fact that dislocation plasticity is much more discrete at the nanoscale. Their observations of inhomogeneous dislocation nucleation under the surface of the loading platen — where the indenter contacts the specimen — and the occurrence of discrete dislocation bursts provide valuable insight into how plasticity occurs in these reduced volumes.

Another advantage of direct observation is the ability to see and address experimental complications. The presence of surface layers (oxides or focused-ion-beam-induced radiation damage) might be expected to inhibit dislocation exhaustion, but the observations presented by Shan and co-workers clearly indicate that this is not the case. By contrast, the smaller-is-stronger creed suggests that pillars should be stronger than the larger substrate that they rest on, and the *in situ* observations provide clear evidence of the pillar punching into the substrate. These observations also highlight the importance of geometry by showing that tapered specimens deform much less homogeneously than has previously been assumed. Such effects greatly reduce the fidelity of *ex situ* experiments unless properly accounted for.

The emergence of micro- and nanoscale materials science has led to the discovery that the intrinsic strength of very small structures is higher than for bulk materials. The *in situ* results reported by Shan and colleagues provide clear evidence of the importance of dislocation starvation and the discreteness of dislocation processes in understanding this phenomenon in nanopillars. More broadly, these experiments show that direct observations can provide much needed clarity in understanding complex material behaviour at the nanoscale.

References

1. Shan, Z. W., Mishra, R., Syed Asif, S. A., Warren, O. L. & Minor, A. M. *Nature Mater.* **7,** 115–119 (2008).
2. Nix, W. D. *Metall. Trans.* **20A,** 2217–2245 (1989).
3. Brenner, S. S. *J. Appl. Phys.* **27,** 1484–1491 (1956).
4. Stelmashenko, N. A., Walls, M. G., Brown, L. M. & Millman, Y. V. *Acta Metall. Mater.* **41,** 2855–2865 (1993).
5. Uchic, M. D., Dimiduk, D. M., Florando, J. N. & Nix, W. D. *Science* **305,** 986–989 (2004).
6. Greer, J. R., Oliver, W. C. & Nix, W. D. *Acta Mater.* **53,** 1821–1830 (2005).
7. Volkert, C. A. & Lilleodden, E. D. *Phil. Mag.* **86,** 5567–5579 (2006).
8. Dimiduk, D. M., Uchic, M. D., Rao, S. I., Woodward, C. & Parthasarathy, T. A. *Model. Simul. Mater. Sci. Eng.* **15,** 135–146 (2007).
9. Dimiduk, D. M., Woodward, C., LeSar, R. & Uchic, M. D. *Science* **312,** 1188–1190 (2006).
10. Greer, J. R. & Nix, W. D. *Phys. Rev. B* **73,** 245410 (2006).
11. Gilman, J. J. *Micromechanics of Flow in Solids* 185–190 (McGraw-Hill, New York, 1969).

BIOMOLECULAR ASSEMBLY

Dynamic DNA

Building blocks of DNA self-assemble into nanostructures in a kinetically controlled way. The versatile molecular system can be programmed to perform diverse dynamic functions.

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Nanotechnologists, inspired by living systems, strive to design artificial biomolecular systems that show similar behaviour. One aspect of biological self-assembly they have found challenging to mimic in synthetic systems, however, involves the dynamic properties of natural processes. Writing in *Nature*, Pierce and colleagues from Caltech describe a powerful framework for programming the growth and dynamic function of nanostructures self-assembled from DNA components[1]. The remarkable adaptability of the system results from the robust kinetic control of interactions between multiple components. The versatility enables the programming of several kinetically controlled behaviours, including the growth of branched junctions and a dendritic tree, the exponential switching in a cross-catalytic circuit, and the movement of a bipedal walker.

The world of designer biopolymers to date has focused on static self-assembly[2],

