properties of the neutrino are responsible for the solar-neutrino problem. One possible explanation is provided by neutrino oscillations resonantly enhanced in their passage through matter —the MSW effect[22]. This implies neutrinos of finite mass and thus goes beyond the standard model of the electroweak theory[33]. □

Received 6 June; accepted 24 August 1990.

1. Claverie, A., Isaak, G. R., McLeod, C. P., van der Raay, H. B. & Roca Cortes, T. *Nature* **282,** 591–594 (1979).
2. Deubner, F. L. & Gough, D. O. *A. Rev. Astr. Astrophys.* **22,** 593–619 (1984).
3. Bahcall, J. N. *Proc. Int. Conf. on Neutrino Physics and Astrophysics* Vol. 2 (eds Cence, R. J., Ma, E. & Roberts, A.) 253 (University of Hawaii, 1981).
4. Ulrich, R. K. & Rhodes, E. J. Jr *Astrophys. J.* **265,** 551–563 (1983).
5. Gough, D. O. & Novotny, E. *Sol. Phys.* **128,** 143–160 (1990).
6. Christensen-Dalsgaard, J. in *Solar Interior and Atmosphere* (eds Cox, A. N. Livingston, W. C. & Mathews, M.) (University of Arizona Press, in the press).
7. Cox, A. N., Guzik, J. A. & Raby, S. *Astrophys. J.* **353,** 698–711 (1990).
8. Schatzman, E. & Maeder, A. *Astr. Astrophys* **96,** 1–16 (1981).
9. Lebreton, Y., Berthomieu, G. & Provost, J. *Advances in Helio and Asteroseismology, IAU 123* (eds Christensen-Dalsgaard, J. & Frandsen, S.) 95–98 (Reidel, Dordrecht, 1988).
10. Spergel, D. N. & Press, W. H. *Astrophys. J.* **294,** 663–673 (1985).
11. Faulkner, J. & Gilliland, R. L. *Astrophys. J.* **299,** 994–1000 (1985).
12. Davis, R., Lande, K., Lee, C. K., Cleveland, B. T. & Ullman, J. *Inside the Sun* (eds G. Berthomieu, G. & Cribier, M.) 171–177 (Kluwer, Dordrecht, 1990).
13. Hirata, K. S. *et al. Inside the Sun* (eds Berthomieu, G. & Cribier, M.) 179–186 (Kluwer, Dordrecht, 1990).
14. Dicke, R. H. & Goldenberg, H. M. *Astrophys. J. Supp.* **27,** 131–182 (1974).
15. Robertson, D. S. & Carter, W. E. *Nature* **310,** 572–574 (1984).
16. Taylor, J. H. & Weisberg, J. M. *Astrophys. J.* **345,** 434–450 (1989).
17. Dicke, R. H., Kuhn, J. R. & Libbrecht, K. G. *Astrophys. J.* **318,** 451–458 (1988).
18. Claverie, A., Isaak, G. R., McLeod, C. P., van der Raay, H. B. & Roca Cortes, T. *Nature* **293,** 443–445 (1981).
19. Woodard, M. F. *Nature* **309,** 530–532 (1984).
20. Bahcall, J. N. *Neutrino Astrophysics* Ch. 1 (Cambridge University Press, 1989).
21. Christensen-Dalsgaard, J. *Proc. Symp. Seismology of the Sun and Sun-like Stars* (ed. Rolfe, E. J.) 431–450 (European Space Agency, 1988).
22. Bethe, H. A. *Phys. Rev. Lett.* **56,** 1305–1308 (1986).
23. Leighton, R. B., Noyes, R. W. & Simon, G. W. *Astrophys. J.* **135,** 474–499 (1962).
24. Brookes, J. R., Isaak G. R. & van der Raay, H. B. *Mon. Not. R. astr. Soc.* **185,** 1–17 (1978).
25. Elsworth, Y., Howe, R., Isaak, G. R., McLeod, C. P. & New, R. *Nature* **345,** 322–324 (1990).
26. Woodard, M. F. & Noyes, R. W. *Nature* **318,** 449–450 (1985).
27. Gelly, B., Fossat, E. & Grec, G. *Astr. Astrophys.* **200,** L29–L31 (1988).
28. Palle, P. L., Regulo, C. & Roca Corte, T. *Astr. Astrophys.* **224,** 253–258, (1989).
29. Bahcall, J. N. & Ulrich, R. K. *Rev. mod. Phys.* **60,** 297–372 (1988).
30. Faulkner, J., Gough, D. O. & Vahia, M. N. *Nature* **321,** 226–229 (1986).
31. Däppen, W., Gilliland, R. & Christensen-Dalsgaard, J. *Nature* **321,** 229–231 (1986).
32. Jimenez, A. *et al. Advances in Helio and Astroseismology, IAU 123* (eds Christensen-Dalsgaard, J. & Frandsen, S.) 205–209 (Reidel, Dordrecht, 1988).
33. Kuo, T. K. & Pantaleone, J. *Rev. mod. Phys.* **61,** 937–979 (1989).

