Organic photonics and electronics

Paul Burn introduces aspects of research at the Centre for Organic Photonics and Electronics (COPE) at the University of Queensland.

One of the fastest growing and important areas of 'soft materials' is organic opto-electronics, and this was recognised by the award of the Nobel Prize in Chemistry in 2000 to Professors Heeger, Shirakawa and MacDairmid for their pioneering work on conducting polymers. The emphasis in their early work was on developing lightweight plastic wires to replace conventional metal wires such as copper. Although the stability and conductivity of conjugated polymers has not matched metal wires, lower conductivity materials based on doped poly(aniline) and poly(thiophene) derivatives are used commercially, and they have also found use in other applications such as microfluidic chips. Organic materials can achieve very high conductivities with some organic charge transfer salts having superconducting properties. More recently it has been discovered that conjugated organic materials can also have semiconducting properties and this has rejuvenated the field and led to some spectacular results.

Organic semiconducting materials are of great interest for opto-electronic applications such as flat panel displays based on organic light-emitting diodes (OLEDs), solar (photovoltaic (PV)) cells, and organic electronics including field-effect transistors (FETs) and sensors. Of these technologies, flat-panel displays based on OLEDs are the most advanced with products now available. Building on the understanding of materials and device requirements developed for OLEDs, the other technologies are moving apace with commercialisation of solar cells, field-effect transistors, and sensors.

Figure 1. Examples of organic semiconducting opto-electronic materials. Pentacene 1 and the aluminium 2 and ruthenium 3 complexes are small molecules that are used in field-effect transistors, OLEDs and dye-sensitised solar cells, respectively. Examples of conjugated polymers include poly(1,4-phenylenevinylene), poly(fluorene) and poly(3-n-hexyl-2,7-thiophene). The R and R' groups of the first two provide solubility and control the intermolecular interactions of the opto-electronic backbone. Molecule 7 is an example of a second-generation dendrimer with a fac-tris(2-phenylpyridyl)iridium(III) core, carbazole-based dendrons and fluorenyl surface groups. When used in an OLED, the core is responsible for light emission with the core and dendron participating in charge transport and the surface groups impart solubility.
effect transistors and sensors being pursued through a range of companies around the world. Organic semiconducting materials have the potential to provide a superior technology package when compared with incumbent materials and devices. For example, flat-panel displays based on OLEDs now have the potential to compete against liquid crystal displays in terms of power consumption, brightness, repetition rate, viewing angle and flexibility. Indeed, the efficiency of some devices is such that they are now being investigated for solid-state lighting.

Organic semiconducting materials fall into three main classes: small molecules, polymers and more recently dendrimers (Fig. 1). In this field, the term ‘organic’ is used loosely as many of the materials also contain metal ions. So, for example, a small molecule may be all ‘organic’, as in the case of pentacene (1, in Fig. 1), or be a metal complex such as 2 and 3 (Fig. 1), with the latter two used in OLEDs and organic solar cells respectively. Small molecules have a number of advantages as materials for opto-electronic applications including syntheses that are generally simpler and easily reproduced; it is easier to manipulate the properties in a predictable manner by functional group manipulation and hence there is a greater choice of opto-electronic chromophores; and it is easier to control the purity of the materials.

Small molecules are generally processed by evaporation under high vacuum. The advantage of evaporation as a manufacturing process is that it is possible to build up complex multilayer devices in a relatively straightforward manner. The deposition of another layer does not remove previously deposited layers. However, the problems with evaporative processing techniques are that simple changes to the structure of a material (to change the opto-electronic properties) can lead to vastly different physical properties. This means that while a parent material can be evaporated, a derivative may not because of a lack of the necessary volatility. In addition, while evaporation can be a final purification step, there is now evidence that some materials can degrade during the process. Finally, simple evaporation are restricted to small devices and in patterning to form pixelated structures, for example, for full-colour displays, material is wasted due to the masking process. That is, for an OLED with red, green and blue pixels, only one-third of each evaporated material is used.

While small molecule organic semiconductors were first out of the blocks, the discovery that polymers could be used in OLEDs has led to an explosion of solution-processed devices. Polymer 4 with $R = R' = H$ (Fig. 1) was the first to be used in an OLED. Unadorned conjugated polymers tend to be insoluble and unless they are prepared via a precursor route, they need to be substituted with solubilising groups as in the case of polymers 5 and 6 (Fig. 1). The two main families of conjugated polymers are the poly[(hetero)arylene vinylene]s (4 in Fig. 1) and the poly[(hetero)arylene]s, of which poly(phenylene) 5 and poly(3-n-hexyl-2,5-thiophene) 6 are examples of this widely studied class. With the discovery of polymer organic semiconductors, the field is now divided into two main camps based on how the materials are processed, namely evaporation and solution processing. Solution processing gives rise to the potential for low-cost large-area manufacturing by techniques such as screen and inkjet printing and web- and spin-coating. The use of inkjet printing for patterning is a powerful technique and less wasteful of material as the polymer is placed only in the positions where it is needed. However, a disadvantage of solution processing is that it is much harder to form multilayer structures which can lead to more efficient devices. For example, the most efficient OLEDs tend to have at least two layers to balance charge injection and transport.

