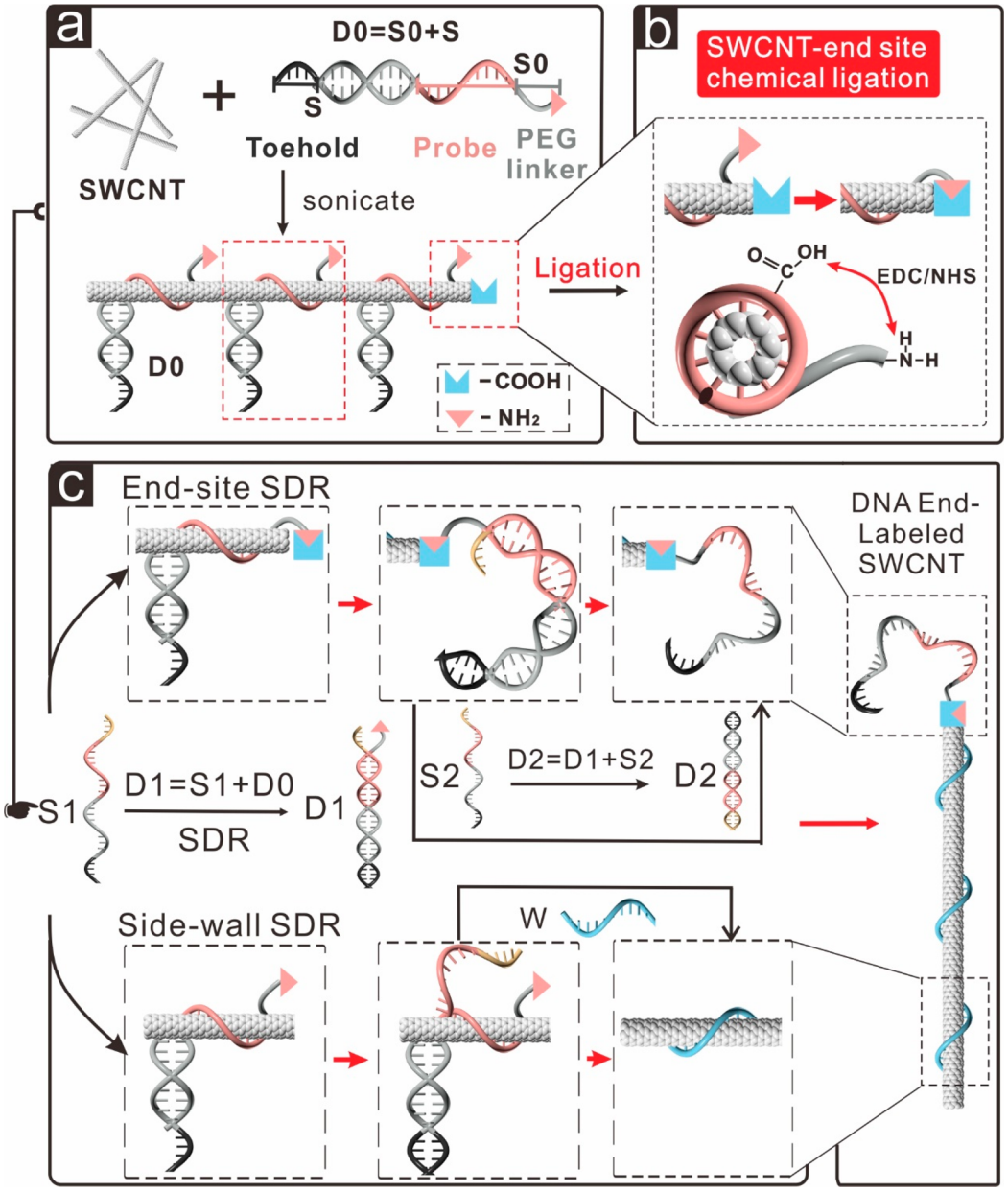

Figure 1. Preparation of end-labeled SWCNTs. (a) Scheme for the synthesis of DNA wrapped SWCNTs. A carboxyl group is shown as a blue "M" construct, and an amino group as a red triangle, complementary in shape to the "M". In the presence of EDC, an amide bond is formed between them in (b), which shows the chemical ligation between an SWCNT end site and DNA. (c) Strand displacement reactions (indicated as SDR) of SWCNT end-bonding DNAs (top); strand displacement reactions of SWCNT side wall wrapped DNAs (bottom).

reactions between the SWCNT and the DNA, the scheme entails adding a toehold[18] to the other end of the DNA strand so that all solubilizing strands, except for the reacted strand, could be removed readily and replaced with unreactive strands of a particular desired sequence.