ACKNOWLEDGEMENTS. We thank all members, past and present, of the Birmingham and Instituto de Astrofisica de Canarios solar oscillations groups for their assistance, and J. Christensen-Dalsgaard, A. N. Cox and D. O. Gough for their comments. This work was funded by SERC and by the CAICYT.

Light-emitting diodes based on conjugated polymers

J. H. Burroughes*‡, D. D. C. Bradley*, A. R. Brown*, R. N. Marks*, K. Mackay*, R. H. Friend*, P. L. Burns† & A. B. Holmes†

* Cavendish Laboratory, Madingley Road, Cambridge CB3 0HE, UK
† University Chemistry Laboratory, Lensfield Road, Cambridge CB2 1EW, UK

CONJUGATED polymers are organic semiconductors, the semiconducting behaviour being associated with the π molecular orbitals delocalized along the polymer chain. Their main advantage over non-polymeric organic semiconductors is the possibility of processing the polymer to form useful and robust structures. The response of the system to electronic excitation is nonlinear—the injection of an electron and a hole on the conjugated chain can lead to a self-localized excited state which can then decay radiatively, suggesting the possibility of using these materials in electroluminescent devices. We demonstrate here that poly(*p*-phenylene vinylene), prepared by way of a solution-processable precursor, can be used as the active element in a large-area light-emitting diode. The combination of good structural properties of this polymer, its ease of fabrication, and light emission in the green–yellow part of the spectrum with reasonably high efficiency, suggest that the polymer can be used for the development of large-area light-emitting displays.

There has been long-standing interest in the development of solid-state light-emitting devices. Efficient light generation is achieved in inorganic semiconductors with direct band gaps, such as GaAs, but these are not easily or economically used in large-area displays. For this, systems based on polycrystalline ZnS have been developed, although low efficiencies and poor reliability have prevented large-scale production. Because of the high photoluminescence quantum yields common in organic molecular semiconductors, there has long been interest in the possibility of light emission by these organic semiconductors through charge injection under a high applied field (electroluminescence)[1–7]. Light-emitting devices are fabricated by vacuum sublimation of the organic layers, and although the efficiencies and selection of colour of the emission are very good, there are in general problems associated with the long-term stability of the sublimed organic film against recrystallization and other structural changes.

One way to improve the structural stability of these organic layers is to move from molecular to macromolecular materials, and conjugated polymers are a good choice in that they can, in principle, provide both good charge transport and also high quantum efficiency for the luminescence. Much of the interest in conjugated polymers has been in their properties as conducting materials, usually achieved at high levels of chemical doping[8], and there has been comparatively little interest in their luminescence. One reason for this is that polyacetylene, the most widely studied of these materials, shows only very weak photoluminescence. But conjugated polymers that have larger semiconductor gaps, and that can be prepared in a sufficiently pure form to control non-radiative decay of excited states at defect sites, can show high quantum yields for photoluminescence. Among these, poly(*p*-phenylene vinylene) or PPV can be conveniently made into high-quality films and shows strong photoluminescence in a band centred near 2.2 eV, just below the threshold for π to π^* interband transitions[9,10].

