Over the past two decades, organic semiconductors have been one of the most rapidly developing research fields. The development of organic semiconductor combines novel materials design for controlling the opto-electronic and processing properties that is in principle simpler than inorganic semiconductors. Small molecules and polymers are the two main types of organic semiconductors studied but more recently dendrimers have shown great potential for application in semiconductor devices. A wide range of organic semiconductor devices have been demonstrated such as light-emitting diodes, solar cells, transistors and lasers. Among these, organic light-emitting diodes (OLEDs) are a key technology for future flat-panel displays (FPDs) and solid lighting, and have great potential to replace current FPDs (such as plasmas and TFT-LCDs) due to their superior video display quality (fast response time) and excellent power efficiency, as the backlight required for LCDs is no longer needed. Many of the major electronics companies are now engaged in OLED development. The first OLED TV, the SONY XEL-1, was launched on the market in December 2007. Although it is only an 11-inch screen, it represents a remarkable piece of technology made from evaporated layers of small molecular organic semiconductors.

**What is an OLED?**
A simple OLED consists of one or more layers of organic semiconductor between two electrodes (Fig. 1). When a voltage is applied, opposite charges (holes and electrons) are injected from the two electrodes, which then move across the device. If they meet up on a light-emitting material, they can form an excited state called an exciton, which can decay radiatively to give a photon. For efficient OLEDs, it is necessary to achieve balanced charge injection (equal numbers of holes and electrons), efficient transport, and capture of all charges injected to form excitons, and for all the excitons to decay radiatively. This has not yet been achieved in OLEDs comprising a single emissive material and hence more complex devices are necessary. For example, if the light-emitting layer predominantly transports holes, then one or more electron transporting layers will be placed between the emissive layer and the cathode and vice versa. With OLEDs, there is no control over the spins of the injected charges (holes or electrons) and hence when they meet up on the same (macro)molecule, both a singlet or triplet excitons can form. For small molecules, the ratio of singlets to triplets is 1:3, (or higher for conjugated polymers). For fluorescent materials, only the singlets can emit light while for phosphorescent materials based on heavy metal complexes, both the singlets and triplets can be captured. Therefore, phosphorescent materials intrinsically have the potential to lead to more efficient devices than their fluorescent counterparts. It is important to note that the emissive chromophore must have a high-solid state PLQY (photoluminescence quantum yield); that is, once the exciton is formed, it must decay to emit a photon of light.

**What is a light-emitting dendrimer?**
Figure 2 illustrates a light-emitting dendrimer, in which an emissive core has three dendrons (branched structures) attached. The dendrons comprise branching points and can
have linking units between the branching points. Dendrimers are defined by their generation, which is the number of levels of branching. Typically, to achieve the required solubility and processibility, surface groups are connected to the distal ends of the dendrons. The emissive chromophores can be located at the core of the dendrimer, within the dendrons, and/or at the surface of the dendrons. All these strategies have been investigated, with the most successful approach having the light-emitting element as the central core. This is mainly because the dendrons can stop the intermolecular interactions that lead to the quenching of the luminescence, which is not possible if the luminescent moiety is at the dendrimer surface.

**Why dendrimers?**

OLEDs based on phosphorescent small molecules have proved to be the most efficient. However, the high-vacuum manufacturing process required for small molecules is time-consuming, wasteful of material, and only used easily for small devices. This has therefore led the drive for solution-processable materials with similar performance, which would then open up the prospect of large-area and low-temperature device manufacturing using spin-coating, ink-jet printing or blade-coating.

**Processing and emission properties**

The first light-emitting dendrimers contained fluorescent cores. The key feature discovered with dendrimers consisting of E-stilbenyl dendrons was the ability to independently control the processing and emissive properties. For example, while dendrimers 1, 2, and 3 emit blue, green and red light, respectively (Fig. 3), they can be all solution processed under the same conditions to give good-quality thin films.

**Charge transport and intermolecular interaction**

In OLEDs there is a trade-off between charge transport and light emission. For good charge transport, the chromophores need to be close, but if the charge-transporting chromophores are also responsible for light emission, close proximity can lead to a change in emission colour and reduction in efficiency. By using the dendrimer generation, these key interactions can be controlled. The effect of generation was first illustrated with three generations of distyrylbenezene-cored dendrimers (1 is the second-generation in the series). For this family of dendrimers, it was found that the higher the dendrimer generation, the higher the device efficiency. It was also found that the emission spectrum became narrower going from the first- to the second-generation dendrimer due to less excimer emission caused by a reduction of the intermolecular interactions of the emissive chromophore.

