which describes the electric-field-induced current of a reactant. The model is based on the following equations:

$$\frac{\partial u}{\partial t}=f(u, v)+D\Delta u+ME\frac{\partial u}{\partial x}$$

$$\frac{\partial v}{\partial t}=g(u, v)$$

with $f(u, v)=\varepsilon^{-1}u(1-u)(u-(v+b)/a)$ and $g(u, v)=u-v$, where u denotes the fast excitation variable and v denotes the slow recovery variable. D is the diffusion coefficient of u, M the ion motility and E the electric field strength. $ME(\partial u/\partial x)$ is the additional flux term. The parameters a, b and ε control the dynamical properties (such as excitability) of the system[10].

To compare the model with the BZ reaction, we take the autocatalytic species $HBrO_2$ as the excitation variable and the catalyst ferroin as the recovery variable. It might seem unreasonable to use an uncharged component to describe electrically induced flux, considering that more realistic models (such as the Oregonator) include the bromide ion, Br^-, which is most affected by the field. But in fact, because of the reaction kinetics, the dynamical behaviour of Br^- is closely related to that of $HBrO_2$ (ref. 1). The modified model used here allows a more general way of describing the effect of an external perturbation such as an applied electric field on a reaction–diffusion system.

The computer investigation agreed well with the experimental data. Figure 3 shows a graphical representation of an annihilation process. The trajectories of coexisting vortex tips are drawn in Fig. 4.

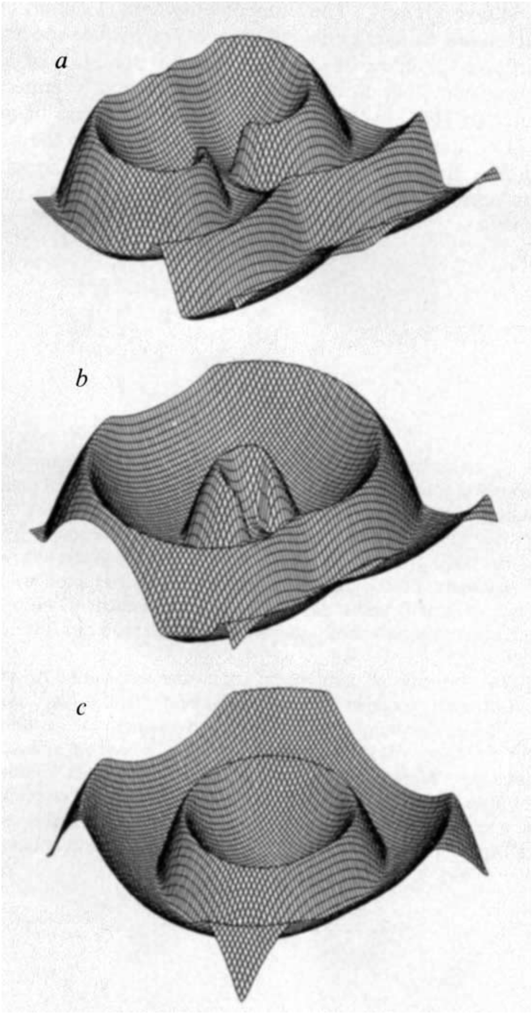

FIG. 3 Three-dimensional representation of the slow recovery variable, v, in a numerical simulation of annihilating vortices with $ME/D=0.3$. *a*, Initial structure. *b*, Region enclosed by the vortex pair is small and has low excitability. *c*, Chemical perturbation disappears in the centre of an expanding circular wave.

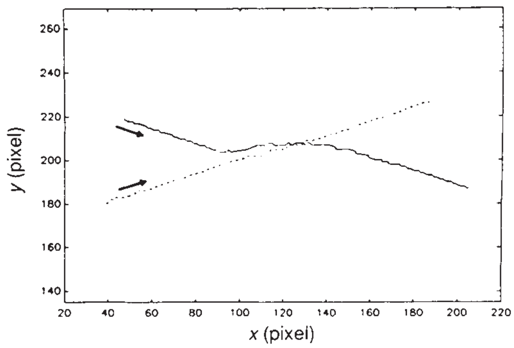

FIG. 4 Calculated traces of crossing vortices. The angle between the symmetry axis of the spiral pair and the field direction is 12° initially and −24° after the interaction. $ME/D=0.15$.