We synthesized PPV (I) using a solution-processable precursor polymer (II), as shown in Fig. 1. This precursor polymer is conveniently prepared from α,α'-dichloro-*p*-xylene (III), through polymerization of the sulphonium salt intermediate (IV)[11–13]. We carried out the polymerization in a water/methanol mixture in the presence of base and, after termination, dialysed the reaction mixture against distilled water. The solvent was removed and the precursor polymer redissolved in methanol. We find that this is a good solvent for spin-coating thin films of the precursor polymer on suitable substrates. After thermal conversion (typically ≥250 °C, *in vacuo*, for 10 h), the films of PPV (typical thickness 100 nm) are homogeneous, dense and

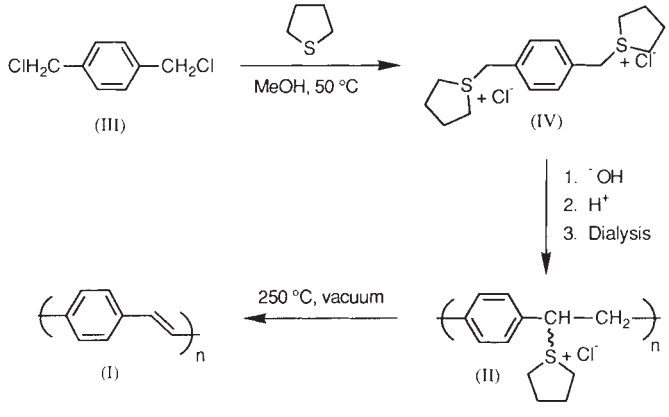

FIG. 1 Synthetic route to PPV.

‡ Present address: IBM Thomas J. Watson Research Centre, Yorktown Heights, New York 10598, USA.

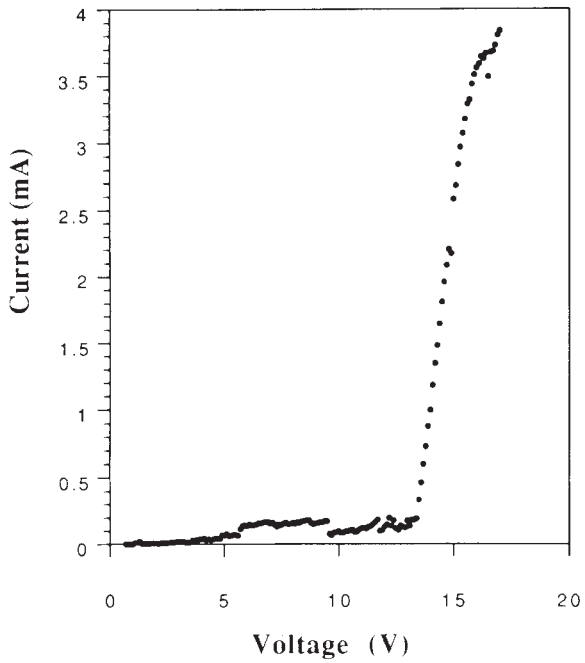

FIG. 2 Current–voltage characteristic for an electroluminescent device having a PPV film 70 nm thick and active area of 2 mm^2, a bottom contact of indium oxide, and a top contact of aluminium. The forward-bias regime is shown (indium oxide positive with respect to the aluminium electrode).

uniform. Furthermore, they are robust and intractable, stable in air at room temperature, and at temperatures >300 °C in a vacuum[11].

Structures for electroluminescence studies were fabricated with the PPV film formed on a bottom electrode deposited on a suitable substrate (such as glass), and with the top electrode formed onto the fully converted PPV film. For the negative, electron-injecting contact we use materials with a low work function, and for the positive, hole-injecting contact, we use materials with a high work function. At least one of these layers must be semi-transparent for light emission normal to the plane of the device, and for this we have used both indium oxide, deposited by ion-beam sputtering[14] and thin aluminium (typically 7–15 nm). We found that aluminium exposed to air to allow formation of a thin oxide coating, gold and indium oxide can all be used as the positive electrode material, and that aluminium, magnesium silver alloy and amorphous silicon hydrogen alloys prepared by radiofrequency sputtering are suitable as the negative electrode materials. The high stability of the PPV film allows easy deposition of the top contact layer, and we were able to form this contact using thermal evaporation for metals and ion-beam sputtering for indium oxide.

