Borrowing from biology

What nature already knows

We seldom stop to think about how our bodies grow, develop and repair themselves. Or wonder how, from the time we are a tiny fertilised egg, our cells construct everything we need.

If humans were a mechanical device, made in a factory, each little part of us (protein, carbohydrate, hormone etc) would have to be laboriously assembled – like Lego. Unfortunately, this would not be quick enough or accurate enough to sustain life. We – and all life as we know it – would not be possible. But nature has a cunning mechanism – self-assembly. The biological lego assembles itself; proteins form naturally when a newly formed sequence of amino acids curves and twists itself into the finished structure.

Nature does this with ease and great accuracy. And it's this ability to self-assemble that MacDiarmid scientists are harnessing to collaborate on new and exciting nanomaterials.

Tiny and tricky to handle

You've found a new semi-conductor. It has great potential in the flexible and wearable electronics industry, potentially enabling computers to be printed on fabric or walls. But the material is tiny (as you'd expect) and making it is time-consuming and tedious. You need to find an efficient way to manufacture it. What do you do? You turn to nature, of course.

This is what happened when a team of MacDiarmid scientists at Victoria University led by Dr Justin Hodgkiss needed to find an efficient way to manufacture a new printable electronic material – an electronic ink called perylene diimide (PDI). PDI can be printed and offers new environmentally friendly and low cost ways of making existing electronic gadgets, plus the potential to enable computers, sensors, displays, or smart ID tags to be printed on walls, packaging, fabrics, or skin. But in order to conduct electricity, PDI needs to assemble in a very precise way. If left to assemble randomly, the material does not work as a semiconductor. Dr Hodgkiss and his team had been experimenting with peptides to get PDI to assemble properly but it just wasn't working. So they turned to their MacDiarmid colleague at Auckland University, Professor Juliet Gerrard.

Clicking two technologies together

Professor Gerrard's team had been experimenting with little pieces of protein – called peptides – to try to enhance protein assembly. They studied the peptides that influenced how a protein assembled different units into the correct size and shape and figured out how to modify the peptides but still retain the ability to self-assemble. By doing this they could control and enhance the way the peptide assembled.

This was just what Dr Hodgkiss' team needed to take their development forward. Working closely under the MacDiarmid umbrella, the two teams found they could improve the coupling between the peptides and the electronic material (PDI). By adding linker units between the peptide and the PDI they engineered a new material that could self-assemble. They managed to get hybrid (part chemical, part biological) materials to self-assemble from a water-based ink.

Professor Gerrard says her team had to design a peptide that would do the job the Wellington team needed. "Often in science we struggle to make something and then realise that biological systems have already worked out how to do it."

Knitting nature with nanoscience

Dr Hodgkiss' team then worked closely with a third MacDiarmid team led by Victoria University physicist Dr Plank. She had been looking at how hybrid materials could be used to form the active part of a transistor device – the building block of modern electronics. Her team used the new hybrid material to make a functioning device that worked as an electronic switch – a highlight result in the team's publication in Advanced Functional Materials.

Dr Plank says that compared to regular semi-conductors (made of silicon) these new materials are 'soft' and that it was initially hard to think of a way to make a device from something so different. "By mimicking biology we could get the material to grow from the 'bottom-up' rather than the usual and slow 'top-down' approach. It is exciting to take a biological assembly method and apply it to a material that can have a function electronically."

We talk about 'the MacDiarmid difference', and this project highlights that difference; the combination of chemistry, biology, and physics really allowed us to realise an ambitious idea and convey it to a broad audience.

Justin Hodgkiss

Our team was fiddling around with how to use our knowledge of proteins to assemble nanomaterials and the Victoria University team was trying to build field effect transistors. It was just a matter of clicking these two technologies together.

Juliet Gerrard

We can take a biological assembly method and apply it to a material that can have a function electronically.

Natalie Plank

A MOF could remove CO_2 from polluting smoke stacks.

Metal-organic frameworks that self-assemble from solution into rhombic dodecahedral crystals.

MacDiarmid Institute
Annual Report
2015

Molecular sponges

Another MacDiarmid team led by Massey University Professor Shane Telfer has developed self-assembling nanomaterials – in this case three dimensional metal-organic frameworks (or MOFs). MOFs are 'molecular sponges' with pores about the size of molecules. This means a MOF could deliver a drug to a specific site within the body, or store gases, such as hydrogen (for fuel) or carbon dioxide (to remove it from polluting smoke stacks). MOFs are mostly free space, like an open porous net, with a metal at the corners and an organic component as the rods or linkers.

