Electroluminescence in polymer films

Optically pumped lasers, using conjugated polymers as their active material, have been reported both in solution[1–3] and in thin films[4,5]. There is now a great deal of interest in the prospects of producing similar, electrically pumped laser diodes[1–6]. Here we report tunnelling-induced electroluminescence experiments on polymer films which indicate that construction of such devices should be possible.

Microcavity devices[5] have the appropriate structure for laser diode operation, with in-phase reflection from the cavity mirrors providing the necessary feedback. The role of superfluorescence remains a subject of debate[6], but more important is the question of whether electrical injection can generate the required excitation densities for lasing to occur. From the threshold optical pump power for the establishment of gain, Hide *et al.*[4] estimate that a current density in excess of 10^6 A m^{-2} will be needed. This is much higher than is normally sustainable within an electroluminescent light-emitting diode (LED), and some have argued that it is fundamentally inaccessible[7].

We note that electroluminescence can be generated by tunnelling injection from a scanning tunnelling microscope (STM) tip. In our own ultra-high vacuum experiments with thin films (approximately 3 nm thick) of poly(1,3-phenylene vinylene-co-2,5-dioctyloxy-1,4-phenylene vinylene) on a gold surface, we observe electroluminescence at a tunnelling current of 100 pA for an STM tip bias of −2.5 V relative to the gold anode. Although the electric field at the sharp tip is relatively high, at this tip bias the mean field across the polymer film is approximately 10^7 V cm^{-1}, not significantly greater than used in many organic LEDs[8]. Electrons from the tip can tunnel directly into unoccupied states of the polymer, and on combination with holes injected from the anode, excitons are formed that can decay radiatively with the emission of light.

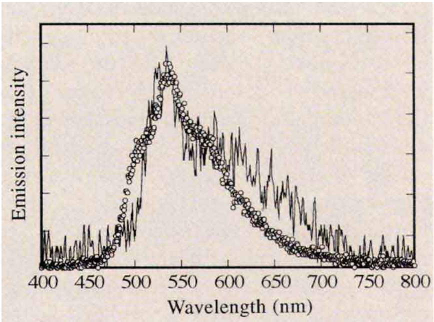

Figure 1 **STM-induced electroluminescence emission spectrum (black line) and cathodoluminescence spectrum (circles), in arbitrary units.**

The electroluminescent emission was collected and dispersed (Fig. 1), and was stable over periods of at least several minutes (the course of the experiment). The equivalence of the cathodoluminescence spectrum (recorded by raising the STM tip ~1 μm above the same spot on the surface and applying a −200 V bias, sufficient to cause field emission from the tip), confirms that the electroluminescence spectrum does indeed arise from the polymer film.

The STM tip was scanned over the surface of the film, and the electroluminescence intensity and topography were simultaneously recorded as a function of position. The smallest features (less than 1 nm for a tunnelling current of 100 pA) resolved in the topographic image provide an upper limit of the tunnelling spot size, an assertion confirmed by the observation of intensity variations in the photon image over similar length scales. Because of the thinness of the film (~3 nm) and the magnitude of the electric field, we expect little spreading within the film of the current injected through this spot. Hence we conservatively estimate that the applied STM tunnelling current of 100 pA flows through an area of roughly 1 nm^2, corresponding to a current density of 10^8 A m^{-2}. This exceeds by two orders of magnitude the estimate in ref. 4. It indicates that there is no intrinsic limit to achieving electroluminescent emission at current densities which (in an optimized device structure) should satisfy the conditions for the establishment of optical gain.

The electroluminescent emission is highly non-uniform on length scales of 10 nm and greater, with variations in both emission intensity and spectral characteristics. Non-uniform emission occurring at similar current densities has also been observed in thin films of poly(*p*-phenylene vinylene)[9], indicating that these results might apply to a large class of conjugated polymers. This non-uniformity in electroluminescence is problematic for device fabrication, and a detailed understanding of the processes that control local emission efficiency is required as part of any development of electrically pumped polymer lasers. Clearly there is still much to do in engineering a polymer laser diode, but we are convinced that this is an attainable target.

