

VIEWPOINT

Polymer electronics: the skill lies in the blending

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Only a few decades after their invention, structural polymers are seen everywhere. Their immense range of successful applications has been possible through three major innovations. The first was molecular design and engineering. The second, texture control, to give chosen 'spaghetti structures', has evolved through the understanding of intermolecular interactions and the nature of polymer processing. The role of texture was a theme of several papers in the recent special issue of *Journal of Physics: Condensed Matter* on organic electronics [1], e.g., in the papers of Lidzey [2] and the modelling approaches of Stoneham *et al* [3]. Thirdly, the blending of polymers has been enormously effective, often for interestingly different reasons from the success of bandgap engineering through the alloying of III–V semiconductors. Electronic polymers have enormous potential, and already show the power of molecular design. There are clear indications that performance can be enhanced by control of texture, and perhaps by self-organisation. So what can blends offer?

In this issue, Ellen Moons [4] shows both the promise and the challenges of exploiting blends of electronically-active polymers. She shows, in particular, that designer-blends can give major improvements in the efficiency of organic devices such as light-emitting diodes (LEDs). What is now evolving into a systematic new approach follows a number of earlier examples: studies of photovoltaic diodes based on polymer blends [5, 6], in polymer LEDs [7–11], in low-threshold cascade [12] or distributed feedback lasers [13]. The new opportunity is to create a technology in which blends for wide-ranging applications can be identified and optimized with understanding and control.

Texture is perhaps more subtle. Yet its effects can be profound on luminescence efficiency. As Rothberg and Bao [14] describe, ordered and disordered regions of a conjugated polymer film differ significantly in their photophysics, especially as regards the decay of excited states produced via direct excitation rather than via energy exchange. They also show how molecular engineering, one other strand in polymer technology, can be used to prevent quenching by aggregation. These two papers show how the powerful ideas known from structural polymers impact on electronic polymers.

Self-organized nanostructures of conjugated polymers are formed naturally in virtually every blend by spontaneous phase separation initiated by a common solvent (spin-casting) or change in temperature (annealing). Such nano- and microstructures are often reflected in the surface topography and three-dimensional morphology of the films. These structures profoundly influence charge generation, transport and recombination. These structures are crucial in controlling physical properties and device performance at the nanoscale and at

the microscopic level. This represents a remarkable window of opportunity. Today, just as serious applications of organic semiconductor organics are emerging, so the striking developments in nanotechnology are offering novel experimental and theoretical analysis tools. Example? The increased understanding of how intermolecular and intramolecular interactions regulate polymer systems also controls the fundamental physics of carbon-based materials and underpins soft-matter physics at large, not least for bio- or bio-mimetic structures.

The character of organic semiconductor devices is often dominated by the interface and surface effects. By blending materials with chosen frontier orbital levels, heterojunctions can be engineered that either allow exciton formation for LEDs or promote exciton dissociation for photovoltaic diodes. The dilution of certain chromophores can boost the photoluminescence (PL) efficiency. In general, the combination of polymers can be optimized for different tasks, to offer 'the best of all possible worlds'.

The most striking difference between organic and inorganic semiconductor is that the organics can be solution-processed. This makes it possible to produce the blends and structures which exhibit the rich photophysics already mentioned. The blending of polymeric semiconductors differs from the alloying of inorganic semiconductors in an important way. For the polymers, there is ubiquitous phase separation on multiple lengthscales, associated with the slight entropy of mixing of long polymeric chains. This is essentially self-organization on the nanoscale, driven by thermodynamics. Within limits, it can be manipulated by controlling environmental parameters and by functionalization of the blended materials. Even though they are disordered, phase-separated polymer blends exhibit supramolecular organization.

Blends have enormous appeal. Yet they are very complicated systems to understand and control for implementation in devices. General, robust methods of control are still being devised. The rich surface structures may not be those intended. Blend stability with respect to changes in temperature, pressure, or solvents, has still not been fully achieved. The phase separation process is 'frozen in' at the time of deposition, by relatively rapid solvent evaporation, and the resulting morphology is not one of stable equilibrium, but a metastable state. Increasing the temperature, especially to above the glass transition point, allows wider exploration of the degrees of freedom. More stable conformations may be undesirable from some points of view, but the wider exploration could identify new opportunities. Further, the applied electric fields can be very important in determining the course of the evolution of blends as phase separation proceeds.

There are reports of successful control of the blend morphology. The major obstacle to full exploitation of blends as a technology is that much of the parameter space is uncharted territory. The effects on blend morphology of environmental variations (temperature, pressure, solvents) is not established, with consequent uncertainties in electrical and optical properties. Perhaps for this reason, many industrial laboratories have hesitated to consider blends as serious candidates for plastic electronics. Yet this is a technology challenge, not an intrinsic limit to what is possible. The new experimental methods now available (scanning probe microscopy; micro-Raman spectroscopy, secondary ion mass spectroscopy, SIMS, with sub-micron mapping resolution, spatially-resolved ultra-fast spectroscopy) should help to overcome the problems.

There would be substantial rewards if sufficient control of the self-organization process were achieved. For example, one might imagine preparing a film from a solution of red-, green-, and blue-emitting (RGB) polymers, and letting them phase-separate on appropriate places on a substrate, so as to enable self-organisation to assist in fabricating an RGB display. Or one could exploit the self-organization/phase-separation process to form photonic structures spontaneously; more generally, systems with light localization effects could be created. More ambitiously, blends could become a major tool in the study of the self-organization processes

which, ultimately, will make it possible to put together molecular, macromolecular, or supramolecular electronic circuits.

The opportunities are not only technological, but include fundamental scientific issues. These range from the nature of the interfaces in the heterogeneous systems to the role of surface energy. They include the thermodynamics of soft matter, the theoretical description of disorder (structural and electronic), and the quantitative understanding of the processes taking place during and after deposition. It is far more demanding to model charge injection, transport and recombination in these systems than for homogeneous organic semiconductors. But the experimentalist can help by answering some of the fundamental questions. How is the charge mobility of electrons and holes changed in a blend? What is the mobility inside an A-rich domain in an A–B blend? What is the PL efficiency in the different domains? What is the probability that an exciton splits into an electron and a hole, and is this higher at the polymer–polymer interfaces? The paper in the special issue by Silva *et al* [15] provides an example of physical insight into the effects of heterogeneity on the photophysics of conjugated polymer systems. In this case, the system is a functionalized polyindenofluorene, rather than a blend. Its state of order, and thus its photophysical behaviour, is controlled by the different functionalizations.

It has even been claimed that the polythene bag was the most important invention of the 20th century. Will there be a comparable invention based on electronic polymers? Possibly so, but there remains an implementation barrier to the wide use of organic semiconductor technology. In the short-term, blends might provide the substantial improvement in device performance needed to overcome this barrier. If so, they would make possible one of the first success stories in real-world nanotechnology.

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