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DNA Triangles and Self-Assembled Hexagonal Tilings

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There are exactly three regular tilings of the plane: one composed of triangles, one of squares, and one of hexagons. We have constructed DNA complexes in the form of triangles that self-assemble into planar structures in the form of regular hexagonal tilings.

To date, only a small number of DNA complexes have been demonstrated to self-assemble into orderly structures. For example, Seeman et al.[1] created double-crossover complexes and Winfree et al.[2] showed that they self-assemble into planar structures in the form of rectangular tilings. LaBean et al.[3] extended the double-crossover motif to create triple-crossover complexes that also assemble into structures of this form. Quadruple-crossover complexes that assemble into structures of this form have also been reported.[4] Yan et al.[5] created 4 × 4 complexes that assemble into planar structures in the form of square tilings, and Liu et al.[6] created triangular complexes that can assemble into orderly structures of several different forms. Recently, Ding et al.[7] also demonstrated the creation of hexagonal structures from triangular complexes using an approach different from the one presented here.

We were inspired to explore triangular complexes by Yang et al.,[8] who used them as markers on structures formed from double-crossover complexes. We created free-standing triangular complexes composed of seven strands of DNA. We designed two such complexes that stick to one another at their vertices. The type-a complex, Figure 1a, has a 90-mer core strand (the same length as the core strand used by Yang et al.), three 52-mer side strands with identical sequences, and three 14-mer horseshoe strands with identical sequences. The type-b complex, Figure 1b, has a 90-mer core strand with sequence identical to that used in the type-a complex, three 52-mer side strands with identical sequences, and three 30-mer horseshoe strands with identical sequences. The unpaired bases at the ends of the side strands in the type-a complex are complementary to the unpaired bases at the ends of the horseshoe strands in the type-b complex, allowing triangles to connect at these sticky ends. In theory, such triangles can form a hexagon, as shown in Figure 1c, and hexagons can form a tiling, as shown in Figure 1d.

The two types of triangular complexes were assembled in separate tubes by annealing. The complexes were then combined at room temperature. Atomic force microscope images of the resulting structures are shown in Figure 2.

Figure 2a shows six triangular complexes assembled into a single hexagonal structure. The distance between opposing sides is approximately 35 nm, which is in good agreement with expectations based on number of base pairs in the structure. Figure 2b (see also Figure 1e) shows two hexagonal tilings, one lying on top of the other. One-half of the triangles of the top tiling lie in the centers of the hexagons of the bottom tiling. The remaining triangles of the top tiling lie directly on top of the triangles of the bottom tiling. Where triangles overlap the structure has greater height, as revealed by bright spots in Figure 2b. In our experience, tilings layered in

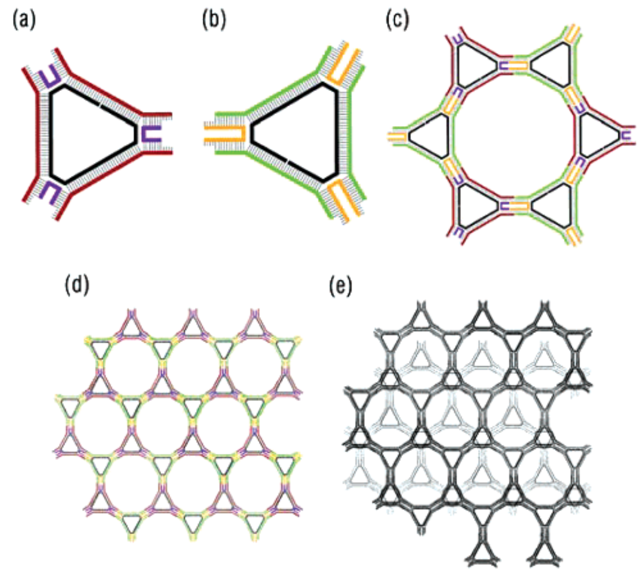

Figure 1. Schematics representing connectivity and base pairing. (a) Type-a triangular complex. Core strand (black), side strands (red), horseshoe strands (purple), Watson−Crick pairing (gray). (b) Type-b triangular complex. Core strand (black), side strands (green), horseshoe strands (orange), Watson−Crick pairing (gray). (c) Hexagonal structure composed of six triangular complexes. (d) Hexagonal tiling composed of hexagonal structures. (e) A pair of overlapping hexagonal tilings. Top layer shown black; bottom layer shown gray. (See also Figure 2b.)

this way are common. Layering of tilings also occurs in the hexagonal lattices of Ding et al.,[7] where the hexagons on successive layers appear to have centers that coincide.

We designed our complexes to form equilateral triangles and to stick to each other but not to themselves. Figure 2a suggests that they do have this form and stick in this way. However, sticking in this way is also consistent with the formation of ring structures containing any even number of triangular complexes. Such structures are perhaps energetically less favorable than a hexagonal structure; nonetheless, they do form. Figure 2c shows a broad view of structures consisting of hexagons together with ring structures with more or fewer than six vertices. It seems likely that the number of such nonhexagonal ring structures could be reduced by using more than two types of triangular complexes.