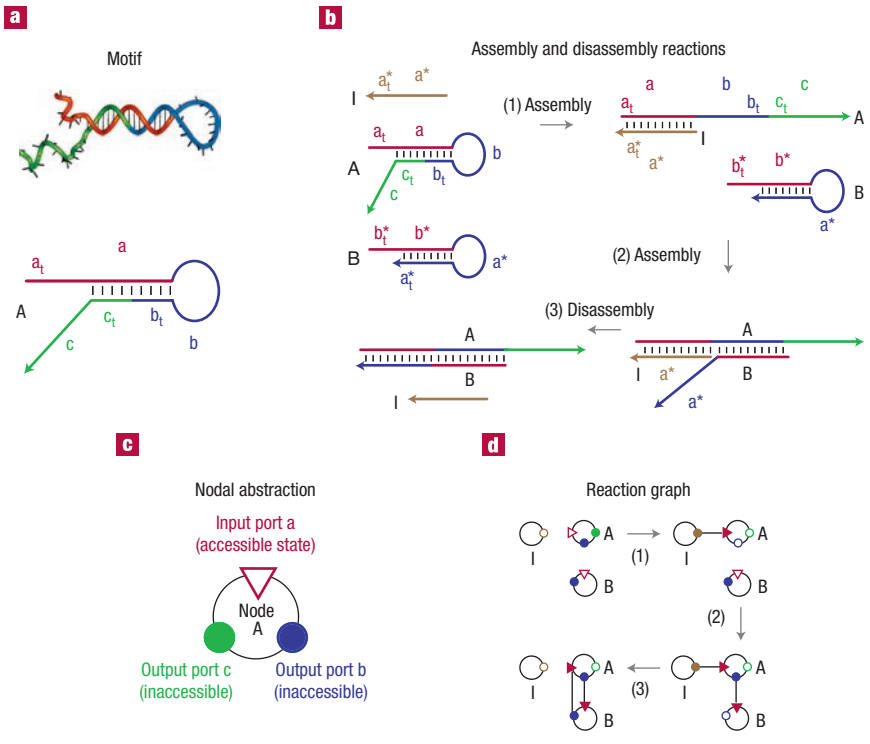

Figure 1 Programming biomolecular self-assembly pathways — an illustration of the components and notation. **a**, The hairpin motif. **b**, Schematic diagram showing assembly and disassembly reactions. **c**, Depiction of hairpin A segment as a node (nodal abstraction). **d**, A reaction graph for the pathway shown schematically in **b**.

where synthetic amino and nucleic acid sequences settle into the desired structure at thermodynamic equilibrium. Computational studies typically select sequences for which the target structure represents the calculated global free-energy minimum, with little consideration of kinetic factors. This simplification has resulted in the successful synthesis of static self-assembly systems, including enzymes[3] and complex nanostructured architectures[4]. In nature, however, biological organization often relies on dynamic self-assembly, where macromolecular assemblies never reach equilibrium, but instead cycle endlessly through various configurations in patterns governed by catalysed steps of free-energy dissipation. For example, tubulin self-assembles into microtubules that alternate between slow growth and rapid shrinkage, as a result of undergoing cycles of guanosine triphosphate (GTP) hydrolysis[5]. This 'dynamic instability' is impossible to achieve in a system at static equilibrium. The Caltech team[1], however, take an important step towards enabling this type of dynamic behaviour.

The jigsaw pieces for the dynamic puzzle created by Pierce and colleagues are DNA hairpin motifs[6] (composed of a loop and stem) that turn out to be exceptionally programmable units. Taking a simple example (Fig. 1a), DNA hairpin motif A is made up of three different sections, labelled a, b and c, which are joined end-to-end. Each section has a nucleation site, called a 'toehold', and these are denoted, a_t, b_t, c_t.

One of the basic reactions described is the use of a single-stranded initiator (I) as a catalyst for the assembly of hairpins A and B (Fig. 1b). The initiator (I) has an exposed toehold, a_t^*, that nucleates at the exposed toehold, a_t, of hairpin A, initiating a branch migration and resulting in the opening of hairpin A. This exposes two other toeholds of hairpin A (b_t and c_t), which then act as initiators for reaction with hairpin B. Following the joining of sections b and b*, of hairpins A and B respectively, a disassembly reaction causes the displacement of the initiator from hairpin A, resulting in the linking together of sections a and a*.

This example shows how the DNA hairpin motifs are metastable kinetic traps — the base-pairing to the loop of the hairpin is prevented unless the stem is broken first. Kinetic 'escapes' are triggered by association of single-stranded domains (the initiator I) with the short complementary toehold at one end of hairpin A. The subsequent branch migration that breaks the intramolecular stem releases a new single-stranded section of hairpin A that is available to trigger the next kinetic escape of hairpin B.

