

unavoidable but using structured, efficiently conducting DNA may offer a solution. In a system built from hundreds of DNA bases, a few consecutive A–T pairs will be inevitable, but this can be a serious problem. The $(AT)_n$ tracts are notorious blockades of charge transport because they combine bases of high potential with high flexibility and poor stacking dynamics. Like a pedestrian waiting for a break in traffic to cross the street, charges cannot pass through until the dynamic stacking of the base pairs give them a clear path. Eventually, base-pair dynamics will allow charges to migrate through or hop over the barrier, much as the pedestrian will eventually be rescued when the traffic light changes. The team led by Majima and Kawai have dealt with this problem by effectively replacing some of the lanes of traffic with islands.

Long-range hole transport through DNA is generally considered to occur by incoherent hops through low-potential regions of the stacked base pairs, for example guanines — the most easily oxidized bases — or transient delocalized domains extending over several bases. The domains are defined by the base sequence. If low-potential well-stacked sites replace the high potential and flexible barriers, then charge will be more effectively transported. The Majima group incorporate deazaadenine (Z A) into the DNA wires they study. Deazaadenine differs from adenine by the substitution of nitrogen with carbon (Fig. 1). This substitution is a long way from the portion responsible for base pairing, so it has minimal effect on DNA stability. It does, however, stack more effectively than adenine and has a potential similar to that of guanine^{11,12}.

The charge transport was measured by observing the rate that charge travelled from a photoexcited hole donor (naphthalimide) at one end of the DNA chain to a hole acceptor (phenothiazine) at the other. By monitoring transient absorption, the researchers could watch the hole arrive at the phenothiazine. Initially, they compared a sequence that is known to facilitate charge transport — a well-stacked mixed sequence DNA — with the poorly stacked $(AT)_n$. As has been observed previously, the $(AT)_n$ sequence slows charge transport. Then, they serially introduced Z A, which increased the transport rate by orders of magnitude. Even long $(^ZAT)_n$ tracks are shown to facilitate efficient charge transport.

Previous work by Saito and co-workers established that Z A and derivatives can improve charge-transport yields^{11,13}. These studies, however, only measured relative yields in the context of single steps. The current work measures rates of charge transport over distances up to 10 nm, with many substitutions and in a variety of sequence contexts. What makes this approach most impressive is the apparent sequence generality. In every sequence investigated, the rate increased with Z A content. There seems to be no trade-off with this substitution; even when G–C pairs were replaced with Z A–T pairs the rate increased. It is not clear whether Z A is improving transport solely because of its low potential — it is likely that improved stacking compared with adenine also has a critical role. Nonetheless, the effect of Z A on transport is indisputable.

Importantly, charge transport across many of the DNA sequences now occurs too fast for measurement. To avoid rapid charge

recombination, an extended adenine tract at the site of injection must be used.

Further studies will undoubtedly test the general application of Z A to the broader family of DNA devices. Nevertheless, it is tantalizing to consider that DNA-based structures may now be possible where the conductance carries no information regarding the sequence. Nanodevices may begin to be constructed with self-assembled DNA wiring. It should be noted, for all scientists studying molecular nanodevices, that deazaadenine is commercially available on a large scale, giving us the opportunity to grab a real bargain! □

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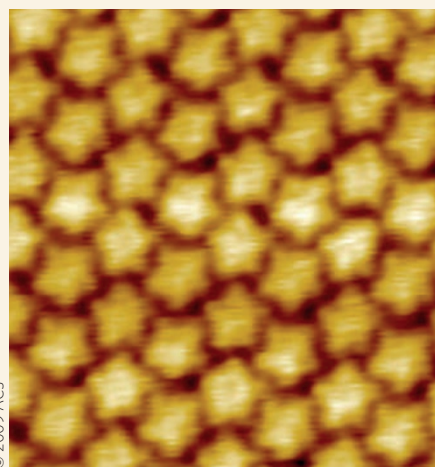
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TWO-DIMENSIONAL CRYSTALS

Tilting and tiling



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Although a surface can be tiled in many different ways, none of them exhibit five-fold symmetry. Similarly, molecules with five-fold symmetry (pentagonal or star-shaped) reduce their order of symmetry to form two-dimensional crystals — a phenomenon that can help in understanding molecular recognition processes at surfaces.

Bauert *et al.* have now used tunnelling electron microscopy to observe the packing arrangement of corannulene — a convex aromatic molecule also known as a buckybowl — on metal surfaces (*J. Am. Chem. Soc.* **131**, 3460–3461; 2009). They also studied its chiral pentachloro and pentamethyl derivatives.

All three molecules close-pack, with their centroids on a hexagonal lattice. The corannulenes form a perfectly ordered monolayer by tilting to one side, but this is not possible in the presence of bulky substituents. The pentachloro derivatives form an array of ‘striped lattices’ (pictured), with pentagonal molecules arranged in antiparallel rows, but the order only extends for a short distance. The pentamethylated molecules form a more disordered ‘rotator phase’ in which the orientation of the molecules, their position with respect to the substrate and their chirality all vary, though their centroids still form a hexagonal lattice.

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