RESULTS AND DISCUSSION

To make SWCNT ends fixed at predesigned positions of DNA origami, we first synthesized DNA-end-functionalized SWCNTs. As noted above, we obtained aqueous soluble SWCNTs by exploiting noncovalent interaction of SWCNTs with single-stranded DNA (ssDNA), which could preserve the original structures of the SWCNTs without disrupting their electronic/optical properties. We have designed a DNA structure (D0) adapting the ssDNA wrapping technique to disperse and separate the SWCNTs used in this study. D0 is composed of a fraction of double stranded DNA with a short single-stranded tail, ssDNA probe portion and PEG linker with an amino group at the 5′ end, which is synthesized from two ssDNA molecules (S0 and S). The aromatic bases of the ssDNA probe portion wrap around the SWCNT surface, which is enabled via $\pi-\pi$ bonding,[19] and the anionic phosphate group enhances SWCNT solubility, leading to the formation of highly soluble DNA-coated SWCNTs (Figure S1). Moreover, the PEG linker designed here is capable of keeping the amino-group dangling with more freedom after D0-wrapping process. Excess amounts of D0 were removed using spin filtration.

Whereas the SWCNTs preserve the original structures, carboxyl groups only exist on the growing end. The carboxyl could be activated subsequently with the EDC/NHS reaction,

