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Solution-phase electroluminescence

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We report emissive devices exhibiting electroluminescence in the solution phase. The principle operating mechanism for these devices—direct electronic carrier injection from the electrodes into the carrier bands of the dissolved polymer—resembles that of a conventional solid-state organic light-emitting diode and is distinct from the solvent-mediated electrochemical devices recently reported by Chang *et al.*

Luminescent polymers have attracted widespread scientific and commercial interest owing primarily to their potential applications in thin-film solid-state emissive devices.[1] Films of luminescent polymers are highly promising from a commercial perspective because they may be deposited directly from solution. Additionally, in the solid-state, they provide intrinsic strength and rigidity thereby obviating the need for additional support structures within devices. Recently, however, Chang *et al.* have reported solution-phase electrochemiluminescent devices (SPECLDs), in which the polymer layer of a conventional solid-state device is replaced by a high-concentration solution of the emissive polymer dispersed in a low molecular weight solvent.[2] Whilst the solvent layer does not have the mechanical advantages of a solid-state film, solution-based devices are nonetheless of interest in certain applications requiring occasional and wholesale exchange of the emissive medium (*e.g.* road signs and street lighting). It has also been suggested by Chang *et al*. that the high levels of disorder found in the solution phase should improve device performance, although they did not provide detailed reasoning.[3]

SPECLDs exhibit relatively high quantum efficiencies ($\sim 1\%$ photons/electrons) at modest applied fields of $\sim 10^6$ Vm^{-1} and are found to be highly sensitive to the choice of solvent. In particular, they require the use of easily oxidizable (or reducible) solvent molecules for their operation. Chang *et al.* proposed an electrochemiluminescence (ECL) based mechanism for device operation in which injection and transport of the majority carriers was mediated by the solvent.[3] The solvent was assumed to undergo oxidation at the anode to form small radical cations with the polymer undergoing reduction at the cathode to form bulky (and relatively immobile) radical anions (negatively charged polarons). The mobile cations were assumed to drift through the bulk of the device and on encountering a radical anion of the luminescent polymer transfer their charge producing an excited state chain segment capable of radiative decay.

As reported by Chang *et al.*, the role of the solvent as a charge transport medium is fundamental to the operation of their devices. They considered the mobility of positive and negative polarons to be too low for adequate electronic charge transport, and concluded that at least one low-molecular-weight species must be present for successful device operation. In this paper, however, we report solution-phase electroluminescent devices in which the solvent plays no part in the charge transport process (other than as a host for the dissolved polymer). Emission in our devices arises from direct bipolar carrier injection from the electrodes into the carrier bands of the dissolved polymer. The operating mechanism is therefore solution-phase electroluminescence (EL)—essentially identical to the conventional solid-state phenomenon[1]—as opposed to (solvent-mediated) electrochemiluminescence.[2,3]

The solution-phase devices used here were fabricated in a planar format (inset of Fig. 2) using commercially available interdigitated gold electrodes of height 1000 Å with 5 μm spacing between anode and cathode.[4] The substrates were washed in spectroscopic grade methanol, acetone and toluene and dried under nitrogen gas before use. A one-percent by-weight solution of poly(9,9-dioctylfluorene) (PFO)[5] in spectroscopic grade toluene was prepared and warmed gently at 35 °C for 5 minutes to ensure full dissolution of the polymer. 5 μL of the polymer solution was then dispensed over the electrode structure and the entire substrate covered with a quartz microscope cover slip to minimize evaporation of the solvent. Non-emissive dummy devices were also fabricated using 5 μL droplets of spectroscopic grade solvent in place of the polymer solution; these devices were used to investigate the charge transport properties of the host solvent. Emission spectra were recorded using a calibrated spectrograph (Ocean Optics).

We draw attention to two features of the emissive devices: the choice of electrode materials and solvent. The electrodes used were commercially available interdigitated gold electrodes from Abtech Scientific. It is difficult to obtain interdigitated electrodes fabricated from dissimilar metals, and therefore no attempt was made to match the work-functions of the electrodes to the carrier bands of the dissolved polymer. Literature estimates for the HOMO and LUMO in PFO indicate injection barriers of 0.7 eV and 2.3 eV at anode and cathode respectively.[6] Consequently, the devices reported here do not in any way represent optimised structures, and considerable improvements in performance are to be expected through the use of alternative electrode materials.

