level of electroluminescent power (24 mW) — quite an achievement for an LED, particularly in comparison with the quantum cascade laser, which has a typical emission of 4 μW just below threshold and 8.5 mW above threshold. It is significant that for injection currents greater than 1 A, the LED showed an efficiency of 6×10^{-3} photons per electron. This is 20 times larger than the internal efficiency of the first quantum cascade laser below threshold, and 60 times larger than the internal efficiency of the first quantum cascade LED.

This demonstration of an enabling technology for light emitters lattice-matched to GaAs integrated circuits opens up a new area of investigation. LTG-GaAs has very short (subpicosecond) radiative lifetimes, and is therefore ideal for digital communications where speed must continue to increase. It is expected that the research initiated here will continue to provide further performance improvements. Even this initial demonstration is a very significant contribution to optoelectronics, and should lead to a better understanding of the properties of LTG-GaAs.

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ORGANIC ELECTRONICS
Molecules as bipolar conductors

Composite films of conducting polymers and fullerenes are attractive for making optoelectronic devices, such as solar cells. A new approach mixes the two components at the molecular level.

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The ability to achieve both p-type (hole conducting) and n-type (electron conducting) properties in semiconducting materials is fundamental to the success of existing electronics, and will also be crucial for the future of 'molecular electronics'. Currently, there is increasing interest in the synthesis of active electronic materials that combine the p-type semiconducting properties of conjugated polymers with the n-type ones of fullerenes. In *Macromolecules*, Jean Roncali and colleagues[1] describe the preparation of conjugated polymeric materials covalently linked to fullerene units, thereby combining these two properties in the same material. This work is a beautiful example of the preparation of exotic materials expected to behave as intrinsic, non-composite p/n-type semiconductors. Such chemical tailoring could lead to the development of other (macro)molecular architectures for electronic applications.

Conjugated polymers, with an unsaturated backbone and extended π-electron delocalization, are some of the most promising organic materials for electronic applications. In general, these polymers can stabilize chemically or photochemically generated mobile radical-cations (the so-called positive polarons), and can be regarded as p-type semiconductors. Fullerenes are another class of molecular materials with outstanding electronic and optical properties. Except, in this case, the behaviour is n-type: fullerenes can accommodate as many as six electrons, and display considerable electron mobilities. Roncali and colleagues have now designed monomers consisting of two bithiophene-based groups attached to a fullerene by alkyl spacers of variable length. These precursors are then polymerized by straightforward electrochemical methods to produce fullerene-derivatized conjugated polymers with a robust three-dimensional structure, enhanced conjugation length and improved stability.

The approach followed by Roncali and co-workers is the so-called multisite concept[2]: the use of bithiophene-based monomeric precursors that undergo polymerization at two different sites with respect to a central fullerene unit. Previous studies have created similar materials[3,4], such as linear conjugated polymers bearing tethered fullerene units (so-called double-cable polymers; Fig. 1). These can be prepared electrochemically, as insoluble films, and chemically, in soluble form[3]. Soluble double-cable polymers have even been used to make prototype thin-film photodetectors and photovoltaic elements. But the multisite approach proposed by Roncali and colleagues seems to bring substantial improvements in terms of polymer conjugation length and stability as well as providing a potentially attractive way to fully control the three-dimensional structure of the material. When comparing their electrochemical behaviour to linear conjugated polymers, either with or without attached fullerene units, the polymeric materials created by Roncali and co-workers are much more durable during potential cycling and can be p-doped (oxidation of the conjugated polymer) at lower potentials.

One of the most mature applications of conjugated polymers and fullerenes is for 'plastic' photovoltaics.

Indeed, thin-film solar cells with energy conversion efficiency of up to 2.5% (under standard solar illumination) have been prepared from conjugated polymer and fullerene blends[5]. Such composites exploit the ultrafast photoinduced electron transfer between conjugated polymers and fullerenes, which enables the separation of long-lived charged carriers necessary for photovoltaic solar-cell operation[6]. But the efficiency of these devices is limited by the ability of the materials to transport charge carriers, which in turn depends on the morphology of the polymer/fullerene composite used as a photoactive layer. The morphologies of existing composites, aside from the double-cable polymers, are not easy to fine-tune.