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Adaptation of colour vision to sunlight

The processes of light and dark adaptation in photopic vision are generally thought to be complete within minutes. Even after nearly all the photopigment in the retinal cone cells of the eye has been bleached by exposure to an intense light, both the density of pigment and the observer's sensitivity are said to recover fully in only 7 minutes[1]. We describe here a much slower process, which reveals itself in an alteration of colour vision after an hour's adaptation to English sunlight.

Before and after exposure to natural sunlight, we measured Rayleigh matches, in which red and green spectral lights are mixed to match a monochromatic orange[2]. Using a Nagel anomaloscope, in which two semicircular fields are viewed simultaneously (see Fig. 1a), a subject adjusted the red/green ratio of the upper half-field to match the standard orange field. Data were also obtained with a computer-controlled colorimeter that allowed a 2° red/green mixture field (690 + 550 nm) to be alternated every 2 s with a monochromatic orange field (590 nm), thresholds being determined with a randomized 'double-staircase' procedure (Fig. 1b). The exit pupils of both instruments were less than 1 mm in diameter and so variations in the natural pupil are unlikely to affect the stimulus.

During the adaptation phase of the experiment the subject read scientific papers illuminated by natural summer sunlight in central Cambridge (typically 80,000 lux). After exposure, Rayleigh matches were shifted in the protan direction — more red being required in the mixture field. A shift of Rayleigh matches in this direction is known to occur for very short periods after photopigment bleaching[3,4], but these previously reported effects last for only seconds or minutes. The present long-term effect, though small (of the order of 2 Nagel units), can be measured reliably for as long as 5 hours after the end of the adaptation period.

In other experiments we have established that the effect shows no measurable transfer between eyes. It can be obtained with an artificial light source (575 W Sirio Daylight Fresnel), giving an illumination of ~40,000 lux at the reading surface; and it survives when the ultraviolet component, or indeed all wavelengths shorter than 460 nm, are removed from this light source.

Because these adapting conditions are often encountered in the natural world and because matches repeatedly return to pre-adapted levels, we assume that the protan shift (alteration of sensitivity to red light) represents a normal mechanism of adaptation rather than subclinical pathology. The effect is unlikely to occur after the receptor level, because a colour match requires that the standard and matching fields lead to the same triplet of quantum catches in the three classes of retinal cone. Subsequent neural events cannot undo this equation[5]. Therefore, a change must have occurred in either the spectral sensitivity of the cone photoreceptors themselves, or one of the ocular pigments that are usually considered to be photostable.

A change in the spectral sensitivity of the photoreceptors could be caused by a very long-lasting photoproduct, or by a reduction in the self-screening of the photopigment. The latter could arise either from a reduction in optical density or from a reduction in the alignment of the photoreceptors with the centre of the pupil. We have some evidence against a change in photoreceptor alignment, in that we find a shift in Rayleigh match but no change in the Stiles–Crawford effect[6] after 30 min of exposure to artificial daylight of 40,000 lux.

Among the ocular pigments conventionally regarded as stable are macular pigment, melanin and lipofuscin. Light exposure might alter the optical density of such a pigment or might prompt a migration of pigment (as has been reported for melanin granules of the pigment epithelium in one mammalian species[7]). By brightness matching experiments in the short-wave region, we have satisfied ourselves that no significant change occurs in macular pigment under the conditions of our experiment; but preliminary measurements suggest that the red/green matching ratio is changed by the same factor for all wavelengths between 570 and 620 nm, a result that does implicate one of the ocular pigments other than the cone pigments themselves.

Rayleigh matches are often said to be bimodally distributed within the normal male population[8,9], although we have not found such bimodality[10] (and there is no longer a molecular genetic reason to expect it[11,12]). The shifts of colour matches reported here are of the same order of magnitude as the individual differences observed when Rayleigh matches are obtained from a group of colour-normal people. Bimodalities might arise artifactually if subsets of subjects differed in their recent history of light exposure (for example by wearing sunglasses or being tested at different times of day). Certainly, the subjects' history of light exposure will need to be controlled in future population studies.