The solvent selected for the emissive devices was toluene. Chang *et al.* deliberately chose solvents with low ionisation energies (such as cyclohexanone and 1,2-dichlorobenzene) for their devices in order to ensure facile oxidation of the solvent. Toluene by contrast is an extremely resistive solvent and oxidation is highly unfavourable.[7] This, for example, creates considerable difficulties in the field of non-aqueous solution electrochemistry where the low conductivity of toluene gives rise to severely distorted voltammograms because of the large potential drop between working and reference electrodes. It is also worth noting that, because toluene is extremely non-polar, very few salts will dissolve at room temperature (all of which are likely to be organic in nature). The probability of accidental contamination with an impurity salt is therefore low and, unless a supporting electrolyte is deliberately introduced into the solution, it will remain electrochemically inactive. We note in passing that Chang and Yang have previously reported polymer gel electroluminescent devices using a non-polar solvent, albeit at concentrations considerably above the gel point.[8]

Fig. 1 shows *in-situ* photoluminescence (PL) and EL spectra for the dissolved polymer in toluene. Similarity between the spectra indicates that emission arises from the same excited state species in both instances (excitons); the differences in the relative magnitudes of the phonon peaks are attributed to cavity effects and differing recombination profiles.[9] No attempt was made to exclude atmospheric oxygen and operational lifetimes were consequently short at around 30 minutes. It should be

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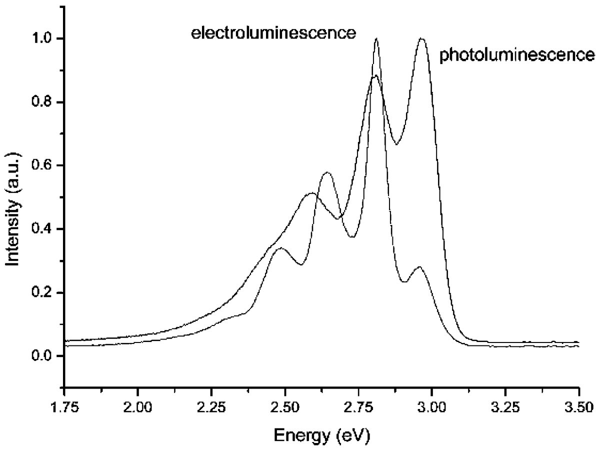

Fig. 1 Photoluminescence and electroluminescence spectra of poly(9,9-dioctylfluorene) in toluene (one percent solution by weight). The near equivalence of the two spectra indicates that emission occurs from the same species in both cases (excitons).

possible to improve this considerably with appropriate encapsulation of the device.

Fig. 2 shows current–voltage characteristics for two dummy devices containing respectively toluene and 1,2-dichlorobenzene (as used in the SPECLDs), and for an emissive device containing toluene and PFO. As expected, oxidation of toluene is unfavourable and the corresponding device is highly resistive. The resistance of the DCB-based device is considerably lower reflecting the lower ionisation energy of the solvent. When PFO is added to the toluene to form the emissive device, the rate of electronic carrier injection increases dramatically. And, because the solvent is unable to sustain a substantial electronic current itself, electronic injection occurs directly from the electrodes into the carrier bands of the polymer. The observation of EL indicates that the injection process is bipolar. The operating mechanism is therefore essentially the same as that for a conventional solid-state organic light-emitting diode. The near-exponential dependence of the current on the drive voltage above 100 V indicates that device behaviour is not described well by simple thermionic emission, Fowler Nordheim tunnelling, or space-charge limited currents.

We note that the drive voltages of the EL devices described here are considerably higher than those reported by Chang *et al.* for their ECL devices (< 10 V for SPECLDs *versus* ~ 100 V for our devices). They suggested that in their devices the light-weight cations of the solvent are free to move through the bulk, whereas the negative polarons formed at the cathode are relatively immobile. The cations therefore drift through the bulk of the device before transferring their charge to a negative polymer chain. Chang *et al.* reported photographs, showing emission close to the cathode, to support this assertion.