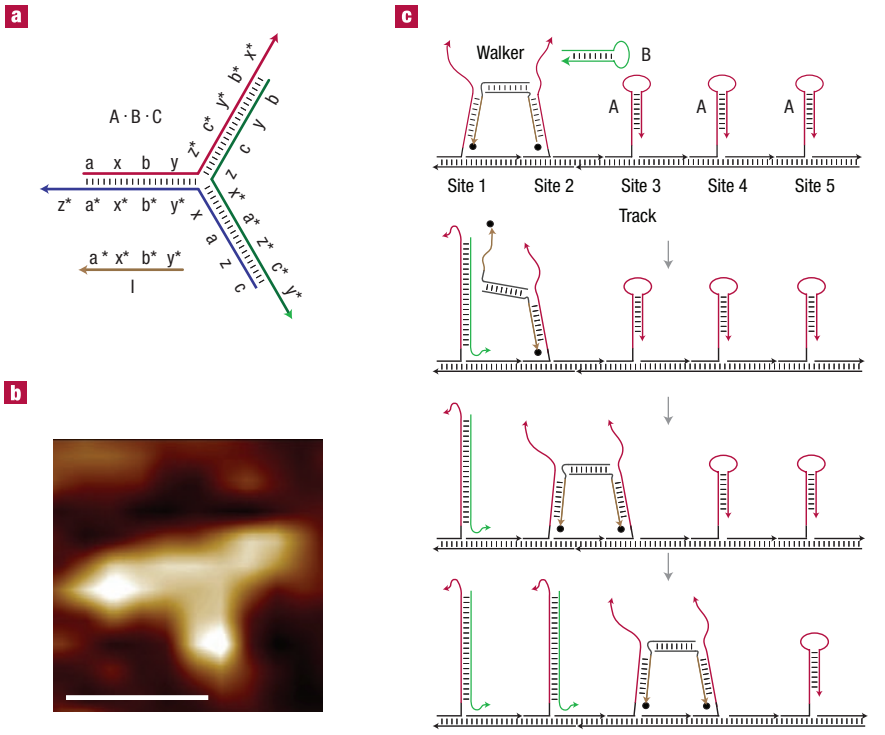

Figure 2 The outcome and mechanisms of various DNA programmes. **a**, The secondary structure of the three-armed junction resulting from the catalytic self-assembly of three segments. **b**, The atomic force microscopy image of a three-armed junction. Scale bar: 10 nm. **c**, The mechanism for the progressive locomotion of the bipedal walker as depicted by secondary structure diagrams.

The strength of the system lies in the robust and modular nature of the assembly and disassembly reactions. This makes it possible to simplify the notation — a node is used to represent a DNA hairpin motif that has an input port and one or two output ports (Fig. 1c). When a single-stranded initiator pairs with the input port, the output ports become accessible and link with input ports on other nodes (as shown in Fig. 1). Subsequently, the nodes can be used to simplify the reactions in terms of reaction graphs (Fig. 1d). This shows that a diverse collection of molecular assemblies is possible from one common programmable framework. The Caltech team demonstrate this generality by applying four different programmes (sequences of assembly and disassembly reactions) and analysing the results by gel electrophoresis and atomic force microscopy.

In the first programme, a three-branch junction is formed by the assembly of an ABC complex (Fig. 2a) in a stepwise catalytic process. To make this junction, the initiator strand activates node A, which links to node B, then this AB complex links to node C and links back to A. This regenerates the initiator and makes an ABC complex, which was observed by atomic force microscopy (Fig. 2b). The second programme is a cross-catalytic circuit — an initiator strand catalyses the formation of an AB complex, and a second activated output port on B is used to catalyse formation of CD; a second activated output port on D is used to catalyse formation of AB. Thus, the presence of second output ports enables exponential instead of linear growth kinetics. The third programme results in exponential chain reaction growth of a binary molecular tree carrying five – of nodes — the final tree has a total of $1 + 2 + 4 + 8 + 16 = 31$ nodes.

The fourth programme shows the fuelled movement of a bipedal walker — two linked single strands walk along a track of fixed A nodes on a double helix (Fig. 2c). Walker legs catalyse linkage of hairpins A with free hairpins B to make AB complexes. If the concentration of B is kept low enough, the walker legs spend most of their time linked to the fixed A nodes. Thus, walkers rarely lift both legs simultaneously and almost never dissociate from the track; instead they amble along it.

An important aspect of dynamic self-assembly in cells involves catalytic breakdown of multimeric structures into regenerated monomers — this occurs in the previously mentioned dynamic instability of self-assembled microtubules[5]. Another step towards synthetic nanosystems that similarly recycle their dynamic potential is the development of methods for coupling the regeneration of 'structural' hairpin motifs (for example, hairpins used to build the dendritic tree) with the consumption of 'fuel' hairpin motifs (hairpin B in the walker example is consumed to regenerate the walker, but not to regenerate another hairpin). Likewise, a switch between slow-growth and rapid-shrinkage states of the polymer (as seen in microtubular dynamic instability) could be implemented as a conformational switch between an intramolecular hairpin versus an intermolecular duplex. The regeneration of the hairpin would be powered by consumption of external fuel hairpin motifs, analogous to the exchange of guanosine diphosphate (GDP) for GTP by microtubular subunits.