Electric fields can thus be used to influence and decompose dissipative structures in excitable systems by inducing drift of key ions, and could be a simple, controllable tool for investigating reaction–diffusion patterns. This could be useful, for similar studies of forced vortex interaction in other systems and could help to elucidate their specific dynamics[11,12]. ☐

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Chemical tuning of electroluminescent copolymers to improve emission efficiencies and allow patterning

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ONE advantage of using conjugated polymers in semiconductor applications is that they can be processed using techniques well established for conventional polymers. We reported recently that poly(*p*-phenylenevinylene) could be used as the active layer in a light-emitting diode[1], producing yellow/green emission. We have now found that related copolymers, comprising a combination of different arylene units, can be chemically tuned to provide a range of materials with considerably improved properties for this and other applications. By incorporating two different leaving groups into a precursor copolymer, we can selectively eliminate one of these, to give a conjugated/non-conjugated copolymer, or both, to give a fully conjugated copolymer. This allows us to induce local

variations in the π–π^* electronic energy gap at both the molecular and supramolecular level. Variations at the molecular level can act to trap excitons, hindering their migration to quenching sites, and we find that these materials give strongly enhanced quantum yields for electroluminescence (by a factor of up to 30). They also allow control of the colour of emission. Variations at the supramolecular level, by patterning the films to control the progress of conversion, allow the production of structures suitable for multicolour displays. The ability to pattern the film also allows for fabrication of optical waveguides, as regions with different energy gaps have different refractive indices.

Much attention has recently been devoted to the development of efficient routes to conjugated polymers[2-9]. Because most organic materials with a high level of conjugation show poor solubility in common solvents, approaches to conjugated polymers have involved the preparation of a processible precursor polymer, the attachment of groups that increase solubility[8,10], or a combination of both.

In our initial work[1] on the light-emitting properties of poly(*p*-phenylenevinylene) (PPV) we observed that the efficiencies (up to 0.01%; photons emitted per electron injected at room temperature) depended on the combination of electrode materials used. We used aluminium with a surface oxide coating or indium/tin oxide as the positive, hole-injecting contact, and aluminium as the negative, electron-injecting electrode. We found that a segmented PPV analogue emitted blue-green light (508 nm) with a twofold improvement in efficiency[11]. Considerably higher efficiencies are obtained with metals of lower work function as the negative electrode: Braun and Heeger[12], working with a soluble dialkoxy derivative of PPV, showed that efficiencies could be raised to 1% through the use of calcium, whose lower work function allows much easier injection of electrons. We find that efficiencies can be raised to above 1%, using some of the copolymers discussed below. This illustrates the importance of controlling the injection electrodes, and we see scope for further improvements by using hole and electron transport layers. Here, however, we are concerned with the optimization of the emissive layer formed from the conjugated polymer.

Both photoluminescence and electroluminescence originate from the radiative recombination of exciton states, in the first case formed by photoexcitation, and in the second by combination of oppositely charged polarons (radical ions) generated by injection of electrons and holes[13]. The quantum yield for photoluminescence in small conjugated molecules can be very high, but the yield in PPV is reduced as the extent of π-electron conjugation is increased[14]. Increased mobility of excitons in the delocalized π-electron system will allow more rapid motion to quenching centres; among the latter, self-localized charged excitations have been experimentally identified as important[15,16]. We set out, therefore, to introduce local variations in the potential that could act as exciton traps and reduce motion to quenching sites, by synthesizing copolymers that have regions of different π–π^* energy within a single chain.

The essence of the synthetic route was to produce a precursor polymer polyelectrolyte with two different leaving groups on the main chain. We illustrate this here for the monomers (I) and (II), copolymerized to form polymer (III), which was then converted to polymers (IV) or (V) by heat treatment under different conditions. Formulae and preparation details are given in Fig. 1. We chose these two monomers because their conjugated homopolymers show substantially different bandgaps, 2.5 eV (496 nm) for PPV and 2.1 eV (590 nm) for poly(2,5-dimethoxy-*p*-phenylenevinylene)[17]. The films of polymers (IV) and (V) were characterized by infrared and ultra-violet/visible spectroscopy. The infrared spectra of (IV) showed the presence of methoxy leaving groups, which disappeared on thermal treatment in the presence of HCl. In the optical absorption spectra of the polymers (IV), the energy of the band edge shifted to the blue with increasing numbers of dimethoxy-*p*-phenylene units. These results confirmed that the polymer (IV) had been randomly