Figures 2 and 3 show typical characteristics for devices having indium oxide as the bottom contact and aluminium as the top contact. The threshold for substantial charge injection is just below 14 V, at a field of 2×10^6 V cm^{-1}, and the integrated light output is approximately linear with current. Figure 4 shows the spectrally resolved output for a device at various temperatures. The spectrum is very similar to that measured in photoluminescence, with a peak near 2.2 eV and well resolved phonon structure[9,10]. These devices therefore emit in the green–yellow part of the spectrum, and can be easily seen under normal laboratory lighting. The quantum efficiency (photons emitted per electron injected) is moderate, but not as high as reported for some of the structures made with molecular materials[2–7]. The quantum efficiences for our PPV devices were up to 0.05%. We found that the failure mode of these devices is usually associated with failure at the polymer/thin metal interface and is probably due to local Joule heating there.

The observation and characterization of electroluminescence in this conjugated polymer is of interest in the study of the fundamental excitations of this class of semiconductor. Here, the concept of self-localized charged or neutral excited states in the nonlinear response of the electronic system has been a useful one. For polymers with the symmetry of PPV, these excitations are polarons, either uncharged (as the polaron exciton) or charged (singly charged as the polaron, and doubly charged as the bipolaron)[15,16]. We have previously assigned the photoluminescence in this polymer to radiative recombination of the singlet polaron exciton formed by intrachain excitation[9,10] and, in view of the identical spectral emission here, we assign the electroluminescence to the radiative decay of the same excited state. The electroluminescence is generated by recombination of the electrons and holes injected from opposite sides of the structure, however, and we must consider what the charge carriers are. We have previously noted that bipolarons, the more stable of the charged excitations in photoexcitation and chemical doping studies, are very strongly self-localized, with movement of the associated pair of energy levels deep into the semiconductor gap, to within 1 eV of each other[9]. In contrast, the movement of these levels into the gap for the neutral polaron exciton, which one-electron models predict to be the same as for the bipolaron[15], is measured directly from the photoluminescence

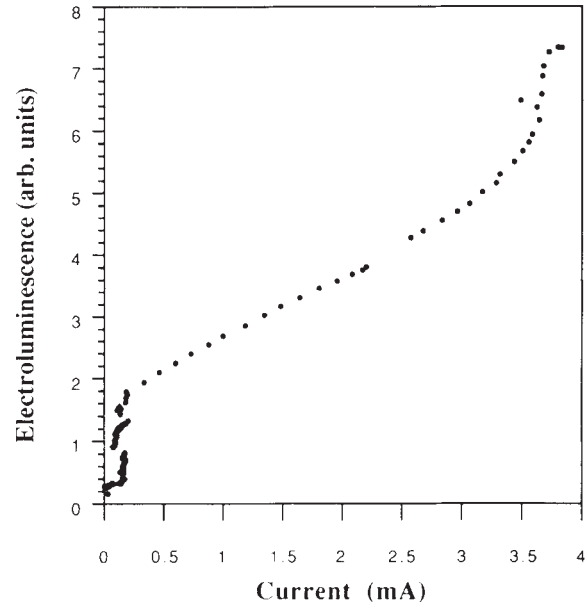

FIG. 3 Integrated light output plotted against current for the electroluminescent device giving the current–voltage characteristic in Fig. 2.

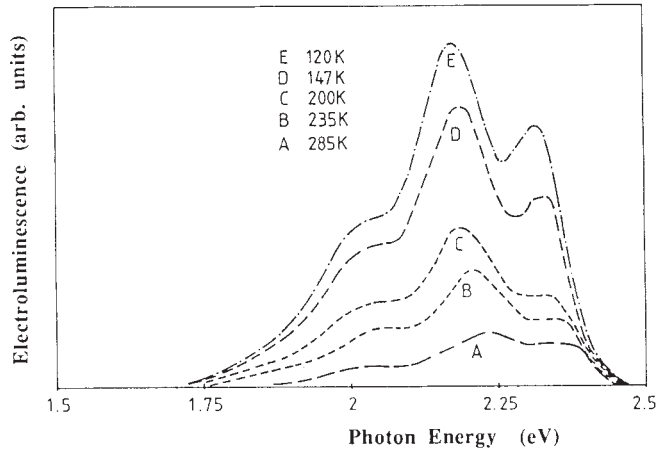

FIG. 4 Spectrally resolved output for an electroluminescent device at various temperatures.

