Zimmerman notes that this is not the case in tetracene, because fission occurs in that material only through thermally activated processes. Can singlet fission therefore occur in rubrene crystals, which are chemical derivatives of tetracene, and if so, by what mechanism? In model tetracene dimers, the yield of this process depends sensitively on the molecular nature of a bridge linking the two molecules. One might therefore expect that in rubrene the side-group substituents could increase the rate of singlet fission with respect to that in unsubstituted tetracene crystals. Further ultrafast spectroscopic measurements in high-purity rubrene crystals are thus warranted.

Generally, it is not yet clear to what extent triplets can contribute to the photocurrent in organic semiconductor heterostructures. Recent ultrafast spectroscopic measurements by Rao and co-workers have shown for pentacene:fullerene bilayer heterostructures that charge is generated following slow diffusion of triplet excitons to the heterojunction. Triplets were shown to be produced by singlet fission on subpicosecond timescales, but charge-induced absorption was only observed on nanosecond timescales, consistent with a diffusion-limited process involving triplets. Considering the short singlet-exciton lifetime, and therefore the long singlet diffusion length that would be required in bulk pentacene, pentacene:fullerene bilayers display surprisingly high power conversion efficiencies in solar cells. Podzorov and co-workers suggest that, on generation of triplets in the bulk of the crystal, the triplets diffuse to the surface by a Dexter mechanism. Taken together, the studies by Rao and colleagues and by Podzorov and co-workers point towards the view that triplet states may indeed be useful to produce photocurrent in photovoltaic diodes. If so, the mechanism of charge separation of triplet excitons at fullerene heterojunctions clearly requires substantial further investigation.

We continue to find new opportunities to understand in greater depth the rich many-body physics of organic semiconductors. A detailed understanding of triplet-exciton generation mechanisms, their transport properties and their dynamics at heterojunctions, will be crucial to the fabrication of organic photovoltaic devices. Certainly, if we could learn to make use of singlet fission as an effective energy up-conversion scheme in solar cells, exciton energies would then really go a long way.

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References

NANOPARTICLE ASSEMBLY

Made to order

The DNA-mediated assembly of anisotropic gold nanoparticles shows the importance of particle shape in the controlled formation of DNA-nanoparticle superlattices.

Sharon C. Glotzer and Joshua A. Anderson

Since the early days of the nanoscience revolution, scientists have recognized the great potential in exploiting the highly specific and recognitive properties of DNA to assemble nanomaterials. The four nucleotide bases of DNA bind only with their complementary counterparts, providing lock-and-key specificity that traditional materials lack. Attaching a DNA oligonucleotide at one end to a nanoparticle confers a ‘sticky patch’ or binding site to the particle that will stick only to its ‘mate’ (see Fig. 1). In parallel work published in 1996, Mirkin and Alivisatos showed that mixing together batches of nanoparticles functionalized with complementary DNA strands resulted in hybridization of the DNA linkers, consequently binding the patchy particles to one another. Without the DNA, the gold nanoparticles would not ordinarily assemble, at least not into anything interesting. In this early work, binding and unbinding was demonstrated, and even nanoparticle dimer and trimer ‘molecules’ were achieved. However, extended aggregates formed from many particles lacked any long-range order.

The first crystal lattices assembled from DNA-linked nanospheres were reported, using slightly different binding strategies, in 2008. An ordered gold-nanoparticle binary crystal with a CsCl structure was obtained by Gang and co-workers, and in a separate
Assembly of crystal structures from non-spherical gold nanoparticles

Mirkin and co-workers now report the DNA-mediated assembly of crystal structures from non-spherical gold nanoparticles. They have synthetically realized and numerically rationalized the assembly of various anisotropic nanoparticles into ordered arrangements that had not been achieved by the assembly of spherical particles. In going beyond spheres, the researchers demonstrate a new level of complexity and control for DNA-mediated nanoparticle self-assembly — an important step in the struggle to manipulate matter at the nanoscale. By exploiting the same self-complementary DNA linking strategies as before, the Northwestern team is able to self-assemble hexagonal packing of gold rods, columns of triangular prisms and face-centred-cubic crystals of rhombic dodecahedrons. These structures are easily predicted given the shapes of the particle building blocks. Maximal DNA hybridization occurs when the particles pack face-to-face because of a preponderance of DNA on the particle faces, as opposed to the edges or vertices, making the faces ‘sticky’ (Fig. 2).

They also obtained both body-centred-cubic and face-centred-cubic crystals of gold octahedrons depending on the length of the DNA linkers, demonstrating the exciting possibility of tailoring both the crystal structure and the lattice constants by simply changing the length of the DNA. Their analysis shows that the face-centered-cubic structure formed at long DNA linker lengths results from the increased flexibility of the longer DNA. With enough flexibility, the outside surface of ‘sticky patches’ around an octahedron becomes spherical, removing the tendency for face-to-face ordering. This result shows that both the shape of the particle and the flexibility of the DNA contribute to the final structure. Also writing in this issue, Cigler et al. report on a similar system of linked nanoparticles with two types of particles — gold nanospheres and protein virus capsids. Cigler et al. show that the interaction of the DNA linkers alone results in the previously seen CsCl structure, but the different interactions between the two types of nanoparticles with each other enables the formation of the NaTl lattice — a composition of two interpenetrating diamond lattices. Computer simulations revealed aggregation of the particles, followed by crystallization of the structures.

Interestingly, Mirkin and co-workers show that their anisotropic nanostructures initially form disordered aggregates and then, on thermal annealing, form ordered lattice structures, similar to the process of...
reported by Cigler et al. In the case of the gold nanorods reported by Mirkin and co-workers, single-angle X-ray scattering data shows that the nanorods’ shape directs crystallization into a two-dimensional lattice, and then on further annealing, three-dimensional order is gradually introduced to form a hexagonal-close-packed lattice.

Although the crystal structures reported by Mirkin and co-workers are relatively simple ones as crystals go, the work opens the door to far more interesting structures that are possible now that the linking of non-spherical building blocks by DNA is in hand. Future work will no doubt explore the self-assembly of more complex structures, where different DNA sequences are used to create specific interparticle bonds using DNA-programmed building-block assembly with unprecedented speed and fidelity, allowing for rapid prototyping and design. In any case, with continued synthetic advances, such as those reported by Mirkin’s team and by Cigler et al., ‘made to order’ nanomaterials are closer than ever.

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