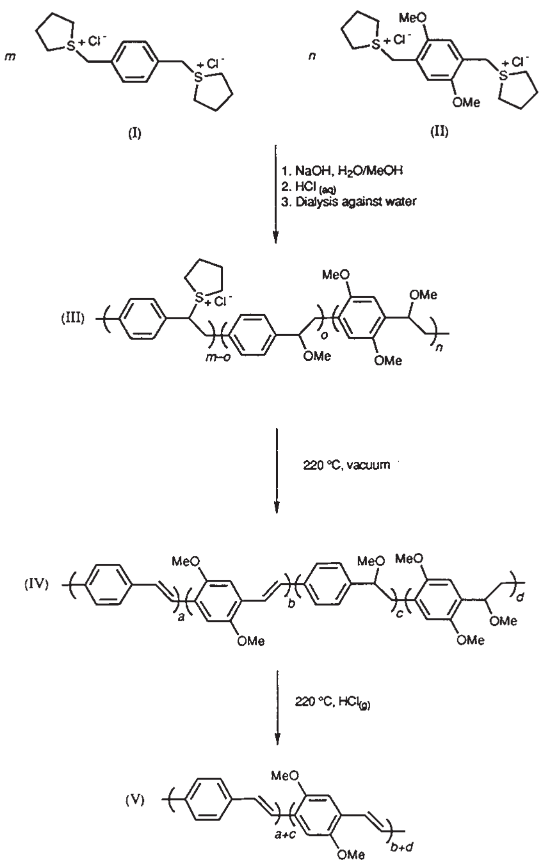

FIG. 1 Synthetic pathway. The symbols *m* and *n* represent the molar equivalents of the monomeric salts (I) and (II) in the reaction. A small number (*o*) of benzylic positions adjacent to the phenylene rings in (III) are substituted by methoxy groups. Thermal elimination of all the sulphonium groups and a few methoxy groups from (III) produces the polymer (IV), which has an arrangement of conjugated units randomly interrupted by saturated units (where *a, b, c* and *d* stand for the total number of each structural type). Further acid-promoted conversion of (IV) produces the conjugated polymer (V).

METHODS. The ratio of units in the copolymer was varied by altering the amount of each monomer unit in the reaction mixture. We copolymerized the two *bis*(sulphonium) salts in a water/methanol mixture with aqueous sodium hydroxide. After termination, polymers (III) were purified by dialysis against water before isolation and dissolution in methanol. Thermal conversion of films of polymers (III) (220 °C *in vacuo*; 2 h) produced homogeneous, dense and uniform films of the polymers (IV) (typical thickness 100 nm). The polymers (V) were formed from (III) by heat treatment under acidic conditions (220 °C, HCl/Ar, 22 h).

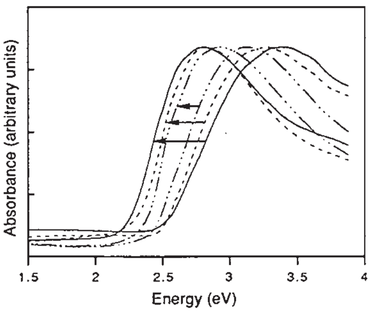

FIG. 2 Absorption spectra of copolymers prepared from ratios of (I) to (II) 9:1 (— - - - - —), 4:1 (- - - -), 7:3 (——) from thermal treatment and acid and thermal treatment. The shift is indicated in the direction of the arrows for each case.