emission to be much smaller, with the levels remaining more than 2.2 eV apart. For electroluminescence then, bipolarons are very unlikely to be the charge carriers responsible for formation of polaron excitons, because their creation requires coalescence of two charge carriers, their mobilities are low and the strong self-localization of the bipolaron evident in the positions of the gap states probably does not leave sufficient energy for radiative decay at the photon energies measured here. Therefore, the charge carriers involved are probably polarons. The evidence that they can combine to form polaron excitons requires that the polaron gap states move no further into the gap than those of the polaron exciton and may account for the failure to observe the optical transitions associated with the polaron.

The photoluminescence quantum yield of PPV has been estimated to be ~8%. It has been shown[10,17] that the non-radiative processes that limit the efficiency of radiative decay as measured in photoluminescence are due to migration of the excited states to defect sites which act as non-radiative recombination centres, and also, at high intensities, to collisions between pairs of excited states. These are processes that can, in principle, be controlled through design of the polymer, and therefore there are excellent possibilities for the development of this class of materials in a range of electroluminescence applications. □

Received 21 August; accepted 18 September 1990.

1. Vincent, P. S., Barlow, W. A., Hann, R. A. & Roberts, G. G. *Thin Solid Films* **94,** 476–488 (1982).
2. Tang, C. W. & VanSlyke, S. A. *Appl. Phys. Lett.* **51,** 913–915 (1987).
3. Tang, C. W., VanSlyke, S. A. & Chen, C. H. *J. appl. Phys.* **65,** 3610–3616 (1989).
4. Adachi, C., Tokito, S., Tsutsui, T. & Saito, S. *Jap. J. appl. Phys.* **27,** 59–61 (1988).
5. Adachi, C., Tsutsui, T. & Saito, S. *Appl. Phys. Lett.* **55,** 1489–1491 (1989).
6. Adachi, C., Tsutsui, T. & Saito, S. *Appl. Phys. Lett.* **56,** 799–801 (1989).
7. Nohara, M., Hasegawa, M., Hosohawa, C., Tokailin, H. & Kusomoto, T. *Chem. Lett.* 189–190 (1990).
8. Basescu, N. *et al. Nature* **327,** 403–405 (1987).
9. Friend, R. H., Bradley, D. D. C. & Townsend, P. D. *J. Phys.* D**20,** 1367–1384 (1987).
10. Bradley, D. D. C. & Friend, R. H. *J. Phys.: Condensed Matter* **1,** 3671–3678 (1989).
11. Bradley, D. D. C. *J. Phys.* D**20,** 1389–1410 (1987).
12. Murase, I., Ohnishi, T., Noguchi, T. & Hirooka, M. *Synthetic Metals* **17,** 639–644 (1987).
13. Stenger-Smith, J. D., Lenz, R. W. & Wegner, G. *Polymer* **30,** 1048–1053 (1989).
14. Bellingham, J. R., Phillips, W. A. & Adkins, C. J. *J. Phys.: Condensed Matter* **2,** 6207–6221 (1990).
15. Fesser, K., Bishop, A. R. & Campbell, D. K. *Phys. Rev.* B**27,** 4804–4825 (1983).
16. Brazovskii, S. A. & Kirova, N. N. *JEPT Lett.* **33,** 4–8 (1981).
17. Bradley, D. D. C. *et al. Springer Ser. Solid St. Sci.* **76,** 107–112 (1987).

ACKNOWLEDGEMENTS. We thank J. R. Gellingham, C. J. Adkins and W. A. Phillips for their help in preparing the indium oxide films. We thank SERC and Cambridge Research and Innovation Ltd for support.