Pierce and colleagues forecast the construction of additional motifs beyond the simple hairpin presented. The challenge is to design increasingly complicated sets of motifs that exhibit robust and versatile behaviour, with low levels of leakage, cross-talk and undesired kinetic traps. Achieving these properties will allow us to shift our attention to high-level molecular programming languages, and hence enable the synthesis of increasingly sophisticated target behaviours. Examples from biological systems that would be useful for mimicking by adaptive nanosystems of the future include recursive subdivision of compartments in cellular division, self-healing, and spatial patterning in organism development.

References

1. Yin, P., Choi, H. M. T., Calvert, C. R. & Pierce, N. A. *Nature* **451,** 318–322 (2008).
2. Whitesides, G. M. & Grzybowski, B. *Science* **295,** 2418–2421 (2002).
3. Dwyer, M. A., Looger, L. L. & Hellinga, H. W. *Science* **304,** 1967–1971 (2004).
4. Rothemund, P. W. *Nature* **440,** 297–302 (2006).
5. Mitchison, T. & Kirschner, M. *Nature* **312,** 237–242 (1984).
6. Dirks, R. M. & Pierce, N. A. *Proc. Natl Acad. Sci.* **101,** 15275–15278 (2004).

QUANTUM INFORMATION

Positively spin coherent

The observation of long relaxation times and high-fidelity preparation promote the spin of a hole in a semiconductor quantum dot to the best position to be a contender for the role of a solid-state qubit.

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One of the main challenges of quantum information research is to find a materials system that satisfies the requirements for use as the basic element — the qubit. Semiconductor quantum dots (QDs), consisting of nanometre-size clusters in which carriers are confined in three dimensions have long been considered an ideal candidate. Owing to the confinement, the electron motion is quantized, and because QDs can be incorporated into large semiconductor devices, they can in principle be easily addressed through external fields. Both the charge and the spin of an electron in a QD have been considered as qubit candidates. However, two recent papers show that an even better bet could be the absence of one electron (known as hole) or more precisely its spin[1,2].

In a spin qubit, the information is stored in the value of the spin (which can be up or down) and its quantum phase[3]. Not only should it be possible to prepare the spin in a precisely defined state, but this state should persist long enough to allow its manipulation. Owing to interaction with the environment, which for a quantum dot is represented mainly by the lattice surrounding the carriers, both the value of the spin and its phase tend to decay, with characteristic times T_1, the spin-relaxation time, and T_2, the decoherence time, respectively. Preparation and relaxation of single-electron spins in QDs have been the subject of a remarkable series of experiments predominantly using gallium arsenide and related semiconductors[4]. The mechanism that leads to spin relaxation has been identified theoretically as the spin–orbit interaction that weakly couples the spin and charge degrees of freedom of the electron. The electron charge, in turn, is coupled to the lattice vibrations (phonons) in the host crystal that can therefore act as a dissipative environment for the spin. It was predicted and confirmed experimentally that this mechanism is strongly suppressed in confined electron states such as those in QDs (ref. 5). At low magnetic field, a T_1 of up to one second has been reported[6].

The trouble with electrons in GaAs, however, is the relatively short decoherence time. The electron spin interacts with up to a million nuclear spins present in a QD through the so-called hyperfine interaction. Whereas a moderate magnetic field prevents the hyperfine interaction from flipping spins (and thus affecting T_1), the decoherence is strongly affected by the nuclei. Using holes may be one solution because of the different type of interaction of hole spins with the environment compared with that of electrons. In a semiconductor crystal, a hole is created in the valence band when an electron is promoted to the conduction band leaving a vacancy behind (Fig. 1). The hole behaves practically like a positively charged particle. However, whereas the conduction band states originate from atomic orbitals with an s-type symmetry and have a maximum of the wavefunction at the locations of the nuclei, the valence band states originate from p-orbitals, which have negligible overlap with the nuclei, and are therefore expected to experience very small hyperfine interaction, leading to a long T_2. Unfortunately, the p-orbital character also leads to an enhanced spin–orbit interaction, which at first sight means that T_1 for holes is too short. This expectation seemed to be confirmed by early measurements of hole spin-relaxation times in extended systems in the subpicosecond regime[7]. However, recent theory and experiments indicate that spin relaxation is much less severe in very small, strongly confining structures[1,2,8].