Occasionally, rings with an odd number of triangles also form. These may result from our use of the same core strand in the two types of triangular complexes. A common core strand allows for the creation of chimeric triangular complexes containing side strands from complexes of different types. It seems likely that the number of such rings could be reduced by using distinct strands in triangular complexes of different types.

In many published works on DNA self-assembly, the assembled structures are planar and composed of double helices running in parallel.[1−3,9−11] While our structures are planar, they do not have

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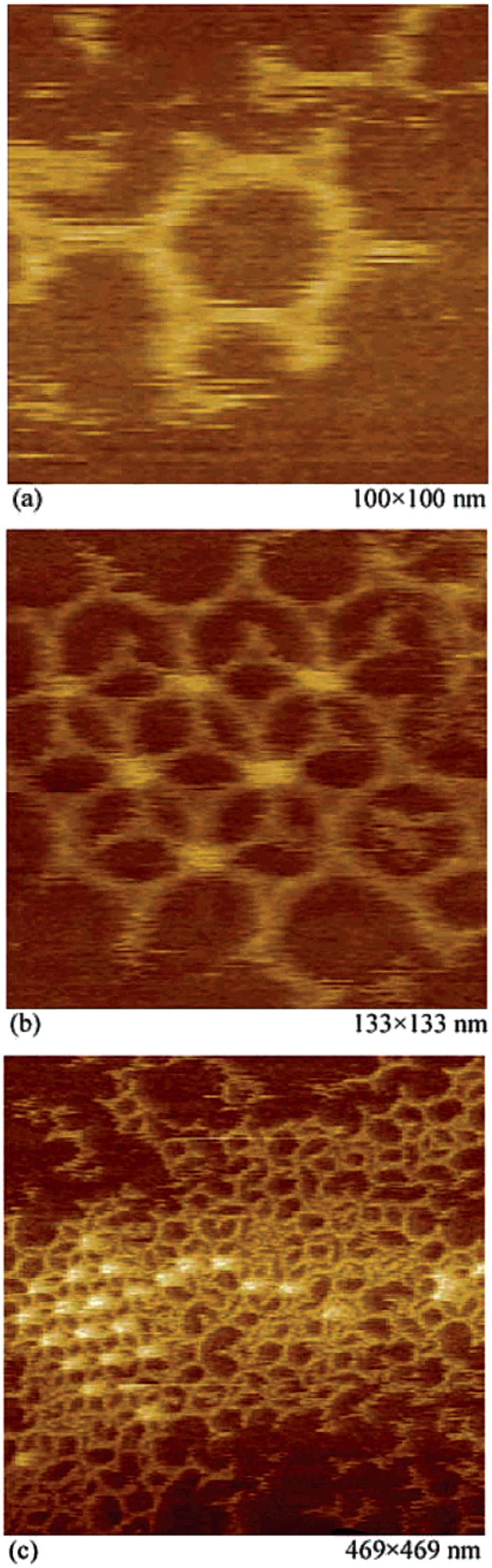

Figure 2. AFM images. (a) Hexagonal structure composed of six triangular complexes. (b) A pair of overlapping hexagonal tilings (see also Figure 1e). (c) Structures composed of hexagonal and nonhexagonal rings. The evenly spaced bright spots on the left side of the image suggest a region of overlapping regular hexagonal tilings; no such regularity is evident on the right side.

this form. In the case of hexagons as shown in Figure 1c, helices run parallel where sticky ends come together, but meet at angles of 150° or 60° where no sticky ends are present. It appears that some helices in our structures are bent. The use of long side strands with a 30-mer complementarity to the core strand in our triangular complexes may be critical in allowing bending to occur. In fact, when triangular complexes employing shorter side strands with only a 21-mer complementarity to a 63-mer core strand were attempted, AFM imaging revealed no structures (data not shown). While existing DNA self-assembled structures use helices as linear elements, bending may allow for the use of helices as curvilinear elements, thus providing greater freedom in the design of future self-assembled DNA structures.

The 4×4 complexes of Yan et al.[5] produce planar structures with helices intersecting at 90° angles. The helices in the 4×4 complex have unpaired stretches of polyT. Images show that helices make right-angle turns, presumably at these sites.[5] Thus, unlike our structures, where helices apparently bend, helices in structures created with the 4×4 complex apparently hinge.

Liu et al.[6] also described structures with nonparallel helices. However, these structures are not planar, and helices are allowed to cross each other without bending. Like our structures, these structures are created from triangular complexes designed to stick to one another at vertices. While the triangular complexes of Liu et al. stick to one another via one helix, our complexes stick via two. This may provide greater integrity. In addition, our structures may be useful when planarity is desired.

Ding et al.[7] have recently created pseudohexagonal structures from triangles. They appear to have avoided the problem of nonhexagonal ring formation by using triangles with sides composed of double crossovers,[1] which may provide greater rigidity than the single-helical sides used in our triangles.

Using the design concepts described here, it seems possible, in principle, to create complexes with arbitrary polygonal shapes. Of immediate interest would be the creation of squares, pentagons, and nonequilateral triangles.

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Supporting Information Available: Sequences for the triangular complexes, protocols for assembly, and AFM preparation. This material available free of charge via the Internet at http://pubs.acs.org.

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