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NANOTECHNOLOGY

Peptides as biological semiconductors

A simple peptide that assembles into desirable nanoscale structures is a striking example of how the whole can be greater than the sum of its parts. What's more, the assembly process is controllably reversible.

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Could a simple, short peptide made of naturally occurring amino acids form structures that have the optical and electronic properties of semiconductor nanocrystals? Reporting in the *Journal of the American Chemical Society*, Gazit, Rosenman and colleagues[1] describe a peptide formed from just two phenylalanine amino acids that does exactly that. This is a remarkable discovery, because although conductive organic polymers are well known (their discoverers won the 2000 Nobel chemistry prize[2]), no one had envisaged that biological peptides could act as semiconductors. The reported dipeptide assemblies[1] represent an intriguing, bioorganic class of 'quantum dot' nanomaterial.

A quantum dot is a nanoscale, ordered structure whose excitons — energy-carrying quasiparticles associated with semiconductors and insulators — are confined in three spatial dimensions. This means that quantum dots have electronic properties intermediate between those of bulk materials and discrete molecules. They are being used in solar cells, light-emitting devices and as fluorescent labelling agents in the biomedical industry.

Most quantum dots are made of inorganic semiconductors, often a single material such as silicon or germanium. Others are 'core–shell' structures, in which a semiconductor such as cadmium selenide (CdSe) or zinc sulphide (ZnS) is surrounded by another material. Such CdSe quantum dots have been particularly successful for a variety of applications, but the toxicity associated with cadmium is increasingly a concern. The search for cadmium-free quantum dots has therefore become a major area of research.

The phenomenon that constrains excitons in quantum dots is known as quantum confinement. A key feature of quantum confinement is that it occurs when the diameter of a particle is about the same size as the wavelength of the particle's electronic wavefunction. For objects made of materials that have highly ordered structures, this occurs at the nanoscale, independently of the material used. In other words, as long as there is quantum confinement, there is no reason that materials other than semiconductors — including peptides — cannot form quantum dots.

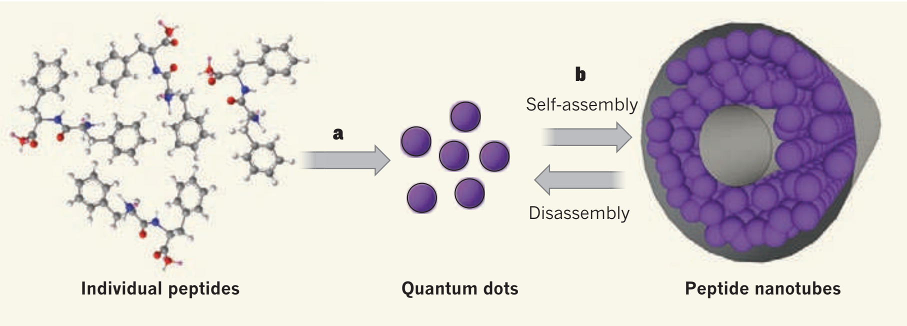

Figure 1 | Simple dipeptides are building blocks for quantum dots and nanotubes. a, Gazit, Rosenman and colleagues[1] report that when they concentrated a solution of diphenylalanine peptides in methanol, the molecules self-assembled into quantum dots. Each quantum dot was composed of two diphenylalanines. **b**, When the authors changed the solvent from methanol to water, the peptides further self-assembled to form nanotubes, each containing millions of quantum dots. The nanotube assembly process was completely reversible — when the solvent was changed back to methanol, the nanotubes disassembled into individual quantum dots.

Enter Gazit, Rosenman and colleagues[1]. They observed that when a solution of diphenylalanine peptide in methanol is concentrated, the peptide molecules self-assemble into nanocrystalline structures (Fig. 1). These assemblies have an average diameter of 2.1 nanometres and consist of two diphenylalanine peptides, corresponding to a total of just four phenylalanine residues per assembly. The authors found that the peptide assemblies have the characteristic optical properties of quantum dots: on exciton formation, they emit light across a very narrow frequency range (that is, they have a narrow photoexcitation peak). But when the authors studied low-concentration solutions of the dipeptide, which contain discrete dipeptide molecules rather than nanocrystalline assemblies, they observed a broad excitation peak. This suggests that individual dipeptide molecules are not quantum dots.

The peptide quantum dots have an intriguing property not found in inorganic quantum dots: when Gazit, Rosenman and colleagues changed the solvent in which the dipeptide nanostructures were dispersed from methanol to water, the structures underwent further self-assembly to form peptide nanotubes. The nanotube dispersion had near-identical optical properties and X-ray diffraction patterns to those of the quantum-dot dispersion, thus proving that the quantum dots are the elementary, quantum-confined building blocks of the nanotubes.