In addition to their intrinsic p/n-type semiconductor character, one of the most exciting features of double-cable polymers and the new fullerene-derivatized polymers is the potential to control, at the same time, both the electronic and morphological properties of photoactive layers. Most notably, the covalent fixation of fullerene units onto the conjugated backbone maximizes contact between the electron donating and accepting counterparts, and should prevent phase separation. It is hoped that in future devices based on these materials, this property will enhance photoinduced charge-carrier generation and allow the creation of nanoscale-patterned structures for maximizing the conduction of both electrons and holes.

It is worth noting that, unlike the double-cable concept, the multisite approach proposed by Roncali and colleagues will not allow the synthesis of easily processable materials. Solubility is an important technological requirement for the easy and cost-effective production of large-area thin-film devices, which can be cast from solutions by techniques such as spin coating. The three-dimensional structure of these novel fullerene-derivatized polymers means their solubility is inherently much lower than double-cable polymers. Nonetheless, organic and hybrid (inorganic–organic) photoelectrochemical cells, for which processability of the materials is less critical, are also of interest[7]. As with the solid-state solar cells discussed above, the addition of fullerenes to the conjugated polymer is expected to dramatically improve the charge-carrier generation, and thus the overall photoelectrochemical device efficiency. This approach could eventually lead to fully electrochemically prepared and electrochemically operated photovoltaic devices. Indeed, preliminary experiments show that the photoelectrochemical response of polymers containing fullerenes is more than twice that obtained with an underivatized reference polymer[1].

For photoelectrochemical applications, the multisite approach presented by Roncali and co-workers possesses two clear advantages. For 'wet' electrochemical devices that operate in contact with an electrolyte, the covalent fixation of the fullerene units will improve the stability of the active layer by preventing their migration into the electrolyte solution. The same is true
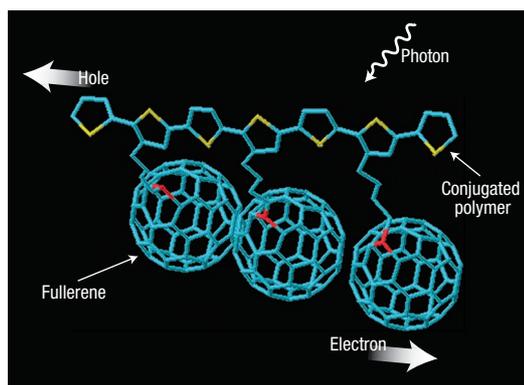

Figure 1 Photoinduced charge transfer in a polymeric material composed of a conjugated moiety with covalently linked fullerene-based units[3]. The structure is designed to behave as a semiconducting double-cable: the conjugated polymer (unsaturated backbone) allows for the transport of holes (p-type conduction), whereas the tethered fullerene units allow for the transport of electrons (n-type conduction). Roncali and colleagues[1] have now created a three-dimensional polymeric-fullerene structure, which also behaves as an intrinsic p/n-type semiconductor with enhanced stability and tunable morphology. (Yellow: sulphur. Blue: carbon. Red: nitrogen.)

of double-cable polymers. In addition, the multisite approach results in more porous polymer structures, and this is expected to facilitate processes—such as the in-out diffusion of ions—that are crucial to the operation of photoelectrochemical cells[7]. Another possible application of the thin-film double-cable polymers and multisite-fullerene engineered materials could be in multilayer devices, for instance, as efficient charge-generating layers. In this case, insolubility will permit the casting of a subsequent layer without affecting the electrochemically deposited one.

Much work has been done to investigate the photophysics of dyads composed of a small electron-donor moiety linked to fullerenes as electron acceptors. It will be of interest to perform similar studies on such macromolecular systems as double-cable polymers and three-dimensional fullerene-derivatized polymers. This will allow us to clarify how much the conjugated polymeric nature influences their photophysical behaviour or the carrier mobility. These newly proposed synthetic approaches are another example that clearly demonstrate the potential of covalent chemistry for controlling various properties of molecular electronic materials. They also suggest that the combination of covalent chemistry and self-assembly concepts, for instance, based on different lock-and-key interactions[8–10], will be crucial for the development of nano-engineered functional materials for electronic applications.

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