DOI: 10.1021/jacs.9b03432
J. Am. Chem. Soc. 2019, 141, 11923−11928

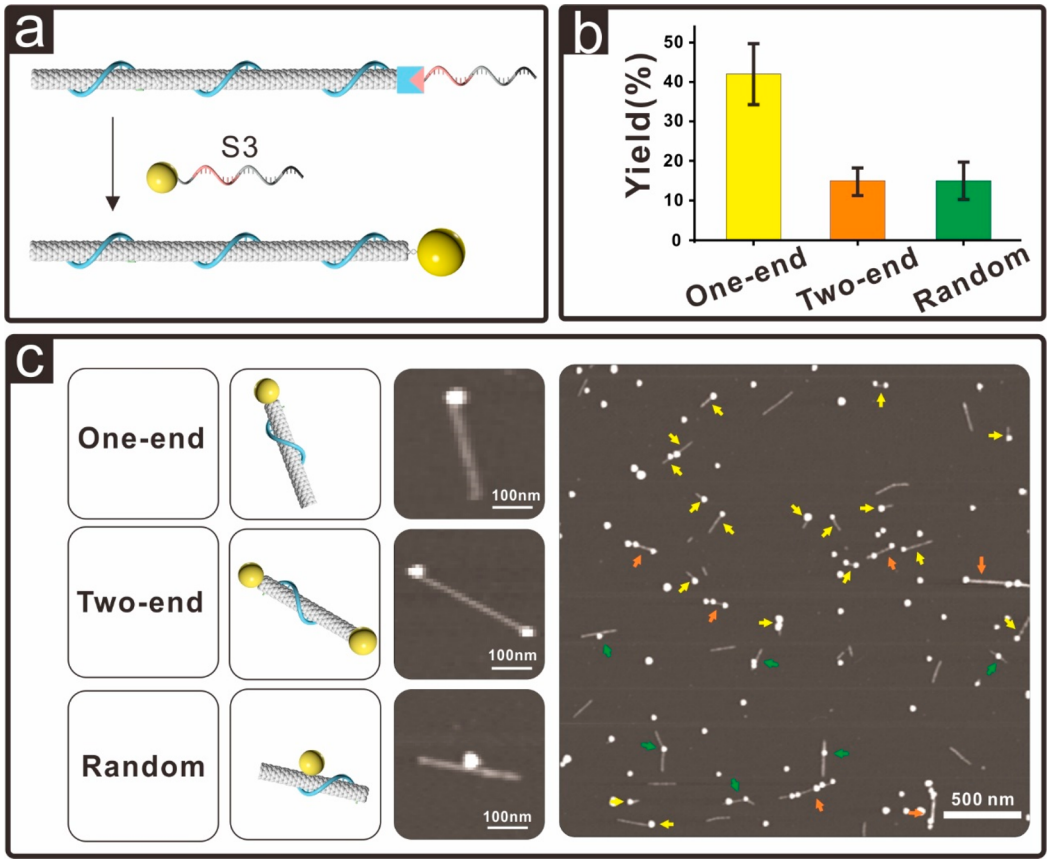

Figure 2. (a) Schematic illustration of interaction of S3-modified AuNP with DNA end-functionalized SWCNTs. (b) Yield of S3-modified AuNP binding with DNA end-functionalized SWCNTs. (c) AFM image of S3-modified AuNP binding with DNA end-functionalized SWCNTs via three binding approaches, including one-end binding, two-end binding, and random binding.

which induced initiation of the amide reaction. Note that the probability of collision between resulting SWCNT-bearing NHS esters and adjacent amino from the wrapped DNA at the end was maximized owing to the proximity effect, which results in higher chemical ligation yield between DNA and SWCNTs (Figure 1b). Following reaction, we added the S1 strand (complementary to S0) to trigger a toehold-mediated strand displacement reaction (SDR), causing the formation of double stranded D1 that is removed from the backbone of SWCNTs. The added ssDNA (W) with sequence $(GT)_{20}$, that has higher-affinity with SWCNTs would concurrently adsorb on the unoccupied backbone of SWCNTs, so that the solubility of SWCNTs would not be disrupted. It is worth mentioning that the terminal D1 is still attached to the SWCNT, owing to the covalent bond between the SWCNT and DNA (Figure 1c). The dangling double-stranded D1 at the end of the SWCNT could transform into ssDNA by a SDR triggered by adding the S2 strand, which was used for the next experiments.

To demonstrate that the DNA strand has successfully bonded to the end of the SWCNTs, we used a gold nanoparticle (AuNP) with a 5 nm diameter as an AFM imaging label. The AuNP labels were modified with thiol-ssDNA S3 (complementary to the strand bonded to the SWCNT) via an Au−S bond. The efficiency and site-specificity of AuNP binding to SWCNTs were measured using AFM, after incubating the AuNP label with DNA end-functionalized SWCNTs. The desired outcome for constructs was AuNP attached to a single SWCNT at the end-sites of SWCNTs (Figure 2a). Hence, more than 300 SWCNTs were analyzed. Of all analyzed SWCNTs (Figure 2b), ∼42% were single AuNP interactions with the SWCNT via one-end binding (yellow arrow). ∼15% were two-end of nanotubes binding to AuNP (orange arrow). Such a high yield of site-specific AuNP attachment on the SWCNTs indicated that we have successfully synthesized DNA end-functionalized SWCNTs. Interestingly, we have also found that one AuNP could connect two SWCNTs in an end-to-end fashion; this feature may have potential applications in nanoeletronics[20] or nanophotonics.[21] In addition, we also noted that some AuNPs randomly binding in the middle of the SWCNTs (green arrow), whose yield (∼15%) is yet lower than that of sequence-specific binding sites (Figure 2b). These nonspecific binding sites may be the SWCNT sidewall defects that containing carboxylic acid groups or unoccupied surface regions of DNA-coated SWCNTs.[12] There are ∼28% of SWCNTs without any AuNPs binding. In contrast, there was no end-binding event occurring in the case of noncomplementary DNA-modified AuNP mixing with DNA end-functionalized SWCNTs (Figure S2). Although not performed here, procedures are known for the elimination of side-wall defects.[22,23]

The assembly process for placement of DNA end-functionalized SWCNTs onto DNA origami rafts contains two steps (Figure 3a). First, DNA end-functionalized SWCNTs were fixed at a specific predesigned position on a DNA origami raft via one-point linkage, wherein the DNA origami raft was modified with ssDNA (S4). DNA hybridization between S0 and S4 allowed SWCNTs to bind to a single site-specific locus on the DNA origami raft. Notably, this capture S4 DNA strand