Diphenylalanine-peptide nanotubes have been reported before. Their observed rigidity seems to be very high[3], they are piezoelectric[4] (they generate charge under mechanical strain) and they have been used as scaffolds to fabricate silver nanowires[5]. Gazit and Rosenman's groups have also previously observed quantum confinement in peptide nanostructures[6], and have demonstrated that diphenylalanine peptides can assemble to form quantum wells (structures in which excitons are confined within two dimensions) that exhibit strong blue luminescence[7]. But the present paper[1] is the first to describe the elementary quantum-confined structures that underpin the earlier findings.

What makes this result even more interesting is that the self-assembly of the peptide quantum dots into nanotubes is completely reversible — the nanotubes disassembled back to individual quantum dots when the authors changed the dispersion solvent from water to methanol[1] (Fig. 1). One can thus modify the peptide architecture at will to fabricate either quantum dots or nanotubes. The synergistic effect of millions of quantum dots in a single nanotube might make them a promising material for new types of optical devices, such as light-emitting diodes and lasers.

The optical and electronic properties of inorganic quantum dots can be fine-tuned by varying the size of the nanostructures. Could the properties of peptide quantum dots also be fine-tuned? The answer is probably yes. Because the size of peptide quantum dots is governed by the specific amino acids in the peptide, a large number and variety of naturally occurring and/or synthetically customized amino acids could be used in countless combinations. In this way, it might one day be possible to tweak the size and properties of peptide quantum dots. Indeed, the authors[1] have already shown that a dipeptide made from a phenylalanine and a tryptophan amino acid forms a quantum dot that has different optical and electronic properties from that of the diphenylalanine analogues.

Peptide quantum dots represent arguably one of the simplest forms of quantum dot, but they also offer distinct advantages over other types. First, they are made of natural amino acids that are synthesized by plants and animals, so they shouldn't be too harmful to the environment. Their degradation products will also be harmless natural amino acids. This is unlike most inorganic quantum dots, especially those made of heavy metals. Second, the preparation of dipeptide quantum dots requires the formation of a single peptide bond, which makes them cheap and easy to produce at very high purity. Finally, given the availability of a wide range of amino acids that have diverse properties, perhaps peptide quantum dots will be discovered that have properties not yet observed in other such materials. Nevertheless, much theoretical work is needed to guide further development of peptide quantum dots. Let us hope that Gazit, Rosenman and colleagues' findings will attract people from other disciplines to further advance this nascent field.

Although nature has produced numerous wonderful peptides and proteins, if peptides had been proposed as potentially useful synthetic materials two decades ago, few people would have taken the idea seriously. But today, the use of peptide and protein materials is thriving in diverse areas that could never have been imagined. If quantum dots can be made from peptides, what other surprises might be in store? As Louis Pasteur best put it: "Chance favours the prepared mind." Gazit, Rosenman and colleagues' work[1] should help us to open our minds to be ready for more remarkable discoveries. ■

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QUANTUM OPTICS

Particles of light

Bose–Einstein condensation, which demonstrates the wave nature of material particles, now offers further illumination of wave–particle duality: it has been observed in light itself. **SEE LETTER P.545**

JAMES ANGLIN


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Figure 1 | The Ancient of Days painted by William Blake. "Nothing represented his harsh view of science better than the implication that, if light corpuscles could be neither created nor destroyed, then the Universe contained a fixed amount of light, which could never be increased."

"Art is the Tree of Life. Science is the Tree of Death." So wrote the visionary English poet and artist William Blake[1] in 1826, contrasting the limitless creativity of art with the limiting rigidity of science. Blake understood the science of his day — well enough, for instance, to lump together "The Atoms of Democritus And Newton's Particles of Light", and compare them both to sand[2]. In Blake's time, both were conceived of as indivisible and indestructible, their motion governed by Newtonian mechanics. Nothing represented his harsh view of science better than the implication that, if light corpuscles could be neither created nor destroyed, then the Universe contained a fixed amount of light, which could never be increased (Fig. 1). On page 545 of this issue, Weitz and colleagues[3] demonstrate that, even if that were true, the wave nature of light would still persist, through the Bose–Einstein condensation of photons. They also demonstrate the creativity that thrives within scientific rigour.

Modern physics teaches that light has wave as well as particle properties. But one of the most basic differences between the wave and particle theories is rarely emphasized in textbooks. Classical light waves are not conserved like the atoms of Democritus, but can easily be excited and absorbed. So, a lamp may run out of battery power, but it does not run out of light. In this respect, Newton's particle theory of light was as false as the caloric theory of heat, according to which heat was a conserved substance held in matter like water in a sponge. In fact, both heat and light are simply convertible forms of energy. And it was the thermodynamics of light that led Planck and Einstein to the quantum unification of wave and particle theories.

Unlike classical particles, quantum particles such as electrons and photons can in general be created and destroyed, and so the issue of whether the amount of light is fixed is now separate from the discussion of wave and particle behaviour. A basic question therefore seems natural: what would light be like if photons were, like atoms, wave-like but conserved? Weitz and colleagues[3] have answered this question experimentally. By confining light within the narrow slice of space between two barely separated mirrors, and filling this slab-like cavity with a dye material, they have achieved thermal equilibration of light as a gas of conserved particles, rather than ordinary black-body radiation. The critical step in