Tropospheric lifetimes of three compounds for possible replacement of CFC and halons

A. C. Brown, C. E. Canosa-Mas, A. D. Parr, K. Rothwell & R. P. Wayne

Physical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK

CHLORINE and bromine have been implicated in the massive springtime depletion of stratospheric ozone over Antarctica[1]. As the source of these halogens is anthropogenic emissions of haloalkanes, the problem has acquired political and economic significance[2]. The chemical industry has been forced to consider urgently possible replacements for conventional halocarbons, and the potential effects on the environment of proposed alternative compounds have been evaluated recently in the Alternative Fluorocarbon Environmental Acceptability Study (AFEAS)[3]. Three such compounds that are not included in the AFEAS report are CF_2BrH (halon 1201). CF_3CFBrH (halon 2401) and $CF_3CF_2CCl_2H$ (HCFC 225ca). Removal of these compounds from the atmosphere will occur primarily by reaction with the hydroxyl radical, OH (ref. 4). Here we determine, from laboratory studies, the absolute rate of reaction between these three species and OH. Such kinetic data are vital for assessing their viability as replacement compounds. We use these data, along with our measurements of ultraviolet absorption cross-sections, to estimate the tropospheric lifetimes of the halons and HCFC 225ca against removal by OH, and their potential for destroying ozone in the stratosphere. Our approach shows how laboratory measurements can provide a useful first estimate of the environmental acceptability of compounds of this sort.

CF_2BrH and CF_3CFBrH are being considered as substitutes for CF_3Br in fire extinguishers, and $CF_3CF_2CCl_2H$ has useful properties as a solvent. The efficiency with which a unit mass of each halocarbon will destroy stratospheric ozone relative to the most important ozone-depleting molecules CFC-11 ($CFCl_3$) and CFC-12 (CF_2Cl_2) will depend strongly on the atmospheric lifetime of the compound. The daytime degradation of these hydrogen-containing molecules, RH, will occur primarily by reaction with the OH radical[4]

$$OH + RH \xrightarrow{k_1} H_2O + R \qquad (1)$$

and it is therefore important to know the rates of the homogeneous gas-phase reactions of OH with RH.

We have determined values of the second-order rate constants, k_1, for the hydrogen-atom abstraction process (1) and their variation with temperature for the three hydrohalocarbon molecules. Our experimental procedure and data analysis are described fully elsewhere[5–7]. We used an absolute discharge flow technique with a movable injection point for the reactant to provide time resolution; OH concentrations were measured by resonance fluorescence. The variation of OH concentration with injector position was monitored with a known excess of hydrohalocarbon added. The logarithm of the OH signal was a linear function of calculated contact time, and the gradient was plotted against the concentration of hydrohalocarbon to give a straight line of slope k_1. Our values for k_1 are given in Table 1 along with the experimental conditions. We used a conventional Arrhenius equation, $\ln k_1 = \ln A - E/RT$, to analyse the temperature-dependence. Thus a plot of $\ln k_1$ as a function of $1/T$ should give a straight line of slope E/R and intercept $\ln A$. Values of the activation energies E in the form E/R and pre-exponential factors A are given in Table 1. Errors on the slope, calculated in a linear least-squares analysis, are the 95% confidence limits. The 95% confidence limits on the intercept were unrealistically large, as is often the case in calculating Arrhenius parameters: we do not quote the errors here. The predictive capacity of the experimental Arrhenius expression is not properly represented by the individual errors on E and A, but rather by the combined expression incorporating both parameters.

We paid particular attention to the possible presence of fast-reacting impurities in the hydrohalocarbon samples, which could seriously affect the measurement of k_1. All of the

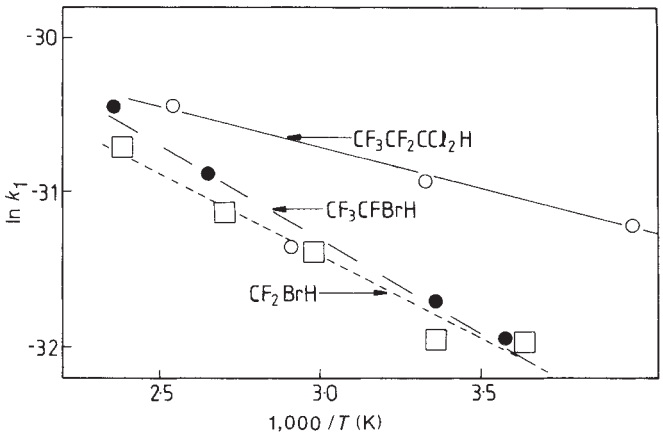

FIG. 1 Arrhenius plots for reactions of RH with OH.