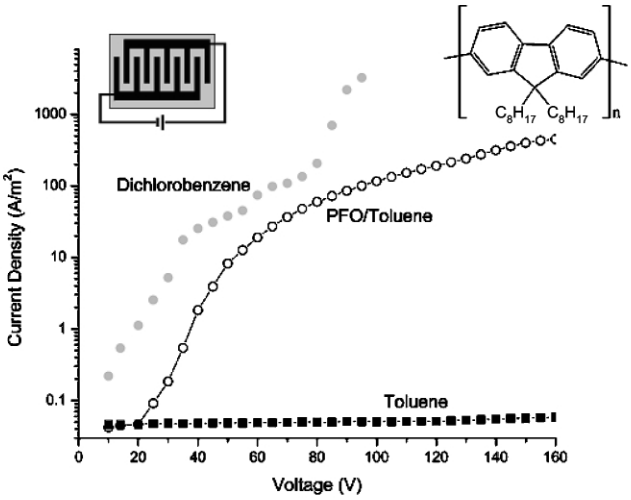

Fig. 2 Current–voltage plots for ‘dummy devices’ containing respectively dichlorobenzene-only and toluene-only, and for an emissive device containing a one percent solution by weight of poly(fluorene) in toluene. Charges are injected directly from the Au electrodes into the carrier bands of the dissolved polymer.

In the EL devices reported here by contrast, charges are transported only in the form of polarons, and large drive voltages are therefore needed to achieve appreciable current injection and light emission. Interestingly, although the drive voltages of ~ 100 V are considerably larger than those needed for the ECL devices, they are broadly in line with the typical field-strengths required for balanced bipolar charge injection in conventional thin-film organic LEDs.[1]

This suggests that polaron mobilities in the solution-phase devices are comparable to the corresponding mobilities in solid-state despite the wider (time-averaged) spacing of individual chains. It is anticipated that there will be three main contributions to the conductivity: hopping between sites on a single polymer chain; modest drift, diffusion, and convection of charged polymer chains; and charge transfer between chains (which depends in turn on their spacing and segmental motion). This is the subject of ongoing investigation and further work is being undertaken to ascertain the exact nature of the charge transport processes in these materials.

In passing, we note that Bard *et al.* have previously reported electrochemiluminescent devices, based on emissive metal chelates,[10] which do not require the addition of an external electrolyte for their operation. In other words, in common with the devices reported here, the active layer comprises in its entirety a luminescor dissolved in an appropriate solvent. The key distinction between the two structures is that metal chelates are salts which dissociate to form ionically conductive solutions, and hence they serve as intrinsic electrolytes. In our devices, the (non-ionic) semiconducting polymer is the only solute and there is no electrolyte present (intrinsic or otherwise). Additionally, and in contrast generally with electrochemiluminescent devices, positive and negative charge carriers do not move freely though the solution, but hop between sites on a large and relatively immobile high molecular-mass host-polymer.

In conclusion, we report solution-phase electroluminescent devices exhibiting direct bipolar injection of electrons and holes into the carrier bands of the emissive polymer. These devices differ in operation from conventional electrochemiluminescent devices and from the solvent-mediated SPECLDs reported by Chang *et al*. In particular, transport of the majority carrier type requires the presence of neither an electrolyte nor an easily oxidised or reduced low molecular weight host solvent. The electroluminescent devices, which are direct solution-based analogues of solid-state organic light-emitting diodes, are of potential interest for a range of optoelectronic applications.

Notes and references

1 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Bredas, M. Logdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121–128.
2 S. C. Chang, Y. Yang and Q. Pei, *Appl. Phys. Lett.*, 1999, **74**, 2081–2083.
3 S. C. Chang, Y. Li and Y. Yang, *J. Phys. Chem. B*, 2000, **104**, 11650–11655.
4 http://www.abtechsci.com.
5 http://www.adsdyes.com.
6 S. Janietz, D. D. C. Bradley, M. Grell, C. Giebeler, M. Inbasekaran and E. P. Woo, *Appl. Phys. Lett.*, 1998, **73**, 2453–2455.
7 L. Geng, A. G. Ewing, J. C. Jernigan and R. W. Murray, *Anal. Chem.*, 1986, **58**, 852–860.
8 S. C. Chang and Y. Yang, *Appl. Phys. Lett.*, 1999, **75**, 2713–2715.
9 H. Becker, S. E. Burns and R. H. Friend, *Phys. Rev. B*, 1997, **56**, 1893–1905.
10 A. J. Bard and G. M. Whitesides, United States Patent 6140138, 2000.