Introduction

Cite this article: Monkman A, Friend RH.

2015 Organic semiconductor spintronics:

utilizing triplet excitons in organic electronics.

Phil. Trans. R. Soc. A **373**: 20150121.

<http://dx.doi.org/10.1098/rsta.2015.0121>

Accepted: 7 April 2015

One contribution of 11 to a discussion meeting
issue 'Organic semiconductor spintronics:
utilizing triplet excitons in organic electronics'.

Subject Areas:

spintronics

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Organic semiconductor spintronics: utilizing triplet excitons in organic electronics

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Organic electronics now supports a rapidly growing industry, including organic light-emitting diode (OLED) displays as used in cell phone displays and up-market TVs. This has been enabled both by successful engineering of materials and devices, and also through the design of new device architectures that allow control of electron spin. This is a rapidly moving field, and some recent advances in the basic semiconductor science are likely to enable new applications.

This issue will focus on the role of the spin state of the bound electron-hole pairs (excitons) that provide light emission in LEDs or separate to give free charge in solar cells. The spins of the two electrons involved in these excitons can be arranged as zero-spin 'singlet' states or spin-1 'triplet' states, and for most organic semiconductors the spin exchange energy raises the singlet state substantially above the triplet, typically by 0.5 eV.

For simple OLEDs, only 25% of the electron-hole recombination events can form spin singlet excitons that can then emit photons, with the remaining 75% forming non-emissive triplet excitons. This is a severe limitation to LED efficiency and a number of approaches are developed to avoid this limitation. First, it turns out that collisions between triplet excitons can result in their 'fusion' to form an emissive spin singlet exciton, and under some conditions this can be the dominant decay channel for triplet excitons. How much this can raise efficiency remains an active research question. Second, direct emission from the triplet exciton (phosphorescence) can be achieved if strong spin-orbit coupling can be introduced. Organometallic compounds containing iridium, platinum and osmium have been found effective, particularly for red and green emission. Third, there has been very recent progress in the design of molecular semiconductors with very

small exchange energies, and in well-designed LED architectures this enable triplets to undergo thermally activated reverse intersystem crossing to the singlet manifold. This ‘thermally activated delayed fluorescence’ approach shows real promise.

Standard single-junction semiconductor solar cells such as those made with silicon have their efficiency limited by the compromise that has to be struck between absorbing as much as possible of the solar spectrum, to maximize the short circuit current and keeping the semiconductor bandgap high to keep the open circuit voltage up. The Shockley–Queisser analysis sets an upper limit to single-junction efficiency at around 33%. Improvements beyond this limit require that the solar spectrum be split into different wavelength ranges that are each matched to the semiconductor. ‘Tandem’ cells have been developed using stacked III–V semiconductors with different bandgaps, but these are inherently expensive. There is however scope to improve the match to a single-junction cell with the solar spectrum by ‘colour conversion’. Up-converting low energy infrared photons that would not be absorbed by the semiconductor to higher energy photons can, in principle, be managed by the same triplet–triplet ‘fusion’ process used in OLEDs. The reverse process, the ‘fission’ of a high-energy spin singlet exciton into a pair of spin triplet excitons (in an entangled spin zero state) is now observed to run very efficiently in molecular semiconductors in which the exchange energy brings the triplet exciton down to one half of the singlet exciton energy. Harnessing these spin triplet excitons remains a current research challenge.

Though the focus of this issue is on the spin management of excitons, there is a growing interest in the use of organic semiconductors for the manipulation of electron spin, usually in conjunction with inorganic ‘spintronic’ systems that can inject spin polarized electron currents. The weak spin–orbit coupling present in organic semiconductors, manifest in the form of very distinct singlet and triplet excitons, allows long electron spin coherence times and is being exploited in a number of novel device structures.

This issue is based on research presented at a Royal Society Theo Murphy meeting held in September 2014.