DOI: 10.1021/jacs.9b03432
J. Am. Chem. Soc. 2019, 141, 11923−11928

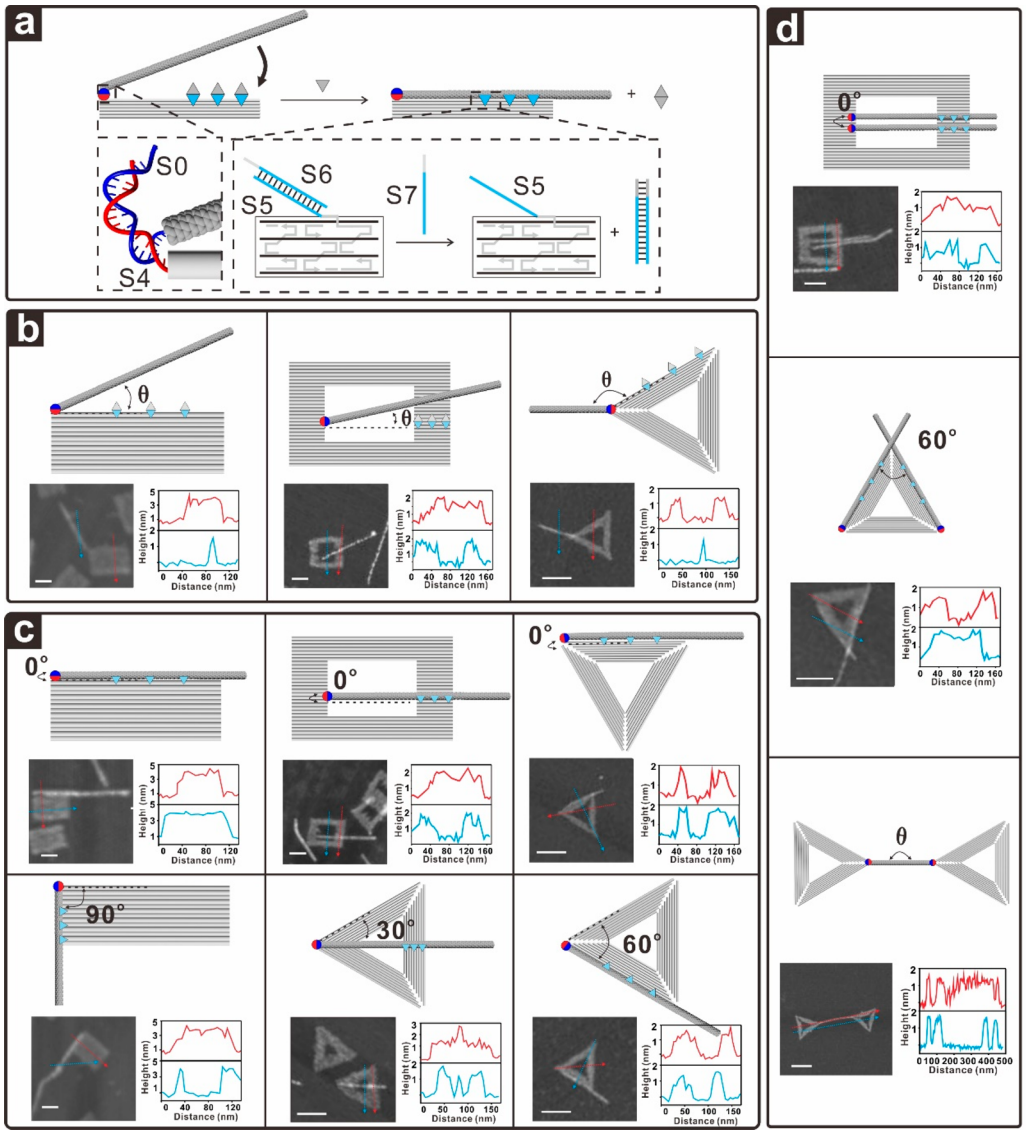

Figure 3. (a) Scheme for placement of DNA end-functionalized SWCNTs onto DNA origami templates. (b) One-point linkage between SWCNTs and DNA origami templates. (c) Control of one SWCNT's orientation on the DNA origami templates. (d) Control of two SWCNTs' orientation on the DNA origami templates and one SWCNT's orientation between two DNA origami templates.

can be extended from any staple strand of the raft. That is to say, the DNA end-functionalized SWCNTs can be fixed at any chosen site on the DNA origami, affording more flexibility in control of SWCNT orientation.