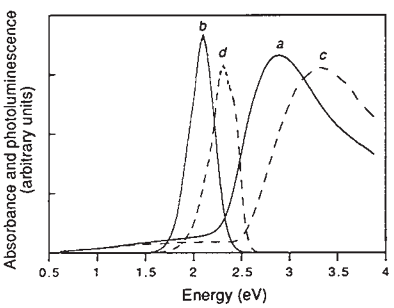

FIG. 4 Absorption (*a*) and photoluminescence (*b*) spectra of a capped sample, and absorption (*c*) and photoluminescence spectra (*d*) of an uncapped sample of copolymer made from a 7:3 mixture of (I) and (II).

segmented into discrete conjugated units, because the sulphonium groups on the benzylic carbons attached to the 2,5-dimethoxy-*p*-phenylene units are readily displaced by methanol. Those attached to the benzylic carbons of the *p*-phenylene units are not. During the thermal conversion, the sulphonium groups are readily lost, whereas the methoxy groups resist elimination. They require both heat and acid. Consequently thermal and acidic treatment of the polymer (III) yields the polymer (V). Elimination of both the sulphonium and methoxy leaving groups is substantially complete, with the result that the energy gap shifts to the red (Fig. 2).

We thus have the choice of conjugated copolymers (V) or conjugated/nonconjugated copolymers (IV). We have looked at the properties of the conjugated/nonconjugated copolymers in electroluminescent diode structures, and find that these offer better device efficiency than PPV. The most striking results are obtained for devices with aluminium/aluminium oxide and aluminium contacts. The device efficiency depends strongly on the monomer feed ratio, increasing from 0.01% (PPV in the same device configuration) by a factor of up to 30 (to 0.3%) as the monomer feed ratio (I) : (II) was reduced to 9 : 1; copolymers arising from lower feed ratios (I) : (II) showed an efficiency that decreased consistent with the lower photoluminescence yield from poly(2,5-dimethoxy-*p*-phenylene vinylene)[18].

Conversion of (III) to (V) can be achieved lithographically, by control of the presence of acid through patterning, and thus copolymer samples with supramolecular variations in π-π^* energy gap can also be prepared. One convenient method is to make use of the hydrogen chloride, a by-product of the thermolysis of the sulphonium groups of polymer (III), to catalyse the removal of the methoxy leaving groups. This merely requires that the acid generated in this way is trapped in the film. We achieved this by masking a thin film of the precursor polymer (III) with strips of evaporated aluminium or another suitable metal (Fig. 3). After thermal treatment and removal of the aluminium mask, the films showed a striking difference in colour (orange where previously coated and yellow elsewhere) and in their photoluminescence spectra (Fig. 4). Such a process is readily amenable to lithographic techniques, with resolution limited only by acid diffusion around the edges of the mask.

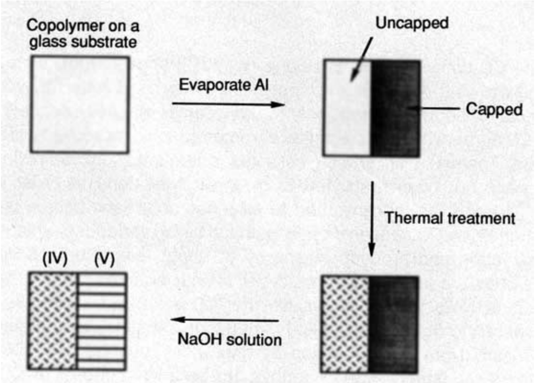

FIG. 3 Schematic diagram showing the process for forming a pattern of polymers (IV) and (V) from polymer (III).

We compared the effective refractive indices of the TE and TM optical waveguide modes in each of two closely neighbouring regions on either side of the boundary at a wavelength of 632.8 nm, and we estimated the difference in the polarization-dependent refractive index n_{TE} and n_{TM} in the two regions. We found a striking difference in n_{TE} (electric field parallel to surface) linked to the change in absorption spectra in the two different regions. For example, a copolymer prepared from a 4 : 1 feed ratio of (I) to (II) treated in the above fashion had $n_{\mathrm{TE}} = 1.81$ in the uncapped region (polymer absorption maximum at 376 nm (3.30 eV)) and $n_{\mathrm{TE}} = 1.96$ in the capped region (polymer absorption maximum at 427 nm (2.90 eV)).

The efficiency of the output of electroluminescent devices that incorporate copolymers can be raised to levels comparable to those of inorganic devices operating in the yellow-green part of the spectrum. Furthermore, the colour of the electroluminescent output can be varied by controlling the chemistry behind the copolymerization and the degree of conversion to the conjugated form. Emission over the spectral range from green-blue[11] to orange-red has already been demonstrated using different copolymers. Supramolecular control of refractive index through control of the π-π^* energy gap also offers scope for guided-wave devices. ☐

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