**Phosphorescent dendrimers**

Despite these important findings, the efficiency of the fluorescent dendrimer OLEDs (DLEDs) was not satisfactory. To improve the efficiency, dendrimers with phosphorescent cores have thus been developed. The pioneering work showed that solution processible dendrimers with biphenyl dendrons and a fac-tris(phenylpyridyl)iridium(III) core (Fig. 4, 4), could give rise to devices with external efficiencies of 16% (external quantum efficiency), 40 lm/W and 55 cd/A at 4.5 V and brightness of 400 cd/cm$^2$, which is very close to the
theoretical limit of 20%. A key point of the DLEDs was that the efficiencies were achieved in simple two-layered devices with only three organic materials rather than the typically more complicated OLEDs based on small molecules (Fig. 5, left). Dendrimer 4 is a green emitter, and changes made to the structures very quickly led to dendrimers that gave efficient red (5, Fig. 4) and sky-blue (6, Fig. 4) emission.

Host-free phosphorescent DLEDs

Finally, by increasing the number of dendrons per ligand from one to two (7, Fig. 5), it was possible to form the simplest but efficient devices that contained only a light-emitting dendrimer layer and an electron transport layer sandwiched between the electrodes. The host-free phosphorescent DLED gave an excellent device performance, 13.6%, 47 cd/A, 30 lm/W at a brightness of 110 cd/m² and 4.8 V. The host-free DLEDs also demonstrate the promise of simple-to-fabricate, and low-cost, high-performance displays and lighting.

Phosphorescent blue DLEDs

With the excellent progress on green and red phosphorescent dendrimers, we have focused our most recent efforts on developing high-efficiency saturated blue phosphorescent metal complexes. Iridium(III) complexes based on aryltriazole ligands (8, Fig. 6), were shown to emit saturated blue light at room temperature. However, we found that the deeper the phosphorescent blue, the less luminescent the complexes were, which was determined to be due to strong coupling of vibrational modes to the excited state. We have therefore been working on incorporating the blue emissive complexes into dendritic architectures to see whether the dendrimer advantages observed for other colours could be transferred to blue emitters. Progressive encapsulation of 8 with one and then two biphenyl-based dendrons, 9 and 10, respectively, led to host-free DLEDs with an external quantum efficiency of 8% for dendrimer 10. However, the emission colour was light blue, not saturated blue as required for full-colour displays.

Attachment of a fluorine atom to the ligands of 8 to give 11 (Fig. 7) shifted the emission colour to a saturated blue. However, attachment of the biphenyl-based dendrons (12, Fig. 7) was found not to be an advantage because in the solid state the dendrons led to the quenching of the luminescence, as their triplet energy was similar to that of the core. To overcome this, we developed a new class of high-triplet dendrons based on 1,2-diphenylethylene units (13, Fig. 7). This gave rise to an excellent film PLQY (49%) for 13. However, the relatively flexible dendrons created another problem - the glass transition temperature was found to be low (-3°C), meaning the dendrimer film is too soft to make a host-free DLED.

Conclusions and outlook

Light-emitting dendrimers are a unique class of macromolecules, comprising tunable molecular components that allow
simple optimisation of the properties. The chemistry used to synthesise our light-emitting dendrimers is generally straightforward and by using a convergent approach, mono-dispersed highly pure materials can be formed. The attached surface groups lead to good solubility of the intermediates during the dendrimer synthesis and processing. Highly efficient red, green and light-blue phosphorescent dendrimers have been developed and used in DLEDs. However, the development of saturated blue host-free DLEDs remains a challenge with new dendron types required. In addition, all DLEDs have been monochromatic and methods need to be developed to allow the patterning required for full colour displays. Therefore, while the development of light-emitting dendrimers has advanced rapidly with the key properties being understood, there are still challenges ahead for materials and devices development.

REFERENCES


Shih-Chun Lo <s.lo@uq.edu.au> and Paul L. Burn, Centre for Organic Photonics and Electronics, School of Chemistry and Molecular Biosciences, The University of Queensland.