In view of the properties of DNA origami, a certain pattern of dsDNA (comprised of S5 and S6) was projected on DNA origami at a fixed distance, which impeded alignment of single site-binding SWCNTs onto DNA origami. It is conceivable that the angle of the SWCNTs with respect to the origami is flexible through such single site assembly of SWCNTs on DNA origami. It has been previously reported that ssDNA-rich areas can be capable of immobilization and alignment of SWCNT by deleting complements to short domains.[12] Hence, S7 (complementary to S6) was subsequently added to trigger SDR, which leads to S6 release from the DNA origami (Figure 3a). As a result, the ssDNA-rich area would wrap the unoccupied sidewalls of single site-specific binding SWCNTs for alignment via noncovalent interaction. This rational design is therefore expected to allow us to realize oriented assembly of SWCNTs on DNA origami.[2]

To modulate alignment of DNA end-functionalized SWCNTs, we have designed three kinds of DNA origami, including triangular origami, rectangular origami, and rectangular origami structures with a landmark window (Figure S3).[25] After mixing S0 end-functionalized SWCNTs with rectangular origami (or rectangular origami structures with a landmark window, triangular origami) with extended capture S4, SWCNTs were assembled onto DNA origami via one-point linkage because of DNA hybridization of S4 and S0 (Figure 3b). By evaluation of SWCNT immobilized on origami (with a yield of ∼4−10%) found in various AFM images (Figure S4−S6), the observed angle of SWCNTs with respect to DNA origami was random as expected (Table S1). Moreover, the diameter of SWCNTs is ∼1 nm, ascribed to the DNA-wrapping process. It is noted that whether SWCNTs are aligned onto origami or not can be judged by the angle of SWCNTs with respect to DNA origami. Then, the addition of S7 initiated SDR and deleted S6 from designed pattern of dsDNA on DNA origami, followed by the ssDNA-rich areas left as hooks aligning the aforementioned SWCNTs onto DNA

DOI: 10.1021/jacs.9b03432
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origami through nonspecific interactions. AFM topographic images in Figure 3c (top) display an angular distribution for SWCNTs at 0°, suggesting that SWCNTs were successfully aligned on DNA origami as designed (Figure S7−S12, with a yield of ∼1−3%). Moreover, the angle of SWCNTs with respect to DNA origami could be further modulated by changing the position of S4 and dsDNA patterns (Figure 3c, bottom). For example, the angle was 90° when dsDNA patterns were designed at short axis from long axis on rectangular origami, the angle was 60° when dsDNA patterns were projected at adjacent side on triangular origami. In summary, specific orientations of DNA end-functionalized SWCNTs assembled on DNA origami can be realized by this method.

More complex alignment architectures (e.g., alignment of two SWCNTs onto single DNA origami) were also achieved by using more sophisticated designs (Figure 3d). To this end, we designed a second binding site to create patterns of dsDNA parallel to the previous binding site or pattern, which allows for parallel alignment of two nanotubes on one rectangular origami with a landmark window (Figure 3d). The angle of 60° between two nanotubes on triangular origami was achieved by placing a designed binding site on both sides, with dsDNA patterns. In addition, a single SWCNT could bridge two triangular origami through single site-specific binding with origami. Observed from the above, controlling the orientation and alignment of single SWCNT onto DNA origami, two SWCNTs onto DNA origami, even one SWCNT onto two DNA origami can be achieved by integrating DNA end-functionalized CNTs with designed DNA origami.

It should be noted that the reactive part of a 100 nm SWCNT is only about 1% of its volume. Likewise, the limiting concentrations of standard (M13) origami constructs are limited by its molecular weight of $\sim 4.5 \times 10^6$. These factors jointly contribute to the low yields seen in experiments involving both of these components. The large DNA origami molecules have been employed in these preliminary experiments to demonstrate the assembly principles in a convenient fashion. However, now that this has been done, smaller DNA components with larger limiting concentrations, can be used in future applications of this chemistry.