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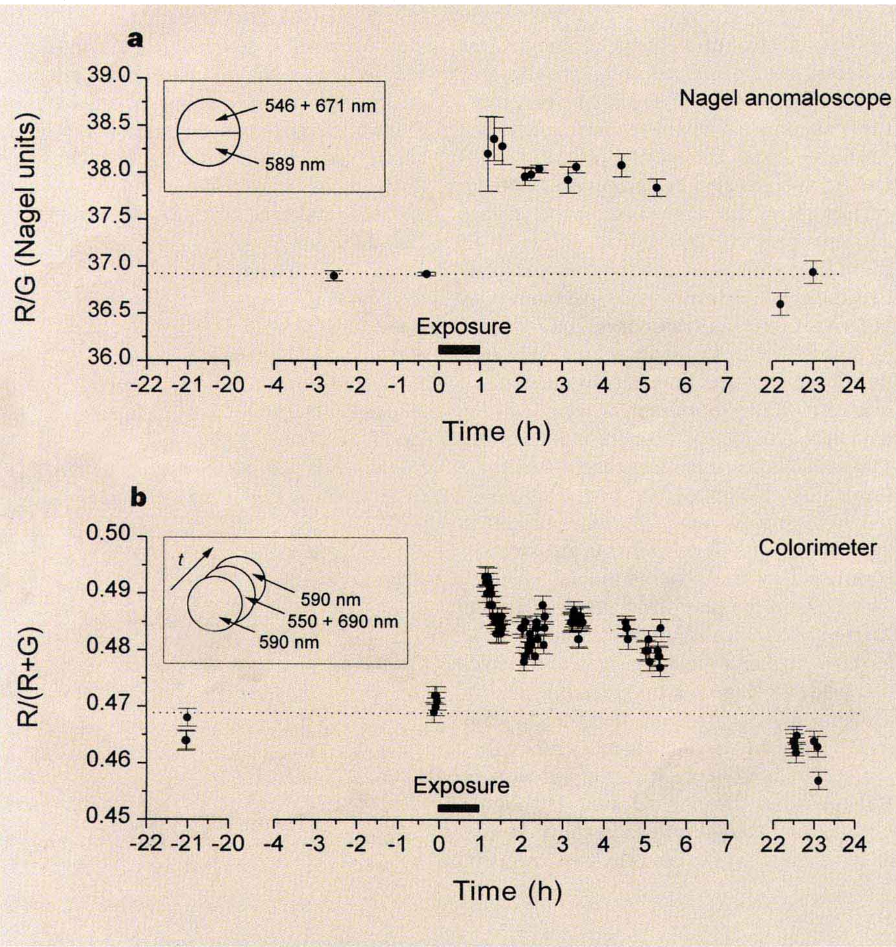

Figure 1 **Long-term shift of Rayleigh matches after exposure to 1 h of natural sunlight in June.** a, **Data obtained using a Nagel anomaloscope. The subject (G. J., female, colour-normal) set a match by adjusting the red/green mixture ratio of the upper half-field (546 + 671 nm) and the brightness of the lower orange half-field (589 nm). Room temperature was held at 21 °C (ref. 13). Each data point is the mean±s.e.m. of 5 matches.** b, **Data measured for the same subject on a three-channel colorimeter. A temporal substitution method was used (see inset), the alternating mixture and standard fields each having a duration of 2 s. Two 'staircases' were randomly interleaved and on each presentation of the mixture field the subject indicated whether it was too red or too green to match the standard. Each data point is the mean of 20 trials, after which the subject had the opportunity to adjust the brightness of the standard. Both panels show the amount of red in the red/green mixture that matched the orange standard as a function of time. Zero on the abscissa indicates the beginning of the 1-h exposure to sunlight. The dotted line is the mean of all matches before exposure. Similar results have been obtained for a male subject (J. D. M.).**

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