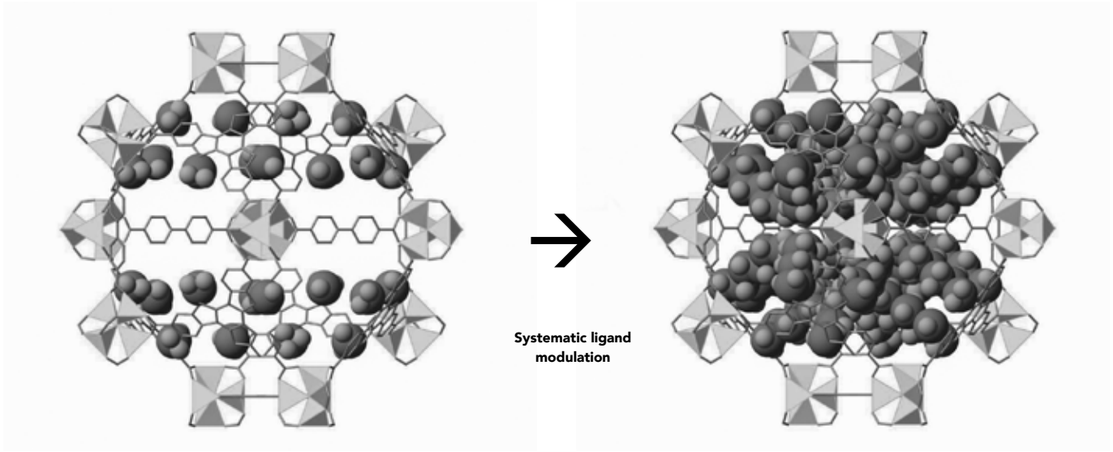
As with the two-dimensional electronic inks, the three-dimensional metal-organic framework materials that Professor Telfer's team are working on also self-assemble. His team has developed a way to get materials to self-assemble from the two-dimensional plane to the third dimension. They are added separately into a reaction mixture, which is then heated to crystallise (assemble) the framework. The metal and organic components come together and arrange themselves into an ordered lattice by self-assembly.

Professor Telfer says there are many applications for MOFs including drug delivery.

"We can make the molecular sponges small enough to be taken up by cells to deliver a payload, such as a drug or an imaging agent. Other applications include gas storage – for example for methane or hydrogen powered vehicles. Instead of an empty fuel tank which would have to be at very high pressure, we can pre-fill the tank with these materials and the gas can be held safely within them."

He says MOFs can also be used for separation/purifications – for example as breathing filters in gas masks for chemical weapon or pesticide detoxification. "We can use them in membranes on a larger scale for industry in the smokestacks of coal-fired power-plants where MOFs could filter CO_2 and other toxins before they get into the atmosphere."

Shane Telfer



**Quanternary
Zn4O-carboxylate MOFs**

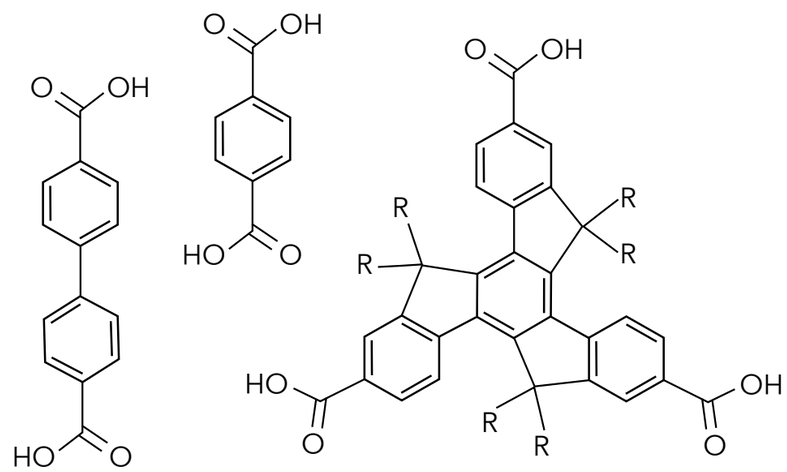
**Stable to water vapour
& tunable gas adsorption**

Abstract 1

Advanced Functional Materials, 2015, 25, 5640-5649

Functional Organic Semiconductors Assembled via Natural Aggregating Peptides

Natural proteins have evolved peptide sequences that adhere to each other with exceptional strength and specificity. In this work, we explore the concept of using such peptide sequences as tectons for encoding the self-assembly of synthetic functional materials. We first identified aggregating peptide sequences by inspection of protein-protein interfaces in the peroxiredoxin family. We then created hybrid bioelectronic materials by tethering these 8-mer peptide sequences to organic semiconducting molecules, along with an additional sequence to act as a trigger for aggregation. We show the hybrid materials self-assemble into nanofibres, whereby the semiconducting units are brought into electronic communication with each other in a way that strongly depends on the peptide interactions. A bioorganic field-effect transistor is fabricated from this class of materials, highlighting the possibilities of exploiting natural peptide tectons to encode self-assembly in other functional materials and devices.



**Systematic ligand modulation
optimises water vapour stability
& gas adsorption capacity**

Abstract 2

J. Am. Chem. Soc., 2015, 137 (11), pp 3901–3909

Systematic ligand modulation enhances the moisture stability and gas sorption characteristics of quaternary metal-organic frameworks.

Complex metal–organic frameworks (MOFs) that maintain high structural order promise sophisticated and tunable properties. Here, we build on our strategy of using combinations of structurally distinct ligands to generate a new isoreticular series of ordered quaternary Zn4O–carboxylate MOFs. Rational design of the framework components steers the system toward multicomponent MOFs and away from competing phases during synthesis. Systematic ligand modulation led to the identification of a set of frameworks with unusually high stability toward water vapour. These frameworks lose no porosity after 100 days' exposure to ambient air or 20 adsorption–desorption cycles up to 70% relative humidity. Across this series of frameworks, a counterintuitive relationship between the length of pendant alkyl groups and framework stability toward water vapour emerges. This phenomenon was probed via a series of gas and vapour adsorption experiments together with Grand Canonical Monte Carlo (GCMC) simulations, and could be rationalized on the basis of the propensity of the frameworks to adsorb water vapour and the proximity of the adsorbed water molecules to the water-sensitive metal clusters. Systematic variation of the pore volume and topography also tunes the CO_2 and CH4 gas adsorption behaviour. Certain of these materials display increases in their adsorption capacities of 237% (CO_2) and 172% (CH4) compared to the parent framework.