CONCLUSION

We have demonstrated that SWCNTs can be placed at particular loci on DNA origami rafts, with a variety of designs. This work adds to the SWCNT toolbox that already allows the selection of surface lattices,[8−10] and the choice of relative orientations.[11] Now it is possible to place SWCNT molecules at specific positions in specific orientations, and it is possible to place more than a single SWCNT within a larger framework. This is an encouraging step for the bottom-up development of SWCNT-based nanoelectronics photonics that combines the electronic properties and optical properties of carbon nanotubes with the semantomorphic level of control offered by DNA.[24−26] For future applications, yields must, of course be increased, and it will be necessary to obtain atomic-level control on the lengths of SWCNTs. At that point, a bottom-up joint carbon-DNA nanoelectronics photonics will be possible.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b03432.

Details of the experiment sections and supplementary figures and tables (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the following grants to N.C.S.: GM-29554 from the National Institute of General Medical Sciences; Grants CMMI-1120890, EFRI-1332411, CCF-1117210, and CHE-1708776 from the National Science Foundation; MURI W911NF-11-1-0024 from the Army Research Office; Grants N000141110729 and N000140911118 from the Office of Naval Research; DE-SC0007991 from the Department of Energy for DNA synthesis and partial salary support; and Grant 3849 from the Gordon and Betty Moore Foundation. The National Natural Science Foundation of China (Grant No. 21722502).

REFERENCES

(1) Iijima, S.; Ichihashi, T. Single-Shell Carbon Nanotubes of 1-nm Diameter. *Nature* **1993**, *363*, 603−605.
(2) De Volder, M. F.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon Nanotubes: Present and Future Commercial Applications. *Science* **2013**, *339* (6119), 535−539.
(3) Shulaker, M. M.; Hills, G.; Patil, N.; Wei, H.; Chen, H. Y.; Philip Wong, H. S.; Mitra, S. Carbon Nanotube Computer. *Nature* **2013**, *501*, 526−530.
(4) Cao, Q.; Han, S. J.; Tersoff, J.; Franklin, A. D.; Zhu, Y.; Zhang, Z.; Tulevski, G. S.; Tang, J.; Haensch, W. End-Bonded Contacts for Carbon Nanotube Transistors with Low, Size-Independent Resistance. *Science* **2015**, *350* (6256), 68−72.
(5) Srinivasan, K.; Zheng, M. Quantum Optics: Nanotube Chemistry Tunes Light. *Nat. Photonics* **2017**, *11*, 535−537.
(6) Saito, R.; Dresselhaus, G. S.; Dresselhaus, M. S. *Physical Properties of Carbon Nanotubes*; Imperial College Press: London, 1998.
(7) Franklin, A. D. Electronics: The Road to Carbon Nanotube Transistors. *Nature* **2013**, *498*, 443−444.
(8) Zheng, M.; Jagota, A.; Semke, E. D.; Diner, B. A.; Mclean, R. S.; Lustig, S. R.; Richardson, R. E.; Tassi, N. G. DNA-Assisted Dispersion and Separation of Carbon Nanotubes. *Nat. Mater.* **2003**, *2*, 338−342.
(9) Tu, X.; Manohar, S.; Jagota, A.; Zheng, M. DNA Sequence Motifs for Structure-Specific Recognition and Separation of Carbon Nanotubes. *Nature* **2009**, *460*, 250−253.
(10) Ao, G.; Streit, J. K.; Fagan, J. A.; Zheng, M. Differentiating Left- and Right-Handed Carbon Nanotubes by DNA. *J. Am. Chem. Soc.* **2016**, *138* (51), 16677−16685.
(11) Maune, H. T.; Han, S.; Barish, R. D.; Bockrath, M.; Goddard, W. A.; Rothemund, P. W. K.; Winfree, E. Self-Assembly of Carbon Nanotubes into Two-Dimensional Geometries Using DNA Origami Templates. *Nat. Nanotechnol.* **2010**, *5*, 61−66.