Conjugated polymers have been investigated for most of the opto-electronic applications with good success. However, there are a number of difficulties with using such materials including synthetic reproducibility, polydispersity, purity, complex film morphologies and the fact that changes to the structures to alter the opto-electronic properties can often lead to differences in the processability. An interesting point to note is that copolymers often lead to more efficient devices than homopolymers. That said, the most efficient solution-processed bulk heterojunction (a mixture of an electron acceptor and donor) solar cells are based on conjugated polymers.

Dendrimers, on the other hand, combine the strengths of small molecules and polymers, in that simple reactions are used to produce well-defined, monodisperse macromolecules, which are solution processable. Dendrimers consist of a core to which one or more dendrons (branched groups) are attached, and at the distal ends of the dendrons surface groups are often found (e.g. 7 in Fig. 1). A further advantage of dendrimer semiconductors over small molecules and conjugated polymers is that the electronic and processing properties can be optimised independently. The surface groups play the primary role in controlling the processing while the dendrons and/or core govern the opto-electronic characteristics. In addition, by using convergent syntheses, the dendrimers can be prepared using a modular approach from dendron and core libraries, thus enabling the incorporation of the structural variations required to achieve the desired properties later in the synthesis. With dendrimers, it is also possible to control the critical intermolecular interactions by either generation or number of dendrons. Finally, the
dimensionality of the dendrimer can be controlled by generation and/or shape of the core, allowing tuning of film morphology. However, like solution-processable conjugated polymers, dendrimers are also difficult to introduce into all solution-processed multilayer devices.

The key to the success of developing organic materials for applications is to be able to control the intermolecular interactions of the active materials at the molecular level in the solid state. For example, for charge transfer salts, the intermolecular interactions govern whether the material is an insulator or a metal and whether it can become superconducting. In terms of organic semiconductors for opto-electronic applications, there is often an exquisite balance between two key properties: charge transport and the optical characteristics of the materials in the solid state. In organic (super)conductors and semiconductors, good order and close intermolecular interactions are required for good charge transport. In contrast, for good light emission, apart from a small number of special materials that form highly luminescent aggregates, it is best to have the luminescent chromophores held far apart to avoid the intermolecular interactions that lead to the quenching of the luminescence. For applications that require emission of light such as OLEDs, lasers and sensors that rely on an oxidative quenching of the excited state, close intermolecular interactions of the emissive components can lead to quenching of emission. For small molecules, this is overcome by using guest-host systems where the emissive chromophore is blended at a low concentration in the host. For polymers, the control is gained essentially by the side-groups attached to the polymer backbone. Dendrimers provide the most precise way of controlling intermolecular interactions as the emissive chromophore can be located at the core of the dendrimer and then the dendron type, generation, dendrimer dimensionality and surface groups can all be manipulated at the molecular level to fine tune the properties. For FETs and organic PV, charge transport (mobility) is a critical
property in terms of device performance. Achieving the necessary order or arrangement in the films over the required length scales by evaporation or solution processing to achieve the high mobilities on the scales needed for manufacturing is one of the big chemistry and materials challenges.

The model of chemists and physicists working together has led to the great steps forward in organic photonics and electronics and this is the model that we have adopted at COPE (Fig. 2). The Centre is a joint venture between the School of Mathematics and Physics (Physics discipline) and the School of Chemistry and Molecular Biosciences (Chemistry discipline) at the University of Queensland. The team includes Associate Professor Paul Meredith (experimental physics), Dr Shih-Chun Lo (chemistry), Dr Ben Powell (theoretical physics), and Professors Paul Burn (chemistry) and Ross McKenzie (theoretical physics) with examples of our research interests reflected in the following articles in this issue of *Chemistry in Australia*. At the Centre, we have created a process that flows from materials design and synthesis through materials characterisation to prototype fabrication and testing. The materials development and testing program is underpinned by high-level theory where we are testing our hypotheses to see whether we can produce predictive models for our materials and device development. The materials program at the Centre has a focus on dendritic macromolecules but we also create small molecules as model systems and work with charge transfer salts and conjugated polymers. We are developing our understanding of structure–property relationships of the materials in the context of exploring a range of applications including organic solar cells, field effect transistors, sensors and OLEDs. COPE is also part of the Queensland node of the Australian National Fabrication Facility (www.anff.org.au), and we work with colleagues both nationally and internationally in collaborative programs.

**REFERENCES**


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