DOI: 10.1021/jacs.9b03432
J. Am. Chem. Soc. 2019, 141, 11923−11928

(12) Mangalum, A.; Rahman, M.; Norton, M. L. Site-Specific Immobilization of Single-Walled Carbon Nanotubes onto Single and One-Dimensional DNA Origami. *J. Am. Chem. Soc.* **2013**, *135* (7), 2451−2454.
(13) Zhao, Z.; Liu, Y.; Yan, H. DNA Origami Templated Self-Assembly of Discrete Length Single Wall Carbon Nanotubes. *Org. Biomol. Chem.* **2013**, *11*, 596−598.
(14) Penzo, E.; Palma, M.; Wang, R.; Cai, H.; Zheng, M.; Wind, S. J. Directed Assembly of End-Functionalized Single Wall Carbon Nanotube Segments. *Nano Lett.* **2015**, *15* (10), 6547−6552.
(15) Weizmann, Y.; Chenoweth, D. M.; Swager, T. M. Addressable Terminally Linked DNA−CNT Nanowires. *J. Am. Chem. Soc.* **2010**, *132* (40), 14009−14011.
(16) Freeley, M.; Attanzio, A.; Cecconello, A.; Amoroso, G.; Clement, P.; Fernandez, G.; Gesuele, F.; Palma, M. Tuning the Coupling of Single-Molecule Heterostructures: DNA-Programmed and Reconfigurable Carbon Nanotube-Based Nanohybrids. *Adv. Sci.* **2018**, *5*, 1800596.
(17) Amoroso, G.; Ye, Q.; Cervantes-Salguero, K.; Fernández, G.; Cecconello, A.; Palma, M. DNA-Powered Stimuli-ResponsiveSingle-Walled Carbon Nanotube Junctions. *Chem. Mater.* **2019**, *31*, 1537−1542.
(18) Yurke, B.; Turberfield, A. J.; Mills, A. P., Jr; Simmel, F. C.; Neumann, J. L. A DNA-Fuelled Molecular Machine Made of DNA. *Nature* **2000**, *406*, 605−608.
(19) Zheng, M.; Jagota, A.; Strano, M. S.; Santos, A. P.; Barone, P.; Chou, S. G.; Diner, B. A.; Dresselhaus, M. S.; Mclean, R. S.; Onoa, G. B.; Samsnoidze, G. G.; Semke, E. D.; Usrey, M.; Walls, D. J. Structure-Based Carbon Nanotube Sorting by Sequence-Dependent DNA Assembly. *Science* **2003**, *302* (5650), 1545−1548.
(20) Qiu, C.; Zhang, Z.; Xiao, M.; Yang, Y.; Zhong, D.; Peng, L. M. Scaling Carbon Nanotube Complementary Transistors to 5-nm Gate Lengths. *Science* **2017**, *355* (6322), 271−276.
(21) Hillenbrand, R. Coherent Imaging of Nanoscale Plasmon Patterns with a Carbon Nanotube Optical Probe. *Appl. Phys. Lett.* **2003**, *83*, 368−370.
(22) Subbaiyan, N. K.; Parra-Vasquezm, N. G.; Cambré, S.; Cordoba, M. A. S.; Yalcin, S. E.; Hamilton, C. E.; Mack, k N.H.; Blackburn, J. L.; Doorn, S. K.; Duque, J. G. Bench-Top Aqueous Two-Phase Extraction of Isolated Individual Single-Walled Carbon Nannotubes. *Nano Res.* **2015**, *8*, 1755−1769.
(23) Streit, J. K.; Lam, S.; Piao, Y.; Hight-Walker, A. R.; Fagan, J. A.; Zheng, M. Separaation of Double-Wall Carbon Nanotubes by Electronic Type and Diameter. *Nanoscale* **2017**, *9*, 2531−2540.
(24) Udomprasert, A.; Bongiovanni, M. N.; Sha, R.; Sherman, W. B.; Wang, T.; Arora, P. S.; Canary, J. W.; Gras, S. L.; Seeman, N. C. Amyloid Fibrils Nucleated and Organized by DNA Origami Constructions. *Nat. Nanotechnol.* **2014**, *9*, 537−541.
(25) Jones, M. R.; Seeman, N. C.; Mirkin, C. A. Programmable Materials and the Nature of the DNA Bond. *Science* **2015**, *347* (6224), 1260901.
(26) Seeman, N. C.; Sleiman, H. F. DNA Nanotechnology. *Nat. Rev. Mater.* **2018**, *3*, 17068.

DOI: 10.1021/jacs.9b03432
J. Am. Chem. Soc. 2019, 141, 11923−11928